

Graphite Nodule and Cell Count in Cast Iron

E Fraś*, M. Górný*, H. F. López**

University of Science and Technology, Mickiewicza 30, Cracow, Poland

**University of Wisconsin-Milwaukee, P.O. Box 784, Milwaukee, WI 53201, USA

Received on: 05.04.2007; Approved for printing on: 27.04. 2007

Abstract

In this work, a model is proposed for heterogeneous nucleation on substrates whose size distribution can be described by the Weibull statistics. It is found that the nuclei density, N_{nuc} can be given in terms of the maximum undercooling ΔT_m by $N_{nuc} = N_s \exp(-b/\Delta T_m)$; where N_s is the density of nucleation sites in the melt and b is the nucleation coefficient ($b > 0$). When nucleation occurs on all the possible substrates, the graphite nodule density, $N_{V,n}$ or eutectic cell density N_V after solidification equals N_s . In this work, measurements of $N_{V,n}$ and N_V values were carried out on experimental nodular and flake graphite iron castings processed under various inoculation conditions. The volumetric nodule $N_{V,n}$ or graphite eutectic cell N_V count, were estimated from the area nodule count, $N_{A,n}$ or eutectic cell count N_A on polished cast iron surface sections by stereological means. In addition, maximum undercooling ΔT_m were measured using thermal analysis. The experimental outcome indicates that volumetric nodule $N_{V,n}$ or graphite eutectic cell N_V count can be properly described by the proposed expression $N_{V,n} = N_V = N_s \exp(-b/\Delta T_m)$. Moreover, the N_s and b values were experimentally determined. In particular, the proposed model suggests that the size distribution of nucleation sites is exponential in nature.

Keywords: Heterogeneous nucleation, Cast iron, Nodule count, Cell count, Weibull statistics

1. Introduction

In flake graphite cast iron, the austenite-graphite eutectic solidification process is concomitant with the formation of eutectic cells that are more or less spherical. These eutectic cells consist of interconnected graphite plates surrounded by austenite. In general, increasing the eutectic cell count in a given cast iron leads to:

- Increasing strength of cast iron (through a reduction in ferrite and an increase in graphite type A) [1],
- A reduction chill of cast iron [2] and as a consequence make possible production machinable castings, free from the high hardness carbide eutectic,
- Increasing pre - shrinkage expansion [3,4]. If the mould lacks sufficient rigidity, expansion of the casting during solidification can cause unsoundness in the form of internal porosity or surface sinking defects, particularly in those parts

of casting last to solidify. The probability of developing unsoundness, increase with the cell count.

Ductile iron is a modern engineering material whose production is continually increasing. Increasing the nodule count in a given ductile cast iron leads to:

- Increasing strength and ductility in ADI iron [5],
- Reduced microsegregation of alloying elements [6,7], and improved microstructural homogeneity. Here, the type of eutectic transformation (stable or metastable) is also influenced due to the re-distribution of alloying elements,
- A reduction in the chilling tendency of cast iron [8,9],
- Increasing pre - shrinkage expansion [3],
- Increasing fraction of ferrite in the microstructure [10].

Since each eutectic cell and nodule of graphite are the product of a graphite nucleation event, cell and nodule count measurements can be used to establish the graphite nucleation susceptibility of a given cast iron.

In the published literature, cell count N_V or nodule count $N_{V,n}$ are often related to the maximum undercooling ΔT_m , by empirical expressions of the type [11].

$$N_{V,n} = \sum_{i=0}^3 \alpha_i (\Delta T_m)^i \quad (1)$$

where α_i , and $i = 0,1,2,3$, are experimentally determined nucleation constants. Since these equations are obtained from fitting experimental data, they do not have a definite physical meaning, even though they have been widely used. Hence, the aim of the present work is to propose a simple analytical model for heterogeneous nucleation. In the proposed model, expressions are derived as a function of ΔT_m , which are qualitatively similar to Eq. (1), however the nucleation constants have a plausible physical interpretation.

2. Theoretical model

Assuming that each nucleus of graphite gives rise to a single nodule of graphite or eutectic cell, the expected volumetric nodule count, $N_{V,n}$ or volumetric cell count, N_V can be described by the nuclei count N_{nuc} (number of graphite nuclei per unit volume of liquid metal) as

$$N_{V,n} = N_V = N_{nuc} \quad (2)$$

In liquid melts, particles - nucleation sites can be described by a continuous random variable of a Weibull distribution with the probability density given by [12]

$$f(l) = n a l^{n-1} \exp(-a l^n) \text{ for } l \geq 0 \quad (3)$$

where l is the nucleation site size, and n is a positive integer

For a given n and an average site size l_a , the parameter a can be written as

$$a = \left[\frac{\Gamma(1 + n^{-1})}{l_a} \right]^n \quad (4)$$

where Γ is the Euler function. N_s and $f(l)$ can be related to each other through the function $\Lambda(l)$ as

$$\Lambda(l) = N_s f(l) \quad (5)$$

Accordingly, the density of nucleation sites can be found by integrating $\Lambda(l)$ as

$$N_s = \int_0^{\infty} \Lambda(l) dl \quad (6)$$

Since not all of the set of sites take an active role in the nucleation process, the minimum site size, l_m for a given undercooling, ΔT_m from which a nucleus can grow is determined by (see Fig. 1)

$$AB = l_m = 2r^* \sin \theta \quad (7)$$

$$r^* = \frac{2\sigma}{\Delta T \Delta S} \quad (8)$$

where r^* is the critical nucleus size, θ is the wetting angle, ΔS is the entropy of solution of graphite, and σ is the nucleus-melt interfacial energy. From Eqs. (7) and (8), the minimum site size can be given by

$$l_m = \frac{\Omega}{\Delta T} \quad (9)$$

where:

$$\Omega = \frac{4\sigma \sin \theta}{\Delta S} \quad (10)$$

Figure 1d shows a cooling curve where the arrows indicate the extent of undercooling at the beginning of solidification. Notice that within the time interval from t_b to t_m or undercooling from $\Delta T = 0$ to

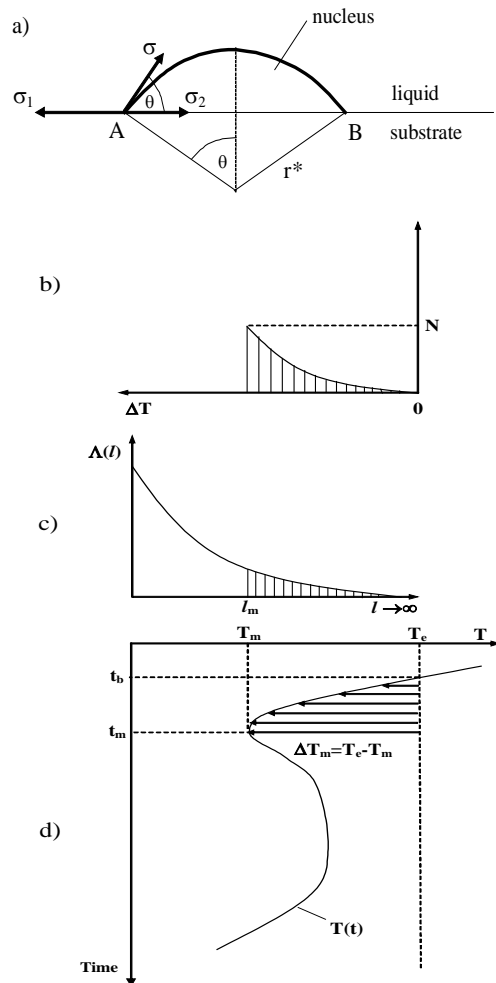


Fig.1 Schematic representation of solid nucleus on a solid substrate (a), nuclei density (b), sites Weibull distribution (c) and cooling curve (d)

$\Delta T = \Delta T_m$ sites with sizes greater than l_m become active for nucleation (Fig.1c). If on all sites of sizes $l > l_m$ nuclei are formed, then at ΔT_m which determines l_m , the nuclei density N_{nuc} can be described by

$$N_{nuc} = \int_{l_m}^{\infty} \Lambda(l) dl \quad (11)$$

Substituting $\Lambda(l)$, (Eq.(5)) in Eq. in (11) and using Eqs. (2),(3), (4) for $n = 1$ yields

$$N_{nuc} = N_{V,n} = N_V = N_S \exp\left(-\frac{b}{\Delta T_m}\right) \quad (12)$$

where b is the nucleation coefficient given by

$$b = \frac{\Omega}{l_a} \quad (13)$$

3. Experimental procedure

The proposed model was experimentally corroborated for the ductile and flake graphite cast iron. In case of ductile iron, the experimental melts were made in a low frequency (50 Hz) induction furnace of 8000 kg capacity. The raw materials employed were iron scrap, steel scrap and ferro-silicon alloys. After melting and preheating at 1485°C, molten iron was poured into a casting ladle where the spheroidization treatment was implemented using the cored wired injection method. Different inoculants in various amounts were used in order to promote various degrees of maximum undercooling. In case of cast iron the liquid was inoculated using FOUNDRYSIL (73-75% Si, 0.75% Al, 0.75-1.25% Ca, 0.75-1.25% Ba) with a 2 - 5 mm granulation added as a 0.5% of the charge weight. Samples of inoculated iron were taken at various successive time intervals of 1.5; 5; 10; 15; 20 and 25 minutes from the instant of inoculation. The chemical composition of the experimental cast irons are given in Tables 1 and 2. The molten cast iron was poured into 6, 10, and 16 mm thick plate molds of 100 mm in length, and in 22 mm thick plates of 140 mm in length. All the plates had a common gating system. The thermocouple terminals (Pt/PtRh10) were placed at the geometrical center of each mold cavity and cooling curves have been obtained.

Table 1.
Chemical composition of ductile iron

No	C, %	Si, %	Mg, %
1	3.62	2.68	0.05
2	3.73	2.57	0.04
3	3.62	2.65	0.03
4	3.71	2.77	0.04
5	3.75	2.77	0.03
6	3.61	2.67	0.04

Table 2.
Chemical composition of cast iron

No	Time after inoculation min.	C %	Si %
I/1	1.5	3.14	1.98
I/2	5	3.18	2.05
I/3	10	3.16	2.04
I/4	15	3.21	2.01
I/5	20	3.20	2.08
I/6	25	3.16	2.08

The maximum undercooling for individual plates was established using

$$\Delta T_m = T_e - T_m \quad (14)$$

where

$$T_e = 1153,9 + 5,25 Si \quad (15)$$

In the above expression, T_e is the stable equilibrium temperature of the graphite eutectic and C, Si are the carbon and silicon contents in cast iron, respectively.

Metallographic evaluations of nodule counts were made on samples cut from the plate geometrical centers. The area nodule count, $N_{A,n}$ (number of graphite nodule per unit area of metal) was measured using a Leica Q Win quantitative analyser. In ductile iron the volumetric nodule count, $N_{V,n}$ was estimated from $N_{A,n}$ using the Wiencek expression [13]

$$N_{V,n} = \sqrt{\frac{N_{A,n}^3}{g_{gr}}} \quad (16)$$

where g_{gr} is the volumetric fraction of graphite, with $g_{gr} \approx 0.12$ at room temperature.

The area cell count N_A , (number of cells per unit area of metal) was determined using the, so-called variant II of the Jeffries method, which after applying the Saltykov formula can be written as [14].

$$N_A = \frac{N_i + 0.5N_c + 1}{A} \quad (17)$$

where: N_i is the number of cells inside a rectangle W , N_c is the number of cells that intersect a W side but not its corners, and A is the surface area of W . The graphite eutectic exhibits a granular microstructure. Hence, as a first approximation it may be assumed that the spatial cell configurations follow the so-called Poisson-Voronoi model [15]. Then, the stereological formula given below for cell density N_V can be employed in this work.

$$N_V = 0.5680 (N_A)^{3/2} \quad (18)$$

4. Results and discussion

Considering the experimental ΔT_m and $N_{V,n}$ and N_V values for a given melt, correlation expressions according to Eq. (12) were derived and nucleation coefficients, N_s and b are given in Tables 3 and 4. In these calculations the correlation coefficients are relatively high ($R \approx 0.88-0.99$) suggesting that in each case, the relationships between N_V , $N_{V,n}$ and ΔT_m described by Eq. (12) are in good agreement with the experimental outcome.

From Tables 2 and 4 it is evident that the inoculation effect expressed in terms of cell count is a function of the time counted from the instant of metal bath inoculation. After 25 minutes from the onset of inoculation, the changes in cell count are negligible and this time can be considered as a reference point. Accordingly, any cell count changes can be correlated to the dimensionless time

$$t = \frac{t}{t_f} \quad (19)$$

where t is the time from the instant of metal bath inoculation and $t_f = 25 \text{ min.}$ is the time beyond which total fading of the inoculation effect is observed

Using a polynomial approximation for data given in Tables 2 and 4, regression expressions can be found

$$b = 96.9 + 122.6 t - 59.2 t^2 \quad (20)$$

$$N_s = 10^6 \left(6.5 - 0.8 t - 5.3 t^2 \right) \quad (21)$$

(21)

Table 3.
Nucleation coefficients for ductile cast iron

No.	Correlation coefficients	Nucleation coefficients	
		N_s cm^{-3}	b $^{\circ}\text{C}$
1	0.88	$4.13 \cdot 10^7$	58
2	0.98	$5.69 \cdot 10^7$	60
3	0.96	$4.01 \cdot 10^7$	42
4	0.98	$4.24 \cdot 10^7$	20
5	0.96	$5.16 \cdot 10^7$	20
6	0.97	$4.85 \cdot 10^7$	43

Table 4.
Nucleation coefficients for flake graphite cast iron

No.	Correlation coefficients	Nucleation coefficients	
		N_s cm^{-3}	b $^{\circ}\text{C}$
I/1	0.99	$6.1 \cdot 10^6$	104
I/2	0.99	$6.8 \cdot 10^6$	119
I/3	0.99	$4.4 \cdot 10^6$	135
I/4	0.86	$5.4 \cdot 10^6$	154
I/5	0.98	$1.3 \cdot 10^6$	152
I/6	0.99	$8.4 \cdot 10^5$	162

Considering Eqs. (12), (20), and (21) an expression can be obtained for the cell count N_V as a function of ΔT_m and t after inoculation as

$$N_V(t) = N_s(t) \exp\left[-\frac{b(t)}{\Delta T_m}\right] \quad (22)$$

Where $N_s(t)$ and $b(t)$ are given by Eqs. (20) and (21), respectively. From equations (20) - (22) results that as ΔT_m increases N_V also increases, while prolonged times, t after inoculation has an opposite effect. It is worth to note Lesoult et al work [16] and Wessen et al work [17] where they were using ductile iron after different metallurgical treatment and where ΔT_m and nodule count $N_{V,n}$ were also estimated. Points in figures 4 and 5 show results of these experimental results. Values of coefficient N_s and b can be estimated similarly as before and are given in Tables 5 and 6. The correlation coefficients R are high and are situated in the range of 0.93 - 0.99. In Fig. 6 it is shown results of calculations for melt No II/6 according to Eqs (1) and (12). It is worth pointing out (Fig.6) that in a wide range of undercooling Eq. (12) has better matching to

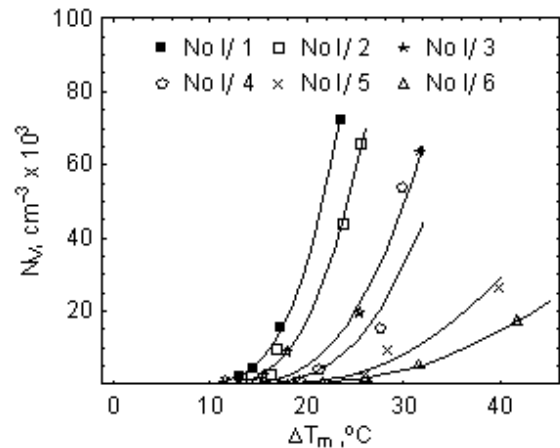


Fig.2. Plots of volumetric eutectic cell count versus maximum degree of undercooling

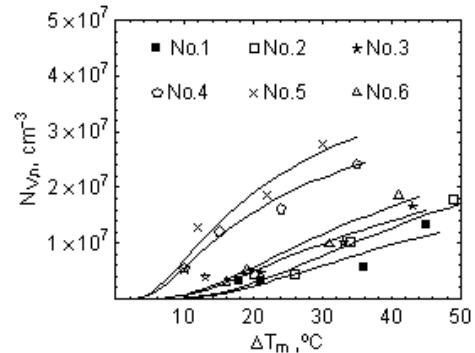


Fig.3. Volumetric nodule count versus maximum degree of undercooling

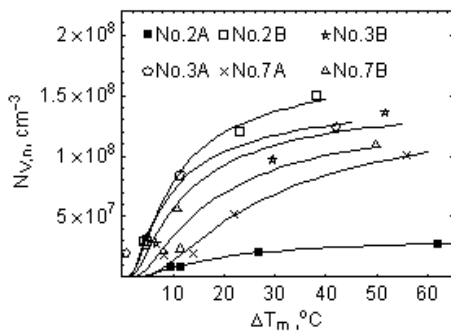


Fig.4. Volumetric nodule count versus maximum degree of undercooling

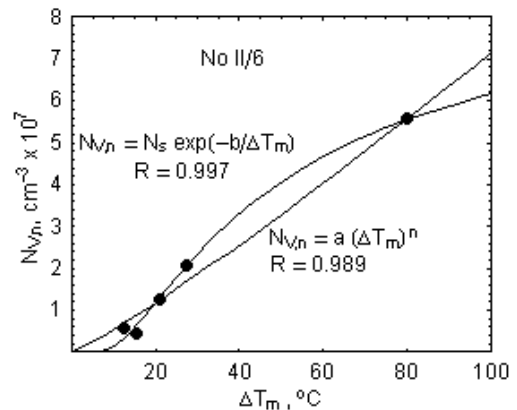


Fig.6. Volumetric nodule count versus maximum degree of undercooling

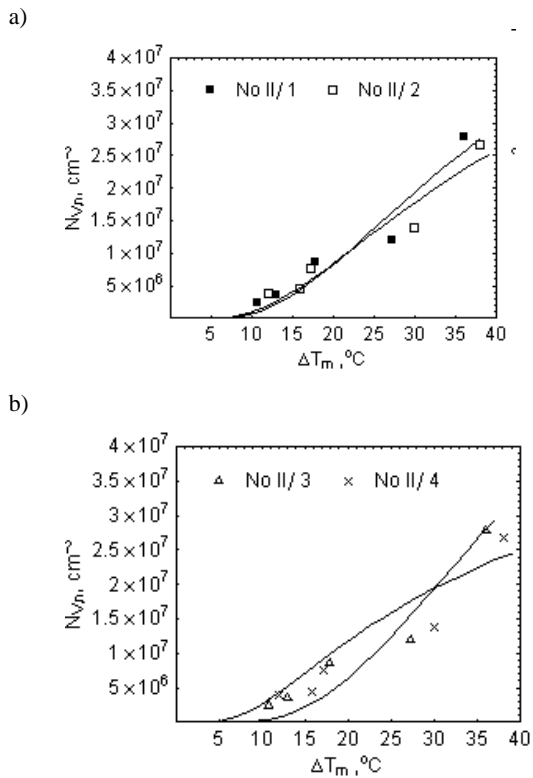


Fig.5. Volumetric nodule count versus maximum degree of undercooling

experimental results than Eq. (1). Moreover, empirical Eq. (1) is a concave function, which approach infinity, while Eq. 12 is a convex function, which approach to $N_s = \text{const}$.

It is also interesting to present experimental results (Fig 7) of an extended investigation made by Mamapaey [18] between eutectic cell count in uninoculated and inoculated flake graphite cast iron and rather small range of undercooling ΔT_m . Once again the correlation coefficients of relationships given in Fig.7 are high ≈ 0.98 .

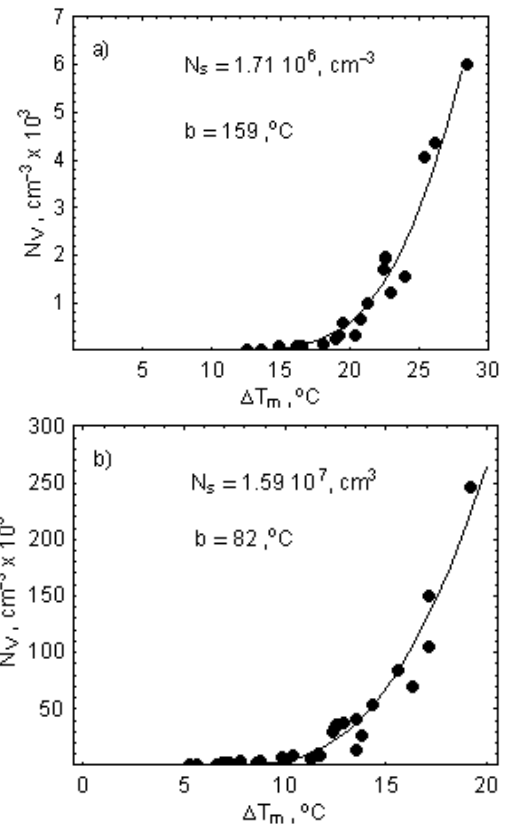


Fig.7. Plots of volumetric eutectic cell count versus maximum degree of undercooling a) uninoculated and b) inoculated cast iron

From Tables 3-6, for the different melts (different chemical composition and different type of metallurgical treatment and in consequence for liquid with different the substrate nucleation size distribution), it is not surprising the fact that nucleation

Table 5.
Nucleation coefficients

No	Nucleation coefficients	
	N_s cm^{-3}	b $^{\circ}\text{C}$
2A	$3.55 \cdot 10^7$	15.43
2B	$1.80 \cdot 10^8$	8.24
3A	$1.51 \cdot 10^8$	9.80
3B	$1.50 \cdot 10^8$	7.36
7A	$1.55 \cdot 10^8$	24.55
7B	$1.45 \cdot 10^8$	14.73
2A, 2B - C = 3.76 %; Si = 2.39 %; 3A, 3B - C = 3.79%; Si = 2.60 %, 7A, 7B - C = 3.66 %; Si = 2.55 %;		

Table 6.
Nucleation coefficients

No	N_s cm^{-3}	b $^{\circ}\text{C}$
II/1	$1.05 \cdot 10^8$	51
II/2	$7.94 \cdot 10^7$	45
II/3	$5.26 \cdot 10^7$	30
II/4	$1.74 \cdot 10^8$	66
II/5	$1.62 \cdot 10^8$	54
II/6	$9.31 \cdot 10^7$	41
II/1 – II/4 C = 3.66%; Si = 2.40%; P = 0.012% II/5 – II/6 C = 3.72%; Si = 2.38%; P = 0.011%		

coefficients N_s and b for a given melt are different from each other. However, in each case and independent from authors of experiments it can be state that N_v or $N_{v,n}$ are an exponential function of ΔT_m and it is evident that they can be described by analytical Eq. (12), thus confirming that the proposed theory is in good agreement with the experimental evidence.

4. Conclusions

1. In this work a theory is proposed that relates the density of nuclei, and hence the graphite nodule and eutectic cell count with the maximum degree of undercooling. This theoretical analysis is experimentally verified.
2. It has been shown that the nodule and eutectic cell count in cast iron can be described by an exponential expression, which is a function of the maximum undercooling, ΔT_m and of the

References

- [1] E. Fraś, C. Podrzucki, Inoculated Cast Iron, (in polish) AGH, nr.675, Cracow, 1978.
- [2] E. Fraś, H. Lopez, A theoretical analysis of the chilling susceptibility of hypoeutectic Fe-C alloys, Acta Metallurgica and Materialia, 1993, vol. 41, no.12, s.3575
- [3] E. Fraś, H. Lopez H, Generation of International Pressure During Solidification of Eutectic Cast Iron. AFS Transactions, 1994, vol. 102, s. 597.
- [4] H. Morrogh, The status of the metallurgy of cast irons, Journal of The Iron and Steel Institute, January, 1968, s.1.
- [5] L. Jincheng, R. Elliot, The influence of cast structure on the austempering of ductile iron. International Journal of cast Metals Researches, 1999, vol.11, p. 407.
- [6] G. Lesoult, M. Castro, J. Lacaze, Solidification of Spheroidal Graphite Cast Iron: III Microsegregation related effects. Acta Materialia, 1999, vol. 47, p. 3779.
- [7] M. Achmadabadi, E. Niyama, T. Ohide, Structural control of 1 % Mn ADI aided by modeling of microsegregation. AFS Transactions, 1994, vol. 97, p. 269.
- [8] A. Javaid, J. Thompson, K. Davis, Critical conditions for obtaining carbide – free microstructure in thin-wall ductile iron. AFS Transactions, 2002, vol. 102, p. 889.
- [9] A. Javaid, J. Thompson, M. Sahoo, K. Davis, Factors affecting formation of carbides in thin-wall DI castings, AFS Transactions 1999, vol. 99, p. 441.
- [10] D. Venugopalan, A Kinetic Model of the $\gamma \rightarrow \alpha + \text{Gr}$ Eutectoid Transformation in Spheroidal Graphite Cast Iron, Metallurgical and Materials Transactions, 1990, vol. 21 A, p.913
- [11] E. Fraś, K. Wiencek, M. Górny, H. Lopez, Graphite Nodule and Eutectic Cell Count In Cast Iron, Theoretical Model Based on Weibull Statistics and Experimental Verification, Metallurgical and Materials Transactions A, 2007, vol. 38A, pp.385-395
- [12] W. Eadie., D. DriJard., E.F., James., M. Roos., B. Sadoulet., Statistical methods in experimental physics, London, 1982, Amsterdam, North-Holland.nodular cast iron, Acta Stereologica, 1986, vol. 5/2, p. 319.
- [13] K. Wiencek, J. Ryś, The estimation of Fe_3C particle density in steel by simple counting
- [14] J. Ryś, Stereology of materials, Fotobit, Cracow, 1995.
- [15] J. Osher, Quantitative Gefuengenanalyse, DVG Leipzig-Stuttgart, 1994.
- [16] G. Lesoult, M. Castro., J. Lacaze, Acta Materialia, 1998, vol.46,p.997.
- [17] M. Wenssen, I. Svensson, R. Agaard, International Journal of cast Metals Researches, 1999, vol.11, p. 351.
- [18] F. Mampaey, International Foundry Congress, Mosow, 1988.