INEXPENSIVE METHOD TO PRODUCE COMPACTED GRAPHITE IRON WITHOUT COSTLY THERMAL ANALYSIS

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ARTICLE TAKEAWAYS:

1. Precise control of sulfur recovery for ductile iron & compacted graphite iron
2. Amount of sulfur addition in magnesium-treated iron needed to obtain a critical nodular graphite/compacted graphite (NG/CG) ratio depends many factors.

For several years, the iron casting environment is driving the need for stronger cast irons with lower weight than gray iron parts, but with improved machinability, thermal-fatigue resistance, damping capacity, casting mold yield, and castability compared to ductile iron parts. Compacted graphite cast irons (CGI) provide a cost-effective solution to meet these challenges. Automotive components, such as disc brake rotors, are prime candidates for conversion to compacted graphite iron production, especially where lighter weight and higher strength are important issues to design engineers. Unfortunately, producing consistent quality compacted graphite iron requires even more stringent controls than ductile iron production. The most popular method of producing CG iron requires the use of complex thermal analysis techniques. The equipment and foundry controls needed to produce CGI as well as associated licensing costs have prevented widespread use of CGI.

A review of worldwide research investigations and foundry experience involving different liquid metal treatment procedures to produce compacted graphite iron was the topic of a 2002 AFS Casting Congress Compacted Graphite Iron Panel. From these panel discussions, the presentation by D. Kelley generated a considerable interest in the "Resulfurizing after Magnesium Treatment". Kelley showed that in a production environment, using a 0.015 to 0.025% sulfur addition (after magnesium addition) to denodulize magnesium treated iron, he was able to consistently produce acceptable CG irons with less than 20 percent nodularity. The key to Kelley's success was the use of a new iron sulfide briquette (Resulf 30), which allowed consistently high sulfur recoveries (85 to 90%). Prior to using these briquettes, granular iron sulfide (iron pyrites) was used with sporadic and inconsistent CGI results; typical recoveries of were only 30 to 40%.

Since sulfur is used to denodulize the irons, there was little concern about contamination of foundry returns. This is not the case when another anti-nodularizing elements, such as titanium, is used in CGI production. This production research was a response to the desire of many foundries to add alternative elements such as titanium to "denodulize" magnesium treated ductile iron.

The simultaneous use of sulfur with inoculating agents is not a new concept. The use of sulfur added with potent oxy-sulfide forming elements was first demonstrated by Naro and Wallace (1970). Naro showed that balanced ratios of rare earths and sulfur, without the presence of ferrosilicon provided drastic reductions in undercooling, completely eliminated chill and promoted favorable graphite shapes in gray irons. In a 1984 study, Strande showed that calcium silicide based inoculants along with increased sulfur additions provided vastly improved machinability in gray iron castings compared to proprietary ferrosilicon based inoculants and similar late sulfur additions.

It was further demonstrated by Riposan (1998) that a small sulfur addition (less than 0.010%), when added concurrently with calcium silicon-based inoculants increased graphite nucleation potential in ductile iron, but without affecting graphite nodularity. Chisamera and Riposan (1998) also showed that the strong sulfide forming tendencies of calcium and rare earth metals, when used in conjunction with controlled sulfur additions, strongly promoted the formation of sulfide compounds assisting their effectiveness as nodular graphite nuclei.

The amount of sulfur addition in magnesium-treated iron needed to obtain a critical nodular graphite / compacted graphite (NG/CG) ratio depends on the residual magnesium content after magnesium treatment as well as holding time prior to pouring. Other important factors are casting wall thickness, mold type and thermal gradient effects.

Kelley also showed that it was also possible to produce both compacted graphite irons and ductile iron from the same base iron melt (suitable for ductile iron production) using cored wire containing a high magnesium containing ferrosilicon. Kelley, et al. also showed that it was possible to use such a magnesium treated ductile iron, with low residual Mg levels (0.025 to 0.04%) but with an addition of "fresh" sulfur which was in the form of a rapid dissolving iron sulfide briquette since loose, granulated iron pyrites produced inconsistent results. Less than 0.02 weight percent sulfur was needed to "denodulize" the iron. Thus, it was possible to have the same furnace melt chemistry and have a controlled transition from ductile iron to compacted graphite iron in the same campaign. The key to his success was having complete control over the magnesium reaction.

Sulfur can be both detrimental and beneficial element in ductile iron and compacted graphite iron. Sulfur's harmful and beneficial effects are related to the amount present before magnesium treatment (nodularizing process) as well as its concentration during graphite nucleation. A high base iron sulfur content is generally considered harmful because it will lower the magnesium efficiency and result in increased dross formation in both ductile and compacted graphite irons. However, in ductile iron, a minimum sulfur level of at least 0.005 to 0.008% is necessary after magnesium treatment to insure proper post-inoculation and reduce the risk of carbides. Thus, after magnesium treatment, the presence of critical sulfur levels is considered beneficial for the promotion of graphite nuclei. Further, the reaction of sulfur with sulfide forming elements such as rare earths and calcium enhance nucleation of graphite in ductile irons. In compacted graphite irons and after magnesium treatment, control of sulfur levels is critical for controlling graphite nodularity and promoting compacted formation.

In Kelley's, two sources of sulfur were used experimentally to resulfurize the magnesium treated iron. These included 1) FeS2 or iron pyrites, nominally containing 49ercent sulfur having a particle size of 70 mesh by down and 2) briquetted iron pyrites (Resulf 30) FeS2 briquettes. Excellent and consistent control of the sulfur recovery has been found to be an essential feature of this technology and it has been demonstrated in foundry conditions, for both ductile iron and compacted graphite iron.

In the early stages of the investigation, granular FeS2 additions after Mg-treatment were used to re-introduce sulfur (resulfurize) to an iron melt. Since iron pyrites are normally available only in very fine mesh sizes, difficulties are often encountered during the addition to ladles, resulting in inconsistent recoveries. The fine sized FeS2 particles, when added to molten irons, tend to become airborne due to convection currents of super-heated air, leading to the generation of obnoxious fumes and odors. For all these reasons, it was necessary to improve control over the sulfur addition. It was found that briquetted FeS2 (Resulf 30) can circumvent the inconsistencies of adding powdery iron pyrites. The "iron pyrite briquettes" are formulated to go into solution rapidly without odor. A second and important benefit of these briquettes is that they supply a "fresh sulfur" source to the iron, which affects the surface activity and speculatively changes the graphite growth mechanism promoting the "compacted" growth mode.

The sulfur additions were calculated from the charts developed by Riposan (1998).

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Granular iron pyrites additions were at a rate of 1.0 pound (0.49 pounds of contained sulfur or 0.032% S) per 1,550 pounds of treated metal, with a target of 0.03% Mg residual after Mg treatment. Iron sulfide briquettes were added at a rate of 0.75 pounds (0.225 pounds of contained sulfur or 0.015% S) per 1,500 pounds of metal.

The influence of initial sulfur level in the base iron was examined for several magnesium addition levels (Mg(add) additions of 0.04 to 0.05%) and a late sulfur addition (S(add) additions were 0.031%) in the form of one pound of finely granulated FeS2. The use of the finely granulated iron pyrites produced poor and inconsistent recoveries. Resulf 30 FeS2 briquettes containing 30% sulfur allowed for consistent sulfur recoveries and control over the final sulfur content.

The results summarized in Table 1 show the various rations of magnesium added, magnesium recovered, initial sulfur and final sulfur levels and the level of CG iron produced using Resulf 30 FeS2 briquettes. The amount of compacted graphite produced was 83.75% with a standard deviation of 5.7 based on 17 heats. The use of iron sulfide briquettes provided significantly improved control of sulfur. Final magnesium levels and sulfur levels were 0.030% and 0.021% respectively. The ratio of Mg (fin) to S (fin) was 1.463 with a standard deviation of 0.30.

TABLE 1: Magnesium and Sulfur Relationships in CG Iron - Resulf 30 Iron Sulfide Briquettes

Initial $S_{(in)}$% Mg(add)	% Mag add S(add)briquettes	% S add S(in)ratio	Mg(add)/ %Mg(fin)	Final S(fin)	Final % ratio	Mg(fin)/S(fin) ratio	Mg(fin)/S(in)	% CG
0.0136%	0.0333%	0.0186%	2.480	0.0296%	0.0209%	1.43	2.24	83.75%
Std Dev.	0.0026%	0.0024%	0.0025	0.0072%	0.0064%	0.30	0.656	

Sulfur additions rates for briquettes were reduced to an average of 0.019% compared to 0.031% for granular powder additions of iron pyrites. The briquetted iron pyrites appeared to provide the consistency for producing compacted graphite with 80% minimum compacted structures. The standard deviation for compacted graphite production decreased to 5.7 compared to 10.82 for granular additions tested under the same conditions.

Because of the favorable results obtained with the Resulf 30 iron sulfide briquettes, a series of heats were made from a gray base iron having an initial sulfur content of 0.057 percent. The averages of 6 heats of resulfurizing a gray base iron after magnesium treatment is shown in Table 2.

TABLE 2: Magnesium and Sulfur Relationships in CG Iron from Gray Base irons - Resulf 30 Iron Sulfide Briquettes

Initial $S_{(in)}$% Mg(add)	% Mag add S(add)briquettes	% S add S(in)ratio	Mg(add)/ %Mg(fin)	Final S(fin)	Final % ratio	Mg(fin)/S(fin) ratio	Mg(fin)/S(in)	% CG
0.057%	0.037%	0.016%	0.64	0.024%	0.014%	1.70	0.410	81%
Std Dev.	0.0011%	0	0.025%	0.0039%	0.0021%	0.42	0.07	6.5

Table 2 shows that it was possible to produce compacted graphite iron from a gray iron furnace chemistry. The compacted graphite irons so produced exhibited microstructures containing an average of 81% compacted graphite. The ratios of Mg (fin) to S (fin) to the percentage of compacted graphite formed increased somewhat to 1.7. This ratio is still well within the standard deviation calculated in Table 1, where the most consistent compacted graphite structures were obtained.

Precise control of sulfur recovery is an essential feature of this technology and it has been demonstrated to be easily achievable in foundry conditions, for both ductile iron and compacted graphite iron. The addition of controlled amounts of sulfur widen the magnesium “window” from which CGI can form. This technique has been found to be a low cost and reliable method to consistently manufacture CGI without costly thermal analysis equipment, licensing fees and without the use of harmful trace elements.

Additional details and findings can be found from the paper entitled “Magnesium-Sulfur Relationships in Ductile and Compacted Graphite as Influenced by Late Sulfur additions”, paper No. 03-093 that was published in 2003 at the AFS, authored by I. Riposan and R. L. Naro.

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