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THERMAL ANALYSIS OF INOCULATED GREY CAST IRONS

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ABSTRACT

A research was done to investigate the effect of 0.05…0.25wt.% addition rate of Ca, Zr ,Al – FeSi alloy, in ladle and in-mould inoculation of grey cast irons. In the present paper, the conclusions drawn are based on thermal analysis. For solidification pattern, some specific cooling curves characteristics, such as undercooling degree at the beginning of eutectic solidification and at the end of solidification, as well as recalescence level, were identified to be more influenced by the inoculation technique. In order to secure stable and controlled processes, representative thermal analysis parameters could be used, especially in thin wall grey iron casting production.

KEYWORDS: Thermal Analysis, Grey Cast Irons, Inoculation, In-mould Inoculation, Ladle Inoculation

1. Introduction

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 under-cooled forms (D-type graphite), to obtain freedom from chill in thin sections, to promote uniformity throughout different sections sizes, to improve machinability and mechanical properties, etc.

The development of inoculants started by the control of calcium and aluminium in ferrosilicon and continued by addition of other active/inoculating elements, such as Sr, Ba, Zr, Ce, etc. Inoculation techniques were also continuously improved, in order to increase efficiency and to reduce the inoculant consumption, to avoid the fading, etc [1, 2].

The chemistry of the base iron and the treatment alloys are very important in controling 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 complex (Mn, X)S compounds formation, which act as the major nucleation sites for graphite in grey cast irons [3-7].

Recently, the 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. On the other hand, the use of thermal analysis can help assess the inoculation requirements for the melt [7-13].

The current experimental investigation in this paper was designed to estimate the cooling curves parameters of low sulphur (0.025%S), low residual aluminium (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 rates (0…0.25wt.%).

2. 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 a relative low carbon equivalent, hypo-eutectic base cast iron (CE = 3.55%), at low content of sulphur (0.025%S) and residual aluminium (0.003%Al), too.

Thermal analysis was used to estimate and quantify nucleation characteristics of different inoculated irons. The thermal analysis was carried out using shell sand Quick-Cups, with a modulus of approximately 0.75cm (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.

***Table 1.** Experimental Procedure Parameters*

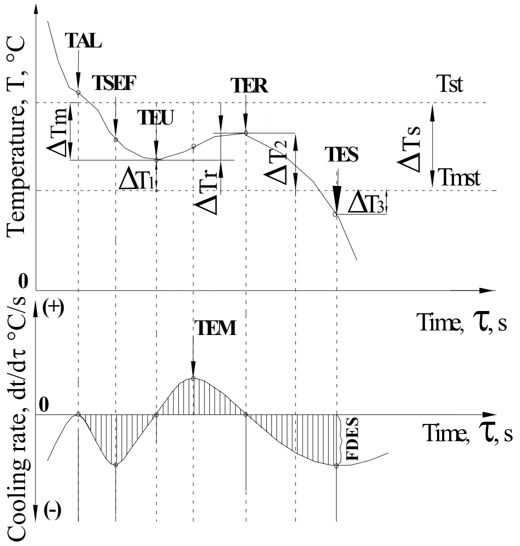
Parameters	**Values**
I. MELTING	
1.1. Melting Furnace	Graphite Crucible Induction Furnace, 10Kg, 8000Hz
1.2. Metallic Charge:	
-Synthetic Pig Iron (94%):	3.48%C, 1.72%Si, 0.50%Mn, 0.12%P, 0.025%S, 4.03%CE
-Steel Scrap (6%):	0.2%C, 0.3%Si, 0.50%Mn, 0.03%P, 0.03%S
1.3. Base Metal	3.02%C, 1.65%Si, 0.49%Mn, 0.11%P, 0.025%S, 0.0026%Al, 0.006%Ti, 0.042%Cr, 0.0078%Mo, 0.028%Ni, 0.044%Cu
II. INOCULATION	
2.1. Inoculant	
-System	Ca, Zr, Al-FeSi, 0.2-0.7mm size
-Chemistry	75%Si, 2.2%Ca, 1.5%Zr, 1.2%Al, Fe bal.
-Additional Rate	0.05, 0.10, 0.15, 0.20 and 0.25wt.%
2.2. Inoculation Technique	
-In-Mould	Quick-Cups [Thermal Analysis System]
-Ladle	Ladle addition, after tapping
III. TEST	
Cooling Curve Analysis	Shell Sand Cup, 0.75cm Cooling Modulus

A complex inoculant in Ca,Zr,Al – FeSi system was used, at various addition rates (0…0.25wt.%). Two inoculation techniques were applied, 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 alloy was employed at 0.05%, 0.10%, 0.15%, 0.20% and 0.25% levels, into the shell sand cup. In the second program, a ladle inoculation was applied with the same prescribed amount of alloy, which was added in the in-mould/cup tests.

3. 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 on these curves is included in Table 2 [7-13].



TAL - temperature of austenitic liquidus, °C;
TSEF - temperature of start of eutectic freezing (eutectic nucleation),°C;
TEU - temperature of eutectic undercooling, °C;
TER - temperature of graphitic recalescence, °C;
TES - temperature of the end of solidification (end of solidus), °C;
TEM - maximum recalescence rate, °C/s;
Tst - graphite eutectic equilibrium temperature, °C;
Tmst - carbide eutectic equilibrium temperature, °C;
ΔTm - maximum degree of undercooling (ΔTm = Tst-TEU), °C;
ΔTr - recalescence degree (ΔTr = TER-TEU), °C;
ΔTs - range of equilibrium eutectic temperature (ΔTs = Tst-Tmst), °C;
FDES - minimum value of the first derivative of cooling curve on the end of eutectic solidification, °C/s;
ΔT_1 = TEU – Tmst; ΔT_2 = TER – Tmst; ΔT_3 = TES – Tmst

***Fig. 1** Typical cooling curve and its first derivative.*

Table 2. *Thermal Analysis Parameters of Hypo - Eutectic Grey Cast Irons*

Param. (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 *Favourable 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 sec *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 [TEU, about 25^{o}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^{o}C, as normal value *Inoculation reduces eutectic undercooling
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 [$\Delta T_1 > + 20^o$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
ΔT_r	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^{o}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 $\Delta T_3 > 20^o$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

There are many elements which individually have favourable or unfavourable 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, while Figures 2 and 3 illustrate the effects of the two major influences, i.e. the inoculation technique (in-mould/cup and ladle inoculation) and the inoculant addition rate (0…0.25wt.% alloy), respectively.

Table 3. *Favourable and Un-Favourable Elements as $\Delta Ts = Tst - Tmst$ Influence*

Equilibrium Temperature	**Favourable Elements**		**Un-favourable Elements**	
	Elements	**Action**	**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		**TEU (^{o}C)**	**TER (^{o}C)**	**TES (^{o}C)**	**$\Delta Tm = Tst - TEU$ (^{o}C)**	**$\Delta T_1 = TEU - Tmst$ (^{o}C)**	**$\Delta T_2 = TER - Tmst$ (^{o}C)**	**$\Delta T_3 = TES - Tmst$ (^{o}C)**	**$\Delta Tr = TER - TEU$ (^{o}C)**	**FDES (^{o}C/s)**
Addition (wt. %)	**Type**									
U.I.	M	1124.7	1125.1	1100.2	38.9	-3.3	-2.9	-27.8	-	-2.3
	L	1122.8	1125.2	1089.9	40.8	-5.2	-2.8	-38.1	2	-1.79
0.05	M	1132.5	1141.5	UD	31.3	4.9	13.9	UD	9	UD
	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-ladle inoculation.

The most pronounced 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 latent heat from 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 rate and inoculation technique. TER level is stabilized in a shorter time comparing to TEU level, as inoculant addition rate increases, especially for in-mould/cup treatment. Conventionally, undercooling is defined with reference to the graphitic equilibrium eutectic temperature (Tst), as $\Delta Tm = Tst - TEU$. If TEU is closed to white eutectic temperature but above it ($TEU > Tmst$) then undercooled graphite might develop. Free carbides occurrence is typical for $TEU < Tmst$ condition. The importance of the position of the start of eutectic reaction (TEU) comparing to metastable (white) eutectic temperature (Tmst) is revealed by $\Delta T_1 = TEU - Tmst$. For the end of eutectic reaction temperature, $\Delta T_2 = TER - Tmst$ parameter 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, respectively (Table 4, Figure 2).

In all cases, the in-mould/cup inoculation is clearly more effective compared to ladle inoculation, represented by 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 increasing of the alloy addition rate led to the increasing of the distance of the both TEU and TER events, from the metastable (white) eutectic temperature. In mould/cup inoculation appears to be more efficient compared to ladle inoculation at low inoculant addition rates, such as 0.05-0.10wt.% level. No big difference in efficiency from the inoculation technique was found for more than 0.20wt.% alloy addition rate. Generally, the efficiency of 0.05-0.15wt.% alloy for in-mould/cup inoculation is comparable to or better than 0.15-0.25wt.% additions in ladle inoculation procedures.

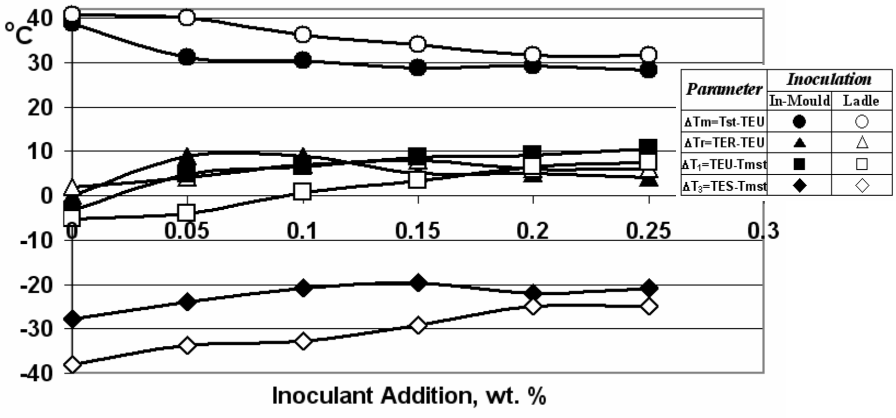


Fig. 2 *Influence of the inoculant addition rate and inoculation technique on the representative thermal analysis parameters*

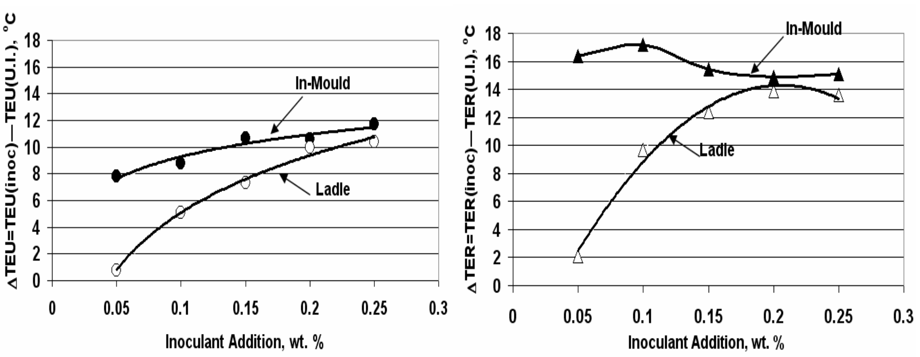


Fig. 3 *Undercooling (a) and Recalescence (b) difference of un-inoculated and in-mould/ladle inoculated irons*

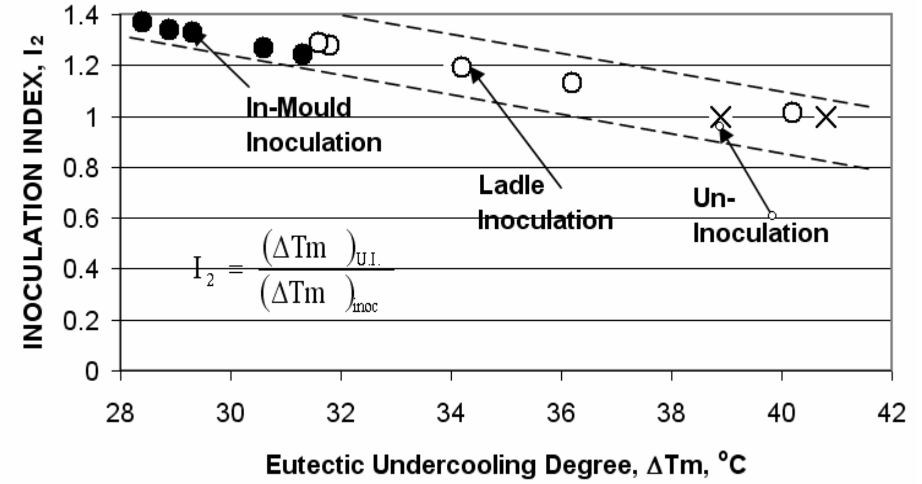


Fig. 4 *Inoculation Index (I_2) of Treated Irons*

The difference between un-inoculated and inoculated irons is strongly affected by the alloy addition rate, much more for ladle inoculation as the lowest eutectic temperature (TEU) shows (Fig. 3). Late inoculation technique is consistently at higher efficiency for the entire range of inoculant additions, but especially at lower levels (less than 0.20wt.%). Late inoculation technique is characterized by lower eutectic undercooling degree (ΔTm) and higher inoculation index (I_2) level, respectively (Fig. 4).

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 is recalescence, the higher is the probability for micro-shrinkage and porosity occurrence, especially in soft moulds media, such as green sand moulds (high metal volume expansion). Figure 2 shows the evolution of the level of recalescence (ΔTr), as inoculant addition rates increase. A peculiar difference appears in the behavior of in-mould/cup and ladle inoculated irons. At no more than 0.1wt.% 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 techniques at more than 0.10wt.% alloy addition rate, when higher recalescence was typical for ladle inoculated irons. Lower differences were obtained between the two techniques for more than 0.20wt.% inoculant.

White iron solidification as intercellular carbides or/and inverse chill formation is also dependent on the position of the temperature of the end of solidification (TES), compared to the metastable (white) eutectic temperature (Tmst). Figure 2 illustrates the evolution of the TES, its position given Tmst (ΔT_3 = TES - Tmst), as the inoculant addition rate increases. Because this difference (ΔT_3 parameter) is generally more than 20^{o}C, 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 favourable as it is correlated to a high amount of graphite at the end of freezing. Increasing of the alloy addition rate improves the behavior of irons at the end of solidification but in a different manner for in mould/cup and ladle inoculation methods. 0.10-0.20wt.% inoculant stabilizes the representative solidification parameters at a favourable level for in mould/cup inoculation comparing to 0.20-0.25wt.%, for ladle inoculation.

4. Conclusions

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

*Eutectic undercooling degree of the electrically melted base iron having 0.025%S, 0.003%Al and 3.5%CE is excessively high (39-40^{o}C), generating a relatively high need for inoculation;

*Under these conditions, the in-mould inoculation had a significant effect compared to ladle inoculation, inclusively at lower inoculant usage (less than 0.20wt.%);

*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;

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

*Generally, the efficiency of 0.05-0.15wt.% alloy for in-mould inoculation is comparable to or better than 0.15-0.25wt.% addition in ladle inoculation procedures;

*The Ca,Zr,Al-FeSi alloy appears to be efficient in low S, low Al, low CE hypo-eutectic grey cast irons, especially for late inoculation.

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