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The effect of selected alloying elements on the hardness and microstructure of ductile cast iron

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THE EFFECT OF SELECTED ALLOYING ELEMENTS ON THE HARDNESS AND MICROSTRUCTURE OF DUCTILE CAST IRON

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ABSTRACT

The effects of cooling rate and alloying element on the matrix structure, nodule count and hardness have been studied in this investigation.

Recommendations for producing ferritic ductile iron have been made and the relationship between hardness and pearlite percentage has been obtained in this study.

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I. INTRODUCTION

The mechanical properties of ductile iron are dominated by the characteristics of the matrix. The effects of the ferrite and pearlite percentages then become important and all conditions which affect these percentages will alter the mechanical properties. The variables which are most important in this respect are: cooling rate, alloying additions, and the number of graphite nodules.

In this investigation, the effect of cooling rate during the eutectoid reaction in both as cast and heat treated ductile iron castings has been studied. Five alloy compositions, each with four section sizes, were used to permit the effects of alloying element and nodule count to be determined. The alloys included elements which promote pearlite (Mn, Sn, Cu) or promote ferrite (Si). The hardness of the matrix has been chosen as the index of the mechanical properties.

A recommendation for producing ferritic ductile iron has been made and the relationship between hardness and pearlite percentage was obtained in this investigation.

II. LITERATURE REVIEW

The structure of ductile cast iron consists of spheroids or nodules of graphite in a matrix which may be a combination of ferrite, pearlite, tempered matensite, intermediate transformation products, etc.

The nodule count and the morphology of the graphite in ductile iron are controlled by metal composition, liquid metal processing, cooling rate during solidification, section size of the casting and, in special instances, by heat treatment.

Similarly, the matrix structures are controlled by nodule count, metal composition, liquid metal processing, cooling rate during and after solidification, section size of the casting, heat treatment, and many other factors.

Some of these factors are reviewed below.

A. THE COMPOSITION OF THE DUCTILE IRON

1. Carbon. The carbon content for commercial ductile iron varies from 3.0 to 4.0 percent[1,2]. Nodule counts are directly affected by the carbon content -- greater numbers of spheroids form at the higher carbon contents[1]. Increasing the carbon content also increases castability by improving fluidity and feeding[1]. But increasing carbon content is also accompanied by a decrease in hardness and other mechanical properties[3].

2. Silicon. The normal range for silicon in ductile iron is 1.80 to 2.80 percent[1,2]. Silicon affects the carbon equivalent value, the nodule count, and also the matrix structure. Silicon is a strong graphite promoter since it increases the temperature difference between the stable (austenite-graphite) and metastable (austenite-cementite) eutectics[4]. The strength of the ferrite increases by the solid solution hardening effect of the silicon[5].

3. Carbon Equivalent. A carbon equivalent of 4.3 percent is desired[1]. As the carbon equivalent increases, the nodule count will also increase. In thin section castings (less than 0.5") a higher carbon equivalent of 4.5 percent may be used. However, in heavy section castings (greater than 1.5") high carbon equivalents will produce a problem with graphite flotation[2].

4. Magnesium. Magnesium is important because it provides desulfurization and nodulization. The residual magnesium is usually in the range of 0.015 to 0.05 percent, depending on the initial sulfur content and other factors. Magnesium contents in excess of 0.05 percent are not necessary and sometimes are detrimental in heavy castings[6]. The typical residual magnesium content is 0.03 percent.

5. Sulfur. The sulfur content of the base iron is held as low as possible for best efficiency in the nodulizing treatment. Nodulizing agents, such as magnesium and cerium, react first with sulfur in the iron; until

substantially all of the sulfur is combined, the nodulizing action cannot take place. During treatment, a quantity of magnesium equal to about 0.75 times the base metal sulfur content is added in addition to the magnesium needed for nodulizing. Ductile iron is produced more easily and economically when the sulfur content of the base iron is lower[2].

6. Manganese. Manganese retards the formation of ferrite and moderately refines the lamellae in pearlite[7]. The usual range of manganese in ductile iron is from 0.15 to 0.8 percent. The low side of this manganese range is desirable for best as-cast ductility and rapid ferritization by heat treatment. Manganese on the high side of the range is desirable for highest as-cast strength and for best response to a hardening heat treatment[2].

7. Copper. Copper is a mild graphitizing element as well as a strong pearlite stabilizer[8]. It is believed to act as a barrier to carbon diffusion by accumulating at the austenite-graphite interface[9]. Copper up to about 1.00 percent will increase the strength and hardness of ductile iron. However copper tends to intensify the harmful effects of certain subversive elements, such as lead, arsenic, and tellurium when these are present[2]. Copper only weakly refines pearlite[7].

8. Tin. Although tin is a carbide stabilizing element, it also is a strong pearlite stabilizer[8]. Tin additions of more than 0.05% are not recommended for heavy

castings because of resulting intercellular inclusions[10]. Like copper, tin acts as a barrier to carbon diffusion by accumulating in the austenite adjacent to the graphite[11].

9. Chromium. Chromium is a strong pearlite promoter because it increases carbon solubility in austenite and thus inhibits the nucleation of ferrite[7]. But because chromium is also a powerful carbide stabilizer, it is not used in ductile iron unless carbides are desired for hardness or wear resistance. With about 0.15 percent or more of chromium in the base iron, the ductile iron castings are difficult to completely ferritize and produce the annealed grade of ductile iron[2].

10. Molybdenum. Molybdenum increases the hardenability of ductile iron and is the most practical addition for refining pearlite in gray iron[7]. Molybdenum is occasionally added to ductile iron in order to obtain high temperature properties, strength and hardness in heavy sections[2].

11. Lead. Lead causes nodule degeneration and inferior mechanical properties in concentrations as low as 0.01 percent[12]. The addition of 0.02 percent Ce causes complete restoration of mechanical properties and the spherulitic nodule form[12].

12. Titanium. Titanium, which occurs very frequently in cast iron, causes the shape of the graphite to deteriorate to a vermicular or flake form. In ductile iron with 0.04 to 0.05 percent magnesium, the presence of

as much as 0.05 percent titanium is tolerable[13]. Since the effect of titanium is influenced considerably by magnesium content, casting section size and other trace elements[12,14], some allowance for these factors is required in considering the amount of titanium that can be tolerated. The addition of approximately 0.04 percent cerium eliminates the detrimental effect of titanium and restores the nodule form and mechanical properties[12,14].

13. Bismuth. Bismuth acts very much like lead, although the minimum amount considered detrimental is much less, 0.003 to 0.005 percent[12]. The presence of 0.02 percent cerium is effective in eliminating the undesirable effects created by bismuth[12]. But other investigations show that the addition of 0.05 percent bismuth to ductile iron does not cause nodule degeneration[14].

14. Nickel. Nickel is a graphite and pearlite stabilizer; in addition, when combined with other alloying elements such as molybdenum, nickel provides a great hardenability effect[7]. Up to 20 percent nickel is sometimes added to ductile iron to produce an austenitic matrix at room temperature[2].

B. LIQUID METAL PROCESSING

1. Melting. Cupola melting is the most common method for melting ductile iron; however, electric induction furnaces are in use in a number of foundries. About 75 percent of the ductile iron producers employ the acid

cupola. In nearly all these instances, the cupola is used for both gray and ductile iron production. Among those foundries which have provided separate melting facilities for ductile iron, the basic cupola is preferred. Approximately 70 to 85 percent of the tonnage of ductile iron produced is melted in basic cupolas[1].

2. Desulfurization. In order to produce a low sulfur base iron which can be used to produce ductile iron castings which are free of excessive amounts of dross and surface crazing, a desulfurization treatment is required. The basic types of desulfurization agents are a) sodium-based agents -- soda ash, sodium hydroxide, sodium carbonate; b) calcium carbide -- CaC_2; and c) lime -- CaO[15].

3. Magnesium Treatment[1]. Although a number of elements can be used to promote at least partial speroidization of graphite in cast iron, magnesium is by far the most effective and economical material. The base iron temperature at treatment is usually 2700-2800°F. The main magnesium nodulizing alloys are

(a) Magnesium-nickel alloys

i. 15% Mg, 85% Ni.

ii. 15% Mg, 55% Ni, 30% Si.

(b) Magnesium-ferrosilicon alloys

i. 9% Mg, 45% Si, 1.5% Ca, balance Fe.

ii. 9% Mg, 45% Si, 1.5% Ca, 0.5% Ce, balance Fe.

(c) High cerium alloys

3% Mg, 45% Si, 1% Ca, balance Fe.

In each of these alloys, other elements which affect the matrix are also introduced, such as nickel (a pearlite stabilizer) and silicon (a ferrite stabilizer). Consequently it is important to select a nodulizing alloy that will help provide the desired matrix structure and iron properties.

4. Inoculation. Post-inoculation is required to produce a high nodule count[1]. A high nodule count produces more growth centers, allowing solidification to occur more rapidly, with less undercooling, and therefore fewer carbides and less vermicular graphite[16]. The higher nodule counts also encourage the formation of ferrite during further cooling of the casting.

The alloys used for inoculation of ductile iron are generally the same as those for gray iron -- standard 75% ferrosilicon with calcium and aluminum, SMZ (with Mn and Zr), Superseed (with strontium), barium containing ferrosilicons, and cerium bearing ferrosilicons[17].

C. COOLING RATE DURING SOLIDIFICATION (SECTION SIZE OF THE CASTINGS)

The effect of cooling rate on the properties of ductile iron is profound, because of its influence on microstructure. A number of effects have been observed to occur as the section size of the casting (or the time to solidify) is increased. These include: a general degradation of graphite shape from spheroidal to compact, irregular, or vermicular forms; the appearance of carbides in the center of heavy sections; graphite flotation; and a degrading of mechanical properties[18]. Thin section castings or faster cooling rates always give a higher nodule number and smaller nodules than heavy section castings[16]. Low nodule counts are generally accompanied by a carbide matrix. As the number of nicules is increased, the amount of ferrite in the as-cast structure is also increased[16].

D. <u>HEAT TREATMENT</u>[1,19]

Because of its excellent response to heat treatment, ductile iron castings can be produced with a wide range of properties. Accordingly, the matrix structure may be all ferrite, ferrite and pearlite, all pearlite, martensite, tempered martensite, or banite, and may, in special alloys, contain carbides or an austenitic matrix. Normally ductile irons are heat treated either to relieve residual stresses, or to develop desired properties. The principal types of heat treatments are 1) stress relief; 2) annealing; 3) normalizing and tempering; 4) quenching and tempering, including austempering and martempering; 5) surface hardening by the flame or induction methods.

In ductile iron, annealing produces a soft ferritic matrix, while normalizing produces a pearlitic matrix. Particularly in annealing and normalizing, the nodule count may play an important role in determining the effectiveness of the heat treatment.

III. EXPERIMENTAL PROCEDURE

The experimental procedure can be described in the following steps:

A. MOLDING

A simple green sand molding process was chosen for this experiment, using the pattern shown in Figure 1. A top riser was used to minimize shrinkage. The diameters of the four cylinders are 0.5", 1", 1.5" and 2". The height of the four cylinders is 4". In order to insert a Chromel-Alumel thermocouple, a hole was drilled through each cylinder at a height of 2". Metal rods were threaded through the holes in each cylinder, extending through each side of the flask. After compaction, the rods were removed, leaving room for quartz protection tubes, Figure 2. Thermocouples inserted in the quartz tubes were located at the thermal center of each cylinder.

B. MELTING AND TREATMENT

The charges were melted using an induction furnace. The compositions of the charge materials are shown in Table I. To study the effect of the alloying elements on the matrix structure, different elements were added to the base metal. These elements and the intended chemical analyses are listed in Table II. After the temperature reached 2750°F, the hot metal from the furnace was tapped

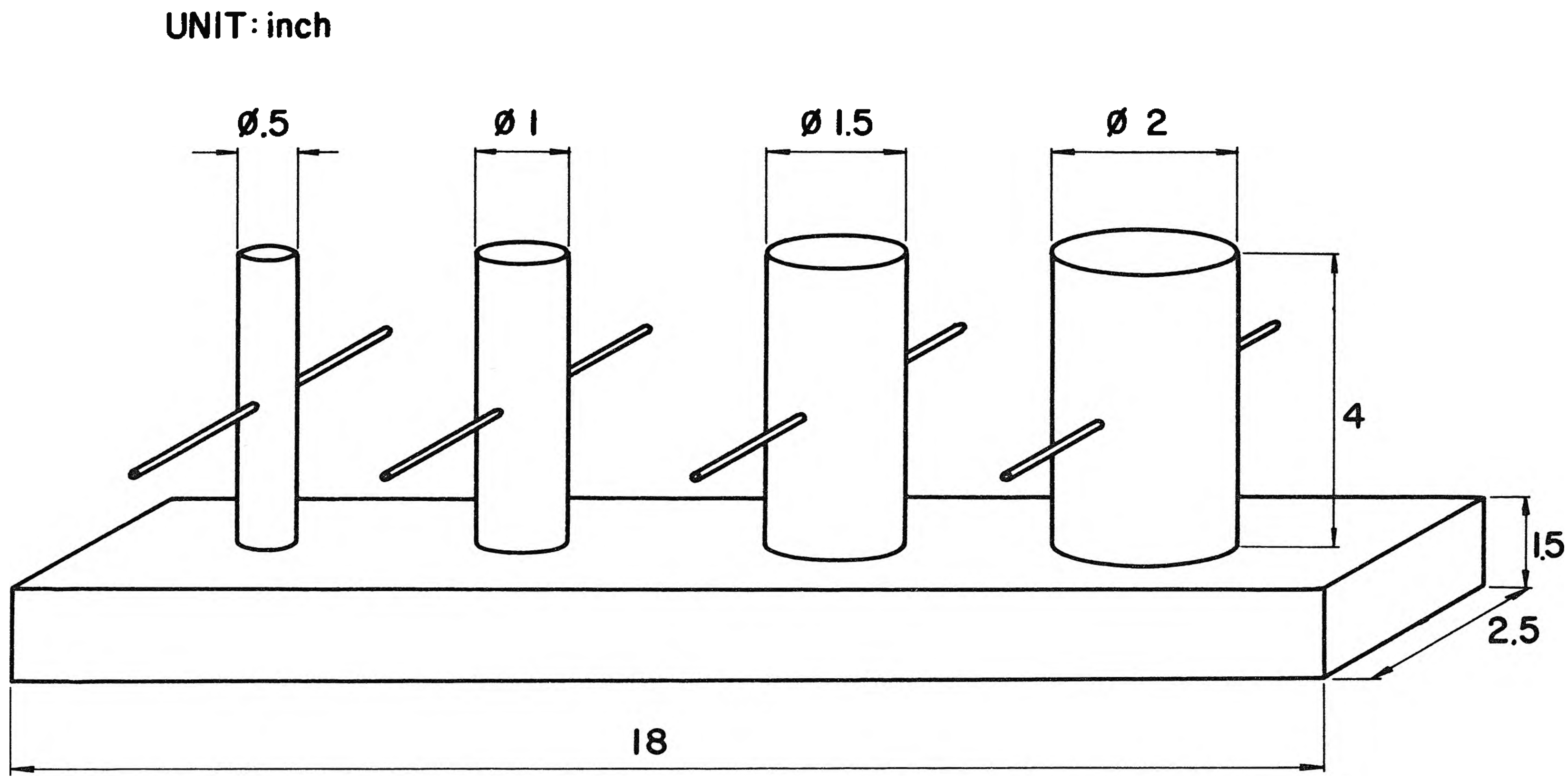


Figure 1. The shape and dimensions of the pattern.

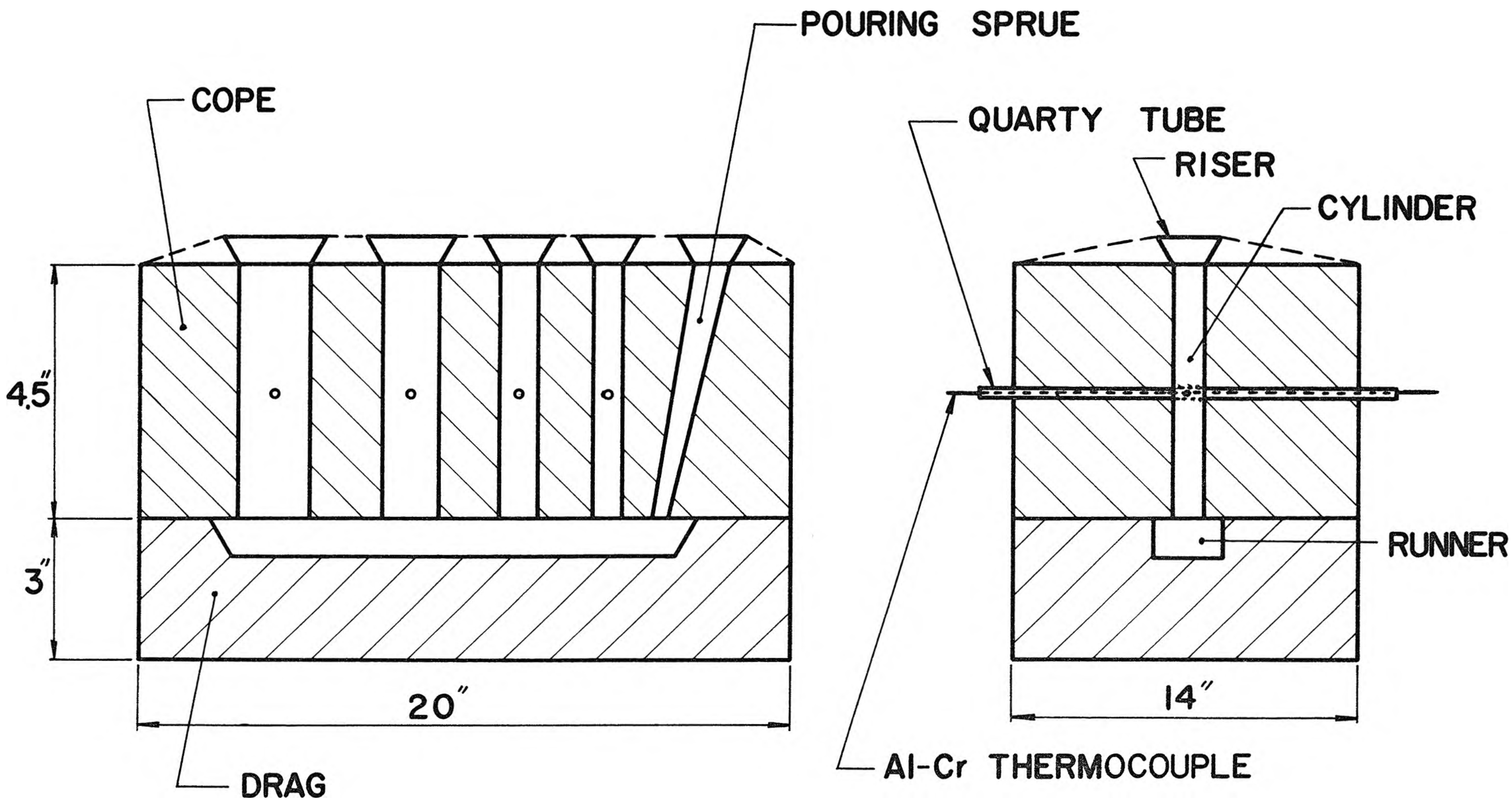


Figure 2. The sketch of green sand mold.

TABLE I

THE CHEMICAL COMPOSITION AND WEIGHTS OF THE CHARGE MATERIALS

Material	%C	%Si	%Mn	%Mg	%Ca	%Al	%Ba	%S	%P	Weight(lb)
Pig iron	4.42	1.00	.22	-	-	-	-	.021	.017	81.8
Steel	.1-.2	-	.4-.6	-	-	-	-	-	-	15.3
Inoculoy 63	-	63.0	11.8	-	2.0	1.5	5.24	-	-	.79
Noduloy 9C	-	45.03	-	8.9	1.-1.5	1.0	-	-	-	1.67
75% FeSi	-	70.	-	-	1.5	1.0	-	-	-	.44

TABLE II

THE INTENDED CHEMICAL ANALYSES AND GENERAL COMPOSITION FOR EACH HEAT

Intended Chemical Analyses			
Heat Number	%C	%Si	
B1	3.6	2.4	
B2	3.6	2.4	+ 1.2% Mn
B3	3.6	2.4	+ 0.5% Cu
B4	3.6	2.4	+ 0.1% Sn
B5	3.6	2.4	+ 1.0% Si

General Composition(%)		
about	0.035	Cr
	0.050	Ti
	0.03	Al
less than	0.01	S
	0.03	P
	0.035	Mg
	0.01	Sn
	0.25	Mn
	2.2-2.4	Si
	3.58-3.77	C

into a preheated ladle and the nodulizing alloy was added to the stream of metal. Finally, the inoculant was stirred into the melt prior to pouring.

C. POURING AND COOLING CURVE MEASUREMENT

After treatment, the hot metal at approximately 2500°F was poured into the mold. The thermocouple protected by the quartz tube was used to monitor the temperature during cooling. The thermocouples were attached through a switching device, so that the cooling curves from all four section sizes were displayed on a strip chart recorder. The average cooling rate of each cylinder was determined in the temperature interval of 1600 to 1200°F. These cooling rates were 810°F/hr for 2" section, 2000°F/hr for 1.5" section, 2400°F/hr for 1" section, and 3600°F/hr for 0.5" section.

D. HEAT TREATMENT

The casting was shaken from the mold after cooling to room temperature. After cleaning and removal of the runner and riser, all cylinders were cut into four parts, with each part 1" in length.

Three heat treatment processes were conducted as follows:

1. H1. Heat to 1600°F and hold for one hour, then furnace cool to room temperature. This gives a cooling rate of 340°F/hr in the temperature range of 1600°F to

1200°F.

2. H2. Heat and hold as H1, then cool to 1200°F at the cooling rate of 100°F/hr, then furnace cool to room temperature.

3. H3. Similar to H2, but with a cooling rate of 25°F/hr from 1600°F to 1200°F.

The cooling rates in H2 and H3 were controlled by manually reducing the temperature of the furnace in 25°F intervals per 15 minutes for H2, and per one hour for H3 over the necessary period of time.

E. SAMPLE PREPARATION

The as-cast samples and the samples after heat treatment were prepared by the following steps:

(1) Mounting in bakelite,

(2) Wet polishing through 240, 320, 400, and 600 grit emery papers,

(3) Polishing laps using coarse and fine alumina on billiard cloth,

(4) Etching in 5% Nital.

F. DATA COLLECTION

1. Nodule Count. The nodule counts were obtained by projecting the reflected image of an unetched specimen on a ground glass screen at 100 X. The individual graphite nodules were crossed out with a red marking pen as they were counted. Every nodule shown on the glass screen was

counted, except those with diameters less than 0.5 mm. Ten regions were counted for each specimen. The arithmetic average of the counts were used as the specimen's nodule count. The nodule count is expressed as the number of nodules per square millimeter.

2. Pearlite Percentage Measurement. Photomicrographs were taken at 75 X magnification to reveal the matrix. The different constituent areas are outlined with a pencil. A grid of evenly placed lines is placed on the photograph. The number of grid line intersections that fall on the constituent areas of interest (i.e. pearlite, graphite, ferrite, and carbide) are counted. Then their percentage of the total number of points is calculated. This procedure for measurement of the pearlite percentage is recommended by the American Foundrymen's Society[20].

3. Hardness Measurement. Rockwell B and Rockwell C hardnesses were obtained from the center of each specimen after the metallographic study. The hardness data were converted to Brinell hardness 3000 Kg using standard hardness conversion tables[21].

IV. RESULTS AND DISCUSSION

According to Hawkes et al.[22], the various graphite formations which occur in ductile iron may be classified according to the reaction by which they are produced; these reactions are listed as follows:

1. At the eutectic temperature -- 2100°F

   Hyper-eutectic:

   Carbon in liquid iron $\longrightarrow$ Graphite --------- (1)

   Hypo-eutectic:

   Liquid iron $\longrightarrow$ Austenite + Graphite -------- (2)

2. Between the eutectic temperature and eutectoid temperature -- 2100 to 1350°F

   Cementite $\longrightarrow$ Austenite + Graphite ---------- (3)

   Carbon in austenite $\longrightarrow$ Graphite ------------ (4)

3. At the eutectoid temperature -- 1350°F

   Austenite $\longrightarrow$ Ferrite + Graphite ------------ (5)

4. Below the eutectoid temperature -- below 1350°F

   Cementite $\longrightarrow$ Ferrite + Graphite ------------ (6)

   Carbon in ferrite $\longrightarrow$ Graphite -------------- (7)

In the reactions (1) and (2), nucleation and growth of the nuclei will determine the graphite nodule's size and number. The cooling rate is an important factor; a fast cooling rate gives a large undercooling, producing more graphite nuclei but also a slow growth rate. A slow cooling rate gives a small undercooling, producing fewer graphite nuclei with a faster growth rate.

In the reactions (3)-(7), carbon diffusion is the rate-determining step. In these reactions, no new graphite nodules form. Carbon atoms should diffuse through the austenite for reactions (3) and (4), or through the ferrite for reactions (5)-(7), to enlarge the graphite nodules. The reactions (1)-(3) are most important in the as cast condition and the reactions (4)-(7) are important in the heat-treating process. Any factor that can slow down the carbon diffusion or trap the carbon in cementite or in austenite will make the matrix pearlitic.

The results are presented below in two sections. First, the effects of section size and alloying element on the cooling rate, nodule count, matrix structure, and hardness of the as cast ductile iron are presented and discussed. Second, the effect of three annealing heat treatments having different cooling rates on these same parameters is described. The data is presented in the Appendix.

A. AS CAST DUCTILE IRONS

The alloying elements and the different cooling rates produced as a result of the four section sizes give a wide range of nodule counts and matrix structures. Figures 3 and 4 show representative photomicrographs of specimens with high (Si, 0.5") and low (Sn, 2") nodule counts and with high (Sn, 1.5") and low (Si, 2") percentages of pearlite. The observations made on the as cast specimens are presented next.

1. The Effect of the Cooling Rate During Solidification (or Section Size) on the Nodule Count for Each Element. (Figure 5) As a general rule, the nodule count decreases as the section size increases. The nodule count of the light section casting is larger than that of the heavy section casting. This result is expected because, except for high silicon, the alloying elements do not have a pronounced effect on the cooling rate - nodule count relationship, since the slopes are about the same. The high Si alloy appears to have a particularly high nodule count, especially at rapid cooling rates. Because the copper and tin act like a barrier to carbon diffusion in the reaction (3) described above, the carbon remains in the austenite and the presence of maganese will make the Fe-C bonding in Fe_3C stronger. This prevents the growth of existing nodules after solidification. Since only nodules having a minimum size are counted, there is a tendency for lower nodule counts to be observed in the alloyed irons.

(a)

(b)

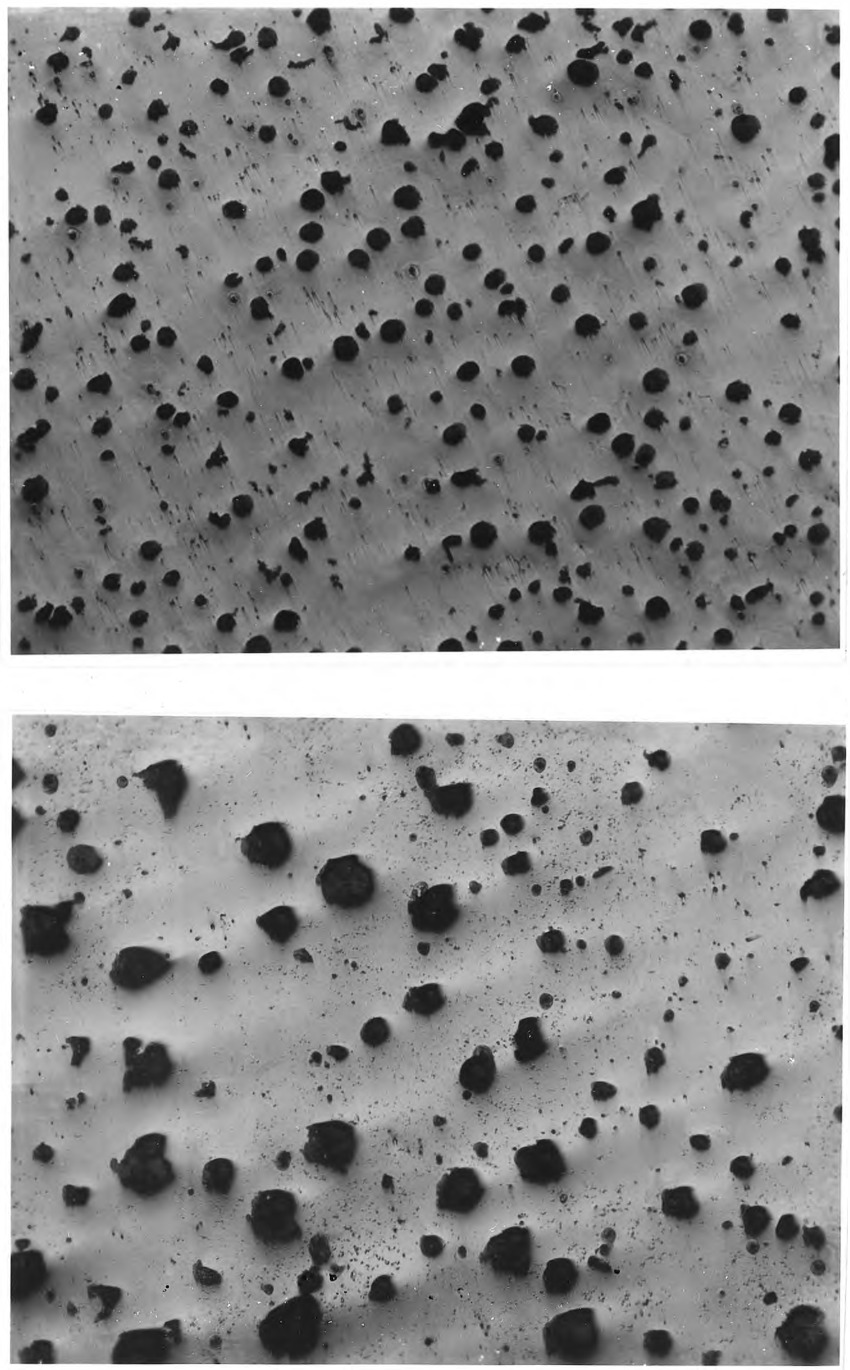


Figure 3. The as cast specimens with (a) high nodule count $213/mm^2$ (Si, 0.5") and (b) low nodule count $41/mm^2$ (Sn, 2"). Unetched, 100 X.

(a)

(b)

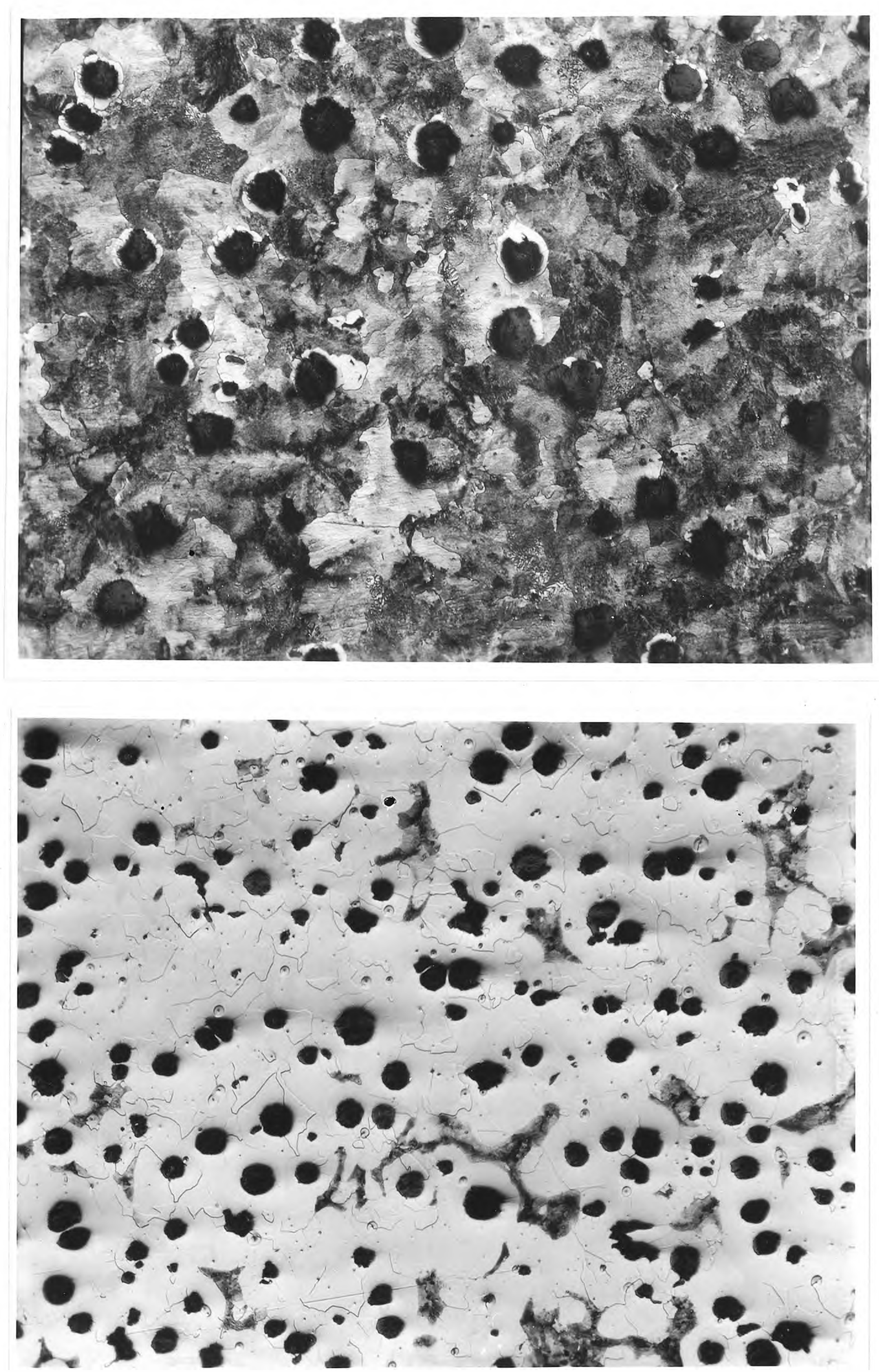


Figure 4. As cast specimens with (a) high pearlite percentage 96% (Sn, 1.5") and (b) low pearlite percentage 11% (Si, 2"). 5% Nital etched, 100 X.

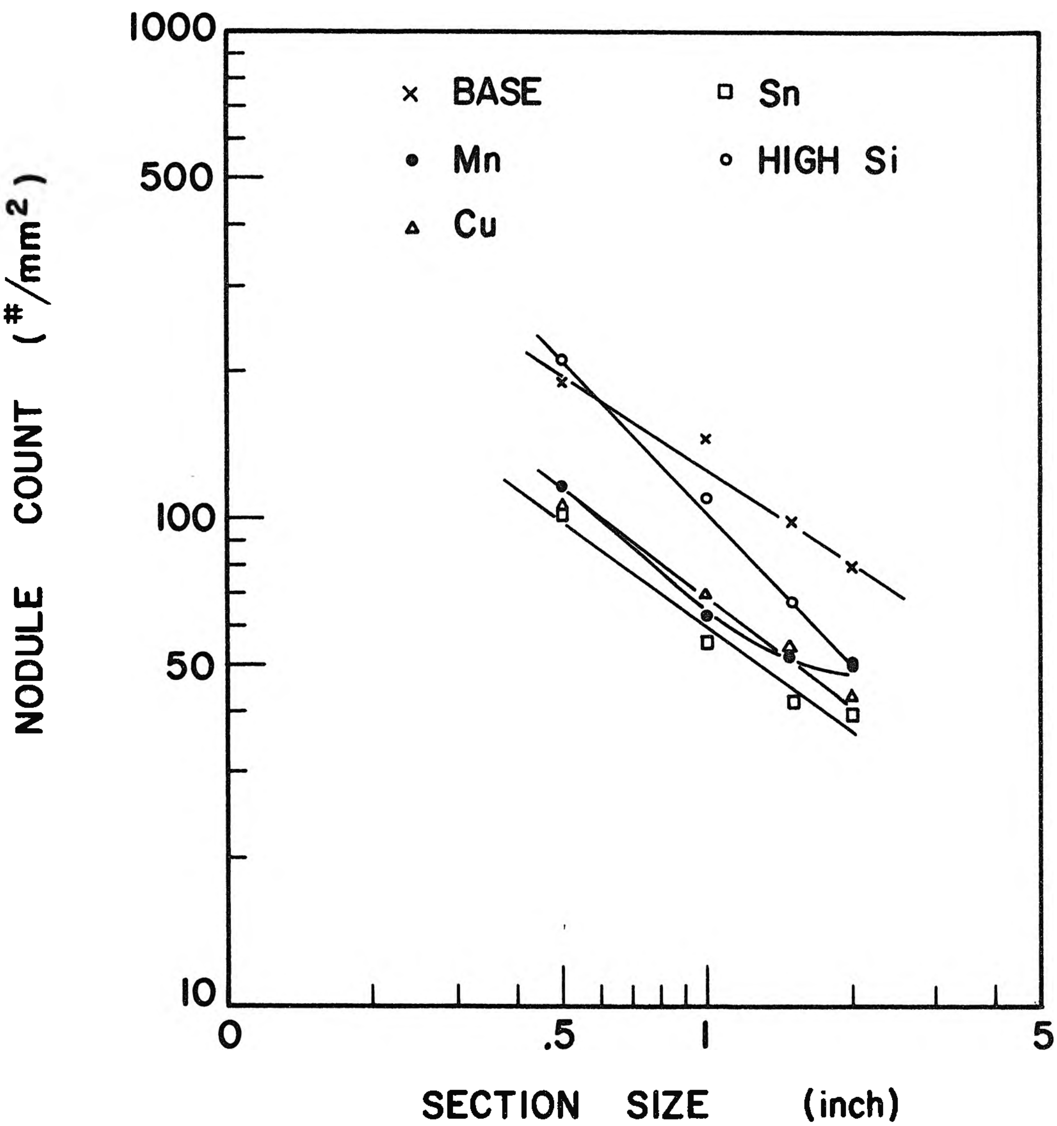


Figure 5. The effect of section size (cooling rate) and alloying elements on nodule count of as cast ductile iron.

2. <u>The Effect of the Section Size on Pearlite for Each Element</u>. (Figure 6) As the section size increases, there is little effect on pearlite percentage, except in the base metal, where the section size of 0.5" gives a large pearlite percentage. For the alloy containing copper, the pearlite percentage increases slightly with the section size.

The same results have been obtained by Cole[23], namely that pearlite is stabilized at higher cooling rates, and ferrite at lower cooling rates (depending on the overall composition) as a result of carbon diffusion. The large castings freeze slowly and generally contain more ferrite, especially in the absence of pearlite stabilizers. In small section castings, on the other hand, the structure is always pearlitic and carbides usually precipitate within the matrix[24,25]. However, when pearlite stabilizers are present in the alloy, there is almost no change in the pearlite percentage upon altering the section size. For the alloy containing a graphite stabilizer, such as silicon, fast cooling rates did not produce a lot of pearlite. In this case the higher nodule counts shorten the diffusion distance of catbon, making it easier to form more ferrite in the matrix.

3. <u>The Effect of Each Alloying Element on Pearlite.</u> (Figure 6) The percentage of pearlite formed is affected by the addition of different elements to the base metal. The percentages are highest with tin, followed by copper,

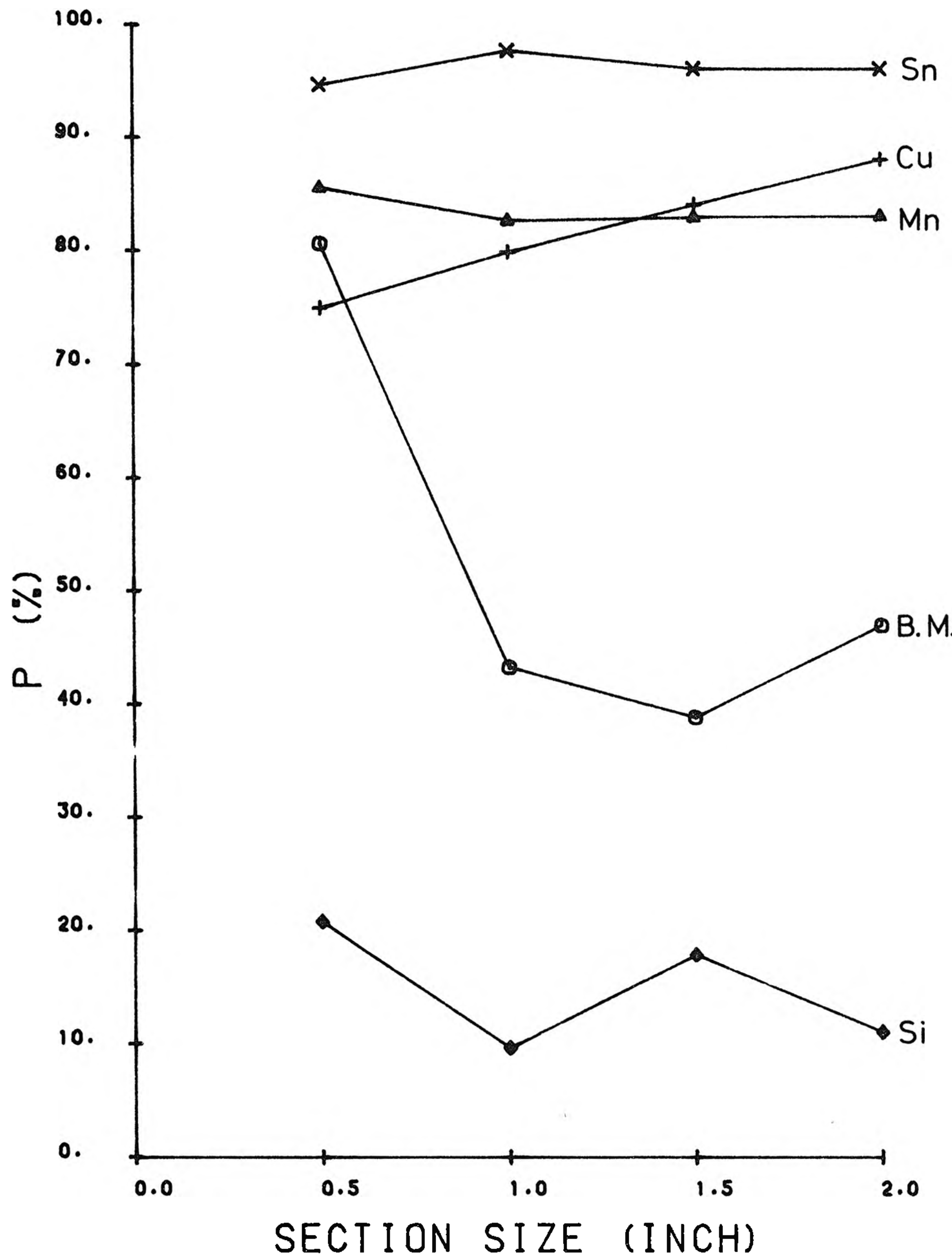


Figure 6. The effect of section size (cooling rate) and alloying elements on the pearlite percentage of as cast ductile iron.

manganese, the base metal, and high silicon, in descending order.

It has been reported by Loper et al.[8] that between 8 and 12 times as much Cu as Sn is needed to obtain equivalent amounts of pearlite in the matrix. Another reference[26] showed that a Cu addition of 0.82% was equivalent to a 1.47% Mn addition in stabilizing pearlite, but the Mn addition resulted in carbides appearing in the microstructure.

In this study, 1.2% Mn (B2), 0.5% Cu (B3) and 0.1% Sn (B4) were added. According to the Loper's paper[8], the pearlite percentage of the sample B4 should be higher than that of sample B3, while the samples B3 and B2 should have about the same pearlite percentage. If we examine Figure 6, we can see that the experimental data perfectly follow those rules.

4. <u>The Effect of Cooling Rate, Nodule Count, and Alloying Element on Hardness</u>. (Figure 7 and Figure 8) According to G. S. Cole[24], "Ductile iron acts like steel with the matrix characteristics dominating the overall mechanical properties. The effect of the ferrite and pearlite ratio then becomes important and all conditions which affect this ratio will alter the mechanical properties. There are three variables which dominate in this respect: (a) cooling rate as the alloy passes through the eutectoid temperature, (b) alloying addition which alters the phase proportion of the ferrite and

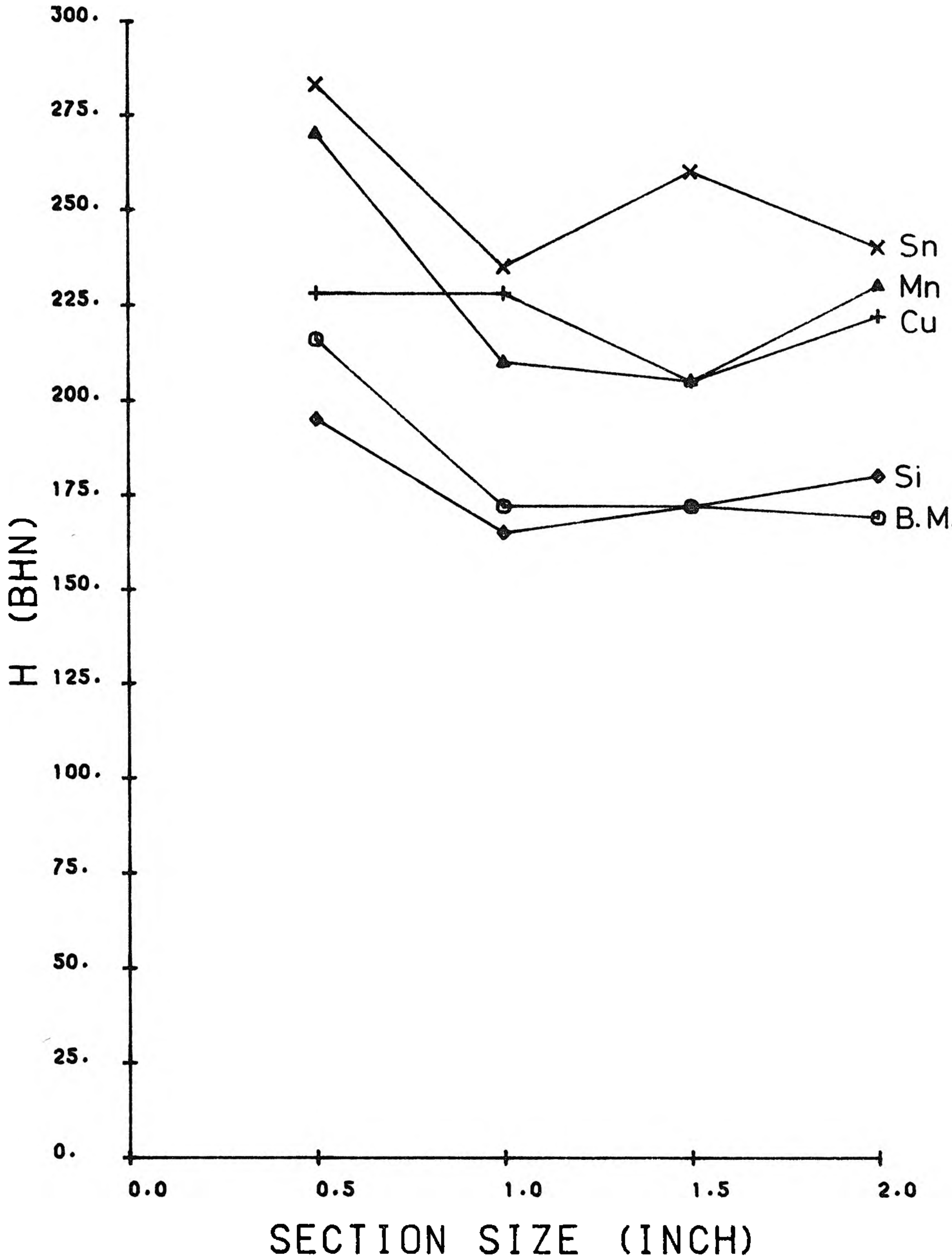


Figure 7. The effect of section size (cooling rate) and alloying elements on hardness of as cast ductile iron.

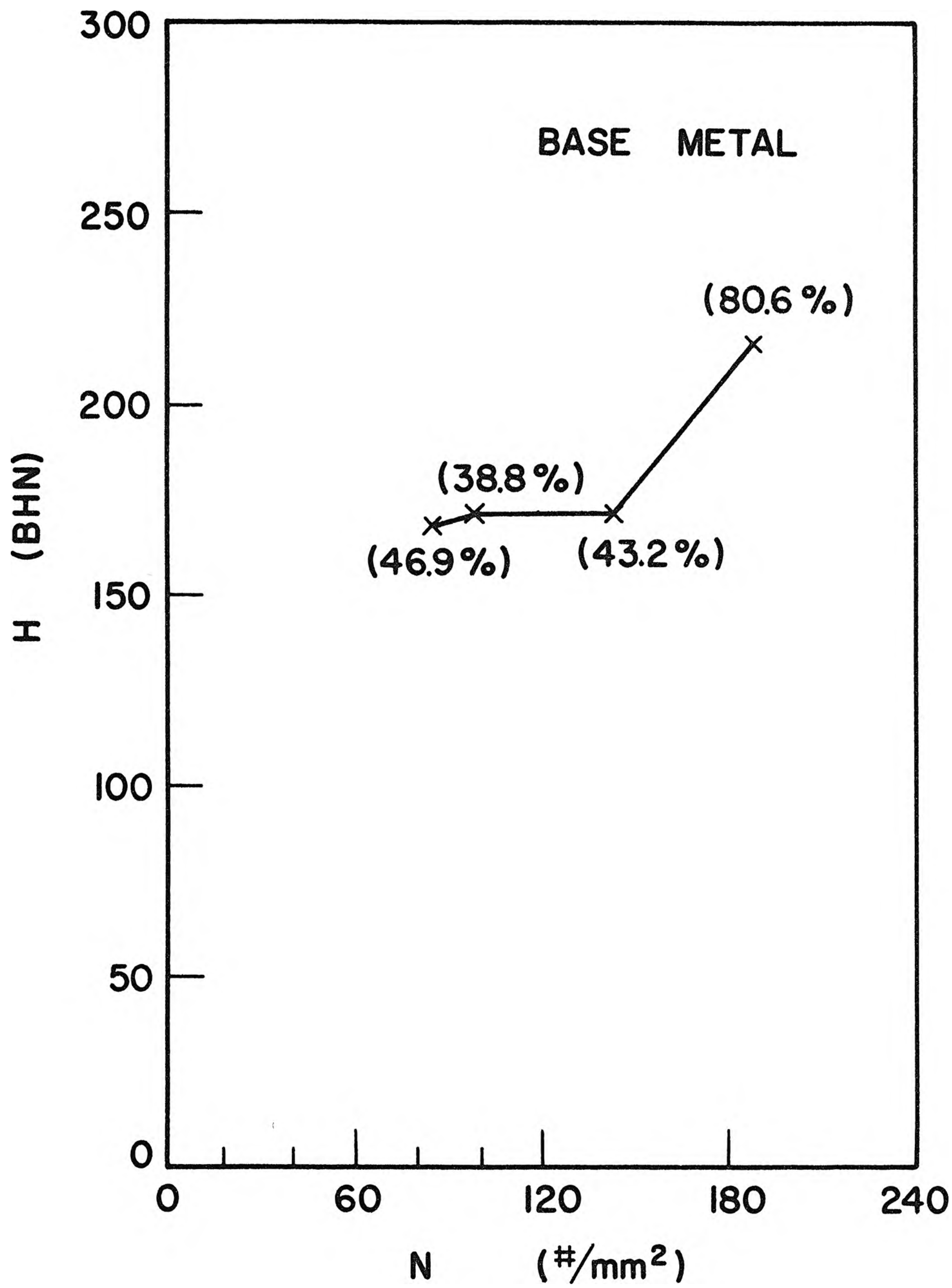


Figure 8. The effect of nodule count on hardness of as cast ductile iron. The number in the quotation marks is the pearlite percentage of the matrix.

and pearlite, and (c) the graphite distribution."

In this study, the thin section 0.5" casting of each heat always has highest hardness. But the hardness of thicker section sizes (1", 1.5" and 2") did not decrease in sequence, except with the base metal.

Comparing the results of the as-cast pearlite versus section size (Figure 6) and as-cast hardness versus section size (Figure 7), we can see that these two figures are very similar to each other. We may say that a higher pearlite percentage gives a higher hardness.

In descending order, the sequence of the as-cast hardness of the five heats are tin-added, copper-added, manganese-added, base metal, and silicon-added. The hardness of the base metal and the silicon-added are very close to each other.

From Figure 8, the as-cast nodule count versus hardness for base metal, the following result can be observed: higher nodule counts do not give a higher hardness if the pearlite percentage is about the same. The only point that shows a higher hardness also has twice the amount of pearlite. The same result was observed in the other alloys studied in the experiment. We may conclude that the nodule count did not affect the hardness in this study.

5. The Carbide Percentages for Each Alloying Element and Section Size. (Table III) We find that 0.1% tin can promote carbide formation in section sizes up to 1", and 1.2% manganese can promote carbide formation in section

TABLE III

THE AS CAST CARBIDE PERCENTAGE

FOR EACH ALLOYING ELEMENT

Section Size	Carbide Percentage (%)				
(inch)	B	Mn	Cu	Sn	Si
0.5	0.0	5.6	0.0	5.4	0.0
1.0	0.0	0.0	0.0	0.1	0.0
1.5	0.0	0.0	0.0	0.0	0.0
2.0	0.0	0.0	0.0	0.0	0.0

sizes up to 0.5". Other alloys produce no carbides in the section sizes that were studied.

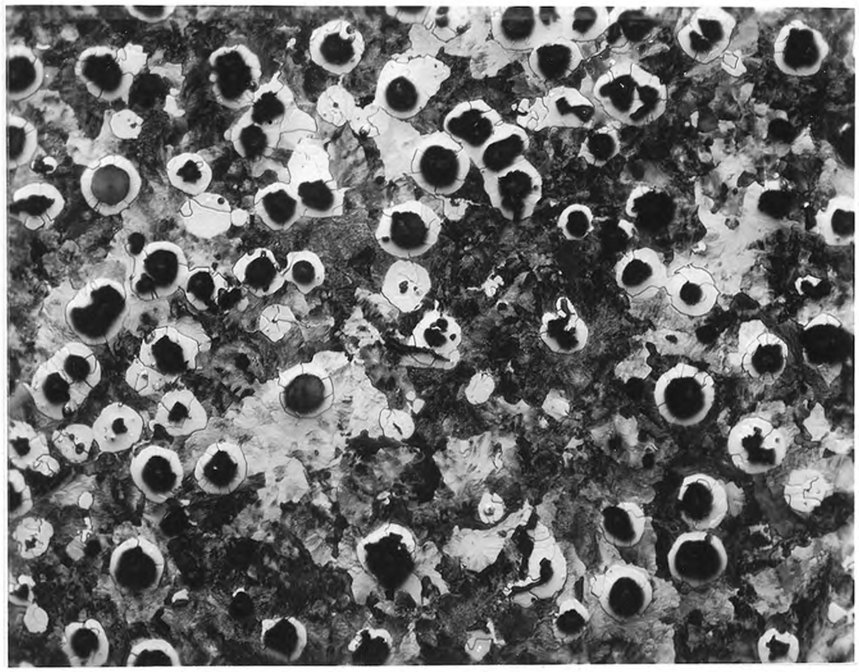
B. HEAT TREATED DUCTILE IRONS

Specimens removed from each cylinder for all of the alloys were annealed using three different cooling rates. The effect of the annealing treatment on the matrix structure of the high Mn alloy is shown in the photomicrographs in Figures 9 and 10. Slower cooling rates are observed to increase the percentage of ferrite in the structure. Other observations are discussed next.

1. The Effect of Heat Treatment on the Nodule Count.

(Figures 11 to 15) There are two mechanisms that can affect the nodule count after heat treatment. First, some of the small nodules grow during the heat treatment, so that they can be counted afterwards (diameter of the
7 nodules larger than 0.5 mm). Second, some of the nodules may dissolve during the heat treatment. Which of these two predominates depends on the alloying element and the section size, with the section size having the greater influence. Generally, for smaller section sizes the growth of small nodules is dominant; for larger section sizes, the dissolution of nodules is dominant. Thus for a small section size, a higher nodule count is usually observed after heat treatment; for a larger section size, a lower nodule count is typically found.

(a)



(b)

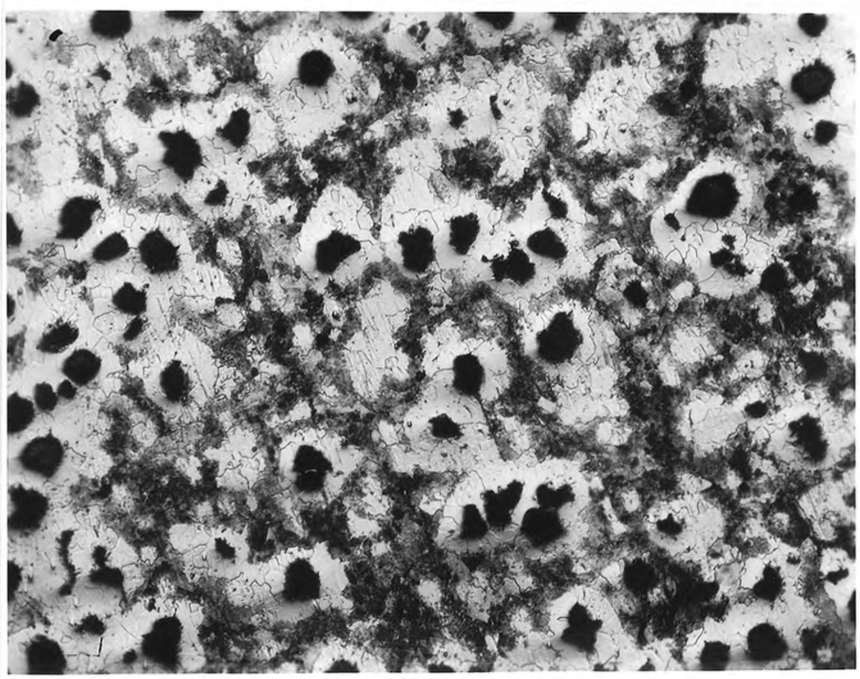


Figure 9. The effect of heat treatment on the matrix of ductile iron (a) as cast, (b) furnace cooling. 5% Nital etched, 100 X, 1.2% Mn added, section size 1".

(a)

(b)

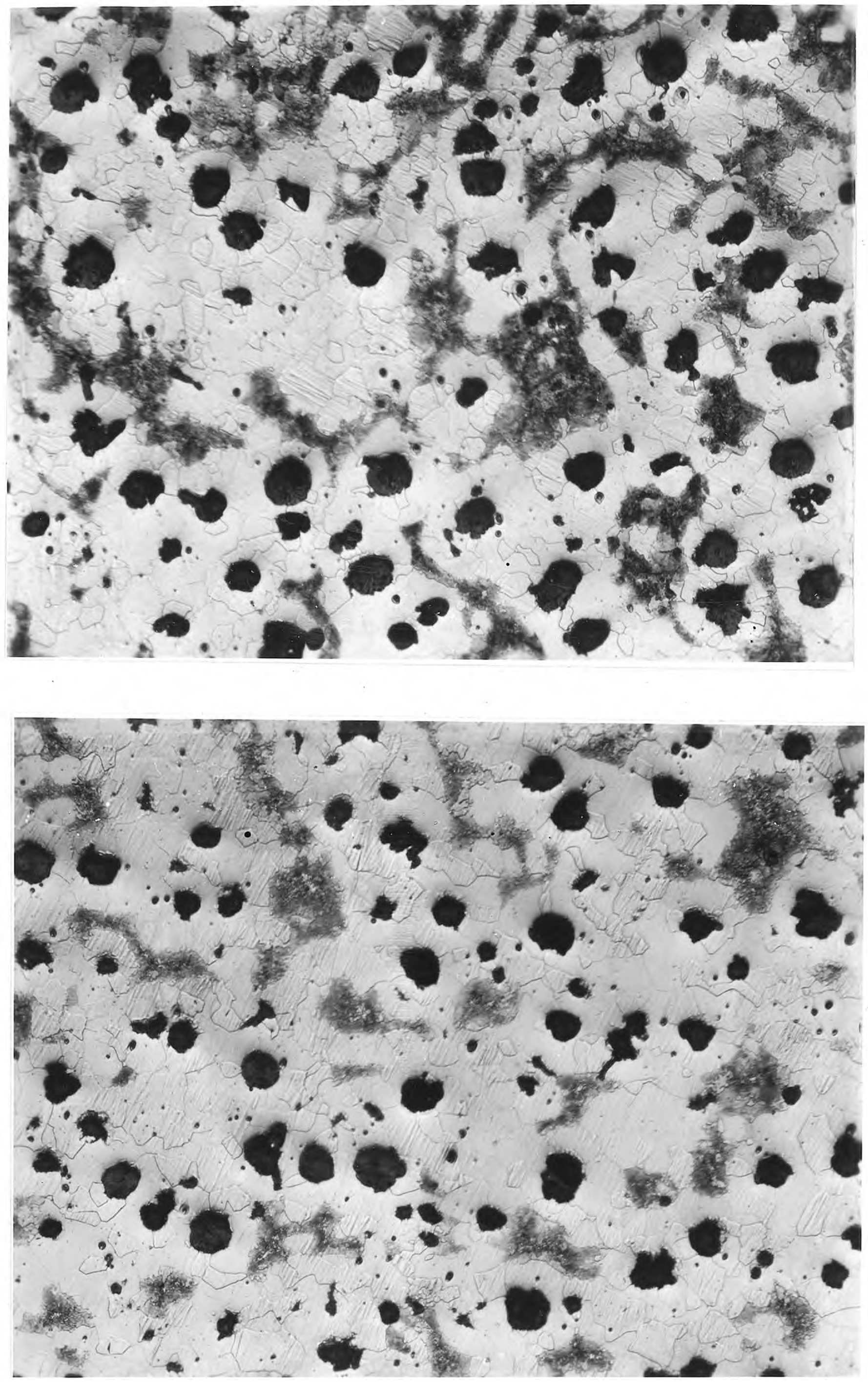


Figure 10. The effect of heat treatment on the matrix of ductile iron (a) 100^{O}F/hr (b) 25^{O}F/hr. 5% Nital etched, 100 X, 1.2% Mn added, section size 1".

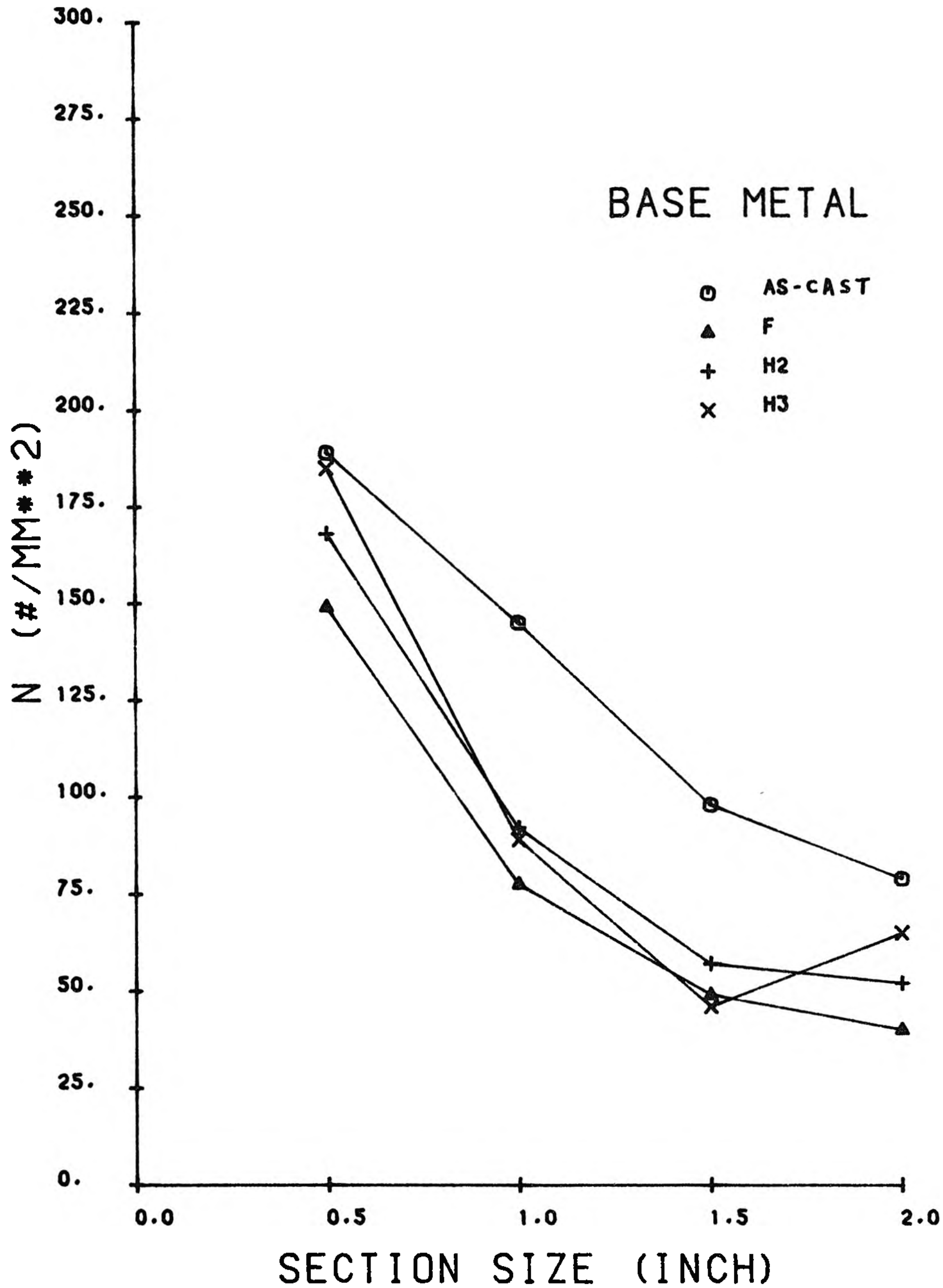


Figure 11. The effect of heat treatment on nodule count of the base ductile iron.

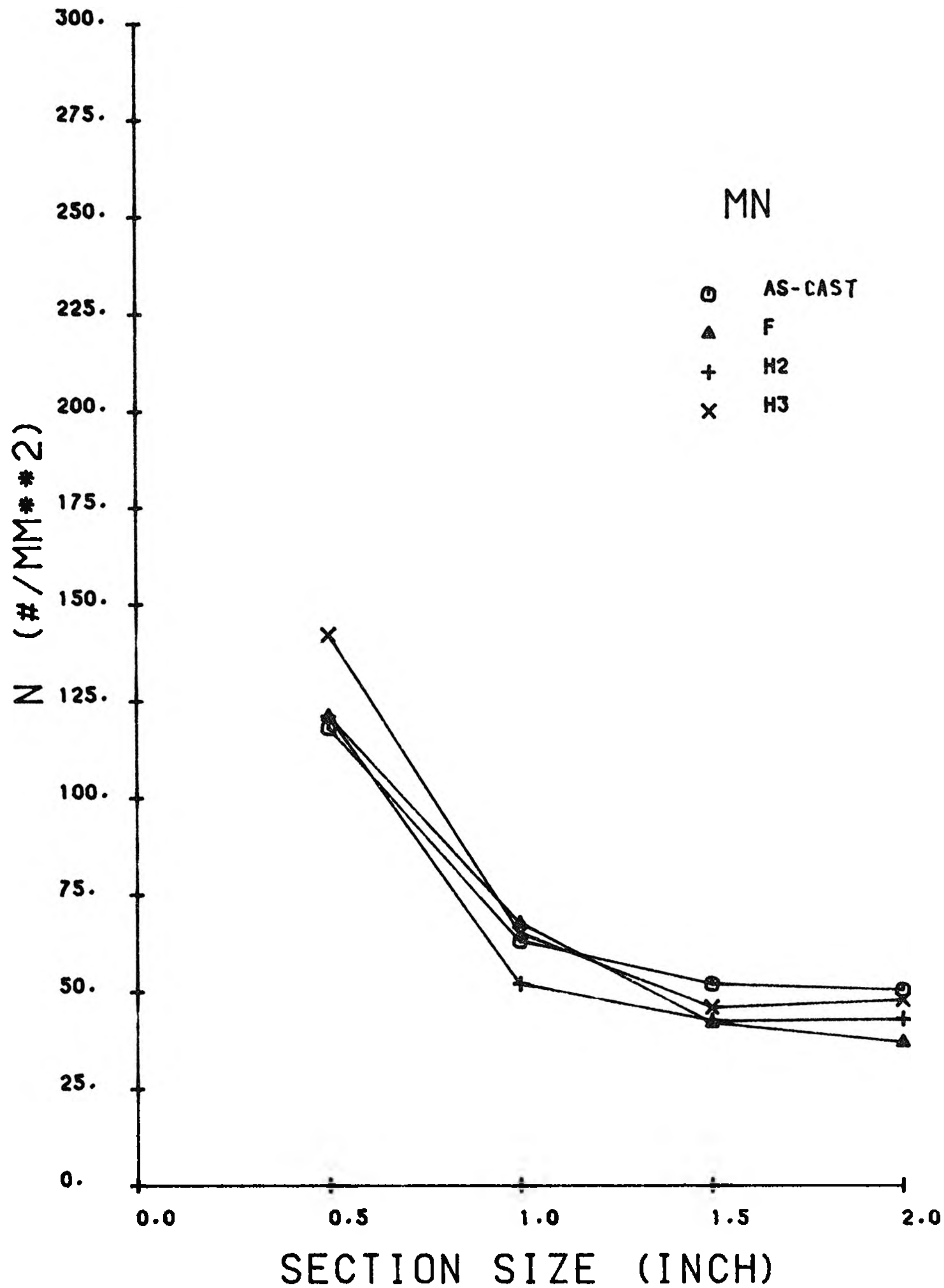


Figure 12. The effect of heat treatment on nodule count of the 1.2% Mn added ductile iron.

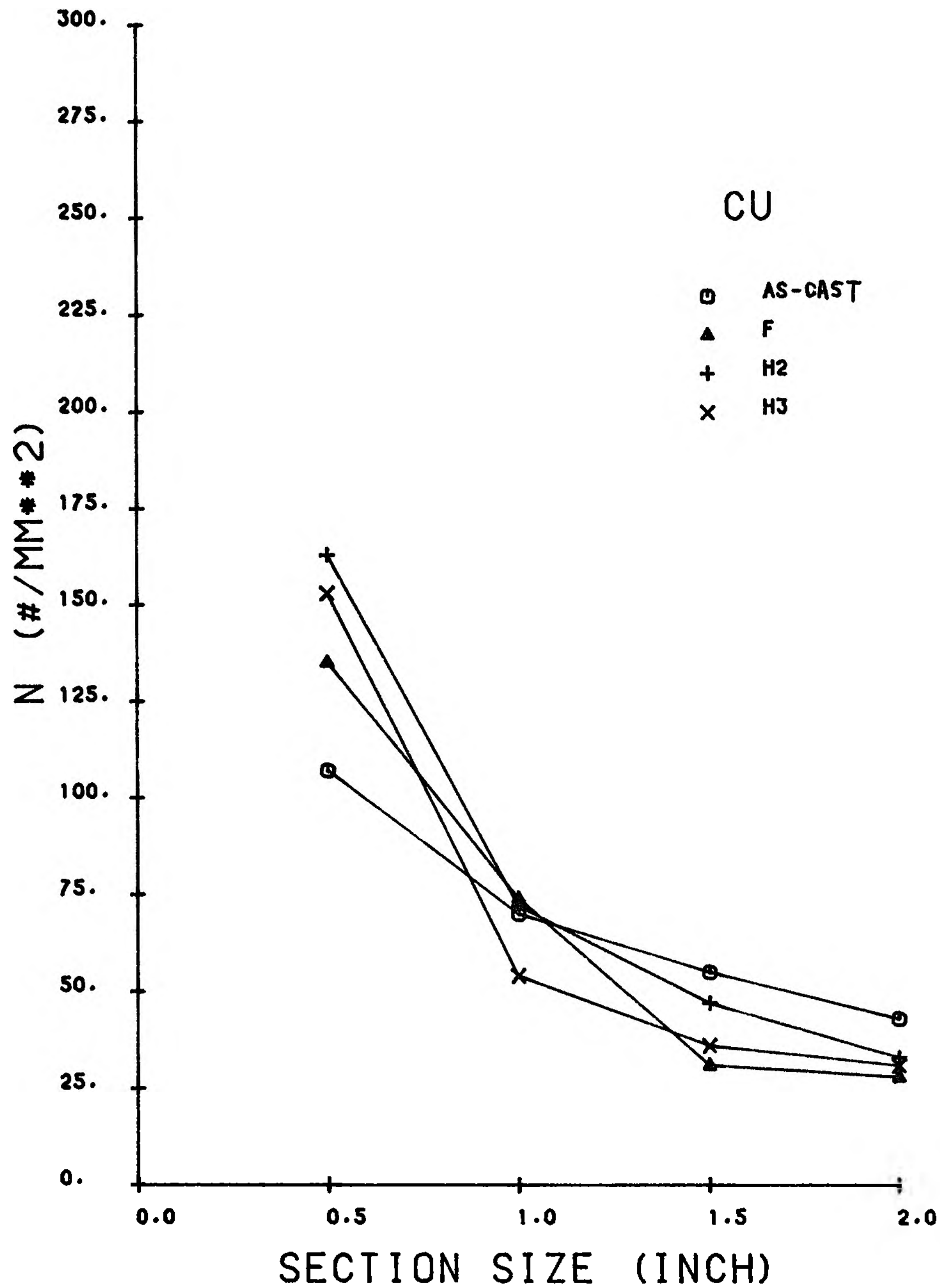


Figure 13. The effect of heat treatment on nodule count of the 0.5% Cu added ductile iron.

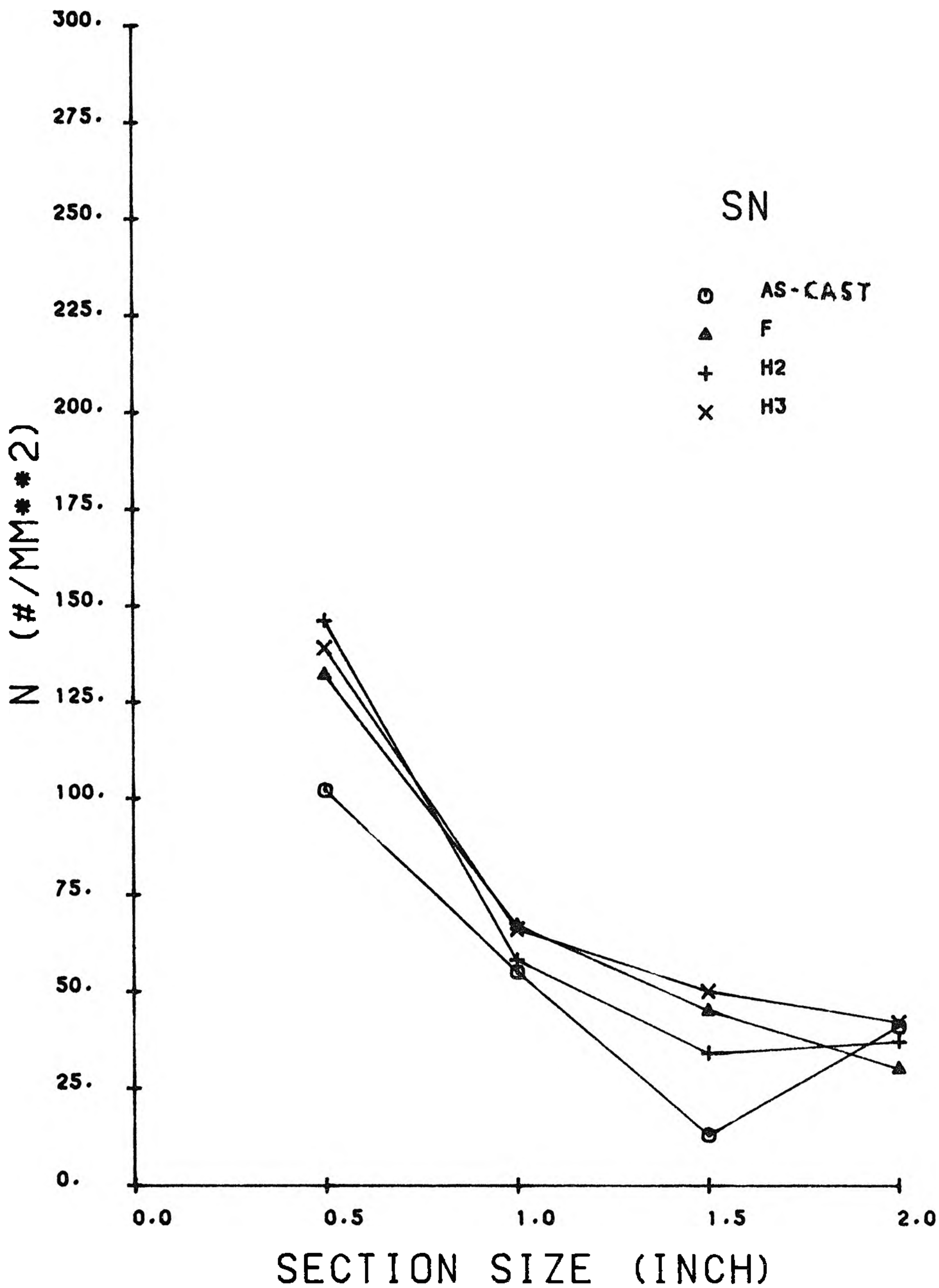


Figure 14. The effect of heat treatment on nodule count of the 0.1% Sn added ductile iron.

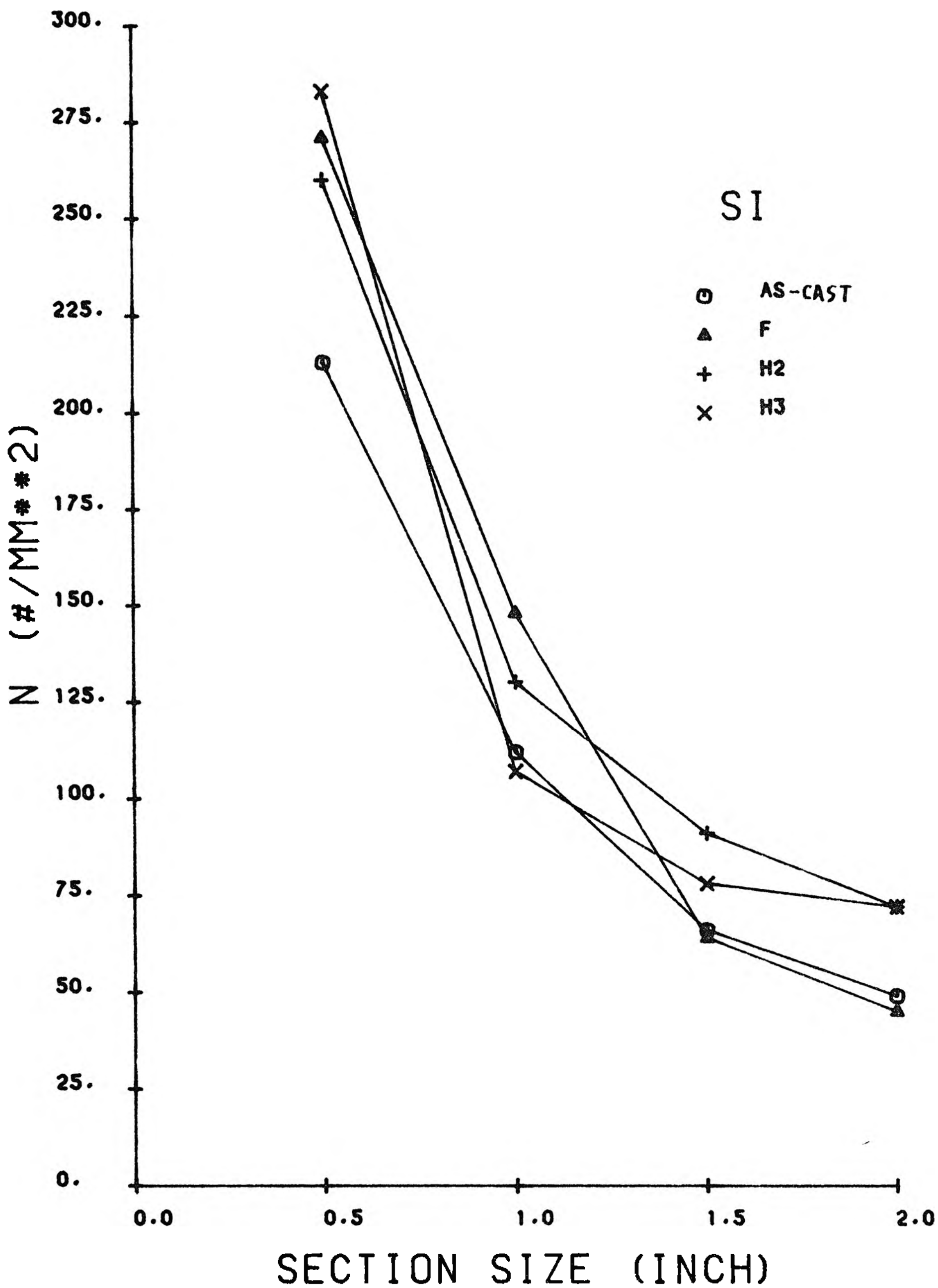


Figure 15. The effect of heat treatment on nodule count of the extra 1% Si added ductile iron.

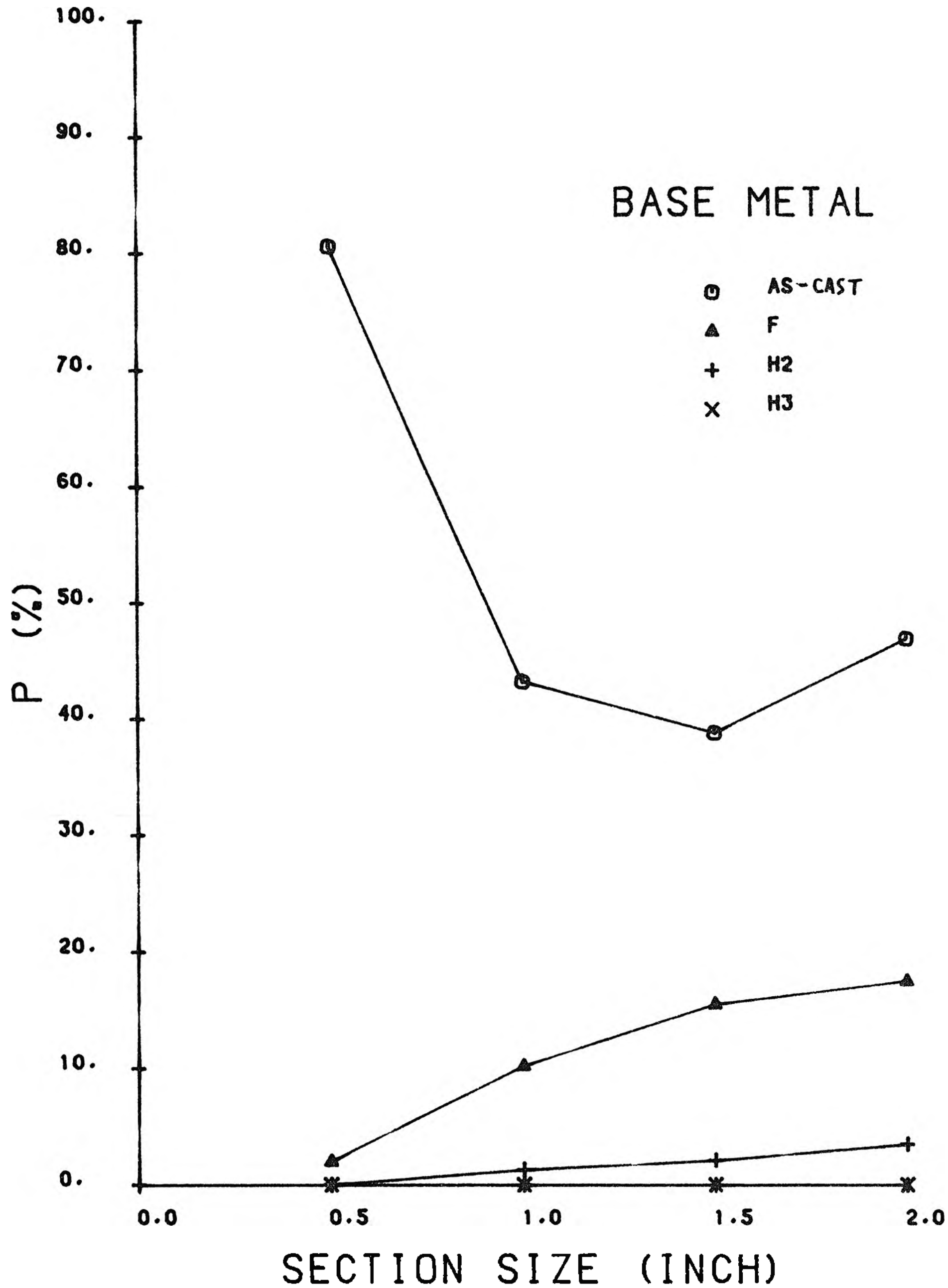


Figure 16. The effect of heat treatment on pearlite percentage of the base ductile iron.

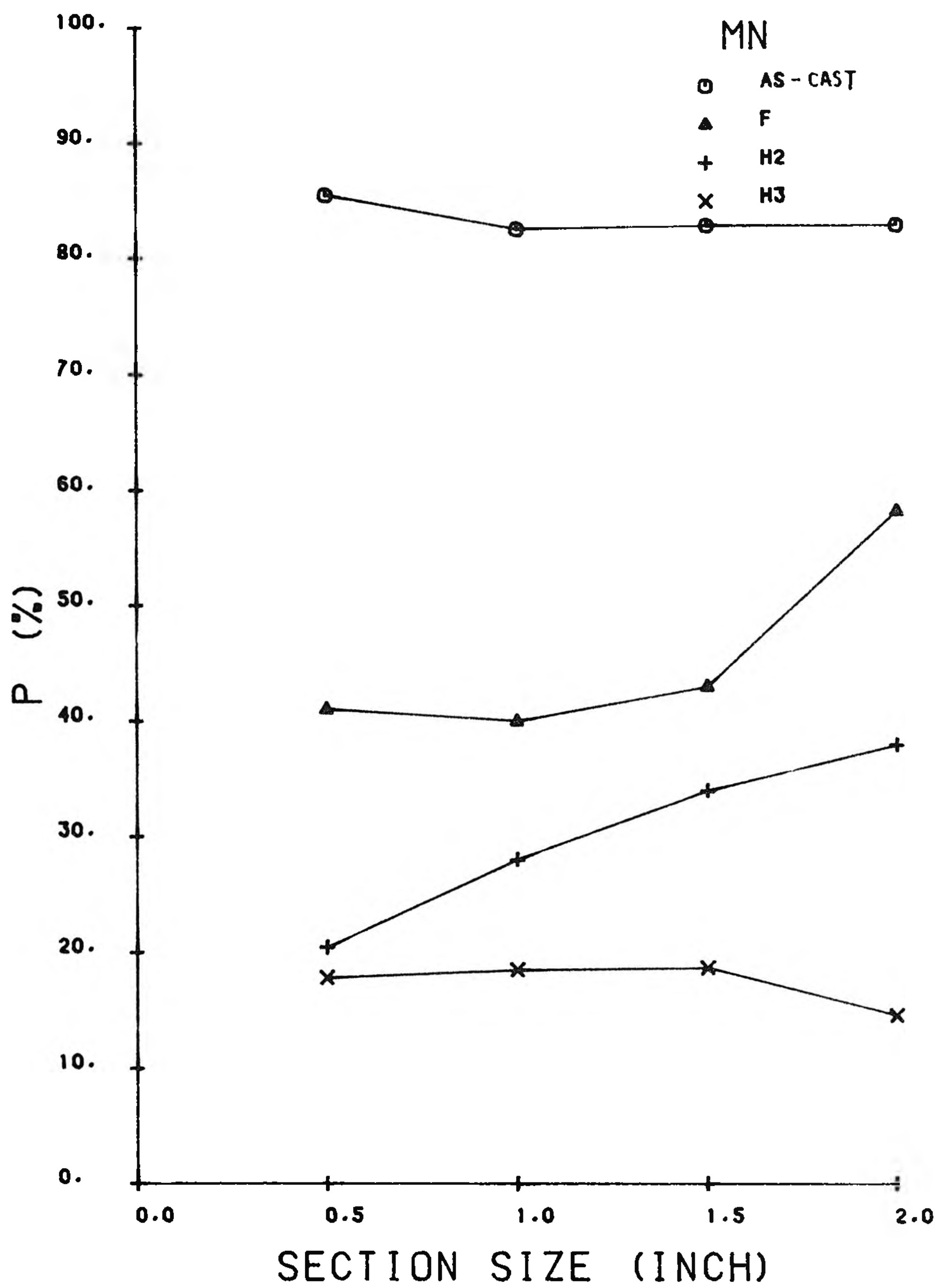


Figure 17. The effect of heat treatment on pearlite percentage of 1.2% Mn added ductile iron.

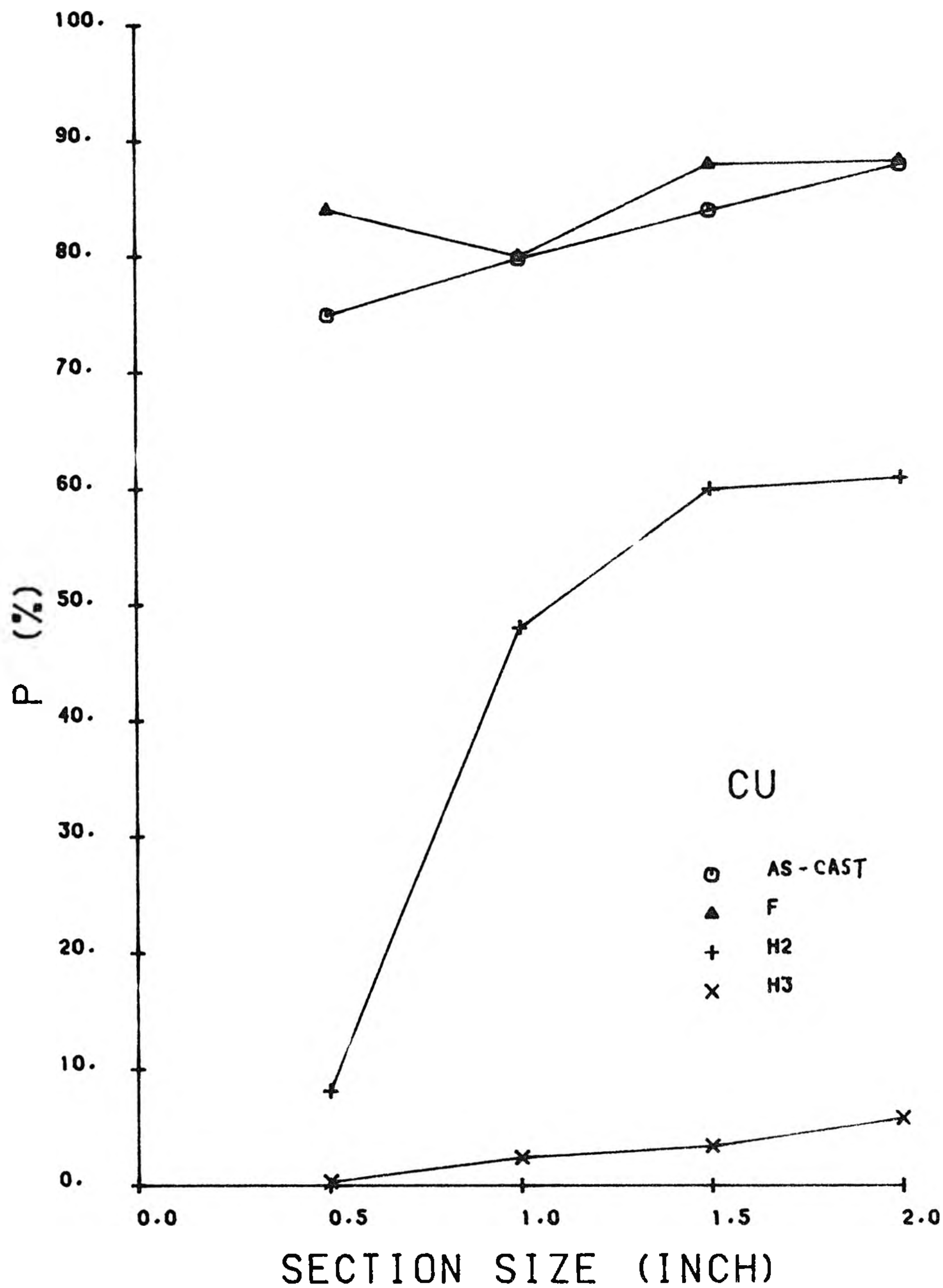


Figure 18. The effect of heat treatment on pearlite percentage of the 0.5% Cu added ductile iron.

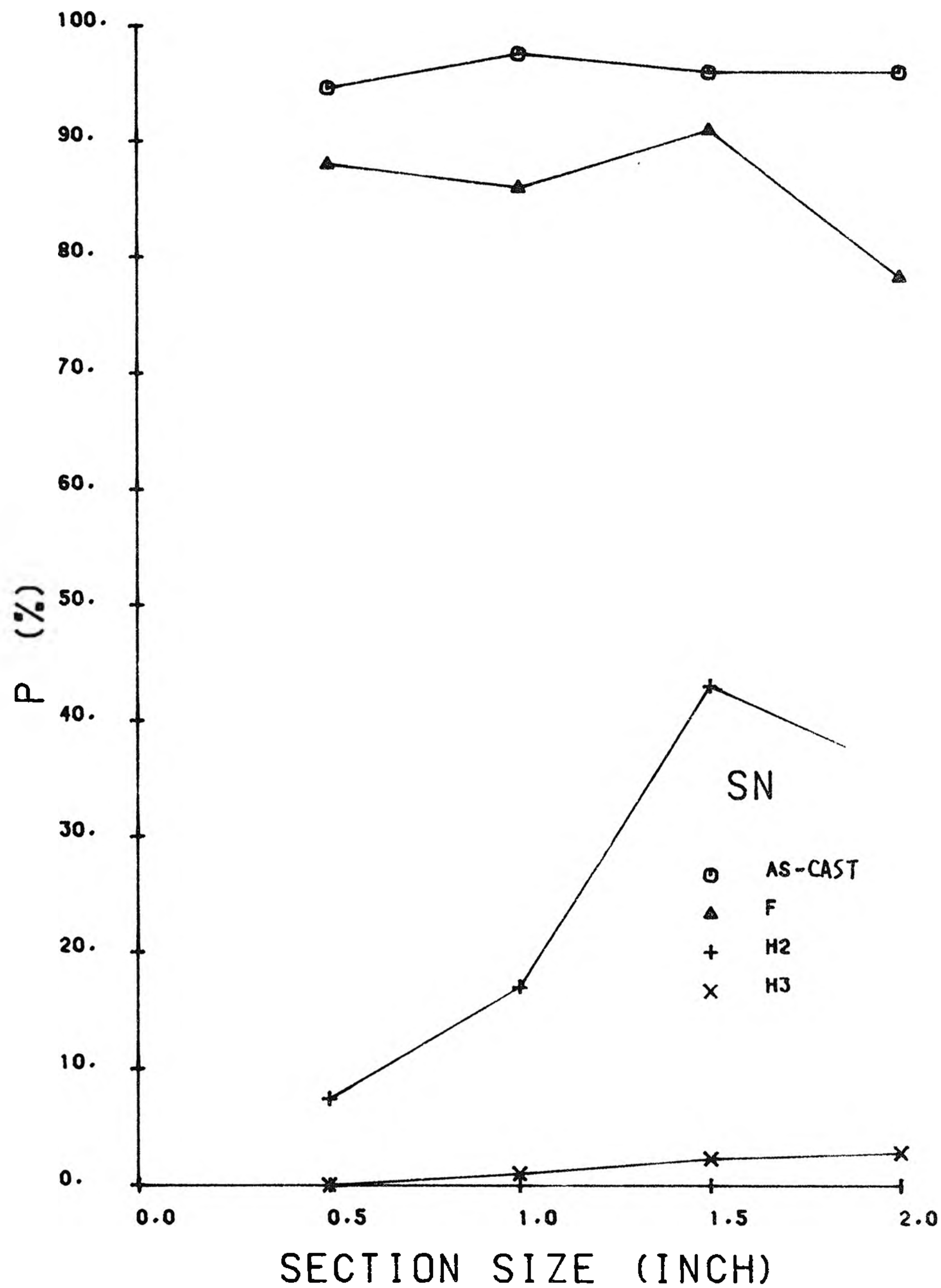


Figure 19. The effect of heat treatment on pearlite percentage of the 0.1% Sn added ductile iron.

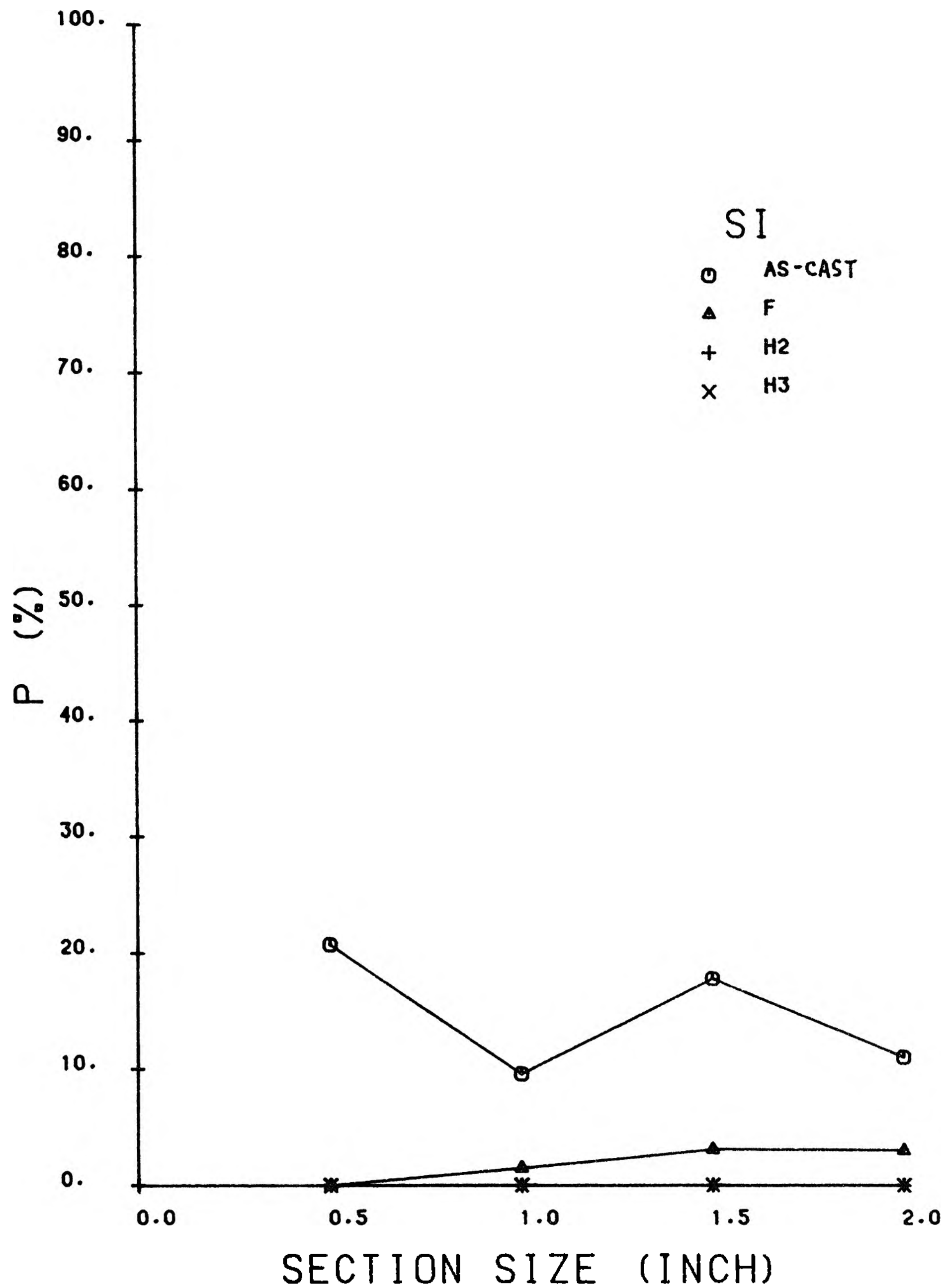


Figure 20. The effect of heat treatment on pearlite percentage of the extra 1% Si added ductile iron.

2. <u>The Effect of Heat Treatment on Pearlite Percentage.</u> (Figures 16 to 20) The following reactions take place during the heat treatment: the cementite decomposition reactions (reactions 3 and 6), the diffusion of catbon from austenite through the austenite boundary to graphite (reaction 4), the decomposition of austenite to form ferrite and graphite (reaction 5), and the diffusion of catbon through the ferrite boundary into graphite (reaction 7).

A slow cooling rate can give the carbon atoms a longer time to diffuse; this will make the matrix more ferritic and the remaining pearlite in the matrix coarser.

3. <u>The Effect of Section Size and Alloying Elements on Pearlite after Heat Treatment.</u> (Figures 16 to 20) The addition of copper and tin to the ductile iron will retard the decomposition of the cementite, because of the segregation of the copper and tin atoms on the austenite boundaries, the carbon atoms cannot diffuse through the austenite boundary to the graphite nodules. The addition of manganese in the ductile iron will make the Fe-C bonding in cementite stronger, also retarding the decomposition of cementite.

But if the cooling rate is slow enough, i.e. the carbon atoms have a longer time to diffuse at a higher temperature, the carbon atoms can diffuse through the barrier, break down the Fe-C bonding, and produce more ferrite. A cooling rate of $25^{o}F/hr$ is sufficient to cause ferritization in all but the high manganese alloy.

Generally, the thicker section castings have lower nodule counts; the longer carbon diffusion distance makes ferritization more difficult. That is the reason why the heavy section castings have less ferrite after heat treatment than the thin section castings.

From the experimental data, we found a critical cooling rate for each element which was necessary to produce a ferritic matrix. These cooling rates are listed in Table IV. Above the critical cooling rate, little ferritization was observed. Below the critical cooling rate, we obtain very good ferritization. For cases with cooling rates near the critical cooling rate, the section size can affect the pearlite percentage. The larger section size has a lower nodule count and higher pearlite, while the smaller section size had a higher nodule count and lower pearlite. For cases with cooling rates above the critical cooling rate, the pearlite percentage is not significantly affected by section size. The relationship between pearlite percentage and section size with heat treated ductile iron is similar to that of the as-cast condition, depending on nodule count and alloying additions. If no pearlite stabilizer is added, higher nodule count castings have lower pearlite, or the thin sections have more ferrite. If a pearlite promoter is added to the alloy, the pearlite percentage displays virtually no change with section size.

TABLE IV

THE CRITICAL COOLING RATE FOR

EACH ALLOYING ELEMENT

Alloying element	Critical Cooling Rate (^{O}F/hr)
Base Metal	340
1.2% Mn	< 25
0.5% Cu	100
0.1% Sn	100
Extra 1% Si	340

4. <u>The Effect of Pearlite and Alloying Elements on Hardness.</u> (Figures 21 to 26) The relationship between hardness and pearlite percentage can be expressed by the following equation:

$$H = A\ \mathrm{Exp}(BP)$$

where H is the hardness, P is the pearlite percentage, A is the hardness at zero pearlite percentage, and B is a constant. The A, B values for each alloying element are listed in Table V.

As shown in Figure 26:

(a) Silicon increases the hardness of the ferrite matrix. This is most easily observed by considering the constant "A" which represents the hardness of a completely ferritic matrix. This may be due to the smaller size of Si atoms, compared to the Fe atoms, causing a greater amount of solid solution strengthening.

(b) Cu, Sn, Mn provide only small increases in the hardness of ferrite, as shown by a similar constant "A". The smaller effect may be due to these atoms having about the same size as iron atoms.

(c) The slope B may indicate the effect of the alloying element on the fineness of the pearlite. A low slope indicates a coarser pearlite. The experimental data indicates that Mn produces finer pearlite, while Sn and Cu produce coarser pearlite. Consequently the high Mn alloy should be harder than the base metal while the high Sn and Cu alloys should have a lower hardness.

TABLE V

A,B VALUES OF H = A Exp(BP)

FOR EACH ALLOYING ELEMENT

Alloying Element	A	B
Base Metal	131.2	0.0061
1.2% Mn	134.6	0.0063
0.5% Cu	136.8	0.0048
0.1% Sn	135.0	0.0057
Extra 1% Si	165.5	0.0053

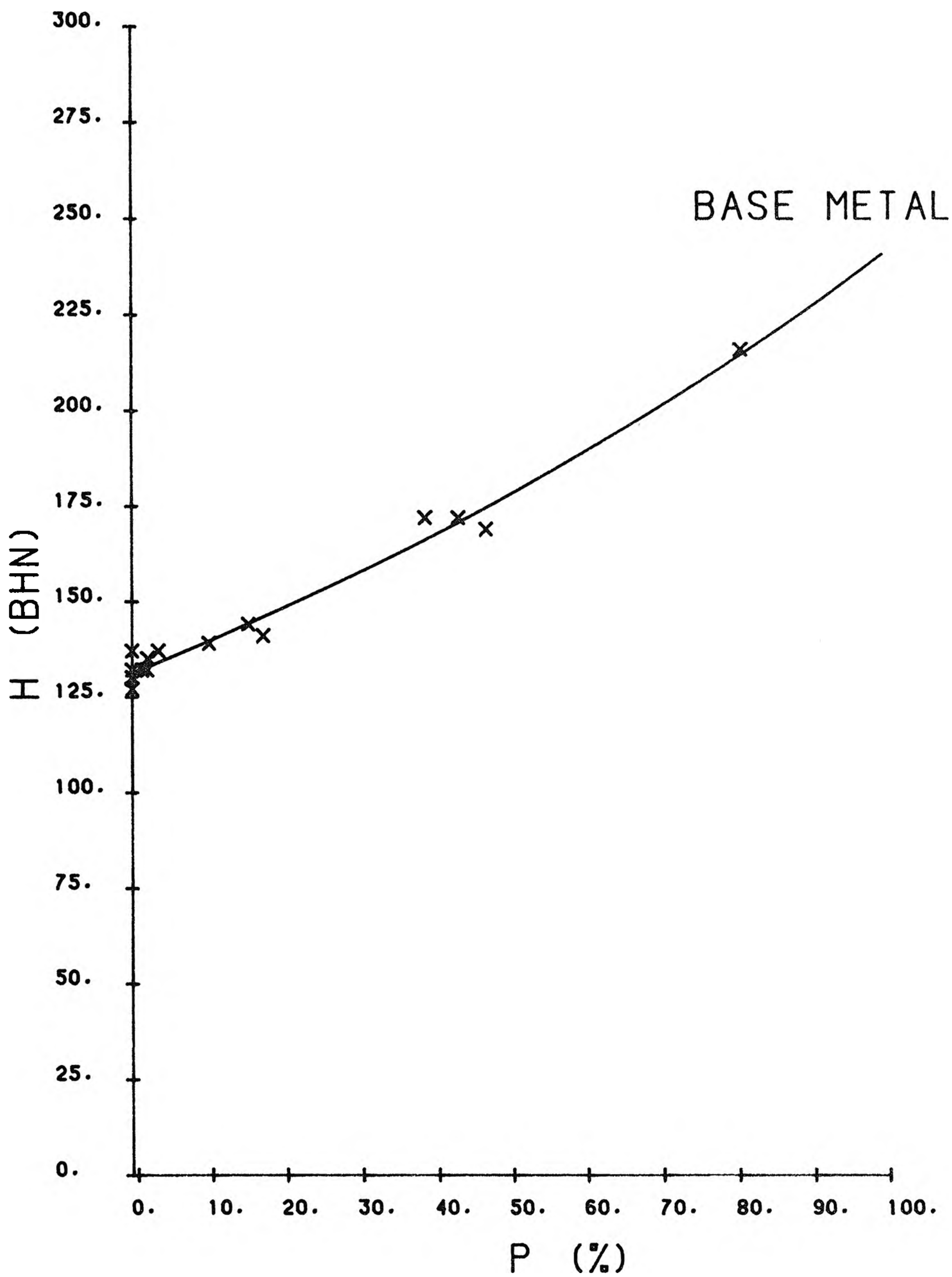


Figure 21. The relationship between hardness and pearlite percentage of the base ductile iron.

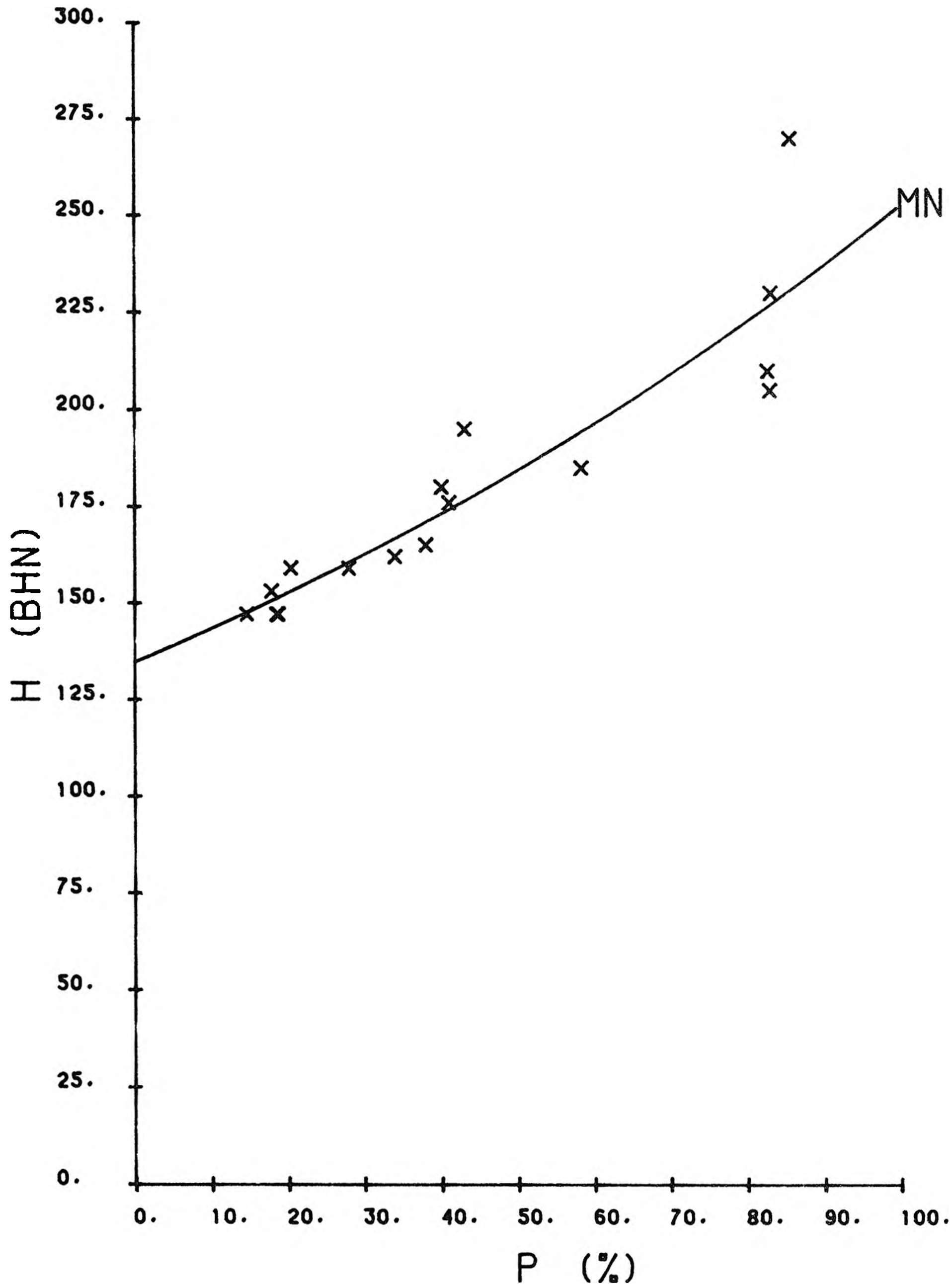


Figure 22. The relationship between hardness and pearlite percentage of the 1.2% Mn added ductile iron.

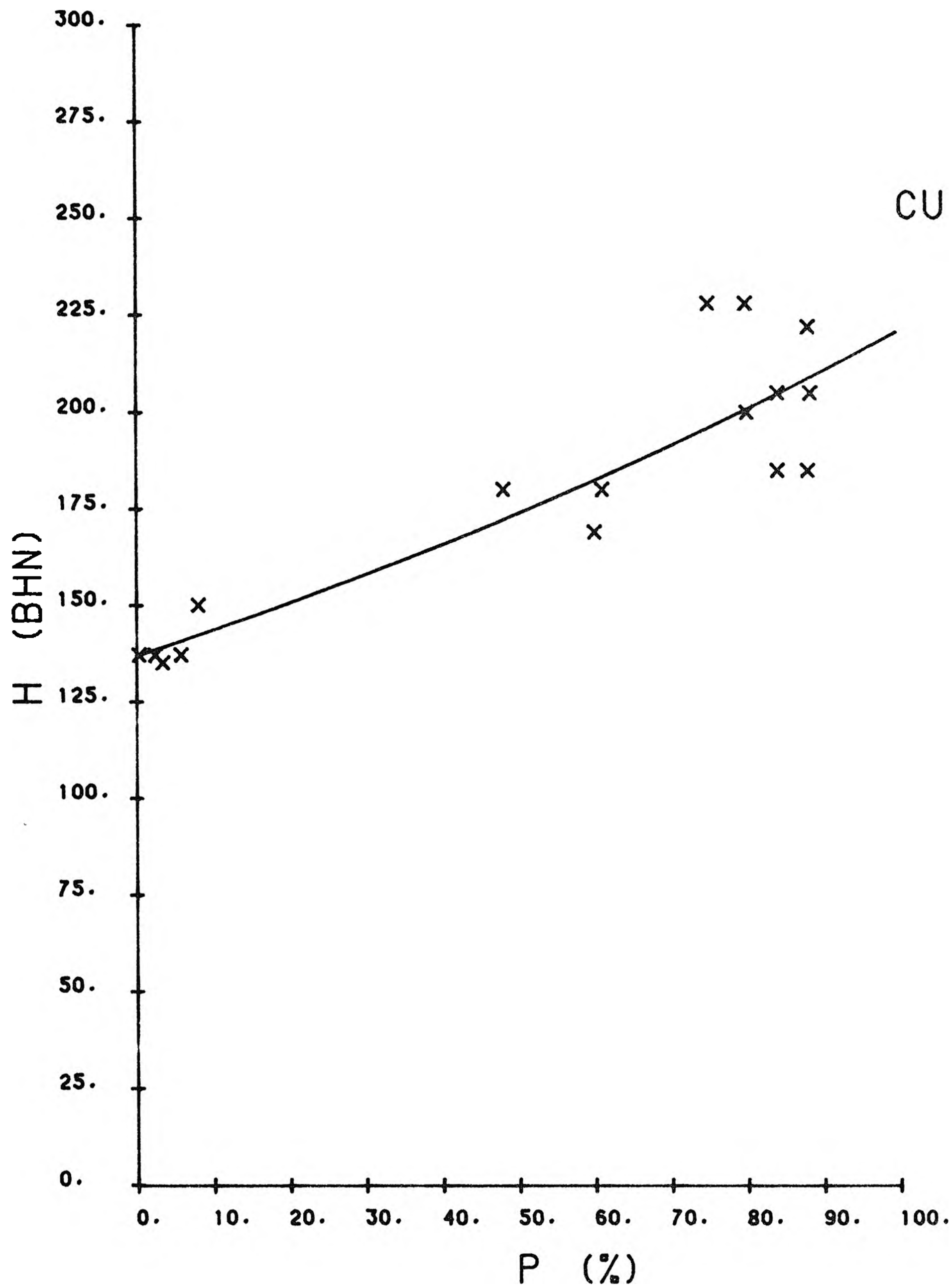


Figure 23. The relationship between hardness and pearlite percentage of the 0.5% Cu added ductile iron.

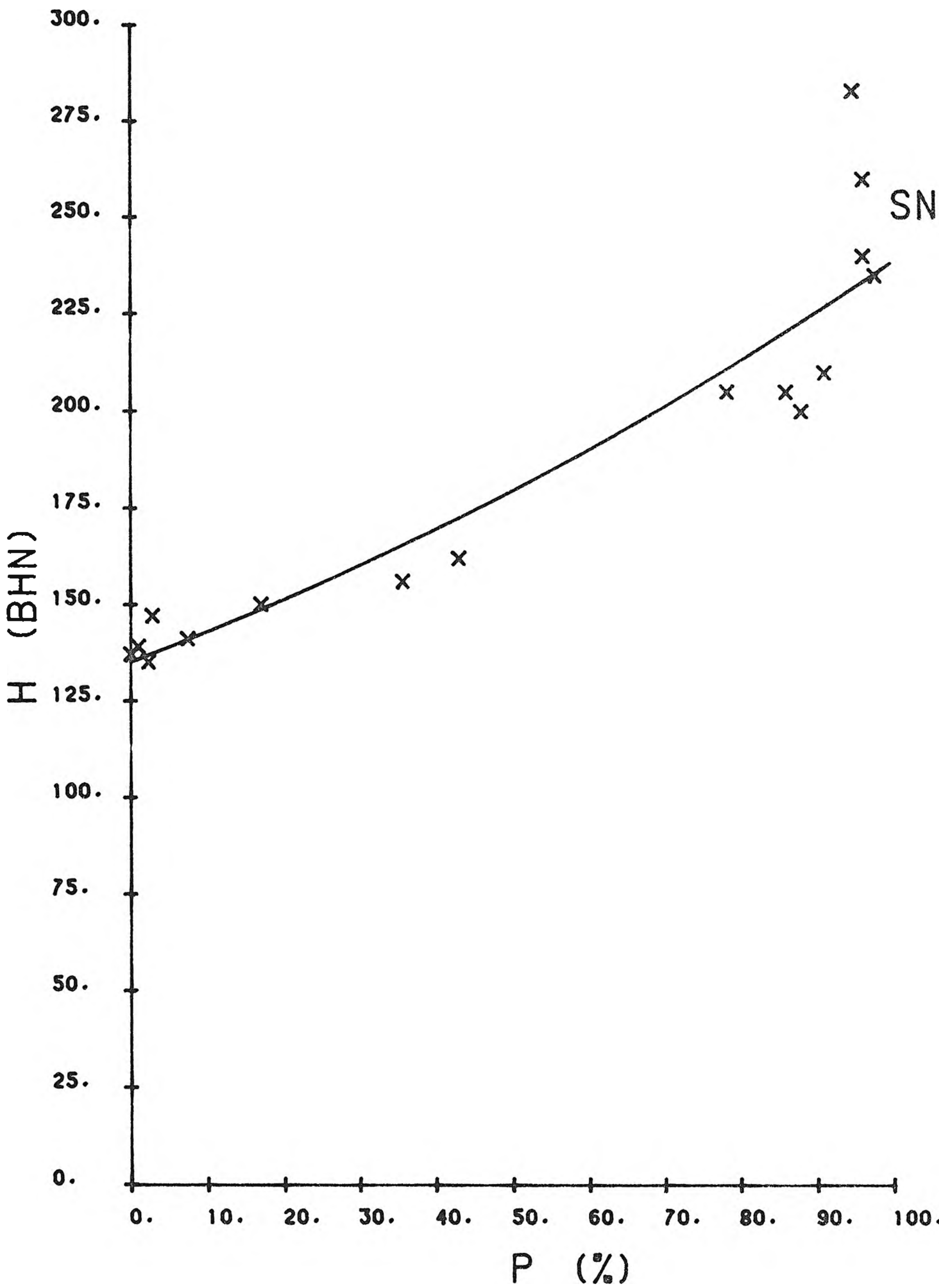


Figure 24. The relationship between hardness and pearlite percentage of the 0.1% Sn added ductile iron.

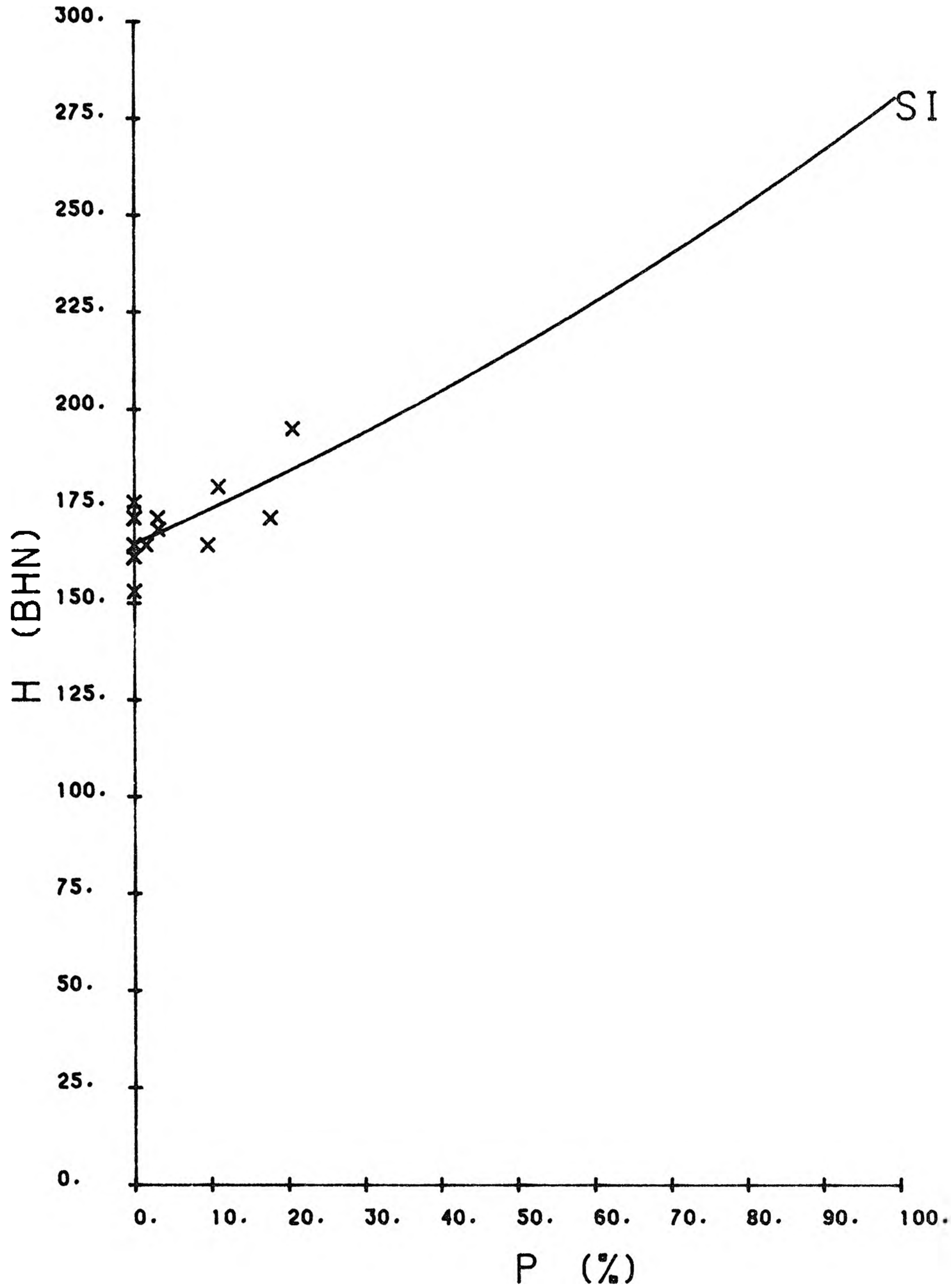


Figure 25. The relationship between hardness and pearlite percentage of the extra 1% Si added ductile iron.

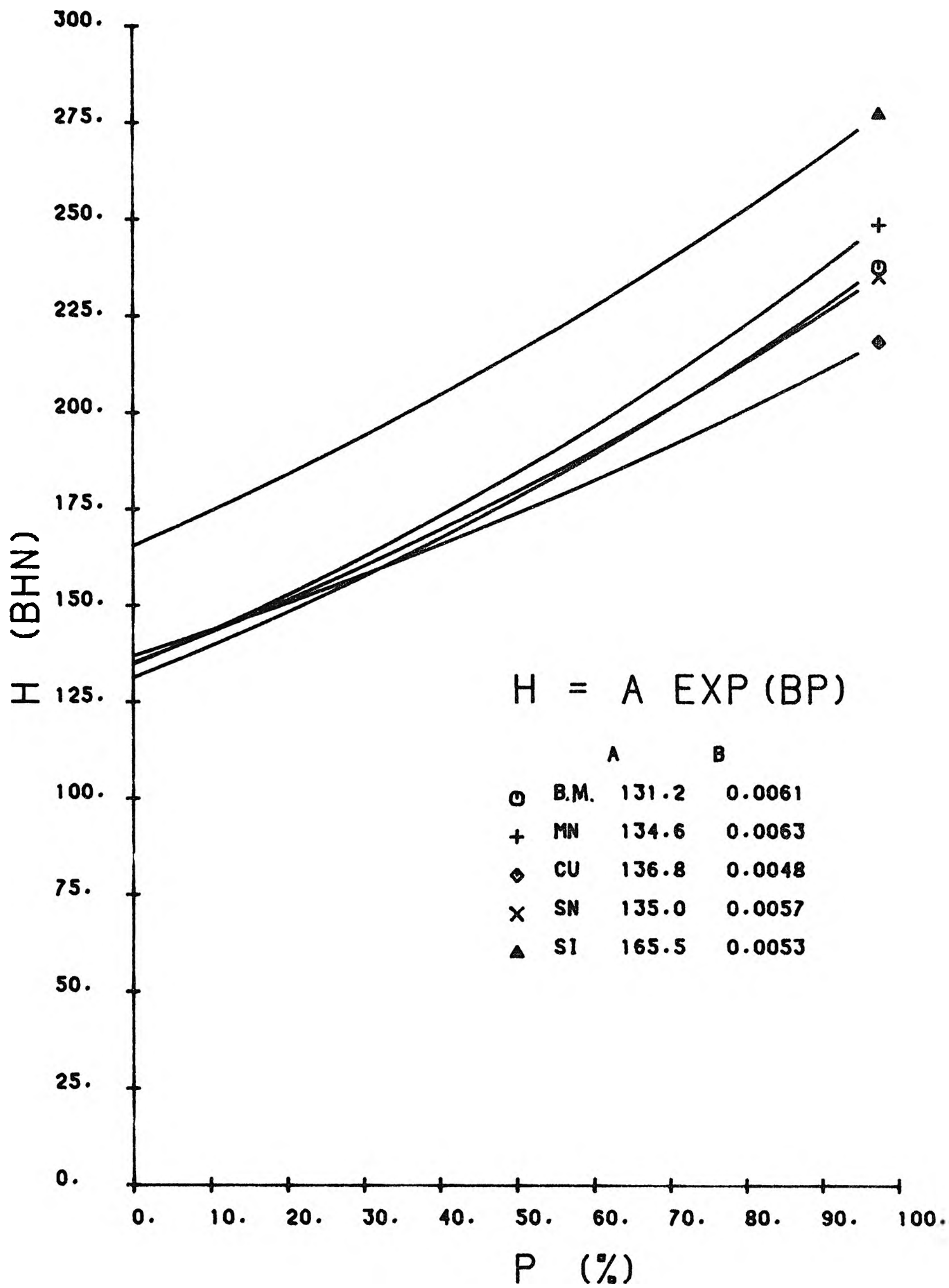


Figure 26. The effect of the alloying elements on the relationship between hardness and pearlite percentage.

V. PRACTICAL SIGNIFICANCE OF RESULTS

In order to obtain the ferritic structure in ductile iron, an annealing process is almost always required. In this study, the austenitizing treatment for each specimen is fixed at 1600°F and one hour. The only variables are the cooling rate during the temperature range 1600 to 1200°F, the section size, and the alloy element. The fastest cooling rate is furnace cooling, i.e. about 340°F/hr; the slowest cooling rate for this study is 25°F/hr.

A. BASE METAL

In the thin section (0.5") of the base metal, furnace cooling can successfully reduce the pearlite percentage to less than 5%. For thick sections (over 1"), the cooling rate should be somewhat slower -- between 340°F/hr and 100°F/hr -- in order to reduce the pearlite percentage to less than 5%. This effect is due to the lower nodule counts and longer diffusion distances in the heavier sections.

B. 0.5% COPPER ADDED

For the thin section (0.5") ductile iron with 0.5% Cu, a 100°F/hr cooling rate can drop the pearlite percentage down to 8%. For casting with section sizes over 1", 25°F/hr cooling rate should be chosen in order to reduce the pearlite percentage to less than 5%. Much slower cooling rates are required due to the pearlite stabilizing effect of copper.

C. <u>0.1% TIN ADDED</u>

The iron containing 0.1% Sn acts similarly to that of the 0.5% Cu alloy. For thin sections (0.5"), $100^{o}F/hr$ is slow enough to drop the pearlite percentage down to 7%. For thicker sections, a cooling rate close to $25^{o}F/hr$ should be used to obtain a pearlite percentage below 5%.

D. <u>1.2% MANGANESE ADDED</u>

The castings containing 1.2% Mn can not obtain a pearlite percentage as low as 5%. Even with the lowest cooling rate used, the pearlite percentage is always higher than 15%. Therefore, the recommendation for ductile iron castings containing more than 1.2% Mn is that the annealing temperature be higher than $1600^{o}F$, a longer holding time be used, and a cooling rate slower than $25^{o}F/hr$ be used. Ideally, the manganese content should be maintained as low as possible.

E. <u>3.4% SILICON ADDED</u>

For thin sections, even furnace cooling drops the pearlite percentage to zero. For thicker sections, the pearlite percentage always is less than 4% whenever funace cooling is applied to the casting. Slower cooling of even thick sections almost completely eliminates pearlite due to the powerful ferrite stabilizing effect of silicon.

Based on these results, it is apparent that alloying elements such as Cu, Mn and Sn will prevent the formation of ferrite even during slow cooling rates. Consequently these alloying elements must be avoided in castings that are to be annealed. This may require careful segregation of melting materials and the proper selection of nodulizing and inoculating alloys. On the other hand, higher silicon contents greatly assist in producing a completely ferritic structure during annealing.

VI. CONCLUSION

The following conclusions can be obtained from this experiment:

A. AS CAST DUCTILE IRON

1. As the section size (the time needed to solidify) increases, the nodule count of the casting decreases. There is a tendency for the nodule count to decrease when a pearlite stabilizer is added.

2. The effect of the section size on pearlite percentage is small, particularly when a pearlite promoter is added to the base metal.

3. The hardness of as cast ductile iron depends on cooling rate through the eutectoid temperature and alloying additions. The nodule count of the castings shows no effect on as-cast hardness.

B. HEAT TREATED DUCTILE IRON

1. In order to produce a ferritic matrix in ductile iron, pearlite promoters, such as manganese, copper and tin, should be avoided.

2. By carefully choosing the furnace cooling rate between 1600 and 1200°F (depending on section size), the castings containing 0.5 percent copper or 0.1 percent tin can be ferritized. But the casting which have 1.2 percent manganese content can not be ferritized by this process.

3. The relationship of pearlite percentage and the hardness of the matrix can be expressed by the equation

$$H = A\ \mathrm{Exp}(BP)$$

where H is the hardness and P is the pearlite percentage. A is a constant which indicates the hardness of a completely ferritic iron and B is a constant whcih may indicate the effect of alloying elements on pearlite fineness.

BIBLIOGRAPHY

1. Heine, Loper and Rosenthal, Principles of Metal Casting 2nd edition, American Foundrymen's Society, 1967, p. 614-641.
2. C. K. Donoho, "Molten Cast Iron for Treating to Produce Ductile Iron", Trans. AFS, Vol. 72, 1964, p. 608-610.
3. T. Watmough, W. F. Shaw, F. C. Bock, "Combined Effects of Selected Elements on the Properties of Ductile Iron", Trans. AFS, Vol. 79, 1971, p. 225-246.
4. J. E. Rehder, "The Critical Temperature Range in Cast Irons", Trans. AFS, Vol. 73, 1965, p. 473-487.
5. J. W. Abr, R. A. Cellitti and J. A. Halgren, "Effect of Silicon Content on the Heat Treatment and Mechanical Properties of Nodular Iron", Trans. AFS, Vol. 73, 1965, p. 344-354.
6. I. Karsay and R. D. Schelleng, "Heavy Ductile Iron Castings Composition Effect on Graphite Structure", Trans. AFS, Vol. 69, 1961, p. 672-679.
7. J. F. Janowak and R. B. Gundlach, "A Modern Approach to Alloying Gray Iron", Trans. AFS, Vol. 90, p. 847-863.
8. T. Levin, P. C. Rosenthal, C. R. Loper, R. W. Heine, "Tin and Copper in Ductile Iron", Trans. AFS, Vol. 79, 1971, p. 493-514.
9. A. de Sy, "Copper in Cast Iron -- Principal Considerations", Trans. AFS, Vol. 67, 1959, p. 321-328.

10. S. I. Karsay, "Control of Graphite Structure in Heavy Ductile Iron Casting", Trans. AFS, Vol. 78, 1970, p. 85-92.

11. B. V. Kovacs, "Pearlite Stabilization in Cast Irons", Ford Motor Co. Research Technical Report SR-80-94.

12. H. Morrogh, "Influence of Residual Elements and Their Neutralization in Magnesium-Treated Nodular Cast Iron", Trans. AFS, Vol. 60, 1952, p. 439.

13. J. C. Sawyer and J. F. Wallace, "Effects and Neutralization of Trace Elements in Gray and Ductile Irons", Trans. AFS, Vol. 76, 1968, p. 386-404.

14. C. E. Bate and J. F. Wallace, "Effect and Neutralization of Trace Elements in Gray, Ductile and Malleable Iron", Part I, Trans. AFS, Research Progress Report, 1967.

15. A. F. Spengler and H. K. Briggs, <u>The Ductile Iron Process</u>, Miller and Company, Compendium IV, 1972, Chapter 8.

16. C. R. Loper and R. W. Heine, "The Effect of Processing Variables on Ductile Iron Quality", Trans. AFS, Vol. 73, 1965, p. 488.

17. J. J. Osorno-Fonnegra, "Variables Affecting the Rate of Solution of Mold Inoculations in Cast Iron", M.S. thesis, 1975.

18. R. W. Reesman and C. R. Loper, "Heavy Section Ductile Iron as Affected by Certain Processing Variables", Trans. AFS, Vol. 75, 1967, p. 1-9.

19. T. L. Burkland and A. H. Rauch, "Prior Structure Effect on Ductile Iron Response to Induction Hardening", Trans. AFS, Vol. 70, 1962, p. 896-908.

20. "Measurement of the Pearlite Content in Ductile Iron", Trans. AFS, Vol. 80, 1972, p. 219-230.

21. "Hardness Conversion Table", Metal Progress, Vol. 118, No. 1, Mid-June 1980, p. 156-157.

22. B. F. Brown and M. F. Hawkes, "Kinetics of Graphitization in Cast Iron", Trans. AFS, Vol. 60, 1952, p. 181-200.

23. M. J. Lalich and C. R. Loper, "Effects of Pearlite-Promoting Elements on the Kinetics of the Eutectoid Transformation in Ductile Cast Irons", Trans. AFS, Vol. 81, 1973, p. 217-228.

24. G. S. Colt, "Solidification of Ductile Iron", Trans. AFS, Vol. 80, 1972, p. 335-348.

25. L. A. Neumeier, B. A. Betts and D. H. Desy, "Tin and Copper Combinations in As-Cast Ductile Iron", Trans. AFS, Vol. 82, 1974, p. 131-138.

26. B. B. Moreton, "Recent Research of Copper in Cast Iron", Foundry Trade J., Vol. 123, 1976, p. 845.

VITA

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He has been enrolled in the graduate school of the University of Missouri-Rolla since August 1980 and he is presently a candidate for the Master of Science degree in Metallurgical Engineering.

APPENDIX

DATA

BASE METAL

	Section Size(")	N	H	P%	F%	C%
As Cast	0.5	189	216	80.6	19.4	0
	1.0	145	172	43.2	56.8	0
	1.5	98	172	38.8	61.2	0
	2.0	79	169	46.9	53.1	0
H1	0.5	149	132	2	98	0
	1.0	77.5	139	10.2	89.8	0
	1.5	49	144	15.5	84.5	0
	2.0	40	141	17.5	82.5	0
H2	0.5	168	137	0	100	0
	1.0	92	132	1.3	98.7	0
	1.5	57	135	2.1	97.9	0
	2.0	52	137	3.5	96.5	0
H3	0.5	185	132	0	100	0
	1.0	89	130	0	100	0
	1.5	46	130	0	100	0
	2.0	65	127	0	100	0

1.2% Mn ADDED

	Section Size(")	N	H	P%	F%	C%
As Cast	0.5	118	270	85.5	8.9	5.6
	1.0	63	210	82.6	17.4	0
	1.5	52	205	82.9	17.1	0
	2.0	50.5	230	83	17	0
H1	0.5	121	176	41	59	0
	1.0	67.6	180	40	60	0
	1.5	42	195	43	57	0
	2.0	37	185	58.3	41.7	0
H2	0.5	121	159	20.4	79.6	0
	1.0	52	159	28	72	0
	1.5	42.5	162	34	66	0
	2.0	43	165	38	62	0
H3	0.5	142	153	17.8	82.2	0
	1.0	65	147	18.5	81.5	0
	1.5	46	147	18.7	81.3	0
	2.0	48	147	14.6	85.4	0

0.5% Cu ADDED

	Section Size(")	N	H	P%	F%	C%
As Cast	0.5	107	228	74.9	25.1	0
	1.0	70	228	79.8	20.2	0
	1.5	55	205	84	16	0
	2.0	43	222	88	12	0
H1	0.5	135	185	84	16	0
	1.0	74	200	80	20	0
	1.5	31	185	88	12	0
	2.0	28	205	88.3	11.7	0
H2	0.5	163	150	8.1	91.9	0
	1.0	72	180	48	52	0
	1.5	47	169	60	40	0
	2.0	33	180	61	39	0
H3	0.5	153	137	0.3	99.7	0
	1.0	54	137	2.4	97.6	0
	1.5	36	135	3.4	96.6	0
	2.0	31	137	5.8	94.2	0

0.1% Sn ADDED

	Section Size(")	N	H	P%	F%	C%
As Cast	0.5	102	283	94.6	0	5.4
	1.0	55	235	97.6	2.3	0.1
	1.5	43	260	96	4	0
	2.0	41	240	96	4	0
H1	0.5	132	200	88	12	0
	1.0	67	205	86	14	0
	1.5	45	210	91	9	0
	2.0	30	205	78.3	21.7	0
H2	0.5	146	141	7.4	92.6	0
	1.0	58	150	17	83	0
	1.5	34	165	43	57	0
	2.0	37	156	35.7	64.3	0
H3	0.5	139	137	0	100	0
	1.0	66	139	1	99	0
	1.5	50	135	2.3	97.7	0
	2.0	42	147	2.8	97.2	0

EXTRA 1% Si ADDED

	Section Size(")	N	H	P%	F%	C%
As Cast	0.5	213	195	20.7	79.3	0
	1.0	112	165	9.6	90.4	0
	1.5	66	172	17.8	82.2	0
	2.0	49	180	11	89	0
H1	0.5	271	172	0	100	0
	1.0	148	172	1.5	98.5	0
	1.5	64	169	3.1	96.9	0
	2.0	45	172	3	97	0
H2	0.5	260	172	0	100	0
	1.0	130	165	0	100	0
	1.5	91	165	0	100	0
	2.0	72	162	0	100	0
H3	0.5	283	176	0	100	0
	1.0	107	165	0	100	0
	1.5	78	162	0	100	0
	2.0	72	153	0	100	0