THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 3 – 2013, ISSN 1453 – 083X

STRUCTURE CHARACTERIZATION OF Ca / Ba, Ca-FeSi INOCULATED, LOW SULPHUR, ELECTRICALLY MELTED, THIN WALL GREY IRON CASTINGS

Lavinia Marilena HARCEA, Iulian RIPOSAN
Politehnica University of Bucharest, 313, Spl. Independentei, RO-060042, Bucharest, Romania
emails: harcea.lavinia@yahoo.com, riposan@foundry.pub.ro

ABSTRACT

Much of the base iron in grey iron foundries is electrically melted in an acid lined induction furnace. The performance of the induction furnace allows superheating above 1500 ^oC, which is appropriate for thin wall casting production. With higher levels of superheat, the base iron characteristics are totally different from cupola melted iron, resulting in changes to the final casting microstructure. Previous experiments illustrated that eutectic undercooling of this type of base iron is excessively high, demonstrating an increased need for inoculation. The high dissolution rate of residual graphite in superheated iron and difficulties in forming complex (Mn,X)S compounds as active nucleation sites of graphite can be due to very low residuals of Al (< 0.003%) and Zr (< 0.0003%), especially at less than 0.03%S content. This results in increased tendencies for chill and undercooled graphite morphologies, even in inoculated irons. The structural characteristics of low-S (0.025%), low-Al (<0.003%) and 4.0 wt.% carbon equivalent for electrically melted grey irons were studied at different solidification cooling rates in wedge castings up to 20mm wall thickness, using Ca and (Ba + Ca) inoculating elements in FeSi based alloys with the same Si and Al contents. Under these conditions, Ca inoculation had minimal effect at less than 8mm wall thickness, while a Ca-Ba combination improved most of the structural parameters, including those in thin wall castings: less than 10% carbides for 2.5 mm and no carbides at more than 5mm section size, which also showed the highest graphite amount with a uniform distribution over the casting section.

KEYWORDS: grey cast iron, S, Al, Ca, Ba, inoculation, graphite, carbides, matrix

1. Introduction

The study on the efficiency of inoculants used in the production of grey irons aims to design a process that will produce a structure that is commensurate with achieving the target mechanical properties [1]. These are strongly influenced by the components in the structure, or control of graphite morphology and its distribution, the composition of the metal matrix and possibility of defects. The key factor for the production of grey irons with high resistance is represented by the graphite morphology control [2].

Recent research results have identified the graphite nucleation sites as being of the (Mn, X)S - type in commercial grey cast iron. Formation of these complex compounds can be more difficult in electrically melted iron, because of the tendency to low sulphur content especially if residual Al or Zr are also very low. After the addition of one or more inoculants to the molten iron, the compound (Mn,X)S becomes more complex at a lower ratio Mn/S, which is suitable for the germination of graphite [2-4].

The purpose of this paper is to evaluate the efficiency of Ca-and-Ca,Ba-FeSi alloys for controlling the structural characteristics of 4.0% carbon equivalent [CE], low S (0.026 wt.%S), low Al (0.0015 wt.%Al), typical of electrically melted commercial iron.

2. Experimental procedure

For this experiment grey cast iron was melted in a 100kg, 2400Hz frequency, electric induction furnace. The iron was superheated to a temperature of

1484°C and poured into a specially designed furan resin mould.

The mould was designed with a central downsprue, which simultaneously supplied the base iron to four separate test reaction chambers, with one acting as an un-inoculated reference and three to test different inoculation variants [5-7].

In this paper two inoculated irons were compared, one treated with Ca-FeSi alloy and the other with Ca, Ba-FeSi alloy to assess the effectiveness of each inoculant in reducing carbides, and to control the graphite morphology. The effective inoculating elements in the two alloys were Ca and Ca-Ba: Ca-FeSi (wt-%: 73.8Si, 1.02Ca, 0.77Al, Fe-bal) and Ca, Ba-FeSi: (wt-%: 72.6Si, 0.94Ca, 0.96Al, 1.68Ba, Fe-bal). The treatment alloys had a fine grain size (20x80 mesh), specifically for addition of the inoculant into the iron stream. The addition rates of the two selected inoculants in the reaction chamber were evaluated at 0.16 wt.% Ca-FeSi alloy and 0.10 wt.%Ca,Ba-FeSi alloy, respectively.

Sample wedges W_3 (ASTM A367-85, 19x38x100mm, CM = 0.35cm cooling modulus) were connected to the reaction chamber. The wedges were analyzed to establish the structural characteristics of grey iron after inoculation. Plate and cylindrical samples were also cast for other analyses. The design of the ASTM W_3 samples promotes the formation of carbides in the apex area because of the high solidification rate [8].

These samples were fractured, polished and analyzed with a conventional microscope for metallography and an automated image analyzer, on the un-etched and those etched with a 2% Nital solution.

The analyses were performed on both the centreline and along the surface at 1mm depth of the test castings. A higher solidification rate is expected at the casting surface, compared to the central region. The amount of graphite and its morphology (Figure 1), the amount of carbides and the metal matrix features were evaluated.

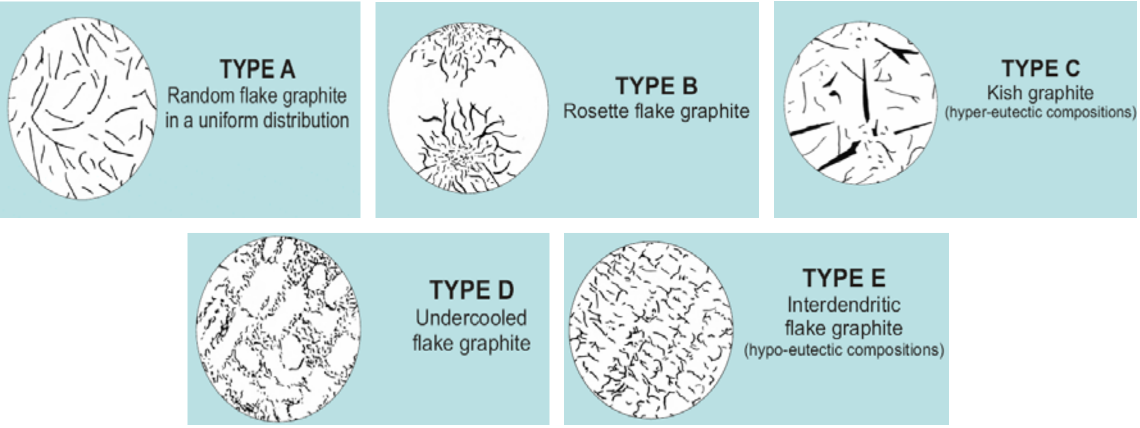


Fig. 1. *Typical graphite morphology in grey irons [ASTM]*

3. Results and discussion

The test iron is characterized by medium levels of C and Si, positioning it close to the eutectic (CE = 4.0%, Sc = 0.93), with low trace elements content, including those known to promote carbides (Tables 1 and 2). A Pearlite factor P_x [9], commonly used to characterize ductile iron, is mainly influenced by Mn, Si and some micro-elements.

One of the most important characteristic of grey cast iron is the level of and the ratio of the elements Mn and S since these affect the germination of lamellar graphite in commercial irons.

Tables 1 and 2 show critical parameters for iron solidification with low eutectic undercooling, as affected by Mn, S and Al content: (% Mn) x (% S) = 0.01 <0.03; Al = 0.0015 < 0.005%; Zr = 0.00044% < 0.0005% [2-4].

Table1. *Chemical Composition of Base Iron (wt-%)*

C	**Si**	**Mn**	**P**	**S**	**Al**	**Cr**	**Mo**	**Ni**	**Co**	**Cu**
3.49	1.73	0.382	0.100	0.0258	0.0015	0.048	0.0087	0.0364	0.0045	0.0566
Nb	**Ti**	**W**	**V**	**Pb**	**Sn**	**As**	**Zr**	**Bi**	**Sb**	**Te**
0.00033	0.0042	0.0066	0.0016	0.0005	0.0041	0.0061	0.00044	0.0011	< 0.0004	0.0016
B	**Zn**	**N**	**Ca**	**Mg**	**Ce**	**La**	**Fe**			
0.00079	<0.0001	0.0095	<0.0002	0.00058	0.0018	< 0.0001	94.1			

***Table 2**. Control Factors of Base Iron Chemistry*

Eutectic Range		**Mn and S Control**		**Pearlitic Factor***, P_x**	**Al Control [min. 0.005%]**
Carbon Equivalent* CE,%	**Carbon Saturation Degree**, S_c**	**Mn / S**	**(%Mn) x (%S)**		
4.04	0.93	14.81	0.01	3.83	0.0015

$*CE = C + 0.3(Si + P) - 0.03.Mn + 0.4S$; $**S_c = C / C_c = C / 4.3 - 0.3(Si + P) + 0.03.Mn - 0.4S$

$***P_x = 3.0 (\%Mn) – 2.65 (Si - 2.0) + 7.75 (\%Cu) + 90 (\%Sn) + 357 (\%Pb) + 333(\%Bi) + 20.1(\%As) + 9.60(\%Cr) +71.7(\%Sb)$ [9.]

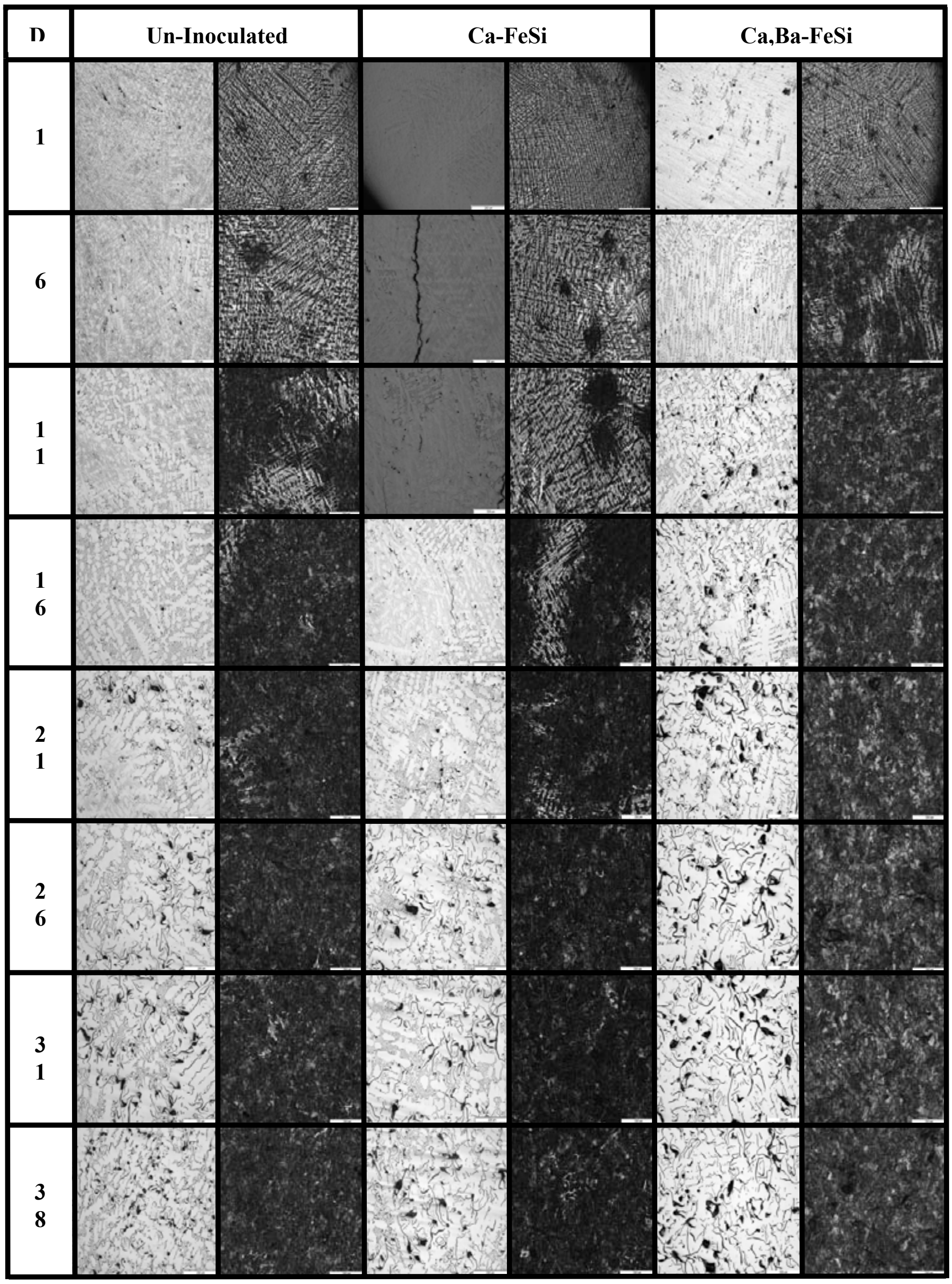


***Fig. 2.** Central zone microstructure of W_3 samples at different distance (D, mm) from the apex, for un-inoculated, Ca-FeSi and Ca,Ba-FeSi inoculated irons [un-etched and Nital etched]*

Figures 2 and 3 show the graphite phase and metal matrix characteristics, of un-inoculated and Ca-FeSi or Ca, Ba-FeSi inoculated irons at different distances from the apex of W_3 wedge sample, along the centreline (Fig. 3) and at the surface (Fig. 4), respectively. At greater distance from the apex sample width increases (section size), and therefore experiences slower cooling rate.

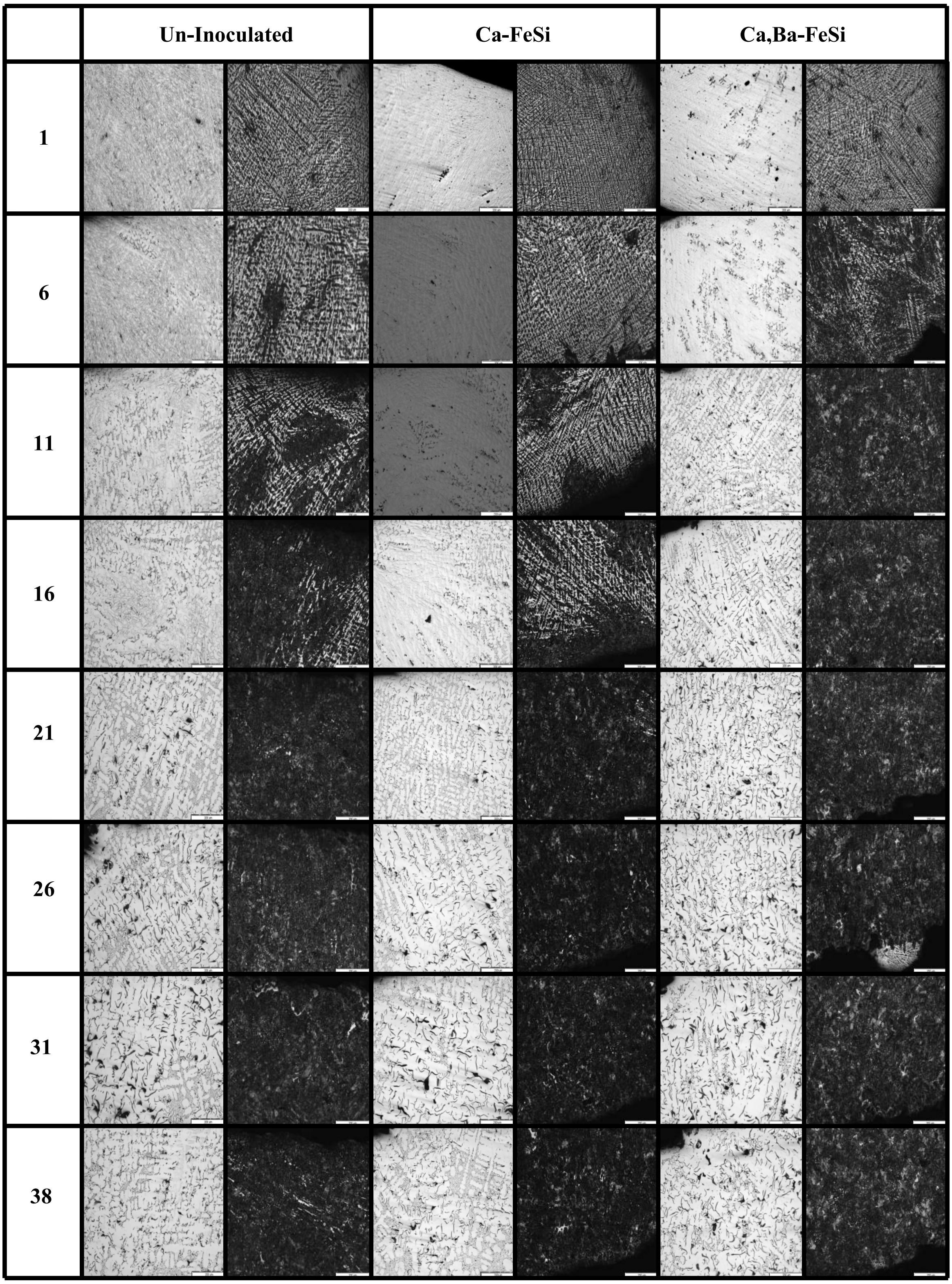


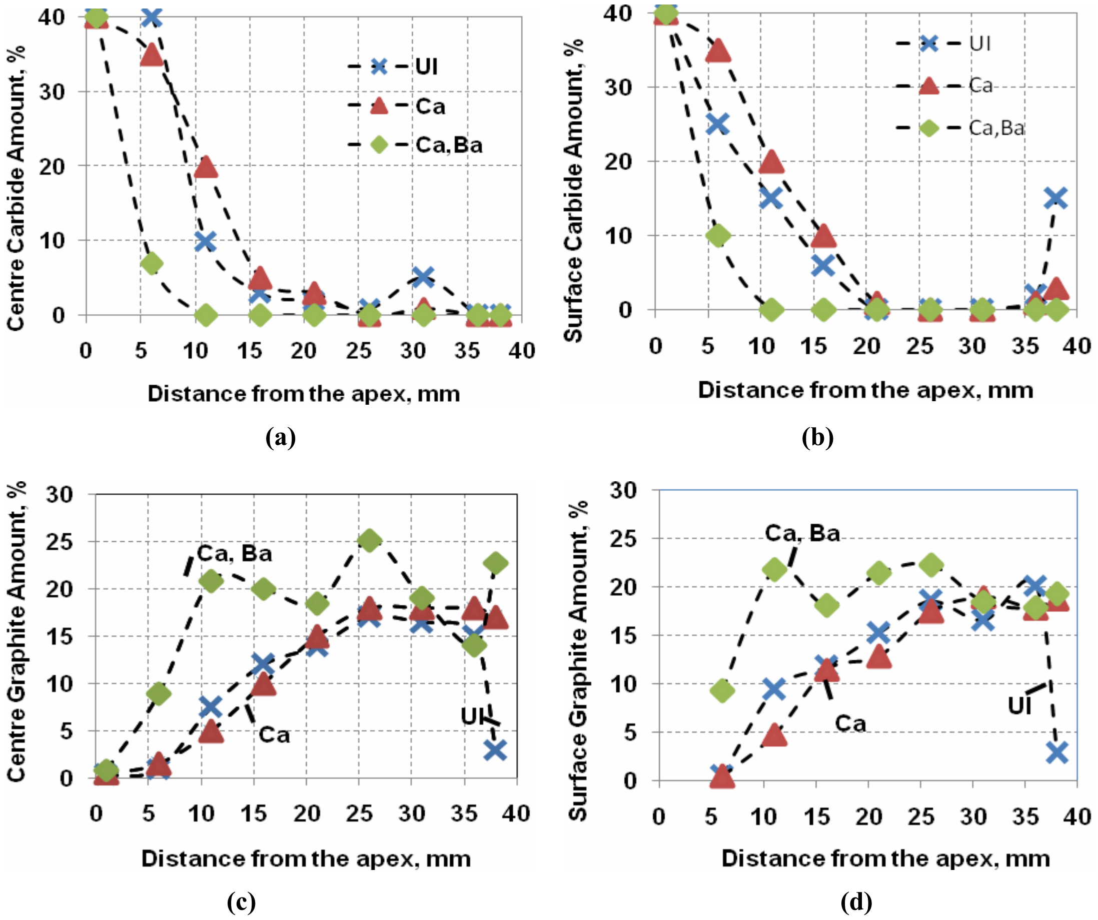
Fig. 3. *Surface zone microstructure of W_3 samples at different distance (D, mm) from the apex, for un-inoculated, Ca-FeSi and Ca,Ba-FeSi inoculated irons [un-etched and Nital etched]*

The influence of cooling rate or the distance from the apex of the wedge casting, the inoculation treatment and type of inoculating element on the amount of carbides and graphite, and undercooled graphite ratio were the focus of this evaluation. Avoiding both carbides and undercooled graphite morphologies (B, D, E), resulting in the preferred Type A, graphite formation is the most important objective of inoculation in grey cast iron production. Generally, well inoculated grey irons are characterized by Type A graphite nucleation with low eutectic undercooling, usually at more than 25 °C above the metastable (carbidic) eutectic equilibrium temperature (T_{mst}). As undercooling increases and the start of graphite nucleation is closer to T_{mst}, the graphite will branch, forming abnormal patterns. These shapes are known as Types B, D and E graphite. A further increase in undercooling will suppress the formation of graphite, resulting in a hard and brittle white iron, carbidic structure, with very poor machinability. An inverse relationship exists between the level of free carbides and distance from the apex of the chill wedge, and the wedge width, respectively. The risk of carbides is lower with increasing wedge width, but is dependent on whether the state of the iron is as base iron or inoculated iron.

The effect from inoculation was able to eliminate free carbides formation at more than 26 mm distance from the apex (13 mm wall thickness) for Ca-FeSi inoculated iron and at 10 mm distance (5mm section size) for Ca, Ba-FeSi treatments, in the centreline area of the wedge castings. As expected, the surface area of these castings is more likely to see metastable solidification conditions and free carbides formation.

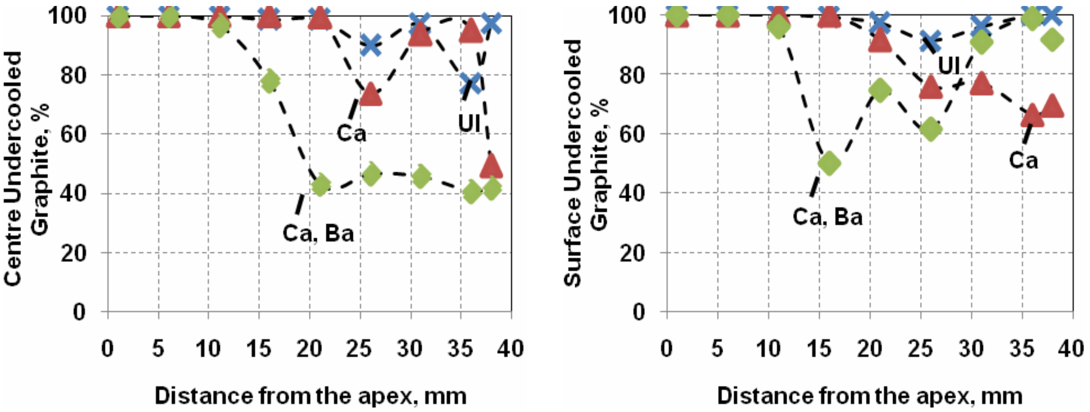
Additionally, the end effect [8] is more visible, especially for un-inoculated iron. Ca-bearing FeSi alloy limited this effect, but only Ca, Ba-FeSi inoculation avoided it. Ca, Ba-bearing FeSi alloy appears to be more effective especially for thin wall castings (less than 5mm section size), despite the critical chemical composition. The conventional inoculant Ca-FeSi does not achieve a clear effect of limiting the carbides at high solidification rates (Figure 4). The amount of graphite formed is related inversely to the variation in amount of carbides, (Fig. 4c and 4d).

At greater distance from the apex (increased section size = lower solidification rate), normally leads to a higher amount of graphite, but it depends on the state of the iron as well as which inoculating elements are employed.



(a) (b)

(c) (d)



(e) (f)

Fig. 4. *Influence of cooling rate and inoculation on the carbide amount (a,b), graphite amount (c,d) and undercooled graphite ratio (e,f) at different distances from the apex of* W_3 *– ASTM A387 wedge casting*

Ca, Ba-FeSi inoculation led to the highest amount of graphite, reflecting the lowest level of carbides, whereas Ca bearing FeSi alloy inoculation had a limited effect in these experimental conditions.

Undercooled graphite morphologies, including B, D and E type graphite (Fig. 1) are seen to be affected by cooling rate, iron treatment and inoculant type (Figs. 4e and 4f). Un-inoculated iron typically has the highest amount of these inferior graphite morphologies, with 100% presence up to 10mm section size, and more than 90% for the larger wedge casting sections, for both analyzed areas (centreline and surface). Ca-bearing FeSi was only effective above 10mm section size, decreasing the undercooled graphite up to 70%. Ca, Ba-FeSi inoculation had a stronger effect, as the undercooled graphite ratio decreased above 5mm section size by up to 40% in the centre areas and by 60% at the surface area of wedge castings.

Ca is considered the base inoculating element, while Ba is known as a strong promoting element that prolongs the effect of graphite germination. Combination of the two inoculating elements shows a beneficial effect on low sulphur irons [10]. Ca, Ba-FeSi alloy is more efficient in reducing carbides and undercooled graphite both at the centre and the casting surface compared to Ca-FeSi inoculant, which was less able to limit undercooled graphite and carbide formation. Ca and Ba inoculated iron had a uniform distribution of graphite over the whole surface of the sample with relatively small differences between the two central and marginal areasDespite the relatively high carbon equivalent (CE = 4.0%), the experimental irons develop iron carbides and an undercooled graphite morphology during solidification. As expected, the un-inoculated iron contained a large number of carbides with a small amount of graphite, most of which was present as undercooled graphite (more than 90% of the sample).

The pearlite / ferrite ratio is determined not only by the solidification rate and later, the cooling rate, but also by the graphite phase characteristics, which influence carbon diffusion during the eutectoid reaction. Normally at higher cooling rate (close to the apex of the wedge casting, equivalent to thinner section), there is a higher pearlite/ferrite ratio. However, undercooled graphite morphologies formed during eutectic solidification, as a result of higher eutectic undercooling, typical of high cooling rates, will also influence the later eutectoid transformation when the iron is 100% solid: increased carbon diffusion is easier because of the shorter distance between graphite particles. This creates a local zone in the matrix with sufficiently lower carbon content to allow ferrite formation, even if free carbides are present (mottled iron structure).

4. Summary

(1) The study confirmed that low-S (0.025%), low-Al (<0.003%) and low-Zr (<0.0005%) electrically melted base iron superheated to 1484 ^{o}C, with a (%Mn) x (%S) <0.03 control factor, is highly prone to free carbides and undercooled graphite formation, even at high carbon equivalent (CE=4.0%), for thin wall castings.

(2) A conventional Ca-bearing FeSi inoculant, added at the lower amount for an in-mould treatment technique (0.16 wt-%) had a limited graphitizing capacity, and only above 10 mm section thickness in the test castings.

(3) Despite adding 40% less in the reaction chamber than Ca-FeSi alloy, Ca,Ba-FeSi alloy was more effective than the Ca-FeSi reducing carbides formation, down to a 5mm section size.

(4) Both inoculant variants showed a limited performance to avoid undercooled graphite formation, with Ca,Ba-FeSi inoculant outperforming Ca-FeSi.

(5) A more effective inoculation treatment is necessary to control both carbides and undercooled graphite formation, especially for castings with less than 5 mm section size.

Acknowledgement

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/107/1.5/S/76903. The authors would like to recognize and thank Dr. Rod Naro, ASI International Ltd, for partially supplying funding for the experiments and Michael Barstow (Consultant) for reviewing and editing this paper.

References

[1]. D. M. Stefanescu - *Properties and Selections: Irons, Steels and High-Performance Alloys*, ASM Handbook, Vol.1 (1990), pp. 3-11.

[2]. I. Riposan, M. Chisamera, S. Stan, D. White - *Complex (Mn,X)S compounds–major sites for graphite nucleation in grey cast iron*, China Foundry, 2009, **6** (4), pp. 352-357.

[3]. I. Riposan, M. Chisamera, S. Stan, T. Skaland - *Graphite Nucleants (Microinclusions) Characterization in Ca/Sr Inoculated Grey Irons*, Int. J. Cast Met. Res., 2003, **16** (1-3), pp. 105-111.

[4]. I. Riposan, M. Chisamera, S. Stan, C. Hartung, D. White - *Three-Stage Model for the Nucleation of Graphite in Grey Cast Iron*, Mater. Sci.Techn., 2010, **26** (12), pp. 1439-1447.

[5]. M. Chisamera, I. Riposan, S. Stan, C. B. Albu, C. Brezeanu, R. L. Naro - *Comparison of Oxy-sulfide Alloy Tablets and Ca-bearing FeSi75 for Late Inoculation of Low Sulfur Grey Irons*, AFS Trans., 2007, **115**, pp. 481-493.

[6]. S. S. Ojo, I. Riposan - *Alloy selection for in the mould inoculation to control chill in ductile iron*, Mater. Sci. Techn., 2010, 28 (5), pp. 576-581.

[7]. L. M. Harcea, I. Riposan - *Chill sensitivity in 4.0% carbon equivalent, low-S, inoculated grey iron in thin wall castings*, Metal. Int., 2013, **18** (Special Issue 6), pp. 99-104.

[8]. S. Stan, M. Chisamera, I. Riposan, E. Stefan, M. Barstow - *Solidification Pattern of Un-inoculated and Inoculated Gray Cast Irons In Wedge Test Samples*, AFS Trans., 2010, **118**, pp. 295 – 309.

[9]. T. Thielman - *Zur Wirkung van Spurenelementen in Gusseisen mit Kugelgraphit*, Giessereitechnik, 1970, No.1, pp. 16-24.

[10]. M. Chisamera, S. Stan, I. Riposan, G. Grasmo, C. Hartung - *Structure Characteristics of Ba/Ca/Sr inoculated hypoeutectic grey cast irons*, Int. J. Cast Metal. Res., 2011, **24** (6), pp. 363-369.