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COOLING RATE DEPENDENCE OF STRUCTURES CHARACTERISTICS IN Ce-INOCULATED LOW-S GREY IRONS

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ABSTRACT

The efficiency of Ce,Ca,Al-FeSi alloy was tested for lower addition rates (0.15-0.25wt.%), as, traditionally, high inoculant addition rates have been used in low sulphur grey cast irons, comparing to the base iron and conventional inoculated irons (Ba,Ca,Al-FeSi commercial alloy). The present work explores chill and associated structures in hypoeutectic grey iron chill wedges, with cooling modulus 0.21 cm and a large variation of the cooling rate, from the apex to the base of W_2 *samples [ASTM A 367, furan resin mould]. The chill tendencies of the experimental irons correlate well with the structure characteristics, displayed as the carbides/graphite ratio of undercooled graphite morphologies. Carbide sensitivity is lower with increasing wedge width, but depends on whether the state of the iron is as base iron or inoculated with different alloys. Undercooled graphite was present for both un-inoculated irons and higher cooling rate inoculated irons. As expected, inoculation as well as an increase in wall thickness of the same wedge sample led to improved undercooled graphite control. The difference in effects of the two inoculants addition is seen as the ability to decrease the amount of carbides and undercooled graphite, with Ce-bearing FeSi alloy outperforming the conventional inoculant, especially at the low alloy addition and high cooling rate solidification.*

KEYWORDS: Grey iron, Low S, Cooling rate, Inoculation, Ce, Structure, Carbides, Graphite morphology

1. Introduction

Inoculation is a means of controlling the structure and properties of cast iron by minimizing eutectic undercooling and increasing the number of active graphite nucleation sites during solidification. The role of an inoculant, usually as a FeSi-based alloy including one or more inoculating elements (Ca, Ba, Sr, Ce, La etc), is to influence the formation, characteristics and, thereby, the quality of nuclei for flake graphite and the eutectic structure, respectively.

It accomplishes this by improving the micro-inclusions that already exist in the iron melt (such as sulphides), rather than by creating new compounds. However, this is possible especially as nitrides, in iron melts with very low sulphur content.

Generally, well inoculated grey irons are characterized by graphite nucleation with a low degree of eutectic undercooling, usually as more than 25°C above the metastable (carbidic) eutectic equilibrium temperature (Tmst), which is the base condition to promote Type A graphite (random graphite flakes form uniformly in the iron matrix).

As the undercooling increases and graphite nucleation start is closer to Tmst, the graphite will branch, forming abnormal patterns. This is known as Types B, D and E graphite ***(Fig. 1).***

A further increase in undercooling will suppress the formation of graphite and results in a hard and brittle white iron carbide structure, at very low machinability.

The avoidance of both carbides and undercooled graphite morphologies (B, D, E) in the advantage of Type A graphite formation is the most important objective of the inoculation in grey cast iron production.

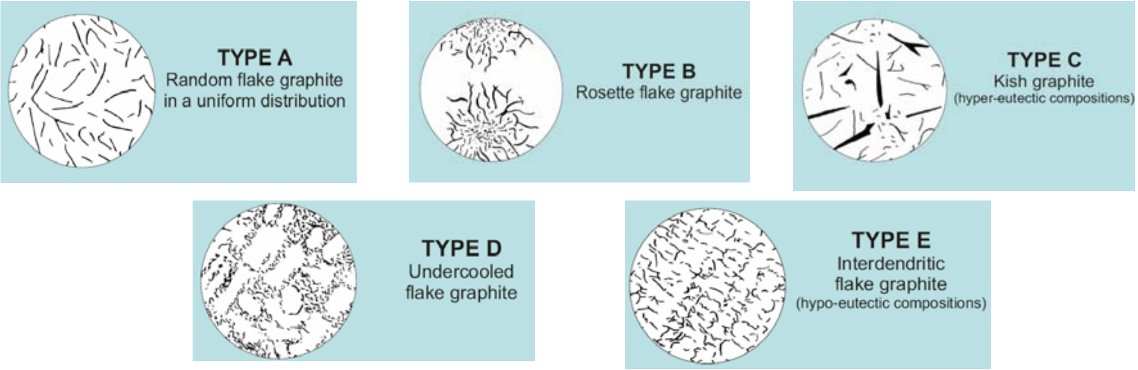


Fig. 1. *Typical graphite morphologies in grey cast iron (ASTM).*

There are a lot of causes for higher eutectic undercooling and undercooled graphite formation in grey irons, such as lower carbon equivalent level (low carbon and / or silicon), detrimental contents of Mn, S and Al [< 0.05%S, < 0.03 as (%Mn) x (%S) control factor, < 0.004%Al] to sustain complex (Mn,X)S compounds formation as major graphite nucleation sites [1-6], melting practice (high steel scrap amount, high superheating and holding time etc) and pouring practice (low pouring temperature, moulds with high thermal conductivity, thin wall castings etc) [7-9].

The actual world practice in grey iron foundries, involving melting shops including the new generation, acid lined, medium frequency coreless induction furnaces (200-1000Hz, > 250 kW/t specific power) and thin wall castings production led to critical conditions for iron solidification, as base iron chemistry [< 0.05%S, < 0.005%Al, < 0.03 (%Mn) x (%S)], more than 1500^{o}C superheating and more than 2^{o}C/sec cooling rate during solidification.

These irons are notoriously difficult to inoculate, in order to avoid carbides and/or undercooled graphite morphologies, especially in economic conditions.

Previous experiments [7,10-12] illustrated the efficiency of some special inoculating variants in low sulphur grey irons, such as Rare Earth (RE) bearing FeSi alloys (Ce, La or Mischmetal variants) or complex inoculants, such as the most representative Ca,Ba,Al-FeSi, Zr,Sr-FeSi, and Ca,Ce,Al-FeSi alloys.

The main objective of the present paper is to examine the effect of Ce,Ca,Al-FeSi alloy on the structure characteristics of low sulphur grey cast irons, comparing to a conventional (commercial) inoculant in Ba,Ca,Al-FeSi alloy system, at lower addition rates procedures (< 0.3wt% inoculant) and a large variation of the cooling rate during solidification, as castings geometry.

2. Experimental procedure

The experimental melts were obtained using an induction furnace (acid lining, 100kg, 2400Hz).

The iron melt was heated to 1540^{o}C held for 10 min, then tapped into the pouring ladle (10kg) at 1530^{o}C allowing a final pouring temperature at 1350^{o}C into furan resin sand moulds.

A proprietary Ce-bearing FeSi alloy [1.5-2.0%Ce, 0.75-1.25%Ca, 0.75-1.25%Al, 70-76%Si, Fe bal] [10] was used, comparing to a conventional (commercial) Ba,Ca,Al-FeSi inoculant (typically chemistry: 1.5%Ca, 1.0%Ba, 1.0%Al, 65%Si, Fe bal), both of them at 0.2-0.7mm grain size range.

Addition rates were as 0.15wt.% and 0.25wt.%, point of addition was into the stream when tapping from the furnace into the pouring ladle.

The following final chemical compositions of the inoculated irons were obtained: 3.15-3.3%C, 1.50-1.55%Si, 0.67-0.70%Mn, 0.020-0.025%S, 0.001-0.002%Al, 0.015–0.018%Ti, 0.0060-0.0100%N, 0.05-0.1%Cr, 0.025-0.050%Ni, 0.009-0.015%Mo, 0.004 – 0.006% V, at carbon equivalent 3.6-3.8% CE.

Chill wedges of the type W_2 (10.2mm base width, 31.8mm height, cooling modulus CM=0.21cm) specified in the ASTM A-367 wedge test were considered (resin sand mould), as usually used chill samples in grey iron foundries.

CM is defined as the ratio between volume and the total external casting surface and is an expression of the capacity to transfer a given quantity of heat through an existing surface to the mould.

Higher CM equates to slower cooling rate (CR) and lower undercooling during eutectic solidification. The equivalent cooling modulus, represented by W_2 wedges, corresponds to round bars with diameter of 8.4 mm.

3. Results and discussion

In a chill wedge, that portion nearest the apex, entirely free of grey areas, is designated as the clear chill zone (W_c).

The portion from the end of the clear chill zone to the location where the last presence of cementite, or white iron is visible, is designated the mottled zone (W_m).

The region from the junction of grey fracture to the first appearance of chilled iron (apex) is designated the total chill (W_t).

The parameters relative clear chill (RCC) and relative total chill (RTC) were also considered:

$$RCC = 100 [W_c / B] (\%) \quad (1)$$

$$RTC = 100 [W_t / B] (\%) \quad (2)$$

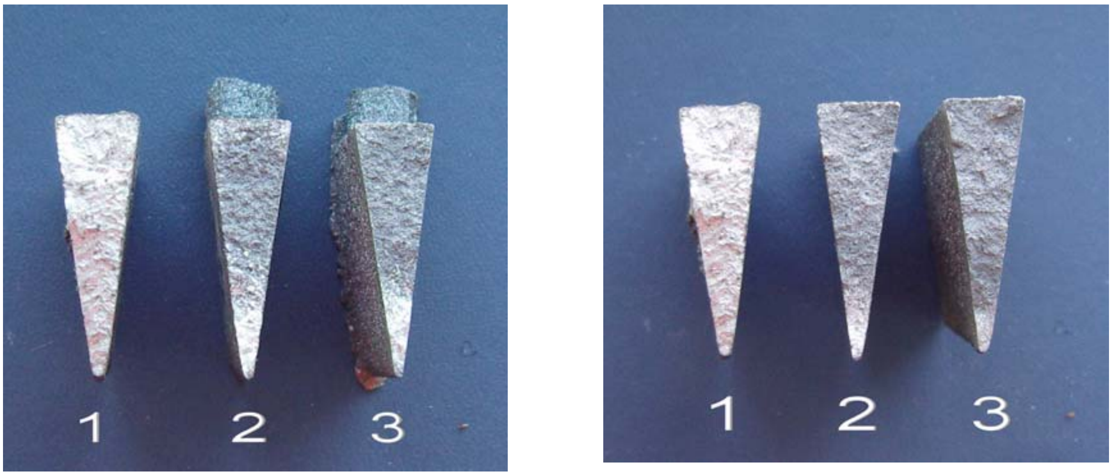
Where B is the maximum width of the test wedge.

A medium solidification rate, represented by a W_2 wedge sample, was also used to evaluate the structure formation in un-inoculated and different inoculated irons, with the two considered inoculants (Ce,Ca,Al-FeSi and Ba,Ca,Al-FeSi alloys) at the two addition rates (0.15wt.% and 0.25wt.%) ***(Table 1).***

Table 1. *Structure characteristics [W_2 – wedge sample, ASTM A367]*

Wedge width (mm)	Inoc. (%)	Carbides, %			Graphite; %			Undercooled Graphite (B+D+E), %			Ferrite, %		
		U.I	**Ba,Ca-FeSi**	**Ce,Ca-FeSi**	**U.I**	**Ba,Ca-FeSi**	**Ce,Ca-FeSi**	**U.I**	**Ba,Ca-FeSi**	**Ce,Ca-FeSi**	**U.I**	**Ba,Ca-FeSi**	**Ce,Ca-FeSi**
1.91	0.15	40	30.0	30.0	1.5	1.5	2.25	100	100	100	0	0	0
	0.25		35.0	30.0		1.75	3.25		100	100		0	0
3.25	0.15	40	29.0	20.0	1.5	2.5	3.5	100	100	100	0	0	4.0
	0.25		22.5	7.5		3.5	4.5		100	100		2.5	4.0
4.89	0.15	39.5	6.5	3.0	1.5	3.25	6.0	100	100	90	0	4.0	5.0
	0.25		4.0	1.5		5.0	6.5		100	80		4.0	2.5
6.62	0.15	35	2.5	2.0	1.75	6.5	8.5	100	90	70	0	5.0	5.0
	0.25		0	0		7.5	9.5		65	40		5.57	2.0
8.18	0.15	39.5	6.5	2.0	1.75	8.5	11.0	100	85	70	0	5.0	5.0
	0.25		0	0		10.0	11.5		50	30		6.5	1.0

Fractures of W_2-samples ***(Fig.2)*** were analyzed metallographically, un-etched and etched with Nital (2%), along the geometrical centerline of the chill wedge and at different distances from the apex of the wedge.



(a) ***(b)***

Fig. 2. *Influence of Ba,Ca,Al-FeSi (a) and Ce,Ca,Al-FeSi (b) inoculation (1 - un-inoculated, 2 - 0.15% alloy and 3 - 0.25% alloy) on the chill wedge W_2-ASTM A367 macrostructure.*

Using chill samples, offering different wall thickness simulated different solidification conditions to be explored. At the farthest distances from the apex of the chill wedge, the cooling rates are very shallow.

The chill tendencies of the experimental irons correlate well with the structure characteristics, displayed as the carbides / graphite ratio and as the presence of undercooled graphite morphologies. Different structures were obtained at the same area (width) of the wedge sample.

Figures 3a and 3b illustrate that an inverse relationship exists between free carbides level and distance from the apex of the chill wedge, and the wedge width, respectively.

Carbide sensitivity is lower with increasing wedge width, but depends on whether the state of the iron is as base iron or inoculated with different alloys and with different additions, too.

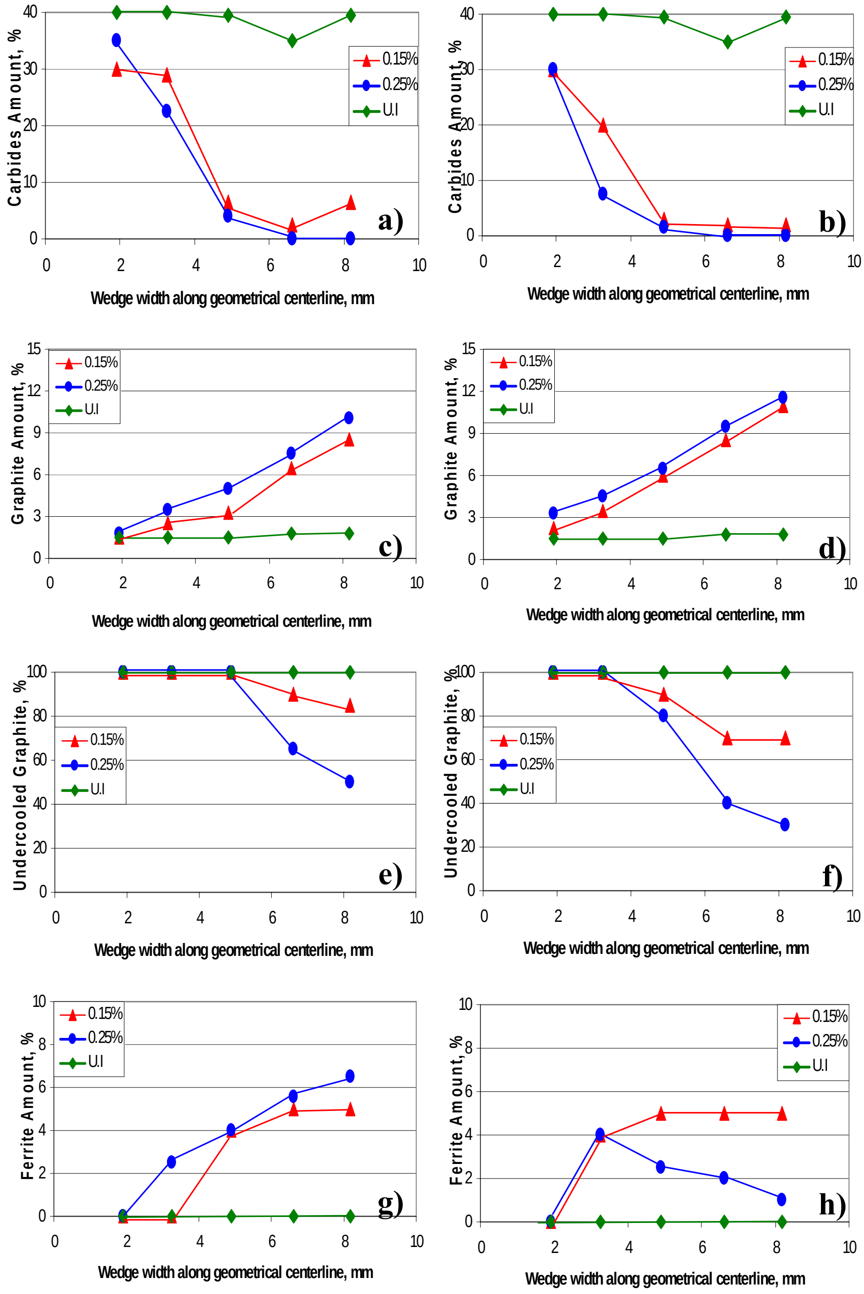


Fig. 3. *Influence of inoculant type (a,c,e,g-Ba,Ca,Al-FeSi; b,d,f,h-Ce,Ca,Al-FeSi) and amount (0.15 and 0.25wt.%) on the structure characteristics along the geometrical centerline of W_2 -ASTM A367 chill wedge comparing to un-inoculated (UI) irons [a, b-carbides amount; c, d-graphite amount; e, f-undercooled graphite amount; g, h-ferrite amount].*

The inoculation was able to totally avoid free carbides formation for more than 6.5mm wall thickness for Ba,Ca-FeSi inoculated irons and 5mm for Ce,Ca-FeSi treatment, with a limited difference for the two inoculant addition rates. Ce-bearing inoculant appears to be more effective especially for thin wall castings (3-4mm), despite the critical conditions of chemical composition.

It was found that despite the white iron appearance, the samples contained different amounts of free carbides and a small amount of graphite, depending on the inoculant type and addition rate ***(Figs. 3c, d)***.

According to the higher capacity to prevent free carbides formation, Ce-bearing FeSi alloy led to higher graphite amount for the same cooling rate solidification conditions and for the two addition rate procedures.

Un-inoculated iron is more sensitive not only to free carbides formation (chill tendency) but also to undercooled graphite appearance at the lower solidification rate (at the base of the wedge sample).

Figures 3e and 3f show an inverse relationship between undercooled graphite levels and the distance from the apex of the chill.

Undercooled graphite was present for both un-inoculated irons and higher cooling rate inoculated irons.

As expected, inoculation as well as an increase in wall thickness of the same wedge sample led to improved undercooled graphite control.

The amount of undercooled graphite decreased with increasing the distance from the apex of the wedge. The Ce,Ca-bearing inoculant outperformed the Ba-Ca-FeSi alloy, especially at low inoculant additions. The difference in effects of the inoculant addition rates is seen as the ability to decrease the amount of undercooled graphite, especially above a 5.0 mm wedge width.

The amount of ferrite ***(Figs. 3g, h)*** is strongly dependent on the presence of undercooled graphite: the highest level of ferrite is typical in the mottled iron area, at the highest undercooled graphite amount.

The association of ferrite and carbides in the same area is an anomaly in the structure (pearlite and carbides normally coexist) and is typically linked to the presence of type D undercooled graphite morphologies. Medium eutectic undercooling led to free carbides and type D graphite formation during eutectic solidification (carbides at the beginning and graphite at the end of the eutectic reaction). The presence of type D graphite favors carbon diffusion during the eutectoid reaction due to the shorter distance between graphite particles and consequently ferrite formation (Ferrite + Pearlite = 100%), despite a high cooling rate during the eutectoid reaction (also typical for the center of type B graphite).

There is a difference depending on how chill is evaluated for inoculated irons macro-structure (fracture analysis, visual white/mottled iron evaluation) versus microstructure (metallographic analysis, free carbides/graphite presence) ***(Fig. 4)***.

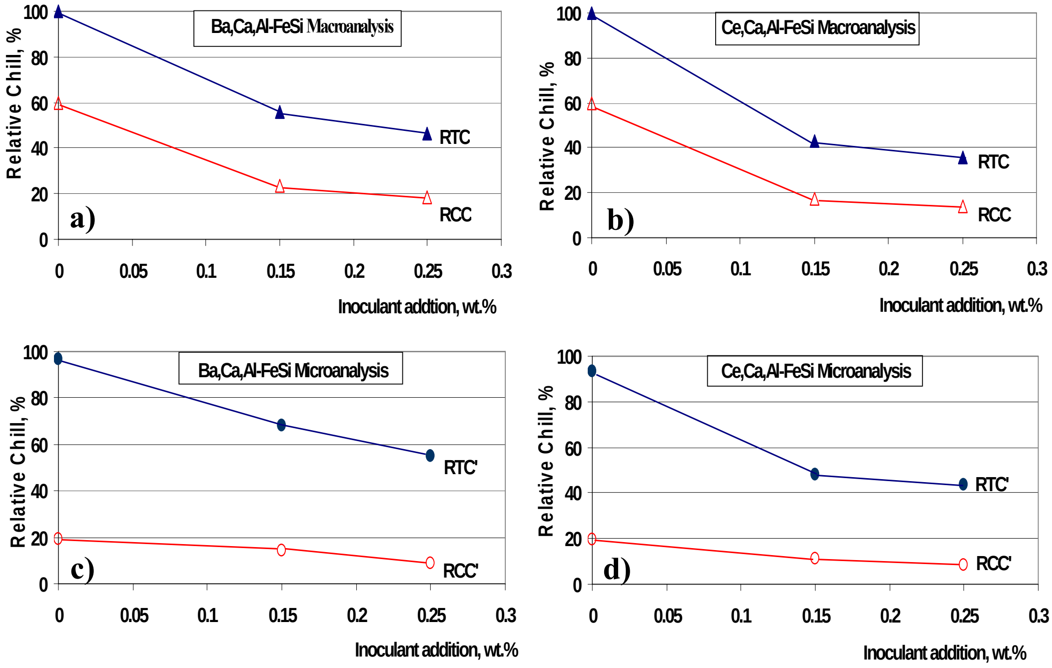


Fig. 4. *Relative clear (RCC) and total (RTC) chill evaluated by macro-analysis (a, b) and micro-analysis (c, d) of un-inoculated and Ba, Ca, Al-FeSi (a, c) and Ce, Ca, Al-FeSi (b, d) inoculated irons [W_2-ASTM A367 chill wedge].*

This difference is higher in inoculated irons, mainly at lower alloy addition rate, for relative clear chill (RCC) evaluation and bearing inoculant, respectively.

Ba, Ca-FeSi alloy inoculated irons.

Specific to the solidification pattern of wedge shaped samples is the end (corner) effect, which is an excessive sensitivity of iron to free carbides and / or undercooled graphite, at the greatest width, corresponding to the B - size parameter.

This phenomenon is more apparent for a lower inoculation potential, such as for 0.15wt.% Ba,Ca-FeSi inoculated cast irons. Ce-bearing FeSi alloy led to the avoidance of this phenomenon, as carbides formation, inclusively at lower addition rate procedure.

High cooling rates, typical for a corner effect [13], led to free carbides and / or undercooled graphite morphologies in all of these cases.

This peculiar solidification pattern of wedge shaped samples could create problems in accurately evaluating chill, especially for thin wall castings and for both relative clear chill and relative total chill criteria.

4. Summary

- The efficiency of a Ce-bearing FeSi inoculant on the structure characteristics (carbide, graphite, metal matrix) of low sulphur [< 0.025%S, (%Mn) x (%S) < 0.02], low aluminium [< 0.002%Al], hypoeutectic [3.6-3.8%CE] electric melt [>1500^{o}C] irons, was tested by comparing if to a conventional inoculant [Ba,Ca,Al-FeSi alloy], at lower addition rates [< 0.3wt.%] and a large variation of the cooling rate during solidification, as casting geometry [1-10mm].
- As expected, an inverse relationship exists between free carbides (in the benefit of graphite) and the undercooled graphite level (in the benefit of type - A graphite) and the distance from the apex of the chill wedge or wedge width, but depending on the inoculant type and addition rate, too.
- The inoculation was able to totally avoid free carbides formation for more than 6.5 mm wall thickness for Ba,Ca-FeSi inoculated irons and 5 mm for Ce,Ca-FeSi treatment.
- Ce-bearing inoculant appears to be more effective especially for thin wall castings (3-4 mm), despite the critical conditions of chemical composition of the base iron.
- According to the higher capacity to prevent free carbides formation, Ce-bearing FeSi alloy led to a higher graphite amount for the same cooling rate solidification conditions and for both of the addition rate procedures. The Ce-Ca-Al-FeSi inoculant outperformed the Ba-Ca-Al-FeSi alloy, especially at low inoculant additions.
- There appears to be a difference in chill (carbides formation) evaluation, for inoculated irons, between macrostructure (fracture analysis) and micro-structure (metallographic analysis).
- The chill tendency at a microstructure evaluation route appears to be important in thin wall castings after inoculation, for both relative clear chill and relative total chill criteria.
- The end (corner) effect, seen as a higher cooling rate at the highest width, leads to free carbides and / or undercooled graphite morphologies / ferrite, more especially for lower inoculation potential, such as Ba,Ca,Al-FeSi alloy and 0.15wt.% addition rate, respectively.

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