Enhanced Quality in Electric Melt Grey Cast Irons

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The paper reviews original data obtained by the authors, recently disconnected published, concerning the specific solidification pattern of low S (<0.05%) irons, with very low Al (<0.005%), melted and superheated in acid lined, coreless induction furnaces, and how superheating affects the iron quality with effective metallurgical treatments for use in these conditions. Solidification undercooling increased with increasing superheat, associated with significant changes in chemical composition, such as C, Si, Mn, Al and Zr, involved in the nucleation of graphite. The concept in the present paper sustains a three-stage model for nucleating flake graphite [(Mn,X)S type nuclei]. There are three important groups of elements [deoxidizer/Mn, S/inoculating] and three technology stages in electric melt iron [superheat/pre-conditioning base iron/final inoculation]. Different materials were used for pre-treatment of the iron melt, to control oxidation levels and/or to promote active graphite nucleation sites, including carbon materials and metallurgical silicon carbide. Special attention was paid to maintain Al and Zr recoveries in the melting furnace for their effects on the iron structure. A double treatment utilizing strong oxide forming elements, such as Al and Zr for preconditioning, followed by inoculation decreased eutectic undercooling parameters. This treatment improved graphite characteristics and avoided carbides. For foundry application, it is recommended to ensure (Mn,X)S compound formation, compatible for nucleating graphite with less eutectic undercooling. Attention is drawn to ensuring a control factor (%Mn) × (%S) equals 0.03 – 0.06, accompanied by 0.005–0.010% Al and/or Zr content in inoculated grey irons.

KEY WORDS: grey iron; S; Al; Zr; Ti; electric melting; furnace superheating; preconditioning; inoculation; graphite nucleation; graphite morphology; carbides; thermal analysis.

1. Introduction

Historically, grey cast irons were melted in a cupola furnace, at more than 0.05 wt.%S, more than 0.5 wt.%Mn and more than 0.005 wt.%Al levels, with favourable conditions for formation of MnS-type compounds, often found as the major nucleation sites for flake graphite. Despite that cupula furnace technology is developing, some problems can become acute in a cupola melting shop. For example, a cupula shaft furnace depends on combustion of valuable raw materials, such as coking coal, generating stack gases including CO/CO₂. Users would have to make enormous investments in order to design and install a really environmentally friendly cupola furnace.

Cupula furnaces are often designed for cost effective high production volumes of the same iron composition but they offer limited flexibility for the same reason. This results in production limits, especially when foundry throughput is reduced, or when cast parts in different qualities (grey iron, ductile iron, compacted graphite iron) are increasingly being demanded from the same foundry production line. Consequently, in many parts of the world, such as in Asia as a whole, many cupula furnaces have been closed down and new investments are being made in induction furnaces rather than coal or gas-fired furnaces.¹

Small and inefficient cupolas with their attendant process issues have been replaced by a new generation of coreless induction furnaces with medium frequency (200–1 000 Hz) and high specific power supplies (more than 250 kW/ton). This has revolutionized the iron foundries: high melting rates (usually less than one hour melt cycle, with high steel charges), so high production at lower furnace capacity; no heel required (100% solid charge); larger furnace capacities are readily available up to 10 – 20 tons; reasonable stirring capability for carbon raiser additions to a high steel scrap charge - lower cost; improved iron quality for large scale production.

The smaller scale cupula melting problems such as suitable coke availability, environmental restrictions, plus the need for a holding furnace to stabilize iron temperature and analysis led to increasing electric melting of grey iron with low sulphur levels (usually less than 0.05 wt.%S) in many parts of the world. The growing production of ductile iron and compacted graphite iron castings needs a lower sulphur base iron. In many cases, a foundry will produce high and low sulphur base irons in the same shift, for grey iron and ductile/compacted irons, respectively. For these producers, a single low sulphur base iron would be very attractive, especially if a single inoculant type could be used for each of
One of the main differences between a cupola melted iron and an electric furnace melted iron is the sulphur content, as melted. It is well established that there is a preferred grey iron sulphur content at approx. 0.05 wt.% to assist the inoculation response. It has been demonstrated that the effectiveness of inoculants in lower sulphur electric melt iron is inferior to the performance in higher sulphur cupola melted irons of similar carbon equivalent. To ensure that an inoculant still performs in lower sulphur electric melt iron a foundry has to choose an appropriate inoculant composition, and then provide an environment in which it can reliably minimize undercooling.

Grey iron is still the most common foundry metallic material, at 45% of total world castings production (Fig. 1). It is especially attractive in the manufacture of vital engine components, using thin walled castings, because of a range of excellent properties such as machinability, heat conductivity and vibration damping capacity, in combination with reasonable strength.

A specific feature of the automotive industry is ongoing demand for lighter iron castings, so thin wall grey iron castings (less than 5 mm wall thickness) are more prevalent. These castings require mandatory high iron pouring temperatures, so the melting furnace superheats to more than 1550°C usually. Even if a cupola melted iron could reach a tap temperature sufficient to allow a pouring temperature of 1450°C the environment in a cupola shaft for the melting iron or steel is mainly reducing. In contrast the latest coreless furnaces have an oxidizing atmosphere and the seemingly unlimited availability of kWh allows the melt deck to reach high molten bath temperatures unthinkable in cupola melting. Superheated electric melt irons with low S and very low Al, typical for these coreless furnaces solidify at high cooling rates in thin wall castings and are particularly prone to free carbides and/or undercooled graphite formation.

The main objective of the present paper is to explore what conditions are needed to improve the quality of electric melt grey iron superheated in acid lined, medium frequency coreless induction furnaces, for thin wall iron castings. A review of original data obtained by the authors, relating to the specific solidification pattern of low sulphur irons, examines how superheating affects the iron quality and which metallurgical treatments are effective.

2. Low Sulphur Grey Cast Irons Characteristics

Only when liquid iron undercools sufficiently (200–230°C), can the smaller sizes of micro cluster (≤50 μm) exist as stable homogeneous nuclei for graphite particles. Under normal conditions, such high undercooling is very difficult to achieve; therefore, the nucleation of graphite is mainly by heterogeneous nucleation.

Various compounds can be formed in the iron melt, depending upon the melting and pouring practices. Thermodynamically, the free energy of formation (ΔG°) (Fig. 2), of oxides/silicates and sulphides allow more stable particles to form in commercial iron melts, than with nitrides and carbides, respectively. Silicate particles are apparently favourable nucleation sites of graphite in grey irons. This is due to their hexagonal crystallographic structure, suitable wetting relationship, a similar lattice registry and relatively high stability of the compounds. The ability of sulphides to nucleate graphite is not obvious, as graphite has a specific hexagonal structure, while sulphides are mainly of the cubic types.

To become part of a nucleation substrate, foreign particles must satisfy two conditions: (a) conform to certain relationships of lattice mismatch or registry; a certain lattice face of the foreign particle (inclusion) substrate has a certain corresponding relationship to the lattice parameter and orientation of a graphite crystal lattice; (b) satisfy the interfacial energy requirement between a heterogeneous nucleus and graphite: only when the foreign particles can be wetted by graphite, can graphite form nuclei on the foreign substrates.

A characteristic parameter of the lattice relationship is plane mismatch (δ). The smaller the mismatch of the two substances, the stronger the nucleation potential between them. In general the relationship has the strongest nucleating ability when δ is < 6%, medium nucleating ability when δ = 6 – 12% and weak nucleating ability at δ > 12%. Mis-match δ (%) between a certain lattice face of some substances and the (0001) face of graphite is shown in Fig. 3, according to paper, which reviewed the literature data.

A possible ranking of nuclei of graphite is as follows: graphite (highest-least energy required), silicates, oxides, sulphides, carbides, nitrates and austenite (lowest). MnS appears to be a medium potency candidate for graphite nucleation, while other sulphides should be more able to nucleate graphite. The silicates of traditional inoculating elements (Ca, Sr, Ba) also have a good ability to act as nuclei of graphite. It was also found that the elements of Ca,
Ce, La, Pr, Nd, Sr, can be present in MnS nuclei to form complex sulphides (Mn,X)S, which provide a good lattice match with graphite and become the most effective nuclei among any of the heterogeneous nuclei. For example, it was found that although the lattice parameter disregistry of MnS/graphite may be rather large (–12.1%), SrMnS as a modified particle has a better fit for graphite nucleation (–5.2%).

A three stage model for the nucleation of graphite in both un-inoculated and inoculated grey irons has been proposed (Fig. 4): (a) Small oxide-based sites (0.1–3 μm, usually less than 2.0 μm) are formed in the melt; (b) complex (Mn,X)S compounds (1–10 μm, usually less than 5.0 μm), where X = Fe, Si, Al, Zr, Ti, Ca, Sr, P, nucleate at these micro-inclusions; and (c) graphite nucleates on the sides of the (Mn,X)S compounds because of the low crystallographic misfit with graphite.

Three groups of elements were found to be important to sustain graphite nucleation in industrial grey irons: (1) strong deoxidizing elements (for example Si, Al, Zr), to promote early forming, very small micro-inclusions, which will then act as nucleation sites for later forming complex (Mn,X)S compounds; (2) Mn and S to enable a MnS type sulphide formation; (3) inoculating elements (for example Ca, Sr, Ba, La, Ce), which act in the first stage and/or in the second stage of graphite formation, to improve the potential of (Mn,X)S compounds to nucleate graphite. The chemistry maps showed that the core (nucleus) and body (shell) parts of the inclusions are distinct in terms of chemical composition (Fig. 5).

Mn and S were found as the basic components of all micro-inclusions found in commercial irons, regardless of their position in the iron structure, iron chemistry, or iron melt treatment. In all of the above conditions manganese sulphides were a complex rather than the simple type. In inoculated irons the (Mn,X)S compounds are more complex, they appear at a lower Mn/S ratio and with higher compatibility for graphite nucleation, especially when one or more

Fig. 3. Mismatch δ (%) between a specific lattice face of some substances and the (0001) face of graphite [I-strongest nucleating ability; II-medium nucleating ability; III-weak nucleating ability].

Fig. 4. Typical morphologies of graphite nuclei in different inoculated grey irons [G-graphite; N-nuclei]. (a) High Purity (HP)–FeSi; b) Sr–FeSi; c and d) Ca–FeSi.

Fig. 5. Typical example of chemical analysis along cross-section of complex (Mn,X)S compound associated with graphite [La,Ca,Al–FeSi inoculated iron] [a-Compo; b-Mn, S; c-O, Al, Si; d-Ca, La].
The nucleation of graphite on MnS particles was also confirmed by microstructure simulation. Recently, silica-rich oxide bi-films were considered to be able to behave as substrates on which oxysulphide particles form, nucleating graphite. The presence of the film provides a favoured substrate onto which graphite can grow. This leads to the development of flake graphite, while undercooled graphite is the true coupled growth form, nucleated at even lower temperatures in the absence of favourable film type substrates in suspension.

In foundry practice grey irons with low S levels, usually solidify with high eutectic undercooling, leading to the formation of carbides and/or undercooled graphite morphologies, especially in thin wall castings, commonly used in the automotive industry.

Figure 6(a) shows important changes to the eutectic undercooling parameters at different sulphur levels, in both base and inoculated irons, and at low aluminium content (0.003 wt.%Al). The $\Delta T_1$ parameter (TEU – Tmst) illustrates the condition of the irons at the start of the eutectic reaction, while $\Delta T_2$ = TER - Tmst at the end of this stage, relative to the metastable (carbidic) eutectic temperature (Tmst). TEU is the lowest and TER the highest eutectic temperature on the cooling curve.

At extremely low sulphur content (< 0.01 wt.%S), typical for ductile base iron, the cast iron solidified without graphite in the structure, as values for both $\Delta T_1$ and $\Delta T_2$ were < 0. Ca–FeSi inoculation changed the iron structure from white to mottled, with carbides forming at the beginning of the eutectic reaction ($\Delta T_1 < 0$) followed by graphite formation at the end of the eutectic reaction ($\Delta T_2 > 0$). In contrast, a high sulphur content in the base iron (0.07–0.09 wt.%S), representing resulphurized electric melt iron or cupola melted iron, supported graphite formation in solidification. The cast iron changed from a white iron (carbides) to a mottled iron (carbides + graphite), while inoculated iron changed from a mottled to a grey (graphitic) microstructure (Fig. 6(a)).

Chill or carbide formation and the characteristics of the eutectic structure are strongly affected by the sulphur content in cast irons. As an example, 3.8–3.9%CE and 0.001–0.003 wt.%Al electric melt irons (acid lined, medium frequency induction furnace), at two sulphur levels, representing as-melted iron (0.024 wt.%S) and resulphurized iron (0.072 wt.%S) show different chill characteristics (Fig. 6(b) and eutectic cell (EC) parameters (Fig. 7), depending on the sulphur content and inoculation treatment. The chilled iron at the apex of the wedge sample consists of different zones. That portion nearest the apex, entirely free of grey areas, is designated as the clear chill zone ($W_c$). The region from the junction of the grey fracture to the first appearance of chilled iron (apex) is designated total chill ($W_t$). In both case studies, the low residual aluminium in the iron melt also had a negative effect on graphite nucleation.

The influence of the element sulphur, individually or in conjunction with manganese content, has a long history in cast iron. Generally, it is accepted that in grey irons, a controlled relationship between manganese and sulphur contents is necessary, and it is expressed in different ways.

$$%\text{Mn} = 1.7(\% \text{S}) + 0.2 - 0.4 \quad \text{(1)}$$

$$%\text{Mn} / \% \text{S} = 5 - 15 \quad \text{(2)}$$

$$\text{(Mn/}\% \text{S}) = 0.03 - 0.06 \quad \text{(3)}$$

The Eq. (3) was recently proposed by R. Gundlach as a result of reviewing the most important historical data, on the influence of manganese and sulphur in grey cast irons and with support of the three-stage model of flake graphite nucleation in commercial irons, based on major role of (Mn,X)S compounds.

For example, the results presented in Figs. 6(b) and 7 refer to grey irons characterized by 0.024 wt.%S with 0.75 wt.%Mn ($\text{[(Mn/}% \% \text{S}) = 0.018] and 0.071 wt.%S with 0.77 wt.%Mn ($\text{[(Mn/}% \% \text{S}) = 0.055]$, respectively. Considerable laboratory and plant data confirmed the usefulness of Eq. (3) for controlling the content of both elements in ranges, such as 0.4–1.2 wt.%Mn and 0.04–0.12 wt.%S.

3. Superheating of Iron Melt in Acid Lined Coreless Induction Furnace

There are different reasons for superheating grey iron in the acid lined, coreless induction furnaces, including the production of thin wall (< 5 mm wall thickness) grey iron castings, which need a 1450°C pouring temperature or high-
er. Any significant analysis correction after melting a steel charge needs power for stirring, especially if recarburizing with cheaper amorphous carbon raisers. Post-furnace metallurgical treatment, or numerous transfers and long holding time all require much higher tap temperatures.

The new generation of coreless induction furnaces are very capable of achieving high superheat temperatures above 1550°C, due to high performance electrical equipment with high specific power rating above 250 kW/t. Also quality improvements allow the acid refractory lining to withstand high temperatures (high purity SiO$_2$ materials, optimum crystalline structure, active agents addition). One application uses a SiC addition in a SiO$_2$ – B$_2$O$_3$ mass leading to improved lining life (20–100%), especially with high rust levels in the metallic charge or even when employing oxygen in a furnace process.$^{27,28}$

Since superheating is necessary and has become more possible in modern foundry melt shops, it is important to investigate the effect on iron quality and possible consequences in a casting. An extensive research programme,

![Fig. 8. The evolution of the liquid iron solution (a) and typical cooling curves and resulted structure of irons (b).](image1)

![Fig. 9. Influence of the superheating temperature and time on the iron chemistry in acid lined induction furnace melting.](image2)
combining laboratory experiments with plant trials, showed that superheating iron in an acid lined, coreless induction furnace will change the liquid iron characteristics. It affects the diffusion of elements and solution homogenization; remnant graphite dissolution; flotation of non-metallic inclusions, especially large particles. After melting, the liquid metal may be flotation of non-metallic inclusions, especially large particles. After melting, the liquid metal may be considered to be in a colloidal state, which consists of: a Fe–C–Si (Xi) base solution; remnant graphite particles (0.1 to 10.0 μm) and non-metallic inclusions (Fig. 8(a)).

The condition of the liquid iron is heavily dependent on the quality of the original charge materials but then change after superheating the bath. Liquid iron evolves from a colloidal liquid state after melting (suspension of graphite particles) through quasi-homogenous up to a quasi-ideal solution. Superheating is useful to dissolve leftover coarse graphite, to float coarse inclusions and to de-activate the residual micro-inclusions as un-controlled nuclei for graphite. Excessive superheating however will ultimately promote undercooled graphite morphologies and iron carbides (Fig. 8(b)).

Detailed results from experimental melting and superheating up to 1 600°C in an acid lined, medium frequency coreless induction furnace, on changes to the solidification characteristics, chemistry and chill tendency, were presented. Melting led to oxidation of most of the important elements (C, Si, Mn, Zr, Al, Cr); C, Al and Zr content continued to decrease up to 1 600°C, while Si and in some cases also Mn and N showed a slight increase especially at temperatures above 1 500°C (Fig. 9). Holding the iron melt at high temperature (1 530°C) contributed to important loss of C, Al and Zr.

Considering the active elements involved in graphite nucleation, according to (Mn,X)S theory, excess superheat did not affect the levels of Mn and S in the melt, but had a severe effect on the residual Al and Zr levels. The loss of Al and Zr after melting led to solidification with high eutectic undercooling and consequently higher tendency for chill (Fig. 10). Eutectic undercooling (ΔTm) is defined as the difference between the eutectic temperature in the stable system (Tst) and the lowest eutectic temperature (TEU). The parameter relative clear chill (RCC) is defined by $\text{RCC} = 100 \left[ \frac{W_c}{B} \right]$, where $B$ is the maximum width of the test wedge.

4. Metallurgical Treatment of Electric Melted Grey Irons

4.1. Pre-Treatment of the Iron Melt in a Melting Furnace

Different materials are used for pre-treatment of the iron melt in the furnace, to control oxidation levels and/or to promote active graphite nucleation sites, including ferro-silicon, metallurgical silicon carbide, and different carbon materials. In electric melt grey iron foundry practice, a range of results support this approach, providing improved casting quality.

Some papers reported the effectiveness of crystalline (graphic) carbon materials or metallurgical silicon carbide to reduce eutectic undercooling or carbide tendency, and promote type A graphite with higher eutectic cell count. Controlled laboratory and plant experiments demonstrated alternative ways to improve the quality of low sulphur, electric melt grey irons, using treatments during melting.

4.1.1. Carbon Materials

The structure (crystalline/amorphous ratio) and chemistry of recarburisers have an important influence on carbon recovery, iron quality, working environment, power/energy consumption, furnace lining life, tap-to-tap time, and alloy recovery. Generally, it is accepted that amorphous forms of carbon materials are absorbed into the melt as iron carbide. They supply carbon, but cannot nucleate graphite. In contrast, addition of crystalline graphite is particularly effective in nucleating graphite during cast iron solidification.

Typically, S-bearing recarburisers are used in the production of grey irons. Low S recarburisers are specifically required for ductile irons, where the recommended sulphur level is typically ten times lower (0.005–0.015 wt.%) than in a grey iron. Higher sulphur content in the iron melt suppresses graphite dissolution and prolongs the suspension period of graphite particles, and, consequently, their contribution to graphite nucleation in the final cast iron. Sulphur level in the melt is important since complex (Mn,X)S compounds were found as the major nucleation sites for flakes in both un-and inoculated grey irons.

Different carbon raisers with various origins structure and chemistry, were evaluated in laboratory conditions to assess the effect on grey iron quality, particularly their graphitizing characteristics. Calcined Petroleum Coke (CPC), rep-

![Fig. 10. Influence of superheating temperature on eutectic undercooling ΔTm (a) and chill tendency (b) [Wc and Ws-wedge samples, ASTM A367].](image-url)
representing amorphous carbon materials (95–98.7 wt.% fixed carbon-FC, 0.6–2.5 wt.%S, 0.5–1.5 wt.%Ash); b) Graphitized Petroleum Coke (GPC) as a crystalline Synthetic Graphite (99–99.7 wt.%FC, 0.06–0.3 wt.%S, 0.1–0.7 wt.%Ash); c) By-Product Partially Graphitized Packing Coke, as granular Petroleum Coke (GPCR) (97.4–97.9 wt.%FC, 0.05–0.10 wt.%S, 2.0–2.4 wt.%Ash) or Metallurgical Coke (GMCR) (83–87 wt.%FC, 0.19–0.34 wt.%S, 11.5–16.7 wt.%Ash) initially used to surround electrodes in electric graphitizing furnaces; d) Resistor Coke, as a by-product from graphite manufacture, where calcined petroleum coke was covered with sand to act as an insulator for the furnace wall. It was selected as a high purity product (MCSX), at more than 95 wt.%FC, less than 0.2 wt.%S and 2–3 wt.%Si; e) Natural Crystalline Graphite, a high purity mined product (96.9 wt.%FC).

The experimental procedure employed consisted of holding the melt (3.0–3.25%CE, 2.5–2.9 wt.%C, 1.6–1.85 wt.%Si, 0.016–0.022 wt.%S) in a 10 kg graphite crucible induction furnace at constant temperature for about five minutes followed by deslagging. The selected carbon material was then added (0.6 wt.%C) to the melt while power was applied to the furnace to maintain the same temperature range (1450–1470°C). After a fixed holding time (5 minutes), mechanical stirring was applied for 2 minutes. Finally, 0.7–0.8 wt.%FeSi175 was added to the furnace before tapping. Chill wedge (W3 ½, ASTM A367) and forced chill (4C, ASTM A367) tests were used to evaluate the chill tendency of the recauburised cast irons.

The highest carbon recovery level was attained with graphitized petroleum coke products (GPC, MCSX). Natural graphite (NG) had the lowest range of carbon dissolution results in molten iron, while calcined petroleum coke (CPC) had an intermediate behaviour, closer to graphitized petroleum coke in these experimental conditions.

Resistor coke (MCSX), previously used as a furnace insulator in high temperature furnaces for graphitizing electrodes was generally found to have an important inoculating influence, giving the lowest chill tendency with less undercooled graphite (type D + E) (Fig. 11). A homogeneous structure is also a desirable characteristic with the recauburised irons using this type of carbon material.

In different experimental conditions, at a higher iron temperature (1480–1500°C) and longer carburizing time (7 min), with a higher recauburiser addition (0.9 wt.%), both graphitized petroleum coke products (granular synthetic graphite-GPC and packing coke as by-product-GPCR) appear to be more effective than calcined petroleum coke (CPC). Graphitized packing metallurgical coke (GMCR) performance depends on its purity, but could be more efficient than amorphous calcined petroleum coke (Fig. 12).

The results confirmed that graphitized petroleum coke products, including recovered (by-product) materials, generally represent higher carbon recovery and inoculation effect in grey irons (lower chill tendency). Medium sulphur and high carbon content amorphous calcined petroleum coke could be a preferred cheaper carbon raiser for low sulphur grey iron, considering inoculation effect, due to it also raising the sulphur level. Recovered granular carbon materials, previously used as conducting media are potential carbon raisers with noticeable inoculation effects in grey iron, especially if they were originally petroleum coke.

4.1.2. Metallurgical Silicon Carbide

Silicon carbide is usually produced in special graphite electric resistance furnaces from high quality raw materials, including high purity quartzite (>99.5 wt.%SiO2), active petroleum coke (<0.5 wt.%Ash, <1.5 wt.%S) and other additions. Two groups of SiC-products are considered: a) α-type at the highest purity (>98 wt.%SiC), surrounding graphite electric resistance (>1800°C), usually for abrasives, heating elements, refractories type applications; b) β-type, at lower purity (>80 wt.%SiC), is the next layer (1400–1800°C) in a section of the electric furnace, usually known as Metallurgical SiC.

Generally, granular metallurgical silicon carbide products include 80–98 wt.%SiC, 0.1–8 wt.%Cfree (graphite), 0.01–1.0 wt.%SiCfree, 0.5–10 wt.%SiO2, 0.02–0.5 wt.%Al, <0.15 wt.%S, <1000 ppmN, <200 ppmH, and very low residual elements. Metallurgical silicon carbide is a unique C and Si bearing material, with 30–35 wt.%Ctotal and 55–65 wt.%Stotal, for a Si:C = 2:1 ratio.

![Fig. 11](image1.png) Chill tendency (TC) and undercooled graphite amount of recauburised irons, depending on final carbon equivalent (CE) and carbon material type [calcined (CPC) and graphitized (GPC) petroleum coke; MCSX-resistor coke; NG-natural graphite].

![Fig. 12](image2.png) Influence of carbon material type on C- recovery (Re, %), specific sulphur increase [AS/ΔC × 103, %] and chill tendency as wedge test (TCW, mm) and forced chill test (TCC, mm) of test irons.
4.1.3. Aluminium Recovery by Charge and after Melting

As a carbon source, it is characterized by lower S, N and H contents, compared to non-graphitic recarburisers. As a Si source, it contributes less Al, compared to FeSi and has a lower level of harmful elements compared to recarburisers and FeSi. Supplementary, metallurgical silicon carbide is inert towards moisture (no storage problems), resistant to oxidizing at temperature (even above 1 500°C) and it does not melt (hence its use in refractories), but dissociates in a ferrous melt.

In iron foundries, metallurgical SiC has three important roles: a) Silicon and Carbon additive, with low Al, S, N, H; b) Preconditioning/pre-inoculation effect; c) Efficient deoxidizer lowering FeO/MnO, in slag and metal. It is used as a furnace addition, in granular form for induction furnaces (80...95 wt.%SiC, 1...10 mm grain size, 2...10 kg/ton addition rate) and as briquettes for cupola charges (35...65 wt.%SiC, 5...20 kg Bricks/ton).

As a ladle addition (in-stream or injected), especially in ductile iron production, finer sized products are used, typically <1.0 mm grain size and >97 wt.%SiC (special products). Due to the need for SiC to dissociate into molten iron, rather than dissolve, the process is temperature sensitive and requires prolonged exposure to the molten iron. For these reasons SiC additions, either at lower temperatures or late in the process, are not widely practiced.

Worldwide foundry experience reports benefits from using metallurgical silicon carbide: reduced chill; improved machinability; improved and more uniform mechanical properties; less scrap, particularly due to hard edges, less shrinkage porosity, gas porosity, graphite degeneration; higher durability of furnace acid lining; increased Mg-yield; reduction in dross formation; higher nodule count.

The preconditioning/inoculation effect of metallurgical silicon carbide is generally promoted by the presence of SiC molecules (not from melting but after dissolution) and residual crystalline carbon, as graphite. This effect benefits the formation of a fine iron structure, lower chill (carbide forming) tendency and reduction, or even elimination, of the inoculant addition. Some experimental programmes claimed a possibility to improve the preconditioning/inoculation performance of metallurgical silicon carbide, by optimizing the chemical composition, especially by increasing the free carbon content.29–41

4.1.3. Aluminium Recovery by Charge and after Melting with In-furnace Additions

It was shown (see Fig. 9) that higher superheating temperatures resulted in loss of carbon equivalent and residual (Al, Zr) levels with a transition from mottled iron to white iron solidification reflected by increased eutectic undercooling (see Fig. 10). As Al was identified to be a key element within complex manganese sulphides acting as graphite nucleation sites in grey irons, experiments were conducted to control Al in coreless furnace melting with superheating.24

The iron bath was held in an acid lined coreless furnace for up to 40 min at 1 520–1 540°C. Composition history of the iron melt was tracked, especially for minor elements Al, Zr, Cr, N. In a special section aluminium, as a key element in graphite nucleation at lower eutectic undercooling, was analyzed accurately, especially after aluminium additions to the molten bath.

Typical changes to the residual aluminium and zirconium with time, when holding the induction melted irons in contact with air in a silica crucible is shown in Fig. 13(a). Even at very low zirconium levels in the iron Zr continued to oxidize to a final content less than 0.00050 wt.%Zr. Aluminium content decreased drastically for the observed heats, with a similar pattern throughout, so the final content was up to two times lower than the initial content. A final content of 0.0004–0.0005 wt.%Zr and 0.0012–0.0016%Al in the irons is insufficient to assist graphite nucleation with low eutectic undercooling.

Having observed that the Al content in the iron melted in acid lined coreless furnace was less than that needed for good graphite nucleation (< 0.0030 wt.%Al), an experimental programme was established to examine this in more detail.25 In total 11 heats, from the same metallic charge, were produced and the Al content was recorded after different Al additions and holding times (Figs. 13(b), 13(c)). This showed that the Al content after melting and measured after holding for 15–20 min at 1 500±10°C would be within a very narrow range of 0.0011–0.0012 wt.% from 0.0023–0.0030 wt.%Al in the metallic charge.

In some of the heats Al was added after an initial holding period to obtain Al-levels from 0.0025 to 0.0060 wt.% followed by 20 minutes holding at 1 530±10°C. The aluminium content in the iron melt was then evaluated at different times. The higher the aluminium quantity added, the higher the final aluminium content, but the level of Al decreased two - three times while holding at high temperatures for 20–25 min. Independent of the added aluminium, its content in the final tapped iron was in the range 0.0015–0.0025 wt.% Al. The experiments showed that despite the presence of 0.004–0.006 wt.% Al in the iron early after melting, and any
subsequent addition of Al, during holding the Al content in the final iron would be too low to sustain graphite nucleation.

4.2. Complex Treatments of Electric Melt Grey Irons

4.2.1. Al, Zr and Ti Preconditioning Comparison

The effect of strong deoxidizing elements such as Al, Zr or Ti on graphite nucleation in base iron and Sr-inoculated grey irons has been investigated in a laboratory programme (SEM analysis, thermal analysis, chill tendency, structure parameters).\(^6,18,25,42-44\) It was found that Al, Zr and Ti have different distribution patterns in the core (nucleus) and the shell (body) of (Mn,X)S compounds, which were found to act as nucleation sites for graphite flakes, with different influences on graphite nucleation. In contrast with Ti resulting in complex shaped (morphology) (Mn,X)S compounds, like Chinese-script, which appear to cause type D graphite formation, Al and Zr led to smaller sized, more compact compounds, enabling type A graphite nucleation (Fig. 14).\(^6\)

4.2.2. Double Treatments (Al/Zr Preconditioning + Inoculation) of Grey Cast Irons

In some of the experiments, Al and Zr were considered individually, for their ability to support complex (Mn,X)S compounds formation, with high activity in graphite nucleation of grey irons. Effectiveness in this area allows carbide control (chill), limits undercooled graphite (D, E type) formation and affects eutectic cell characteristics.\(^18\) Hypoeutectic grey irons (3.6–3.8%CE), at 1.65–1.85 wt.%Si, 0.45–0.6 wt.%Mn, 0.09–0.1 wt.%S, 0.001–0.01 wt.%Al, 0.0005–0.013 wt.%Zr, (\%Mn) × (\%S) = 0.04–0.06 were electric melted.

Metallic Al was added to the furnace prior to tap as a preconditioner followed by a ladle addition of 1.0 wt.%Ca–FeSi inoculant. 15 mm diameter bars for structure analysis and 4C chill test samples (ASTM A367) were cast in furan resin moulds at 1330–1350°C. Similarly, Zr was tested as a pre-conditioner (0.03 wt.% Zr addition as FeSiZr alloy in the stream during furnace tap), followed by 0.3 wt.% Sr–FeSi inoculation in the ladle. Experimental test samples, non-pre-conditioned and Zr-pre-conditioned iron, un-inoculated and Sr-inoculated, were poured at 1380–1400°C (furan no-bake bonded mould): wedge test sample (20 mm width, 50 mm height, 75 mm length) and round test bar (20 mm diameter).

Low residual Al level (0.001–0.003 wt.%) results in higher chill, more undercooled graphite and lower eutectic cell count, in inoculated irons. A 0.007–0.010 wt.% Al content in the melt is important to promote type A graphite nucleation, with reduced chill, at a higher eutectic cell count (Figs. 15(a), 15(b), 15(c)). In another experimental programme, (Figs. 16(a), 16(b), 16(c)), Zr-preconditioning also contributed to reduced chill (carbides) and to an increased eutectic cell count. Al has a vital role mainly in the first stage of graphite nucleation, forming very small oxide-based inclusions. Zr has a double role in this process: early Zr-oxide based micro-inclusions help (Mn,X)S compounds nucleation and improve the structure of these sulphides to enhance their ability to nucleate flake graphite with less undercooling.\(^42\)

![Graphite nuclei and graphite particle morphologies in Ti, Al or Zr preconditioned and Sr–FeSi inoculated grey cast iron.](Fig. 14)

![Chill (a), undercooled graphite amount (b) and eutectic cell count (c) of un – and - Al-preconditioned grey cast irons [UI-un-inoculated; Ca-inoculated irons].](Fig. 15)
Consequently, not only inoculation but also the pre-conditioning (Al or Zr) of the base iron could have a positive effect on the solidification pattern of cast irons. These elements were incorporated in a complex FeSi based alloy, very efficient for pre-conditioning grey irons for thin wall castings, at low addition rates.45)

An experimental programme, 24) exposed an iron melt with 3.9–4.0%CE (3.4–3.5 wt.%C, 1.5–1.7 wt.%Si, 0.7–0.8 wt.%Mn, 0.012–0.015 wt.%S, 0.002–0.005 wt.%Al, 0.0005 wt.%Zr) heated to and tapped at 1530°C, to different pre-conditioning and/or inoculation treatments. The pre-conditioning treatment was applied in the furnace, just before tap. A small 0.10 wt.% addition of a Al,Zr,Ca–FeSi complex alloy was used as a pre-conditioner.45) Similarly 0.2 wt.% of a commercial Ca,Ba,Al–FeSi inoculant 46) was added to the ladle during furnace tap. The base (reference) iron, pre-conditioned iron, inoculated iron and double treated (pre-conditioned + inoculated) iron were all monitored using conventional Quik-cup™ thermal analysis.

These experimental irons were also poured at 1350°C into wedges of the type W1, W2 and W3, in resin sand moulds as specified in the ASTM A367 standard test methods of chill testing cast iron. Standard W-wedge samples were designed to represent a large range of solidification conditions of foundry castings. In this experimental programme, W1, W2 and W3 samples were selected to represent thin to medium section castings, known to be critical for chill control in electric melted, hypoeutectic grey irons.

The elements Al and Zr can participate in the pre-conditioning treatment by using a Al,Zr,Ca–FeSi alloy. This treatment supports the formation of (Mn,X)S compounds as effective nucleation sites for graphite, and thermal analysis confirms this benefit: a lower \( \Delta T_m \) with higher \( \Delta T_1 \), which becomes slightly positive, as an undercooling expression for the beginning of the eutectic reaction, favourable for no carbides, with undercooling at the end of solidification, \( \Delta T_3 \), becoming less negative (less desirable for contraction defects and intercellular carbides) (Fig. 17(a)).24,30)

The greatest improvement was with a double treatment incorporating Al,Zr,Ca–FeSi alloy pre-conditioning followed by Ca,Ba,Al–FeSi inoculation. The effect of this combination was more powerful when compared to the results of single iron treatments of either inoculation, or especially pre-conditioning (Fig. 17(a)).

Thermal analysis of this complex grey iron treatment shows that despite higher superheat to 1530°C and relatively undesirable hypoeutectic iron chemistries, with low levels of S, Al and the \((\%\text{Mn}) \times (\%\text{S}) < 0.015\) factor, typical for electric melting, it is still possible to achieve good levels for the control factors: \( \Delta T_m < 25°C \), \( \Delta T_1 > 10°C \) and \( \Delta T_3 < –20°C \) (less negative). The development of the thermal analysis parameters in Quik-cup™ tests, from the base (reference) iron up to double treated iron, agrees with a favourable decrease in chill tendency in the experimental irons, depending on the different cooling modulii of the wedge samples (CM) (Fig. 17(b)), and eutectic undercooling expression \( \Delta T_m \) (Fig. 17(c)).24,30)

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. At higher cooling modulus, equivalent to a slower cooling rate, the iron’s chill tendency is less, with different iron chill values in Fig. 17(b) agreeing with their counterparts in the thermal analysis chart (Fig. 17(a)).

A case study (automotive foundry) illustrates the efficiency of Al and Zr bearing-FeSi pre-conditioning of electric melt grey irons inoculated with Sr–FeSi or Ca,Zr–FeSi.25,45) In the initial foundry process, the melting procedure in a 6.5 t medium frequency induction furnace used 50 wt.% Steel
of metallurgical treatments of molten iron. Cooling and recalescence are the most important objectives. Inoculation or supply of feed metal cannot compensate the ability of micro-shrinkage and porosity is high if the expansion due to freezing. Too high a recalescence might be harmful especially in green sand moulds, as the volume expansion is high especially if the eutectic point, carbides were a major problem, occurring in sections of 5 mm or less.

An addition of 0.1 wt% Al,Zr,Ca–FeSi alloy to the furnace before tap, in constant conditions for melting/ inoculation/pouring procedure decreased eutectic undercooling, the graphite structure was improved and the tensile strength increased (Fig. 18). Undercooling refers to the ΔTm parameter, while recalescence represents the difference between the highest (TER) and lowest (TEU) eutectic temperatures, and reflects the amounts of austenite and graphite that precipitate during the first part of eutectic freezing. Too high a recalescence might be harmful especially in green sand moulds, as the volume expansion is high and might increase the size of the mould cavity. The probability of micro-shrinkage and porosity is high if the expansion of graphite or supply of feed metal cannot compensate for the increased volume. Decreasing both eutectic undercooling and recalescence are the most important objectives of metallurgical treatments of molten iron.

5. Recommendations for Foundry Application

For foundry application, it is recommended to ensure (Mn,X)S compound formation, compatible for nucleating graphite with less eutectic undercooling: smaller/more compact/higher count particles with a suitable crystallographic fit with graphite. In this respect, three technological steps appear to be necessary to produce high performance grey iron, especially in electric melting (Table 1). These affect solidification with less eutectic undercooling and recalescence; graphite nucleation with less undercooling for promoting type A graphite and avoiding type D graphite; fewer carbides; higher eutectic cell count. All these factors are critical for thin wall grey iron castings to avoid carbides and/or type D graphite.

The first of these is superheating of the molten iron, depending on the charge characteristics and melting practice, to eliminate un-desired heredity influence of charge, to dissolve all charge materials and allow removal of suspended inclusions, slag, etc. This step is recommended especially for lower quality charge, including less known metallic or/ and non-metallic materials, possible suppliers of coarse residual graphite or micro-inclusions, etc. Very important is also sulphur correction, in order to obtain a beneficial Mn and S relationship in complex (Mn,X)S compounds formation, found as the major graphite nucleation sites in commercial grey cast irons. It is recommended to use (%Mn) × (%S) control factor, according to Table 1 data.

The second step is pre-conditioning the iron with oxide forming elements (Al and/or Zr), which will have been reduced to very low levels during induction melting, especially for low quality charges and/or poor melting practice, unsuitable inoculation and/or pouring practice. Both Al and Zr support type A graphite formation with less undercooling and fewer free carbides, with zirconium having the highest effect. In order to minimize the pinholing, especially in green sand moulds and to obtain an efficient graphitization process, an Al content of 0.005–0.010 wt.% in final iron (Fig. 19) the surface tension of molten iron is high enough while hydrogen pick-up from green sand mould is limited.

The third and final step is inoculation with Ca or Sr or Ca + Ba – FeSi inoculants, to control eutectic undercooling and recalescence during solidification, responding to the base iron quality and casting characteristics. According to the Table 1 recommendations, for a preferred range of Mn and S [controlled factor (%Mn) × (%S) = 0.03–0.06] and

Scrap, 50% Cast Iron Scrap, Graphite, FeSi, FeMn, FeS in the charge. The thermal regime required a 1500°C tap temperature and pouring within a 1400–1450°C temperature range. A single treatment employed 0.3 wt.% Sr–FeSi or Ca,Zr–FeSi inoculation during ladle filling. Typical chemical analysis: 3.36 wt.%C, 2.13 wt.%Si, 0.64 wt.%Mn, 0.094 wt.%S, (%Mn) × (%S) = 0.06, 0.042 wt.%P, 0.097 wt.%Cr, 0.13 wt.%Cu, 0.01 wt.%Ni, 0.011 wt.%Mo, 0.005 wt.%Sn. Despite a favourable iron composition and inoculation practice, carbides were a major problem, occurring in sections of 5 mm or less.

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| Table 1. Three Steps in Electric Iron Melt Processing. |
|---|---|
| No. | Step | Characteristics |
| 1 | Melting | *Minimum 1 500°C superheat/Induction furnace |
| | | *Scrap steel and Iron charge |
| | | *S correction for optimum (%Mn) × (%S) Factor [0.03–0.06] |
| | | - generally, in a 0.4–1.2 wt.%Mn/0.04–0.12 wt.%S range |
| 2 | Preconditioning | *Al, Zr, Ca–FeSi alloy |
| | | *0.1 wt.% addition before tap (usually) |
| | | *0.005–0.010 wt.%Al/Zr in final iron |
| 3 | Inoculation | *Different inoculation techniques |
| | | *Normal/lower addition rates |
| | | *Sr-FeSi/Ca-FeSi/Ca,Zr-FeSi/Ca,Ba-FeSi alloys |

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The performance of the induction furnace can be characterized as electric melt, in an acid-lined induction furnace of irons from the same base iron (grey/ductile/compacted) usually < 0.03 wt.% S. It also allowed production of a range of grey iron at sulphur levels less than 0.05 wt.% S, more common in world grey iron foundries. This resulted in increased worldwide production (more than 250 kW/ton), which revolutionized the medium frequency (200–1000 Hz) and high specific power generation of acid-lined, coreless induction furnaces with lower furnace acid lining and higher availability to balance the sulphur content.

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6. Summary

(1) Historically, grey irons were cupola melted, with at least 0.05 wt.% S and 0.005 wt.% Al, leading to favourable conditions for MnS-type compound formation, as the basis for nucleation sites for flake graphite. Usually, the challenge in a cupola shop was to avoid excessive sulphur levels. This could be addressed by using better quality coke and less coke per charge, or employing an external desulphurization step in the process, and then adjust the manganese content to balance the sulphur content.

(2) Smaller, inefficient cupolas were replaced by a new generation of acid-lined, coreless induction furnaces with medium frequency (200–1000 Hz) and high specific power supplies (more than 250 kW/ton), which revolutionized the iron foundries. This resulted in increased worldwide production of grey iron at sulphur levels less than 0.05 wt.% S, more usually < 0.03 wt.% S. It also allowed production of a range of irons from the same base iron (grey/ductile/compacted) from the same furnace.

(3) The actual base metal of grey iron moulds could be characterized as electric melt, in an acid-lined induction furnace from a steel scrap charge, usually recycled with amorphous carbon. The performance of the induction furnace has created a new opportunity to superheat above 1500°C, which is appropriate for thin wall casting production. With higher levels of superheat, the characteristics of the base iron are totally different to cupola melted iron, even if it could be tapped at 1500°C, resulting in deterioration in the final casting quality.

(4) Experiments showed that induction melting led to oxidation of most of the important elements (C, Si, Mn, Zr, Al, Cr); C, Al and Zr content continued to decrease up to 1600°C, while Si and in some cases also Mn and N showed a slight increase, especially above 1500°C. Holding iron at high temperatures (1530°C) aggravated the loss of C, Al and Zr. A slight gain in Mn, Cr and N could be observed during holding.

(5) Raising the iron temperature in an acid-lined, coreless furnace will cause important changes beyond the iron chemistry, affecting the liquid iron characteristics. Especially there is a transition from a colloidal liquid state after melting (mainly as graphite particles in suspension) to a quasi-ideal solution with no surviving graphite, and a lower quantity of de-activated micro-inclusions relative to their ability to act as heterogeneous nucleation of graphite.

(6) The high dissolution rate of residual graphite in superheated iron (favoured by low sulphur content) and difficulties in complex (Mn,X)S compounds formation as active nucleation sites of graphite, due to very low content of residual Al (< 0.003 wt.% ) and Zr (< 0.0003 wt.% ) to sustain MnS-type particles formation, especially at less than 0.03 wt.% S content (despite normal manganese level) resulting in higher eutectic undercooling solidification and consequently high chill and undercooled graphite morphologies sensitivity, inclusively in inoculated irons.

(7) Recycled granular carbon, which was previously used as conducting media, is a potential carbon raiser able to pre-condition or inoculate grey iron, especially if it originally had been petroleum coke. Graphitized resistor petroleum coke, with high carbon content and a controlled amount of SiC (up to 5 wt.%), not only is capable of high carbon recovery but also lowers chill tendency and prevents undercooled graphite (type D + E), in low sulphur cast irons.

(8) Worldwide foundry experience claims benefits for a metallurgical silicon carbide addition in electric furnaces, seen as reduced chill, improved machinability, improved and more uniform mechanical properties. Other related benefits are less casting scrap, particularly due to hard edges, shrinkage and gas porosity, all with higher furnace acid lining life. It was reported that preconditioning or inoculation, using metallurgical silicon carbide, could be improved by increasing free carbon in the chemical composition.

(9) A double treatment initially uses strong oxide forming elements, such as Al and/or Zr to replace levels depleted by electric melting. This preconditioning step is followed by inoculation with Ca, Ba, or Sr, in a FeSi alloy to decrease eutectic undercooling and recalescence, improve the graphite characteristics, and avoid carbides. For consistent inoculation results in grey irons ensure the control factor, (%Mn) × (%S) = 0.03 – 0.06, meets these ranges [0.4–1.2 wt.% Mn and 0.04–0.12 wt.% S], with 0.005–0.010 wt% Al and/or Zr.

(10) The concept in the present paper sustains a three-stage model for nucleating flake graphite [(Mn,X)S type nuclei]. There are three important groups of elements [strong deoxidizer/Mn, S/inoculating] and three technology stages in electric melt commercial grey iron [furnace superheat/pre-conditioning base iron/final inoculation treatment].

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