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Inoculation of Cast Iron

Technical Paper

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The addition of an inoculant to molten cast iron is advisable and even necessary in most cases, in order to be able to produce castings which fulfill the quality requirements. The mechanical properties and machinability of cast iron with lamellar, compact and nodular graphite greatly depend on the formation of the basic and secondary structure. Both are significantly influenced by the inoculation treatment. Therefore the mechanism of inoculation and the graphite nucleation during the solidification of cast iron will be explained here in more detail.

What is meant by inoculation of cast iron?

"Inoculation of molten cast iron" refers to the introduction of nuclei into the melt in order to influence the solidification process or structural formation in the casting in a specific way. Nuclei are fine particles that are ≤ 4 µm in size and which serve as crystallization centers for the graphite precipitation.

The literature contains various theories concerning inoculation, which will not be explained in more detail here, of which the oxide nucleation theory is regarded as the most significant and most probable. [1, 2]. According to this theory, the precipitation of SiO2 nuclei occurs during the inoculation, and the graphite can then grow onto these nuclei. However, these nuclei also depend on the existence of foreign nuclei. These are formed, in particular, by those elements that have a high oxygen affinity (see also the Inoculants section).

The setting of a favorable nucleation state is designed to influence both the graphite precipitation (number, size, form) as well as the formation of the basic structure in a targeted manner (promoting the grey solidification, prevention of a ledeburitic chill).

Effective inoculation leads to uniform mechanical material properties in different wall thicknesses, especially to a restriction of the hardness scatter. It can also influence the feeding characteristics due to its effect on the austenite-graphite eutectic.

Nevertheless, the inoculation effect is in direct correlation to the previous history of the melt to be cast, i.e. its metallurgic initial state, the temperature-time course and the chemical composition.

Inoculation can occur in several stages, but has its greatest impact shortly before or during pouring. Depending on the nuclei effectiveness and cooling conditions, inoculation occasionally takes place in the furnace or in the intermediate vessel, though preferably while filling the ladle, in the pouring stream or in the mold.

Besides iron, unalloyed or low-alloy cast iron contains about 1.5% to 3% silicon and 2% to 4% carbon. During the cooling, the melt attains the eutectic composition (4.3% carbon) after a certain time and then the eutectic solidification begins immediately, at least under conditions of equilibrium. The precipitating carbon is then fully present as graphite. In practice, however, these conditions of equilibrium are not achieved. The reasons for this include variations in the chemical composition, the wall thickness or cooling speed and the pouring temperature, with the result that the melt in most cases cools below the stable eutectic temperature before the solidification of the eutectic begins.

The aim of inoculation is now to ensure that sufficient nuclei are present for the crystallization of graphite at the beginning of this eutectic solidification and that the formation of iron carbide (cementite, Fe3C) is largely prevented. The addition of an inoculant is thus to be equated with an addition of crystallizers to the molten iron, thus enabling graphite crystallization with minimal undercooling below the stable eutectic temperature.

This consequently enables the formation of evenly distributed A graphite in cast iron with lamellar graphite and the formation of many small graphite nodules in the Mg-treated cast iron.

Fig. 1: Typical cooling curve of a hypoeutectic gray cast iron [3]

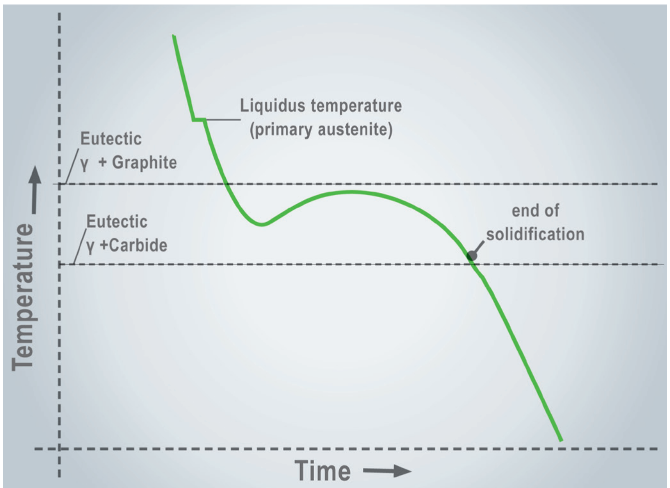
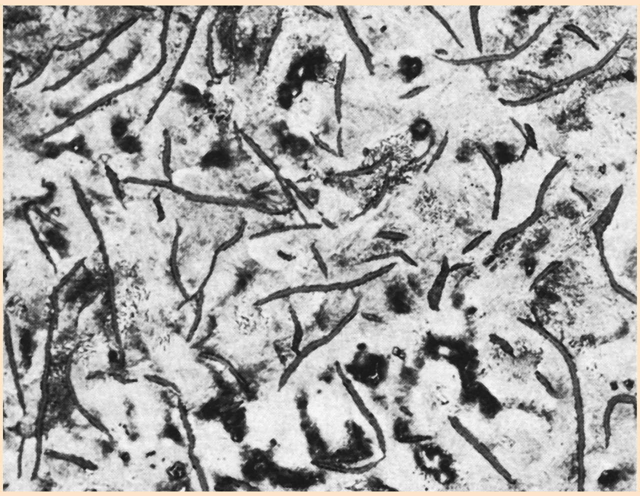


Fig. 2: Gray solidified structure with A-graphite



Inoculants

In practice, inoculants are mostly special alloys based on ferro-silicon. They contain additions of inoculation-effective elements with a high affinity to oxygen, such as calcium, aluminum, barium, zircon, strontium and rare earth metals. This is because successful inoculation is always associated with a depletion of the oxygen dissolved in the melt.

However, some inoculants also contain elements such as bismuth, titanium, manganese, sulfur and oxygen, for example, which can also have a positive effect on the graphite nucleation. A selection of the wide range of inoculants available from ASK Chemicals Metallurgy is shown in **Table 1**. Furthermore, inoculants based on FeSi with additions of graphite are also available via which, in addition to the resultant oxides, graphite nuclei are introduced into the melt. When using graphite as an inoculant, it must be noted that this involves crystallized graphite, which is produced at high temperatures (2500°C).

Some of these inoculation-effective constituents of the inoculants, in particular calcium and aluminum, are already contained in certain quantities as “natural” content in the so-called “inoculation FeSi”. The complex-alloyed special inoculants then contain higher contents and/or the additional elements mentioned above, which, besides the inoculation effect, also partly affect the dissolution performance of the inoculant.

The use of pure ferro-silicon as an inoculant has proven to be ineffective.

Table 1: Inoculants of ASK Chemicals Metallurgy

<table>
<tr><th>Effective elements</th><th colspan="2">DI and GI</th><th>DI (Ductile Iron)</th><th>GI (Grey Iron)</th><th>CGI (Compact Graphite Iron)</th></tr>
<tr><td>Al</td><td colspan="2" rowspan="2">Inogen 75</td><td>VP 216/116 (GERMALLOY™)</td><td>–</td><td rowspan="2">Inogen 75</td></tr>
<tr><td>Ca</td><td>–</td><td>–</td></tr>
<tr><td>Ba</td><td>SB 5</td><td rowspan="2">Inoculoy 63</td><td>–</td><td>–</td><td>–</td></tr>
<tr><td>Mn</td><td rowspan="2">ZM 6</td><td>–</td><td>VP 316 (OPTIGRAN™)</td><td rowspan="2">–</td></tr>
<tr><td>Zr</td><td rowspan="3">Optinoc™ Z</td><td>–</td><td>–</td></tr>
<tr><td>Ca</td><td>–</td><td rowspan="3">SMW 605</td><td>–</td><td>–</td></tr>
<tr><td>Bi</td><td>–</td><td>–</td><td>–</td></tr>
<tr><td>CerMM</td><td>–</td><td>CSF 10</td><td>–</td><td>–</td></tr>
<tr><td>Sr</td><td>SRF 75</td><td>–</td><td>–</td><td>–</td><td>SRF 75</td></tr>
<tr><td>Ti</td><td>–</td><td>–</td><td>–</td><td>LC Graphidox</td><td>LC Graphidox</td></tr>
</table>

Fading Effect

The effect of the inoculation treatment depends on temperature, but above all on time. The term fading is also used. The fading time begins with the addition of the inoculant and ends when the eutectic solidification temperature is reached.

A reduction in the number and a coarsening of the inoculation-effective inclusions results during this time due to re-oxidation, concentration compensation as well as the dissolution of nuclei. This also explains the influence of the solidification times on the inoculation result. While the normal wall thickness areas of castings of 5mm to 50mm solidify in seconds to a few minutes, the crystallization of thick-walled, heavy castings with wall thicknesses bigger than 60mm can take hours, depending on the casting temperature. These differences in the solidification times entail a greater fading effect of the inoculation for bigger castings and hence a reduction in the number of nuclei able to grow, which leads in turn to a longer crystallization time. Both factors have the result that the eutectic grains or graphite nodules present in heavy section castings are generally fewer in number but larger in size **(Fig. 3).**

Because of the omission of appreciable fading times and of the then lower iron temperature in the case of late inoculation enables very good inoculation results to be achieved with minimum inoculant additions at the same time. The maximum inoculation effect of late inoculation is generally not attainable with ladle inoculation.

The most effective late inoculation methods applied in practice are pouring stream and mold inoculation. In these cases, the inoculant is either dosed precisely into the pouring stream or placed in the mold and dissolved evenly by the molten iron during the overall casting process.

The fact that the subsidence or fading effect depends on the inoculant composition also merits particular consideration. Thus, for example, very powerful inoculants usually subside very quickly as well. On the other hand, a very long-lasting inoculant effect was ascertained for inoculants containing barium and cerium. This aspect is, above all, to be noted for multi-stage inoculation.

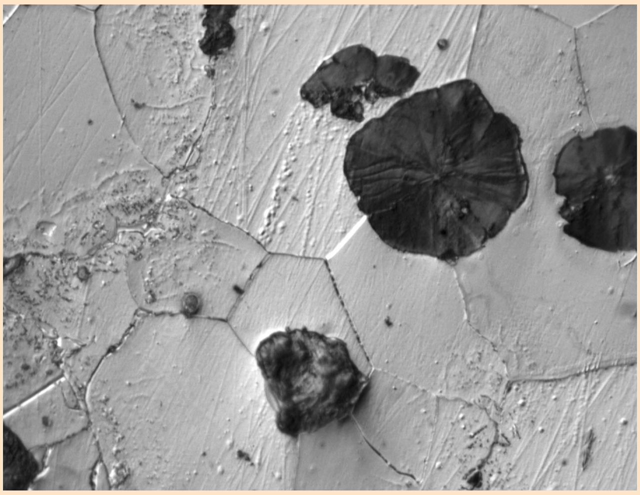


Fig. 3: Very large nodules in casting of DI (20 nodules/mm^2, nodule diameter up to 100 µm)

Effect on the Graphite Formation

Via the state of nucleation of the molten cast iron, the inoculation has an effect on the number, size and partly the form of the graphite precipitations.

Inadequate inoculation and resultant increasing undercooling initially lead in cast iron with lamellar graphite to the formation of B-graphite (rosette graphite) or also D- and E-graphite (undercooling graphite), see **Fig. 5** and **Fig. 6**. The result is the formation of ferrite areas, which lead to a reduction in strength and a deterioration of the machinability.

If the undercooling continues on account of increasing cooling speed or a poorer state of nucleation, results in a mottled or even white structure, in which the graphite is present partially or fully as iron carbide (Fe_3C).

In the case of cast iron with nodular graphite, a poor state of nucleation is discernible via a reduced number of nodules, poorer nodularity and also via the structure with higher pearlite content and, in the less favorable case, with increasing chill.

With the same cooling conditions (wall thickness), for example, a DI casting inoculated with SMW 605 containing bismuth exhibits significantly higher numbers of nodules than an iron inoculated with an inoculant containing barium, as shown in **Fig. 7.** Nevertheless, it must be noted that, with the same wall thickness and same amount of inoculant, the specific number of nodules is, in turn, also determined by the type of inoculant (inoculation-effective elements).

Fig. 8 shows the effect of the wall thickness or cooling speed on the specific number of nodules in relation to various inoculants. Owing to the very rapid solidification, all inoculants are still fully effective in thin wall thicknesses, while a fading effect occurs as the wall thickness increases, hence leading to a reduction in the number of nodules. In other words, you can never get the same number of nodules in heavy section castings than in thin-walled castings, even with optimum inoculation. In very thick areas, sometimes only 40 to 60 nodules per mm^2 are encountered, for example, while nodule numbers > $500/mm^2$ are perfectly possible in casting areas of only a few millimeters. The reduction in the number of nodules is also accompanied by a coarsening of the graphite, see also **Fig. 3** and **Fig. 9**. What is shown here as an example of Ductile Iron is applicable for the

Fig. 4: Cooling curve of an iron with inadequate nucleation state – significant undercooling below the stable eutectic temperature

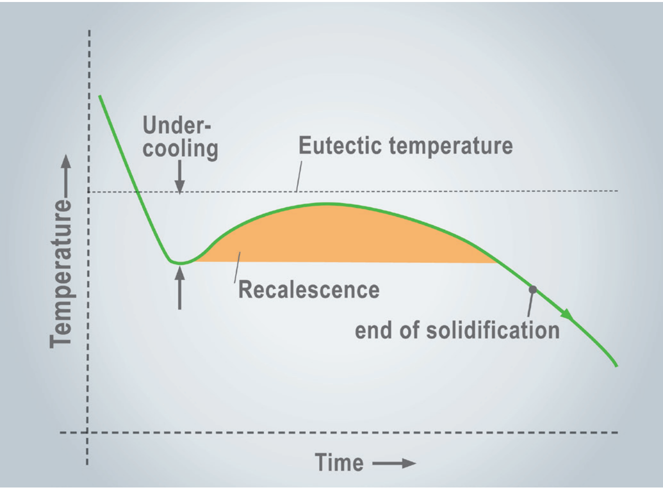


Fig. 5: B-graphite

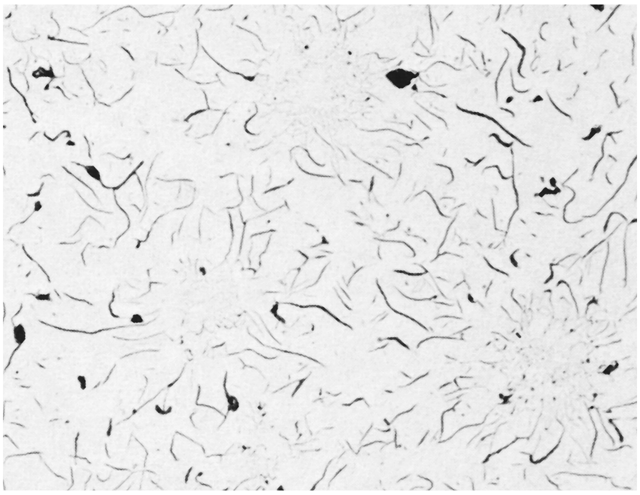


Fig. 6: D-graphite

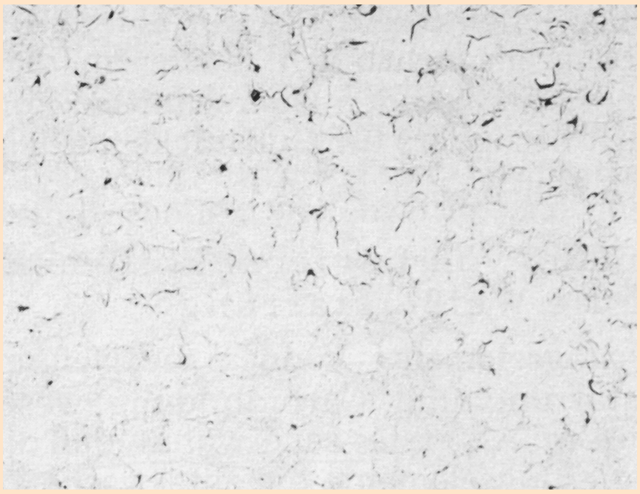


Fig. 7a: Late inoculation with 0.15% SMW 605

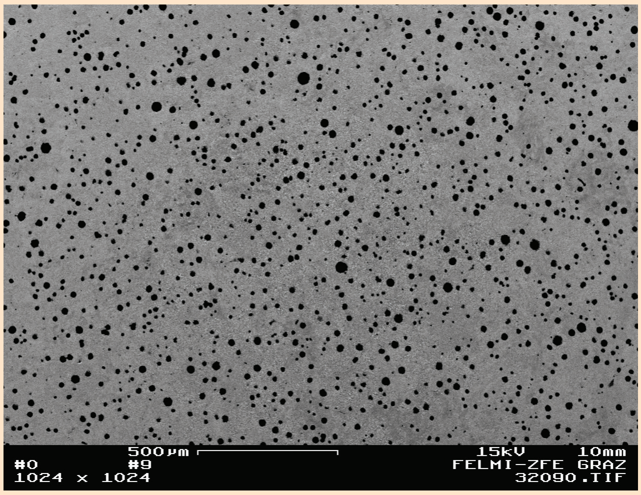


Fig. 7b: Late inoculation with inoculant containing barium

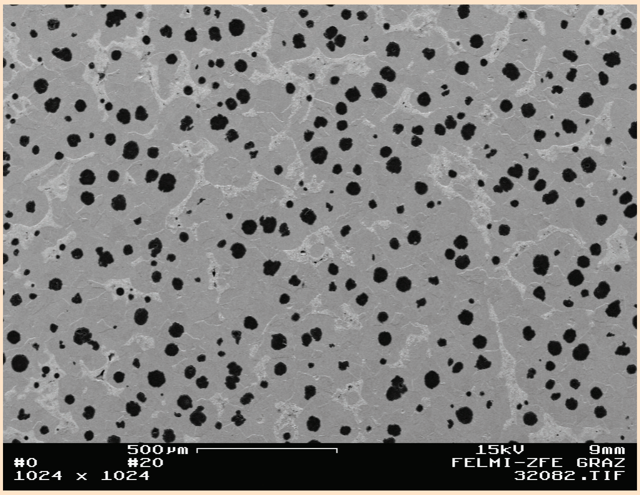


Fig. 8: Effect of the wall thickness and the inoculation-effective elements on the number of nodules after late inoculation

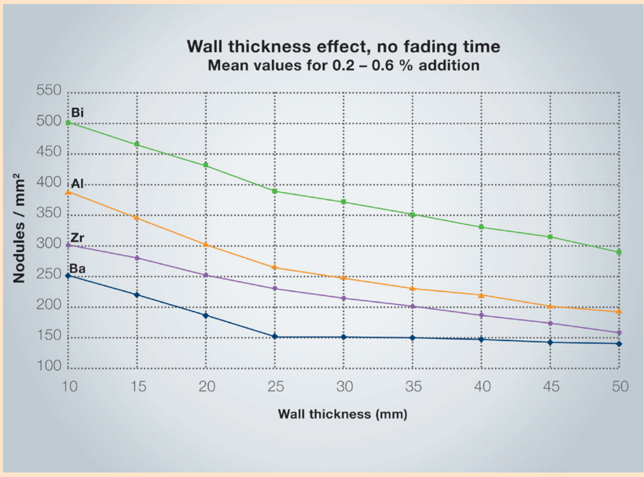
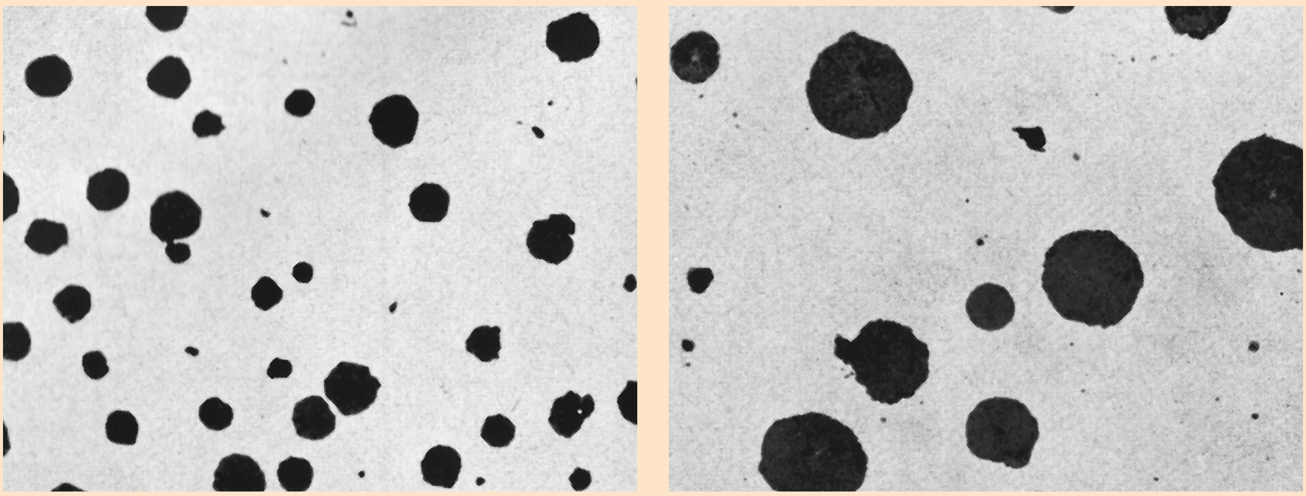


Fig. 9: Comparison of nodule numbers and nodule size for different wall thicknesses [4]



Effect on the Matrix

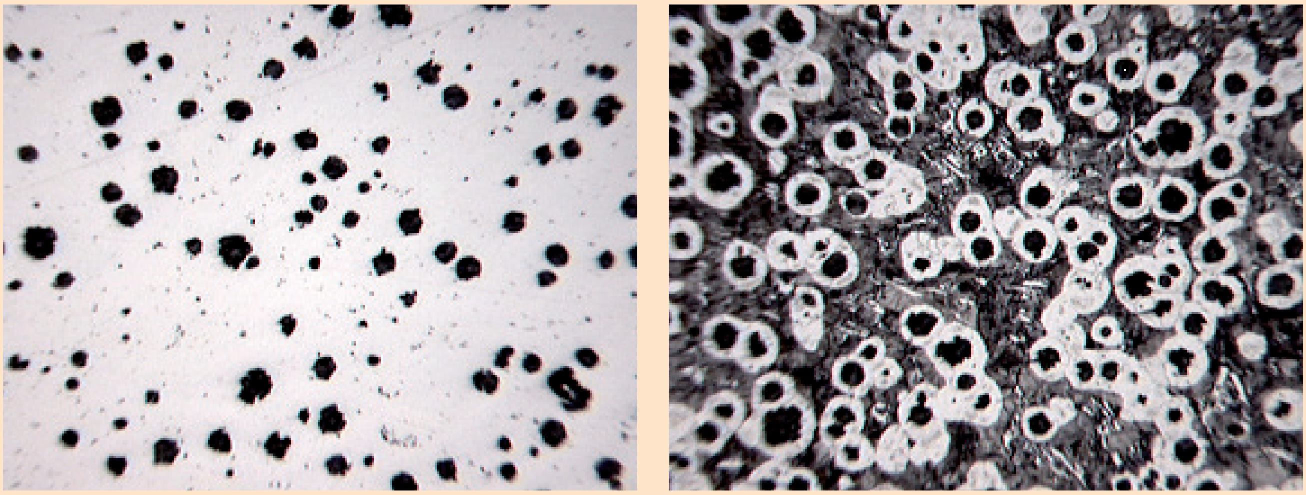
Cast iron with lamellar graphite

In most cases, the formation of a fine-grained, pearlitic matrix without chill and the formation of fine A graphite is aimed for cast iron with lamellar graphite.

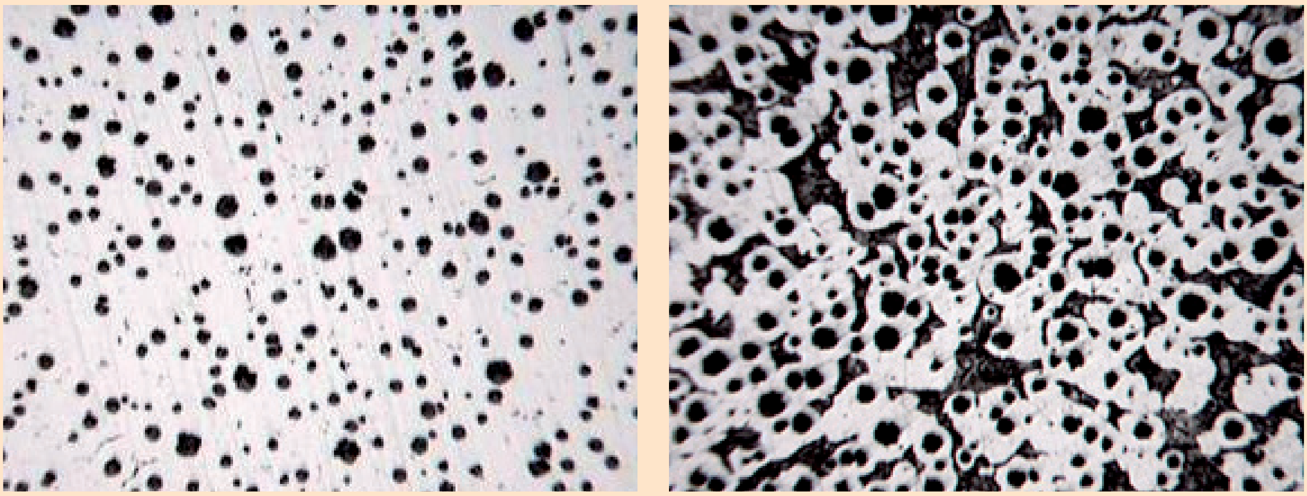
Effective inoculation or a good nucleation distribution affects the solidification process positively in this respect and, taking into account the other influential variables (chemical analysis, cooling conditions), leads to the desired structure as well as the formation of uniformly finely distributed A-graphite. Almost uniform mechanical properties with very good machinability are therefore ensured, even in different wall thicknesses.

Fig. 10: DI after ladle inoculation (above) and with additional mold inoculation (below); wall thickness 10mm, magnification 100:1

0.3% ladle inoculation, approx. 100 nodules/mm², 10% cementite, 20…30% ferrite, rest pearlite



0.2% ladle inoculation, approx. 300 nodules/mm², no cementite, 70…80% ferrite, rest pearlite



Cast iron with nodular graphite

Cast iron with nodular graphite would mostly solidify white or mottled if not inoculated, owing to its fundamentally greater tendency towards undercooling due to the magnesium treatment.

The grey solidification is only brought about by the inoculation. As a result, the specific number of nodules is increased, the nodularity improved, the ferritization tendency increased and, above all, the tendency towards chill or carbide formation reduced.

As an illustration, **Fig. 10** compares the inoculation result after ladle inoculation with 0.3% inoculant (after the magnesium treatment), as well as ladle inoculation with 0.2% and 0.1% additional mold inoculation. The additional mold inoculation has increased the number of nodules, improved the nodule shape and increased the ferrite content.

In medium- and thick-walled castings, the structural formation is also significantly improved by late inoculation. In the case of thick-walled castings made from Ductile Iron (besides the creation of ingot molds), the mold inoculation is often the only option for increasing the number of nodules and largely avoiding undesired segregations, intergranular carbides and graphite degeneration.

Inoculation Methods

Pre-inoculation / Pre-conditioning

This refers to the addition of so-called pre-conditioning agents or other nucleation-effective substances as early as the furnace or during tapping. This involves establishing favorable conditions for optimum structural and graphite formation right at the start of the metallurgical process in the iron.

VL(Ce)2 containing Ce-Zr-Mn is typically used as a pre-conditioning agent, contributing to a reduction in the oxygen content and an improvement in the nucleation distribution. Other preconditioning agents may contain barium or aluminum, for example.

The use of silicon carbide can also be referred to as preconditioning in a certain sense, as this also ensures a basic iron rich on nuclei.

Ladle inoculation

This is the classic inoculation method, the inoculant being added during tapping or pouring, e.g. after a magnesium treatment. Depending on the amounts of iron, inoculants with grain sizes of between 0.6mm and 6mm are mostly used for this type of inoculation. It must be ensured that the inoculant is not placed on the bottom of the ladle but added as steady as possible to the iron stream.

Wire inoculation

In wire inoculation, the inoculation is performed with the help of a cored wire filled with granular inoculant. The wire is fed to the melt via a controllable feeding machine, thus ensuring a precise dosing of the inoculant both via the wire length and the feeding speed. The wire inoculation can be carried out both in a ladle and in the pouring channel of a casting device.

Pouring stream inoculation

Here, the inoculant is added to the iron stream directly during pouring. In most cases pouring stream inoculation devices are used, which enable a quantitatively uniform addition of the inoculant to the pouring stream over the entire casting process. What are known as the pouring stream grain sizes are mostly between 0.2 mm and 0.7 mm. The amount added should not be more than 0.15%, as the inoculant has to be completely dissolved in a very short time. The advantage compared to the ladle inoculation is the late addition time and hence largely avoiding the fading of the inoculation effect. Pouring stream inoculation is above all used in automatic molding systems.

Mold inoculation

Mold inoculation is the addition of inoculant as late as possible and hence also the inoculation method in which the fading effect is reduced to a minimum. In mold inoculation, the inoculant is introduced in the pouring basin or directly into the gating system of the mold. The dissolution therefore occurs under air exclusion directly in the iron over the entire pouring time. Preferably casted inoculant blocks should be used, otherwise there is a risk of flowing in of non-dissolved inoculant grains with negative consequences for the cast structure.

Checking and Monitoring the Inoculation and the Inoculation Result

To avoid errors during inoculation, simply monitoring the inoculation effectiveness after pouring the casting is inadequate, i.e. it must be planned as part of the quality assurance and adapted to the individual production steps and operating conditions. The data logging and evaluation should satisfy the requirements of statistic process control. This begins as early as the choice, the incoming goods inspection and the storage of the inoculant. It also includes, for example, temperature measuring, time recording and dosing devices (e.g. periodic checking of the added inoculation amounts, control of the frequencies for vibrating channels, and the feed during wire inoculation). [5]

Various options are available to the caster for monitoring the inoculation result. These are, on the one hand, the conventional methods of evaluating casting wedge samples (depth of the chill) and the fabrication of metallographic ground samples (graphite and structural formation, number of eutectic grains, number of nodules). On the other hand, thermal analysis systems are nowadays available, which besides the representation of the cooling curve, also provide further evaluation options for assessing the inoculation result.

References

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[4] K. Reifferscheid: Gießerei Praxis (1973) Issue 22/November, pp. 393-398

[5] VDG Information Sheet p. 210 “Impfen von Gusseisenschmelzen”

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