What is an inoculant and what does it do?

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ABSTRACT

Inoculation of cast iron is a critical processing step that can determine if a casting passes quality inspection or not. This process is more critical in the production of ductile iron than in grey iron.

As a concept, inoculation has been around since the 1930s. Over the years, many different theories have been presented to explain how inoculation works. At the same time, many different inoculation compositions have been tested and used in foundry operations.

Today the inoculation process involves an addition of between 0.05 to 1% of a specialized FeSi alloy containing controlled amounts of one or more elements, including Al, Ca, Ba, Sr, Ce, La, Mn, Bi, S, O, and Zr. The inoculant provides nucleation sites that promote graphite precipitation and growth, together with iron solidification based on a stable Fe-C system. This inoculation effect can be measured using a chill wedge or thermal analysis.

In this paper, the concept of inoculation will be presented along with a description of the common understanding of what an inoculant is today, how the effect and performance of an inoculant can be measured, and what factors can affect inoculation performance.

INTRODUCTION

The thesaurus gives the following alternative words for inoculation: vaccination, injection, shot, immunization, booster, vaccine, jab, graft, grafting and prevention. [1] When looking at alternative words, one can find two meanings or directions to explain inoculation -- one related to providing protection and the other creating a substrate. As this paper will show, both meanings make sense and effectively describe what is achieved by inoculating cast iron. Effective inoculation will provide protection against chill while providing a substrate that allows the graphite to grow.

HISTORY [2]

The need for inoculation started at the beginning of the 20th century when foundries needed improved mechanical properties. In addition, the transition from cupola to inductive melting with high additions of steel scrap in the charge accelerated the need for inoculation.

This early connection between the charge and melt history and their subsequent effect on final properties dates to the early 1900s. The term heredity was used to explain why some melts gave good properties while others gave poor results.

For cast iron to compete against steel, higher strengths needed to be developed. In grey iron this is most easily achieved by reducing the C content. Inductive melting and the use of steel in the charge allowed for easier production of cast iron with a lower carbon equivalent (C.E.). Together, the transition to inductive melting, more steel in the charge, and lower C.E. grey iron created a need for inoculation.

During initial inoculation experiments with various ladle additions, it was observed that late additions of ferrosilicon (FeSi) had a positive effect on the graphite structure. At that time, the content of aluminum and calcium in the FeSi was not controlled. During 1930s and 1940s, several publications referred to the positive results obtained from ladle additions of FeSi containing one or more of elements, such as Ca, Mg, Al, Ni and Cr.

Following extensive research that improved the effectiveness of these FeSi-ladle additions, the term inoculation appeared. One of the earliest patents for these ladle additions was awarded to C. O. Burgess of Union Carbide Research Laboratories in 1936, followed in 1942 by US Patent 2,290,273 [3].

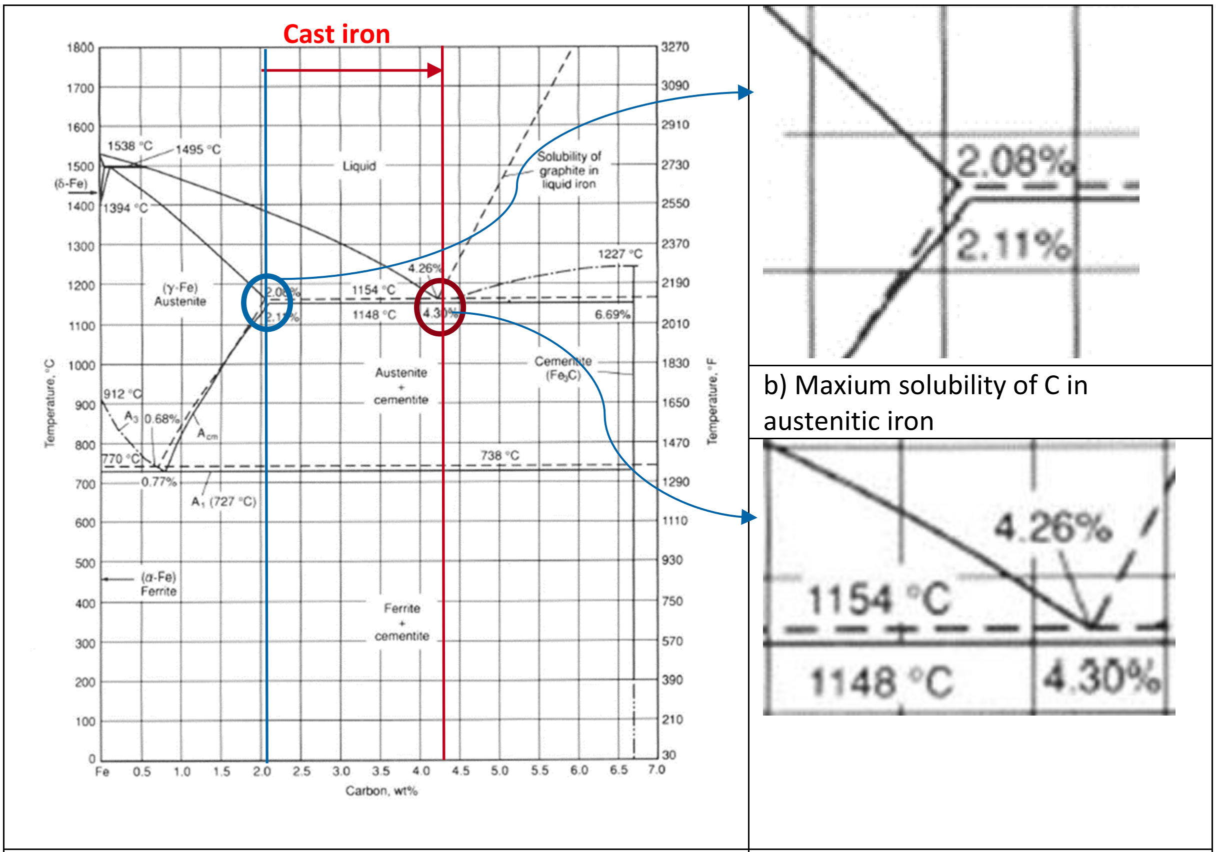
Following the invention of ductile iron in the 1940's, a greater understanding of the need and function of both inoculation and inoculants has been gained in both grey and ductile iron. Numerous elements and materials have been tested and found to be successful inoculants, yielding the variety of inoculants found in present-day practice. A more detailed analysis of the typical inoculants used today is presented later in this paper.

SOLIDIFICATION OF CAST IRON

To understand why inoculation is so important in cast iron, a closer look at what is cast iron and how cast iron solidifies is needed. The phase diagram presented in figure 1a [4] below shows that cast iron is a two-component alloy of iron and carbon. The right side marked with a red arrow -- covering the composition range from 2% to 4% C -- shows the phase diagram for cast iron. The blue circle shows the solubility limit for carbon in iron while the red circle indicates the eutectic point. A close-up of these points can be seen in figures 1b and 1c.

Cast irons are often classified according to their composition, or more specifically, their position in relation to the eutectic point.

Regardless of the composition of the cast iron, a carbon-rich phase will form during solidification if the carbon content is higher than the amount that can remain in solution in the iron matrix. What differentiates cast iron from other materials is that carbon can form two carbon rich-phases -- graphite and cementite. The formation of graphite is considered stable solidification. The formation of cementite is considered meta-stable solidification.



a) Iron–carbon phase diagram

b) Maxium solubility of C in austenitic iron

c) Eutectic point

Figure 1: Iron-carbon phase diagram. [4]

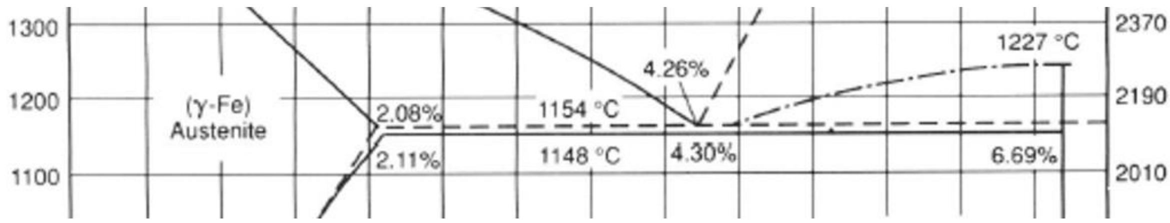


Figure 2: Close-up of the eutectic point. [4]

As seen in figure 2, the temperature difference between these two types of solidification is only 6°C. Fast cooling will promote the formation of iron carbide while slower cooling will promote graphite.

In the real world, cast iron is not a two-component system, but a multicomponent system composed of elements deliberately added plus impurities that affect the stable (t_{EG}) and meta-stable eutectic temperature (t_{EM}), as shown in figure 3. [5]

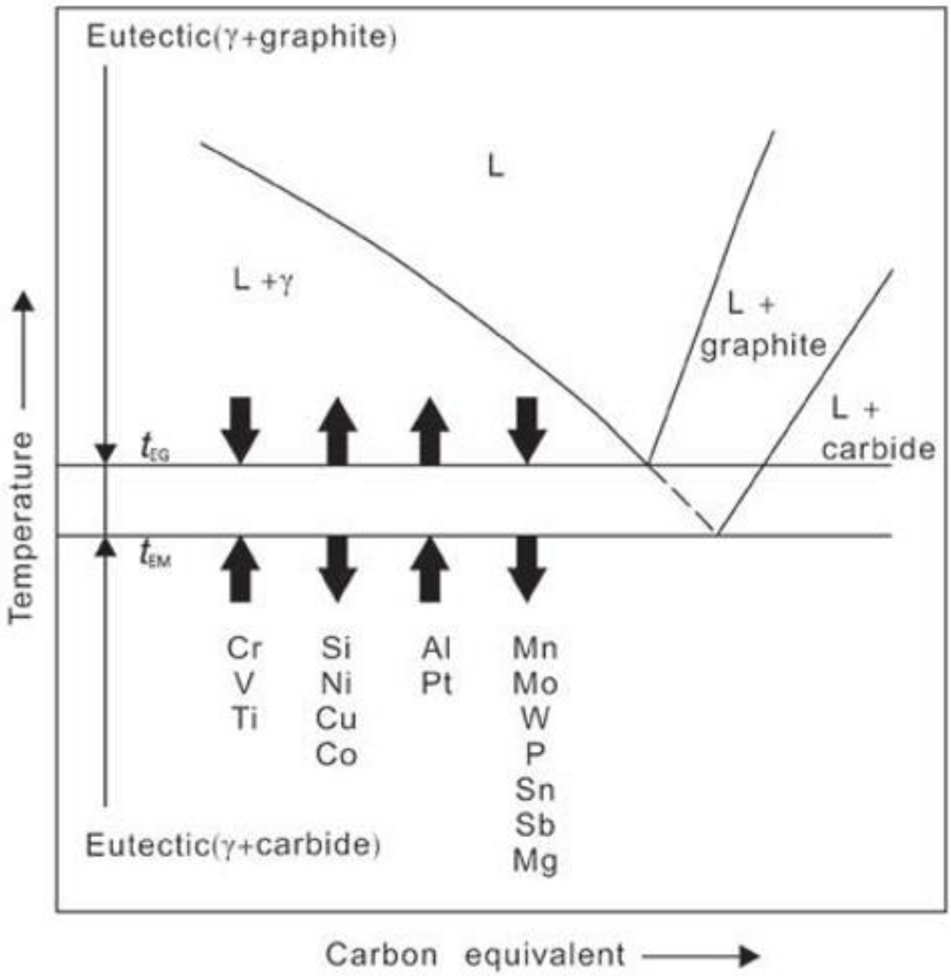


Figure 3: Effect of various alloying elements or impurities on the stable eutectic temperature t_{EG} and meta-stable eutectic temperature t_{EM}.[5]

Although these additional elements make the solidification of cast iron more complex, they also help open the temperature window between stable and meta-stable solidification from around 6°C to around 40°C.

It is the because of these two modifications of C-rich phases that the inoculation of cast iron is such an important production step. Without inoculation, there is a higher risk of forming iron carbides and not achieving the target properties. The main job of an inoculant is therefore to help facilitate stable solidification and the formation of graphite.

CONCEPT OF INOCULATION

The purpose of inoculation is to promote heterogeneous graphite nucleation by introducing elements that form suitable substrates that will act as nuclei and initiate graphite growth. By promoting a stable solidification process, inoculation encourages C to come out of solution in a favorable form of graphite and not as iron carbide.

The effect of inoculation is presented in figure 4 below showing the cooling curves for uninoculated iron as a black-dotted line and inoculated iron as a blue solid line. Inoculation reduces the degree of undercooling needed before graphite forms (red arrow). In addition, inoculation prolongs the formation and growth of graphite, increasing the solidification time. (green arrow).

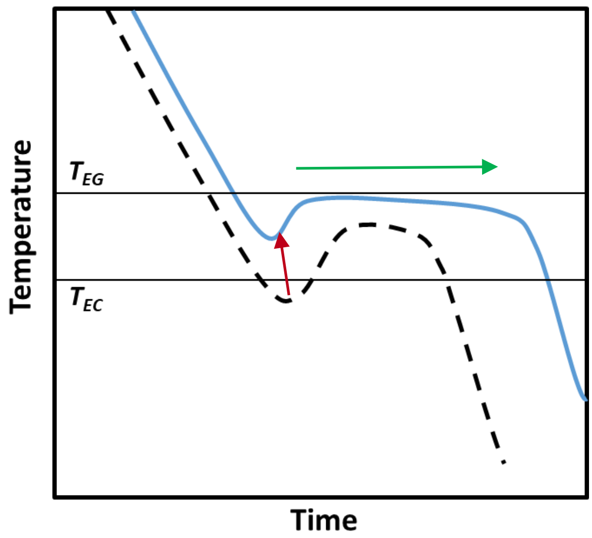


Figure 4: Effect of inoculation on cooling curve.

As a result, inoculation transforms the structure from carbidic or undercooled graphite to fully flake or spheroidal graphite, as shown in figure 5.

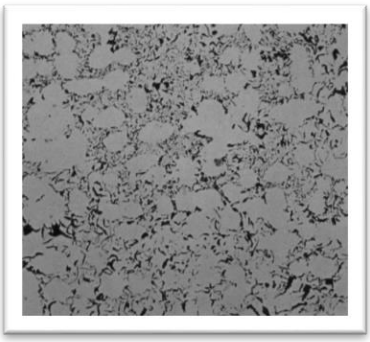
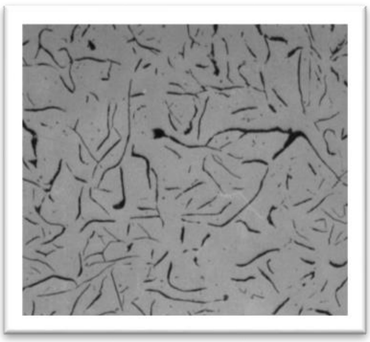
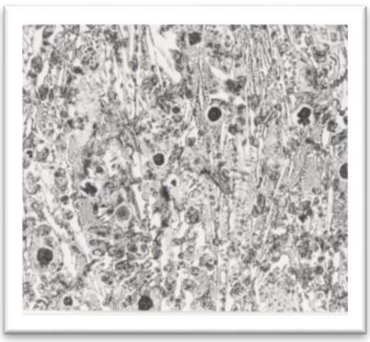
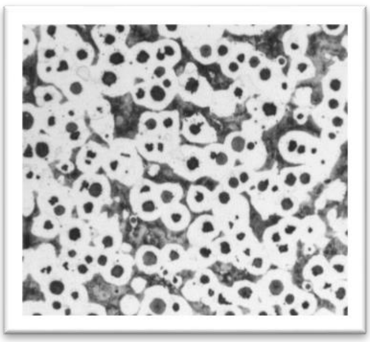
Grey iron		
	Uninoculated	Inoculated
Ductile iron		

Figure 5: Effect of inoculation on graphite structure in grey and ductile iron

The goals of inoculation are therefore to: [5,6,7,8,9,10,11,12]

- Avoid formation of carbides (cementite)
- Promote the formation of graphite
- Reduce segregation
- Reduce shrinkage
- Improve machinability
- Promote a homogenous structure
- Increase ductility

Inoculation can take place either at tapping, in the ladle, in the stream during casting, or in the mold. Inoculating alloys are available in granular form, packed in a wire, or cast/pressed into various shapes. The size is adjusted based on the point of addition and the time and temperature available for dissolution. As a rule, additions can be reduced when inoculation takes place as close as possible to the pouring of iron into the mold.

In the commercial production of cast iron, both grey and ductile iron are inoculated, but grey iron may require smaller inoculating additions, depending on its chemical composition, melting method and charge make-up. As shown in figure 6 below, the degree of grey-iron undercooling prior to inoculation decreases as the carbon equivalent is increased. [12]

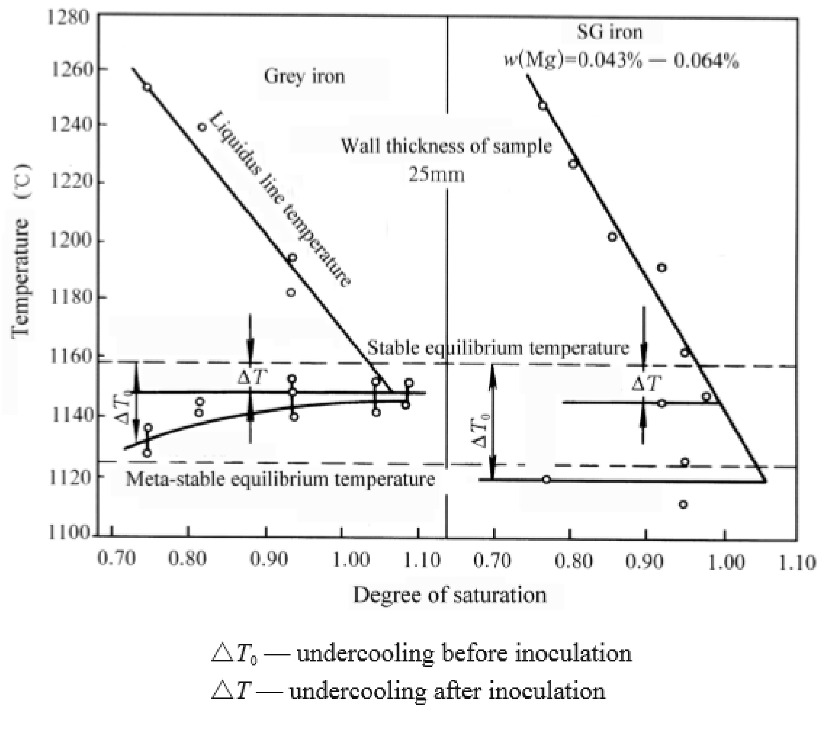


Figure 6: Relationship between chemical composition and degree of undercooling in grey and ductile iron. [12]

Figure 6 also shows that the amount of undercooling in ductile iron does not depend on the carbon equivalent. Since the Mg treatment ties up and removes S and O during ductile-iron nodularisation, the degree of undercooling is generally higher than the undercooling in grey iron. As a result, ductile iron almost always needs inoculation with additions generally larger than with grey-iron inoculation.

The effect of inoculation can be measured in several ways, including:

- measuring the degree of undercooling using thermal analysis.
- measuring the chill-reduction tendency using a chill wedge
- analyzing the microstructure using a quantitative and qualitative evaluation of the structural features

Measurements can be made at a fixed time or throughout the process.

WHAT IS AN INOCULANT?

In the beginning it was thought that the inoculating effect was connected to Si, but studies using high-purity FeSi showed that this material had limited influence. Instead, the inoculating effect of FeSi was attributed to the Ca and Al impurities in FeSi. [8,13]

Many compositions have been tested and used as inoculants since the start of inoculation in the 1930's. Today, the typical inoculant uses FeSi as a carrier with one or more active elements. The amount varies depending on the element, but all inoculants either contain a minimum of Ca and Al or Sr.

Table 1 provides an overview of the common active elements in inoculants today along with their composition range and the typical analysis. An effective inoculant always has Ca, Ba or Sr, but can also contain elements like Al, Zr, Mn, Bi, Ce, La, Mg, and Ti. The most commonly used inoculant worldwide is Ca- and Al-bearing FeSi.

Table 1: Overview of main elements in commercially available inoculants with range and typical level.

Element	Range	Typical
Si	27 - 80	50/75
Ca	0.3 – 15	1 – 2
Al	0.5 – 5	1 / 3
Sr	0.5 – 9	0.6 – 1
Ba	0.4 – 12	1/2.5/9
Zr	0.5 – 8	1.5/3.5
Ce	0.2 – 11	1.8/11
Mg	0.1 – 40	
RE	0.1 – 40	1/2/10
Ti	4 – 11	10
Bi	0.4 – 1.3	<1/>1
La	0.5 – 2.3	2

As shown in this table, almost all effective inoculating elements have a high affinity for O and/or S.

Some of these elements are more commonly used in grey iron and some find greater use in ductile. For example, Sr-containing inoculants were developed for grey iron by

BCIRA J. Dawson. [14] Since this invention in 1960s, Sr has been the most popular inoculating element for use in grey iron, particularly irons having high S. Al-containing inoculants are primarily used in ductile iron. However, Al is also important for graphite nucleation in grey iron. [15]

Although some inoculants were developed for specific irons and applications, they will work in most applications and iron compositions. Foundries also tend to want to have only one inoculant for practical reasons.

<u>How does an inoculant work?</u>

All inoculants use FeSi (actually Si) as a carrier to deliver the active elements to the cast iron while, at the same time, creating a suitable environment for heterogenous nucleation and the precipitation of graphite.

All of the elements listed in table 1 above have limited solubility in iron so they are tied to Si when they dissolve. At the same time, when a FeSi-bearing inoculant dissolves, the iron melt will then be enriched locally with Si. Since Si reduces the solubility of C, Si encourages C to come out of solution and form graphite. In addition, the zone around the dissolving FeSi has elements that have a high affinity for S and O. These compounds form the suitable substrates needed for graphite growth. [16]

<u>Fading of inoculation</u>

The effect of inoculation lasts for a limited time period. Immediately following dissolution and the reaction that forms inclusions, the inclusions will start growing and will eventually become too big to provide the suitable nuclei needed for graphite formation. This is known as the Ostwald -Ripening effect. [17,18]

In addition, the zone with the higher Si level becomes more uniform over time and reduces the driving force for C to precipitate. [16]

Different inoculants fade differently. This was recognized early during presentations by several authors such as H. Morgan. A. Moore, J.V. Dawson, A.G. Fuller. [9, 19, 20, 21] Some inoculants provide a strong effect initially but fade quickly, while others give more consistent inoculation over a longer period of time.

WHAT AFFECTS INOCULATION PERFORMANCE?

This section presents examples from the literature as well as results from R&D trials and projects carried out by Elkem Foundry Products:

<u>Effect of Chemistry</u>

Since the inoculation addition rate throughout the casting process is normally fixed, it is important that the performance of any inoculant be consistent. This performance is connected to the presence of the active element(s) in iron. To have consistent results, it is therefore important that the level of the active element(s) be defined, preferably with a minimum and a maximum level. The studies by McClure and Bilek et al revealed the importance of an element such as Ca on inoculation performance. [8, 13]

<u>Effect of same active element</u>

As mentioned earlier, Sr-containing inoculants were developed for inoculating grey iron in the 1960s. Today, numerous Sr-containing inoculants are available in the market and are widely used commercially. Figure 7 below shows chill levels obtained from 7 different Sr-containing inoculants.

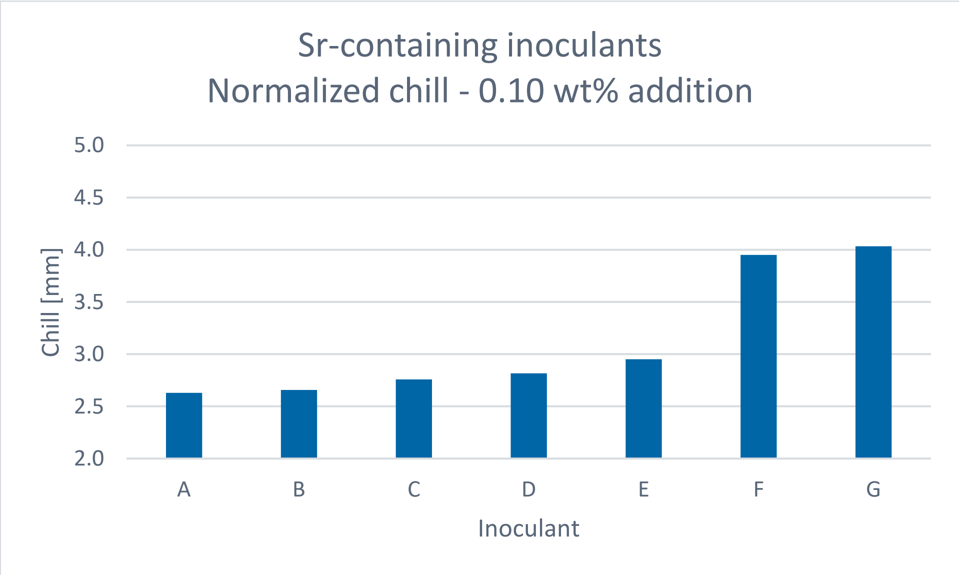


Figure 7: Variation in chill level seen for 7 commercially available Sr-containing inoculants.

As figure 7 above shows, there appears to be two groups of inoculants -- inoculants A, B, C, D and E which give a chill level in the range of 2,5 to 3 mm and inoculants F and G that give a chill level of about 4 mm – 50% more chill than the first group. This difference will not be noticeable for most foundry conditions.

Figure 8 shows the chill result obtained by increasing the amount of Sr in the inoculant.

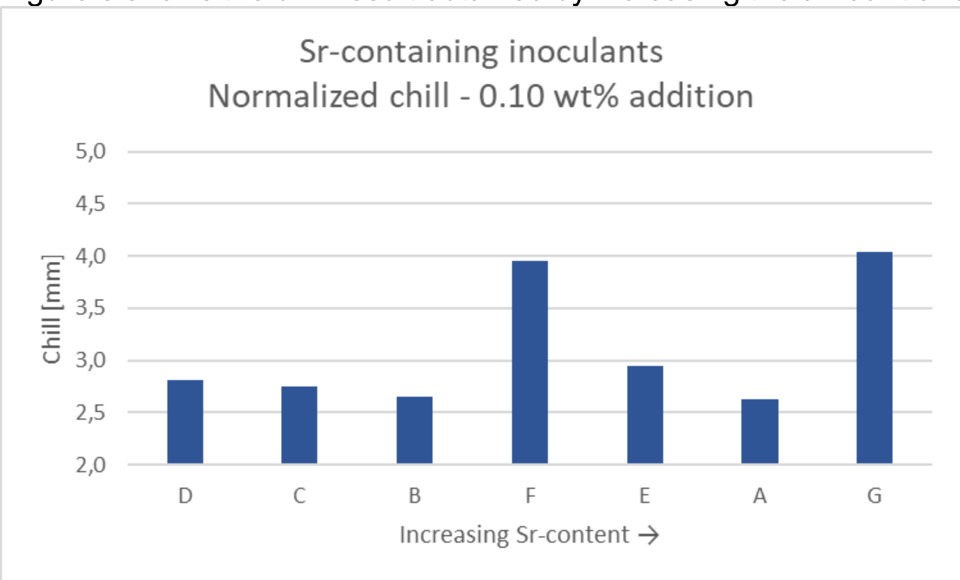


Figure 8: Chill results obtained by increasing the Sr level of an inoculant.

The difference in the Sr level between inoculants C and G is 100%; however, the effectiveness is not connected to the level of the active element. This is in line with observations by Hummer and an explanation by T. Skaland that there is an optimum range for the various active elements. If this range has a correct stochiometric relationship, compounds will form that have a good lattice match with graphite. [12,18]

As a result, an inoculant must not only contain active elements, it must have an optimum range of those elements. This range is different for different inoculants. For Ca, the optimum range has been found to be 0.4 to 1.0%. And since Sr and Ba form compounds with the same optimum graphite match as Ca, the optimum range is presumed to be the same for these elements.

Increasing the levels of active elements beyond the optimum stochiometric relationship that gives the best crystal match with graphite increases the risk of forming compounds with greater lattice mismatch, reducing the effectiveness of the substrates formed. Since these active elements all have a high affinity for S and O, there is a risk that they will create nucleation sites for graphite that produce ineffective inclusions, also known as slag inclusions.

Different types of inoculants with different active element(s)

Another factor that might affect inoculant performance is the combination of active elements contained in the inoculant. Some combinations of active elements work better than others, depending on the application. In most cases, inoculants can be used in both grey and ductile iron, but normally some inoculants give better results in grey while some are better for ductile. For example, the Sr and Al inoculants are primarily used in grey while Al, Ce-Ca, La-Ca, Bi-R.E. inoculants were developed for ductile iron. Zr-Ba-Ca inoculants are normally effective in both grey and ductile iron.

In figure 14 below, the effect of different combinations of active elements can be seen in the same melt.

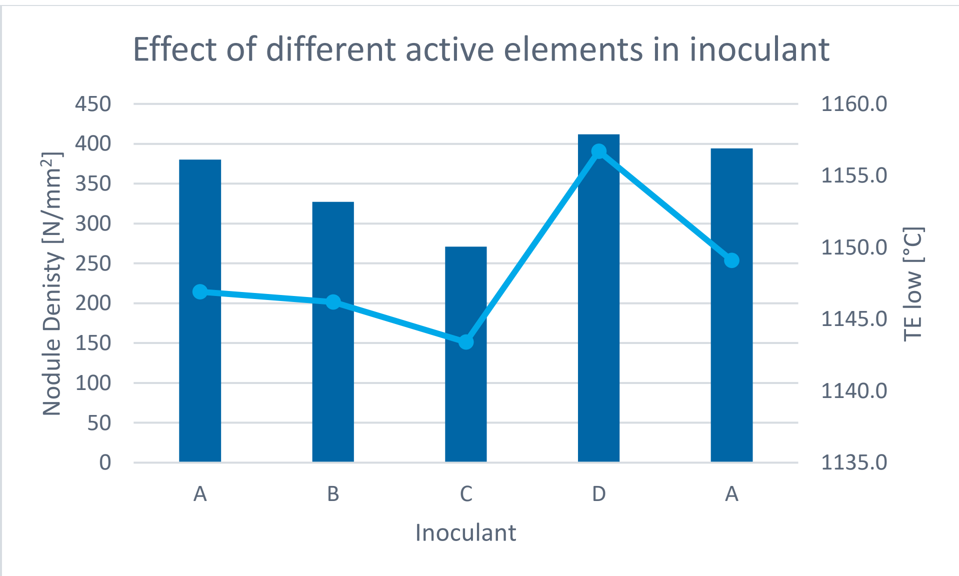


Figure 9: Effect of different type of active elements on inoculation performance.

In figure 9 above, the nodule density and TElow are shown for 4 different inoculants. The nodule density was measured in a 25-mm tensile bar while the TElow is the average of 4 individual thermal analysis cups poured at the same time as the tensile bar. The same inoculant was used in the first and last pouring ladles as a check on reproducibility. The inoculants A, B, C and D all have different combinations of active elements. As the figure shows, some combinations of active elements provided better results than the others.

As shown in this example, the choice of an inoculant should depend on the application as well as the chemistry.

<u>Effect of time of addition</u>

Another important factor on the performance of an inoculant is the timing of the inoculant addition. As a rule, the inoculant should be added as close as possible to pouring the casting. This makes sense considering how the inoculants work by creating a zone with high Si levels around the inoculant particle as it dissolves. This dissolution creates favorable conditions for nucleation of graphite. Increasing the time before solidification starts allows more time to even out the local variations in the temperature and the composition. Figure 10 reveals the effect of time of addition on the microstructure.

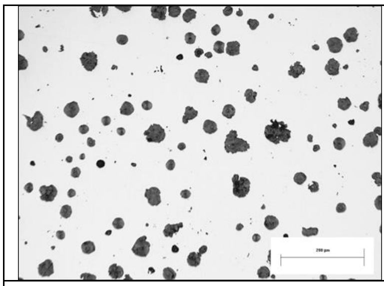
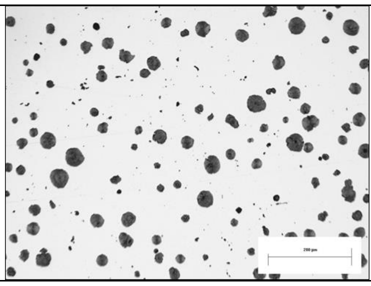
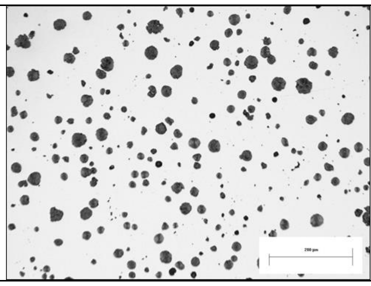
		
Uninoculated	Lade inoculated	Inoculated in pouring cup and mould

Figure 10: The most effective inoculation is achieved when inoculation takes place as close as possible to pouring the casting.

<u>Effect of temperature</u>

The inoculating temperature has a similar effect on inoculation effectiveness. By inoculating as close as possible to pouring, foundries can inoculate iron with lower temperatures. This will improve inoculating results, assuming that the inoculant is sized for late additions. This effect is more pronounced in thin than in heavy sections, as shown in Figure 11. The nodule density in casting sections of around 10 mm increase by 1% for every 1°C drop in temperature at the time of inoculation. For thick casting sections, the nodule density increases only 0.4% for every 1°C drop in temperature.

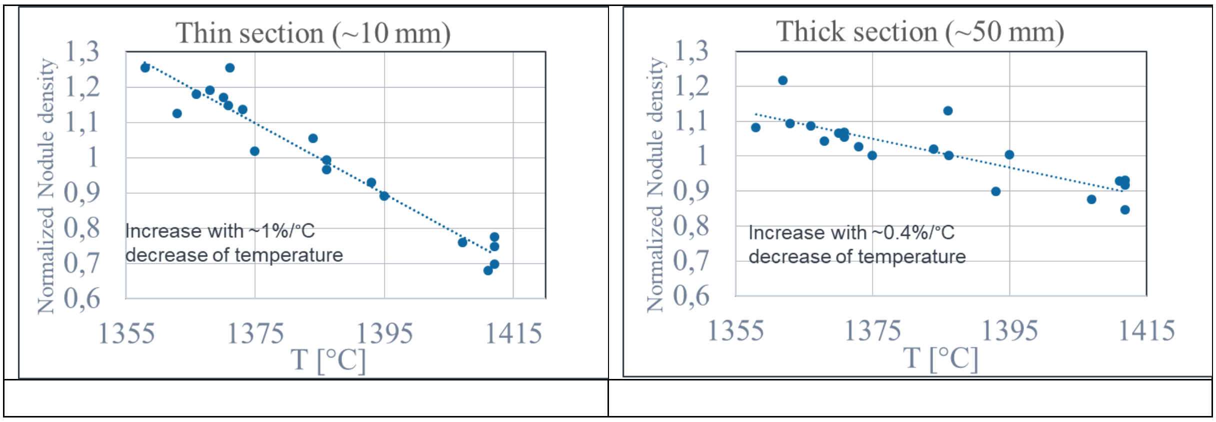


Figure 11: Effect of temperature on inoculation effect in thin (10 mm) and thick sections (50 mm)

This effect assumes that the temperature is sufficient to allow for the inoculant to be dissolved during addition.

Effect of Mg-treatment history

The effectiveness of ductile-iron inoculation can also be affected by the Mg-FeSi used. In his 1979 paper, A.G Fuller showed that cerium additions can improve graphite fading characteristics. [21] In figure 12, the inoculation performance is affected by the type of MgFeSi used in combination with different types of inoculants. This suggests that there might be a synergistic effect between MgFeSi and an inoculant, and that care should be taken when selecting an inoculant with any particular MgFeSi.

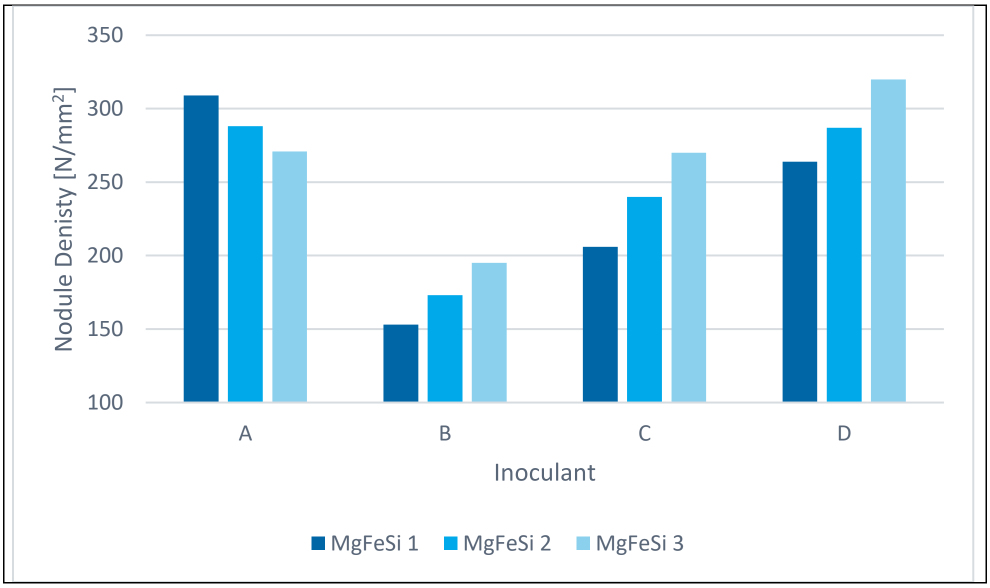


Figure 12: Difference in nodule density from 4 different inoculants combined with 3 different Mg-FeSi alloys (having different R.E. levels and compositions).

SUMMARY

The purpose of inoculation is to provide a suitable substrate that allows graphite to grow with less undercooling. Inoculation is more important and requires larger additions in ductile iron than in grey iron. Typically, inoculants are FeSi alloys containing one or more deoxidizing elements that provide a suitable environment for inoculation to take place.

Inoculation effects can be measured a number of ways, including thermal analysis, chill tests, and microstructure and eutectic-cell evaluation. The inoculation effects depend on chemistry, time, temperature, addition rate, and the history of the iron being treated. These effects should be carefully considered in devising an effective inoculation strategy for grey- and ductile-iron castings.

ACKNOWLEDGMENT

We thank John Crane for his valuable help and support.

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