ABSTRACT
Traditionally, cast iron microstructures have been controlled by measuring and adjusting the chemistry of the liquid iron, the individual chemical elements being like the pieces of a jigsaw puzzle that the foundry can assemble to infer the microstructure. However, spectrographic analysis is not able to provide information about the activity of the individual elements, to measure critical elements such as oxygen, or to indicate the efficiency of the inoculant. Some pieces of the puzzle are always missing; the picture is incomplete. In contrast, thermal analysis ‘listens’ to the graphite as it precipitates and grows. Regardless of the underlying chemical factors, if a graphite particle grows as worm, it will show a worm’s heat. If it grows as a nodule, it will show a nodule’s heat. Thermal analysis allows the foundry to see how the graphite is growing – similar to a micro but faster, and with a larger sample size. While the spectrometer has for many years been the ultimate judge in the foundry, the present paper proposes an evolution toward control by microstructure rather than by chemistry. Indeed, for the determination of feedforward and feedback process control actions, it is proposed that chemistry should be regarded as subordinate to microstructure determination by thermal analysis.

Keywords: Thermal Analysis, Process Control, Compacted Graphite Iron, Ductile Iron

INTRODUCTION
As one of the largest consumers of castings, the automotive industry is undergoing a transformation. Governments around the world are implementing increasingly stringent fuel economy and emissions standards, with fuel economy in the US increasing from 27.5 mpg in 2010 to 54.5 mpg in 2025 and CO₂ emissions in Europe decreasing from 130 g/km (42 mpg) in 2010 to 95 g/km in 2020 (57 mpg). This legislation is motivating a wide range of new technologies including lightweight cast components and body panels, downsized gasoline and diesel engines, electric powertrains, improved aerodynamics and reduced rolling resistance.

The demand for more from less in the automotive industry places a parallel demand on the foundry industry. In order to enable design engineers to reduce safety factors and trim component weight, microstructures must be consistently controlled in a narrower range. And, in order to ensure cost effective production and global competitiveness, castings must be produced right-first-time, satisfying the property requirements with a minimum of alloying and feeding. One important element in achieving these goals is the continued transition from after-the-fact quality control toward online process control.

PROCESS STABILITY AND CONTROL STRATEGY
The need for process control is defined by the microstructure and property requirements of each casting. In the case of Compacted Graphite Iron (CGI), complex components such as cylinder blocks and heads require a narrow range of 0-20% nodularity, with no flake graphite, in order to provide the optimum combination of castability, strength, machinability and thermal conductivity. For ductile iron, safety critical components must be produced with more than 90% nodularity and a high graphite particle count, without resorting to excess alloying that can cause casting defects and cost inefficiencies. In both cases, the microstructure requirements must be maintained until the end of casting, even as the magnesium, inoculant and temperature fade.

Traditionally, the control of cast iron microstructures has been achieved through chemistry measurement. However, chemical analyses provided by a spectrometer only show the total amount of each element and do not provide any information about compounds that could serve as nuclei or the activity of the elements such as the dissolved magnesium, oxygen and sulphur that influence the growth behavior of the graphite. Therefore, chemistry results provide only limited information about the expected solidification of the iron.

The reliance on chemical analysis is also limited by the changing conditions in the production environment, as changes in the raw material mix and changes in melting and holding techniques influence the active oxygen and sulphur content of the iron. The net result is that the stable microstructure range for both CGI and ductile iron is a moving target. Ironically, ensuring that the chemistry is the same in every ladle will result in microstructure variation. The most effective strategy to reliably remain within the specified microstructure range is to measure the behavior of the iron in each ladle and to dynamically adjust the magnesium and inoculant additions according to the needs of the iron. Depending on the production...
conditions and process flow, this dynamic adjustment can be applied by feedforward or feedback control. Chemical analysis remains important for the control of the base iron chemistry, alloying, and tramp elements, but for microstructure control, chemistry should be regarded as subordinate to the measured solidification behavior.

The influence of the magnesium and inoculation on cast iron microstructures is illustrated in Figure 1, which also serves to introduce the term “Modification”. The graphite morphology in cast iron is determined by the combined influence of all nodularising elements, such as magnesium, rare earths, calcium, etc., and all subversive elements, such as oxygen, sulphur, titanium, etc. Therefore, the horizontal axis of the microstructure chessboard is referred to as “Modification” rather than simply as magnesium. In terms of thermal analysis, when the cooling curves respond to the growth of graphite, it is as a result of the influence of all variables rather than simply the magnesium, so the term “Modification” provides a more holistic representation of the graphite growth. The microstructure chessboard shows how the foundry can influence the graphite morphology and particle count by varying the Modification and Inoculation additions and therefore provides a quantitative basis for defining the control limits of the stable windows for CGI and ductile iron production.

In contrast to CGI, high quality ductile iron exists in the top-right corner of the chessboard and therefore affords some opportunity for the overtreatment of both Modification and Inoculation to buffer the risk against low nodularity, low nodule count, patchy graphite distribution and carbide formation. However, excess Modification and Inoculation also increases the risk of casting defects and burdens the foundry with unnecessary ferroalloy consumption and unnecessarily large feeders. Therefore, the objective of ductile iron production is to control the iron within a narrow and low Modification and Inoculation window that reduces alloy consumption, defect formation and porosity in order to ensure the consistency of the microstructure and the material properties, and to maximize the economic efficiency related to mould yield and machinability.

**THERMAL ANALYSIS**

The mantra of process control is: *you can’t control what you can’t measure*. Accordingly, process control must begin with an accurate measurement of the iron.

In order for a liquid to transform to a solid, it must release heat. The basis of thermal analysis is that this liberation of heat, illustrated in cooling curve shown in Figure 2, can be measured and correlated to the solid phases that are precipitating and growing. As the iron transforms from the liquid state to primary austenite, the liberated heat causes an arrest in the natural cooling of the iron. The temperature, at which this arrest occurs, shown at Point A in Figure 2, provides a direct measurement of the Carbon Equivalent. Therefore, the first information provided by thermal analysis of hypoeutectic irons is the Carbon Equivalent, which is important in determining the shrinkage behavior of the iron. The Carbon Equivalent also indicates the risk for graphite flotation and for exploded graphite in ductile iron.
Physically, the eutectic is simply defined as the temperature at which the austenite and the graphite grow simultaneously. Under equilibrium conditions, slow cooling provides enough time for the graphite to precipitate out of solution, and therefore, the graphite can precipitate at a higher temperature: reaction kinetics play no role. However, in series production, the carbon atoms require a driving force to squeeze them out of solution. This force is provided by temperature (undercooling) and aided by the addition of inoculant – as more inoculant is added and more nuclei are formed, less undercooling is needed to push the carbon out of solution.

With reference to Figure 2, as the Carbon Equivalent increases, the CE plateau (austenite plateau) at Point A moves downward. The decrease is approximately 1°C for each 0.01 increase in CE. At the same time, as the inoculation increases, the additional nuclei make it easier for graphite to precipitate, so the eutectic undercooling defined by Point B moves upward. The point at which the CE plateau (A) merges with the undercooling (B) is the eutectic, regardless of the CE value. Under production conditions, depending on the inoculation level of the iron and the cooling conditions of the thermal analysis sample (or casting), CE values of up to approximately 4.55 can be measured before the eutectic is reached. In the example of Figure 2, it can be seen that the CE is approximately 0.14 units below the eutectic. If eutectic solidification is targeted for this casting, the foundry can adjust the carbon and the inoculant to bridge the 0.14 gap. Again, as with the Modification and Inoculation window, it is seen that even the eutectic is a moving target and that chemical analysis cannot be relied upon to determine the proximity of the iron to the eutectic point. Thermal analysis is required to define the true eutectic point. Chemical analyses and phase diagrams should be regarded as subordinate to the measured solidification behavior.

Beyond the initial arrest in the cooling curve caused by the formation of primary austenite, the precipitation of carbon atoms to form graphite particles triggers a second change in the cooling curve. As carbon atoms are consumed from the liquid, the solidification temperature of the austenite increases. This constitutional undercooling effect influences the speed of the solidification of the austenite. The sequence of events is (i) the speed of the graphite growth determines the rate of consumption of carbon from the liquid, (ii) the rate of consumption of carbon from the liquid determines the speed of the austenite growth, (iii) the speed of the austenite growth determines the rate of heat released, and (iv) the released heat determines the shape of the cooling curve. Working backwards, the shape of the cooling curve can be used to determine the graphite morphology.

The amount of heat liberated by the deposition of each carbon atom is the same, regardless of whether the atom precipitates onto a flake, a ‘worm’, or a nodule. Further, the amount of heat liberated by the graphite, which only represents approximately 3% by weight and 10% by volume, is dwarfed by the dominance of the heat released by the austenite and the heat lost from the sample vessel to the atmosphere. But despite this, the graphite growth still dictates the shape of the cooling curves - not directly by releasing heat, but indirectly by consuming carbon from solution and controlling the austenite growth. The reason that the graphite is so influential is that the number of carbon atoms that are precipitating is so immense. Each 50 μm graphite nodule, as shown in Figure 3, consumes more than $10^{25}$ carbon atoms and, in a simple thermal analysis sand cup, more than $10^{25}$ carbon atoms will precipitate from solution in less than two minutes. Ultimately, it is the difference in the speed at which the flakes, worms and nodules grow that determines the rate of carbon consumption from the liquid, the speed of the austenite growth, and thus, the shape of the cooling curves.

**Figure 2:** In hypereutectic irons, the heat released by primary austenite results in a thermal plateau at Point A. Thereafter, the onset of the eutectic solidification of graphite and austenite defines the undercooling at Point B, and the graphite growth beyond.

The Carbon Equivalent result determined by thermal analysis is different from the CE value derived from chemical analysis (usually defined as C + ⅓(Si)) and from the definition of the eutectic CE value shown in the iron-carbon phase diagram. This difference is because both the chemical value and the phase diagram are defined under thermodynamic conditions, which means that the iron is under equilibrium, as could be achieved by the controlled slow cooling of a thermal analysis sample over many hours. However, under normal production conditions, the iron cools much faster than equilibrium. The CE result provided by thermal analysis therefore represents the actual physical or kinetic solidification that occurs in the casting.
Gray iron flakes grow in a eutectic cell, with many flakes branching from a single nucleation site. The flakes grow in direct contact with the liquid iron, with the carbon atoms precipitating on the A-face (Prism plane) of the basic graphite building block, in a coupled eutectic. The single nucleation event, combined with many points of direct contact with the liquid, results in fast growth that allows the flakes to precipitate and grow with little or no undercooling. In contrast, the precipitation of each graphite nodule in ductile iron requires a unique nucleation event, followed by initial growth through the precipitation of carbon atoms onto the C-face (Basal plane) of the basic graphite building block, in a divorced eutectic, and final growth by the diffusion of carbon atoms through a solid austenite shell. The individual nucleation results in more undercooling than gray iron while the low surface area to volume ratio and eventual diffusion-controlled growth through the austenite results in slower growth.

The growth mechanism of compacted graphite particles is intermediate between that of gray iron and ductile iron. Similar to gray iron flakes, compacted graphite particles grow in branched eutectic cells, from single nucleation sites, in direct contact with the liquid iron. The many branches and direct contact with the liquid provide a high surface area for the deposition on new carbon atoms, resulting in fast growth. The predominant deposition of carbon onto the A-face results in the characteristic elongated aspect of the compacted graphite particles while the concurrent deposition of carbon atoms onto the C-face results in the irregular bumpy surface of the particles. In contrast to ductile iron, where aggressive inoculation is preferred to maximize the nodule count, the inoculation of CGI is lower in order to suppress the tendency to form nodular graphite. The net result is that CGI generally shows more undercooling than ductile iron, followed by fast growth due to the high surface contact with the liquid iron, providing a steeper recalescence in the cooling curve.

As illustrated in Figure 4, the differences in the nucleation and growth of gray iron, ductile iron and CGI provide distinct differences in the thermal analysis cooling curves, and these differences can be used to determine solidification behavior and to decide upon control actions. Rather than measuring the chemistry to infer the graphite microstructure, the philosophy of process control by thermal analysis is to directly measure the solidification behavior of the iron, as determined by the graphite growth. Regardless of the underlying chemical factors, if the graphite particles grow as worms, the iron will show a worm’s heat. If the graphite particles grow as nodules, the iron will show a nodule’s heat. It only remains to ‘listen’ to the graphite.

The three primary output values from the thermal analysis are the Carbon Equivalent, the Modification index and the
Inoculation index. The Modification and Inoculation index values are determined from the evaluation of more than 100 different parameters extracted from the cooling curves, the derivatives and the heat evolution (power) curves. The Modification and Inoculation index values are used to define the size and location of the calibration window on the microstructure chessboard for each component during the calibration phase, and to quantify the location of each ladle during series production. Together with the CE result, the Modification and Inoculation values define the microstructure and the risk for casting defects such as porosity and carbides. The use of dimensionless indices simplifies the process for the operators and allows the foundry engineers to focus on production optimization rather than allocating resources to the fundamental task of interpretation of cooling curves.

MEASUREMENT TECHNIQUES AND DEVICES

Thermal analysis is a heat balance. The ultimate shape – and thus the resolution – of the cooling curve is determined by the balance between the heat liberated during solidification and the heat lost to the sampling vessel and the atmosphere. It is evident that the amount of heat liberated by the solidification of a 200 gram sample of cast iron is fixed. If the 200 gram sample is contained in a vessel that cools quickly, the heat liberated by the solidification will be less able to prevail over the heat loss than it would be in a vessel that cools more slowly. The result is that the faster cooling of the vessel will provide less resolution in the cooling curves. Fast cooling caused by the vessel can also alter the true solidification behavior of the iron by inducing chill or by influencing the undercooling. In order to extract as much information as possible from the heat liberated by the solidification, it is necessary to design the thermal analysis vessel such that it neither masks nor dilutes the information provided by the solidification. The other major requirement of a thermal analysis vessel is that it must ensure consistent sampling conditions. Because the differences in the liberated heat between a good microstructure and an out-of-spec microstructure can be very small, it is critical that all variations measured are due to differences in the iron and not due to differences in the sampling technique.

While conventional sand cups provide adequate resolution for the determination of the austenite arrest temperature, the geometry and cooling conditions of sand cups introduce some limitations on the ability to accurately determine the graphite microstructure. For example, the filling of sand cups is liable to variation in the fill volume and differences in the starting temperature of the iron. The pour-in filling technique also introduces a source of variation, as the exposure of the pouring stream to the atmosphere causes inconsistent amounts of oxidation and air entrainment during the filling of the cup. Once the cup is filled, the high heat capacity of the thick sand walls, shown in Figure 5 (a), causes the vessel to act as a heat sink, influencing the solidification behavior and effectively competing against the heat liberated by the solidification. The open surface of the sand cups also results in large radiation heat losses from the surface and imbalanced heat losses from the top, the exposed sides, and the thicker bottom, which is also influenced by the measurement stand. The net result is that the design of conventional sand cups can contribute to measurement variation and limit the resolution of the cooling curves.

(a) Conventional thermal analysis sand cup with open surface and variable wall thicknesses.

(b) Immersion sampling steel cup with regulated heat loss, showing the protective tube for the containment of the reusable thermocouples.

Figure 5: Immersion sampling and pre-heating of the vessel provide more consistent sampling conditions and higher resolution in the cooling curves.

In order to improve upon the thermal analysis sampling technique, SinterCast has developed the immersion sampling device shown in Figure 5 (b) for the thermal analysis of cast irons. The thermal analysis sample is obtained by immersing the Sampling Cup into the iron for approximately three seconds. This sampling technique minimizes oxidation and simultaneously pre-heats the
vessel to eliminate any influence on the natural solidification potential of the iron. The immersion filling also simplifies the sampling procedure, as the overflow provided by the upper annulus of the sample cup ensures consistent filling. In comparison to conventional sand cups, the Sampling Cup is fabricated entirely from stamped and drawn steel sheet and has a predominantly spheroidal containment area. The steel walls containing the molten iron provide a double-wall Dewar type insulation of the sample. The void space between the walls varies symmetrically along the height of the vessel to regulate heat loss, with the gap at the bottom being minimized to balance the heat loss from the surface of the iron. The upper portion of the Sampling Cup also provides a barrier to reduce radiation heat losses from the open surface. These design features promote a uniform spheroidal solidification behavior. Beyond the design of the Sampling Cup, six separate Go / No-Go checks are made on the cooling curves prior to the onset of solidification to ensure that the sampling conditions are consistent and not influenced by the start temperature. Together, the design of the thin-wall Sampling Cup and the immersion sampling technique ensure a constant sample volume, prevent oxidation of the iron during pour-in filling, provide a uniform solidification profile and yield a more accurate measurement of undercooling because of the elimination of chill-induced solidification.

Two different cooling curves are obtained from two thermocouples contained within the protective tube in the Sampling Cup. The thermocouples are mounted in the sampling hardware and are reused up to 250 times as the consumable Sampling Cups are positioned, used, and dispensed. One of the thermocouples is located in the thermal center of the Sampling Cup while the second is located at the bottom of the protective tube, thus providing two different measurement conditions.

The walls of the Sampling Cup are coated with a reactive coating that consumes active magnesium in order to simulate the fading of magnesium in the ladle. This patented Mg-fade simulation allows for the simultaneous measurement of the solidification behavior at the start of casting (through the center thermocouple) and also after a predetermined loss of magnesium (through the bottom thermocouple). Strategically, the strength of the reactive coating is chosen for either CGI or ductile iron analyses to provide the desired difference between the cooling curves of the center and bottom thermocouples. In addition to the inherent differences in the cooling curves of gray iron, CGI and ductile iron, as shown in Figure 4, this patented wall reaction provides additional insight into the solidification behavior of the iron to quantitatively determine the coordinates on the microstructure chessboard and to decide upon control actions that ensure that the iron remains within the specification window from the start until the end of casting.

**PROCESS CONTROL**

Thermal analysis provides the ability for the foundry to see inside the iron and, with the additional insight, to decide upon control actions. Depending on the process flow, the control action can either be a feedforward addition of magnesium and/or inoculant prior to casting, a feedback adjustment of magnesium and/or inoculant in subsequent the base treatments, feedback control of furnace CE, or a combination of these actions.

Production experience with Compacted Graphite Iron has shown that the stable window for simultaneously avoiding flake graphite and shrinkage defects in complex castings such as cylinder blocks and heads is too small to reliably reach the start-cast coordinates directly with the base treatment. Even with advanced knowledge of the parameters that determine the base treatment result, such as historical recovery, sulphur, ladle weight and temperature, variation in the base treatment is too large to always remain within the narrow control range. Figure 6 shows actual series production data for the variation of base treatment Modification (‘MGM’) results during the production of heavy-duty CGI cylinder blocks from 281 ladles. The base treatment was conducted by the addition of cored wire into a 2,300 kg ladle based on statistically optimized algorithms including input from (i) MGM results from previous ladles; (ii) sulphur content of the base iron; (iii) ladle weight; and, (iv) ladle temperature. The calibrated Modification limits required to achieve the specified microstructure, properties and soundness in the heavy-duty blocks range from 38 to 46, but the results in Figure 6 (a) show that the actual base treatment result varies from 26 to 44 – more than two times wider than the permissible casting range. The actual Modification range after the corrective addition of magnesium cored wire is shown in Figure 6 (b), with all of the 281 production ladles falling within the specification range. The average corrective magnesium addition for this series of 281 ladles was approximately 30 grams per tonne, showing that the final correction step is a precise addition that manipulates the third and fourth decimal points in order to deliver consistency to the moulding line.

For the reliable high volume production of CGI, the control strategy must be to intentionally undertreat the iron during base treatment to the extent that, even if all variables combine to produce the maximum recovery, the iron will still not be overtreated. This strategy provides the opportunity to make bespoke additions of Mg and inoculant wire to adjust each ladle prior to casting. In contrast, if the target for the base treatment result shown
in Figure 6 (a) was shifted upward in an attempt to target the center of the MGM casting range of 38 to 46, many of the ladles would be overtreated, resulting in the formation of shrinkage defects, ultimately causing leakage scrap after machining. The only recourse to avoid such scrap would be to resort to excessive feeding, but the cost of such feeding is generally more than the cost of the process control, especially when exothermic feeders are required. It must also be considered that not all areas of complex castings can be reached by feeders, so that not all defects can be eliminated. But beyond these considerations, shifting the base treatment target to the center of the MGM casting range is not sufficient, because this would also result in some ladles being undertreated, causing flake graphite. In order to avoid flake graphite, the base treatment target would need to be increased to the point where no ladles fell below the minimum MGM limit. In turn, this would necessitate more feeding, further increasing the cost and increasing the risk for more scrap.

As shown in Figure 7, the CE, Modification and Inoculation results are also provided to serve as the basis for on-line process control. These results are displayed as running bar charts with the current analysis on the far right, and the previous results trailing to the left. The absolute CE value is displayed in the upper run chart while additional CE information indicating the proximity of the CE result to the true eutectic is reported in the “Δ-Eutectic” field provided in the final result window at the bottom of the display. With reference to the previous explanation of the eutectic in Figure 2, the Δ-Eutectic value shows the degree of separation between the austenite arrest (Point A) and the minimum undercooling (Point B). In the example of Figure 7, the Δ-Eutectic result shows that the CE is 0.18 units below the eutectic, allowing the foundry to make carbon, silicon and/or inoculant additions to adjust the iron toward the eutectic composition to optimise the castability. Likewise, the Modification and Inoculation results are provided as simple index values corresponding to the pre-calibrated target window for each product on the microstructure chessboard. These index values provide the basis for automatic or manual feedforward control of the in-stream inoculation and/or feedback control of subsequent base treatments to iteratively adjust the iron into the target window.

In a ductile iron pilot application that has been running for more than a year, the process has evolved such that the foundry obtains a thermal analysis sample from the first ladle of each furnace campaign and from every other ladle thereafter, until the end of the 16 ladle campaign. The CE
results have been adopted to trim the carbon content in the furnace throughout the campaign, while the Modification and Inoculation results are used for dynamic feedback control of the tundish cover base treatment process. The optimization of the base treatment has resulted in a 7.5% reduction in the FeSiMg alloy consumption and, although the average inoculant addition has not changed, the dynamic control has resulted in more consistency in the graphite distribution and the particle count. The foundry is also contemplating the acquisition of an in-stream inoculant dispenser to allow for the dynamic feedforward control of the in-stream addition based on the Inoculant index results. In addition to the improved microstructure consistency, the external machining company has stated that the tool life has improved as a result of the process control.

The potential to reduce the magnesium and inoculant consumption provides a direct and obvious cost reduction, but the most significant opportunity for cost reduction is the ability to reduce scrap levels and feeding. Incremental magnesium and inoculant additions beyond the minimum amount needed to satisfy the microstructure specification increase the risk of scrap and the shrinkage sensitivity of the iron. For each component, the foundry must determine the safety margin in the size of the feeders to compensate for the worst case condition, which occurs when the variation in the process results in the highest Modification. Process control provides the opportunity both to reduce the variation and to shift the location of the target window toward lower levels, thus providing a double-opportunity for reducing the worst case condition.

Depending on the sales price of the casting and the mould yield, every 1% reduction in scrap or improvement in mould yield can provide a cost benefit of $10–20 per tonne of castings. Accordingly, the application of additional process control for ductile iron production should be approached as a cost-benefit opportunity rather than as an absolute cost.

CONCLUSION

The global foundry industry continues to become more polarized. Commodity components are under pressure to be made less expensively while high tech components are under pressure to be made with better and more consistent properties. The challenge for the high tech foundry industry is that the stable microstructure ranges for engineered castings such as Compacted Graphite Iron and ductile iron are moving targets. Despite all efforts and discipline, experience has shown that process consistency can’t be ensured by reproducing the same chemistry in every ladle. This realization leads to the concept of dynamic process control; to measure the solidification behavior of the ladle and to adjust the iron prior to casting. As the starting point for process control, thermal analysis provides the opportunity for the foundry engineers to see into the iron and to understand the true solidification behavior. With this insight, bespoke feedforward and/or feedback control actions can be determined and implemented before the castings are poured to improve consistency and cost efficiency.