Ductile Iron News

Ductile Iron Society

To Promote the production and application of ductile iron castings *Issue 2, 2001*

DIS Announces New Member

Performance Improvements for Foundries

S·S technologies THE AUTOMATION ENGINEERS

S-S Technologies specializes in minimizing operational downtime associated with project implementations. Customers benefit from tested, reliable solutions, and enjoy higher productivity and reduced operating costs.

Read the complete article on S-S Technologies

FEATURES

DEPARTMENTS

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Company Overview
S-S Technologies specializes in minimizing operational downtime associated with project implementations. Customers benefit from tested, reliable solutions, and enjoy higher productivity and reduced operating costs.

With a staff of approximately 220 industrial automation professionals, we offer more than 18 years experience in:

- Manufacturing Execution Systems (MES)
- Plant Information Management
- Packaged Software Deployment
- Simulation
- Industrial Control System (PLC, DCS, PC) Design
- Enterprise Integration
- Planning & Scheduling
- Quality Management

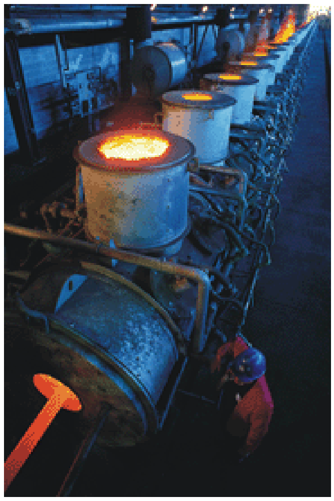
S-S Technologies has offices in Ontario, Alberta, Quebec, Michigan, New Jersey and Kentucky.

Foundry Expertise
S-S Technologies' team of automation specialists has extensive experience engineering automation solutions for Foundries across North America. Our focus is on results, and we are committed to providing the highest quality, cost-effective solutions for our clients' automation requirements. S-S Technologies' project experience encompasses the following areas:

Mold and Pour

- Molding Machine Performance Improvements
- Melt and Sand Cooling Water Control Systems
- Core Room Services Control Systems
- Casting Conveyor Systems§ Machine Performance Monitoring
- Flaskless Molding Machine Controls Upgrades

- Turntable Pneumatic to Hydraulic Conversion
- Turntable Capacity Solution



Melt Shop

- Electric Arc Furnaces

Finishing

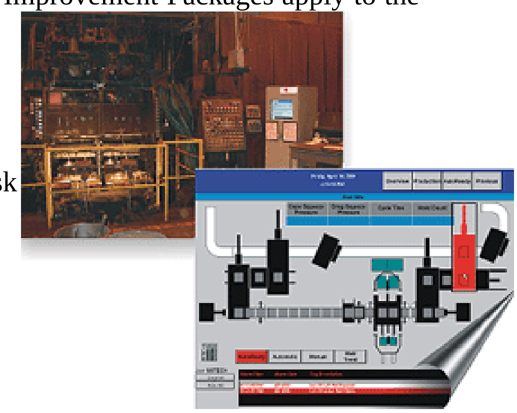
- Autogrinders
- Intake Manifold Loading
- Flexible Automation

Machining

- NC Turret Drilling and Tapping Machines
- Machining Centers

Molding Machine Performance Improvement Packages
S-S Technologies has extensive experience rebuilding foundry machines to "like new" condition. In several cases, the machine's frame was successfully strengthened, and comprehensive Electrical and Mechanical upgrades were performed.

S-S Technologies' Performance Improvement Packages apply to the following machines:



- Matchplate Molding Machines
- Cope and Drag Tight Flask Molding Machines
- Flaskless Molding Machines

With the Performance Improvement Package, our customers realize the following immediate benefits:

- Reduced Cycle Time
- Improved Uptime and Production Capacity
- Improved Mold Quality
- Advanced Diagnostics
- Mold Shift Reduction and Improved Alignment

In some cases, S-S Technologies' Performance Improvement Package includes a "Cycle-Time Improvement Guarantee" ensuring a cycle-time reduction of a minimum of 5 seconds from the fastest available time achieved before the machine upgrade.

FoundryPlus - Mold/Pour Manufacturing Execution System

S-S Technologies also offers customers the "FoundryPlus - Mold/Pour MES" solution. FoundryPlus is designed to provide foundries with up-to-date information for measuring productivity and implementing programs aimed at improving customer service, increasing production throughput and reducing operating costs.

FoundryPlus includes such modules as: Production Scheduling, Downtime Tracking, Data Acquisition and Production Reporting.

For more information on S-S Technologies and our Foundry capabilities please contact info@sstechnologies.com.

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CTIF Announcement

PRESS RELEASE

In December 2000, the **"SESAMM"** bibliographical database compiled by the Centre Technique des Industries de la Fonderie has opened up a real gateway to the foundries and metallurgy fields by going online through its Internet site (http://www.ctif.com).

For over 50 years the CTIF, the foundries' research and development center based at Sèvres near Paris has had a documentation center that is one of a kind in the foundry field. There, a team of information scientists and linguistic observers has been compiling a database specializing in foundries and metallurgy to meet the expectations of its trade members.

"SESAMM's" multi-criteria search engine will enable 33000 relevant bibliographical entries to be consulted in the fields of ferrous and non-ferrous alloys, metal molded parts, competing processes (plastic, forge..), innovations, markets, techniques and processes, and research and development. *Document title display is free of charge, but there will be a charge for consulting detailed notes (references and abstracts).* A subscription will pay for rights to access periodically published topic files that will enable subscribers to build up their own customized desk research. The other welcome feature of this database is the trilingual glossary of specialist terms (in French, English, German), which will provide a helping hand with making bibliographical searches.

SESAMM has been designed to be user-friendly and simple to use, and will be a boon to those wishing to keep abreast of technical events and find bibliographical references.

For further information :
http://www.ctif.com/version_us/html/sesamm.html

Additional information resources for the foundry industry:
The new Web site of the CTIF (http ://www.ctif.com)

At a time of great change (with the appearance of new information and communications technology) and major challenges (globalisation of trade), it is necessary for all companies, and particularly small to medium-sized businesses in the foundry industry, to be constantly adding to their information resources in order to be best able to take on their competitors.

For this reason the CTIF has undertaken a huge project using the Internet in order to boost its information and support activities for the foundry trade.

Therefore, following on from the success of its initial Web site (opened over 3 years ago), the CTIF has embarked upon a project (now almost complete) aimed at progressively bringing its various information and technical support services 'online' on a Web site that has been redesigned for the occasion. In order to be able to guarantee users of the accuracy and validity of the information supplied, the data offered online has been carefully selected by the teams of the CTIF.

For the main part of its content, the site is available in both French and

English.

Today, it can boast over 50 000 hits per week.

The main features of the site :

1- Presentation of the French foundry profession and its constituent companies

- The organisation of the foundry profession in France
  The main bodies concerned are listed, most of which are directly accessible by Internet from the CTIF site.
- Key statistical information
  The site gives most of the results achieved by the French foundry profession including overall production, world ranking and distribution of product tonnage by business sector and by market segment etc.
- The French foundries
  A database containing information on all of the French foundries makes it possible to find a company not only through its company name or geographical location but also, for those having included the type of products they manufacture, by the types of alloy produced and/or by any casting processes used.

2 - Finding a supplier for the foundry sector

A database of suppliers of materials and products for foundries makes it possible to find a supplier by entering his company name or the description of one of his products.

3 - Keeping up to date with official standards in the foundry industry

The site introduces all of the official standards for the foundry trade (with the exception of hydraulics) including references, fields of application, precedence, and any possible variations with superseded documents.

Moreover, the database makes it possible to carry out a search by the major themes of the applicable standards (for example aluminium alloy, supply and inspection, etc). The online availability of a "Standards News" service is being looked at. This service would provide information about the work and surveys currently underway.

4 - Introduction to the activities of the CTIF and the services it offers

All of the CTIF's activities are introduced, including its surveys, training opportunities, design services, laboratory-related activities, strategic planning, certification, in-house diagnosis and advice for companies, as well as quality and environment-related activities. Certain research and development results with transfer possibilities are also available.

5 - A gateway to other "foundry" resources on the Internet

A range of hypertext links enables the surfer to pass directly from the CTIF site to those of the main bodies within the French foundry industry, and also to a certain number of others (selected by the CTIF) on an international level.

*6 - Presentation of the basic technical documents distributed by **Editions Techniques des Industries de la Fonderie** (Foundry Industry Technical Publications)*

Visitors will find a database making it possible to order and pay online, and including a presentation of all of the technical documents distributed by the E.T.I.F.

7 - Presentation and downloading of technical softwares

A range of technical foundry-related softwares, designed by the CTIF and likely to be useful to companies on a day-to-day basis (including fault diagnosis, item weight calculation, burden optimisation, and calculation of feed and runner systems, etc) is available, and may be downloaded from the CTIF site to make evaluation easier.

8 - Database of translations of technical documents produced by the CTIF

Using a multi-criteria selection system, it is possible to search the library of translations produced by the CTIF to see if documents exist for a particular theme.

9 - Presentation of various certified reference materials

The chemical compositions of all of the certified reference materials (produced by the CTIF) likely to be of interest to the foundry profession are to be found here.

10 - Gateway to the documentary library of the CTIF

The creation of a gateway to the documentary library of the CTIF has been looked at. It makes it possible to directly consult the bibliographical database of the CTIF on-line, (this being one of the most extensive to be found in the foundry field).

http://www.ctif.com/version_us/html/sesamm.html

11 - Gateway to the european database related to the question of energy in foundry

The european database EUROFINE can be consulted through the CTIF website. It provides very complete information concerning the energy in the foundry field by displaying freely integral texts on different technical topics.

12 - Additional ways to contact the CTIF

The CTIF Web site offers additional means to directly contact the CTIF via electronic mail:
* Either via the central electronic mailbox of the CTIF
info@ctif.com
* Or by those of your usual contacts
xxx@ctif.com

For all further information please contact:

Alain Reynaud
CTIF - Sèvres
e-mail: reynaud@ctif.com
Fax: 33-1-45-34-14-34

The Web site of the CTIF: http://www.ctif.com

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Summary of Ductile Iron Marketing Group Presentation

Annual Meeting of Ductile Iron Society, June 2001
James D. Mullins

This presentation was made at the society's recent annual meeting to show members how successful one of the ongoing programs has been. The Ductile Iron Marketing Group (DIMG) has been in existence for more than 16 years. Its purpose is help foundry members and their suppliers by increasing the size of the total ductile iron engineered castings market through dissemination of information to engineers, designers and buyers of metal parts. It is difficult at best to estimate the impact that the group has had; however the market for ductile iron castings has shown relatively steady growth almost every year. Many other metals have seen overall market declines. Whereas ductile iron has replaced many steel forgings, fabrications and castings as well as has been the material of choice to replace gray iron and aluminum castings.

The Ductile Iron Society along with Rio Tinto Iron & Titanium America are the principal contributors to this marketing association, where 100% of the monies collected go towards marketing in one form or another. The participating members donate all work effort put into the group, so there is no additional cost to the budget for us to operate.

The methods used to offer our publications and advice are as follows:

- Web site - (www.ductile.org/dimg)
- Advertising in national metals publications
- Mailing publications to satisfy ad inquiries
- Exhibiting at Design and Engineering shows
- Responding to questions relating to ductile iron castings and properties by telephone, e-mail, and fax

There are four publications, which are also available as downloadable files on our web site:

* Ductile Iron Data book, >200 pages of information about the various types of ductile iron castings, properties, specifications, ordering and applications.

* A Design Engineers Digest of Ductile Iron, an introduction to ductile iron, 40 pages.

* Why Convert to Ductile Iron, 2 pages (card form).

* Designs in Ductile Iron, cost saving conversions to ductile iron, 27 pages.

The first three listed publications are printed and donated free of charge to the marketing group by Rio Tinto Iron & Titanium and all of the publications are current as of the year 2000.

The website has been extremely popular as a marketing tool for us and has been noted as being very helpful to those who use it to locate information. It has shown increasing traffic that is now over four thousand unique visitors per month from all over the world. The most viewed pages have been from the Ductile Iron data Book. The web site contains e-mail addresses, which are used often by casting users to ask questions and obtain information.

The group spends most of its contributed money on direct advertising and press releases of our publications. To this end we have used the following publications:

- New Equipment Digest
- Industrial Product Bulletin
- Product Design & Development
- Literature for Industry
- Machine Design
- Design News
- Industrial Equipment News
- Design Fax

We have received over 1500 inquiries for information and/or publications during our 2000/2001 fiscal year. Additionally this past year we have advertised and are giving away an SAE paper that was published by one of our member companies using data generated by one of the Ductile Iron Society's research projects. This paper gives cyclic fatigue property data that can be readily used in computer aided product design. This data has been lacking and the society has been pushing to get it out on the market.

We also have direct contact with potential ductile iron casting users through exhibiting at design and engineering shows such as SAE Show, National Design & Engineering Show, and Primary Metals Show, where we give out publications and answer questions concerning the use of ductile iron.

The Ductile Iron Society maintains our web site and mails out all printed publications that are requested through the website or through our advertising.

Increasing the size of the Ductile Iron Market benefits all members of the society. In turn all members should promote the efforts of the group, use the publications in their own market programs and refer customers and potential customers to the website for information. Volunteers are also always needed to man the booth at shows. All DIS members should look at the website frequently and get involved with the marketing of ductile iron.

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FEF College Industry Conference

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Properties of Thin-Wall Ductile Iron Castings

Chantal Labrecque & Martin Gagné
Rio Tinto Iron & Titanium, Sorel, Québec, Canada
DIS Presentation June 2001

Introduction
This research project has been initiated to develop a simple technique to achieve a carbide free structure in a thin-wall test casting having the attributes of a production part. Once this first objective completed, the second part consisted in Correlating the microstructure and the mechanical properties to the chemical composition and the cooling conditions. The following summarizes the principal observations and conclusions of this research work.

Experimental Procedures
The experimental casting is shown in Fig. 1. It consists in four sections each having four vertical plates of different thicknesses: two plates of 3, one of 6 and one of 10 mm. Because of the orientation of the plates, a draft angle is introduced to facilitate the mold-pattern separation. Thus the section thickness is thinner at the top and bottom compared to the center. Two alumina foam filters are also inserted in the mold.

The charge is melted in an induction furnace (350 lb), heated to 1530°C and Mg treated with 2%-FeSiMg5% using the plunging technique. The inoculation is carried out in two steps. The first one is achieved by adding 0,75%-FeSi75% in the metal stream during the metal transfer to the ladle. The second inoculation step takes place in the pouring box where 0,5% Si64/Bi1/RE1 is mixed with the liquid metal before flowing into the mold. The filling time is approximately 6-7 seconds.

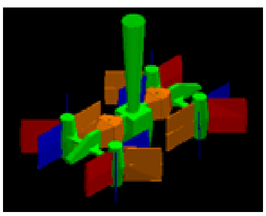

Figure 1: Drawing of the Casting.

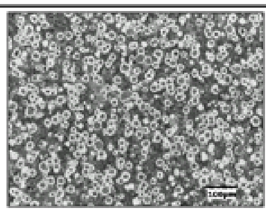

Figure 2: Typical Microstructure at the Center of a 3mm Plate.

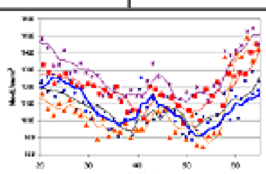

Figure 3: Nodule Count Distribution in 3mm Plates, Various Melts.

Results
Melts are produced within the following chemical compositions: 3.6 to 4.0% C; 2.35 to 3.0% Si. The Mn content is kept below 0.1% except for one test for which 0.36% Mn is added. The % Pearlite, the Nodularity and the Nodule Count distribution across the vertical central plane are measured

in the 3 and 10-mm plates of each casting. The typical microstructure of the centre of a 3-mm plate is presented in Fig. 2. The nodularity level achieved in the 3-mm plates is always higher than 90% and the pearlite content varies from 25 to 55%. The residual Bi content in the casting is 15 ppm. This small amount does not affect the nodularity in the 3 and 10-mm plates. The difference of nodule count (same vertical position) between the 3 and 10-mm plates lies in the range of 600 and 700 Nod. /mm2. The nodule count distribution in different 3-mm plates is presented in **Fig. 3.** Nodule count increases with the reduction of the plate thickness toward the edges. This is expected because of the increased cooling rate associated with the reduction of section thickness. However, it is also observed that the nodule density increases in the center of the plates. Such a phenomenon is not seen in the 10-mm plates. The physical parameter that controls Nodule count is the cooling rate; however at the center this high cooling rate is ascribable to the solidified iron surrounding the liquid iron acting as a heat sink. This is similar to the inverse chill phenomenon but in this case, no carbide occurs.

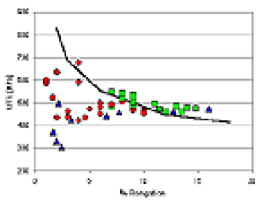

Figure 4: Mechanical Properties vs. Section Size and Filter Effect.

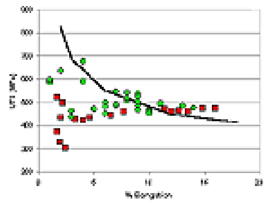

Figure 5: Mechanical Properties vs. %Si.

The mechanical properties were measured in the 3 and 10-mm plates. The results are correlated to the section size, and the filtering effect (Fig. 4), and to the silicon content (Fig. 5). These are compared to those of the ASTM A536 standard (continuous line). Figure 4 shows that the properties of the 10-mm plates are closer to those of the standard than the 3-mm plates. For equivalent UTS values, the thin wall iron casting exhibits lower ductility. This is ascribable to the higher nodule count and to the lower ferrite content of the 3-mm plates when compared to the 10-mm plates. One of the experimental castings was produced without a filter. The mechanical properties of these plates (Fig. 4) lay below the general distribution of the properties. This is indicative of the benefit of filtering to reduce the occurrence of defects that decrease the mechanical properties. Finally, in Figure 5, the relation between silicon content and mechanical properties is presented. It appears that the lower the silicon content, the better are the mechanical properties even for thin wall casting (compare to Fig. 4 to identify the 3 mm plates). Thus using very high silicon concentration may not be necessary to produce a good quality thin-wall ductile iron casting. The inoculation technique has to be very efficient and the pouring temperature and rate high. In these experiments, the pouring rate was more than 3 lb/s.

Conclusions

- Significant microstructural variations exist within a 3-mm casting. This is ascribable to different cooling rates as well as different filling conditions. Designers have to be aware of the range of properties that may be found in such castings.
- High cooling rates (not %Si) control the nodule density and distribution.
- For ~ 3-mm casting, % Si controls the Position of max. Nodule Count, % Pearlite.
- Filtering improves the consistency of static mechanical properties

(UTS and %El)

- It was possible to produce a good quality thin-wall D.I. casting having a %Si lower than usually recommended. It might be beneficial to keep the %Si as low as possible in order to get better mechanical properties in thin wall Ductile Iron castings.

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"Reduction of Shrinkage Scrap and Notes About Risering"

by: James D. Mullins
Mar. 2001

In general, shrinkage is one of the most troubling of all foundry problems. Most often it is not seen until after the casting is machined and then found in critical junction areas of the casting causing it to be scrap and the customer to be unhappy.

Shrinkage happens when the molten metal cools, it contracts and requires additional feed metal to replace or fill in the contracted area. If this feed metal is not available, either a large gassy looking type hole (primary shrinkage) or a smaller spongy and dendritic porosity (secondary shrinkage) occurs. When ductile iron is poured into strong molds, with heavier sections, shrinkage is often minimized or eliminated due to the expansion of graphite forming from the liquid. However, most engineered castings have sections that are less than 1-inch thickness, which causes more problems with solidification and feeding out possible shrinkage prone areas. This is a result of mold walls cooling and reducing feed metal passage or transfer.

Continuous shrinkage problems in a specific part can be a result of a poor part design or incorrect set up and /or processing in the foundry. These type problems can be addressed and solved. However, this is not what this article is going to address.

If the shrinkage is of the sporadic type it is usually a result of a number of variables probably only slightly out of control. The usual production variables are: Green sand strength and mold density (ramming), weighting and clamping of molds, pouring temperature variation, overall chemistry, but primarily carbon, silicon and magnesium levels, changes in nodule count, graphitic carbon content and carbide content, and type and/or functioning of risers (piping). Each of these items are covered in detail below:

- Mold strength and density - changes from day to day in clay and moisture levels and mold ramming will allow the expansion pressure from the graphite growth in the metal to dilate the mold wall more or less depending on the strength and overall density of the mold.
- Weighting and clamping of molds - will have a similar effect as previously mentioned allowing mold wall movement.
- Pouring temperature variation - each part number will have its own special pouring temperature requirements, because of casting section sizes, gating system design and riser functioning. Testing should be done to determine what this range is, so that it is checked frequently and controlled properly. Higher pouring temperatures are usually beneficial to casting quality, such as less gas defects, but increase primary shrinkage amounts that must be compensated for by the risering system.

Chemistry is important. Having the correct carbon for the section size (without carbides) usually reduces the amount of shrinkage formed. Higher silicon levels will usually increase shrink, but reduce carbides. Excessive amounts of magnesium and magnesium plus rare earths can increase shrinkage. Other elements such as chromium that promote carbides usually increase shrinkage.

- Nodule count (good nucleation) - having the necessary amount of nodules for a given section modulus is important as it determines the amount of pressure generated during graphite growth. Too few nodules may not cause much expansion pressure leading to excessive metal shrinkage. Inoculant fading or under inoculation may cause this. Too many nodules (excessive inoculation) can create excessive metal pressure and again shrinkage. Over-inoculation especially with strong inoculants and faster cooling of the liquid can produce too many nodules.

- Higher graphitic carbon contents generally reduce shrinkage, because of more expansion produced on nodule formation whereas larger amounts of carbides reduce the available amount of graphitic carbon and increase shrinkage. The overall volume of graphite in ductile iron can vary from 10 to 12 %.

Remember that trying to follow the rules of risering and proper feeding will not always guarantee success, but ignoring them will often result in failure. In this regard we offer a few risering suggestions to help reduce shrinkage problems:

- Bottle-shaped risers are advantageous as they work at lower and wider range of pouring temperatures than other riser types and can significantly improve casting yield.

- Small exothermic ram-up core type risers strategically placed work well and can also improve yield, but the iron needs to be hot to make them work as they are usually placed in areas of the mold where cold metal occurs (top of cope).

- Blind & hot risers are preferred to open & cold risers, because they generally work better. Insulating and exothermic sleeves work well but also need higher temperature to function.

- All risers function better (pipe better) at higher metal temperatures. This is especially true of top (cold) risers but also is appropriate for hot (gated) risers.

- Using chills in isolated sections can often give better results than risers can, when used properly. Often chills are less costly to use and remove than risers are.

- When examining risers in the finishing room they should have a characteristic shrinkage hole or pipe in or near the top. Oftentimes if there is no hole, the riser probably did not work. Risers with large flat areas on the top are very susceptible to freezing off (forming a surface skin). This is why bottle shaped (also called Heine) risers work well - they begin to form a shrinkage hole very quickly, allowing wider pouring temperature ranges and continue to supply feed metal through solidification. When new parts are sampled it is often wise to saw up the risers (vertically) and through the neck (contact) to see how well they have or have not worked.

- Often when there are two or more risers in close proximity - one will have a shrinkage hole and another does not. This can mean that one riser is feeding the other(s) and the other(s) often can be removed.

Improving casting yield by improving risering and eliminating scrap is one of the best sources of cost reduction in the foundry. Keep this listing handy to help solve shrinkage problems.

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Carbon Additives

CHARACTERIZATION
There are at least seven types of carbon additives commonly used in iron and steel melting. They are generally characterized (or identified) by their origin, their chemistry, and their physical properties.

The origin is straightforward: Where did it come from? How much temperature has it been subjected to? How is it characterized? We can identify two graphitic types of carbon: natural graphite and synthetic (manufactured) graphite. For carbons (un-graphitized), there are calcined petroleum cokes (CPC), metallurgical coke (Met.Coke), electrically calcined anthracite (ECA), carbon electrodes, and silicon carbide (SiC). These constitute the bulk of carbon alloyed in iron and steel.

The chemical properties of carbon/graphite are: ash content, volatile matter, moisture content, and sulfur content. Historically, what's left is the available carbon for alloying. Also included would be gas contents: nitrogen, hydrogen, and oxygen. Some of the gas can be chemically reacted, yet a significant portion remains mixed or entrapped within the carbon/graphite particle.

Physical tests include sizing, density, and resistivity. Other more intricate tests are spectrographic analyses, and x-ray diffraction and crystallite sizing. The x-ray diffraction would be used mostly to differentiate various graphites.

NATURAL GRAPHITE
Natural graphite is mined and of two types. One is graphite particles or flakes imbedded in rock. The rock is crushed, then the graphite is separated by flotation from the host rock. This graphite can be quite pure but has an attending high cost. It has been subjected to high geothermal temperature and pressure (often over 7000^{o}F or 3900^{o}C). The second type is vein graphite extracted from mines throughout the globe. An example would be Mexican graphite. It too, has been subjected to high geothermal temperatures and pressures. While vein graphite has lower costs, it also can contain high ash contents and gases

SYNTHETIC OR MANUFACTURED GRAPHITE
The next type of graphite is synthetic or man-made graphite, as graphitic electrodes, either as machinings from newly produced electrodes, or from scrap electrodes crushed and sized. The raw electrodes are made from calcined petroleum coke (roughly 85%) plus petroleum paste, iron oxide, and small amounts of other additives to enhance graphitization. This mixture is then carbonized at approximately 2000 to 2200^{o}F (1100 - 1200^{o}C) in a carbon furnace. They are then removed from the furnace, rough machined, re-furnaced into an Acheson-type furnace, and heated through electrical resistance to 4000 to 4500^{o}F (2200-2500^{o}C) for an extended period of time (from several days to weeks). This converts the carbon electrode into a graphite electrode.

Other graphitic plates and shapes are similarly treated and are used as anodes or cathodes, generally available as scrap products.

Another synthetic graphitic material is a desulfurized calcined petroleum coke that has been subjected to a high temperature thermal process, 4500 to 4800 degrees F (2500 - 2650 degrees C), that desulfurizes the CPC and converts most of the carbon to graphite

CARBONS (UNGRAPHITIZED)

Calcined petroleum coke (CPC) emanates as a by-product from oil refineries. Most of the CPC is utilized in the aluminum industry as anodes to reduce aluminum oxide to metallic aluminum. Several grades are available, based on chemistry. CPC has a high carbon content but it also contains measurable amounts of sulfur, gases (notably nitrogen and hydrogen), and sometimes metallics like Va or Ni. Sulfur can reach 5 to 6 %. However, iron and steel won't tolerate much more than 1.5 to 2.0 %. Nitrogen levels can also reach 2.0%, or 20,000 ppm. CPC has been coked at roughly 1800 to 2200^{o}F. (1000 - 1200^{o}C).

Also available is an ethylene coke made from high purity feed-stock with notably lower S (.10%) and N (.50%). The high purity of the precursor feed-stock yields a high purity coke suitable for carbon alloy additions in ferrous metals.

Metallurgical coke derives from foundry or blast furnace coke. Carbon additions are screened from the larger furnace coke and are perhaps the least expensive of carbon additions. Metallurgical coke contains some sulfur (.6 to .8%), a measurable amount of ash which impedes carbon recovery, and varying amounts of gas. It emanates from blend of coals, which are coked at 1600 to 2000^{o} F. (900 - 1100^{o}C.).

Electrically calcined anthracite (ECA) is made from anthracite coal and electrically calcined in special furnaces. It's end use is generally in ferro-alloy electrodes, often as a paste in Soderburg furnaces. The heat of its formation can vary, depending how close it passes to the furnace electrodes, or how fast it passes through the furnace.

Carbon electrodes originate similar to graphitic electrodes, except that they have not been graphitized. They are used primarily as ferro-alloy electrodes and have been subjected to 2000 to 2200^{o}F. (1100 - 1200^{o}C.) of temperature. Carbon electrodes are hard, often machined with diamond tooling. The carbonizing process removes only small percentages of sulfur and gases available in the precursor CPC. They are scrapped, crushed, and sized before usage as a carbon additive.

Silicon carbide can also be used as a carbon addition. Its chemistry is roughly 30% C and 60% Si and is known more for its deoxidizing potential. However, both its C and SI are available as alloy additions.

CHEMISTRY OF CARBON ADDITIVES

Concerning chemistry of carbon, testing has historically provided an ash content whereby a measured sample is placed in a crucible, heated to 1700^{o} F. (950^{o} C.) for several hours to burn off the carbon, after which the remaining ash content is weighed and calculated as loss of ignition. This is specified under ASTM C561-91. The color of the ash can also be noted. For instance, a reddish hue indicates the presence of Fe.

Volatile matter testing involves heating a sample of carbon or graphite to 1700^{o}F. (950^{o}C.) for 5 to 7 minutes, cooled, and reweighed to calculate the weight loss, yielding the % volatile content. ASTM D 3175-77 Revision 3105 (1990) is one of the specifications.

Moisture content involves a material sample dried in an oven at 230^{o}F. (110^{o}C.)for 2 hours, cooled, then the dried sample is reweighed to calculate % moisture loss. ATSM C562-85, Revision 2606 (1987) is the specification.

The % sulfur in carbon or graphite is generally provided by Leco furnace testing, burned with oxygen whereby the combusted gas is bubbled through a titrator which converts to % S. Specification are under Leco sulfur testings.

Once the above tests have been performed, the customary reporting of available carbon can be determined: 100% minus % ash, minus % volatiles, minus % moisture, minus % sulfur, equals the carbon available. There is also a fixed carbon test which basically is 100%, minus % ash, minus % volatiles, minus % moisture, equals % fixed carbon; however, this does not accommodate any appreciable sulfur nor gas contents which of course are not available carbon.

The gases contained in carbon or graphite are generally measured by high temperature thermal conductivity using various Leco instruments. (Reference: nitrogen analyses comparison, Casting Industry Suppliers Assoc., 1990). Nitrogen can be determined by the Kjeldahl chemical digestion procedure (ASTM D 3179-89). Further, there is a chemiluminescence procedure which converts nitrogen to nitric oxide, then measured by a photo multiplier tube. Gases are generally reported in parts per million (ppm). It should be noted that this technology is undergoing alterations to improve the accuracy as time passes. Also note that the chemical Kjeldahl procedure involves lengthy time to fully dissolve the carbon or graphite sample (often a week) and is therefore, subjected to operator variation. Further note that significant gas contents are likewise weighed in the original test sample. 10,000 ppm of nitrogen, for instance, is 1.0 % nitrogen which is not part of carbon available for dissolution in iron or steel.

PHYSICAL TESTING OF CARBON/GRAPHITE ADDITIVES

Under physical testing, sizing is accomplished by screening out various fractions on a series of stacked screens, weighing each fraction, then dividing by the original sample weight to calculate the % retained on each screen. In general, sizing of carbon/graphite additives is ½ inch maximum, down to 100 mesh minimum. Additives can be procured in various sizings; for instance - 3/8"x 30 mesh, or 8 mesh x 60 mesh. Furnace additions generally are larger than ladle additions.

Density is another comparative measurement. Pure graphite has a density of 3.36 grams per cubic centimeter, whereas pure carbon is lower. There are cases where carbon densities have been over 3.40 gm/cc but this must be approached with caution: the carbon had a high ash content and there were metallics in the ash, increasing the density. To reiterate, density is simply a comparison.

Resistivity is measured in a Wheatstone or Kelvin bridge instrument whereby an electrical current is passed through a sample and the electrical resistance is measured. Resistance is the inverse proportion to electrical conductivity and can easily differentiate graphite from carbon.

In X-Ray Diffraction testing, a candidate sample is bombarded with x-rays which form a distinctive pattern of peaks on a graph. Pure graphite will create narrow, long vertical lines indicating a high degree of graphitization whereas less graphitized material will create lower, broader peaks of less graphitization. Carbon (ungraphitized) does not exhibit any peak, or little more than a bump in the pattern. Impurities can influence the peak pattern, flattening them out to a small degree.

In conjunction with x-ray diffraction, cystallite sizing of the graphite can be calculated, indicating in angstroms, how large the graphite flakes are. This has value in determining whether the graphite will inoculate irons. For instance, a crystallite sizing measurement of less than 100 angstroms indicates the sample is a carbon, which will not create an inoculating effect in irons. Synthetic graphite has been calculated at 300 to 500 angstroms and is known to suppress undercooling, reducing chill i.e., aiding in the inoculation effect. High purity graphite has been calculated at over 1000 angstroms. Graphitic materials are often added in conjunction with ferro-silicon based inoculants to create the desired effect.

Spectrographic Analyses have been run on carbon/graphite materials to determine various residual levels of the many elements carried in additives. Sometimes measured in percentage, some elements are reported in parts per million. The spectrograph has emerged in the last two decades with rapid measurements to further characterize carbon graphitic additives used to alloy iron and steel.

SUMMARY

The above chemical and physical tests of carbons and graphites properly characterize the additives, and judicious use of these results will determine which additive corresponds best to your needs. No attempt is made to compare costs. In general, melt shops should use these characterizations to procure the carbon alloy best suited to their application.

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Nodulizing and Inoculation Approaches for Year 2000 and Beyond - Part 1

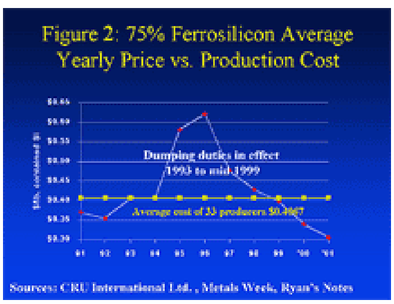
by Dr. R. L. (Rod) Naro
ASI International, Ltd. - July 30, 2001

Original Paper presented June 15, 2000
DIS Meeting, Wichita, Kansas

Abstract: Nodu-Bloc, a new iron-magnesium briquette, offers ductile iron foundries a powerful alloy that can be used to replace traditional magnesium ferrosilicon (MgFeSi) as well as other magnesium containing master-alloys. Controlled laboratory tests show that Nodu-Bloc can replace up to 50 weight percent of MgFeSi. Field trials with Nodu-Bloc confirm these results and show that Nodu-Bloc replacement of MgFeSi can provide significant cost savings. Foundries converting to Nodu-Bloc will experience reduced melting costs because less MgFeSi is consumed, less steel and pig iron is required in the charge and far greater levels of foundry returns can be utilized. Foundries can easily save up to $10 or more per ton on molten ductile iron processing costs by incorporating Nodu-Bloc technology.

Introduction: Since the commercialization of ductile iron in 1948, foundries have used numerous methods to introduce magnesium into molten cast iron. **Figure 1** lists some of the approaches and techniques used over the years. Although some of these processes gained a brief following, and some have even been used successfully, most have fallen out of favor because of numerous shortcomings. Today, the majority of ductile iron castings made throughout the world are produced using ladle-metallurgy practices with MgFeSi alloys. It is estimated that MgFeSi alloys are used in 65% of all ductile irons produced worldwide. In the United States, MgFeSi alloys account for an estimated 75% of ductile iron production. The remaining ductile iron production is made using either the magnesium-converter process or magnesium containing wire injection.

During the first decade of the new millennium, ductile iron production is forecast to surpass U.S. gray iron production, with shipments exceeding 5 million net tons by 2006 [(1)]. The supply of domestically produced MgFeSi becomes important in assessing whether this important raw material will be available in sufficient quantities to sustain the forecasted growth.

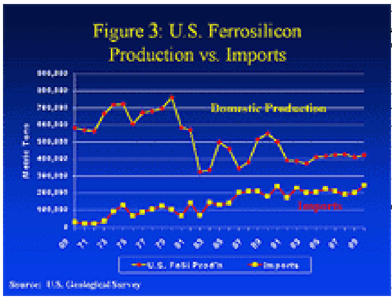


With the International Trade Commission 1999 ruling to rescind dumping duties on ferrosilicon alloys, foreign-produced ferrosilicon alloys have flooded the market, setting near-record low prices and pushing domestic producers out of the market. See **Figure 2**. Just last year, American Alloys, a producer of MgFeSi as well as ferrosilicon, was forced into bankruptcy and has closed. **Figure 2** shows the average production costs of

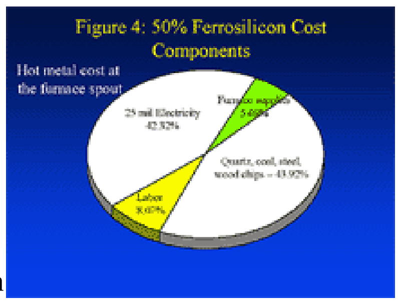
33 ferrosilicon producers taken from a recent survey conducted by the Commodities Research Unit, a British economic research firm.

At the present time, all five remaining U.S. ferrosilicon producers are operating at a profit loss. Their combined, before tax operating income for the last four years is summarized in **Table 1**.[(2)] The U.S. producers provided this information at ITC hearings in an unsuccessful attempt to restore dumping duties on ferrosilicon-based products. In addition to increased competition from foreign firms, the slowing economy and rising energy costs have worsened the plight of domestic producers. Consequently, some haven't found continued operations to be financially worthwhile.

If, indeed, the supply of domestically manufactured MgFeSi is reduced or curtailed because of plant closures, alternate nodulizing approaches may be necessary to sustain the projected growth of ductile iron.



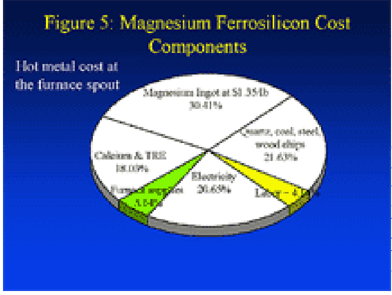
Economics of Ferroalloy Production:
The U.S. ferroalloy industry was a major market force up until the early 1980s. **Figure 3** shows U.S. production of ferrosilicon alloys compared with imports for the time frame 1969 to the present. The decline in production can be linked to several factors. Because of electricity-rate increases, pollution-control costs and strong competition from foreign ferrosilicon producers, several domestic producers have gone bankrupt, have closed plants or reduced manufacturing output. **Table 2** shows the decline in installed furnace capacity to manufacture ferrosilicon alloys during the past 20 years.



In the United States, MgFeSi production is dependent on the production of 50% ferrosilicon. Fifty percent ferrosilicon is produced in a submerged-arc furnace and then alloyed with magnesium, calcium and rare earths, also known as mischmetal. The relative cost to produce 50% ferrosilicon, based on a nominal 25-mil power rate ($0.025/kilowatt), is shown in **Figure 4**. Electricity and raw materials represent 42.32 percent and 43.92%, respectively, of molten metal cost at the furnace spout; labor accounts for a modest 8.07% of the cost. Major cost reductions for producing 50% ferrosilicon can only be achieved by renegotiating electrical power rates. Reducing labor costs has only a minimal effect on overall production costs.

The amount of electricity needed to produce one ton of 50% ferrosilicon is 4,500 kilowatts. A single 22-megawatt submerged arc furnace using 25-mil electricity, running 24 hours per day, uses $11,500 of electricity per day, or $4.1 million annually. However, the current energy crunch doesn't bode well for ferrosilicon producers to have access to such low-cost electricity in the future. In fact, during the summer of 2001, at least three plants have curtailed production of silicon-based alloys and have sold their contracted electricity back to the power generator.

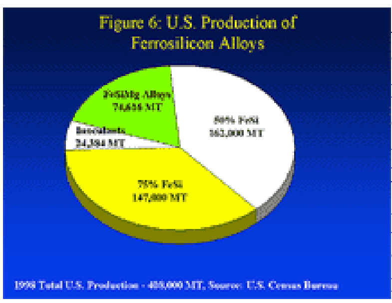
MgFeSi is made by ladle treatment of 50% ferrosilicon. Magnesium ingots are plunged into the ladle, followed by additions of calcium silicon and rare



earths. The relative cost to produce MgFeSi is shown in **Figure 5**. Two ingredients, magnesium ingot and related raw materials required for 50% ferrosilicon production account for 70.07% of the molten metal cost while electricity and labor now represent 20.65% and 4.14%, respectively.

Because electricity has such a significant effect on production costs, foreign ferroalloy producers that have inexpensive, government-subsidized electricity, have a distinct production-cost advantage. In the survey of ferrosilicon production costs at thirty-three Western World ferrosilicon plants by the Commodities Research Unit, high electricity costs were cited as the reason all U.S. ferrosilicon producers were ranked as high-cost producers. Two-thirds or twenty-four of the ferrosilicon producers surveyed by CRU had lower production costs. All of these overseas producers had significantly lower power costs.

Currently, only three producers of MgFeSi remain in the United States. Globe Metallurgical, Calvert City Metals and Alloys (CCMA) and Keokuk Ferro-Sil produce MgFeSi as well as other silicon-based alloys. Keokuk Ferro-Sil, Inc. just started to produce MgFeSi alloys in October 2000 while another, Globe Metallurgical in Beverly, Ohio[3], the largest domestic MgFeSi producer, is for sale. The owner, an investment-holding company, has decided that its return on investment isn't adequate and that there isn't much hope that market conditions will improve in the near term. Quite simply, there is an excess worldwide capacity to produce silicon-based ferroalloys. This oversupply will continue to depress world prices in the foreseeable future. If Globe Metallurgical is sold, and if the new owner decides to convert the plant to silicon metal production, future U.S. supplies of MgFeSi will be jeopardized[4] .



Although considerable production capacity still exists in the United States to manufacture MgFeSi, whether that capacity will be utilized for MgFeSi production remains to be seen. The various grades of U.S. ferrosilicon production are shown in **Figure 6**. It's apparent that capacity exists to convert much of the current 50 and 75 percent ferrosilicon production to MgFeSi should the need arise. However, this premise is based on U.S. ferrosilicon producers weathering the continued onslaught of imports and remaining in business.

U.S. ferrosilicon producers have recently (August 2000) appealed to the International Trade Commission to re-instate dumping duties and restrictions on ferrosilicon imports, but no ruling is expected soon. Even if a favorable ruling occurs, other non-affected ferrosilicon producing countries would probably step into the U.S. market. Favorable currency exchange rates and a strong dollar typically are excellent incentives for overseas producers to export ferrosilicon into the U.S. market. Further, there doesn't appear to be any shortage of ferrosilicon producers who can export to the U.S.

Without import restrictions, U.S. ferrosilicon production could disappear or be drastically reduced, possibly causing U.S. ductile iron producers to be totally dependent on foreign-produced alloys. If this occurs, the number of available grades and sizes of MgFeSi may be limited. Because ocean transportation is used to ship foreign produced MgFeSi to the United States, it is unlikely that multiple grades and sizes would be available because of the logistics problems associated with ocean transportation. Only one or two grades of the most commonly used alloy chemistries, of one specific size, would most likely be available.

MgFeSi Replacement: To meet the growing demand for ductile iron and to circumvent potential reliance on foreign-produced MgFeSi, progressive foundries need to explore alternate nodulizing methods. Nodulizing processes that utilize pure magnesium have attracted more attention in recent years. Eliminating or reducing the amount of silicon based nodulizers has a number of benefits for ductile iron producers. Silicon is often an unwanted element and at many foundries, control of silicon levels is an economic and technical challenge. High silicon levels typically are the result of one or more of the following: over-treatment with MgFeSi alloys, improper ladle design, treatment method, treatment temperature and base sulfur level.

ASI International, Ltd. has developed a new generation of iron-magnesium alloys (Nodu-Bloc) that address potential MgFeSi shortages and as well as provide improved ductile iron silicon control. These new iron-magnesium alloys can reduce or even completely eliminate dependence on MgFeSi alloys. The iron-magnesium alloys provide all the cost advantages of pure magnesium processes along with the ease and forgiving nature of ladle-treatment production techniques. More importantly, by using these low silicon alloys, higher levels of foundry returns can be used in the furnace charge make-up, resulting in significantly reduced melting costs.

Nodu-Bloc iron-magnesium alloys are manufactured using well-developed powder-metallurgy techniques. Pure magnesium, high-purity iron powder and other additives are carefully blended and compacted under extremely high pressure. Since a furnace smelting process isn't employed, magnesium levels can consistently be controlled in the range of +/- 0.05%. In addition, controlled amounts of calcium, barium, rare earths and copper can easily be incorporated into the briquettes for those applications requiring special chemistries.

Popular Nodu-Bloc iron-magnesium alloy chemistries are listed below:

Nodu-Bloc Grade 11 - 11% Mg, 0.7% Ca, 0.7% Ba, 3.0% Si, 0.7% C, Balance - Iron
Nodu-Bloc Grade 15 - 15% Mg, 3.0% Ca, 6.0% Si, 2.0% C, Balance - Iron
Nodu-Bloc Grade 20 - 20% Mg, 5.5% Ca, 13.0% Si, 2.0% C, Balance - Iron

Nodu-Bloc briquettes have an almond shape and measure 1.25 inch by 1.0 inch by 1/2 inch, each having a volume of approximately 5 cubic centimeters (see **Figure 7**). Recently, a somewhat larger pressed disc measuring 4.75 inches in diameter and 1.25 inch thick (350 cc's) and containing either 11 percent or 15 percent magnesium has been developed. A schematic of two discs covering MgFeSi in a ladle bottom is shown in **Figure 8**. The Nodu-Disc's have a similar formulation to the smaller briquettes and can be used as a "reactive cover" material for either iron-magnesium tablets or standard MgFeSi. The consistent weight of the discs may be advantageous in some applications where weighing charge additions might prove cumbersome. The shape of the pressed disc also provides a more favorable surface area-to-volume ratio, which reduces reactivity in molten iron.

A comparison of Nodu-Bloc iron-magnesium briquettes with 5 percent MgFeSi is shown in **Table 3**. The density of Nodu-Bloc iron-magnesium briquettes, for a given magnesium level, is considerably higher than MgFeSi. However, as with MgFeSi, alloy floatation, especially with the 20 % Nodu-Bloc product, may be a problem. Silicon deficiencies can simply be corrected by adding additional returns to the charge. In many cases, improved foundry return utilization can result in significantly reduced melting costs.

Although silicon control is necessary in producing high quality ductile iron, many ductile iron foundries are reluctant to add sufficient returns to their furnace charges for fear of high silicon.Sometimes, these returns are simply sold to scrap dealers at a significant loss. Utilizing these returns, in conjunction with Nodu-Bloc replacement of MgFeSi, allows more flexibility in post-inoculation. Higher addition rates of post-inoculants for improved structure and carbide reduction can now be made while maintaining nominal silicon levels. Higher-base silicon levels from improved return utilization will significantly improve refractory live. Lastly, by lowering silicon levels and precisely controlling these levels, foundries will have improved control over mechanical properties such as charpy impacts.

Experimental Laboratory Testing and Development: To investigate the effects of various levels of Nodu-Bloc substitution for MgFeSi, several experimental ductile irons heats were prepared. Three levels of Nodu-Bloc substitution (15%, 30% and 50%) were evaluated as partial replacement for a nominal 6 percent MgFeSi alloy. The effects of Nodu-Bloc substitution on slag and fume formation, magnesium recovery, sulfur removal and final microstructure were evaluated during this laboratory-testing phase [5].

Heats of ductile-base iron were prepared in a 2,500 pound induction furnace with the base iron charge shown below:

220 kilograms (485 pounds) pig iron (Sorel grade)
330 kilograms (727.5 pounds) ductile iron returns
550 kilograms (1212.5 pounds) steel scrap
25 kilograms recarburizer (55.1 pounds) (crushed electrode grade, 99.9% C, 0.05% S)
8 kilograms (17.63 pounds) 75% Ferrosilicon

Experimental ductile iron treatments were poured into a conventional, 300 kilogram (660 pound) tundish ladle. Two base iron sulfur levels were used, 0.013% and 0.033%. Treatment temperatures were 1,500^{o}C (2,732^{o}F), and tundish ladle filling times were 40 seconds. The tundish ladle had a removable lid and a sandwich divider wall in the ladle bottom. The nominal height to diameter ratio of the ladle was 2.5-to-1. Nodu-Bloc briquettes containing 21% magnesium were used for the trials along with a 5.9% magnesium containing ferrosilicon containing 1.0 percent total rare earths. The Nodu-Bloc briquettes were first charged into the ladle. The appropriate amount of MgFeSi was then added as a cover. Finally, 2 kilograms (4.4 pounds) of calcium-bearing 75% ferrosilicon was also used as a sandwich cover. Post-inoculation was accomplished using a 0.30% barium-containing ferrosilicon as a stream inoculant in a 68 kilogram (150 pound) transfer ladle.

Results for the 0.013% sulfur base iron tests are shown in **Table 4**. The 15% and 30% Nodu-Bloc replacement levels showed no significant change or reduction in magnesium recovery. However, magnesium recovery for the 50% replacement level declined somewhat. The relatively lengthy treatment ladle filling time may have accounted for this reduced recovery.

It was noted during testing that more surface dross was observed at the highest Nodu-Bloc replacement level of 50%. It was also noted was that with increasing Nodu-Bloc replacement level, treatment reaction intensity increased. Although more flashing and flaring were observed, the overall reaction is best described as being "brighter," not more violent. Since a tundish ladle was used, the increased reactivity would not be regarded as a problem in a normal tundish operation. However, with open sandwich ladles, the increased reactivity of 21% magnesium Nodu-Bloc could result in some risk of metal splashing. Although not laboratory tested, the 11 and 15% grades of Nodu-Bloc would provide reduced reactivity.

Test results for the higher 0.033% sulfur base iron are shown in **Table 5**. For these heats, 0.8 kg (1.76 lbs) of iron pyrites was added to the furnace. The 30% Nodu-Bloc replacement levels showed no change in magnesium recovery. However, magnesium recovery for the 50% replacement level declined somewhat. Nodu-Bloc replacement at both the 30% and 50% levels seemed to be much more effective in removing sulfur than 100% MgFeSi additions. Typically, with a 2.5% MgFeSi addition to a high (0.033% sulfur) base iron, final sulfur levels typically are above 0.02%. In these experiments, the addition of 2.5% MgFeSi decreased the base sulfur content from 0.033% to 0.023%. The 30% and 50% Nodu-Bloc replacement treatments reduced the final sulfur levels to 0.017% and 0.019%. These results tend to indicate that Nodu-Bloc has a somewhat more powerful capability to desulfurize a high sulfur base iron compared with just MgFeSi. In more practical terms, foundries running high base sulfur levels would benefit from using Nodu-Bloc since nodulizing and desulfurization can both be accomplished without any increase in silicon level.

Microstructural results for the series of experimental treatments are summarized in **Table 6**. The microstructures of all 25 mm section test bars poured with the 0.013% sulfur base iron were all normal and contained nodule counts ranging from 184 to 237/mm^2. Pearlite content was measured between 60 to 70% for all samples. No differences in nodule count or nodularity were noted even at the highest Nodu-Bloc replacement level. In fact, the 50% Nodu-Bloc replacement showed the highest nodule count (237 N/ mm^2) and best nodularity even though magnesium recoveries were somewhat reduced. Similar microstructural results were observed with the 0.033% sulfur base iron samples; nodule counts ranged from 164 to 178 N/ mm^2.

One of the subtler laboratory observations was reduced temperature loss when Nodu-Bloc was used. For example, at a 30% Nodu-Bloc replacement of MgFeSi, the nominal reduction in total alloy addition rate is 0.30 weight percent. Reducing additions of nodulizing alloys results in less temperature loss from the heating and melting of alloy additions. The heat conservation resulting from 0.30% less MgFeSi is estimated to be in the range of 20^{o}C to 30^{o}C (36^{o}F to 54^{o}F). Higher levels of Nodu-Bloc replacement would undoubtedly result in additional temperature conservation.

Production Results: To date, several foundries have substituted Nodu-Bloc for MgFeSi as an integral part of their daily production while many others are in the process of evaluating Nodu-Bloc. The production experience of three vastly different ductile iron foundries, each of which had different needs, is discussed in detail in this section.

Foundry A is a medium-sized, high-production foundry producing ductile iron parts for the automotive and truck industries. Daily production capacity is 280 tons. Although Foundry A has a casting yield which ranges from 45% to 55%, they generate more returns, in the form of gates, risers and pouring basins, than they can remelt. They needed an economical way to increase returns utilization without the accompanying increase in silicon levels. To accomplish these goals, an economical, low-silicon nodulizer needed to be found. Nodu-Bloc 15 met these goals.

Foundry A utilizes three 10-ton induction furnaces for melting. A 2,000 pound capacity open ladle with a height-to-diameter ratio of 2.5-to-1 is used for ductile iron treatments. Extensive tests with Nodu-Bloc iron-magnesium briquettes containing 15% magnesium were conducted. It was found that a 25% Nodu-Bloc replacement, based on total magnesium, allowed the foundry to use an additional 400 pounds of returns per furnace charge and reduce steel scrap levels by an equivalent 400 lbs.

Nodulizing is accomplished using the sandwich technique. The appropriate amount of MgFeSi is weighed and placed in a charging container. Next, the Nodu-Bloc iron-magnesium briquettes are place over the MgFeSi. The charge container is then dumped into a pocket in a completely empty, heated ladle. Foundry grade 75% ferrosilicon is then added to the pocket as additional cover material, followed by twelve pounds of cover steel. Residual magnesium levels ranged from 0.035% to 0.040%.

Table 7 shows a comparison of the furnace charge makeup as well as levels of nodulizers employed prior to and after incorporation of Nodu-Bloc. Little-to-no difference in magnesium flare or reactivity was noted by operating personnel when Node-Bloc was used. The favorable height to diameter dimensions of the sandwich ladle most likely accounted for the modest reaction.

The 25% magnesium Nodu-Bloc replacement provided identical microstructural results compared to nodulizing with 100 percent MgFeSi. Nodule count, nodularity and matrix structures remained unchanged. Average nodule count is 275 with an average nodularity rating of 95%. Average casting section size is five-eighths of an inch with section sizes ranging between a quarter inch to two inches.

The foundry has realized significant cost savings by utilizing 11.21% more returns in the charge make-up. Production costs have been reduced by $7.45 per net ton. The level of daily savings achieved by using a combination of Nodu-Bloc, reduced levels of MgFeSi and increased foundry returns in the furnace charge is $1,489 daily. Annually, these savings approach $375,000. It should be noted that the level of savings is largely dependent on how the foundry values its returns. In this example, the foundry placed a value of $90 per ton on its returns. Thus, with these types of savings, Nodu-Bloc iron-magnesium briquettes have now been incorporated into daily production. Trials have been run with Nodu-Discs and have produced encouraging results. Additional trials with the discs are scheduled for in the near future.

Foundry B is a much smaller jobbing foundry producing a variety of ductile iron castings. Daily production is about 25 tons. Because of the jobbing nature of their business, optimizing casting yield becomes difficult due to the fluctuating nature of their production schedule. Foundry B melts with two 4,000-pound induction furnaces.

Twenty percent magnesium containing Nodu-Bloc briquettes were evaluated as a replacement for 6% percent MgFeSi for cost-reduction purposes. Foundry B also had a silicon problem and could not utilize all of the returns generated. It was often forced to liquidate excess returns by selling them to the local scrap yard. This practice had an adverse effect on their balance sheet since it involved a significant write-down of assets.

Nodulizing is accomplished in a 750-pound tundish ladle having a height-to-diameter ratio of 2-to-1. MgFeSi is first weighed into a charging container. Then Nodu-Bloc 20% iron-magnesium briquettes are place over the MgFeSi. The charge container is then dumped into the completely empty, heated tundish ladle. Foundry-grade 75% ferrosilicon is then placed over the nodulizers. Finally, 22 pounds of cover steel is added to the ladle.

Table 8 shows the furnace charge makeup as well as levels of nodulizers employed by Foundry B both prior to and after incorporation of Nodu-Bloc. During the foundry trials, no appreciable difference in magnesium flare or reactivity occurred during the nodulizing operation.

The 46% magnesium Nodu-Bloc replacement provided identical microstructural results compared with nodulizing with 100% MgFeSi. This small foundry has realized significant cost savings by utilizing 10% more returns in the charge make-up. Ductile iron production costs have been reduced by $10 per net ton. The level of daily savings achieved by using a combination of Nodu-Bloc, reduced levels of MgFeSi and increased foundry returns in the furnace charge is $295 daily. On an annual basis, these savings approached $75,000, which pleased foundry management. Needless to say, Nodu-Bloc iron magnesium briquettes have now been incorporated into daily production.

Foundry C is also a small, jobbing foundry producing mostly ductile iron castings along with gray iron castings. The foundry uses two one-ton induction furnaces for melting. Foundry C's prime objective was to reduce ductile iron production costs by eliminating costly nodular grade pig iron and replacing it with its own foundry returns. This foundry, not unlike many other small foundries, tends to over treat their ductile iron with MgFeSi and, consequently, is always battling a silicon problem. The reasons for over treatment include MgFeSi is used for desulfurization since base iron sulfurs approach 0.02 percent, non-ideal treatment ladle dimensions, and lengthy ladle filling times due to the tilting mechanism on the induction furnaces.

Nodulizing is accomplished in a 2,000-pound open ladle using the sandwich process. The height to diameter ratio of the ladle is only 1.25-to-1. The treatment is completely empty and pre-heated. Nodu-Bloc 15% briquettes are added to the ladle first, then MgFeSi is placed over the iron-magnesium briquettes, and finally, one 3-pound Nodu-Disc is added as cover. Lastly, 22 pounds of foundry grade 75% ferrosilicon is placed over the nodulizers for "cover".

Table 9 shows the furnace charge makeup as well as levels of nodulizers employed by Foundry C both prior to and after incorporation of Nodu-Bloc. During the foundry trials, only minor differences in magnesium flare and reactivity occurred during the nodulizing operation. However, some metal splashing has occurred on an infrequent basis, mainly due to the shallow depth of the treatment ladle. Residual magnesium levels continued to be in the range of 0.05 to 0.055%.

The 57% magnesium Nodu-Bloc replacement provided identical microstructural results compared with nodulizing with 100% MgFeSi. This small foundry has realized significant cost savings by completely eliminating over 1,000 pounds of nodular pig iron from its charge make-up. Production costs have been reduced by $33.49 per net ton. The level of daily savings achieved by using a combination of Nodu-Bloc, reduced levels of MgFeSi and increased foundry returns in the furnace charge is $502 daily. On an annualized basis, these savings are in excess of $126,500. As with Foundries A and B, Nodu-Bloc iron-magnesium briquettes and discs have now been incorporated into daily production.

Discussion: Laboratory testing of Nodu-Bloc replacement for MgFeSi confirmed that it is a viable replacement for MgFeSi alloys up to 30% substitution. Magnesium recovery and microstructure evaluations showed that Nodu-Bloc replacement was identical to 100% MgFeSi treatment. At higher replacement levels, the nodulizing reaction was more vigorous and some reduction in magnesium recovery occurred. However, microstructures were identical or slightly better than the lower 30% substitution level. The laboratory findings also suggest that Nodu-Bloc is a more potent desulfurizer that MgFeSi, particularly when base iron sulfur levels are 0.025% and higher. Although the laboratory trials utilized the most potent form of Nodu-Bloc, (21% magnesium content), the 11% and 15% grades would show reduced reactivity.

The summary of production results at three different foundries mostly confirmed the laboratory findings. Two of the three foundries used a higher replacement level than 30% level and continued to produce high-quality ductile iron castings with excellent microstructures. The three case history foundries all were able to increase their use of ductile iron returns in their charges. The savings levels achieved ranged from $7.50 per ton to over $30 per ton. It should be noted that the savings level calculations greatly depends on what value the foundry places on its ductile iron returns.

Nodu-Bloc replacement of MgFeSi allows foundries to continue to use time-proven ladle metallurgy practices while also realizing the cost savings of pure magnesium processes. All of this is achieved without the need for costly wire feeding equipment and alloys or installation of a converter. Additionally, should supplies of U.S. produced MgFeSi be reduced due to producer plant closings, Nodu-Bloc replacement of MgFeSi is one method to stretch supplies. Additional research work continues to strive for methods that will allow even greater replacement levels of MgFeSi.

Conclusions:

1.) Extensive laboratory testing of Nodu-Bloc 21% iron-magnesium briquettes has shown that up to 30 percent replacement of MgFeSi could be accomplished. Good and comparable magnesium recovery and microstructures were obtained from substituting 1.5 weight percent addition rates of MgFeSi with 1.0 weight percent MgFeSi and 0.10 weight percent Nodu-Bloc. Higher addition rates may result in increased reactivity, possible metal splashing and reduced recoveries, but these are dependent on ladle design and other foundry variables.

2.) Nodu-Bloc is a very attractive product for silicon control in ductile iron production, since the iron-magnesium briquettes will introduce only trace contributions of silicon to the final castings. This may be of great advantage to foundries producing ferritic ductile iron with requirements for impact resistance where final silicons of 2.5% are often necessary to avoid brittleness.

3.) Production results from three different foundries, showed that Nodu-Bloc replacement of MgFeSi of up to 50% was feasible.

4.) Nodu-Bloc iron-magnesium briquettes appear to be provide greater efficiency in desulfurization than MgFeSi in medium sulfur base irons (0.02 to 0.05%). In such cases, Nodu-Bloc may be an attractive alternative to competitive treatment processes such as converter and cored wire. The mixture Nodu-Bloc and MgFeSi will still provide the most best advantages of MgFeSi versus pure magnesium when it comes to facilitating good nucleation response of the treated metal.

Part II of this paper will address new advances in post-inoculation practices of ductile iron using newly developed inoculants that contain a significant amount of oxy-sulfide forming elements.

References:

1.) Modern Castings, January 2000
2.) Ryan's Notes, April 12, 1999
3.) Ryan's Notes, March 19, 2001
4.) Ryan's Notes, July 30, 2001
5.) T. Skland, Elkem Research Laboratory, Norway

Table 1. "Plight of the U.S. Ferrosilicon Industry"
U.S. FeSi Producer Statistics
(International Trade Commission Questionnaire Responses)

	2000 est.	1999 est.	1998 actual	1997 actual
Shipments (Metric tons of contained silicon for both 50% and 75% Ferrosilicon)	180,000	180,000	186,497	189,755
75% FeSi Prices (Price per lb. of contained silicon)	$0.3483*	$0.3991	$0.4281	$0.4765
Operating Income (Loss) in Millions	($30.7)	($10.6)	($2.8)	%15.4
*Average 75% FeSi for Year 2000				

Table 2. U.S. FeSi Producer Statistics
Ferrosilicon Production - 20 years of contraction

	1980	2000	+/-%
Ferrosilicon Producers	7	5	
No. of Furnacea	39	9	(77%)
Installed KVA Capacity	804	224	(72%)
Production (Metric Tons)	585,551	408,000	(30.3%)

Table 3. Comparison of Nodu-Bloc Iron-magnesium Briquettes to MgFeSi

		MgFeSi	Iron-magnesium Briquettes
Melting Temperature		2,350 to 2,450°F	<2.050°F
Size (typical)		1 in x 1/4 in.	1.25 x 1.0 x .5 in.
Density	5.5% grade	4.05 grams/cc	
	11% grade	3.50 grapms/cc	4.55 grams/cc
	15% grade		4.1 grams/cc
	20% grade		3.3 grams/cc
Reactivity in Open Ladle		Moderate	Moderate & "brighter"
Alloy chemistry control capability		Fair	Excellent

Table 4. Research Laboratory Test Results
0.013% Sulfur Base-Iron

Tap No.	Mg Substitution Level	% Mg	% Sulfur	Recovery
#1 - 2.5% Addition or 16.5 lbs. MgFeSi	0% - Base	0.056	0.0235	44%

#2 - 8.36 lbs MgFeSi & .44 lbs Nodu-Bloc	15%	0.044	0.009	53%
#3 - 7.04 lbs MgFeSi & .88 lbs Nodu-Bloc	30%	0.038	0.007	49%
#4 - 4.84 lbs MgFeSi & 1.43 lbs Nodu-Bloc	50%	0.031%	0.008	40%

Notes:

1. Magnesium FeSi alloy - 5.9% Mg, Nodu-Bloc - 21% Mg
2. 300 kg Tundish Ladle, Base Sulfur Level - 0.013%
3. Treatment Temperature - 1,500^{o}C (2,732^{o}F), Tundish filling time - 45 sec.
4. Post-inoculation - 0.30% Ba containing 75% FeSi stream inoculation into transfer ladle

Magnesium Recovery calculations based on the formula:

$$\% \text{ Mg recovered} = \frac{(\%) \text{ Mg residual} + \text{base iron sulfur reduction}}{\% \text{ Mg addition}} \times 100\% \ (\%)$$

Table 5. Research Laboratory Test Results
0.033% Sulfur Base-Iron

Tap No.	Mg Substitution Level	% Mg	% Sulfur	Recovery
#1 - 2.5% Addition or 16.5 lbs. MgFeSi	0% - Base	0.056	0.0235	44%
#2 - 10.67 lbs MgFeSi & 1.474 lbs Nodu-Bloc	30%	0.055	0.017	47%
#3 - 8.25 lbs MgFeSi & 2.36 lbs Nodu-Bloc	50%	0.039	0.019	35%

Notes:

1. Magnesium FeSi alloy - 5.9% Mg, Nodu-Bloc - 21% Mg
2. 300 kg Tundish Ladle, Base Sulfur Level - 0.033%
3. Treatment Temperature - 1,500^{o}C (2,732^{o}F), Tundish filling time - 45 sec.
4. Post-inoculation - 0.30% Ba containing 75% FeSi stream inoculation into transfer ladle
5. Magnesium Recovery calculations based on the formula:

$$\% \text{ Mg recovered} = \frac{(\%) \text{ Mg residual} + \text{base iron sulfur reduction}}{\% \text{ Mg addition}} \times 100\% \ (\%)$$

Table 6. Research Laboratory Microstructure Results
0.013% Sulfur Base-Iron - 25 mm Section Size

Nodu-Bloc Substitution Level	**0%**	**15%**	**30%**	**50%**
Nodule Count (mm^2)	184	188	201	237
Nodularity %	85%	85%	89%	89%
Ferrite Content %	41	42	42	46
Pearlite %	59	58	58	54
Shape Factor	0.80	0.80	0.81	0.81
Mean Diameter (in microns)	21.0	21.3	21.2	19.5

Notes:
1) Test casting section size - 25mm

Table 7: Production Experience of Foundry A using 15% Nodu-Bloc Iron-magnesium Briquettes

	Original Charge	Nodu-Bloc Modified Charge
Foundry Returns	2,100 lbs	2.500 lbs
Steel scrap	1,500 lbs	1,100 lbs
Carbon	55 lbs	40 lbs
Silicon Carbide	4 lbs	4 lbs
MgFeSi	27 lbs	21 lbs
Nodu-Bloc 15%	0 lbs	2.9 lbs
75% Foundry FeSi	11 lbs	11 lbs
Cover Steel	11 lbs	11 lbs
Final Chemistry		
% Carbon	3.70% - 3.85%	3.70% - 3.85%
% Silicon	2.60% - 2.70%	2.60% - 2.70%
% Sulfur	0.007% - 0.009%	0.007% - 0.009%
% Magnesium	0.030 - 0.040%	0.03 - 0.040%

Nodule Count (mm^2)	275	275
Nodularity	95%	95%
Carbides	None	None
Notes: 1) 1,900 lb. open ladle, sandwich treatment method		

Table 8: Production Experience of Foundry B using 20% Nodu-Bloc Iron-magnesium Briquettes

	Original Charge	Nodu-Bloc Modified Charge
Foundry Returns	750 lbs	900 lbs
Steel scrap	750 lbs	600 lbs
Carbon	28 lbs	23 lbs
Silicon Carbide	5 lbs	5 lbs
MgFeSi	12 lbs	6.5 lbs
Nodu-Bloc 20%	o lbs	2.1 lbs
Proprietary Inoculant	3.25 lbs	
75% Foundry FeSi	---	2.75 lbs
Cover Steel	22 lbs	22 lbs
Final Chemistry		
% Carbon	3.60% - 3.75%	3.60% - 3.75%
% Silicon	2.5% - 2.65%	2.50% - 2.65%
% Sulfur	0.0075%	0.0075%
% Magnesium	0.035 - 0.045%	0.035 - 0.045%
Nodule Count (mm^2)	225	250
Nodularity	95%	98%
Carbides	None	None
Notes: 1) 750 lb. tundish treatment ladle		

Table 9: Production Experience of Foundry C using 15% Nodu-Bloc Iron-magnesium Briquettes

	Original Charge	Nodu-Bloc Modified Charge
Foundry Returns	0 lbs	1,000 lbs
Steel scrap	200 lbs	200 lbs
Nodular Pig Iron	1,800 lbs	800 lbs
Carbon	2 lbs	6 lbs
75% FeSi lumps	16 lbs	0 lbs
MgFeSi	49 lbs	21 lbs
Nodu-Bloc 15%	0 lbs	8 lbs
Nodu-Disc 15%	0 lbs	3 lbs
75% Foundry FeSi	20 lbs	20 lbs
Notes: 1) Base iron sulfur level - 0.025%		

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Offsetting Macro-shrinkage in Ductile Iron What Thermal Analysis Shows

By: David Sparkman, May 30, 2001
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Abstract
The natural shrinkage that occurs during the solidification of Ductile Iron can be offset by the expansion caused by the formation of graphite. Though this has been known for some time, thermal analysis has some interesting contributions to understanding exactly what is going on, and offers some opportunities for better control of late graphite expansion in moderate section sizes. Different modes of solidification are examined and measured, and the early and late graphite content are calculated using thermal analysis. Carbon flotation is seen as a fourth form of solidification that is both hypereutectic and hypoeutectic.

Introduction to Macro-shrinkage and Expansion

Ductile Iron consists of primarily two materials: a steel matrix surrounding graphitic nodules. The steel matrix can be ferritic, pearlitic or martensitic, or a combination of any two. The majority of ductile castings are generally ferritic with less than 10% pearlite. A small amount of retained austenite is generally present and in combination with micro carbides, retains about 20% of the carbon1. This carbon can then be transformed into graphite during heat-treating.

The steel matrix will typically shrink 1.2 % when cooling from 2000 degrees to room temperature. Offsetting this is the transformation of dissolved carbon into nodules of graphite, which occupy 12% more volume as graphite than as carbon.

One insidious form of shrinkage is a suck-in. It is caused by the same factors as shrinkage, but shows no internal porosity as the volume loss is transferred to the surface of the casting. Suck-ins are caused by the combination of a high shrinkage iron, and a thin or weak casting wall that cannot resist the internal pull. This could be due to a combination of a casting designed hot spot and/or hotter than normal iron. Eutectic and hypereutectic iron is more susceptible to this problem than hypoeutectic iron. Though these castings might not show internal shrinkage, they should be counted as having shrinkage nonetheless.

Two other forms of voids appear in iron: micro-shrinkage, and gas or blows. The micro-shrinkage appears in the grain boundaries[5 10 11] as the final solidification takes place, and is caused by micro-segregation where the grain boundaries become enriched in low melting elements and phases[8]. Gas is caused by Nitrogen and Hydrogen being present in the iron[9].

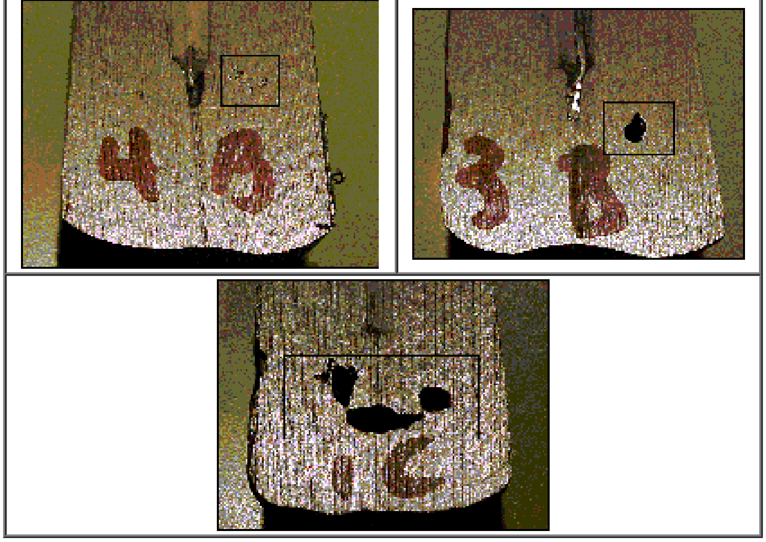


Figure 1. These are three examples of different levels of macro-shrinkage in thermal analysis cups. Shrinkage occurs at the point of the last metal to solidify, so is located around the thermal couple for easy detection. Some suck-in occurred in the first and second sample.

Literature Review

Skaland and Grong[1] suggest that up to 20% of the carbon in iron does not transform to graphite or pearlite, but is tied up as micro partials of carbides that only convert to graphite on heat treating. They base this on the results of studies of heat-treating, which increases both the total graphite and the nodule count. This suggests that 20% of the carbon present must be discounted, as it will not form graphite during solidification.

Heine[3] suggests that higher nodule counts lead to less shrinkage, but that above about 4.70, carbon floatation sets in, and then the nodule counts will vary greatly from the depleted zone to the flotation zone. He also reported two Liquidus arrests in strongly hypereutectic irons[4].

Stefanescu et al[5] suggest that shrinkage be broken down into macro-shrinkage caused by feeding problems, micro-shrinkage caused by contraction of the solid metal, and by micro-porosity caused by gas evolution within the iron. In this paper, we will use Stefanescu's definitions of shrinkage and examine what can be done to minimize macro-shrinkage.

Graphite Growth in Solidifying Iron

Graphite is a hexagonal-closepack form of carbon that can grow in both the liquid and solid forms of iron. In theory, in irons above the eutectic composition of carbon, the graphite first nucleates in the liquid, and then continues to grow in the solid. In irons below the eutectic composition, the graphite does not start to grow until the iron reaches eutectic temperature. As seen in a micro, the larger nodules are from growth initiated in the liquid, and the smaller nodules are from growth that does not start until solidification temperatures are reached. During heat-treating, the existing nodules increase in size, and very small nodules appear[1].

The graphite nodules that form in the liquid in hypereutectic irons continue to grow as the iron cools, so the amount of growth that occurs in the liquid is smaller than what would be assumed by examining the micro.

The expansion from the graphite that grows in the liquid, generally pushes liquid back into the riser or down sprue, and does not offset shrinkage. This is because hypereutectic irons do not form thick walls before the eutectic temperature is reached, and of course, there are no dendrites to block this reverse feeding.

Late graphite is defined as graphite that grows during or after the eutectic solidification. This late graphite can exert internal pressure to offset the shrinkage we would like to prevent.

So in order to minimize shrinkage, it is necessary to maximize the formation of late graphite without having to reduce the actual amount of graphite. Understanding what happens in a non-steady state solidification of Ductile Iron suggests a few ways that this can be done.

In a hypoeutectic mode of solidification, austenite forms as a solid with a lower than average carbon content. This increases the carbon content of the remaining liquid until it reaches the eutectic composition. Likewise, in a hypereutectic mode of solidification, graphite nodules form in the liquid, removing carbon from the liquid until it is reduced to the eutectic composition

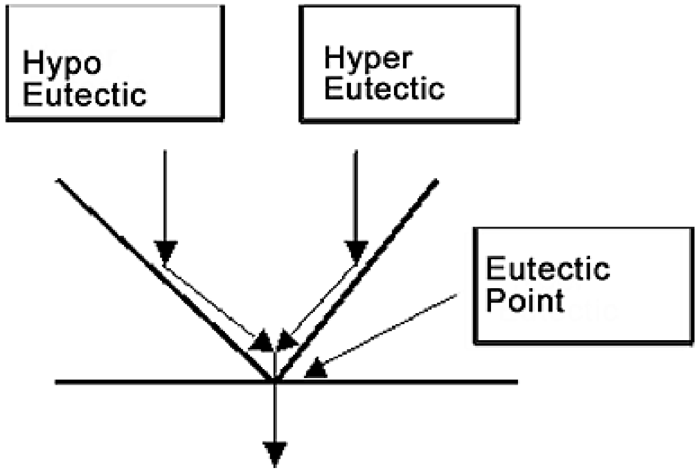


Figure 2. Phase diagram showing movement of carbon concentration in liquid metal as iron solidifies.

It would seem from figure 2 that the maximum amount of carbon that can be formed in late graphite is determined by the eutectic composition, and as long as the iron is at eutectic or above, the amount of late graphite will be the same. But there are some methods that can actually increase the amount of late graphite. The first is to reduce the silicon, the second is to reduce the pearlite, and the third is to run slightly hypereutectic and make use of magnesium's ability to suppress the formation of graphite. The first two methods will also significantly change the properties of the iron, so they may not be possible to implement. The third, which involves running a C.E. from 4.40 to 4.55, opens some possibilities.

Thermal Analysis shows how this third method works and how it actually decreases shrinkage. TA also shows the pitfalls of higher C.E.s and where adding more carbon may actually increase shrinkage.

Increasing Graphite to Avoid Shrinkage
Thermal analysis reveals that under dynamic conditions, the amount of late graphite can be increased considerably by hitting a hypereutectic chemistry between 4.33 and 4.60 that solidifies without a graphitic liquidus. To actually benefit from this window, the C.E. should be slightly hypereutectic (4.4+) and safely away from a higher C.E. that would form a graphitic liquidus. Our research indicates that this point is about 4.6+, though it may change with section size and magnesium level.

In qualifying curve types in thermal analysis, there are three basic shapes: One that shows an austenitic liquidus and a eutectic arrest, one that shows a graphitic liquidus and eutectic arrest, and one that only shows a eutectic arrest.

Surprisingly, the eutectic only mode is very common in iron used for small and medium size casings. When testing the chemistry for these eutectic only irons, it was found that the carbon equivalent varied from the eutectic composition of 4.33 all the way up to 4.58. The samples above 4.66 carbon equivalent generally show a graphite liquidus.

It is speculated that the magnesium is inhibiting the graphite liquidus up to about a 4.6 carbon equivalent. The level of magnesium in the iron may also have an effect on how much of a carbon equivalent can be suppressed. This means that an iron with a C.E. of 4.55 can behave as a eutectic iron but will add an additional 22 points of carbon to counteract the shrinkage. But an iron with a C.E. of 4.65 will behave not much differently than one of 4.33 C.E. in suppressing shrinkage.

C.E.	Silicon	Carbon	Graphite in Liquid	Late Graphic	Improvement Over Eutectic
4.20	2.40	3.40	0.00	2.72	-3.5%
4.25	2.40	3.45	0.00	2.76	-2.1%
4.30	2.40	3.50	0.00	2.80	-1.1%
4.33	2.40	3.53	0.00	2.82	Base Line
4.35	2.40	3.55	0.00	2.84	0.7%
4.40	2.40	3.60	0.00	2.88	2.1%
4.45	2.40	3.65	0.00	2.92	3.5%
4.50	2.40	3.70	0.00	2.96	5.0%
4.55	2.40	3.75	0.00	3.00	6.3%
4.60	2.40	3.80	0.00	3.04	7.8%
4.65	2.40	3.85	0.32	2.82	0%
4.70	2.40	3.90	0.37	2.82	0%

Figure 3. Assumptions: 20% carbon retained in matrix, no graphitic liquidus forms till above 4.60 C.E. Above 4.70 C.E. there is a risk of carbon flotation.

This would account for the frequency that eutectic freezing modes are found. The Eutectic is no longer just a point, but a small range from 4.33 to about 4.60 due to the presence of magnesium. This can result in an increase of 13% more carbon forming in the late solidification, or shrinkage being reduced by 1.6% of the total volume of the carbon. This suggests that the amount of shrinkage in castings can vary considerably over a small carbon range.

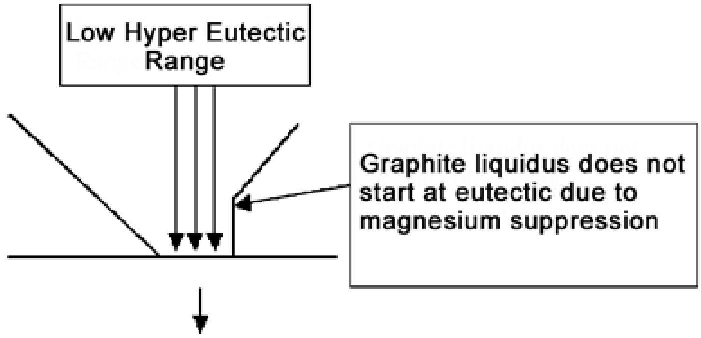


Figure 4. Expanded region of eutectic zone due to magnesium suppression of graphite formation.

Once the carbon equivalent becomes higher than the suppressed value, then the effect will be lost, the extra carbon will be removed by graphite formed in the liquid, and macro-shrinkage will increase.

This goes against the idea of counteracting shrinkage by simply increasing the carbon content. It suggests that we, instead, should increase the carbon until the iron is slightly hypereutectic, but does not yet exhibit a graphite liquidus.

Carbon Flotation in small castings
As the carbon content increases into the graphitic liquidus area, a stronger graphitic liquidus occurs that may not simply reduce the carbon content to eutectic, but may actually remove enough carbon to reduce the C.E. level below the eutectic. This results in an unusual thermal analysis curve that has both a graphitic liquidus and an austenite liquidus followed by the eutectic arrest. This then proves even further that increasing the carbon beyond the graphitic liquidus may drastically increase shrinkage.

Heine and others have previously documented multiple arrests in their research, but these arrests were not identified as anything other than graphitic arrests4. This is the first time that multiple liquidus arrests have been identified in a single sample.

The dynamics of inoculation, magnesium, carbon content, and other alloys make a system that needs to be tightly controlled to supply the necessary amount of carbon and alloys and yet prevent a graphitic liquidus from increasing shrinkage and porosity.

Results
Samples were taken from many foundries in this research. Two are presented as demonstrating the interrelationships of freezing mode, shrinkage, late graphite and nodule count. The results are from the thermal analysis instrument using the same calibration for both foundries. While the readings are approximant, they are in agreement with the measurements of the foundries, i.e. the 77% nodularity was recorded as an 80%.

Table 1 and 2 show typical results from two different foundries having different chemistry aims and inoculation practices. The test data shows considerable interrelationship between shrinkage, and nodule count in the hypoeutectic irons, and in table 1, the shrinkage seems to be related to both nodule count, and the double arrest.

The Hypo-hypereutectic arrest in table 1 greatly reduced the available late graphite and increased the shrinkage. The nodule count relates well to the nodularity. This foundry would do well to reduce their carbon slightly and avoid hypereutectic freezing modes. Late graphite control would greatly benefit shrinkage in this foundry.

Mode	Nodularity	Nod Count	Late Graphite	Shrink	Undercooling
Eutectic	84	330	100	1	8
Hypoeutectic	86	330	86	0	5
Hypo-Hyper	93	380	69	12	9
Eutectic	85	380	100	6	7
Hyper	77	330	76	2	11
Hyper	78	300	75	nm	9

Table 1 Generally hypereutectic iron (nm - not measured)

In table 2 there is a completely different chemistry practice with a slightly higher inoculation practice. Late graphite comes out during about 93% of the solidification, but it is not enough to offset the lower carbon level and higher inoculation practice. This foundry would do well to decrease their inoculation down to the 300 levels if possible. If chill problems prevent this, then they might consider raising the C.E. to produce eutectic mode solidification.

Mode	Nodularity	Nod Count	Late Graphite	Shrink	Undercooling
Hypoeutectic	84	470	93	Nm	1
Hypoeutectic	88	470	87	19	1
Hypoeutectic	89	470	92	18	1
Hypoeutectic	87	450	96	17	0
Hypoeutectic	91	470	95	22	0
Hypoeutectic	90	370	92	9	1
Hypoeutectic	94	320	95	1	0
Hypoeutectic	86	370	92	9	1
Hypoeutectic	94	320	91	2	0

Table 2 Generally hypoeutectic iron (nm - not measured)

Discussion

Shrinkage has many causes. The question is: Is shrinkage an intermittent problem or a consistent problem? Consistent problems are problems that require a redesign of the gating and risering system, additions of chills, and even a redesign of the casting or change in the carbon equivalent of the iron. An intermittent problem is generally where the foundryman is at a loss for a solution. While tramp elements that cause significant alloy segregation in the grain boundaries[8] can cause small micro-shrinkage by lowering the grain boundary freezing temperature, this discussion is directed more toward graphite control to offset normal macro-shrinkage.

There are four solidification modes that can occur in ductile iron: hypoeutectic, hypereutectic, eutectic, and a combination of hyper-hypoeutectic. These classifications are applied to the shape of the thermal analysis curve, not the chemistry. These curves may differ from what can be expected from chemistry because of the speed of cooling and the suppression of graphite formation due to magnesium. Faster cooling will shift the mode from hypereutectic toward eutectic, and from eutectic toward hypoeutectic.

In the hypoeutectic mode there is an austenitic liquidus arrest, followed by a eutectic arrest. In the hypereutectic mode there is a graphitic liquidus arrest followed then by a eutectic arrest. In the eutectic mode there is only a eutectic arrest. In the hyper-hypoeutectic mode there is first a graphitic liquidus arrest followed by an austenitic liquidus arrest, and then finally, the eutectic arrest.

Hypereutectic Mode

In a hypereutectic mode iron, graphite nodules first form in the liquid. This is a moderately low energy reaction that may go on for some time. The heat generated from the graphite slows the cooling rate, and therefore prolongs the length of the arrest. Since no solid metal is precipitated during this arrest, the walls of the casting are thin to non-existent depending on the temperature gradient.

During this cooling time, the expansion due to the graphite may simply push iron back into the riser, or, if it is a riserless casting or the gating is frozen off, will cause some mold wall movement, if the wall is still thin or the liquid is still a large portion of the casting. Since hypereutectic irons will not form thick casting walls before entering the eutectic arrest, they should be risered, or there will be mold wall movement! This goes against conventional thinking, but such previous thinking was probably based on hypereutectic chemistry, and a eutectic freezing mode where no graphite forms in the liquid.

The formation of graphite nodules in the liquid reduces the remaining carbon in the iron down to the eutectic level. Assuming a 3.9 carbon and a 2.4 silicon iron (C.E. of 4.7), this will lead to a carbon level remaining in the liquid of 3.53% with the balance of 0.37% going to expansion in the liquid riser or mold wall movement.

4.33 C.E. - (2.4 Si / 3) = 3.53 C

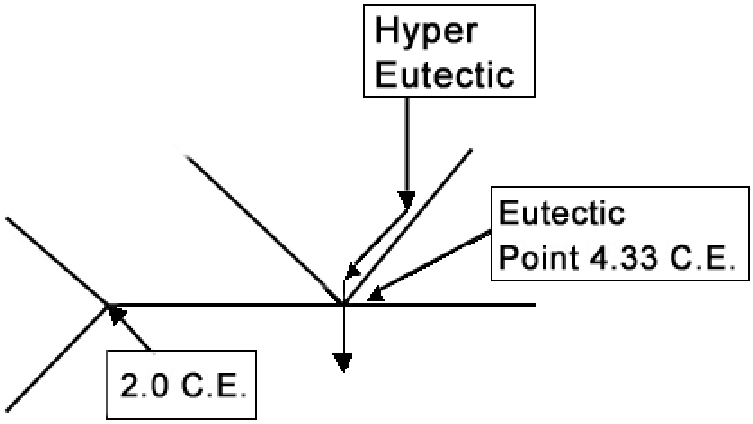


Figure 4. Hypereutectic liquid iron is depleted of carbon down to the eutectic point by formation of graphite

Once the graphite liquidus is finished, the eutectic forms and the remaining carbon down to the capability of the austenite to hold carbon (2% C.E.) is rejected from the austenite in the form of graphite. Again assuming a 3.9 carbon and a 2.4 silicon iron, this will lead to the formation of about 2.7% graphite in the iron at eutectic.

2.0 C.E. - (2.4 Si / 3) = 1.2 % C in austenite
3.9 C - 0.37 graphite - 1.2 C in austenite = 2.33% graphite formed at eutectic temperature
3.9 C - 0.37 graphite in liquid - 0.78 retained carbon = 2.75 graphite for expansion.

Figure 5. Note the large area of the graphitic arrest in the Cooling Rate graphic. This represents a considerable amount of graphite coming out. The energy production of the graphitic liquidus is not as great as an austenite liquidus. This iron would be subject to macro-shrink, but the micro-shrink is ok. The graphite shape is also poor with several clusters of fast growing graphite present.

The remainder of the carbon can transform into graphite as the iron cools further. The amount of retained carbon in the unheat-treated room temperature iron is about 20%1 plus whatever carbon is retained in pearlite or carbides. If we assume no pearlite, then the total expansion of the graphite that benefits fighting shrinkage would be 2.75%, and the wasted graphite expansion would be 0.36% or 13% of the total expansion of graphite.

Hypoeutectic Mode
In a hypoeutectic mode, an austenite liquidus forms, and dendrites grow into the liquid, increasing the carbon content of the remaining liquid. This iron will develop a stronger casting wall to resist mold wall movement, but will have less graphite formed to offset macro-shrinkage. For an iron with 3.4 carbon and 2.1 Silicon (C.E. of 4.1), a little less than 10% of the casting will be solid before the eutectic is reached.

2x + (1-x)* 4.33 = 4.1 C.E. (lever rule)
x = 9.87%

At the eutectic, the graphite formed would be 2.1%

2.0 C.E. - (2.1 Si / 3) = 1.3 % C in austenite
3.4 C - 1.3 C in austenite = 2.1% graphite formed at eutectic temperature

3.4 C - 0.68 retained carbon = 2.72 graphite for expansion.

Applying similar logic to the previous example, we would gain a total of 2.72% graphite to fight expansion. This is not much different than the hypereutectic mode result.

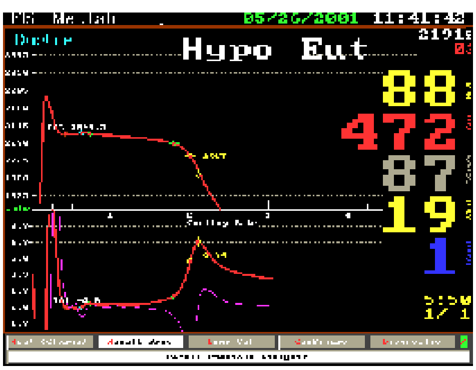


Figure 6. Hypoeutectic mode solidification: austenite liquidus and eutectic

Eutectic Mode

In the eutectic mode, there is no liquidus arrest. Due to the presence of magnesium, a single arrest (eutectic) mode can occur between 4.3 C.E. and as high as a 4.6 C.E. Assuming 2.4 silicon, this iron could contain from a 3.5 to a 3.8 carbon. At the eutectic, this would produce a range from 2.3 to 2.6% graphite: a variation of 13%.

2.0 C.E. - (2.4 Si / 3) = 1.2 % carbon in austenite
3.5 C - 1.2 C in austenite = 2.30% graphite formed at eutectic temperature
3.8 C - 1.2 C in austenite = 2.60% graphite formed at eutectic temperature
3.5 C - 0.70 retained carbon = 2.80% graphite for expansion.
3.8 C - 0.76 retained carbon = 3.04% graphite for expansion.

Applying similar logic to the previous examples, we would gain a total of between 2.80% and 3.04% graphite to fight expansion. There is no liquid expansion problem, and the 3.8% carbon example has 13% more beneficial graphite then the slightly higher 3.9% carbon hypereutectic iron.

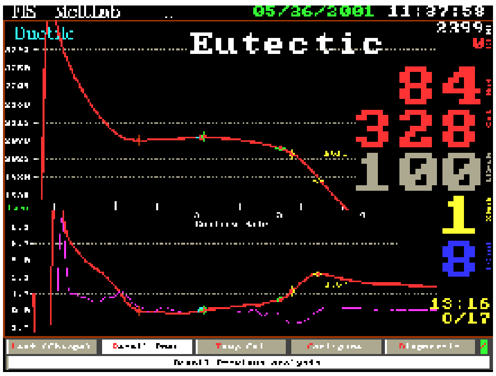


Figure 7. Single arrest eutectic mode solidification

Hyper-Hypoeutectic Mode

This mode occurs more often than suspected. A large graphitic liquidus starts a reaction that removes so much carbon from the liquid, (possibly through flotation) that the remaining liquid turns hypoeutectic, and an austenite liquidus follows. This material has the worst aspects of a hypereutectic iron (mold wall movement, no appreciable wall thickness, low graphite contribution to fight shrink) and has all the bad aspects of a hypoeutectic iron (even lower graphite contribution to fight shrink).

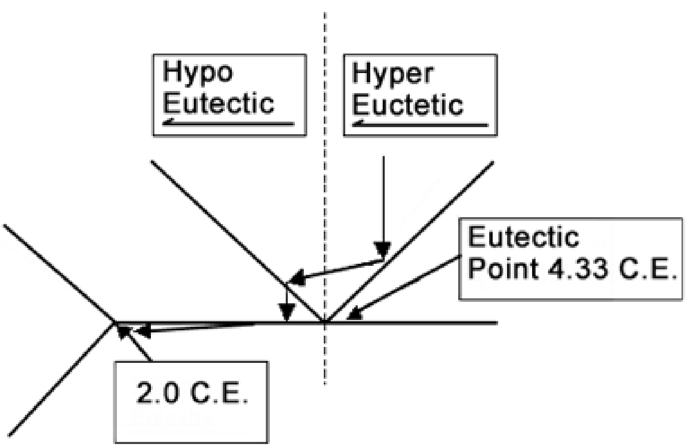


Figure 8. Expanded region of eutectic zone due to magnesium suppression of graphite formation.

Assuming a 3.9 carbon and a 2.4 silicon iron (C.E. of 4.7), and that the iron falls to a 4.25 C.E. this will lead to a carbon level remaining in the liquid of 3.45% with the balance of 0.45% going to expansion in the liquid riser or mold wall movement.

4.25 C.E. - (2.4 Si / 3) = 3.45 C

The eutectic forms, and the remaining carbon down to the capability of the austenite to hold carbon (2% C.E.) is rejected from the austenite in the form of graphite. Again assuming a 3.9 carbon and a 2.4 silicon iron, this will lead to the formation of about 2.6% graphite in the iron at eutectic.

2.0 C.E. - (2.4 Si / 3) = 1.2 % carbon in austenite
3.9 C - 0.45 graphite in liquid - 1.2 C in austenite = 2.25% graphite formed at eutectic temperature
3.9 C - 0.45 graphite in liquid - 0.78 retained carbon = 2.67 graphite for expansion.

The remainder of the carbon can transform into graphite as the iron cools further. The amount of retained carbon in the unheat-treated room temperature iron is about 20%1 plus whatever carbon is retained in pearlite or carbides. If we assume no pearlite, then the total expansion of the graphite that benefits fighting shrinkage will be 2.67%, and the wasted graphite expansion will be 0.45% or 17% of the total expansion of graphite.

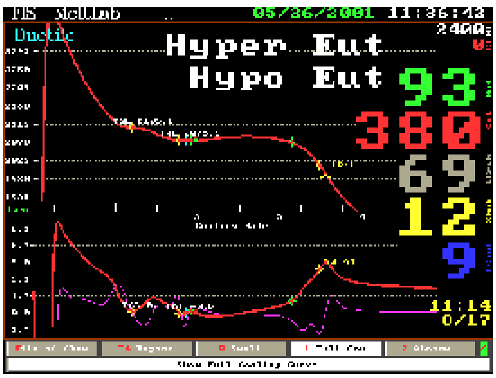


Figure 9. The two liquidus arrests are followed by the eutectic arrest. The first liquidus arrest is large but not energetic (graphitic). The second liquidus arrest is small but very energetic (austenite).

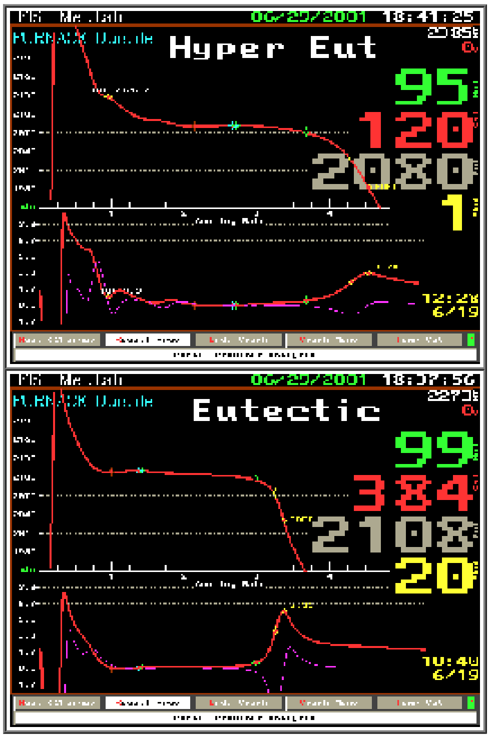
Conclusion
Macro-shrinkage is the result of the interaction of several complex influences in the iron. If the shrinkage is constantly present from day to day, then the gating and risering vs. the iron chemistry needs to be revised. But if the problem comes and goes, and the chemistry seems to be consistent during these episodes of shrinkage, then the problem is most likely in the control and timing of the graphitizing process.

Magnesium opens up the C.E. range of a eutectic iron by inhibiting the formation of a graphite liquidus. This opens up the possibility to have more carbon in the iron to offset shrinkage so long as no graphitic liquidus occurs. This phenomena needs to be studied more in terms of effective magnesium vs. carbon level vs. inoculation.

Small-localized carbon flotation may be far more common than previously thought, and can result in slow cooling sections anytime that the graphitic liquidus occurs in that section size. This can account for 15 to 20% less graphite being available to counteract the macro-shrinkage. This can also occur in iron when the carbon equlivant is on the high side of safe, and the effective magnesium is on the low side of the normal operating range. Inoculation may also influence the appearance of the graphitic liquidus.

The eutectic mode of freezing with irons that are above the eutectic in chemistry will give the most "late graphite" to counteract macro-shrinkage. There is as much as a 13% gain in late graphite possible with this mode of solidification. Likewise, irons of the same C.E. level that are lower in silicon will have more graphite to counteract shrinkage.

Thermal analysis provides a unique picture of how all these factors combine together to produce different modes of freezing. It can identify irons susceptible to carbon flotation, as well as when the iron will have a graphitic liquidus.



Before and after in-stream inoculation

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Ductile Iron News

Ductile Iron Society

To Promote the production and application of ductile iron castings

Issue 2, 2001

Nodulizing and Inoculation Approaches for Year 2000 and Beyond - Part 1

Tables: Below are all the tables associated with the Nodulizing Article.

Table 1. "Plight of the U.S. Ferrosilicon Industry"
U.S. FeSi Producer Statistics
(International Trade Commission Questionnaire Responses)

	2000 est.	1999 est.	1998 actual	1997 actual
Shipments (Metric tons of contained silicon for both 50% and 75% Ferrosilicon)	180,000	180,000	186,497	189,755
75% FeSi Prices (Price per lb. of contained silicon)	$0.3483*	$0.3991	$0.4281	$0.4765
Operating Income (Loss) in Millions	($30.7)	($10.6)	($2.8)	$15.4
*Average 75% FeSi for Year 2000				

Table 2. U.S. FeSi Producer Statistics
Ferrosilicon Production - 20 years of contraction

	1980	2000	+/- %
Ferrosilicion Producers	7	5	
No. of Furnaces	39	9	(77%)
Installed KVA Capacity	804	224	(72%)
Production (Metric Tons)	585,551	408,000	(30.3%)

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Table 3. Comparison of Nodu-Bloc Iron-magnesium Briquettes to MgFeSi

		MgFeSi	Iron-magnesium Briquettes
Melting Temperature		2,350 to 2,450^{o}F	<2, 050^{o}F
Size (typical)		1 in. x 1/4 in.	1.25 x 1.0 x .5 in.
Magnesium %		3.5% to 11%	11%, 15% and 20%
Density	5.5% grade	4.05 grams/cc	
	11% grade	3.50 grams/cc	4.55 grams/cc
	15% grade		4.1 grams/cc
	20% grade		3.3 grams/cc
Reactivity in Open Ladle		Moderate	Moderate & "brighter"
Alloy chemistry control capability		Fair	Excellent

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Table 4. Research Laboratory Test Results
0.013% Sulfur Base-Iron

Tap No.	Mg Substitution Level	% Mg	% Sulfur	Recovery
1. 1.5% Addition or 9.9 lbs MgFeSi	0% - Base	0.042	0.010	48.70%
2. 8.36 lbs MgFeSi & .44 lbs Nodu-Bloc	15%	0.044	0.009	53%
3. 7.04 lbs MgFeSi & .88 lbs. Nodu-bloc	30%	0.038	0.007	49%
3. 4.84 lbs MgFeSi & 1.43 lbs Nodu-Bloc	50%	0.031%	0.008	40%

Notes:
1.) Magnesium FeSi alloy - 5.9% Mg, Nodu-Bloc - 21% Mg
2.) 300 kg Tundish Ladle, Base Sulfur Level - 0.013%
3.) Treatment Temperature - 1,500oC (2,732oF), Tundish filling time - 45 sec.
4.) Post-inoculation - 0.30% Ba containing 75% FeSi stream inoculation into transfer ladle
Magnesium Recovery calculations based on the formula:

$$\%\ \text{Mg recovered} = \frac{(\%)\ \text{Mg residual + base iron sulfur reduction}}{\%\ \text{Mg addition}} \times 100\%\ (\%)$$

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Table 5. Research Laboratory Test Results
0.033% Sulfur Base-Iron

Tap No.	Mg Substitution Level	% Mg	% Sulfur	Recovery
#1 - 2.5% Addition or 16.5 lbs MgFeSi	0% - Base	0.056	0.0235	44%
#2 - 10.67 lbs MgFeSi & 1.474 lbs Nodu-Bloc	30%	0.055	0.017	47%

#3 - 8.25 lbs MgFeSi & 2.36 lbs Nodu-Bloc	50%	0.039	0.019	35%

Notes:

1. MgFeSi alloy - 5.9% Mg, Nodu-Bloc - 21% Mg
2. 300 kg Tundish Ladle, Base Sulfur Level - 0.033%
3. Treatment Temperature - 1,500oC (2,732^{o}F), Tundish filling time - 45 sec.
4. Post-inoculation - 0.30% Ba containing 75% FeSi stream inoculation into transfer ladle
5. Magnesium Recovery calculations based on the formula:

% Mg recovered = (%) Mg residual + base iron sulfur reduction / % Mg addition x 100% (%)

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Table 6. Research Laboratory Microstructure Results
0.013% Sulfur Base-Iron - 25 mm Section Size

Nodu-Bloc Substitution Level	0%	15%	30%	50%
Nodule Count (mm^2)	184	188	201	237
Nodularity %	85%	86%	89%	89%
Ferrite Content %	41	42	42	46
Pearlite %	59	58	58	54
Shape Factor	0.80	0.80	0.81	0.81
Mean Diameter (in microns)	21.0	21.3	21.2	19.5
Notes: 1.) Test casting section size - 25mm				

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Table 7: Production Experience of Foundry A using 15% Nodu-Bloc
Iron-magnesium Briquettes

	Original Charge	Nodu-Bloc Modified Charge
Foundry Returns	2,100 lbs	2,500 lbs
Steel scrap	1,500 lbs	1,100 lbs
Carbon	55 lbs	40 lbs
Silicon Carbide	4 lbs	4 lbs
MgFeSi	27 lbs	21 lbs
Nodu-Bloc 15%	0 lbs	2.9 lbs
75% Foundry FeSi	11 lbs	11 lbs
Cover Steel	11 lbs	11 lbs
Final Chemistry		
% Carbon	3.70% - 3.85%	3.70% - 3.85%
% Silicon	2.60% - 2.70%	2.60% - 2.70%
% Sulfur	0.007% - 0.009%	0.007% - 0.009%
% Magnesium	0.030 - 0.040%	0.03 - 0.040%
Nodule Count (mm^2)	275	275
Nodularity	95%	95%
Carbides	None	None
Notes: 1.) 1,900 lb. open ladle sandwich treatment method		

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Table 8: Production Experience of Foundry B using 20% Nodu-Bloc

Iron-magnesium Briquettes

	Original Charge	Nodu-Bloc Modified Charge
Foundry Returns	750 lbs	900 lbs
Steel scrap	750 lbs	600 lbs
Carbon	28 lbs	23 lbs
Silicon Carbide	5 lbs	5 lbs
MgFeSi	12 lbs	6.5 lbs
Nodu-Bloc 15%	0 lbs	2.1 lbs
Proprietary Inoculant	3.25 lbs	
75% Foundry FeSi	---	3.75 lbs
Cover Steel	22 lbs	22 lbs
Final Chemistry		
% Carbon	3.60% - 3.75%	3.60% - 3.75%
% Silicon	2.50% - 2.65%	2.50% - 2.65%
% Sulfur	0.0075%	0.0075%
% Magnesium	0.035 - 0.040%	0.035 - 0.045%
Nodule Count (mm^2)	225	250
Nodularity	95%	98%
Carbides	None	None
Notes: 1.) 1,900 lb. open ladle sandwich treatment method		

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Table 9: Production Experience of Foundry C using 15% Nodu-Bloc Iron-magnesium Briquettes

	Original Charge	Nodu-Bloc Modified Charge
Foundry Returns	0 lbs	1,000 lbs
Steel Scrap	200 lbs	200 lbs
Nodular Pig Iron	1,800 lbs	800 lbs
Carbon	2 lbs	6 lbs
75% FeSi Lumps	16 lbs	0 lbs
MgFeSi	49 lbs	21 lbs
Nodu-Bloc 15%	0 lbs	8 lbs
Nodu-Disc 15%	0 lbs	3 lbs
75% Foundry FeSi	20 lbs	20 lbs
Notes: 1.) Base iron sulfur level - 0.025%		

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Ductile Iron News
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Issue 2, 2001

News Briefs

MEETINGS

The **Fall T&O meeting** of the Ductile Iron Society will be held on October 3-5, 2001 at the Pioneer Resort and Marina in Oshkosh, Wisconsin. There will be a visit to Neenah Foundry.

The next **Research Committee Meeting** will be held on January 8-9, 2002 at the Ramada O'Hare in Rosemont, Illinois.

The **June 2002 meeting** has not been scheduled yet.

The **World ADI Conference** will be held on September 25-27, 2002 at the Galt Hotel in Louisville, Kentucky.

The **June 2003** meeting has not been scheduled yet.

There will be a **Keith Millis Symposium** on October 20-23, 2003 at the Crowne Plaza Resort in Hilton Head Island, South Carolina.

BUSINESS

Superior Graphite Co. Awarded Saturn's 2000 Outstanding Quality Achievement Award.

Jerry White, Quality Assurance Manager, (left) and Brian Mitalo, Sales Manager Metallurgical Products (right) accepting Saturn's 2000 Supplier Outstanding Quality Achievement Award.

Saturn Corporation held its annual Supplier Recognition Award Ceremony on June 19, 2001 at the Franklin Cool Springs Marriott in Tennessee.

During the ceremony, Saturn's 2000 Supplier Outstanding Quality Achievement award was presented to Superior Graphite Co.'s Jerry white, Quality Assurance Manager, and Brian Mitalo, National Sales Manager Metallurgical Products. Superior Grapite Co. won this award by meeting Saturn Corporation's stringent quality criteria, which included; zero parts per million defect rate, on-time delivery, and no recalls.

By winning this award, Saturn Corporation is formally recognizing Superior Graphite Co.'s commitment to superior performance in the areas of quality, service and price. "You made us who we are," Jerry Childers, UAW coordinator for Material Management, said to the gathering of Saturn suppliers. "So when you see those Saturn commercials on TV celebrating our ten year anniversary, remember you are a part of the Saturn family. You are a big part of why we're still here ten years later."

FEATURES

DEPARTMENTS