WHY CUSTOM BLENDED GRAY AND DUCTILE IRON ADDITIVES OUTPERFORM TRADITIONAL INOCULANTS

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ARTICLE TAKEAWAYS:

1. Blended inoculants outperform smelted inoculants
2. The importance of Sulphur during inoculation
3. Calcium, Rare Earth, Sulphur containing inoculants

For many decades ferrosilicon producers have sought to make improvements in gray and ductile iron inoculants. This developmental work was the result of changes in the primary iron melting method. Medium frequency coreless induction melting rapidly replaced cupola melting due to environmental requirements. More steel and purchased scrap were being used in the charges to replace some or all of the pig iron previously used, and a general increase in the average melting temperature resulted in greater metal oxidation state. Further, cupola melted irons typically responded far better to inoculation than irons melted in coreless induction furnaces.

Ferrosilicon-based inoculants are made using quartzite, coal, wood chips and steel scrap in large submerged arc furnaces (see Figure 1).

Figure 1. *Ingredients used to make Ferrosilicon*

Mineral oxides rich in elements from Group IIA, IIIB and IVB in the Periodic Table of Elements, such as strontium, barium, calcium, titanium, cerium and magnesium are often added to the smelting furnace or to the pouring ladle to achieve the desired inoculant chemistry. However, there is a finite limit to the amount of these elements that can be added to or else the smelting and reduction reactions will be negatively impacted. Other important inoculating elements that have been shown to be critical for improving inoculation and that cannot be added to the smelting furnace, are sulphur and oxygen.

If the sulphur and oxygen content of the molten iron that is to be treated with an inoculant is insufficient, an abundance of carbides and chill may result. Thus, the only feasible way to insure that the molten iron has sufficient levels of oxygen and sulfur is to mechanically blend sulfur and oxide rich elements into the inoculant additive.

Group IIA, IIIB and IVB in the Periodic Table of Elements react with dissolved oxygen and sulfur to varying degrees to form atomic clusters of oxy-sulphide particles that have a similar crystalline structure to graphite. These surfaces greatly assist in graphite nucleation and prevent "undercooling" during solidification process. Undercooling can lead to carbides, poor graphite shape, low nodule quantity in ductile (S.G.) irons and have an adverse effect on mechanical properties and machining characteristics.

In the last decade, to improve the performance of high potency rare earth based-inoculants, a thin coating of ferrous sulphide and ferrous oxide was applied as a surface treatment to the ferrosilicon-based inoculant. However, this approach provided only a limited amount of oxy-sulfide particles that would adhere to the surface of individual inoculant particles. In addition, this "coating" easily was removed during shipping prior to being used. The only method by which suitable additions of oxygen and sulfur can be incorporated into any inoculating agent is by using suitable blending techniques and selecting proper particle sizing.

An example of adding controlled amounts sulfur with of rare earths (as cerium) on improving inoculation and reducing carbides was first demonstrated by R.L. Naro and J.F. Wallace in 1970 and the results are shown in Figure 2.

This research showed the importance of controlling both gray iron sulphur and rare earth levels in the molten iron. Balanced ratios of rare earths (cerium) and sulphur, without the presence of ferrosilicon drastically reduced undercooling, completely eliminated chill and promoted favorable graphite shapes in grey irons.

Using this concept, patented technology (U.S. Patent 6,293,988B) has been developed and is based on a ferrosilicon-free inoculant, mechanically blended alloy that contains high levels of calcium and stoichimetric amounts of sulfur and oxygen, similar to the Naro and Wallace research findings. Using proprietary blending techniques, this new alloy has demonstrated remarkable abilities to reduce shrinkage, improve inoculation (reduced chill, elimination of carbides) improve nodule count and nodule shape.

Alternate methods to introduce sulphur and oxides onto the surface of a cerium/calcium containing ferrosilicon based inoculant is the limited amount of these materials than can be coated onto the surface of the ferrosilicon particle substrate, thereby limiting the critical amounts of sulphur and oxygen needed to boost inoculant potency. Adding late additions of sulphur and oxygen provides a clean, fresh source of sulfur and oxygen. The combination of fresh sulfur and oxygen allows the other proprietary inoculating elements (calcium, aluminum, barium, etc) to react in-situ and provide multiple times the nucleation sites of other, less potent inoculants.

Sphere-o-Dox (SOD) has shown remarkable abilities to solve many troublesome inoculation situations. SOD is a proprietary blend of oxy-sulphide 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-potency rare earth containing inoculants at numerous foundries, but it can be used as an inoculant enhancer to improve the performance of all ferrosilicon-based inoculants, such as standard calcium-bearing, barium-bearing or rare earth containing alloys. As a result, greater efficiencies during inoculation treatment have been obtained at significantly lower addition rates, in both grey iron and ductile irons, resulting in significant metal treatment cost savings.

An example of how SOD 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, carbides have been a serious problem.

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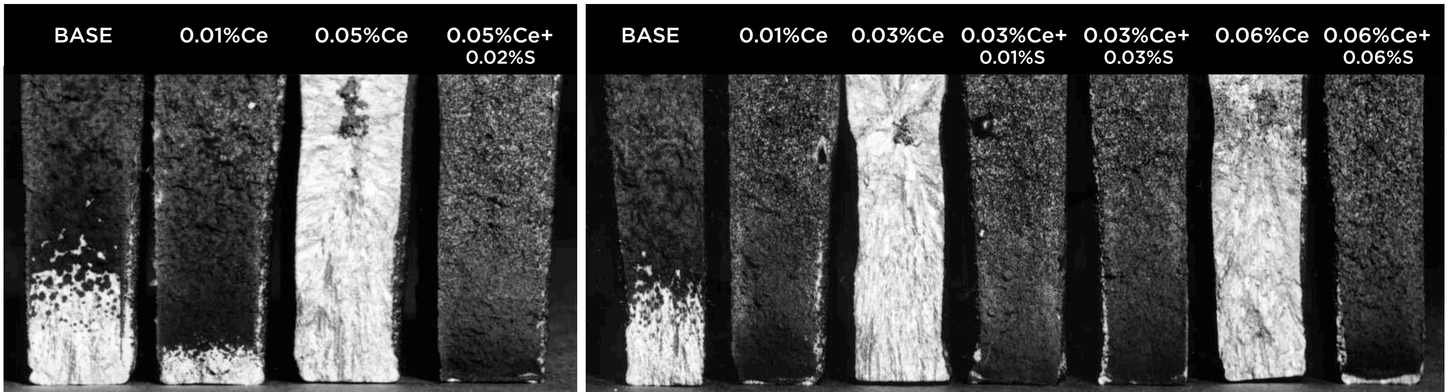

***Figure 2.** Effect of oxy-sulphide forming elements (Ce and S) on the chilling tendency of a 4.3 carbon equivalent grey iron*

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 ferritic 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 in-mold inoculant insert was used in each shell mold. All attempts 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 SOD added as a separate, independent addition to enhance the performance of the inoculants. The occurrence of carbides in thin sections was eliminated only when SOD was used.

The properties of the standard inoculant practice compared to using the modified practice using Sphere-o-Dox as an inoculant enhancer is shown below:

	STANDARD PRACTICE	ENHANCED INOCULATION	PERCENTAGE IMPROVEMENT
Nodule Count	250	300	20.0%
% Nodularity	95	97	2.11%
% Ferrite	20	58	190.0%
% Pearlite	60	32	- 46.7% Reduction
% Carbide	20	0	- 100% Reduction

The mechanical properties obtained from these same castings, are shown below:

	UTS (PSI)	YS (PSI)	% ELONGATION	BHN
Customer Specification	65,000 Min.	45,000 Min.	12% Minimum	156-217
SOD Enhanced Inoculation	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.

This example of a Sphere-o-Dox case history has been equally successful in casting pearlitic ductile iron grades and is just one example of how a custom-blended inoculant, containing sulfur and oxygen, can result in significantly improved inoculation.

Presently, many foundries throughout the world have incorporated using this non-ferrosilicon based oxygen and sulfur containing inoculant to increase the potency of their current inoculation practice to not only reduce their inoculant cost per ton, but also to improve mechanical properties and machining properties.

Note: *This article is a longer version of an article that originally appeared in the January 2018 issue of Foundry Management & Technology. Reprinted by permission of Penton Media, Inc.*

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