# PRECONDITIONING OF ELECTRICALLY MELTED GREY CAST IRONS

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*Cercetarea a fost elaborată pentru a investiga efectul elementelor puternic dezoxidante precum Al sau/şi Zr în precondiţionarea fontelor cenuşii, topite electric, neinoculate şi inoculate. Atât Al cât şi Zr susţin formarea grafitului de tip A la un grad de subrăcire mai scăzut şi fară carburi libere. Unele studii de caz prezintă eficienţa precondiţionării cu Al şi Zr-FeSi a fontei cenuşii, topite electric, divers inoculate. Un adaos de 0,1% de aliaj Al,Zr-FeSi în topitură în cuptorul cu inducţie înainte de inoculare si turnarea unor piese cu 3-5mm grosime de perete a avut urmatoarele efecte: scaderea subracirii si recalescentei eutectice, imbunatatirea caracteristicilor grafitului, eliminarea carburilor si crestrea rezistentei la tractiune, in conditiile eliminarii tratamentului termic.*

*Laboratory research has been conducted to investigate the effect of strong deoxidizing elements such as Al or/and Zr in preconditioning of electrically melted un-inoculated and inoculated grey cast irons. Both Al and Zr sustain the A-type graphite formation with a lower degree of eutectic undercooling and free carbides. Some foundry case studies are also presented to illustrate the efficiency of Al and Zr bearing-FeSi preconditioning of electrically melted and differently inoculated grey irons. An addition of 0.1wt% Al,Zr-FeSi alloy to the melt in the induction furnace before inoculation and casting of 3-5 mm sections decreased eutectic undercooling and recalescence, improved graphite characteristics, avoided carbides and increased tensile strength, while heat treatment was eliminated.*

**Keywords:** grey cast iron, preconditioning, inoculation, Al, Zr, foundry case studies

### 1. Introduction

The main objective of grey iron production technology is to secure the formation of a large number of nuclei which can initiate nucleation of graphite. This will give a low degree of undercooling in order to prevent solidification very close to the metastable eutectic temperature (D and E type graphite formation) or

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below it, where carbide (white) structures are formed. Charge materials and melting practice will influence the structure of the resultant base iron melt, while later treatments, such as preconditioning and inoculation will influence the solidification behaviour of the castings.

After melting, the resulting metallic liquid is characterized by a colloidal condition which includes: Fe-C-Si ($X_i$) base solution (1-2wt%C), residual graphite particles (0.1-10 μm), and other non-metallic inclusions. The colloidal condition of the iron melt is preserved for a long time by the presence of the remnant graphite particles. The dissolution rate of the residual graphite particles is very low immediately after melting, especially due to the high stability of the C-C connections and the presence of the superficial active elements (S, O) on the surface of the residual graphite particles (dissolution is hindered).

The heating of the iron melt in the furnace will bring about important changes of the liquid iron characteristics; such as diffusion of elements and homogenization, remnant graphite dissolution, and non-metallic inclusions flotation (at least of the large particles). The iron melt will evolve, due to the heating effect from the colloidal condition stage (just after melting) to a quasi-homogeneous solution [Fe-C-Si ($X_i$) and C-atoms as groups or clusters] up to the quasi-ideal solution at the highest superheating level (Fig. 1). Remnant graphite particles will gradually disappear, while non-metallic inclusions and phases will be drastically reduced, both in quantities and sizes [1, 2].
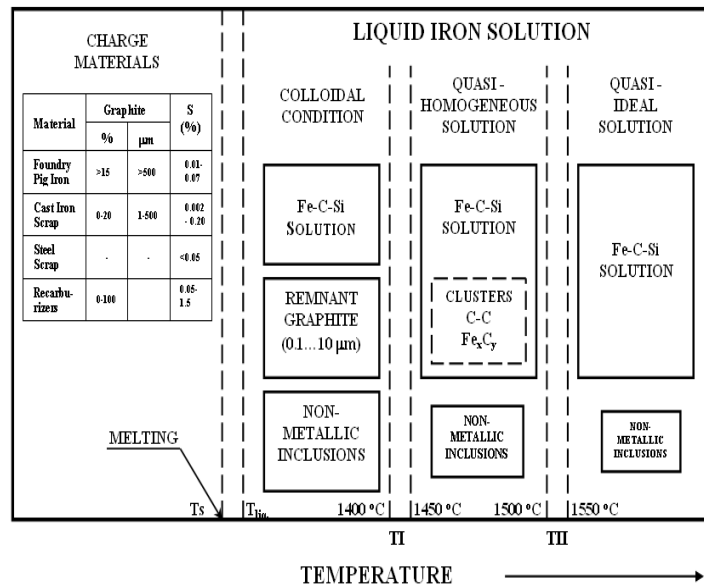


Fig. 1. The evolution of the liquid iron solution

Thermal analysis is applied to evaluate the state of the base iron, the necessity for inoculation (inoculant type and addition rate) and the response of the final inoculated iron to this specific treatment. As Fig. 2 shows, increased superheating promotes higher eutectic undercooling and visible change of graphite morphology, inclusively as transition from grey iron through mottled iron
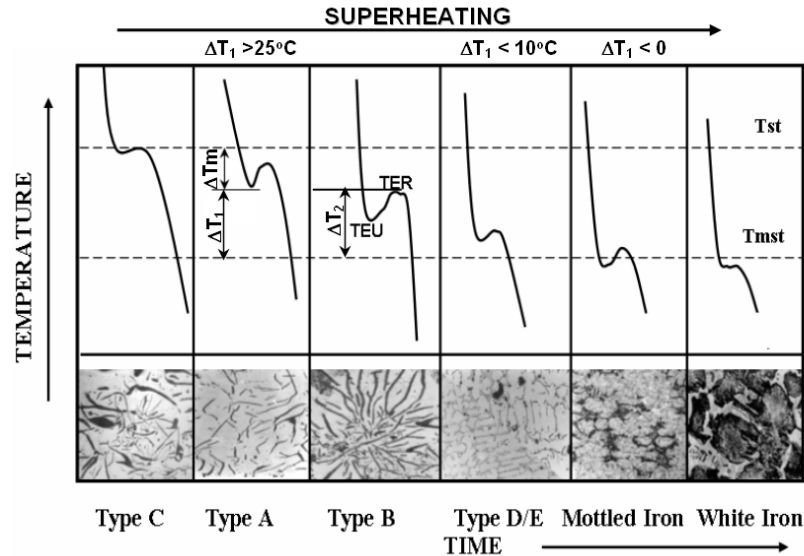


Fig. 2. Typical cooling curves and lamellar graphite morphologies in cast irons

up to white iron structure. High superheating level is useful to sustain the dissolution of coarse remnant graphite, to float coarse micro-inclusions and to deactivate the remnant micro-inclusions as they are able to act as un-controlled nuclei for graphite. But new and controlled nucleation sites of graphite must be promoted, to avoid undercooled graphite morphologies and chill tendency.

A possible ranking of graphite nuclei is as follows: graphite (highest-least energy required), silicates, oxides, sulphides, carbides, nitrides and austenite (lowest). Graphite substrates or non-metallic micro-inclusions covered by a graphite layer can nucleate eutectic graphite during solidification with minimal undercooling [3, 4]. The ability of sulphides to nucleate graphite is hindered because these substrates belong mainly to the cubic system. However, the nucleation potency of sulphides can be enhanced by inoculating elements to transform MnS into complex (Mn,X)S compounds. These might have a better lattice match to graphite, a low coagulation capacity, good stability and adequate interfacial energy [3-10].

A three-stage model for the nucleation of graphite in both un-inoculated and inoculated grey irons has been proposed (Fig. 3): (i) Small oxide-based sites (usually less than 2.0 μm) are formed in the melt; (ii) complex (Mn,X)S compounds (usually less than 5.0 μm) nucleates at these micro-inclusions; (iii) graphite nucleates on the sides of the (Mn,X)S compounds with low crystallographic misfit with graphite.  It was found that three groups of elements are important to sustain
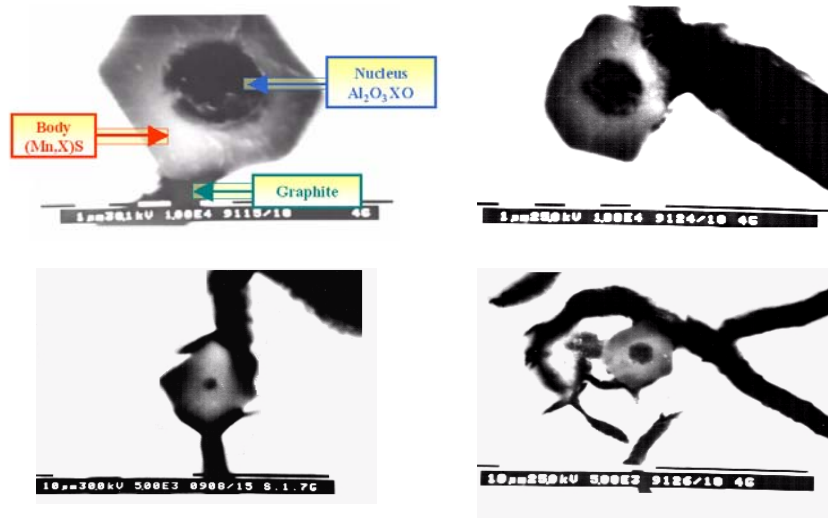


Fig. 3. Three-stage model for the nucleation of graphite in gray irons

graphite nucleation in industrial grey cast irons:  (i) strong deoxidizing elements, such as Al and Zr, to promote early formed very small micro-inclusions, which will act as nucleation sites for later formed complex (Mn,X)S compounds; (ii) Mn and S to sustain MnS type sulphide formation; (iii) inoculating elements which act in the first stage and/or in the second stage of graphite formation, to improve  the capability of (Mn,X)S compounds to nucleate graphite [8-10].

The current experimental investigation was designed to evaluate the possibility to control the solidification pattern of electrically melted grey cast irons subjected to preconditioning with Al or/and Zr and inoculation, both under laboratory experiments and plant trials.

## 2. Results and Discussion

### A. Laboratory experiments
Laboratory experiments were performed to compare the effect of strong deoxidizing elements, such as Ti, Al and Zr, to determine their individual capacity

towards preconditioning of un-inoculated and Sr-FeSi- inoculated grey cast irons [11, 12].

Iron melts were made in an acid lined induction furnace. Irons were characterized by the chemistry including 3.15-3.30wt% C, 1.50-1.65wt% Si, 0.55-0.65wt% Mn, 0.095-0.10wt% S, 0.002-0.003wt% Al and 0.003-0.005wt% Ti, giving carbon equivalent of 3.7-3.9wt% CE and Mn/S ratio of 5.5-6.5. Al-metal (99.5wt% Al), Ti-metal (99.5wt% Ti) and FeSiZr (43.5wt% Si, 30.8wt% Zr, 0.56wt% Al) were used as preconditioning agents. The three strong deoxidizing elements (Al, Ti or Zr) were added at the same level (0.03wt% each) into the metal stream during tapping at $1450^{o}$C into acid lined small poring ladles of 3 kg. Non-preconditioned irons (as reference) and a range of preconditioned irons (Al, Ti, Zr) were also inoculated in the ladle with same low aluminium Sr-FeSi alloy (76.9wt% Si, 0.8wt% Sr, 0.01wt% Al, <0.0005wt% Ti). 0.3wt% inoculant was added at 1400-1420 $^{o}$C after deslagging on the melt surface and mechanically stirred for about one minute (steel rod). Un-inoculated and Sr-inoculated irons were poured into test castings made from furan no-bake bonded moulds. A round bar specimen of 20 mm diameter and 100 mm height was cast for structure analysis and cooling curve recording (K-type thermocouple was incorporated). The aluminium content was 0.002-0.004wt% Al range in the base iron and at 0.027-0.028wt% Al level in final cast irons. Similarly, the titanium content was varied from 0.003-0.005wt.% Ti in base irons to 0.011-0.017wt% Ti in Ti enriched irons. Zirconium was only detected in Zr-preconditioned irons, the content in the melt was in the range of 0.011-0.013wt%.

For inoculated irons, it is assumed that the majority of the micro-inclusions play a role in the nucleation of graphite in size range between 1 and 10 μm, mainly depending on the preconditioner type, as Fig. 4 shows. Zr generates twice the number of particles as Al and four times the number of Ti. The morphology of graphite nucleation sites is also dependent on the preconditioner type. Generally, the compounds have a polygonal shape (mainly irregular or quasi-regular shape) especially in Al and Zr preconditioned irons. Particles with indented outline (like a dendrite) characterize Ti-preconditioning irons (Fig. 5).

The graphite particles started growing on the surface irregularities of the nuclei, such as edges, peaks or other irregular areas where the energetic state is higher. The graphite particles are interacting with their nucleation site covering it partly or entirely.
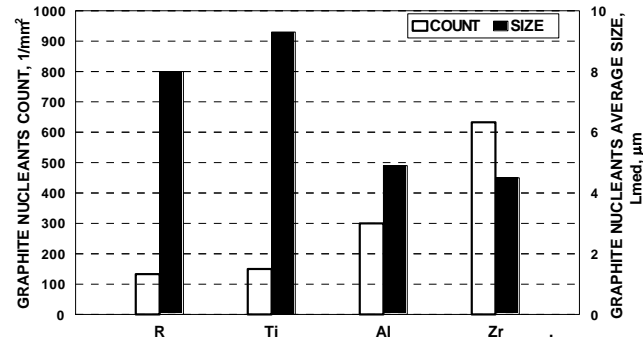
Fig. 4. Graphite nuclei count and average size in inoculated irons [R is reference]

As it appears, the particles with a higher compactness degree and smaller size favour a more simple involvement of graphite with lower branching tendency, such as type A graphite (Al and especially Zr preconditioned irons).

The big size particles having a complex morphology give a higher branching tendency of graphite, such as type D graphite (un-inoculated and Ti treated irons) (Fig. 5).
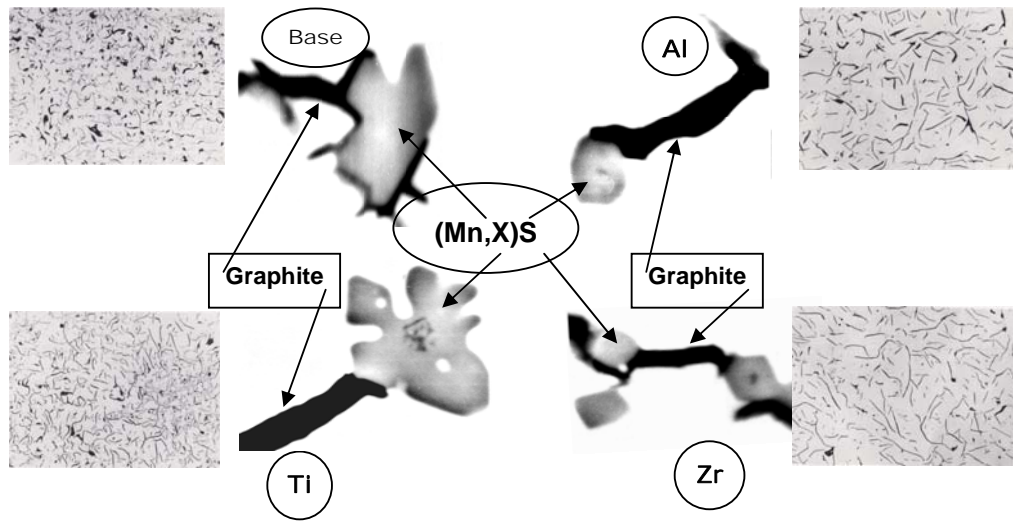


Fig. 5. Graphite nuclei and graphite particles morphologies

Not only inoculation, but also the preconditioning before inoculation of the base iron is important to control undercooling referring to the metastable

(carbide) eutectic temperature (Tmst) of cast irons (Fig. 6). At negative values, the $\Delta T_1$ parameter indicates the free carbides formation at the beginning, while $\Delta T_2$ parameter indicates at the end of eutectic reaction, respectively.

Applied inoculation moved the cooling curves from white iron characteristics to mottled iron for non-preconditioning melts and grey iron for all cases of preconditioned melts. In experimental conditions, all of un-inoculated irons start the eutectic reaction under the carbide eutectic temperature ($\Delta T_1 < 0$), but at different levels depending on the preconditioning agent: Al and Zr are better than Ti. Inoculation was more effective in all of preconditioned irons, but also with Al and Zr being more effective.

A forced chill test specimen (50 mm high and 75 mm long) was used for chill tendency evaluation (Fig. 7). The chilled iron consists of two zones. The
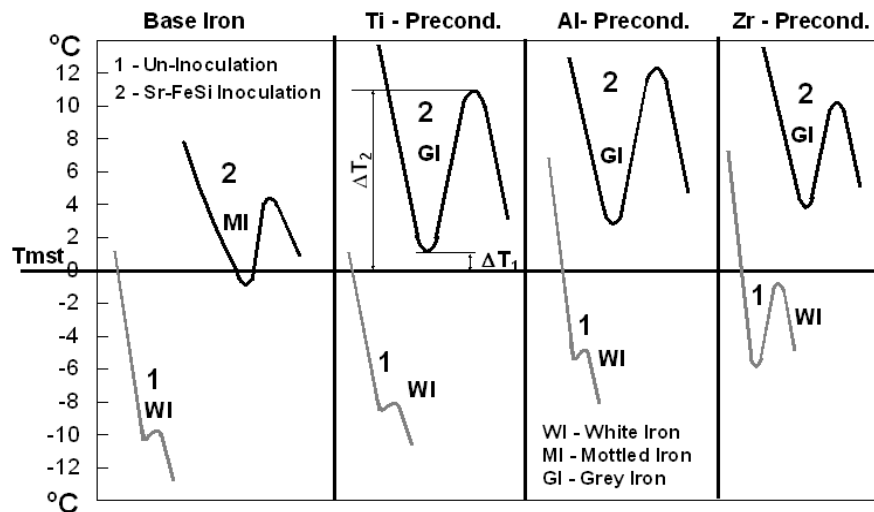


Fig. 6.  General aspect of cooling curves

white iron from the chilled face to the first appearance of a grey spot was designated as clear chill. The distance from the chilled face to the last appearance of a spot of white iron was designated as total chill. The portion of the chill affected zone between the clear chill and the total chill was designated as the mottled zone. At lower carbon equivalent level (3.70-3.72wt% CE), un-inoculated irons are characterized by high chilling tendency. Inoculation gave, as expected, overall lower chill than no inoculation. Al and Zr preconditioning of the base iron during the tapping period appears to have a beneficial effect on both chill measures, with zirconium having the most impact. Ti preconditioning had a limited benefit. The mottled zone was also affected by inoculation: the zone was larger for all of un-inoculated irons, but at lower incidence if base iron was pre-

conditioned with Al or Zr. A lower difference between un-inoculated and inoculated irons is typically for Al or Zr preconditioning.

It has been shown that small levels of aluminium in final grey iron castings is beneficial for the solidification process as required undercooling for nucleation is reduced. Recent research has given more knowledge about the fundamental effect of aluminium in the grey iron nucleation process [8-10]. This effect is significant even at very low aluminium levels (~0.003wt%) in both inoculated and un-inoculated grey iron. Increasing the residual aluminium content in iron melt helps the initiation of graphite nucleation with lower undercooling. A 0.005-0.010wt% Al content in melt therefore appears to be beneficial, even up to 0.015wt% Al can be secure in some cases, without occurrence of the detrimental pinhole effect. The optimum aluminium level suppresses or at least reduces carbides and chill, while the graphite morphology is improved: A-type graphite
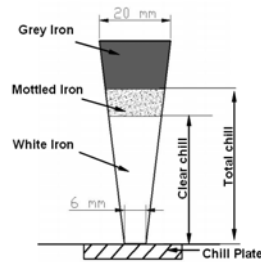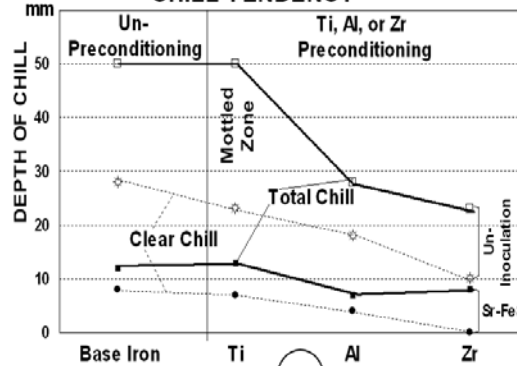
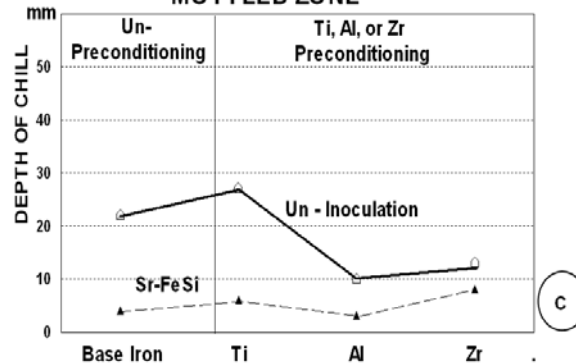Fig. 7. Influence of Ti, Al or Zr preconditioning on the chill parameters
(a-Test specimen; b-Clear and Total chill; c-Mottled zone)

flakes are promoted and B-D-E type graphite morphologies are suppressed. During casting operation it is important to control the constituent levels of the melt, including aluminium.

It could be better to adjust the aluminium content by use of Al-bearing preconditioner and subsequently add appropriate inoculants. The improved nucleation effect is also possible by use of aluminium containing inoculants, provided there is adequate control of the base iron conditions. It is important to verify the Al, S and Mn levels in the case of problems with undercooled graphite morphology.

### B. Foundry cases studies

As both aluminium and zirconium sustain the type–A graphite nucleation at lower degree of eutectic undercooling and suppress generation of free carbides, also in thin wall castings, these elements were associated in a complex alloy: 62-69wt% Si, 3-5wt% Al, 3-5wt% Zr, 0.6-1.9wt% Ca, balanced by Fe. This preconditioner was tested under different foundry conditions [13].

Electrically melted grey cast irons, especially thin wall castings (2-5 mm sections) were considered for production of automotive or general engineering specific products and rainwater pipe fittings. Major problems were reported; carbides in thin sections, shrinkage or breakages of castings during transit. High steel charges, variable charge quality or/and extended hold period incidences characterize these foundries.

Fig.s 8 and 9 illustrate some representative benefits of Al,Zr-FeSi preconditioning by furnace addition, at 8-10 minutes before tapping and after deslagging, respectively. Good results were also obtained by Al, Zr-FeSi alloy addition to transfer ladles, before inoculation.

Thermal analysis was applied to monitor the liquid iron quality, especially the eutectic undercooling parameters. Micro-samples were taken from the last ladle/castings, to evaluate the graphite morphology and occurrence of carbides. Standard tensile test bars were used to evaluate the tensile strength level.

By creating stable and long-lasting particles within the melt, Al,Zr-FeSi increases the nucleation potential of the iron at an early stage in the treatment process. This helps to eliminate variations caused by charging, holding and temperature differences between melts and creates a significantly more consistent and stable iron from the melting unit. By increasing the low eutectic temperature, and maintaining this over a long period (up to 40 minutes), the iron is more responsive to subsequent inoculation.

Foundries globally have reported the following advantages from the use of Al,Zr-FeSi preconditioning:

a) Increase of tensile strength, typically between 10-15% improvement;
b) Elimination of types B, D and E graphite forms and promotion of type A
   graphite;
c) No loss of properties on long holding times; ]
d) Reduction of chill levels in thin section castings;
e) Reduced shrinkage tendency;
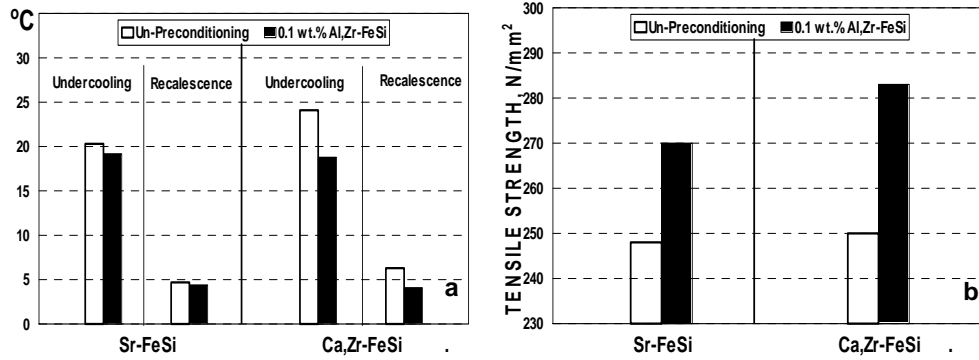f) Reduction in pig iron usage.

Fig. 8. Effects of Al,Zr-FeSi preconditioning on the cooling parameters (a) and
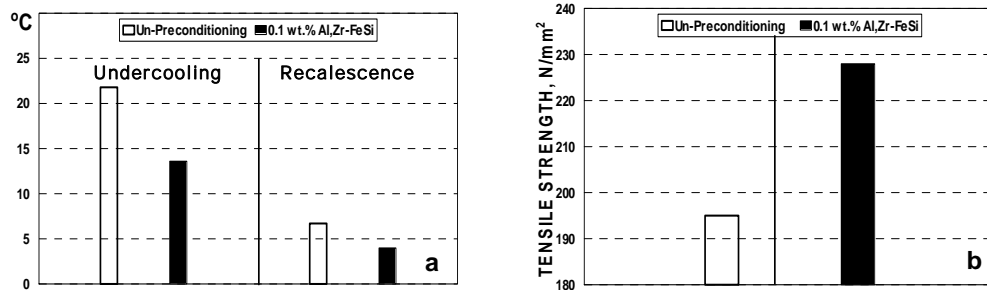tensile strength (b) of Sr-FeSi and Ca,Zr-FeSi inoculated irons [Foundry A]

Fig. 9. Effects of 0.1 wt% Al,Zr-FeSi preconditioning on cooling parameters (a) and
tensile strength of Ca,Ba-FeSi inoculated irons [Foundry B]

## 3. Conclusions

- After melting, the resulting metallic liquid may be considered to be in a colloidal condition, which includes: Fe-C-Si ($X_i$) base solution with 1-2wt% C, residual (remnant) graphite particles (0.1-10 μm); non-metallic inclusions.

- The liquid iron condition is mainly dependent on the nature of the charge materials and can be changed by superheating the melt. Liquid iron evolves from a colloidal liquid state after melting (suspension of graphite particles) through a quasi-homogeneous state into a quasi-ideal solution.

- Controlled superheating is useful to sustain the dissolution of coarse remnant graphite, to float coarse inclusions and to de-activate the remnant micro-inclusions as their ability to act as un-controlled nuclei for graphite. Excessive superheating levels promote undesired undercooled graphite morphologies and free carbides.

- For electrical melting, three technological steps appear to be necessary to produce high performance grey cast iron: [1] Furnace super-heating of the molten iron, depending on the charge characteristics and melting practice, to eliminate un-desired heredity influence of charge; [2] Pre-conditioning of the base iron, especially for low quality charge materials or/and melting practice, low performance inoculation or/and pouring practice; [3] Inoculation, as final treatment, especially to control eutectic undercooling and recalescence during solidification.

- Al or Zr preconditioning of the base iron led to improved characteristics for solidification when measuring the most significant temperatures of thermal cooling curves, giving a positive trend for eutectic and final solidification.

- It was found that 0.005-0.010wt% Al content in the melt is important to sustain type A graphite nucleation, with lower occurrence of undercooled graphite and reduced chill, without pinholes incidences.

- Foundry case studies for casting of 3-5 mm sections showed that addition of 0.1wt% Al,Zr-FeSi alloy to the melt in the induction furnace decreased the eutectic undercooling and recalescence, improved graphite characteristics, avoiding carbides, increased tensile strength and heat treatment was eliminated.

- Al,Zr-FeSi preconditioning of electrically melted base iron appears to be beneficial especially for critical foundry conditions, such as high steel charges, variable charge quality, superheated irons, extended hold periods, low sulphur or/and excessive low aluminium residual content.

**Acknowledgments**

R E F E R E N C E S

[1] *I. Riposan, M. Chisamera and M. Barstow*, "Undesirable Structures in the Inoculated Grey Irons".  Proceedings of the AFS Cast Iron Inoculation Conference, Sept. 29-30, 2005, Schaumburg, Illinois, pp. 119-129

[2] *St. Stan, I. Riposan, M. Chisamera and M. Barstow*, "Undesirable Graphite Morphologies Incidence in Inoculated Grey Irons", Advanced Materials Research, **Vol. 23** (2007), pp.  307-310, Trans.  Techn.  Publications, Switzerland, online at http:// www.scientific.net

[3] *C. R. Loper Jr.*, "Inoculation of Cast Iron-Summary of Current Understanding", *AFS Transactions,* **Vol. 107**, pp. 523-528 (1999)

[4] *C. R. Loper Jr  and  R. B. Gundlach*, "Inoculation What is it and How Does Inoculation Work"? *AFS* International Inoculation Conference, Paper No. 1, Rosemont, Illinois (1998).

[5] *T. Skaland, O. Grong  and  T. Grong,* "A Model for the Graphite Formation in Ductile Cast Irons", *Metallurgical Transactions*, **Vol. 24A, 2321** (1993)

[6] *D.M. Stefanescu*, "Inoculation of Thin Wall Castings, AFS International Inoculation Conference, Paper No.16, Rosemont, Illinois (1998)

[7] *M. Chisamera, I. Riposan  and M. Barstow*, "The Importance of Sulphur to Control Graphite Nucleation in Cast Iron", AFS International Inoculation Conference, Paper No.  3, Rosemont, Illinois (1998)

[8] *I. Riposan, M. Chisamera, St. Stan and T. Skaland*, "Graphite Nucleant (Microinclusion) Characterization in Ca/Sr Inoculated Irons", International Journal of Cast Metals Research, **Vol. 16**, No.1-3, pp.  105-111 (2003)

[9]  *I. Riposan, M. Chisamera, St. Stan, T. Skaland  and M.I. Onsoien*, "Analyses of Possible Nucleation Sites in Ca/Sr Over Inoculated Grey Irons", *AFS Transactions,* **Vol. 109**, pp. 1151-1162 (2001)

[10] *I. Riposan, M. Chisamera, St. Stan and T. Skaland*, "A New Approach to Graphite Nucleation Mechanism in Grey Irons", Proceedings of the AFS Cast Iron Inoculation Conference, Sept. 29-30, 2005, Schaumburg, Illinois, pp. 31-41

[11] *I. Riposan, M. Chisamera, St. Stan, C. Ecob  and D. Wilkinson*, "Role of Al, Ti, Zr in Grey Iron Preconditioning/Inoculation", Journal of Materials Engineering and Performance, **Vol. 18(1)**, February 2009, pp. 83-87

[12] *I. Riposan, M. Chisamera, St. Stan, P. Toboc and C. Ecob,* "High Efficiency Preconditioning of Electrically Melted Grey Cast Irons", 68th World Foundry Congress, Chennai, India, February 7-10, 2008, Paper 53

[13] Preseed Preconditioner Booklet, ELKEM Foundry Products Division, www.foundry.elkem.com (2007).