THE EFFECT OF LADLE ADDITIONS OF ALUMINUM, CALCIUM, SILICON, AND GRAPHITE ON THE EUTECTIC SOLIDIFICATION, MICROSTRUCTURE, AND PHYSICAL PROPERTIES OF HYPOEUTECTIC GRAY CAST IRONS

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Howard L Womochel
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By

DENTON DELBERT MCGRADY

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ABSTRACT

A study was made of the relative effectiveness of pure aluminum, calcium, silicon, and graphite as inoculants for gray cast irons of a nominal composition of 2.85% carbon, 2.25% silicon, 0.90% manganese, 0.17% phosphorus, and 0.07% sulfur. Cast irons melted in an indirect-arc rocking furnace were inoculated with aluminum and calcium and compared to untreated irons of identical analysis. Comparative data are included on graphite distribution, chemical analysis, cell size, chill depth, transverse strength, deflection, and triangular resilience.

Cast iron melted in a high frequency induction furnace were poured into dry sand molds and time-temperature solidification curves automatically recorded for untreated iron and for irons inoculated with 0.6% aluminum, 1.0% calcium, 0.55% silicon, and 0.5% fine graphite. Comparative cooling curves are presented for the induction furnace irons along with associated data on physical properties, microstructure, and chill depth.

Small wedge-shaped castings from a blank iron and from an iron inoculated with calcium were quenched into cold water at the start of the eutectic formation and the resulting microstructures studied for difference in primary dendrite size and distribution.

The following general observations and conclusions are made.

(1) The use of aluminum as a ladle addition caused a marked reduction in chill, but had very slight or negligible effect on graphite

distribution and no effect on physical properties. Cell size was not changed by the late addition of aluminum and the amount of carbon and sulfur in the cast iron remained the same. Aluminum raised the temperature of the initial formation of the eutectic by about 50°F. on the average. The microstructure showed largely type D graphite. (2) Cast irons inoculated with 0.55% pure silicon were not significantly different from the corresponding blank irons. (3) The use of 0.5% of fine graphite as an inoculant raised the temperature of initial eutectic formation by about 60°F. on the average. (4) The late addition of 1.0% of pure calcium metal to the ladle resulted in a cast iron that contained a large proportion of type A graphite, that showed a marked reduction in chill and in cell size, and that exhibited a definite increase in physical properties. (5) The use of ladle additions of calcium raised the temperature of initial eutectic formation by 60-80°F. as compared to a corresponding blank iron. The calcium inoculated irons showed eutectic cells forming from a large number of nuclei as compared to blank irons which contained relatively few centers of eutectic cell formation. The addition of calcium decarburized and desulfurized the molten cast iron and evidence was obtained to indicate that the decarburization was caused, at least in part, by the formation of calcium carbide. The size and distribution of the primary dendrites of austenite was not appreciably changed by inoculation with calcium. (6) Strong evidence was obtained that inoculation is a nucleating process and this study points to either a carbide or a sulfide as the nucleating agent. (7) The elimination of undercooling does not necessarily result in an improvement in graphite distribution. (8) The rate of growth of the eutectic cells is an important factor in graphite shape and distribution.

(9) Successful inoculation is accompanied by an elevation of the range of eutectic temperature and by a decrease in cell size. (10) The spacing of the primary dendrites, although it varies somewhat in normal and abnormal irons, cannot be taken as the principal cause of variation in graphite distribution. (11) A decrease in carbide stability as measured by chilling tendency is not necessarily related to graphite distribution. (12) The possibility exists that a group of elements related to calcium may also be effective as inoculant for gray cast iron.

Howard L Womochel

Approved, Major Professor

PREFACE

This study is a continuation and extension of the general problem initiated by Womochel et al with regard to the relative effectiveness of various active metals and other elements as inoculants for gray cast iron. Because of the complex nature of the alloy and the consequent large number of variables, the literature contains very little fundamental information about this topic.

This research was undertaken in order to better determine the nature of the time-temperature solidification curves, particularly in the region of the eutectic transformation. Parallel observations of microstructure and physical properties were also made.

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INTRODUCTION

Cast iron has served the needs of mankind since the Chinese produced cast-iron tools for the farmer and wood-worker some 2,200 years ago. Howe (24) writes that the period of cast-iron metallurgy began in the 14th century with the production of ornamental castings in Sussex. Vannoccio Biringuccio, (6) writing in the first edition of his "Pirotechnia" published in 1540, reports a process of steelmaking in which masses of wrought iron were immersed in a bath of molten cast iron. Biringuccio writes..."blooms weighing 30-40 lbs. each of iron... are put while hot into this bath of molten iron...then keep it in this melted material with a hot fire for four to six hours..." By the end of the 16th century cannon weighing as much as three tons were cast. In 1735 Darby showed how to make cast iron by means of coke, thus replacing the previously used wood charcoal. Thus for six centuries foundrymen have made iron castings to supply man's requirements for domestic and agricultural use - and more recently for engineering purposes.

With the exception of steel ingots, cast iron articles constitute the largest tonnage of castings made of any metal or alloy. The majority of these articles are made of grey cast iron. The casting method is admirably suited to making products of intricate nature, and the alloy itself is readily machinable. The products of the iron foundry vary from pipe fittings to automotive cylinder blocks, and their weight varies from a fractional pound to more than 50 tons.

Following the early works (25) of such pioneers as Sorby, Martens, Tschernoff, Brinell, Osmond, and Hadfield before the turn of the 20th century, and the studies of Howe, Sauveur, Stead, Campbell and others in the early 1900's, cast iron was subjected to increasingly intensive study as to microstructure and associated physical properties. By 1910 Moldenke (35) had written a book about malleable castings.

Patents (29) on the late addition of small amounts of certain metals and alloys were granted in the United States about 1920. These late-addition materials, or inoculants, were usually added in relatively small amounts to the molten metal in the ladle just before pouring the castings. The improvements in graphite form and physical properties were much greater than would logically be expected on the basis of simple alloy effects or slight change of chemical composition alone.

Perhaps the high point in the study of the effect of inoculants on graphite distribution in gray cast iron came in 1948 with the simultaneous discovery in England and the United States of "ductile" cast iron. This new engineering material, which has graphite present in the form of nodules or spherulites rather than as the usual flake form, has been described as the outstanding foundry development of the century.

Certainly the past twenty years, and particularly this decade, has been a period of fruitful work in explaining some of the basic transformations in cast iron. Hultgren (26) states, "The question of whether the graphite which is observed in cast iron after solidification is formed directly from the melt or as a decomposition product of an

initially precipitated solid carbide constituent has been the subject of experiment and discussion for a considerable time. For the primary graphite in hypereutectic irons, and also for the coarse eutectic graphite, formation directly from the melt now seems to be the generally accepted mechanism. This is not so, however, for the fine graphite, nor for the spherulitic graphite produced during cooling under special conditions."

Along the same line of thought Morrogh (33) has written, "The graphite phase in gray cast irons can be obtained in the flake form, in the undercooled form, and as spherulites. The conditions necessary for the formation of these structures are well known, but the fundamental reasons for these modifications are not established. The view that the flake or lamellar form of graphite in gray castiron forms as a hypereutectic or eutectic constituent directly from the melt seems to be widely accepted. It is, however, not easy to see why the graphite originating from a eutectic transformation should be so unlike a typical eutectic constituent in appearance. The undercooled form of graphite presents even more problems."

In discussing the decomposition of cementite during the solidification of cast iron, Berman and Kondic (5) state, "Many methods of producing commercially different forms of graphite in cast iron are known, but no generally acceptable explanation has been offered for the mechanism of graphite formation, nor are the reasons for obtaining different cast-iron structures under certain conditions fully understood.... There is still disagreement on whether graphite forms directly from the eutectic liquid or is a product of the decomposition

of cementite.... Any general theory of graphite formation in cast iron must be based on the solution of this problem."

It thus appears that the methods and conditions for altering the form of the graphite in cast iron are reasonably well known, but that considerable work yet remains before establishing a satisfactory understanding of the basic reasons for these modifications of graphite based on fundamental principles and concepts. A comprehensive survey and critical review of various theories explaining the mechanism of inoculation of gray cast iron has been presented by Womochel (48) and need not be repeated in detail here.

The purpose of this investigation is to make a fundamental study of the effect of late additions of aluminum, calcium, silicon, and graphite on the eutectic solidification, microstructure, and physical properties of gray cast irons.

II.

GENERAL HISTORICAL SURVEY

Since the earliest work on the iron-carbon diagram (1890-1900) the general mechanism of freezing of cast iron has been known. The phenonemon of graphitization was the point in question and the existence of cementite and graphite together in the same alloy was the condition demanding explanation.

Piwowarsky (37) reports that as early as 1906 Benedicts (4) had suggested the possibility of the formation of flake graphite from the solidified cast iron. Howe concurred with this concept during the years 1909-1911. In his book published in 1916 Howe (23) used the general idea of the stable and metastable equilibria and described quite clearly the sequence of events occuring during the freezing of iron-carbon alloys without, however, giving details as to the manner in which graphite flakes were formed. In 1906 Wust and Petersen (47) had shown that the carbon content of the eutectic is lowered by the presence of silicon and in 1913 Sauveur (39) plotted a diagram based on this work which related the silicon percent to the percent of carbon in the eutectic. (A 2% Silicon iron is shown as having a eutectic at 3.8% of carbon). Howe (25) states that he considers the work of Tiemann (42) as being the first to clearly identify primary cementite in white or hypereutectic cast iron. Between 1915 and 1931 the work of Ruer and Goerens (38), Goerens (15), and Hanemann (18, 19), based on a study of the thermodynamics of both the iron-carbon and iron-iron carbide system, showed that the possibility existed that under certain conditions graphite in gray cast iron could form directly from the melt.

Honda and Murakami (22) and Honda and Endo (21) wrote during the period 1920-1929 that graphite in gray cast iron is a result of decomposition of the carbide component of the eutectic. In 1924 Heyn and Bauer (20) studied the variation in graphite content of three cast irons containing different amounts of silicon and concluded that the graphite form was dependent on cooling rate and that the greatest part of the graphite had formed during the eutectic halt, not only for the low-silicon, hypoeutectic iron but for the eutectic and the hypereutectic cast irons as well. As research on the subject of graphitisation was continued two schools of thought gradually evolved - one maintaining that a graphite-austenite eutectic formed directly from the melt, and the other that cementite-austenite eutectic always formed first and that the formation of graphite was a secondary reaction. Hurst (27) writing in 1926 presented the arguments on both sides and pointed out the unsatisfactory state of knowledge at that time and the need for additional research on the topic. Hanemann, (18) as a result of quenching experiments published in 1931, concluded that graphite formed directly from the melt and he published two photomicrographs one of which showed nests of graphite flakes surrounded by ledeburite and the other a single graphite flake extending at each end into ledeburitic areas. Boyles (8) in 1937 showed by a series of quenching experiments that graphite is not present before the eutectic solidification begins. From studies made in 1924 by pouring silicon containing iron in a thin stream into cold water, Northcott (36) concluded that the absence of elemental carbon in the samples indicated that for hypoeutectic cast irons the graphite forms from the carbide phase, not disproving, however, the possibility of direct graphite formation. Hanemann (18) in 1931 and later studied the time required for decomposition of cementite, and concluded that relatively long times (hours) were required even at temperatures above 1000°C. More recent work (5) has indicated that as little as four minutes may be needed at temperatures close to the eutectic.

The discussion as to the mechanics of formation of the various types of graphite possible in grey cast iron has continued until the present day. Recently (1954) Morrogh (33) published work supporting the carbide decomposition hypothesis to explain type D graphite and in the same issue of the journal Hultgren, Lindblom, and Rudberg (26) presented data to support the idea of direct formation of fine graphite from the melt.

Ladle additions to improve the properties of cast iron are reported in the literature as far back as 1900 in the work of Wust (46) who studied lead, zinc, tin, aluminum, sodium, and magnesium additions as related to degassing, purifying, and improvements in density. In 1908 Moldenke (34) investigated the use of ferrosilicon, calcium, and vanadium and recommended these materials for deoxidizing and increasing the density of cast iron.

It has been known since about 1920 that late additions of small amounts of ferrosilicon, calcium-silicon, and other "inoculants" to the ladle just previous to casting can, under proper conditions, greatly

improve the graphite structure of cast iron (41). The original U.S.A. patent (29) to A. F. Meehan, which was granted in 1922, along with later patents and additions, covered in general the late additions to white and grey cast iron of calcium-silicon, calcium, and other alkaline earth materials either separately or in combination.

An extensive literature about the mechanics of graphite formation and hypotheses to explain the effects of inoculation has developed in the past 30 years.

Outstanding work based on a fundamental approach to understanding the formation of graphite in grey cast iron and the effect of inoculants has been published during the past decade. A series of papers by Alfred Boyles was brought up to date and expanded into a book (10) published by the American Society for Metals in 1947. The research and discussion of Eash, Schneidewind, D'Amico, MacKenzie, Lownie, Loria, and many others has been of great value. The research of the British Cast Iron Research Association (BCIRA) as presented in papers by Morrogh, Norbury, Williams, et al is of excellent quality. The Royal Institute of Technology and the Swedish Institute of Metals Research in Stockholm have contributed important data by authors such as Hultgren, Lindblom, and Rudberg. The work of Wittmoser, Ward, Pelsel, and Piwowarsky continues in Germany, and that of de Sy in France to mention only a few.

The discovery in 1948 that late additions or ladle inoculation of low-sulfur gray cast iron with cerium or magnesium could produce a nodular graphite form has not only created a new engineering material but has served to focus attention and intensify interest in recent years on fundamental studies of the inoculation phenomenon.

III.

DISCUSSION OF FACTORS AFFECTING GRAPHITIZATION

The physical properties of gray cast iron are largely determined by the character of the matrix proper and by the size and distribution of the flakes of graphite throughout this matrix. The approach to the problem of graphitization in cast iron has customarily been on the basis of binary or ternary equilibrium diagrams involving iron, carbon, and silicon. Cast irons are known, however, to behave much differently from pure alloys. Indeed it may well be that there is need for additional careful study of the iron-carbon-silicon alloy system.

Figure 1 shows the classification chart for graphite distribution in gray cast iron as standarized by the American Foundrymen's Society and the American Society for Testing Materials. Because of superior physical properties, a uniform distribution and random orientation, as illustrated in type A, is usually preferred. However gray cast iron may also have graphite present in other forms as illustrated by types B, D, and E. A cast iron having a type D graphite pattern has inferior properties to an iron of the same chemical analysis, but with type A graphite.

Figure 2 shows a section of the iron-carbon-silicon thermal equilibrium diagram at 2.0% silicon. Cast irons display the phenomenon of metastability, by which the solidification may proceed in either the stable iron-graphite system or in the metastable iron-iron carbide system. The effect is no doubt caused by the presence of several elements with rather diverse influences on solidification or freezing.

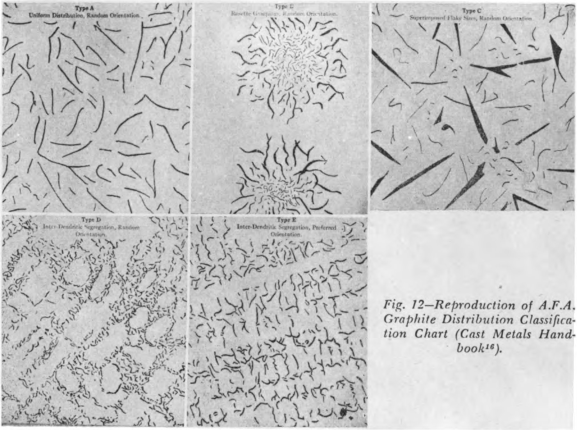


Fig. 12—Reproduction of A.F.A. Graphite Distribution Classification Chart (Cast Metals Handbook[16]).

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

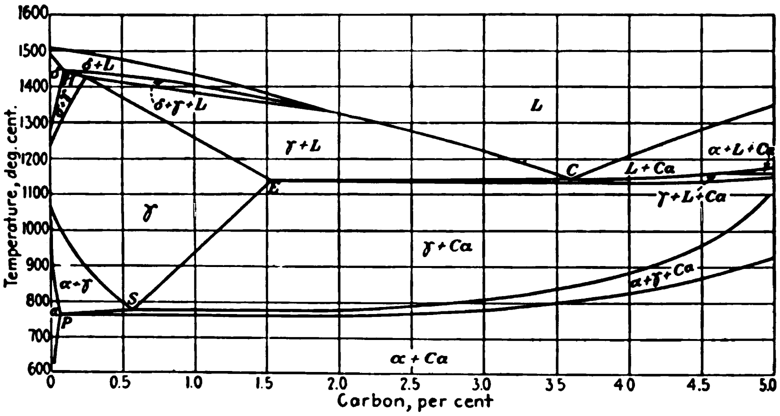


FIG. 4—IRON-CARBON DIAGRAM IN PRESENCE OF 2.00 PER CENT SILICON (GREINER, MARSH AND STOUGHTON).

Figure 2. Section Through the Ternary Iron-Carbon-Silicon Diagram at 2.0% Silicon.

The mere presence of a stable graphite phase in gray cast iron is not sufficient to determine or control its quality. It is, rather, the size, shape, distribution, and orientation of the graphite masses which most concerns the metallurgist, for these are factors basic to the quality and strength of his product.

Knowledge of the factors that influence graphitization is inadequate at present. Among some topics which might well merit additional study and discussion Altekar (30) has included:

1. Mode of occurence of carbon in molten cast iron.
2. Possibility of bringing about molecular groupings in the melt.
3. Mechanism of formation of carbides.
4. Mechanism of stabilization of carbides by the presence of carbide-stabilizing elements.
5. Mechanism of decomposition of carbides, with and without the presence of graphitizers.
6. Control of the freezing of the eutectic.
7. Phenomenon of undercooling in cast irons.

The achievement of nodular graphite in as-cast iron as the result of inoculation or late additions to the ladle, has had a most helpful effect in attracting the attention of research workers and has resulted in a large number of diverse explanations for the microstructures obtained. No overall comprehensive explanation has been offered to explain the several variations of graphite form in gray cast iron.

It would seem logical that the various types of graphite bear a definite relation to each other. The conditions that change one graphite type to the other can perhaps be classified into two main parts—— thermal factors and chemical factors. Manipulation of the several alternatives under each of the main factors could give any size, distribution, and orientation of graphite flakes.

A. CHEMICAL FACTORS AFFECTING GRAPHITIZATION

Each element present in cast iron is effective, to a greater or lesser extent, in influencing the formation of graphite in cast irons. However, the effect of a particular element may be increased or minimized by the presence of some other element or group of elements. Thus no classification of these elements based upon their individual effects is entirely rigorous.

The work of Boyles (10) and Piwowarsky (37) is prominent in the considerable literature that now exists on this subject. Boyles, by means of a series of quenches from successively advancing stages of solidification, was able to follow closely the initiation and progress of graphitization during eutectic freezing. The photomicrographs in Figure 3, from the work of Boyles, well illustrate the mechanism of solidification of hypoeutectic cast irons and may be summarized as follows:

1. Primary dendrites of Austenite solidify from the liquidus temperature down to the range of temperature of the eutectic.
2. Crystallization of the eutectic begins at centers which grow outward spherically in all directions and form a cell-like structure.
3. Constituents formed during the formation of the eutectic occupy the interstices of the dendrites. Thus graphite flakes

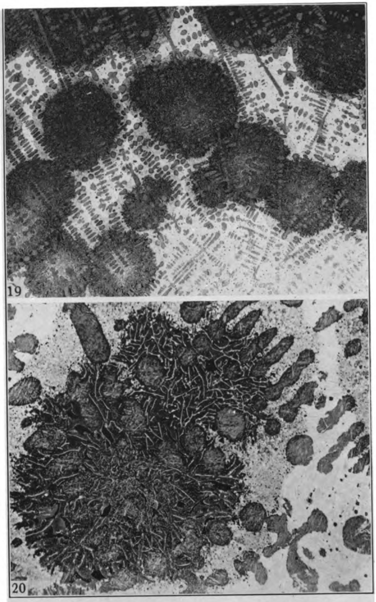


Fig. 19—Sample No. 20. Quenched from 2010° F. Heat-tinted. × 20.
Fig. 20—Detail of Structure in Fig. 19. Heat-tinted. × 100.

Figure 3. Microstructures Obtained by Quenching Partly Solidified Hypoeutectic Gray Cast Iron. Heat Tinted. Upper Picture x20. Lower Picture x100. After Boyles (10).

are restricted by the amount, size, and orientation of the primary dendrites of austenite.

4. Segregation takes place in two ways---first, between the primary dendrites and the liquid, and second, in the solidifying eutectic between the core and the radially growing boundary.
5. Graphite flakes start to appear with the gradual freezing of the eutectic and the flakes increase in size and number down to the point of complete solidification.

In high purity Fe-C-Si alloys the amount of both carbon and silicon profoundly influences graphitization. Larger amounts of carbon not only increase the amount of eutectic at the expense of primary austenite, but also increases the readiness and amount of graphitization. Silicon is generally considered to replace one-third of its own weight in carbon and to lower the solubility of carbon in austenite.

The presence of silicon increases the eutectic temperature and extends the range of temperature during which the eutectic freezes. Although the presence of silicon facilitates the process of graphitization, it is probably not indispensable.

It is readily seen that carbon and silicon together determine the relative amounts of primary austenite and eutectic and that the influence of those elements that segregate into the eutectic is reduced for the higher compositions. The presence of more primary austenite leads to a very restricted interdendritic spacing for the formation of graphite flakes. For cast irons containing higher amounts of carbon and silicon, and consequently fewer primary dendrites, the graphite flakes are characterized by random orientation and comparatively unhindered growth.

Boyles found that the graphitization of pure Fe-C-Si alloys always resulted in type D graphite because of the strong tendency of the eutectic to graphitize, and he showed that it was the presence of sulfur, manganese, and hydrogen that made the commercial cast irons solidify so differently from the pure ternary alloys. Sulfur and hydrogen are carbide stabilizers and the introduction of either one of them into pure alloys resulted in an increase in size of graphite flakes. There was an optimum carbide stabilizing action which resulted in a maximum flake size, and additional concentrations of sulfur or hydrogen thereafter decreased flake size and eventually resulted in white cast iron.

Supposedly the carbide stabilizers acted to increase flake size by their ability to delay graphitization by making the carbide more persistent. This prevented a rapid graphitization. Too great a carbide stability however sharply reduces the availability of carbon for the formation of flake graphite. Both sulfur and hydrogen are reported to segregate in the eutectic where they exert all their influence.

Manganese considerably modifies the effect of sulfur. A complex series of FeS and MnS solid solutions are formed. The influence of sulfur on graphitization when thus excluded from the freezing eutectic because of the presence of manganese, is not definitely known.

Thus three elements---sulfur, manganese, and hydrogen---changed the high purity ternary alloys into cast irons. Boyles investigated this trio rather thoroughly and found that their manipulation could produce any type or combination of types of graphite flakes.

Another class of elements are used to affect graphitization. These elements are generally added late as ladle additions and, although added in very small amounts, have the ability to bring about a remarkable change in graphitization. These elements are either graphitizers or carbide stabilizers. Why certain elements stabilize the carbide and others promote its decomposition is still an unresolved question. Bolton (7) has suggested the following possible ways in which a ladle addition may act:

1. It may form a mixed carbide more stable then cementite.
2. It may form a mixed carbide that is very unstable and which may accelerate the decomposition of all carbides.
3. It may affect eutectic carbon concentration.
4. It may affect the eutectic temperature.
5. It may obstruct atomic movement in the matrix.

The effect of some elements on the persistence of carbide is not consistent and some elements which are generally regarded as a carbide stabilizer under one set of conditions may act as a graphitizer under another set of conditions. The influence of boron, bismuth, tellurium and many other elements remains ambiguous.

Boyles observed that the immediate factors that influenced graphite flake size were the rate at which graphite became available and the rate of solidification. By maintaining a constant rate of slow cooling, and varying carbide stability by chemistry, Boyles was able to change the rate of carbon availability and thus obtain a wide range of flake sizes.

Thus it is contended by Boyles, Morrogh, and others that the conditions for the formation of fine graphite flakes can occur in two ways. First, when a very high nucleation rate and a high carbon availability are present, a simultaneous formation of numerous centers of graphitization throughout the melt results in closely spaced, small, underdeveloped flakes of graphite. This contention is justified by the observation that high purity alloys of Fe-Si-C, Ni-C, and Co-C always show finely dispersed graphite, and that this condition persists until a carbide stabilizer in suitable amount is added. The second condition for the formation of small flakes of graphite occurs if an excessive persistence of carbide causes the growth of the flakes to lag behind the advancing front of solidification, whereupon the flakes are pinched off because the rate of solidification exceeds the rate of availability of carbon or of decomposition of cementite. In the case of extreme stability of the carbide it may be decomposed very abruptly at lower eutectic freezing temperatures, or may even persist indefinitely to produce white cast iron.

The stability of carbide is sensitive to thermal treatment as well to chemical variations.

B. Thermal Factors Affecting Graphitization

Thermal factors that operate during the freezing of the melt also affect graphitization during the solidification of the eutectic. Some of these closely interrelated factors are:

1. Superheating temperature.
2. Time at maximum temperature.

3. Pouring temperature.
4. Rate of cooling in the mold.
5. Temperature of start of graphitization.
6. Duration of graphitizing period.
7. Temperature at end of graphitization.
8. Amount of undercooling of the melt.

Superheating of the melt results in a fine type D graphite. Piwowarsky has suggested that superheating causes a breakdown of the molecular carbides in the melt thus greatly increasing the urge to graphitize. Studies by Zapffe (49) and Morrogh (31) have shown that the fine graphite which results from superheating is caused by an increased absorption of hydrogen by the melt.

Perhaps the rate of cooling of the melt and particularly of the eutectic is the most important thermal factor, for it in turn seems to control other conditions such as the temperature at which graphite starts to form, the duration of graphitization, and the extent of undercooling. Generally speaking the greater the rate of cooling, the lower the initial temperature of graphite formation, the shorter the duration and the more severe the undercooling.

A compilation of conclusions about the effect of rate of cooling on graphitization based on the work of Schneidewind (40), Bolton (7), D'Amico (12), Piwowarsky (37), and Morrogh (30) is given below:

1. The rate of cooling affects the temperature of the eutectic arrest. Very slow cooling may result in a eutectic temperature as high as 1200°C (2190°F) whereas with fast cooling it may occur at 1000°C (1832°F).

2. The greater the rate of cooling and the lower the arrest temperature, the shorter the duration of graphitization, and the finer the graphite pattern.
3. The higher rates of cooling result in more severe undercooling.
4. With extensive undercooling the growth of graphite flakes is hindered, possibly by the viscous nature of the melt.
5. Very high cooling rates produce a metastable product.
6. With gradual variation in cooling rate, a gradual and ordered change in the graphite pattern takes place.
7. For a particular iron every type of graphite is formed at a definite temperature. Raising the temperature of graphitization yields longer and coarser flakes whereas lowering the temperature of graphite formation results in finer and more numerous flakes.
8. The eutectic freezing of cast iron can be made to occur over a wide period of time and over an extended range of temperature.

The above conclusions, although compiled from various sources, are in agreement and emphasize the fact that graphitization depends upon time-temperature conditions. From these conclusions it is seen that carbide stability brought about by control of cooling rate progressively decreases flake size. The graphite flakes continue to get smaller until undercooling is sufficient to allow only finely dispersed type D graphite. The limit of undercooling is the complete suppression of graphitization in any form and the formation of white iron.

Eash (13) and Morrogh (31, 33) have shown that type D graphite results from decomposition of carbides immediately after solidification

of a white eutectic. On the other hand Hultgren (26) supports the possibility of direct formation of graphite from the melt by eutectic reaction.

Little information is available about the carbide phase in cast iron. It is evident however, that the persistence of the carbide is a factor of major importance in the process of graphitization.

A study of the literature indicates the possibility that during the freezing of the eutectic either:

1. Direct graphitization may proceed without the formation of a carbide phase. This may be true with high-carbon, high-silicon irons containing only small amounts of stabilizers, or even in the presence of usual amounts of stabilizers when these are diluted by a large amount of eutectic as in near-eutectic alloys. (Hanemann (18); Boyles (9); Piwowarsky (37); Hultgren (26).)
2. The formation of graphite may be preceded by the formation of carbides. (Eash (13); Morrogh (31, 33).)

In summary it may be said that graphitization is greatly affected by the relative persistence of the carbide phase and that this persistence can be altered by chemical variations, by variations in cooling rate or by simultaneous manipulation of both factors. Available evidence indicates that increasing the cooling rate, lowering the eutectic temperature, constricting the range of temperature of eutectic freezing, reducing the duration of graphitization and increasing the persistence of carbides by chemical control, all tend to promote finer graphite flakes in an orderly manner starting with type A and proceeding to type B, E, and D.

IV.

EXPERIMENTAL PROCEDURE

Part A. - Rocking Furnace Heats

The experiments discussed in Part I of this report were made in an indirect-arc rocking furnace of 250 lb. capacity. The cold furnace was charged with pig iron, low-carbon steel scrap, and 27% ferrosilicon. The composition was adjusted immediately after the meltdown by an appropriate addition of 80% ferromanganese, 25% ferrophosphorus, and 50% iron sulfide.

The analysis of the pig iron used was:

%	C	Si	Mn	P	S
Lot 1	4.15	1.18	0.72	0.128	0.039
Lot 2	4.12	1.23	0.88	0.24	0.033

A typical charge consisted of:

110 lbs. of pig iron, Lot 1
43 lbs. of pig iron, Lot 2
61 lbs. of steel plate
12.7 lbs. of 27% ferrosilicon
0.7 lbs. of ferromanganese
0.6 lbs. of ferrophosphorus
0.2 lbs. of iron sulfide

All of the melts were heated to a temperature of 2850°F. An optical pyrometer reading was made through the spout of the furnace. After tapping the heat into 50 lb. pre-heated ladles, the metal was

allowed to cool to the pouring temperature of 2650-2675°F.

The ladle additions of metallic aluminum and calcium were made after securely wiring the active metal to a 1/2 inch diameter steel rod about 6 ft. long which was bent at 90° some 1 ft. from the end. The active metal was then plunged quickly under the surface of the ladle and agitated until all reaction ceased. Blank ladles were treated with a 5 inch length from a similar rod. Some two or three minutes elapsed between tapping the furnace and pouring the molds.

Metal from each ladle was cast into four or five standard 1.2 inch vertical test bar molds. Chill specimens were poured in pairs, either as small wedges or as chill blocks.

The data on physical properties was secured from the transverse breaking load on 18 inch centers and from the deflection. The greatest effect of inoculation is noticed at the surface of castings, the breaking of the unmachined transverse bar is thus a sensitive way of revealing effects of inoculation.

Carbon equivalents (%C + 1/3% Si) of cast irons compared in this paper will usually not vary more than 0.1%. This is a measure of control that compares favorably with that of similar experiments reported in the literature.

The amount of carbon and silicon was determined for each ladle, and the analysis for manganese, phosphorus, and sulfur was made for each heat or, frequently, for each ladle if subject to variation as a result of inoculation. No attempt was made to determine the amounts of active metal retained in the cast iron as a result of inoculation. Work reported in the literature has given residual magnesium and calcium as low as 0.008%. (3) Retention of any considerable amount of active metal is apparently not necessary in order for the effect of an inoculant to be quite pronounced.

Part B. - Induction Furnace Heats

In order to proceed with a second series of heats made in a small 20 kw. induction furnace, it was first necessary to produce some melting stock. To this end the rocking furnace was charged as follows:

90 lbs. of Pig Iron, Lot 1
93 lbs. of Pig Iron, Lot 2
15 lbs. of low carbon steel strip
2.2 lbs. ferrosilicon (27% Si)
1.0 lbs. ferromanganese (80% Mn)
0.22 lbs. iron sulfide (50% S)

The analysis of the pig used was:

Analysis Pig Iron

	% C	Si	Mn	P	S
Pig Iron, Lot 1	4.15	1.18	0.72	0.128	0.039
Lot 2	4.22	1.67	0.48	0.19	0.018

The 200 lbs. of metal in the rocking furnace was poured into four 50 lb. cylinders about 4 inches in diameter and 20 inches long. The analysis of the slugs thus made was found to be:

	% C	Si	Mn	P	S
Slug 3-Top	3.67	1.56	--	--	0.059
Bottom	3.66	1.58	0.92	0.129	0.050
Slug 4-Bottom	3.66	1.51	0.845	0.152	--
Slug 5-Bottom	3.50	1.78	--	--	--
Slug 6-Bottom	3.57	1.72	--	--	--

Sections were cut from the large cylinders of melting stock in order to charge the induction furnace. The cold charge to the induction furnace consisted of all of the ingot iron and ferrosilicon, and part of the melting stock. A typical induction furnace charge of 31 lbs. consisted of:

12.06 lbs. slug 3
12.06 lbs. slug 4
1.30 lbs. ferrosilicon (27% Si)
5.60 lbs. ingot iron punchings
0.09 lbs. ferromanganese (80% Mn)
0.06 lbs. ferrophosphorus (25% P)
0.03 lbs. iron sulfide (50% S)

As soon as the original charge had melted sufficiently, the remaining melting stock was added. Additions of the ferromanganese, ferrophosphorus, and iron sulfide was made as soon as complete melting of all the charge had occurred. All heats were brought to a temperature of 2850°F. and were then poured into a small hand ladle. The blank heats each had five inches of iron rod stirred into them until melted, and the inoculated heats had the active metal added as described previously. Pouring temperature was 2650°F. by optical pyrometer measurement. There was poured from each induction heat two wedge chills, two block chills, and three standard transverse bars as in Part A. In addition a small cylinder one inch in diameter and five inches long was poured. The cylinder contained a pair of chromel-alumel thermocouples and a dual record was made on the strip-chart of a high speed electronic recorder of the progress of solidification as indicated by latent heat evolution at both thermocouples. Chemical analysis of the various irons was made as in Part A.

Part C. - Physical Properties

1. Transverse Strength

The dry sand molds used in this work were made from a well-mixed aggregate of lake sand, cereal, water, and linseed oil. The core sand molds were baked at 475°F. for four hours. The transverse bars were washed with a non-carbonaceous silica slurry and again baked as before. The other molds used were not washed.

Standard transverse bars 1.2 inches in diameter were poured from each heat. The bars were cast in vertical core-sand molds and were wire-brushed before testing on 18 inch centers. The diameter of the bar and the deflection at the breaking point was measured. From these data the corrected breaking load was calculated and the triangular resilience determined as 1/2 (corrected breaking load) (deflection).

2. Chill Tests

(a) Wedge chills

Two wedge chill specimens per heat, each about 4 x 2 x 1/2 inches, were poured into core sand molds. The pair was broken at a similar section and chill data based on the average depth of clear chill (white) and total chill (white and mottled) measured in 1/32 inch units.

(b) Block chills

Two block chills each about 4 x 2 1/8 x 3/4 inches, were poured for each heat into a core sand mold containing a heavy metal chill face. Pairs of block chills were broken at comparable positions and chill data taken as the average of clear and total chill in 1/32 inch units.

3. Photomicrography

(a) General

Small specimens were taken near the fracture of representative transverse bars so that the microstructure could be studied from the surface into the center of the bar. The samples were processed on coarse and fine grit dry abrasive paper followed by a fine abrasive used in water suspension on a wax wheel. Final polish was on a silk cloth using AB Metpolish #1 for hard metals. The etchant was either 2% nital or 4% picral. The etched samples were dipped into boiling water and immediately dried.

(b) Cell size

Cell size was measured at 25x by comparison of a heavily etched sample with a chart offered by Adams (1). This procedure requires a heavily etched sample in which the cell size is outlined by the lighter areas of steadite.

(c) Heat tinting

Certain samples were given a final polish and a very light etch and were then placed in an electrically heated muffle furnace at 400-500°F. for 1 to 8 hours. Time and temperature of heat tinting were necessarily varied for each different sample.

4. Temperature Measurement

Cooling curves were recorded on the strip chart of a high speed electronic recorder. The recorder had two scales which were calibrated in millivolts and which operated independently each with its own amplifier system at a response rate equivalent to some 1000°F. per second.

Two chromel-alumel thermocouples of 22-gauge wire were attached to the recorder by means of extension lead wires. The thermocouples were insulated by a fine-bore porcelain tube and were enclosed in a somewhat larger tube of fused silica (Vitreosil). The welded hot junction of the thermocouple was protected by a thin layer of alundum refractory cement which was applied wet and then baked at a bright red heat.

The recorder and thermocouple were calibrated by comparison with the freezing point temperature of high purity zinc, aluminum, and copper. The recorder was also compared at intervals to a portable millivoltmeter potentiometer which had been checked with the melting point of pure electrolytic copper using a noble metal thermocouple of platinum - platinum 10% rhodium for which a bureau of standards certificate of calibration was available. Reproducible accuracy of the different chromel-alumel thermocouples, based on the noble metal thermocouple, the portable potentiometer, and the automatic high-speed recorder, was taken as ± 5°F.

5. Chemical Analysis

Chemical analysis of the various irons for carbon, silicon, manganese, phosphorus, and sulfur was made by standard methods.

V.

DISCUSSION OF EXPERIMENTAL DATA AND RESULTS

Part A

Rocking Furnace Irons

1. Aluminum Additions.

In order to determine the effect of aluminum as a ladle addition, two ladles of molten cast iron were inoculated with 0.07% and 0.5% aluminum respectively and two additional ladles were untreated to serve as blank irons.

A tabulation of results of heat T-34 is given in Table 1. The chemical analysis of the iron was not altered by the addition of aluminum. A comparison of the two blank irons and the two irons inoculated with aluminum indicated that no significant changes occurred in the transverse strength, deflection, or triangular resilience. However, for the iron inoculated with 0.5% aluminum, therewas a marked drop in clear and total chill. A cell size of 2-3 was found for both the aluminum treated irons and the blank irons.

A study of the microstructure of the transverse bar near the point of fracture revealed that the iron inoculated with 0.07% aluminum had a similar microstructure to the blank irons. Both irons showed type D and E graphite at the surface, with type A increasing in amount toward the center of the bar. The ladle addition of 0.5% aluminum resulted in a more abnormal microstructure than found in the corresponding

TABLE 1

Data on Aluminum Inoculation of Rocking Furnace Iron T34

Iron No.	Addition %	Analysis %					Trans. lbs.	Defl. in.	Resl.	Block Chill 1/32 inch	Cell Size
		C	Si	Mn	P	S					
T34-1A	0.5 Al	2.82	2.27	0.82	0.12	0.064	2450	0.194	238	2-8	2-3
T34-2A	0.07 Al	2.84	2.28	0.87	--	0.062	2465	0.211	260	11-30	2-3
T34-1B	Blank	2.84	2.33	0.86	0.12	0.064	2478	0.212	260	8-31	2-3
T34-2B	Blank	2.82	2.31	0.87	--	0.061	2455	0.212	258	14-33	2-3

blank iron, and the inoculated iron was definitely type D and E graphite at positions on the diameter where the blank iron was partly type A mixed with type D and E. Both samples tended toward type A graphite at the center. A study of the microstructure at 500x showed no apparent difference in matrix structure. Both samples showed little or no ferrite associated with the type D and E graphite.

2. Calcium Additions.

A study of the effect of calcium as an inoculant was made in heats T35, T39, and T40. A 200 lb. heat of cast iron was melted in the rocking furnace using the same charge as for heat T34. Results for the ladle addition of 0.8% calcium as compared to the blank iron are shown in Table 2. A loss of carbon resulted from the addition of calcium metal to the molten cast iron. A marked decrease in chill was also obtained.

An additional study of calcium inoculation was made in heat T39. There was added 0.75% and 1.0% calcium respectively to a pair of ladles for comparison with a pair of untreated ladles from the same heat. Results are shown in Table 3. Again the addition of calcium served to decarburize the iron and produced a marked decrease in chill. Heat T40 was run to obtain information about the effect of a small addition of 0.1% and to secure some blank irons of comparable analysis to the calcium inoculated irons of heat T39. The addition of the smaller amount of 0.1% calcium resulted in only a small decrease of carbon in the iron as shown in Table 4. A definite drop in chill was obtained.

Table 5 presents data for comparison of three cast irons inoculated with different amounts of calcium with two blank irons of similar analysis. Iron T39-1C, which was inoculated with 1.0% calcium, showed a microstructure

TABLE 2

Data on Calcium Inoculation of Rocking Furnace Iron T35

Iron No.	Addition	%C	%Si	%S	Block Chill 1/32 inch
T35-C	0.8% Ca	2.68	2.40	0.063	4-8
T35-B	Blank	2.78	2.38	0.060	18-33

TABLE 3

Data on Calcium Inoculation of Rocking Furnace Iron T39

Iron No.	Addition %	Analysis % C	Si	Mn	P	S	Block Chill 1/32 inch
T39-1C	1.0 Ca	2.72	2.46	0.87	0.19	0.042	2-3
T39-2C	0.75 Ca	2.74	2.48	0.88	--	0.040	4-6
T39-1B	Blank	2.91	2.45	0.86	--	0.053	10-22
T39-2B	Blank	2.85	2.51	--	--	0.050	13-27

TABLE 4

Data on Calcium Inoculation of Rocking Furnace Iron T40

Iron No.	Addition	% C	% Si	% Mn	% S	Block Chill 1/32 inch
T40-1C	0.1% Ca	2.70	2.43	0.83	0.053	5-12
T40-1B	Blank	2.74	2.47	0.86	0.054	12-28
T40-2B	Blank	2.72	2.48	0.86	--	14-24
T40-3B	Blank	--	2.46	--	--	9-14

TABLE 5

Comparative Data on Calcium Inoculation of Rocking Furnace Irons

Iron No.	Addition %	Analysis %					Trans. lbs.	Deflec. in.	Resl.	Block Chill 1/32 inch	Cell Size
		C	Si	Mn	P	S					
T39-1C	1.00 Ca	2.72	2.46	0.87	0.19	0.042	3313	0.313	518	2-3	4-5
T39-2C	0.75 Ca	2.73	2.48	0.88	--	0.040	3389	0.341	578	4-6	4
T40-1C	0.10 Ca	2.70	2.43	0.83	--	0.053	3245	0.292	474	5-12	4-5
T40-1B	Blank	2.74	2.47	0.86	--	0.054	2390	0.191	228	12-28	3
T40-2B	Blank	2.72	2.48	0.86	--	--	2455	0.197	241	14-24	3

of type A graphite from the center to the very edge of the transverse bar. Iron T40-1C, to which a ladle addition of 0.1% calcium was made, had type A graphite predominating and had almost as good a microstructure as iron T39-1C to which 1.0% calcium was added. The corresponding blank irons, T40-1B and T40-2B, showed considerable type D and E graphite particularly near the surface. Cell size of the calcium treated irons was 4-5 in all cases as compared to 3 for the blank irons. As shown in Table 5 all of the cast irons inoculated with calcium showed a marked reduction in chill and superior results for the transverse breaking load, the deflection, and triangular resilience.

Data on the relative effectiveness of aluminum and calcium as inoculants is shown in Table 6. The ladle addition of 0.5% aluminum did not alter the chemical analysis of the iron and had no beneficial effect on microstructure or physical properties except to sharply reduce the amount of chill.

The use of calcium as an inoculant resulted in a marked improvement in microstructure and an increase in physical properties. Cell size was reduced and chill depth was lowered in calcium inoculated cast irons as compared to the corresponding blank iron. Calcium additions to molten cast iron resulted in some decarburization of the cast iron and in a reduction of sulfur.

Table 7 compiles the available information on the effect of ladle additions of calcium on the carbon and sulfur content of cast irons. Generally speaking an increase in the amount of calcium used in the ladle addition resulted in a larger loss of carbon and sulfur. The use of 1.0% of calcium as an inoculant, for example, resulted in a drop in carbon from 3.04% to 2.84% and decrease in sulfur from 0.065% to

TABLE 6

Comparison of Inoculating Effect of Aluminum and Calcium on Rocking Furnace Irons

Iron No.	Addition %	Analysis %					Trans. lbs.	Defl. In.	Resl.	Block Chill 1/32 inch	Cell Size
		C	Si	Mn	P	S					
T34-1A	0.5 Al	2.82	2.27	0.82	0.12	0.064	2450	0.194	238	2-8	2-3
T34-2B	Blank	2.82	2.31	0.87		0.061	2455	0.212	258	14-33	2-3
T40-1C	0.1 Ca	2.70	2.43	0.83		0.053	3245	0.292	474	5-12	4-5
T40-2B	Blank	2.72	2.48	0.86			2455	0.197	241	14-24	3
T39-2C	0.75 Ca	2.73	2.48	0.88		0.040	3389	0.341	578	4-6	4
T40-1B	Blank	2.74	2.47	0.86		0.054	2390	0.191	228	12-28	3
T39-1C	1.0 Ca	2.72	2.46	0.87	0.19	0.042	3313	0.313	518	2-3	4-5
T40-2B	Blank	2.72	2.48	0.86			2455	0.197	241	14-24	3

TABLE 7

Effect of Calcium Inoculation on Carbon and Sulfur Content of Cast Iron

%Ca Added		Blank Ladle	Treated Ladle	%C lost	%S lost
0.10	%C	2.74	2.70	0.04	
	%S	0.054	0.053		0.001
0.22*	%C	2.93	2.87	0.06	
0.44**	%C	3.09	3.00	0.09	
	%S	0.066	0.057		0.009
0.75	%C	2.85	2.73	0.12	
	%S	0.050	0.040		0.010
0.80	%C	2.78	2.68	0.10	
	%S	0.063	0.058		0.005
1.00	%C	2.91	2.72	0.19	
	%S	0.053	0.042		0.011
1.00	%C	3.04	2.84	0.20	
	%S	0.065	0.056		0.011
1.11**	%C	3.08	2.84	0.24	
	%S	0.064	0.050		0.014

Data by *McClure, **Kahn

0.056%. Thus in this instance, the loss of carbon was 0.20% and of sulfur 0.01% and represented a decrease of one part in fifteen (6.5%) for carbon and of one part in six (17%) for sulfur.

At the conclusion of all of the heats inoculated with calcium a strong odor similar to acetylene gas was noticed. Investigation revealed that the source of the odor was an accumulation of gray powder which covered the ladle. A small pile of this powder, when moistened with a few drops of water, bubbled vigorously and gave off a gas which could be ignited and which continued to burn for some time. The gray powder, when dissolved in water, gave a very basic reaction to litmus paper.

Because of the decarburizing effect of calcium,it seems probably that calcium carbide is formed by reaction in the molten cast iron. This would account for the reduction of carbon in the cast iron and for the gray powder that covered the ladle after it cooled.

It is generally accepted that silicon and carbon are interrelated in the graphitization of cast iron. The term used is "carbon equivalent" and is equal to the percent carbon pluc 1/3 percent silicon. Table 8 summarized the carbon equivalents of the rocking furnace irons inoculated with aluminum and calcium along with those for the corresponding blank irons.

TABLE 8

Comparison of Carbon Equivalents of Rocking Furnace Irons

Iron No.	Addition %	%C	%Si	Carbon Equivalent (C+1/3 Si)
T34-2A	0.07 Al	2.84	2.28	3.60
T34-1B	Blank	2.84	2.33	3.62
T34-1A	0.5 Al	2.82	2.27	3.58
T34-2B	Blank	2.82	2.31	3.59
T40-1C	0.1 Ca	2.70	2.43	3.51
T40-2B	Blank	2.72	2.48	3.55
T39-2C	0.75 Ca	2.73	2.48	3.56
T40-1B	Blank	2.74	2.47	3.56
T39-1C	1.0 Ca	2.72	2.46	3.54
T40-2B	Blank	2.72	2.48	3.55

Part B

Induction Furnace Irons

1. Time-Temperature Solidification Curves.

The range of temperature of eutectic formation is of particular interest in the graphitization of cast iron. Some of the results of earlier work by Boyles with respect to the effect of inoculants on cooling curves are shown in Figure 4. Some authors have held that cast irons with type D graphite solidify at a lower temperature than irons with a normal graphite structure. Boyles (10) supported the idea that inoculation of cast iron furnished nuclei from which eutectic centers of crystallization could form.

The work of Eash (13) has also received much attention and discussion. Figure 5 shows of a series of cooling curves for some induction furnace irons of low carbon content. Eash states his conclusions in part as follows:

"Ladle inoculated gray irons, having random flake graphite, solidify in the stable iron - graphite system. The flake graphite forms during the freezing of the graphite-austenite eutectic."

"Gray irons, having fine graphite in a dendritic pattern, solidify in the metastable iron-carbide system as white irons. The eutectic carbide subsequently decomposes in the solid state to form iron and graphite."

The work of these two investigators had produced much discussion and will be treated more fully later in this paper.

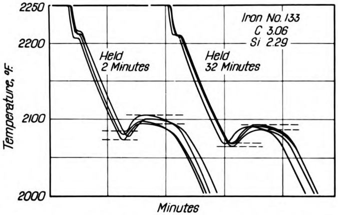


Fig. 48—Cooling Curves of Castings Made From Iron No. 133. Curves on left from castings poured 2 minutes after inoculation. Curves on right from castings poured 32 minutes after inoculation.

Figure 4. Time-Temperature Curves for Solidification of Hypoeutectic Cast Iron. After Boyles and Lorig (11).

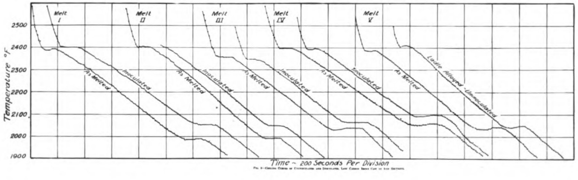


Figure 5. Time-Temperature Curves for Solidification of Hypoeutectic Cast Irons. After Eash (13).

A series of experimental tests were devised to determine the effect of ladle additions of aluminum, calcium, silicon, and graphite on the eutectic transformation in cast irons. In order for results to be comparable it was necessary to carry out all details of charging the furnace, melting, and pouring the cast iron in exactly the same manner for each heat.

Three blank runs, T45, T46, T47 were made with similar results in all cases as shown by the cooling curves of Figure 6. The untreated blank irons started the eutectic formation at about 1970°F. Some 5° to 10°F. undercooling was observed and the duration of the eutectic reaction estimated at 50 to 55 seconds.

The effect of aluminum as an inoculant is indicated in the cooling curves of Figure 7 for heats T50 and T51. The initial temperature of eutectic formation was raised to 2010° - 2040°F. No undercooling was recorded, but an initial nearly level portion of the cooling curve was of some 30 seconds duration. Total time of the eutectic reaction was estimated at 50 seconds.

The results of cooling curves when calcium was used as a ladle addition, as carried out in heats T48 and T49, are shown in Figure 8. The initial temperature of eutectic formation was increased to some 2050°F. and the cooling curves showed no horizontal portion at all. Rather the eutectic formation took place over a range of temperature of some 80°F. during a time interval of about 75 seconds. It is interesting to note at this point that the irons inoculated with calcium had apparently completed the eutectic reaction and were completely solidified at a level of temperature where the blank irons were just starting to show evidence of eutectic formation.

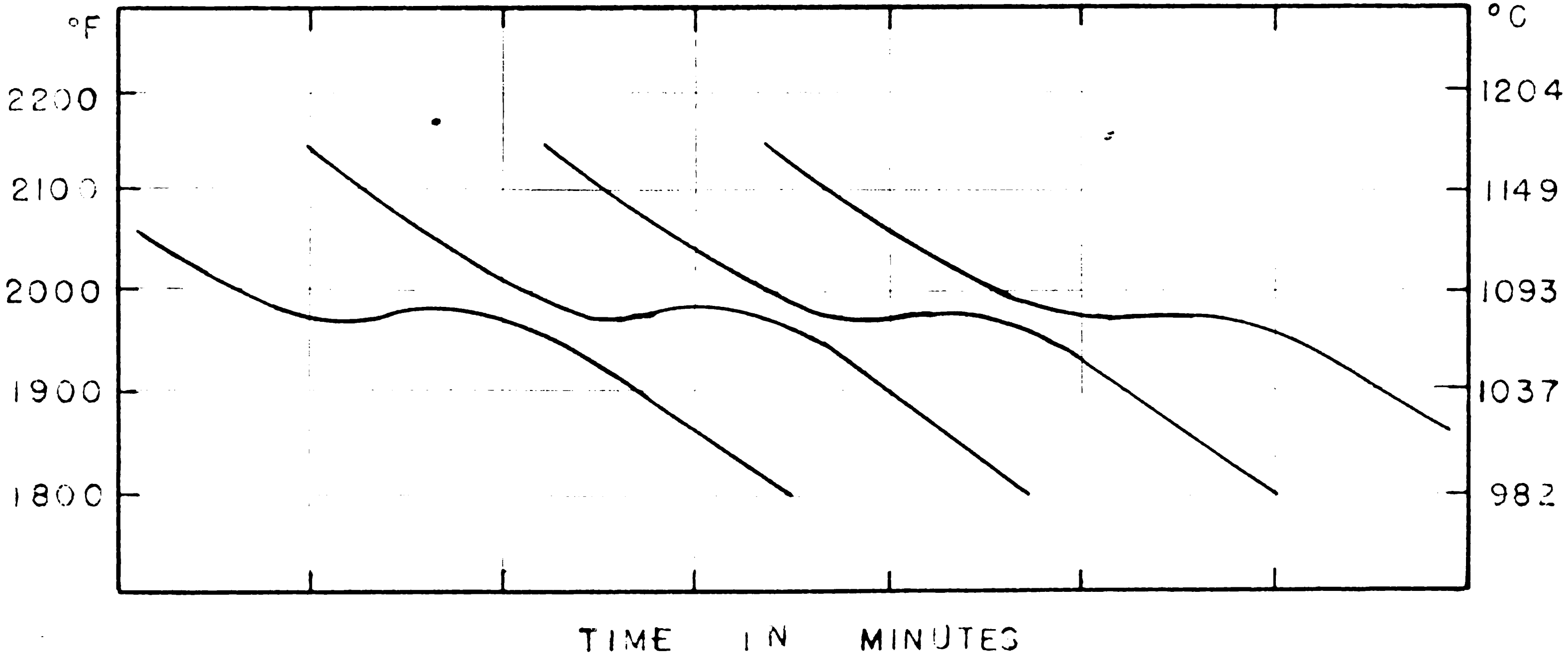


FIG. 6.— COOLING CURVES FOR UNINOCULATED CAST IRON.

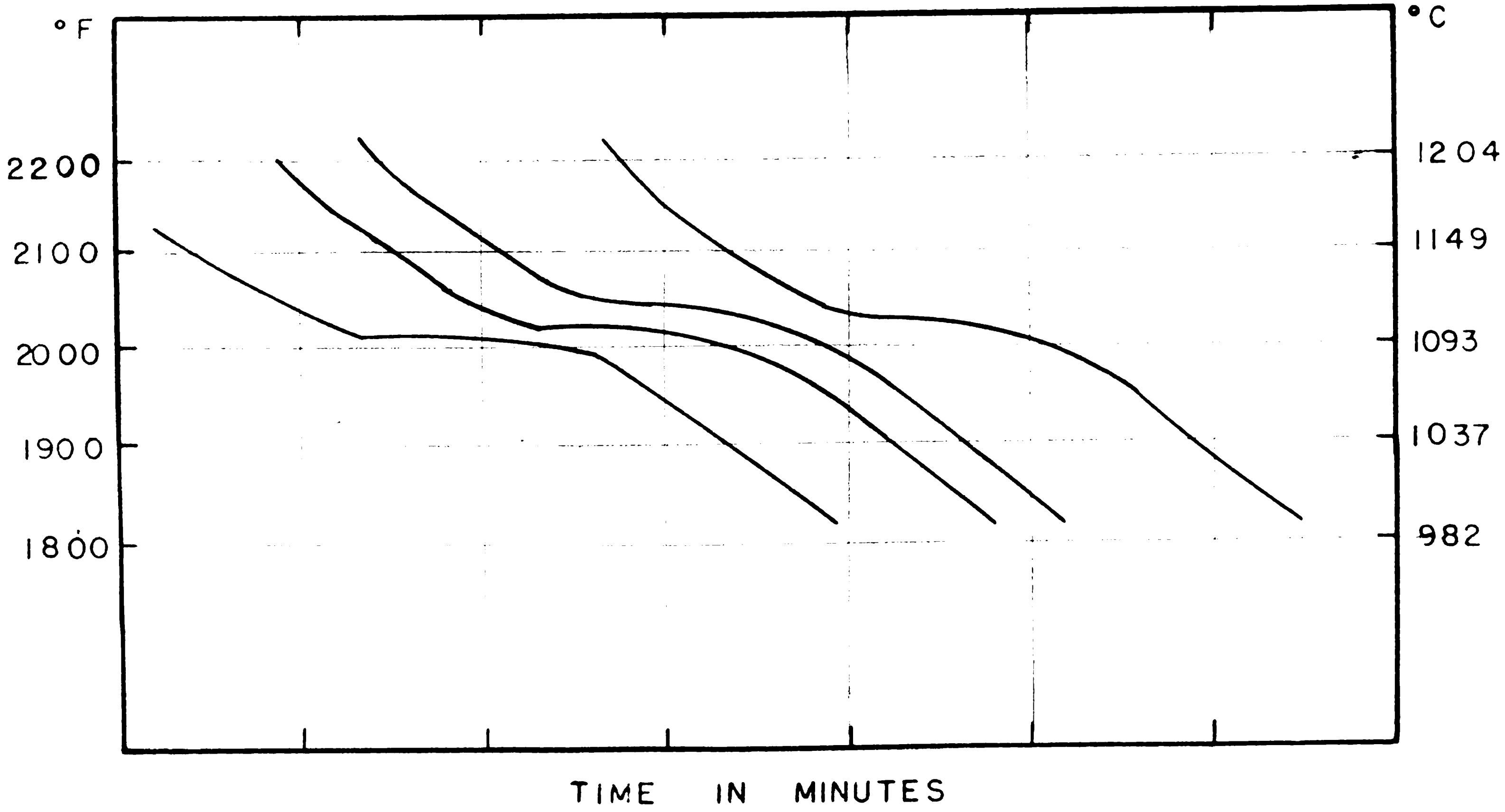


FIG. 7 — COOLING CURVES FOR CAST IRON INOCULATED WITH ALUMINUM.

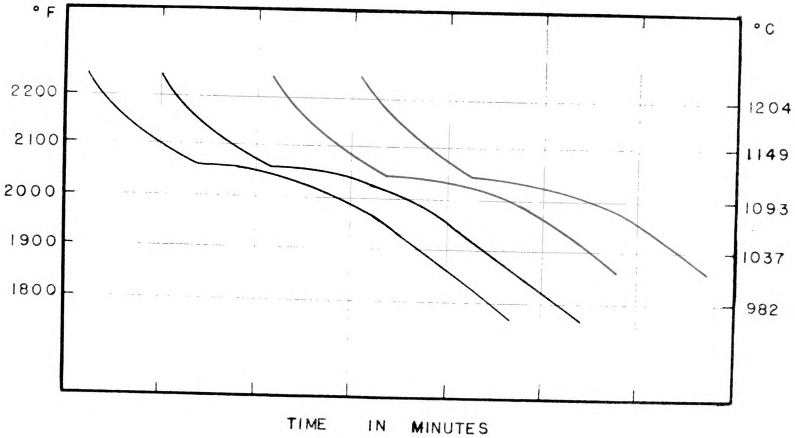


FIG. 8.— COOLING CURVES FOR CAST IRON INOCULATED WITH CALCIUM.

The use of pure silicon as an inoculant for cast iron in heat T55 produced a cooling curve very similar to the blank irons except that no undercooling was recorded. The temperature at the start of the eutectic reaction was 1980°F. and the curve held horizontal at constant temperature for some 40 seconds.

In connection with a study of graphite as an inoculant, cooling curves on a second pair of blank irons, L7 and L8, were determined. These curves are shown in Figure 9. An initial eutectic temperature of about 1990°F. was recorded along with an undercooling of 5°-10°F. The duration of the formation of the eutectic in the blank irons was again about 50 seconds.

Figure 10 shows the cooling curves obtained from a series of four heats, L4, L5, L6, and L9, in which fine graphite was used as an inoculant. The initial temperature of eutectic formation was increased to the range 2020°-2050°F. The duration of the eutectic reaction was about 70 seconds.

A summary of the results of cooling curves obtained is shown in Figure 11. These are typical or average curves based on the studies just discussed. A tabulated summary of the effect of each inoculant on the initial temperature of eutectic formation and on the duration of the entire eutectic formation is given in Table 9.

These data show that calcium was the most effective inoculant in raising the range of temperature of eutectic solidification. Graphite was also effective in this way but not to quite such a marked degree as calcium. Aluminum was less effective than either the calcium or graphite, although better than silicon which showed little or no effect on the temperature of eutectic formation.

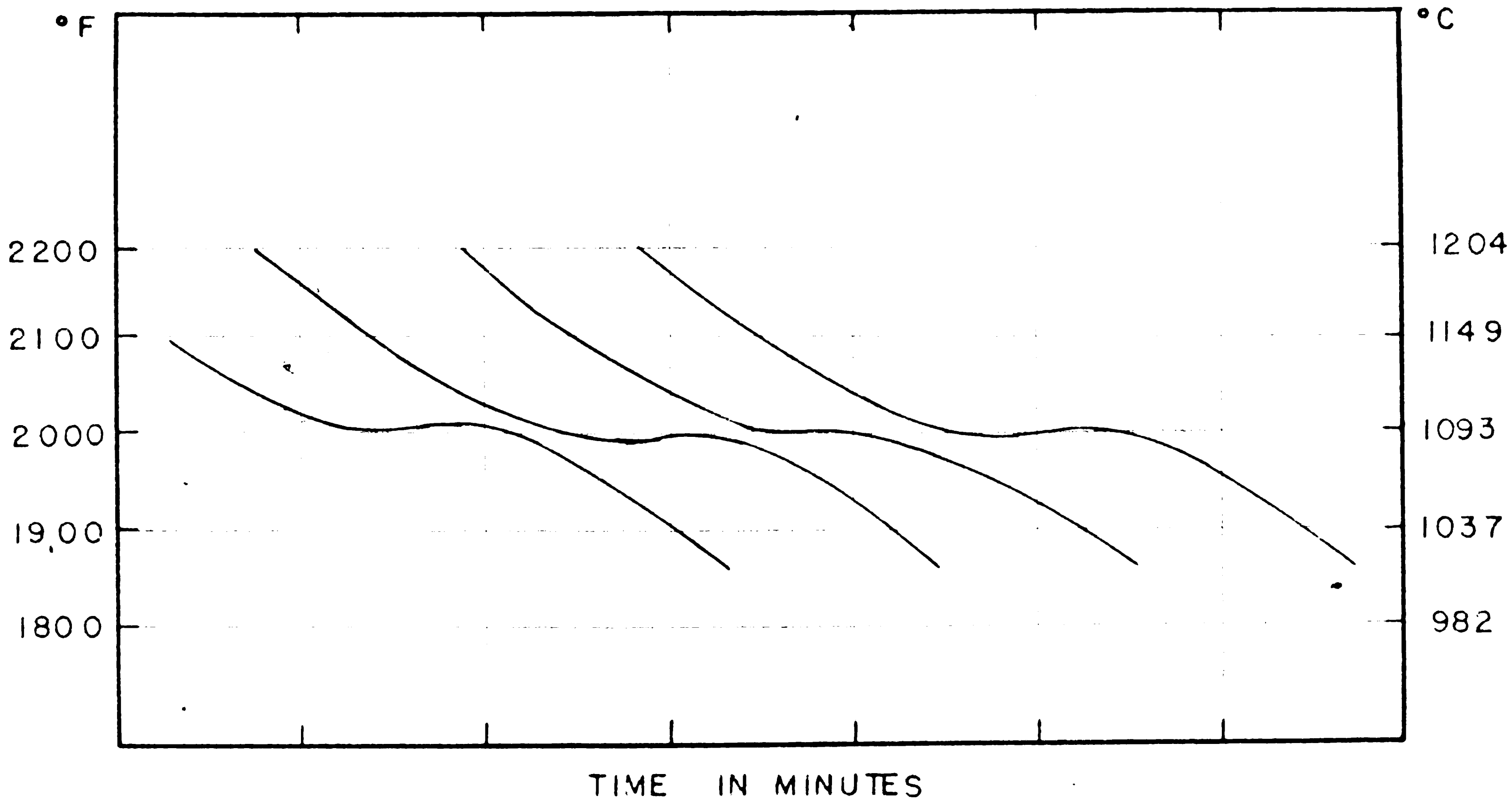


FIG. 9.— COOLING CURVES FOR UNINOCULATED CAST IRON. (SECOND SERIES).

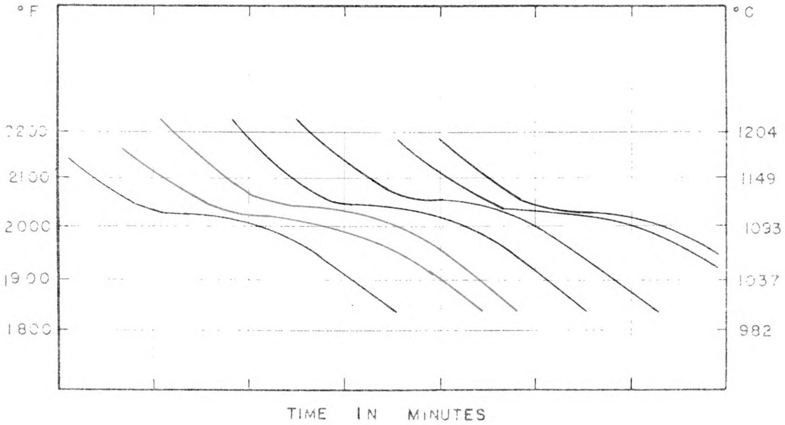


FIG. 10.— COOLING CURVES FOR CAST IRON INOCULATED WITH FINE GRAPHITE.

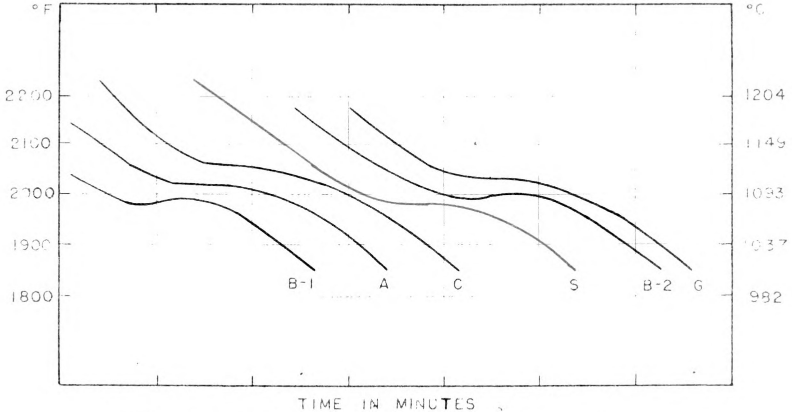


FIG. 11. — COMPARISON OF TYPICAL COOLING CURVES.

B-1 BLANK HEAT, NOT INOCULATED.
B-2 BLANK HEAT, SECOND SERIES, NOT INOCULATED.
A INOCULATED WITH 0.6 % ALUMINUM.
C INOCULATED WITH 1.0 % CALCIUM.
G INOCULATED WITH 0.5% FINE GRAPHITE.
S INOCULATED WITH 0.55% SILICON.

TABLE 9

Comparison of Effect of Ladle Additions of Aluminum, Silicon, Calcium, and Graphite on the Initial Temperature of Eutectic Formation of Induction Furnace Irons.

Iron No.	Addition %	°F at Start of Eutectic	Duration of Eutectic (Seconds)	Ave. °F	Ave. Seconds
T-45	Blank	1970	60		
T-46	Blank	1970	50		
T-46	Blank	1970	50		
T-47	Blank	1968	55	1970	54
T-55	0.55 Si	1980	42	1980	42
T-50	0.6 Al	2007	45		
		2015	45		
T-51	0.6 Al	2047	60		
		2033	50	2025	50
T-48	1.0 Ca	2057	78		
		2057	84		
T-49	1.0 Ca	2038	70		
		2038	70	2048	76
L 7	Blank	1966	50		
		1986	48		
L 8	Blank	1995	40		
		1990	60	1984	50
L 4	0.5 Gr	2020	60		
		2020	60		
L 5	0.5 Gr	2040	72		
		2050	78		
L 6	0.5 Gr	2055	78		
		2035	66		
L 9	0.5 Gr	2037	78	2039	70

2. Microstructure and Physical Properties.

The blank cast irons of heats T45, T46, and T47 were very abnormal in graphite distribution. Figure 14 is typical of this type of microstructure. Very little type A graphite was observed, even at the center of the transverse bars. The physical properties of these blank irons are listed at the top of Table 10 and a summary based on average results is shown in Table 12. The blank irons as a group showed a large amount of chill and were relatively low in transverse strength, deflection, and triangular resilience.

Heats T50 and T51 to which 0.6% aluminum was added as an inoculant showed a microstructure very similar to the blank irons. No improvement in graphite distribution resulted from the ladle addition of aluminum. The physical properties, as tabulated in Table 11 for comparison with corresponding blank irons, were not significantly changed.

The addition of 1.0% calcium as an inoculant to heats T48 and T49 produced a cast iron having type A graphite predominating throughout the cross section of the bar. Figure 13 is typical of this type of microstructure. Table 11 shows that the physical properties of the calcium treated irons are definitely superior to those of the corresponding blank iron of similar chemical analysis.

The physical properties of an iron to which a late addition of 0.55% silicon was made were not appreciably different from the properties of a blank iron of similar analysis.

Table 12 is a summary of average results for the blank irons and for the irons to which aluminum, calcium, and silicon were added as inoculants. Table 13 is a comparison of carbon equivalents of the several inoculated irons and the corresponding blank irons.

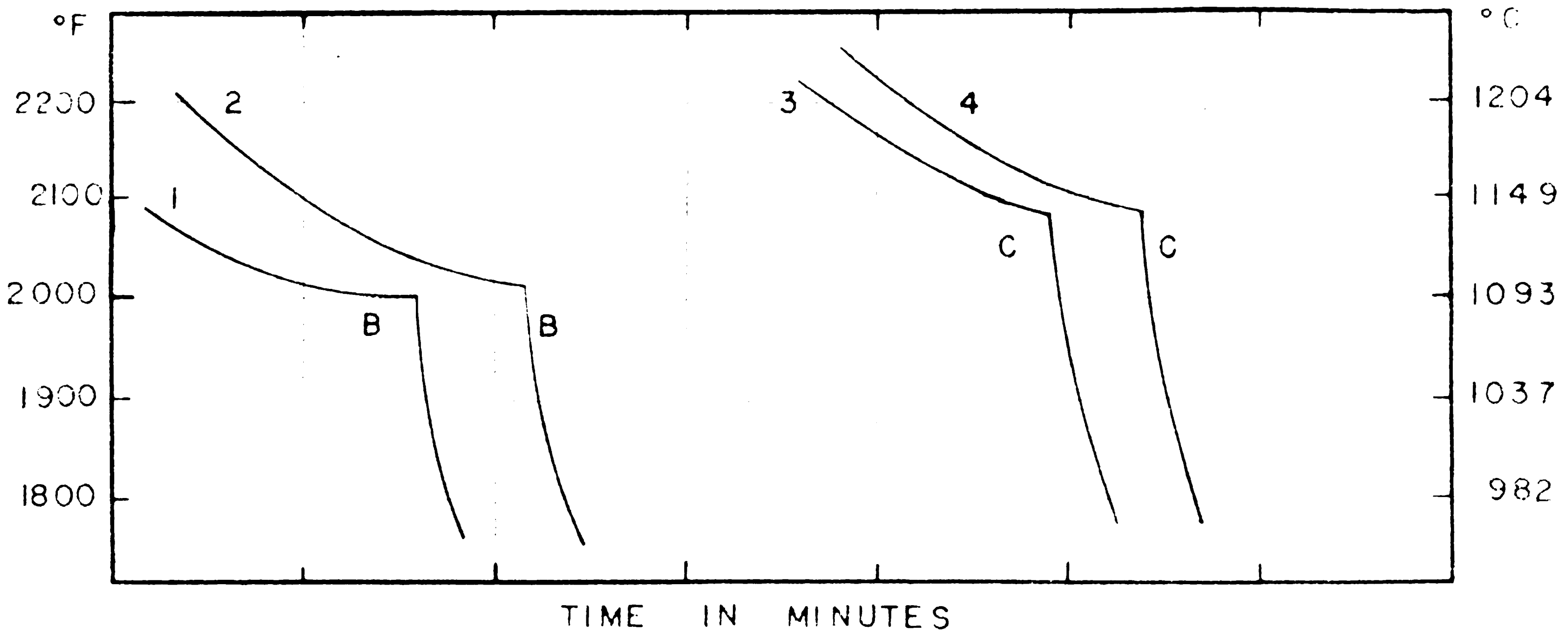


FIG. 12.-COOLING CURVES FOR WATER QUENCHED WEDGE SAMPLES

B - BLANK HEAT, NOT INOCULATED.
C - INOCULATED WITH 1.0% CALCIUM METAL.

Figure 13. Typical Microstructure of Type A Graphite Distribution. Iron T53M Inoculated with 1.0% Calcium and Cooled in a Dry Sand Mold. x100

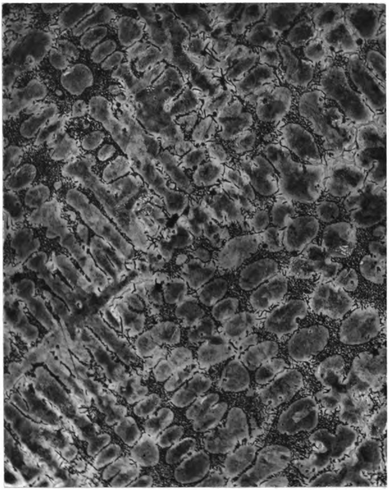


Figure 14. Typical Microstructure of Type D Graphite Distribution. Uninoculated blank heat T54M of same analysis as iron in Figure 13. Cooled in a Dry Sand Mold. x100

TABLE 10

Comparative Data on Calcium, Aluminum, and Silicon Inoculation of Induction Furnace Cast Iron

Iron No.	Addition %	Analysis %					Trans. lbs.	Defl. in.	Resl.	Block Chill 1/32 inch
		C	Si	Mn	P	S				
T45	Blank	2.80	2.22	0.94		0.064	2402	0.192	230	16-36
T46	Blank	2.84	2.08	0.91		0.068	2610	0.205	267	23-46
T47	Blank	2.83	2.16	0.92		0.065	2500	0.209	261	21-44
T48	1.0 Ca	2.82	2.19	0.93		0.056	3175	0.355	563	6-10
T49	1.0 Ca	2.84	2.16	0.97		0.055	3485	0.407	710	6-10
T49B		3.04	2.15			0.068				
T50	0.6 Al	2.83	2.17	0.93		0.067	2410	0.193	233	6-18
T50B		2.86	2.18			0.070				
T51	0.6 Al	2.84	2.10	0.87		0.068	2605	0.222	289	3-9
T53	1.0 Ca (Quench)	2.78	2.20			0.058	3365	0.374	630	7-13
T54	Blank (Quench)	2.78	2.26			0.067	2380	0.178	212	18-44
T55	0.55% Si	2.83	2.05			0.058	2460	0.201	247	20-48

TABLE 11

Comparison of Inoculating Effect of Calcium, Aluminum, and Silicon on Induction Furnace Irons

Iron No.	Addition %	Analysis %					Trans. lbs.	Defl. in.	Resl.	Block Chill 1/32 inch
		C	Si	Mn	P	S				
T48	1.0 Ca	2.82	2.19	0.93		0.055	3485	0.407	710	6-10
T47	Blank	2.83	2.16	0.92		0.065	2500	0.209	261	21-44
T49	1.0 Ca	2.84	2.16	0.97		0.055	3485	0.407	710	6-10
T47	Blank	2.83	2.16	0.92		0.065	2500	0.209	261	21-44
T50	0.6 Al	2.83	2.17	0.93		0.067	2410	0.193	233	6-18
T47	Blank	2.83	2.16	0.92		0.065	2500	0.209	261	21-44
T51	0.6 Al	2.84	2.10	0.87		0.068	2605	0.222	289	3-9
T46	Blank	2.84	2.08	0.91		0.068	2610	0.205	267	23-46
T55	0.55 Si	2.83	2.05			0.058	2460	0.201	247	20-48
T46	Blank	2.84	2.08	0.91		0.068	2610	0.205	267	23-46

TABLE 12

Summary of Average Results of Calcium, Aluminum, and Silicon Additions to Induction Furnace Irons

	Trans. lbs.	Defl. in.	Resl.	Block Chill 1/32 inch
Average of Blank Heats	2473	0.196	242	20-42
Average of 1.0% Ca Heats	3330	0.381	636	6-10
Average of 0.6% Al Heats	2507	0.207	261	4-14
Average of 0.55% Si Heats	2460	0.201	247	20-48

TABLE 13

Comparison of Carbon Equivalents of Induction Furnace Irons

Iron No.	Addition %	%C	%Si	Carbon Equivalent (C+1/3 Si)
T48	1.0 Ca	2.82	2.19	3.55
T47	Blank	2.83	2.16	3.55
T49	1.0 Ca	2.84	2.16	3.56
T47	Blank	2.83	2.16	3.55
T50	0.6 Al	2.83	2.17	3.55
T47	Blank	2.83	2.16	3.55
T51	0.6 Al	2.84	2.10	3.54
T46	Blank	2.84	2.08	3.53
T55	0.55 Si	2.83	2.05	3.51
T46	Blank	2.84	2.08	3.53

3. Water-Quenched Irons.

Previous investigators in this field have stated that one of the factors affecting graphitization of cast iron is the amount and size of the primary austenite dendrites that form previous to the eutectic reaction. In order to make some experimental observations about the effect of inoculation on primary dendrite size and distribution, wedge-shaped samples were quenched in cold water from a temperature level such that the eutectic cells were just starting to form. This quench treatment was carried out for both a cast iron inoculated with 1.0% calcium (T53) and for a comparable untreated iron (T54). The cooling curves automatically recorded as shown in Figure 12 were used as a guide in judging the desired temperature for quenching.

An identical wedge was also poured into a dry sand mold for both heats T53 and T54 and allowed to slow-cool without being disturbed. The slow-cooled inoculated wedge had a microstructure as shown in Figure 13 and the corresponding untreated iron as shown in Figure 14.

A careful study of the microstructure of both irons was made at identical locations in the wedge and at a point near the thermocouple. Results for the cast iron inoculated with 1.0% calcium are shown in the photomicrographs of Figures 15 and 16. In addition to the primary dendrites of austenite that have quenched to martensite, this microstructure shows many darker centers scattered throughout the molten metal remaining at the time of quench. These darker centers are the beginning of eutectic cells, and it is in these expanding centers that graphite flakes form.

Figures 17 and 18 were taken of the blank iron for purposes of comparing with Figures 15 and 16 of the inoculated iron. The microstructure

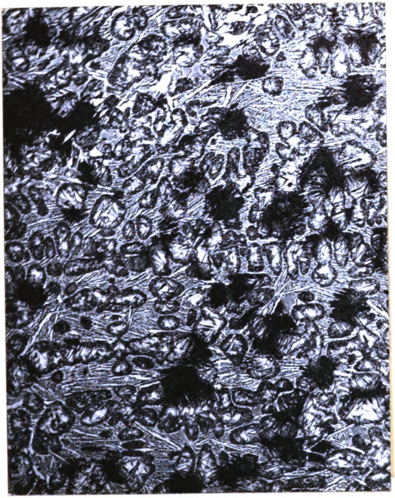


Figure 15. Dendrite Size and Distribution in Iron T53 Inoculated with 1.0% Calcium. Wedge-shaped Sample Quench at Start of Eutectic Formation. x100.

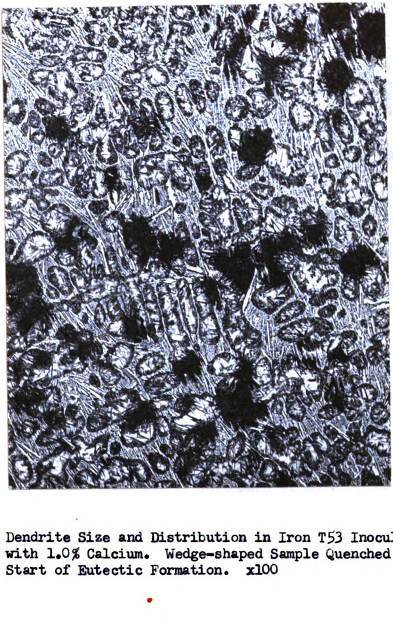


Figure 16. Dendrite Size and Distribution in Iron T53 Inoculated with 1.0% Calcium. Wedge-shaped Sample Quenched at Start of Eutectic Formation. x100

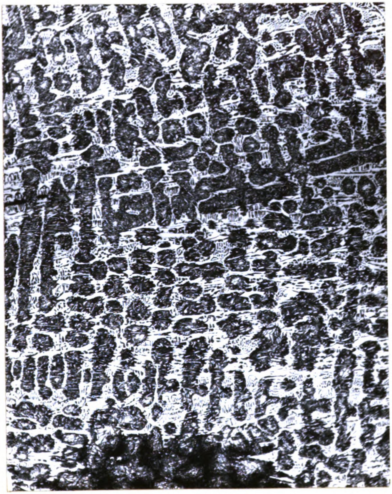


Figure 17. Dendrite Size and Distribution in Uninoculated Blank Heat T54 of Same Analysis as Iron in Figures 15 and 16. Wedge-Shaped Sample Quenched at Start of Eutectic Formation. x100.

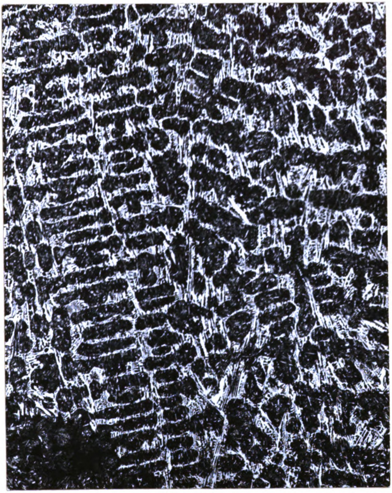


Figure 18. Dendrite Size and Distribution in Uninoculated Blank Heat T54 of Same Analysis as Iron in Figures 15 and 16. Wedge-Shaped Sample Quenched at Start of Eutectic Formation. x100.

of the blank iron also shows primary dendrites of austenite that have transformed to martensite as a result of the quench into water. Only a few of the darker centers of eutectic cells were observed, and these were of much larger size on the average. The edge of one of these larger eutectic cells that are just in the early stages of formation may be seen at the bottom of the photomicrographs of the untreated cast iron in Figures 17 and 18. A comparison of the microstructure showed that the blank irons had only one or two larger eutectic cells in the typical field of view whereas at an identical location in the inoculated irons no less than 25 or 30 eutectic cells were observed.

After a careful and detailed study of comparable microstructures, it was concluded that in this case inoculation had no gross or major effect on primary dendrite size and distribution. The inoculated irons did seem to have just a little more molten eutectic metal at the time of quench and perhaps the pattern of the primary dendrites was somewhat more broken and less compact. However these indications were rather slight.

The effect of inoculation on the numbers of eutectic cells formed is illustrated in the macrophotograph of Figure 19. These samples were taken from the wedges quenched at the start of eutectic formation for heat T53, inoculated with 1.0% calcium, and heat T54, uninoculated. The untreated cast iron on the left shows fewer and larger eutectic cells than does the inoculated cast iron at a comparable location, The effect of inoculating this cast iron with 1.0% calcium was to create nuclei or centers of eutectic formation. Because all of the flake graphite is formed in the eutectic cells during the progress of solidification, the number and distribution of these cells has an

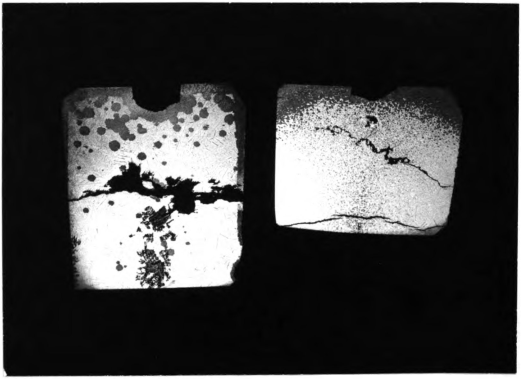


Figure 19. Effect of Inoculation on Number of Eutectic Cells.
Blank Iron T54, on left, not Inoculated.
Iron T53, on right, Inoculated with 1.0% Calcium.
Both irons quenched in water at start of eutectic formation. x2

Figure 20. Graphite Flakes Formed in Eutectic Cells of Specimen T53 Quenched at Start of Eutectic Formation. Inoculated with 1.0% Calcium. x250

Figure 21. Graphite Flakes Formed in Eutectic Cells of Specimen T53 Quenched at Start of Eutectic Formation. Inoculated with 1.0% Calcium. Same Spot as Figure 20. x500.

important bearing on graphitization in cast iron.

Additional studies of the wedges quenched from inoculated heat T53 were made at higher magnifications. Figure 20 and 21 were taken at the same location on the sample and at 250x and 500x respectively. Graphite flakes may be seen in the darker eutectic cell areas at the center of Figure 20. These same flakes of graphite are shown in more detail in the center area of Figure 21. The dispersion of very fine graphite flakes in the remaining portion of the darker areas was probably formed during the quench.

Figure 22 shows a photomicrograph taken at 1500x where ledeburite in adjacent to what is apparently an extremely fine graphite dispersion. This fine dispersion of graphite was either a result of the very rapid decomposition of the cementite phase of the ledeburite, or was formed at a relatively low range of temperature during the quench with the remaining portion of the liquid transforming to quenched ledeburite.

The photomicrographs of Figure 23 and 24 were taken near the top surface of the quenched wedge from inoculated heat T53. Through the center area of Figure 23 it is possible to see a fine graphite structure having the same general physical outlines as the adjacent areas of quenched ledeburite.

Figure 24 shows some light areas of iron carbide found in a location near the top surface of the wedge. The area near the top surface shown in these photomicrographs was subjected to a more rapid rate of cooling than was the case for locations within the wedge.

Figures 25 and 26 were taken at the same spot located near the center of the quenched wedge poured from inoculated heat T53. The

Figure 22. Ledeburite Adjacent to Fine Graphite Constituent in Specimen T53 Quenched at Start of Eutectic Formation. x1500.

Figure 23. Microstructure of Iron T53 Near Top Surface of Wedge Quenched at Start of Eutectic Formation. x500.

Figure 24. Microstructure of Iron T53 Very Close to Top Surface of Wedge Quenched at Start of Eutectic Formation. x500.

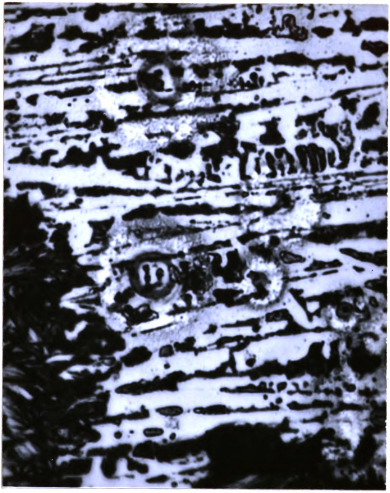


Figure 25. Microstructure of Iron T53 Near Center of Wedge Quenched at Start of Eutectic Solidification. Heat Tinted. x1800.

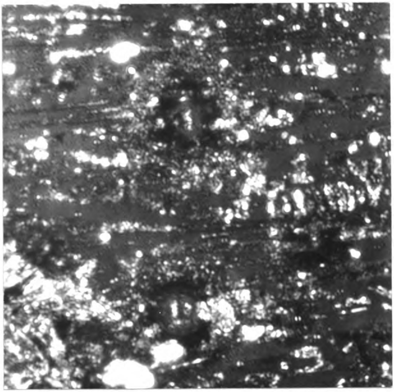


Figure 26. Same spot as Figure 25. Polarized Light. x1800.

eutectic solidification had just started in this zone when the sample was quickly cooled to room temperature by quenching in water. The darker area on the lower left of Figure 25 is martensite formed from the original primary dendrites of austenite. The generally light-colored area in the photograph represents a location that was molten metal of nearly eutectic composition at the time of quench. This molten phase transformed into a fine ledeburite structure. Of particular interest in Figure 25, taken at 1800x, is what appears to be several centers of eutectic nucleation scattered throughout the ledeburite areas. This specimen was heat tinted at 450°F. for two hours. Figure 26 is the exact spot shown in Figure 25, but with polarized illumination. The actual diameter of the more sharply delineated ring in these centers is in a range of magnitude of from 0.00005 to 0.0002 inches.

Figure 27 was drawn after the work of Hanemann (18) on the decomposition of cementite. Recent work published by Berman and Kondic (5), as shown in Figure 28, provides evidence that iron carbide can decompose in much shorter periods of time than previously recognized. Berman and Kondic state as follows:

"From the series of cooling and heating curves it is evident that the time required for the decomposition of cementite near the eutectic temperature is of the order of minutes, and not of hours as Hanemann found. By drawing a line through the points representing the beginning of graphitization at different temperatures (as obtained by microscopic examinations of quenched specimens) and by drawing a similar line through the points representing the end of graphitization, it was possible to establish the time temperature decomposition diagram of cementite below the eutectic temperature. (Figure 28). Extrapolating these lines up to the eutectic temperature shows that complete graphitization should take place within four minutes; this time is very similar to that found to be required for total decomposition of cementite, as the experiments on the duration of arrest at the eutectic temperature have shown. The graphite formed during either direct cooling or subsequent reheatings was of type D."

Earlier in their article (5), Berman and Kondic discuss the general problem of graphitization of cast iron by means of a diagram shown in Figure 29. They state in part.

"Solidification of iron-carbon alloys can readily be followed from a semi-hypothetical free-energy/composition diagram (Figure 29), in which the curves representing the free energies of liquid iron, austenite, cementite, and graphite are plotted as functions of their carbon content. At temperature T_1 the free energy of the liquid of any composition is less than that of any component which could solidify. Thus, at this temperature liquid is the only phase present. On cooling to T_2 primary austenite begins to form, since the free-energy curve for the liquid has a common tangent with that for solid austenite. The eutectic will not begin to form until the temperature falls to T_3, at which point there is a common tangent to the austenite, graphite, and liquid free-energy/composition curves, or if graphite is hard to nucleate, to the austenite, cementite, and liquid curves at a slightly lower temperature T_4. Thus it appears theoretically that either graphite can form straight from the liquid state or, when graphite is not easily nucleated, cementite may form first, subsequently decomposing

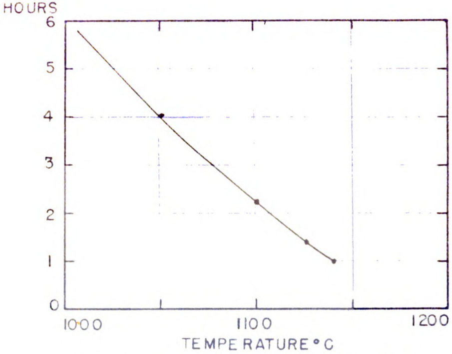
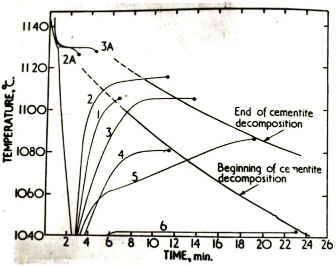


FIG. 27.— DECOMPOSITION TIME FOR CEMENTITE (HANEMANN)



—Time/temperature decomposition diagram

Figure 28. Time for Decomposition of Cementite of Temperatures Below the Eutectic. (Berman and Kondic) (5).

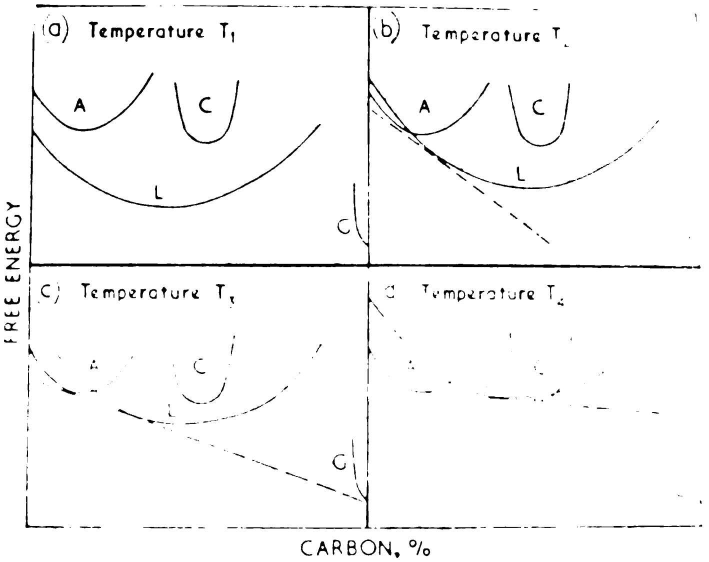


Fig. 1 Free-energy composition diagram of Fe-C system (not drawn to scale)

Figure 29. Free-energy/Composition Diagram of Iron-Carbon System. (Not drawn to scale). After Berman and Kondic (5).

into graphite. The problems of graphitization seems to be reduced to finding out the conditions under which graphite may be nucleated directly from the melt and the time required for the decompositions of cementite at and near the eutectic."

Morrogh and Williams (32) have previously reported...."that some curves, obtained on hypo-eutectic irons giving undercooled graphite, have an inflection before the eutectic arrest which is quite distinct from the charge in slope due to the separation of primary austenite. This inflection was clear and reproducible and began about 10°C above the eutectic arrest. The crystallization of the acicular form of carbide is clearly responsible for this inflection."

In a recent publication Morrogh and Williams (33) present additional experimental data and photomicrographs to support the formation of an acicularcarbide, resembling a hypereutectic deposition, before the eutectic arrest. The crystallization of austenite probably ceases when these carbide needles begin to form. The deposition of carbide continues until at the eutectic arrest some of the carbide begins to graphitize to give undercooled graphite. The eutectic arrest corresponds to the solidification of the remaining liquid and the graphitization of most of the carbide formed before and during the eutectic arrest. However, Morrogh and Williams do not contend that all iron-carbon-silicon alloys solidify by this mechanism, but state---"When a hypo-eutectic white iron is able to undercool to give acicular carbide of hypereutectic form it can transform readily to give undercooled graphite. It would seem that the hypereutectic carbide formed under such conditions is very unstable... It is conceivable, therefore, that the graphitization process leading to the formation of undercooled graphite is made possible by the extreme instability of the hyper-eutectic carbide phase.... The boundary between the undercooled graphite area and the white iron is seldom smooth and regular, and often seems to take its form from the carbide particles. This may be taken as further evidence of the prior existence of the carbide... This solidification sequence is in agreement with accepted ideas on undercooling of eutectics... In eutectiferous systems undercooling can cause the appearance of the primary phases from each side of the eutectic in the same specimen.

"Undercooled graphite in relatively high-silicon alloys has been shown to arise from the decomposition of a mixture of silico-carbide and cementite, suggesting that assumptions made elsewhere about the construction of the iron-carbon-silicon diagram are invalid."

Although the above explanation of the formation of undercooled graphite is widely held, it is not completely accepted by all of the investigators in this field. A recent publication of work carried out at the Swedish Institute for Metal Research (Stockholm) by Hultgren, Lindblom, and Rudberg (26) stated that... "in the irons studied the appearance of the graphite-austenite aggregates, their composition, and their general manner of development, related to the cooling curves, indicates direct formation from the melt by eutectic reaction.

"....the graphite is not uniformly coarse or fine but varies in a characteristic manner, in close correlation with the temperature at which it makes its appearance.

"The birth and growth of units of a eutectically composed graphite-austenite constituent, coarse or fine and always of a roughly spherical

shape, modified by pre-existing dendrites, has as its counterpart in the cooling curves a gradual smooth change in direction...

"The present investigation is essentially one of cooling experiments, and the conclusion is that the undercooled graphite observed is not a decomposition product of ledeburite but is formed directly from the melt..."

It may thus be said that a study of graphitization of various cast irons by a number of investigators has produced the following two general conclusions.

1. Although type A graphite flakes can form as a eutectic constituent directly from the melt, the dendritic or type D graphite is a result of decomposition of a very unstable hypereutectic or eutectic iron-carbide or silico-carbide.
2. All types of graphite in cast iron form directly from the melt as a graphite-austenite eutectic. The variations in size of graphite flakes is directly related to the temperature of formation. A lower temperature results in a finer dispersion of graphite.

Mention has already been made of the previous work of Boyles and Eash on the effect of inoculation on cooling curves which is shown in Figures 4 and 5. Boyles used for his studies a cast iron containing about 3.0% carbon, 2.3% silicon, 0.75% manganese, 0.055% sulfur, and 0.09% phosphorus. Samples weighing 200 grams were taken from machined transverse bars and were remelted in a furnace, after which cooling curves were plotted. Boyles used calcium-silicon as an inoculant with the results shown in Figure 4. Boyles stated as follows in regard to these cooling curves:

"It will be noted that there is, on the average, a difference of about 10°F. between the eutectic arrest point shown by the castings poured 2 minutes and those poured 32 minutes after adding calcium-silicon. This is not a very large difference in view of the scatter shown by duplicate determinations. Both types of castings show a dip in the cooling curve during eutectic solidification, the difference between high and low points amounts to about 20°F. for the castings poured 2 minutes after inoculation and about 23°F. for those poured 32 minutes after inoculation. From these data it would not appear that any pronounced difference in undercooling occurred in the two types of castings under consideration. There was, however, a very marked difference in the type of structure exhibited by these two groups of castings, all of which were examined microscopically."

Eash in his studies of cooling curves used low carbon cast irons containing about 1.75% to 2.40% carbon, 1.51% to 2.67% silicon, 0.85% manganese, 0.17% sulfur, and 0.16% phosphorus. Eash melted his irons in an induction furnace, heated them to 2885°F., and poured them at 2700°F. into open-top, dry-sand molds about three inches in diameter and seven inches long. The heat was divided into two parts, one of which served as a blank. The remaining portion of the metal was inoculated with 0.6% of 85% ferrosilicon. The average cooling rate was 0.33°F. per second. Eash states in reference to the cooling curve of Figure 5:

"Comparison of each pair of curves showed that the outstanding difference between the "as-melted" and the inoculated irons was the higher eutectic freezing temperature of the latter. The eutectic freezing temperature of the ladle treated specimens was 36° to 76°F. higher than for untreated irons, the difference depending upon the composition."

Hultgren, Lindblom, and Rudberg (26) in a discussion of the work of Eash, state:

"Eash concluded from his cooling experiments that undercooled "dendritic" graphite is formed by the decomposition of ledeburite. Eash shows that the cooling curves for an iron in which fine undercooled graphite is formed has an arrest some 15-30°C lower than that in the curve for the same iron inoculated with ferro-silicon and thus giving coarse flake graphite. He points out that the equilibrium eutectic temperature is known to be higher for graphite eutectic than for cementite eutectic; the lower arrest temperature is therefore held to prove that cementite eutecitc is formed on solidification in this case, and that the fine graphite results from a subsequent decomposition of cementite. From the results of the present work, on the other hand, it is quite natural to find that the graphite formed at a lower temperature is finer than that formed at a higher temperature, without a change in mechanism. The temperature at which a cooling curve levels off when a reaction occurs need not be the equilibrium temperature for that reaction, when arranged to take place reversibly, but must in general be lower and depends to a considerable extent on the rate of heat extraction imposed by the cooling conditions. A close approach to equilibrium temperature, uninfluenced by cooling conditions, can only be expected for those processes in which the rate of removal of reaction heat alone controls the speed of the reaction.

This condition may obtain, in some cases, for the solidification of a pure substance, which involves no compositional changes and no diffusion up to, or away from, the reaction front."

The results of the research conducted for this paper indicated that silicon is not a necessary component of an effective inoculant for gray cast iron. It has been shown that it is possible to greatly reduce chill without producing type A graphite. When, however, type A graphite was produced, then a reduction of chill also resulted. All of the material tried as inoculants in this study were effective in removing the undercooling of 5-10°F. observed in the blank irons. Aluminum both raised the initial temperature of formation of the eutectic and eliminated the undercooling effect without, however, producing any improvement in graphite distribution or increase in physical properties. It has thus been demonstrated that the elimination of undercooling and the increase in the initial temperature of eutectic formation, either alone or in combination, is not a sufficient condition for the formation of type A graphite. The additional requirement of a good inoculant, that it be able to furnish suitable nuclei for the formation of eutectic cells, has been clearly demonstrated. Results of this study showed that pure silicon and pure aluminum were not effective as inoculants, but that metallic calcium, used as a ladle addition, was capable of providing an ample supply of suitable nuclei with resulting improvement in graphite distribution and physical properties. Evidence has been presented to show that calcium carbide was formed during the inoculation of cast iron with metallic calcium. The possibility exists that CaC_2 may be the effective nucleating agent, particularly if it exists in a colloidal dispersion in the molten cast iron or is absorbed on the surface of the primary solid. The decrease in sulfur associated with the formation of calcium carbide should not be overlooked as a possible additional graphitizing effect. Sulfur is known to be a strong carbide stabilizer.

For the cast iron melted in the induction furnace and inoculated with pure aluminum, there was a tendency for the graphite flakes to be somewhat thicker. This tendency to thickening of the flakes of graphite was not observed on similar cast irons melted in a rocking furnace. This tendency may be caused by variations between the smaller 30-lb. heats of the induction furnace. The larger 200-lb. heats of the rocking furnace permitted blank irons from the same heat. Additional observations on the effect of aluminum on the graphite structure of cast irons melted in the induction furnace are necessary before final conclusions can be reached.

Figure 23 shows the microstructure of Iron T53 near the top surface of the wedge poured from a cast iron inoculated with 1.0% calcium and quenched at the start of the eutectic formation. This area near the top surface was cooled at a more rapid date than the interior of the sample. Evidence of a very fine graphite structure coherent in general outline and contiguous with a ledeburite eutectic, both of which fill the area between the primary dendrites of austenite, indicates that this portion of fine graphite resulted from a decomposition of the immediately adjacent iron carbide portion of the ledeburite eutectic.

The results of the studies carried out for this paper have demonstrated that the formation of type A graphite in cast iron depends upon the presence of a large number of suitable nuclei from which eutectic cells can form. Evidence was also obtained indicating that under certain conditions graphite could form by carbide decomposition.

Aluminum and calcium, used as inoculants for gray cast iron, were both capable of reducing chill. Because the aluminum was not able to initiate the formation of flake graphite or to provide suitable nuclei for eutectic cells, it would appear that the marked chill reduction observed in the aluminum treated irons came about as a result of greater instability of the carbide. It may well be that aluminum operates to accelerate the decomposition of cementite once it is formed.

Calcium metal, on the other hand, was very effective as an inoculant for gray cast iron. Not only was the initial temperature of eutectic formation raised some 80°F. and undercooling eliminated, but a suitable nucleating material was produced during the process of inoculation from which eutectic cells and type A graphite flakes could form. Evidence of the remarkable nucleating effect produced by using metallic calcium as a ladle addition is shown in Figure 19.

It has been shown that when many suitable nuclei were present, not only was the graphite-austenite eutectic initiated and completed at a much higher temperature, but the entire reaction proceeded over a longer period of time. In the case of many small, closely spaced nuclei there was no demand for a high rate of movement of the spherical liquid-solid interface and it was possible for diffusion of carbon from the molten metal in front of the leading edge of the flakes and from the austenite immediately adjacent on either side to keep pace.

For fewer nuclei more widely spaced, the rate of growth of the spherical front of the eutectic cell could easily exceed the diffusion rate of carbon to the graphite flake with the result that the flakes were continually cut off or segmented.

VI.

SUMMARY AND CONCLUSIONS

The results of the work undertaken in this research showed that rocking furnace irons inoculated with calcium had a much smaller cell size than the corresponding blank irons, whereas comparable aluminum treated irons showed no change in cell size.

The ladle additions of calcium to both rocking furnace and induction furnace irons produced a decarburization and a desulfurization of the molten metal. The possibility exists that the calcium carbide or the calcium sulfide thus formed might serve as a nucleating agent for eutectic cells.

The rocking furnace irons inoculated with calcium showed superior physical properties and had a type A graphite structure. Similar cast irons melted in the rocking furnace but inoculated with aluminum showed a marked reduction of chill but had type D graphite present. There was no improvement in physical properties for the aluminum treated irons and the use of aluminum did not significantly reduce the amount of carbon and sulfur in the molten metal.

The use of pure calcium as an inoculant for cast iron melted in an induction furnace produced an abundant supply of suitable nuclei from which eutectic cells could form. Under similar conditions a corresponding blank iron contained relatively few nuclei.

Induction furnace cast irons, when inoculated with aluminum, had a higher temperature of initial formation of eutectic as compared to the blank irons, but showed no increase in physical properties and no marked change in graphite distribution, other than a possible thickening of the graphite flakes. Silicon inoculated cast irons showed no change in initial temperature of eutectic formation and no improvement in graphite distribution or physical properties. The ladle addition of fine graphite resulted in an increase in the temperature of initial eutectic formation. The use of calcium as a ladle addition raised the temperature at which the eutectic started to form by 50 to 75°F.

Aluminum used as a ladle addition for cast iron melted in the induction furnace was effective in producing a marked reduction of chill although the graphite was of type D. Similar irons inoculated with silicon showed only minor differences in chill when compared to a blank iron of the same analysis. Calcium inoculated irons also showed a very sharp reduction in chill as well as the presence of type A graphite.

The use of pure silicon and pure aluminum as inoculants for gray cast iron produced no significant changes in transverse strength, deflection, or triangular resilience as compared to similar blank irons, whereas the use of calcium resulted in a definite improvement in these physical properties.

Specific observations and conclusions from this report are:

Aluminum

1. Aluminum caused a marked reduction in chill.
2. Aluminum was not effective in promoting type A graphite distribution.

3. The use of aluminum did not improve physical properties.
4. Aluminum ladle additions raised the temperature of initial eutectic formation by about 50°F. on the average.
5. Aluminum additions did not change the amount of carbon and sulfur in the iron.
6. Aluminum did not change the cell size of the cast irons.

Silicon

1. The use of pure silicon as an inoculant was not effective. Cast iron inoculated with silicon was not significantly different from the corresponding blank iron.

Graphite

1. The use of fine graphite as an inoculant raised the temperature of initial eutectic formation by about 60°F. on the average.

Calcium

1. Calcium caused a marked reduction in chill.
2. Calcium was very effective in improving graphite distribution and its use resulted in a large proportion of type A graphite.
3. The use of metallic calcium as an inoculant resulted in a decided increase in physical properties.
4. The use of ladle additions of calcium raised the temperature of initial eutectic formation by 60° to 80°F. as compared to a corresponding blank iron.
5. Calcium inoculated irons showed eutectic cells forming from a large number of nuclei as compared to a blank irons which contained relatively few centers of eutectic cell formation.
6. The addition of calcium decarburized and desulfurized the cast

iron to some extent.

7. Evidence was obtained that the decarburization of the cast iron produced by the use of calcium metal as an inoculant was caused, at least in part, by the formation of calcium carbide.
8. Calcium treated irons showed a reduction in cell size.
9. The size and distribution of the primary dendrites of austenite was not appreciably changed by inoculation with calcium.

GENERAL OBSERVATIONS

Certain general indications and observations as to the nature of the inoculation process are possible as a result of this investigation.

1. The elimination of undercooling does not necessarily result in an improvement in graphite distribution.
2. Strong evidence was obtained that inoculation is a nucleating process.
3. Results of this study point to either a carbide or a sulfide as the nucleating agent.
4. The rate of growth of the eutectic cells is an important factor in graphite shape and distribution.
5. Successful inoculation is accompanied by an elevation of the range of eutectic temperature.
6. A decrease in carbide stability as measured by chilling tendency is not necessarily related to graphite distribution.
7. Aluminum and calcium are remarkably different in their effect on cast iron, and the possibility exists that a group of elements related to calcium may be effective as inoculants.

8. The spacing of the primary dendrites, although it varies somewhat in normal and abnormal iron, cannot be taken as the principal cause of variations in graphite distribution.
9. Successful inoculation is accompanied by a decrease in cell size.

Although a careful study of the microstructure of the quenched iron was made, it has not been possible to reach a final conclusion as to the mechanism of formation of type D graphite. It is the writer's opinion based on this study that final and conclusive evidence regarding the mode of formation of type D graphite cannot be obtained from quenching experiments inasmuch as no quenching process can produce an instantaneous arrest of transformation.

An inspection of the microstructures resulting from this investigation affords evidence that the solidification of abnormal irons is highly critical. Evidence of the highly critical nature of the process is provided in Figure 21 which shows immediately adjacent areas of type A graphite, a highly reticulated type D graphite, massive graphite, and a ledeburite structure of massive cementite and austenite.

VII.

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