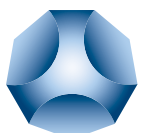Authors: Werner Maschke and Dr. Manfred Jonuleit

Oxygen and Sulfur – Metallurgical Partners in Cast Iron Melts

Technical Paper

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Introduction

The aim of every foundry operation is to produce castings in good quality in small or large series.

This is achieved by specifying individual process steps for melting and casting iron alloys precisely and performing this in a reproducible way. The better this succeeds in representing the initial state of an iron melt reproducibly (target value), the less the melt (actual value) will have to be treated or the less the treatments of the melt will have to be varied.

It is tried-and-tested practice to treat the iron melt with FeSi based alloys – the actual state of a melt is adapted to the target value by what is known as "magnesium treatment," by inoculation and possibly also by a preconditioning of the iron.

The dissolved and total oxygen contents change during the melting of a cast iron batch in the induction furnace **(Fig. 1) [1] [2]**. Oxygen and sulfur are needed to attain a carbide-free casting during the melt treatment with FeSi alloys.

Three treatment steps have proven effective in practice. These individual steps are performed in a chronological sequence, separately from one another and coordinated to one another:

- Preconditioning
- Magnesium treatment
- Inoculation

Preconditioning

The aims of preconditioning are:

- Setting a low content of dissolved oxygen in the melt

- Binding the sulfur in the melt to the cerium as a component of the lanthanides

Cerium compounds

The addition of cerium – in the form of a treatment agent VL (Ce) 2 – leads to the formation of thermodynamically stable sulfides and oxides. This becomes clear through the solubility products (K at 1600 °C) [3]:

CeS	2.5×10^{-5}
Ce_2O_3	1.0×10^{-17}
Ce_2O_2S	1.1×10^{-20}

These cerium compounds are stable in the temperature range around 1500 °C. They are very fine (Ø 1–3 µm), spherical and remain evenly distributed in the iron melt owing to their high specific weight (approx. 6.5 g/cm³). Ce-O-S compounds consequently boost heterogeneous nucleation catalysis and are demonstrated as "nuclei" in the graphite.

A second aspect of preconditioning with cerium is that a formation of MgO and MgS – these representing components of the casting defect "dross" [4] – is reduced by binding oxygen and sulfur before the magnesium treatment.

Amount of cerium added

The level of the cerium addition is calculated according to the need for neutralization of so-called interfering elements such as Ti, Pb, Bi, etc. for intermetallic compounds as well as according to the content for binding the dissolved oxygen and sulfur to cerium-oxide sulfides.

Reliable data on the content of dissolved oxygen is not usually available to the foundrymen. The literature contains values between 1 and 10 ppm. Likewise, the amount of interfering elements in the foundries is not constant, and their quality not always known.

Test operations have revealed that a cerium requirement of 0.002 to 0.006% (20–60 ppm) is sufficient. The treatment agent VL (Ce) 2 with approx. 2% cerium is used as a cerium carrier [5].

Furthermore, providing ferritic melts such as EN-GJS-400-18/-18-LT with an addition of bismuth (Bi) to VL (Ce) 2 has proven effective in practice.

Yet bismuth has the status of an interfering element and "degenerates" the nodule form of the graphite. However, bismuth in combination with cerium forms a large number of nuclei and leads to numerous "small" nodules [6].

The FeSi alloy SMW 605 with approx. 1% bismuth and approx. 0.5% cerium is used as a bismuth carrier. Additions from 0.001 to 0.002% bismuth (10–20 ppm) are sufficient for the desired effect [7].

Treatment of the iron melt with magnesium (magnesium treatment)

To allow the graphite to crystallize in nodule form, the surface tension and hence the interfacial tension between the graphite and melt must be high. Oxygen and sulfur reduce the surface tension. Deoxidation with magnesium, calcium, rare earths, etc. leads almost to a doubling of the surface tension.

Some methods of introducing the treatment agent (FeSiMg, NiMg or pure Mg) into the iron melt have become established in practice. The most frequently applied methods are currently

Sandwich	(FeSiMg e.g. VL 53, VL 63)
Cored wire	(FeSiMg / Mg and mixtures)
Converter	(Pure Mg)
Flowtret, Inmould	(FeSiMg e.g. Noduloy 3, VL 7)
Open ladle	(NiMg e.g. VL1, VL4 or FeSiMg e.g. VL53, VL63)

## Material conversion of the magnesium

Magnesium is transformed via a liquid phase into a gaseous phase in the iron melt at approx. 1500 °C. An iron melt temperature of 1500°C energes a considerable magnesium vapor pressure of 10 atm and explains why the majority of the magnesium provided is lost through evaporation at the bath surface. Only **a small partial amount** of the magnesium is dissolved from the iron melt.

The temperature-dependent decrease in the dissolved magne sium is referred to as "fading." Depending on the prevalent boundary conditions, the magnesium decrease is 0.001 to 0.005% Mg/min.

A **further partial amount** of the magnesium supplied leads to the formation of a reaction slag due to deoxidation **(Fig. 1)**, which contains differing constituent amounts of MgO, SiO_2, CaO and FeO, depending on the treatment agent.

Fig. 1: Progression of the oxide content, the temperature and the number of eutectic cells during melting of iron in an induction furnace (NFI) **[2].**
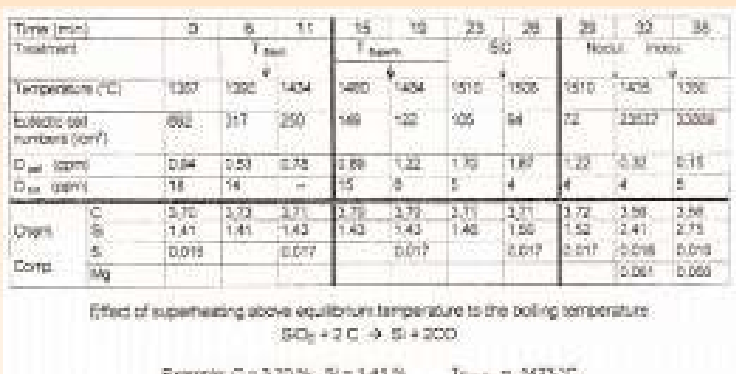
These reaction products are – aided by the turbulence of the melt – flushed onto the bath surface during the magnesium treatment and extracted from there later on.

The separation of the reaction products can be accelerated by an FeSiMg alloy mixed with flux – Dispersit. Finally, a further partial amount of the magnesium supplied rises "unused" as a vapor bubble through the iron melt and reaction slag and combusts with the atmospheric oxygen.

The following therefore applies for the material conversion of the magnesium during the magnesium treatment*:

$<Mg>$	➜	$[Mg]$	➜	$\{Mg\}$	(1a)
$[Mg]$	➜	(MgO)		(Reaction slag)	(1b)
$\{Mg\}Melt$	➜	$\{Mg\}Slag + \{O_2\}Air$	➜	$\{MgO\}Smoke$	(1c)

*) [x] Material x – dissolved in the metal bath   (x) Material x – dissolved in the slag
   {x} Material x – in gaseous state   <x> Solid material x

Reactions of the magnesium with sulfur

The introduced magnesium naturally also reacts with sulfur, the material conversion magnesium-sulfur occurring completely in the iron melt according to

$$[Mg] + [S] \quad ➜ \quad [MgS] \qquad (2a)$$

with partial amounts of the formed magnesium sulfide remaining in the iron melt or being transferred into the slag:

$$[MgS]Melt \quad ➜ \quad (MgS)Slag \qquad (2b)$$

The transfer of the magnesium sulfide from the metal phase into the slag phase is incomplete despite its low density of 2.6 g/cm^3, as analysis results reveal.

This leads to the question of quantitative evaluation of the magnesium sulfide remaining in the melt. If we assume for the "residual sulfur contents" determined with spectral analysis in an analysis sample, a reaction progression as defined by equation 2a, a stoichiometrically equivalent magnesium sulfide content can be assigned to these residual contents according to

S total   ~   MgS equivalent

The depletion of the sulfur is taken into account when determining the magnesium requirement for a magnesium treatment via the formula:
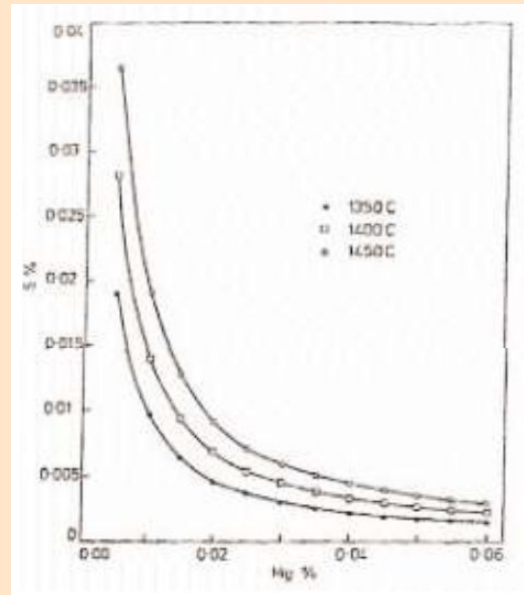
1 part by weight S binds 0.76 part by weight Mg, or
1 part by weight Mg binds 1.32 parts by weight S.

Solubility of magnesium and sulfur

The solubility of magnesium and sulfur in the melt depends on the temperature and is described by the solubility product

$$K (T°K) = [\% \text{ Mg}] \times [\% \text{ S}]$$

Fig. 2: Solubility hyperbolas % [Mg] x [S] = const. at 1350, 1400 and 1450 °C according to [8]

The solubility product for a carbon-saturated iron melt is according to **[8] [9] [10]**

$$K = [\% \text{ Mg}] \times [\%\text{S}] = - 1.3 \times 10^{-3} + 8.6 \times 10^{-7} \times t \text{ [°K]}$$

According to this equation, the K values can be derived for the following temperatures as:

K   1500 °C 22.5 x 10^{-5}
K   1371 °C 11.4 x 10^{-5}
K   1315 °C 6.6 x 10^{-5}
K   1250 °C 1.0 x 10^{-5}

The numerical values verify that the dissolved magnesium and dissolved sulfur are precipitated out again as magnesium sulfide as the temperature of the iron melt falls and are still fully present in suspended form in the melt as magnesium sulfide at 1250 °C.

Magnesium sulfide in the melt

The content of suspended magnesium sulfide in the iron melt is calculated in a numerical example:

Before the Mg treatment   SA = 0.0117%

After the Mg treatment   SE = 0.0068%

This means that 0.0049% sulfur is bound in the slag as MgS.

Sulfur content in the MgS			0.0068%
Magnesium content in the MgS	0.76 x 0.0068	=	0.0052%
Magnesium sulfide MgS in the melt	MgS equivalent	=	0.0120%

This calculation shows that we find e.g. 120 g magnesium sulfide in a GJS melt – a large quantity, which can be reduced by a desulfurization of the base iron with CaC_2 or magnesium or by a preconditioning of the melt with cerium.

Reactions between the melt and air oxygen

Suspended magnesium sulfide (MgS) rises in the treated melt and reacts at the surface according to:

(MgS) + ½{O$_2$}	➜	(MgO) + (S)	(3)
(S)	➜	[S]	
[S] + [Mg]	➜	(MgS)	
(MgS)Melt	➜	(MgS)Slag	
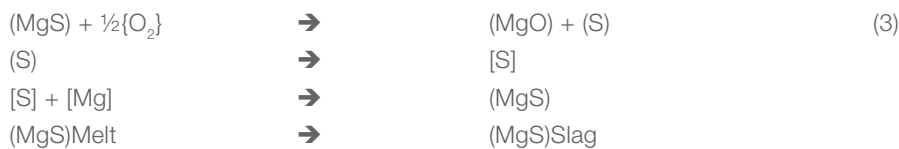
this resulting in a re-sulfurization of the melt, while the formed magnesium oxide remains in the ladle slag. If sufficient amounts of free magnesium are still present in the iron melt, magnesium sulfide will be formed again.

This will also in result in magnesium burn-off, i.e. loss of magnesium in the melt. The magnesium evaporates out of the melt according to:

|		
[Mg] + {½O$_2$}	➜	{MgO}

Reactions of magnesium with oxygen

The oxygen is present in iron melts both in dissolved form and in bound form as oxides (iron oxide, silicic acid, higher oxides) (Fig. 1). It finds its way into the iron via the charging materials, through reaction of the iron melt with the refractory materials of the melting furnaces and ladles and with the atmosphere. During melting in an induction furnace, the oxygen content of the cast iron melt can be influenced via the crucible reaction (equilibrium reaction):

Crucible reaction: $(SiO_2) + 2[C]$ ➜ $[Si] + 2\{CO\}$ (4)

Below the C/Si isotherm given for an iron melt with x %C and y %Si (equilibrium temperature), the silicon determines the dissolved amount of oxygen – solid silicic acid (SiO_2) precipitates out. Above the equilibrium temperature, carbon dominates the oxygen content of the melt; SiO_2 is reduced upon $\{CO\}$ formation [11].

Partial reactions: $[Si] + 2\,[O]$ ➜ (SiO_2)
$[C] + [O]$ ➜ $\{CO\}$
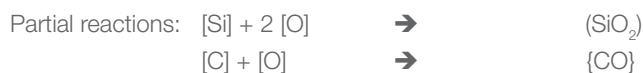
According to [2], the dissolved oxygen content in an iron melt with 3.7% C and 1.4% Si decreases below the equilibrium temperature and increases again after exceeding the equilibrium temperature with rising temperature (boiling temperature). Inverse ratios apply for the oxygen content bound as SiO_2 [11]. This situation can be verified by a decrease in the number of eutectic cells or the increased tendency towards chill, which is coupled with the decline in the nuclei necessary for graphite precipitation (Fig. 1). Regarded as a whole, however, the total oxygen content of a melt will decrease up to the temperature to be set for a magnesium treatment.

Nevertheless, in the event of an incorrect melting process, a high proportion of bound oxygen can still be present in the form of silicic acid (SiO_2). If this is the case, a slagging of the SiO_2 particles by MgO is to be expected as a result of a magnesium treatment according to:

$2(MgO)$ $+$ (SiO_2) ➜ $(2MgOSiO_2)$ (5)

The supply of MgO is inevitably given by the reaction.

$\{Mg\}$ $+$ $[\tfrac{1}{2}O_2]$ ➜ (MgO) (6)

0.2% ladle inoculation, approx. 300 nodules/mm^2, 10% comerlite, 70…80% ferrite, rest pearlite

A comparably low residual magnesium content in the GJS iron of at most 0.030% with a sulfur content of approx. 0.010% is set with such an FeSiMg alloy – VL 53 (S).

All reaction products containing silicic acid form large-area, contiguous structures that are referred to as "oxide skins" by foundry-men.

It is advantageous to have as low as possible a content of bound oxygen in the melt prepared for the magnesium treatment.

The dissolved oxygen is brought to a minimum value by a magnesium treatment; this a prerequisite for the formation of graphite in nodule form. The contents of dissolved oxygen and dissolved magnesium are inversely proportional **[12]**.

A cast iron with nodular graphite is usually evaluated via the magnesium content.

However, we can also include the oxygen activity (a_o), whereby according to **[12]** the value 10^{-7} applies as a limit value:

$a_o > 10^{-7}$ Cast iron with lamellar graphite
$a_o < 10^{-7}$ Cast iron with vermicular or nodular graphite

According to this, a higher magnesium value in the iron is a reliable guarantee of successful magnesium treatment. However, too-high magnesium contents in the iron lead to casting defects, such as the formation of ledeburite, edge hardness, increased shrink hole tendency, dross, etc.

Flanking measures – such as preconditioning with cerium in VL (Ce) 2 – which contribute towards a decrease in oxygen activity are therefore desirable.

Preconditioning of the melt with cerium and/or bismuth cannot be achieved in every foundry. To utilize the positive effect, an FeSiMg alloy with increased content of cerium has been developed – specially for the TC method (Tundish Cover):

approx. 9% Mg and approx. 3% Ce

A comparably low residual magnesium content in the GJS iron of at most 0.030% with a sulfur content of approx. 0.010% is set with such an FeSiMg alloy – VL 53 (S).

Treatment of the iron melt with FeSi alloys (inoculation)

If the limit value of the oxygen activity (ao) is not fallen below due to a magnesium treatment of the iron, this can be attained with an inoculant through the subsequent deoxidation **[13]**. Here the inoculation method or the inoculation alloy that guarantees a high number of spheres or nodule density with high reproducibility is most advantageous **[13]**. Inoculation in the mold is preferable to inoculation in the pouring stream or even in the ladle **[20]**.

Treatment of iron melts – techniques

We do not intend to describe or discuss the numerous process variants at this point. Reference will only be made to fundamentals – also in conjunction with the three metallurgical steps

Preconditioning
Magnesium treatment
Inoculation

Complete dissolution of the treatment agent in the iron melt is crucial for the success of an FeSi or Mg addition. The alloy yield must be reproducible and as high as possible for reasons of cost.

With the cored wire treating method **(Fig. 3) [14] [15] [16]**, a necessary amount of alloy is added to an iron melt defined by amount, temperature, and sulfur and cerium content.

The feeding speed ensures that the cored wire only releases its powder content (magnesium, FeSi alloy, other) as deep as possible in the iron melt. These released particles then only have a short time to dissolve or melt on their way to the bath surface.

Nowadays, the cored wire technology is used for magnesium treatment of the iron as well as for inoculation in the ladle and in the pouring stream. For cost reasons, the alloy is added to the iron stream when filling the treatment ladle for preconditioning the melt.

The most reliable inoculation method with the greatest inoculation effect – due to the chemical analysis of the inoculation alloy and the fusing characteristics – is inoculation in the mold **[14] [17] [18] [19]**. Nevertheless, this presupposes that the runner and gating system is set up for the process of mold inoculation **(Fig. 4+5) [20].** Every individual casting undergoes an equally good inoculation treatment with this method.

We should not fail to mention that the significant deoxidation of a mold inoculation allows a comparably low residual magnesium content in the iron melt.
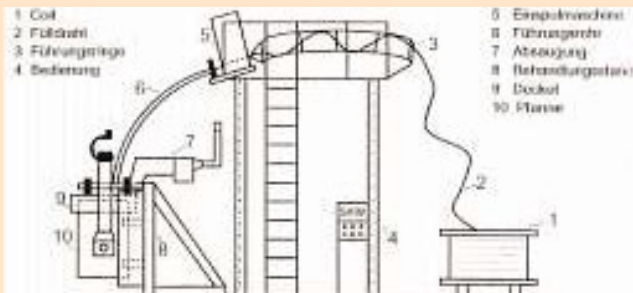
Fig. 3: Wire treatment (schematic) [20]

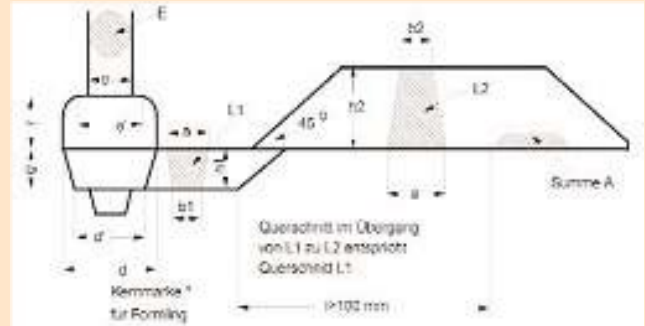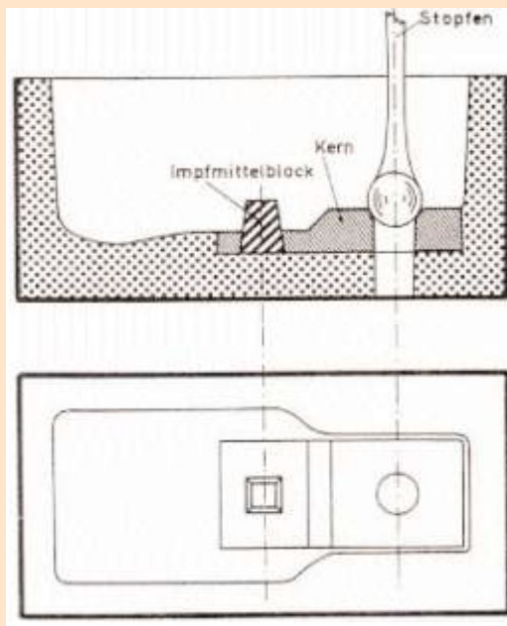Fig. 4: Gating system for the mold inoculation of machine-molded castings (without filter) [20]

Fig. 5: Mold inoculation block in the casting box for medium and large castings [20]

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Summary

The treatment of iron melts with the aim of producing Compact Graphite and Ductile Iron with FeSi and FeSiMg alloys or treatment agents is associated with a deoxidation of the iron melt. A three-stage metallurgical treatment of the iron melt is proposed:

- Preconditioning with cerium
- Magnesium treatment with FeSiMg alloys using wire
- Inoculation of the treated iron melt in the mold with a highly effective special alloy (FeSiAlCa)

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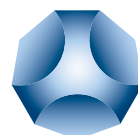
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