INFLUENCE OF LADLE ADDITIONS OF CALCIUM, STRONTIUM AND BARIUM ON THE MICROSTRUCTURE AND PROPERTIES OF HIGH STRENGTH HYPOEUTECTIC GRAY CAST IRON

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ABSTRACT

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by Ramkrishna D. Chaudhari

The relative effectiveness of inoculation with pure calcium, strontium and barium for hypoeutectic gray cast iron was studied. The base irons were of the following composition: 2.90 % C; 2.25% Si; 0.90% Mn; 0.16% P and 0.07% S. An indirect arc rocking furnace was used as a melting unit. The inoculated irons are compared with untreated irons of identical analysis and comparative data obtained on graphite distribution, transverse strength, deflection, triangular resilience and chill depth.

Wedge shaped castings from irons inoculated with barium, strontium and corresponding blank irons were quenched in water at the start of eutectic solidification and the resulting microstructures studied to determine the influence of the inoculant on the nucleation of eutectic solidification.

Silicon base alloys were also used as inoculants and the results obtained by using barium free ferro-silicon were compared with the results obtained by using barium-silicon and calcium-silicon. A possibility of nucleation of eutectic solidification by the carbides of calcium, strontium and barium is considered.

The major findings of this study are:

(1) Addition of pure barium did not change the number of eutectic cells formed and was not effective in changing the graphite distribution and properties.

(2) Strontium additions increased the number of eutectic cells. The deflection was increased and the chilling tendency was decreased but no significant increase in the transverse strength was observed unless the additions were high in quantity.

(3) Calcium was the most effective inoculant in improving the graphite distribution and properties.

(4) Addition of each of the three elements produced decarburization and desulfurization of the melt.

(5) All the irons inoculated with alloys containing barium produced a marked reduction in chill depth.

(6) Except for the difference in chill depth, the irons inoculated with calcium-silicon were superior to all other irons of this study.

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I. INTRODUCTION

Gray iron is used by the industry in substantially greater tonnages than all other cast metals combined. Among the foundry alloys, gray irons are unique because of their wide range of properties and structures. The variations in properties cannot be explained fully by changes in chemical composition.

The literature presenting experimental evidence to understand the factors which influence the properties of cast iron is voluminous and the data presented vary from author to author. The properties of gray iron depend upon both--(a) the amount and manner of distribution of graphite, and (b) the nature of the metal matrix.

The problem of graphitization is usually discussed in terms of binary or ternary equilibrium diagrams involving iron, carbon and silicon. Cast iron can be described more or less as a six component system consisting of carbon, silicon, manganese, sulfur, phosphorus and iron, though in practice even the unalloyed grades may contain significant amounts of many other elements.

It has been generally understood for many years that the late addition of certain silicon alloys to molten iron produces changes in the graphite distribution. This results in improved mechanical properties and decreased chilling tendency. The practice of using such additions is commonly referred to as "inoculation."

Calcium-silicon and ferrosilicon were among the first materials used for inoculation. Calcium-silicon was first proposed by Meehan and many patents were granted to Meehan and others in the early 1920s. A chronological list of these patents is given by Grange and others (1).

Even though inoculation has been practiced for such a long time to improve the properties of gray cast iron, the mechanism and kinetics that lead to such an improvement are not completely understood. The discovery in 1948 that the late additions or ladle inoculation of low sulfur gray cast iron with cerium or magnesium could produce a nodular graphite form has served to focus attention and intensify research on fundamental studies of the inoculation phenomena in recent years.

Until very recently, silicon was regarded as an essential constituent and active agent in inoculating alloys. McClure, Khan, McGrady and Womochel (2) were the first to publish evidence showing that the element silicon as such is of no value as an inoculant. In this and a subsequent paper (3) it was clearly shown that the effectiveness of commercial grades of ferrosilicon as inoculants depends on their active metal content, especially that of calcium. Calcium-silicon and pure calcium were observed to be the best inoculants. This work regarding calcium as the most effective inoculant has been confirmed later by Lux and Tannenberger (4).

Having accepted the idea that calcium is the most effective inoculant, the need for further examination of the mechanism of inoculation in the light of the agency of calcium becomes evident. The elements calcium, strontium and barium belong to the same group IIA in the Periodic Table. It was, therefore, thought that the elements strontium and barium, which are relatively unknown in the field of inoculation, should be tried as inoculants. It was also clear that the change in properties, if any, obtained by the use of these inoculants might lead to a better understanding of the mechanism of inoculation.

The main purpose of this investigation is to study the relative effectiveness of inoculation with strontium, barium and calcium

and analyze the mechanism of inoculation in the light of the results obtained.

II. GENERAL FEATURES

For the convenience of the reader, the general features of the solidification and graphitization principles of cast iron and the various ideas advanced to explain the mechanism of inoculation are presented in brief in this section.

a) Graphite Distribution in Cast Iron:

An attempt to classify all the different types of graphite patterns found in cast iron resulted in the American Foundrymen's Society--American Society for Testing of Materials chart for graphite distribution in cast iron. This chart is shown in Figure 1 (5). High strength hypoeutectic iron (2.60-3.1% C) may exhibit types A, B, D or E of graphite distribution.

The uniformly distributed Type-A is usually associated with the best mechanical properties. The pattern of Type-D is undesirable because of the resultant planes of weakness in the iron. Appearance of Type-D graphite in an iron is frequently accompanied by the formation of a soft ferritic matrix. An iron with Type-D graphite has a poor wear resistance or strength as compared to an iron of the same chemical composition but with Type-A graphite. To illustrate, the readings on the wear in the bore of a gray iron motor block, given by Smith (6), are reproduced below:

(1) Normal flake graphite (Type A) distribution:

Wear 0.000664" per 10,000 miles.

(2) Dendritic, Type D graphite distribution:

Wear 0.003730" per 10,000 miles.

The principle concern of the metallurgist producing high strength iron is to obtain a maximum of normal or Type A graphite. In this

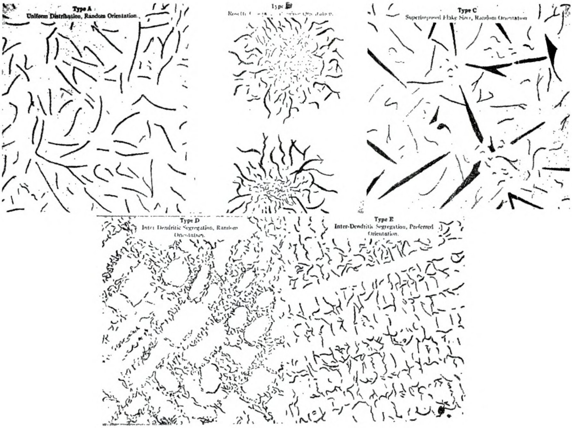


Figure 1. The AFS-ASTM Classification Chart for the types of graphite distributions in cast iron. 50X. (Reference 5).

work, graphite patterns B, D and E will be referred to as abnormal. This is justified because most commercial irons of carbon content less than 3.10% may contain varying amounts of the four types in the same casting.

b) Solidification of Cast Iron:

As mentioned earlier, the problem of solification and graphitization is usually approached on the basis of binary or ternary equilibrium diagrams involving iron, carbon and silicon. Two forms of the iron-carbon diagram are recognized: the stable, in which carbon is present as graphite; and the metastable, in which carbon is present as cementite Fe_3C. This phase has a higher free energy than the equivalent Fe and C and hence the iron-graphite system is recognized as the true equilibrium diagram.

Graphitization is profoundly influenced by both carbon and silicon in high purity Fe-C-Si alloys. Silicon is generally considered to replace one-third of its own weight in carbon. The presence of silicon increases the eutectic temperature and extends the range of temperature during which the eutectic freezes.

Prior to the work of Boyles (7, 8), the manner of solidification of gray iron was not completely understood. Many metallurgists believed that gray iron solidified in a metastable manner and cementite decomposed to give graphite. Boyles arrested the transformation in small melts by quenching from successively advanced stages of solidification. He was thus able to follow the initiation and progress of graphitization during the eutectic freezing.

From the work of Boyles, the solidification of hypoeutectic cast iron can be summarized as follows:

(1) Primary austenite solidifies in the form of dentrites from liquidus temperature down to the eutectic temperature range.

(2) Crystallization of the eutectic liquid begins at centers which grow outward spherically in all directions and form a "cell" like structure.

(3) Constituents solidifying from the eutectic liquid occupy the interstices of the primary dendrites. The graphite flakes are thus restricted by the amount, size and orientation of the primary dentrites.

(4) Segregation takes place in two ways--first, between the primary dendrites and the liquid, and second in the solidifying eutectic between the core and the radially growing boundary.

(5) Graphite flakes start to appear with the gradual freezing of the eutectic and the flakes increase in size and number down to the point of complete solidification.

This is very well illustrated in Figure 2 which shows the photomicrographs taken by Boyles. It could then be said that the variation in size and distribution of graphite flakes depends also on the relative rates of growth of the austenite and graphite from the eutectic liquid. For example, a high rate of austenite formation in the growing cell might produce small (Type D) flakes by restricting the growth of a developing flake.

Eash (9), on the other hand, presented evidence to show that irons highly abnormal in character solidified in the metastable manner and Type D graphite resulted in the solid iron by decomposition of cementite at a temperature close to but below the solidus line. Similar findings were reported by Morrogh and Williams (10, 11) and by Owen and Street (12).

It was believed by these investigators that the metastable solidification leading to the formation of Type D graphite was associated with an undercooling of the liquid iron. Morrogh (13, 14) agreed

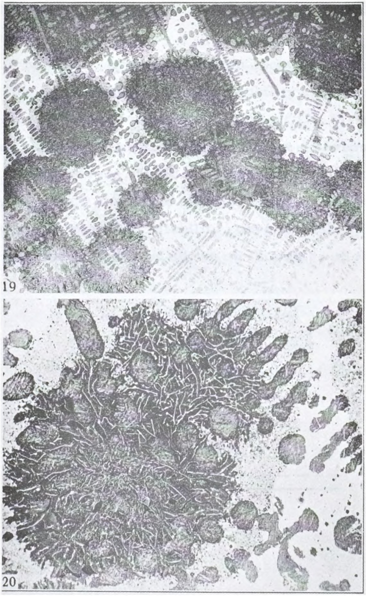


Figure 2. Microstructures obtained by quenching partially solidified hypoeutectic gray cast iron. Heat tinted. Upper picture 20X, lower picture 100X. [From Boyles (8)].

later that in many cases undercooled graphite forms directly from the melt. This was also suggested earlier by Hultgren, Lindblom and Rudberg (15).

There is relatively little information about the solubility of cementite in liquid iron and usually the solubility curve for cementite is drawn parallel with that for graphite. Hillert (16, 17) has suggested that the tentative free energy diagrams of the iron-carbon system indicate that the two curves should intersect below the eutectic temperature. Figure 3 shows the eutectic region of the iron-carbon diagram showing the probable solubility curve for cementite in liquid. The graphite line is also shown on this diagram .

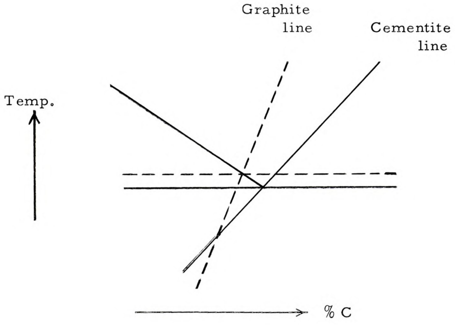


Figure 3. Graphite and cementite lines near the eutectic region in Fe-C diagram. Exploded view (schematic). After Hillert (17).

Very slow cooling of the eutectic liquid causes graphite and austenite to form and it never becomes supersaturated with respect to cementite. Cooling of the liquid below the eutectic temperature for austenite + cementite makes it supersaturated with respect to cementite but it is still more supersaturated with respect to graphite. With further decrease in temperature supersaturation with respect to cementite increases more rapidly than the supersaturation with respect to graphite.

Below the temperature where the two solubility curves intersect the liquid can be said to be more supersaturated with respect to cementite than graphite. At this stage the graphite in equilibrium with the liquid is metastable with respect to cementite. Hence, at a cooling rate which will undercool the melt to below the temperature indicated by the intersection of the two lines, cementite should form. As a consequence, whether cementite will be nucleated or not depends on the lowest temperature reached and hence on the rate of cooling.

c) Factors Influencing Graphite Distribution:

The important factors having influence on graphite distribution have been listed by Womochel (18) as follows:

1. Carbon content of the iron.
2. Superheating temperature.
3. Holding time at temperature.
4. Method of melting.
5. Pouring temperature.
6. Sulfur and manganese contents.
7. Gas content-hydrogen, oxygen and nitrogen.
8. Cooling rate in the mold and the extent of undercooling.
9. Degree of inoculation.

It is generally believed that high strength irons with carbon less than 3.10% are much more susceptible to the formation of Type D

graphite than are the higher carbon hypoeutectic irons. High superheating temperatures and long holding time at such temperatures in the furnace promote the formation of abnormal structures. Schneble and Chipman (19) observed that the effects of superheating are governed by the surrounding atmosphere because melting, superheating and casting in vacuo did not change the structure.

It is also believed that electric furnace irons are more susceptible to the formation of Type D graphite than are the cupola irons. The temperature used in practice for pouring high strength irons is around $2650^{\circ}F$. Timmons and Crosby (20) advocated that pouring temperatures below $2650^{\circ}F$ for these irons have an adverse effect on graphite distribution.

The effect of sulfur on graphite formation has been studied by a number of investigators. The work of Boyles (7, 8) and Garber (21) suggested that in the absence of appreciable sulfur and manganese, an Fe-C-Si alloy solidified in a highly abnormal manner with pronounced Type D graphite and a matrix almost entirely ferritic. Sulfur additions modify the nucleation of graphite and the growth rate of the "eutectic" austenite. Graphite size increases with only about 0.04% S but additions of more than 0.1% cause the graphite size to decrease and the distribution changes to Type D. Increase in sulfur beyond this level causes eutectic carbide to form and the structure changes gradually to white iron with further increases in sulfur.

Manganese alone in the absence of sulfur, acts as a carbide stabilizer and hence manganese, above that necessary to react with sulfur, assists in the development of a pearlitic matrix.

The influence of gas content on the microstructure of iron has been the subject of numerous investigations and a highly controversial matter. Boyles (8) studied the influence of hydrogen by melting in vacuo and in atmospheres of varying hydrogen content. He concluded that a certain amount of hydrogen is essential for the formation of a

normal structure in cast iron but excessive amounts tend to promote unfavorable distributions of graphite.

Oxygen content of cast iron is usually between 0.0005-0.0030% and should be insignificant (22). However, Williams (23) suggested that addition of active metals can cause changes of a temporary nature in the melt by combining with oxygen.

Dawson, Smith and Bach (24) have shown that nitrogen is a powerful carbide stabilizer but the normal variations in the content of this element in cast iron are not likely to have any marked effect. Ivanov (25) has stated that, other conditions being equal, an increase in the nitrogen content of 0.001% is accompanied by an increase in tensile strength by 0.8-1.0 kg/mm^2 (110-140 p.s.i.).

In general, an increase in the cooling rate increases the degree of undercooling and the degree of abnormality, tending toward white solidification of the iron. Graphite distribution of Type D is rarely found throughout an entire casting because of variations in cooling rate in the volume of the casting.

In the ordinary course of events an electric furnace cast iron of less than 3.10% carbon will show abnormal structures, particularly near the surface of the castings. These undercooled fine graphite structures are unsatisfactory and led to development of the process generally known as inoculation.

d) Inoculation:

Inoculation has been practiced in industry for:

1) Improvement in mechanical properties caused by a change in the graphite distribution to Type A flakes and matrix to pearlitic.

2) Overcoming variations in melting practice to obtain more or less consistent properties. In the absence of inoculation, the properties of gray iron are likely to vary from one heat to another.

3) Reducing chill on the high strength irons. This will allow pouring in thin section without the risk of forming white iron or an iron with abnormal graphite distribution.

In the general sense, inoculation may be defined as the addition of substances to melts for the purpose of forming nuclei for crystallization. Morrogh and Williams (11) pointed out that the term nuclei is widely used but its precise meaning rarely defined. It may refer to small solid particles or just some physical or chemical condition that favors the desired type of solidification. Between these concepts we may think of residual lattices in the liquid where some of the atoms may be linked together in a manner similar to that in the solid.

The improvement in properties by inoculation results from a change in graphite distribution and accompanying changes in the matrix structure. The graphite distribution changes from Type-D to E and finally to A. This change depends on the cooling rate (or the extent of undercooling) and the amount and quality of inoculant added. If the inoculant does not contain appreciable amounts of active metals, more amounts may be required for the formation of Type A graphite at the surface of the casting.

Boyles (8) stated that it is important to distinguish between three different types of nucleation which occur during solidification:

a) the nucleation of primary austenite dendrites,

b) the nucleation of eutectic cells, and

c) the nucleation of individual graphite flakes.

It was believed for a long time that the graphite flakes in gray iron eutectic were separated from one another. However, it is now generally understood that within each eutectic cell there is a continuously branched single skeleton of graphite (26). With increased undercooling, the growth rate of each eutectic cell increases and there is a corresponding increase in the frequency of branching of

the skeleton giving finer appearance of the structure in the microsection.

Inoculation does not influence the primary dendrite size and distribution. Principle effect of inoculation is to nucleate eutectic solidification and it has been observed that inoculation increases the number of eutectic cells (27). A large number of eutectic cells is believed to favor the formation of graphite-austenite eutectic rather than the carbide-austenite eutectic which occurs with considerable undercooling (28).

Another aspect of inoculation is that the effect of all inoculants is temporary and will disappear gradually with holding time in the ladle or furnace. The duration of the effect varies with the inoculant used and other circumstances. It is usually between 5 to 30 minutes.

Many attempts have been made to suggest a satisfactory explanation for the effectiveness of late additions but no conclusive evidence has been obtained to establish any of these. Most of the ideas have been based on a nucleation mechanism as implied by the term inoculation.

Before going into the details of other theories, a brief reference may be made to the silicate slime and the undercooling theories which, in the light of recent research, do not appear probable.

According to the silicate slime theory the addition of silicon alloys produces a colloidal dispersion of silica or silicates which nucleate graphite during solidification, promoting Type A distribution. Eash (9) and Morrogh and Williams (11) and others (8) presented cooling curves showing that the irons with Type D graphite solidify at a temperature range which is lower than that for irons with normal graphite structure. The undercooling theory (9, 11) states that the uninoculated iron undercools and solidifies in a metastable manner while the inoculated iron is prevented from undercooling by nuclei provided by the ladle treatment.

As mentioned earlier, Type D graphite is most likely to form at the surface of a casting while considerable Type A may be seen in the center. Since the mold wall is made up of silica and silicates and since its rough surface should be ideal for nucleation, Womochel (18) considers this as a powerful argument opposing both the silica slime and the undercooling theories. This author used pure silicon to inoculate iron and demonstrated that the ladle additions of silicon are not effective. Lux and Tannenberger (4) also suggest that all effective inoculants should actually reduce SiO_2 and hence nucleation of eutectic graphite by SiO_2 appears improbable.

For the purpose of discussion later in this report, the graphite nucleus theory, the gas theory and the surface tension or surface energy theories are dealt with below.

A) The Graphite Nucleus Theory: This theory was developed by Piwowarsky (29) to explain the increased tendency to undercooling as the result of superheating and has been discussed by Lownie (30) and others (8, 11, 18). It is believed that graphite particles are present in the melt and act as nuclei to initiate graphitization during solidification. These nuclei are destroyed by superheating. In support of this view it is pointed out that direct graphite additions serve to inoculate iron.

Eash (9) added his support to this theory by suggesting that the inoculating effect of silicon alloys is due to localized silicon concentrations reducing the carbon solubility. These localized areas might cause the iron to become hypereutectic and deposit particles of kish graphite which serve as nuclei. But this is improbable because of the recent evidence that additions of pure silicon are not effective in changing the graphite pattern (2).

B) The Gas Theory: Assuming that gases in cast iron produce changes in the structure, it is proposed that small amounts of

inoculating agents act as deoxidizers or more generally as degasifiers. The fact that the effect of inoculation gradually wears off if the metal is held for some time in liquid condition agrees with the idea that the addition acts as a temporary degasifier.

It is also believed that local concentration gradients are set up due to imperfect solution and diffusion of the inoculant and these might produce nuclei for graphitization. When the added material is fully dissolved and uniformly distributed, the temporarily created nuclei disappear and the inoculant becomes ineffective.

Williams (23) suggested that the effects produced by inoculation are caused mainly by oxygen present in the iron. It may be assumed that the added inoculant displaces the equilibrium of the iron by combining with oxygen. The deoxidized metal then gradually regains oxygen and the effect of inoculation wears off. As pointed out earlier, hydrogen is certainly involved in influencing the graphite distribution and this may be of more significance than oxygen.

C) The Surface Energy Theory: This is used more or less to explain the formation of spherulitic graphite in iron but it may be said that the same general features apply to explain the change in graphite distribution from Type D to Type A. Buttner, Taylor and Wulff (31) observed that a normal gray iron gave a wetting contact angle against a graphite crucible whereas a definite non-wetting contact angle was observed when the same iron was treated with magnesium. This change in wetting characteristics was attributed by these authors to an increase in the interfacial energy between the liquid iron and the mold material.

Keverian, Taylor and Wulff (32) proposed that surface active elements are present in normal cast iron and if these are adsorbed at the graphite-melt interface, the adsorption would lead to low interfacial energies. When these elements are eliminated by combining with magnesium, the graphite melt interfacial energy increases.

The nucleation is relatively easy in an iron with low graphite-melt interfacial energy and only a slight degree of undercooling required before enough energy is available to create a new interface. In the case of high graphite-melt interfacial energy, there is a definite barrier to nucleation and a greater degree of undercooling is necessary before enough energy can be made available to create the interface. A degree of undercooling intermediate between that necessary for the formation of flake graphite and spherulitic graphite, occurs for the formation of Type D graphite (32).

The literature dealing with practical aspects of the use of various alloys as inoculants is voluminous. Lownie (30) has listed most of the important alloys used as inoculants. The range of properties of cast irons depends mainly on the various ways in which the eutectic transformation can be influenced by variations in composition, cooling rate, metal treatment and thermal history of the melting process. The data presented in the literature generally varies from author to author mainly because of the varying conditions under which experiments are carried out.

In this respect, Morrogh (14) stated:--"The research worker in the academic laboratory has often introduced more confusion than the experimenting foundryman. It is sometimes easier to control variables on the large scale than in the small scale experiment."

In the bibliography presented here, no attempt has been made for a complete presentation. The references cited are either typical or are pertinent to the experiments of this report.

III. SCOPE OF INVESTIGATION

Inoculation has been practiced for a very long time to improve the properties of gray cast iron but the mechanism and kinetics leading to such an improvement are still uncertain. It was proved only recently that calcium is a vital element in inoculation. Hence all attempts to explain the effects of inoculation must begin with this element and its possible compounds in cast iron. It was demonstrated that calcium carbide is formed and nucleation of graphite by calcium carbide was suggested as a possibility (2, 3).

The experimental part of this investigation consisted in using calcium, strontium and barium as inoculants and studying the relative effectiveness on graphite distribution and properties of high strength hypoeutectic gray cast iron. Strontium and barium which belong to the same group as calcium were chosen for these experiments because of the importance of calcium and with the idea that this might lead to a better understanding of the mechanism of inoculation.

The nucleation of eutectic solidification by a compound or compounds of calcium, strontium and barium was examined on theoretical basis and a possible mechanism suggested.

The composition of base iron was kept constant within experimental limits. The results were obtained by comparison of inoculated heats with blank or untreated heats. Barium and strontium were also compared directly with calcium by using equal and equivalent amounts for the purpose of inoculation.

In the later part of this investigation, commercial alloys such as barium-silicon, calcium-silicon and ferrosilicon were also used as inoculants. It is significant that after this work started more than

two years ago, a complex inoculant, containing barium as one of the constituents, has been put on the market by a leading manufacturer in this field. This inoculant was also used in one of the experiments for direct comparison with other inoculants.

Graphite distribution was studied as related to flake types only. Formation of nodular graphite was considered beyond the scope of this investigation.

IV. EXPERIMENTAL PROCEDURE

All heats of this research program were melted in an indirect arc rocking furnace of 250 lb. capacity. The charge consisted of pig iron, structural steel scrap, ferrosilicon, ferromanganese and iron sulfide. Analysis of the charge materials is shown in Table 1. A typical charge consisted of--

110 lb. pig iron, lot no. 1
55 lb. pig iron, lot no. 2
60 lb. steel
11.1 lb. ferrosilicon
0.6 lb. ferromanganese, and
0.24 lb. iron sulfide.

All the constituents except ferromanganese and iron sulfide were charged in the cold furnace. The ferromanganese and iron sulfide were added immediately after the charge in the furnace was molten. All heats were brought to a temperature of 2850-2875°F which was determined by optical pyrometer readings through the spout. This degree of superheat was selected as being representative of general practice and it provided sufficient latitude to transport the metal to molds, skim the ladle, read the temperature with an immersion pyrometer (Pt/Pt-Rh thermocouple) and pour at a temperature of 2650-2700°F.

The metal was tapped into two pairs of preheated, 50 lb. ladles. A $1\frac{1}{4}$" diameter, $3\frac{1}{2}$" long bar was poured before adding the inoculant. Chemical analysis of this bar indicated the extent of decarburization resulting from the active metal addition. The ladle additions of metallic barium, strontium and calcium were made after securely

Table 1. Analysis of the Charge Constituents

Constituent	Percent				
	C	Si	Mn	P	S
Pig Iron, Lot no. 1	4.12	1.23	0.88	0.24	0.033
Pig Iron, Lot no. 2	4.22	1.67	0.48	0.19	0.018
Structural Steel	0.14	0.195	0.42	0.021	0.021
Ferrosilicon (25%)	0.44	27.40	0.84	0.033	0.018
Ferromanganese (Std.)	6.75	1.00	80.00	0.30	-----
Iron Sulfide	----	----	-----	----	50.00

wiring the active metal piece to a $\frac{3}{8}$" diameter steel rod, about 8' long and bent 90° at about 1' from the end. The active metal was then plunged into the molten metal in the ladle and agitated until all reaction ceased.

In the later part of this investigation, when some alloys were used as inoculants, the additions were made by tapping a small amount of metal into the ladle and then adding the inoculant continuously as the ladle was filled. During this operation, an effort was made to carry the inoculant under the surface with the stream of molten iron.

In making additions of the various alloys, crushed sizes of the alloys were generally kept comparable in each case. The commercial size 8 mesh and down was employed. As a consequence of high silicon content of the inoculating alloys, the amount of ferrosilicon in the cold charge was reduced to bring the final silicon content of all heats to the same level.

The operations from tapping to pouring the molds took two to three minutes in all cases. Metal from each ladle was cast into:

a) One wedge shaped casting 2" x 1" in cross-section at the top and tapering to 2" x $\frac{1}{4}$" at the bottom with an overall length of 5". This was not poured in all heats but in only a few which involved quenching experiments.

b) Two rectangular chill blocks each approximately 2$\frac{1}{8}$" x $\frac{3}{4}$" x 3$\frac{7}{8}$".

c) Five vertical, 1.2" diameter, 21" long standard transverse test bars for breaking on 18" centers.

For each heat, a newly prepared set of ladles was used. A mixture of about 50% sand and 50% fireclay, with adequate water was used for the lining of new ladles. These were dried at about 300°F to drive out all moisture and then fired under a gas torch for about 2 hours before use.

All molds were made from a well-mixed aggregate of lake sand, cereal, water, and linseed oil. The molds were baked for four hours at a temperature of 450°F. The 1.2" diameter test bar molds were finally washed with a Black Diamond GW core wash and the baking cycle repeated for the purpose of drying.

A high speed electronic temperature recorder was used for automatic recording of the time temperature curves of two wedge shaped castings from each pair of ladles. Two chromel-alumel thermocouples of 22 gage wire were attached to the recorder by means of extension lead wires. The thermocouples were insulated by thin porcelain insulators and fused quartz tubes. The hot junction of the thermocouple was protected by a thin layer of alundum refractory cement which was applied wet and then baked at a bright red heat. The couple was located on the thinner side of the mold at a distance of 1" from the top (heavy end of the casting). The tip of the thermocouple projected $\frac{1}{8}$ " inside from the mold wall.

The wedge shaped molds were poured over quenching water tanks. When the eutectic solidification was in progress, as indicated by the time-temperature curves, the molds were broken and the partially solidified castings dropped into the quenching tanks, for the purpose of arresting eutectic transformation.

The water quenched wedges were sectioned at a point slightly below the thermocouple entry point by an abrasive wheel cutter. The cutting operation was carried out very slowly with ample supply of coolant to avoid tempering of the martensite formed during quenching. The pieces were then prepared for macro- and microexaminations. The main object of this examination was to know the number of eutectic cells formed.

The mold for casting chill block had a heavy metal chill face. Pairs of chill blocks were fractured at comparable positions after

making a small saw cut at a corner on the gray iron side. Chill depths are reported for clear and total chill in $\frac{1}{32}$ inch units. In general, the agreement between chill specimens from the same ladle was very good. The chill test shows only the tendency of the iron to solidify white instead of gray. It is incorrect to assume that irons showing the same chilling tendencies as a result of ladle additions will have similar mechanical properties.

The data on mechanical properties was obtained from the transverse breaking load on 18" centers and from the deflection of the test bars. Bars were cleaned with wire brush before testing.

The most potent influence of inoculation on microstructure is at the surface of the casting. For this reason, the transverse test bar, tested in an unmachined condition, is a very suitable test specimen for the purpose of demonstrating inoculation action. The transverse breaking load, the deflection and in particular, the triangular resilience [= $\frac{1}{2}$ (Trans. breaking load x deflection)] provide a more sensitive index of variations.

The superiority of transverse breaking load in representing the quality of the iron has been discussed by Womochel (18) and was reported again recently by Kayama and Masaki (33). As a consequence of this, tensile tests were not carried out. The results reported include the corrected transverse breaking load, the deflection and the triangular resilience. Bars showing defects in the fracture and consequently low results for breaking load and deflection were not included in the average. All the results reported are the average of three to five bars.

For microscopic examination, small specimens were taken from near the fracture of representative transverse bars so that the change in structure from the surface to the center could be studied. After polishing the specimens on successive grades of emery papers,

they were processed further on a wax wheel. Final polish was given on a silk cloth using AB Metpolish for hard metals. The specimens were etched lightly in 2% nital. A large number of samples from different heats were examined but photomicrographs of all irons were not made. For the purpose of illustration and discussion only the typical structures were photographed.

The results of the transverse test compared well with the variations in microstructure. The presence of a large percentage of Type A graphite, particularly at the surface of the casting, appears to be very effective in producing a high transverse breaking load and a high deflection.

The drillings for chemical analysis were obtained from the grey iron end of the chilled blocks and the $1\frac{1}{4}$" diameter, $3\frac{1}{2}$" long bar that was poured before adding the inoculant. Analysis of the drillings from the latter sample indicated the extent of decarburization or desulfurization that resulted due to the additions. Carbon and in many cases sulfur were determined from the two types of samples above.

Manganese and phosphorus were determined for each heat and not for each ladle. Except in the cases when the inoculants employed were alloys, silicon determinations were also made for each heat. Chemical analysis was carried out by a commercial laboratory.

The amount of calcium, strontium or barium retained in the solid iron can be determined by either the spectrographic or gravimetric methods. Spectrographic analysis needs a standard sample containing known amount of calcium, strontium or barium and the gravimetric method is time consuming and uncertain. Moreover, retention of a substantial amount of the inoculant is probably not necessary for producing profound changes in the microstructure and properties. After discussing this matter, McElwee and Barlow (34) concluded that the effects of inoculants cannot be measured by analyzing the iron for residuals.

However, gravimetric analysis was carried out on some irons inoculated with calcium and barium. The results showed that the amount of calcium or barium retained is less than 0.01%. This matter is discussed later in this report.

V. EXPERIMENTAL RESULTS

1. Blank Irons

Blank irons without any treatment were poured in the usual manner to obtain data for the purpose of comparison with the data obtained from the inoculated irons. As the work was in progress, it became evident that the decarburization resulting from the addition of active metals lowered the carbon content of the inoculated irons considerably in some of the cases, and these irons could not be compared with blank irons poured from the same heat. It was considered essential to have some blank irons with lower carbon contents. This was achieved by manipulating the cold charge constituents in some later heats.

The subject of obtaining consistent results is important in this type of work. The data obtained from all the blank irons poured in the course of this investigation is presented in Table 2. It is seen that the transverse breaking load varied from 2381 to 2553 lbs. or that the difference was 172 lbs. It may, therefore, be said that the transverse breaking load results are insignificant unless the difference between two irons with different treatments exceeds 172 lbs. If the irons R5X1 and R5X2 which have higher carbon equivalence ($\%C + \frac{\%Si}{C}$) are excluded, the variation in deflection is 0.016". The variation in resilience is 40 inch pounds. The chill results are quite erratic and it appears that small differences in pouring temperature may be responsible for this. In the subsequent data, conclusionsregarding chill depth are confined only to those cases where the difference in chill is very marked.

Variations in properties cannot be attributed to variations in sulfur or manganese as these are controlled within very narrow limits

Table 2. Chemical Analysis and Properties of Blank Irons

Number	Percent					Transverse load lbs.	Deflection in.	Resilience in. lb.	Chill $\frac{1}{32}$ in. units
	C	Si	Mn	P	S				
R5X1	3.06	2.37	0.87	0.16	0.062	2413	0.218	263	17-50
R5X2	3.11	2.37	0.87	0.16	0.060	2404	0.210	252	15-33
R6X1	2.92	2.25	0.89	0.16	0.066	2381	0.185	224	18-39
R6X2	2.93	2.25	0.89	0.16	0.065	2451	0.198	243	18-36
R7X1	2.81	2.22	0.87	0.165	0.070	2421	0.196	238	24-44
R8X1	2.87	2.27	0.89	0.168	0.072	2480	0.188	233	28-52
R8X2	2.86	2.27	0.89	0.168	0.070	2553	0.189	240	29-46
R9X1	2.92	2.27	0.91	0.175	0.062	2549	0.200	255	32-61
R9X2	2.90	2.27	0.91	0.175	0.065	2501	0.201	251	23-42

for all irons. The general impression regarding uninoculated irons being erratic in their behaviour particularly with respect to chilling tendency is seen to be quite true from the results shown in Table 2. The uniformity of behaviour particularly with respect to chilling tendency is one of the justifications for inoculation of such irons.

In general, the carbon equivalents ($\%C + \frac{\%Si}{3}$) of irons compared in this report will not vary more than 0.1%. This is a degree of control which compares favorably with that of similar experiments reported in the literature. Whenever such comparison was not possible between blank and inoculated irons from the same heat, another blank iron was selected from Table 2 for comparison.

It was stated earlier that an uninoculated iron of carbon content between 2.60 and 3.10% will generally show Type D graphite at the surface of the casting. In agreement to this, the microstructure of the cross-sections of the transverse bars of the blank irons of Table 2 showed completely abnormal graphite distribution of Type D at the surface. The graphite distribution at the center was also largely abnormal though there was a slight tendency for a change towards normality. Typical structures of one blank iron R6X2 at the surface and at the center are shown in Figures 4 and 6.

2. Calcium Additions

In this section, the calcium inoculated irons are compared with blank irons of similar analysis. As pointed out earlier, pure calcium as a ladle addition has been extensively studied (2-4, 18, 27) and hence it was not considered essential to carry out more experiments with calcium.

The amounts of calcium used were 0.1%, 0.2%, and 0.33%. Two ladles were treated with 0.1%, three with 0.2% and one with 0.33% calcium. The calcium used was in the form of stick and it was

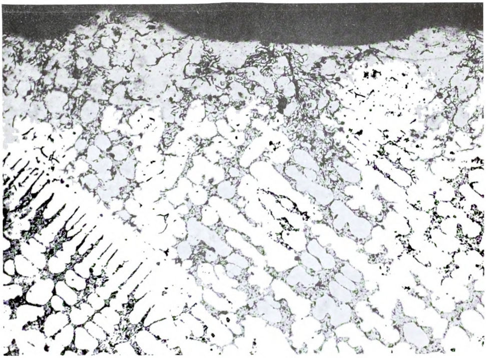


Figure 4. Microstructure of Blank Iron R6X2, at the surface. Nital etch. 100X.

Figure 5. Microstructure of Iron R32C, at the surface. Treated with 0.2% calcium. Nital etch. 100X.

99.5% pure. The results obtained with transverse test bars are shown in Tables 3 and 4. The use of calcium as an inoculant resulted in a definite improvement in the microstructure and properties. Analysis of the small bar poured before adding calcium indicated a significant loss of carbon. The loss in sulfur was observed to be 0.01% or less. The loss of carbon in the calcium inoculated irons is shown in Table 5. The reduction in carbon has been attributed to the formation of calcium carbide (2, 3, 18, 27).

Thermodynamic data by Richardson and Jeffes (35) and by Richardson (36) indicate that the tendency of forming calcium sulfide is greater than that of calcium carbide. Even if the loss in sulfur is only about 0.01%, it represents nearly 15% decrease in total sulfur whereas the maximum loss in carbon amounts only to about 4% of the total carbon present.

As stated by McGrady (27), a strong odor similar to acetylene gas was noticed at the conclusion of heats inoculated with calcium. The source of this odor was an accumulation of gray powder which formed in the ladle. This powder, when moistened with a few drops of water gave off a gas which could be ignited. When dissolved in water, this powder gave a basic reaction to litmus paper.

The formation of calcium carbide thus established, it was suggested that it probably acts as a nucleating agent for the formation of a large number of eutectic cells. By quenching wedge shaped castings at the start of eutectic transformation, McGrady showed that an addition of calcium results in the formation of a large number of centers of eutectic formation. The possibility of calcium carbide acting as a nucleating agent for graphite will be discussed later in this report.

Table 3. Chemical Analysis of Irons Inoculated with Calcium

Iron	Addition (% Ca)	Percent C	Si	Mn	P	S
R4C1	0.1	2.90	2.31	0.87	0.16	0.055
R9X2	Blank	2.90	2.27	0.91	0.17	0.062
R32C	0.2	2.94	2.24	0.92	0.16	0.05
R6X2	Blank	2.93	2.25	0.89	0.16	0.065
R22C	0.33	2.93	2.20	0.94	0.166	0.056
R6X2	Blank	2.93	2.25	0.89	0.16	0.065

Table 4. Properties of Irons Inoculated with Calcium

Iron	Addition (% Ca)	Trans. load lbs.	Deflec. in.	Resil. in.lb.	Chill $\frac{1}{32}$ in. units
R4C1	0.1	3058	0.340	520	5-13
R9X2	Blank	2501	0.201	251	23-42
R32C	0.2	3110	0.343	533	5-11
R6X2	Blank	2451	0.198	243	18-36
R22C	0.33	3037	0.376	570	3-8
R6X2	Blank	2451	0.198	243	18-36

Table 5. Decarburizing Effect of Calcium

Iron	Addition (% Ca)	%C Before Addition	%C After Addition	Loss
R4C1	0.1	2.99	2.90	0.09
R4C2	0.1	2.95	2.89	0.06
R31C	0.2	2.94	2.90	0.04
R32C	0.2	3.02	2.94	0.08
R21C	0.21	2.94	2.83	0.11
R22C	0.33	3.05	2.93	0.12

Table 6. Decarburizing Effect of Strontium

Iron	Addition (% Sr)	%C Before Addition	%C After Addition	Loss
R5S2	0.1	3.11	3.06	0.05
R8S2	0.2	2.86	2.82	0.04
R31S	0.2	2.93	2.90	0.03
R4S	0.22	2.96	2.91	0.05
R9S2	0.24	2.90	2.82	0.08
R32S	0.43	2.95	2.90	0.05
R6S	0.8	2.90	2.84	0.06

Microstructure of the cross-sections of transverse test bars of calcium inoculated irons showed a definite change toward normal graphite distribution at the surface and completely normal, Type-A, in the interior. Figures 5 and 7 show the typical structures of the iron R32C. These two microphotographs together with those in Figures 4 and 6 are typical and will be used for further comparisons and discussion in this report.

3. Strontium Additions

The effect of strontium as an inoculant was studied in four different heats. The quantity of strontium used varied from 0.1 to 0.8%. A pair of ladles was poured each time and strontium was added to one ladle from each pair. The other ladle served as blank. The strontium metal used was in the ingot form and had the following analysis:

Strontium:	Assay 99%	
	Magnesium	0.35
	Calcium	0.3
	Barium	0.3
	Iron	0.05
	Aluminum	0.02
	Nitrogen	0.05

The addition of strontium caused decarburization and desulfurization of the melt. The reduction in sulfur observed was 0.012% or less. The decarburizing and desulfurizing effects were similar to those due to calcium but the amount of carbon lost was less in the case of strontium inoculated irons. The amount of carbon lost in various heats that involved strontium additions is shown in Table 6. The strong odor of acetylene gas, noticed after the conclusion of heats inoculated with calcium, was also noticed after the conclusion of heats inoculated with strontium and hence the reduction in carbon was attributed to the formation of SrC_2.

Figure 6. Microstructure of Blank Iron R6X2, in the interior. Nital etch. 100X.

Figure 7. Microstructure of Iron R32C, in the interior. Treated with 0.2% calcium. Nital etch. 100X.

The results obtained from the transverse test bars of the strontium inoculated and the corresponding blank irons are shown in Tables 7 and 8. The results of strontium inoculated irons, compared with those of matching blank irons, are shown in Tables 9 and 10.

To study the effect of inoculation with strontium on eutectic solidification, wedge shaped castings were poured in heats R-8 and R-9. The procedure followed was described earlier in this report. The water quenched wedges were sectioned, polished and etched deeply in nital. The deep etching revealed the eutectic cells that were in the process of development before the wedge was quenched in water.

Macrostructures of the sectioned wedges of the strontium inoculated and corresponding blank iron from heat R-9 are shown in Figure 8. It is clearly seen that the number of eutectic cells formed is much greater in the strontium inoculated iron. After taking the macrophotograph shown in Figure 8, these wedges were repolished and etched lightly to examine the microstructure. Figure 10 shows the microstructure of the strontium inoculated wedge. The graphite is seen in the eutectic cells which are the darker areas in the microstructure. The primary dendrites of austenite are seen as areas of martensite formed during the water quench.

Similar microstructure of the corresponding blank iron wedge is shown in Figure 11. The microstructures of Figures 10 and 11 were taken at comparable positions. A careful study of the microstructures over a large area showed that the number of eutectic cells in the strontium inoculated iron is probably more than about 10 times the number of eutectic cells observed in the corresponding blank iron. The primary dendrite size and distribution was similar in the two irons.

Table 7. Chemical Analysis of Irons Inoculated with Strontium

	Addition	Percent				
Iron	(% Sr)	C	Si	Mn	P	S
R5S2	0.1	3.06	2.37	0.87	0.16	0.060
R5X2	Blank	3.11				0.060
R8S2	0.2	2.82	2.27	0.89	0.168	0.065
R8X2	Blank	2.86				0.070
R9S2	0.24	2.82	2.27	0.91	0.175	0.052
R9X2	Blank	2.90				0.062
R6S	0.8	2.84	2.25	0.89	0.16	0.052
R6X2	Blank	2.93				0.065

Table 8. Properties of Irons Inoculated with Strontium

Iron	Addition (% Sr)	Trans. load lbs.	Deflec. in.	Resil. in. lb.	Chill $\frac{1}{32}$ in. units
R5S2	0.1	2416	0.245	296	8-33
R5X2	Blank	2404	0.210	252	15-33
R8S2	0.2	2528	0.222	281	10-29
R8X2	Blank	2553	0.189	240	29-46
R9S2	0.24	2718	0.259	352	8-26
R9X2	Blank	2501	0.201	251	23-42
R6S	0.8	2790	0.265	369	9-20
R6X2	Blank	2451	0.198	243	18-36

Table 9. Chemical Analysis of Strontium Inoculated and Comparable Blank Irons

Iron	Addition (% Sr)	Percent				
		C	Si	Mn	P	S
R5S2	0.1	3.06	2.37	0.87	0.16	0.060
R5X1	Blank	3.06				0.062
R8S2	0.2	2.82	2.27	0.89	0.168	0.065
R7X1	Blank	2.81	2.22	0.87	0.165	0.070
R9S2	0.24	2.82	2.27	0.91	0.175	0.052
R7X1	Blank	2.81	2.22	0.87	0.165	0.070
R6S	0.8	2.84	2.25	0.89	0.16	0.052
R8X2	Blank	2.86	2.27	0.89	0.168	0.070

Table 10. Properties of Strontium Inoculated and Comparable Blank Irons

Iron	Addition (% Sr)	Trans. load lbs.	Deflec. in.	Resil. in. lb.	Chill $\frac{1}{32}$ in. units
R5S2	0.1	2464	0.262	323	8-33
R5X1	Blank	2413	0.218	263	17-50
R8S2	0.2	2528	0.222	281	10-29
R7X1	Blank	2421	0.196	238	24-44
R9S2	0.24	2718	0.259	352	8-26
R7X1	Blank	2421	0.196	238	24-44
R6S	0.8	2790	0.265	369	9-20
R8X2	Blank	2553	0.189	240	29-46

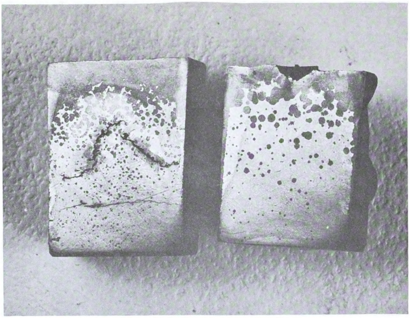


Figure 8. Macrostructures of irons quenched at the start of eutectic solidification. Left picture: Iron R9S2, treated with 0.24% strontium. Right picture: Iron R9X2, untreated. Nital etch. Approximately 1.5X.

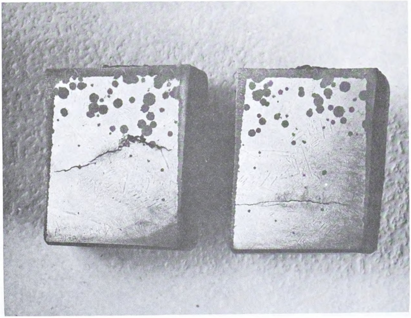


Figure 9. Macrostructures of irons quenched at the start of eutectic solidification. Left picture: Iron R9B1, treated with 0.24% barium. Right picture: Iron R9X1, untreated. Nital etch. Approximately 1.5X.

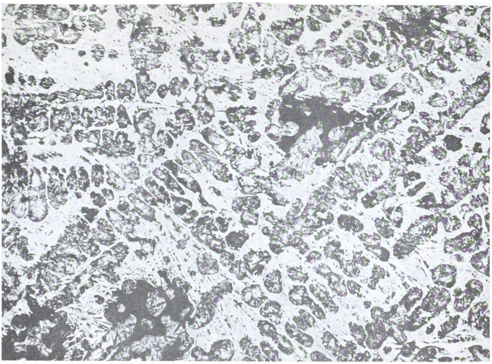


Figure 10. Dendritic size and distribution in Iron R9S2, treated with 0.24% strontium. Nital etch. 100X. From the specimen shown on left in Figure 8.

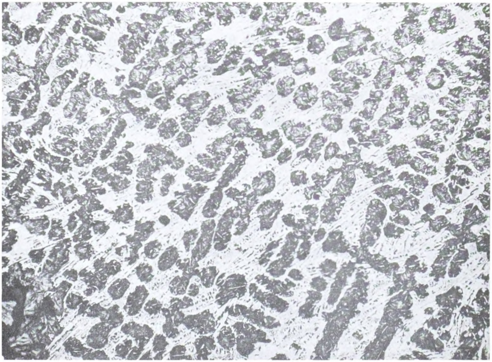


Figure 11. Dendritic size and distribution in Iron R9X2, untreated. Nital etch. 100X. From the specimen shown on right in Figure 8.

Microstructures of the cross-sections of the transverse test bars of irons inoculated with 0.1 and 0.2% Sr were almost similar to those of the corresponding blank irons. In the case of 0.24% Sr inoculated iron a slight but definite change at the surface was noticed. The iron inoculated with 0.8% Sr had more or less completely normal graphite distribution in the interior. Figures 12 and 13 show the microstructures of the 0.8% Sr inoculated iron at the surface and the interior respectively.

Examination of Tables 8 and 10 shows that strontium additions of 0.1 and 0.2% were not effective in increasing the transverse breaking load but the deflection and hence the resilience was higher than in the case of corresponding blank irons. At the surface, the microstructure of these two irons was almost similar to the one of Figure 4. In the center, it appeared slightly better than that of Figure 6 and the higher deflection obtained with these irons might be attributed to this small difference in microstructure.

It is also seen from Tables 8 and 10 that strontium additions were effective in reducing the depth of chill in each case. The sections of the fractured chill blocks of the strontium inoculated and the corresponding blank iron from heat R-9 are shown in Figure 14.

4. Barium Additions

The effect of barium as an inoculant was studied in four different heats. The actual quantities of barium used were 0.1, 0.2, 0.24 and 1.0% respectively in the four heats. The general procedure followed was similar to that followed for strontium. Barium metal used was in the form of sticks and had the following analysis.

Barium: Assay 99%

Magnesium	0.2
Calcium	0.2
Strontium	0.2
Iron	0.05
Aluminum	0.01
Nitrogen	0.10

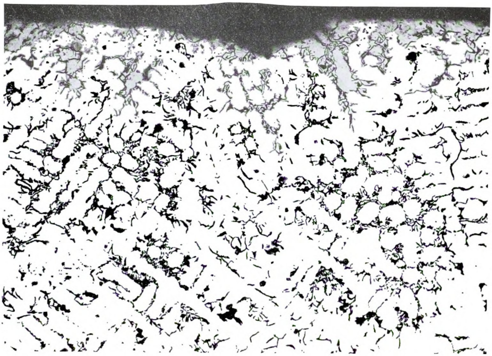
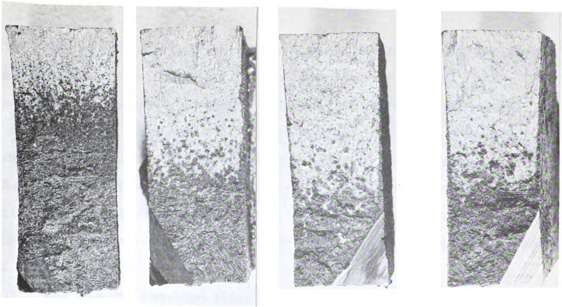


Figure 12. Microstructure of iron R6S, at the surface. Treated with 0.8% strontium. Nital etch. 100X.

Figure 13. Microstructure of iron R6S, in the interior. Treated with 0.8% strontium. Nital etch. 100X.



(a) (b) (c) (d)

Figure 14. Chill block fractures. Approximately 1.25X.
(a) - Iron R9S2, treated with 0.24% strontium.
(b) - Iron R9X2, untreated, from the same heat as in (a).
(c) - Iron R8B1, treated with 0.2% barium.
(d) - Iron R8X1, untreated, from the same heat as in (c).

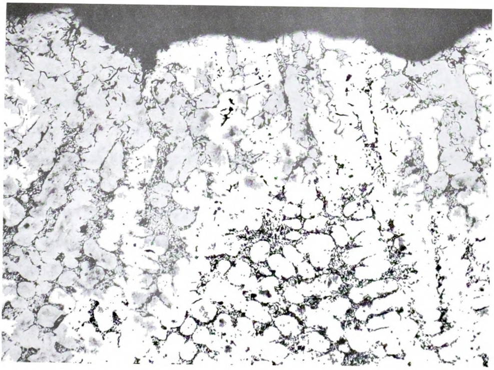


Figure 15. Microstructure of Iron R6B, treated with 1.0% barium. Nital etch. 100X.

The addition of barium caused a decarburization and desulfurization of the melt. In the case of an iron inoculated with 1.0% barium, a maximum reduction of 0.014% in sulfur was observed. Table 11 shows the extent of decarburization caused by different amounts of barium. At the conclusion of these heats the same general observations which indicated the formation of carbide in the case of calcium and strontium, were made. The reduction in carbon resulting from barium additions was, therefore, attributed to the formation of BaC_2.

The results obtained after breaking the transverse test bars from the barium inoculated and the corresponding blank heats are shown in Tables 12 and 13. The properties obtained with the barium inoculated irons were compared with those of properly matching blank irons. This comparison is shown in Tables 14 and 15.

Effect of inoculation with barium on eutectic solidification was studied in heats R-8 and R-9. Macrostructures of the sectioned wedges of the barium inoculated and the corresponding blank iron from heat R-9 are shown in Figure 9. It is clear from this picture that the addition of barium didn't make any significant change in the number of eutectic cells. These wedge sections were repolished and etched lightly to examine the microstructure. The microstructures of the barium inoculated and the corresponding blank wedges were very much similar to that of Figure 11 and hence they are not presented.

All the irons inoculated with different amounts of barium had microstructures similar to that of a typical blank iron shown in Figures 4 and 6. For the purpose of illustration, one microstructure at the surface of the cross-section of transverse test bar, from heat R-6 in which 1.0% Ba was used for inoculation, is shown in Figure 15.

In agreement with the observed microstructures, examination of Tables 13 and 15 also shows that barium was not effective at all.

Table 11. Decarburizing Effect of Barium

Iron	Addition (% Ba)	%C Before Addition	%C After Addition	Loss
R5B1	0.1	3.07	3.07	0.00
R8B1	0.2	2.90	2.86	0.04
R9B1	0.24	2.90	2.84	0.06
R22B	0.32	2.96	2.84	0.12
R4B	0.34	2.95	2.85	0.10
R21B	0.7	3.02	2.85	0.17
R6B	1.0	2.97	2.81	0.16

Table 12. Chemical Analysis of Irons Inoculated with Barium

	Addition	Percent				
Iron	(% Ba)	C	Si	Mn	P	S
R5B1	0.1	3.07	2.37	0.87	0.16	0.058
R5X1	Blank	3.06				0.062
R8B1	0.2	2.86	2.27	0.89	0.168	0.062
R8X1	Blank	2.87				0.072
R9B1	0.24	2.84	2.25	0.91	0.175	0.055
R9X1	Blank	2.92				0.062
R6B	1.0	2.81	2.25	0.89	0.16	0.052
R6X1	Blank	2.92				0.066

Table 13. Properties of Irons Inoculated with Barium

Iron	Addition (% Ba)	Trans. load lb.	Deflec. in.	Resil. in.lb.	Chill $\frac{1}{32}$ in. units
R5B1	0.1	2424	0.218	264	12-36
R5X1	Blank	2413	0.218	263	17-50
R8B1	0.2	2365	0.180	228	25-54
R8X1	Blank	2480	0.188	233	28-52
R9B1	0.24	2420	0.197	238	28-47
R9X1	Blank	2549	0.200	255	32-61
R6B	1.0	2410	0.176	212	20-59
R6X1	Blank	2381	0.188	224	18-39

Table 14. Chemical Analysis of Barium Inoculated and Comparable Blank Irons

Iron	Addition (% Ba)	Percent C	Si	Mn	P	S
R5B1	0.1	3.07	2.37	0.87	0.16	0.058
R5X1	Blank	3.06				0.062
R8B1	0.2	2.86	2.27	0.89	0.168	0.062
R8X2	Blank	2.86	2.27	0.89	0.168	0.070
R9B1	0.24	2.84	2.25	0.91	0.175	0.055
R8X2	Blank	2.86	2.27	0.89	0.168	0.070
R6B	1.0	2.81	2.25	0.89	0.16	0.052
R7X1	Blank	2.81	2.22	0.87	0.165	0.070

Table 15. Properties of Barium Inoculated and Comparable Blank Irons

Iron	Addition (% Ba)	Trans. load lb.	Deflec. in.	Resil. in. lb.	Chill $\frac{1}{32}$ in. units
R5B1	0.1	2424	0.218	264	12-36
R5X1	Blank	2413	0.218	263	17-50
R8B1	0.2	2365	0.180	228	25-47
R8X2	Blank	2553	0.189	240	29-46
R9B1	0.24	2420	0.197	238	28-47
R8X2	Blank	2553	0.189	240	29-46
R6B	1.0	2410	0.176	212	20-59
R7X1	Blank	2421	0.196	238	24-44

The results on breaking load and deflection of any barium inoculated iron were similar to those of a corresponding blank or matching blank iron. It is seen from the results of Table 15 that the barium inoculated irons showed a slight reduction in chill as compared with the blank irons of similar analysis. However, this slight reduction in chill depth cannot be accepted as conclusive because of the erratic behavior of chill specimens. Figure 14 shows the sections of fractured chill blocks of the barium inoculated and the corresponding blank iron from heat R-8.

5. Comparison of Calcium and Strontium

Three different experiments were carried out to compare the relative effectivensss of strontium and calcium. In one experiment, equal amounts of strontium and calcium were used and equivalent amounts were used in the other two. In each experiment, metal was poured in a pair of ladles. One of the ladles was treated with calcium and the other with strontium.

It was observed that the reaction with calcium starts immediately after adding the inoculant whereas with strontium it starts after about 3-4 seconds and is less violent than that with calcium. The quantity of SrC_2 found in the ladle after the conclusion of heat was small as compared with the quantity of CaC_2 found in the calcium treated ladle.

The results obtained from the transverse tests are shown in Tables 16 and 17. These results clearly show that calcium is much superior to strontium as a ladle addition. The typical microstructures of Figures 5 and 12 also indicate the superiority of calcium over strontium.

Table 16. Chemical Analysis of Irons Inoculated with Calcium and Strontium

Iron	Addition	Percent C	Si	Mn	P	S
R4C2	0.1 % Ca	2.89	2.31	0.87	0.16	0.056
R4S	0.22 % Sr	2.91				0.060
R31C	0.2 % Ca	2.90	2.24	0.92	0.16	0.05
R31S	0.2 % Sr	2.90				0.055
R32C	0.2 % Ca	2.94				
R32S	0.43 % Sr	2.90				

Table 17. Properties of Irons Inoculated with Calcium and Strontium

Iron	Addition	Trans. load lb.	Deflec. in.	Resil. in. lb.	Chill $\frac{1}{32}$ in. units
R4C2	0.1 % Ca	3044	0.337	513	6-12
R4S	0.22 % Sr	2568	0.243	312	10-35
R31C	0.2% Ca	3136	0.353	552	5-11
R31S	0.2% Sr	2496	0.239	298	10-30
R32C	0.2% Ca	3110	0.343	533	5-11
R32S	0.43% Sr	2610	0.244	318	12-29

6. Comparison of Calcium and Barium

The experimental work of this project was started with the experiments described in this section. At that time, the ineffectiveness of barium as a ladle addition in improving the properties of high strength hypoeutectic gray cast iron was not known.

Three different experiments using equal amounts of calcium and barium in one and equivalent amounts in the other two, were carried out. After adding the inoculant, it was observed that with barium, the reaction is less violent than that with calcium. The transverse test results are presented in Tables 18 and 19.

For heat R-2, preparations such as setting up the molds, cutting the pieces of barium and calcium required a little more time and the metal could not be poured at the proper time. This superheating was probably responsible for the low breaking loads of this heat. However, this was the only heat in which the metal was superheated to an unusual degree.

The quantity of BaC_2 found in the ladle after the conclusion of heat was less than the quantity of CaC_2 found in the ladle treated with calcium. The transverse breaking load results were well correlated with the microstructure at the surface of the test bars. These microstructures were similar to those of Figures 5 and 15.

After studying the results presented so far, it is readily seen that calcium is the most effective inoculant of the three elements calcium, strontium and barium. Strontium is seen to be only partially effective and barium is not effective at all in improving the properties and graphite distribution in high strength hypoeutectic gray cast iron. This matter will be discussed later.

Table 18. Chemical Analysis of Irons Inoculated with Calcium and Barium

Iron	Addition	Percent C	Si	Mn	P	S
R4C1	0.1% Ca	2.90	2.31	0.87	0.16	0.055
R4B	0.34% Ba	2.85				0.056
R21C	0.21% Ca	2.83	2.20	0.94	0.166	
R21B	0.7% Ba	2.85				0.056
R22C	0.33% Ca	2.93				
R22B	0.32% Ba	2.84				

Table 19. Properties of Irons Inoculated with Calcium and Barium

Iron	Addition	Trans. load lb.	Deflec. in.	Resil. in. lb.	Chill $\frac{1}{32}$ in. units
R4C1	0.1% Ca	3058	0.340	520	5-13
R4B	0.34% Ba	2447	0.202	247	26-57
R21C	0.21% Ca	3017	0.380	572	4-9
R21B	0.7% Ba	2277	0.205	233	15-40
R22C	0.33% Ca	3037	0.376	570	3-8
R22B	0.32% Ba	2161	0.211	228	10-25

7. Comparison of Barium-silicon and Calcium-silicon

In commercial practice the active metals are added as alloys and in order to gain some information on barium additions in the form of an alloy, these experiments were performed. The inoculating alloys used in practice are silicon base alloys. The alloys used in this work were supplied by the Union Carbide Metals Company. The barium-silicon and calcium-silicon used had the following analysis:

Barium-silicon: 51.78 Si; 44.02 Ba; 1.65 Fe; 0.22 C; the Al and Ca contents are not known but typical values are 0.5 Al and 1.0 Ca.

Calcium-silicon: 61.8 Si; 32.70 Ca; 0.99 Al and 1.60 Fe.

The addition of these high silicon alloys increases the final silicon content of the iron. The amount of ferrosilicon in the cold charge was therefore reduced so that the final silicon content after adding inoculants was comparable in all heats. Two experiments were carried out and the quantities of the Ba-Si and Ca-Si added in each experiment had equal amounts of silicon. This required a use of higher quantity of Ba-Si.

A pair of ladles was used in each experiment. One was treated with Ba-Si and the other with Ca-Si. The inoculants were added when the metal was being tapped into the ladles and hence it was not possible to check the extent of decarburization and desulfurization. The results obtained are shown in Tables 20 and 21. From this data it is seen that the silicon pick-up was not complete when the inoculant was Ca-Si. This is in agreement with the results reported about Ca-Si in the literature (2).

From the results of the first experiment it is clear that except for the differences in chill depth, effects of the two inoculants were

identical. The second experiment involved the use of larger amounts and Ca-Si appeared more effective in increasing the breaking load and deflection. In both cases, the iron treated with Ba-Si had low chill depth.

It was seen earlier in section 4 that barium, when added as a pure metal, is not effective in reducing chill. It has been reported in the literature that aluminum additions are effective in reducing chill (2, 3). Lownie (37) used a mixture of Ba-Si and Fe-Si and found that an iron inoculated with the mixture gives lower chill depth than the one inoculated with either Ba-Si or Fe-Si alone. Lownie did not explain why the combination works better. The Fe-Si used by him had 87.0 Si, 1.6 Al and 0.8 Ca.

The exact aluminum and clacium contents of the Ba-Si used in this research were not known but the typical value for aluminum content given by the supplier is 0.5%. As a consequence of these considerations and of the results shown in Tables 20 and 21, the low chill depth of irons inoculated with Ba-Si may be attributed to the combined presence of barium, aluminum and calcium in the inoculant.

The microstructures of the cross-section of the two transverse test bars at the surface was better than the microstructure shown in Figure 5. These two microstructures of the irons inoculated with Ba-Si and Ca-Si are shown in Figures 16 and 17. The graphite distribution was completely normal in the interior in both irons.

8. Comparison of Barium-silicon and Ferrosilicon

To compare the effect of Ba-Si and Fe-Si as inoculants, barium free ferrosilicon of the following analysis was used. The Ba-Si used was from the same lot as in section 7 above.

Ferrosilicon: 75.94 Si; 1.26 Al and 1.76 Ca.

Table 20. Chemical Analysis of Irons Inoculated with Barium-silicon and Calcium-silicon

		Percent				
Iron	Addition	C	Si	Mn	P	S
R10BS2	0.5% Ba-Si	2.90	2.27	0.92	0.165	0.060
R10CS2	0.42% Ca-Si	2.90	2.18	0.94	0.164	0.060
R11BS2	0.96% Ba-Si	2.84	2.29	0.84	0.158	0.055
R11CS2	0.8% Ca-Si	2.86	2.12			0.060

Table 21. Properties of Irons Inoculated with Barium-silicon and Calcium-silicon

Iron	Addition	Trans. load lb.	Deflec. in.	Resil. in. lb.	Chill $\frac{1}{32}$ in. units
R10BS2	0.5% Ba-Si	3195	0.378	603	2-3
R10CS2	0.42% Ca-Si	3205	0.364	583	7-12
R11BS2	0.96% Ba-Si	3161	0.366	578	2-4
R11CS2	0.8% Ca-Si	3360	0.394	662	7-11

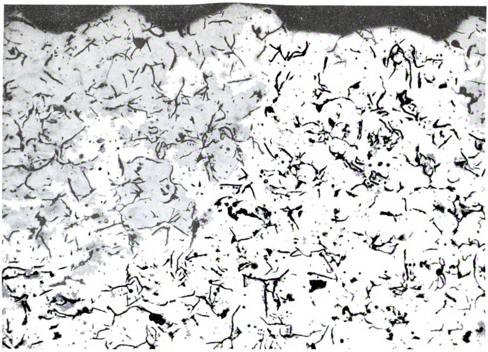


Figure 16. Microstructure of iron R11BS2, at the surface. Treated with 0.96% barium-silicon. Nital etch. 100X.

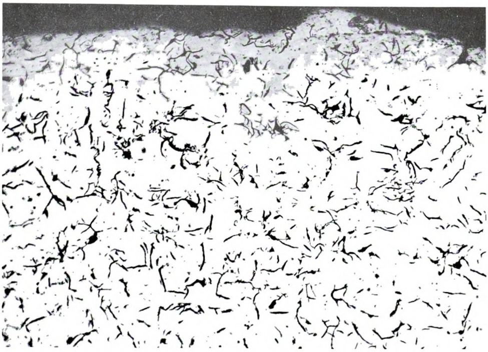


Figure 17. Microstructure of iron R11CS2, at the surface. Treated with 0.8% calcium-silicon. Nital etch. 100X.

The general procedure followed here was similar to that described in section 7. The results are shown in Tables 22 and 23. It is seen that Ba-Si as an inoculant was better than Fe-Si. The microstructures of the treated irons were similar to those of Figures 16 and 18. The silicon pick-up was comparable in both cases. The depth of chill was higher for the iron inoculated with barium free ferrosilicon and this again leads to the idea that a combination of barium, aluminum and calcium probably acts as a better chill reducer.

9. Comparison of Ferrosilicon and Inoculoy

Inoculoy is an inoculant containing barium and has been put on the market by the Vanadium Corporation of America. The analysis of the inoculant as supplied by the manufacturer was: 61.36 Si; 10.06 Mn; 5.26 Ba; 2.24 Ca and 1.24 Al.

One experiment was carried out using the ferrosilicon used in the experiments described in the last section. The results obtained are shown in Tables 24 and 25.

It is seen from the results shown in Tables 24 and 25 that the two inoculants are almost identical. The graphite distribution of the surface of the cross-section of the transverse test bar was slightly abnormal in both cases. These microstructures are shown in Figures 18 and 19. In both cases the graphite distribution was normal in the interior.

The iron inoculated with Inoculoy showed a lower chill depth than the iron inoculated with Fe-Si. McClure *et al.* (2) used silico-manganese free of calcium and aluminum and showed that inoculation with Si-Mn did not improve the chilling tendency. Hence the low chill depth of an iron inoculated with Inoculoy cannot be attributed to the presence of manganese in the Inoculoy. It may, therefore, be said

Table 22. Chemical Analysis of Irons Inoculated with Barium-silicon and Ferrosilicon

Iron	Addition	Percent C	Si	Mn	P	S
R10BS1	0.5% Ba-Si	2.92	2.24	0.93	0.169	0.058
R10FS1	0.34% Fe-Si	2.90	2.27	0.97	0.170	0.065
R11BS1	0.96% Ba-Si	2.92	2.24	0.85	0.155	0.052
R11FS1	0.65% Fe-Si	2.90	2.20			0.062

Table 23. Properties of Irons Inoculated with Barium-silicon and Ferrosilicon

Iron	Addition	Trans. load lb.	Deflec. in.	Resil. in. lb.	Chill $\frac{1}{32}$ in. units.
R10BS1	0.5% Ba-Si	3197	0.370	591	2-3
R10FS1	0.34% Fe-Si	3080	0.347	534	7-11
R11BS1	0.96% Ba-Si	3240	0.355	575	3-3
R11FS1	0.65% Fe-Si	2974	0.330	491	8-12

Table 24. Chemical Analysis of Irons Inoculated with Ferrosilicon and Inoculoy

Iron	Addition	Percent C	 Si	 Mn	 P	 S
R7FS2	0.4% Fe-Si	2.82	2.46	0.87	0.165	0.057
R7I2	0.4% Inoculoy	2.85	2.43			

Table 25. Properties of Irons Inoculated with Ferrosilicon and Inoculoy

Iron	Addition	Trans. load lb.	Deflec. in.	Resil. in. lb.	Chill $\frac{1}{32}$ in. units.
R7FS2	0.4% Fe-Si	3154	0.327	516	5-8
R7I2	0.4% Inoculoy	3184	0.330	525	2-4

Figure 18. Microstructure of iron R7FS2, at the surface. Treated with 0.4% ferrosilicon. Nital etch. 100X.

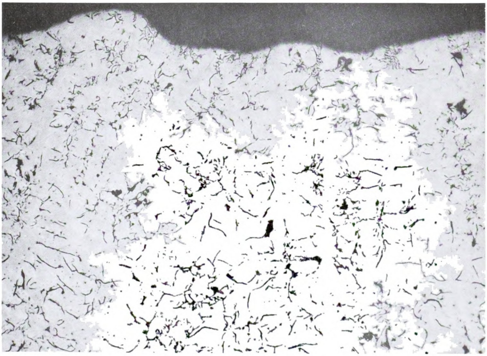


Figure 19. Microstructure of iron R7I2, at the surface. Treated with 0.4% Inoculoy. Nital etch. 100X.

that the improved chilling tendency of this iron must be due to the combined presence of barium, aluminum and calcium in the Inoculoy.

VI. DISCUSSION

It is seen from the results reported in the last chapter that the changes in graphite distribution and properties obtained by inoculating a high strength hypoeutectic gray cast iron with calcium, strontium and barium were different in each case. Among the three elements, calcium was found to be the most effective whereas barium had no effect at all. Strontium was seen to be only partially effective.

Let us try to examine why these three elements produced dissimilar effects. It was stated earlier that an effective inoculant increases the number of eutectic cells. The inoculant, either by direct or indirect action, is expected to provide the nuclei for the large number of eutectic cells. McGrady and others (3) showed that aluminum additions increase the number of eutectic cells but do not bring about any change in the graphite distribution. Hence it may be said that the nucleation of a large number of eutectic cells alone is not sufficient and additional factors are involved in the mechanism of inoculation.

Washchenko and Rudoy (38) state that the shape and distribution of graphite are connected with the influence of the additions on the changes in the surface tension in cast iron. These authors observed that carbon reduces the surface tension in hypoeutectic cast iron and increases it in hypereutectic cast iron. The minimum surface tension coincides with the eutectic composition of the cast iron. Silicon has a low surface activity in cast iron and it lowers the surface tension by only a small amount. In accordance with the intensity of their influence on the surface tension of cast iron, the major elements are arranged in the following order: Si, C, P, Mn and S.

Both the nucleation and the surface phenomena may, therefore, be important to explain the action by which inoculants work. For the sake of continuity, the general discussion will be restricted to calcium only. The major differences with strontium and barium will be pointed out wherever necessary.

The proposed nuclei for eutectic solidification include graphite, carbides, sulfides, oxides, nitrides or the interface between the liquid and the primary austenite dendrites. Semenchenko (39) has stated that in any phase solidifying from the liquid state, the probability of formation of a nucleus containing surface active impurities will be less than the probability of the formation of a "pure nucleus." Ivanov (25) carried out certain experiments, the complete details of which are not given, and concluded that liquid cast iron contains graphite formations averaging 10 microns in size.

The free energies of formation of sulfides, oxides, nitrides and carbides are shown in Table 26. From the data in this table, it is clear that the affinity of calcium for oxygen, sulfur and nitrogen is higher than that for carbon. The amounts of oxygen, nitrogen and sulfur present in cast iron are very small as compared with the amount of carbon. Decarburization probably results because of mass action. All the compounds listed in Table 26 are believed to be either insoluble or having very low solubility in cast iron.

Oxygen is believed to increase the chilling tendency of cast iron. It was stated earlier in this report that sulfur and nitrogen act as carbide stabilizers in cast iron. It appears that calcium, by combining with oxygen, sulfur and nitrogen, should favor the solidification of the graphite-austenite eutectic. The change in graphite distribution probably depends upon the nucleation mechanism and the surface energy changes achieved by the formation of oxides, sulfides and nitrides.

Table 26.* Free Energies of Formation of Various Compounds

			ΔF_T = free energy of formation kcal/gm. atom of S, N, O or C	
	Compound	Melting Point °K	ΔF_{298}°K	ΔF_{1400}°K
Sulfides	CaS		-245.27	-194.00
	SrS	>2270	-237.00	
	BaS	>2470	-222.00	
Oxides	CaO	2873	-144.35	-117.25
	SrO	2688	-133.85	-108.20
	BaO	2196	-126.30	-101.50
Nitrides	Ca_3N_2	1468	-93.20	-40.00
	Sr_3N_2	1300	-77.00	
	Ba_3N_2		-73.40	
Carbides	CaC_2	2573	-16.20	-25.70
	SrC_2	>2200		
	BaC_2	>2050		

*Compiled from (35, 40 and 41)

Keverian, Taylor and Wulff (32) stated that nucleation is relatively easy in an iron with low graphite-melt interfacial energy and only a slight degree of undercooling is required before enough energy is available to create a new interface. In the case of high graphite-melt interfacial energy there is a definite barrier to nucleation and a greater degree of undercooling is necessary before enough energy can be made available to create the interface. These authors suggested that a degree of undercooling intermediate between that necessary for the formation of flake graphite and spherulitic graphite occurs for the formation of Type D graphite.

The last statement above does not appear correct if we consider that Type D graphite structure should have maximum surface area of graphite because of its more frequently branched finer structure. Spheroidal form of graphite has the minimum surface area because of its shape. Type A graphite structure should have the surface area which is intermediate between that of the spheroidal and the Type D forms.

From the considerations of surface area, it appears that the graphite-melt interfacial energy should be the lowest for Type D graphite structure. This does not agree with the general observation that the graphite-austenite eutectic in Type A graphite iron begins solidifying earlier than the graphite-austenite eutectic in Type D graphite iron.

Washchenko and Rudoy (38) believe that the tendency of cast iron towards undercooling is connected with the stability of the liquid phase and depends on the presence of those elements which change the carbon adsorption. The increased undercooling tendency of the spheroidal graphite cast iron cannot be considered to be the cause for the spheroidization of the graphite.

It has been proposed that calcium carbide acts as a nucleating agent for graphite in the graphite-austenite eutectic solidification (2). A theoretical investigation that can indicate the possibility of calcium carbide acting as a nucleating agent does not appear in the literature. It was, therefore, decided to check if calcium carbide can be expected to nucleate graphite.

To start with, it is essential to know about the structure of graphite. The carbon atom possesses four valence electrons ($2s^2 2p^2$) and it acquires the stable neon structure with the completed second quantum group of eight electrons by forming four electron pair bonds. These four bonds are disposed tetrahedrally. The octet can also be completed by the following ways:

i) one double and two single bonds: $>C=$
ii) two double bonds: $=C=$
iii) one triple and one single bond: $-C\equiv$

The bond lengths for the three types are given in Table 27.

Table 27.* Bond Lengths in Carbon

Bond		Bond length (Å)
Single:	C—C	1.54
Double:	C=C	1.34
Triple:	C≡C	1.20

*From Wells (42)

In graphite, the atoms are arranged in hexagonal array in layers so that the third layer is vertically over the first. The distance between the adjacent layers is 3.35 Å. The weak forces between the

layers are of a van der Waals nature. The bonding is two single and one double type. The distance between the closest neighbors in a layer is 1.42 Å, obtained from the bond order $1\frac{1}{3}$. In general, the a spacing or the distance between atoms in the hexagonal layers is much more constant than the c spacing or twice the distance between the adjacent layers (26, 42).

Wells (42) has discussed the structure of various carbides. Carbides are generally divided into four main groups:

1) the salt-like carbides of metals of the earlier Periodic groups.
2) the carbides of the 4f and 5f elements.
3) the interstitial carbides of transition metals of the IV, V and VIth groups.
4) a less well defined group of carbides comprising metals of groups VII and VIII and also some of those of elements of group VI.

The first group includes the following carbides: Be_2C, Al_4C_3, CaC_2, SrC_2 and BaC_2. These are again divided into two subgroups. The carbides in which the C_2^{2-} ions may be distinguished are CaC_2, SrC_2 and BaC_2 and these form one subgroup. All the three carbides have a similar structure of the CaC_2 type. They are decomposed by water and since the negative ions are unstable, acetylene is evolved.

The room temperature form of the CaC_2 structure is face centred tetragonal. The structure is sodium chloride type but it is tetragonal because of the parallel alignment of the C_2 groups. This structure is shown in Figure 21.

Bredig (43) proved that the three carbides CaC_2, SrC_2 and BaC_2 are face-centred cubic at high temperatures. The calcium ions occupy positions entirely analogous to those of the sodium ions in rock salt

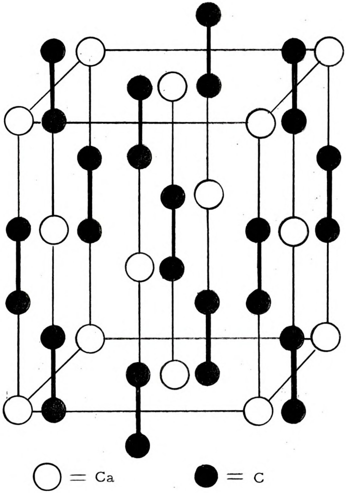


Figure 20. The Calcium Carbide Structure.
[From Hume-Rothery (26)]

while the centres of the C_2 groups are assumed to occupy the places of the chloride ions of NaCl. Table 28 summarizes the data on the cubic forms of the three carbides.

Table 28.* Cubic Forms of Calcium, Strontium and Barium Carbides

Carbide	High temp. form	Temp. above which stable (°C)	a_0 (Å)
CaC_2	F.C.C.	> 450	5.92
SrC_2	F.C.C.	> 370	6.24
BaC_2	F.C.C.	> 150	6.54

*From Bredig (43) and Hansen (44)

The graphite-austenite eutectic in cast iron starts solidifying at a temperature of about 1150°C and if CaC_2 does act as a nucleating agent, its cubic form is obviously important. It is believed that the C_2 anions are not aligned in any specific direction but they rotate freely all the time, thereby acquiring spherical symmetry (43).

The centers of all C_2 pairs in the CaC_2 structure lie on (111) type planes. If the spherical symmetry of carbon atoms in the C_2 pairs does exist, then at a particular instant it is likely that the carbon atoms of the C_2 pairs are on the (111) plane. These carbon atoms of the C_2 pairs may combine with carbon atoms from the liquid and nucleate graphite. An approximate hexagonal formation on the (111) plane is shown in Figure 21.

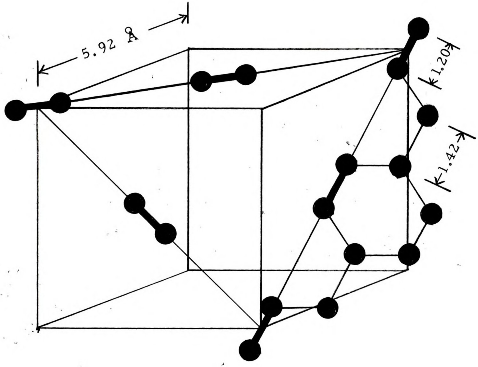


Figure 21. Possible formation of a ring like structure of carbon atoms on a (111) plane in CaC_2.

The CaC_2 structure involves a triple bond between the two carbon atoms. The fourth valence electron from each of the two carbon atoms is used up in bonding with the calcium atom (42). It, therefore, appears that a carbon atom must break its bond with the calcium before it can combine with another carbon atom from the liquid. This may not happen unless some structural changes occur in graphite as bonded to calcium at temperatures above 1150°C.

The distance between the carbon atoms in the C_2 pairs in CaC_2 is 1.20 Å whereas the distance between two carbon atoms in graphite is 1.42 Å . From Figure 21, it is seen that if the distance between two C_2 pairs on (111) plane increases, the possibility of the formation

of the ring like structure of carbon atoms will decrease. The information on lattice parameters, shown in Table 28, suggests that the distance between the ends of two C_2 pairs in SrC_2 and BaC_2 should be greater than it is in CaC_2. If the nucleation of graphite takes place in the manner proposed, then the increasing deviation from the possibility of the hexagonal ring formation in SrC_2 and BaC_2 might explain the partial effectiveness of strontium and the ineffectiveness of barium additions.

Richards and Rostoker (45) observed that the size of the graphite flakes in an iron casting is increased by vibrating it during solidification. The interface between the liquid and the primary austenite dendrites is one of the nuclei proposed for the solidification of the graphite austenite eutectic. Vibration of the casting will lead to smaller primary dendrites. The increased surface area of the small dendrites should favor an increase in the rate of nucleation of the eutectic (46).

In the absence of any external nuclei the atoms of the solidifying phase, prior to solidification, are linked together in a similar manner to that in the solid. Vibration might favor such linkages and increase the rate of eutectic nucleation. Hence an interface between the primary austenite dendrites and the liquid may not be important in nucleating eutectic solidification. Another argument that may be advanced against the possibility of eutectic nucleation at the interface is the observation made in this work and by McGrady (27) that inoculation did not make any significant change in the size and distribution of the primary dendrites.

In all experiments of this research, the inoculants were added when the iron was at a temperature of about 2850°F. This temperature is lower than the boiling point of barium whereas both calcium and

strontium have their boiling points below 2850°F as seen from Table 29. However, it is very doubtful that the ineffectivensss of barium as an inoculant resulted from this factor.

Table 29.* Melting and Boiling Points of Calcium, Strontium, and Barium

	Melting Point		Boiling Point	
	°C	°F	°C	°F
Calcium	838	1540	1440	2625
Strontium	768	1414	1380	2620
Barium	714	1317	1640	2980

*From Metals Handbook (47)

Aluminum has a very high boiling point (4220°F) but it was observed to be effective in increasing the number of eutectic cells (3). In aluminum carbide, Al_4C_3, each carbon atoms is surrounded by aluminum atoms and the shortest distance between two carbon atoms is 3.16 Å (42). The nucleation of graphite by the carbon atoms in Al_4C_3 appears improbable. It is possible that the homogeneous nucleation centers increase by some indirect effect caused by the additions of aluminum.

The formation of barium carbide as a result of barium additions was discussed earlier. The atomic diameter of barium is large in comparison to that of calcium or strontium. The lattice parameter of BaC_2 as seen from Table 28 is large and therefore the C_2 pairs in BaC_2 are widely spaced and probably do not stand any chance to nucleate eutectic solidification.

It was stated earlier than an analysis of the treated iron to determine the calcium and barium indicated the residual content of these elements to be below 0.01%. Calcium carbide resulting from the addition of calcium rises to the top surface and it is probable that a small amount of calcium carbide remains in colloidal dispersion in the liquid metal at the time of pouring. This small amount in colloidal dispersion can be expected to nucleate eutectic solidification. If the metal is held in the ladle for a long time after the addition of calcium, the dispersed calcium carbide might also rise to the top surface. The disappearance of the effect of inoculation can then be expected.

It has been observed that larger additions of calcium to an iron of carbon equivalence higher than that of the high strength iron composition used in this research result in the formation of nodular graphite (48). The higher carbon equivalence might change the graphite-melt interfacial energy as suggested by Washchenko and Rudoy (38) and the net result, after inoculation with calcium, may be the formation of nodules but a discussion of this matter is beyond the scope of the present investigation.

Once nucleated, the growth rate of the eutectic cells is important. In a fast growing eutectic cell, a corresponding increase in the frequency of branching of the graphite can be expected to give a finer appearance of the Type D structure in the microsection. On the other hand, a slow growth of an eutectic cell means infrequent branching of the graphite giving an appearance of large flakes of Type A in the microsection.

In the presence of a small number of eutectic cells, each cell will grow at a fast rate. A slow growth of each eutectic cell will result if the number of eutectic cells is large. McGrady and others (3) have shown that an increase in the number of eutectic cells does not

necessarily change the graphite distribution. It was suggested earlier in this discussion that the graphite-melt interfacial energy can be expected to be lower in Type D graphite distribution than in Type A graphite distribution. As a consequence, it appears that a slow growth rate of an eutectic cell might result when the graphite-melt interfacial energy increases.

An adsorption of the inoculant, or of the compounds formed after adding the inoculant to molten iron, on the graphite-melt interface would lead to a decrease in the interfacial energy. An increase in the interfacial energy may take place if some of the existing elements present in normal cast iron are eliminated as a result of inoculation. From Table 26 it may be seen that such elements could be oxygen, sulfur and nitrogen. These elements, by combining with the inoculant, may not concentrate on the graphite melt interface and the net result might be an increase in the graphite-melt interfacial energy.

Keverian, Taylor and Wulff (32) explained the formation of spheroidal graphite by stating that the spheroidizing additions combine with the surface active elements to form stable compounds and make them ineffective in lowering the interfacial energy. However, these authors considered the undercooling behavior of an iron with Type D graphite and suggested that the graphite-liquid interfacial energy is the lowest in an iron with Type A graphite distribution.

The reasons for the difference in the inoculating abilities of calcium, strontium and barium may be summarized as:

1) Calcium: The nucleation of graphite by carbon atoms in the calcium carbide can be expected to take place as proposed and cause an enormous increase in the number of eutectic cells. The large number of eutectic cells decreases the growth rate of each individual eutectic cell. The change in graphite-melt interfacial energy may also be a contributing factor in decreasing the growth rate of the

eutectic cells. The slow growth rate leads to the formation of Type A graphite distribution and this, in turn, leads to an improvement in properties.

2) Strontium: The nucleation of graphite by carbon atoms in the strontium carbide may be a little difficult because the C_2 pairs in SrC_2 are spaced at a greater distance from each other than they are spaced in CaC_2. In agreement with this, the increase in the number of eutectic cells obtained by strontium additions was relatively small. This small number of eutectic cells and the change in graphite-melt interfacial energy may reduce the growth rate of the eutectic cells only to a small extent. The partial effectiveness of strontium additions can thus be explained.

3) Barium: It was seen that pure barium additions are not effective in increasing the number of eutectic cells and in changing the graphite distribution. The C_2 pairs in BaC_2 are more widely spaced than they are in CaC_2 or SrC_2. The nucleation of graphite by carbon atoms in BaC_2 might be extremely difficult. The graphite-melt interfacial energy change alone may not influence the growth rate of the eutectic cells. This explains the ineffectiveness of pure barium additions.

It was observed that an iron inoculated with an alloy containing barium gave the lowest chill depth. Failing to obtain any improvement in the chilling tendency by the additions of pure barium, the low chill depth was attributed to the combined presence of barium, calcium and aluminum.

It may be possible that though the addition of barium is not effective in increasing the number of eutectic cells, it might help in reducing the growth rate of the eutectic cells nucleated by the calcium present in the Ba-Si or the Inoculoy.

The amount of calcium present in the Ba-Si and Inoculoy is small and hence a doubt may be expressed if such a small amount can nucleate the large number of eutectic cells. However, it can be said that when calcium is added in the form of a silicon-base alloy, the CaC_2 formed probably stands a better chance of remaining in the liquid.

The low chill depths obtained from irons inoculated with the complex alloys Ba-Si and Inoculoy were attributed to the combined presence of barium, calcium and aluminum in these inoculants. The partial effectiveness of strontium suggests that a combination of strontium with calcium and aluminum may be better than the combination of barium with calcium and aluminum.

VII. SUMMARY AND CONCLUSIONS

The process of inoculation has been in use for a considerable length of time but no satisfactory explanation of the mechanism by which an inoculant works is available. The recent discovery suggesting the importance of calcium in the process of inoculation of gray iron stimulated interest in further studying the inoculation phenomena. This research was based on the use of calcium, strontium and barium as inoculants in the production of high strength hypoeutectic gray cast iron. It was believed that the results might lead to a better understanding of the mechanism by which the inoculants change the graphite distribution in cast iron.

The importance of theoretical studies is great,nevertheless it must be emphasized that the main discoveries in the field of cast iron are made by continuous improvements in industrial production. Gray iron is one of the most complex alloys and the large number of variables involved make experiments difficult. In the present investigation, the melting and casting procedure employed was more or less similar to commercial practice.

It appears that an inoculant will improve the graphite distribution and properties if--(1) it can help in the nucleation of a large number of eutectic cells, and (2) control the growth rate of these eutectic cells. A slow growth rate of the eutectic cells is expected to promote the desirable graphite distribution of the Type A.

Specific observations and conclusions from this investigation are:

(1) Calcium is the most effective inoculant among the three elements calcium, strontium and barium employed as inoculants.

(2) Additions of all the three elements caused decarburization and desulfurization of the melt.

(3) The element barium when added alone was not effective as an inoculating addition.

(4) The addition of strontium produced an increase in the deflection and reduced the chill depth but the breaking load did not change significantly unless the additions were high in quantity.

(5) As a result of decarburization, carbides were produced in all the three cases.

(6) The carbide structures, because of the possibility of obtaining a concentration of carbon atoms on a (111) type plane, may be helpful in nucleating eutectic solidification of graphite. However, a knowledge of the structural changes that may occur in the vicinity of 1150°C is essential to accept the possibility of nucleation of eutectic cells by the carbides.

(7) The difference in the inoculating abilities of the three elements may be related to the spacing of the C_2 pairs in the respective carbide structures.

(8) The inoculating alloys containing barium were found to be better chill reducers than either calcium or calcium-silicon.

(9) The low chill depth of irons inoculated with alloys containing barium was attributed to the combined presence of barium, aluminum and calcium in the inoculating alloys containing barium.

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APPENDIX

ADDITIONAL COMMENTS ON THE NUCLEATION OF GRAPHITE BY CARBON ATOMS IN CaC_2

After the preliminary typing work of this thesis was complete, publication of a paper by Lux[1] made it necessary to attach an appendix. This paper explained how carbon atoms in calcium carbide could act as heterogeneous nuclei for the growth of graphite. The major idea was quite similar to the one already suggested in this thesis.

It is stated that there is no question of a triple bond between the carbon atoms in CaC_2 as could perhaps be concluded from the formation of acetylene. The C_2 molecules become ions having ten valence electrons with a stable electron configuration $(:C\vdots\vdots C:)^{-}$ and the C-C distance in CaC_2 can be assumed to be approximately the distance of closest approach found in graphite.

A small percentage of the carbon atoms in an iron-carbon melt is considered to be present as C_2 molecules. On this basis it is suggested that the nucleation of graphite can occur by--(1) C_2 molecules originating from the melt or (2) by diffusion of C_2^{2-} anions out of the CaC_2 lattice which is believed to be unstable.

To support the idea of nucleation of graphite by carbon atoms in CaC_2, it is pointed out that the shortest distance between the (111) planes occupied by carbon ions in CaC_2 is $a_o/\sqrt{3} = 5.92/\sqrt{3} = 3.41$ Å whereas the distance between the adjacent layers in graphite is 3.36 Å.

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[1] B. Lux, Modern Castings, v. 45, May 1964, p. 222.

It is, therefore, suggested that layers of graphite can grow from parallel (111) planes of the CaC_2.

Various hypothetical ideas are discussed to explain the inoculation mechanism. The statements to which an objection may be raised are discussed below.

(1) From the thermodynamic data it is seen that calcium oxide is the most stable compound while the sulfide is also more stable than the carbide. Presence of other elements in the inoculant, having high affinity for oxygen should favor the formation of CaC_2.

The writer of this thesis considers this statement ambiguous. It is known that no other element in gray iron has as high a tendency as calcium to form oxide. It, therefore, appears improbable that other elements having affinity for oxygen could favor the formation of CaC_2. It may be said that the formation of CaO is unavoidable and takes place immediately after adding the inoculant. Other compounds can form by reacting with the excess calcium. It is possible that the activation energy is lower for the carbide reaction than the sulfide or nitride reactions at the liquid iron temperature.

(2) Presence of silicon in the inoculant is expected to form hypereutectic silicon rich zones in the melt and the tendency for carbon precipitation in these zones will favor CaC_2 formation.

This statement also appears incorrect. If the addition of silicon could cause precipitation of carbon in the hypereutectic zones, why is the addition of pure silicon ineffective in increasing the number of eutectic cells? As stated earlier in this thesis, it may be said that when calcium is added in the form of a silicon base alloy, the probability of getting it into the liquid iron is increased and the number of CaC_2 particles that may act as nuclei is also increased.

(3) It is suggested that strontium and barium carbides can also facilitate the heterogeneous nucleation of graphite during the solidification of the eutectic.

It was discussed earlier that the structures of the carbides of calcium, strontium and barium are of the same type but the lattice parameters are different. The addition of pure barium was found to be ineffective and this was related to the wide spacing of the C_2 pairs in the barium carbide.