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HIGH ACTIVE INOCULANT FERROALLOY TO CONTROL GRAPHITE MORPHOLOGY AND NUCLEATION ABILITY IN CAST IRON

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ABSTRACT
The use of denodularising elements to control graphite nodularity has been applied for quite a long time in order to produce Compacted Cast Iron. Experiences from production of CG Iron using these elements (Ti, Al, Sb, Sn etc.) showed that returns containing denodularising elements can have negative influence on the quality of newly made CG and NG Irons, when such returns are used. For this reason, the industrial production of CG Iron is in difficulty now. For many foundries , the aim is to use magnesium treatment ductile iron and add something to "denodularize" it. The idea of adding FeS in association with a silicon base inoculant to reduce the magnesium and to improve the graphite nucleation is a possibility. Sulphur can replace classical denodularising elements in order to control graphite nodularity. Also, the favorable effect of a sulphur containing inoculant on the graphite nucleation has been compared with Bi, usually used to increase the count of graphite nodules in Ductile Iron.

1.ANTISPHEROIDISING ELEMENTS IN COMPACTED AND COMPACTED/NODULAR GRAPHITE CAST IRONS

Previous works have suggested two main categories of cast irons: a) Standard CG Iron (max. 20 % NG) and Standard NG Iron (max. 20 % CG) on the one hand and b) Conventional CG Iron (50 ... 80 % CG + 20 ... 50 % NG) and Conventional NG Iron (50 ... 80 % NG + 20 ... 50 % CG) on the other (NG - nodular graphite; CG - compacted graphite) [1, 2]. Every one of these four types of cast iron has particular properties making it suitable for several applications.

The use of antispheroidising (denodularising) elements (AE) increases structural stability of CG Cast Iron (in order to extend the range of CG formation) and increases CG/NG ratio control (in order to obtain Conventional Irons). For this purpose, Ti is especially used, but good results have also been obtained by using other elements (Al, Sn, Sb etc.).

When Mg and Ce are used as spheroidising elements and Ti and Al as antispheroidising elements, the stability of the production of standard CG Cast Iron (max. 20% NG) is higher than in the situation when only magnesium is used [3]:

$$Mg : Mg + Ce : Mg + AE : Mg + Ce + AE = 1 : 1.3 : 1.5 : 1.8 \quad (1)$$

Denodularising elements which are useful in controlling the morphology of the graphite, remain in the return scraps and may have a negative influence on the new NG and CG Irons. The accumulation of denodularising elements, due to the presence of returns, in CG Iron is expressed by equation (2), without taking into consideration the oxidation of the melt [4]:

$$E_i = m \cdot \left[1 + \sum_{i=1}^{n} \left(\frac{R}{100} \right)^i \right] \qquad [\%] \tag{2}$$

Where: E_i is the concentration of element **E** after **i** cycles of treatment (charges), %;
R - returns, %;
m - ratio of element **E**, brought about treatment, %;

For example, when treating cast iron with a FeSiCaMgTi alloy containing 8-10 % Ti, the use of 1.0 % of the alloy introduces m=0.08 % Ti into the cast iron. When using R=30 % returns in the charge, the accumulation of Ti (E=Ti) is in the form E_1=0.104 %, E_{10}=0.114 %.

Experiment has highlighted that CG Returns containing Ti and Al are not recommended in the case of Ductile Iron with high ductility and toughness. When a nodulariser containing RE is used in the production of ferrito-pearlitic and pearlitic Ductile Irons, it is possible to use up to 25 % CG Returns, which favors the increase of the nodule number and reduces the tendency towards metastable solidification.

It can be concluded that Antispheroidising Elements could be useful for making of CG Iron (Standard and Conventional) and Conventional NG Iron, if they are not accumulated in returns. It was shown that sulphur addition after Mg - treatment can change the nodularity in CG Iron and a more stable structure for this type of iron can be obtained by this way [3,5-8].

2. S-INOCULATION OF Mg-TREATED IRONS TO CONTROL GRAPHITE MORPHOLOGY

Some experiments were carried out at POLITEHNICA University of Bucharest-ROMANIA in order to make a comparison between the action on the morphology of graphite of general denodularising elements (O, S) and the classical (Ti, Al) ones. These elements were therefore introduced in the liquid iron after treating it with nodularising elements (Mg, Ce). The results are clearly proving that sulphur ladle or mould inoculation of Mg-treated irons makes it possible obtain various values of NG/CG ratio, without using the classical denodularising elements (Ti, Al) [6].

In some laboratory experiments, the irons were treated by the Sandwich-technique with FeSiCaMgCe alloy, followed by ladle inoculation with 0.5 wt % FeSi75 and variable quantities of sulphur (as FeS). The treated irons were cast in stepped-wedge samples (g = 5...20 mm thickness) and in round pieces (Ø10...30 x 100 mm) in sand and metal moulds. The variation of NG/CG ratio under the influence of the sulphur inoculation of the Mg-treated iron (0.024 ... 0.03 % Mg_{res}) and of the wall thickness of the samples are shown in Figure 1 [6].

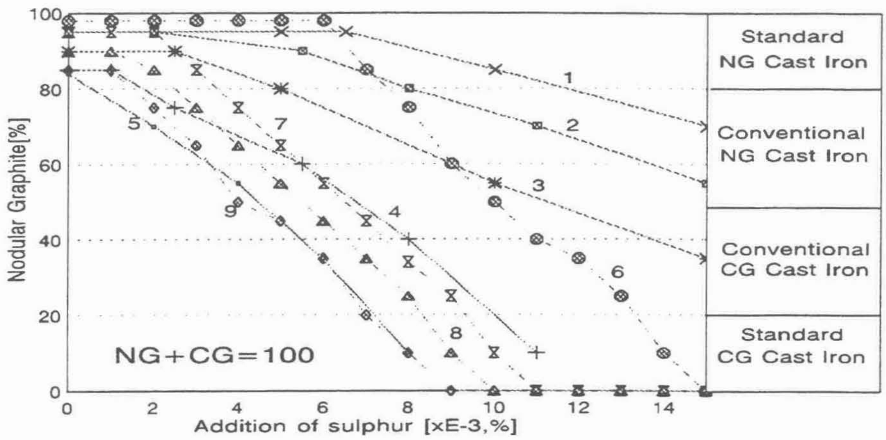
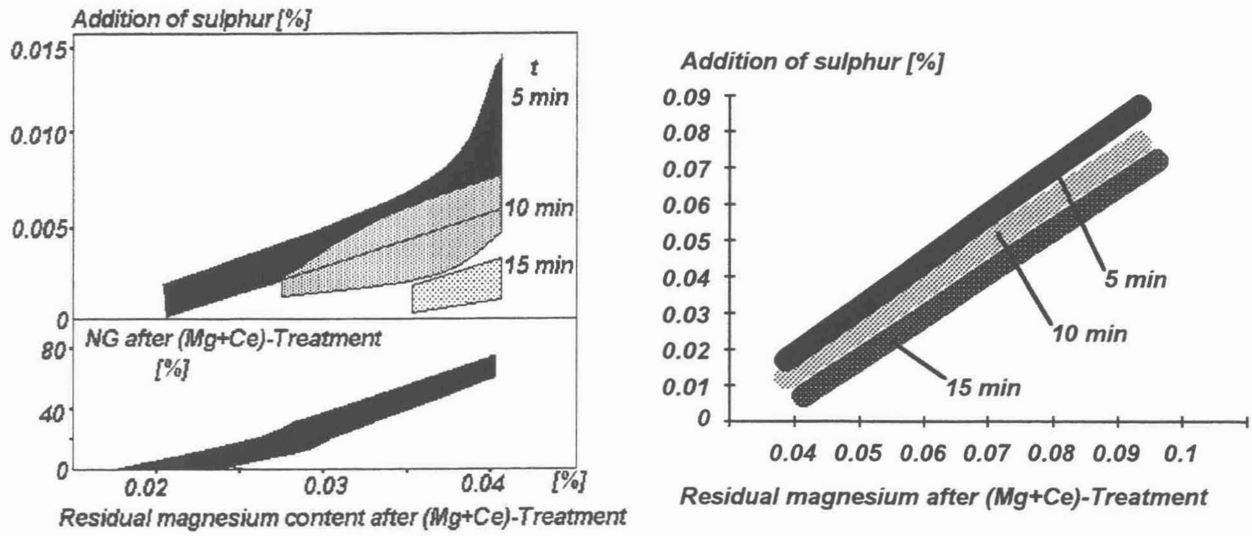


FIG. 1 Graphite Nodularity according to the Sulphur-addition after Mg-Treatment 1- WS1_C; 2-WS1_B; 3-WS4_C; 4-WS4_B; 5-RS4_A; 6-RM3_C; 7-RS2_C; 8-RS3_C; 9-RS5_C; WS-Stepped Wedge Samples-Sand Mould; RS-Round Samples-Sand Mould; RM-Round Samples-Metal Mould; 1-5 mm; 2-10 mm; 3-17 mm; 4-20 mm; 5-30 mm; A-0.024 % Mg_{res}; B-0.027 % Mg_{res}; C-0.03 % Mg_{res}

During plant experiments, Standard CG Iron (max. 20 % NG) was obtained by melting in 3.5 t capacity acid crucible induction furnaces. The irons were treated with FeSiMgCaCe alloys by Sandwich and Tundish-Cover techniques (so that residual magnesium content after this treatment was kept under 0.04 % Mg), followed by ladle inoculation with 0.01 ... 0.015 % S (FeS), accompanied by addition of 0.3 ... 0.5 % FeSiCaBaAl. For a variation of wall thickness of the casting between 5...45 mm, Standard CG Cast Iron made in this way has a distinctive structural stability.

Required sulphur for inoculation of Mg-treated irons depends on the residual magnesium content after Mg-treatment, holding time prior to pouring, wall thickness of the casting and type of the mould (sand or metal mould). Some relationships in this respect are presented in Fig.2, for two main situations [3,7,8].



a) b)

Fig.2 Required sulphur for (Si-alloy + FeS) inoculation after (Mg + Ce) treatment of cast irons which contain Mg_{res}=0.02 ... 0.04 % (a) and Mg_{res}=0.04 ... 0.1 % (b).
(Sand mould; 10...30 mm thick samples; τ - holding time)

If the initial residual magnesium content after Mg(Ce)-Treatment does not exceed by more than 20 % the content corresponding to the lower limit of stability of Standard NG Cast Iron (max. 0.04 % Mg_{res}), required sulphur can be determined by the color of the fracture samples. In this case, normal additions should be in the range of 0.005 ... 0.02 % S in order to obtain Standard CG Iron.

At the higher initial magnesium content (0.04 ... 0.1 % Mg), proper to obtain NG Cast Iron, larger additions (0.02 ... 0.05 % S) are needed in order to make Standard CG Iron; required sulphur is dependent on a prior assessment of the initial magnesium content.

In order to make Standard CG Iron, it is recommended to use Mg or Mg-Ce treatment, so to get a ratio of 0.025 ... 0.04 % Mg in iron melt. In this way, the formation of lamellar graphite, on the one hand, and a stability of graphite nodularity, on the other hand, are avoided. Low additions of sulphur (usually under 0.015 % S as FeS) make it possible to obtain Standard CG Cast Iron under reproducible conditions.

3. S-INOCULATION TO IMPROVE GRAPHITE NUCLEATION IN DUCTILE IRON

It is known that sulphides act as primary nucleation support both in gray and ductile irons (Table 1), so sulphur is an important agent in the inoculation process of ductile iron, which becomes low in oxygen, sulphur and nitrogen after Mg-Treatment.

Some experiments have been made under laboratory conditions in order to find out the influence of inoculants on the graphite nucleation in ductile iron, when Si-Alloys are associated with FeS (0.002 ... 0.01 wt % S added). The inoculation treatment has been made by using different procedures (in ladle, pouring basin, reaction chamber). The FeS was associated with Si-base Inoculants (FeSi, SiCa) by a mixing method (free and under pressure), or by incorporating the FeS in the inoculated melt during its processing (MGS-type Inoculant).

Some results obtained by in-mould inoculation of Ductile Irons (0.055 ... 0.065 % Mg_{res}) are presented in Fig.3 (mechanical-free mixture of FeS + Si-Alloys) [6], Fig.4 (FeS + Si-Alloys pressure insert) and Fig.5 (S-incorporated Inoculant), for 1/4 " section of castings.

Single-sulphur addition (as FeS) has a slow inoculation effect in Mg-treated cast irons. The experiences pointed out the necessity of adding sulphur in association with elements able to form stable sulphides. (FeSi75 + FeS) association is a better inoculant than FeSi or FeS only, but it is less effective than (SiCa + FeS), which is the best solution in this respect - i.e. it gives the greatest increase in nodules number and decreases the size of the chilled area. It was also shown that the graphitizing capacity of (SiCa + FeS) Inoculant is similar to (FeSi + Bi) addition.

It can be concluded that the lower sulphur addition (up to 0.01 wt % S) in association with Silicon-Base Inoculants, after Mg-Treatment can be the solution to improve the graphite nucleation process in ductile iron, without affecting nodularity. This inoculation can be applied in various ways, especially by sulphur incorporation into an insert (pressure processed) or into the inoculant melt, in association with Si-base alloys.

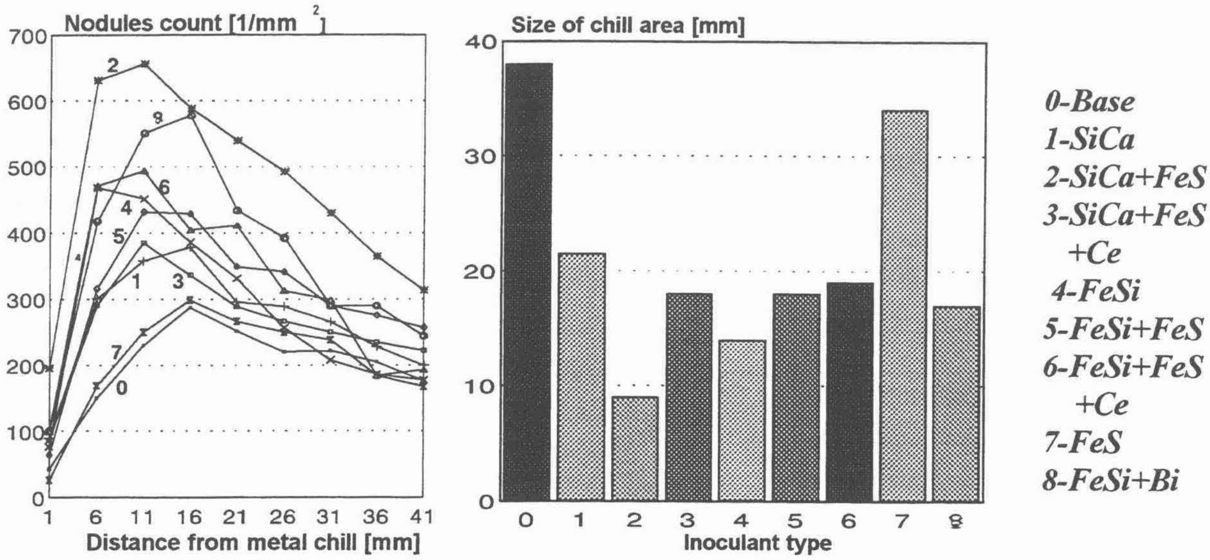


Fig.3 (FeS + Si-Alloys) Mixture - Inoculation of Ductile Irons; (6.5 mm wall thickness)

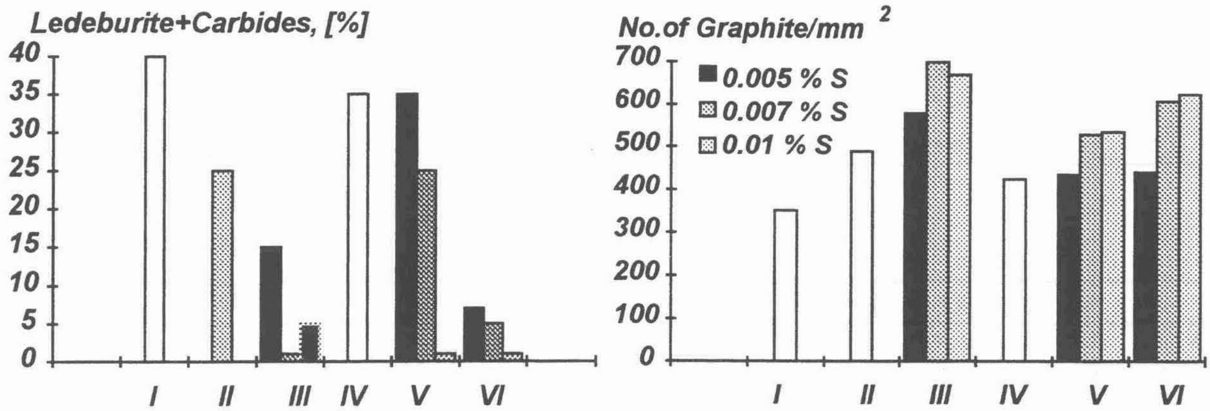


Fig.4 (FeS + Si-Alloys) - Insert Inoculation of Ductile Irons
(I-Uninoculated Ductile Iron; II-SiCa; III-SiCa+FeS; IV-FeSi; V-FeSi+FeS; VI-SiCa+FeS+Ce; 6.5 mm wall thickness)

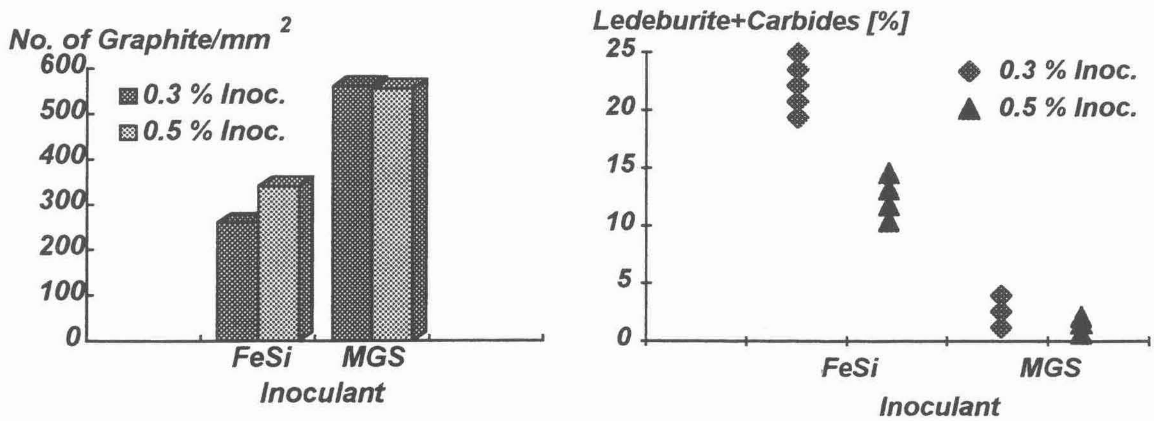


Fig.5 MGS - Inoculation of Ductile Irons
(MGS = S - Incorporated Inoculants; 6.5 mm wall thickness)

TABLE 1 Graphite nucleation possibilities in cast irons

No.	Type of compounds - conditions		Source
	Gray Iron (GI)	Ductile Iron (DI)	
1	-	RE-S; MgS; (RE+Mg)S*	[11]
2	CeS-inoculated GI; BN-B addition; S-addition is effecting in reducing undercooling and chill; S<0.03 wt %-higher chill;	-	[9]
3	-	(Ca-Mg)S	[10]
4	MnS-uninoculated GI; RE-S and (RE,Mn)S-Rare Earth inoculated GI; S<0.03 wt %-higher chill;	MgS at Mg-treatment (RE+Mg)S at MgRE treatment Low base S-higher carbide and lower nodules count; RE-S greater frequency	[12] [13] [14]
5	MnS-uninoculated GI; (Sr, Ce, Ba, Ca) sulphides-inoculated GI	-	[15]
6	At S<0.03 wt % , FeSi, FeSiSr and FeSiBa have little effect; graphite inoculation-has no effect	Graphite inoculation - has no effect	[16]
7	-	Zr, Ti, Al-nitrides Zr, Ti-sulphides SiO_2, Al_2O_3	[17]
8	CaO, CaS, Al_2O_3, ZrO_2	-	[18]
9	-	(Mg, Ca, Ce) oxides-sulphides	[19]
10	BN, AlN, CaO, ZrS_2, TiS, MnS, Al_2O_3, BaS, Ba_2O_3,CaC_2, CaS (oxides-sulphides)-RE	-	[20]
11	-	S addition in DI	[21]
12	MnS, SiO_2-uninoculated GI (Mn,X)S-complex sulphides in inoculated GI (X=Ca, Ce, La, Nd, Pr, Sr etc.)	-	[22]

4. GENERAL CONCLUSIONS

a) Sulphur Inoculation of Mg-treated irons makes it possible to obtain various values of the NG/CG ratio, without using classical denodularising elements (such as Ti, Al), thus making the use of iron returns less dangerous because these elements.

b) The amount of S-additive in Mg-treated irons needed to obtain a certain NG/CG ratio depends on the residual magnesium content, holding time prior to pouring, wall thickness of the casting and type of the mould.

c) The lower sulphur addition (usually up to 0.01 wt % S) in association with silicon-base inoculants (especially SiCa) after Mg-treatment can be the solution to improve the graphite nucleation process in ductile iron, without affecting the nodularity.

d) S-Inoculation can be made by different procedures (in ladle, pouring basin, reaction chamber), especially by sulphur incorporation into insert (pressure processed) or into the inoculant melt, in association with Si-base alloys.

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