The advantages of a Well Designed MgFeSi Treatment Alloy in Ductile Iron and the Growth of Pure La MgFeSi in the Americas.

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ABSTRACT

MgFeSi was recognized many decades ago as an excellent material to introduce Mg into the cast iron melt. One advantage is that MgFeSi offered the possibility to add Mg resulting in a quieter reaction with higher recovery rates than pure Mg addition methods and cored wire methods, also considered to be pure Mg.

One of the main goals with MgFeSi treatments is to minimize the overall addition of Mg to tight reproducible low levels and to reduce the shrinkage tendency and slag defects observed with high final Mg levels. This can be achieved through a combination of optimization of MgFeSi composition, improved ladle design and cover material, automation of the treatment process and use of thermal analysis as process control tools. When developing the correct alloy for a foundry, the goal is to achieve an overall treatment that will reduce fume and flare, slag generation, maximize Mg recovery and minimize the need for subsequent inoculation. The advantages of this optimized process over other treatment methods is compared.

Pure La MgFeSi has been used as an in mold alloy for about 40 years, but the use as a ladle alloy has only occurred in the last 15 years. The growth of MgFeSi alloys containing pure La has grown due to a unique nodule size distribution that reduces shrinkage and overall need for less RE. With an optimized nodule count at significantly lower overall additions than mischmetal, the cost of using MgFeSi alloyed with pure La has become an additional cost advantage.

Keywords: ductile iron, Mg-treatment, MgFeSi-alloys, optimized recovery, pure La MgFeSi, improved microstructure, less porosity

INTRODUCTION

The competition to develop alternative alloys for use in iron in the 1940’s, resulted in the accidental discovery of nodular graphite structure by Henton Morrogh at BCIRA, and Keith Mills at International Nickel. It was the production method of Keith Millis et. al initially tested in the early 40’s, patent granted in 1949 using Magnesium to obtain spheroidal graphite, later referred to as Ductile Iron, which became the commercially viable production method.

Since 1948, additional research has shown that several other elements are capable of making ductile iron. However, Mg remains the main element added to the melt to tie up S and O, allowing the graphite to grow as spheres instead of flakes. To this day Mg remains a cost effective and preferred nodularizing element. With the advent of lower S Ductile Iron production the need for desulphurizing using high levels of Mg has been reduced. Furthermore, there are many different ways of adding Mg-sources, each having its own efficiencies. Figure 1, is a general overview of various Mg treatment...
processes, from pure Mg methods to MgFeSi in the mold. Each axis identifies process efficiencies described by Magnesium Recovery, Violence of Reaction, Fume and Slag formation and Inoculation effects.  

![Process Efficiency Diagram]

Fig. 1. Comparisons for Mg Treatment Process Efficiencies. 

Adding Magnesium to iron creates challenges for the foundry men due to its lower density than iron, limited solubility in cast iron, a boiling point below the freezing point of cast iron, and a vapor pressure above 1 atmosphere as seen in Fig. 2 for temperatures relevant for production of ductile cast iron. This means that methods of Mg addition that use a high Mg content generally result in a more violent reaction and lower Mg recovery as was identified on Figure 1.

![Fig. 2. Relationship between temperature and vapor pressure of pure magnesium.]

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This more violent reaction results in more fumes that by today’s environmental standards, must be contained in separate, specially designed fume collection cabinets and systems. These systems can be elaborate and expensive compared to a quieter, more efficient MgFeSi reaction that uses existing fume collection capacity built into most melting furnaces. The violence of the higher Mg reactions can also have a negative effect on iron quality due to the lack of nucleation by destruction or removal of essential primary and secondary products. Without complex nuclei formed during treatment, the graphite structure and shrinkage tendency of the iron will be negatively influenced. This is one of the
main advantages of lower Mg containing MgFeSi alloys as identified in Figure 1, as Inoculation effect efficiency.

EVOLUTION OF MGFESI TREATMENT METHOD

The development of the basic slag cupola made it possible to melt a low S base iron. Furthermore, the need at many locations to return to higher production rates eventually led to the development of the continuous desulfurization processes. Nitrogen gas stirring via porous plugs was developed. Calcium carbide, and eventually lime-fluorspar desulfurizing reagents were used.

Simultaneously, induction melting and holding furnaces were becoming more cost effective and provided a flexible melting arrangement very suitable for production of ductile iron. Access to charge materials with low sulphur levels also made it possible to make base iron for ductile iron production with S-level, below 0.02wt%. Today 0.01wt% base S is common with foundries being cautious to avoid S levels well below this level due to nucleation issues and a propensity for iron carbide formation. In fact it was discovered that Nuclei changes, as base S decreases the effective nucleus type shifted from a mostly round (Mg, Ca) S particles to a polygon (MgSiAl) N particle.

As the production and demand of ductile iron increased the need to find consistent and cost efficient production processes continued. Two directions have evolved to accommodate this need. One focuses on making a cost effective treatment process by introducing a low amount of pure magnesium or high magnesium containing master alloys. The other direction looked at developing a cost efficient way through introducing dilute magnesium alloys to get a calm reaction and reduce the negative impact of high residual magnesium content on shrinkage tendency and carbide formation. Treatments methods representing the direction of minimizing the addition of magnesium are ladle treatment and in mould treatment.

Since the start of ductile iron production the simple ladle treatment has undergone various developments. All of them aiming at improving the yield and consistency of the treatment and thus favoring adding as little magnesium as possible. This started with the master alloy added to the bottom of the ladle and iron poured over. Recovery improvements were made with the addition of alloy pockets to contain the MgFeSi alloy and with cover materials to delay the start of the Mg reaction until more iron could be added. The introduction of the thermal efficient tundish treatment ladle allowed the treatment to be conducted at considerably lower temperatures, with a substantial reduction in MgFeSi usage. An overview of these principle ladle treatments types can be seen in Fig.3.

![Fig. 3. Overview of the most common ladle treatments; pour over, Sandwich Cover and Tundish Cover](image-url)
Mg Fade was recognized early as a problem as shown in Fig 4. In the mould nodularizing treatment represents a solution to this problem. This method was invented by C.M. Dunks in 1977\textsuperscript{12}. Here the treatment is made in a dedicated reaction chamber in the mould thus making each mould a separate treatment. This way of treatment offered the advantage of eliminating the fading effect allowing a minimum of magnesium to be added and eliminating the need for subsequent inoculation due to the extraordinary resistance to carbide formation. The process demanded that pouring times be highly consistent, which led to ongoing developments with automatic pouring. With slag formation inside the mold, filters were introduced to the iron foundry industry that had previously been used in steel casting manufacture.

The in the mould nodularizing treatment represents the ultimate optimization when it comes to minimum alloy usage due to, treatment at the lowest possible temperature with maximum recovery and avoidance of any subsequent inoculation. In the mould nodularizing treatment also provided a ductile iron with very low shrinkage and carbide tendency.\textsuperscript{13}

As a method it is suitable for cast iron foundries making large series of the same casting as it requires some set up work to design the gating system which includes alloy pockets. In mould treatment also has the further advantages of avoiding the very high cost of purchasing and operating a dust collector system, avoids the high maintenance costs of holding treated iron in a holding furnace.

**WHY MGFESI MASTER ALLOY?\textsuperscript{6}**

Magnesium was found to be soluble in metals like nickel, copper and silicon. Since the treatment method at that time involved adding the alloy to the top of the melt, it was an advantage to have an alloy with similar or higher density than the molten cast iron to facilitate that the magnesium would be submerged in the melt prior to reacting. The development of MgFeSi provided an alloy system with density lower than the NiMg alloys, but significantly higher than pure magnesium metal. Magnesium is soluble in liquid FeSi and forms stable magnesium-rich phases with silicon upon solidification, which are trapped between the normal phases in FeSi. When added to the molten iron, these phases release more slowly in small doses into the iron, greatly reducing the violence of the reaction.
To be suitable as a carrier alloy for Mg into ductile iron, FeSi alloy should ideally have a high density, a low melting point, ample Si to provide a high Mg recovery into the MgFeSi and subsequently into the iron, and low cost. Looking at the phase diagram for FeSi in Fig. 5 there are compositions which could be suitable for production of MgFeSi. High Si content (75% FeSi) allows high Mg contents but the alloys are very violent when added to iron and are more costly than lower Si alloys. At 20wt% silicon, Mg additions are extremely violent with low recovery. As a result, the composition with around 50wt% silicon is the preferred and most common.

Fig. 5. Phase diagram of FeSi indicating common composition for production of MgFeSi in green and inoculants in blue.

The early MgFeSi master alloys contained around 10wt% Mg, but it was soon discovered that the recovery could be improved when the Mg-content was decreased to around 5wt%. At treatment temperature of 1450°C the vapor pressure of a 5wt% Mg-containing MgFeSi would be less than 1 atmosphere while for a 10wt% Mg containing MgFeSi would be around 1.5 atmosphere.

For a sandwich treatment process this change from 10wt% Mg to 5wt% Mg in the MgFeSi could provide a 50% improvement in Mg-recovery as indicated by Fig. 6. Of even more importance was the ability to control final Mg levels with less variation.

Fig. 6. Comparison of Mg-recovery for 5% containing versus 10% containing MgFeSi at different treatment temperatures.
INTRODUCTION OF CALCIUM IN MGFESI

Calcium was later added to MgFeSi to decrease reaction and reduce the boiling and loss of magnesium. Calcium was one of many elements that research later showed to have the ability to produce spheroidal graphite similar to that of magnesium and cerium. Calcium has a similar strong affinity to sulfur and oxygen as magnesium, but compared to magnesium, calcium has a higher vapor pressure at the operating temperatures for production of ductile iron. By adding calcium to MgFeSi a second Mg-containing phase was introduced into the structure: CaMgSi$_2$. The presence of this phase as can be seen in Fig. 7 provided a calmer reaction and thus a positive effect on the Mg-recovery.

![Fig. 7. Overview of the typical structure and phases present in MgFeSi.]

Research showed that the calcium level should not greatly exceed 2wt% as this would inhibit the reaction between the MgFeSi and iron and potentially give undissolved MgFeSi.

INTRODUCTION OF RARE EARTHS IN MGFESI

During the discovery phase of ductile iron, rare earth elements (RE) and especially cerium, were shown to be an alternate route to produce nodular structures. Rare earth elements were later incorporated into MgFeSi. Optimized levels were shown to reduce the chance of edge carbides and increase nodule count. Importance of trace elements such as Pb, Sb, Bi, As, P and Ti were seen as crucial to control in order to make good ductile iron. Small rare earth additions to ductile iron such as via MgFeSi or NiMgRE were developed as a means to neutralize the damaging effect to the graphite structure that these elements could cause. The content of the rare earth elements in MgFeSi increased over the years as the amount of MgFeSi required for treatment declined with time.

Mischmetal (MM) and rare earth silicides became the most common types of rare earth sources used. These normally contained the elements cerium (Ce), lanthanum (La), neodymium (Nd), and praseodymium (Pr). Using the individual rare earth elements as pure metals was initially cost prohibitive. Also at that time several rare earth sources were available with different compositions. Studies made by Lalich showed that source and relationship between the various main rare earth elements to be of importance.

Introduction of calcium and rare earths to MgFeSi built in several effects into one alloy. Both calcium and the rare earth elements are strong deoxidizers and desulfurizers and support magnesium in tying up S and O allowing for reduction in the magnesium content needed to neutralize S and O. In addition the higher vapor pressure of both Ca and rare earth elements make it possible to work with a higher amount of iron in the treatment ladle as the reaction is calmer. A third common effect of calcium and
rare earths is the improved inoculation effect and the positive influence seen in nodule count and reduced carbide formation. A fourth effect of the rare earth elements is the ability to tie up subversive trace elements.

Thin Casting of the MgFeSi alloy was introduced to optimize yield on sizing and also to maximize the number and minimize the size of the Mg rich phases. Both effects further reduced the Mg reactivity.

INTRODUCTION OF PURE LA IN MGFESI

Over subsequent years, new applications for rare earth elements were developed in other industries, often requiring a single rare earth rather than a mixture. Demands for separation of Pr and Nd in particular as pure metals resulted in improved availability of Ce and La as a mixture or pure metals. The first use of pure La in MgFeSi dates back to the early in mold process days, where reduced shrinkage tendency was demonstrated by the introduction of pure La MgFeSi. The use of pure La in MgFeSi as a ladle application was introduced around the turn of the century and has grown to become a large proportion of the market based upon studies and industry success with reduced shrinkage tendency and improved machined surface finish. This work by Skalund\textsuperscript{25} details studies conducted during the development stages of pure La MgFeSi for ladle application. During these studies a 1.5% addition rate was used with no subsequent additional inoculant revealing that castings produced with 0.5 and 1.0% La had minimal iron carbides and porosity. In comparison these castings produced with varying amounts and type of Ce, MM RE exhibited porosity as shown in Figure 8.

![Fig 8: Shrinkage porosity in section cut through the cross bar casting for different nodularizer alloys. (a) RE-free, (b) 0.5%La, (c) 1.0%La, (d) 0.5%Ce, (e) 1.0%Ce, (f) 1.0%MM.](image-url)
The reduced amount of La metal needed in this MgFeSi also provided a cost advantage, as was particularly evident during the Global Rare Earth Supply Crisis between 2010 and 2012. Fig 9 reveals the influence of these two factors on the growth and application of pure La MgFeSi in North America.

FLEXIBLE MGFESI DESIGN FOR DIFFERENT FOUNDRY CIRCUMSTANCES

MgFeSi chemistry and size can be readily altered to suit foundry requirements. Foundries producing very thin castings that require higher tap and pouring temperatures, and are prone to carbides may consider an alloy with larger proportions of RE and Ca. Smaller ladles will normally benefit from smaller MgFeSi alloy sizing. Foundries producing very thick castings may select an MgFeSi without rare earth to avoid chunky graphite, or with low rare earth since the foundry also intends to balance the rare earth content with a known amount of tramp element such as Sb to optimize nodule count and nodule quality. Larger alloy sizes may be requested for very large ladles. A trend towards MgFeSi having a smaller top end size is evident. This type of size distribution will allow for a higher bulk density used in well-designed MgFeSi treatment pockets having an optimized shape and size. The use of clean, dense steel and/or 50% FeSi (possibly containing inoculating elements) rather than a cheap, low quality cover is also important for maximizing recovery and iron nucleation with the latter option.
CASE STUDIES WITH THE USE OF AN IMPROVED MGFESI PROCESS USING PURE LA

One important variable that influences Mg recovery and consistency is an ideal ladle fill time. A fill time that allows all or most of the iron to fill the ladle before the MgFeSi alloy starts to react, as opposed to reacting while the ladle fills is critical.

Means to achieve this are to either:

- Fill approximately ¾’s of the ladle very rapidly and back off the last ¼ to achieve the near exact tap target weight
- Altering the timing and location of the MgFeSi reaction by using a transfer ladle with a pre-measured amount of iron tapped from the furnace. The iron is then transferred to a treatment and pour ladle near the pouring area in a fraction of the time than from a furnace and with the additional benefit of a lower treatment temperature

In both cases, developing a quieter, less violent MgFeSi treatment process with a more optimal alloy pocket design and more effective cover materials will result in a delayed reaction. Taller pockets with reduced area increase the depth of cover material delaying the start of the reaction more effectively. Cover alloys based on 50% FeSi dissolve far more slowly than higher Si alloys expanding that effect. The use of FeSi materials as cover may reduce overall costs for foundry operations using Cupola melting due to far higher recovery of Si in the ladle.

The following three case studies are only a few of many examples whereby innovative technical customer support and the use of a pure La MgFeSi have been successful to either improve the existing foundry MgFeSi process or to replace a pure Mg/Cored wire process.

CASE 1: IMPROVEMENTS IN THE MgFeSi PROCESS WITH FEWER EMISSIONS USING A LOWER Mg-CONTENT

Since the conversion many years ago from 10wt% Mg MgFeSi alloys to 5wt% Mg content, there has been a further general trend for foundries to request small increases in wt% Mg in an attempt to use less alloy. However, more recently we have observed that this simply creates more fume, flare, and slag. Repeatedly, tests have been run reducing the Mg content from 5.8 to 4.6 to even 3.5 wt% Mg, without any need to add more alloy. Final Mg levels remain similar or sometimes even higher with the lower Mg content MgFeSi.

A good example of this is a foundry in the Southern US. This foundry employs an open sandwich ladle with a fairly good pocket design. They pour mostly 50-400 lbs. castings on a large inline molding machine. They were happy with the quality of the iron, but the 5.85% MgFeSi with a 1.3% addition rate produced excessive smoke emissions. The foundry tested a 4.0% Mg pure La containing MgFeSi alloy and achieved the same final Mg levels, with greater consistency, using the same addition rate. The Mg Recovery went from 56% to 76% while reducing the amount of smoke generated by an estimated 66%. They later started using a 50% FeSi based Ca/Ba alloy as cover and now run a 1.25% addition rate. Reducing emissions was the most important item for this shop, but they now also see less slag and buildup in the ladle. This foundry is very satisfied and continues to use these products successfully.
CASE 2: IMPROVEMENTS IN TREATMENT PROCESS BY CHANGING FROM MG CONVERTOR TO A PURE LA MGFESI PROCESS.\textsuperscript{26}

In 2009 a large Cupola, Disa automotive heated pressure pour foundry in southeastern US was considering changing from pure magnesium converter process to an MgFeSi process for producing ductile iron. The reasons for the interest:

- Converter too big and awkward
- Too many problems with carbides and shrink
- Pure Mg process requires massive amounts of inoculation

It was recommended for the facility to use an open top ladle with properly engineered alloy pocket in the bottom using a low %Mg MgFeSi with pure lanthanum as rare earth and a 50% FeSi with calcium and barium for the cover material. This would give a treatment process that is very efficient, low fume generation, and high quality iron (low carbide and shrink propensity).

Visits were conducted to several facilities in Europe to view current processes using open top pocket ladles using versions of the recommended alloy system. After review the foundry decided to begin running tests with the recommended system in a 10Mt ladle in 2010. Since the start of using a 4.5% Mg pure La containing MgFeSi to produce ductile iron in 2011 results have been very favorable with the foundry stating that they have the best quality iron of all foundries they bench mark.

CASE 3: IMPROVING THE IRON QUALITY BY CHANGING FROM CORED WIRE TO A PURE LAMGFESI GRADE.\textsuperscript{27}

In 2014 a foundry in the US that produces large ductile iron castings using the Cored Wire (CW) method (treatment volume ranging from 10 to 25 MT) made a decision to test ladle treatment using MgFeSi. There were a number of reasons this foundry decided to consider another treatment method:

- Reduction or elimination of shrinkage;
- Improved Mg recovery – the typical recovery when using CW was at 30-35%;
- Improved mechanical properties, specifically the Tensile Yield and Elongation;

It was recommended a pure La containing MgFeSi with 3.5% Mg (1.6% wt) using a 0.4% inoculating cover alloy (FeSi50 based alloy with 1% Ca, 1% Al and 1% Ba) be tested. Since the foundry used their usual pouring ladles with H:D ratio of around 1.2 the decision was made not to install the treatment pocket and use an additional 0.6% of slitter steel on top of MgFeSi and the cover alloy. All materials were loaded into the ladle while it was tilted at 45 degrees to better contain alloys and to minimize the area. No additional ladle inoculation was required but production molds still received standard inoculation using in-mold inserts.

The reaction during treatment was very quiet and was continuing for an additional minute after the iron tapping was complete. While the entire cored wire treatment process took close to 15 minutes, it was less than 5 minutes (including the time to de-slag the ladle) when ladle treatment process was used. The Mg recovery increased to 75-90%, while the nodule count (in a sample taken from a 75 mm Y-block) increased from 70-80 Nods/mm\textsuperscript{2} to 170-180 Nods/mm\textsuperscript{2}. Mechanical properties were also tested in a 75 mm Y-block – elongation increased 1.5-2 times.
After switching to the ladle treatment method the foundry was able to optimize the gating and risering setup on a number of parts that resulted in producing those castings shrink-free without risers. Improvements made to thermal analysis curves of FSM compared to Cored Wire are shown in figure 9.

| Cored wire.  
9 tonne treatment,  
140 metres of 30% Mg wire.  
Residual Mg 0.045%  
Mg recovery 46% |
|-----------------|
| FSM – Pure La Containing (1.6% addition, 3.5% FSM, open ladle)  
Residual Mg 0.057%  
Mg recovery 90% |

Fig.9. Thermal Analysis results FSM to CW

**AUTOMATION**

Foundries are seeking ways to remove variation from the treatment process and to improve iron quality. Many foundries have automated their FSM alloy addition and are now realizing the benefits of FSM treatment with higher levels of quality through automation as shown in Figure 10.
SUMMARY

1. MgFeSi ladle process has been used for over half a century and remains the dominant process with the highest Mg recoveries.
2. The use of Pure La only MgFeSi, launched over 10 years ago, has shown tremendous growth. The product has further improved the already superior iron nucleation properties of MgFeSi with still lower tendency for porosity over Pure Mg processes.
3. The MgFeSi process is very flexible and can be modified by the location, usage and grade of material.
   a. Lower Mg content alloys (for example, 6.0 wt% Mg down to 4.0 wt% Mg) has the potential in some processes to be a self-compensating recovery effect, whereby the % Mg recovery increases with reduced reaction violence and slag generation.
   b. Altering the timing and efficiency of the MgFeSi reaction can have a major effect on Mg recovery.
4. The advantages of a MgFeSi treatment process are extensive when compared to Cored Wire and Mg Convertor Process:
   • Faster Treatment time, less space.
   • Higher Magnesium recovery.
   • Better Nucleation / Inoculation / Casting Quality.
   • In many cases lower cost, when all factors are considered.
   • Automated solutions available.

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