# CAST IRON INOCULATION ENHANCING BY OXY - SULPHIDES FORMING ELEMENTS CONTRIBUTION

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## ABSTRACT

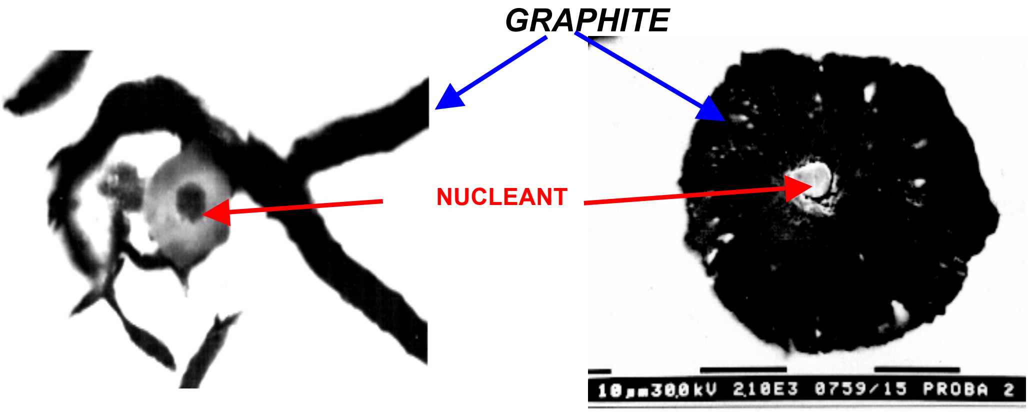
The paper focused on the separate addition of an inoculant enhancer alloy [S, O, oxy-sulphides forming elements] with a conventional Ca-FeSi alloy, in the production of grey and ductile irons. Carbides formation tendency decreased with improved graphite characteristics as an effect of the [Ca-FeSi+Enhancer] inoculation combination, when compared to other Ca / Ca,Ba / Ca,RE-FeSi alloy treatments. Adding an inoculant enhancer greatly enhances inoculation, lowers inoculant consumption up to 50% or more and avoids the need to use more costly inoculants, such as a rare earth bearing alloy. The Inoculation Specific Factor [ISF] was developed as a means to more realistically measure inoculant treatment efficiency. It compares the ratio between the improved characteristic level and total inoculant consumption for this effect.

## INTRODUCTION

Cast iron is more than 70% of the total world metal casting production. Important changes in iron castings production worldwide have occurred and some critical production conditions must be considered, such as: thin wall castings [<5mm wall thickness] production; electrically melting at low sulphur content, higher superheating and limited/no foundry pig iron in the charge; less rare earth elements available due to the world crisis in this field.

Inoculation is one of the most important metallurgical treatments when added to the molten iron immediately prior to casting, with direct effects on the primary structure (austenite, carbides, eutectic cells, graphite characteristics). Generally, inoculation is applied to promote solidification without excessive eutectic undercooling, which favours carbides formation usually with undesirable graphite morphologies. Several factors influence inoculation efficiency: charge materials [pig iron/steel scrap ratio, choice of recarburizers, preconditioners]; melting furnace iron bath temperature profile; base iron chemical composition [Si, Mn, S] and iron residual elements [Al, Ti, O, N]; inoculating elements/inoculant type/inoculation procedure; holding time/pouring procedure; casting characteristics (modulus). [1]

Figure 1 shows typical heterogeneous graphite nucleation in grey [lamellar graphite] iron (a) [2] and ductile [nodular graphite] iron (b) [3]. It was found that with both graphite morphologies, complex compounds act as nucleation sites in commercial cast irons, in a general three-stage graphite formation. In grey cast iron, small oxide-based sites (0.1-3μm, usually less than 2.0 μm) are formed in the melt; (2) complex (Mn,X)S compounds (1-10μm, usually less than 5.0 μm), where X = Fe, Si, Al, Zr, Ti, Ca, Sr, P, nucleate at these micro-inclusions; (3) graphite nucleates on the sides of the (Mn,X)S compounds because of their low crystallographic misfit with graphite. [2, 4-8] The role of complex (Mn,X)S compounds in graphite formation in commercial grey cast irons was later confirmed in other papers. [9-14]



(a) (b)

**Fig. 1. Graphite nucleation in grey (a) [2] and ductile (b) [3] cast irons**

According to M.H. Jacobs et al [15] graphite nodules nucleate heterogeneously on particles formed in the melt, and exhibited a duplex sulphide/oxide structure. Later, T. Skaland found complex hexagonal silicate phases of $XO\text{-}SiO_2$ or $XO\text{-}Al_2O_3\text{-}2SiO_2$ on the surface of the previously formed Mg-silicates making them more favorable sites for subsequent graphite nucleation. In post-inoculated ductile irons, X can be one of the following: Ca, Ba, or Sr.[16]

In ductile iron, two types of micro-inclusions (0.8-8.0 µm size) have been identified (Ca-S-X and Mg-Si-O-X) with the majority in both matrix and nodules, came from the second system. [3] It was found that a residual aluminum of 0.005 to 0.020% appeared to be beneficial for improving ductile iron solidification characteristics without the incidence of pinholes. [17, 18] Limited and controlled S-additions after Mg-treatment, led to impressive, positive inoculating effects, as expressed by chill reduction and increased nodule count, especially as [SiCa + FeS] variant. [19, 20] Further consideration in ductile iron inoculation was to introduce both S and O in a FeSi-based alloy, accompanied by strong oxy-sulphide forming elements such as Ca and Ce during inoculation treatment [Ca,Ce,S,O-FeSi inoculant]. [21] The addition of an inoculant enhancer alloy, based on a proprietary blend of CaSi or FeSi, Al and oxy-sulphide forming elements with the conventional FeSi-based inoculants improved inoculation potency, and caused a reduction of chill and shrink tendency. [22-24]

The main objective of the present paper is to evaluate the effects of a complementary addition of an inoculant enhancer alloy [S, O and oxy-sulphides forming elements] with the conventional Ca-FeSi alloy, in the production of grey and ductile irons, with higher solidification cooling rates. The main focus was on the carbides forming tendency and the characteristics of the graphite phase, in comparison to Ca / Ca,Ba / Ca,RE-FeSi alloys, in an in-mould inoculation technique.

## EXPERIMENTAL PROCEDURE

An acid refractory-lined, coreless induction furnace (100kg, 2400Hz) was used for iron melting and superheating to 1500-1520$^0$C. A tundish cover Mg-treatment technique was applied along with a 2.5 wt-% Mg-bearing FeSi [wt.%: 44.7Si, 5.99Mg, 0.26TRE, 1.02Ca, 0.91Al) addition into a 10kg nodulizing ladle to produce ductile iron. Both irons were inoculated by an in the mould technique, by the use of three commercial inoculants added to the reaction chamber in the mould: Ca-FeSi [wt.%: 73.8Si, 1.02Ca, 0.77Al], Ca,Ba-FeSi [wt.%: 72.6Si, 0.94Ca, 1.68Ba, 0.96Al] and Ca,RE-FeSi [wt.%: 73.5Si, 0.87Ca, 1.86TRE, 0.83Al] (TRE-total rare earth elements).

Another inoculation variant consisted of also adding an oxy-sulphide inoculant enhancer alloy: S,O,Al,Mg-CaSi alloy for ductile iron and S,O,Al,Ca-FeSi alloy for grey iron.[22] The inoculant enhancer was added to complement the 75% Ca-bearing FeSi in the reaction chamber at the following rate: 75% Standard Ca-bearing, 75% FeSi and 25% inoculant enhancer. For grey iron, inoculant additions in the mould were kept constant at a targeted 0.10 wt.% level for all of the conventional inoculants. When the inoculant enhancer [S,O,Al,Ca-FeSi) was employed, total addition rates were targeted at 0.05 wt.%. [27] For ductile iron, different inoculant rates were selected, depending on their known inoculating power: 0.18wt-%Ca-FeSi, 0.10wt-%Ca,Ba-FeSi and 0.04wt-%CaRE-FeSi, respectively. When the inoculant enhancer [S,O,Al,Mg-CaSi) was employed, total addition rates were 0.04 wt.%. [28]

$W_3$ chill wedge samples [ASTM A367-85 specification, CM = 3.5 mm cooling modulus], plate samples (4.5mm thickness) and round test bars (25mm diameter) were gated off each inoculation reaction chamber. The designed pattern [26] allows simultaneously testing of four inoculation variants, for the same base iron. The test castings all were poured at $1450^0$C in furan resin moulds [within 3 minutes after Mg-treatment for ductile iron]. A furan resin (3.0 wt.%) and p-toluenesulphonic acid (PTSA) (6.53 wt.% S content and 1.5 wt.% addition) bonded silica sand (95.5 wt.%) [FRS-PTSA] moulding system was used.

## RESULTS AND DISCUSSION

Table 1shows the chemical composition of the thin plate samples. Based on the final chemistry, the experimental irons are in the higher range of hypo-eutectic compositions (carbon equivalent CE = 3.70–3.90%) for grey irons and a near eutectic position for ductile irons (CE = 4.10 – 4.35%). Two major effects of minor elements were considered on the cast iron structure, mainly in ductile iron, in conjunction with base chemistry: pearlite promotion and anti-nodularising effect). The Thielman's factors were calculated in this respect, $P_x$ and K, respectively. [25]

All $W_3$ samples were polished and examined to determine the graphite parameters on un-etched samples and then etched with Nital to determine the percentages of free carbides and pearlite/ferrite ratios. The structure variation on the centreline in the direction from the apex up to the base of $W_3$ wedge sample was evaluated by conventional metallographic analysis and image analysis, at three points (center and 1.0 mm distance left-right), for each distance from the apex; the averages of the structure parameters were then determined.

**Table 1. Base Chemical Composition of Thin Plate Specimens [wt.%]**

| IRON | C | Si | Mn | S | Mg | TRE* | CE** | K*** | $P_x$**** |
|---|---|---|---|---|---|---|---|---|---|
| Grey | 3.05-3.20 | 2.05-2.10 | 0.38-0.40 | 0.035-0.042 | | | 3.70-3.90 | | 6.2-6.6 |
| Ductile | 3.20-3.50 | 2.40-2.70 | 0.55-0.65 | 0.015-0.017 | 0.043-0.058 | 0.005-0.007 | 4.10-4.35 | 0.6-0.8 | 2.2-2.5 |

*TRE-total rare earth elements; **CE-carbon equivalent [CE = %C+0.3 (%Si + %P) – 0.03 %Mn + 0.4%S]; K***= 4.4 (%Ti)+2.0 (%As)+2.4 (%Sn)+5.0 (%Sb)+290 (%Pb)+370 (%Bi)+ 1.6 (%Al); $P_x$**** = 3.0 (%Mn)–2.65 (%Si - 2.0)+7.75 (%Cu)+90 (%Sn)+357 (Pb)+333(%Bi) + 20.1 (%As)+9.60 (%Cr)+71.7 (%Sb)

Since the range of $P_x$ was between 6.2 to 6.6, the experimental grey irons are sensitive to pearlite formation, despite having a low manganese content. High content of manganese in ductile iron [typically the upper limit] led to a medium level of $P_x$ factor [2.2-2.5], representing pearlitic irons, despite the low content of minor elements. As K < 1.0, the ductile iron chemistry favours nodular graphite formation in Mg-treated irons, without any rare earth elements addition. [1, 26, 27]

The graphite phase characteristics were improved, as important effect of inoculation treatment, in both grey and ductile cast irons. Increasing the amount of the type-A graphite [reduced type-D graphite presence] in grey irons and improving the nodular graphite compactness (sphericity) with increased nodule count [consequently higher ferrite amount] in ductile irons are important features of all inoculated irons.

The inoculation Specific Factor [ISF] [28] was used, as a technique to more realistically measure inoculant treatment efficiency for comparing the combined influence of inoculant type and consumption level. The resulting inoculation difference, ΔX (interpreted to be the improved characteristic) is divided by the actual inoculant consumption [% Inoculant], (which contributed to the positive result) for the Inoculation Specific Factor [ISF] value.

$$ISF_{[K]} = \Delta K / [\%\ Inoculant] = [\%K_{[UI]} - \%K_{[I]}] / [\%\ Inoculant] \quad (1)$$

$$ISF_{[NC]} = \Delta NC / [\%\ Inoculant] = [NC_{[I]} - NC_{[UI]}] / [\%\ Inoculant] \quad (2)$$

Where $ISF_{[K]}$ is the inoculation specific factor to decrease carbides amount and $ISF_{[NC]}$ to increase nodule count; $K_{[UI]}$ and $NC_{[UI]}$, carbides amount and nodule count in un-inoculated irons and $K_{[I]}$, $NC_{[I]}$ in inoculated irons, respectively.

It was found that the $ISF_{[K]}$ parameter, for illustrating the potency of inoculants to decrease the amount of free carbides, is dependent on the inoculation variant and the solidification cooling rate, expressed by wedge casting section size (greater section size, lower cooling rate) for both grey iron and ductile iron. In grey cast iron (Fig. 2), low $ISF_{[K]}$ values were characteristic of the Ca-bearing FeSi inoculant, followed by Ca,Ba-FeSi and Ca,RE-FeSi inoculation, at comparable positions. These modified Ca-FeSi inoculants reduced the levels of carbide, by reference to un-inoculated iron, for all section sizes (cooling rates) even though they all had essentially the same Ca level. Higher $ISF_{[K]}$ values were obtained when the inoculant enhancer was employed. The incorporation of the S,O,Al,Ca-FeSi alloy with the three Ca bearing-FeSi alloys [(Ca + En) to (Ca,RE + En) and (Ca,Ba + En)] significantly increased the Inoculation Specific Factor for all wedge section widths of the grey iron.

The S,O,Al,Ca-FeSi alloy improved the performance of the Ca,Ba and Ca,RE–FeSi alloys to a greater extent than the simple Ca-FeSi alloy, and this difference became more marked as the cooling rate increased (decreased section size). It was also observed that the

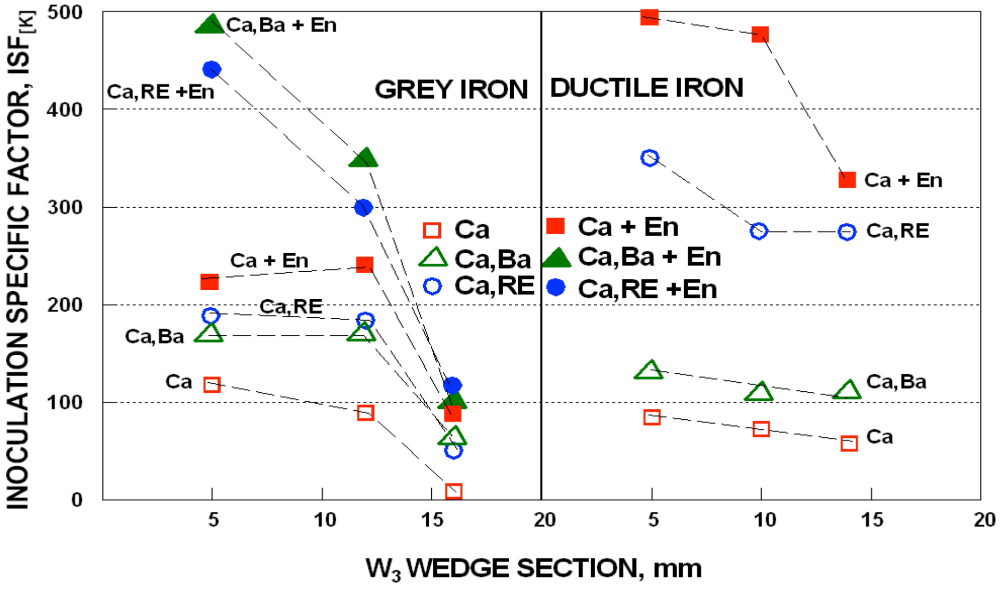


**Fig. 2. Effect of Inoculant Variant on the calculated Inoculant Specific Factor [$ISF_{[K]}$], as capacity to decrease carbides at different section size of $W_3$-ASTM A367 wedge**

Ca,Ba-FeSi outperformed the Ca,RE-FeSi alloy when the same level of S,O,Al,Ca-FeSi alloy was employed. A good correlation was found between the theoretical generated sulphide volume values [27] and the inoculation specific factor to decrease the carbides sensitivity (ISF$_{[K]}$) for the various inoculants combinations. The addition of the inoculant enhancer significantly increased the theoretical volume of generated sulphides and the ISF$_{[K]}$ factor, also.

A graph of Inoculation Specific Factor ISF$_{[K]}$ versus wedge casting section size (cooling rate) of different inoculated ductile irons shows that a distinct difference resulted from the different inoculating elements involved (Fig. 2). The incorporation of the more potent inoculating elements Ba and rare earth [RE] into a conventional Ca-FeSi75 alloy led to increasing inoculation power of the Ca,Ba-FeSi and Ca,RE-FeSi alloys, with visible performance advantage of the rare earth bearing inoculant, for grey iron treatment. The [Ca-FeSi + Enhancer] inoculation variant led to the highest inoculation specific power [lowest chill tendency], 5-6 times higher compared to Ca-FeSi and 3-4 times compared to Ca,Ba-FeSi, respectively. This combined addition (a total of 0.04 wt-% alloy addition, comprised of individual additions of 0.03% Ca-FeSi with 0.01% S,O,Al,Mg-CaSi to the inoculant chamber), was up to 50% more effective than the equivalent consumption of REE-bearing Ca-FeSi inoculation.

If Ca,Ba-FeSi alloy shows only a little performance in nodule count increasing comparing to simple Ca-FeSi alloy, at the higher cooling rate, Ca,RE-FeSi is visible more efficient, similarly with its capacity to reduce carbides formation sensitiveness (Fig. 3). Inoculant enhancer [S,O,Al,Mg-CaSi alloy] addition on the commercial Ca-FeSi alloy [1:3 ratio] led to increasing of the inoculant specific factor in this respect, ISF$_{[NC]}$, up to 5 times; the same effect such as for ISF$_{[K]}$ factor.

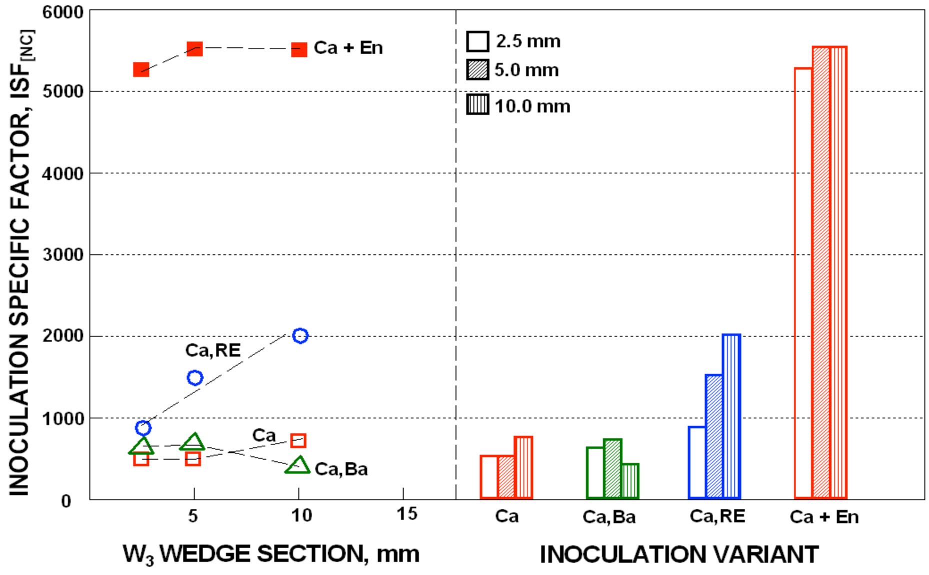


**Fig. 3. Effect of Inoculant Variant on the calculated Inoculant Specific Factor [ISF$_{[NC]}$], as capacity to increase nodule count in ductile irons [W$_3$-ASTM A367 wedge sample]**

## CONCLUSIONS

1. Complex compounds act as nucleation sites in commercial cast irons, in a general three-stage graphite formation, but in a different sequence: (1) a first micro-compound formation as oxide/silicate in grey iron and sulphide in ductile iron; (2) the second compound nucleated on the first one, as complex manganese sulphide in grey iron and complex silicates in ductile iron; (3) graphite nucleation on the sides of the stage two compounds, which have low crystallographic misfit with graphite.

2. The co-addition of an inoculant enhancer alloy [S, O and oxy-sulphides forming elements] to the conventional Ca-FeSi alloy, in grey and ductile irons production, greatly enhances inoculation, lowering inoculant consumption up to 50% or more and without resorting to more costly inoculants, such as RE bearing alloy.
3. The Inoculation Specific Factor [ISF] pointed out that the addition of any of the commercial inoculants plus the inoculant enhancer offered outstanding inoculation power [increased ISF] even at higher solidification cooling rates.

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