Undercooling, Cooling Curves and Nodule Count for Near-eutectic Thin-walled Ductile Iron Castings

Wojciech KAPTURKIEWICZ,* Andriy BURBELKO and Marcin GÓRNY

AGH University of Science and Technology, Reymonta 23, 30-059 Krakow, Poland.

(Received on August 31, 2013; accepted on November 5, 2013)

A solidification model for ductile iron, including Weibull formula for nodule count, has been presented. The principal assumptions of the kinetic nature of growth, depending on undercooling in respect of the eutectic equilibrium temperature and austenite liquidus line, have been adopted, disregarding the diffusion processes, which was justified by the rapid course of the crystallization process in a thin-walled casting. From this model, the following parameters can be determined: cooling curves, kinetics of austenite and eutectic nucleation, austenite and eutectic growth velocity, and volume fraction.

The correctness of the mathematical model has been experimentally verified by comparison with literature data in the range of the most significant factors, which include temperature field, the value of maximum undercooling, the value of minimum and maximum temperature on a cooling curve, maximum undercooling, the recrystallization and graphite nodule count interrelated with the casting cross-section.

KEY WORDS: modeling; ductile iron; solidification; thin walled casting.

1. Introduction

Nodular graphite cast iron, also known as ductile iron, ductile cast iron, nodular graphite iron and spheroidal graphite iron (SGI), has major applications in critical engineering parts due to its excellent properties and castability. The mechanical, physical and utilization properties of this cast iron depend on the number of the graphite grains and on the individual matrix constituents. The prediction of local properties of castings is an old dream of foundrymen and casting designers which nowadays is becoming every day more true due to the development of our computational abilities. To predict the mechanical properties of nodular graphite iron it is necessary to simulate the refinement and volume fraction of the individual structural constituents present in this cast iron.

Most of the computer modeling programs described in literature is devoted to eutectic transformation under the pre-assumed stationary conditions of carbon diffusion in austenite. In Refs. 5 and 6) a physical model of solidification of the nodular graphite cast iron which quantitatively accounts for the formation of non-eutectic austenite during cooling and solidification of hyper-eutectic as well as hypo-eutectic cast iron has been presented. In investigations described in Ref. 7), process modeling techniques have been applied to describe the multiple phase changes occurring during solidification and subsequent cooling of near-eutectic nodular graphite cast iron, based on the internal state variable approach.

According to Ref. 8), at the eutectic temperature, austenite dendrites and graphite spheroids nucleate independently in the liquid. This mechanism has been confirmed in the experiments and modeling by both-for hypo-eutectic and eutectic, as well as hyper-eutectic SGI. The non-stationary diffusion in nodular graphite iron casting has been presented in Ref. 13).

In Refs. 14 and 15) some formulae have been introduced for uninodular models assuming that a basic unit of solidification is formed by a graphite nodule and austenite shell covering this nodule, whereas multinodular models assume that each unit of solidification is formed by a grain of dendritic austenite containing several graphite spheroids.

The aim of this study was to develop a simple kinetic, non-diffusional model of SGI solidification, using knowledge available so far for near-eutectic composition, confronted with experiments in respect of both the cooling curves as well as graphite nodule count in a real thin-walled casting.

2. Model of Process

The model combines a macro-model (heat transfer in casting) with micro-model (nucleation and growth of grains). Heat transfer in casting depends on the cooling conditions created by foundry mold.

According to the analysis of reference literature presented above, it has been assumed that, irrespective of the fact that molten metal may have the chemical composition corresponding to the eutectic one (carbon equivalent $C_E \approx 1.0$), it is possible that austenite dendrites and graphite spheroids will nucleate independently in the liquid. The mechanism of the diffusion growth of nodular graphite (allowed for in Ref. 13), among others) has been disregarded, assuming that the leading factor in the process of the grain growth is the kinetic undercooling at an austenite-liquid phase boundary.
including the growth of both eutectic grains and austenite dendrites (for which an approximate spherical growth with amendment in Kolmogorov equation has been adopted). It has also been assumed that the eutectic nucleate count is equivalent to graphite nucleate count.

2.1. Heat Transfer

The macro temperature field in casting-mold system is:

$$\frac{dT}{dt} = aN^2T + \frac{q}{c_v} \quad \text{(1)}$$

where \(T, \tau\) – temperature and time, \(s, \lambda\) – thermal conductivity, \(W \cdot m^{-1} \cdot K^{-1}, \rho\) – density, \(kg \cdot m^{-3}\), \(q\) – heat generation rate of phase transformations, \(J \cdot m^{-3} \cdot s^{-1}\); \(c\) – volumetric specific heat, \(J \cdot m^{-3} \cdot K^{-1}\) (lower index \(i\) denotes casting - \(c\) or mold - \(m\)).

The impact of the casting mold was allowed for using a Chvorinov’s rule, calculating the heat flux into the mold with regard to the mold parameters.

2.2. Volume Fraction

In order to calculate the true volume fraction of solid, one must include the effect of grain impingement. The true volume fraction of solid \(f_s\) can be described by Kolmogorov equation:

$$f_s = 1 - e^{-\omega} \quad \text{(2)}$$

where \(\Omega\) - so-called "extended" volume of all solid grains. Value of the \(\Omega\) is non-dimensional and is calculated as a relation between the total volume of ideal shape of all grains and volume of the mother phase.

According to Kolmogorov:

$$\Omega = \frac{4\pi}{3} s \int_0^{t'} \alpha'(t') \left( \int u(t') dt' \right)^{3/2} dt' \quad \text{(3)}$$

where \(t'\) - nucleation time, \(s, \alpha'(t')\) - rate of the grain nucleation, \(m^{-3} \cdot s^{-1}\); \(u(t)\) – linear velocity of the growth, \(m^{-1} \cdot s^{-1}\);

$$\left( \int u(t') dt' \right) \text{ – grain radius, } m \quad s - \text{non-dimensional shape coefficient (e.g. } s = 1 \text{ for globular grains and } s = 0.3 \text{ for dendrite grains).}$$

2.3. Nucleation

It is well known that liquid cast iron contains undissolved particles of various sizes. Hence, upon alloy undercooling beyond a critical value, sizes of these particles exceed the threshold level needed for stable growth. Hence, growing nuclei are continually developed until the time when the metal attains its maximum level of undercooling. Afterward, with the progress of recalescence, no new nuclei form because all the particles larger than the critical size (which corresponds to maximum undercooling) were already exhausted. Activation of smaller particle substrates as active nuclei will require undercooling, which will have to exceed the maximum value. To compute the density of the formed austenite nuclei \((m^{-3})\) the following relationship has been adopted:

$$N_s = \Psi_s \Delta T_{s}^{2} \quad \text{(4)}$$

where \(\Psi_s\) – nucleation coefficient of austenite grains, \(m^{-3} \cdot K^{-2}\); \(\Delta T_{s}\) – undercooling with the reference to equilibrium austenite temperature, \(K\).

For number of graphite nodule count \(N_v\) \((m^{-3})\) the Weibull formula has been used:

$$N_v = N_i \exp(-b/\Delta T_v) \quad \text{(5)}$$

where \(N_i\) – overall nucleation site density in the melt, \(m^{-3}\); \(b\) – nucleation coefficient, \(K\); \(\Delta T_v\) – undercooling with the reference to equilibrium eutectic temperature, \(K\).

\(N_i\) can be identified with a maximum value of nodule count, which is theoretically possible, if all the substrates for nucleation are used separately. A similar equation, but with the \((1-f_s)\) factor (where \(f_s\) – solid fraction) was used by Dardati et al.59 in 2009, after Boeri (PhD thesis in 1989).

2.4. Growth of Grains

The austenite linear growth velocity \((m \cdot s^{-1})\) the classic law \((22, 23)\) is used:

$$u_s = \mu_s \Delta T_{s}^{2.5} \quad \text{(6)}$$

where \(\mu_s\) – austenite growth coefficient, \(m \cdot s^{-1} \cdot K^{-2.5}\).

Rate of growth for eutectic grains:

$$u_v = \mu_v \Delta T_{v}^{2} \quad \text{(7)}$$

where \(\mu_v\) – eutectic growth coefficient, \(m \cdot s^{-1} \cdot K^{-2}\).

2.5. Equilibrium Temperature and Segregation

The equilibrium temperatures \(T_\gamma\) for solidifying austenite and \(T_v\) for eutectics (\(°C\)) can be represented with the linear functions of carbon, silicon and phosphorus concentration in liquid cast iron \((22, 23)\)

$$T_\gamma = 1.636 - 113(C_L + 0.25Si_L + 0.5P_L) \quad \text{(8)}$$

$$T_v = 1.154 + 5.25Si_L - 14.88P_L \quad \text{(9)}$$

where \(C_L, Si_L, P_L\) – weight percent of \(C, Si\) and \(P\) in liquid, respectively.

The solute concentration in the solidifying phases is strongly influenced by the magnitude of the diffusion coefficients. Hence, for solute of relatively high diffusivity (e.g. carbon in austenite), the solute concentration in the liquid phase can be approximated with the mass balance.

Alternatively, the Scheil equation has been used in dealing with low diffusivity solutes, such as in the case of silicon or phosphorus in austenite.

A set of the above equations, after transformation to a differential form, was solved by the finite difference method, applying an iteration procedure (secant method). The simulation program operating in Delphi environment was prepared for one dimensional (1D) casting geometry.

The verification of the model was confronted with the results of an experiment which in more detail was described in Refs. 16 and 17.

2.6. Parameters of Experiment and for Modeling

The parameters adopted in modeling are given below and in Tables 1 and 2. The first three parameters in Table 1 concern the nucleation and growth, the next ones – thermal conductivity, specific heat and density of casting and mold material. The results of experiments (and cooling curves from the experiments) shown in Table 3 were taken for comparison with the modeling.
where

\[ \Delta T_s = k \cdot \frac{S_c}{N_v} \]

and \( g = N_s \) = 1.5 \times 10^5 mm\(^{-3}\) and with \( \lambda = 0.55 \) (simulation I), for the thickness of 4 and 8 mm, the value of \( \lambda = 0.70 \) (simulation II, experiments), \( 17) \) and for the thickness of 6 and 10 mm (simulation III experiments) \( 16) \) - the value of \( \lambda = 1.03 \) W·m\(^{-1}\)K\(^{-1}\).

### Table 1. Parameters for modeling.

<table>
<thead>
<tr>
<th>Property</th>
<th>Meaning</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Psi,_{s} )</td>
<td>Nucleation coefficient of austenite grains</td>
<td>( 5 \times 10^6 )</td>
<td>cm(^{-3}) K(^{-2})</td>
</tr>
<tr>
<td>( \mu_s )</td>
<td>Austenite growth coefficient</td>
<td>( 5 \times 10^{-9} )</td>
<td>cm s(^{-1}) K(^{-2})</td>
</tr>
<tr>
<td>( \mu_e )</td>
<td>Eutectic growth coefficient</td>
<td>( 1 \times 10^{-7} )</td>
<td>cm s(^{-1}) K(^{-2})</td>
</tr>
<tr>
<td>( \lambda_c )</td>
<td>Thermal conductivity</td>
<td>0.37</td>
<td>W cm(^{-1})K(^{-1})</td>
</tr>
<tr>
<td>( c_s )</td>
<td>Specific heat</td>
<td>0.753</td>
<td>J cm(^{-3})K(^{-1})</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Density</td>
<td>7.3</td>
<td>g cm(^{-3})</td>
</tr>
<tr>
<td>( L_s )</td>
<td>Austenite solidification heat</td>
<td>1952.4</td>
<td>J cm(^{-1})</td>
</tr>
<tr>
<td>( L_e )</td>
<td>Eutectic solidification heat</td>
<td>2028.8</td>
<td>J cm(^{-1})</td>
</tr>
<tr>
<td>( \lambda_m )</td>
<td>Thermal conductivity</td>
<td>0.0103</td>
<td>W cm(^{-1})K(^{-1})</td>
</tr>
<tr>
<td>( c_m )</td>
<td>Specific heat</td>
<td>1.09</td>
<td>J cm(^{-3})K(^{-1})</td>
</tr>
<tr>
<td>( \rho_m )</td>
<td>Density</td>
<td>1.73</td>
<td>g cm(^{-3})</td>
</tr>
</tbody>
</table>

### Table 2. Chemical composition of cast iron, wt%. 

<table>
<thead>
<tr>
<th>Melt</th>
<th>Chemical composition, wt %</th>
<th>Cast temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Si</td>
<td>P</td>
</tr>
<tr>
<td>1</td>
<td>3.62</td>
<td>2.68</td>
</tr>
<tr>
<td>2</td>
<td>3.73</td>
<td>2.57</td>
</tr>
<tr>
<td>3</td>
<td>3.62</td>
<td>2.65</td>
</tr>
<tr>
<td>4</td>
<td>3.51</td>
<td>2.70</td>
</tr>
<tr>
<td>5</td>
<td>3.57</td>
<td>2.64</td>
</tr>
<tr>
<td>6</td>
<td>3.65</td>
<td>2.10</td>
</tr>
<tr>
<td>Mean value of ( F, L )</td>
<td>3.58</td>
<td>2.48</td>
</tr>
</tbody>
</table>

### Table 3. Experimental data.

<table>
<thead>
<tr>
<th>Plate thickness ( d, ) mm</th>
<th>( N_v) ( \times 10^3, ) mm(^{-3})</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>100</td>
<td>Ref. 17), Fig. 3</td>
</tr>
<tr>
<td>2</td>
<td>81</td>
<td>Ref. 16)</td>
</tr>
<tr>
<td>2.8</td>
<td>50</td>
<td>Ref. 17), Fig. 3</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>17.5</td>
</tr>
<tr>
<td>4</td>
<td>35</td>
<td>Ref. 16)</td>
</tr>
<tr>
<td>4.3</td>
<td>28</td>
<td>17.5</td>
</tr>
<tr>
<td>6</td>
<td>18.6</td>
<td>Ref. 16)</td>
</tr>
<tr>
<td>8</td>
<td>12</td>
<td>Ref. 17), Fig. 3</td>
</tr>
<tr>
<td>10</td>
<td>10.6</td>
<td>Ref. 16)</td>
</tr>
<tr>
<td>10.6</td>
<td></td>
<td>10.6</td>
</tr>
</tbody>
</table>

Coefficient of eutectic saturation \( S_c \) (Table 2) was calculated as:

\[
S_c = \frac{\%C - 0.3 \times \%Si - 0.36 \times \%P}{4.26 - 0.3 \times \%Si - 0.36 \times \%P} \tag{10}
\]

where \( \%C, \%Si, \%P \) – weight percent of \( C, Si, P \).

Own trials and prior information stated in the literature\( 12)\) showed a variation in the boundary conditions (heat transfer coefficient and heat flux on the surface of casting). From own simulation tests and a comparison with the temperature curves obtained by the experiment it follows that the boundary conditions change during solidification (which can be allowed for as a function dependent on the fraction solidified according to \( 17)\) but to a larger extent they change with a change in the casting thickness. After the tests it has been assumed that these changes will be expressed with different values of the conductivity coefficient for mold material \( \lambda_m \). It has been assumed that for the casting thickness of 1.5, 2.8 and 3 mm, the value of the coefficient \( \lambda_m = 0.55 \) (simulation I), for the thickness of 4 and 8 mm, the value of \( \lambda_m = 0.70 \) (simulation II, experiments), \( 17)\) and for the thickness of 6 and 10 mm (simulation III experiments) \( 16)\) - the value of \( \lambda_m = 1.03 \) W·m\(^{-1}\)K\(^{-1}\).

### 3. Discussion of Results

The development of computer programs, based on the assumed mathematical model of the solidification process of casting made from nodular graphite iron, had as a main objective checking the viability and reproducibility of this model, and investigating some of its specific features. Selected elements of the model (temperature field and number of grains) were verified by experiments. The successful results of this verification have confirmed the assumptions made previously that the developed model faithfully reflects the reality. Assuming now the correct functioning of mathematical model and of the respective simulation program enabling practical operation of this model, numerous process-related results were obtained. Although, so far, not all of them have been checked in practical application, they can still give important information on the mechanism of the examined process.

The simulation computations were carried out on plates for which the experimental data were available. The thermophysical parameters were taken from the data given in literature. The plate geometry and the starting test conditions were adapted to those applied previously in the experiments. \( 16,17)\)

Studies\( 16,20)\) based on a comparison with the experiment have indicated that, to have the results consistent with the experiment, the values of \( N_v \) and \( b \) must be individually selected for each melt. An analysis of the melting results summarized in Table 3, using the developed simulation program, has showed that (with similar and typical conditions for liquid metal treatment), one value of \( N_v \) can be assumed, and the value of the coefficient \( b \) will be functionally dependent on the casting thickness – **Fig. 1**.

Using the simulation program, a relationship shown in **Fig. 1** has been derived. All of the following simulation calculations were obtained at a constant value of \( N_v = 1.5 \times 10^5 \) mm\(^{-3}\) and with the nucleation coefficient \( b \) according to the above functional relationship.

**Figures 2(a), 3(a) and 4(a)** show cooling curves for the plate thickness of 2.8, 6 and 10 mm; the corresponding course of undercooling \( \Delta T_s \) and nodule count \( N_v \) are shown in Figs. 2(b), 3(b) and 4(b). The indicated values refer to the middle part of casting. The curves drawn in solid line rep-
resent the simulation results, while dots show the experimental values according to Ref. 16) or Ref. 17). The simulation lines in Figs. 2(a) and 2(b) were plotted for a mean value of the chemical composition for melts F, J and L (Table 2), whereas in the case of the plate thickness of 6 and 10 mm – for melt 2. Figures 2(a), 3(a) and 4(a) also show the run of an equilibrium temperature curve of eutectic transformation $T_e$ as a result of $\text{Si}$ and $\text{P}$ segregation during the solidification.

The temperature curves from both simulation (solid line) and experiment (dotted line) show a point of visible change of cooling curve gradient, marked with letter $A$. Its presence is due to the effect of the nucleating and growing grains (dendrites) of austenite.

Some attention deserves the fact that studies in both variants, i.e. simulation and experiment, were carried out on the Fe–C–Si–P alloy of practically eutectic composition (the point of eutectic saturation $S_e = 1.05 – 1.07$ for Ref. 16) data and 1.01 – 1.03 for Ref. 17) data) which, considering an equilibrium course of the solidification process, allows us to expect total absence of the austenite in structure. Yet, modeling carried out for a non-equilibrium system has revealed an important share of austenite (disclosed in further drawings). Another proof is the result of modeling excluding the possibility of austenite nucleation – Fig. 3(a), where the plotted cooling curve is basically different from both the

\[
b = -0.0843d^6 + 3.3558d^3 - 24.587d^2 + 116.57d - 105.34
\]
experimental curve (dots) and simulation curve (solid line). The characteristic point \( A \) (change of the line curvature), which reflects the thermal effect caused by the growing dendrites of austenite, is also present in Figs. 2(a) and 4(a). These results confirm previous data reported in the literature.\(^{21}\)

Figures 5–9 show the values obtained by simulation for the data given in Table 2 compared with the experimental data given in Table 3 and in publications.\(^{16,17}\)

Simulations were carried out for the thermo-physical parameters given in Table 1. Own trials and prior information stated in the literature\(^{12}\) showed a variation in the boundary conditions (heat transfer coefficient and heat flux on the surface of casting). From own simulation tests and a comparison with the temperature curves obtained by the experiment it follows that the boundary conditions change during solidification (which can be allowed for as a function dependent on the fraction solidified according to),\(^{12}\) but to a larger extent they change with a change in the casting thickness. After the tests it has been assumed that these changes will be expressed with different values of the conductivity coefficient for mold material \( \lambda_m \). It has been assumed that for the casting thickness of 1.5, 2.8 and 3 mm, the value of the coefficient \( \lambda_m = 0.0055 \) (simulation I), for the thickness of 4 and 8 mm, the value of \( \lambda_m = 0.007 \) (simulation II, experiments),\(^{17}\) and for the thickness of 6 and 10 mm (simulation III experiments)\(^{16}\) - the value of \( \lambda_m = 0.0103 \text{ W \cdot cm}^{-1}\text{K}^{-1} \).

Figure 5 shows, for the examined casting thicknesses, the value of minimum temperature \( T_{\text{min}} \) at an instant of the maximum undercooling \( \Delta T_{\text{max}} \), Fig. 6 shows the maximum temperature \( T_{\text{max}} \) achieved after \( \Delta T_{\text{max}} \), while Fig. 7 shows the value of recalescence, that is, the difference between \( T_{\text{max}} \) and \( T_{\text{min}} \). Figure 8 shows dependence the maximum undercooling \( \Delta T_{\text{max}} \) of plate thickness, while Fig. 9 shows the nodule count as a function of the casting thickness. All the results obtained indicate the following:

- obvious dependence of the measured quantities on the casting thickness;
- simulation results are close to measurement results between the values obtained by simulation and experiment.

For the casting thickness of 6 and 10 mm, the values obtained in three different melts were shown. The largest differences between these values are for the recalescence (Fig. 7), which can be explained by measurement uncertainty, as in simulation calculations the differences in the recalescence values between the melts did not exceed 2 K. Of course, these differences can also be ascribed to some simplifications in the model adopted, but it has to be remembered that recalescence in the measurements (Fig. 4 in Ref. 17) was also characterized by a large scatter of values (about 22 K).

The final number of nodule count depends on the value
of maximum undercooling which, in turn, depends on process parameters. For the similar pouring temperature, casting configuration and mold material, it depends on the casting thickness only, as shown in Fig. 7. With increasing casting thickness, the value of the maximum undercooling is decreasing, analogically to the nodule count. The values obtained by modeling have been compared with the values measured in experiments.\textsuperscript{16,17} Besides comparison of the cooling curves, this is the most significant criterion to evaluate the correctness of a mathematical model of the process and of the developed simulation program.

Figure 10 shows small differences in the final volume of austenite and eutectic on the casting cross-section, where the distinguishing feature is a relatively high volume content of austenite (about 20\%) in alloy of the eutectic saturation ratio equal to 1.05, which de facto means a eutectic alloy. As mentioned previously, it is the consequence of allowing for non-equilibrium conditions of the solidification process. It is also a confirmation of the above mentioned literature data. The results of simulation calculations indicate some variations in the content of primary austenite depending on the casting thickness, as shown in Fig. 11. There is also a variation in austenite volume for castings of the same thickness values (6 and 10 mm) but poured from different melts, although \( S_p \) values are similar. This is probably due to a stronger influence of the Si content than would result from the \( T_c \) or \( S_p \) dependence. This, however, requires a separate analysis.

4. Conclusions

In the developed model of nodular graphite iron casting solidification, the correctness of the mathematical model has been verified with experimental data given in the literature in the range of the most significant factors, which include temperature field, the value of minimum and maximum temperature on a cooling curve, maximum undercooling, recalescence and the graphite nodule count interrelated with casting cross-section. The verification was carried out on thin-walled castings of 1.5−10 mm, where the boundary conditions are the source of very significant deviations from the equilibrium process (undercooling of 30−80 K).

It has been shown that in eutectic cast iron (\( S_p \approx 1 \)) the nucleation and growth of austenite grains are of great importance. The cooling curves obtained by modeling excluding and including the possibility of austenite nucleation are quite different and the experimental curve is close to the case with austenite.

Undoubtedly, an experimental verification of other results obtained by simulation is recommended, especially as regards the content of austenite and eutectic on the casting cross-section.

Acknowledgements

This work was supported by NCN project No. N N508 621 140.

REFERENCES

2) S. M. Yoo, A. Ludwig and P. R. Sahm: Solidification Processing, Renmor House, Univ. of Sheffield, Sheffield, (1997), 494.
19) W. Oldfield: Trans. ASM, 59 (1966), 945.