Some Metallurgical Aspects of Producing Ductile Iron and Holding Treated Metal

I. Henych
George Fischer Ltd.
Schaffhausen, SWITZERLAND

INTRODUCTION
The foundry industry is more and more exposed to a strongly increasing demand for improving environmental and working conditions and for increasing casting quality. This demand comes with a reduced acceptance of the customers to honor it by higher casting prices. Therefore, the need for mechanization and automation of foundry procedures is steadily increasing.

Because of continuously growing ductile iron production and growing international competition at decreasing margins between costs and realized prices, it became more and more important for ductile iron foundries to take cost reducing technological measures into consideration. One of these technological means which—aside from economical effectiveness—strongly influences casting quality is automatic pouring of treated nodular iron melt. This technology, developed in the last ten-year period, offers economical as well as metallurgical advantages to foundrymen.

AUTOMATIC POURING OF TREATED MELT
The successful automatic pouring technology provides solving of two main process areas:

• Holding of treated ductile iron melt for long time period.
• Automation of pouring process.

Holding of treated iron has been connected with specific problems as:

• Fading of magnesium in the melt.
• Slag deposits in holding furnace cavities as well as slag inclusions on components of pouring devices as stoppers, intermediate ladles, etc.

Extensive practical experiences show that automatic pouring can only be successfully operated in complex systems which include—besides such suitable equipment as an inert gas-operated channel holding/pouring furnace—a suitable magnesium treatment technology and observe some more points of metallurgical technology.

Economical Effects

• Reduction of personnel for handling of melt and pouring.
• Improvement of casting yield up to 7% (no ladle returns, etc.).
• Reduction of tapping temperature, saving of energy, refractories, etc.
• Reduction of magnesium consumption for treatment.
• Reduction of foundry rejects, optimum pouring temperature, optimum magnesium content, clean melt, etc.

Metallurgical Effects

• High constancy of pouring temperature.
• Optimum magnesium content for all castings.
• Coagulation and separation of dispersed reaction products.
• Homogenization of the treated melt in the holding-pouring furnace.

Pouring
Besides other metallurgical procedures such as making a suitable material charge, obtaining the required chemical composition of iron, etc., magnesium treatment and handling and pouring of treated iron are the most important steps to a successful production of high quality ductile iron castings.

Pouring Temperature
The pouring temperature should be low from the point of nodule count, shrinkage, relation between volume of liquid metal and casting, thermal stress of sand and refractories. From the point of fluidity, dross formation, surface defects like cold shots and incoagulation, however, the temperature should be higher.

More important for the quality of castings, as practice shows, is the critical initial temperature for the formation of magnesium silicate dross which is on the order of 2600F (1426C). As a compromise, pouring temperature is determined to be not below 2530F (1390C).

Magnesium Contents
The magnesium in ductile iron is not to be considered an alloying element. Magnesium makes it possible to influence the shape of graphite. It is to be kept just as high as absolutely necessary for obtaining a sufficient nodularity. Due to the accuracy of spectrometer analysis the Mg-level can vary from foundry to foundry (Fig. 1).

Too high a magnesium content increases the tendency to porosity, carbidic formation during solidification, and magnesium silicate dross formation, as well as decrease of nodule count in the castings. There are also indications that increasing Mg contents supports blow formation (pinholes).

Transfer of Treated Melt
Each transfer of treated iron from one ladle to another results in temperature loss of 18–40F (10–20C), also in loss of magnesium. The Mg loss is usually between 0.007–0.010% per transfer.

The iron stream and the turbulence during transfer (as well as during pouring) cause an intensive contact of the iron with air oxygen which results in oxidation of Mg.

The reaction products are MgO and possibly Mg silicates (MgO-SiO2, Mg2SiO4, Mg5SiO8). Besides the economical aspect of Mg and temperature losses, the reaction products could also generate casting defects. The agitation of melt in the holding furnace or pouring spout has a similar effect to melt transfer from one ladle to the other.

The magnesium treatment is always accompanied by intensive slag formation and slag incrustation in the treatment and transfer ladles. This slag contributes to oxidation of the melt and makes it more difficult to keep the castings free of nonmetallic inclusions.
Magnesium Treatment

To obtain nodular shape of graphite, it is necessary to treat the iron with certain elements like Mg, Ba, Ce or Ca. Magnesium is normally used for the industrial production.

Introduction of Metallic Mg to the Melt

At 1.74 g/cm³ the density of magnesium is much lower than that of molten iron. Having a boiling point of 2016°F (1102°C), and a density which is much below that of molten iron, the vapor pressure of the magnesium is about 10 bar at 2696°F (1480°C), which is the normal treatment temperature of the iron (Fig. 2). In the vast majority of cases the magnesium is added to the melt in the form of master alloys. The vapor pressure is then reduced in proportion to the dilution of magnesium share so that a simple and safe treatment operation becomes possible.

The use of master alloys results in an introduction of other elements such as silicon, nickel and possibly also aluminum into the melt being treated, so the range of possible applications of these alloys is limited. The use of silicon-based master alloys for the purpose of automatic pouring and holding of magnesium treated melt proved to be unsuitable. This is because of treatment slag characteristic, the impossibility of overtreating the ductile iron melt for corrections of Mg residual content of the held melt as well as due to the low desulfurization rate of master alloys.

Master alloys make it necessary for the base iron melts to have a low sulfur content, which can only be achieved by using a basic melting plant or low sulfur charging materials or by having a previous desulfurization treatment.

The experiences show that only treatment with pure magnesium makes it possible to meet the requirements of long time holding of treated ductile iron melt.

The use of pure magnesium is only possible with special equipment where the reaction of magnesium with the iron melt and the produced pressure of Mg vapor can be controlled.

The pure magnesium converter method is widely used in foundries for more than 12% of the world’s ductile iron production.
Pure Magnesium Converter Process

The reaction chamber for the controlled evaporation of the pure magnesium is the most important component of the converter vessel. The chamber is formed by a graphite-clay plate of approximately semi-circular section set into the lining of the rear part of the converter. It can be charged with magnesium lumps and, if required, other additives through a charge opening. The reaction chamber is connected with the treatment vessel via a number of holes located in different heights above the rear end of the vessel. Easy access to the reaction chamber from outside and a simple reliable chamber lock simplify and safeguard the addition of treatment agent.

The molten iron is charged with the converter in horizontal position. The lumps of magnesium are placed in the reaction chamber and the locking plunger is brought down to seal the reaction chamber opening.

The vessel is then tilted to vertical position to initiate the evaporation of the pure magnesium in the reaction chamber. During the magnesium treatment the converter spout is closed by a pneumatically operated lid. A part of the vapor generated during the treatment process escapes into the atmosphere through the vent opening in the lid.

The magnesium treatment in the vessel is carried out at atmospheric pressure. For tapping the treated metal a skimmer brick is usually fitted across the converter spout. This skimmer brick ensures that the slag generated during the treatment is retained in the converter.

By tilting the converter vessel into its vertical position, the reaction is started.

A limited amount of liquid iron, defined by the dimension of the openings in the reaction chamber wall and by the height of the iron level, flows into the reaction chamber (Fig. 4). The magnesium stored in the reaction chamber starts to vaporize and causes a vapor pressure in the reaction chamber. The increasing vapor pressure stops entering of iron through the top hole as soon as the pressure in the chamber is in accordance with the ferrostatic pressure over the top chamber hole. A certain amount of iron, however, will still enter the chamber through the lowest opening because the ferrostatic pressure there is higher. The vapor pressure further increases, such that magnesium vapor escapes through the top openings and is pressed through the iron bath, effecting an intense stirring of the melt. The supply of thermal energy still increases the pressure in the reaction chamber until a pressure equilibrium is obtained, also at the lowest opening. A further supply of iron through that opening is now no longer possible. Due to the consumption of heat by the magnesium vaporization, the temperature in the chamber becomes reduced and the pressure drops. This results in the iron starting to enter the chamber again through the lowest opening. As soon as the vapor pressure in the chamber is higher than the ferrostatic pressure at the lowest opening, the iron flows back through that opening; simultaneously the vapor escapes through the top hole until pressure equilibrium is again adjusted due to the reduced amount of heat.
converter vessel is equal to atmospheric pressure. Because of this self-regulating pressure relation, a nearly constant amount of magnesium vapor per time unit will permeate through the melt during the entire vaporization period. Thereby, the produced vapor is absorbed largely by the melt and effects a vigorous stirring of the melt resulting in an excellent separation of the reaction products.

As a result of the high affinity of magnesium for oxygen and sulfur, some of the introduced magnesium reacts with oxygen

$$2 \text{ Mg } + \text{ O}_2 = 2 \text{ MgO}$$

and sulfur

$$2 \text{ Mg } + \text{ S}_2 = 2 \text{ MgS}$$

The magnesium sulfides and oxides pass into the slag or escape into the atmosphere. The oxygen content of the molten cast iron is so low that the magnesium consumption for deoxidation can be neglected. The iron is first desulfurized to approximately 0.02% S, then it starts to pick up magnesium (Fig. 6).

The magnesium addition required for desulfurization and adjustment of the necessary residual magnesium content in the iron is calculated by the formula

$$\text{Mg}_{\text{Z}} = [(\text{S}_{\text{A}} - \text{S}_{\text{B}}) \times 0.76 + \text{Mg}_{\text{R}} / \text{Mg}_{\text{A}}] \times 100 \%$$

where $\text{Mg}_{\text{Z}} = \text{Mg} \%$ magnesium addition in 

$\text{Mg}_{\text{R}} = \text{Residual magnesium content required} \%$

$\text{Mg}_{\text{A}} = \text{Mg} \%$ recovery, see Fig. 5

The design of the converter vessel is responsible for very low temperature losses during the treatment (Fig. 7). The temperature drop, associated with carburization, is approximately 5°F (3°C) per 0.1% C addition (Fig. 8).

Fig. 5. Pressure and temperature relation in the reaction chamber of the converter.

Fig. 6. Pure magnesium treatment and desulfurization.

Fig. 7. Pure magnesium addition in relation to initial sulfur contents.

Fig. 8. Temperature losses during treatment with pure magnesium converter.

AFS Transactions
Magnesium Fading

Fading of magnesium dissolved in molten iron is caused by the following reactions shown in Figure 9.

- System melt atmosphere
  Vaporization of Mg and oxidation with atmospheric oxygen
- System melt-slag-atmosphere
  Dissolved oxygen in the slag reacts with Mg in the melt
  MgS in the slag is oxidized by atmospheric oxygen and forms MgO
  Elementary sulfur reacts with Mg dissolved in the melt
- System melt-oxides
  Mg reduces lower oxides from refractory
  Mg reduces lower oxides from slag
- System melt-refractory-pore
  Mg reacts with gas-oxygen in refractories as well as with gas-oxygen in slag inclusions
- System melt-melt
  Dissolved Mg reacts with free sulfur and oxides present in the melt

System Melt-Atmosphere

The vapor pressure of Mg above bath surface, even at the usual low Mg concentration for ductile iron can reach 480 torr (Fig. 10).

At atmospheric conditions Mg vapor escapes from the melt and becomes oxidized by air oxygen to MgO which escapes partly as microscopic MgO particles in the atmosphere or is bound in the slag. In case of having an inert gas atmosphere in a closed system like a holding furnace, the gas pressure must be at least as high as the partial pressure of Mg vapor. In practice, due to leakages in the system and the necessary variations of gas pressure in the pouring furnace some additional Mg losses due to vaporization are to be taken into consideration.

![Fig. 9. Magnesium reaction of Mg fading.](image)

![Fig. 10. Magnesium vapor pressure in treated ductile iron.](image)

![Fig. 11. Free energy for the reaction of one mole Mg.](image)
in both investigated slag systems, the probability of forming compounds (Fig. 17) in this ternary system is rather high. The master alloy slag will probably form nearly eutectic low melting olivine with a melting point of 2820°F (1550°C). But pure magnesium treatment slag forms magnesiowustite with a melting point of approximately 3500°F (1930°C).

**System SiO$_2$-MgO-CaO-Al$_2$O$_3$**

Because of the chemical composition this system is relevant for pure magnesium treatment only. The investigation shows that possible compounds remain in the area of high melting materials even when considering more complex systems (Fig. 18). In this case or compound of 2CaO-SiO$_2$ can be expected. The melting temperature of the possible products lies between 3542 and 3812°F (1950-2100°C).

### Slag Problems in Holding Furnace

The slag incrustations inside of furnace cavities (especially in inlets and outlets, as well as in inductor channels) have been—besides Mg fading—the serious hindrance for using this technology in the foundry. The practical experiences show that the best available solution for holding and automatic pouring of Mg treated melt is at the present time the channel-type, double-syphon, gas-pressure-operated furnace.

![Diagram](image)

*Fig. 16. Possible compositions in treatment slags in the system MgO-MnO-SiO$_2$.*
The critical areas where the slag deposits lead to operational difficulties are (Fig. 19): 1) upper part of inlet channel (4); 2) channel inlet areas (1 and 3); and 3) inductor channel mouth (2).

**Upper Part of Inlet Channel**
Due to the turbulences oxides are formed in the funnel of inlet channel during filling into the furnace. Part of these oxides, as well as dispersed treatment slag, coagulate and build slag deposits in the upper part of the inlet channel. This slag incrustation can be easily removed and does not cause serious problems in operation.

**Channel Inlet Areas**
Slag deposits can be caused by changing speed of filling stream, lining and certain turbulences in the inlet area as well. The decreasing stream speed and possibly turbulences support the coagulation of dispersed slag. The coagulated slag particles are transported to the channel inlet lining where they become stuck.

It is obvious that low melting glass-like acid slag tends more to this effect than high basic, high melting slag. The experiences show that it is possible to keep the furnace in operation for three and more months without major cleaning of furnace cavities, provided that the melt is treated with pure magnesium. The weekly skimming of the melt surface in the furnace is necessary to remove approximately 80 grams of slag per one metric tonne of the iron processed.

FeSiMg treated iron requires extensive cleaning of furnace cavities every few days.

**Induction Channel**
Similar to the critical areas described above, the agitation of the melt in the area of induction channel mouth causes coagulation of dispersed slag and slag deposits. Due to the temperature increase (Fig. 20) in the induction channel—which can reach 180–360°F (100–200°C)—the low melting components of the slag are being melted or nearly melted. Such consistency of slag supports the formation of slag deposits in the induction channel area. The operational experiences show that this problem is especially severe in the case of master alloy treated melts and almost not known for pure magnesium treated melts.

![Figure 17. Possible compositions in treatment slags in the system Fe$_2$O$_3$-MgO-SiO$_2$.](image)

<table>
<thead>
<tr>
<th>Treatment Fe Si Mg 6%</th>
<th>Converter</th>
</tr>
</thead>
<tbody>
<tr>
<td>S (Init.) = 0.015%</td>
<td>S (Init.) = 0.08%</td>
</tr>
<tr>
<td>(Final) = 0.010%</td>
<td>(Final) = 0.005%</td>
</tr>
<tr>
<td>SiO$_2$ = 30.2%</td>
<td>17%</td>
</tr>
<tr>
<td>MgO = 25.35%</td>
<td>42.9%</td>
</tr>
<tr>
<td>CaO = 0.001%</td>
<td>0.56%</td>
</tr>
<tr>
<td>MnO = 1.4%</td>
<td>2.6%</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ = 36%</td>
<td>14%</td>
</tr>
<tr>
<td>Al$_2$O$_3$ = 6.8%</td>
<td>5.94%</td>
</tr>
<tr>
<td>S = 0.06%</td>
<td>17%</td>
</tr>
<tr>
<td>TiO$_2$ = 0.17%</td>
<td>—</td>
</tr>
<tr>
<td>Basicity = 0.84</td>
<td>Basicity 2.56</td>
</tr>
</tbody>
</table>

**Transformed to Fe$_2$O$_3$-MgO-SiO$_2$ System**

<table>
<thead>
<tr>
<th>Fe Si Mg</th>
<th>Converter</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO = 27.7%</td>
<td>58%</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ = 39.3%</td>
<td>19%</td>
</tr>
<tr>
<td>SiO$_2$ = 33%</td>
<td>23%</td>
</tr>
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</table>

**Melting Point of Compounds**

- 1550°C
- 1930°C
- 2820°F
- 3500°F
SiO₂ - MgO - CaO - Al₂O₃ (5%) 

The practical experiences in operation show that successful automatic pouring is only possible when suitable equipment and a suitable magnesium treatment method are used. The magnesium treatment with pure magnesium converter process in combination with channel-type holding and pouring furnace is in operation in 17 foundries all over the world. The experiences show that this system makes it possible to reduce the above-discussed problems to a minimum.

The moderate tendency to fading, high basic and high melting dry treatment slag generate essentially less problems than glass-like acid treatment slag produced during FeSiMg treatment.

Furthermore, the system makes it possible to overheat the nodular iron melt if necessary for correction of magnesium in the holding furnace without raising the silicon content.

The converter process enables one to obtain considerable economical benefits due to an essential reduction of magnesium treatment costs, reduction of personnel, reduction of foundry rejects, improvement of casting yield, as well as due to the long life

**Typical Content**

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>42.9%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>17%</td>
</tr>
<tr>
<td>CaO</td>
<td>0.56%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.94%</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>14%</td>
</tr>
<tr>
<td>MnO</td>
<td>2.6%</td>
</tr>
<tr>
<td>S (MgS)</td>
<td>17%</td>
</tr>
<tr>
<td>Basicity</td>
<td>2.65</td>
</tr>
</tbody>
</table>

**Transformed to CaO-SiO₂-Al₂O₃-MgO System:**

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>64.6%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>25%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.9%</td>
</tr>
<tr>
<td>CaO</td>
<td>0.8%</td>
</tr>
</tbody>
</table>

**Melting Point of Possible Products:**

1950°C - 2100°C
3542°F - 3812°F

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*Fig. 16. Possible composites in treatment slags in the system SiO₂-MgO-CaO-Al₂O₃.*
of refractories in the holding furnace and converter vessel. Service life of refractories of one to two years can be expected for the furnace itself and one year for the inductor channel.

In the ten years that the system has been in use, it has become state of the art in the foundry industry and offers many technological and economical benefits to foundrymen.

SUMMARY
The automatic pouring system meets the contemporary need for improvement of environmental and working conditions as well as the demand for improvement of casting quality and cost-saving foundry technology. The technology makes it possible to:

- Reduce the personnel.
- Improve casting yield.
- Reduce tapping temperature.
- Reduce magnesium consumption.
- Reduce foundry rejects.
- Improve control of the technological parameters of pouring through high consistancy of pouring temperature, optimum magnesium contents, separation of dispersed reaction products, etc.

Because of the slag characteristics, high desulfurization rate and cleanliness of treated melt the pure magnesium converter process in combination with inert gas-operated channel-type holding-pouring furnace with double siphon proved to be an optimum solution. This system works successfully in 17 foundries all over the world.

Due to the high acidity (basicity approximately 0.84) of treatment slag, low desulfurization rate, high nucleus count the treatment with silicon based master alloys proved to be less suitable for long time holding and automatic pouring. The tendency to magnesium fading, considerable problems with slag deposits in the furnace, and difficulties by corrections of magnesium contents by overtreatment generates serious problems in operation.

The investigation of metallurgical parameters shows that the automatic pouring has to be considered as a metallurgical system which consists of magnesium treatment, long time holding and automatic pouring of magnesium treated melt. The automatic pouring device itself shall respect all the metallurgical demands specific for magnesium treated melt.

Fig. 19. Critical areas for slag incrustations in channel-type automatic pouring furnace.
Fig. 20. Temperature change effected in the inductor channel.