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The effect of nickel upon the stability of iron carbide and upon the microscopic structure of white cast iron compositions

Milo J. Stutzman
Iowa State College

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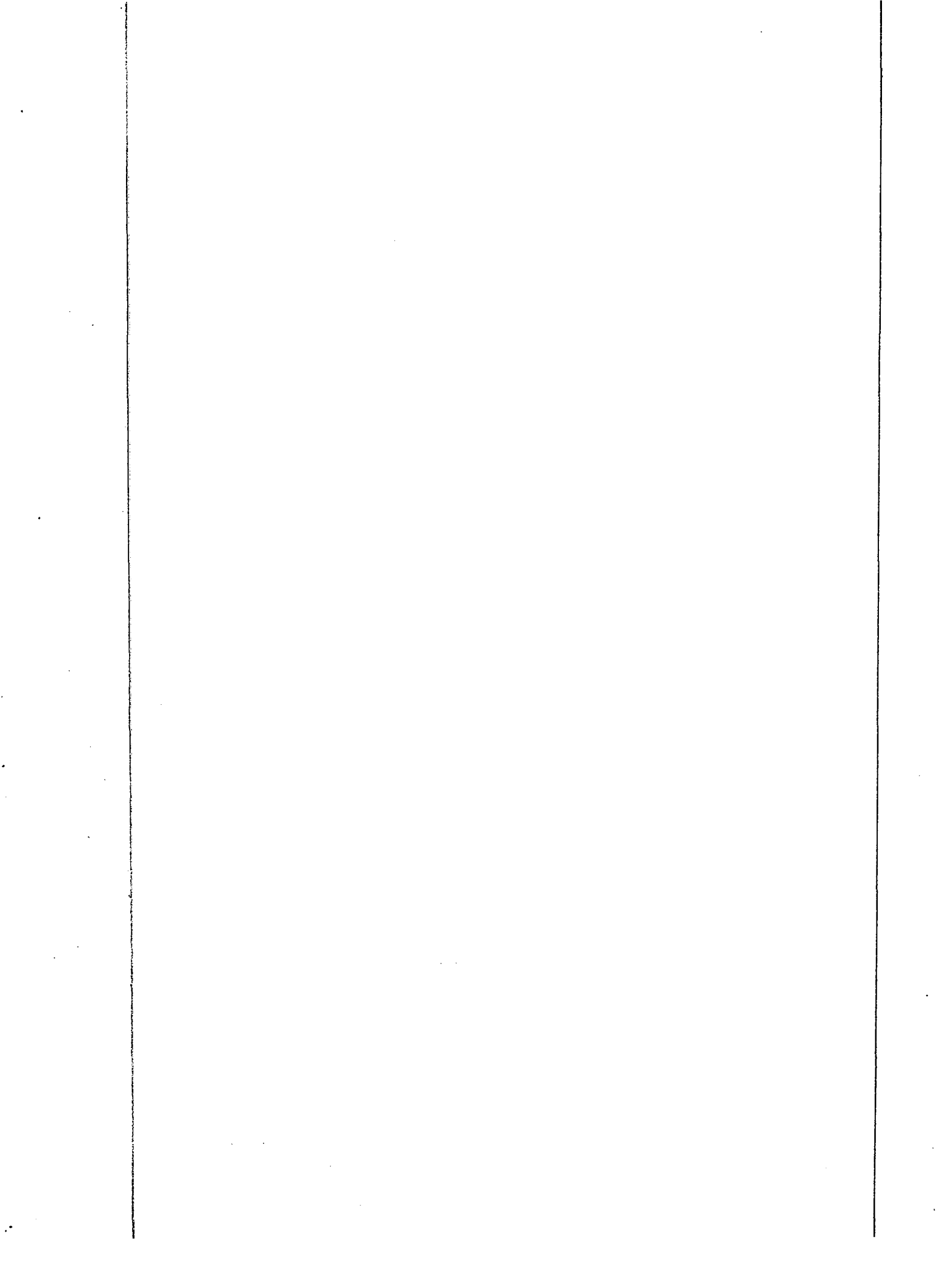
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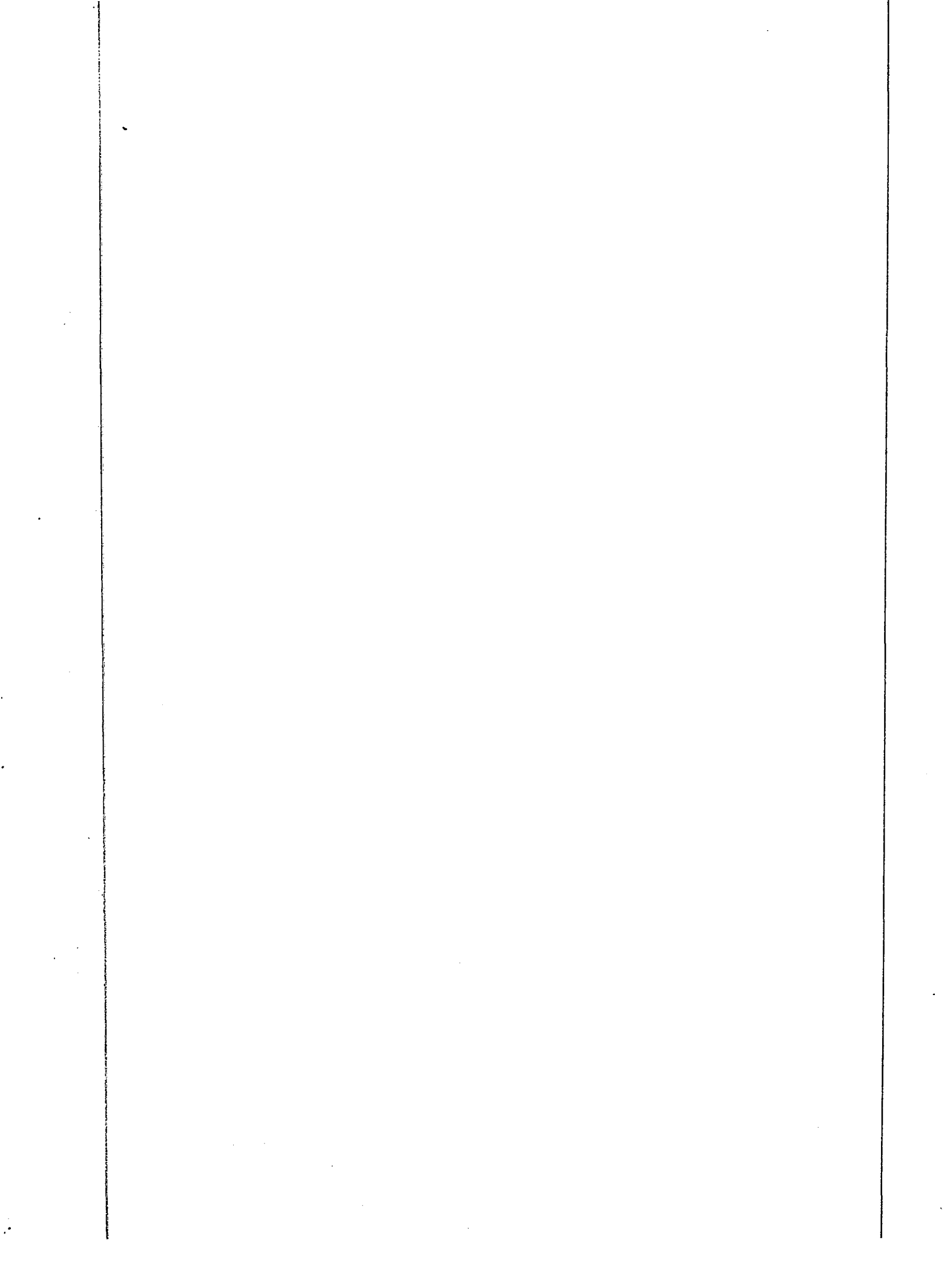
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THE EFFECT OF NICKEL UPON THE STABILITY OF IRON CARBIDE
AND UPON THE MICROSCOPIC STRUCTURE OF WHITE
CAST IRON COMPOSITIONS

BY

Milo J. Stutzman

A Thesis submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In charge of Major work.

Signature was redacted for privacy.

Head of Major Department.

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Dean of Graduate College.

Iowa State College

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THE EFFECT OF NICKEL UPON THE STABILITY OF IRON CARBIDE
AND UPON THE MICROSCOPIC STRUCTURE OF WHITE
CAST IRON COMPOSITIONS

By Milo J. Stutzman

I. INTRODUCTION

In 1923 and '24 when the investigation on the shortening of the annealing cycle for malleable cast iron, by Hayes and Diederichs (1) was being carried out in this laboratory, it became apparent that a study of the physical and chemical factors affecting the rate of graphitization was needed. Since that time some work has been published on the effects of both the physical and chemical factors. In 1925 Hayes, Diederichs and Flanders (2) investigated the effects of annealing temperatures on the rates of graphitization and on the properties of the malleable iron produced. In the same year Schwartz and Guiler (3) made a qualitative investigation of those elements that inhibit graphitization. In 1926 Kikuta (4) studied both the physical factors and the elements of regular malleable cast iron compositions and their effects on both the rates of graphitization and the physical properties.

The effect of chemical composition on the rate of graphitization and the physical properties of the product is now

being investigated in this laboratory, for those elements found in commercial malleable iron and for alloying elements. The work discussed in this paper is on the effect of nickel additions to commercial malleable iron.

II. REVIEW OF THE LITERATURE

A. The Mechanism of Graphitization:

The mechanism of graphitization as outlined by Hayes and co-workers (1) of this laboratory, takes place in two stages: first, the graphitization of the free cementite at a temperature above the A_1 stable and during cooling from the high temperature to the eutectoid and second, the graphitization to ferrite and graphite at the A_1 stable, or below.

Figure 1 shows the iron-carbon diagram with the stable iron-carbon eutectoid and the carbon solubility line drawn as proposed by Hayes and Diederichs (1). This is for a one percent silicon alloy, and may be used only for qualitative values of alloys of about the same composition. For quantitative data a ternary diagram is necessary. Line AJ represents the solubility of carbon from carbon in austenite and the line AC represents the solubility of carbon from iron carbide in the same solution. Consider a sample of 2.20 percent carbon with the regular structure of white cast iron. The first step then of the graphitization is the graphitization of the free cementite at the high temperature, for example, at 925 degrees centigrade. According to this theory for the mechanism of graphitization the graphite particle first forms in contact with the cementite. Additional carbon then precip-

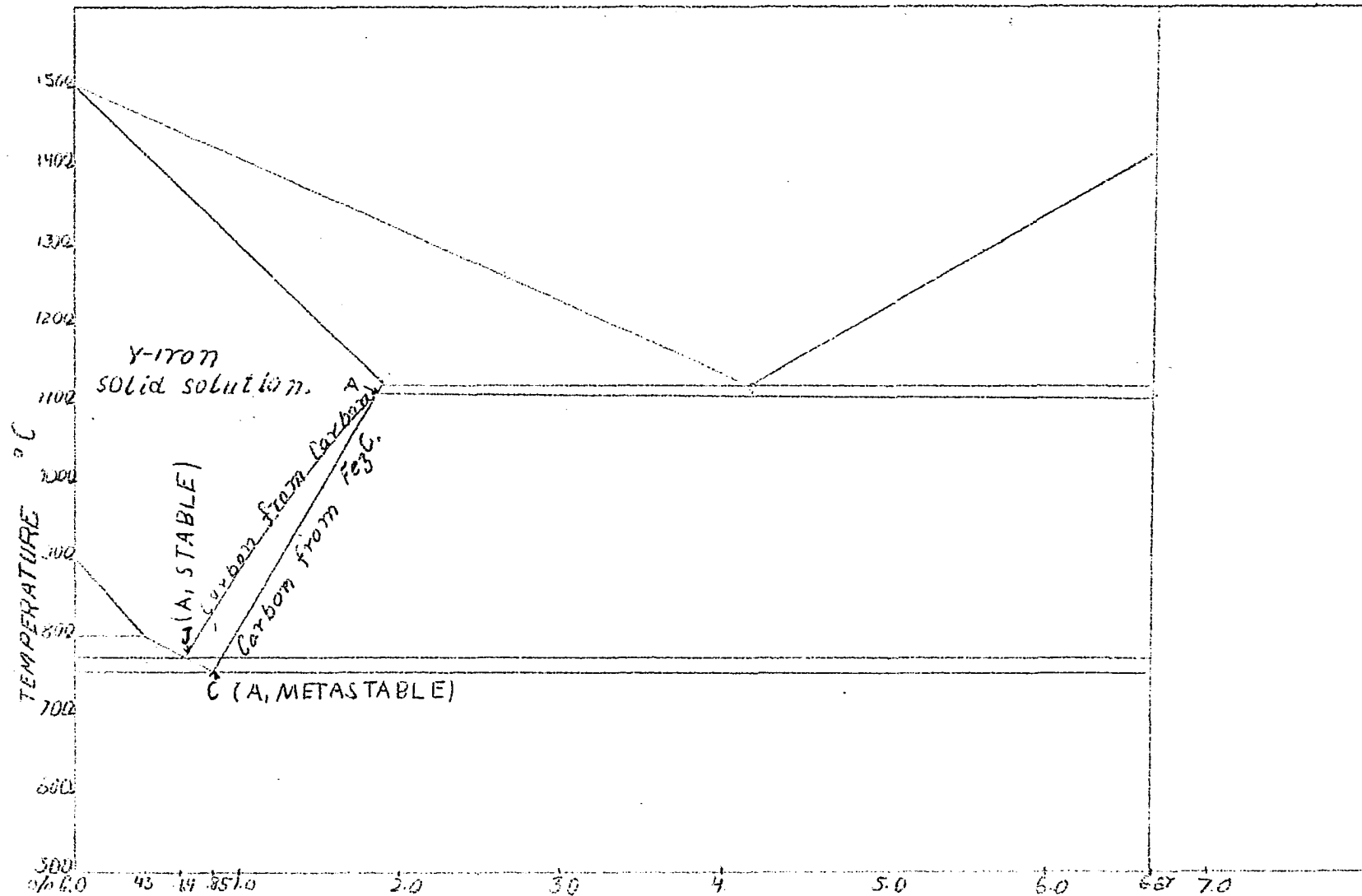


FIG. 1 IRON-CARBON STABLE META-STABLE SYSTEMS

itates on these already formed nuclei from the solid solution which contains more carbon than corresponds to the solubility of carbon from carbon. This then allows more of the free cementite to dissolve and carbon to precipitate, until all of the free cementite is used up.

The next step in the annealing process is the cooling from the high temperature to the eutectoid. According to the law of mass action, the further a reaction is from equilibrium at constant temperature the greater the rate of reaction. In the present reaction if the cooling is too rapid the composition will cross the line AC and free carbide will again be precipitated. If the cooling is too slow the reaction will be slowed up due to the approach of equilibrium conditions. Thus the cooling should be such as to keep the composition just below the solubility of carbon from the iron carbide.

At the iron-carbon eutectoid ferrite and graphite separate. The first ferrite will be precipitated about the carbon nucleus and the graphite deposited upon it. But it has been shown in this laboratory by Hayes, Diederichs and Flanders (1) that at the iron-carbon eutectoid fine graphite particles are precipitated throughout the solid solution with the precipitation of ferrite. However, time is required for

the reaction to be complete and if the time is not sufficient pearlite will result, due to the action of the meta-stable iron-iron carbide eutectoid.

B. Physical Factors Effecting the Rates of Graphitization:

The effect of the annealing temperature on the time required and the microstructures produced was studied by Fisher (6), White (5), Hayes, Diederichs and Flanders (1), and by Kikuta (4). White showed very clearly by photomicrographs the change that takes place at the high temperature and that the logarithm of the time required for the disappearance of free carbide bears a straight line relation to the temperature. This checks the results of Hayes and of Kikuta. Hayes has also shown that the carbon is precipitated in good form if the temperature is not higher than 992°C. (1820°F.), and the iron shows good physical properties. The rate of heating has little or no effect on either. However, if poor carbon form is obtained by too high a temperature it can not be changed by heat treatment. The following table taken from the data of Kikuta shows the time required for the disappearance of free cementite at the different temperatures:

Annealing Temperature	Time of 1st Stage.
875°C. (1607°F.)	9 hrs. 0 min.
900°C. (1652°F.)	4 30
925°C. (1691°F.) X	2 50
950°C. (1742°F.)	2 0
975°C. (1787°F.)	1 20

The effect of pouring temperature on the rate of graphitization at the high temperature is shown by the following data taken from the work of Kikuta:

Pouring Temperature	Time of 1st Stage.
1300°C. (2372°F.)	5 hrs. 0 min.
1350°C. (2462°F.)	5 30
1400°C. (2552°F.)	6 20
1450°C. (2642°F.)	7 0
1500°C. (2732°F.)	8 0
1550°C. (2822°F.)	8 20

This increase in the time required for annealing with an increase in the pouring temperature was explained by

Kikuta as due to driving out of the metal the oxides of carbon, which are known to act as a catalyst on the graphitization processes. This might also be the effect of the coarser white iron structure which results in the formation of more massive cementite, which in turn would require more time to be absorbed. In thick sections of malleable iron castings this is found to be the case. The cementite is much larger grained and thicker and upon annealing requires more time to graphitize. Because of the difficulties of machining and working the white iron, Kikuta studied the effect of time of cooling on the form of cementite and the time for annealing, by pouring the alloys into dry sand, green sand, and iron molds at different temperatures. The structures thus obtained were similar to those found in the heavy portions of regular castings. The following table gives the results of this investigation:

Note: Mistake, should be sand instead of iron

	Time at 925°C.		Time at Eutectoid.
	#1	#2	#1
Green sand	5 hrs.	—	—
Dry sand	6	8 hrs.	15 hrs.
Iron at 400°C. (752°F.)	7 1/2	—	—
Iron at 600°C. (1112°F.)	9	11 1/3	21
Iron at 800°C. (1472°F.)	9 1/3	14	
Iron at 1000°C. (1832°F.)	10	15 1/3	

C. Effects of Chemical Composition on
The Rates of Graphitization;

While the work of Hayes and Diederichs (1) on the shortened annealing cycle for malleable iron was being carried out in this laboratory, the lack of reliable data on the effect of chemical composition on graphitization soon became evident. In 1925 Hayes and Flanders (2) studied the effect of sulfur on the speed of graphitization. In the same year Schwartz and Guiler (3) determined qualitatively, by additions of alloying elements to commercial white cast iron and annealing with a regular commercial anneal, those elements which inhibit graphitization. The following list of elements were found to have appreciable effects in inhibiting the graphitization reaction: antimony, boron, chromium, cerium, lanthanum, rare earths, selenium, tellurium and tin.

The work of most value on the effects of chemical composition on annealing times is that of Kikuta. He studied the effects of the elements found in regular commercial malleable iron, carbon, silicon, manganese, sulfur and phosphorus. The results of this work are shown in figure 2 and in the following summary:

1. Silicon increases the rate of graphitization both in the critical range and at the high temperature. This is shown

in curves I, II, III, IV of figure 2. Kikuta expresses the first stage of the graphitization as a logarithmic function of the concentration of silicon. The equation is,

$$t = (A) (S^B)$$

where t is the time for the absorption of the free carbide at a temperature of 925°C. (1697°F.), S the weight per cent of silicon and A and B constants dependent on the concentration of the other elements, and when the carbon content is 2.00 per cent this expression becomes,

$$t \text{ (in hours)} = (10.64) (S^{-2.773})$$

and when carbon equals 2.50 per cent,

$$t = (6.356) (S^{-2.05}).$$

With carbon equal to 2.85 per cent

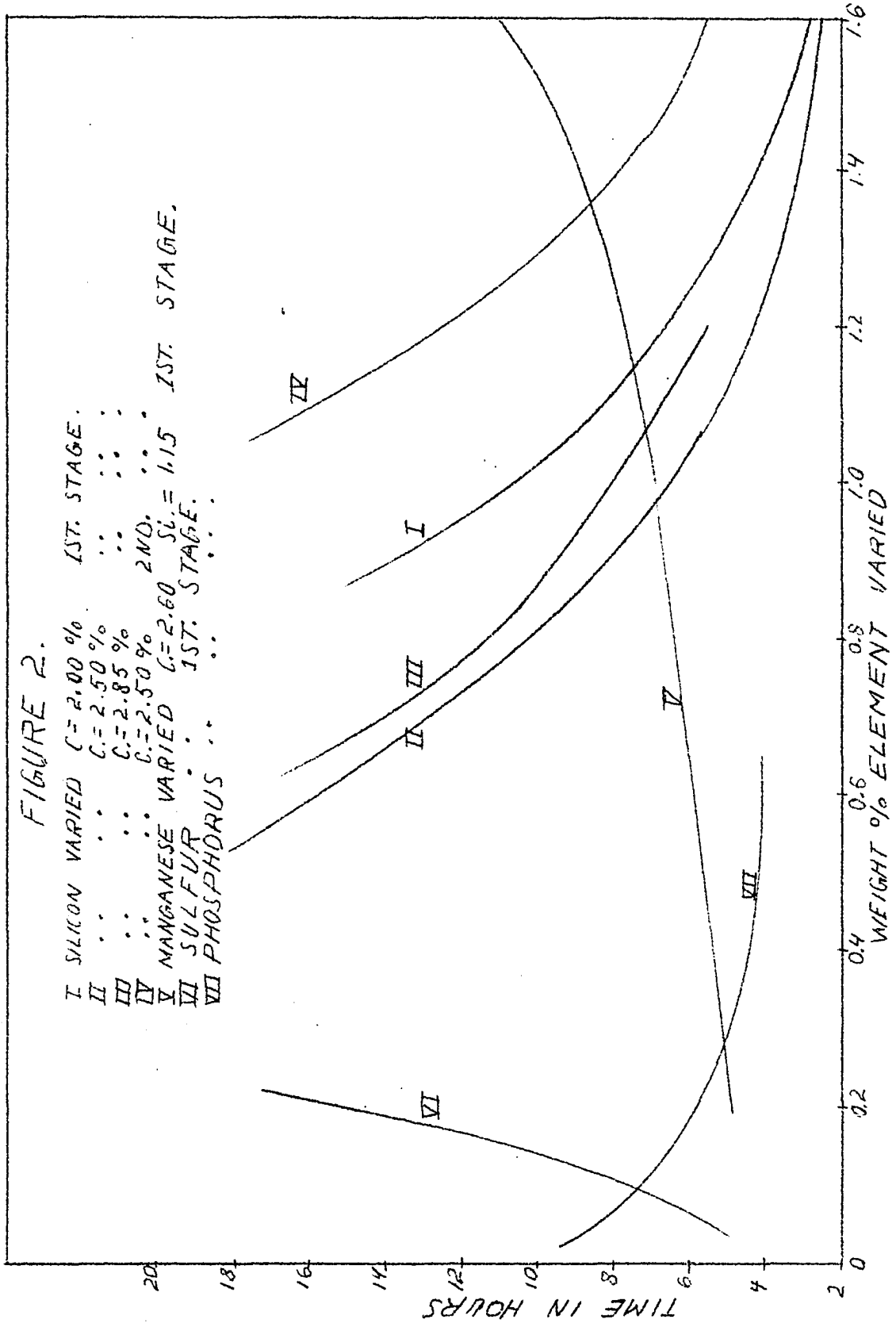
$$t = (8.040) (S^{-0.487}).$$

The second stage of the graphitization was carried out at a temperature below the A_{r1} point. The effect of silicon is shown in curve IV of figure 2. The time may be expressed by the equation,

$$t = (A) (e^{-BS}).$$

For an alloy containing 2.50 per cent carbon this expression becomes,

$$t = (1.514) (10^{-2}) (e^{-2.09 S}).$$



2. Carbon increases the rate of graphitization in the critical range with little or no effect on it at the high temperature.

3. Manganese retards the rate of graphitization in both stages. The effect is more marked in the critical range than at the high temperature. The effect on the first stage is shown in curve V, figure 2. He states that manganese should not be more than 0.5 per cent for good malleable iron.

4. Sulfur, like manganese, retards graphitization in both the critical range and at the high temperature. The effect is, however, much greater than in the case of manganese. This is shown for the first stage in curve VI of figure 2. According to Kikuta, for good malleable iron it should not exceed 0.16.

5. According to Kikuta, phosphorus increases the rate of graphitization in the first stage and hinders it in the second stage, and suggests that it should not exceed 0.3 per cent for good malleable cast iron. The measurements of Kikuta on the effects of phosphorus are not significant because of variations in manganese and sulfur content of the alloys used in this study.

6. From a review of the literature it is found, as stated by Kikuta, that those elements which are associated with the carbide tend to retard graphitization and those that are associated with the solid solution accelerate it.

A theory may be suggested for the mechanism of these effects of alloying elements. From the laws of solutions it is known that the addition of one constituent to another, in such concentrations as they are miscible with each other, decreases the activity of the diluted constituent. Thus if an alloy element be added to white cast iron and be associated with the iron carbide, the activity of the iron and the carbon in the carbide will be decreased. These activities, at equilibrium, are equal to the activities of carbon and iron from the gamma iron solid solution. The activity of the iron from the solid solution of gamma iron may be considered constant for these variations of its concentration. The activity of the carbon from the graphite will be a constant, and equal to the activity of carbon from the solid solution at equilibrium. Thus by dilution the activity of the carbon from the iron carbide solution may be decreased until it is equal to or even less than the activity of the carbon from graphite. In such a case the reaction would proceed in the reverse direction.

As the graphitization of a white cast iron proceeds the alloying element is concentrated in the remaining carbide, and thus exerts a greater retarding effect as the reaction progresses and may even stop the reaction entirely when the

activity of the carbon from the iron carbide equals that from graphite. This has been found to be the case with some alloys.

For the case where the alloyed element is miscible with the gamma iron solution and nonmiscible with the carbide the activity of the iron will be decreased. Iron from the iron carbide will then be dissolved and leave the activity of the carbon from the iron carbide greater. The effect of a change of the gamma iron solvent as affected by the addition of an alloying element, on the activity of the solubility of carbon either from iron carbide or from graphite, can not be stated. However the activity of the carbon from graphite is a constant. The activity of carbon from iron carbide is increased by a decrease of the activity of the iron. Then the difference between the activities of carbon from iron carbide and from graphite is increased and the rate of reaction increased.

It has also been suggested by some writers that the effect may be due to changed rates of migration of the carbon particles.

D. Alloys of Iron and Nickel:

Investigations of the iron-nickel alloys have been investigated by the commercial interests in compositions found

in steels, gray cast iron, invar and monel metal. The characteristic Widmanstätten structure of meteoric iron has attracted attention of some of the most outstanding metallurgists. In figure 3 is shown the iron-nickel phase diagram first proposed by Osmond and Cartard (7) and later revised by Hanson and Hanson (8). Iron and nickel form completely miscible solution both in the liquid and in the solid state. The transition points of iron are lowered by the addition of nickel. Nickel is more soluble in gamma iron than in the alpha. The magnetic A_2 change is lowered in the alpha iron but appears again in the high nickel gamma solution, and reaches a maximum at about 70 per cent nickel. According to the diagram of Osmond there is a eutectoid at 360°C. (680°F.) and 40 per cent nickel. Hanson placed it at 34 per cent nickel, as shown in figure 3. As to just what happens in this region of the diagram is not well known. As was shown by Benedicks (10), on slow cooling, iron nickel alloys of compositions between 7 and 36 per cent nickel, segregate into two constituents with a structure very similar to that of meteoric iron.

The most complete work that we have on iron-nickel alloys is that of Kase (9), who worked with Honda on the phase diagrams of iron, nickel and carbon. He does not consider the

magnetic A_2 transition a phase change since it is not a change in the lattice arrangement. By means of the dilatometer, magnetic and thermal analysis he traced the transitions of iron to below room temperature. The phase diagram which he proposes for the iron-nickel system is shown in figure 4. He does not consider a eutectoid exists at ordinary temperatures. The separation of two constituents, found in iron-nickel alloys, he explains as the lack of the concentrated gamma solution to change over to the alpha state because of the high resistance to lattice changes of the metal at the lower temperatures.

In figure 5 is shown the nickel-carbon phase diagram as determined by Kase. Nickel was saturated with carbon at definite temperatures, quenched and analyzed for combined carbon. No attempt was made to determine the state of the carbon that separated from the solutions on cooling. It is thought, however, that nickel carbide is stable in the liquid solution at temperatures above 1500°C . (2732°F .) but metastable at lower temperatures. The diagram is very similar to the iron-carbon system with a lower solubility of carbon in the solid solution at the eutectic and below. There was no indication of separation of nickel carbide in any of the alloys prepared as shown by microscopic analysis.

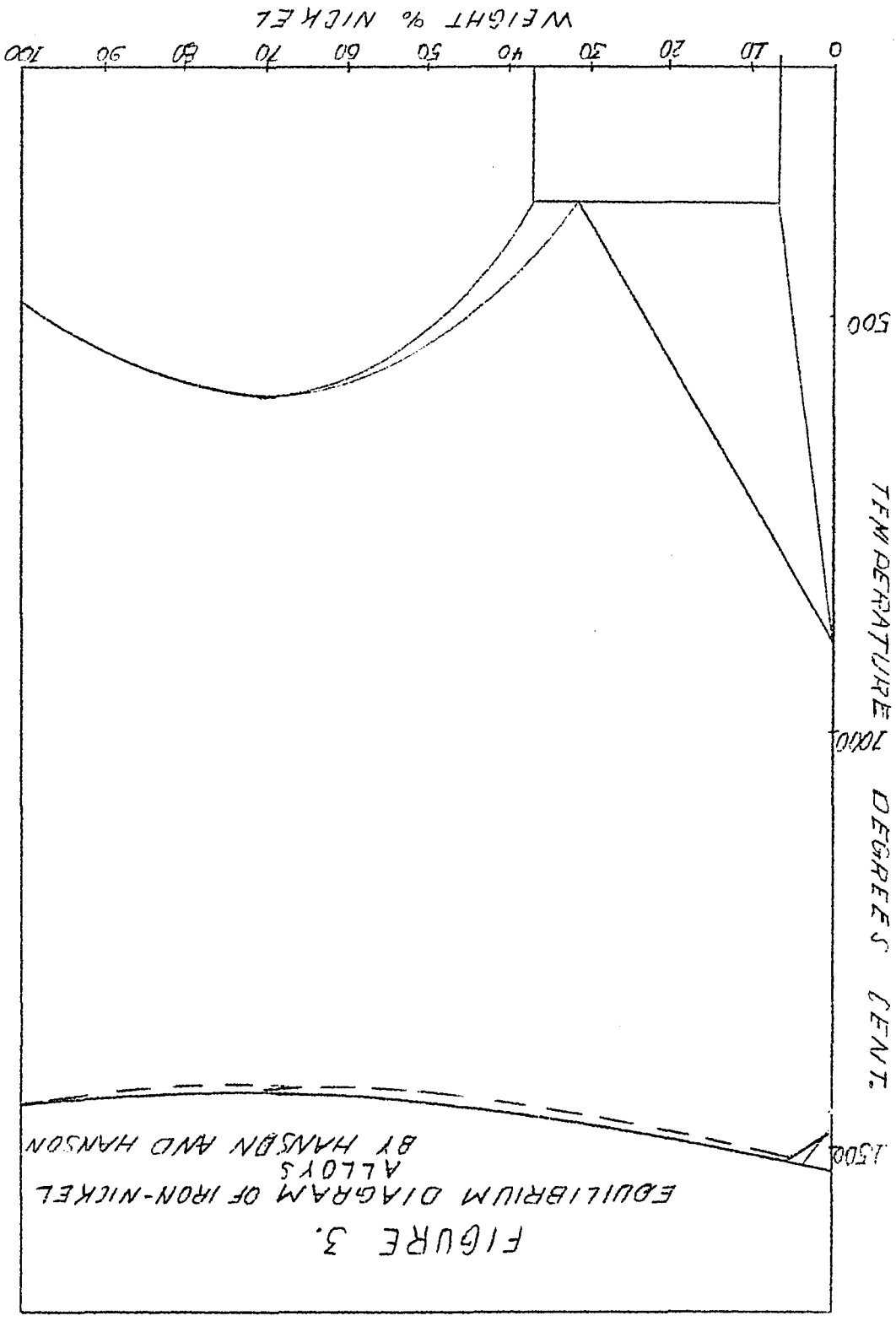
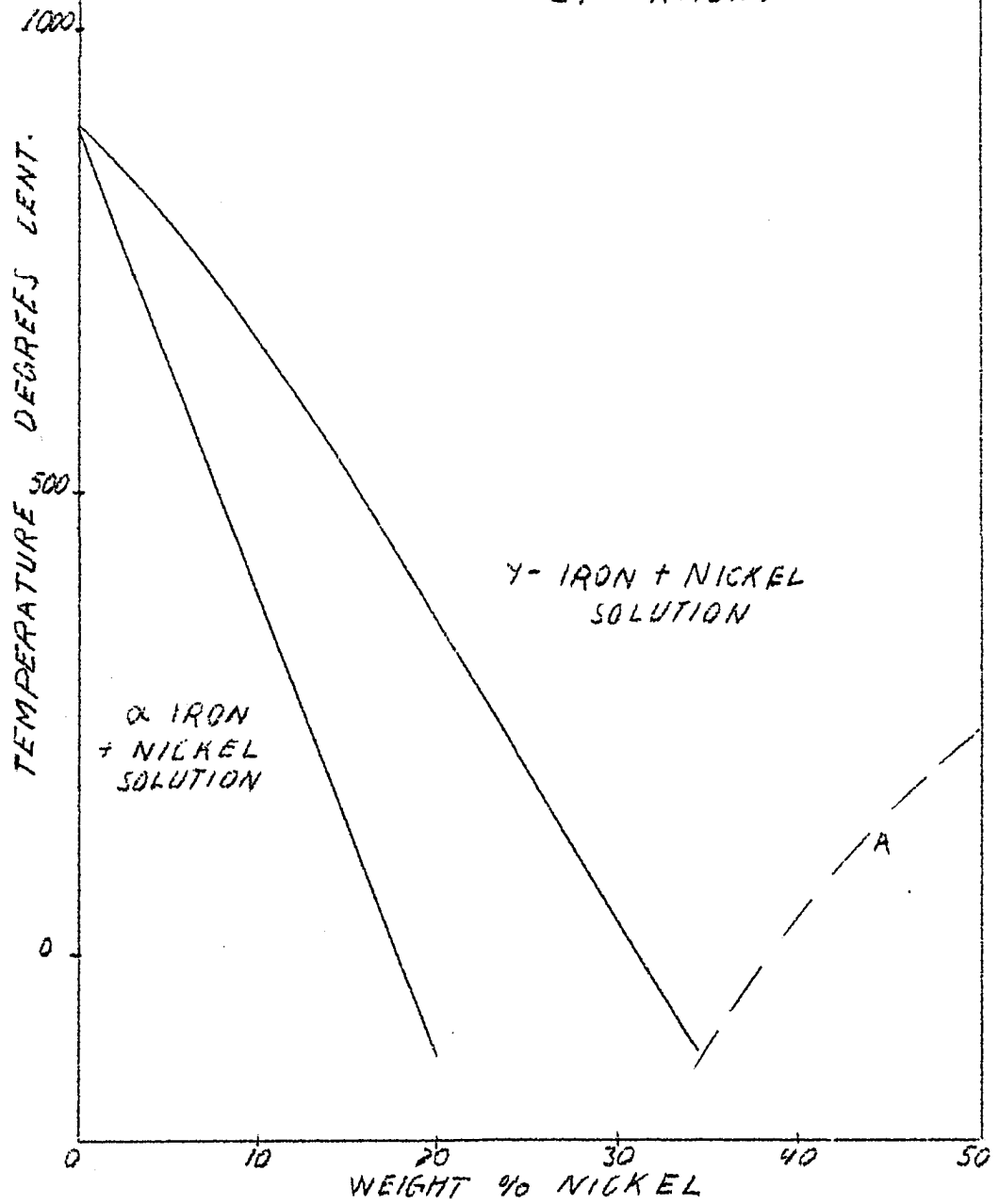


FIGURE 3.
EQUILIBRIUM DIAGRAM OF IRON-NICKEL
ALLOYS
BY HANSEN AND HANSON

FIGURE 4.

EQUILIBRIUM DIAGRAM OF IRON-NICKEL
ALLOYS.
BY KASE.



In the ternary system of iron-carbon and nickel, Kase determined the effects of nickel and carbon on the A_1 , A_2 and A_3 points of iron. These results are shown in figures 6 and 7. He then determined the solidification points and the carbon contents of iron-nickel-carbon alloys and drew the ternary iron-carbon-nickel diagram. Figures 8, 9, 10 and 11 show iron nickel diagrams in two dimensions with varied amounts of carbon. It will be seen that the alpha iron region is reduced by the addition of carbon to iron-nickel alloys.

Use has been made of nickel to improve the properties of steel for many years. In the last few years it has come into a similar use in gray cast iron. From the diagram shown above the effect of nickel on the transition temperatures of steel and thus to produce troostite, sorbite, martensite and austenite will be seen. Thus, according to the Bureau of Standards Circular (11), nickel steels may be divided into three classes:

1. Pearlitic steel. Steels containing not more than 10 per cent nickel act normally toward heat treatment.
2. Martensitic steels. Steels containing between 10 and 26 per cent nickel when air cooled become martensitic. These are sometimes known as self hardening steels.

FIGURE 5.

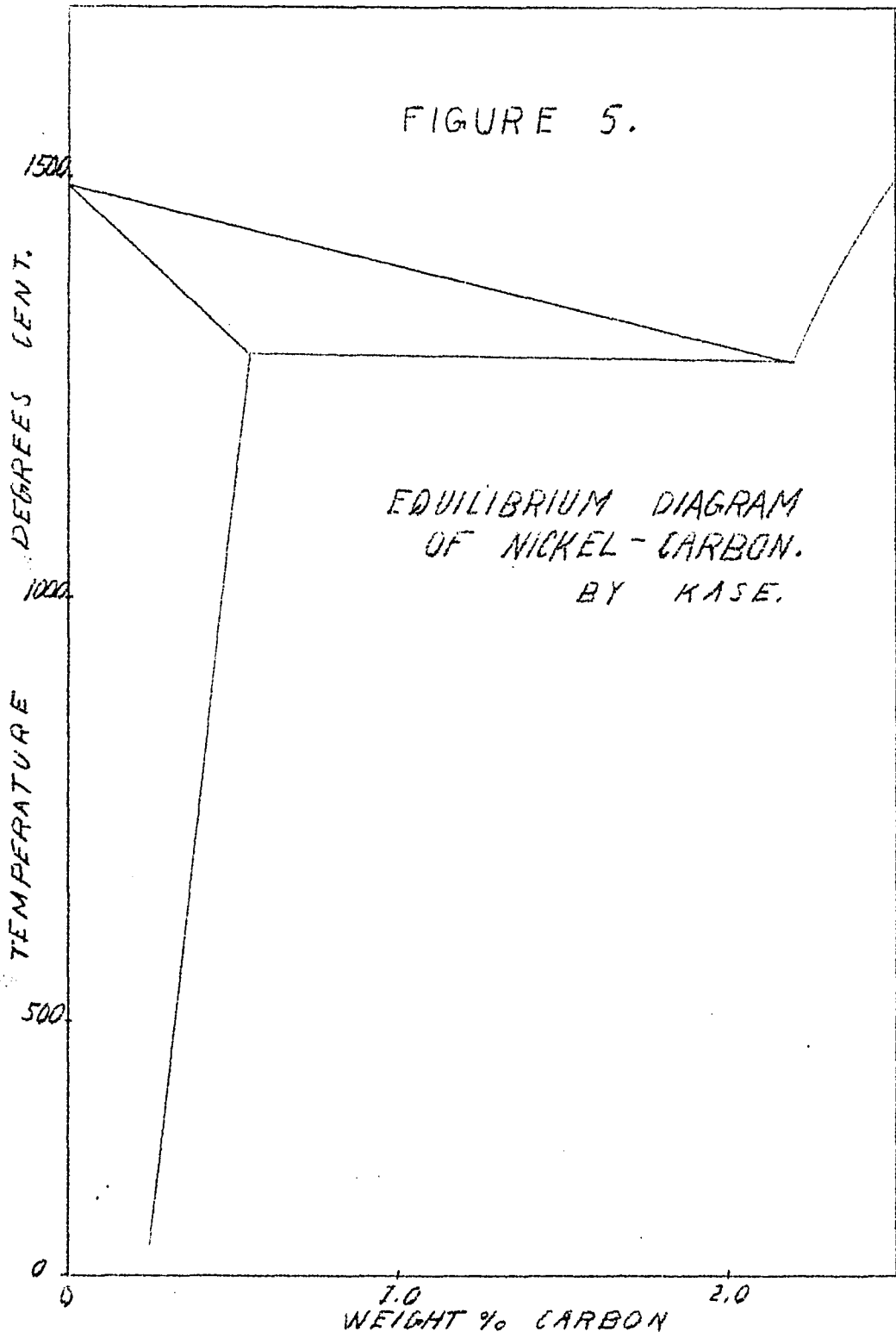
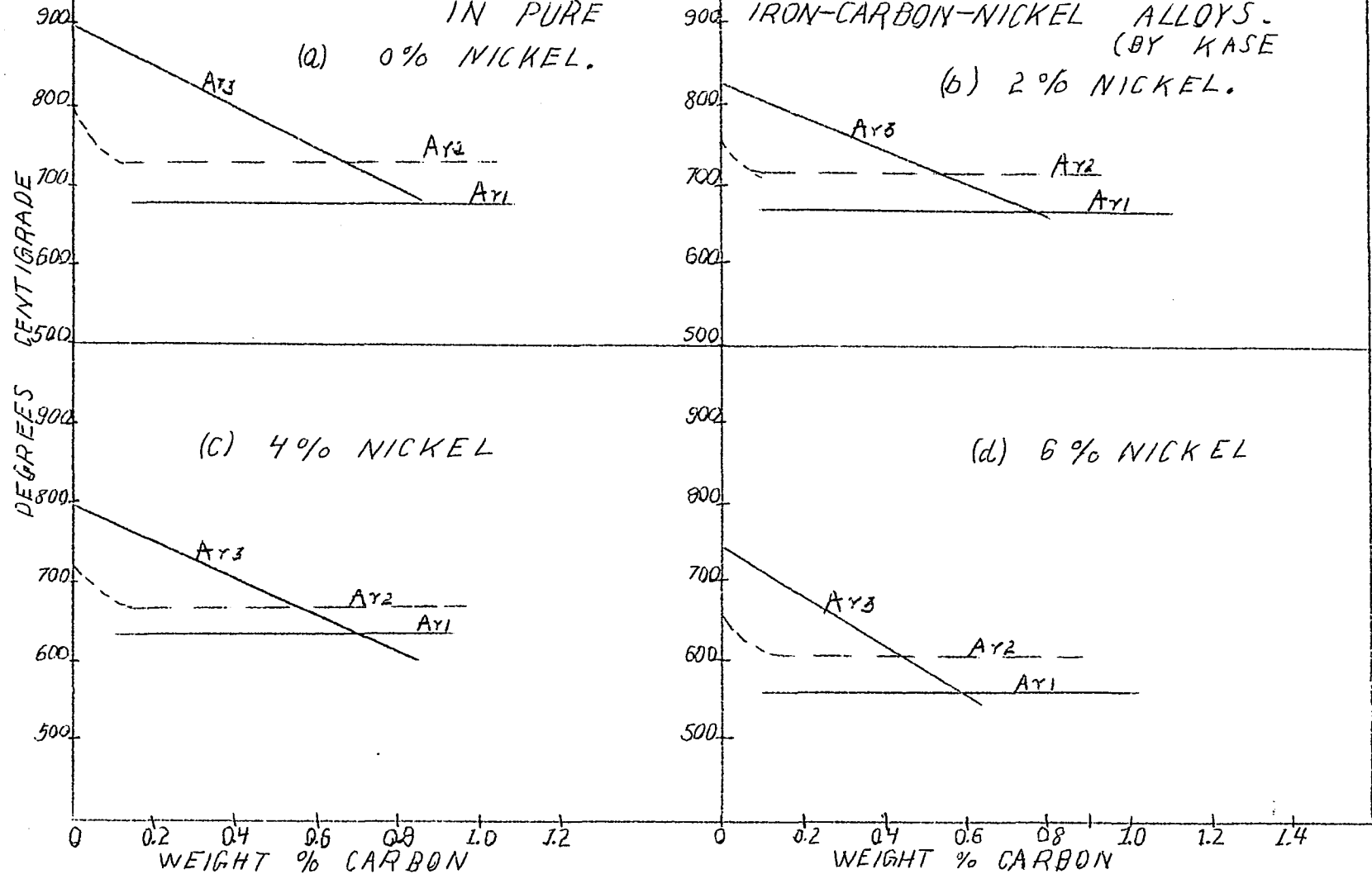
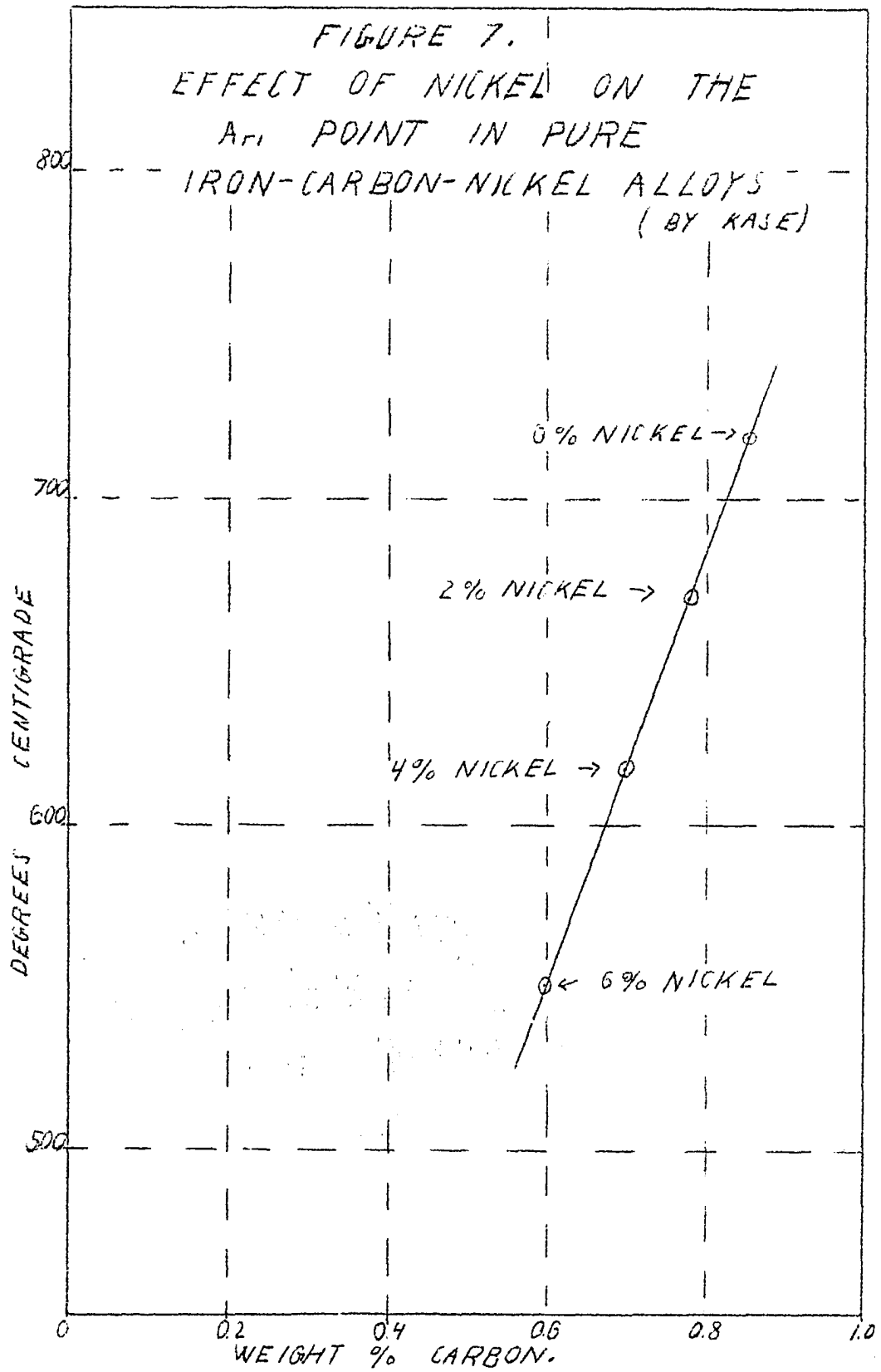
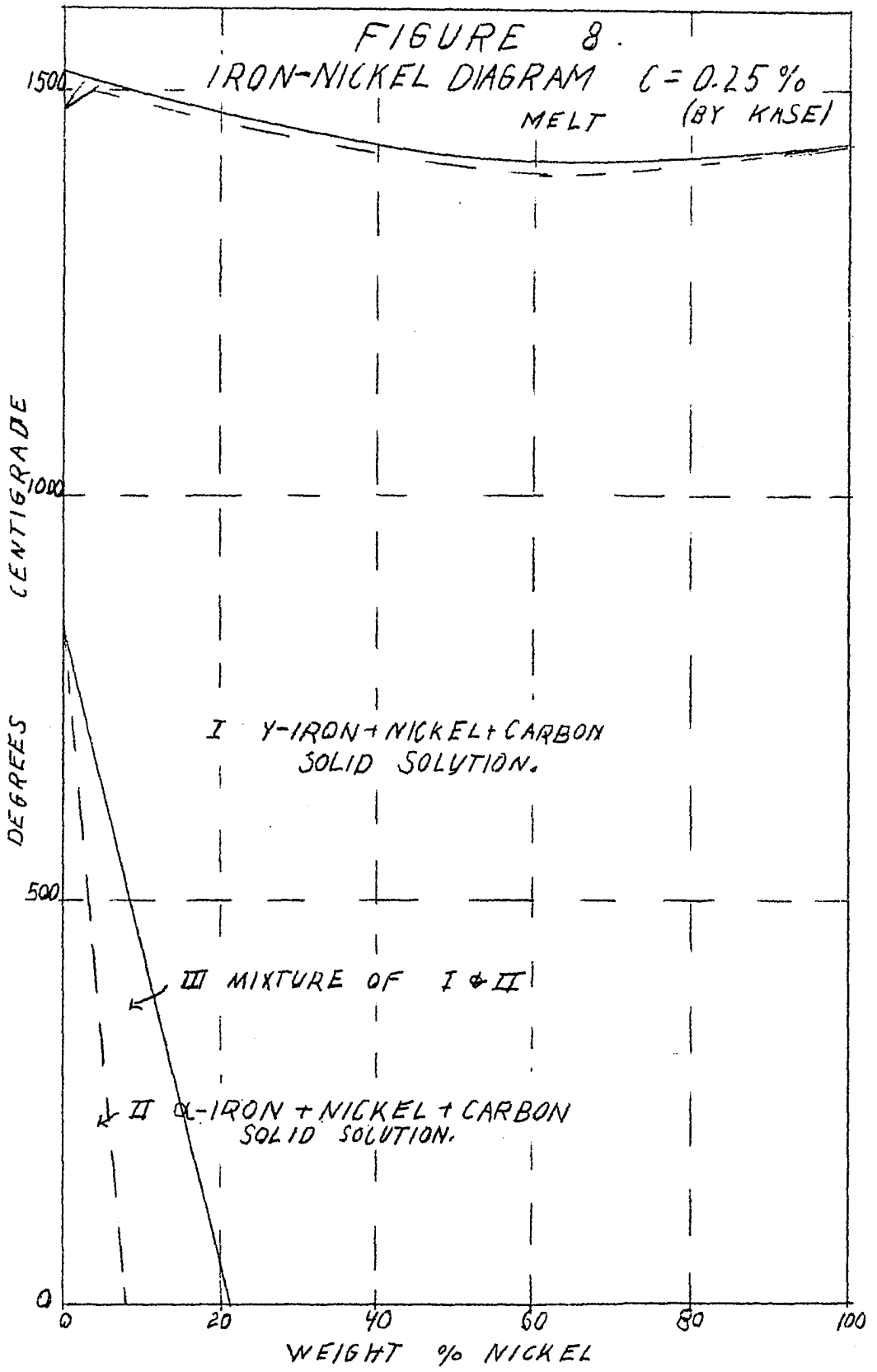
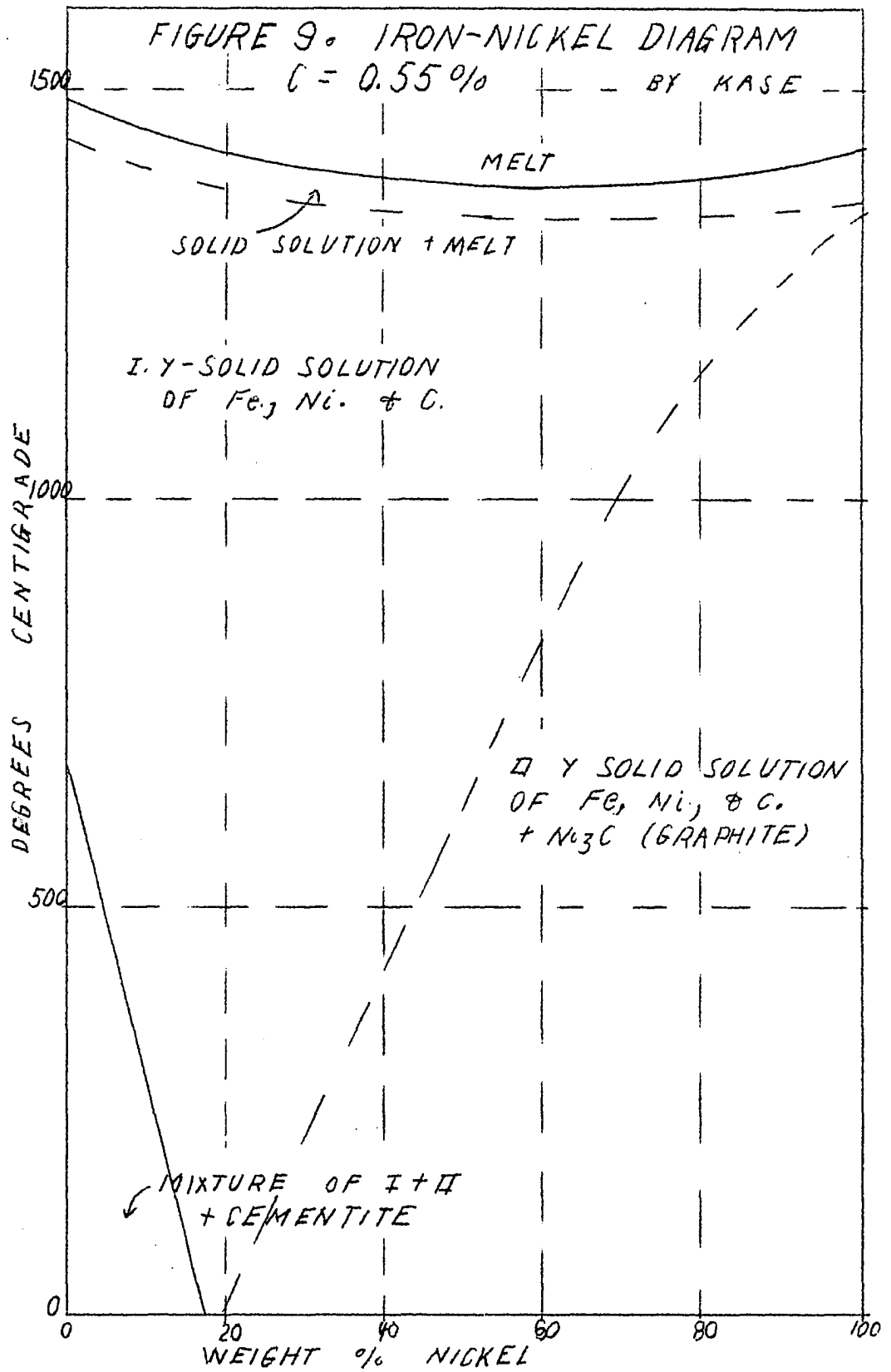


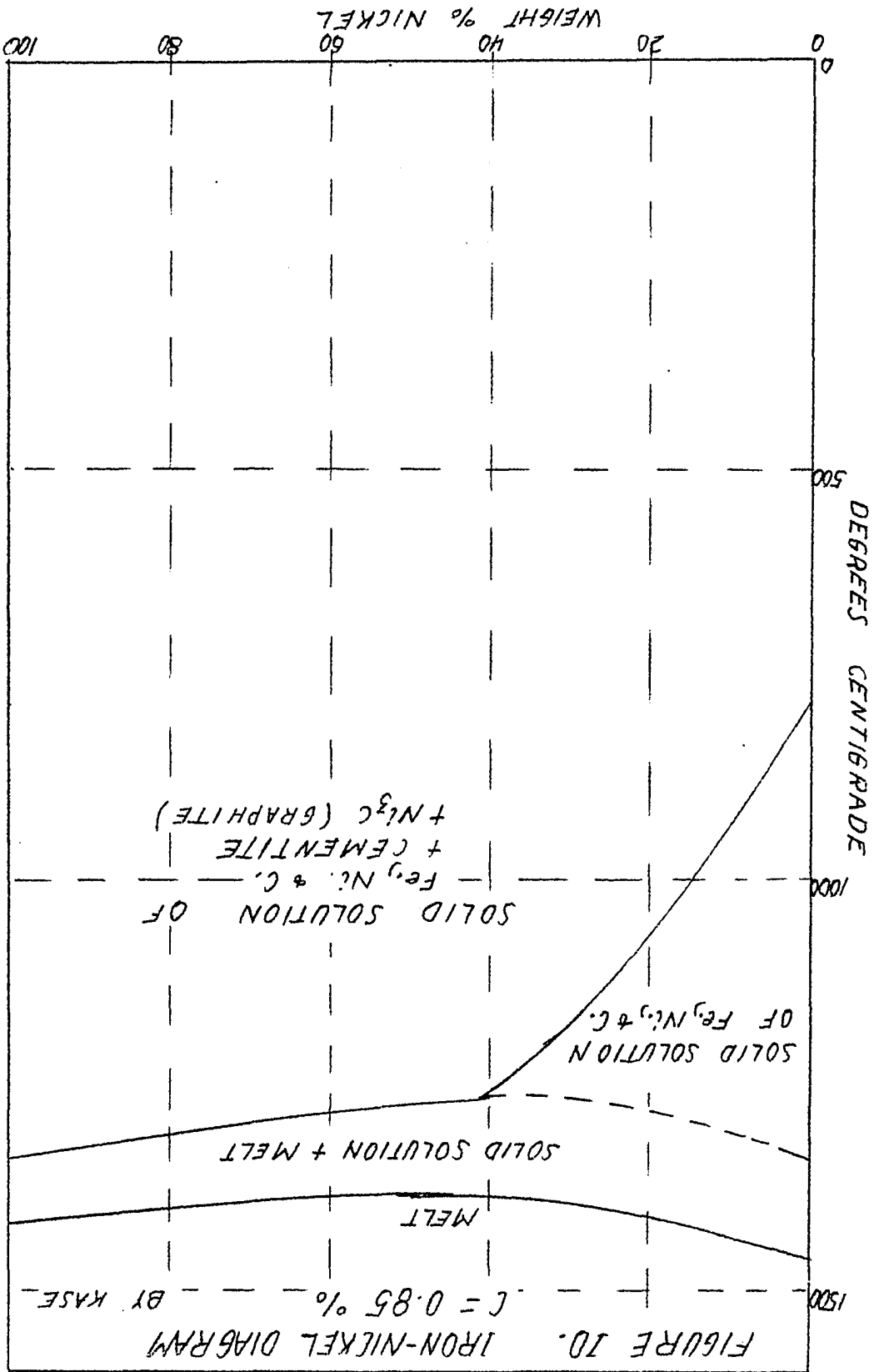
FIGURE 6. EFFECT OF NICKEL ON THE A_{r1} , A_{r2} , & A_{r3} POINTS
IN PURE IRON-CARBON-NICKEL ALLOYS.

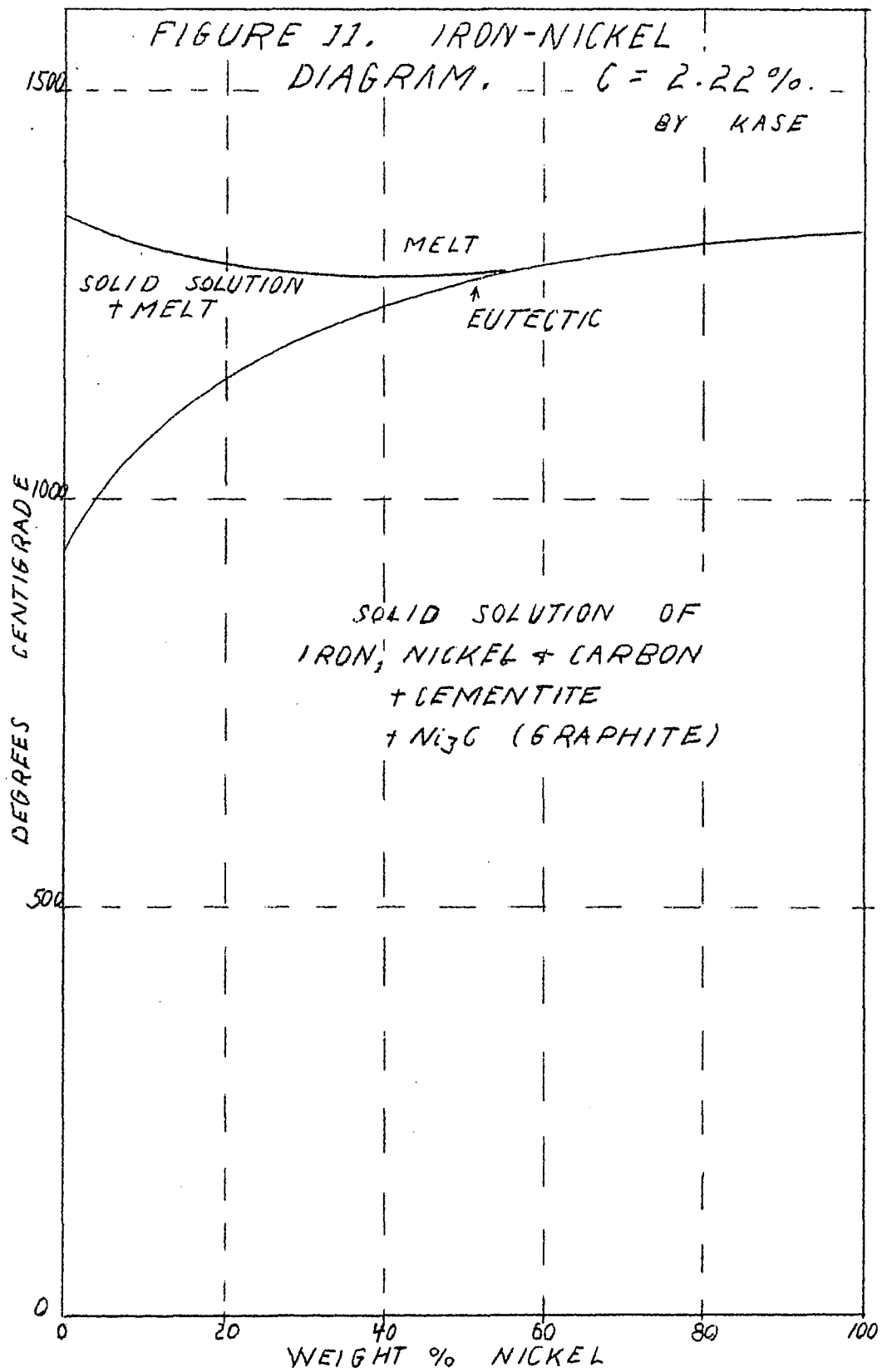












3. Austenitic steels. Steels containing more than 26 per cent nickel are austenitic in structure. These can not be hardened by heat treatment.

Figure 12, taken from Guillet's work, shows very nicely the three classes of nickel steels. When a special steel of high tensile strength, hardness and ductility is desired, hypo-eutectoid steels containing from 1 to 5 per cent nickel are often used. Nickel in these percentages increases the tensile strength and the hardness without loss of ductility. It also refines the grain and lowers the critical range which permits of a lower quenching temperature and gives greater resistance to wear. The following data taken from the Bureau of Standards Circular give a good idea of the effect of nickel on the properties of steel: A sample of steel that contained no nickel and had been quenched from 787°C. (1450°F.) in H₂O and then drawn at 704°C. (1300°F.), gave a yield point of 53,000 pounds per square inch, tensile strength of 90,000 pounds per square inch, an elongation of 25 per cent in two inches and a reduction of area of 62.5 per cent. The same steel with 3.5 per cent nickel added to it, quenched at 787°C. (1450°F.) in water and then drawn at 681°C. (1260°F.) gave a yield point of 83,000 pounds per square inch, tensile strength of 108,000 pounds per square inch, elongation of 25 per cent

in two inches and 66 per cent reduction of area. The data here shown is typical of the effects produced by the additions of nickel to steels.

In recent years nickel is being used in gray cast iron where a special alloy of relative high strength, good machinability and resistance to wear is desired as in the blocks and pistons of motors. Wickenden and Vanick (12) of the International Nickel Company, studied the effects of nickel and chromium on gray cast iron. The following is a summary of their work for nickel:

1. Below 4 per cent nickel, this element has little or no effect on the total carbon but begins to decrease it slightly at 5 per cent and above.
2. Nickel accelerates graphite formation and reduces the combined carbon to 0.80 per cent, and then acts mildly to reduce it below this value.
3. Due to the influence of nickel to break down iron carbide, it is very effective in reducing the chill in cast iron. This prevents the producing of mottled iron or hard spots. One per cent nickel is quite positive in its effect. This is one of the most useful functions of nickel in cast iron.
4. With less than 5 per cent nickel, it serves to refine the grain. With from 5 to 10 per cent of nickel it again coarsens the grain.

5. Nickel tends to break up the cementite network and thus by preventing the growth of thick particles it prevents the formation of hard spots.
6. Nickel, by its effect on the critical points, tends to harden the iron matrix. At the same time, by reducing the combined carbon, it tends to soften the iron.
7. Nickel, by eliminating hard spots in the iron, greatly improves its mechanability.
8. Nickel is effective in improving the tensile strength of cast iron. It is, however, more effective in the lower silicon than in the high silicon alloys. In a 1.40 per cent silicon alloy the tensile strength is increased from 21,850 to 33,325 pounds per square inch by the addition of 3.88 per cent nickel. In a gray iron with 2.00 per cent silicon the increase is from 22,950 to 28,862 pounds per square inch by the addition of 5.00 per cent nickel. And in one containing 2.60 per cent silicon the increase is from 20,962 to 27,087 pounds per square inch by the addition of 5.70 per cent nickel. In all of these alloys the carbon was between 2.40 and 2.70 per cent.
9. Nickel definitely improves the toughness of gray cast iron as measured either by transverse deflection test or by other methods of measuring. The greatest improvement is obtained with alloys containing between 3 and 5 per cent nickel.

10. Gray cast iron containing not more than 5 per cent nickel is not affected as to shrinkage in the mold, forming of porous metal and blow holes or as to fluidity of the molten iron.

11. When the nickel content is increased to between 5 and 15 per cent the product becomes martensitic and is very hard. When the nickel content is increased to above 15 per cent the iron becomes austenitic, which again reduces the hardness but leaves the material very tough.

From the effects of nickel on the properties of steel and gray cast iron as shown above, and from its complete miscibility in the gamma iron and non miscibility in the iron carbide, one would predict that by additions of nickel to malleable iron, the rate of graphitization would be increased, the microscopic structure would be improved and the physical properties would be bettered. The present investigation was carried out to establish more definitely the effects of nickel on the malleablizing processes and the properties of the product produced.

?
Proof

III. PREPARATION OF ALLOYS

The materials used in the preparation of the alloys used in this investigation were electrolytic nickel and commercial white cast iron of the following compositions:

	I.	II.	III.
Carbon	2.25%	2.35%	2.50%
Silicon	0.96	0.90	0.86
Sulfur	0.033	0.033	0.055
Manganese	0.21	0.21	0.56
Phosphorus	0.155	0.155	0.140

For the study of the rates of graphitization, weighed quantities of nickel and cast iron were melted in an Ajax induction furnace. The metal was placed in magnesia crucibles and melted, stirred twice with an Armco iron rod and poured at a temperature of about 1500°C. (2732°F.) into sand moulds. The sand molds were prepared by making holes in moderately packed molding sand and then drying them. The rods thus cast were about five eighths of an inch in diameter and from 8 to 10 inches in length. The bars were cast in the vertical position.

For the physical tests, regulation test bars were cast horizontally in green sand molds that were allowed to stand in air for two days. Two bars were cast in each mold. The melts were made in plumbago crucibles in the Ajax electric induction furnace. All the bars were allowed to cool to below the crit-

ical temperature before they were removed from the molds. The alloys were analyzed for nickel and found to be within 0.15 per cent of the value calculated from the weights of metal melted.

IV. THE EFFECT OF NICKEL ON THE RATE OF GRAPHITIZATION AT THE HIGH TEMPERATURE

The purpose of the high temperature anneal in the manufacture of malleable iron is to eliminate the free iron carbide at a sufficiently high temperature to allow the reaction to progress as rapidly as possible and at the same time precipitate the carbon in good form. It has been shown that, in commercial white cast iron of 1 per cent silicon, the carbon is precipitated in good rounded spots when the temperature is not above 992°C. (1820°F.). The temperature used for the high temperature anneal in this work was 935°C. (1717°F.).

The 5/8 inch bars, cast as described under the preparations of alloys, were used for this study. They were broken into pieces about one inch in length. One sample of each composition was polished and photographed as cast to show the dendritic white cast iron structure. The other samples were packed with powdered graphite in graphite crucibles to prevent oxidation. Each crucible contained one sample each of several compositions. These were then placed in a vertical Hump furnace, which had been previously brought to temperature. Not more than ten minutes were required to bring the furnace again to the annealing temperature. At intervals of a half hour the furnace was opened and a crucible removed. The samples were

then allowed to air cool in the crucibles. Not more than five minutes were required for the samples to reach a temperature below red heat. The time recorded is the actual time the samples were in the furnace.

The samples were then numbered to indicate the series and the time of the anneal. The first number represents the series and the last number the time in half hours, of the anneal. Because of the extreme hardness of the white cast iron samples they were marked before annealing by grinding notches in the edges of the samples.

These samples were then polished and studied, etched and unetched, to determine to the nearest half hour the time required for the disappearance of free iron carbide. Photomicrographs were taken of these samples to show the progress of graphitization and the effect of nickel on its rate. Representative samples are shown in figures 13 to 44.

Sample number 16, shown in figures 13 to 16, contained no nickel but was remelted in the same manner as the other alloys. The photomicrographs show that there is appreciable free iron carbide left at the end of six hours. The time required for complete graphitization of this alloy was between eleven and twelve hours.

The following table gives the time required for complete graphitization, the nickel content, and the figures referring to the photomicrographs where they are shown. In each case

the first figure refers to the photomicrograph of the bar as cast.

Sample Number	Weight % Nickel	Time of 1st stage	Figures
16.	0.0%	11-12 hrs	13 to 16
15	1.0	6	_____
8	1.5	4	_____
17	1.9	3.5	16 to 20
2	2.5	3	_____
18	2.5	2.5	21 to 24
3	3.0	1.5	_____
19	3.2	1.5	25 to 28
20	3.9	1.0	29 to 32
9	4.0	1.0	_____
6	4.0	1.0	_____
5	5.0	0.5	_____
10	5.9	0.5	33 to 36
11	6.3	0.5	_____
12	7.3	0.5	37 to 40
14	8.8	0.5	41 to 44
13	10.3	0.5	_____

No attempt was made to determine the time to less than a half hour. Those samples marked 0.5 hours contained no free carbide after one half hour at the annealing temperature.

It was shown by Kikuta (4) that the effect of silicon on the time required for the first stage of graphitization followed a logarithmic relation. The equation he used, as shown before, was

$$t = A \cdot S^B$$

where t is time in hours, A and B constants and S the weight per cent of silicon.

It is found that the effect of nickel on the time for the first stage of graphitization may be expressed by the equation,

$$t = A e^{BN} \quad (1)$$

where t is time in hours, A and B are constants, N the weight per cent of nickel in the alloy of composition as shown under preparation of alloys, and e is natural logarithm. A may be eliminated from this equation when two values of t and N are known. Equation 1 then becomes,

$$2.303 \log (t_1/t_2) = B(N_1 - N_2).$$

or

$$B = \frac{2.303}{N_1 - N_2} \log (t_1/t_2). \quad (2)$$

Samples 15, 17, 18, 19 and 20 were selected for the evaluation of the constants A and B . For samples 18 and 20,

$$N_1 = 3.9, \quad t_1 = 1.0$$

$$N_2 = 2.5 \quad t_2 = 2.5.$$

Substituting these values in equation 2 gives,

$$B = -0.656.$$

And for samples 17 and 19,

$$N_1 = 3.2 \quad t_1 = 1.5$$

$$N_2 = 1.9 \quad t_2 = 3.5$$

And, $B = -0.653.$

Averaging these two values gives,

$$B = -0.654$$

Substituting this value of B in equation 1 gives,

$$t = A e^{-0.654N}.$$

The following table shows the values of A obtained by substituting values of N and t in equation 1 and solving for A.

Sample Number	N	t	A
15	1.0	6.0	11.7
19	3.2	1.5	12.1
17	1.9	3.5	12.1
Average			12.0

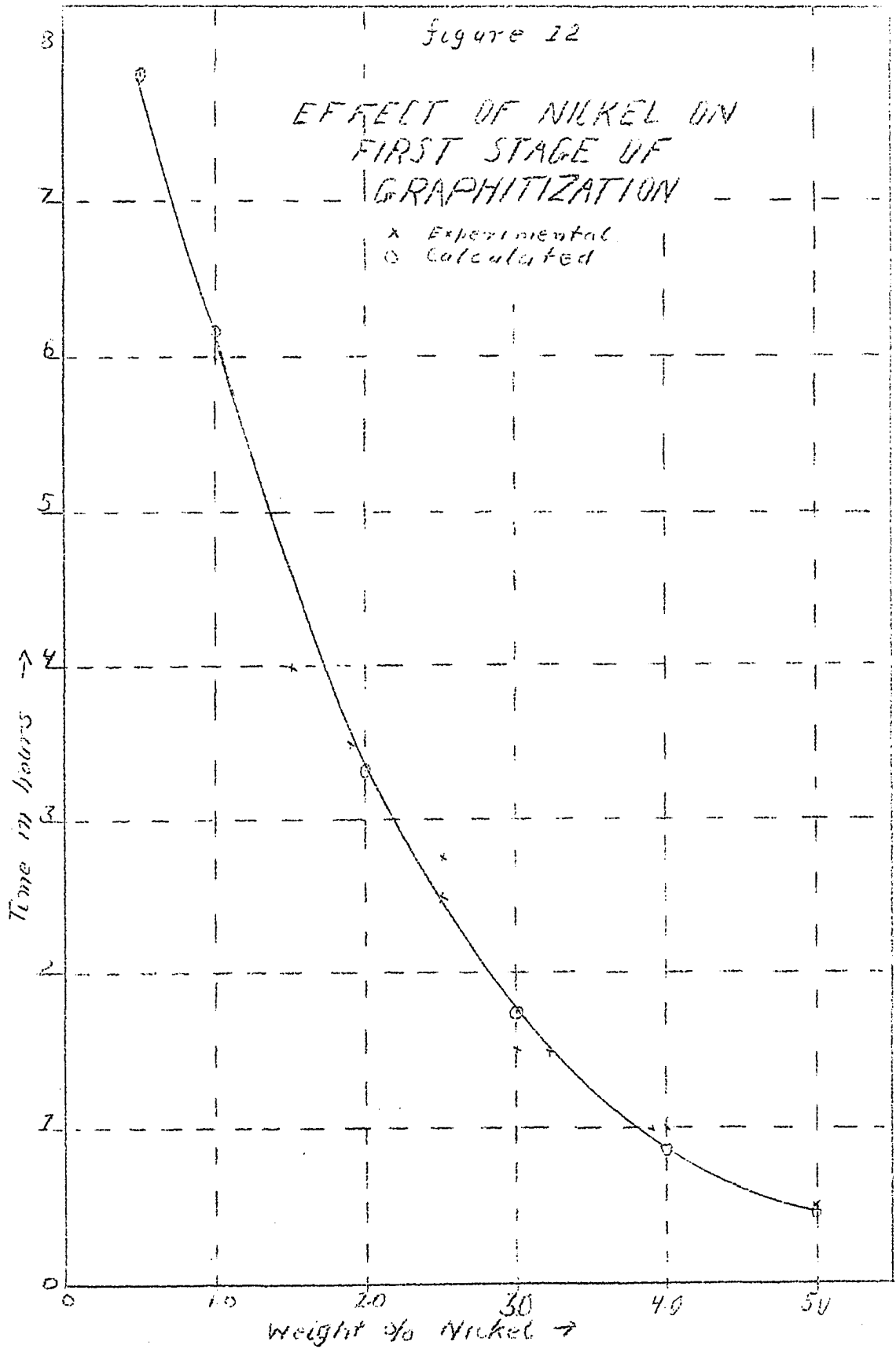
Substituting this value of A in the above equation gives,

$$t = 12.0 e^{-0.654N} \quad (3)$$

Values of N were then substituted in equation 3 and solved for t. The values thus obtained are shown in the following table.

N	t	N	t
0.0	12.	3.0	1.74
0.5	7.86	4.0	0.865
1.0	6.18	5.0	0.445
2.0	3.34	6.0	0.236

In figure 12 the calculated values of t are plotted on the curve, the calculated values being marked 0. The experimental values are plotted on the same figure and marked X. It is therefore shown that the experimental data agree very closely with those calculated from the equation. However this equation would not give concordant values for alloys that were far variant in silicon or carbon content.



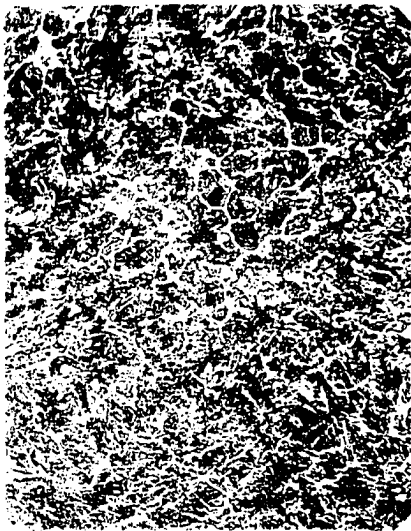


Figure 13. Sample 160.
0.0% Ni cast.



Figure 14. Sample 166.
0.0% Ni. Annealed at
936°C. (1717°F.), for 3
hrs., air cooled, nitric
acid etched. 100 X.

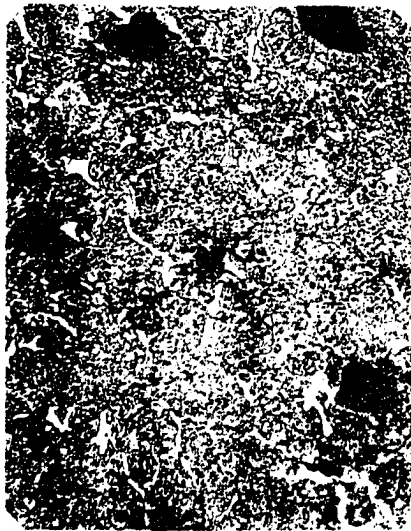


Figure 15. Sample 168.
0.0% Ni. Annealed at
936°C. (1717°F.), air
cooled, etched with 5%
HNO₃. 100 X.

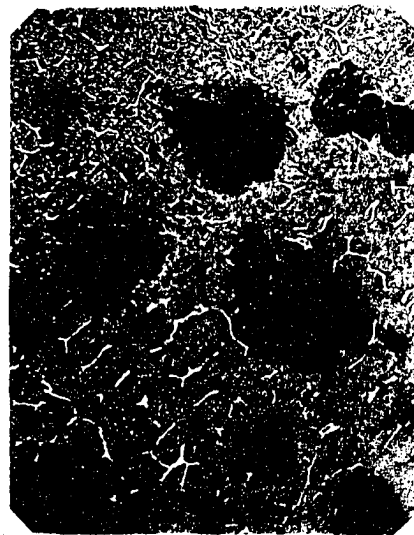


Figure 16. Sample 1612.
0.0% Ni. Annealed at
936°C. (1717°F.), for 6
hrs., air cooled, etched
with nitric acid. 100 X.

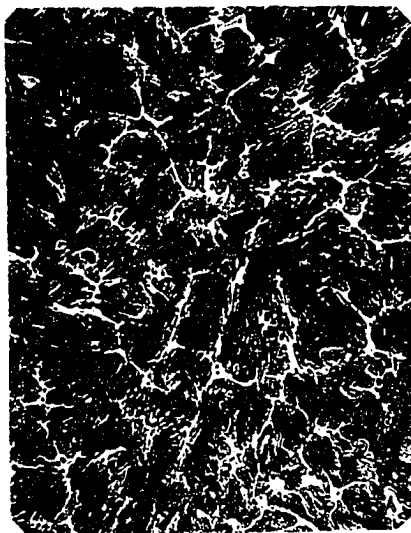


Figure 17. Sample 170.
1.9% Ni as cast.
Nitric acid etched. 100X.



Figure 18. Sample 174.
Same as 170 annealed at
936°C. (1717°F.) for two
hours, air cooled, nitric
acid etched. 100 X.



Figure 19. Sample 176.
Same as 170 annealed for
3 hrs. at 936°C. (1717°F.),
air cooled, nitric acid
etched. 100 X.



Figure 20. Sample 178.
Same as 170, annealed for
4 hrs. at 936°C. (1717°F.),
air cooled, nitric acid
etched. 100 X.



Figure 21. Sample 180.
2.5% Ni as cast.
Nitric acid etched. 100 X.



Figure 22. Sample 183.
Same as 180 annealed at
936°C. (1717°F.), for 1 1/2
hours, air cooled, nitric
acid etched. 100 X.

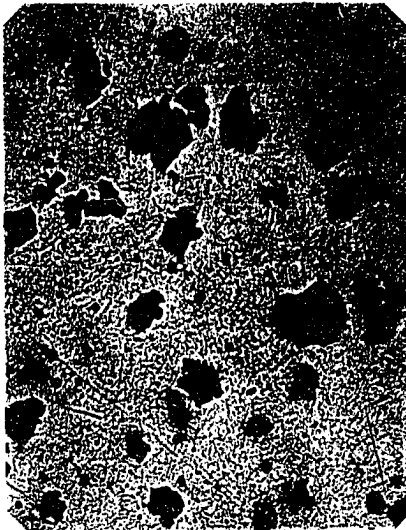


Figure 23. Sample 184.
Same as 180 annealed at
936°C. (1717°F.), for 2 hrs.
Nitric acid etched. 100 X.



Figure 24. Sample 184.
Same as figure 23, un-
etched. 100 X.

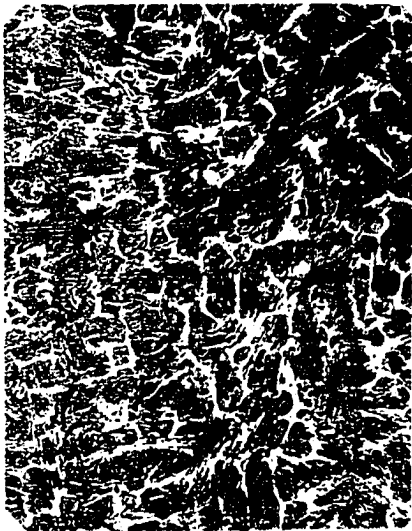


Figure 25. Sample 190.
3.2% Ni as cast.
Nitric acid etched. 100 X.

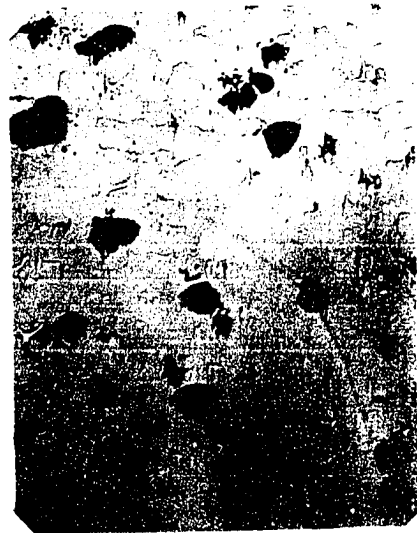


Figure 26. Sample 193.
Same as 190 annealed at
936°C. (1717°F.), for 1½
hrs., air cooled and
nitric acid etched. 100 X.

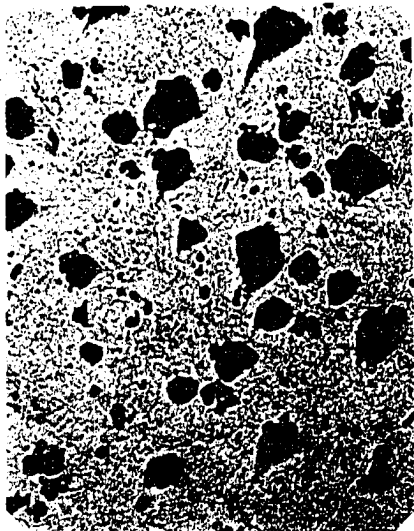


Figure 27. Sample 194.
Same as 190 annealed at
936°C. (1717°F.) for 2
hours, air cooled and
nitric acid etched. 100 X.



Figure 28. Sample 194.
Same as 190 annealed at
936°C. (1717°F.) for 2
hours and air cooled.
Unetched. 100 X.



Figure 29. Sample 200.
3.90% Ni as cast.
Nitric acid etched. 100 X.



Figure 30. Sample 202.
Same as 200 annealed at
936°C. (1717°F.) for 1
hour and cooled in air.
Nitric acid etched. 100 X.



Figure 31. Sample 203.
Same as 200 annealed at
936°C. (1717°F.) for 1
hours, air cooled and
nitric acid etched. 100 X.



Figure 32. Sample 203.
Same as figure 31 but un-
etched. 100 X.



Figure 33. Sample 100.
5.9% Ni as cast.
Nitric acid etched. 100 X.



Figure 34. Sample 101.
Same as 100 annealed at
936°C. (1717°F.) for $\frac{1}{2}$
hour. Unetched. 100 X.



Figure 35. Sample 101.
Same as 100 annealed at
936°C. (1717°F.) for $\frac{1}{2}$
hour and air cooled.
Nitric acid etched. 100 X.

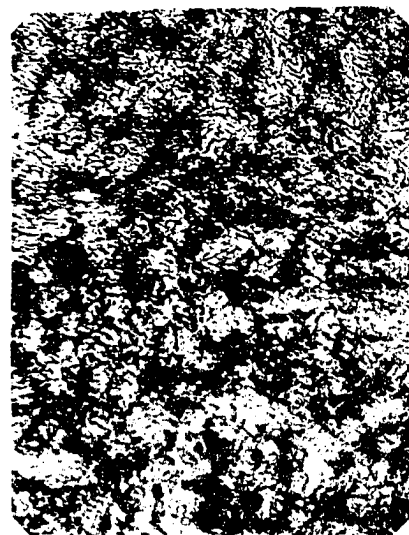


Figure 36. Sample 101
Same as 100 annealed at
936°C. (1717°F.) for $\frac{1}{2}$
hour and air cooled.
Nitric acid etched. 100 X.



Figure 37. Sample 120.
7.3% Ni as cast.
Nitric acid etched. 100 X.



Figure 38. Sample 121.
Same as 120 annealed at
936°C. (1717°F.) for $\frac{1}{2}$
hr., air cooled and nitric
acid etched. 100 X.

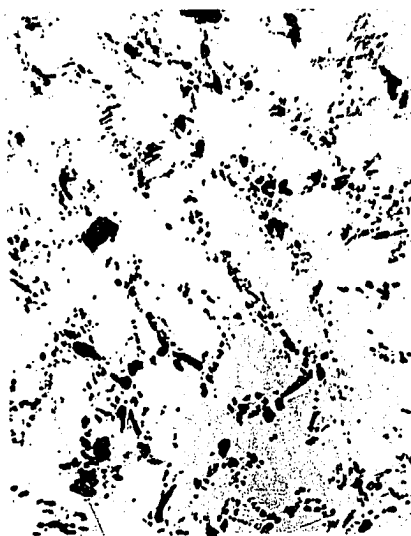


Figure 39. Sample 121.
Same as 120 annealed at
936°C. (1717°F.) for $\frac{1}{2}$
hour, air cooled and un-
etched. 100 X.



Figure 40. Sample 121.
Same as 120 annealed at
936°C. (1717°F.) for $\frac{1}{2}$
hour, water cooled and
nitric acid etched. 100 X.

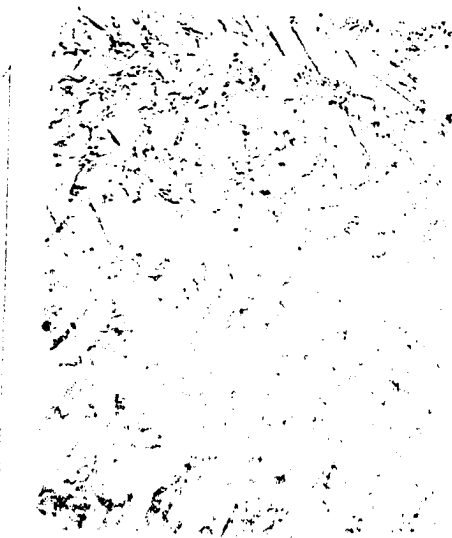


Figure 41. Sample 140.
8.8% Ni as cast.
Nitric acid etched. 100 X.



Figure 42. Sample 140.
Same as figure 41.
580 X.



Figure 43. Sample 141.
Same as 140 annealed at
936°C. (1717°F.) for $\frac{1}{2}$
hour, air cooled and
nitric acid etched. 100 X.

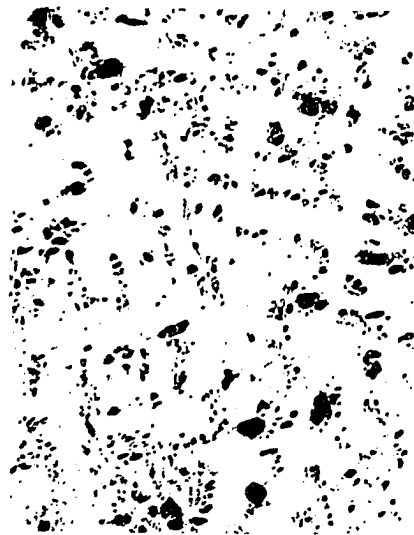


Figure 44. Sample 141.
Same as 140 annealed at
936°C. (1717°F.) for $\frac{1}{2}$
hour, air cooled and un-
etched. 100 X.

V. THE EFFECT OF NICKEL ON THE RATE OF GRAPHITIZATION IN THE CRITICAL RANGE

It was shown under the theories of graphitization that the cooling rate from the high temperature to the eutectoid, most effective on the rate of graphitization is dependent on the distance of the carbon content of the solid solution from the carbon solubility line. To keep this at a maximum would require cooling at such rate as to keep the composition very close to the solubility of carbon from iron carbide. On the other hand this would tend to slow up the reaction due to the decreased rate of migration and reaction at the lower temperature. Thus by slower cooling the time required for complete graphitization may be decreased to a minimum and then again increase.

The second stage of graphitization takes place only when the temperature is at or below the iron carbon eutectoid. If the temperature is far below the eutectoid the rate of graphitization will be again decreased by the decreased rate of migration and reaction. It is thus desirable to complete the graphitization at a temperature not too far below the temperature of the iron-carbon eutectoid.

Differential heating and cooling curves were run on seven alloys to determine the critical temperature. The samples used had been previously annealed to contain only

ferrite and pearlite. In the following table and in figure 77 are shown the effects of nickel on the temperature of the critical range for alloys containing 1 per cent silicon.

Sample Number	Weight % Nickel	Thermal Effects	
		Cooling	Heating
16	0.0	737°C. (1350°F.)	793°C. (1460°F.)
15	1.0	704	1300
19	3.2	675	1250
20	3.9	659	1220
5	5.0	648	1200
11	6.3	604	1120
12	7.3	604	1120

The average rate of heating and cooling used in these determinations was 11.1°C. (20°F.) per minute. The values of A_1 given by Kase (9) for pure iron-carbon-nickel alloys are, with 0 per cent nickel 700°C. (1292°F.), and for a 6 per cent nickel 550°C. (1022°F.). The value for the A_1 point as given by Hayes (1) for a 1 per cent silicon alloy is 759°C. (1400°F.). The value here obtained for a 6.3 per cent nickel alloy with 1 per cent silicon is 604°C. (1120°F.). The difference between this value and that of Kase for a 6 per cent nickel alloy with very low silicon is 54°C. (98°F.). The difference between the value of Hayes and that of the pure iron-carbon system is 59°C. (108°F.). This would indicate that the effect of nickel on the temperature of the A_1 point is practically the same in 1 per cent silicon alloys as in pure iron carbon alloys.

To study the effect of nickel on the rate of graphitization through the critical range, each of four crucibles were packed with samples varying in nickel content from 0 to 10 per cent. The samples were packed in powdered graphite to prevent appreciable oxidation. They were then placed in the Hump annealing furnace and the temperature held at 945°C. (1735°F.) for 16 hours to graphitize all the free iron carbide. At this stage one crucible was removed, cooled in the air and the samples marked A. The current to the furnace was then reduced and the temperature allowed to fall to 648°C. (1200°F.) in 10 hours. The second crucible was then removed, cooled in air and the samples marked B. The temperature of the furnace was then allowed to fall to 538°C. (1000°F.) in five hours and the third crucible was removed, cooled in air and the samples marked C. The fourth crucible was left in the furnace 10 hours longer, when the temperature was only slightly above room temperature. These samples were then marked D.

Photomicrographs of representative samples of this experiment are shown in figures 45 to 76. It will be noted that nickel increases the rate of graphitization when present in less than 5.5 to 6 per cent. Samples containing more than 6.0 per cent do not graphitize so readily due to the lowering of the critical range to such an extent that rates of diffusion and reaction are decreased.

Samples 16A, B, C and D are shown in figures 45 to 48. In 16B considerable ferrite has formed. C and D have experienced no further change.

Samples 17A, B, C and D are shown in figures 49 to 52. Sample 17 contains 1.9 per cent nickel and shows more ferrite in the B, C and D treatments than did 16B, C or D. Sample 17C shows more ferrite than does 17B.

Samples 18A, B, C and D are shown in figures 53 to 56. They contain 2.5 per cent nickel. There is a decided increase in the proportion of ferrite over that in sample 17.

Sample 19 contains 3.2 per cent nickel. As is shown in figures 57 to 60, graphitization is practically complete in samples 19B, C and D.

Sample 20, containing 3.9 per cent nickel, is shown in figures 61 to 64. It is completely graphitized by the B, C and D heat treatments.

Sample 10, containing 5.9 per cent nickel, is shown in figures 65 to 68. Number 10C and D are completely graphitized but B is not. This is probably due to the lowering of the critical range to below 648°C. (1200°F.).

Sample number 12, containing 7.3 per cent nickel, is shown in figures 69 to 72. Here as in sample 10 complete graphitization occurs in C and D but not in B.

Sample 14, containing 8.8 per cent nickel, is shown in figures 73 to 76. No ferrite is formed in B and only small amounts in C or D.

From the above experiment it is concluded that nickel increases the rate of graphitization in the critical range to the extent that alloys as used here containing between 3 and 6 per cent nickel can be completely graphitized in less than twelve hours.



Figure 45. Sample 16A.
Annealed at 945°C. (1735°F.)
for 16 hours, air cooled
and nitric acid etched. 100 X.



Figure 46. Sample 16B.
Same as 16A. Remained in
furnace 10 hrs. while
temperature dropped to
648°C. (1200°F.), air cool-
ed and nitric acid etched.



Figure 47. Sample 16C.
Same as 16B, cooled from
648°C. (1200°F.) to 538°C.
(1000°F.) in 6 hrs. Nitric
acid etched. 100 X.

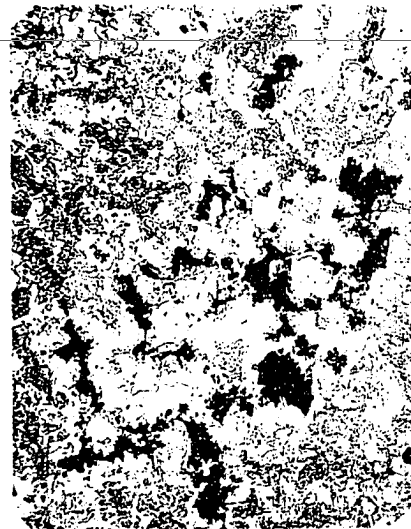


Figure 48. Sample 16D.
Same as sample 16C but
allowed to cool to room
temperature in furnace.
Nitric acid etched. 100 X.

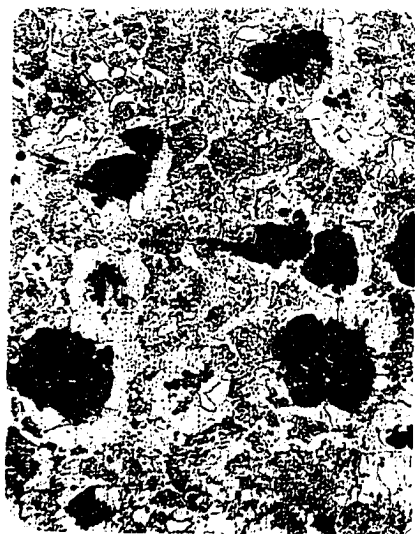


Figure 49. Sample 17A.
1.9% Ni. Annealed at 945°C.
(1735°F.) for 16 hours, air
cooled and nitric acid
etched. 100 X.



Figure 50. Sample 17B.
Same as 17A cooled in fur-
nace to 648°C. (1200°F.)
in 10 hrs., then air cooled.
Nitric acid etched. 100 X,



Figure 51. Sample 17C.
Same as 17B cooled in
furnace to 538°C. (1000°F.)
in 6 hours. Nitric acid
etched. 100 X.

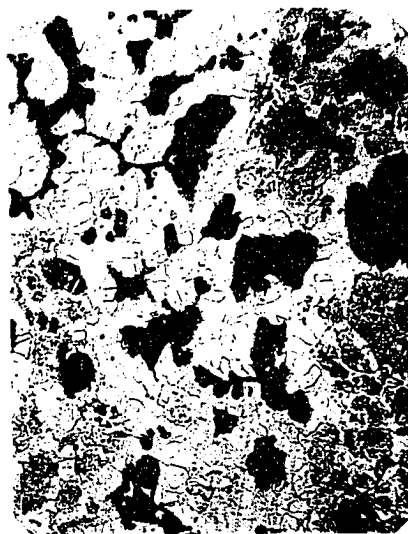


Figure 52. Sample 17D.
Same as 17C cooled to room
temperature in furnace in
10 hrs. Nitric acid etched.
100 X.



Figure 53. Sample 18A.
2.5% Ni. Annealed at 945°C.
(1735°F.) for 16 hrs., air
cooled and nitric acid
etched. 100 X.



Figure 54. Sample 18B.
Same as 18A cooled in fur-
nace to 648°C. (1200°F.)
in 10 hours. Nitric acid
etched. 100 X.



Figure 55. Sample 18C.
Same as 18B cooled in
furnace from 648°C. (1200°F.)
to 558°C. (1000°F.) in 6
hrs. Nitric acid etched.
100 X.



Figure 56. Sample 18D.
Same as 18C cooled to room
temperature in furnace in
10 hrs. Nitric acid etched.
100 X.



Figure 57. Sample 19A.
3.20% Ni. Annealed at 945°C.
(1735°F.) for 16 hrs., air
cooled and nitric acid
etched. 100 X.

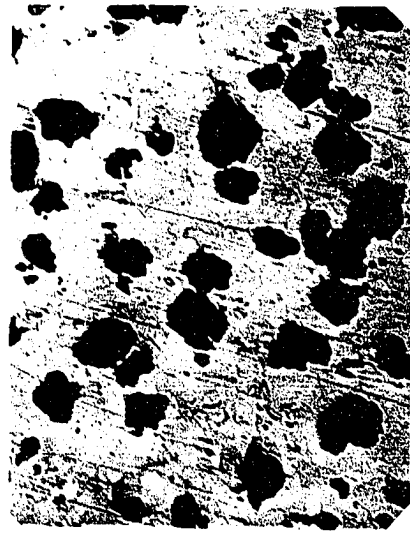


Figure 58. Sample 19B.
Same as 19A cooled in fur-
nace to 648°C. (1200°F.)
in 10 hours. Nitric acid
etched. 100 X.

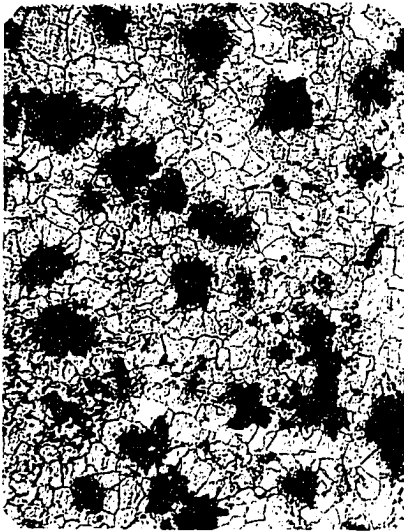


Figure 59. Sample 19C.
Same as 19B cooled from 648°C.
(1200°F.) to 538°C. (1000°F.)
in 5 hours in furnace. Nitric
acid etched.

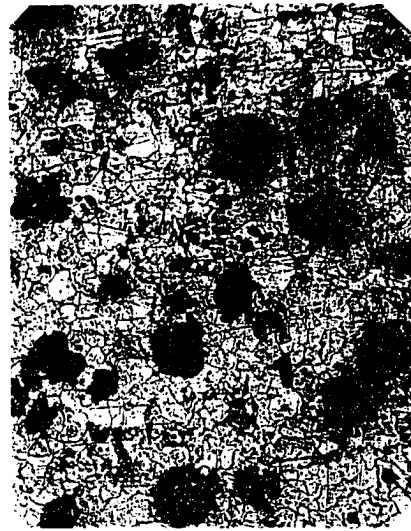


Figure 60. Sample 19D.
Same as 19C cooled to room
temperature in furnace in
10 hours. Nitric acid
etched. 100 X.

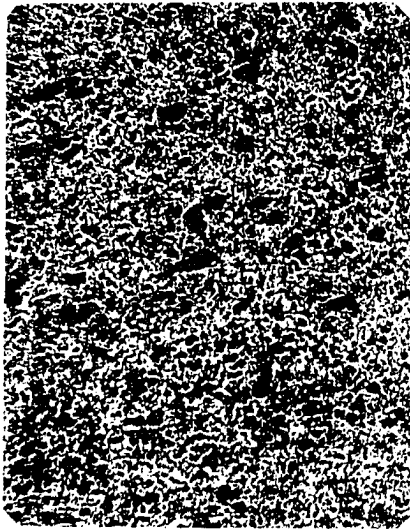


Figure 61. Sample 20A.
3.9% Ni. Annealed at 945°C.
(1735°F.) for 16 hours, air
cooled and nitric acid
etched. 100 X.



Figure 62. Sample 20B.
Same as 19A cooled in fur-
nace from 945°C. (1735°F.)
to 648°C. (1200°F.) in 10
hours and air cooled.
Nitric acid etched. 100 X.



Figure 63. Sample 20C.
Same as 20B cooled in fur-
nace from 648°C. (1200°F.)
to 538°C. (1000°F.) in 6
hours and cooled in air.
Nitric acid etched. 100 X.



Figure 64. Sample 20D.
Same as 20C cooled to room
temperature in furnace.
Nitric acid etched. 100 X.

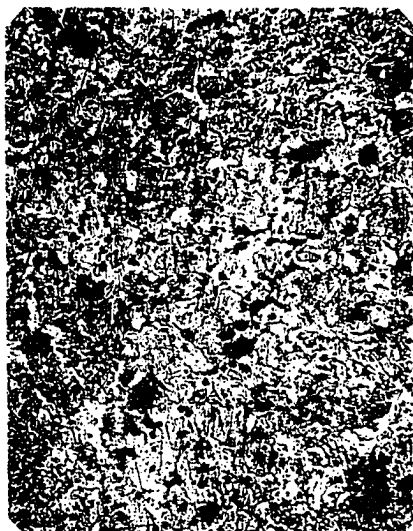


Figure 65. Sample 10A.
5.9% Ni. Annealed at 945°C.
(1735°F.) for 16 hours and
then cooled in air. Nitric
acid etched. 100 X.



Figure 66. Sample 10B.
Same as 10 A cooled in fur-
nace from 945°C. (1735°F.)
to 648°C. (1200°F.) in 10
hours, air cooled and nitric
acid etched. 100 X.



Figure 67. Sample 10C.
Same as 10B cooled from 648°C.
(1200°F.) to 538°C. (1000°F.)
in furnace in 6 hours, air
cooled and nitric acid etched.
110 X.



Figure 68. Sample 10D.
Same as 10C but cooled from
538°C. (1200°F.) to room
temperature in furnace in
10 hours.

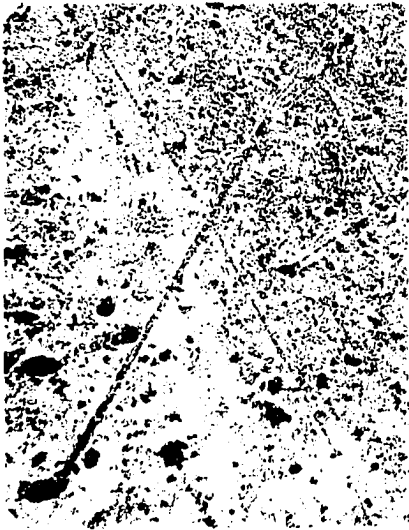


Figure 69. Sample 12A.
7.3% Ni. Annealed at 945°C.
(1735°F.) for 16 hours, air
cooled and nitric acid etched.
100 X.

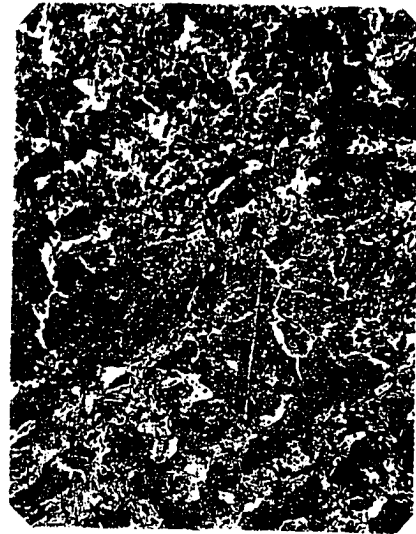


Figure 70. Sample 12B.
Same as 12A but cooled in
furnace from 945°C. (1735°F.)
to 648°C. (1200°F.) in 10
hours, air cooled and nitric
acid etched. 100 X.



Figure 71. Sample 12C.
Same as 12B cooled in fur-
nace from 648°C. (1200°F.)
to 538°C. (1000°F.) in 6
hours, air cooled and nitric
acid etched. 100 X.

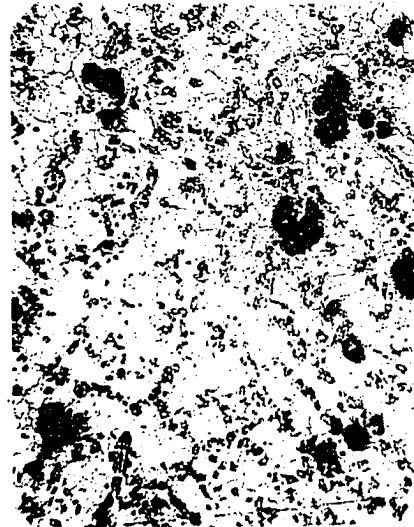


Figure 72. Sample 12D.
Same as 12C cooled from
538°C. (1000°F.) to room
temperature in furnace in
10 hours and nitric acid
etched. 100 X.

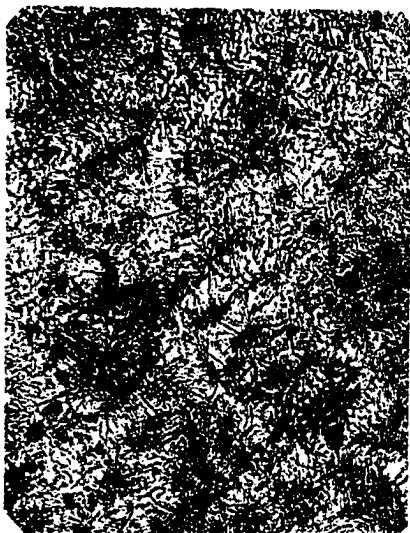


Figure 73. Sample 14A.
8.8% Ni. Annealed at 945°C.
(1735°F.) for 16 hours and
air cooled. Nitric acid
etched. 100 X.



Figure 74. Sample 14B.
Same as 14A cooled in fur-
nace from 945°C. (1735°F.)
to 648°C. (1200°F.) in 10
hours, air cooled and nitric
acid etched. 100 X.

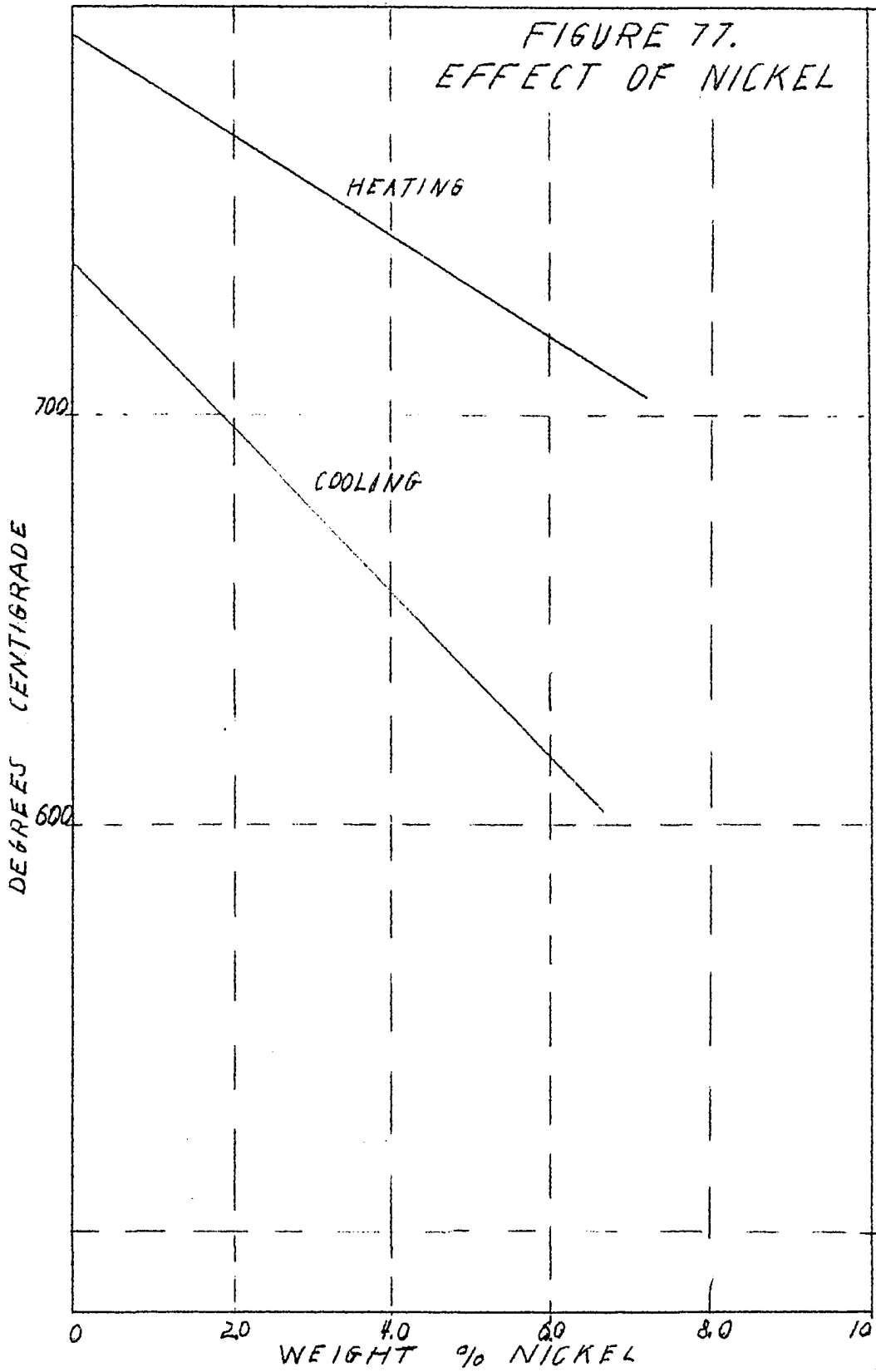


Figure 75. Sample 14C.
Same as 14B, furnace cooled
from 648°C. (1200°F.) to
538°C. (1000°F.) in 6 hours,
air cooled and nitric acid
etched. 100 X.



Figure 76. Sample 14D.
Same as 14C, furnace cooled
from 538°C. (1000°F.) to
room temperature in 10 hours
and nitric acid etched. 100 X.

FIGURE 77.
EFFECT OF NICKEL



VI. DETERMINATION OF THE MINIMUM ANNEALING TIME

From the study of graphitizing rates at the high temperature and in the critical range, it is estimated that alloys containing between 3 and 6 per cent nickel and 1 per cent silicon can be graphitized completely in less than 11 hours. The following experiments were run to determine the minimum time for complete graphitization. In all of these experiments the samples were packed in powdered graphite in graphite crucibles to prevent oxidation. The heat treatments were carried out in a Hump furnace, hand controlled. The temperature was measured with an iron-constantan thermocouple.

1. Heat Treatment H.

Nine samples containing nickel additions between 3.0 and 4.5 per cent and the original white cast iron bar that had been remelted without additions of nickel and one that had not been remelted were used in this experiment. The samples were placed in the furnace and brought to the temperature of 959°C. (1760°F.). The temperature was then allowed to rise to 1027°C. (1885°F.) in four hours. The power was then turned off and the temperature allowed to fall to 556°C. (1035°F.) in four hours. The total time of the anneal was 8 hours.

Photomicrographs of the original bar (not remelted) are shown in figures 78 and 79. There is appreciable free iron carbide present and large areas of pearlite. These may be compared to samples 31 and 26, containing 3.46 and 3.04 per cent nickel and shown in figures 80 and 81. Both of these samples are completely graphitized under the above treatment.

2. Heat Treatment G9.

Sample 25, containing 4.18 per cent nickel, was used in this experiment. It was heated to 981°C. (1800°F.) and allowed to cool to 939°C. (1725°F.) in one hour and then to 593°C. (1100°F.) in 6 hours. The total time of the anneal was 7 hours. The photomicrograph of this sample is shown in figure 82. It is completely graphitized and the carbon is precipitated in good form and the ferrite grain fine but of good form.

3. Heat Treatment G11.

Sample 25, containing 4.18 per cent nickel, was used in this experiment. It was placed in the furnace and heated from 912°C. (1675°F.) to 997°C. (1830°F.) in 30 minutes. The power was then turned off the furnace and the temperature allowed to drop to 593°C. (1100°F.) in 6 hours and 30 minutes. The total time of the anneal was 7 hours. A photomicrograph of this sample is shown in figure 83. It is completely graphitized.

4. Heat Treatment F.

Samples 9, 11, 19, 20 and 21, containing 4.0, 5.3, 3.2, 3.9 and 9.1 per cent nickel, were used for this anneal. The samples were held at 939°C. (1725°F.) for 30 minutes and then cooled to 593°C. (1100°F.) in 7 hours and 30 minutes. The total time of the anneal was 8 hours. Sample 19 contained appreciable free iron carbide. Samples 9 and 20 were completely graphitized. A photomicrograph of sample 9 is shown in figure 84. A photomicrograph of sample 11 is shown in figure 85. It is either not completely graphitized or the rigidity of the metal was so great at the temperature of completion that the ferrite grains failed to form regularly. Sample 21 contained considerable combined carbon in the form of hardening bodies. It shows a martensitic structure.

It is thus shown that white cast irons containing 1 per cent silicon, 2.25 per cent carbon and from 3 to 6 per cent nickel can be completely graphitized in from 7 to 9 hours. In all cases the carbon was precipitated in good form and the ferrite, though much refined in grains, seemed of good structure.



Figure 78. Stock bar.
Heat treatment H. Time, 8
hours. 0 % nickel. Not re-
melted. Nitric acid etched.
100 X.



Figure 79. Stock bar.
Not remelted. 0 % nickel.
Heat treatment H. Time, 8
hrs. Nitric acid etched.
100 X.

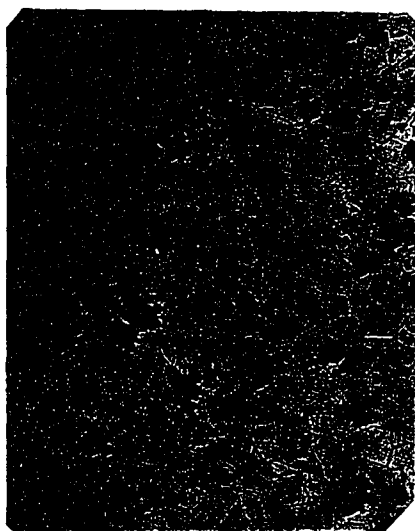


Figure 80. Sample 31H.
3.46% Ni. Total time of an-
neal, 8 hours. Nitric acid
etched. 100 X.

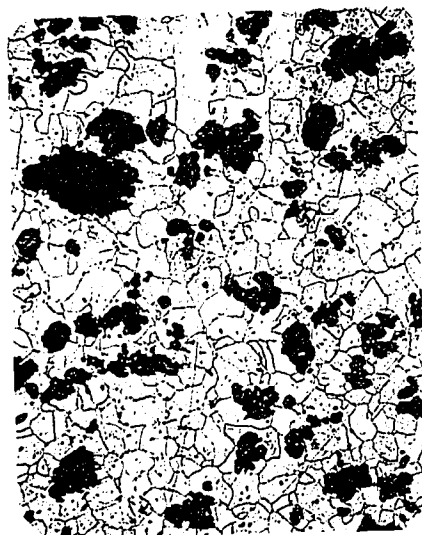


Figure 81. Sample 26H.
3.04% Nickel. Total time
of anneal, 8 hours. Nitric
acid etched. 100 X.



Figure 82. Sample 25 G9.
4.18 Ni. Total time of an-
neal, 7 hours. Nitric acid
etched. 100 X.

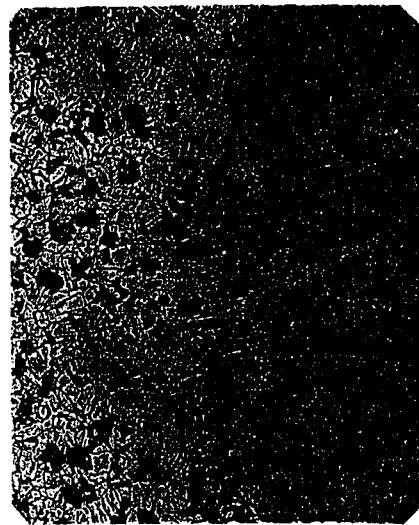


Figure 83. Sample 25 G11.
4.18 Ni. Total time of an-
neal, 7 hours. Nitric acid
etched. 100 X.

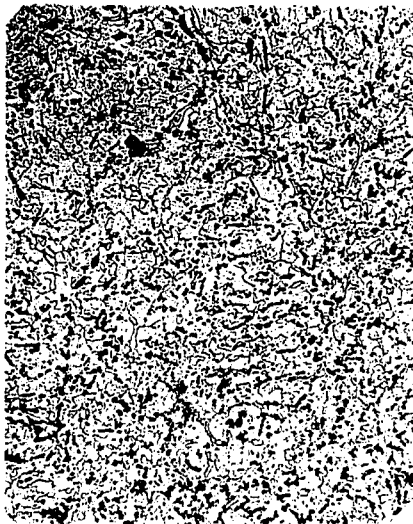


Figure 84. Sample 9F.
4% Ni. Total time of an-
neal, 7½ hours. Nitric
Acid etched. 100 X.

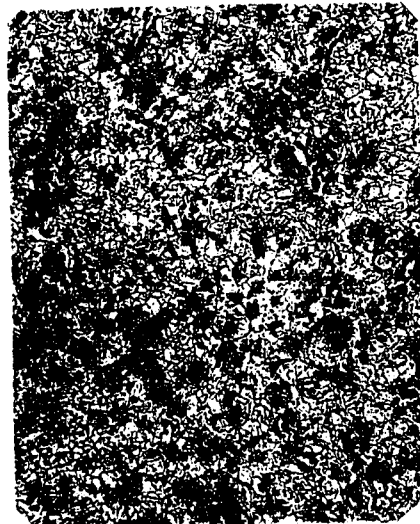


Figure 85. Sample 11F.
6.3% Ni. Total time of an-
neal, 7½ hours. Nitric
acid etched. 100 X.

VII. THE EFFECT OF NICKEL ON THE MICROSTRUCTURE OF WHITE AND MALLEABLE CAST IRON

Nickel has little or no effect on the microstructure of the free iron carbide in white cast iron. As might be anticipated from the effect of nickel on steel and its solubility in the gamma iron solid solution, the matrix of white cast iron may be changed to martensite or to austenite by additions of nickel. This change is shown by the photomicrographs in figures 13, 17, 21, 25, 29, 33, 37, and 41. Sample 19 containing 3.2 per cent nickel is shown in figure 21. Sample 20, containing 3.9 per cent nickel, is shown in figure 25. Sample 19 has the regular white cast iron matrix, while sample 20 is martensitic. Sample 14, containing 8.8 per cent nickel is shown in figure 41 at 100 magnification and in figure 42 at 580 magnification. The matrix in this sample contains only a few larger well-formed martensitic needles, embedded in austenite.

The effect of nickel on the microstructure of malleable cast iron in amounts from 0 to 3 per cent, is to refine the grains of the ferrite and to increase the number of carbon nuclei. This is shown by the photomicrographs in figures 34 to 60. The size of the carbon spots are reduced and the number increased.

Sample 19, containing 3.2 per cent nickel, and sample 20, containing 3.9 per cent nickel, show a definite change in the microstructure of the malleable iron product. This is shown by the photomicrographs in figures 57 to 64. In sample 20 the carbon is precipitated in much finer spots than in sample 19, and is evenly distributed throughout the samples. The ferrite grains are refined in about the same proportion as in the lower nickel alloys.

Samples 10, 12 and 14, containing 5.9, 7.3 and 8.8 per cent nickel, are shown in figures 65 to 76. The carbon in these alloys, while finely divided and not flakey, is not evenly distributed and appears to be precipitated in the position formerly occupied by the free iron carbide. Sample 10 shows further refinement of the ferrite grains, but sample 12 shows an increase in ferrite grain growth.

It should be noted that the change in the carbon precipitation occurs simultaneous with the change in the structure of the white cast iron matrix. This would indicate that the martensitic matrix contained a larger number of carbon nuclei, and thus the carbon is precipitated at a greater number of centers.

VIII. DISCUSSION OF RESULTS

It has been shown above that there are two types of alloying constituents with reference to the first stage of graphitization of white cast iron. In the first class, are those elements which are associated with the carbide as a carbide, or as miscible solid solutions. In the second class are those elements which are not associated with the carbide but are miscible in the gamma iron phase.

If in the first case a stable carbide of the alloying element is formed, the iron carbide may be replaced in part or completely by this more stable carbide, which may not graphitize at all under regular annealing conditions. If a stable compound of the element and carbon is not formed, it may be associated with the iron carbide as miscible solid solutions of the element and iron carbide, of a compound of iron and the element, and iron carbide or of the two carbides. In all of these cases the effect will be the same. The iron carbide will be diluted by the alloying constituent, thus decreasing the activity of the carbon from the iron carbide, in proportion to its distribution between the two phases and the amount present. The activity of carbon from the carbide phase may even become less than its activity from graphite. In this case the re-

action would proceed in the reverse direction. As graphitization progresses the added constituent will be concentrated in the remaining iron carbide, and thus its effect would be increased until it may stop the reaction entirely. This would result in only partial graphitization at the high temperature.

In the second case the added constituent is not associated with the carbide and is miscible in the proportions added with the gamma iron solid solution. This would result in a dilution of the iron in the solid solution thus a decrease in its activity. Under equilibrium conditions the activity of iron and carbon from the solid solution and from iron carbide must be equal. With a decrease in the activity of iron from the solid solution there will be an equal decrease in its activity from the iron carbide. In order for iron carbide to be precipitated there must be a proportional increase in the activity of the carbon from the solid solution, which will, at equilibrium, equal the activity of carbon from the iron carbide. The difference in the activity of the carbon from iron carbide and from carbon is thus increased by dilution of the iron solid solution. This will result in an increased rate of graphitization. However, an increase in the activity of carbon from iron carbide does not infer that its solubility

must increase. The added constituent will affect the solubility of iron carbide, only, in that it changes the properties of the solvent.

Nickel is of the second class of added constituents. It has a face center cubic lattice, similar to that of gamma iron. It is immiscible with iron carbide, but is miscible with both alpha and gamma iron. Its solubility in gamma iron is greater than its solubility in alpha.

In the first stage of graphitization, nickel affects the rate of reaction in accordance with the above discussion. It is dissolved in the gamma iron and increases the rate of graphitization. The time t in hours for the disappearance of free iron carbide in a 1 per cent silicon and 2.2 per cent carbon alloy may be calculated from the equation,

$$t = 12 e^{-0.654N}$$

Where e is natural logarithm and N the weight per cent of nickel.

Added elements divide themselves into two classes as they affect the second stage of graphitization, those which are more soluble in alpha than in gamma iron and those which are more soluble in gamma than in alpha iron. In the first case, as ferrite is formed the alloy constituent will be diluted in the gamma phase and thus, as the reaction progresses,

its tendency to accelerate or retard the reaction will be decreased. In the second case, as ferrite is formed the alloying constituent will be concentrated in the gamma phase and thus the tendency to retard or accelerate the reaction will be increased.

Nickel is of the second type of alloying constituent. It is thus concentrated in the gamma phase as the reaction progresses and its effect to accelerate the reaction is increased. This explains the results found for nickel alloys in the second stage of graphitization. They were either completely graphitized or contained relatively small portions of ferrite. This is in accordance with the theory that the rate of reaction would be increased as the second stage of graphitization proceeded.

It was found: that nickel addition to white cast iron containing 1 per cent silicon and 2.2 per cent carbon greatly increases the rate of graphitization of both stages; that these alloys respond to graphitization during comparatively rapid rates of cooling through the critical range; and that these alloys with 3.5 to 5 per cent nickel additions can be completely graphitized in seven hours.

BIBLIOGRAPHY

1. Hayes and Diederichs, The Mechanism for the Graphitization of White Cast Iron and its Application to the Malleablization Process, Bulletin 71 Engineering Experiment Station, Iowa State College, Ames, Iowa.

The various phases of this work were published as they were completed in the Trans. Am. Soc. Steel Treating and the Trans. Am. Foundrymen's Assoc. as follows:

- (a) Experiment on the Rapid Graphitization of White Cast Iron and a Theory for the Mechanism of Graphitization, Anson Hayes, W. J. Diederichs and W. M. Dunlap, Trans. Am. Soc. Steel Treating, Vol. 3, p. 624, 1923.
- (b) Evidences of an Iron-Carbon Eutectoid and Resulting Modification of the Equilibrium Diagram, Anson Hayes and W. J. Diederichs, Trans. Am. Soc. Steel Treating, Vol. 3, p. 918, 1923.
- (c) Identification of the Thermal Effects of the Iron-Carbon Eutectoid and Extrapolation of the Heating and Cooling Values to Zero Rates, Anson Hayes, H. E. Flanders and E. E. Moore, Trans. Am. Soc. Steel Treating, Vol. 5, p. 183, 1924.
- (d) Possibilities of Producing Malleable Iron and Intermediate Products of Value in Short Annealing Periods, Anson Hayes and W. J. Diederichs, Trans. Am. Soc. Steel Treating, Vol. 6, p. 491, 1924.
- ✓(e) Structural Evidences of an Iron-Carbon Eutectoid, Anson Hayes and H. E. Flanders, Trans. Am. Soc. Steel Treating, Vol. 6, p. 623, 1924.
- ✓(f) The Mechanism of Graphitization of White Cast Iron and its Application to the Malleablizing Process, Anson Hayes and W. J. Diederichs, Trans. Am. Foundrymen's Assoc., Oct., 1924.

2. Hayes and Flanders, On the Causes of Variations in Rates of Graphitization of White Cast Iron, Trans. Am. Foundrymen's Assoc., Vol. 33, p. 634, 1925.
3. Schwartz and Guiler, Chemical Elements that Inhibit Graphitization, Trans. Am. Foundrymen's Assoc., 33, 639, 1925.
4. T. Kikuta, On the Malleable Cast Iron and the Mechanism of its Graphitization, Science Reports Tohoku Imp. Univ. 15, 115, 1926.
5. Albert E. White, Manufacture of Malleable Iron, Trans. Am. Soc. Steel Treating, 11, 245, 1927.
6. Edward P. Fisher, Relation of Temperature to the Form and Character of Graphite Particles in the Graphitization of White Cast Iron, Trans. Am. Foundrymen's Assoc., 30, 397, 1923.
7. Osmond and Cartaud, Sur les Fers Meteoriques, Rev. Metal, 1, 69, 1904.
8. D. Hanson and Hilda Hanson, The Constitution of Iron-Nickel Alloys, J. Iron and Steel Inst., 102, 39, 1920.
9. Tuston Kase, The Equilibrium Diagram of the Iron-Carbon-Nickel System, Science Reports Tohoku Imp. Univ., 14, 173, 1925.
10. Carl Benedicks, Metallographic Research, (Book) pages 99 to 150.
11. Nickel and its Alloys, Circular of the Bureau of Standards No. 100.
12. Thos. H. Wickenden and J. S. Vanick, Nickel and Nickel Chromium in Cast Iron, Trans. Am. Foundrymen's Assoc. 33, 347, 1925.