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**INVESTIGATION ON THE PRODUCTION  
OF NODULAR IRON WITH CALCIUM**

**By**

**Luiz Antonio de Araujo**

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science.

Signed:

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Approved:

*Clark B. Carpenter*

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Golden, Colorado

Date: June 2, 1951

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## INTRODUCTION

What would be the advantage of producing an iron in which the graphite would be distributed in spheroidal form, instead of flakes?

In a common gray cast iron, the graphite flakes are long and thin, and when viewed in cross-section, pointed at the ends. These flakes form a multitude of discontinuities and notches in the matrix which are responsible for the low tensile strength and brittleness of the iron. Furthermore, the sharp ends of the flakes act as points of considerable stress concentration or "stress-raisers".

In nodular iron, these irregular, sharp-edged flakes are replaced by spheres or near-spheres of graphite and the metallic mass is much less broken up and the sharp "stress-raisers" are eliminated.

This type of spheroidal graphite can be produced with any type of matrix structure, i.e., wholly ferritic or wholly pearlitic, or a mixture of the two.

With the present state of knowledge, there are at least 9 ways of producing graphite spherulites:

1. In hypoeutectic or hypereutectic irons by treatment of the melt with magnesium.
2. In hypereutectic irons by treatment of the melt with cerium.

3. In the solid phase by annealing white heart malleable castings high in sulfur and low in manganese.

4. In cobalt-carbon and nickel-carbon alloys, by treatment of the melt with calcium, cerium, bismuth, magnesium, zinc, or cadmium.

5. In very low sulfur cast irons, simply by rapid cooling of the molten metal.

6. In tellurium-treated irons, spherulites are formed just beyond the chilled zone.

7. Bismuth has been used effectively as a nodulizing element in gray irons having a low sulfur content.

8. R. A. Flinn of the American Brake Shoe Company<sup>23/</sup> announced, at the A.S.M. convention in 1950, the successful production of nodular graphite irons by treating the molten metal with titanium carbide, boron carbide, and calcium carbide.

9. Nodular iron can be produced by inoculation of the melt with calcium, either in the elementary form or combined with silicon; this method is the subject of the present work.

## HISTORY

Although the occurrence of graphite in spheroidal or nodular form is by no means new, having been presented in the technical literature as early as 1912<sup>1,2,3/</sup> and later in 1935 by Nipper<sup>4/</sup> and subsequently by Hanemann and Schröder<sup>5/</sup> in 1936, only since 1948 has the production of nodular graphite been successfully and uniformly obtained in the laboratory and in the foundry.



Fig. 1 - Graphite Nodule Obtained by Hanemann by Treating  
Cast Iron with Titanium Carbide

The earliest process of producing spheroidal graphite in gray iron, developed by J. E. Johnson<sup>2,3/</sup> is noteworthy:

The iron is blown in a converter at relatively low temperatures in order that the silicon content be reduced, but the carbon content only slightly decreased. The blast has the effect of causing considerable absorption of oxygen in the melt which is retained upon solidification.

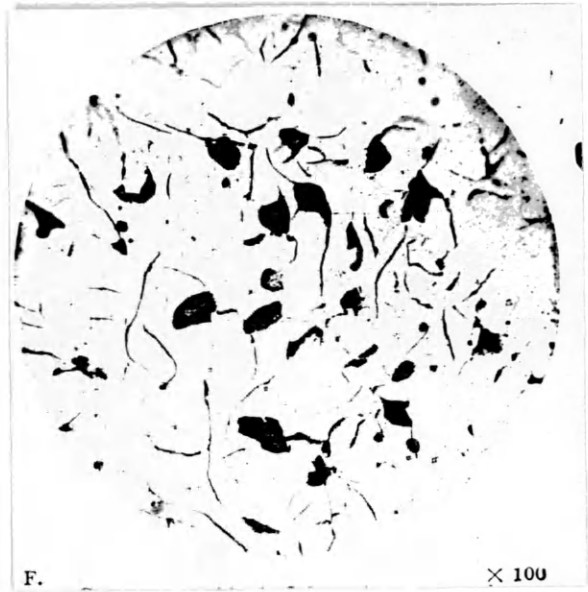


Fig. 2 - Graphite Structure Obtained by Johnson After Treating Molten Iron with Oxygen

The graphite in the iron assemblies, for the most part, in spheroids. In Johnson's process, the iron was remelted and enough silicon added to give the desired degree of graphitization. The spheroidizing tendency was not affected by the addition of silicon.

Johnson explained the formation of graphite spheroids by stating that the presence of oxygen in the cast iron lowered the temperature of graphitization relative to that of solidification in such a way that when the graphite separated from the melt, it was imprisoned within a relatively rigid mass, thus having little opportunity to spread out into broad flakes, with the only recourse being to form compact spheroids.

Also, in this connection, dealing with the production of compacted graphite (spheroidal) irons, it is interesting to observe that in his book, "Hochwertiges Gusseisen" ("High-Strength Cast Irons"), Piwowarsky<sup>21/</sup> refers to an application for a patent by C. Aden<sup>22/</sup> who describes a process in which "in a high-strength gray iron (eutectic or hypereutectic) with a minimum of 1% of silicon, immediately after solidification, the graphite precipitates completely or in part, in spheroidal form".

Morrogh and Williams<sup>7/</sup>, who later discovered the first practical process of consistently producing nodular iron by inoculation with cerium, had in 1946 reported to the Iron and Steel Institute of London, on the occasional occurrence of spherulitic graphite structures in as-cast gray irons, although it was not possible to control their production and distribution.

In a communication to the Iron and Steel Institute, dated December 1947, H. J. Morrogh and W. J. Williams<sup>6/</sup> announced their process of consistently obtaining nodular graphite structures in cast irons without heat treatment.

This announcement came to the attention of researchers throughout the world, who confirmed the experiments of the British Cast Iron Research Association and also tried new inoculating elements.

C. K. Donoho<sup>8,9/</sup> in a paper presented to the A.F.S. Michigan Regional Conference in October 1948 made public the experiments conducted at the American Cast Iron Pipe Company in the production of nodular iron with magnesium.

The work of Reese<sup>10/</sup>, Kuniansky<sup>11/</sup>, Smith<sup>12/</sup>, Myskowsky and Dunphy<sup>13,14/</sup> and especially of Professor Albert De Sy<sup>15,16,17/</sup> have

contributed much to the understanding of the necessary conditions for obtaining nodular iron.

As proof of the considerable interest devoted to the subject, it is sufficient to say that the most recently compiled bibliography<sup>18/</sup> lists more than one hundred articles in English, French, German, and Russian.

## THEORIES OF NODULIZATION

To date, there are two different theories regarding the formation of nodules in cast iron when inoculated with a nodulizing agent.

The theory advanced by Morrogh is chronologically the first. The British investigator<sup>3,4/</sup> stated his theory after studying the solidification behavior of nickel-carbon and cobalt-carbon alloys in comparison with the iron-carbon alloys. According to him, the most important factor in nodule formation is the delay in the formation of graphite due to the carbide stabilizing effect of the nodulizing agents.

Therefore, with slight modifications, the mechanism of nodule formation is the same as that in the malleabilizing process, i.e., the iron solidifying as white iron, followed by a decomposition of the supercooled carbides which were in spheroidal form.

Consequently, Morrogh inclined to the view that extraneous nuclei (other than graphite) are not required and that the spots observed microscopically in the center of the spherulites are optical effects coinciding exactly with the basal plane of a radial crystallite.

Professor Albert De Sy<sup>13/</sup> suggested that solid particles suspended in the melt tend to act as nuclei for the crystallization of phases of the same crystalline structure as the particle. Thus, in common gray iron, the hexagonal flake graphite is nucleated by hexagonal particles of silicon dioxide in the melt.

De Sy explains the formation of other types of graphite structures by the delay in the formation of silicon dioxide through the addition of deoxidizers that are more powerful than silicon.

Such deoxidizers are cerium and magnesium and other nodulizing agents, and their oxides will have a cubic crystal structure, which according to the De Sy theory, will nucleate austenite in preference to graphite, and in this manner suppress the early formation of graphite.

Normally, in a hypoeutectic iron, solidification begins by the formation of austenite dendrites growing from the melt until the remaining liquid is of eutectic composition. The solidification of the eutectic starts independently of the previously solidified dendrites at definite crystallization centers; flake graphite and solid gamma iron form simultaneously.

Professor De Sy believes that the spherulites may form in fully solid or fully liquid metal, but never at a solid-liquid interface, where graphite flakes presumably form.

#### FACTORS PRO AND CON CONCERNING THE DIFFERENT THEORIES OF NODULIZATION

One of the greatest differences between nodular iron and flake graphite iron is in the shrinkage characteristics. Nodular iron tends to pipe deeply, behaving more like steel than gray cast iron.

This is a point in favor of the hypothesis that in ductile cast iron, the spherulites of graphite separate in the liquid; in normal gray irons the separation of graphite at the eutectic

point causes an expansion which counterbalances the natural shrinkage, necessitating special precautions for proper feeding and for avoidance of contraction cavities, in nodular iron.

If part of the graphite in nodular iron is formed at a temperature where the metal is still in the liquid state, the beneficial influence of its formation is wasted so far as its effect in counteracting shrinkage is concerned.

Another point favoring this hypothesis is that if cerium-treated iron is cast centrifugally in hand molds, there is a marked inward segregation of the graphite nodules. This is a good indication that the first nodules of graphite separate in the liquid.

Likewise, several investigators<sup>3,17/</sup> have reported a marked segregation of nodules in the top surfaces of castings when using hypereutectic nodular irons made by the cerium process.

With magnesium-treated irons, the effect, although noticeable, is not so marked.

Morrogh<sup>3/</sup> after studying these phenomena, stated:

"Previously, it has been supposed that nodular graphite can form only in cast irons as a result of the decomposition of solid iron carbide. If the hypereutectic spherulites form by such a process, the decomposition of the carbide must be extremely rapid."

"It is difficult to imagine how this (the segregation of hypereutectic nodules at the inner surfaces of centrifugally cast treated irons) could have occurred, except by the existence of the spherulites before the eutectic had solidified."

On the other hand, as evidence that nodular cast irons solidify white and graphitize after solidification, Morrogh<sup>23/</sup>

cites the dimensions and shapes of small castings. These castings, having thin sections, solidify at the center a short time after the outer surface of the casting. The entire section solidifies, therefore, as white iron, and graphitizes uniformly. When the feeding is good and there are no porosity cavities, the sides of these castings bulge outward slightly under the pressure of graphitization.

### THE NATURE OF THE GRAPHITE NODULE CORES

Morrogh and his associates are inclined to say that the "core" observed at the center of the spherules in carefully polished specimens of nodular iron is merely the result of an optical effect. The graphite nodules consist of crystallites growing radially outward from the center and the crystallites are so oriented that their basal planes are perpendicular to the radius of the sphere whose form the nodules approach. When the polished section lies above or below the center of the spherulite, the basal planes of the crystallites in the center of the exposed surface are parallel to the polished section, giving the appearance of a distinct "core" or nucleus.

Professor De Sy has presented evidence (see Fig. 3), through the use of the electron microscope (which excludes optical effects), that a non-graphitic nucleus does exist, as well as chemical evidence that it is a magnesium compound when the nodular iron has been produced by magnesium inoculation.

J. E. Rehder<sup>19/</sup> of the Bureau of Mines, Ottawa, Canada, observed that the nuclei appear to be harder than the graphite composing the remainder of the nodules.

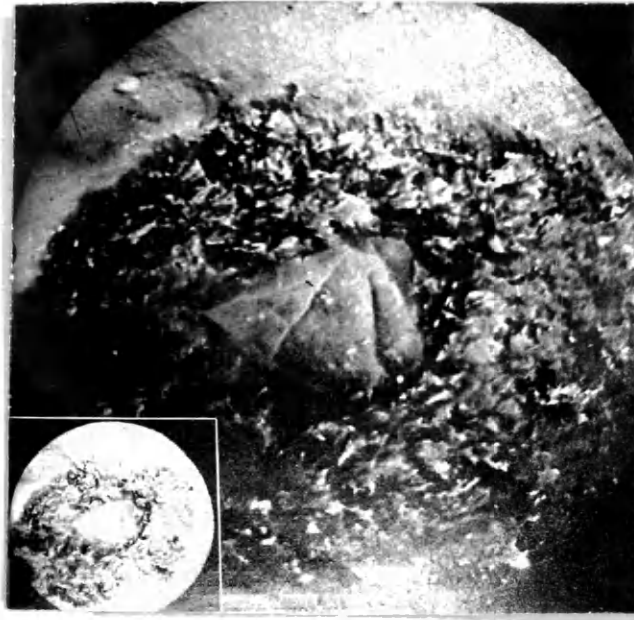


Fig. 3 . Photomicrograph Obtained Through the Electron  
Microscope of the Core of the Graphite Nodule. 20,000 x

Also, Mr. Bhagwan Maniar<sup>25/</sup> has presented evidence of the presence of magnesium in the nodules of irons treated with a 15% magnesium-nickel alloy.

According to the majority of the investigators, a substance to be an effective nodulizing agent should be an effective desulphurizer, a carbide stabilizer, and should be added to the melt in an easily soluble form.

It is interesting to observe that, according to the following table, the majority of the substances known so far to be effective nodulizing agents, are essentially insoluble in the iron lattice.

	a I b		a II b		a III b		a IV b		a V b		a VI b		a VII b		a VIII b		h
I														1H			2He
II	3Li ▲		4Be ●		5B ○		6C □		7N □		8O ○		9F				10Ne
III	11Na ▲		12Mg ▲		13Al ●		14Si ●		15P ●		16S ○		17Cl				18Ar
IV	19K ▲		20Ca ▲		21Sc		22Ti ●		23V ●		24Cr ●		25Mn ■		26Fe	27Co ■	28Ni ■
		29Cu □		30Zn □		31Ga		32Ge ●		33As ●		34Se		35Br			36Kr
V	37Rb ▲		38Sr ▲		39Yt		40Zr ○		41Nb ●		42Mo ●		43Tc		44Ru ■	45Rh ■	46Pd ■
		47Ag ▲		48Cd ▲		49In		50Sn ●		51Sb ●		52Te		53I			54Xe
VI	55Cs ▲		56Ba ▲		58Ce ○		72Hf		73Ta ●		74W ●		75Re		76Os ■	77Ir ■	78Pt ■
		79Au □		80Hg ▲		81Tl ▲		82Pb ▲		83Bi ▲		84Po		85At			86Rn
VII	87Fr		88Ra ▲		89Ac		90Th		91Pa		92U						

■ Open  $\gamma$ -field      □ Expanded  $\gamma$ -field      ▲ Insoluble  
 ● Closed  $\gamma$ -field      ○ Contracted  $\gamma$ -field

Fig. 4 . Periodic Table Showing Behavior of Elements  
in Binary Iron Alloys

## EXPERIMENTAL WORK

### Introductory

The experiments in nodulizing cast iron with calcium were conducted at one foundry in Denver and at the laboratories of the Colorado School of Mines.

As the base metal for inoculation, a cast iron having the following limits in composition was used:

Carbon	3.28 - 3.50%
Manganese	0.76 - 0.89%
Silicon	1.35 - 2.28%
Sulphur	0.04 - 0.05%

This type of iron is used as the charge to the Tropenas Converter. It was selected due to its fairly uniform composition heat after heat due to the careful selection of the scrap used in making up the charge, and especially due to its low sulphur content. The low sulphur content reduces to a minimum the amount of calcium which would be used up without beneficial effects, as desulphurizer, before any nodulizing action can take place. Three arbitration test bars of treated iron from each heat were cast in sand molds. After cooling down to atmospheric temperature, the castings were shaken out of their molds and brought to the School laboratories for analysis, testing and microscopic examination.

### Alloys Used in the Experiments

Experiments 1 to 8 inclusive were made using a calcium-copper alloy containing 10% calcium as the nodulizing agent.

The quantity used in the first experiment was 5 pounds of alloy per 100 pounds of metal, which corresponds to 0.5% Ca addition. The amount of alloy used was progressively increased up to 12 pounds of alloy per 100 pounds of metal.

Experiments 9 to 13 were made using a commercial calcium-silicon alloy, containing 20% Ca, commonly used in the steel industry as a deoxidizer and degasifier. The quantities added ranged from 3 pounds per 100 pounds of molten metal to 5 pounds of alloy to 100 pounds of iron.

The last experiments were made using pure calcium metal, in the form of turnings. The amount of calcium used was from 2 ounces up to 1/2 pound to 100 pounds of metal.

Immediately after inoculation, 1/2 pound of a commercial ferrosilicon, containing 25% Si, was added as a graphitizing agent in all experiments except 13 and 14.

The 100-pound shank ladle was preheated, in the first experiments by the use of an oil burner and later by filling it once with molten metal, before making the inoculation.

The bars were removed from the molds only after cooling down to room temperature.

### TESTING

All specimens were tested in the as-cast condition. The test bars, after being removed from the mold, were thoroughly cleaned and identified.

For metallographic examination, a section near the in-gate end of the bar was cut with a power saw and polished. Photographic records of the unetched structures were made.

### Flexure Test

The standard 1.20 inch diameter test bars were tested according to the A.S.T.M. specification A-48-41, under a transverse load with the supports spaced 18 inches apart.

Two bars of each heat were tested and the average values of the breaking load and maximum deflection are listed on Table I.

TABLE I  
FLEXURE TEST

Sample No.	Max. Deflection In.	Breaking Load Lbs.	Observations
Base Iron No. 1	0.250	2520	
Base Iron No. 2	0.256	2200	
No. 1	0.220	2510	Inclusions.
No. 2	0.202	2450	Large inclusions of Cu alloy.
No. 3	0.304	3190	
No. 5	0.249	2980	Blowholes.
No. 9	0.191	2510	Blowholes. Inclusions of inoculant.
No. 10	0.394	4500	Small inclusions.
No. 11	0.214	2890	Extremely porous.
No. 12	0.252	3210	Inclusions, blowholes.
No. 13	0.276	3020	Large inclusions.
No. 14	0.310	4500	Large inclusions about 1/3 section.
No. 15	0.294	3800	Inclusions, porosity.

### Tensile Test

Tensile test bars were machined from the transverse test bars to the dimension of Bar Type B of the A.S.T.M. Specification A-48-41.

The mean diameter of the specimens was measured with a micrometer and the gauge length was then punched. After the test, the broken ends were fitted together carefully and the elongation measured with calipers.

Every test was conducted in triplicate and an average of the values found is presented in tabular form in Table II.

As it is marked under the column Observations, considerable trouble was encountered with porosity in the test bars. This is attributable to the relatively small time interval between the additions of alloy and the pouring of the test bars and also to the violent stirring employed in trying to aid the contact of the inoculant and the molten metal.

TABLE IITENSION TEST

Sample No.	Load at Fracture Lbs.	Elongation %	Observations
Base No. 1	18,600	None	
Base No. 2	20,820	3%	
No. 3	16,000	None	
No. 5	11,250	None	Two large blowholes.
No. 9	11,200	None	Inclusions, porosity.
No. 10	25,750	5%	Inclusions of the inoculant.
No. 11	20,950	5%	Porosity.
No. 12	25,200	6%	Blowholes.
No. 13	23,300	10%	Inclusions.
No. 14	23,050	8%	Blowholes, porosity.
No. 15	26,800	12%	

TABLE III  
BRINELL HARDNESS

Sample No.	Brinell Hardness Number 3,000 Kg
Base No. 1	302
Base No. 2	233
No. 3	212
No. 5	241
No. 9	228
No. 10	249
No. 11	242
No. 12	235
No. 13	225
No. 14	262
No. 15	235

Brinell Hardness

On the fractured test bars a section was ground flat and three Brinell impressions made. The mean diameter was measured and the Brinell hardness calculated. The average values of the values found are presented in Table III.

## CHEMICAL ANALYSIS

Borings taken with a drill press were carefully collected for analysis.

Total carbon was determined by the gravimetric method. Graphitic carbon was determined by dissolving out the matrix in Nitric Acid 6N and burning the carbon residue in the same apparatus used for the total carbon determination.

Manganese, silicon and sulphur were also determined.

The determination of the minute amounts of calcium in the iron would be more precise with standard calcium containing cast irons for spectrographic analysis.

The determination of the minute quantities of residual calcium in the treated iron would be more precise if spectrographic analysis were employed. The impossibility of obtaining standard samples at the time forced the use of the normal gravimetric method.

EXPERIMENT NO. 1Heat Data

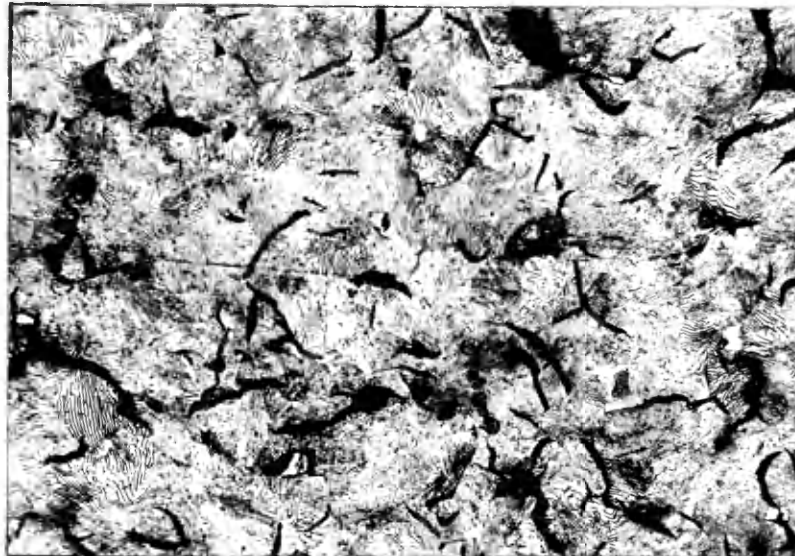
Five pounds of calcium-copper alloy, broken into pieces the size of a walnut, was placed in the bottom of a 100-pound ladle, which was preheated to a dull red temperature.

Microstructure

The distribution and form of the graphite flakes were not substantially altered by the inoculation.

Comments

The alloy was undissolved in the bottom of the crucible. Also, large inclusions of calcium-copper alloy were found in the test bars tested.



Magnification: 250 x

EXPERIMENT NO. 3Heat Data

An increased quantity of alloy was added. To 100 pounds of metal, were added in succession:

Calcium alloy	6.0 pounds
Exothermic ferrosilicon	0.5 pound

Microstructure

No change in graphite formation.

Comments

The alloy did not react with the molten iron; the bulk of it remained at the bottom as an unfused mass.



Magnification: 250 x

EXPERIMENT NO. 4Heat Data

Seven pounds of calcium-copper alloy was finely ground and placed at the bottom of a ladle preheated with an oil flame.

Microstructure

No modification of the form or distribution of graphite was observed.

Comments

The alloy did not go into solution, but agglomerated in a sluggish mass at the bottom of the ladle.



Magnification: 250 x

EXPERIMENT NO. 5Heat Data

In this experiment, finely ground alloy was added by placing it in the bottom of a preheated ladle.

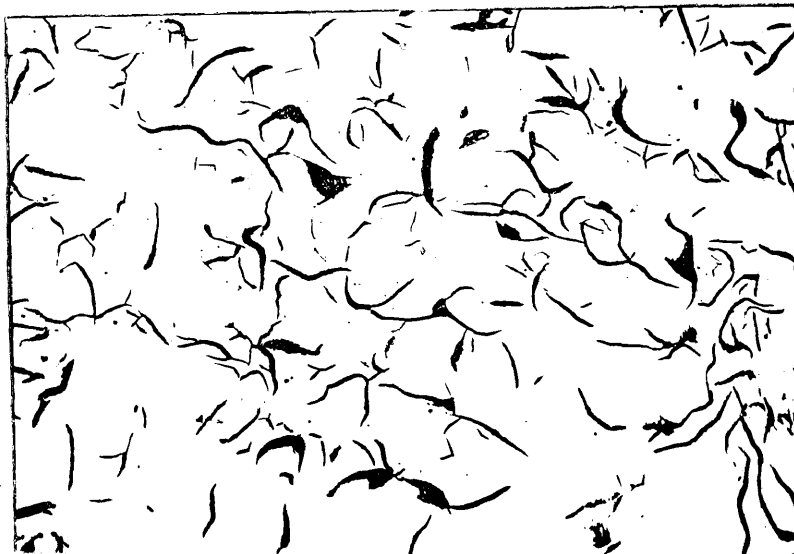
Calcium-copper alloy added	8	pounds
Ferrosilicon	0.5	pound

Microstructure

No significant modification on graphite distribution occurred.

Comments

As in the previous experiments, the alloy collected in the bottom of the ladle and did not react with the iron.



Magnification: 250 x

## EXPERIMENT NO. 7

### Heat Data

Ten pounds of alloy was added to the stream while the iron was being transferred from the collecting ladle to the 100-pound shank ladle.

After stirring thoroughly, 1 pound of ferrosilicon was added.

### Microstructure

Although the graphite flakes appeared thicker and in some places almost round, there were no distinct nodules.



Magnification: 250 x

## EXPERIMENT NO. 8

### Heat Data

The same amount of calcium-copper alloy used in Experiment No. 7 was added to the stream. The ladle was preheated by filling it once with molten metal.

### Microstructure

Similar to that in Experiment No. 7.

### Comments

Despite all precautions taken, there was no reaction between the iron and the alloy.



Magnification: 250 x

### OBSERVATION

It was soon observed that despite all the precautions taken, such as fine grinding of the alloy, preheating of the ladle and of the inoculating agent, using the iron from the cupola furnace at the highest temperature possible under the prevalent conditions, the bulk of the alloy remained undissolved, although painstaking cares were observed in stirring the alloy in the ladle.

At the conclusion of the experiments, an attempt was made to add the finely ground alloy in the stream as the iron was poured from the waiting ladle into the small shank ladle.

In these photomicrographs we can observe a refining of the pearlitic structure without effect on the graphitic form or distribution.

Inclusions of the copper-calcium alloy were observed in many of the bars tested. These inclusions resulted from the violent stirring prior to pouring in the mold.

## EXPERIMENTS WITH CALCIUM-SILICON ALLOY

Since the quantity of calcium present in the alloy originally tried was far too low to react effectively in a nodulizing reaction, a commercial calcium-silicon alloy containing 20% calcium, commonly used in the steel industry as a deoxidizer and degasifier, was then tried.

It was expected, in view of the recent developments in the field announced by Professor De Sy,<sup>26/</sup> that using an alloy of a composition similar to that used by the Belgian investigator (Professor De Sy used an alloy with 24 to 26% calcium and 56 to 59% silicon, with the remainder copper and nickel), it would be possible to obtain nodular structures in cast iron.

One striking difference, however, between the two methods, is that De Sy used an induction furnace as the means of melting the cast iron. In the present work, aimed at practicality, the cast iron was melted in a cupola furnace. With an induction furnace, the experimenter is able to maintain the temperature constant while the inoculant is being dissolved and the process of nodulization is taking place. In the present case, the rapidly cooling metal in the ladle, combined with the relatively large volume of alloy used, resulted in the incomplete solution of the inoculant with its consequent inefficiency in the formation of graphite nodules.

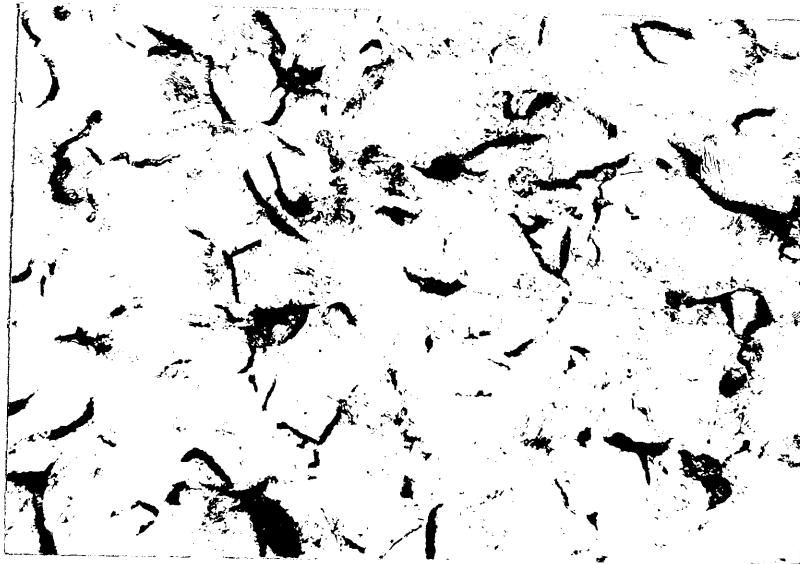
EXPERIMENT NO. 12Heat Data

Five pounds of calcium-silicon alloy was placed at the bottom of a 100-pound shank ladle previously heated in an oil flame. The chemical analysis was as follows:

Carbon	3.18%
Manganese	0.91%
Silicon	2.05%
Calcium	0.02%
Sulfur	0.05%

Microstructure

Although the physical properties were improved, the form of the graphite flakes was not altered.



Magnification: 250 x

EXPERIMENT NO. 13Heat Data

In this experiment, 7 pounds of calcium-silicon alloy was added to the stream while the iron was being transferred to the shank ladle. The chemical analysis was as follows:

Carbon	3.36%
Manganese	0.76%
Silicon	2.02%
Sulfur	0.081%

Microstructure

The graphite agglomerated in large flakes, some of which were roughly round.

Comments

A great part of the alloy floated to the top of the melt, burning with a brilliant flame.



Magnification: 250 x

EXPERIMENT NO. 14Heat Data

The addition of 7 pounds of calcium-silicon alloy was divided into two parts, one being placed in the bottom of the preheated ladle, and the other being added to the stream.

Microstructure

The same as in Experiment No. 13.

Comments

Due to the presence of blowholes in the test bars, they were not tested.



Magnification: 250 x

In view of the negative results of experiments 8 through 13, the writer began experimentation with an induction furnace at the Colorado School of Mines, using pure calcium as an inoculant.

It was observed that calcium metal is a much safer inoculating agent than magnesium. Only a small flare, without projections of molten metal or violent explosions, resulted from the contact of molten iron and the metal.

Using the same base iron used at the foundry, and adding calcium metal turnings to the stream of molten iron being poured into a mold, nodular structures were observed when as little as 0.65% calcium was added.

EXPERIMENT NO. 15Heat Data

Three ounces of pure calcium metal was added to the stream when the 100-pound shank ladle was being filled with molten iron. The chemical analysis was as follows:

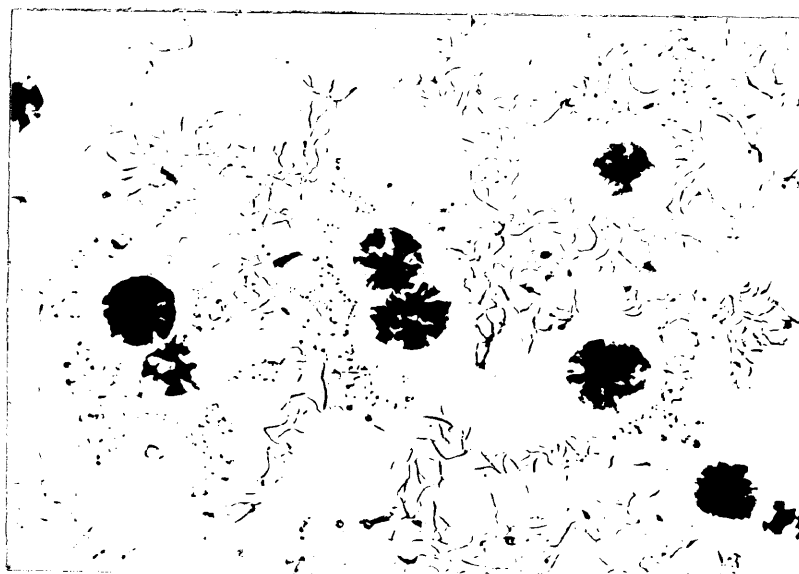
Carbon	3.02%
Manganese	0.55%
Silicon	2.28%
Calcium	nil

Microstructure

Some nodules were observed throughout the section.

Comments

Some boiling action took place when the calcium reacted with iron. Only a small flare was observed.



Magnification: 250 x

EXPERIMENT NO. 18Heat Data

To iron remelted in an induction furnace, pure calcium was added in the proportion of 0.65% by weight. The analysis was the following:

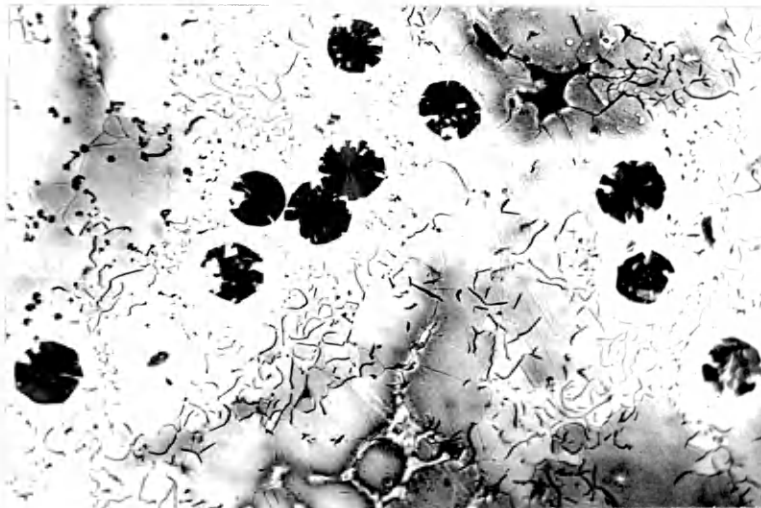
Carbon	2.76 %
Manganese	0.55 %
Silicon	2.28 %
Calcium	0.008%

Microstructure

A number of incompletely formed nodules were observed, as illustrated.

Comments

It is supposed that if the quantity of calcium added were greater, complete nodulization would have taken place.



Magnification: 250 x

According to De Sy,<sup>26/</sup> the amount of calcium in the alloy used is 0.96% of the weight of the metal treated to obtain a completely nodular structure.

Following this, an attempt was made to mix some pure calcium with the calcium-silicon alloy used in the previous experiments in order to raise the proportion of the active element in relation to the total volume of the addition. Experiments 13 to 15 were conducted with this idea in mind.

As can be seen from the tables, the physical properties of the test bars were improved, even though, the violent stirring before pouring without allowing the metal to settle resulted in a large proportion of defective bars due to blowholes and porosity.

## SUMMARY AND CONCLUSIONS

In striving to find a safer and more economical substitute for the alloy treatment in current use in the production of nodular cast iron, several calcium alloys were used, alone or in combination, with the metal itself being used to inoculate cast iron.

It was found that with the alloys used, the quantity required in order to obtain nodulization was far greater than the amount which the metal was capable of dissolving.

In the last experiments, the addition of calcium had a marked effect on the physical properties of the iron, although a completely nodular structure was not obtained.

When a suitable means of maintaining the temperature or of even superheating the iron was provided, the nodulization took place, although only partially, due to the small amount of calcium added (0.65%). Such a means of heating the melt was the induction furnace.

At the present stage in normal foundry practice, however, the use of calcium in metallic form cannot compete successfully with the magnesium process, although the addition of calcium can be made more safely, and without danger of injury to the workers or to the equipment.

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