



EFFECT OF AN OXY-SULPHIDE INOCULANT ENHANCER ON GRAPHITE PARAMETERS IN THE MOULD INOCULATED COMPACTED GRAPHITE CAST IRON

M. C. FIRICAN*, I. C. STEFAN, I. RIPOȘAN

POLITEHNICA University of Bucharest, 313 Spl. Independentei, RO-060042, Bucharest, Romania

*Corresponding author;

e-mail: firicanmihailciprian@gmail.com

ABSTRACT

In compacted/vermicular graphite cast iron production, inoculation is applied to limit the formation of carbides, but usually this treatment also promotes nodular graphite with improved nodularity. The main objective of the present paper is to examine the graphite phase characteristics in these irons, as affected by different in the mould inoculation variants, for resin sand mould castings. Graphite shape factors illustrate the loss of compactness of the graphite particles in the surface layer of the casting and its variation with cooling rate changes, especially with the circularity expression. In the surface layer, up to 0.5 mm from the cast surface, inoculation increased graphite nodularity, with the performance of the inoculant enhancer alloy [OS-IE] treated iron also promoting a high nodularity through the section of casting. A specific effect of inoculation with this alloy is the formation of a high number of small graphite nodules, which is accompanied by higher nodularity and the highest levels for the circularity and sphericity shape factors. Inoculation with the (Ca+OS-IE) dual addition led to the highest compacted/vermicular graphite formation sensitivity, with limited nodular graphite formation.

KEYWORDS: inoculant, inoculant enhancer, inoculation, compacted graphite cast iron, calcium ferrosilicon, oxide forming elements, graphite, shape factors, nodularity, sulfur, oxygen

1. Introduction

Of the present production, iron castings represent more than 70% of all castings worldwide mainly due to the package of physical and mechanical properties associated with competitive costs. In the family of cast irons, compacted/vermicular graphite iron is increasingly attractive for industrial applications. Vermicular or compacted graphite cast iron (C/VGI or CGI) is a type of cast iron in which the graphite is shaped between flake/lamellar and nodular/spheroidal. Compared with flake graphite in grey iron, compacted/vermicular (C/V) graphite is shorter and thicker and shows a curved, more rounded shape intermediate between flake and fully nodular graphite. The name vermicular graphite (VG) relates to the unusual graphite shape, which resembles a worm hence the inference, wormlike graphite. The alternate name, CGI, is associated with a measurement of the graphite shape, the ratio of width

to length, which in CGI is much higher than that of grey iron.

The graphite shapes in CGI consist of vermicular graphite and also some nodular or spheroidal graphite; generally, more than 70% compacted graphite must be present, with the remainder nodular graphite, not flake graphite. Graphite nodularity, usually expressed as a nodular/vermicular graphite ratio (%) is an important control factor for this grade of iron. The presence of lamellar (flake) graphite is prohibited, while the amount of nodular graphite must also be restricted.

Compacted/vermicular graphite cast iron is obtained by a treatment of the base iron in two steps: a compacting or nodulizing first treatment followed by a second graphitizing step using an inoculant, similar to ductile iron production. Elements known for their nodulizing capability, such as magnesium and/or rare earth elements (Ce, La, Pr, Nd, Y) are employed in the first step, while inoculating elements,



such as Ca, Ba, Sr, Ce, La are used in the final treatment.

A residual content of 0.01–0.03% of nodulizing elements is necessary, depending on the presence of anti-nodularizing elements and solidification (cooling) rate, which is influenced by the characteristics of both the castings and mould media. The first treatment must ensure an adequate nodulizing potential to avoid lamellar graphite formation or an excess of nodular graphite, and the role of the second treatment is to avoid carbides forming as well as encourage graphitization. In ductile iron production, inoculation is applied after Mg-treatment to enhance graphite nodularity, which for specific CGI castings could be more than is acceptable.

Several studies proposed and then investigated whether graphite nucleation occurs on sulfide and/or oxide particles, which are formed after the molten iron treatment [1-4]. They found that compounds of magnesium-calcium sulfides act as nucleation sites for graphite particles in irons treated with Mg-bearing ferrosilicon alloys. Consequently, some elements, such as sulphur and oxygen appear to be important to sustain nodular graphite formation.

The main objective of the present paper is to examine the effects of in the mould inoculation of a Mg, RE-MgFeSi treated compacted/vermicular graphite iron, at low anti-nodularizing potential of the base iron. Three inoculant variants were tested: (a) a conventional Ca-FeSi alloy, (b) an oxy-sulphide inoculant enhancer alloy [(OS-IE)] added with a conventional Ca-FeSi alloy, and (c) the OS-IE alloy added as the inoculant treatment.

2. Experimental procedure

The base iron was melted in a coreless induction furnace (acid lined, 150 kg, 2400 Hz). The charge mix contained 50 wt.% high purity pig iron and 50 wt.% cast iron scrap with a 520 g graphite powder addition to correct the iron analysis (fig. 1). The thermal regime during the iron melt process was as follows: superheat temperature $T_s=1550$ °C; Mg treatment temperature $T_m=1530$ °C; pour temperature $T_p=1350$ °C.

The base iron was tapped into a tundish cover nodulizing ladle containing FeSiMgRE alloy (table 1). After the nodulizing treatment the melt was poured into a specially designed test mould with a central downsprue feeding Mg-treated iron simultaneously to four separate reaction test chambers: (1) as an un-inoculated reference; (2) 0.1 wt.% Ca bearing FeSi alloy; (3) 0.02 wt.% oxy-sulphide inoculant enhancer; (4) 0.04 wt.% Ca bearing FeSi alloy + 0.015 wt.% [(OS-IE)] alloy. Table 1 illustrates the chemical composition of the inoculants used.

W₃ chill wedge samples (ASTM A367-85 specification, dimensions 19 x 38 x 100 mm, cooling modulus, CM = 3.5 mm), plate samples (4.5 mm thick) and round bar samples (25 mm diameter) were cast in furan resin sand moulds. A Furan resin (3.0 wt.%) - P-Toluol Sulphonic Acid (PTSA) (6.53 wt.%S content and 1.5 wt.% addition) bonded silica sand (95.5 wt.%) [FRS-PTSA] moulding system was used. No reclaimed moulding material was used and the moulds contained approx. 0.1 wt.%S. In this study, round bar samples were used for structure analysis and thin plate samples for chemical analysis of the final castings.

3. Results and discussion

The final chemical composition of the treated irons is slightly hypereutectic, with a carbon equivalent CE = 4.3 – 4.4% (table 2). All the castings contained the nodulizing element Mg at a low level, appropriate for compacted graphite cast iron ($Mg_{res} = 0.019 - 0.023\%$). There is a small difference in the content of trace elements in the heats. The cumulative influence of the pearlite forming elements in the Mg-treated irons (Factor P_x) and anti-nodularising elements effect (Factor K) [5] is included in table 2. It could be concluded that the content of anti-nodularising elements in the Mg-treated irons is sufficiently low ($K < 0.7$). The pearlite factor $P_x = 3.9 - 4.9$ indicates a medium pearlite forming tendency, for conventional solidification conditions.

Micrographs included in figure 2 illustrate the typical structure of these experimental irons at the same solidification rate 3.96 mm from the surface in a 25 mm round bar. This structure is characteristic for the experimental cast irons chemistry, at around 0.02% Mg_{res} .

$$CE = \%C + 0.3(\%Si + \%P) - 0.03\%Mn + 0.4\%S \quad (1)$$

$$P_x = 3.0 (\%Mn) - 2.65 (\%Si - 2.0) + 7.75 (\%Cu) + 90 (\%Sn) + 357 (\%Pb) + 333 (\%Bi) + 20.1 (\%As) + 9.60 (\%Cr) + 71.7 (\%Sb) \quad (2)$$

$$K = 4.4 (\%Ti) + 2.0 (\%As) + 2.4 (\%Sn) + 5.0(\%Sb) + 290(\%Pb) + 370(\%Bi) + 1.6(\%Al) \quad (3)$$

A mixture of compacted and nodular graphite morphologies characterizes these structures, with a relatively high nodularity level (fig. 3). According to figure 3, graphite nodularity is influenced by the applied treatment (un-inoculated and inoculated irons), solidification rate (greater distance from the surface, slower cooling rate) and inoculation choice [Ca-FeSi, OS-IE only or (Ca-FeSi + OS-IE)].

For all of tests, the lowest graphite nodularity (less than 20%) was obtained at the casting surface, despite the highest cooling rate characteristic of this

area, as a result of high heat transfer from the metal to the mould. Generally, a higher solidification cooling rate promotes greater graphite nodularity in Mg-treated irons.

Conversely the same area of casting experiences S-transfer from the mould since P-Toluol Sulphonic Acid (PTSA) influence is at the highest level, which can explain the reduction in graphite nodularity. It is assumed that SO₂ will result from the combustion of

PTSA in the resin sand at the casting temperature. SO₂ is absorbed at the metal surface, after it has dissociated into atoms. It either diffuses into the molten metal, or will be reduced by iron to form FeS and FeO in solution, which can react with magnesium in the molten iron. As a consequence Mg is partially consumed prior to solidification, and the nodulising potential of the treated iron decreases [6].

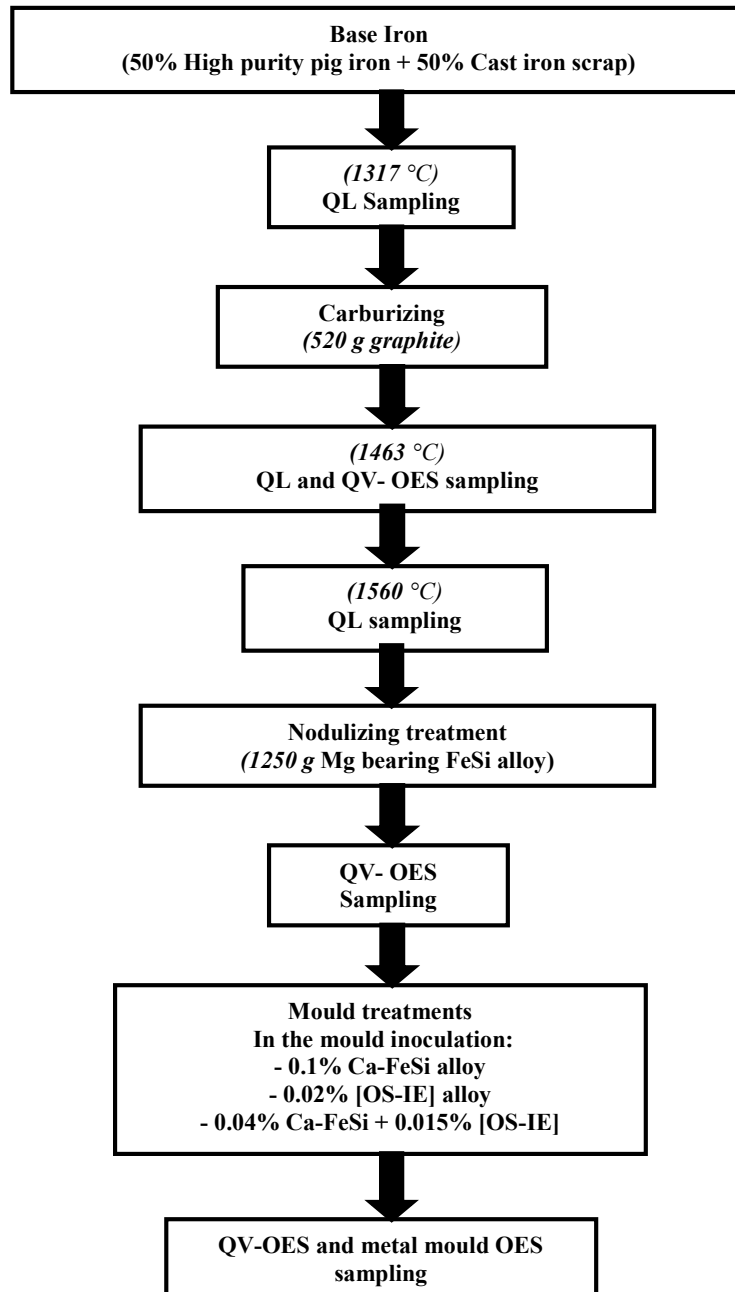


Fig. 1. Technical schedule [OES/QV - Optical emission spectroscopy; QL - Quick Lab]

It was found that for the furan resin-PTSA moulding system, sulphur delivered by the mould is an important contributor to graphite degeneration in

the surface layer of Mg treated iron castings. Uncoated FRS-PTSA moulds, which have sulphur in the binder, promoted degenerate graphite in the

surface layer of the test castings, with the thickness of this layer increasing as residual magnesium content decreased: compacted graphite iron is more sensitive to this abnormal surface layer compared to nodular graphite iron, as is a ductile iron with a marginal nodularising potential for similar solidification conditions [7-9]. The lowest nodularity in the surface layer of a casting was obtained in the un-inoculated iron, while inoculation generally increased the

graphite nodularity in the experimental conditions in this layer for all the treatment variants. The highest nodularity appears in the iron treated with only the inoculant enhancer alloy [OS-IE], despite a sulphur contribution from this material. This effect is due to the activity of sulphur in the enhancer alloy, which combines with active elements in the melt, promoting the formation of numerous small particles that can act as nucleating agents for graphite.

Table 1. Chemical composition of the treatment alloys (wt.%)

Alloy	Si	Ca	Mg	Al	TRE	Ce	La	Ba	S	O
FeSiMgRE [Nodulizer]	44.71	1.02	5.99	0.91	0.25	0.15	0.10	0.035		
Ca-FeSi [Inoculant]	73.80	1.02		0.77						
OS-IE [Enhancer]	36.90	16.29	1.96	5.74					8.11	2.67

*TRE-total rare earth elements

Table 2. Chemical composition of cast irons

Inoculation	Chemical Composition [wt.%]							Control Factors	
	C	Si	Mn	P	S	Mg	CE	K	P _x
Un-inoculated	3.59	2.49	0.43	0.040	0.023	0.020	4.42	0.645	3.879
Ca-FeSi inoculation	3.58	2.48	0.41	0.058	0.029	0.019	4.42	0.551	4.416
[OS-IE] inoculation	3.58	2.45	0.47	0.046	0.021	0.023	4.40	0.649	4.694
Ca-FeSi + [OS-IE] inoculation	3.45	2.44	0.38	0.057	0.030	0.019	4.28	0.502	4.954

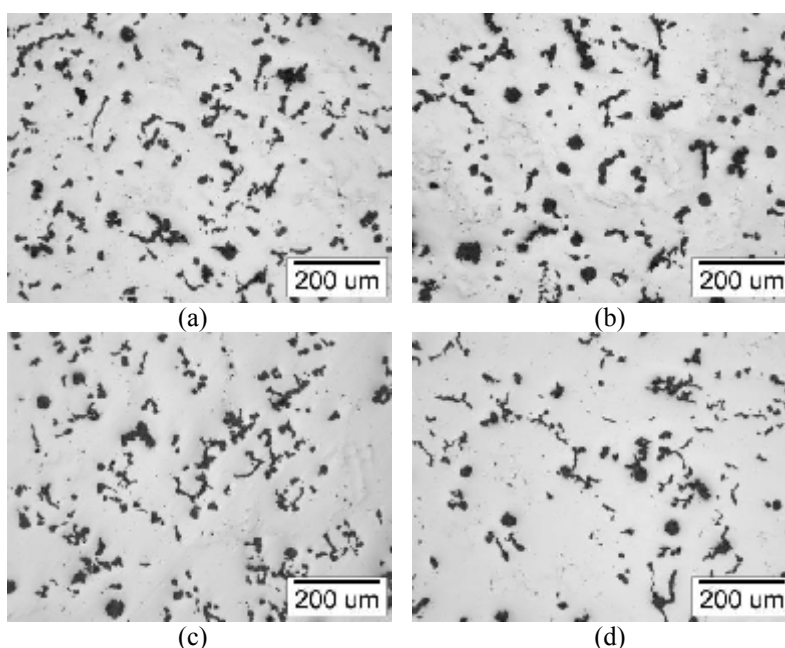


Fig. 2. Graphite structure at 3.96 mm from the surface [a)-un-inoculated; b) Ca; c) OS-IE; d) Ca+OS-IE; un-etched]

According to figure 3, the surface layer with lower nodularity thickness is generally no more than 0.5mm. After this, the graphite nodularity is within the 35-50% range, with limited influence from the cooling rate, as defined by distance from the casting surface. Two groups of irons appear to be, concerning the graphite nodularity level: un-inoculated and OS-IE treated irons (40-50%) and Ca and (Ca+OS-IE) treated irons (35-40%), respectively.

Table 3 and figure 4 include the main shape factors used for evaluating the graphite morphology

on a section of the 25 mm diameter round bar samples. The graphite characteristics were evaluated with Automatic Image Analysis [analySIS® FIVE Digital Imaging Solutions software]. Two groups of representative shape factors were considered with higher levels of circularity and sphericity describing more graphite particle compactness, with a value of 1.0 for spherical particles. Circularity and sphericity are different approaches to describe the roundness of a particle. Elongation and aspect ratio at lower levels defined a higher degree of compactness.

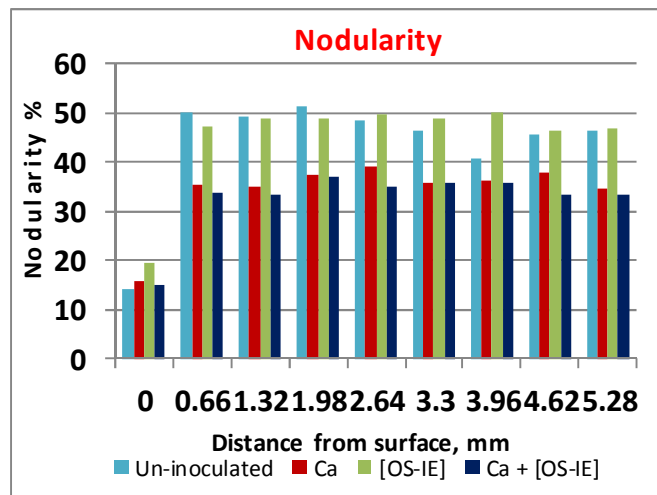


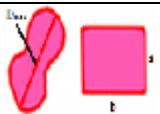



Fig. 3. Graphite nodularity at different distances from the sample surface and different inoculation treatments

Table 3. The main shape factors used for graphite morphology evaluation

No.	Parameter	2D- Geometrical features	Definition
1	Circularity (F_c) [$F_c=4\pi A/P_r^2$] $F_c \leq 1$		Provides informations about the particle "roundness" by using the area (A) and the real perimeter (P_r) of the measured particle
2	Sphericity (F_s) $F_s \leq 1$		Describes the spheroidal shape or "roundness" by using the central moments, $\mu_{p,q}$ $\mu_{p,q} = \iint (x-x_c)^p (y-y_c)^q f(x,y) dx dy$ p,q-central moment indices x_c, y_c -center of gravity coordinates
3	Elongation (E) [$E= D_{max}/a$] $E > 1$		The ratio of the maximum diameter (D_{max}) and the equivalent rectangle shortest side (a) (the rectangular which has the same area and perimeter as the particle)
4	Aspect Ratio [$AR=b/a$] $AR > 1$		The maximum ratio of height (b) and width (a) of a rectangular boundary for the measured particle

Graphite shape factors values confirmed the influence of the casting surface layer at the lower degree of compactness of graphite particles, as all are

different compared to the body of the castings, beyond any influence of the mould (surface *versus* body): $F_c = 0.49 - 0.58 < 0.63 - 0.73$, $F_s = 0.26 - 0.28$

$< 0.35 - 0.43, E = 2.4 - 2.7 > 1.7 - 2.2$ and $AR = 2.0 - 2.2 > 1.6 - 1.8$. Considering the graphite shape factors, inoculation appears to have a clear beneficial effect on circularity characterization, with limited benefits for sphericity, but with inconclusive influence regarding the second group of shape factors (elongation, aspect ratio). As distance from the casting surface increases the solidification rate decreases leading to a slow decline of the degree of graphite particles compactness (decreasing F_c and F_s and increasing E and AR shape factors) in the body of the castings. There is limited influence from the

inoculation treatment or the inoculant choice. Generally, a small addition of the complex alloy bearing sulfur and oxygen, associated with other active elements, such as calcium, aluminium and magnesium appears to support graphite nucleation with a high degree of compactness. One specific effect of the inoculation with this OS-IE alloy is the formation of a high number of small graphite nodules. A very high nodule count is usually accompanied by more spherical nodules, which explains the high nodularity in this test and the highest levels for circularity and sphericity shape factors.

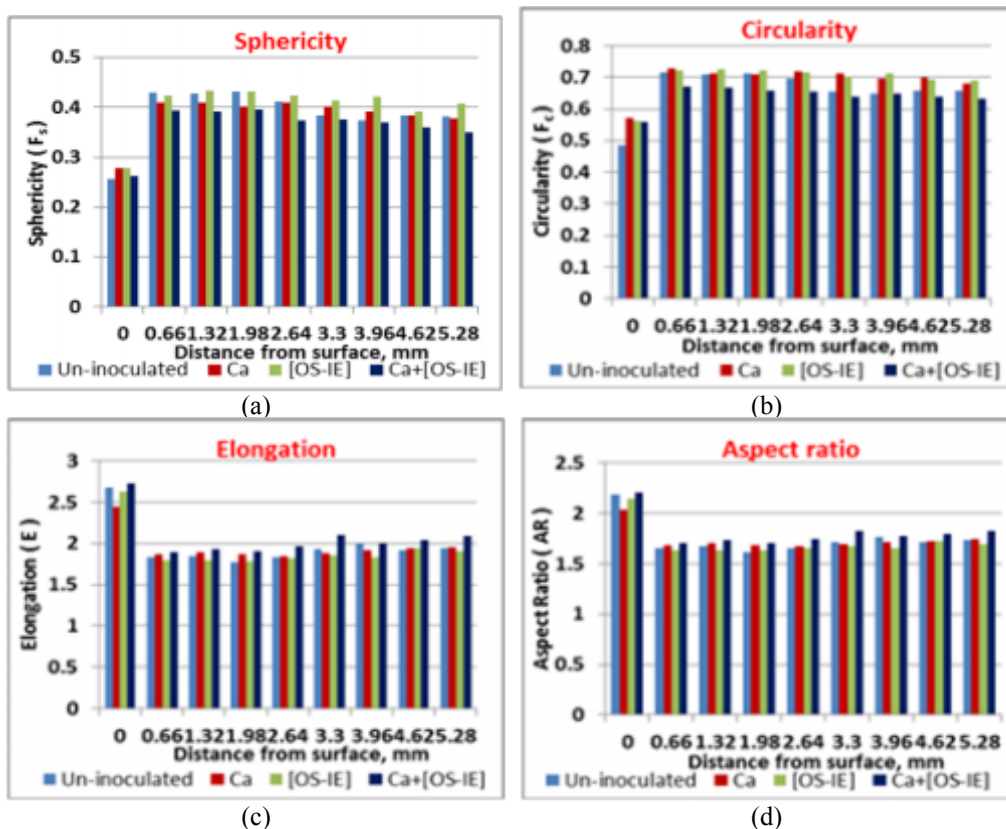


Fig. 4. Shape factors variation for uninoculated and inoculated irons

In contrast, solidification in these test conditions, using (Ca+OS-IE) inoculation led to the highest compacted/vermicular graphite formation sensitivity, with restricted nodular graphite formation, at under 35% nodular graphite content in this iron.

4. Conclusions

*In Mg,RE-FeSi treated, compacted/vermicular graphite cast iron, at 0.019–0.023% Mg_{res} , cast in a Furan resin - P-Toluol Sulphonic Acid (PTSA) bonded silica sand [FRS-PTSA] moulds, the graphite phase characteristics are influenced by inoculation, in both the surface layer and in the body of the castings.

*Even with the highest solidification rate at the surface layer the structure has the lowest graphite nodularity (10-20%), due to the mould binder sulfur content, in contrast to 35–50% nodularity in the casting body, for 25 mm round bar sample solidification conditions.

*Graphite shape factors illustrate the loss of compactness of the graphite particles in the surface layer of the casting and how it varies with the cooling rate, especially the circularity factor.

*The inoculation changes have a complex influence on the graphite phase characteristics, in the surface layer versus the casting body, depending on the chosen graphite parameter.



References

*In the surface layer of the casting, up to 0.5 mm depth, inoculation with only the inoculant enhancer alloy [OS-IE] increased the graphite nodularity, promoting a high nodularity, even through the section of casting.

*A specific effect of inoculation with this alloy [OS-IE] is the formation of a high number of small graphite nodules, which is associated with higher nodularity. This was represented by the highest levels for circularity and sphericity shape factors.

*Inoculation with the (Ca+OS-IE) dual addition led to the highest compacted/vermicular graphite formation sensitivity, with limited nodular graphite formation.

Acknowledgments

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 through the Financial Agreements POSDRU/159/1.5/S/132395 and POSDRU/159/1.5/S/134398.

- [1]. **Chisamera M., Riposan I.** - *Sulphur Inoculation of Mg-treated Cast Iron - on Efficient Way to Control Graphite Morphology and Nucleation Ability*, Fifth International Symposium on the Physical Metallurgy of Cast Iron, Oct. 1994, Nancy, France; Advanced Materials Research, 1997, vol. 4-5, p 293-300.
- [2]. **Skaland T.** - *Nucleation Mechanism in Ductile Iron*, Proceedings of AFS Conference on Cast Iron Inoculation, Schaumburg, sept. 2005, p.13-30.
- [3]. **Chisamera M., Riposan I. Barstow M.** - *The Importance of Sulphur to Control Graphite Nucleation in Cast Iron*, AFS Inoculation Conference, April 1998, Chicago, USA, paper no. 3.
- [4]. **Lalich M. J., Hitchings J. R.** - *Characterization of Inclusions as Nuclei for Spheroidal Graphite in Ductile Cast Iron*, AFS Trans., 1976, vol. 44, p 653-664.
- [5]. **Thielman T.** - *Zur Wirkung van Spurenelementen in Gusseisen mit Kugelgraphit*, *Giessereitechnik*, 1970, 1, p. 16-24.
- [6]. **Xiaogan H.**, *Nodular iron surface deterioration due to PTSA in resin*, AFS Trans., 1992, vol. 100, p. 9-15.
- [7]. **Chisamera M., Riposan I., Ivan N., Stan S.** - *No-Bake Mould Iron Casting Skin Management – Effect of Magnesium Residual and Mould Coating*, Proc. of the 71st World Foundry Congress, May 2014, Bilbao, Spain.
- [8]. **Riposan I., Chisamera M., Stan S.** - *Control of Surface Graphite Degeneration in Ductile Iron for Windmill Applications*, *Int. J. Metalcasting*, 2013, 7 (1), p.9-20.
- [9]. **Ivan N., Chisamera M., Riposan I.** - *Mg-bearing coating of resin sand – PTSA moulds to control graphite degeneration in the surface layer of ductile iron castings*, *Mat. Sci. Techn.*, 2012, 28 (11), p. 1246-1253.