Thermal analysis control of in-mould and ladle inoculated grey cast irons

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Abstract: The effect of addition of 0.05wt.% to 0.25 wt.% Ca, Zr, Al-FeSi alloy on in-ladle and in-mould inoculation of grey cast irons was investigated. In the present paper, the conclusions drawn are based on thermal analysis. For the solidification pattern, some specific cooling curves characteristics, such as the degree of undercooling at the beginning of eutectic solidification and at the end of solidification, as well as the recalescence level, are identified to be more influenced by the inoculation technique. The degree of eutectic undercooling of the electrically melted base iron having 0.025% S, 0.003% Al and 3.5% Ce is excessively high (39 – 40℃), generating a relatively high need for inoculation. Under these conditions, the in-mould inoculation has a more significant effect compared to ladle inoculation, especially at lower inoculant usage (less than 0.20 wt.%). Generally, the efficiency of 0.05wt.% – 0.15wt.% of alloy for in-mould inoculation is comparable to, or better than, that of 0.15wt.% – 0.25wt.% addition in ladle inoculation procedures. In order to secure stable and controlled processes, representative thermal analysis parameters could be used, especially in thin wall grey iron castings production.

Key words: thermal analysis; grey cast irons; in-mould inoculation; ladle inoculation

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Inoculation has a vital role to play in the continuing progress of cast iron. The objectives of various additions to the iron melt are to control the graphite size and shape, to promote A-type flakes instead of fine undercooled forms (D-type graphite), to obtain freedom from chill in thin sections, to promote uniformity throughout different sizes sections, to improve machinability and mechanical properties, etc. The development of inoculants started with the control of calcium and aluminum in ferrosilicon and continued with the addition of other active/inoculating elements, such as Sr, Ba, Zr, and Ce. Inoculation techniques have been continually improved in order to increase efficiency, to reduce inoculant consumption, and to avoid fading, etc [1, 2].

The chemistry of the base iron and the treatment alloys is very important in controlling the structure formation at lower eutectic undercooling conditions. It was found that Mn and S, strong deoxidizing elements (Al and Zr), and inoculating elements (Ca, Sr, Ba, Re, etc.) have a key role in the formation of complex (MnX)S compounds, which act as the major nucleation sites for graphite in grey cast irons [3-7].

Recently, thermal analysis became an important tool to reflect the solidification behavior of cast irons. The cooling curve itself, as well as its derivatives and related temperatures, and calculated parameters are patterns that can be used to predict the characteristics of irons. In addition, the use of thermal analysis can help assess the inoculation requirements for the melt [7-13].

The experimental investigation in this paper was designed mainly to estimate the cooling curves parameters and structure characteristics of low sulfur (0.025% S), low residual aluminum (0.003% Al), hypo-eutectic grey irons (3.5% – 3.6% Ce), subjected to in-mould and in-ladle inoculation by the same type of inoculant (Zr, Ca, Al-FeSi) added at various percentage (0 to 0.25wt.%).

1 Experimental procedure

Table 1 shows the representative experimental procedure parameters. The charge was melted in a graphite crucible medium-frequency induction furnace, mainly as a synthetic pig iron contribution, to ensure a low level of trace elements. It was obtained as a relative low carbon equivalent, hypo-eutectic base cast iron (Ce = 3.55%), with a low content of sulfur (0.025% S) and residual aluminum (0.003% Al).

Thermal analysis was mainly used to estimate and quantify the nucleation characteristics of different inoculated irons. The thermal analysis was carried out using shell sand Quick-Cups, with a modulus of approximately 0.75 cm (30 mm diameter bar equivalent). The cooling curve and its first derivative were considered for un-inoculated and inoculated irons at different inoculant addition rates. The structure characteristics were also evaluated.

A complex inoculant in Ca, Zr, Al-FeSi system was used, at various addition rates (0 to 0.25 wt.%). Two inoculation techniques were applied to in-mould (M) and in-ladle (L) alloy addition, as representative for high performance grey cast iron production. In the first experimental program, Zr, Ca, Al-FeSi

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Table 1 Experimental procedure parameters

Parameters	Values
Melting	
1 Melting furnace	Graphite crucible induction furnace, 10 kg, 8,000 Hz
2 Metallic charge:	
-Synthetic pig iron (94%)	3.48% C, 1.72% Si, 0.50% Mn, 0.12% P, 0.025% S, 4.03% Ce
-Steel scrap (6%)	0.2% C, 0.3% Si, 0.50% Mn, 0.03% P, 0.03% S
3 Base metal	3.02% C, 1.65% Si, 0.49% Mn, 0.11% P, 0.025% S, 0.0026% Al, 0.006% Ti, 0.042% Cr, 0.0078% Mo, 0.028% Ni, 0.044% Cu
Inoculation	
1 Inoculant	
-System	Ca, Zr, Al-FeSi, 0.2 – 0.7 mm size
-Chemical composition	75% Si, 2.2% Ca, 1.5% Zr, 1.2% Al, Fe bal.
-Addition rate	0.05, 0.10, 0.15, 0.20 and 0.25 (wt.%)
2 Inoculation technique	
-In-Mould	Quick-Cups (Thermal analysis system)
-Ladle	Ladle addition, after tapping
Test	
Cooling curves analysis	Shell sand cup, 0.75 cm cooling modulus
Structure characteristics	Round bar specimen (20 mm diameter, 150 mm high)

alloy was employed at 0.05 wt.%, 0.10 wt.%, 0.15 wt.%, 0.20 wt.% and 0.25 wt.% levels, respectively, into the shell sand cup. In the second program, a ladle inoculation was applied with the same prescribed amounts of alloy that were added in the in-mould/cup tests.

The base iron was also poured into test casting moulds made from green sand. The test castings were all poured at 1,430 ºC. For in-mould inoculation, the specially designed test mould included a central down-sprue, which supplied un-inoculated grey iron to a reaction chamber. A round bar specimen (20 mm diameter, 150 mm high) was gated off the inoculation reaction chamber. As molten iron flowed into the reaction chamber, it was inoculated and the inoculated iron then flowed into the test bar. The same prescribed amounts of the inoculant were added in the reaction chamber as in the shell sand cup tests [14].

2 Results and discussion

Figure 1 shows the aspect of a typical cooling curve and its first derivative for a hypoeutectic grey iron (Ce < 4.3 %). The signification of the most important events and parameters

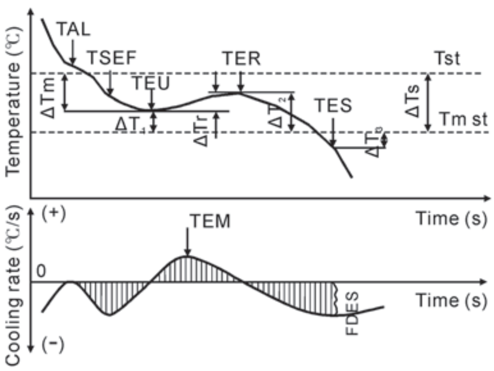


Fig. 1 Typical cooling curve and its first derivative of hypoeutectic grey cast iron

on these curves is included in Table 2 [7-13]. There are many elements which individually have favorable or un-favorable influence on the equilibrium temperatures in stable (Tst) and metastable (Tmst) systems (Table 3). Silicon appears to be the most important influencing element in un-alloyed irons especially at very low content of trace elements [Tst = 1153 + 6.7 (%Si); Tmst = 1147 – 12 (%Si)] [8, 9].

Table 4 includes the most important experimental parameters, as thermal analysis data. Figures 2 and 3 illustrate the effects of the two major influence factors, i.e. the inoculation method (in-mould/cup and in-ladle inoculation) and the inoculant addition amount (0 to 0.25 wt.% alloy), respectively.

The most obvious effect of inoculation is that the temperatures of eutectic undercooling (TEU) and graphite recalescence (TER) are increased. When TEU is reached, the generated heat from released specific heat and latent heat (from the first austenite dendritic solidification and the start of eutectic freezing) just balance the heat losses. The eutectic reaction then occurs and the released energy causes the temperature to rise until TER is reached. Un-inoculated irons are characterized by low TEU and TER temperatures. Although inoculation increases both of these temperatures, the amount of the increase is dependent on the inoculant addition amount and inoculation method. TER level is stabilized in a shorter time compared to TEU level, as the inoculant addition amount increases, especially for in-mould/cup treatment.

Conventionally, undercooling is defined with reference to the graphitic equilibrium eutectic temperature (Tst), as ΔTm = Tst – TEU. If the TEU is close to, but above, the white eutectic temperature (TEU > Tmst) then undercooled graphite might develop. Free carbide occurrence is typical of the condition TEU < Tmst. The importance of the position of the start of eutectic reaction (TEU) compared to the metastable (white) eutectic temperature (Tmst) is revealed by ΔT_1 = TEU – Tmst. For the end of eutectic reaction temperature the

Table 2 Thermal analysis parameters of hypoeutectic grey cast irons

Param. in Fig. 1	Signification	Comments
Tst	Stable (graphite) eutectic equilibrium temperature	*Theoretical temperature for C to precipitate as graphite *It should be as high as possible (Tst = 1153 + 6.3 %Si)
Tmst	Metastable (white) eutectic equilibrium temperature	*Temperature when C is chemically combined with iron (Fe_3C) *It should be as low as possible (Tmst = 1147–12 %Si)
ΔTs	Range of equilibrium eutectic temperature ΔTs = Tst – Tmst	*ΔTs should be as large as possible *Favorable elements: Si, Ni, Cu, Co, Al
TAL	Liquid temperature commences solid precipitation, as pro- eutectic austenite	*First arrest temperature (no recalescence has occurred) *The first derivative is zero *TAL should have a well defined plateau, 2–10 s *TAL can sometimes be reduced by inoculation
TSEF	Temperature of the start of eutectic freezing (nucleation)	*Derivative has a minimum, between TAL and TEU, grey iron. *It should not be too deep
TEU	Lowest eutectic temperature	*The minimal point from which the temperature is increasing *The first derivative is zero *Inoculation increases TEU (about 25˚C above Tmst)
TER	Highest eutectic temperature	*The maximum temperature after the increase in temperature *The first derivative is zero *High cooling rates may not achieve this temperature
ΔTm	Conventional eutectic undercooling degree ΔTm = Tst – TEU	*Comparing to graphite eutectic temperature (Tst) *The maximum eutectic undercooling *A high undercooling means: -D-graphite might develop -More austenite, risk of macro shrinkage and outer sunk -Free carbides (chill) if ΔTm > ΔTs *Higher the ΔTm of base iron, the higher the need for inoculation: base iron, ΔTm = 20–35˚C , as normal value *Inoculation reduces eutectic under-cooling
ΔT_1	Undercooling comparing to Tmst ΔT_1 = TEU – Tmst	*Beginning of eutectic reaction *Carbides (chill), if $\Delta T_1 < 0$ (TEU < Tmst) *Undercooled graphite (D-type) if $\Delta T_1 > 0$ (TEU close to Tmst) *Inoculation increases ΔT_1 parameter (ΔT_1 > + 20˚C normally)
ΔT_2	Undercooling comparing to Tmst ΔT_2 = TER – Tmst	*End of eutectic reaction, no white iron if $\Delta T_2 > 0$ *Higher ΔT_2, lower incidence of D-type graphite *Inoculation increases ΔT_2, at lower power comparing to ΔT_1
ΔTr	Recalescence degree ΔTr = TER – TEU	*It reflects the amount of austenite and graphite that are precipitated during the first part of eutectic freezing *Too high recalescence might be harmful, in soft moulds *Ideal values depend on the type of mould and the casting modulus: ΔTr = 2 – 5 ˚C , as a guideline *Inoculation normally reduces recalescence
TES	Temperature of the end of solidification (solidus)	*All metal has solidified *Lowest value of the negative peak on the first derivative *Lower (TES), higher sensitiveness to contraction defects
ΔT_3	Undercooling at the end of solidification ΔT_3 = TES – Tmst	*Usually at negative values, as TES < Tmst *Intercellular carbides, inverse chill and micro-shrinkage occurrence, especially if ΔT_3 > 20˚C (more negative) *Inoculation normally decreases ΔT_3 and the incidence of contraction defects
FDES	The depth of the first derivative at solidus	*The depth of the negative peak *It should be less than –3.5 (i.e. deeper) for grey irons (high amount of graphite at the end of solidification) *Inoculation normally has a positive influence
TEM	Maximum recalescence rate	*Maximum value of the first derivative between TEU and TER

Table 3 Influence of favorable and un-favorable elements on Tst and Tmst

Equilibrium temperature	Favorable elements	Action	Un-favorable elements	Action
Tst	Si, Ni, Cu, Co, Al, Pt	Increase Tst	Cr, V, Ti, Mn, Mo, Sn, Sb, W, Mg, P	Decrease Tst
Tmst	Si, Ni, Cu, Co, Mn, Sn, Sb, W, Mg, P	Decrease Tmst	Cr, V, Ti, Al, Pt	Increase Tmst

Table 4 Thermal analysis representative parameters

Inoculation: Addition amount (wt.%)	Inoculation: Type	TEU (˚C)	TER (˚C)	TES (˚C)	ΔTm = Tst –TEU (˚C)	ΔT_1 = TEU –Tmst (˚C)	ΔT_2 = TER –Tmst (˚C)	ΔT_3 = TES –Tmst (˚C)	ΔTr= TER –TEU (˚C)	FDES (˚C/s)
U.I.		1124.7	1125.1	1100.2	38.9	-3.3	-2.9	-27.8	-	-2.3
		1122.8	1125.2	1089.9	40.8	-5.2	-2.8	-38.1	2	-1.79
0.05	M	1132.5	1141.5	Undone	31.3	4.9	13.9	Undone	9	Undone
	L	1123.6	1127.3	1093.9	40.2	-4.0	-0.3	-33.7	4	-2.12
0.10	M	1133.5	1142.3	1106.3	30.6	6.4	15.2	-20.8	9	-3.13
	L	1127.9	1134.9	1094.4	36.2	0.8	7.8	-32.7	7	-2.40
0.15	M	1135.4	1140.6	1107.2	28.9	8.7	13.0	-19.5	5	-3.13
	L	1130.1	1137.6	1097.4	34.2	3.4	10.9	-29.3	8	-2.88
0.20	M	1135.3	1140.1	1104.1	29.3	9.1	13.9	-22.1	5	-2.77
	L	1132.8	1139.1	1101.2	31.8	6.6	12.9	-25.0	6	-3.22
0.25	M	1136.4	1140.2	1105.1	28.4	10.6	14.4	-20.7	4	-3.23
	L	1133.2	1138.8	1100.8	31.6	7.4	13.0	-25.0	6	-3.45

*M – In-mould/cup inoculation; L – In-ladle inoculation.

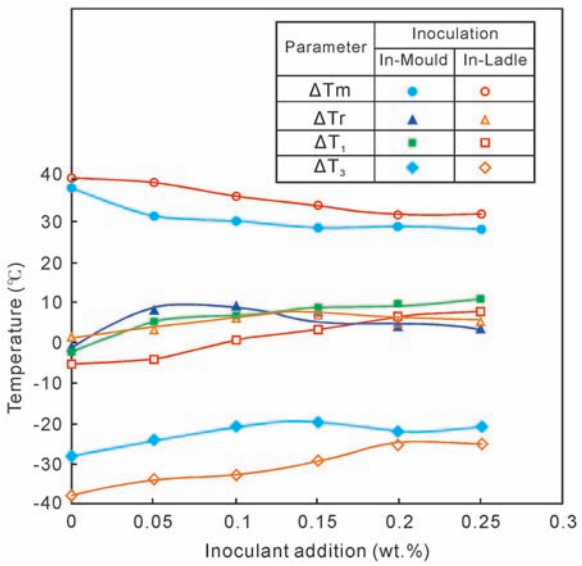


Fig. 2 The influence of the inoculant addition amount and inoculation method on the representative thermal analysis parameters

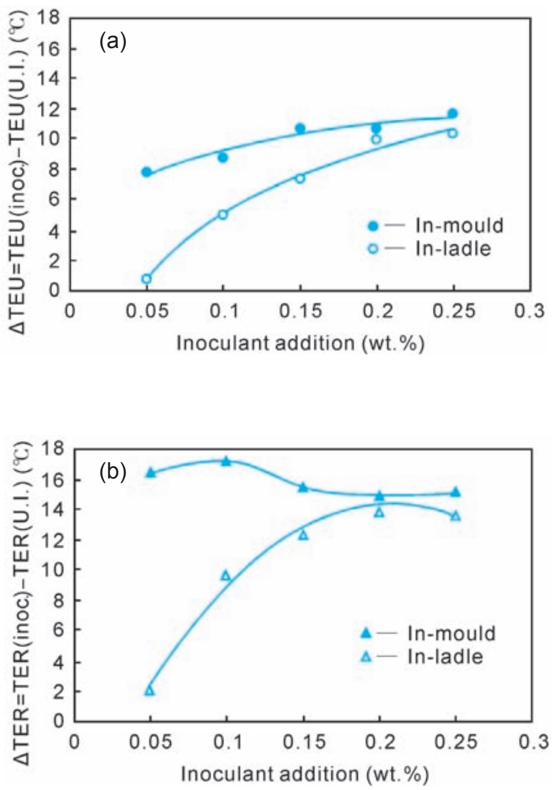


Fig. 3 Undercooling (a) and recalescence (b) difference between un-inoculated and in-mould/in-ladle inoculated irons

parameter ΔT_2 (ΔT_2 = TER – Tmst) was introduced.

The efficiency of inoculation is measured by its ability to decrease the ΔTm level and to increase the ΔT_1 and ΔT_2 levels, as shown in Table 4 and Fig. 2. In all cases, the in-mould/cup inoculation is clearly more effective than the in-ladle inoculation, as represented by the variation of the ΔT_1 and ΔT_2 parameters. In both experimental programs, the un-inoculated irons start and end the eutectic reaction in the white iron field ($\Delta T_1 < 0$, $\Delta T_2 < 0$). Inoculation is known to move the solidification pattern to the grey iron feature. The increase of the alloy addition amount led to an increase in the distance of both the TEU and TER events, from the metastable (white) eutectic temperature.

In-mould/cup inoculation appears to be more efficient compared to in-ladle inoculation at low inoculant addition amount, such as 0.05 wt.% to 0.10 wt.% levels. No big difference in efficiency from the inoculation technique was found for more than 0.20 wt.% alloy addition. Generally, the efficiency of 0.05 wt.% to 0.15 wt.% alloy for in-mould/cup inoculation is comparable to, or better than, that of 0.15 wt.% to 0.25 wt.% additions in in-ladle inoculation procedures.

The difference between un-inoculated and inoculated irons is strongly affected by the alloy addition amount, much more so for in-ladle inoculation as the lowest eutectic temperature (TEU) shows (Fig. 3). The in-mould/cup inoculation method is consistently more efficient for the entire range of inoculant additions, but especially at lower levels (less than 0.20 wt.%). It is characterized by lower eutectic undercooling degree (ΔT_m) and higher inoculation index (I_2) level (Fig. 4).

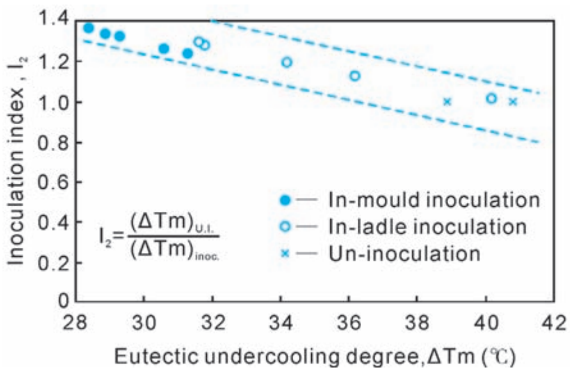


Fig. 4 Inoculation Index (I_2) of treated irons

In many cases, graphitic recalescence (ΔTr = TER – TEU) is also an important parameter to evaluate the behavior of inoculated irons. It is a function of the amount of austenite and graphite that are precipitated during the first part of eutectic freezing. The higher the recalescence, the higher the probability for micro-shrinkage and porosity occurrence, especially in soft mould media, such as green sand moulds (high metal volume expansion). Figure 2 shows the evolution of the level of recalescence (ΔTr), as the inoculant addition amount increases. A peculiar difference appears in the behavior of in-mould/cup and in-ladle inoculated irons. At no more than 0.1 wt.% alloy addition, high recalescence level characterizes the in-mould treated irons especially due to the higher TER temperature. An opposite result was obtained for these two inoculation methods at more than 0.10 wt.% alloy addition amount, when higher recalescence was typical for the in-ladle inoculated irons. Lower differences were obtained between the two techniques for more than 0.20 wt.% inoculant.

White iron solidification as intercellular carbides and/or inverse chill formation is also dependent on the temperature of the end of solidification (TES), compared to the metastable (white) eutectic temperature (Tmst). Figure 2 illustrates the variation of the ΔT_3 (given by ΔT_3 = TES – Tmst), as the inoculant addition amount increases. Because this difference (ΔT_3) is generally more than 20ºC, these irons will be sensitive to chill tendency and micro-shrinkage formation.

Beneficial end of solidification means high solidus temperature and low level of the ΔT_3 parameter (usually at low negative value, as TES < Tmst in the most of cases). A low value of FDES (more negative level) is also favorable as it is correlated to a high amount of graphite at the end of freezing. Increasing of the alloy addition amount improves the behavior of irons at the end of solidification but in a different manner for in mould/cup and ladle inoculation methods. The 0.10 wt.%–0.20 wt.% inoculant stabilizes the representative solidification parameters at a favorable level for in mould/cup inoculation comparing to 0.20 wt.%–0.25 wt.%, for in-ladle inoculation.

The effects of inoculation were also analyzed by comparing the microstructures of irons treated with different amounts of Ca, Zr, Al-FeSi alloy, obtained by both inoculation methods, using the 20 mm diameter bars. The graphite morphology was drastically improved. The amount of undercooled graphite decreased with increasing inoculant addition amount, up to mainly type-A graphite, as Table 5 and Fig. 5 show. The presence of ledeburite and cementite was eliminated for 0.05 wt.% and 0.15 wt.% addition amounts (Table 5). Again, the in-mould inoculation was more effective in avoiding undercooled graphite morphologies and free carbides, compared to in-ladle inoculation. A predominantly pearlitic structure (90%–100% pearlite) was obtained in all cases: 90 %–98 % pearlite for in-ladle inoculation compared to 98 %–100 % pearlite for in-mould inoculation.

Table 5 Structure characteristics

Inoculant addition amount (wt.%)	Undercooled graphite amount (%)		Carbides amount (%)	
	In-ladle inoculation	In-mould inoculation	In-ladle inoculation	In-mould inoculation
0	100	100	20	30
0.05	70	40	10	< 2
0.10	50	20	5	0
0.15	30	5	0	0
0.20	15	7	0	0
0.25	15	5	0	0

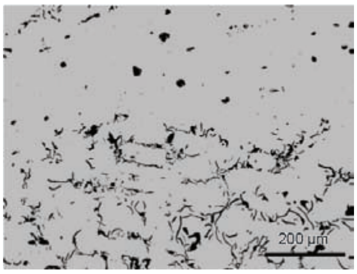
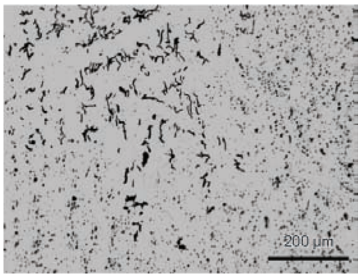
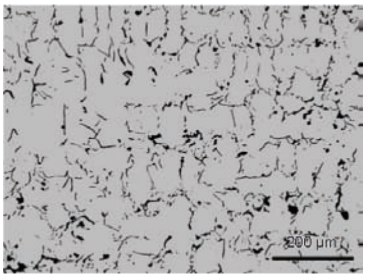
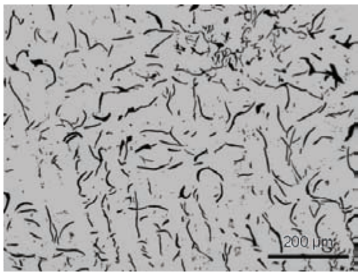
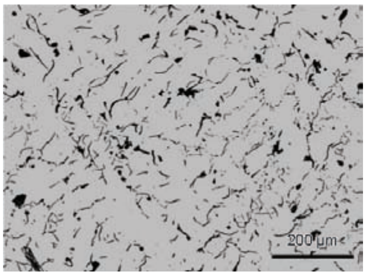
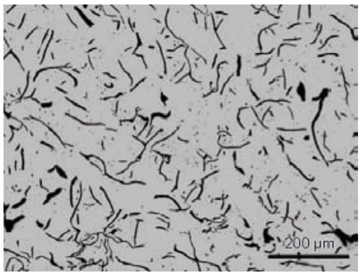
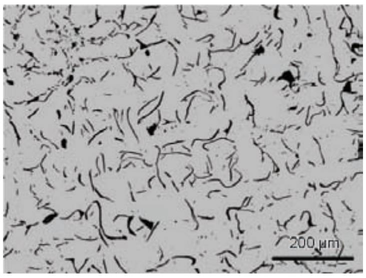
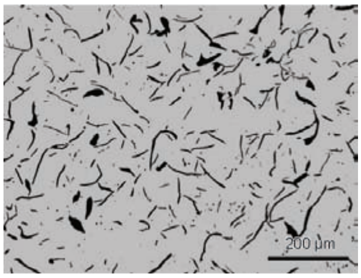
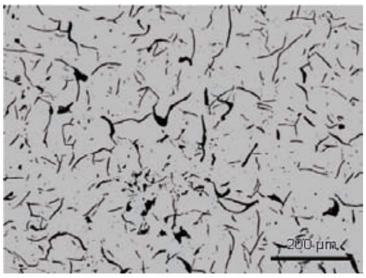
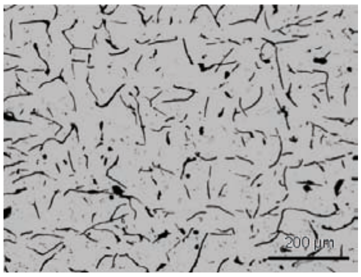
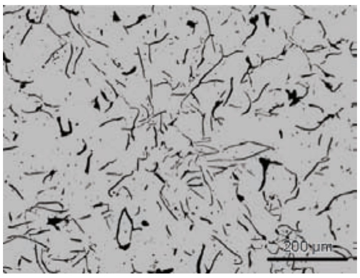
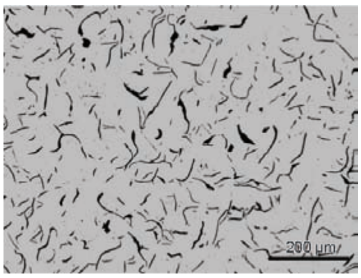
Inoculant addition wt.%	Inoculation technique	
	In-ladle	In-mould
U.I.		
0.05		
0.10		
0.15		
0.20		
0.25		

Fig. 5 Graphite morphology in un-inoculated and inoculated grey cast irons (0.05 wt.% to 0.25 wt.% alloy)

3 Conclusions

(1) The present study clearly indicates that thermal analysis methodology can be very successfully used to optimize and control the complicated cast iron solidification processes.

(2) The degree of eutectic undercooling of the electrically melted base iron having 0.025% S, 0.003% Al and 3.5% Ce is excessively high (39 – 40 ℃), generating a relatively high need for inoculation.

(3) Under these conditions, the in-mould inoculation had a more significant effect than the in-ladle inoculation, especially at lower inoculant usage (less than 0.20 wt.%).

(4) Lower levels of eutectic undercooling (ΔTm), recalescence (ΔTr), and the undercooling at the end of solidification (ΔT_3) are characteristic for in-mould treatment at lower inoculant addition rates.

(5) The difference between un-inoculated and inoculated irons is strongly affected by the alloy addition rate, much more so for in-ladle inoculation.

(6) Generally, the efficiency of 0.05 wt.% – 0.15 wt.% alloy for in-mould inoculation is comparable to, or better than, that of 0.15 wt.% – 0.25 wt.% addition in in-ladle inoculation procedures.

(7) A Ca, Zr, Al-FeSi alloy inoculation appears to be efficient in low S, Al, Ce, hypoeutectic grey cast irons, especially with in-mould inoculation.

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