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RELATIVE PERFORMANCE OF Ca, Ba-FeSi INOCULANTS TO CHILL CONTROL IN LOW-S GREY CAST IRONS

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ABSTRACT

Low sulphur irons (< 0.05%S) production is more and more promoted in many parts of the world, as small and less efficient cupolas were replaced by the new generation of induction furnaces, while a single low sulphur base iron is very attractive for grey/ductile/compacted irons production. The problem is that at low S-levels, grey irons usually solidify with high eutectic undercooling, favorable for carbides formation, especially in thin wall castings (automotive industry). Relative performance of different Ca, Ba and Al bearing FeSi alloys was calculated to evaluate their efficiency to control chill tendency, in critical base irons [< 0.035%S, (%Mn) x (%S) < 0.02, 0.002%Al]. Relative clear/mottled/total chill measurement criteria were applied, for chill wedges with different cooling modulus (CM = 0.11 – 0.35 cm). The results showed that some inoculants performed better than the other alloys bearing the same base inoculating elements and have different positions for different chill evaluation criteria and wedge size (cooling modulus) parameters reference. An optimum association of Ca, Ba and Al contents at a proper Ba/Ca ratio is more efficient comparing to the increasing of the inoculating elements leveling FeSi-based alloys for inoculation of lower sulphur, electrically melted irons.

KEYWORDS: Grey iron, Low S, Cooling rate, Inoculation, Ca, Ba, Al, Structure, Carbides, Graphite

1. Introduction

Inoculation is a treatment of the molten iron to control the structure and properties of castings by promotion of active nucleation sites available for the growth of graphite flakes in grey irons at lower eutectic undercooling, thereby minimizing the risk of forming chill (hard iron carbides) and/or un-favourable graphite morphologies, such as D-type (undercooled) graphite, particularly in thin sections.

Chilled structures are typically for high eutectic undercooling and are hard and brittle and interfere with machining, necessitate additional heat treatment operations, resulting in non-conformance with specifications and, in general, increase the total cost of production.

Lowering the eutectic undercooling may lead to avoiding of carbides, but, if it is still high, the promoted graphite will branch, forming abnormally patterns, such as Types B, D and E graphite.

At enough lower eutectic undercooling level, random graphite flakes form uniformly in the iron matrix, which is known as Type A graphite.

The most effective inoculants are FeSi alloys containing small amounts of one or more of the elements such as Ca, Ba, Sr, generally at concentrations above 0.5wt.% each one. It is considered that inoculating elements contents above 1.5wt.% give improved inoculation under some conditions but may also give a greater tendency to produce slag [1, 2].

Recent research results have identified three groups of elements with important contributions in formation of graphite nucleation sites as (Mn,X)S - type in commercial grey cast iron: (a) oxide forming elements (Mn, Si, Al, Zr etc) to produce small oxide base sites (usually less than 3µm) in the first stage; (b) Mn and S to sustain MnS-compounds (generally up to 10 µm size) nucleated by stage one particles; (c) inoculating elements, such as Ca, Ba, Sr, Ce, La etc which act in the first stage or/and in the second stage of graphite formation, to improve the capability of (Mn,X)S compounds to nucleate graphite [3-5].

The nucleation of graphite flakes on MnS particles was also confirmed by microstructure simulations [6, 7].

Traditionally, the sulphur level in grey iron was above 0.05%, as the cupola was the typical melting furnace in the cast iron foundries, where the metallurgical coke acts as an efficient re-sulphurizer of the iron melt, but with excessive contribution in many cases.

The new generation of coreless induction furnaces replaced cupolas in the iron melting shops (no metallurgical coke), the expensive pig iron was replaced by steel scrap (lower sulphur), while the high quality carbon riser (lower sulphur) is more and more used, inclusively in grey iron production.

Consequently, less than 0.05%S content is typically now for the base iron in high performance grey iron castings production. The re-sulphurization of the iron melt to attend a control factor at (%Mn) x (%S) = 0.03-0.05 level [8] is necessary, but in some cases this is not possible, as ecology limitation or for the necessity to use the same base iron for grey/compacted/ductile irons castings production.

The problem is that at low S-levels, grey irons usually solidify with high eutectic undercooling, favourable for carbides and / or undercooled graphite morphologies, especially in thin wall castings (automotive industry) [9-13]. Lower residual aluminium content in the iron melt (less than 0.004%Al), also typically for the acid lining coreless induction furnaces melting increases the difficulty of (Mn,X)S compounds formation [3-5, 10, 13].

Grey irons with sulphur contents below about 0.05% may only respond to certain specialized inoculants, or necessitate the increasing of the inoculant addition rate, but promoting some detrimental effects, such as the increasing of slag defects. Recently, a strong research activity was recorded, to improve the chemical composition of FeSi-based inoculants, in order to increase their inoculation capability according to low sulphur grey iron characteristics.

New inoculating elements were considered, especially from rare earth (RE) group (Ce, La), or some elements were associated with traditionally inoculating elements, such as Zr + Sr, Zr + Ca or RE + Ca. The review of the conventional inoculants composition was also considered, in order to optimize inoculant’s chemistry according to the new conditions of the grey iron melt.

The current experimental investigation in the paper was designed to evaluate the relative performance of the Ca, Ba and Al bearing FeSi alloys at different association of inoculating elements as efficiency in chill control of grey iron; a critical iron chemistry [< 0.035%S, (%Mn) x (%S) < 0.02, 0.002%Al] for graphite nucleation was also considered, for solidification in different cooling rate conditions.

2. Experimental procedure

Experimental heats at low sulphur level (0.030-0.035%S) and very low residual aluminium content (0.002%Al) were produced in an acid lined coreless induction furnace (100kg, 2400Hz). Un-inoculated and ladle inoculated (0.15wt.% Ca,Ba,Al-FeSi alloys) were considered, at the following final chemical compositions (wt.%): 3.25-3.35C, 1.60-1.65Si, 0.55-0.56Mn, 0.08-0.11P, 0.09-0.10Cu, 0.03-0.04Ni, 0.08-0.09Cr, 0.01Mo, 0.005V, 0.005-0.006Ti, for carbon equivalent (CE) 3.75-3.85, and (%Mn) x (%S) = 0.017-0.020 as control factor.

Different Ca, Ba, Al-FeSi alloys were used, for the 70-75wt.%Si range and appropriate aluminium contents (0.7-0.9wt.%), typically for foundry grade ferrosilicon, but at different inoculating elements (Ca, Ba) levels. The traditionally Ca and Ba inoculating elements were included in the usual range for the commercial inoculants (up to 4wt.% each one), but varied as Ba/Ca ratio (0.8-4) and content associations, for Ca + Ba = 1.7-6.2wt.% in the inoculants chemistry.

The iron melt was heated up to 1530-1540^{o}C for 10 minutes, and then was tapped into the inoculation ladle (10 kg). Inoculants were added, at 0.2-0.7 mm grain size during tapping into the pouring ladle. Inoculated irons were poured (furan resin moulds) at a strong controlled temperature (1350^{o}C) after a 2.0-2.5 min holding time.

The very narrow chemistries range of the tested irons and very low minor (trace) elements contents, the strong control on the thermal regime and treated iron melt volume, and controlled compositions and grain sizes of the inoculants led to an accurate evaluation of the inoculants effect, inclusively as the Ba/Ca ratio influences. Wedge W_1, W_2 and W_3 samples according to ASTM A367, were used (furan resin mould) as “Test Method A-Wedge”. Standard wedges are characterized by size and cooling modulus (CM), which involved different solidification cooling rates, for the same pouring practice and moulding media. For the three considered wedges, representative for thin-medium wall thickness castings, the main characteristics are the follows: W_1 (B=5.1mm base width, 25.4mm height, CM=0.11cm cooling modulus), W_2 (10.2mm base width, 31.8mm height, CM=0.21cm) and W_3 (18.6mm base width, 38.1mm height, CM=0.35cm). Cooling modulus (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 cooling modulus equates to slower cooling rate and lower undercooling during eutectic solidification.

3. Results and discussion

The measurement of chill was recorded according to a controlled procedure, to avoid hot shaking effect on the solid state transformation. Later the wedges were fractured and their fractures analyzed. That portion nearest the apex, entirely free of grey (graphite) areas, is designated as the clear chill zone (W_c), including only carbides in the structure ***(Fig. 1).***

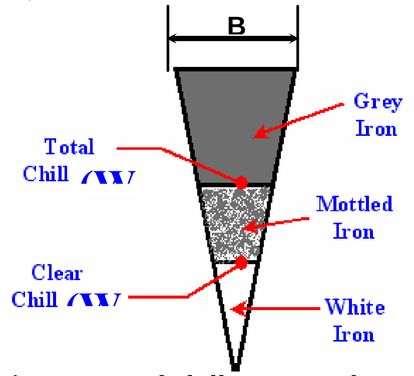

Fig. 1. *Typical chill zones on the wedge test samples [B-base width].*

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), including both carbides and graphite. The region from the junction of grey fracture (no carbides, only graphite) to the first appearance of chilled iron (apex) is designated the total chill (W_t).

The parameters relative clear chill (RCC), relative total chill (RTC) and relative average mottled chill (RMC) were also considered:

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

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

$$RMC = 100\,[0.5\,(W_c + W_t) / B]\ (\%) \quad (3)$$

where B is the maximum width of the test wedge.

Table 1 summarized the obtained results for the three chill evaluation criteria (RCC, RMC, RTC), of un-inoculated and different inoculated irons (A….I inoculants).

The increasing of the cooling modulus (CM) from W_1 (CM=0.11cm) through W_2 (0.21cm) up to the W_3 (0.35cm) led to the decreasing of the cooling rate, and, normally, also of the chill tendency of both un-inoculated and inoculated irons. Un-inoculated irons are characterized by having high chilling tendency. It could be considered as excessive for 3.75-3.85%CE irons.

Table 1*. Relative clear (RCC), mottled (RMC) and total (RTC) chill*

Alloy	Ca+Ba (%)	Ba/Ca	W_1 [B=5.3mm; CM=0.11cm]			W_2 [B=10.2mm; CM=0.21cm]			W_3 [B=18.6mm; CM=0.35cm]		
			RCC (%)	RMC (%)	RTC (%)	RCC (%)	RMC (%)	RTC (%)	RCC (%)	RMC (%)	RTC (%)
U.I	-	-	100	100	100	100	99.0	98.0	51.5	75.8	100
A	1.70	0.89	55.5	77.8	100	34.0	66.0	98.0	20.0	34.0	48.0
B	2.01	0.62	64.5	82.3	100	36.0	67.0	98.0	24.0	39.3	54.5
C	2.22	1.00	50.5	75.3	100	30.5	64.3	98.0	20.0	35.0	50.0
D	2.40	1.40	52.0	76.0	100	30.5	64.3	98.0	18.5	33.5	48.5
E	2.97	2.06	48.5	74.3	100	33.0	65.5	98.0	20.0	36.0	52.0
F	3.85	3.53	62.5	81.3	100	37.0	50.5	64.0	20.0	33.5	47.0
G	3.85	1.08	55.5	77.8	100	29.0	63.5	98.0	18.7	33.9	49.0
H	4.55	1.76	54.5	77.3	100	34.0	51.8	69.5	17.0	31.5	46.0
I	6.20	1.82	59.5	79.8	100	35.0	52.3	69.5	19.5	33.8	48.0
Average	CL_K		**55.9**	**78.0**	**100.0**	**33.2**	**60.6**	**87.9**	**19.7**	**34.5**	**49.2**
St. Dev.	S_K		**5.38**	**2.70**	**0.00**	**2.72**	**6.88**	**15.25**	**1.89**	**2.17**	**2.62**

High furnace superheating (1540^{o}C), low Al content (0.002%) and less than 0.02 as (%Mn) x (%S) control factor led to difficulties in complex (Mn,X)S compounds formation, as graphite nucleation sites, and, consequently, to excessive chill. Inoculation gave, as expected, overall lower iron chill than with no inoculation, even at lower inoculant (0.15wt.%) in-ladle additions. A 0.15wt.% inoculant addition had a very big influence on chill tendency compared to un-inoculated irons, especially at the higher cooling rate (or lower cooling modulus of wedge samples). At low cooling modulus (CM=0.11cm, W_1 samples), typically for thin wall castings (4.4mm corresponding diameter for a bar sample), an important inoculation effect was obtained for relative clear chill (RCC) evaluation, as RCC decreased from 100% to 50-65%, much more than for relative mottled chill RMC (from 100% to 75-85%), while the relative total chill RTC was not affected. W_2 type wedges are representative for 8.4 mm diameter bars castings, large used in mechanical engineering. Inoculation was more effective for these castings as relative clear chill evaluation, comparing to relative mottled chill and especially to relative total chill evaluation, where only some inoculants were efficient. The largest considered wedge sample (W_3), correspondent to 14mm diameter bar castings is visible affected by inoculation for all of chill evaluation criteria and inoculants used.

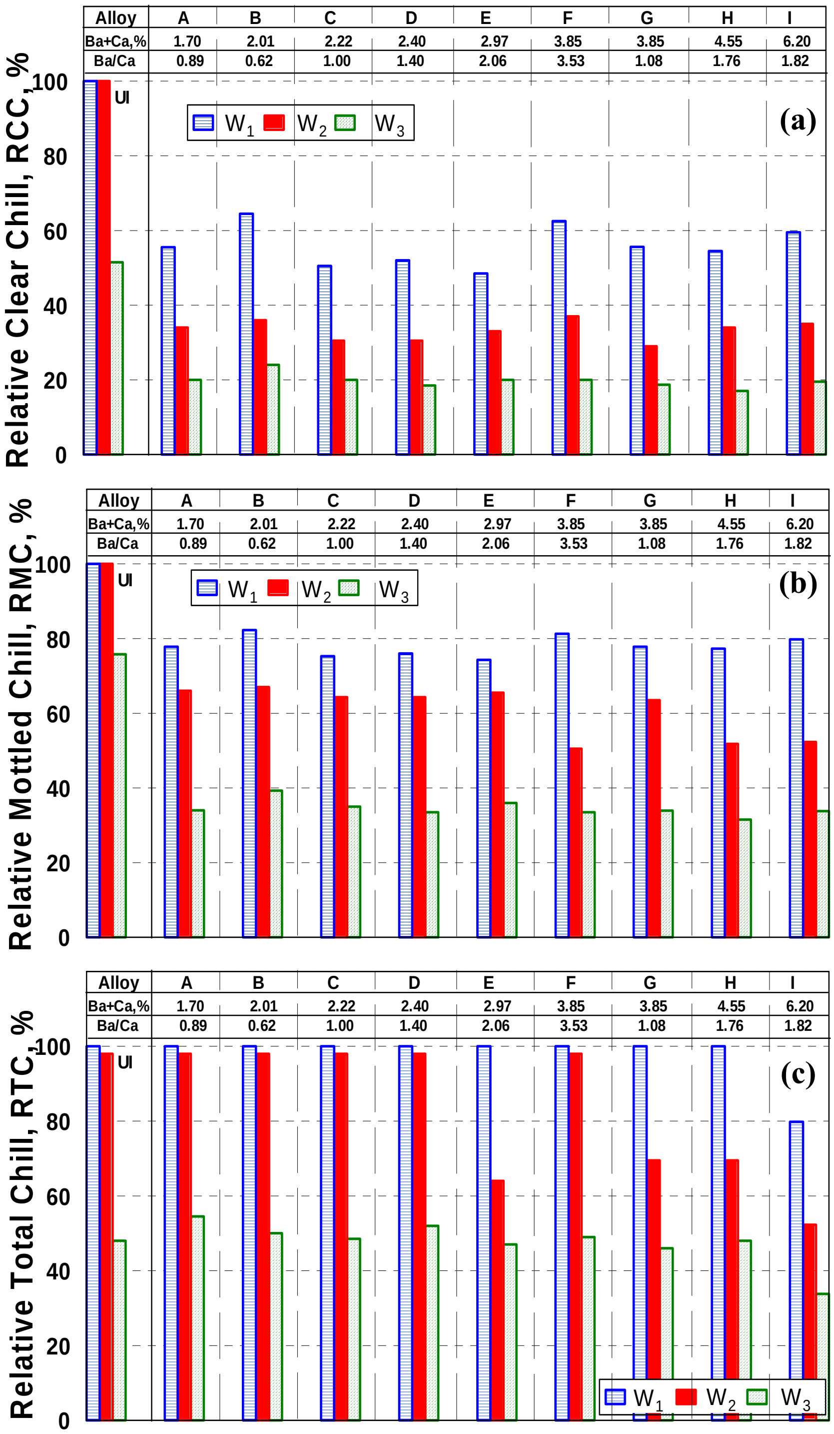

Fig. 2. *Relative clear chill (RCC) (a), relative mottled chill (RMC) (b) and relative total chill (RTC) (c) of un-inoculated (UI) and inoculated (A….I) irons, for W_1, W_2 and W_3 samples.*

A number of trends in chill sensitivity could be identified, as the influence of inoculating elements (Ca, Ba) total sum and especially as ratio, specific content of each element and their associations (***Fig. 2***).

Generally, the increasing of the total content of inoculating elements (Ca + Ba sum) in the compositions of Ca,Ba,Al-FeSi alloys does not appear to have an important beneficial influence as chill tendency decreasing of the low sulphur and low aluminium, electrically melted grey irons, with some peculiar exceptions.

It is more visible for intermediary solidification conditions, such as for W_2 (CM=0.21cm) samples and for relative mottled chill (RMC) evaluation criteria, respectively. The relative performance of inoculants to control representative chill tendency parameters was calculated to determine the efficiency of the experimental alloys [14].

The relative performance (RPi) of inoculants –i- is estimated as:

$$RPi = \frac{\sum_k (X_{ik} - CL_k)}{S_k} \quad (4)$$

where X_{ik} is measured value of property –k- using inoculants –i-;

CL_k is average value for property set –k-;

S_k is standard deviation from the set.

The reducing of chill tendency performance is averaged and used as one parameter –*k*-, for each chill evaluation criteria (RCC, RMC, RTC) and each wedge samples (W_1, W_2, W_3). Average performance has level 0%.

The performances of inoculants increase as chill tendency decreases, so positive values for relative performance ***(Tables 2 and 3, Figures 3 and 4)*** means a lower chill comparing to the average level for the group of considered alloys. This tool was used to determine and distinct the close performance of the alloys in all the analyses carried out in this work.

The results showed that some inoculants performed better than the other alloys bearing the same base inoculating element (Ca and Ba), depending on the total Ca + Ba content and the ratio of the two inoculating elements (Ba / Ca), respectively. Inoculants have different positions for different chill evaluation criteria (RCC, RMC, RTC) and wedge size (cooling modulus) parameters.

Thin wall castings (< 5mm wall thickness), represented here by W_1 wedge sample (0.11cm cooling modulus and corresponding to 4.4mm diameter bars), are the most affected by different alloys chemistries.

Table 2. *Relative performances of Ca,Ba-FeSi alloys to reduce chill tendency*

Alloy	Ca+Ba (%)	Ba/Ca	W_1 [B=5.3mm; CM=0.11cm]			W_2 [B=10.2mm; CM=0.21cm]			W_3 [B=18.6mm; CM=0.35cm]		
			RCC (%)	RMC (%)	RTC (%)	RCC (%)	RMC (%)	RTC (%)	RCC (%)	RMC (%)	RTC (%)
A	1.70	0.89	+7.2	+7.0	0.0	-28.6	-78.9	-66.3	-13.5	+23.1	+46.6
B	2.01	0.62	-159.9	-159.9	0.0	-102.2	-93.4	-66.3	-225.1	-221.3	-201.2
C	2.22	1.00	+100.1	+99.7	0.0	+100.2	-54.1	-66.3	-13.5	-23.1	-29.6
D	2.40	1.40	+72.2	+73.8	0.0	+100.2	-54.1	-66.3	+65.8	+46.1	+27.5
E	2.97	2.06	+137.2	+136.8	0.0	+8.2	-71.6	-66.3	-13.5	-69.2	-105.9
F	3.85	3.53	-122.8	-122.8	0.0	-139.0	+146.6	+156.7	-13.5	+46.1	+84.7
G	3.85	1.08	+7.2	+7.0	0.0	+155.4	-42.5	-66.3	+55.2	+27.7	+8.5
H	4.55	1.76	+25.8	+25.5	0.0	-28.6	+127.7	+120.6	+145.1	+138.3	+122.8
I	6.20	1.82	-67.1	-67.2	0.0	-65.4	+120.4	+120.6	+12.9	+32.3	+46.6

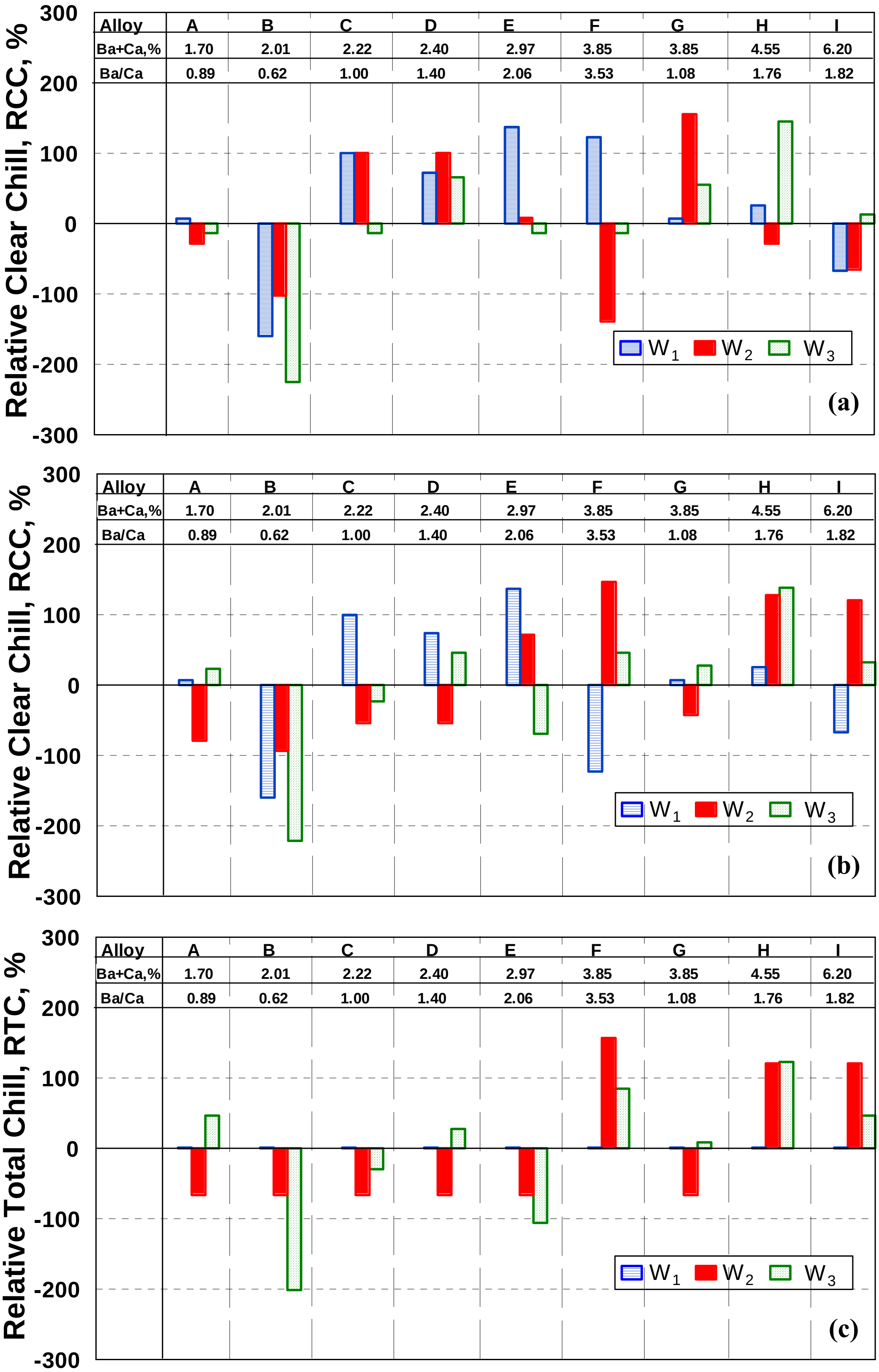

Fig. 3. *Relative performance as chill tendency decreasing of Ca,Ba-FeSi alloys for W_1, W_2 and W_3 wedge samples, as relative clear chill (RCC) (a), relative mottled chill (RMC) (b) and relative total chill (RTC) (c) evaluation criteria.*

Table 3. *Relative performances of inoculants as chill evaluation criteria and wedge size*

Alloy	Ca+Ba (%)	Ba/Ca	Chill evaluation criteria				Wedge samples			
			RCC	RMC	RTC	Total	W_1	W_2	W_3	Total
A	1.70	0.89	-11.6	-16.3	-6.6	-11.5	+4.7	-57.9	+18.7	-11.5
B	2.01	0.62	-162.4	-158.2	-89.2	-136.6	-106.6	-87.3	-215.9	-136.6
C	2.22	1.00	+62.3	+7.5	-32.0	+12.6	+66.6	-6.7	-22.1	+12.6
D	2.40	1.40	+79.4	+21.9	-12.9	+29.5	+48.7	-6.7	+46.5	+29.5
E	2.97	2.06	+44.0	-1.33	-57.4	-4.9	+91.33	-43.2	-62.9	-4.9
F	3.85	3.53	-91.8	+23.3	+80.5	+4.0	-81.9	+54.8	+39.1	+4.0
G	3.85	1.08	+72.6	-2.6	-19.3	+16.9	+4.7	+15.5	+30.5	+16.9
H	4.55	1.76	+47.4	+97.2	+81.1	+75.2	+17.1	+73.2	+135.4	+75.2
I	6.20	1.82	-39.9	+28.5	+55.7	+14.8	-44.8	+58.5	+30.6	+14.8

In clear chill (white iron structure, no graphite presence) control, the highest performance characterized Ca,Ba,Al-FeSi alloys at medium inoculating elements content [2-3% (Ca + Ba)] and Ba/Ca = 1 - 2 ratio.

The increasing of the inoculating elements content does not appear to be an economical solution for these irons, independently of their ratio in the chemical composition of these complex alloys. The same behaviour appears in relative mottled chill evaluation (mixture of carbide and graphite zone size), while for total chill control (RTC) these inoculants have not enough power in tested conditions.

Thin to medium size wall thickness castings characterized by W_2 wedge sample (0.21cm cooling modulus, corresponding to 8.4mm diameter bars) present different requirements for Ca,Ba,Al-FeSi alloys as chill control, depending on the chill evaluation criteria.

As clear chill approach, the ratio of the two inoculating elements appears to be the most important parameter. The best performance characterized inoculants with Ca and Ba in a relative equilibrium (Ba/Ca = 1.0-1.5), at medium (2.2-2.5%) or high (3.85%) total content of Ca and Ba. In the both chemistry ranges, lower or higher Ba/Ca ratio visible decreased the performance of these inoculants. Mottled and total chill control in these castings required inoculants with higher content of inoculating elements, generally more than 4%.

W_3 wedge sample usually characterizes medium size (more than 10mm wall thickness) castings. Also in this case the ratio of the two inoculating elements is important, as the higher performance inoculants are generally characterized by Ba/Ca = 1.5-2.0 ratio, mainly at more than 4% total content.

Generally, in low sulphur grey cast irons, the higher is the wall thickness (cooling modulus) of castings, the higher is the content of inoculating elements necessary for higher performance of inoculants in Ca-Ba system.

In critical solidification condition, such as thin wall castings, the performance of Ca-Ba bearing FeSi alloys is better for an equilibrium of Ca and Ba contents, the best position is typically for 3% (Ca + Ba) and Ba/Ca = 2 ratio alloy, which performed better than the other alloys, inclusively at higher content of inoculating elements. The high calcium and barium bearing inoculants did not perform well during fast casting of small samples under the conditions in this trial.

Independently of wedge size and chill evaluation criteria, less than 2% (Ca + Ba) and Ba/Ca < 1.0 ratio are not recommended in low sulphur grey cast irons, with critical conditions for graphite nucleation at lower eutectic undercooling.

As iron castings are usually complex parts, at a large range of wall thickness, including from thin (some millimeters) up to thick (hundreds millimeters) walls, it is very difficult to select a performance inoculant to control the structure in so different solidification conditions.

Figure 4 shows the total relative performance of the tested alloys, for a large range of cooling modulus (0.11-0.35cm) and different chill evaluation criteria.

The best performance inoculant to produce a high quality complex grey iron castings (large wall thickness variation) is characterized by 4.5% (Ca + Ba) total content at 1.75 specific Ba/Ca ratio, while the second variant refers to an alloy at lower but controlled content of the two representative inoculating elements: Ca + Ba = 2.4% and Ba/Ca = 1.4.

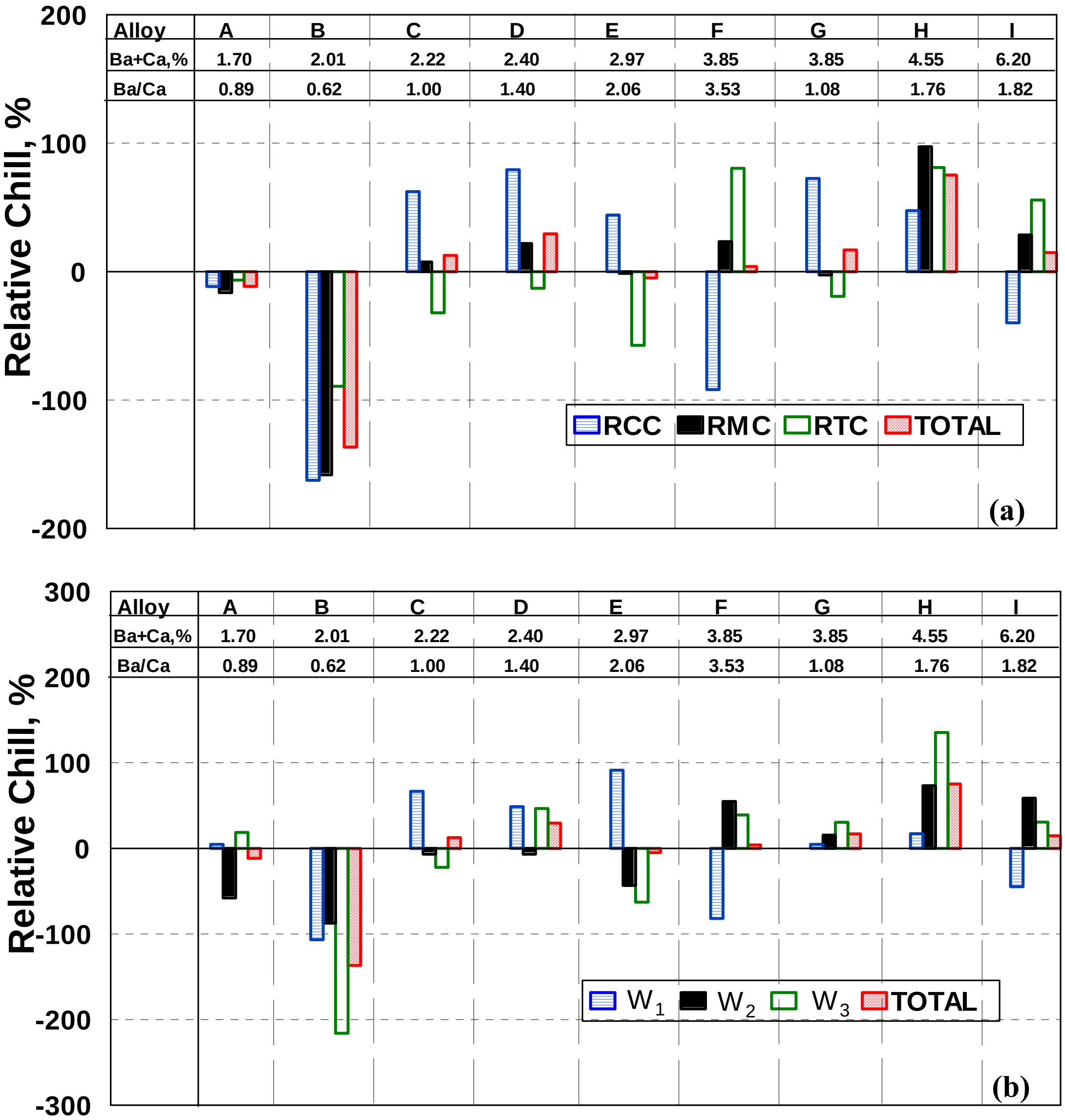

Fig. 4. *Relative performance as chill tendency decreasing of Ca, Ba, Al-FeSi alloys for different chill evaluation criteria (a) and different wedge sample size (b).*

4. Summary

The relative performance of Ca,Ba,Al-FeSi alloys, at different association of inoculating elements (Ca, Ba), was tested in chill control in low S grey irons (< 0.035%S) for different solidification cooling rates (W_1, W_2 and W_3 wedges, ASTM A 367) and chill evaluation criteria (RCC, RMC, RTC). Based on this work the following main conclusions can be drawn.

- Chill tendency of electrically melted base iron having 3.75%CE, 0.03%S, (%Mn) x (%S) < 0.02 control factor and 0.002%Al residual is excessively high, demonstrating a relatively high need for inoculation power.
- The results showed that some inoculants performed better than the other alloys bearing the same base inoculating element (Ca and Ba), depending on the total Ca + Ba content and the ratio of the two inoculating elements (Ba/Ca), respectively.
- Un-favourable chemical composition of the inoculated irons as Mn, S and Al contents for (Mn,X)S compounds formation to act as graphite nucleation sites is difficult to be covered by increasing of inoculating elements (Ca, Ba) content, especially for high cooling rate solidification and clear chill parameter control.

- Inoculants have different positions for different chill evaluation criteria (RCC, RMC, RTC) and wedge size (cooling modulus) parameters reference.
- Independently of wedge size and chill evaluation criteria, less than 2% (Ca + Ba) and Ba/Ca < 1.0 ratio are not recommended in low sulphur grey cast irons, with critical conditions for graphite nucleation at lower eutectic undercooling.
- In thin wall castings production, the performance of Ca-Ba bearing FeSi alloys is better for an equilibrium of Ca and Ba contents, the best position is typically for 3% (Ca + Ba) and Ba/Ca = 2 ratio alloy, which performed better than the other alloys, inclusively at higher content of inoculating elements.
- The best performance inoculant to produce a complex grey iron castings (large wall thickness variation) is characterized by 4.5% (Ca + Ba) total content at 1.75 specific Ba/Ca ratio, while the second variant refers to an alloy at lower but controlled content of the two representative inoculating elements: Ca + Ba = 2.4% and Ba/Ca = 1.4.
- The use of relative performance of inoculants is a tested tool to determine and distinct the close performance of the alloys in all the analyses carried out in this work.

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