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CHILL SENSITIVENESS AND THERMAL ANALYSIS PARAMETERS RELATIONSHIP IN HYPO-EUTECTIC, Ca AND Ca-La INOCULATED COMMERCIAL GREY CAST IRONS

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Abstract

Previous experiments showed a specific distribution of Al, La, and Ca on the section of complex (Mn,X)S compounds, found as major nucleation sites for graphite flakes in low-S cast irons (< 0.03%S), and a possible contribution of La to improve their capacity to nucleate graphite, avoiding carbides formation. In the present work, standard thermal [cooling curves] investigations were undertaken to explore Ca and La-Ca bearing FeSi alloys inoculation effects [10 measurements for each inoculant], in 3.7 – 3.8%CE and optimum S and Mn relationship [0.046 – 0.056%S, (%Mn) x (%S) = 0.024 – 0.029]. Representative temperatures on the cooling curves and under-cooling degrees referring to the meta-stable eutectic temperatures were determined and correlated with the chill [carbides/graphite formation sensitiveness], in different solidification conditions [cooling modulus, wedge shape castings, resin sand mould]. Supplementary addition of La to Ca-bearing inoculants had limited, but specific benefits in these cast irons: lower eutectic recalescence and maximum recalescence rate, higher GRF1 and lower GRF2 graphitizing factors, and lower value of the first derivative at the end of solidification. Consequently, it resulted in a premise for lower shrinkage sensitiveness and lower chill (carbides) sensitiveness, especially at the highest solidification cooling rate (thin wall castings).

Keywords: *Solidification; Thermal analysis; Cooling curve analysis; Grey cast iron; Cooling modulus, Inoculation; Ca; La; Carbides; Graphite*

1. Introduction

Cast iron continues to be the most produced metallic material in the world foundry industry [cca 70% of the total, more than 75 million tons castings each year], including different graphite morphologies, such as lamellar, nodular (spheroidal), vermicular (compacted), or temper carbon, with grey (lamellar graphite) cast iron in the first place (cca 48% rate). Reducing necessity of the metal and energy consumption led to the re-design of the metal parts, and as result, thin wall grey iron castings (less than 5mm wall thickness) are more and more produced, especially in the automotive industry. On the other hand, melting procedures of this cast iron diversified, as furnace type, energy form and metallurgical treatments, resulting a large range of iron melt temperature [1300 – 1600^{o}C] and sulphur content [0.015 – 0.15%S). Transition from cupola furnace melting [moderate overheating and usually more than 0.08%S content] to electrically melting, especially in induction furnaces, typically at higher melt overheating and lower sulphur content characterizes the actual world cast iron industry.

It was found that for commercial grey cast irons, solidified in foundry conditions, complex manganese sulphides, in (Mn,X)S system, act as major graphite nucleation sites for graphite [1]. Higher iron melt temperature (>1500^{o}C) and lower sulphur content (<0.03%S), typically for electric induction furnace melting, are non-favourable conditions for (Mn,X)S formation, and, as a result, solidification will occur at excessive under-cooling referring to equilibrium eutectic temperature. In these conditions, solidification pattern will be characterized by higher sensitiveness to free carbides and/or under-cooled graphite morphologies formation, both of them at negative effects on the mechanical properties of iron castings.

Three stage lamellar graphite formation in commercial cast irons, illustrated by the authors in previous papers [1 - 5] pointed out the importance of three groups of active elements, involved in this process. Strong oxide forming elements, such as Al

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or/and Zr, promoted low size (< 3µm) first compounds, which would act as nucleation sites for (Mn,X)S later formation, usually up to 10µm size (both Mn and S content was important), major nucleants for graphite. The third group of elements, such as Ca, Ba, Sr, Ce, La etc., would act in the first or/and the second stage, to sustain their formation or/and to increase their capacity to nucleate graphite, such as the decreasing of the characteristic parameter of the lattice relationship, plane mismatch. The smaller the mismatch of the two substances, the stronger the nucleation potential between them.

The nucleation of graphite on MnS-type particles was also confirmed by microstructure simulations [6]; role of Mn/S ratio [7]; silica rich oxide bi-films to behave as substrates on which oxy-sulphide particles form [8]; especially for > 0.02%S in grey iron [9].

In previous papers [10, 11] it was illustrated that for critical solidification conditions, such as lower sulphur content [0.018 – 0.026%S, (%Mn) x (%S) = 0.008 – 0.015] and more than 1500^{o}C overheating temperature in the induction furnace, grey iron castings were sensitive to carbides and under-cooled graphite formation. In these conditions, La bearing FeSi alloys acted as effective inoculants, with better efficiency comparing to the conventional commercial inoculants, as Ca-FeSi system.

The main objective of the present work is to apply the thermal [cooling curves] investigations to explore the effects of supplementary addition of La to commercial Ca-bearing FeSi inoculant on solidification parameters, in electrical melted hypo-eutectic grey cast iron (3.7 – 3.8% carbon equivalent) with optimum level of sulphur content [0.046 – 0.056%S, (%Mn) x (%S) = 0.024 – 0.029] and with or without anti-graphitizing action after inoculation.

2. Experimental procedure

Two heats of experimental cast irons were obtained in graphite crucible electric induction furnace [10kg, 8000Hz], with cast iron scrap as metallic charge material, in similar conditions as chemical composition (3.76 – 3.77% carbon equivalent), thermal regime (1550^{o}C overheating and metallurgical treatments), ladle inoculation, 0.25wt.% alloy addition, (0.2 – 0.8mm size grains) (Fig. 1). The iron melt was tapped into the pouring ladle, with inoculating alloy added in the metal stream, during the ladle filling, at 1426 – 1429^{o}C inoculation temperature. Two inoculating systems were considered: commercial Ca bearing FeSi alloy (wt.%: 0.75Ca, 1.25Al, 75Si, bal Fe) and Ca, La bearing FeSi

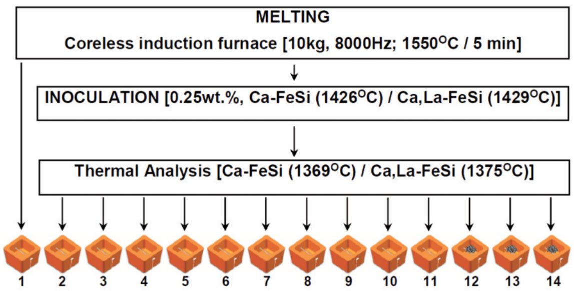


Figure 1. *Experimental schedule [1: un-inoculation; 2 – 11: inoculation; 12 – 14: inoculation + Te addition]*

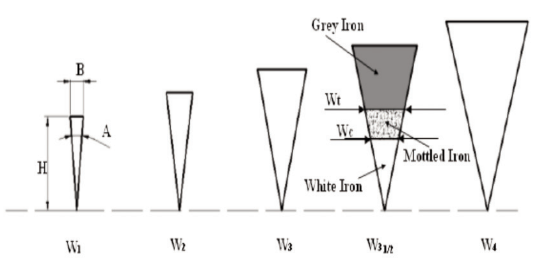
alloy (wt.%: 1.2Ca, 0.96Al, 4.0La, 67Si, bal Fe). The two tested inoculants had similar Ca and Al content, while supplementary La addition to commercial Ca-bearing inoculant was different.

Un-inoculated and inoculated iron melts were poured in standard ceramic cups (7.3mm cooling modulus) including a thermocouple for thermal (cooling curve) analysis of the solidification process. Cooling modulus was the ratio between the volume and total surface area of castings, and it expressed the capacity to transfer the heat from casting through mould media outwardly. Lower cooling modulus value led to higher solidification cooling rate, with important effects on the eutectic and eutectoid structure formation and characteristics.

The used cooling modulus for ceramic cup were

Wedge No.	Wedge dimensions, mm			Angle, deg (A)	Calculated Parameters	
	Width (B)	Height (H)	Length (L)		Wedge Section Area, S (mm^2)	Cooling Modulus, CM (mm)
W_1	5.1	25.4	101.6	11.5	64.8	1.1
W_2	10.2	31.8	101.6	18.0	162.2	2.1
W_3	19.1	38.1	101.6	28.0	363.9	3.5
$W_{3½}$	25.4	44.4	127.0	32.0	563.9	4.5
W_4	31.8	50.8	152.4	34.5	807.7	5.4

(a)



(b)

Figure 2. *Dimensions (a) and geometry (b) of Standard Test Wedges (ASTM A367) [Wc -clear chill; Wt -total chill] [12, 13]*

similar, with 30 mm diameter standard bar casting, typically used for grey cast irons quality evaluation.

Appropriate pouring temperature (1369 – 1375^{o}C) allowed a similar thermal regime as mould behaviour. For both inoculation variants, similar 14 ceramic cups were used: one for un-inoculated iron (1 - UI); ten for inoculated irons [2 – 11 cups]; other three cups [12 – 14], also filled with inoculated irons, included Te, at known strong anti-graphitizing factor.

The two experimental heats, as un-inoculated and inoculated irons were also poured in wedge type casting, type W_1, W_2, and W_3, according to ASTM A 367, in resin sand mould media, to evaluate the chill tendency, the sensitiveness to form free carbides instead of graphite, respectively. The standard size and cooling conditions are illustrated by Figure 2 [12, 13].

3. Results and discussion

3.1. Chemical Composition

Tables 1, 2, and 3 show the chemical composition of the two experimental heats, as Ca-FeSi inoculation (Heat 1) and Ca, La-FeSi inoculation (Heat 2). According to the Table 1 data, both tested cast irons had close chemistry as the base chemical composition, including carbon equivalent (CE = 3.76 – 3.77%) and control factors as sulphur and manganese content (0.046 – 0.055%S, 0.52 – 0.53%Mn, 9.5 – 11.5 Mn/S, (%Mn) x (%S) = 0.024 – 0.029, ΔMn = 0.13 – 0.15).

$$CE = C + 0.3\,(\%Si) - 0.027\,(\%Mn) + 0.3\,(\%P) + 0.40\,(\%S) - 0.063\,(\%Cr) - 0.015\,(\%Mo) + 0.053\,(\%Ni) + 0.22\,(\%Al) + 0.026\,(\%Co) + 0.074\,(\%Cu) - 0.135\,(\%V) + 0.11\,(\%Sn) + 0.115\,(\%Sb)\,[\%] \quad (1)$$

$$\Delta Mn = (\%Mn) - 1.7(\%S) + 0.3 \quad (2)$$

As in commercial grey cast irons complex, manganese sulphides (Mn,X)S appeared to have the major role in graphite nucleation in industrial castings conditions, Mn and S acted as important factors to promote solidification at lower eutectic. As a result, a Mn/S ratio around 10, control factor (%Mn) x (%S) = 0.02 – 0.03, and ΔMn < 0.2 in these experiments acted as favourable conditions for graphitic solidification [1].

Table 2 summarizes the content of some active elements in the final inoculated cast irons, which could play an important role in heterogeneous graphite nucleation. Lower content of typical oxide forming elements, acting in the first stage of graphite nucleation (micro-oxide formation), such as < 0.004%Al, < 0.0007%Zr and < 0.015%Ti led to difficulties in the initiation of graphite formation. On the other hand, less than 0.008%N content did not favour the participation of nitrides in graphite nucleation., the contribution of Ca, La-FeSi to inoculation in La was visible.

Minor elements content (Table 3) was kept at a low level and close content in the two experimental

Table 1. *Base chemical composition, pearlitic factor (Px) and carbon equivalent (CE)*

Heat	Inoc	Chemical composition, wt.%					Mn and S			Px	CE, %
		C	Si	Mn	P	S	Mn/S	(%Mn) x (%S)	ΔMn		
1	Ca	3.19	1.75	0.53	0.13	0.046	11.45	0.024	0.15	4.48	3.76
2	Ca - La	3.23	1.61	0.52	0.14	0.056	9.51	0.029	0.13	4.76	3.77

Table 2. *Content of active elements in cast irons, wt.%*

Heat	Inoc	Al	Zr	Ti	N	Mg	Ca	La	Ce
1	Ca	0.0032	0.00061	0.0107	0.0074	0.0013	0.006	0.0001	0.0008
2	Ca - La	0.0037	0.00047	0.0141	0.0073	0.00078	0.0037	0.0049	0.0005

Table 3. *Representative minor elements content in cast irons, wt.% [Heat 1 / Heat 2] presence in the cast iron chemical composition*

Cr	Ni	Mo	Cu	Co	V	W	Pb
0.045/0.038	0.034/0.029	0.0067/0.0049	0.051/0.055	0.005/0.004	0.0039/0.0046	0.005/0.002	0.00098/0.00089
As	Zn	Te	B	Bi	Nb	Sn	Sb
0.0045/0.0033	0.0007/0.0005	0.0008/0.0008	0.001/0.001	0.0014/0.0014	0.0056/0.0085	0.0045/0.0047	0.0013/0.001

heats. Mn, Si, and some minor elements had important role in pearlite forming sensitiveness (Px factor), according to Equation 3. [14] In the experimental conditions, Px = 4.5 – 4.8, illustrating a predominant pearlite amount formation.

$$Px = 3\,(\%Mn) - 2.65\,(\%Si - 2) + 7.75\,(\%Cu) + 90\,(\%Sn) + 357\,(\%Pb) + 333\,(\%Bi) + 20.1\,(\%As) + 9.60Cr + 71.7\,(\%Sb) \quad (3)$$

According to the obtained chemical composition, the experimental heats were characterized by a medium hypo-eutectic position on the Fe-C, good ratio as manganese and sulphur content, and low level of active and minor elements.

3.2. Thermal (Cooling Curve) Analysis

Figure 3 illustrates a typical cooling curve and its first derivative. Important solidification events were identified of the experimental hypo-eutectic cast irons: the temperature of the start of austenite formation (TAL, °C) and of eutectic freezing (nucleation) (TSEF, °C); the lowest (TEU, °C) and the highest (TER graphitic recalescence, °C) temperature of eutectic reaction; the temperature of the end of solidification (end of solidus) (TES, °C); recalescence (ΔTr = TER – TEU, °C) and the maximum rate of recalescence (TEM, °C/s); minimum value of the first derivative of the cooling curve at the end of eutectic solidification (FDES, °C/s).

The relative position of these solidification events, comparing with metastable (carbidic) (Tmst) temperature was expressed by under-cooling parameters (°C), such as:

a) ΔT_1 = TEU – Tmst, under-cooling at the beginning of eutectic reaction, referring to the lowest eutectic temperature,

b) ΔT_2 = TER – Tmst, under-cooling at the maximum eutectic temperature (eutectic recalescence), and

c) ΔT_3 = TES – Tmst, under-cooling at the end of solidification.

Figure 4 includes typical cooling curves for representative tested irons, as un-inoculated iron [ceramic cup 1] and Ca, La-FeSi inoculated irons, without Te [ceramic cup 8] and with Te addition into the ceramic cup 14 (see Fig. 1).

Stable (Tst) and metastable (Tmst) eutectic temperatures could be calculated depending on the chemical composition of the cast irons (Si as a major influencing factor) or could be measured, by inciting to graphitic solidification by over-inoculation (Tst measurement) or to carbidic solidification by addition of a strong anti-graphitizing agent, such as Te or S (Tmst measurement). In the present work, a Te addition in inoculated cast irons was applied, and the real Tmst was measured on the cooling curve (Tmst = TEU = TER, no recalescence]. It is important to be noticed that solidification above Tmst led to graphite formation, while at solidification under Tmst only carbide could be formed. Two solidification events were the most important for the structure characteristics and the integrity of iron castings: ΔT_1 and ΔT_3.

ΔT_1 parameter illustrated the position of the lowest eutectic temperature comparing to the metastable eutectic temperature; negative value of this parameter showed the occurrence of free carbides in the cast iron structure, in the specific solidification cooling rate.

A more negative level of ΔT_1 parameter caused higher sensitiveness to carbide nucleation, instead of graphite formation. Carbides were characterized by the highest hardness in the cast iron structure, leading to the lowest machinability of castings, negative affecting their cost. Also, free carbides presence led to lower mechanical properties and fracture incidence, especially in impact conditions.

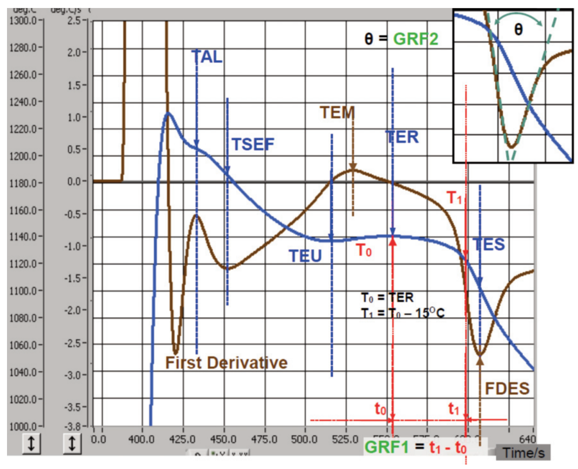


Figure 3. *Representative parameters on the cooling curve and its first derivative (Ca, La-FeSi inoculation)*

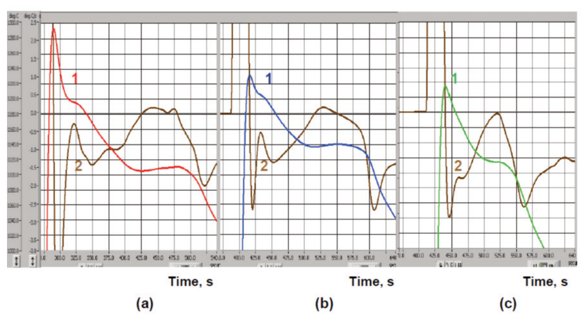


Figure 4. *Typical cooling curves (1) and their first derivatives (2) of non-inoculated (a) and Ca, La-FeSi inoculated cast irons [b) Inoculation; c) Inoculation + Te]*

Contrary, for positive position of ΔT_1 parameter carbides were not formed, being favourable conditions for graphite formation. On the other hand, it is also important the position of ΔT_1 parameter above the zero level: positive, but lower values ment that TEU was closed to Tmst, so graphite could be formed, instead of carbide, but at higher eutectic undercooling. Lower ΔT_1 value favours a higher incidence of under-cooled graphite morphology (such as D-type ASTM), favouring ferrite formation and decreasing of the mechanical properties and wear resistance .

Figure 5 shows the level of the ΔT_1 parameter for un-inoculated and inoculated cast irons, with the two systems of alloys, with and without Te-addition after inoculation. The solidification behaviour of the experimental cast irons at the lowest eutectic temperature was highly depending on the status of the iron melt (with or without inoculation) and anti graphitizing action after inoculation, but it was less depending on the inoculant system.

For both inoculants, the iron melt inoculation before solidification resulted in visible improvement of the cast iron quality, as ΔT_1 increased from negative value (-15°C) up to positive values (17 – 20°C). This way, inoculation suppressed the free carbides formation and promoted favourable conditions for graphite nucleation, in the applied solidification parameters: ceramic mould media and casting at 7.3mm cooling modulus.

Te addition into the ceramic cup, before iron pouring, contributed to important decreasing of inoculated cast irons ΔT_1 values, up to -2.5 ─ +2.5°C, respectively. As a result, carbides formation was promoted and solidification was moved to carbidic system.

For the same addition rate, the inoculant type, as La supplementary addition to Ca bearing FeSi alloy, did not appear to have an important influence on normal solidification. At lower scale, La appeared to have a limited beneficial effect if a strong anti-graphitizing factor acted after inoculation.

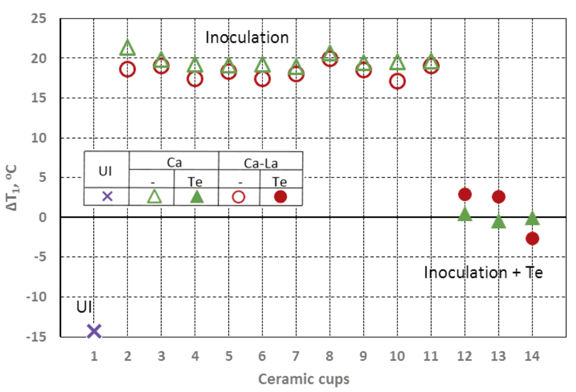


Figure 5. *Under-cooling (ΔT_1 = TEU - Tmst) at the lowest eutectic temperature (TEU) comparing to metastable eutectic temperature (Tmst) [1: non-inoculation; 2 – 11: inoculation; 12 – 14: inoculation + Te addition]*

Complex chemical composition, typical for commercial grey cast iron (more than 30 elements presence, in a large range of content, see Tables 1-3) favoured a segregation process during solidification, between primary austenite and eutectic cells, on the one hand, and especially inside or outside of eutectic cells (in the space between them).

A lot of elements had a limited solubility in the solidified iron comparing to the iron melt, so they would be concentrated in the last solidified iron part, in the last available space, i.e. between eutectic cells, such as C, P, Mn, Mo, V, Cr etc. This last solidified iron melt, usually at a lower temperature than the metastable eutectic temperature in commercial cast irons, included different phases, such as free carbides, phosphides, steadite etc. On the other hand, these last solidified liquid iron micro-volumes formed micro-shrinkages (holes, contraction defects), without possibility to avoid them, by feeding with liquid. The inter eutectic cells defects, including segregated phases and micro shrinkages, had negative effects on the quality of iron castings.

ΔT_3 parameter offered information on the sensitivity to formation phase and the presence of contraction defects at the end of solidification, with inter-eutectic cells distribution. Generally, for grey cast iron solidification, ΔT_3 parameter had negative values, as usually the temperature at the end of solidification (TES) was lower than metastable eutectic temperature (Tmst). Lower (more negative) ΔT_3 values, higher the sensitiveness to structure and contraction defects at the end of solidification was.

Figure 6 shows the obtained values for ΔT_3 parameter for the tested cast irons. Non inoculated cast iron (UI) solidified at a very low temperature, as TES was more than 40°C below Tmst (ΔT_3 = -42.5°C). Inoculation significantly affected the last part of the solidification process, as this treatment decreased the under-cooling at this moment up to ΔT_3 = -5 …-15°C, much more for Ca-FeSi inoculated cast irons. Anti graphitizing treatment of the inoculated irons (Te addition before solidification) drastically affected the end of solidification, illustrating by ΔT_3 increasing up to -40…-47°C.

A relationship between the under-cooling at the end of solidification (ΔT_3) and in the first part of eutectic reaction, corresponding to the lowest eutectic temperature (ΔT_1) is shown in Figure 7. Both under-cooling parameters had negative values, corresponding to the highest under-cooling on the entire solidification process for basic iron (non-inoculated iron), which consumed below metastable eutectic temperature, promoting carbides instead of graphite (including the area between eutectic cells) and contraction defects between eutectic cells.

Inoculation affected both considered under-cooling parameters, resulting in ΔT_3 to be no less than -17°C and ΔT_1 more than 17°C. Higher ΔT_1 level (lower under-cooling at the beginning of eutectic reaction), lower under-cooling at the end of solidification (less negative values), for both inoculating systems, with a good relationship between them was.

Te addition, as anti graphitizing treatment of the iron melt after inoculation, led to the intermediary level of the under-cooling parameter ΔT_1 (close to zero or just below it), but the highest under-cooling at the end of solidification was restored, similarly to the non-inoculated cast irons.

The position of TEU and TER temperatures (visible especially as zero point level on the first derivative of the cooling curve) as the lowest and the highest (recalescence) eutectic temperatures, were important not only for comparing the stable (Tst) and

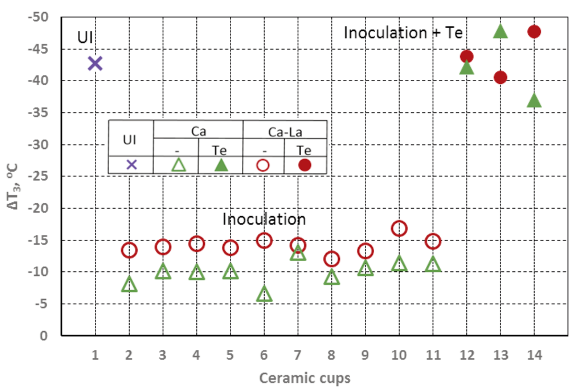


Figure 6. *Under-cooling (ΔT_3 = TES - Tmst) at the end of solidification (TES temperature) comparing to metastable eutectic temperature (Tmst) [1: non-inoculation; 2 – 11: inoculation; 12 – 14: inoculation + Te addition]*

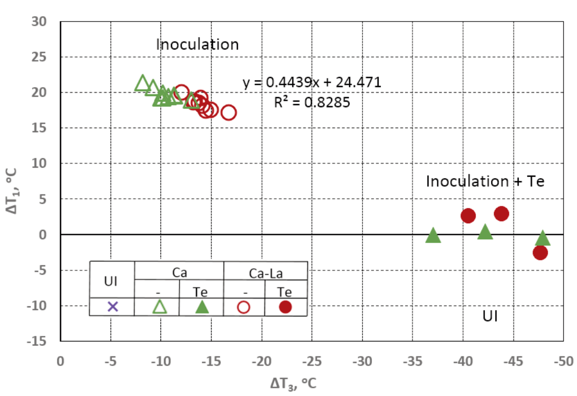


Figure 7. *Relationship between the under-cooling at the end of solidification (ΔT_3) and the under-cooling in the first part of the eutectic reaction, corresponding to the lowest eutectic temperature (ΔT_1) of non-inoculated (UI) and inoculated cast irons*

metastable (Tmst) eutectic temperatures, expressed by eutectic under-cooling parameters but also as a difference between them.

The heat delivered by eutectic cells, including austenite plus graphite, contributed to temperature increasing during eutectic reaction, so the TER parameter (the maximum temperature in eutectic reaction) was visibly higher compared to TEU. Known as eutectic recalescence, ΔTr = TER – TEU parameter is important especially for the integrity of iron castings, produced in soft mould media, such as a green sand mould.

Expressing the level of eutectic (graphite + austenite) precipitation during the eutectic reaction, recalescence was also a measure of the resulted graphitic force applied on the mould walls, resulting in an enlargement of the mould cavity and of the shrinkage (holes in the casting) during solidification, respectively. Too high amount of graphite precipitated during the first stage of eutectic reaction meant that there was a deficit in graphite precipitation at the end of eutectic reaction. Consequently, there was not enough available graphite to compensate the contraction process and to avoid micro-shrinkage, respectively. For this reason, in many industrial cases it is important to obtain a reduced level of the eutectic recalescence ΔTr. One of the important criteria as quality of an inoculant is its capacity to lead to a reduced eutectic recalescence after this treatment, usually applied to avoid free carbides formation and under-cooled graphite occurrence in grey cast irons.

Figure 8 compares the values of eutectic recalescence (ΔTr, °C, on the cooling curve) and the maximum rate of recalescence (TEM, °C/s, on the first derivative of the cooling curve) of the two inoculated cast irons. It is visible that Ca, La-FeSi inoculation led to lower values for recalescence (ΔTr = 3…5°C) and the maximum rate of recalescence (TEM = 0.18…0.24°C/s), comparing to commercial Ca-FeSi alloy (ΔTr = 5…6°C, TEM = 0.26….0.34°C/s), at 25-30% as average. As strong anti-graphitizing treatment, Te treatment led to graphite avoidance, so all of carbon content, non-dissolved in austenite formed carbides. In this condition, TEU was equal to TER, so recalescence did not appear on the cooling curve.

Graphitization process [graphite formation during solidification] could also be characterized by Graphitic Factors, GRF1 and GRF2 [15] and the value of the first derivative at the end of solidification FDES, obtained by measurement on the cooling curve and its first derivative.

GRF1 referred to graphite formation immediately after the attending of the maximum recalescence (TER) (Fig. 3) and it was expressed by registered time for 15°C temperature decreasing after TER point [higher GRF1 ment that the nucleation and the growth of eutectic occur in longer times, resulting in a higher graphite amount formation].

According to Figures 9 and 10, inoculation visibly contributed to increasing the capacity of cast iron to form graphite (instead carbides) during solidification, as GRF1 parameter increased for both inoculating systems with 70-85%, as average from 25.5 level in non-inoculated iron up to 43.7 level for Ca-FeSi inoculation and 47.4 level for Ca, La-FeSi inoculation, respectively. For all of the ten measurements, Ca, La-FeSi inoculation led to higher graphitizing factor GRF1 than it was obtained for Ca-FeSi inoculation (43.6 – 50.5 comparing to 40.7 – 46.0 range). As it was expected, Te addition after inoculation cancelled the graphitizing effect of this metallurgical treatment, so GRF1 factor returned to the same level as it was without inoculation (20-30).

Graphitizing factor GRF2 and the value of the first derivative at the end of solidification (FDES) illustrated the behaviour of cast iron at the end of

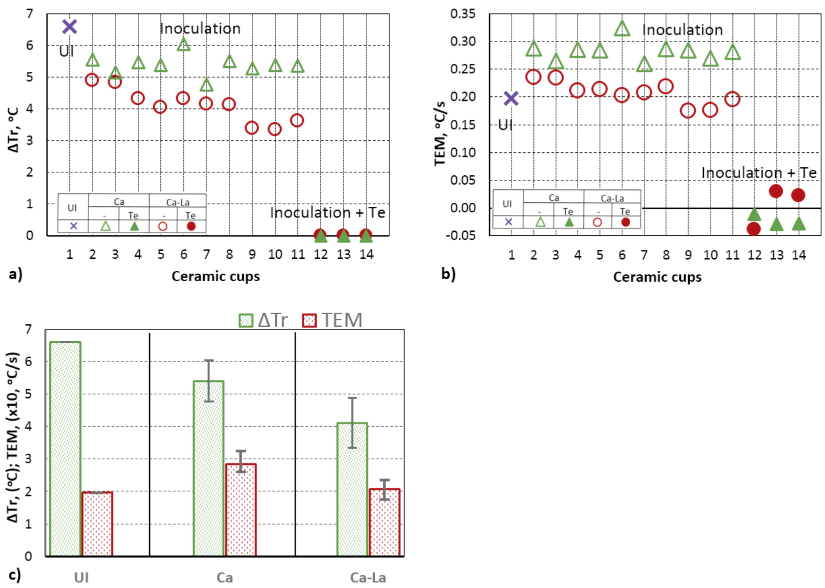


Figure 8. *Eutectic recalescence ΔTr (a), the maximum recalescence rate TEM (b) and as the range and average values (c) of the two inoculated cast irons [UI-un-inoculated cast iron]*

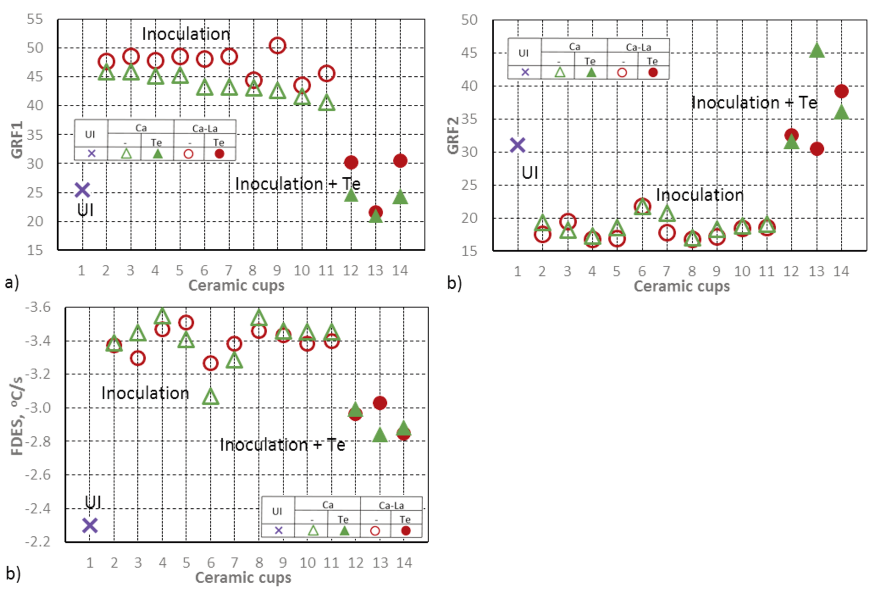


Figure 9. *Graphitizing factors GRF1 (a, seconds) and GRF2 (b, angular degrees), and the first derivative at the end of solidification FDES (c, $^{0}C/s$) [UI - non-inoculated cast iron]*

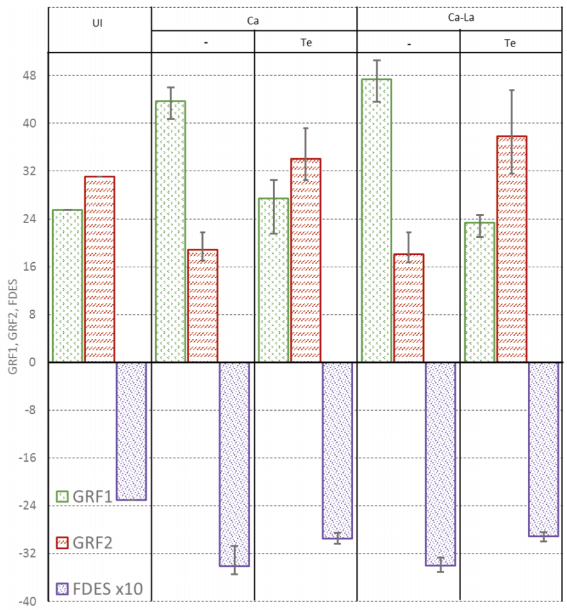


Figure 10. *Average and range of Graphitizing factors GRF1 (seconds), GRF2 (angular degrees) and the first derivative at the end of solidification FDES (^{0}C/s) of non-inoculated (UI) and inoculated (Ca, Ca-La) cast irons (Te-tellurium addition after inoculation)*

solidification (Fig. 3). GRF2 indirectly expressed the thermal conductivity and it was illustrated by the angle of the first derivative at TES, calculated by the use of FDES parameter. Low values of FDES [more negative] and GRF2 were related to a high thermal conductivity, which meant a higher amount of graphite precipitated at the end of solidification, and, as a result, cast iron was more resistant to micro-shrinkage formation. This part of graphite was an important favourable factor to decrease the sensitiveness of iron castings to contraction defects formation [16, 17].

Lower levels of GRF2 and FDES factors indicated higher cast iron quality. In this case, inoculation decreased the GRF2 values from 31 up to 16 – 20 range, for both inoculants, with Ca, La-FeSi as performance: 16.7- 21.8 (18.1 as average) versus 17.0–21.8 (18.9 as average).

Tellurium addition after inoculation increased the GRF2 factor up to the level even above of the non-inoculated iron (30 – 45). Similarl behaviour was recorded also as FDES parameter. If non-inoculated cast iron was characterized by FDES = - 2.30^{o}C/s, inoculation moved this parameter to – 3.3 ….- 3.6 ^{o}C/s, while Te addition after inoculation was in the intermediary range (- 2.8…-3.0^{o}C/s).

It can be seen that the performance of Ca, La-FeSi alloy, comparing to Ca-FeSi inoculant, was higher for GRF1 evaluation comparing to GRF2 or FDES, not only after inoculation, but also (at a reduced power) if a strong anti-graphitizing factor acted after inoculation (Te addition).

3.3. Chill tendency

Chill (carbide formation sensitiveness) was evaluated by simultaneous pouring of typical test castings (W_1, W_2, W_3), defined by ASTM A 367 (Fig. 2). The wedge shape of these castings caused a strong variation of the solidification cooling rate, from the base (the lowest level) up to the apex (the maximum level). As Fig. 2b shows, the portion nearest to the apex, entirely free of grey spots, was designated as the clear chill zone (Wc), while the portion from the end of the clear zone to the location where the last spot of cementite or white iron was visible was designated as the mottled zone. The region from the junction of grey fracture to the first appearance of chilled iron was designated as the total chill (Wt). In the present work the relative total chill [RTC = 100 (Wt / B), %] was considered, where B was the maximum width of the test wedge.

The W_1, W_2, and W_3 wedge samples defined in Fig. 2a were used to evaluate the solidification characteristics of thin wall castings. In order to acquire more accuracy in evaluation of the obtained results, each casting was measured including following characteristics: B-parameter, volume (V), and total area (A), to obtain the real values for cooling modulus and relative total chill, respectively. Previous experiments pointed out that these measurements were necessary to obtain a more realistic evaluation on the obtained results.

Figure 11 a) shows the obtained results for inoculated cast irons, as relative total chill (RTC), influenced by the solidification cooling rate, expressed by the cooling modulus of casting (higher cooling modulus, lower cooling rate) and by inoculating system (Ca, La-FeSi versus Ca-FeSi). As expected, the decreasing of the solidification cooling rate by increasing the cooling modulus resulted in the decreasing of the carbides formation incidence, expressed by decreasing the relative total chill. This was found true for both inoculating systems, with Ca, La-FeSi performance (cca 20% more efficient). The superior inoculating power of Ca, La-FeSi alloy was more visible for W_1 type wedge sample and for the highest solidification cooling rate, respectively. This behaviour is very important for thin wall castings category (less than 5mm wall thickness), that is increasingly produced in the world foundry industry, especially for the automotive industry.

Figure 11 b) illustrates the importance of inoculation in chill tendency control and also the relationship between the chill tendency of grey cast iron and the eutectic under-cooling ΔT_1, referring to the lowest eutectic temperature TEU, comparing to the metastable eutectic temperature Tmst.

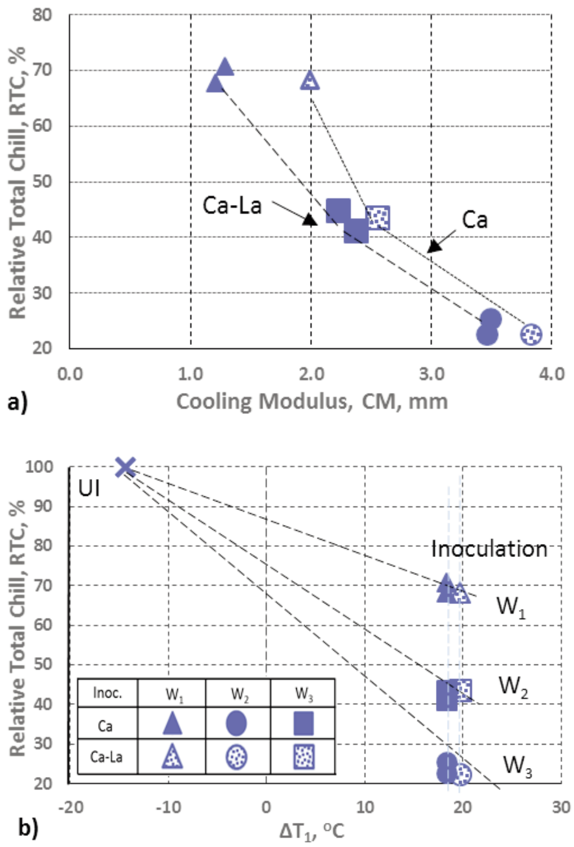


Figure 11. *Relative total chill RTC (a) and relationship RTC – ΔT_1 (b) [W_1, W_2, W_3- wedge castings, Fig. 2)*

4. Conclusions

The evaluation of the effects of supplementary La addition to commercial Ca-FeSi inoculants on the quality of electrically melted, hypo-eutectic (3.7 – 3.8% carbon equivalent) grey cast iron at optimum Mn and S relationship was recorded by thermal (cooling curve) analysis (10 measurements) and chill tendency test and the following conclusions can be drawn:

1) In experimental conditions, the solidification behaviour of cast irons at the lowest eutectic temperature (ΔT_1) was strongly dependent on the status of the iron melt (with or without inoculation) and anti-graphitizing action after inoculation, but it was less dependent on the inoculant system.

2) Inoculation significant beneficial affected the last part of the solidification process (ΔT_3), much more for Ca-FeSi inoculated cast irons.

3) Te addition, as anti-graphitizing treatment of the iron melt after inoculation, led to the intermediary level of the under-cooling parameter ΔT_1 (close to zero or just below it), but it restored the highest under-cooling at the end of solidification ΔT_3, similarly to the non-inoculated cast irons.

4) Higher ΔT_1 level (lower under-cooling at the beginning of eutectic reaction) and lower under-cooling at the end of solidification ΔT_3 (less negative values) was observed for both inoculating systems, with a good relationship between them.

5) Ca, La-FeSi inoculation led to lower values for eutectic recalescence ΔTr (3…5°C), comparing to commercial Ca FeSi alloy (5…6°C), at 25% as an average, favourable especially for soft mould use.

6) For all of ten measurements, Ca, La-FeSi inoculation resulted in a higher graphitizing factor GRF1 than it was obtained for Ca-FeSi inoculation (47.4 comparing to 43.7 as average), expressing a higher capacity to form graphite immediately after attending the maximum eutectic temperature (recalescence).

7) Inoculation decreased the graphitizing factor GRF2 (from 31 up to 16 – 20) and the value of the first derivative at the end of solidification FDES (from -2.3 up to -3.3-3.6°C/s), for both inoculants, with Ca, La-FeSi as a performance in the improving of the cast iron quality.

8) The decreasing of the solidification cooling rate by increasing of the cooling modulus caused the decreasing of the carbides formation incidence for the both inoculating systems, with Ca, La-FeSi performance (cca 20% more efficient). The superior inoculating power of Ca, La-FeSi alloy was more visible for W_1 type wedge sample and for the highest solidification cooling rate, respectively.

9) A good relationship was obtained between the chill tendency of grey cast iron and the eutectic under-cooling ΔT_1, referring to the lowest eutectic temperature TEU, comparing to the metastable eutectic temperature Tmst.

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OSETLJIVOST NA HLAĐENJE I PARAMETRI TERMALNE ANALIZE KOD HIPOEUTEKTIČKOG KOMERCIJALNOG SIVOG LIVA SA DODATKOM Ca I Ca-La KAO INOKULANATA

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Apstrakt

Prethodni eksperimenti su pokazali da postoji specifična raspodela Al, La i Ca na preseku složenih (Mn,X)S jedinjenja, gde je utvrđeno da ti delovi predstavljaju glavna mesta za nukleaciju ljuspastog grafita u livenom gvožđu sa niskim sadržajem sumpora (< 0.03%S), a da prisustvo La može da poboljša sposobnost nukleacije grafita bez formiranja karbida. U ovom radu je urađena standardna termalna analiza (krive hlađenja) da bi se ispitao efekat inokulacije FeSi legura dodavanjem Ca i Ca-La (10 merenja za svaki inokulant), sa 3,7-3,8% CE (ekvivalentni sadržaj ugljenika) i sa optimalnim odnosom S i Mn [0.046 – 0.056%S, (%Mn) x (%S) = 0.024 – 0.029]. Reprezentativne temperature na krivama hlađenja i stepeni pothlađenja koje se odnose na metastabilne eutektičke temperature su određeni i povezani sa osetljivošću na hlađenje (osetljivost na formiranje karbida/ grafita) za različite uslove prilikom očvršćavanja (modul hlađenja, odlivak u obliku klina, kalup od mešavine peska i gline). Dodavanje La inokulantima koji su sadržali Ca je imalo ograničenu, ali posebnu prednost za liveno gvožđe: niža eutektička reakciona toplota i maksimalna brzina dostizanja reakcione toplote, viši GRF1 i niži GRF2 faktori za dobijanje grafita, kao i niža vrednost prvog derivata na kraju očvršćavanja. Shodno tome, kao rezultat postignuta je niža osetljivost na skupljanje i niža osetljivost na hlađenje (karbidi) posebno pri najvećoj brzini hlađenja prilikom očvršćavanja (odlivci sa tankim zidovima).

Ključne reči: *Očvršćavanje; Termalna analiza; Analiza krive hlađenja; Sivi liv (liveno gvožđe); Modul hlađenja; Inokulacija; Ca; La; Karbidi; Grafit*