EFFECT OF LADLE ADDITIONS OF SOME ALLOYS AND ACTIVE METALS ON THE PROPERTIES AND MICROSTRUCTURE OF GRAY CAST IRON

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EFFECT OF LADLE ADDITIONS OF SOME ALLOYS AND ACTIVE METALS ON THE PROPERTIES AND MICROSTRUCTURE OF GRAY CAST IRON

BY

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I. Introduction

Graphite Distribution in Cast Iron.

The properties of gray cast iron are determined by: 1) the character of the microstructural matrix and 2) the amount and manner of distribution of the graphite flakes in the matrix.

The matrix of an unalloyed high strength gray iron of properly balanced silicon and carbon contents may approach one hundred percent pearlite. Under certain conditions undesireable ferrite appears in the microstructure. This ferrite is generally associated with an unfavorable graphite distribution, see Fig 16. The combination of ferrite and graphite distribution of the type illustrated is detrimental to all of the properties of cast iron.

Fig 1 is the American Foundrymen's Society- American Society for Testing Materials Chart for graphite distribution in gray iron. This chart illustrates the various possible graphite distributions in cast iron of a wide range of carbon contents. High strength hypoeutectic iron (carbon range 2.60-3.10%) may exhibit types A, B, D or E of graphite distribution.

Type A with a random distribution of the graphite is the preferred arrangement. The pattern arrangement of type D is undersireable because of the resultant planes of weakness in the iron. There is reason to believe that types B and E are less serious manifestations of the conditions causing the type D arrangement. Type D graphite is vari-

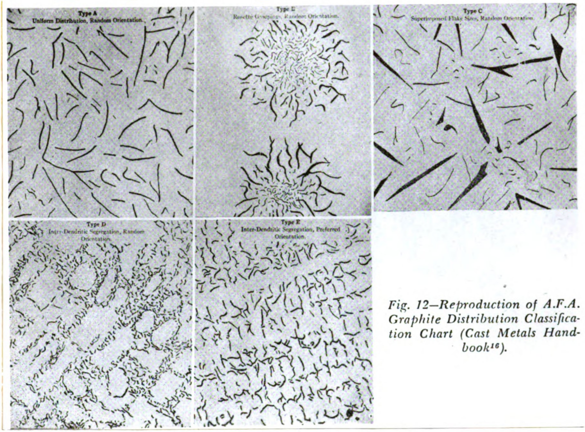

Fig 1. American Foundrymen's Society Chart for Graphite Distribution in Cast Iron.

ously referred to in the literature as: abnormal, lacy, dendritic, interdendritic, undercooled, reticular, eutectiform, refined, and modified. Type B graphite distribution is generally described as the rosette or whorl type. In this report the undesireable kinds of graphite distribution will be referred to as "abnormal" with the understanding that abnormal structures contain types B, D and E, generally with a preponderance of D. This terminology is justified by the fact that most commerical irons of carbon of less than 3.10% may contain varying amounts of the four graphite types in the same casting. The principle concern of the metallurgist producing high strength iron is to obtain a maximum of normal or A graphite.

There are many factors which have an influence on the graphite distribution in cast iron. As an introduction to this paper it will be necessary to review the literature concerning these factors, and also the subject of the solidification of gray iron. These matters have been discussed extensively in the literature and are generally understood by metallurgists concerned with the production of cast iron. However, the literature is so voluminous and in many cases so conflicting that it appears advisable to review these subjects as briefly as possible for the convenience of the reader and for the purpose of relating the data presented in this paper.

Solidification of Gray Cast Iron.

As a simplification, cast iron is regarded as a ternary alloy of Fe-C-Si, and is considered to solidify and transform in accordance with the diagram of Fig 2 when the silicon content is in the vicinity of 2%, as it is in the case of the majority of commercially produced irons. Fig 2 represents a vertical section through the ternary solid at 2% silicon. Two forms of this diagram can be recognized: the stable, and the metastable. In the metastable diagram the carbon rich phase is cementite, Fe_3C, labeled in Fig 2 "Ca". In the corresponding stable diagram carbon is present as graphite. It is understood that Fe_3C has a higher free energy than the equivalent Fe and C, and that the true equilibrium diagram is the stable diagram.

White cast iron solidifies and transforms in accordance with the metastable diagram. Whether or not gray cast iron solidifies in the stable or metastable manner was not determined prior to the publication of a paper by A Boyles[1] in 1937.

In the experiments described in this paper Boyles determined the manner of solidification of hypoeutectic irons by arresting transformation in small melts by quenching from temperatures between the liquidus and solidus. Photomicrographs from his paper are presented in Fig 3. These structures make clear the solidification of a hypoeutectic

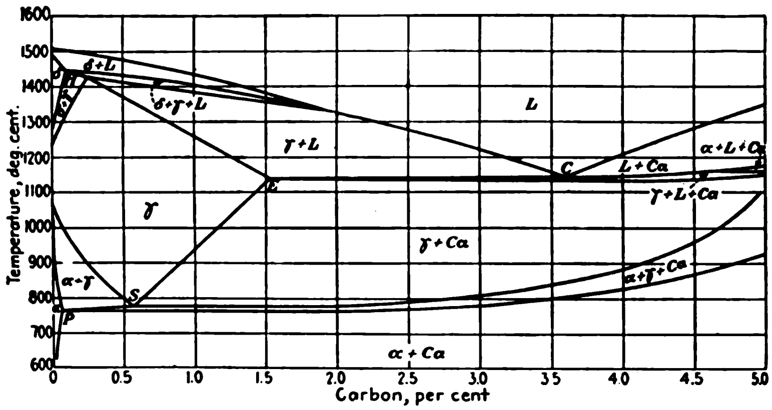

FIG. 4—IRON-CARBON DIAGRAM IN PRESENCE OF 2.00 PER CENT SILICON (GREINER, MARSH AND STOUGHTON).

Fig 2. Section through Iron-Carbon-Silicon Ternary Diagram at 2.00% Silicon.

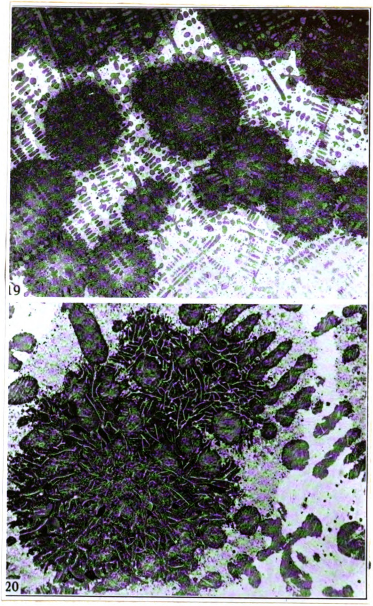

Fig 3. Microstructures Obtained by Quenching Partially Solidified Hypoeutectic Iron. Heat Tinted. Upper Picture x 20. Lower x 100. After Boyles.

iron. In the low magnification micrograph at the top it is apparent that the iron solidifies by the formation of primary dendrites of austenite, and that the eutectic solidifies in the remaining liquid (represented by the light etching background) from centers of crystallization to form spherical masses which upon completion of solidification constitute the "cells" of the cast iron microstructure. Examination of these growing cells at higher magnification (lower picture) reveals that the graphite flakes form during the growth of the cells, and while the iron is still partially liquid. It also appears that flake growth takes place at the liquid-cell interface, a manner of development which, by inhibiting sidewise growth, produces flakes rather than the thermodynamically more stable nodular or temper carbon shape of graphite. All graphite in the iron is seen to be located between the primary dendrites.

This mechanism suggested an attractive explanation for the variation in size and distribution of flakes-namely variations of in the relative rates of growth of the austenite and graphite. For example a high rate of austenite formation in the growing cell might produce small (type D) flakes by "pinching off" the developing flake, or a high availability of graphite for flake growth and a high nucleation rate at the interface might produce the same results.

This conception was modified for certain irons by the publication of a paper by J. T. Eash[2] in which evidence was presented in the form of quenching experiments to show that irons highly abnormal in character solidified in the metastable manner and that graphite of the D type formed in the solid iron by the decomposition of cementite at a temperature close to but below the solidus.

Papers confirming the findings of Eash have been published by Morrogh and Williams[3] and more recently by Owens and Street.[4] It is believed by these investigators that the metastable solidification leading to the formation of type D graphite is associated with an "undercooling" of the liquid iron. As a consequence type D graphite is frequently referred to as "undercooled graphite".

Although the possibility of the solidification of type D irons in the metastable manner by undercooling cannot be disputed, there are certain discrepencies in this theory which require explanation and which will be discussed later in this report in connection with other data.

Factors Influencing Graphite Distribution.

The following factors may be listed as having an important influence on graphite distribution:

1. Carbon content of the iron
2. Superheating temperature
3. Holding time at temperature
4. Method of melting
5. Pouring temperature

6. Sulphur and manganese contents

7. Gas content - hydrogen, oxygen, nitrogen

8. Cooling rate in the mold and extent of undercooling

9. Degree of inoculation

It is generally understood that high strength irons with carbons less than 3.10% are much more susceptible to the development of type D graphite than are the higher carbon irons.

There is evidence to support the conclusion that high superheating temperatures and long holding time at temperature in the furnace promote the formation of abnormal structures in some irons. Sefing and Searls[5], Schneble and Chipman[6] and Krynitsky and Saegar[7] have published papers leading to this conclusion.

The opinion is frequently expressed that electric furnace irons are more susceptible to D graphite formation than are cupola irons. Direct experimental evidence to support this contention is not to be found in the literature.

Timmons and Crosby[8] have investigated the effect of pouring temperature on the properties of high strength irons and have concluded that pouring temperatures below 2650^{0} have an adverse effect on the properties of irons of less than 3.00%C and that low pouring temperatures "tend toward the dendritic, whorl, and eutectiform types of distribution".

Boyles[1,9] has investigated the effect of sulphur and manganese additions to iron-carbon-silicon alloys very low in their sulphur and manganese contents. It was found that in the absence of appreciable S that the iron solidified in a highly abnormal condition with pronounced type D graphite and a matrix almost entirely ferritic. An addition of .018% of S or more altered the structure to one containing a large amount of type A graphite and pearlite. Boyles explained this effect as an influence on carbide stability resulting in variations in the rate of nucleation and availability of carbon during the simultaneous solidification of the eutectic cell and the graphite flakes as postulated in the above discussion of solidification. Manganese was found to have an important but variable effect on graphite distribution dependant on conditions.

The influence of gas content on the microstructure of iron has been the subject of numerous investigations and is a highly controversial matter. The subject is rendered difficult for research by the problem of analytical determination of the gaseous elements. The situation is particularly difficult in the case of oxygen because of the reactions occuring between the melt and the oxides of the furnace and ladle linings.

To review the literature dealing with the subject of gases in ferrous alloys and of oxygen in particular is beyond the scope of this paper. The bibliography of the British Cast Iron Research Association lists more than a thousand references. However, a few of the conclusions pertinent to this paper will be cited from the recent literature.

Boyles[1,9] has determined the influence of hydrogen by melting in vacuo and in atmospheres of varying H content. He concluded that a certain H content is essential to the formation of a normal structure in cast iron, and that excessive amounts tend to promote unfavorable distributions. The influence of H was attributed to an effect on the rate of graphitization.

The subject of oxygen in cast iron has been treated recently in articles by Heine,[10,11] and Bach,[12] and Loria and Lownie.[13] From a study of these and other articles to be discussed later the following conclusions may be advanced that are pertinent to this paper:

1) Above approximately 2600°F the O content of cast iron is governed by the carbon content; below this temperature by the Si and Mn contents.[10]

2) The O content of cast iron is small being approximately .0025% in irons of about 2% silicon.[13]

3) Although the O content is small it is significant, and changes of a temporary nature in the melt can be effected by the addition of active metals such as aluminum."

4) Thermodynamic equilibria are inapplicable because cast iron cannot be in equilibrium with iron oxide or silicate slags except at high pressures.

Foundrymen have long believed that iron can be "oxidized" and that oxygen increases chilling tendency. Experiments described in the literature both confirm and oppose this conception. This matter will be discussed at greater length later in the report.

Nitrogen in cast iron has been discussed by Dawson, Smith, and Bach.[14] It is concluded that N has a strong stabilizing effect on massive cementite and pearlite; that it affects the graphite flake size and shape, the flakes becoming shorter and thicker with increasing N content thus accomplishing an improvement in mechanical properties; and that aluminum additions reduce the effects of nitrogen presumably by the formation of a nitride.

The situation regarding gases in cast iron can be summarized by quoting Loria and Lownie.[13] "In spite of this voluminous literature interpretation of the data is still hazy even for steel......For cast iron the situation is even more nebulous."

D'Amico and Schneidewind[15] have determined the effect of cooling rate in the mold on solidification temperature (extent of undercooling) and on microstructure by casting irons in a metal mold preheated to various temperatures to produce various cooling rates. It was concluded that a variation of the solidification temperature approaching 100°F could be produced, and that as the degree of undercooling increased the degree of abnormality increased so that the severely undercooled irons exhibited type D graphite.

This conclusion is in accord with Eash[2] and others[3,4] regarding the effect of undercooling on graphite distribution.

It is evident from this discussion that the lower carbon high strength irons are extremely sensitive alloys, and that they are likely to develop type D graphite as the result of the operation of a considerable number of factors. In the ordinary course of events an electric furnace cast iron of less than 3% carbon will show abnormal structures particularly near the surface of the castings unless the iron is inoculated. The principle means available to the metallurgist for controlling the microstructure of these irons is the inoculation process. The purpose of the research described in this paper is to investigate the inoculation treatment.

The Inoculation of Gray Iron.

In the general sense in which the word is employed in physics, inoculation may be defined as the addition of substances to melts for the purpose of forming nuclei for crystallization.

Since it is by no means certain that the effect of inoculation of iron is explainable solely on the basis of nucleation effects, it has appeared advisable to use a broader definition for the term, and the following has appeared in the literature.

Inoculation is the process in which an addition is made late in the heat of molten cast iron or in the ladle for the purpose of improving the microstructure and properties of the iron to a degree not explainable on the basis of the change in composition.

As an illustration, an iron of 2.80% and 2.25% Si when melted to this composition with no late additions will have markedly different properties from an iron produced by withholding a portion of the silicon from the cold charge and making up the deficiency with an addition of silicon to the ladle in the form of one of several commercially produced and complex alloys of silicon.

The value of late treatments has been appreciated and the process employed for a good many years, coming into general use in the late nineteen-twenties. A number of alloys for inoculation, notably calcium silicide, have been patented. The use of calcium-silicide constitutes the basis for the well known Meehanite process, the basic patent for which has expired.

Table I, taken from an article by Lownie,[18] lists most of the alloys employed as inoculants.

Table I

Classification of Typical Ladle Inoculants

Group I		Group II
Ca-Metal	Si C	Cr-Si-Mn-Ti-Ca
Ca-Si	Si-Mn	Cr-Si-Mn-Zr
Ca-Si-Ti	Si-Mn-Zr	Mo-Si
Fe-Si	Si-Ti	Ni-Si
Graphite	Si-Zr	

Certain alloys containing relatively large amounts of aluminum should be add ed to this list, such as an important proprietary alloy of Si-Al-Ti-Fe. The above listings are of the principal constituents of the alloys, many of the alloys containing relatively small amounts of active metals particularly Al, Ti and Ca.

A significant thing about this list is that with two exceptions, all of the alloys contain silicon, and silicon is commonly regarded as the essential constituents of inoculants. Most of the theories advanced to explain inoculation effects are based on the action of silicon. A large proportion of the papers dealing with inoculation have employed ferro-silicon as the addition agent, and in many of these cases the composition of the alloy employed has not been specified, indicating that the essential constituent of the alloy is considered to be the silicon.

The literature concerning the use of these alloys is voluminous, particularly that dealing with the practical aspects of inoculation. In the bibliography presented here no attempt has been made for a complete presentation. The articles selected for discussion are either typical or are particularly pertinent to the experiments described in this report.

The writer has been unable to find any discussion of the use of calcium metal as an inoculant in the recent literature.

Many references have been made to the use of graphite as a ladle addition. The consensus of opinion is that the addition of graphite to the ladle decreases the chilling tendency and improves the properties somewhat. This conclusion is supported by very little experimental data. Dahlberg[16] has recommended the use of 8 mesh graphite as being most suited for ladle additions. The opinion is prevalent that the effects of graphite additions are soon lost by holding in the ladle, presumably by complete solution of dispersed graphite, and the suggestion is made that the addition be made immediately before pouring into the mold.

Ferro-silicon has been used in many of the investigations of inoculation reported in the literature. The alloy is generally employed in the grades ranging from

75% Si to 95% Si. Ferro-silicon is available in low and high active metal contents (Al and Ca in particular) but very few if any of the writers have specified the exact composition or even the grade employed, the feeling evidently being that silicon is the essential constituent in the inoculating alloy.

Crosby[17] has experimented with inoculation with increasing amounts of silicon, presumably in the form of ferro-silicon, as the alloy used is not specified. He reports an improvement in properties up to an addition of approximately 60% of the total silicon content of the iron (3.05% C, 2.38% Si). Beyond this proportion of silicon as a late addition the properties fell off rapidly. Graphical representation of the data from this paper summarizes the effect of inoculants on the mechanical properties in general and Fig. 4 presents this information. It is observed that the strength properties are improved while there is some reduction in hardness. The effect of inoculation on chill depth is not represented here, but it is generally understood that the use of inoculants effects a marked reduction in chilling tendency, and this reduction is one of the important justifications for ladle treatments. See Fig 14. In addition it will be understood by the reader that the improvement in properties resulting from increasing the inoculation results from a change in the microstructure from type D to E and finally to A.

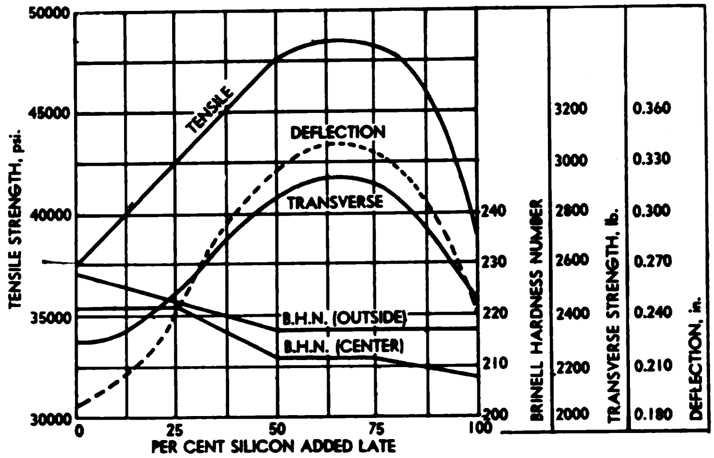

Fig. 17—Effect of Late Additions of Silicon on Physical Properties of Cast Irons Shown in Table 12.

Table 12

Effect of Late Silicon Additions to Cast Iron

Per Cent Silicon Added as Late Addition	0	25	50	75	100
Total Carbon, per cent......	3.07-3.09	3.10-3.11	3.04-3.04	3.04-3.06	3.08-3.10
Combined Carbon, per cent..	0.58	0.61	0.63	0.67	0.64
Graphitic Carbon, per cent..	2.50	2.50	2.41	2.38	2.45
Manganese, per cent......	0.88	0.90	0.89	0.89	0.88
Silicon, per cent, Original......	2.17	1.50	1.00	0.50	...
Late.........	...	0.58	1.15	1.57	2.13
Total.......	2.17	2.08	2.15	2.07	2.13
Transverse Strength, lb....	2266-2332	2420-2530	2840-2895	2990-2860	2442-2510
Deflection, in.....	0.187-0.194	0.233-0.250	0.314-0.335	0.350-0.320	0.245-0.250
Brinell Hardness.	228-228	223-223	217-217	217-217	217-217
Tensile Strength, psi...........	36,650-38,650	42,000-43,120	47,600-47,500	48,200-48,600	39,400-39,550

Fig 4. Effect of Late Silicon Additions. After Crosby.[17]

It should be mentioned in connection with chilling tendency that inoculants are of two types; the graphitising type, represented by Group I of Table I; and the "alloying element" containing type, typified by the members of Group II. Alloys of this second type may or may not be graphitizing depending on the nature of the elements contained. Most of the inoculating agents are designed to reduce chill or to permit the addition of carbide stabilizing elements such as chromium, either with a reduction in chilling tendency or with no increase in chilling tendency. The experiments reported in this paper are concerned only with agents of the first group.

Another aspect of inoculation that deserves emphasis is that the effect of all inoculants is temporary, and will disappear gradually with holding time in ladle or furnace. It is variously stated that the duration of the effect is from 5 to 30 minutes. It no doubt varies with the alloy used and with other circumstances. As mentioned above the effect of graphite additions is particularly short-lived.

In reviewing the literature on inoculation the reader is impressed by the lack of information dealing with the relative effectiveness of the various inoculating agents. This is surprising in view of the wide range of compositions of alloys recommended in the literature. Flinn and Reese[25] have determined the relative effectiveness of several inoculants containing silicon and found them to be roughly equivalent except for one alloy which was particularly low in silicon and gave inferior strength. They state that all successful inoculants contain silicon.

Theories of Inoculation

In view of the importance of inoculation in a practical way and of its theoretical implications concerning the fundamental nature of cast iron, many attempts have been made to develop a satisfactory explanation for the effectiveness of late additions. Lownie[18], Morrogh and Williams[3] and Crome[19] have presented summaries and discussions of the various theories. A brief review of some of the theories will be presented here.

Most of the ideas have been based on a nucleation mechanism as the name "inoculation" implies. It is argued that the molten iron requires a certain nucleation if the freezing is to occur in the stable manner producing type A graphite. This conception was strengthened by the publication of cooling curves indicating that irons with type D graphite solidify at a lower temperature than irons with normal structures. Curves showing this have been published by D'Amico and Schneidewind[15], Eash[2], and Boyles and Lorig[20] as well as by others. Fig 5. presents curves from the latter reference. The group of curves to the left represent an iron inoculated with calcium silicide; those to the right the same iron held at temperature for a period of time sufficient for the inoculation effect to disappear. The fact that the inoculated iron solidifies over a range of temperature, which is higher than that of the other iron, is interpreted by Eash,[2] Morrogh and Williams,[3] and by others as indicating that the iron which is not inoculated undercools, while the inoculated iron is prevented from undercooling by nuclei provided by the ladle treatment. These investigators have quenched the "undercooled" irons from just below the supposed solidification temperature and found that the iron is white. This is interpreted as evidence that the undercooled iron solidifies in the metastable manner as previously mentioned in this report. This conception is widely held at present.

Having accepted the nucleation hypothesis, it has been necessary to designate the nucleating substance. Two principle ideas have been advanced as to the nature of the nuclei 1) the silicate slime theory originally proposed by VonKeil[21] and coworkers, and 2) the graphite theory of Piwowarsky.[22,23]

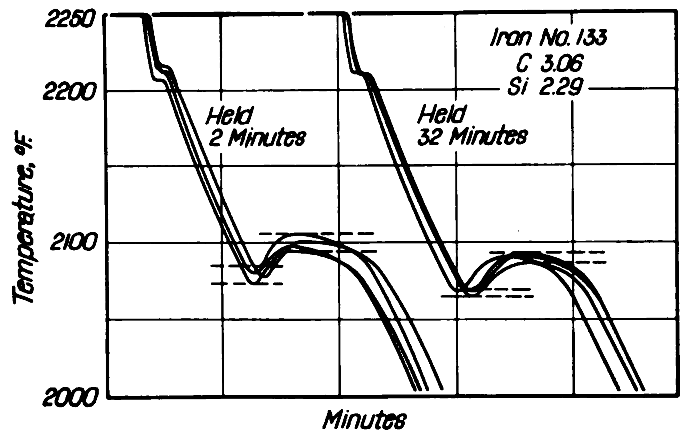

Fig. 48—Cooling Curves of Castings Made From Iron No. 133. Curves on left from castings poured 2 minutes after inoculation. Curves on right from castings poured 32 minutes after inoculation.

Fig 5. Time-Temperature Curves for Solidification of Hypoeutectic Cast Iron. After Boyles and Lorig.[20]

The silicate slime theory proposes that the addition of silicon alloys produces a colloidal dispersion of ferrous or other silicates which nucleate solidification and graphite formation thus promoting type A graphite. This theory is supported by experiments of Diepschlag[24] who conducted melts under aluminous and silicate slags and found that the former, supposedly by absorption of silicate nuclei, produced finer graphite. Experiments reported by Morrogh[3], and one reported in this paper fail to confirm this finding. Inability to demonstrate the presence of silicate inclusion in solid cast iron is another serious objection to this hypothesis.

One recognized tendency of abnormal iron is to show a pronounced type D structure at the surface of the casting or at any other point of rapid cooling in thin sections. The 1.2" diameter transverse bar will show type D at the surface and considerably type A graphite at the center with the poorest structure at the immediate surface if the iron is not completely inoculated and is hypoeutectic. (See Fig 11 and Fig 12). Since the mold wall is made up of silica and silicates and since its rough surface should be ideal for nucleation, the present writer feels that this is a powerful argument opposing both the silica slime theory, and the under-cooling conception of the formation of type D structures.

The graphite nucleus theory is supported by the argument that late graphite additions reduce chill and promote coarse graphite flakes. However, there is very little actual data in the literature to support this contention; in fact some of the experiments described in this report fail to confirm this point. It has been argued that the addition of silicon containing alloys promotes precipitation of graphite in highly localized regions of the melt by reducing solubility for carbon, and that this solid graphite nucleates the solidification of the melt and the formation of coarse random flakes. However, all available evidence indicates that the limit of solubility of the melt for graphite is not approached. This is shown by the fact that graphite additions dissolve rapidly in melts of low carbon irons. The persistance of the effects of inoculation by silicon alloys over periods of 30 minutes would indicate the unlikelihood of the local concentration mechanism.

It has been pointed out in the literature that any nucleation hypothesis for cast iron must include three distinct nucleation reactions 1) the nucleation of primary dendrites 2) nucleation of eutectic cells, and 3) nucleation of the graphite flakes. Anyone or all of these can conceivably influence graphite distribution and any complete nucleation theory should involve all three processes.

It is the opinion of the writer that too little attention is given to the previously mentioned mechanism of formation proposed by Boyles[9] who has argued that small and large flakes can be formed as a result of variations in the relative rates of formation of austenite and graphite. This matter is deemed of sufficient importance to justify an extended quotation from this paper: "On the other hand, the availability of carbon may be limited by a slow rate of dissociation. The growth of the flakes then lags behind the advancing front of solidification. The flakes are pinched off, so to speak, by the freezing of the metal and as a result small flakes are formed. Such cases are approaching graphitization in the solid state and the fine graphite so produced differs in appearance from that formed by rapid graphitization. Between the two extremes of very rapid and very slow carbide dissociation, a great range of flake sizes may be produced with the same rate of cooling. Somewhere in this series, the flakes will have a maximum size."

For the past several years it has been customary to minimize this conception of pattern flake formation and to accept without reservation the undercooling, meta-stable mechanism of type D formation as proposed by Eash[2], and previously discussed in this paper. Although it is very difficult to disprove this undercooling theory, there are certain discrepencies and unanswered questions in the mind of the writer concerning this mechanism. Five of these are discussed here:

1) The time-temperature curves presented by Boyles (see Fig 5) are typical of many of those found elsewhere in the literature. Both the irons show a pronounced dip just prior to the maximum. Elementary text books of physics refer to this dip as a result of undercooling and state that the dip is followed by a recalesence to the correct solidification temperature. This being true it is hardly logical to refer to the iron solidifying to give type D graphite as undercooled as distinct from the other iron. Both irons exhibit almost the same amount of undercooling.

2) Not all of the curves are similar to those of Fig 5. D'Amico and Schneidewind[15] have published the curves of Fig 6, and Eash[2] those of Fig 7. It appears from Fig 7 that no undercooling is taking place in some of the irons, in the usual sense of the word "undercooling". The curve of Fig 6 most closely represents solidification in accordance with the diagram for the ternary alloy (Fig 2). Many investigators appear to have overlooked the fact that ternary alloys

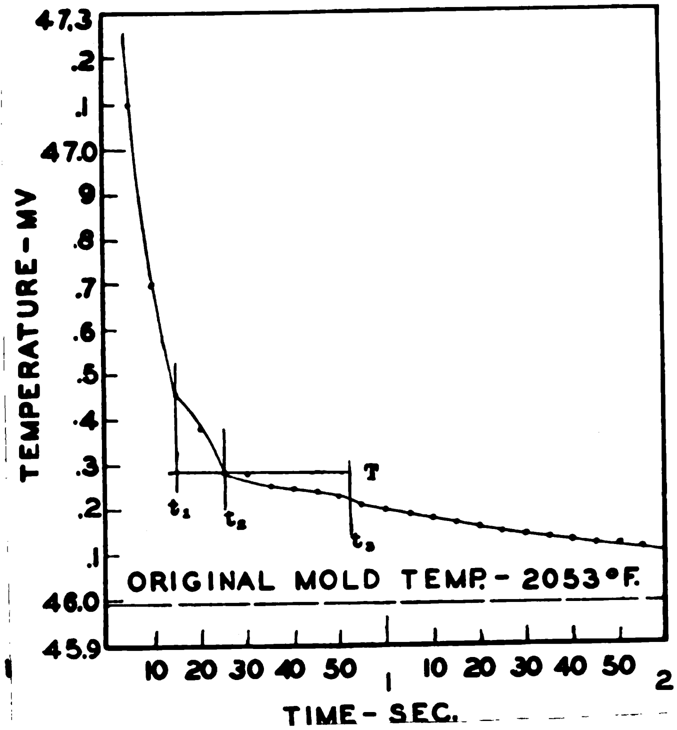

Fig 6. Time-Temperature Curve for Solidification of a Hypoeutectic Cast Iron. After D'Amico and Schneidewind.[16]

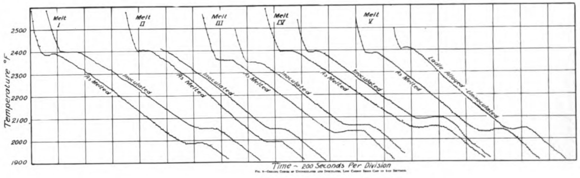

Fig 7. Time-Temperature Curves for Solidification of Hypoeutectic Irons. After Eash.[2]

have complex time-temperature curves, and that in such alloys liquid and two solid phases are in equilibrium over a range of temperature supposedly represented by the three phased field, Gamma + Liquid + Ca of Fig 2. One is compelled to wonder if the horizontals or maxima of some of these curves do not represent an equilibrium between recalesence and heat loss by the system rather than a non-variant equilibrium. The diverse nature of curves presented by the several investigators raises some question about the extent of the range of solid and liquid equilibrium.

This point appears to be particularly significant to the writer in view of the fact that the principle support for the undercooling theory rests on the microstructure of alloys supposedly quenched just below the "eutectic temperature", evidently regarded as the solidus temperature by these investigators. For example Morrogh and Williams[3] in presenting evidence to confirm Eashs' finding regarding metastable solidification of type D irons stated that the eutectic arrest for a particular sample occured at 1133°C and that the sample was quenched after solidification at 1132°C, a difficult achievement. Eash also refers to the "eutectic temperature" and speaks of quenching at a temperature 16° below the "eutectic temperature" and finding the alloy completely white.

3) The photomicrographs presented by these investigators are particularly confusing. As an example Fig 8 taken from the article by Morrogh and Williams represents the microstructure of a sample quenched just below the eutectic temperature. This structure is almost identical with structures presented by Boyles as representing samples quenched just above the eutectic temperature.

Owens and Street[4] in presenting evidence to support the contention of Eash, and Morrogh and Williams, have published the photomicrograph of Fig 8A. This structure was obtained by quenching "partway through the eutectic arrest" and shows a considerable area of type D graphite in the bottom portion of the picture immediately adjacent to the inter dendritic accicular structure which Boyles has taken in his work as representing liquid metal at the moment of quenching. It appears to the writer that this is evidence contrary to the thesis of Eash, and of Owens and Morrogh, who have contended that type D graphite develops after the alloy is solid and in a manner distinct from that of type A graphite.

4) The most pronouncedly abnormal structures with type D graphite occur at the extreme surface of castings. This, in the light of our under-

FIG. 11.—STRUCTURE OF SLOWLY COOLED INGOT QUENCHED IMMEDIATELY AFTER SOLIDIFICATION. SHOWING TRANSFORMED AUSTENITE DENTRITES AND WHITE IRON EUTECTIC OF ACICULAR PATTERN. ETCHED IN PICRIC ACID. × 60.

Fig 8. Microstructure of Iron Quenched from Below the Solidus Temperature. According to Morrogh and Williams.[3]

Fig. 1—Acicular carbide and undercooled graphite. Etched in picral ×300

Fig 8A. Microstructure of Hypoeutectic Iron "Quenched Part-way Through the Eutectic Arrest." According to Owens and Street.[4]

standing of undercooling, should be the region most difficult to undercool because of the opportunity for nucleation on the mold surface, a surface ideally constituted for the purpose. It would appear logical to attribute the abnormal structure to the rate of cooling in the manner proposed by Boyles rather than directly to undercooling and metastable solidification.

5) Many microstructures of low carbon irons show type A and type D graphite structures immediately adjacent to one another. It is very difficult to reconcile this occurance with the undercooling theory. Since the fine graphite adjacent to type A flakes appears to originate at the center of the cells, it should be possible to find cells with a white interior and a gray periphery in the microstructure of irons quenched during solidification. To our knowledge no such peculiar distribution of the cementite and graphite has appeared or been described in the literature.

The writer has embarked on this somewhat lengthy discussion of the shortcomings of the undercooling-metastable theory because some of the observations made during the experimental work of this thesis suggest another explanation for the displacement of the time temperature curves observed by these investigators. This matter will be discussed later.

Many attempts have been made to formulate an acceptable "gas theory" of inoculation. That gases have an important effect on microstructure and properties has been discussed in this report. Hydrogen, nitrogen, and oxygen appear to be effective in changing properties and microstructure of cast irons. It is argued that the effects of superheating are a result of increased solubility for these gases with increase in temperature. The effects of inoculants can be attributed to deoxidation, inasmuch as the commercial alloys all contain elements commonly regarded as reducing agents or deoxidizers in the metallurgy of steel. The undue chilling of abnormal iron in particular has been attributed to oxidation, and the reduction of chill by inoculants as a matter of deoxidation. It is very doubtful that cast iron containing large amounts of carbon, silicon, and manganese could long contain an excess above the normal amount of oxygen. Attention has already been called to this matter by citing Loria and Lownie[13] who claim an equilibrium value for oxygen in the presence of 2% silicon to be .0025%.

The problem of formulating a theory for the mechanism of inoculation and its effect on graphite distribution has been greatly complicated by the discovery of nodular iron, which is produced by a double ladle treatment - generally an initial addition of an alloy containing magnesium or cerium followed by treatment with ferro-silicon. Morrogh and Williams[26] have discussed the theory of this process at great length. Many of the conclusions in their paper which relate to gray cast iron have been discussed in connection with the previous reference to another paper by these authors.[3]

Objective of Research

Two facts become apparent from the literature survey presented here 1) There is a lack of information concerning the relative effectiveness of the alloys recommended in the journals as inoculants 2) A great deal of uncertainty exists as to the mechanism or theory of inoculation.

Morrogh and Williams[26] have commented on this lack of information and have listed forty-one "graphite formation anomalies". This list includes the effect of practically every element introduced to iron melts even including the graphitizing action of silicon, a most fundamental principle of ferrous metallurgy. Also included in this list are all of the practical and theoretical aspects of inoculation, and of the solidification of cast iron.

The writer has long been of the opinion that much of this uncertainty has resulted from failure to determine the relative effectiveness of inoculating substances in a careful and systematic manner. It is believed that such a study should provide information of practical value by showing the best alloys for inoculation, and that the performance of the various alloys, should they vary in the degree of effectiveness, should provide valuable clues as to the mechanism of inoculation and of the solidification of various types of gray iron. Accordingly research of this nature was undertaken by the writer and his associates in the engineering school of Michigan State College in 1946. It is the purpose of this report to summarize the results of the investigations previously reported by McClure[27] and Khan[28], and to present new data dealing with the inoculating substances, and with the melting conditions listed in the table of contents under the heading of Experimental Results. This data was acquired by comparison of inoculated heats with blank heats with no ladle treatment, by comparing iron inoculated with various substances, and by comparing irons melted under varying conditions.

II Experimental Proceedure

All of the heats described in this report were melted in a 250 lb capacity, indirect arc, rocking furnace unless otherwise noted. A typical charge is:

100.00 lbs pig Lot 1 (C4.15, Si 1.18, Mn .72, P.128,S.039%)
38.00 lbs pig Lot 2 (C4.12,Si 1.23, Mn.88, P.24, S.033%)
56.00 lbs of structural steel scrap
7.20 lbs of 27% ferro-silicon
.60 lbs of 80% ferro-manganese
.15 lbs of 50% iron sulphide

In a few cases ingot iron punchings were substituted for some of the steel. All of the constituents of the melt were charged in the cold furnace except the ferro-manganese and the iron sulphide which were added as soon as there was a melt down.

All melts were brought to the temperature range of 2850-2900°F and tapped into 50 lb ladles. The nominal tapping temperature being 2875°F as determined by optical pyrometer readings through the spout. This degree of superheat was selected as being representative of general practice, and as providing sufficient temperature latitude to transport the metal to the molds, skim the ladle, read the temperature with an optical pyrometer, and pour at the temperature selected for these experiments, 2650°F to 2675°F.

All ladle additions, unless otherwise indicated, were made by tapping a small amount of metal into the ladle and then adding the inoculating alloy continuously as the balance of the iron entered the ladle. During this operation an effort was made to carry the inoculant under the surface with the stream of molten iron.

In the case of ladle treatments with active metals special proceedures were required. These will be described for the individual cases.

The time interval between tapping and pouring varied in general from 2 to 3 minutes. This time was required for the metal to drop from the tapping temperature, and for transportation, skimming, and determination of temperature.

Metal from each ladle was cast into vertical, dry sand core, 1.2" standard test bar molds, washed with a non carbonacious silica wash. All transverse test bar results are the average of three or more bars unless otherwise indicated. Bars showing defects in the fracture and abnormally low results for breaking load and deflection were not included in the average. The number of tests bars poured varied from three to five. Bars were cleaned with a wire brush.

Small wedge chill test specimens were used in some experiments, in others a chill block having the dimensions 3/4" x 2¼ x 3-7/8" was employed. Two or more chill specimens were poured from the ladle, and the results for chill are the average of the two specimens. In general the agreement between chill specimens from the same ladle was very good. In the case of two ladles an appreciable difference was found between the check specimens. In these two cases the maximum chill is reported.

Tensile test results and hardness tests are not reported in all cases. As the work continued it became evident that the transverse breaking load, the deflection, and in particular the triangular resilience provided a more sensitive index of variations than did the tensile strength. (Triangular resilience = $\frac{\text{Trans. Breaking Load}}{2}$ x Deflection). The most potent influence of inoculants on microstructure is at the surface of the casting. This renders the transverse bar, tested in the unmachined condition, a very suitable test specimen for the purpose of demonstrating inoculation action.

The subject of reproduceability of results is important in considering both chill tests and transverse tests. Table II is presented to show the degree of reproduceability of properties. This table gives test results along with chemical analysis data on several of the blank heats - that is heats which were melted and poured without ladle treatment for the purpose of comparison with various other irons of similar analysis but ladle treated.

Table 2.

Iron	C	Si	Trans.	Deflec.	Res.	Chill.
T32-2	2.81	2.28	2543	.219	278	16-30
T25-2	2.84	2.24	2575	.230	296	12-18
T25-1	2.86	2.22	2663	.240	320	14-18
T33-2	2.84	2.28	2680	.233	304	16-31
T27-1	2.84	2.39	2490	.232	289	12-20
T27-2	2.85	2.43	2541	.241	306	12-22
T30-B	2.86	2.60	2521	.222	280	12-20

In this table and subsequent tables "Trans" is transverse breaking load for the 1.2 inch bar, "Deflec" is deflection in inches, "Res" is the triangular resilience in inch pounds, and "Chill" the chill depth in 1/32 of an inch units. The figures before the dash give the depth of clear chill, and those after the dash, the total chill.

If all of the results in this table are considered it will be concluded that results for transverse breaking load are not significant unless the difference between two irons with different treatments exceeds 200 lbs. However, in all cases the difference in silicon contents between irons for comparison will be much less than the range included here. The maximum variation in deflection is .022 inch; and in resilience, 42 inch pounds. The variation in chill is large. It would appear that clear chill is somewhat more consistent than total chill, and that conclusions regarding chill depth should be confined to those cases where the difference in chill is very marked. Variations in properties cannot be attributed to variations in sulphur or manganese as these are controlled within narrow limits for the several irons, and the slight variation cannot be correlated with properties. It should be noted that there is a general impression that uninoculated irons are erratic in their behavior particularly with respect to chilling tendency and that uniformity of behavior, particularly with respect to chill, is one of the justifications for inoculation.

In making comparisons between irons in this paper an effort has been made to keep the carbon equivalents ($C + \frac{Si}{3}$) within one tenth of one per cent. This is a degree of control which compares very favorably with that of similar experiments reported in the literature.

Carbon and silicon contents were determined on each ladle. Sulphur, manganese, and phosphorous contents were determined only on one ladle from each heat unless these elements were involved in the additions, or when there was reason to believe that their contents were altered by the ladle addition.

Photomicrographs were not made of all of the irons. Typical structures are presented for the purpose of illustration and discussion. Since the microstructures of any one sample, unless it is fully inoculated, are quite variable it becomes a very difficult matter to select an area on the polished surface which is representative. The microstructures of all significant irons were examined, and it was concluded that the results of the transverse tests were well correlated with the variations in microstructure, except in one instance which will be discussed later. The presence of a large percentage of type A graphite, particularly at the surface of the casting, seems to be very effective in producing a high transverse breaking load and a high deflection. This observation is in accord with the experience of others.

Some of the conclusions reached in this investigation are based on additions of active metals or of alloys containing active metals. In this phase of the research no attempt has been made to determine the amount of the active metal retained in the solid iron. This is justified by the fact that the retention of substantial amounts of the metals is not necessary in order that profound changes in the microstructure and properties be produced. For example in producing nodular iron the amount of residual magnesium has been reported as varying from .020 to .085. McElwee and Barlow[29] have discussed this matter and have concluded that the effects of inoculants cannot be measured by analysis of the iron for residuals - the chemical changes being insignificant or imperceptable.

In view of this feeling and in view of the time consuming nature and of the uncertainty involved in the determination of small quantities of active metals, it was decided to defer analytical studies until their value was indicated by the present research for continuing investigations.

In making additions of the various alloys an attempt was made to keep the crushed sizes of the alloys comparable in each case. In general the commercial size, 8 mesh and down, was employed.

III Experimental Results

Since the amount of data in this report is considerable, the results are presented as a number of separate experiments for the convenience of the reader.

Each comparison of irons is given in two tables, the first tabulating the available analytical data, and the second the mechanical properties.

Comparison of Ferro-silicon and Calcium-silicon.

The two most widely employed inoculants have been ferro-silicon and calcium-silicon. Very little of data is to be found in the literature regarding the relative effectiveness of these two alloys. Lorig[30] has compared irons treated with .2% additions of calcium-silicon with irons treated with .6% additions of ferro-silicon. In his experiments the irons were superheated over a range of temperature up to 3000°F. The specific grade or analysis of the ferro-silicon was not stated. Lorig concluded that .2% additions of the calcium alloy were equivalent to .6% additions of the ferro-silicon for superheating temperatures up to 2900°F. Beyond this temperature the irons treated with the ferro-silicon were somewhat superior in mechanical properties.

In view of the industrial importance of these two alloys and of the lack of comparative information, ferro-silicon and calcium-silicon were selected by McClure[27] and the writer for the initial experiments of this investigation.

Some difficulty is experienced in selecting the relative amounts to be used in making a comparison between alloys as diverse in chemical analysis as are these two. The situation is rendered more difficult by the fact that the silicon pick up is more complete when ferro-silicon is employed than is the case with calcium silicon. It was decided that the most satisfactory basis for comparison would be afforded by use of amounts of the alloys such that the silicon pick up would be the same in each case. This would involve using somewhat larger amounts of calcium-silicon. This basis of comparison has been proposed by Morrogh and Williams[3] for various alloys. In the experiments performed by the author this required using amounts of the two alloys in the proportion of .30% addition of Si as ferro-silicon to .35% addition of Si as calcium-silicon in the first comparison, and .60% to .70% in the second.

The following proceedure was used. A 200 pound heat was melted and brought to 2875°F as described above under experimental proceedure. Two pairs of 50 pound ladles were tapped from the heat. One member of the first pair (iron no. T2-F1) was inoculated with .30% Si addition as ferro-silicon and the second with .35% Si addition as calcium -silicon (T2-C1). This proceedure was repeated for the second pair of the ladles using .60% Si as ferro-silicon (T2-F2) and .70% Si as calcium silicon (T2-C2).

Chemical analysis data are presented in Table 3, and mechanical property data in Table 4. As previously mentioned manganese, phosphorous and sulphur were not determined on all ladles. In these tables the irons to be compared are grouped as pairs.

<u>Data on Ferro-silicon and Calcium Silicon as Inoculants.</u>

Table 3

Iron	Addition	C	Si	Mn	P	S
T2-F1	.30% Si as FeSi	2.95	2.00			
T2-C1	.35% Si as CaSi	2.94	1.95			
T2-F2	.60% Si as FeSi	2.90	2.17			.056
T2-C2	.70% Si as CaSi	2.84	2.21	.99	.102	.046

Table 4

Iron	Inoc.	Trans.	Deflec.	Res.	Tensile	Chill
T2-F1	Fe-Si	2665	208	277	46,910	30-45
T2-C1	Ca-Si	3597	361	651	58,750	13-18
T2-F2	FeSi	2905	261	379	51,470	12-20
T2-C2	CaSi	3728	394	745	59,200	4-8

Analysis of Fe-Si

Si	92.73
Al	1.68
Ca	.25

Table 4 shows the marked superiority of calcium-silicon over ferro-silicon. All mechanical properties are superior in the case of the irons treated with the high calcium alloy. The increase in triangular resilience is particularly noteworthy being 100% or more. It is also evident that the high calcium alloy is much more effective than ferro-silicon in reducing chilling tendency.

Examination of the microstructure of the cross sections of the transverse bars revealed an entirely normal (type A) graphite distribution in the interior of the bars treated with the heavy addition of calcium-silicon (T2-C2). The corresponding bars (T2-F2) treated with ferro-silicon showed a tendency towards type D and type E graphite distribution, see Fig 9. At the immediate surface the calcium-silicon iron was found to have a microstructure consisting mainly of type A graphite with only a slight tendency towards D, see Fig 10. The structure at the surface of the ferro-silicon iron was highly abnormal with considerable ferrite, Fig 11.

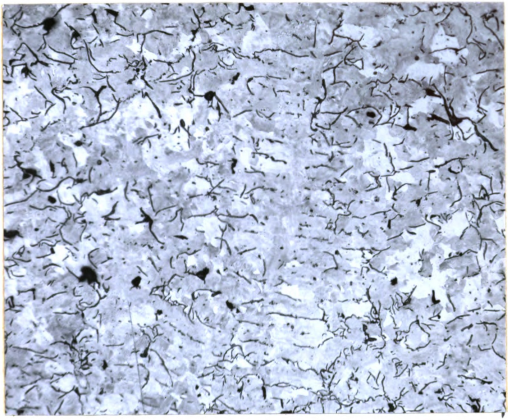

Fig 9. Microstructure of Interior of Iron T2-F2, Treated with .6% Ferro-Silicon. Nital, 100x.

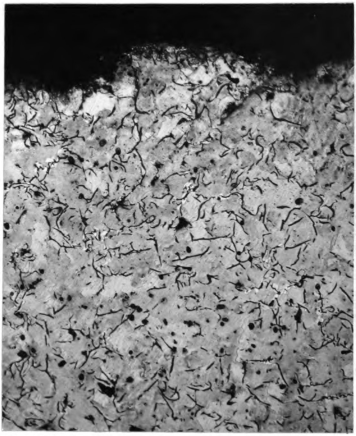

Fig 10. Microstructure at Surface of Iron T2-C2, Treated with .7% Calcium Silicon. Nital, 100x.

Fig 11. Structure at the Surface of Iron T2-F2, Treated with .6% Ferro-silicon. Nital 100x.

The above pictures are from experiments conducted independently by the writer, and are in good agreement with microstructures presented previously by McClure.

In general the microstructures of Figures 9, 10 and 11 are typical. Incomplete inoculation manifests itself as a tendency towards D and E graphite distribution with associated ferrite, and this tendency is shown to be particularly marked at the surface. In the succeeding experiments microstructures will not be presented in all cases, and reference can be made to these photomicrographs as being representative. As previously mentioned a good correlation exists between the transverse breaking loads, deflections, and their products, the triangular resilience, and the microstructure. These values will be taken as measuring the effectiveness of the various ladle treatments in subsequent experiments.

The results of Table 4 are in good agreement with those of McClure who performed the initial experiments of this gray iron research program. His results showed the superiority of CaSi over FeSi for a wide range of percentages of additions.

It is remarkable that this superiority of calcium silicon over ferro-silicon has received little attention in the literature. This difference appears to be very significant both in a practical and a theoretical way. Since the difference in price is not appreciable (20 to 21 cents per pound) it would appear advisable to use calcium silicon more generally than has been the case subsequent to the expiration of the patent covering its use. An additional conclusion of practical importance which can be drawn from these results is that somewhat larger additions of inoculants are required than is usually supposed to be the case. Additions of .20% total inoculant are frequently recommended in the literature, and to the writers knowledge some foundries are using even less. However, it should be mentioned that the employment of heavy treatments involves some practical difficulties in addition to the increased cost. The use of large amounts of calcium silicon forms a dry layer of oxides on the surface which is difficult to remove, and which, if carried into the mold, may contribute to casting dirtyness and surface imperfections.

These results appeared to the writer to have considerable theoretical significance. The superiority of the alloy containing the larger amount of active metal was indicative of an important role of the active metal in inoculation. Accordingly a series of experiments have been carried out in which the effect of active metals have been determined. It is remarkable that in most of the theorizing which appears in the literature, that the agency of active metals has been almost entirely neglected.

The analysis of the ferro-silicon used in this experiment was: Si 92.73%, Al 1.68%, Ca .25%. The calcium silicon was: 63.97% Si, 31.72% Ca, 1.70% Fe, .08% Zr, .16% Ti, 1.09% Al.

Calcium Silicon and SMZ

SMZ (Silicon-Manganese-Zirconium) is widely recommended and employed in industry as an inoculant. Lownie[31] states that SMZ is somewhat more effective than ferro-silicon but fails to give the analysis of the latter alloy or supporting data. Morrogh and Williams[3] make similar statements but also neglect to give data or analysis of the ferro-silicon. Burgess and Bishop[32] present data on irons inoculated with SMZ but give no information as to its effectiveness relative to other inoculants.

In view of the importance of SMZ as a commercial inoculant experiments were undertaken to compare the alloy with calcium-silicon. The proceedure followed was that of the previous experiment. A 200 lb heat was divided into two pairs of ladles - the members of the first pair were inoculated with .30% Si as SMZ and

.35% as Ca-Si. The members of the second pair of ladles were inoculated with .60% Si as SMZ and .70% as Ca-Si respectively. The somewhat greater addition of ca-Si was necessitated by the lower silicon pick up from the latter alloy.

Chemical analysis of the irons is presented in Table 5, and mechanical property data in Table 6. The analysis of the alloys employed is tabulated below Table 6. In this and the other cases of this report the alloy analysis given is that supplied by the producer of the alloy.

<u>Calcium Silicon and SMZ</u>

Table 5

Iron	Addition	C	Si	Mn	P	S
T8-S1	.30% Si as SMZ	2.80	1.97	.94		
T8 -C1	.35% Si as CaSi	2.86	1.96	.92		
T8 -S2	.60% Si as SMZ	2.86	2.30	.96		.056
T8 -C2	.70% Si as CaSi	2.82	2.22	.91	.084	.046

Table 6

Iron	Inoc.	Trans.	Deflec.	Res	Tensile	Chill
T8-S1	SMZ	3023	283	430	48,100	12-22
T8-C1	CaSi	3327	322	536	50,390	14-22
T8-S2	SMZ	3138	326	511	49,010	10-15
T8-C2	CaSi	3516	365	644	57,490	12-17

Ca Si	SMZ
63.92 Si	62.79 Si
31.72 Ca	6.45 Mn
1.70 Fe	5.45 Zr
.08 Zr	2.19 Ca
.16 Ti	1.50 Al
1.09 Al	.19 Ti

These results indicate that SMZ is somewhat inferior to Ca-Si as far as the mechanical properties are concerned when the additions are made to give approximately the same recovery of silicon. The difference in chilling tendency is not sufficient to permit a final conclusion, but it is indicated that SMZ is slightly more effective than Ca-Si in reducing chill.

A rough comparison of SMZ and FeSi is afforded by comparing Iron T2-F2 of table 4 with Iron T8-S2 of Table 6. It would appear that SMZ is somewhat superior to FeSi of the grade employed particularly with respect to deflection.

Figures 12 and 13 show the surface microstructures of the .30% SMZ iron (T8-S1) and the .35% Ca-Si iron (T8-C1) respectively. It is evident that these amounts of the alloys are not sufficient to produce normal structures at the surface of castings of 1.2 inch section. The microstructure of the Ca-Si treated iron is somewhat

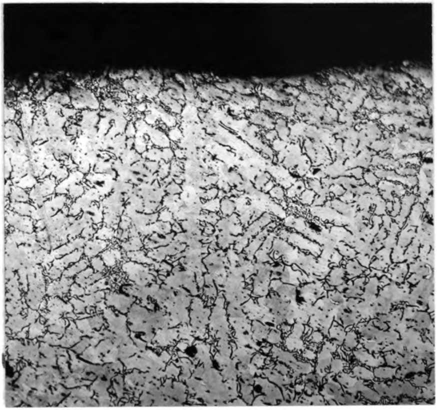

Fig 12. Microstructure at Surface of Iron T8-S1. Treated with .3% SMZ. Nital 100x.

Fig 13. Microstructure at Surface of Iron T8-Cl. Treated with .35% Calcium-Silicon. Nital 100x.

superior to that of the SMZ iron. These results indicate that the present practice of recommending relatively small amounts of inoculants is in error if maximum properties are desired, and in particular if wear resistance is a consideration.

Silico-manganese as an Inoculant.

Silico-manganese is not commonly used as an inoculant. However, it is listed in Table 1 by Lownie[18] as being an inoculant, and is also mentioned as an inoculating substance in the article dealing with gray cast iron in the American Society for Metals Handbook, page 515, 1948 edition. The fact that SMZ is an effective inoculant may be taken as an indication of some value in a late addition of manganese.

Boyles[9] has discussed the effect of sulphur and manganese on graphite distribution and has suggested that the precipitation and distribution of manganese sulphide inclusions is related to graphite distribution. These relationships are indicative of the possibility of some effect of a late addition of manganese.

The following experiment was undertaken to determine the effect of silico-manganese additions. Heat T3 was melted and ladles 1 and 2 were treated with a 1.0% addition of silico-manganese (.5 lb of alloy per 50 lb ladle). Blank heat T4 was melted with the composition of the cold charge adjusted with respect to silicon and manganese to give approximately the same final analysis as for heat T3.

Results for these heats are given in Tables 7 and 8. The composition of the silico-manganese employed is given below Table 8.

Data on Silico Manganese and Blank Heats

Table 7

Iron	Addition	C	Si	Mn	P	S
T3-1	1.0% Si Mn	2.88	2.31	1.06	.075	
T3-2	1.0% Si Mn	2.93	2.34	1.07		.060
T4-1	Blank	2.94	2.34	.98		
T4-2	Blank	3.00	2.33	1.00	.077	.062

Table 8

Iron	Inoc.	Trans	Deflec	Res	Tensile	Chill
T3-1	Si-Mn	2364	184	217	-	32-52
T3-2	Si-Mn	2375	188	223	-	24-44
T4-1	Blank	2580	218	282	-	16-35
T4-2	Blank	2631	223	294	-	18-34

Analysis of Si Mn

Mn	66.5
Si	18.5
C	1.25
Fe	13.00
Ti	.17

Ca and Al present only as traces.

The results would be interpreted as indicating that silico-manganese of the composition employed is not of value as an inoculant and that the with-holding of silicon and manganese from the charge for the purpose of making late additions is detrimental to the properties of the iron including chilling tendency.

As a check on these results the first two ladles of heat T6 were treated with 1.0% additions of silico-manganese, using the first two ladles of blank heat T5 for comparison. Results are presented in Tables 9 and 10.

<u>Data on Silico-Manganese and Blank Heats</u>

Table 9

Iron	Addition	C	Si	Mn	P	S
T6-1	1.0% Si Mn	3.04	2.26	.94	.075	.073
T6-2	1.0% Si Mn	3.04	2.30	1.02		
T5-1	Blank	3.05	2.21	.99		
T5-2	Blank	3.07	2.20	.97	.075	.072

Table 10

Iron	Inoc.	Trans	Deflec	Res	Chill
T6-1	Si-Mn	2485	218	272	18-38
T6-2	Si-Mn	2506	240	301	16-30
T5-1	Blank	2546	215	274	20-42
T5-2	Blank	2588	224	290	20-42

These results are not in complete agreement with those of the first silico-manganese series. The silico-manganese heats of this second series are slightly superior in deflections and slightly lower in chilling tendency than the corresponding blanks. These small differences must be attributed to individual variations in heats as discussed above in connection with the subject of reproduceability of results.

The conclusion from these results is that silico-manganese of this grade is without value as an inoculant. It is noteworthy that the silico-manganese employed is free of calcium and aluminum.

High and Low Active Metal Ferro-silicons.

The superiority of alloys containing calcium, aluminum, and zirconium as demonstrated by the above data indicated the desirability of determining the relative effectiveness of low and high active metal content ferro-silicons. High and low aluminum grades were obtained from a major producer with the analysis given just below Table 12. Irons of the compositions presented in Table 11 were produced by inoculating with .50% Si additions of the two alloys for comparison with one another, and for comparison with a blank heat. Results are given in Table 12.

Data on Grades of Ferro-silicon

Table 11

Iron	Addition	C	Si	Mn	P	S
T26-3	.5% Si,Low Al alloy	2.85	2.34	.85	.115	.066
T26-4	.5% Si,High Al alloy	2.90	2.34			
T27-1	Blank	2.84	2.39	.83	.122	.066
T26-2	.5% Si, High Al alloy	2.86	2.29	.85	.115	.066

Table 12

Iron	Inoc.	Trans.	Deflec.	Res.	Chill
T26-3	Low Al,FeSi	2591	.230	298	13-29
T26-4	High Al,FeSi	2920	.280	409	8-13
T27-1	Blank	2490	.232	289	12-20
T26-2	High Al,FeSi	2919	.288	420	8-14

Low Aluminum FeSi	High Aluminum FeSi
93.00 Si	90.57% Si
.45 Al	2.20% Al
.10 Ca	.46% Ca

Comparison of Iron T26-3, inoculated with the low active metal content alloy, with T27-1, the uninoculated blank, shows that the low aluminum and calcium alloy has a negligible value as an inoculant. Consideration of the data for the irons inoculated with the high active metal content shows the pronounced superiority of the high active metal alloy.

These data afford strong evidence for a theory of inoculation based on the action of active metals, particularly aluminum and calcium. They also indicate the serious nature of failure to state the analysis of inoculants with respect to these elements when used in research. Such failure is usual in work reported in the literat ure. Many of the discrepancies noted in the literature may be attributed to variations in the active metal contents of the alloys employed.

Although the ferro-silicons used here are designated as "high" and "low aluminum" alloys, it should be noted that calcium as well as aluminum is varied in the composition.

Silicon as an Inoculant

Consideration of the above data pointed to an important role of the active metals in inoculation, and indicated the desirability of determining the effect of pure silicon as a ladle addition. The following

experiments were performed: 1) Two ladles were tapped from heat T24 and one ladle was treated with a .50% addition of high aluminum ferro-silicon and the other with a .50% addition of purified silicon. 2) A ladle from heat T26 was treated with .50% purified silicon for comparison with two blank or uninoculated irons. Results are presented in Table 13 and 14. The high aluminum ferro-silicon is the one employed in previous experiments with the analysis given on page 48. The "purified" silicon employed was the highest grade commercially obtainable (99.8% Si, balance iron).

Data for Purified Silicon

Table 13

Iron	Addition	C	Si	Mn	P	S
T24-S	.5% Si as pure Si	2.78	2.61	.91	.130	.059
T24-F	.5% Si as Hi Al FeSi	2.75	2.62	.91	.130	.059
T26-1	.5% Si as pure Si	2.87	2.32	.85	.115	.066
T25-2	Blank	2.84	2.24	.80	.122	.062
T27-1	Blank	2.84	2.39	.83	.122	.066

Table 14

Iron	Inoc.	Trans	Deflec.	Res	Chill
T24-S	.5% Si	2601	.218	284	8-21
T24-F	.5% Si as Hi Al FeSi	3059	.312	476	3-3
T26-1	.5% Si	2533	.210	266	13-36
T25-2	Blank	2575	.230	296	12-18
T27-1	Blank	2490	.232	289	12-20

Comparison of the results for irons T24-S and T24-F shows that pure silicon is much inferior in all respects to the ferro-silicon.

Comparison of the values obtained for the blank heats T25-2 and T27-1 with T26-1, treated with .50% of silicon, indicates that silicon has no value as an inoculant, and suggests that with-holding a portion of the silicon and adding it late may be slightly detrimental rather than beneficial to properties.

These data render it difficult to support the silica slime theory of inoculation particularly if the nucleating agent is considered to be a ferrous silicate particle. It also tends to discredit a theory based on precipitation of graphite particles resulting from local concentrations of silicon. It would appear that the silicon in commercial inoculants is simply a convenient carrier for active metals or that the simultaneous addition of silicon with aluminum and calcium is in some way capable of improving graphite distribution and reducing chill.

Fig. 14 shows chill block fractures of T24-S, treated with purified silicon and T24-F, treated with "high aluminum" ferro-silicon, and shows the powerful chill reducing tendency of the active metals contained in the ferro-silicon.

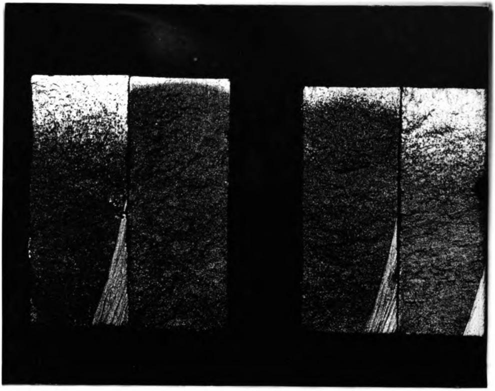

Fig 14. Fractures of Chill Blocks. Pair to left are of Irons T24-S, treated with .5% purified silicon and of T24-F, treated with .5% of high aluminum ferro-silicon, and shows the pronounced effect of aluminum on chilling tendency. Right hand pair are of Iron T30-A, treated with 1.1% aluminum and of T30-B the corresponding blank.

Calcium as a Ladle Addition.

In view of the evident importance of the active metals in the inoculation mechanism Khan[28] and the writer undertook experiments to determine the effect of calcium and aluminum additions as a contribution to the general project. Data from Khan's report are presented here along with confirming data acquired independently by the writer.

Khan inoculated ladles with .21% Ca, .44% Ca, and .68% Ca for comparison with blank ladles from the same and other heats. The calcium additions were accomplished by wiring the metallic calcium to an iron rod and plunging the metal beneath the molten iron in the ladle immediately after tapping. When solution and reaction were complete, the ladle was skimmed, the temperature allowed to drop to 2650°F and the iron poured in the usual manner.

The chemical analysis of the irons from Khan's report are recorded in Table 15 and the mechanical properties in Table 16. It is evident from these data that calcium is very effective as a ladle addition. The properties of iron No. T9C5-9 are superior to the properties of all other irons of this report excepting those inoculated with calcium silicon. The calcium silicon treated irons of Tables 4 and 6 show superior properties but have somewhat lower carbon equivalents.

Data on Calcium.

Table 15

Iron	Addition	C	Si	Mn	P	S
T9B1-4	Blank	3.07	2.30	.95	.1	.063
T9C1-4	.21% Ca	3.04	2.29			.062
T9B5-9	Blank	3.09	2.30			.066
T9C5-9	.44% Ca	3.00	2.30			.057
T12B1-5	Blank	2.90	2.23			.057
T11C1-5	.68% Ca	2.92	2.31			.052

Table 16

Iron	Inoc.	Trans.	Deflec.	Res.	Chill
T9B1-4	Blank	2679	.251	334	7-22
T9C1-4	.21% Ca	2988	.283	425	5-17
T9B5-9	Blank	2656	.261	345	1-17
T9C5-9	.44% Ca	3261	.343	561	1-4
T12B1-5	Blank	2202	.196	216	12-30
T11C1-5	.68% Ca	3013	.361	545	1-8

The writer has checked the data reported by Khan by treating a ladle with .50% Ca and comparing the resulting data with two blank irons of approximately the same analysis. Results are presented in Tables 17 and

18 and are in agreement with those of the preceeding report.

Table 17

Iron	Addition	C	Si	Mn	P	S
T1-2	95 grms Ca .5%	3.02	2.40	.86	.098	.055
T1-B2	Blank	3.03	2.38	.86	.102	.058
T4-2	Blank	3.00	2.33	1.00	.077	.062

Table 18

Iron	Inoc.	Trans.	Deflec.	Res.	Chill
T1-2	Ca	3024	.385	584	6-8
T1-B2	Blank	2521	.262	330	12-20
T4-2	Blank	2631	.223	295	18-34

All of this data is significant and is strongly indicative of the major role played by Ca additions in determining the graphite distribution and properties of cast iron. Consideration of the data for the other experiments shows that those ladle additions which are free or relatively free of calcium (silico-manganese, purified silicon, and "low aluminum" ferro-silicon) are without value as inoculants, while there is a correlation between the calcium contents and the effectiveness of the other inoculants employed.

These data show that silicon additions are not necessary to the production of excellent properties in high strength cast iron.

Aluminum Additions.

Those inoculants which have been effective in the research covered by this report contain substantial amounts of aluminum along with the calcium. The high aluminum ferro-silicon contains 2.20% Al, .46 Ca; and the SMZ, 1.50% Al and 2.19% Ca. The effect of aluminum additions were determined by Khan[28] and the writer, and were checked by the writer.

Aluminum additions were made in the same manner as the calcium additions - by wiring the aluminum to an iron rod and by plunging beneath the surface of the metal in the ladle. The addition of the aluminum gave the surface of the metal a peculiar ropy appearance somewhat like that of molten brass in the ladle. The aluminum addition was approximately 1.1% in both cases.

The data reported by Khan[28] are presented in Tables 19 and 20. The effect on mechanical properties is small but the effect on chill tendency is remarkable.

Data on Aluminum Additions.

Table 19

Iron	Addition	C	Si	Mn	P	S
T13A6-10	1.1% Al	2.90	2.23			.067
T13B6-10	Blank	2.95	2.26			.068

Table 20

Iron	Inoc.	Trans.	Deflec.	Res.	Chill
T13A6-10	Al	2481	.213	266	0-1
T13B6-10	Blank	2280	.184	210	7-24

The properties for the irons of Table 19 are lower than those obtained for other irons of about the same carbon equivalent in this report. The low values may be a result of prolonged superheating.

Check data on this aluminum experiment is given in Tables 21 and 22. It would appear that aluminum additions of 1% have no effect, or a negligible effect on properties with the exception of the effect on chill, which is pronounced.

Table 21

Iron	Addition	C	Si	Mn	P	S
T30-A	1.1% Al	2.86	2.58	.87	.122	.064
T30-B	Blank	2.86	2.60	.87	.122	.062

Table 22

Iron	Inoc.	Trans.	Deflec.	Res.	Chill
T30A	Al	2588	.216	280	3-5
T30B	Blank	2521	.222	280	12-20

More data on aluminum additions are needed with a range of size of additions before a final conclusion is justified. However, it would appear that the effect of aluminum is distinct from that of calcium. Aluminum is seen to be the most effective element for reduction of chill. This ability to reduce chill was noted in the case of the irons inoculated with high aluminum ferro-silicon, see Fig. 14.

No adverse effect of the aluminum additions were observed on the castings. Foundrymen have long believed that large aluminum additions are detrimental to casting properties and tend to promote pin hole defects in the casting surface, particularly when the casting is poured in green sand molds. The absence of such defects in the castings of these experiments may be due to the fact that all of the castings were made in dry sand cores.

Aluminum is capable of reducing chilling tendency without improving graphite distribution or mechanical properties, thus indicating that high chilling tendency is not a necessary concomitant of abnormal graphite distribution. This is surprising in view of the fact that abnormal irons as usually produced exhibit a high chilling tendency. This observation renders it difficult to base a theory of inoculation on a reduction of carbide stability.

Effect of Acid and Basic Melting Conditions.

It has long been understood that at higher melting temperature there is a reduction of silicon from furnace linings by carbon in the melt with a resulting loss in carbon and an increase in silicon. Heine[10,11] has discussed this matter and has placed the temperature at which this reaction starts at 2671°F. This reaction is accompanied by a boiling of the melt presumably from the liberation of carbon monoxide from the reduction. The resulting changes in the carbon and silicon contents contribute to the difficulty of controlling the carbon and silicon within narrow limits in commercial melting equipment.

Diepschlag[24] has claimed that melting in furnaces with aluminous linings produces irons with different properties than those melted in silica linings. As previously mentioned Morrogh and Williams[3] have failed to confirm this finding.

In view of the possible effect of the silica reduction and gas evolution, and in view of the contradictory nature of the reports on the effect of furnace linings, experiments were undertaken to determine the effect of strongly acid and basic melting on the microstructure and properties of cast iron.

Melts for this purpose were made in a 30 lb, high frequency induction furnace using a magnesia crucible for the basic melts and a silica crucible for the acid melts. During and after the melt down small additions of calcium oxide were made to the basic heats, and small additions of silica to the acid heats for the purpose of assuring basic and acid melting conditions. Charges consisted of electric furnace remelt, steel and ferro alloys. No inoculants were added. Since some desulphurizing occured in the basic heats the work was repeated using sulphur additions (slightly larger in the case of the basic melts) for the purpose of adjusting sulphur contents. Results are presented in Tables 23 and 24.

Data on Acid and Basic Melting.

Table 23

Iron	Addition	C	Si	Mn	P	S
TA-1	Acid, 90 grms SiO_2	2.83	2.38	.79	.111	.039
TA-2	Acid, 90 grms SiO_2	2.82	2.34	.80	.111	.058
TA-5	Basic,30 grms CaO	2.82	2.30	.81	.114	.029
TA-6	Basic,30 grms CaO	2.82	2.43			.070

Table 24

Iron		Trans.	Deflec.	Res.	Chill
TA-1	acid	2455	.193	236	24-52
TA-2	acid	2311	.182	210	20-42
TA-5	Basic	2495	.185	232	30-52
TA-6	Basic	2447	.178	218	22-48

From these data it is concluded that acid and basic melts are equivalent - the variation in the properties being negligible. Since the tapping temperature 2875°F was well above the temperature set by Heine for the beginning of reduction of silica, and since boiling of the melt occured before tapping, it is concluded that the reduction of silica from the furnace lining is without effect on structure and properties.

Magnesium as a Ladle Addition.

Magnesium additions to molten iron are of interest in connection with the productions of nodular or ductile iron, which is formed by an addition of magnesium, usually as a nickel magnesium alloy, followed by an inoculation with ferro-silicon. No satisfactory theory has been advanced to explain the effectiveness of this double treatment in producing an iron with the graphite entirely in the form of spheres or "nodules". However, it is understood that magnesium is an active desulphurizer and that low sulphur content is one of the requirements of ductile iron production.

Khan[28] and the writer have attempted to determine the effect of magnesium additions to molten iron without the subsequent addition of ferro-silicon. The technique employed for the addition of calcium and aluminum, whereby the metal is plunged and held beneath the surface of the molten bath, cannot be employed in the case of magnesium because of the low boiling point (1100°C) of this element and the consequent violence of the reaction. In the experiments described here the magnesium, in the form of ½" rods of commercially pure metal, were dropped through a flanged tube with flange covering the ladle onto the molten metal. Even under these conditions the reaction is extremely violent, and the pick up of magnesium somewhat uncertain. For these reasons the use of pure magnesium has been generally abandoned in industry, and the magnesium is introduced in the form of an alloy. In these experiments magnesium was used instead of the alloy in order to avoid the complicating presence of the alloying element.

Results from the experiments reported by Khan are presented in Tables 25 and 26. It is apparent that the magnesium treatment has effected a small improvement in properties, a marked decrease in chilling tendency, and a considerable desulphurization.

<u>Data on Magnesium</u>.

Table 25

Iron	Addition	C	Si	Mn	P	S
T13 B1-5	Blank	2.93	2.26			.057
T13 M1-5	1.10% Mg	2.94	2.26			.029

Table 26

Iron	Inoc.	Trans.	Deflec.	Res.	Chill
T13 B1-5	Blank	2188	.173	188	21-35
T13 M1-5	1.10% Mg	2333	.199	233	8-18

Microstructures of T13-B, the untreated blank and of T13-M, the magnesium treated iron are presented in Figs 15 and 16. The magnesium addition has an adverse effect on graphite distribution and has promoted the formation of associated ferrite. The extent to which the microstructural changes are due to the lowering of the sulphur content is problematical. The sulphur remaining in T13-M should be sufficient to permit a normal structure in the iron according to Boyles.[1,9]

These results as far as microstructure is concerned are in agreement with the opinion of Morrogh and Williams[26] who have regarded the formation of highly abnormal type D graphite and associated ferrite as a step in the direction of the formation of nodular graphite structures by magnesium and cerium additions.

In attempting to check the results reported by Khan the writer performed the following experiments. Three ladles were tapped from heat T32. The first ladle was treated with .50% Mg, the second was untreated to serve as a blank, and the third ladle was treated with 1.0% Mg plus an amount of S calculated to replace the sulphur re-

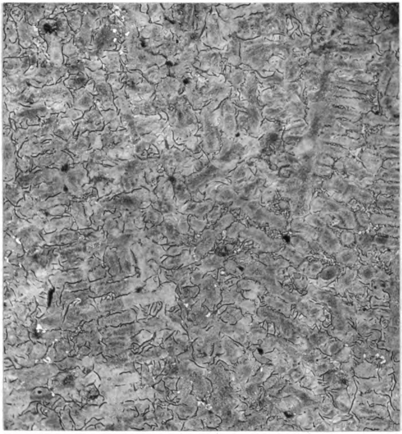

Fig 15. Microstructure of Blank Heat T13-B at the Surface. Nital 100x.

Fig 16. Microstructure of Iron T13-M, Treated with Magnesium. Nital 100x.

moved by the magnesium. The sulphur was added in the form of iron sulphide after the magnesium reaction had ceased, and amounted to an addition of .04%S.

Results are reported below in tables 27 and 28 and are seen to be negative as far as properties and chill tendency are concerned. Examination of the irons under the microscope revealed no influence on structure. Figures from the sulphur determinations show only a minor desulphurization by the magnesium addition. It would appear that either the addition of magnesium is without effect, or that the recovery of the magnesium was too small to be effective. The latter conclusion would appear to be justified by the small amount of desulphurization produced. Magnesium additions as pure metal have been found to be uncertain in the industrial production of nodular iron, and have been abandoned in favor of nickel-magnesium alloys. The writer regards these results as inconclusive, and is of the opinion that further work with magnesium is justified in view of the importance of developing a theory for the mechanism of nodule formation.

Table 27

Iron	Addition	C	Si	Mn	P	S
T32-1	.50% Mg	2.86	2.28			.061
T32-2	Blank	2.81	2.28	.87	.105	.064
T32-3	1.00% Mg - .04% S	2.83	2.21	.85		.083

Table 28

Iron	Inoc.	Trans.	Deflec.	Res.	Chill
T32-1	.50% Mg	2530	208	264	16-32
T32-2	Blank	2543	219	280	16-30
T32-3	1.00% Mg - .04S	2537	220	279	16-32

The photomicrograph of Fig 16 shows the microstructure of iron T13-M, treated with magnesium, to be more abnormal than that of the corresponding untreated iron T13-B of Fig 15. However, the properties of the magnesium treated iron are somewhat superior to those of T13-B, and the chill tendency is markedly less. This is an instance of failure of microstructure and properties to correlate, and a further example of lack of correlation between degree of abnormality and chilling tendency.

Graphite Additions.

The idea is widespread in the foundry industry that benefits are to be derived from late additions of graphite to molten iron, particularly with respect to a reduction in chilling tendency. This conception has been fostered by advertising claims made in the trade journals, but it is not made clear as to whether the chill reduction is due to an inoculation effect or to an increase in the carbon equivalent. The only experimental evidence in the literature is found in an article by Dahlberg[16] who recommended the use of eight mesh graphite, and reported an increase in mechanical properties and a decrease in chilling tendency with very small additions of graphite.

The following experiment was performed to determine the effect of appreciable graphite additions. Heat T29 was melted down to a low carbon content and a ladle treated with a .44% addition of graphite for comparison with blank heats of similar analysis. Results are presented in Tables 29 and 30 and would indicate that the effect of graphite additions are negligible if they exist at all. The idea that the effect of graphite additions is of very short duration, and that the graphite addition should be made as the metal enters the mold has been suggested to the writer. This possibility should be checked before a final conclusion is reached, as the matter of graphite in a colloidal dispersion serving as a nucleating substance is of theoretical interest. In the above experiment the graphite was added at the furnace spout.

Data on Carbon Additions.

Table 29

Iron	Addition	C	Si	Mn	P	S
T29-2	.44% C	2.82	2.30	.89	.110	.064
T32-2	Blank	2.81	2.28	.87	.105	.064
T33-2	Blank	2.84	2.28	.86	.122	.062

Table 30

Iron	Inoc.	Trans.	Deflec.	Res.	Chill.
T29-2	Graphite	2699	.242	326	12-18
T32-2	Blank	2543	.219	280	16-30
T33-2	Blank	2680	.233	311	16-31

The Effect of Various Inoculants on Cell Size.

The cell size of cast iron refers to the size of the eutectic units in the solid iron. Boyles[1] has described the manner of solidification of a hypoeutectic iron as: 1) the formation of primary dendrites of austenite in the liquid 2) the neucleation of the eutectic which solidifies as spherical "cells" between and around the primary dendrites 3) the development of graphite flakes in the cells simultaneously with the growth of the cells, with the flakes growing at the liquid solid interface, and 4) the segregation of some elements in the remaining liquid surrounding the growing cells - notably phosphorous, sulphur, and hydrogen.

This conception of the solidification is based on experiments in which transformation is arrested by quenching at temperatures between the liquidus and solidus to produce microstructures like that of Fig 3, in which the light etching background represents liquid at the moment of quenching.

As previously discussed, Boyles has proposed a theory to explain graphite size variations on the basis of variations in the rate of formation of the austenite and graphite flakes of the eutectic cells. It is apparent that the number and size of the cells in the solidified iron is an important theoretical consideration, inasmuch as it indicates the possibility of a cell nucleation by inoculants.

The cell size in irons is not made evident by ordinary polishing and etching proceedures. Two methods have been employed for the delineation of cell boundaries: 1) Heat tinting, and 2) overetching with nital to bring out the cell size by the position of steadite, which is located in the cell boundaries as a result of the segregation of phosphorous, and which is light etching.

Boyles[1] has successfully employed heat tinting in certain irons, but does not give specific instructions for applying this method, and such directions are not to be found elsewhere in the literature beyond the statement that temperatures up to 900°F may be employed for heat tinting the polished surface. The writer has been unable to apply the heat tinting method successfully for measuring the cell size of the irons of this report. This may be a result of the hypoeutectic character of these irons with the consequent limitation on the interdendritic space. Heat tinting at a temperature of 800°F was found to bring out the primary dendrites but not the cell boundaries.

The second method, which determines the cell boundaries by the distribution of steadite, is dependent on the phosphorous content of the iron. Steadite does not appear in the microstructure unless the phosphorous content is approximately .10% and it increases in amount with increasing phosphorous. High strength irons of the type investigated in this report are generally produced with phosphorous contents of less than .15% and the irons of this investigation have been melted in conformation with this practice. This has made it somewhat difficult to apply this steadite distribution method, but a number of irons were examined this way for cell size.

Adams[38] has discussed the steadite method, which as previously mentioned employs deep etching with nital to create a contrast between the light etching steadite in the cell boundaries and the matrix. He has presented a chart with numbers ranging from 1 to 7 where the low numbers indicate large cell size. On this chart, size no. 2 represents an average cell diameter of approximately one inch at a magnification of 25; no. 3, a cell diameter of three quarters of an inch; and no. 4, of one half inch. Using the deep etching method and this chart, the writer has determined the cell size of a number of the significant irons of this report. Data is presented in Table 31 where the treated irons are compared with the corresponding blanks in the second column or with other irons.

Data from Cell Size Determinations.

Table 31

Iron	Addition	Cell	Iron	Addition	Cell
T11-C2	.68% Ca	4	T11-B3	Blank	3
T1-2	.50% Ca	4	T1-B2	Blank	2
T2-C2	.70% CaSi	3	T2-F2	.60% FeSi	2
T24-F	.50% FeSi	3	T24-S	.50% Pure Si	2
T29-2	.44% C	2	T25-2	Blank	2
T30-A	1.10% Al	2	T30-B	Blank	2
T13-M3	1.10% Mg	4	T13-B3	Blank	3

The ferro-silicon used to treat iron T2-F2 was an intermediate active metal content alloy containing 1.68% Al and .25% Ca (See Table 3 and 4 Page 37, and Page 38). The ferro-silicon addition to iron T24-F was the high active metal alloy containing 2.20% Al and .46% Ca (See page 50). With this in mind consideration of the data on the first four pairs of iron of the table would indicate that the addition of calcium or of alloys containing appreciable calcium has the effect of reducing the cell size.

Comparison of graphite treated iron T29-2 with blank heat T25-2 of very nearly the same analysis indicates that the graphite addition has no influence on cell size.

The aluminum treated iron T30-A has the same cell size as T30-B, the corresponding blank.

An addition of 1.10% magnesium to iron T13-M3 appears to have reduced the cell size from 3 to 4 when comparison is made with the blank T13-B3.

On the basis of the above data it would be concluded that the addition of calcium to gray iron effects a reduction in the cell size, and that the possibility of a similar reduction by magnesium exists. It would be advisable to continue this study using a series of higher phosphorous irons, to give a better delineation of cell size, before a final conclusion is reached.

Decarburization by Calcium.

During the experiments in which pure calcium was added to the ladle, Khan[28] and the author observed that the calcium addition tended to reduce the carbon content of the iron. This conclusion was based on comparison of the analysis of blank ladles tapped at the same time with the analysis of the treated ladles. Table 32 gives data from Khan's report and includes data on the calcium treated ladle (Heat T1) from the work performed independently by the writer. Data on ladles treated with large amounts of Ca Si are also included (Heats T2 and T8).

Data on Decarburizing Effect of Ca.

Table 32

% Ca	Blank	% C	Treated	% C	Loss
.21	T9 B1-5	3.07	T9 C1-5	3.04	.03
.44	T9 B6-10	3.09	T9 C6-10	3.00	.09
.63	T10 B1-5	2.96	T10 C1-5	2.80	.16
.68	T11 B1-5	3.10	T11 C1-5	2.92	.18
.87	T10 B6-10	2.99	T10 C6-10	2.83	.16
1.11	T11 B6-10	3.08	T11 C6-10	2.84	.24
.50	T1 - B2	3.03	T1 - 2	3.02	.01
.22	T2 - F2	2.90	T2 -C2	2.84	.06
.22	T8 - S2	2.86	T8 -C2	2.82	.04

The last column under "Loss" gives the reduction of carbon content brought about by the addition of calcium. The last two pairs of irons at the bottom of the table give results for irons treated with calcium-silicon (31.7%Ca) when compared with accompanying ladles treated with ferro-silicon.

These results are fairly consistant with the exception of the data from heat T1, and furnish strong evidence for a decarburizing action of calcium. It is difficult to attribute this effect to any mechanism other than one involving the formation of a calcium carbide of high stability and low solubility. This possibility is discussed below.

IV Discussion

The following observations can be made from the data of the experiments of this report:

1. The element silicon is not effective as an inoculating agent.

2. Silico manganese, which is relatively free of calcium and aluminum, is not effective as an inoculant.

3. The inoculating ability of various commercial grades of ferro-silicon increases with the calcium and aluminum contents. Low calcium grades have very little effect.

4. Silicon-manganese-zirconium alloys containing somewhat more calcium than is found in commercial ferro-silicon are more effective than ferro-silicon.

5. The most effective inoculant employed in these experiments is the calcium-silicon alloy with approximately 30% of calcium.

6. Although aluminum is a very powerful chill reducer, its addition to cast iron does not promote type A graphite distribution.

7. Metallic calcium additions to the ladle bring about marked improvements in properties and graphite distribution of cast iron. Calcium is superior to all other inoculating agents tested in these experiments, with the exception of calcium-silicon, when added in the amount of approximately .4%.

8. Metallic calcium is effective in reducing the chill-

ing tendency of cast iron.

9. Metallic calcium is effective in reducing the cell size of cast iron microstructures.

10. Calcium additions effect a reduction of the carbon content of molten iron.

A survey of the literature and the data of this report indicates that zirconium, titanium, aluminum, lithium, magnesium and possibly cerium are either not effective in changing graphite distribution or tend to produce type D graphite in cast iron. Thus it appears that calcium is unique in its effect of promoting large randomly distributed graphite flakes, and that calcium is an active agent in commerical inoculants.

This conclusion and the above observations regarding silicon render it difficult to support the silica slime or the graphite nucleus theory of inoculation, and suggests the need for further examination of the mechanism of inoculation in the light of the agency of calcium.

What are the ways in which calcium might influence graphite formation? The following are among the possibilities:

1. By deoxidation.

2. By nucleation.

3. By carbide formation.

4. By adsorption of calcium or a calcium compound on an interface existing during solidification and graphite formation with a resultant influence on the energy distribution in the system.

Of the several elements ordinarily occuring in ferrous materials calcium ranks high in its affinity for oxygen. This affinity for oxygen can be expressed in terms of the free energy of oxide formation. Data on these free energies have been plotted by Richardson and Jeffes[33] and their information is presented graphically in Fig 17. These curves show the variation with temperature of the free energy change accompanying the conversion of one gram molecule of oxygen at one atmosphere pressure into the equivalent quantity of oxide. These data are indicative of the high deoxidizing ability of calcium., However, such data must be interpreted with caution since it cannot be applied to alloys without reservation. Bach[12] has pointed out that the activities of any particular element are influenced by variations in the concentrations of the elements in the system, and that our information regarding thermodynamic relations even for the simple Fe-Si-O system is far from reliable or complete. Nevertheless, it does appear probable that a reduction in oxygen content would be accomplished by the addition of calcium.

The failure of aluminum and some other active metals to influence graphite formation in a favorable manner in gray iron can be advanced as an argument against the deoxidation hypothesis. Heine[10,11] has presented evidence to show that aluminum effects a deoxidation of cast iron, and the failure of aluminum to influence graphite formation renders it difficult to support the deoxidation mechanism as the principle

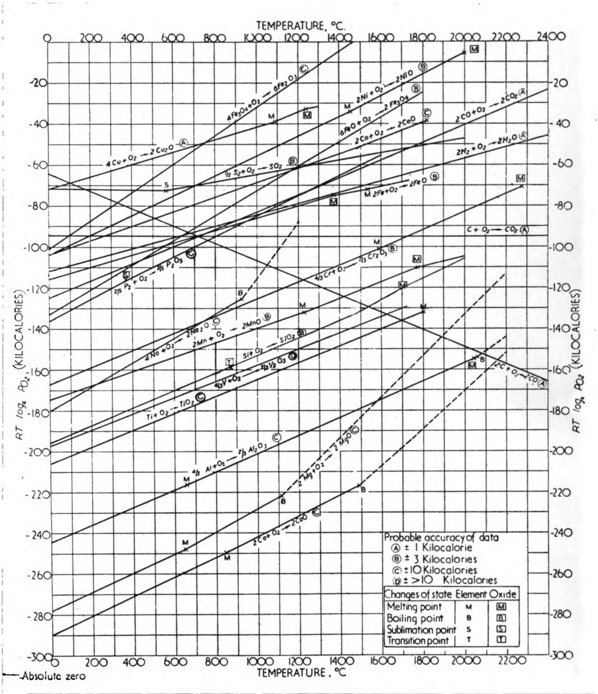

Fig 17. Relation between Free Energy and Temperature. After Richardson and Jeffes.[33]

factor in determining graphite distribution unless it is argued that the oxygen content of the iron is very critical. Chilling tendency has been attributed to oxidation and both calcium and aluminum are chill reducers.

The possibility of calcium additions producing a nucleation is indicated by the decrease in cell size accompanying an addition of this element. Boyles [1,9,20] has discussed the relationship between cell size, rate of development of the cells, and graphite distribution, and it is possible that the sudden formation of a large number of centers of crystallization of the eutectic by nucleation would in influence the rate of solidification and thereby the manner of formation and distribution of graphite.

It is conceivable that colloidally dispersed calcium oxide would serve as a nucleus for initiating cell growth or flake development. Another possibility, which deserves consideration, is the existence of calcium carbide or a complex carbide containing calcium in molten iron treated with calcium or calcium alloys. Calcium carbide, because of certain structural considerations, would be ideally constituted for nucleation of graphite flakes, and possibly for nucleation of eutectic cells.

As previously mentioned the writer and his associates have observed a decarburizing action of heavy calcium additions. This can be taken as an indication that a carbide of low solubility is produced in molten iron. Examination of the ladles in which calcium additions or heavy calcium silicon additions have been made discloses a gray compound on the top of the interior surface of the ladle which resembles the familiar "calcium carbide" and which evolves acetylene gas to such an extent that the odor is readily detected and recognized in the foundry where calcium-silicon additions are being made. Finally, a freshly fractured gray iron casting, which has been inoculated with calcium silicon, gives off a faint but unmistakeable odor of acetylene, the gas evolved when calcium carbide is moistened. These observations suggest the formation of calcium carbide in the iron.

Wells[34] has discussed the structure of metallic carbides. Three types are recognized:

1. Interstitial - Ti, Zr, V, Mo, Ta, W
2. Transition - Cr, Mn, Fe, Co, Ni
3. Electropositive metal carbides, similar to ionic crystals, and including carbides of Mg, Al, and Ca.

It is significant that magnesium, aluminum, and calcium, three metals known to be effective in influencing gray iron behavior, are grouped in one class. The ionic crystal nature of the carbides of these elements suggests a high stability, and a low solubility in ferrous melts.

Wells has pictured the structure of calcium carbide, CaC_2, as shown in Fig 18. The unbalanced structure of a growing crystallite of calcium carbide might be ideally suited for adsorption at interfaces between graphite and solid metal, and between graphite and liquid iron with the non-metallic or

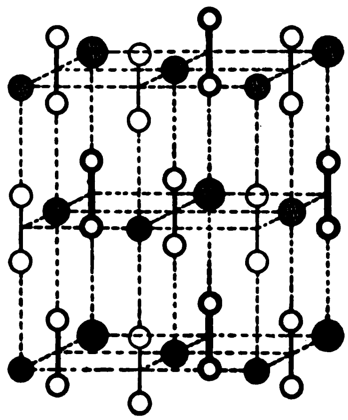

Fig 18. Representation of Structure of Calcium Carbide. After Wells.[34]

graphite rich face on the graphite phase, and the pronouncedly metallic face of the crystallite oriented towards the metal phase. Such absorption would promote formation and growth of the graphite flakes by lowering the surface energy. Wells has suggested that the structure of calcium carbide is unique as it is the only carbide which evolves acetylene.

Hughes[35] has suggested that adsorption occurs in the formation of nodules in magnesium treated irons but does not identify the adsorbed substance.

Buttner, Taylor and Wolf[36] have observed a difference in the tendency of magnesium treated nodular irons in their ability to wet graphite ladles, as opposed to untreated iron which do not wet such ladles, and have suggested an absorption phenomena.

The existence of a new carbide phase, such as calcium carbide, in the alloy system would be expected to alter the phase diagram and the time-temperature curves for the alloy system. Such changes in the time-temperature curves accompanying inoculation have been observed as a shifting of the eutectic arrest to a higher temperature, but this change has been attributed to a nucleation effect which prevents undercooling. The writer has discussed discrepencies in this conception at some length (refer to page 21) and has pointed out that the displacement of the time-temperature curve is not necessarily a matter of undercooling but may be due to other causes.

The existence of a new carbide either simple calcium carbide or a more complex carbide may well account for the observed displacement of the time-temperature curves to a higher temperature. Hume-Rothery[37] has discussed the elevation of the eutectic temperature by the formation of intermediate phases of increasing stability in a series of alloys. The possibility of the active metals influencing the phase diagram and the time-temperature curves deserves consideration and further investigation. However, one serious objection may be advanced to this hypothesis - the extremely small amount of calcium and aluminum contained in the various grades of ferro-silicon which have some value as inoculants. The data of page 48 on the effectiveness of low and high alloy ferro-silicons shows that the high active metal ferro-silicon (2.20 Al and .46% Ca) has appreciable value as an inoculant. With an addition of the inoculating alloy of .55%, which contains a total active metal addition of only .0138% to the iron, it is apparent that the amounts of aluminum and particularly of calcium involved are extremely small, and certainly this raises some question about the ability of such small amounts to produce a perceptible change in the time-temperature curves. The alterations in the time-temperature curves reported by Eash[2] (see Fig 7) were produced by ferro-silicon of unstated composition. Nevertheless, we are compelled to attribute the effectiveness of ferro-silicon to the contained active metals in the absence of any effect of additions of purified silicon or of a silicon alloy relatively low in active metal content.

In completing the discussion of these experiments attention should be called to the low values obtained for the transverse strength of certain of the blank irons of the data reported by Khan.[28] Referring to page 53, Tables 15 and 16, it is found that iron T12 B1-5 shows a transverse strength of 2202 pounds, which is far below the average for similar untreated irons of this report. Other irons of Khan's report show similar low values and render some of the data of his report questionable, particularly when a direct comparison of calcium treated ladles with ladles from the same heat was not possible because of the decarburizing action of the larger calcium additions. Irregularities of properties of these irons can be attributed to variations in temperature and time at temperature, and to the possibility of a critical temperature at which there is a sharp drop in properties and a sudden increase in the degree of abnormality of the irons.

That uninoculated irons are likely to show variations in properties which cannot be explained on the basis of composition is evident from other reports in the literature. Adams[38] has made a survey of the correlation of microstructure, analysis, and properties of commercially produced irons and has reported a wide variation in properties for irons of inappreciable variation in microstructure and composition. As an example data from his report is given for two irons, each of which show D graphite distribution at the surface, in Table 32 below:

Table 32

Iron	C	Si	Trans
100	2.83	2.13	2710
210	2.86	2.15	2215

Other data in the Adams report show similar wide variations. In the case of the irons described above the difference in properties was ascribed to a small variation in flake size at the immediate surface of the casting.

That superheating is detrimental to the properties of gray iron has long been understood. This matter has been investigated by Seffing and Surls[5], Schneble and Chipman,[6] and Lorig.[30] Although the conclusion that superheating is detrimental is accepted by gray iron metallurgists generally, exact information regarding this phenomena is lacking because of the failure of the several investigators to control the composition changes in carbon and silicon which accompany superheating. In the report by Lorig the variations in carbon content exceed .20% and in that by Schneble and Chipman the variation is as much as .37% C. These variations in compositions make it difficult to interpret the data, and these papers have been critisized extensively in the literature. More exact data is required on this important subject, and better means of control of composition and temperature in commercial melting units are necessary for facilitating gray iron research.

In the work conducted independently by the writer very careful attention to time and temperature control was given with the degree of success evident in the data of Table 2, page 31. As previously noted, the uninoculated irons are particularly eratic in their chilling tendency.

The irons melted in the experiments reported by Khan were produced with different pig irons than those employed for the irons of this report. This may account in part for the tendency towards low values for the blank irons of the previous report. Morrogh and Williams[3] have ascribed such variations in tendency to produce D graphite in pig irons to variations in titanium content.

In this work the effect of the inoculating substance could have made more spectacular by reducing the properties of the blank irons by higher superheating temperatures and longer times at temperature. However, the writer deemed it advisable to conform more closely to commercial practice. High heating temperatures promote composition changes, irregularities in properties, and undue lining wear, and the advantages of the high temperatures have yet to be demonstrated.

The adverse effects of superheating have been attributed to 1) the solution or distruction of nuclei, and 2) to an increase in the amount of dissolved oxygen, hydrogen, and nitrogen. Since inoculants are capable of correcting the bad influence of superheating on microstructure and properties, any successful theory of inoculation must be related to the effects of superheating. Boyles[1] has claimed that a certain optimum amount of hydrogen is essential to the formation of normal structures in iron, and many others have discussed the possible effects of oxidation. The formation of oxides,nitrides, and hydrides of calcium and other metals, and their possible influence on behavior provide interesting material for speculation.

V Summary and Conclusions

A survey of the literature has revealed that silicon is regarded as the essential constituent of gray iron inoculants, that no satisfactory theory for the inoculation mechanism has been proposed, and that comparitive data on the relative effectiveness of the various commercial inoculants are lacking. Accordingly a general investigation has been undertaken in which commercial inoculants and the elements occuring in these alloys have been compared as to their effectiveness as a step in the direction of formulating a theory and of providing data of practical value regarding the most effective inoculating proceedure.

This investigation has indicated that the element silicon is not effective as an inoculant. Data has been acquired which shows that the inoculating power of alloys increases with the aluminum and calcium contents. It has been shown that aluminum is particularly effective in reducing chilling tendency, and that calcium is effective both in decreasing chilling tendency and improving graphite distribution and the mechanical properties of high strength gray iron.

The most effective of the commercial inoculants has been established as calcium-silicon. The advisability of using larger quantities of the inoculating alloys than is generally recommended is demonstrated.

Observations have been made which indicate that calcium forms a carbide in molten iron. The literature has disclosed that calcium is unique among the elements found in inoculating alloys in two respects: 1) its free energy of oxide formation under standard conditions is the lowest of the several elements and 2) its carbide has a structure believed by chemists to be different from that of other active metal carbides. The possibility of formulating theories on the basis of deoxidation and of carbide formation is discussed.

Specific conclusions and observations from this report are:

1. The element silicon is not effective as an inoculating agent.

2. Silico manganese, which is relatively free of calcium and aluminum, is not effective as an inoculant.

3. The inoculating ability of various commercial grades of ferro-silicon increases with the calcium and aluminum contents. Low calcium grades have very little effect.

4. Silicon-manganese-zirconium alloys containing somewhat more calcium than is found in commercial ferro-silicon are more effective than ferro-silicon.

5. The most effective inoculant employed in these experiments is the calcium-silicon alloy with approximately 30% of calcium.

6. Although aluminum is a very powerful chill reducer, its addition to cast iron does not promote type A graphite distribution.

7. Metallic calcium additions to the ladle bring about marked improvements in properties and graphite distribution

of cast iron. Calcium is superior to all other inoculating agents tested in these experiments, with the exception of calcium-silicon, when added in the amount of approximately .4%.

8. Metallic calcium is effective in reducing the chilling tendency of cast iron.

9. Metallic calcium is effective in reducing the cell size of cast iron microstructures.

10. Calcium additions effect a reduction of the carbon content of molten iron.

11. Acid and basic melting conditions are equivalent in their effects on gray iron melts.

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