Method to Improve Inoculant Efficiency

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Since the early 1960's, ferrosilicon producers have made significant progress in the development of improved gray and ductile iron inoculants. Much of this work was the result of changes in melting methods. Coreless induction furnaces were rapidly replacing cupolas because of air pollution control requirements. Steel and purchased scrap were being used in the charges to replace some or all of the pig iron previously used and melting temperatures increased resulting in greater metal oxidation. Further, cupola melted irons typically responded far better to inoculation than irons melted in coreless induction furnaces. All these factors made it necessary for ferrosilicon producers to develop more effective graphitizing additives. As a result, new complex proprietary inoculants designed to improve the nucleating and fading characteristics of the older products became available.

Ferrosilicon based inoculants are manufactured in large submerged arc furnaces. Ingredients used for ferrosilicon production are shown in Figure 1 and consist of quartzite, steel scrap, wood chips and coal.

Figure 1: Ingredients used to make Ferrosilicon

Mineral oxides rich in elements from Group II and III in the Periodic Table of Elements, such as strontium, barium, calcium, titanium and cerium and magnesium are then either added to the smelting furnace or to the pouring ladle to achieve the desired inoculant chemistry. As will be shown, it is physically impossible to control or add other necessary elements that assist in the graphitization process into molten ferrosilicon during the smelting or pouring process. The necessary level of Group II mineral oxides additions will negatively impact the smelting and reduction reactions. Other necessary elements that cannot be added to the smelting furnaces are sulfur and oxygen.

Gray and ductile iron inoculants incorporating rare-earths are generally recognized as being very potent in reducing carbides and improving graphite structure. However, it is extremely important that the molten iron contains sufficient residual sulfur levels. If the sulfur content in the iron is too low, an abundance of carbides and chill will result. In the last decade, to improve the performance of these inoculants, a minute coating of ferrous sulfide and ferrous oxide was added as a surface treatment. The end result was a modified inoculant that formed potent oxy-sulfide substrates upon which graphite could nucleate more easily.

Recently, rare earth metals have become increasing expensive and difficult to obtain with China currently having over 95% of the world's production. Using technology that was shown over 40 years ago in a research paper by R.L. Naro and J. F. Wallace, a new concept was developed that showed greatly improved inoculation effectiveness in both gray and ductile irons. The new technology is based on a ferrosilicon-free inoculant alloy, containing 16% calcium and suitable amounts of sulfur and oxygen and other graphitizing elements. Using proprietary blending techniques, this new alloy has demonstrated remarkable abilities to reduce shrinkage, improve inoculation (reduced chill, elimination of carbides) improve nodule counts and nodule shape, and improve mechanical properties, (elongation, impact properties, yield and tensile strength). It has been recently found that Sphere-o-Dox, while it can be used as a solo inoculant addition, can also be used as an inoculant enhancer. It can be added with standard calcium bearing foundry ferrosilicon to yield outstanding results, equaling results shown with rare-earth oxy-sulfide inoculants.

Inoculants for gray and ductile irons are typically based on ferrosilicon. It is the base ingredient to which Group II and IIIA elements in the Periodic Table of Elements are added (most notably calcium, strontium, barium, titanium, zirconium, and rare earths). However, there is a finite as well as an economic limit as to the amounts of these elements that can be added. Group II and IIIA elements can and will react with dissolved oxygen and sulfur to varying degrees to form atomic clusters of oxy-sulfide particle that have a similar crystalline structure to graphite. These surfaces greatly assist in graphite nucleation and prevent undercooling, that can lead to carbides and poor graphite shape and nodule quantity in ductile irons.

The elements that have the greatest tendency to react with sulfur and oxygen are cerium and calcium. The free energy of formation of oxides and sulfides with both of these elements is quite similar. However, the present day cost of cerium (which is a rare earth element) is over seventy-five times higher than calcium.

The effectiveness of all inoculants is directly related to the dissolved levels of sulfur and oxygen in the molten metal. It has been demonstrated by numerous investigators that high purity ferrosilicon that contains no Group II or IIIA elements is not effective in inoculating gray or ductile irons. The dissolved levels of sulfur and oxygen inherent in molten metal often determine the effectiveness of conventional inoculants. If sufficient levels of sulfur and/or oxygen are not present, then the number of substrate particles that need to be generated to effect sufficient nucleation is significantly compromised. Since it is difficult if not impossible to manufacture a smelted ferrosilicon that contains controlled levels of sulfur and oxygen, the only alternative is to apply a surface coating of oxy-sulfide particles, or, alternatively, by blending ferrous sulfide and ferrous oxide into inoculant.

Sphere-o-Dox (U.S. Patent No. 6,281,988B1) has shown remarkable abilities to solve many troublesome inoculation situations. Sphere-o-Dox is a proprietary blend of oxy-sulfide forming elements that provide a high volume of graphite forming nuclei when added to molten gray or ductile irons. Not only has it replaced high-performance rare earth containing inoculants at numerous foundries, but it can be used as an inoculant enhancer to improve the performance of standard inoculants, such as standard calcium bearing 75% ferrosilicon.

An example of how Sphere-o-Dox can be used as an inoculant enhancer is illustrated by the experience of Foundry A. Foundry A is a medium sized foundry making thin (0.25 inches or less) section, shell molded castings. For years, carbide have been a serious problem. Attempts at switching inoculants and/or blending inoculants met with little to no improvement. The end consumer of the castings had to anneal all castings to eliminate carbides. To reduce costs, the customer requested that the castings must be produced as-cast to avoid costly heat treatment and improve machinability.

Foundry A produces ductile iron to a 65-45-12 specification. Melting is done in a 6,000-pound medium frequency induction furnace. A 1,200 pound tundish ladle is used for magnesium treatment; 1.75% GloMag R6-8 magnesium ferrosilicon is added to a 1,000 pound tundish ladle, and covered with 7 pounds of cover steel. The standard post-inoculation practice consisted of adding 4.5 pounds of Calsifer 75, a calcium bearing 75% ferrosilicon. A K15 cast insert is used in each shell mold. Attempts at using numerous inoculant blends failed to eliminate carbides. The most successful combination of inoculants was found to be 3.0 pounds of Calsifer 75, 3.5 pounds of VP216, and 0.6 pounds of Sphere-o-Dox that was used an inoculant enhancer. The occurrence of carbides in thin sections was dramatically reduced or eliminated only when Sphere-o-Dox was used.

Table 1 compares the pertinent properties of the standard inoculant practice compared to using the modified practice that incorporates Sphere-o-Dox S as an inoculant enhancer:

	Standard Practice	Enhanced Inoculation
Nodule Count	250	300
% Nodularity	95	97
% Ferrite	20	58
% Pearlite	60	32
% Carbide	20	0
% Graphite	0	10

The mechanical properties obtained from these same castings is shown in Table 2:

	UTS (PSI)	YS (PSI)	% El	BHN*
Specification	65,000 Min.	45,000 Min.	12% Min.	156-217
Enhanced Inoc.	68,600	48,000	19.9	162

Both the microstructural and mechanical property improvements elicited very favorable results for the end customer. In addition, elimination of the annealing cycle and improvement in machinability resulted in significant cost savings.

Another example of how Sphere-o-Dox can be used as an inoculant enhancer is the experience of Foundry B. Foundry B became concerned about rare-earth metal availability and its subsequent effect on its rare earth containing inoculant. A 4,500 pound tundish ladle with 6% magnesium ferrosilicon is used for ductile iron production. The treated iron is transferred into unheated stopper rod pouring ladles where post-inoculation was performed using 4 pounds of a proprietary rare-earth inoculant containing sulfur and oxide surface treatments.

After numerous qualification tests, which included in-depth thermal analysis, pouring test castings that had both thin sections and an isolated heavy section prone to shrinkage, and fading tests, Foundry B made a complete change in their inoculation practice. Post inoculation is now done with 3 pounds of foundry grade, calcium bearing ferrosilicon and 1 pound of Sphere-o-Dox (used as an inoculant enhancer). This combination of inoculants produced identical results to the more costly rare earth inoculant.

Foundry B pours 400 tons per day and estimates that they are saving over $8.00 per ton with the new inoculant procedure. On an annual basis, savings are estimated to be $750,000. Foundry B found that the introduction of controlled amounts of sulfur and oxygen can provide in vastly improved inoculation that equals or exceeds the proprietary rare-earth based inoculant.

These are two examples of how standard calcium bearing 75% ferrosilicon inoculants can be enhanced by adding Sphere-o-Dox. Additional laboratory testing and results can be found in U.S. Patent 6,866,696B1.