Effect of Chemical Composition on Number of Eutectic Colonies in Ni-Mn-Cu Cast Iron

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Abstract
Determined were direction and intensity of influence of alloying additions on the number of eutectic graphite colonies in austenitic cast iron Ni-Mn-Cu. Chemical composition of the cast iron was 1.7 to 3.3% C, 1.4 to 3.1% Si, 2.8 to 9.9% Ni, 0.4 to 7.7% Mn, 0 to 4.6% Cu, 0.14 to 0.16% P and 0.03 to 0.04% S. Analysed were structures of mottled (20 castings) and grey (20 castings) cast iron. Obtained were regression equations determining influence intensity of individual components on the number of graphite colonies per 1 cm² (LK). It was found that, in spite of high total content of alloying elements in the examined cast iron, the element that mainly decides the LK value is carbon, like in a plain cast iron.

Keywords: Eutectic graphite colonies, Solidification, Austenitic cast iron, Cast iron Ni-Mn-Cu

1. Introduction

Number of eutectic colonies significantly affects several technological, mechanical and service properties of cast iron [1-4]. It is especially important in the case of austenitic cast iron, because in principle the casting structure is finally formed during eutectic transformation.

The number of eutectic graphite colonies is influenced mostly by temperature and concentration overcooling of a liquid alloy [5, 6]. Therefore, the number of the created colonies is decided not only by cooling speed of castings within the eutectic solidification range, but also by chemical composition of the alloyed cast iron.

There are several opinions, sometimes discordant ones, about influence of individual elements on geometrical parameters of eutectic cells.

By intensifying graphite nucleation, carbon increases the number of eutectic colonies. Along with increasing carbon concentration in a hypoeutectic cast iron, overcooling degree of the eutectic transformation drops and thus speed of the eutectic growth decreases as well. As a result, branching degree of the graphite skeleton is reduced and larger graphite particles are observed on metallographic polished sections, as well as a change of its distribution from interdendritic type D or E to uniform type A [7].

The fact is that silicon significantly changes equilibrium solidification temperatures of graphite eutectic mixture and ledeburite, but it practically does not influence the real beginning temperature of eutectic solidification in castings. Thus, it can be assumed that at commonly used concentration (1.5 to 2.5% Si), silicon, as opposed to carbon, does not influence the number of created graphite nuclei and to a small degree changes the eutectic growth speed. The effect of silicon on size of the eutectic colonies is also insignificant [8].

Manganese is conductive to reduction of the number of graphite nuclei, and thus the number of eutectic colonies, but does not influence their size. Higher concentration of this element in cast iron results at the same time in higher branching degree of the graphite skeleton.
Effect of nickel on size and number of eutectic cells is negligibly small. It is believed that this element reduces size of eutectic graphite, favouring its solidification with interdendritic distribution.

Copper increases the number of eutectic cells. In general, its influence on size and features of eutectic graphite colonies is not observed [9].

2. Scope of the research

One of the most often used indices characterising features of eutectic cells is the number of these cells per surface area unit of a polished section. As a measurement area, accepted was a square or a rectangular with defined surface area F. The number of eutectic colonies \( N_f \) per one surface area unit is determined from the equation:

\[
L_K = \frac{(z + 0.5w + 1)}{F}
\]

where:
- \( z \) – number of cells completely included inside the measurement area,
- \( w \) – number of cells partially included inside the measurement area.

Analysis of chemical composition influence on the number of eutectic graphite colonies was based on structure examinations of 40 castings. Separately analysed was mottled cast iron (20 castings) and a cast iron in that no chills occurred (20 castings). Ranges of chemical compositions of all the alloys are given in Table 1.

| Element | Concentration [%] | minimum | maximum | average |
|---------|-------------------|---------|---------|---------|
| C       |                   | 1.9     | 3.8     | 3.1     |
| Si      |                   | 1.4     | 2.6     | 2.0     |
| Ni      |                   | 3.1     | 9.4     | 5.5     |
| Mn      |                   | 3.2     | 6.3     | 3.9     |
| Cu      |                   | 0.1     | 5.9     | 3.2     |
| P       |                   | 0.14    | 0.16    | 0.15    |
| S       |                   | 0.03    | 0.04    | 0.03    |
| \( S_C \)|                  | 0.60    | 1.08    | 0.97    |

Preliminary observations showed strong influence of solidification speed of castings for number and size of eutectic colonies. In order to eliminate this factor, all the measurements were carried-out at ca. 5 mm from the surface of shafts dia. 30 mm cast in shell moulds. The presented results are average values of 5 measurements taken for each casting.

3. Results

It results from literature data [4] that the number of eutectic graphite colonies is strictly related to eutecticity degree of the cast iron. This is obvious in the case of partially chilled castings made of a hypoeutectic cast iron with low value of saturation coefficient \( S_C \). As this coefficient increases, the number of eutectic colonies increases because of increasing susceptibility of the cast iron to graphitization.

In the examined castings, individual eutectic graphite colonies appear when \( S_C \) exceeds 0.60. With increasing \( S_C \) value, the number of colonies also increases. Examples of this tendency is shown in Fig. 1.

![Fig. 1. Eutectic graphite colonies in cast iron containing:](image)

In the castings made of cast iron with \( S_C \) values of 0.62 (Fig. 1a), 0.69 (Fig. 1b), 0.76 (Fig. 1c) and 0.95 (Fig. 1d), numbers of eutectic graphite colonies falling in average per 1 cm\(^2\) of the surface are 90, 200, 310 and 520, respectively. Their size changes slightly only and depends rather on concentration of individual elements in the cast iron. Quantitative evaluation of influence of the eutectic saturation degree on the number of colonies was based on analysis of 18 partially chilled castings. The obtained results are shown in Fig. 2. The trend line calculated on their ground is in form of a second degree polynomial:

\[
L_K = -1340 + 3515 \cdot S_C - 1708 \cdot S_C^2 [cm^{-2}],
\]

where:
- standard deviation: \( \sigma = 45 \text{ cm}^{-2} \)
- determination coefficient: \( R^2 = 0.71 \)
- Fisher's test: \( F_{(1,19)} = 48.7 \)
- significance level: \( p < 0.01 \)

The relatively large scatters of the measurement results in relation to the calculated values indicate that influence of individual elements on the \( S_C \) value is different from their effect on the number of graphite eutectic cells in mottled cast iron. It can be explicitly said on the ground of (2) that increase of \( S_C \) value is accompanied by increase of the number of cells. However, intensity of this process decreases as the composition comes near to the eutectic composition.
Direction and intensity of influence of individual elements on the number of eutectic colonies in the mottled cast iron was determined by linear stepwise regression. The obtained equation is as follows:

\[ L_{K_P} = -685 + 265 \cdot C + 77 \cdot Si + 18 \cdot Ni - 20 \cdot Mn + 17 \cdot Cu \text{[cm}^{-2}] \]  

where:

- standard deviation: \( \sigma = 45 \text{ cm}^{-2} \)
- determination coefficient: \( R^2 = 0.88 \)
- Fisher’s test: \( F_{(5,15)} = 31.9 \)
- significance level: \( p < 0.001 \)

It can be decidedly said that carbon is the element most strongly affecting the number of eutectic colonies. Effect of silicon, the second element with respect to the influence intensity, is over three times weaker. Both these elements increase the number of eutectic colonies. Nickel and copper influence the \( L_{K_P} \) value in similar way, although much weaker. It is only manganese that slightly reduces the number of colonies.

Total influence of all the elements can be expressed using (3) by the equation for carbon equivalent:

\[ E_{kw_{C,P}} = C + 0.29 \cdot Si + 0.07 \cdot Ni - 0.08 \cdot Mn + 0.06 \cdot Cu \text{[%]} \]  

from where:

\[ L_{K_P} = -685 + 265 \cdot E_{kw_{C,P}} \text{[cm}^{-2}] \].

Analysis of influence of chemical composition on the number of eutectic colonies in non-chilled cast iron (20 castings) was carried-out for each element separately. Value of the coefficient \( S_C \) ranged from 0.92 to 1.08.

Carbon is the element that, from among the analysed ones, to a highest degree affects the number and sizes of graphite colonies. In the alloys containing 3.01% C (Fig. 4a); 3.29% C (Fig. 4b); 3.45% C (Fig. 4c) and 3.65% C (Fig. 4d), the number of eutectic cells per 1 cm² is 420, 460, 530 and 575, respectively. Assuming a linear relationship, increasing carbon concentration by 0.1% results in increase of the average number of eutectic cells per 1 cm² of a metallographic polished section by over 25, see Fig. 4e.

Influence of silicon on the number of eutectic colonies was evaluated on the ground of structure analysis of four alloys containing 1.4; 1.6 and 2.0% Si, see Fig. 5. The number of eutectic cells per 1 cm² of a polished section was 520 (Fig. 5a), 540 (Fig. 5b), 530 (Fig. 5c) and 550 (Fig. 5d), respectively. Increasing silicon concentration by 0.1% Si results in slight
increase of the number of eutectic cells, in average by 3 cells per 1 cm$^2$, see Fig. 5e.

Fig. 5. Effect of silicon concentration on number of eutectic colonies:

a) 3.66% C, 1.4% Si, 6.5% Ni, 4.0% Mn, 2.8% Cu, ($S_C = 1.07$),
b) 3.71% C, 1.6% Si, 6.7% Ni, 4.0% Mn, 2.8% Cu, ($S_C = 1.11$),
c) 3.63% C, 1.8% Si, 6.5% Ni, 4.0% Mn, 2.7% Cu, ($S_C = 1.09$),
d) 3.56% C, 2.0% Si, 6.6% Ni, 3.9% Mn, 2.7% Cu, ($S_C = 1.10$),
e) diagram of the relationship

Influence of manganese on the number of eutectic colonies was determined, like in the previous case, on the ground of structure analysis of four alloys containing 3.4; 4.4; 5.2 and 6.3% Mn, see Fig. 6.

As opposed to carbon and silicon, manganese reduces the number of eutectic colonies. In the range between 3.4 and 6.3% Mn, increasing manganese concentration by 0.1% reduces the number of eutectic cells in average by 3 cells per 1 cm$^2$.

Like silicon, nickel increases the number of eutectic colonies, see Fig. 7. Comparison of structures of the castings containing 3.1; 4.7; 6.2 and 7.7% Ni indicates that increasing nickel concentration by 0.1% increases the number of eutectic cells in average by 3 cells per 1 cm$^2$, see Fig. 7e.

Influence of copper on the number of colonies is more complex, see Fig. 8. In the alloys containing 0.1; 1.7; 4.2 and 2.9% Cu, copper increases the number of eutectic colonies. The average number of colonies per 1 cm$^2$ is 360 (Fig. 8a), 410 (Fig. 8b) and 510 (Fig. 8c), resp. This means that between 0.1 to 4.2% Cu, increasing copper concentration by 0.1% increases of the number of eutectic cells in average by over 3 cells per 1 cm$^2$. However, in the cast iron containing 3.30% C, 2.4% Si, 4.1% Ni, 3.7% Mn and 5.8% Cu the number of cells decrease to 480 per 1 cm$^2$, see Fig. 8d. In this alloy, exceeded was limit solubility of copper in the melt (presence of primary cupric phase), so it is supposed that this fact directly results in decreased number of eutectic cells. As a result, the trend line describing copper influence is in form of a second degree polynomial, see Fig. 8e.
Fig. 7. Effect of nickel concentration on number of eutectic colonies:

a - 3.35% C, 2.2% Si, 3.1% Ni, 3.4% Mn, 2.9% Cu, (SC = 1.01),

b - 3.31% C, 2.1% Si, 4.7% Ni, 3.3% Mn, 2.9% Cu, (SC = 1.01),

c - 3.24% C, 2.0% Si, 6.2% Ni, 3.2% Mn, 2.8% Cu, (SC = 1.00),

d - 3.27% C, 2.0% Si, 7.7% Ni, 3.2% Mn, 2.8% Cu, (SC = 1.04),

e - diagram of the relationship

The influence intensity and direction of individual elements on the number of created eutectic colonies can be different depending on kind and concentration of the other additions composing the cast iron. With this respect, like in the partially chilled castings, a complex analysis was carried-out taking into account simultaneous influence of all the elements on the number of graphite eutectic colonies present in the examined cast iron. The analysis was performed for 19 alloys, see Figs. 3 to 7. The cast irons with exceeded limit solubility of copper were not considered in the analysis. Values of the saturation coefficient SC ranged from 0.92 to 1.08. Because of relatively large number of independent variables (5 variables) in respect to the number of cases (19 castings), a linear model of the relationship was accepted. The following equation was obtained:

\[ \text{LK}_{\text{NZ}} = -375 + 174 \cdot \text{C} + 22 \cdot \text{Si} - 20 \cdot \text{Mn} + 31 \cdot \text{Cu} \, [\text{cm}^{-2}], \]  

where:

- standard deviation: \( \sigma = 18 \, \text{cm}^{-2} \)
- determination coefficient: \( R^2 = 0.84 \)
- Fisher's test: \( F_{(5,13)} = 15.8 \)
- significance level: \( p < 0.001 \).

Fig. 8. Effect of copper concentration on number of eutectic colonies:

a - 3.52% C, 2.6% Si, 4.2% Ni, 3.8% Mn, 0.1% Cu, (SC = 1.05),

b - 3.43% C, 2.5% Si, 4.2% Ni, 3.8% Mn, 1.7% Cu, (SC = 1.04),

c - 3.36% C, 2.5% Si, 4.1% Ni, 3.7% Mn, 4.2% Cu, (SC = 1.06),

d - 3.30% C, 2.4% Si, 4.1% Ni, 3.7% Mn, 5.8% Cu, (SC = 1.08),

e - diagram of the relationship

The predominant role of carbon permits presenting influence of chemical composition on the number of eutectic colonies by means of carbon equivalent, that, after transforming (3), takes the form:

\[ \text{Ekw}_{\text{C}, \text{NZ}} = \text{C} + 0.13 \cdot \text{Si} + 0.16 \cdot \text{Ni} – 0.11 \cdot \text{Mn} + 0.24 \cdot \text{Cu} \, [%], \]  

from where:

\[ \text{LK}_{\text{NZ}} = \text{Ekw}_{\text{C}, \text{NZ}} \]  

The points on the diagram refer to the real number of eutectic colonies in the examined castings. No significant qualitative differences were found in comparison to the results obtained for single elements (equations describing trend lines, see Figs. 4e to 8e). Significant quantitative differences appear in the case of carbon and manganese only. In comparison to the analyses for single elements, values of the regression coefficients in the equation (6) indicate more intensive influence of both carbon and manganese.
4. Summary

Results of the performed analyses indicate that in the alloyed cast iron Ni-Mn-Cu, like in the case of the plain cast iron, carbon is the element that mostly decides the number of eutectic colonies. However, intensity of this effect decreases with increasing eutectic saturation degree of cast iron. In the alloys with low $S_C$ (mottled cast iron), increasing carbon concentration by 0.1% results in increased number of eutectic colonies, in average by 26.5 cells per 1 cm$^2$ of the casting surface, see (3). This results mainly from graphitizing action of carbon. In non-chilled castings, increase of the number of colonies is smaller, reaching in average 17, see (6). However, carbon is still the element of the most intensive influence on LK. It seems that in this case the number of graphite colonies grows because carbon increases speed of graphite nucleation.

Influence of the other elements on the number of eutectic colonies is much weaker. Direction and intensity of their effect is determined by values of regression coefficients of the equations (3) and (6). It was determined on their ground, how much the number of eutectic colonies per 1 cm$^2$ of a casting will change when concentration of individual elements changes by 0.1%, see Table 2.

In partially chilled castings (mottled cast iron), silicon increases the number of graphite colonies in the way comparable with carbon. Increasing silicon concentration by 0.1% results in increased LK value in average by 7.7 per 1 cm$^2$. Effect of the other elements is much weaker. Nickel and copper (within solubility limits in a liquid alloy) increase the number of colonies, but manganese decreases it. It is to be supposed that the effect of individual elements results from their influence on chilling tendency of the cast iron.

In the castings with no chills, the effect of individual elements is slightly different. The influence of silicon decreases, but that of nickel and copper increases. It seems that the influence of these elements on LK results from their influence on carbon activity in the liquid alloy.

Table 2.
Effect of elements (0.1%) on LK

| Element (0.1%) | Mottled cast iron | Grey cast iron |
|----------------|-------------------|---------------|
| C              | 26.5              | 17.4          |
| Si             | 7.7               | 2.2           |
| Mn             | -2.0              | -2.0          |
| Ni             | 1.8               | 2.8           |
| Cu             | 1.7               | 3.1           |

It results from the presented research that in the alloyed cast iron Ni-Mn-Cu, in spite of high total content of the elements stabilizing austenite, it is carbon that decides the number of eutectic graphite colonies.

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