THE RELATIVE EFFECTS OF THE INOCULANTS CALCIUM-SILICON AND FERRO-SILICON IN THE PRODUCTION OF NODULAR CAST IRON

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THE RELATIVE EFFECTS OF THE INOCULANTS CALCIUM-SILICON AND FERRO-SILICON IN THE PRODUCTION OF NODULAR CAST IRON

By

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I. Introduction

The commercial grades of gray cast iron range in tensile strength from 20,000 psi minimum to 60,000 psi minimum, with practically no ductility. Ductility as defined in the Metals Handbook is "the property that permits permanent deformation before fracture by stress in tension." The size, shape, and location of the graphite flakes is largely responsible for the lack of ductility and the limited strength of these cast irons.

Malleable cast iron is produced from specific metal mixtures. The metal as-cast is composed of a very hard structure known as cementite. It is necessary to heat treat all as-cast malleable iron to obtain a structure consisting almost entirely of ferrite and graphite in the form of nodules. Malleable irons having this structure possess ductility, whereas the commercial cast irons have practically none. However, malleable cast iron is much more costly to produce.

The structure of the iron as-cast may be changed by the addition of materials to the molten metal as it is being poured into the ladle of just before it is poured into the mold. The change in physical properties that is obtained is of such an extent that it cannot be explained by just the change in composition resulting from the use of these materials. These materials are known as inoculants. Two inoculants that have been used for many years are calcium-silicon and ferro-silicon.

Morrogh and Williams in 1948 published their results on the utilization of cerium for the production of cast iron with nodular graphite in the as-cast contition. During the discussion of this paper, T. H. Wickenden of the International Nickel Company announced

a method utilizing magnesium for the production of cast iron with nodular graphite in the as-cast condition. The magnesium or cerium addition is followed by the addition of a graphitizing inoculant. This type of inoculant is one which contains elements that promote the appearance of carbon in the form of graphite. Some of these are ferro-silicon, calcium-silicon, ferromanganese-silicon, zirconium-silicon, silicon manganese-zirconium, and nisiloy.

The advantages of nodular iron--high strength, (100,000 psi), some ductility in the as-cast condition, increased shock resistance over commercial gray irons, and production cost equivalent to gray iron--have been widely acclaimed. As yet there is neither enough control nor basic knowledge of the process for its adaptation on a commercial basis.

Some recent work done at Michigan State College[6] has indicated the superiority of calcium-silicon over ferro-silicon as the inoculant in commercial gray irons. As either of these graphitizing inoculants can be used in the production of nodular cast iron, an investigation as to their relative effectiveness is the purpose of this research.

II. Survey of Literature

Some of the terms designating this new type of cast iron are: spheroidal-graphite cast iron; spherulitic cast iron; ductile cast iron; and nodular cast iron. As reviewed in an article from the American Foundryman magazine[7] nodular irons may be ductile or relatively non-ductile, hard or relatively soft, magnetic or non-magnetic, heat resisting or not particularly heat resisting, etc. Therefore it is not possible to characterize them by any one property and in this way to name them.

A nodular structure is "characterized by nodules". A nodule is "a rounded mass of irregular shape". These definitions from Webster's Collegiate Dictionary could describe the graphite in malleable cast irons as well. The nodular graphite in malleable cast irons is usually referred to as "temper carbon nodules", thus implying that these nodular graphite structures are produced by heat treatment.

There are two forms of nodular graphite distinguishable in malleable cast irons. The form which occurs when manganese sulphide is present is described as "graphite flake aggregate temper carbon nodules". This structure is characterized by an aggregate of small, apparently randomly orientated graphite particles, and is typical of American or blackheart malleable iron.

When the sulphur that is present is predominantly in the form of iron sulphide, the temper carbon nodule is described as spherulitic. This form of nodule is found in the European whiteheart malleable and also in the as-cast nodular cast irons.

"Spherulitic" does not mean the same as "spheroidal". Spher-

ulites may have many shapes. Usually the spherulites of graphite in cast iron are approximately spheroidal in outline. "Each spherulite consists of a number of graphite crystallites radiating from a common center, the basal planes of each hexagonal graphite crystallite being oriented so that they are approximately at right angles to radii of the spheroid of which the spherulite can be considered to be composed."(8)

Therefore when we speak of "nodular iron" or "nodular cast iron" in reference to the cast iron that is obtained with the proper magnesium or cerium treatment, it is implied that all or a substantial part of the graphitic carbon is in the form of spherulitic nodules in the as-cast condition.

The production of nodular cast iron is not so simple as just adding magnesium to iron. The base iron must be within a particular range, and an optimum amount of magnesium must be retained.

Some of the recommended base iron compositions are listed in Table I.

Table I - Base Iron Compositions (Per Cent)

TC	Si	Mn	P	S	Referance
3.0-3.5	2.0-3.0	0.5-1.0	.15	.03	3
3.2-3.6	1.8-2.5	0.3	.05	-	13
3.2-3.6	1.8-2.5	0.1	.04	-	13
3.1-3.6	2.0-2.3	0.1-0.2	.02-.03	-	13
3.2-3.6	1.8-2.5	0.3-0.4	.05	.03-.04	9
3.2-3.5	2.0-2.3	.42-.80	.06-.13	.01	14
3.6-4.2	1.6-2.0	0.1	.1	.04	11

In the cerium process it is necessary that the iron be hypereutectic, that is, the carbon content should be higher than the value ~~4.3 - 1/3 (% Si + % P)~~ $C = 4.3 - (1/3\ \%Si + \%P)$. In the magnesium process the iron may be either hyper- or hypoeutectic. It is believed that there may be no fundamental difference between the magnesium and cerium treatments other than that more cerium is required to produce a given effect.(35) Ziegler, Meinhart, and Goldsmith(3) comment that a carbon content under 3.0 per cent will result in a stronger metal, but it will be more difficult to machine. By increasing the amount of carbon while the rest of the composition remains essentially the same, Myskowski and Dunphy(4) with a series of photomicrographs show that the size of the nodules increases. Morral(20) recommends a carbon content of at least 3.5 per cent to prevent excessive shrinkage. As a general rule the carbon content is around 3.5 per cent.

For the cerium process it is recommended(36) that the silicon content after the double treatment should be in excess of 2.3 per cent, but not greater than 3.3 per cent. When nickel and copper are present the minimum silicon content may be slightly lower, but not lower than 1.8 per cent provided both or either of these elements is present to give an equivalent silicon content of 2.3 per cent. This is assuming 1 per cent silicon equals 3 per cent nickel or copper. Similarly for the magnesium process Ziegler, Meinhart, and Goldsmith(3) state that less than 2.0 per cent silicon will produce white iron, while over 3.0 per cent will cause ferrite to be too brittle.

The general effect of increasing amounts of manganese is

the inhibiting of the formation of ferrite, even with fairly high silicon contents. Stated another way, manganese acts as a carbide stabilizer. For the cerium process it is recommended[36] that the manganese content should be between 0.5 per cent and 0.9 per cent except when the element is used to obtain special properties and structures. For the magnesium process Ziegler, Meinhart, and Goldsmith[3] state that a manganese content of less than 0.3 per cent has resulted in poorer physical qualities than when it was kept between 0.5 and 1.0 per cent. They offer no explanation for the effect on physical qualities with less than 0.3 per cent manganese. There is some disagreement as to the effect of manganese with respect to magnesium. Holdeman and Stearns[9] comment that if the sulphur content is initially high, a higher manganese content such as 0.8 per cent will reduce the necessary amount of magnesium. Max Kuniansky[11], on the other hand, with reference to the production of nodular cast iron on a commercial basis, states that by keeping the manganese low, a lesser percentage of magnesium alloy was necessary. He recommends a 0.40 per cent maximum manganese content. The sulphur composition of the base iron he used is low, 0.04 per cent. The general purpose of manganese in commercial gray iron is to act as a scavenger with regard to the sulphur. As magnesium or cerium act as desulphurizers in nodular iron, the manganese will act primarily as a carbide stabilizer.

It is believed[36] that phosphorus has a harmful effect on the properties of nodular cast iron. With phosphorus contents in excess of 0.5 per cent the solubility of cerium is

reduced to a figure below the minimum required for the production of nodular irons. The recommended range is 0.1-0.5 per cent phosphorus. On the other hand, E. K. Smith[15] referring to some experiments using the magnesium treatment for nodular iron states that phosphorus is not a deterrent to nodule formation. However, the phosphorus contents in these heats ran from only 0.28 per cent to .045 per cent. Ziegler, Meinhart, and Goldsmith[3] state that phosphorus is not effected by magnesium. Contrary to this, Rehder[23] states that magnesium additions produce a definite dephosphorizing action. Some addition agents are more effective than others with as much as 70 per cent dephosphorization being possible. He also states that the section sensitivity, with regard to the per cent minimum nucleating magnesium required, is less at lower phosphorus content.

In order to produce nodulizing effects it is necessary to use a low sulphur base metal (0.03 per cent sulphur, maximum) or to desulphurize with soda ash, or to add excessively large amounts of magnesium.

Table 2 lists some of the magnesium alloys that have been used, the per cent magnesium that has been added, and the per cent magnesium that is found in the iron on final analysis. A more complete picture of the efficiencies of various magnesium alloys is shown in Table 3. It must be remembered that these alloying efficiencies are dependent on the temperatures of the melt at the time of addition[16] (increasing temperature decreasing the recovery) and most certainly on the sulphur content of the iron.[15, 17]

Table 2 - Some Magnesium Alloys Used

Alloy	Per Cent Mg Added	Per Cent Mg Retained	Reference
80Ni-20Mg	0.25	0.03-0.1	9
50Ni-50Mg	0.35-0.55	0.05-0.07	10
50Cu-50Mg	0.35-0.55	0.05-0.07	10
80Ni-20Mg	0.25	0.18	3
50Cu-50Mg	1.5	0.12	15

Table 3 - Alloying Efficiencies of Various Magnesium Alloys (9)

Alloy		Approx. Alloying Efficiency, Per Cent
Mg-Cu	50-50	5-8
	30-70	8-15
	20-80	9-15
	10-90	20-25
Mg-Ni	50-50	5-8
	20-80	25-40
	10-90	30-40
Mg-Sb	20-80	5
Mg-Al	55-45	15
	20-80	8
Mg-Li	90-10	5
Mg-Zn	50-50	5
	25-75	5
Mg-Cu-Zn	50-35-15	5
Mg-Bi	50-50	5
	15-85	10
Mg-Si	63-27	3-10
Cell Magnesium	100	5

Table 4 shows the magnesium recovery from various addition agents as determined by three investigators. Data on original sulphur contents are lacking, but it is probable that the sulphur contents before additions are in the range 0.02-0.04 per cent.[23]

Table 4 - Magnesium Recovery[23]

Addition Agent		Average Recovery, per cent Donoho	Holdeman & Stearns	Rehder
Cu-Mg	50-50	12	5-8	10-14
	70-30	13	8-15	-
	80-20	15	9-15	-
	90-10	-	20-25	30-35
Ni-Mg	50-50	8	5-8	-
	82-18	27	25-40	30-35
	90-10	-	30-40	-

J. E. Rehder[23] comments that the data of table 4 are out of date and of little commercial interest, but nothing has been published of other results. The actual amount of sulphur remaining in the iron after the magnesium treatment has a major effect on the amount of residual magnesium in the iron necessary to the formation of nodular graphite. When the following assumptions are made relative to determining the magnesium that actually takes part in the formation of nodular graphite, it follows that the amount of magnesium as magnesium sulphide should be subtracted from the total magnesium present.

1. Assume that MgS exists as such.
2. MgS does not take part in the nucleation process for nodules.
3. All the sulphur present is as MgS.

The nucleating magnesium will be equal then to the total magnesium

minus per cent sulphur x 0.75. Rehder[23] believes the nucleating magnesium exists as a carbide. Also a certain minimum nucleating magnesium content is necessary for a completely nodular structure to be formed. Below this amount some proportion of nodular graphite below 100 per cent is formed. Above this minimum amount free carbide appears in light sections and then in heavier sections as the minimum amount is exceeded. The nucleating magnesium is apparently independent of actual sulphur content and type or method of magnesium addition. It is probably dependent on other chemical composition and method and type of post-inoculant.

DeSy[24] gives a formula for estimating the amount of magnesium to be added.

$$Mg(added) = \frac{Mg(residual) + 0.75(S_1 - S_2)}{Y}$$

It is necessary to know the apparent recovery (Y) and also the sulphur content of the original iron. The residual magnesium is fixed. When speaking of the residual magnesium and sulphur it is necessary to place the location of the samples. A curve plotted for mechanical properties vs. Mg(residual) shows a marked maximum. The general ideal conditions necessary for an element to be capable of forcing the spherulitic crystallization of graphite, according to DeSy[24], are as follows.

1. Should be a strong deoxidizer.
2. A stabilizer of carbides.
3. Should not form components which may precipitate in the

hexagonal system in the liquid.

4. If not soluble in iron, should be capable of emulsification with iron as liquid or gas.
5. Element should be a graphitizer.

Bogart[25] from his talk "Observations on Nodular Iron" states that mechanical properties reach a maximum at about 0.025-0.045 per cent residual magnesium. Best properties are obtained at the lowest magnesium residual which produces a fully nodular structure. The Ford Motor Company operates with residual magnesium around 0.035 per cent with additions ganged to allow for interval between inoculation and pouring.

With the holding of 50 pound melts at constant temperature it has been found that the magnesium nodulizing effect largely disappears in about ten minutes. There is a gradual deterioration of the nodulizing effect instead of a sharp line of demarcation as between treated and untreated metals.[5,9] It is possible that with larger ladles and dropping temperatures the effect would persist for a longer time.

J. E. Rehder, Albert DeSy, and Harold Bogart have been in agreement on the existance of a nucleus for nodular graphite formation. H. Morrogh has been opposed to this belief. Rehder in summarizing his work[25] believes as follows.

1. Nodular graphite is the result of growth on specific nuclei.
2. There are radial and non-radial graphite types.
3. A nucleus exists in every nodule.
4. The nucleus is hard and relatively chemically inert.

5. The nucleus is hexagonal in crystal habit.
6. Size and size distribution of nodules is influenced by the nodulizing agent used.
7. Nodules contain Si, Fe, and Ti, with the existance of TiO_2 and Fe_2O_3 confirmed by x-ray diffraction.
8. The nucleus may be a carbide or a nitride.

Morrogh[35] believes that extraneous nuclei (other than graphite) are not required, and that the spots in the center of the nodules are due to optical effects. These effects may possibly be a result of the plane of polishing coinciding exactly with the basal plane of a radial crystallite.

Albert DeSy has advanced the hypothesis that the crystal system of the nuclei or solid particles suspended in molten gray iron determines whether nodular graphite or flake graphite will precipitate. Table 5 shows the crystal systems of austenite, cementite, and graphite, and some compounds which are generally solid at the temperature of the cast iron eutectic. These compounds may be present in suspension in the cast iron as a result of the melting or as additions of deoxidizing or inoculating materials.

Table 5 - Crystal Systems[2]

Cubic		Tetragonal	Orthorhombic	Hexagonal	Rhombohedral
Austenite			Cementite	Graphite	
MgO	MgS	CaC_2	$(MnO)_2SiO_2$	FeS	$CaSi_2$
CaO	CaS	TiO_2	$(FeO)_2SiO_2$	SiO_2	Al_2O_3
SrO	SrS	CrC_2	$(FeO.MnO)SiO_2$	SiC	
BaO	BaS	CeC_2			
MnO	MnS	LiC_2			
FeO	Li_2S	$ZrSiO_4$			
CeO_2	TiC				
H_2O	ZrC				
TiN	ZrN				

In order to obtain nodular graphite Fe_3C must be precipitated, and this carbide decomposed toward the end of or after the solidification of the eutectic. If the iron is deoxidized with elements having a greater affinity for oxygen than silicon, which do not crystallize in the hexagonal system, and which precipitate in the solid state above the eutectic temperature, the compounds will act as nuclei for austenite. As a result of the lack of graphite forming nuclei, the tendency will be towards solidification in the metastable system at the eutectic, i. e. austenite, cementite, and liquid. Such elements are Mg, Li, Ba, Ca, Sr, V, Ce,and Ti.

Von Keil and his co-workers(26) have suggested that a submicroscopic silicate slime nucleates the melt to give coarse graphite, while the absence of the slime allows the formation of undercooled graphite. Norbury and Morgan(27) in order to explain the effect of Ti and CO_2 suggested that this process modified the slime in such a way as to make it soluble, thus allowing the formation of fine undercooled graphite. About this time the process of inoculation was introduced. The silicate-slime theory could not explain the inoculating effects of ferrosilicon or calcium silicon, or graphite. Piwowarsky(28) developed a graphite-nuclei theory to explain the tendency towards undercooling as a result of superheating. As graphite dissolves very rapidly above the liquidus, this theory was weakened. Eash(29) goes along with the graphite-nuclei theory in that the inoculating effect of ferrosilicon is due to localized silicon concentrations reducing the carbon solubility. Morrogh and Williams(26) believe that calcium-silicon acts similarly to ferro-silicon in this manner.

The only reference giving the composition of the melt and per cents of addition agents utilizing calcium-silicon as the inoculant was by DeSy[31]. This data is found in Table 8. Other references[9, 1] mention that calcium-silicon has been used but is not so effective as other inoculants. Usually 75-90 per cent silicon in the ferro-silicon inoculant has been used to give a 0.4-0.6 per cent silicon addition.

III Original Research

The purpose of this research was to determine the relative effects of calcium-silicon and ferro-silicon inoculants in the production of nodular cast iron. It was decided to choose a base iron composition similar to those generally used, to make a magnesium addition as 80Ni-20Mg alloy, and to inoculate this molten metal with calcium-silicon or ferro-silicon in amounts such that equivalent silicon per cents are available for pick-up.

Table 6 - Base Iron Composition

C	Si	Mn	P	S
3.75	2.60	0.40	0.10	0.03 Max

The above base iron composition has been used in the casting of step blocks for dilatometer studies of the annealing of nodular iron.[3] In the one inch section a predominantly pearlitic background was obtained.

The per cent magnesium to be added was selected from the survey of literature to be 0.40 per cent magnesium in the form of an 80Ni-20Mg alloy. This magnesium alloy was added to the furnace crucible. It was believed that the temperature drop on pouring a 30 pound heat into a preheated ladle plus the loss in temperature obtained on the addition of magnesium would be too great. The inoculant was also added to the furnace crucible.

A 35 KVA Ajax High Frequency Induction Furnace with a basic crucible was used. A 30 pound charge was melted for each pour. The magnesium alloy was added through a "stove pipe" fixture hung over the open crucible. This was a 3 foot length of pipe about 2

inches in diameter that was welded to a flanged bottom 3 inches long and 8 inches in diameter. The flanged bottom covered the open top of the crucible, and hung about an inch above it. Half way up the 3 foot length of pipe was a slide on which the magnesium alloy was placed. By pulling out the slide the alloy would drop into the molten metal. The purpose of the fixture was to afford a quick and safe method for adding the alloy plus protection from the resulting flash and any molten metal that might splash out.

After the magnesium alloy was added, the fixture was swung clear of the crucible and the inoculant added. The power was turned on for mixing and also to raise the temperature of the melt.

A standard chill block was cast for each heat. It was decided to use a keel block casting for the purpose of obtaining sound tensile bars. Diagram I shows the dimensions of the keel block pattern. It is an adaptation of the type suggested to the A.F.S. and A.S.T.M. committees for consideration as an alternate standard.(30)

The molds for the keel blocks and the chill specimens were made of a core sand mix and baked at 350°F overnight (12 hours).

The furnace charge was made up of the following constituents.

Table 7 - Furnace Charge Compositions (Per Cent)

Hanna Malleable Pig		Ferro-silicon		Ingot Iron	
C	4.2	C	0.44	Fe	100
Si	1.52	Si	27.4		
S	0.025	S	0.018		
P	0.099	P	0.033		
Mn	0.36	Mn	0.84		

The inoculants were commercial grades of ferro-silicon and calcium-silicon. Their compositions are listed in Table 8.

Table 8 - Per Cent Composition of Inoculants

Ferro-Silicon		Calcium-Silicon	
Si	92.73	Si	63.9
Al	1.68	Ca	31.4
Ca	0.25	Fe	1.7
		Ti	0.16
		Al	1.05

As the Hanna malleable pig was in 50 pound pigs it was necessary to cut it into slices about 3/4 inch thick and then break the corners off so that the slice would fit into the crucible. A slice weighed approximately 2 and 3/4 pounds. Three or four pigs were cut up at the same time and their identity maintained so that approximately an equal amount of each pig went into a charge. The 27 per cent ferro-silicon was selected at random from the bin and entered the charge in chunks about one inch square. The ingot iron was selected at random from the bin and was in the form of punchings one inch in diameter and from 1/8 - 1/4 inch thick.

The ingot iron was placed in the crucible first. For heats J-1 through J-5 all the 27 per cent ferro-silicon was charged next. On top of this was charged Hanna malleable pig in slices and chunks to fill the crucible. The power was then turned on. For heats J-6 through J-11 the ingot iron was on the bottom and next was Hanna malleable pig to fill the crucible. The 27 per cent ferro-silicon was added later in the melt. In both procedures the rest of the pig was added as the melt down progressed.

After the melt down the slag was removed and a temperature reading taken with an optical pyrometer. Up to heat J-4 no attempt was made to control ultimate melt down temperature as furnace and melt down characteristics were unknown. After heat J-4 an attempt was made to hold the melt-down temperature to 2785°F and also to make the Ni-Mg addition at this temperature. The pipe fixture was swung over the open crucible, the power turned off, and the magnesium alloy addition made. The power was turned off in case any of the molten metal splashed out and shorted out the furnace. The alloy was in chunks about ½ inch square. After the addition the fixture was swung away from the crucible, the slag removed, the power turned on, and the inoculation made. The stirring action of the induced currents in the molten metal was utilized to assure thorough mixing of the inoculant in the metal. From one to two minutes were allowed for mixing. The power was turned off, the slag removed, and the heat poured.

In heats J-1 through J-5 the heat was poured in the following manner.

1. Small amount poured in a cast iron mold to get a completely chilled sample for the carbon determination.
2. Chill block mold poured.
3. Three keel block molds poured.
4. Rest of the heat pigged.

For heats J-6 through J-12 a small plug, one inch in diameter by 1½ inches high, was poured just after the first slag was removed and before any magnesium or inoculating additions were made. The purpose was to determine the melt down composition of carbon,

silicon, and sulphur. The remainder of the casting procedure was the same as above.

At the time this investigation was started, the only references that were found on the use of calcium-silicon as an inoculant stated that it had been tried but was not as effective as ferro-silicon.* Due to the lack of information using a Ca-Si inoculant and the lack of experience of this investigator on producing nodular irons, it was necessary first of all to develop a procedure using the equipment and material that was available. For heats J-1 through J-6 the per cent magnesium added was varied. In heat J-5, 0.15 per cent magnesium was added. Micro examination of a specimen showed flake graphite and nodules. The flake graphite was located on the surface of the casting (see Figure 5). Morrogh and Williams[26] describe a similar occurance and attribute it to the inoculating effect of the mold wall on a low cerium content casting. Heats J-1, J-4, and J-6 were treated with 0.40, 0.20, and 0.30 per cent magnesium respectively. The Brinell hardness of J-1 was 330. The hardnesses of J-4 and J-6 were 300. 0.30 per cent

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* Late in the investigation a note[31] was found giving the following composition.

Table 9 - Analysis Using Ca-Si as the Inoculant

C	Si	Mn	S	P
3.33	2.73	0.9	0.02-0.04	0.10

0.5 per cent magnesium alloy was added. This we assumed to be a 50-50 alloy because of the large amount added. 0.2 per cent of a Ca-Si alloy was added as an inoculant. The letter went on to say that this gave a nodular iron. No information was included on the type of Ca-Si alloy or if the 0.2 per cent referred to the available silicon in the inoculant.

magnesium addition was selected as this amount was common in the practice of adding 80Ni-20Mg. The 0.20 per cent addition seemed too close to the 0.15 per cent that gave the flake graphite-nodular graphite structure.

Through the heat J-6, Ca-Si had been the inoculant. The microstructure of all these heats was nodular graphite, pearlite, and a considerable amount of interdendritic cementite. We were attempting to achieve a pearlitic matrix with the graphite in nodules. Heat J-7 was made using Fe-Si inoculant, again adding an amount to make available 0.4 per cent silicon. The microstructure of this heat was the one desired. It was known then that the melt down and addition procedure would give the desired results and control could be maintained. The log of heat J-11 is given in Table 10 as an example of the procedure followed.

The calculated composition of heat J-9 was changed so as to be more in line with the base composition of Table 6. This resulted in a lower carbon and a lower silicon content. The desired microstructure was again obtained using Fe-Si as an inoculant. From the previous heats it was now apparent that the silicon loss for this melt down procedure was about 0.1 per cent. This loss was taken into consideration on calculating the charge for heat J-10. As a result the melt down silicon content differed by 0.06 per cent from that of heat J-9. It was suspected by now that the silicon pick-up from the Ca-Si inoculant was not as much as that from the Fe-Si inoculant. Therefore an amount of Ca-Si inoculant was added to make available 0.5 per cent silicon. The silicon pick-up for heat J-10 was the same as that for J-6, 0.16 per cent. The

microstructure of J-6 and J-10 was similar; nodular graphite, pearlite, and interdendritic cementite.

The charge for J-11 was calculated to give the same final composition as J-9. This was accomplished by adding a greater amount of ferro-silicon (27 per cent silicon grade) in the initial charge. The amount added was the difference between the final silicon contents of J-9 and J-10. This difference was 0.28 per cent and was rounded off to 0.30 per cent. Again 0.5 per cent silicon as Ca-Si was added as the inoculant. The silicon pick-up this time was 0.24 per cent. The final compositions of J-9 and J-11 were similar. The microstructure was of the desired type and matched those of J-7 and J-9. The charge for heat J-12 was the same as J-11. This heat was made with the idea in mind that the calcium was going into the melt and enforcing the carbide stabilizing tendency of the magnesium that was already there. By adding Ca-Si in an amount that would make available the same amount of silicon for pick-up that was actually found in heat J-11, the amount of calcium entering the melt would be less and the desired microstructure might be obtained. The Brinell hardness of this heat was 269 and the microstructure was nodular graphite, pearlite, and interdendritic cementite. There was less interdendritic cementite present in this heat (J-12) than in heat J-10.

Sampling Procedure

The $1\frac{1}{4}$ x $1\frac{1}{2}$ x 6 inch test blanks were cut from the keel blocks and machined into standard .505 test bars. Drillings were made with a $\frac{1}{4}$ inch drill as shown in Figure 11 in the riser part of the keel

block. Drillings were also taken from the base iron plug. Samples for carbon determination were prepared by breaking up intentionally chilled treated iron with a hammer and mortar.(32) This chilled iron was obtained by pouring a small amount into a cast iron pig in the course of casting the keel blocks.

Chemical Determination and Preparation of Specimens

The carbon determinations were made by combustion and volumetric analysis. Duplicate samples were run for each heat. The process was checked continually with Bureau of Standards cast iron samples.

The silicon in one gram samples was determined by evaporation with perchloric acid.(33) Silicon contents of heats J-1 through J-12 were determined from drillings in the keel block. The melt down silicon contents of heats J-6 through J-12 were determined similarly from the one inch diameter plug samples.

The manganese in 0.75 gram samples was determined by the ammonium persulfate oxidation method. (p. 196 Reference 33)

The phosphorus in 2 gram samples was determined by the alkalimetric method. (p. 220 Reference 33)

Sulphur was determined by combustion and volumetric analysis. Samples were run from the base iron plugs and the keel blocks.

The metallographic specimens were mounted in bakelite and polished using the Schaeffler technique.(37) The etchant in all cases was 4 per cent picral.

An attempt was made to polish samples using alcohol instead of water with the AB Micro Polish on AB Micro Cloth. This was done in

view of the apparently water soluble inclusions mentioned by J. E. Rehder.(34)

In order to identify the intercellular-type material, microhardnesses were taken of the ferrite in the rings about the nodules, known cementite, and the intercellular-type material. An attempt was also made to differentiate any iron phosphide that might have been present from cementite by etching a sample in 4 per cent picral, then in 8 per cent chromic acid, and finally heat tinting the etched sample.

The chill blocks were broken in a vise using a 10 pound sledge hammer. No notch was necessary. Due to the characteristic light gray fracture of nodular cast irons it was difficult to see the amount of chill. The broken surface was removed with a cut-off wheel and the burned surface removed with a surface grinder. The surface was wet polished on 280 and 400 grit paper and then etched. All the samples for macro-examination were etched with a mixture of 12 per cent sulfuric acid, 38 per cent hydrochloric acid, and 50 per cent water at 160°F.

Macro-examination Results

As all the keel blocks showed a shrinkage cavity as shown in Figure 10 and the sawed surface of the test blanks indicated porosity, one of the keel block castings was sectioned transversally and etched for macro-examination. The porosity showed up, but did not extend far enough into the test bar blank to influence the tensile results of the finished test bars.

All the chill bars except those of heats J-7, J-9, and J-11

were completely chilled. The chill bars of these heats are shown in Figure 12. All of the heats represented by these bars had the same melt down procedure, and addition temperature. Heat J-7 had a higher final silicon content than J-9, but the same amount of inoculant (0.4 per cent silicon as Fe-Si) was added and the amount of silicon pick-up was essentially the same for both heats. Heat J-11 had a higher melt down silicon content than J-7 or J-9 to offset the low silicon pick-up when using Ca-Si inoculant. The final silicon content of this heat was the same as J-9.

More chill is noticeable in the sample from heat J-11 inoculated with Ca-Si than for heat J-9 inoculated with Fe-Si. The least amount of chill is noticeable in the sample from heat J-7 which contained 0.16 more silicon than J-9 or J-11. Inverse chill is also noticeably associated with this sample.

Micro-examination Results

Figures 1, 2, 3, and 4 are photomicrographs illustrating typical structures found in this series of heats. The structure of Figure 4 is typical of all heats of Brinell hardness around 300. The structure of J-12 showed much less interdendritic cementite and had a Brinell hardness of 269. All of these heats but J-12 were too hard to cut with the power hack saw. Figures 2 and 3 are from heats with the same final composition, but heat J-9, Figure 2 was inoculated with Fe-Si, and heat J-11, Figure 3 with Ca-Si. The size and spacing of the nodules are similar and there is about the same amount of intercellular material. There are a few more nodules without ferrite rings in Figure 1 than in Figure 2. More nodules

are visible in Figure 1 from heat J-7 than in Figures 2 or 3. Also there is more ferrite present. The amount of intercellular material seems to be about the same.

Photomicrographs were taken at x1500 magnification to investigate the nature of the intercellular material. In all cases there was found adjacent to the white intercellular material flake graphite, non-metallic inclusions, and what is believed to be segregated iron phosphide. The non-metallic inclusion is presumed to be Fayalite, $2FeO.SiO_2$ as this type of mineral melts at 2201°F, is medium to dark gray in color by reflected white light, and is colorless, light green, yellowish green, or yellowish brown in color by transmitted white light. Seemingly attached to these inclusions are flakes of graphite.

The etching followed by heat tinting procedure was to distinguish between iron phosphide and cementite in phosphide eutectic of cast iron. The iron phosphide should be colored darker. It is usually difficult to detect steadite when the phosphorus content is about 0.10 to 0.12 per cent. This amount of phosphorus is assumed to stay in solid solution. In cast iron carbon and phosphorus are both soluble in gamma iron to about the same extent 1.7 per cent. With the high carbons of this series of heats, probably what happened is that during solidification the phosphorus was segregated to the outside of the growing austenite areas, which habit is characteristic of normal gray iron. After solidification it would be found in the last portion to solidify. Figure 6 could very well illustrate such a series of events. Two possible ways of explaining this are (one), as the concentration of phosphorus is high in these

areas, and carbon and phosphorus are incompatible at high concentrations, one has to precipitate out. The graphite flakes are visibly attached to non-metallic inclusions in and near to this area. Apparently the inclusions nucleate the graphite. (Two), it is believed that the graphite nodules have an area of influence. As these areas of segregation are removed from the areas of nodules, it might be that the influence of the nodule is not great enough to prevent flake graphite from forming. Close examination of Figure 1 will show nodules immediately adjacent to those areas showing segregation. A possible reason for the cementite persisting is the belief that phosphorus might retard the graphitizing reaction of silicon. There is also the possibility of magnesium segregating to this area and causing the stabilization of cementite. The inoculants of this series of heats do not appear to be affecting these areas of segregation.

After the samples were polished with alcohol as the carrier for the micropolish instead of water, inclusions similar to those mentioned by Rehder[34] were visible. The fine graphite flakes in the intercellular-type areas were more clearly defined. Figure 8 and Figure 9 are photomicrographs at 50X magnification of unetched specimans from heats J-9 and J-11 respectively. The intercellular-type location of the flake graphite is noticeable in both. The size of the flake graphite seems to be about the same, but there seems to be more in J-9 than J-11. The flake graphite in J-9 seems to be more continuous.

Statistical Approach to Variance in Nodule Size

The number of the nodules in Figure 8 was 129 and in Figure 9 was 124. The diameters of the nodules were measured and tabulated in a frequency distribution. From this tabulation the means and standard deviations for the respective heats were calculated. From these results an approximation was made to the standard error of the difference of the means. The ratio of the difference between the mean diameters to the standard error was assumed to follow a normal distribution. From this the probability of occurance of a difference as large or larger than the observed difference was calculated to be 0.3182. The observed difference in mean diameters may well have been due to chance variation. This data is tabulated in Table 13.

Tensile Test Procedure and Results

0.505 inch diameter shoulder-type tensile bars were tested on a 100,000 pound mechanical tensile testing machine. The ultimate strengths, per cents elongation, and hardnesses are found in Table 14. Two tensile bars were made up from heats J-7, J-9, and J-11. These heats were chosen as heats J-9 and J-11 had like compositions and structures. J-9 was inoculated with Fe-Si and J-11 with Ca-Si. J-7 was also inoculated with Fe-Si, but had a higher silicon content. One of the two tensile bars from both heats J-9 and J-11 broke outside the two inch test length.

IV Discussion of Results

An effort was made to control as many of the variables as possible that might influence the characteristics of the final casting. All the constituents of the charges and the late additions were from the same lots. The total melt down times were essentially the same, one hour and forty minutes. The final melt down temperature was 2785°F for heats J-6 through J-12, with the exception of heat J-7. The final temperature of J-7 was 2950°F. A 0.3 per cent magnesium addition as 80Ni-20Mg was added at 2785°F. The range of equivalent carbons was 4.40-4.57. Flake graphite, nodular graphite, cementite, steadite, and ferrite were the microconstituents present.

Microstructure and Chemical Composition

Having as many variables as possible under control, it was assumed that different amounts and types of inoculants would produce differences in the microstructure of two like irons. The following differences might be apparent.

1. The quantity and distribution of flake graphite.
2. The number and size of nodules.
3. The amount and location of intercellular material.
4. The size of pearlite spacing.

Fine graphite dispersion can be attributed to undercooling. Magnesium and cerium promote this undercooling in nodular irons. Two other factors affecting graphite dispersion that are usually considered are time (cooling rate) and composition. For the series of heats J-6 through J-12 the magnesium addition and melt down temperature were about the same (undercooling control). The

cooling rates were essentially the same, i.e., same size casting poured at the same temperature. In some heats the same amount of silicon was available for pick-up from the inoculant. Where the melt down compositions were the same there was a noticeable difference in the microstructures obtained using different inoculants (Figures 2 and 4). However, fine flake graphite was noticeable in both, located in the last areas of the austenite to solidify. This suggests a form of carbon segregation which has been mentioned in connection with gray irons(38).

An ordinary gray iron that would solidify with a white or mottled structure could be forced to solidify with a gray structure by the addition of a graphitizing inoculant. The effect of this addition would be of such an extent that it could not be attributed to the change in composition alone.

The charge of J-10 was calculated to give the same composition as J-6 but 0.10 per cent more silicon as Ca-Si was added. It was hoped that this added silicon in the inoculant would force the decomposition of the interdendritic cementite. However, the same amount of late-addition silicon was picked up and the structure was the same as J-6 (Figure 4).

The amount of silicon going into the melt averaged 40 per cent of that available from the Ca-Si against 100 per cent of that available from the Fe-Si for the addition procedure followed in these heats.

It was thought that a higher melt down silicon content together with the amount of silicon from the Ca-Si usually picked up, would produce an iron with the desired structure. This was

substantiated in heat J-11 (Figure 3).

There were now available for comparison two nodular irons of the same final composition obtained through the use of the different inoculants.

The only difference in flake graphite distribution was that it appeared to be more continuous in Figure 8 (J-9). This could be a result of the greater silicon pick-up from Fe-Si.

The number of nodules was about the same, 129 (J-9) and 123 (J-11). There was a difference in the mean size of the diameters of the nodules. Those from heat J-11 were larger. However, this difference was not significant.

The amount and location of the intercellular material was the same (Figure 8 and 9). The intercellular material in J-9 and J-11 was assumed to be steadite. In the etched microphotographs of Figures 2 and 3 the segregation and intercellular material seems greater in Figure 3 (J-11).

The size of the pearlite spacing was the same.

Chill Characteristics

The addition of the inoculant Fe-Si was more effective in reducing chill for the procedure used in this investigation. The lesser chill reduction obtained with Ca-Si could be a result of the lower silicon pick-up, a carbide stabilizing effect of the calcium, or a combination of both.

Tensile Properties

The Brinell hardnesses of J-9 and J-11 were the same, 255.

J-9 inoculated with Fe-Si had one per cent more elongation. The ultimate tensile strength of J-9 was greater. The lower ultimate tensile strength and per cent elongation of the heat J-11 inoculated with Ca-Si might be attributed to larger intercellular areas. Figures 2 and 3 indicated such a difference, while the unetched photomicrographs of Figures 8 and 9 did not.

V Summary and Conclusions

It is essential that a graphitizing inoculant be used in the production of nodular cast iron. Two of the inoculants that have been used are Fe-Si and Ca-Si. The references to the use of these inoculants on nodular iron stated that Ca-Si was not so effective. However, no evidence was presented in support of these statements.

The method of inoculation used in this investigation has substantiated the reports that Ca-Si was not so effective as Fe-Si. The inoculants were added to the surface of the molten metal. The stirring action of induced currents was utilized for mixing. A 100 per cent pick-up of silicon from Fe-Si was possible while 40 per cent was the average pick-up with Ca-Si.

When the effects of Ca-Si and Fe-Si were compared with regard to chill reduction, tensile strength, and elongation in nodular irons of the same final composition, the inoculant Fe-Si showed a greater tendency (1) to reduce chill, (2) to increase tensile strength, and (3) to give a greater per cent elongation.

The size and number of nodules appeared to be the same. The Brinell hardnesses were the same.

Table 10 - Log of Heat J-11

Charge

27.2 pounds Hanna malleable pig
405 grams ingot iron
600 grams 27 per cent ferro-silicon
113.6 grams Ca-Si (0.5 per cent Si addition)
204.3 grams Ni-Mg (0.3 per cent Mg addition)

Composition by Calculation (Without Si of Inoculation)

C	Si	S	P	Mn
3.87	2.61	0.02	0.09	0.36

2:45 Hydrogen on
405 grams ingot iron on bottom
10 slices pig to fill crucible
3:05 Power on 18 KW
4:05 Conical chunk floating on surface. Turned over with skimmer.
4:13 Mushy chunks floating on surface of bath. Broken up with skimmer. Some kish.
Added half the 27 per cent ferro-silicon.
Added 8 small chunks of pig.
4:25 Mushy chunks floating on top of bath. Broken up with skimmer. Some kish.
Added rest of 27 per cent ferro-silicon.
Added rest of small pieces of pig.
4:38 Some mushy chunks floating on bath. Broken up with skimmer. No kish.
4:45 Small amount of slag floating on bath. No kish.
Pushed to side of crucible.
2785° F.
Power off. Skimmed off slag. Poured base iron sample.
4:47 2785° F.
Power off.
4:48 Added 80Ni-20Mg. About 30 seconds later the reaction was over. Skimmed.
4:48 Power on 15 KW. Added 40Ca-60Si.
4:49 Power off.
Skimmed as much slag off as possible.
4:50 Poured.

Total melt down time one hour and 45 minutes.

Table 11 - Furnace Charges (Pounds)

Heat	Hanna Malleable Pig	27% Fe-Si	Ingot Iron	Inoculant Amount	Inoculant Type
J-7	27.9	1.08	0.892	.132	Fe-Si
J-9	27.2	1.01	1.68	.132	Fe-Si
J-11	27.2	1.32	.892	.251	Ca-Si
J-12	27.2	1.32	.892	.124	Ca-Si

0.45 pounds Ni-Mg added to heats J-7 through J-12

Table 12 - Chemical Compositions (Per Cent)

Heat	Total Carbon	Melt Down Silicon	Final Silicon	Inoculant Amount Si	Inoculant Type
J-6	3.72	2.20	2.36	.40	Ca-Si
J-7	3.78	2.36	2.90	.41	Fe-Si
J-9	3.73	2.24	2.74	.41	Fe-Si
J-10	3.65	2.30	2.46	.50	Ca-Si
J-11	3.73	2.53	2.77	.50	Ca-Si
J-12	3.75	2.46	2.56	.25	Ca-Si

0.3 per cent magnesium added as 80Ni-20Mg

Average manganese 0.32

Calculated phosphorus 0.09

Average melt down sulphur 0.03

Average final sulphur 0.018

Table 13 - Statistical Results on Nodular Diameters

Figure 8 Heat J-9	Cell Boundaries	Figure 9 Heat J-11
7	0-1	11
42	1-2	29
35	2-3	30
26	3-4	40
19	4-5	13
129		123
2.56	Mean	2.62
1.15	Standard Deviation	1.15
	Standard Error	0.145
	Probability of Occurance	0.318

Table 14 - Tensile Properties

Heat	Tensile Strength (psi)	Elongation (%)	BHN	Note
J-7-2	92,700	3.0	241	
J-7-4	95,650	3.0	255	
J-9-2	95,150	-	255	A
J-9-4	101,200	3.0	255	
J-11-5	92,600	2.0	269	
J-11-6	69,000	-	269	B

Note A This tensile bar broke 3/4 inches below the supporting shoulder. There was a slag inclusion located at the fracture.

Note B This bar broke just below the supporting shoulder. The cause of fracture was not determined.

Table 15 - Microhardness (DPH Numbers)

Heat	Ferrite Ring	Cementite	Intercellular Material
J-4	247.0	919.5	
J-5	193.0	919.5	
J-7	223.5	988.0	802.5
			919.5
			988.0

Table 16 - Metallographic Data

Magnification	Objective	Eyepiece	Bellows Setting (cm.)
50X	5.6x0.12 N.A.	5X	46.3
100X	8.0x0.20 N.A.	7.5 H.P.	45.5
1500X	85.0x1.25 N.A.	10X	42.8

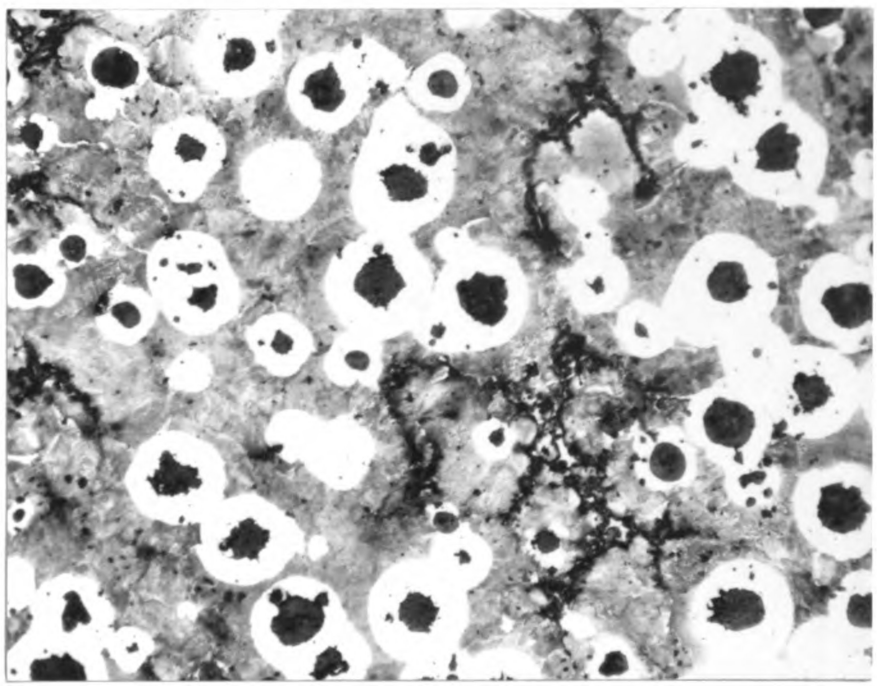

Figure 1

Heat J-7, As-cast structure, etched, 100X

Inoculant: 0.4 per cent Si as Fe-Si

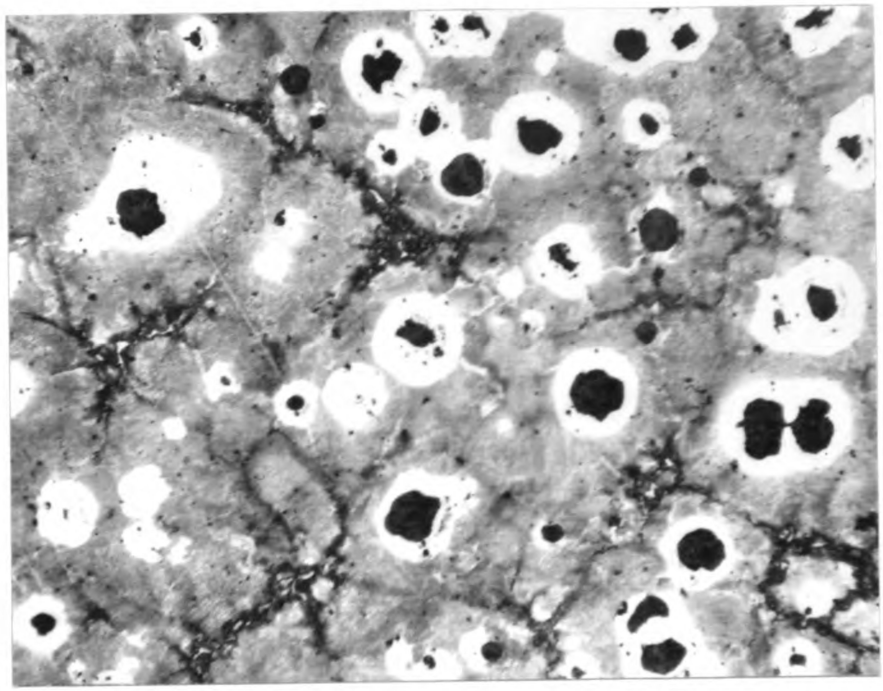

Figure 2

Heat J-9, As-cast structure, etched, 100X

Inoculant: 0.4 per cent Si as Fe-Si

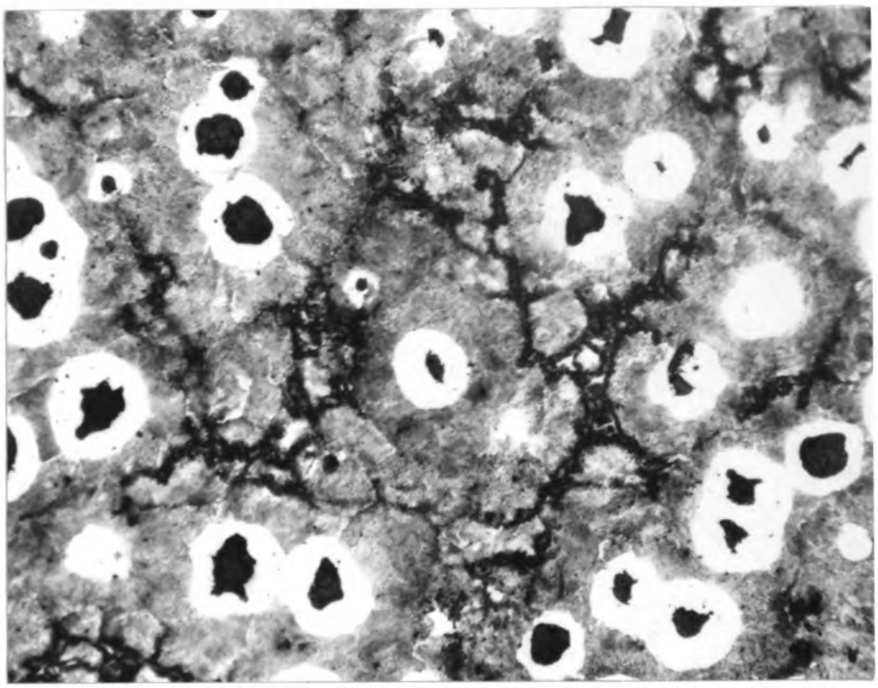

Figure 3

Heat J-11, As-cast structure, etched, 100X

Inoculant: 0.5 per cent Si as Ca-Si

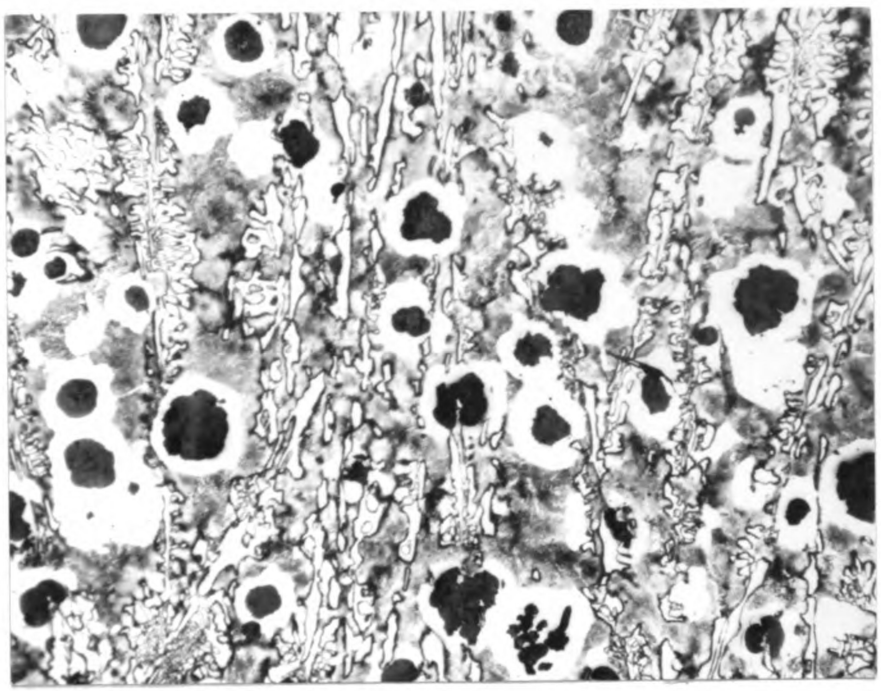

Figure 4

Representative of heats J-1 through J-6, etched, 100X

Inoculant: 0.4 per cent Si as Ca-Si

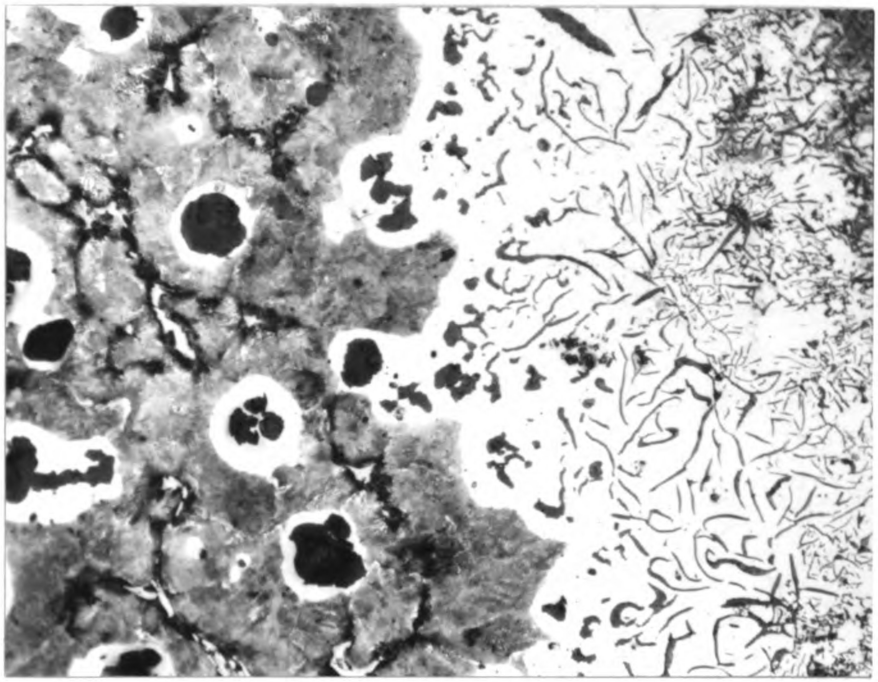

Figure 5

Heat J-5, As-cast structure, etched, 100X

Inoculant: 0.4 per cent Si as Ca-Si

0.15 per cent Mg as 80Ni-20Mg

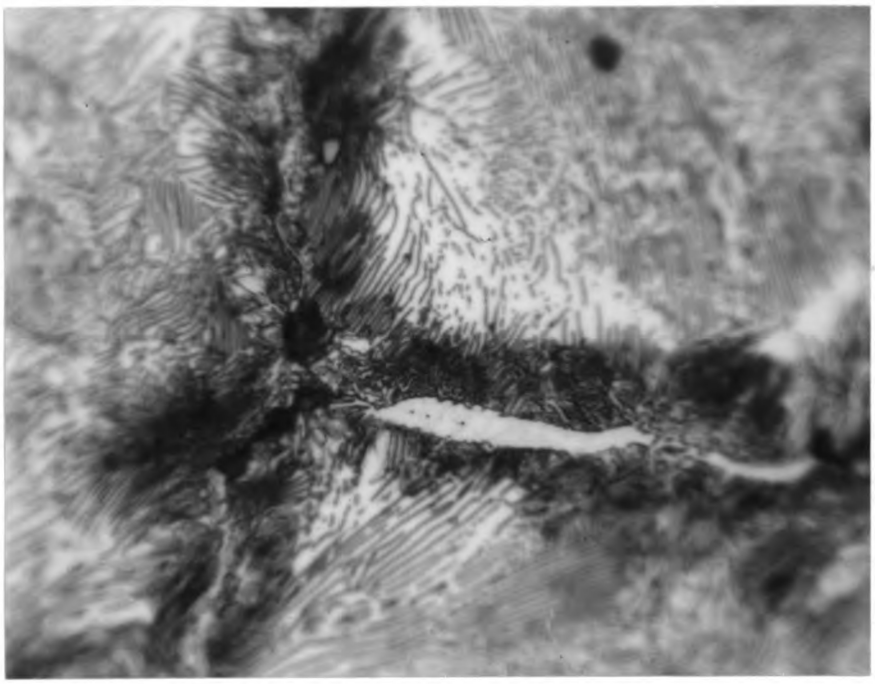

Figure 6

As-cast structure showing area of segregation around intercellular area, etched, 1500X

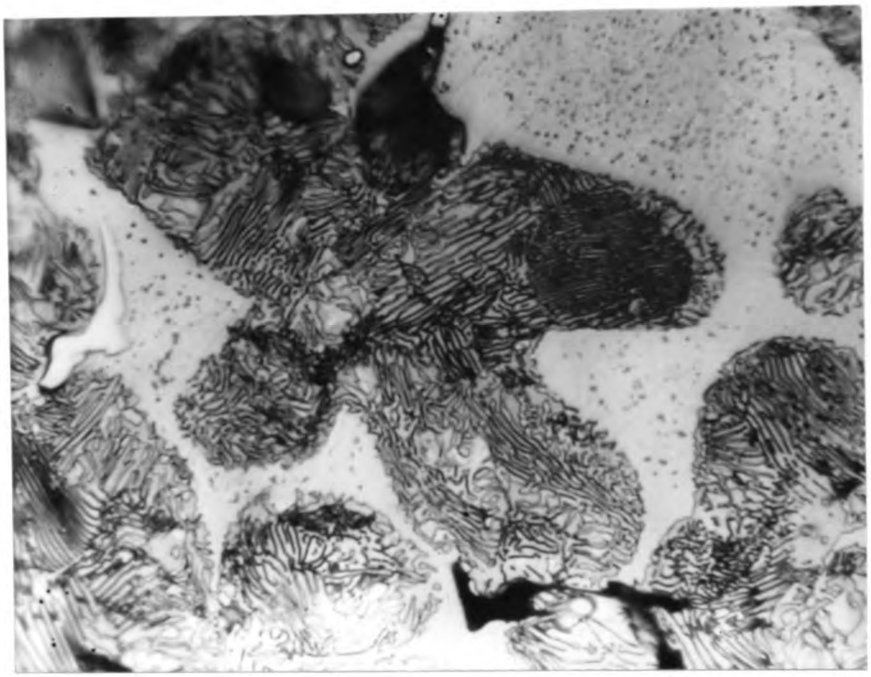

Figure 7

As-cast structure illustrating intercellular area of what is assumed to be steadite, etched, 1500X

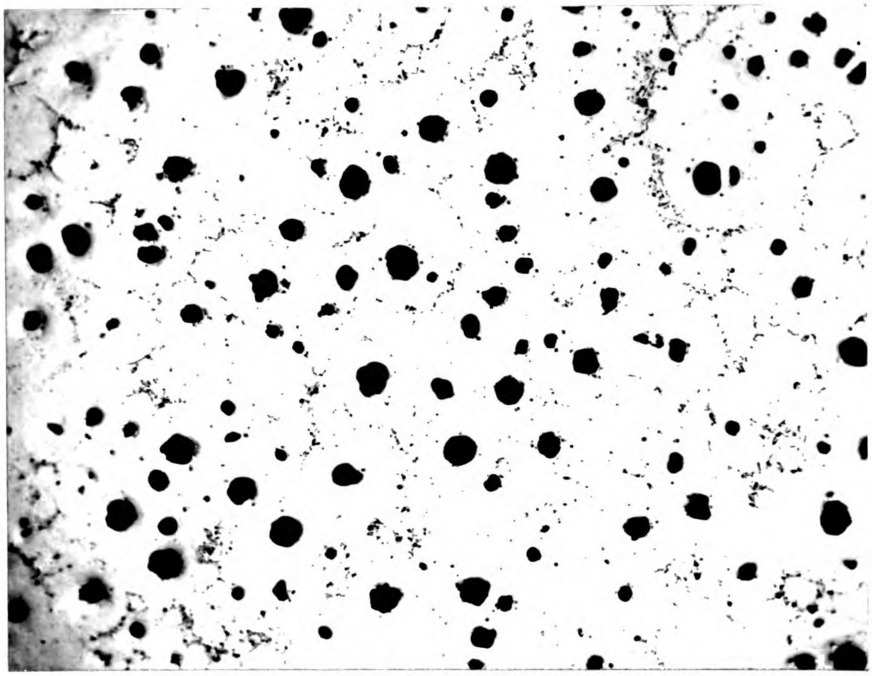

Figure 8

Heat J-9, As-cast structure, unetched, 50X

Inoculant: 0.4 per cent Si as Fe-Si

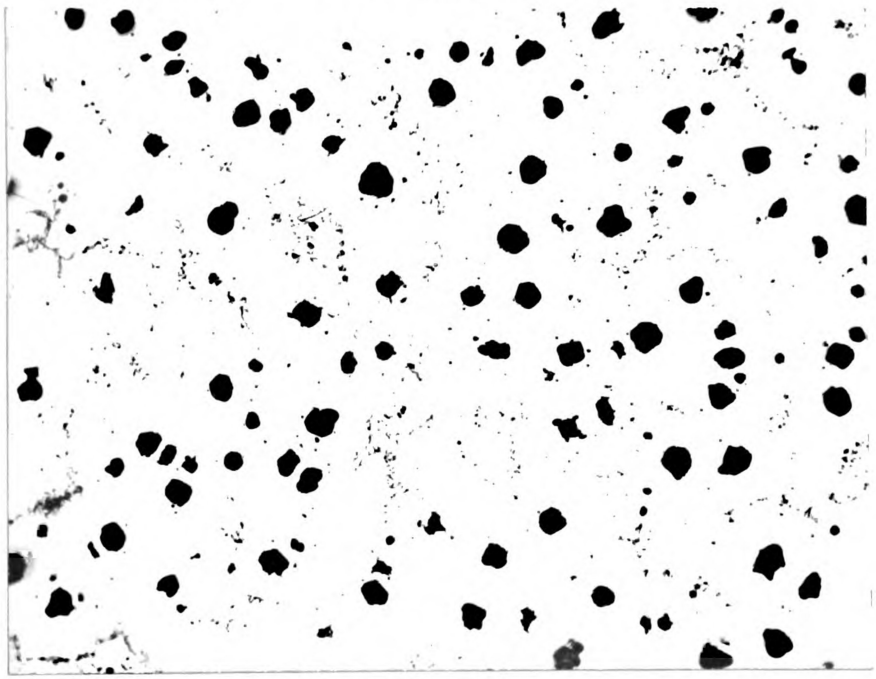

Figure 9

Heat J-11, As-cast structure, unetched, 50X

Inoculant: 0.5 per cent Si as Ca-Si

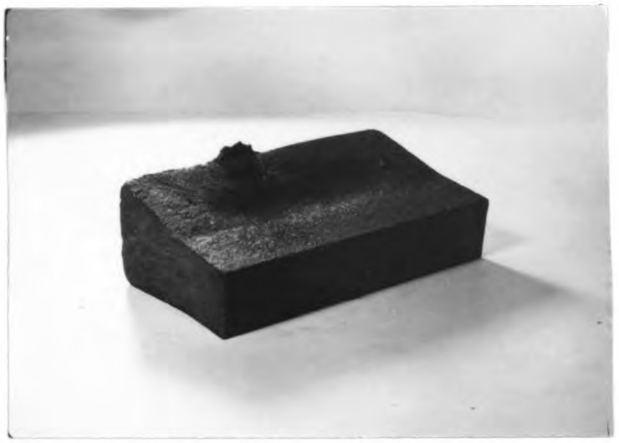

Figure 10

Keel block lying on its side to illustrate shrinkage

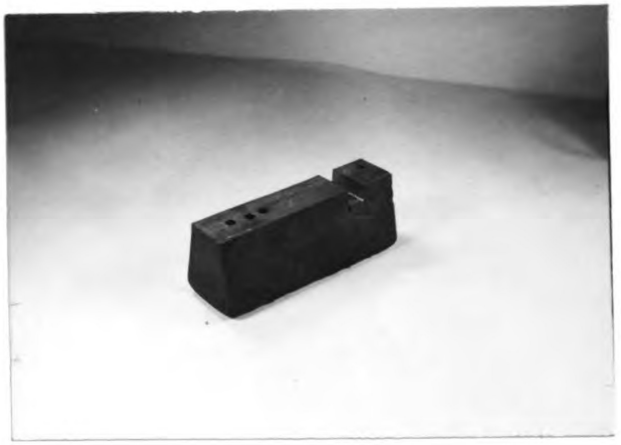

Figure 11

Riser of keel block, inverted to show sampling locations

Figure 12

Left....Chill block from heat J-9

Center..Chill block from heat J-11

Right...Chill block from heat J-7

Figure 13

Arrangement of equipment for melting, making additions, and pouring

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