INOCULATION OF GREY AND DUCTILE IRON

S.O. OLSEN and T. SKALAND

Elkem, Norway

ABSTRACT

The objective of the present paper is to review some major aspects related to cast iron inoculation. The paper describes important conditions In the production of cast iron which call for the addition of an inoculant to ensure the reliable production of sound, strong, and machinable castings. The principal differences between inoculated and un-inoculated cast irons are described, and these differences are exemplified by characteristic microstructures and mechanical properties. Also, some practical considerations related to various methods of inoculant addition to liquid iron is explained.

The fundamental mechanisms of inoculation and graphite nucleation in cast iron during solidification are described. The important connection between minor alloying and trace elements such as Calcium, Barium, Strontium, Sulphur and Oxygen are explained, and in this connection, evidence for graphite nucleation from complex heterogeneous silicate particles is shown. Examples of ferrosilicon based inoculants for highly efficient inoculation of both grey and ductile irons are shown. and the decisive effects of minor alloying elements added through such alloys explained.

Finally, the principal mechanisms and effects of the well-known phenomena of inoculant fading are explained, and also the important interaction in ductile iron between magnesium treatment and fading of inoculation.

1. INTRODUCTION

For the production of high-quality cast iron an inoculation treatment is of decisive importance. The basic function of inoculation is to increase nucleation, thereby promoting growth of the graphite eutectic and reducing undercooling and minimizing the risk of forming hard eutectic carbides in the structure. The aspects of inoculation have been the object of numerous publications for decades, which above all dealt with the inoculation of cast iron with flake graphite, but less so with the inoculation of cast iron with nodular graphite. Though the characteristics of an effective inoculation naturally show up in both materials in the same way, such as a reduction in undercooling and an increase in the number of nuclei, inoculation may influence both types of cast iron in different ways.

2. WHAT IS INOCULATION OF CAST IRON?

Inoculation is a means of controlling the structure and properties of cast iron by minimizing undercooling and increasing the number of nucleation events during solidification. An inoculant is a material added to the liquid iron just prior to casting that will provide a suitable phase for nucleation of graphite during the subsequent solidification. Traditionally, inoculants have been based on graphite, ferrosilicon or calcium silicide. The most popular inoculant today is ferrosilicon containing small quantities of elements such as Al, Ba, Ca- Sr and Zr

The purpose of inoculation is to aid in providing enough nucleation sites for the carbon to precipitate as graphite rather than iron carbide (cernentite). This means to prevent undercooling to temperatures below the metastable eutectic where carbidic structures are formed. The iron solidification mechanism is prone to form chilled iron structures when inoculation is inadequate, and there are several reasons why chilled structures are undesirable. Chilled structures interfere with machining, necessitate additional heat treatment operations, results in non-conformance with specifications and, in general, increase the total cost of production. Figure 1 shows an example of an un-inoculated casting versus an inoculated casting, while Figure 2 gives a listing of the most important effects of inoculation in cast iron.

3. INOCULATION OF GREY IRON

Most hypo-eutectic grey cast irons, particularly those of high duty applications, are inoculated. The effect of inoculation is to increase the number of eutectic cells growing during eutectic solidification. A finer cell structure result and the iron have better mechanical properties without any significant increase in hardness. A high number of eutectic cells also favour the formation of the graphite/austenite eutectic rather than the carbide/austenite eutectic which occurs with considerable undercooling. In practice this means the avoidance of chill in thin sections.

Inoculation changes the structure of cast iron by altering the solidification process. A look at the solidification of hypoeutectic grey iron - that is, iron with a carbon equivalent below 4.3% - helps in understanding the effects of inoculation.

The first metal to solidify in hypoeutectic grey iron is primary austenite. As cooling continues, the remaining iron grows richer in dissolved carbon. Eventually, this liquid reaches the eutectic composition of 4.3% carbon equivalent, at which final or eutectic solidification starts under equilibrium conditions. Equilibrium solidification, however, does not occur under most foundry conditions. Because of variations in chemistry, pouring temperature, solidification rate, section thickness, and other conditions, the metal will cool below the eutectic temperature before the start of final solidification. If the undercooling is slight, random graphite flakes form uniformly in the iron matrix. This is known as Type A graphite. As the undercooling increases, the graphite will branch, forming abnormal patterns. This is known as Type B graphite. A further increase in undercooling will suppress the formation of graphite and result in a hard iron carbide structure.

The role of inoculation is to produce nuclei in the liquid iron which enhance the graphite nucleation at very small undercoolings. This will, in turn, promote the formation of Type A graphite structure in grey cast irons and a high number of small graphite nodules in ductile cast irons.

The recognized method of increasing the number of cells growing is to treat the liquid iron as late as possible before casting. This is usually carried out by making additions of ferrosilicon, calcium silicide or graphite to the ladles of metal. By inoculation it is possible to produce a grey iron from one which would otherwise have been white due to a low carbon equivalent value. In flake graphite irons the high strength arising from the low carbon equivalent may be combined with the relative softness and machinability associated with grey irons. Of the inoculants mentioned above, ferrosilicon containing 72-78% Silicon is the most widely used and it has been shown that the inoculating power of commercial ferrosilicon is strongly affected by its content of minor elements.

The sulphur content of flake irons is usually limited to 0.15%. Manganese added as ferromanganese, silicomanganese, Mn-metal, etc. can be used to control the effect of sulphur in grey irons. Without manganese, sulphur forms FeS late in the solidification sequence and this can restrict graphite cell growth which leads to increased undercooling and even white iron formation. Manganese added to balance sulphur according to the relationship:

$$\%Mn = \%S \times 1.7 + 0.3\%$$

causes the sulphur to partition between Fe and Mn. This forms inclusions predominantly of MnS early in the solidification sequence. This means they are distributed uniformly through the structure and can act as nuclei for eutectic graphite. If the sulphur content is less than 0.03%, although balanced with Mn, the number of MnS inclusions is too small to produce effective nucleation. Unless late inoculation is used, type D graphite may form. There is an upper limit to which Mn may be used to control S because at high S levels it is not combined completely with Mn which leads to type D graphite formation and, with low pouring temperatures, sub surface blowhole defects associated with manganese iron silicate slags may occur.

Figure 3 illustrates the importance of Mn : S ratio on the cell count and chilling tendency in un-inoculated iron. These results show that the iron structure changes from high chilling propensity, low cell count and type D graphite at low S levels to low chilling propensity, medium cell count and Type A graphite at moderate S levels and high chilling tendency, high cell count and Type D graphite at very high S levels. These structural features arise as a result of a dual action of S. It provides nucleation sites and, when present in excess, it restricts eutectic cell growth. Many foundries melting electrically find it necessary to add FeS in order to increase the S level to 0.05% to achieve effective inoculation.

The most popular inoculant for grey iron in ferrosilicon. Pure Si and pure FeSi alloys are not effective as inoculants in cast iron. Effective inoculation depends on the presence of minor elements such as Calcium, Barium or Strontium. Figure 4 gives a listing of the most important factors that causes chill in grey irons.

Graphite flakes may occur in many variants and patterns of distribution depending on the metal composition, nucleation, and cooling rate of the iron. Specific terms have been given to these forms and patterns of graphite. The micrographs in Figure 5 show some typical structures in grey irons using an optical microscope The random flake structure (type A) is a uniform distribution of flakes, promoted by good conditions for inoculation. This is normally the desired graphite structure in most commercial grey irons.

The rosette flake structure (type B) Is characterized by a pronounced radial growth pattern, with the individual cell structures readily apparent. Ferrite is often present in the centre of the cells. Type B graphite is encouraged by rapid solidification, as in thin sections, and absence of inoculation of the metal The type C graphite (Kish graphite) is normally found in hypereutectic irons, characterized by coarse plates in heavy sections and star shapes or clusters in light sections.

The undercooled graphite structure (type D) is characterized by a fine graphite pattern sharply delineating the primary dendrites. Type D graphite is promoted by rapid solidification in thin sections, absence of inoculation, low sulphur content, high superheating temperatures, prolonged holding times and high titanium content.

For optimum inoculation effectiveness in medium to high sulphur grey irons it is recommended to use a Strontium bearing inoculant. Strontium reduces chill without the large increase in cell number common to other inoculants. In thin sections, minimum chill is most likely obtained with a Sr-bearing inoculant, The advantage of producing lower eutectic cell numbers than other inoculants for the same level of chill suppression makes unsoundness less likely. Maximum performance is achieved in cupola iron with natural high sulphur or in resulphurized electric melted iron.

4. INOCULATION OF DUCTILE IRON

The addition of magnesium and cerium to cast iron to produce nodular graphite structures have a strong carbide promoting effect. Inoculation is required to offset this effect, even when the carbon and silicon contents of ductile iron are high. Also, inoculation increased to number of graphite nodules in ductile iron. Inoculants for ductile iron are based on silicon-rich alloys. since graphite is not an effective inoculant for these irons under normal condition. Ferrosilicon and many of the proprietary silicon-based inoculants that are effective in grey irons are also effective in ductile irons, and the presence of such minor elements as aluminium, calcium, barium and strontium are just as important in promoting their inoculating effects. Ferrosilicon containing strontium is not generally recommended for inoculating irons containing both cerium and magnesium, but it is very effective in irons containing only magnesium.

Inoculation of ductile irons will reduce the tendency to chill and mottle, so promoting ductility and reducing the danger of cracking during knock-out or fettling and the need for heat treatment to remove carbides, Also, inoculation increases the number of graphite nodules formed, with general improvements in properties, and encourages the formation of fully spheroidal graphite nodules, giving maximum strength and ductility.

It is often very difficult to measure the:, chill depth at the fracture of a ductile chill test piece owing to the similarity in the appearance of the chilled and un-chilled zones. However, efficient inoculation produces a comparatively large number of graphite nodules in the structure. Samples for comparison of the number of nodules must be from similar section in similar castings. The cast section thickness must be constant and the pouring temperature standardized. Nodule counts should be made by lightly etched, polished specimens using a projection microscope with a square grid to facilitate counting. For each specimen at least three areas must be counted. Also, modern automatic image analysis (AIA) techniques have proven very efficient in measuring nodule count in ductile irons.

Figure 6 shows some examples of good and bad inoculated ductile irons. To the left side are examples of thin and thick sections of carbide free, well-inoculated castings. The middle micrographs shows intercellular carbides resulting from either poor inoculation, rapid cooling or segregation of highly chilled ductile irons where the major part of the structure is carbides (cementite).

The nodularizing treatment of ductile iron is a desulphurizing and deoxidizing process. Nevertheless, it is not necessarily desirable to remove the sulphides and oxides from the liquid iron to the top slag. To obtain effective nucleation during the subsequent inoculation it is advantageous to inhibit the reaction products from agglomerating and floating, and rather promote a tine dispersion of micro-particles in the iron. Such micro-particles will act as potential sites for heterogeneous graphite nucleation during solidification. Hence, an effective nodularizing process, which also gives a good basis for inoculation, is characterized by low S and O values, i.e. the difference between analytical levels of S and 0 t before and after treatment should preferentially below.

A violent treatment process (e.g. converter or cored wire treatment) tent togive magnesium oxide reaction products from the deoxidizing reaction. MgO-particles have a strong tendency to agglomerate forming larger slag clusters that float readily, hence giving effective deoxidation with large quantities of top-slag. A major disadvantage is that, due to sulphide and oxide agglomeration and flotation, a significant part of the potential nuclei particies will also be removed from the iron. This may cause problems avoiding carbides in thin section castings even after adding an effective inoculant material.

Treatment processes applying magnesium-ferrosilicon alloys give less violent reactions and hence less effective removal of potential nuclei from the melt. Also, due to interfacial energy phenomena, magnesium silicates tend to form smaller particles than magnesium oxide. This means that a larger fraction of oxides remains as a fine particle dispersion in the iron after treatment (i.e. magnesium sulphides and silicades). These particles are very small and highly numerous. Normal number densities lie in the area of some 100 thousands per cube milimetre with an average size is about 0.5 to 1 micron in diameter. Such small particles will float very slowly according to Stokes 'law, and hence they will remain in the liquid during handling and pouring. Figure 7 represents schematic segments of Iiquid iron treated with Mg-metal and Mg-FeSi, respectively. As will be described later, particles formed during nodularizing treatment makes an important basis for the effectiveness of the subsequent inoculation.

The chilling tendency may be increase or decreased by adjusting the graphitization potential of the iron. This is achieved by alloying, which influences the two eutectic temperatures. This influence is concentration dependent as shown in Figure 8 The behaviour indicated in the figure is for the normal solute concentrations used in cast irons. Graphitizing elements increase and decrease the graphite eutectic temperature, and carbide eutectic temperature respectively. Carbide stabilizers decrease the graphite eutectic temperature and increase the carbide eutectic temperature . Some elements (Mo, Mn) move the eutectic temperatures in the same direction and should have little effect on chilling tendency.

Alternatively, segregation that accompanies solidification, particularly in heavy section castings, can promote intercellular carbide formation. Carbide stabilizing elements segregate to cell boundaries, whereas graphitizing elements segregate away from these areas. Consequently, there is considerable change in the two eutectic temperatures in the intercellular regions due to segregation effects. It is important to realize that carbide formation occurs, for different reasons and remadies are different. Raising the level of graphitizers in the iron is effective in reducing chill. However, it is not necessarily the best method of avoiding intercellular carbides because graphitizers segregate away from the cell boundaries. A more effective solution is to reduce the level of carbide stabilizers particularly those that segregate strongly. In addition, it is advisable to reduce the degree of segregation by increasing solidification and to shorten diffusion distances by reducing graphite interparticle distances. This can best be done by high efficiency inoculation of the iron.

5. METHODS OF CAST IRON INOCULATION

Inoculation is an essential process in the production of many higher strength grey irons and almost all ductile irons. Control of the inoculation practice is very important, and the correct technique must be used to obtain satisfactory and consistent results. Inoculants must be well mixed with the molten iron to obtain uniform and complete solution. Good mixing can be obtained by ether adding to the tapping stream from the furnace or when transferring from ladle to ladle. The practice of placing the inoculant in the of the ladle before starting to fill is not recommended. If long holding times after inoculation cannot be avoided inoculation may be topped up with an extra, smail addition. Alternatively, some form of the late inoculation may be considered.

In all cases the surface of the metal to be inoculated should be clean and free from slag. The temperature should be sufficiently high to enable the inoculant to dissolve and disperse uniformly and rapid. The amount of inoculant required must be carefully measured by volume or by weight.

Inoculation methods after the metal has left the ladle and enters the mould or within the mould itself, is referred to as late inoculation. Late inoculation, correctly applied, gives the maximum effect obtainable from an hence much lower chilling tendencies than by ladle inoculation alone. Late inoculation dhould be used when it is impossible to achieve and maintain adequate inoculation in the ladle. Late inoculation requires separate, extensive trials to establish a suitable process for each casting and, when established, the process must be strictly fallowed to avoid difficulties. Late inoculation is a specialized process, and each application must be considered on its merits. Since each casting is individually treated, rigorous trials must be carried out and the process is introduced. Late inoculation may be used in addition to ladle inoculation in order to obtain an extra effect, but preliminary trials must first be made to ensure that it will be successful.

Figure 9 shows examples of different ways of adding inoculants. The alloys can be added either to the transfer ladle, the pouring ladle, the metal stream during mould filling or inside to mould. For ladle additions between 0.3 and 1 wt% of inoculant of a sizing between 0.5 to 15 mm is to be added depending on the procedure, holding times, etc. For stream additions, between 0.05 to 0.2 wt% is normally added of a sizing between 0.2 to 1 mm (normally 0.2-0.7 mm). In the mould additions can be either as granular inoculant (0.5-5 mm) or as solid briquettes or inserts of inoculant.

6. GRAPHITE NUCLEATION MECHANISMS

In inoculation technology the road between trial and error approach to a well-founded theoretical one is still incompletely mapped and obscure. The complexity of the thermodynamics, kinetics and interfacial phenomena involved prevents a single, comprehensive theory to be formed from which a workable alloy recipe can be deducted. Nevertheless, since cast iron microstructure control is the present key issue where suitable additions of oxide and sulphide forming elements to the melt are involved, heterogeneous nucleation appears as an essential theoretical feature.

Whereas nodularizing, for instance through a magnesium treatment, is required for graphite spheroidization, inoculation is a way of controlling microstructure by minimizing undercooling and increasing the number of graphite nodules during cast iron solidification. Added to the liquid iron just prior to casting the inoculant provides a suitable phase for the graphite nodule nucleation upon cooling. The most prominent inoculants presently used are ferrosilicon alloys containing small quantities of elements, such as Ca, Al, Ba, or Sr. The micro-inclusions formed are complex and of a heterogeneous chemical nature. After nodularizing, magnesium containing sulphides and silicates can form, and the cominating constituent phases are MgS, $MgO.SiO_2$ (enstatite) and $2MgO. SiO_2$ (forsterite)

After inoculation with Ca, Ba or Sr-containing ferrosilicon, hexagonal silicate phases of the $XO\text{-}Al_2O_3\text{-}2SiO_2$ or the $XO.SIO_2$ type form at the surface of inclusions from nodularization. The presence of phases of this nature will enhance the nucleating potency of the inclusions with respect to graphite. It is important to note that inoculation of ductile iron does not provide formation of new nuclei particles in the iron, but rather modify the surface of existing micro-products from the nodularizing treatment. High purity ferrosilicon dces not show an inoculating effect. This highlights the fundamental importance of the minor elements contained in the alloy, and in search for more efficient inoculants the recognition of theory as a guiding principle should be duly observed.

7. FADING OF INOCULATION

7.1 Principal Effects of Fading

The effects of inoculation are at a maximum immediately after the inoculant. The rate of inoculant fading which depends upon the composition of the inoculant and of the iron to which it is added, may be lost in the first few minutes after the addition. The principal effects of fading are:

- to cause greater undercooling to take place during eutectic soldification and to lead to a great tendency to chilling in grey and ductile irons, particularly in thin sections;
- to reduce the number of eutectic cells growing in flake graphite irons resulting in a less uniform size distribution of graphite in the casting and a reduction in mechanical properties;
- to reduce the number of nodules formed in ductile iron and to cause a deterioration in their shape. If sufficiently severe, the deterioration in shape may affect the mechanical properties of the castings.

There are some well-established facts conceming fading which are of practical significance:

- all inoculants will fade during time;
- there is no period after inoculation during which fading does not occur. To obtain the maximum effect, metal should be cast as soon as possible after the addition of inoculant;
- some inoculants fade more slowly than others;
- inoculating effects vary according to inoculant composition. It is desirable that foundries should carry out tests to determine which is the most suitable inoculant for their specific purpose.

7.2 Coarsening of Inclusions

It is a well-known fact that graphite nucleation occurs from non-metallic inclusions in the melt. A significant coarsening of these inclusions occurs within the time interval between inoculation and solidification of the cast iron. This coarsening of inclusions will result in a reduction in the inclusion number density, consequently reducing the graphite nucleation frequency. Hence, the fading of inoculaation can be explained by this coarsening of the inclusion population with time. Due to coarsening, the total number of possible nucleation sites for graphite during solidification is reduced.

7.3 Effects of Various lnoculants

Inoculants lose their ability to reduce chill and nucleate graphite if the metal is held for extended periods before casting. However, inoculants have different fading characteristics. Barium-containing inoculants produces a high initial number of nucleation sites. Compared to other inoculants, it maintains a high nucleation rate throughout the holding period, thus making it excellent inoculants for ladle treatments. Ba-containing inoculants are effective chill reducers for both low and high sulphur grey irons as well as ductile irons. Other effective inoculants that maintain the inoculation effect are the Strontium-containing types. Figure 10 lists some causes and facts about fading and shows typical fading characteristics for different inoculants in grey and ductile iron.

8. FERROSILICON BASED INOCULANTS

Figure 11 shows an overview of Elkem ’s present commercial inoculant portfolio. One or more of the important elements Calcium Barium and Strontium are found in small and accurate contens in alloys.

Also some inoculants contain either Zirconium or Rare Earth’s (Cerium) to improve performance. The chemical composition and reliability of the analysis from lot to are important if a ferroalloy is to be considered as a good and consisdent inoculant. Many foundrymen insist on silicon and phosporus analyses in pig iron, but pay little attention to the analyses in pig iron, but pay little attention to the analysis of an inoculant. The preceding paragraphs indicate guite cleary that the minor constituents in ferro alloys, not the major constituents (usually silicon) are critical for the performance as inoculants. All the Elkem inoculants are alloys that have been smelted and alloyed to the quoted specifications, and to further additions have to mechanically blended with the alloy. The analysis guaranted by the specification ensures consistent inoculant properties from lot to lot. The inoculants listed in the Table differ by analysis, price and application, but a satisfactory result may be obtained using any of the range. Elkem's foundry experts can give detailed information an each inoculant and its individual features, and also suggestions to the most suitable alloy for a specific foundry condition.

Foundrisil and Barinoc inoculants contain the levels of calcium and barium that has been found to maximize chill reduction while forming minimum amounts of slag. As a result Foundrisil and Barinoc are more powerful than straight calcium inoculants and just as effective as inoculants containing larger amounts of these two elements. The combined effect of calcium and barium also gives better chill control than calcium by itself. Foundrisil and Barinoc are efficient chill reducers for both low and high sulphur grey irons as well as ductile irons. In low sulphur irons Foundrisil exceeds the performance of most other commercial inoculants as can be seen from Figure 12. Foundrisil and Barinoc produce a high initial cell number which during holding is maintained at a higher level than other calcium silicide and ferrosilicon inoculants. The limited amounts of calcium, barium and other reactive elements minimize dross formation.

Inoculants lose their ability to reduce chill if the metal is held for extended periods before casting before casting. However, inoculants have different fading characteristics. Foundrisil and Barinoc produce a high initial number of nucleation sites. Compared to other inoculants, they maintain a high number of nucleation sites throughout the holding period. This makes Foundrisil and Barinoc excellent inoculants for ladle additions.

Under certain foundry conditions, Barinoc may give better inoculation effect than Foundrisil, especially during extended holding periods. The higher barium content may help nucleation in heavy section casting, although higher barium also increases the risk of slag and dross formation. Hence under normal conditions of medium section sizes and holding times less than 15 minutes, Foundrisil is recommended as the cleanest and best performing inoculant.

Superseed and Superseed Extra reduce chill without the large increase in cell number common to other inoculants. In thin sections minimum chill is most likely obtained with Superseed. The advantage of producing lower eutectic cell numbers than other inoculants for the same level of chill suppression make unsoundness less likely. In ductile iron Superseed gives a high nodule count, which may be used to an advantage in inoculation of ductile iron not treated with cerium-bearing magnesium ferrosilicon.

Inoculants minimize the undercooling during solidification of grey by increasing the number of nuclei available for growth of the graphite eutectic. Although most inoculants used in grey iron increas the number of eutectic cells in proportion to their effectiveness in reducing chill, Superseed and Superseed Extra are exceptions in this respect. Powerful chill reduction is combined with unqiue low cell refining properties compared to other inoculants, as can be seen from Figure 13. The reduced tendency of shrinkage defects is another of the advantages of Superseed. Superseed Extra may be an even more powerful choice, especially in irons containing nitrogen, since the zirconium content will combine with nitrogen forming zirconium nitrides. Such nitrides may act as additional nuclei giving even more refining of the graphite structure.

Zircinoc is an intermediate performance inoculant capable of reducing chill in areas of the casting which cool more rapidly. The application of Zircinoc will refine the graphite shape in thin or heavier sections. Electric melted irons lower in sulphur will respond more to the inoculation by zircinoc than to other simple or higher performance inoculants. Zircinoc is suitable for additional modest control of soluble nitrogen in iron and for ladle pouring conditions where oxidation cannot be avoided. Zircinoc can also be used in ductile irons to promote higher nodule counts and reduce chill, but high additions greater than 0.6 wt% are not recommended due to the interference of Zr with the nodularizing effect of magnesium. Figure 14 shows some of the major characteristics of Zircinoc in cast iron.

Rare Earth bearing inoculants as Reseed is effective in combating the carbide promoting tendencies of residual elements such as chromium. The presence of rare earth's in inoculants increases nodule counts, decreases chilling tendency, and fading rate in ductile irons. However, excessive additions promote carbide formation. Figure 14 shows some of the major characteristic of Reseed in cast iron.

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