1933

The influence of copper on the graphitization behavior of white cast iron

Louis Lykken
Iowa State College

NOTE TO USERS

THE INFLUENCE OF COPPER ON THE GRAPHITIZATION BEHAVIOR OF WHITE CAST IRON

By

Louis Lykken

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

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1933

ACKNOWLEDGEMENT

The writer wishes to thank Dr. Anson Hayes for the suggestion of this problem. Also, the writer takes this opportunity to express his sincere gratitude to Dr. W. H. Jennings for his advice and counsel during the progress of this work. In addition, the author desires to thank the Physical Chemistry research staff for their aid, personal interest and friendship.

TABLE OF CONTENTS

THE INFLUENCE OF COPPER ON THE GRAPHITIZATION BEHAVIOR OF WHITE CAST IRON

I. PREFACE

White Cast Iron contains only combined carbon (Fe_3C), and it is, therefore, practically free from free "graphitic" carbon. It is essentially a conglomerate made up of massive cementite (Fe_3C) dispersed in a matrix of intimately mixed ferrite (Fe) and cementite, known as pearlite. Any impurities found in white cast iron may be found in the massive cementite phase as well as in the pearlitic phase. Elements found in the free cementite may be present as admixed carbides or as isomorphic forms of the iron carbide. The foreign substances found in the pearlitic matrix, may be found in cementite portion (in a manner similar to the presence in the massive cementite), or the ferrite portion as a solid solution in the iron. The usefulness of white cast iron is entirely due to the practical possibility of changing it into the more ductile malleable iron by a suitable graphitizing heat treatment.

When the white cast iron is heated above the critical temperature it is converted into an aggregate of austenite and massive cementite. If the temperature is maintained several hundred degrees above the critical the free cemen-

tite is decomposed into austenite, or ferrite, and temper carbon (C):

$$Fe_3C \rightarrow 3Fe + C.$$

The austenitic solid solution is stable at this high temperature; but, when the temperature is slowly lowered through the transformation range, or, when the temperature is brought to just below the transition temperature and maintained there, the austenite is gradually converted into temper carbon and an austenite of a lower carbon composition. In passing the eutectoid point, the remaining solid solution resolves itself into ferrite and more temper carbon.

In the old established process, the white casting is heated some 200°F above the eutectoid point and maintained at the temperature for a day or more. After this preliminary heating the casting is allowed to cool to handling temperature over a period of a week. A newer process consists in heating the white cast iron for a predetermined time at approximately 1700°F and then cooling the material to a temperature below the lower critical point. This cooling may be accomplished by quick cooling or quenching to just above the eutectoid transition and cooling through the transition point at the rate of approximately 100°F per day. The material may also be cooled from the high temperature to just below the critical temperature, in a period of a few hours, followed by holding the temperature

just below the critical point until the graphitization is complete.

The anomalous response of steel and white cast iron to the usual graphitizing treatment is generally explained by their difference in chemical composition. Most authorities concede that the breaking up of the cementite into ferrite (or austenite) and graphite (or temper carbon) takes place more readily (1) when the amount of combined carbon is increased, (2) when the temperature is raised, (3) when the exposure to a high temperature is prolonged, and (4) when the alloy contains more silicon and less manganese and sulfur. These influences may also be altered by the presence of special elements, or by a change in the proportion of the "extra" elements usually found in the white cast iron alloy. Accepted explanation of the mechanism of graphitization, or of the effect of the enumerated conditions on the graphitization, is still lacking. It is generally supposed that decomposition of the free or pearlitic cementite proceeds according to the equation:

$$Fe_3C \rightarrow 3Fe + C.$$

The carbon produced may form a solid solution with any gamma iron present, or it may remain as temper carbon. The impelling force in this reaction is thought to be due to the fact that the solubility of carbon from carbon in

austenite is less than the solubility of carbon from cementite in austenite. The presence of an additional amount of any element may influence this reaction by changing the stability of the resulting cementite and by changing the solubility of carbon in the resulting austerite. Thus silicon accelerates the graphitization in part through the formation of a cementite (containing some silicon) that is less stable than ordinary pure Fe_3C. Similarly the presence of some FeS and Mn_3C in the cementite is thought to be the cause of the deleterious action of excess sulfur and manganese on the graphitizing process.

H. A. Schwartz (40) in his recent summary on malleable iron gives the latest interpretation of the malleablizing process. He states that the process of annealing of white iron castings, is one of solution of the carbide, decomposition of the dissolved carbide, migration of the carbon atoms to centers of deposition, and finally, crystallization of the temper carbon and remaining austenite or ferrite. Experiment has shown that the migratory rate is the determining factor. Any retarding of the graphitization process is thought to be due to formation of intergrainal films. Excess of added elements changes the properties of this film and in turn influences the rate

of graphitization.

From the mode of preparation, white cast iron will contain various foreign elements; chiefly: Silicon, Phosphorus, Manganese and Sulfur. The silicon accelerates graphitization at all temperatures. Phosphorus acts the same as one-half the amount of silicon above the critical, and just opposite to silicon below the transition temperature. Above the critical, manganese, in excess of twice the sulfur, retards graphitization about one-tenth as much as silicon accelerates; manganese retards more below the critical than above it. Sulfur retards the malleablizing process more below the critical temperature than above it (40). The influence of other elements is best found in summaries by Schwartz and Guiler (50) and Everest (51). Of the twenty odd common elements studied, only silicon, aluminum and nickel favor graphitization of the cementite.

Many physical conditions and factors influence graphitizing process. Kikuta (52) finds that the decomposition of the free carbide is accelerated by a rise in annealing temperature. As the pouring temperature is raised the graphitization is retarded. The more rapid the cooling from pouring temperature, the more rapid is the rate of graphitization.

II REVIEW OF PERTINENT LITERATURE.

A. Effect of Copper on the Graphitization of White Cast Iron.

Scattered through the mass of literature on the influence of various elements, on the graphitization behavior of white cast iron, there is very little mention of copper. H. Sawamura (38) states that copper has a slight graphitization tendency. In his article on the theories of graphitization, H. A. Schwartz (41) states that it is believed that copper tends to favor graphitization of white castings. Recently the same writer (40) points out that copper (in general) is an accelerator of graphitization but the effects are small. In 1929 Godefroid (12) reported some work on the influence of copper on the temper process; he states that addition of copper to malleable iron has usually been prohibited. Godfroid finds that a true structure is obtained after copper additions, but desirable castings are not produced. The most recent contribution was made by Sawamura (39). In his paragraph that has to do with copper, Sawamura (39) writes: "Copper favors graphitization in practically pure white iron, and its effect is moderate up to 2 per cent of this element; but further addition of copper makes no practical differ-

ence to its effects. It also promotes the effect of 0.30 per cent silicon in the alloys containing 2.50 per cent carbon". However, Sawamura's results are mainly qualitative and bear no relation to a regular commercial annealing process.

B. Effect of Copper on the Graphitization of Gray Cast Iron.

The earliest reference to this subject is due to Lipin (28). Working with copper additions to pig iron, Lipin concludes that the copper does not tend to retain carbon in the combined form. H. Wedding (47) stated in 1906 that copper hinders the formation of pearlite causing the cementite to segregate; no mention is made as to the stability of the carbide. Working with a series of copper additions to a high-silicon, low-carbon gray iron, Hamasumi (17) found that graphitization is not affected by the copper. In reporting their work on the iron-copper-carbon system, Ishwara, Yonekura and Ishigaki (24) found that copper promotes graphitization of steel containing high carbon. In the same year, Mikailof (29)

reported that copper hinders the formation of cementite only when the silicon content is low. Hurst (22) summarizes the work up through 1926 stating that there appears to be no change in combined carbon content in cast irons to which copper has been added.

While considering copper-bearing pig iron, Coleman (10) found that copper tends to form ferrite and carbon. Blackwood reports that 0.50 per cent copper shows some graphitizing tendencies. Similar results were obtained by Hotari (21) who states that he found an increase of graphite with an increase of copper; so copper accelerates graphitization. Contrary to most previous work, Bauer and Sieglerschmidt (4) found that small additions of copper and nickel, apparantly retard the carbide decomposition. In his review, Good (13) summarizes: "Copper has some slight graphitizing tendency". In 1930, Smith and Aufderhaar (43) found that copper does not have a noticeable effect on the carbon. Norbury (32) states that copper produces only slight changes in gray cast iron.

Reed (36) brings out conflicting evidence in his marvelous work on the iron-carbon eutectoid. He reports no graphitizing effect in high carbon steels containing copper.

Guillet and Ballay (15) report that copper has very little action on the graphitization of cementite. However, these authors state that copper seems to act as an accelerator in the graphitization process. In a later work, Hurst (23) says that copper acts similar to nickel, but it is more moderate.

C. Related Ideas from the Iron-Copper-Carbon System.

No attempt will be made to review the iron-carbon-copper system. It suffices to say that this system has been thoroughly studied by Ishiwara, Yonekura and Ishigaki (24) in 1926. The results published by these workers is pretty well in accord with known facts. However, there seems to be some dispute concerning carbon content of the eutectoid and solubility of copper in presence of carbon. It is the writers opinion that most of this disagreement is caused by the presence of varying amounts of other elements, and by the great tendency of copper to form supersaturated solid solutions with iron, which do not attain equilibrium readily (8).

These supersaturated solid solutions give rise to the age-hardening effect of copper-bearing steel and iron (8), (30), (25).

In 1926, Ishiwara, Yonekura and Ishigaki (24) reported that the carbon concentration on the eutectoid line does not seem to undergo a variation on the account of the presence of copper. This is refuted by Reed (36) in his recent work on the iron-carbon eutectoid. He found that copper displaces the eutectoid concentration to the right (1,13%C and 8.72% Cu gives a pure eutectoid structure). Although the pearlite, in iron or steel alloyed with copper, has a well-laminated structure, it is now generally agreed that the pearlite-ferrite laminae are heterogeneous (mixture of ferrite and copper-iron solid solution) (24), (36).

As early as 1906, Breuil (7) found that copper in a steel produced a finer type of structure and a more marked pearlite. Clevenger (9) states that copper in a steel retards the formation of pearlite and produces a finer grain. More recently, Hayashi (18) found that a copper-bearing steel consists of ferrite and pearlite, the pearlite becoming finer with increase of copper. Ishiwara and his co-workers (24), as well as Stogov and Mesiken (44), state that copper up to 5 per cent has no effect on the cast steel

structure. That copper has no influence on the structure up to one per cent, is the conclusion of Bauer, Vogel and Holthaus (3). However, Kinnear (25) finds that copper-bearing steel or iron has a fine structure. More recently, Reed (36) has found that "free ferrite persists in the microstructure as cast; while in the annealed state, copper promotes migration of cementite to the grain boundaries."

Clevenger (9) has reported that the addition of copper hardens the ferrite and that segregation is produced by more than 2 per cent copper. Summarizing the influence of copper on corrosion, Smith and Aufderhaar (43) state that the maximum resistance to corrosion is produced by one per cent copper.

D. Relation of the Critical Temperature to the Composition and Malleabilization Temperatures of White Cast Iron.

In this review, the writer will only consider actual values of the A_r (A_{r321}) temperature in iron or steel containing 0.60 to 1.00 per cent of silicon. The reason for the choice of this range is that malleable iron universally contains the amount of silicon referred to.

As early as 1906, Breuil (7) found that the A_r point of steel was greatly intensified by copper. In his work on copper alloys, Sahmen (37) found that the presence of copper, in practically pure iron, did not influence the transition of beta to alpha iron. Clevenger (9) states that 4.5 per cent copper lowers the A_r point of steel 95°C. In his book on the Metallurgy of Cast Iron (1926), Hurst (22) summarizes the situation by saying "The position of the A_r point ..... is little affected by the addition of copper". Ishiwara, Yonekura and Ishigaki (24) reported that one per cent copper lowered the A_r value 20°C, in a eutectoid steel; 2 per cent copper lowered the critical cooling temperature 25°C. "Copper lowers the transition points of steel" is the finding of Hayashi (18). In the same year (1928), Stogov and Mesikin (44) found that the A_r could be lowered to 640°C and that a hysteresis of 90°C could be developed. The influence of copper on the critical point of gray (high silicon) cast iron is given by Hotairi (21). More recently, Reed (36) found that 8.72% copper (copper eutectoid) lowers the A_r point 91°C.

Several workers have determined the A_{321} point of white cast iron (and malleable iron) containing an amount silicon suitable for malleabilizing:

Authors	Year	%Si	A_1
Hague and Turner (16)	1910	0.66	726°C
" "	1910	0.97	730°C
" "	1910	1.19	734°C
Phillips (35)	1932	0.90	745°C
Hayes and Diedericks (20)	1924	0.95	760°C
Stutzman (45)	1933	0.95	765°C

From these values, and from the general influence of copper on the critical, it might be expected that several per cent of copper will lower the A_r value below 700°C

III DEVELOPMENT OF WORK

A. Aim and Objective.

The foregoing pages have presented the general fact that chemical and physical conditions have a marked influence on the time needed to produce malleable castings. An investigation of the influence of copper additions on the graphitizing behavior of commercial white cast iron seemed to be of some importance, because, (1) of the lack of quantitative information on this subject and because (2) the use of copper bearing iron and steel is becoming to be more important. In order that no difficulties should arise due to the temperatures used in the annealing process, it was deemed necessary to determine the influence of copper on the transition temperature of the cast iron used. Also in order to investigate fully the influence of the copper content on the decomposition of the massive cementite, as well as on the breakdown of the solid solution, it was decided to subject the desired samples to the two-cycle malleablizing heat treatment developed by Hayes and Diedericks (19) in this laboratory.

The object of this research was to determine the time of graphitization and microstructure of commercial white cast iron containing various amounts of copper.

B. Details of Alloy Preparation.

Preliminary Alloys. Two sets of alloys were made in this investigation. The first set was made up for the express purpose of making a preliminary study of the effect of copper on the microstructure of commercial white iron before and after a prolonged anneal. The materials used in the preparation of the preliminary alloys were electrolytic copper wire and commercial white cast iron test-bars of the following composition:

Total Carbon	2.45%
Silicon	0.87%
Manganese	0.210%
Sulfur	0.031%
Phosphorus	0.141%

About 2000 grams of the cast test-bars were melted in a six-inch plumbago crucible heated by the secondary coils of a 30 K. W. Ajax induction furnace. The calculated weight of copper was then added to the molten iron, and the melt stirred and skimmed with an Armico iron rod. When the melt reached a temperature of 2400°F (as shown by a standard optical pyrometer), the molten metal was poured into a vertical cyclindrical cavity contained in a wet samd flask. This produced vertical cast bars that

were 10 inches long and one-half inch in diameter. The bars were allowed to cool to below red heat before they were removed from the mold. Some difficulty was experienced in getting sound bars as some of them were found to be hollow. No attempt was made to make up for any loss of carbon, silicon, sulfur or phosphorus during the melting process. It was attempted to make alloys containing various amounts of copper from 0 to 3 per cent. These samples were numbered from one to ten.

Final Alloys. This new set of alloys was made up from commercial white cast iron, in the form of test-bars, of the following composition:

Total Carbon ---------- 2.51%;
Silicon ---------- 0.88%;
Manganese ---------- 0.24%;
Sulfur ---------- 0.042%;
Phosphorus ---------- 0.136%;

Commercial electrolytic copper wire was used as the source of the added portions of copper. The ferro-alloys, used to build up the composition of the alloys, had the following composition:

Ferromanganese ----------	80% Mn;
Ferrosilicon ----------	50% Si;
Ferrous sulphide -------	37.5% S;
Gas Carbon (10 mesh) ---	100.0% C;
Armico Iron ----------	99.8% Fe.

Three thousand grams of white cast iron were broken up and placed in a six-inch plumbago crucible supported inside the secondary coils of a 30 K. W. Ajax induction furnace. The contents of the covered crucible were heated to melting point in 20 to 30 minutes using 8 to 15 K. W. of power. When the iron was just fluid, the calculated weights of copper and ferro-alloys were quickly added (separately) with plenty of stirring with an Armico iron rod. Using 14 to 15 K. W. power, the heating was continued until a temperature of 2500°F was reached. The temperature was read by using a Leeds and Northrup optical pyrometer, and by sighting vertically thru a 3/4 inch opening in the crucible cover. The molten alloy at 2500°F was quickly poured into a damp sand flask that was inclined approximately 10% from the horizontal. This process gave a casting consisting of three bars, 5/8-inch in diameter and 15 inches in length. The casting was allowed to cool in the flask until it had reached a temperature below red heat. The flasks were made up during the period of heat-

ing from well-mixed foundry sand that had been suitably dampened.

The procedure was repeated using the same amounts of ferro alloys and an amount of copper wire sufficient to make an alloy of the desired composition. Samples numbered 11 through 21 were made to contain from 5 to 0 per cent of copper. Samples 22 through 25 were made to contain one per cent of copper and from 2.8 to 3.8 per cent carbon. Alloys from number 26 through 29 were to contain one per cent copper, and silicon varying from 1.0 to 1.2 per cent. Numbers 30 and 31 were to have a composition of one per cent copper, in each case, and 2.2 per cent carbon and 0.75 per cent silicon, respectively. Unless otherwise specified, the composition of each sample was made up to give:

Carbon	2.50%
Silicon	0.87%
Manganese	0.24%
Sulfur	0.03%
Phosphorus	0.14%

After the casting had cooled, it was broken into pieces one inch in length. The middle portion of the central bar was reserved for making the chemical analyses. Some of the sample pieces showed distinct shrinkage areas near the center.

C. Methods and Results of Analysis of Cast Alloys.

Chemical Analysis. The bars reserved for chemical analysis were cleaned by a power wire brush and then turned down on a lathe at a slow speed using a high speed tool. The turnings used for analysis consisted of all but the central portion (1/4-inch in diameter) of the bar.

The methods used, in the chemical analysis, were those of the U. S. Steel Corporation as described in their latest book entitled: "Methods of Analysis of Steel." The carbon was determined by absorbing the CO_2 (in Ascarite) formed by the combustion of the sample at 1000°C in an atmosphere of O_2. Silicon was analyzed for by the nitric-sulfuric acid dehydration method combined with the hydrogen fluoride volatization method. The copper content was found by titration of the precipitated cuprous thiocyanate with potassium iodate and sodium thiosulphate. Sulfur was determined by oxidation to sulphate ion with nitric acid and precipitation as barium sulphate after reducing the iron to the ferrous state. In the analysis for manganese, this element was oxidized to permanganate ion (using ammonium persulphate in presence of silver nitrate) and titrated with standard sodium arsenite solution. The phosphorus was dissolved in nitric acid, oxidized to phosphate ion with permanganate ion and pre-

cipitated as phospho-molybdate; this yellow precipitate was titrated with standard base and acid. The fracture of each sample was examined and classified as white, mottled or gray.

In order that the analytical results be as accurate as possible, each method was regularly checked against standard samples furnished by the Bureau of Standards. Each determination was repeated until consistent results were obtained. A summary of the chemical analysis is given in the following table.

Microscopical Analysis. The methods here described were used in the preparation and examination of all microsections considered. After the sample under examination had been cleaned, it was ground down to give a flat fresh surface. About 1/8-inch was removed during the grinding. The rough surface was ground down to a shiny surface containing only a few fine scratches. This grinding was accomplished by using a water suspensions of 60-, 180- and 600-mesh carborundum on a cloth-covered, rotating disk. A scratch free surface was procured by polishing on a wet (rotating) chamois that was saturated with a rouge suspension.

TABLE I
CHEMICAL COMPOSITION OF ALLOYS

Alloy No.	Per Cent Chemical Composition						Fracture of Casting
	Cu	C	Si	S	Mn	P	
1	3.00	2.01	0.65	0.03	0.20	0.141	White
2	2.12	2.05	0.65	0.03	0.20	0.141	White
3	1.46	2.09	0.65	"	"	"	"
4	0.94	2.08	0.65	"	"	"	"
5	1.05	2.06	0.65	"	"	"	"
6	0.72	2.09	0.65	"	"	"	"
7	0.50	2.06	0.65	"	"	"	"
8	0.39	2.09	0.65	"	"	"	"
9	0.30	2.11	0.65	"	"	"	"
10	0.04	2.10	0.65	"	"	"	"
11	4.47	2.33	0.81	0.033	0.24	0.119	White
12	3.10	2.52	0.84	0.029	0.22	0.120	"
13	2.26	2.49	0.81	0.036	0.25	0.120	"
14	1.94	2.54	0.81	0.033	0.25	0.123	"
15	1.35	2.52	0.82	0.028	0.25	0.123	"
37	1.03	2.60	0.85	0.061	0.25	0.127	"
17	0.76	2.59	0.85	0.036	0.23	0.120	"
18	0.60	2.60	0.84	0.034	0.23	0.120	"
19	0.40	2.60	0.84	0.033	0.25	0.120	"
20	0.17	2.60	0.87	0.031	0.25	0.120	"
21	0.01	2.63	0.84	0.033	0.25	0.110	"
22	0.92	2.84	0.84	0.036	0.24	0.115	White
23	0.92	3.08	0.82	0.030	0.25	0.115	Mottled
24	0.94	3.28	0.83	0.030	0.24	0.115	Gray
25	0.98	3.47	0.83	0.036	0.25	0.115	"
26	0.91	2.71	0.95	0.036	0.28	0.115	Mottled
27	0.94	2.61	1.07	0.033	0.26	0.115	"
28	0.97	2.58	1.14	0.034	0.25	0.115	Gray
29	0.95	2.54	1.22	0.033	0.24	0.120	"
30	0.94	2.08	0.83	0.030	0.25	0.107	White
31	0.92	2.50	0.68	0.030	0.25	0.107	"
R*	0.00	2.51	0.88	0.042	0.24	0.136	White

* Commercial stock test-bars.
The values for S, Mn and P for alloys 1 to 10 are calculated values.

The polished sample was prepared for microscopical examination by immersion in ethyl alcohol containing 5% of nitric acid. Two to five seconds were required to bring out the pearlitic structure. To detect the presence of massive cementite, the polished sample was immersed in a boiling soduim picrate solution for five to ten minutes. When desired, photomicrographs were taken on aninverted, projecting microscope. The sodium picrate etched surface was taken as the criterion for determining the presence or absence of cementite. The nitric acid etch was used to determine the presence of pearlite and ferrite.

Photomicrographs of the cast bars, and of important stages in the heat treatment are reproduced in the appendix.

D. Preliminary Trials and Investigations.

When this work was started, there was a prevalent idea in this laboratory that the addition of copper to cast iron would give a heterogeneous micro-structure. Two alloys, containing approximately two and four per cent of copper, were made up from some malleable iron

stock. Microscopical analysis gave no evidence of any other than the usual dendritic structure that is so typical of white cast iron. These bars were never used in any heat treatment. However after having been exposed to the corrosive vapor of the analytical laboratory for several years it was noted that there had been practically no corrosion of the ground surfaces. Pieces of ordinary wrought iron that had been kept in the same space showed a marked rust formation. This is an attest to the well known influence of copper on the corrosion properties of ferrous alloys.

Later the preliminary copper-bearing white cast iron alloys (series 1 to 10) were subjected to a heat treatment at 1650°F. The samples were packed in clay crucibles well packed with gas carbon. The heat treatment was carried out in a Hump (vertical) controlled furnace (described in section F). The samples were maintained at 1650°F for a period of 120 hours, and then cooled in the furnace. Some samples were taken at intervals of 15 to 20 hours. Examination under the microscope showed that the massive cementite had disappeared in all samples that had been heated 15 hours. (The samples had a copper content of 0.04% to 3.00%). The samples heated for 120 hours and cooled in the furnace indicated the presence of 10% to

50% of good pearlite. There seemed to be no relation between the copper content and amount of pearlite in the micro section. The ferrite and pearlite seemed to be homogeneous. No evidence was found of the separation of free copper or any other body save carbon and ferrite. Evidently the copper stays dispersed in some manner even after a prolonged anneal above the critical temperature.

In order to get some preliminary information regarding the proposed heat treatment of the alloy series 11 to 31, several trial anneals were made on the commercial white cast iron (used in making the just mentioned alloys). The arrangement and manner of heating were the same as described in section F (following). The first trials consisted in heating for 12 hours at 1700°F, cooling to 1300°F in 6 or 8 hours and then maintaining the temperature at 1300°F for a suitable length of time. No trace of pearlite was found in any sample after <u>one</u> hour at 1300°F! It was thought that the pearlite might have spheroidized but all available microscopical etching methods failed to show the presence of cementite in any form. The matrix seemed to be normal ferrite except for the presence of some grains that seemed to be ful of minute specks, when viewed under a magnification of 500 diameters.

The heat treatment was repeated except that the mat-

erial was cooled to 1200°F. However, the samples appeared to be completely graphitized after one or two hours at 1200°F. However, if the white cast iron samples were heated for twelve hours at 1700°F, cooled to 1450°F in six hours, cooled to 1275°F in five minutes (open-furnace quench), and then maintained at 1275°F, then 5 hours at 1275°F were required before the pearlite disappeared from the samples so annealed. No further change took place after heating at the lower temperature for 40 hours. The latter heat treatment just described was repeated using some copper bearing cast iron (numbers 12 and 20); similar results were obtained since both samples contained pearlite after two hours at 1275°F but none after five hours. This seemed to indicate that the commercial white cast iron (composition given under final alloy preparation; III, section B) could be fully graphitized by heating at 1700°F until the massive cementite is decomposed and then cooling to 1300°F or lower at a rate slower then 50°F per hour.

E. The Influence of Composition on the Critical Point of White Cast Iron.--Investigation and Results.

The proposed heat treatment would consist in heating

for a period of time above the alpha-gamma transition temperature (the A_{r321}; this will be designated in this paper as just the A_r point) cooling slowly thru the transition point and then maintaining the temperature just below this critical temperature. The nature of this heat treatment makes necessary a fair knowledge of the A_r point of each of the alloys to be heat treated. As pointed out under Part II, Section D, the literature contains no facts regarding the influence of copper content on the A_r point of ordinary white cast iron. Since a series of cast irons (of desired composition) containing varying amounts of copper was at hand, it was decided to determine the A_r and A_c, point of this alloy series.

To this end, differential heating curves and cooling curves were run. The instrument used was a Leeds and Northrup apparatus for the determination of thermal transition temperatures. In order to avoid irregularities in the heat of transition, the samples used were annealed at a temperature of 1650°F until all the massive cementite had been broken down and the samples appeared partially malleablized. After annealing, the samples were properly machined to fit the instrument and were well insulated with sheet mica. Preliminary to making a record, the samples were heated, in the instrument, well above the critical

temperature. A cooling curve was then run at the rate of 20°F to 25°F per minute. When the temperature had fallen several hundred degrees below the A_r point a heating curve was run at the same rate used in cooling. This procedure was repeated until duplicated values were recorded. All samples were run in such a manner that the conditions were strictly comparable. The temperature at which a marked change in slope (on the differential curve) began, was taken as the transition temperature. In most cases this was simplified as the curves showed an abrupt change in slope.

The composition, of the cast iron samples used, (Series 1 to 11) is given under Part III, section C. An average composition is;

Total Carbon	2.05%
Silicon	0.65%
Manganese	0.21
Sulfur	0.031
Phosphorus	0.141

In the following Table 2, and in figure 1, is shown the influence of copper on the A_r and A_c temperatures for the cast irons used:

TABLE 2.

Sample #	%Cu	Thermal Values			
		Cooling		Heating	
		A_r(°F)	Rate	A_c(°F)	Rate
10	0.04	1365	20°F/min	1405	20°F/min
8	0.39	1350	"	1405	" "
7	0.50	1345	"	1400	" "
6	0.72	1340	"	1395	30°F "
6	0.72	1345	"	1400	20°F "
4	0.94	1330	"	1390	19°F "
3	1.46	1310	"	1385	17°F "
1	3.00	1290	"	1390	19°F "

The results of this investigation clearly show; that copper lowers the A_r value of cast iron in a linear fashion between 0 and 2 per cent of copper; that the A_c point is slightly lower in direct proportion to the amount of copper up to 1 per cent, and that the amount of copper has no perceptible influence, on the A_c and A_r temperatures, above 1 and 2 per cent copper, respectively. This is in general accord with values reported in the literature on iron-copper and iron-copper-carbon alloys. The hysteresis lag increases with the amount of copper; this is also in accord with generally known facts. According to the work of Hayes (19) and of Stutzmen (45), one per cent silicon raises the A_r point 110°F and one per cent nickel lowers the transition 60°F. Therefore copper lowers the A_r point

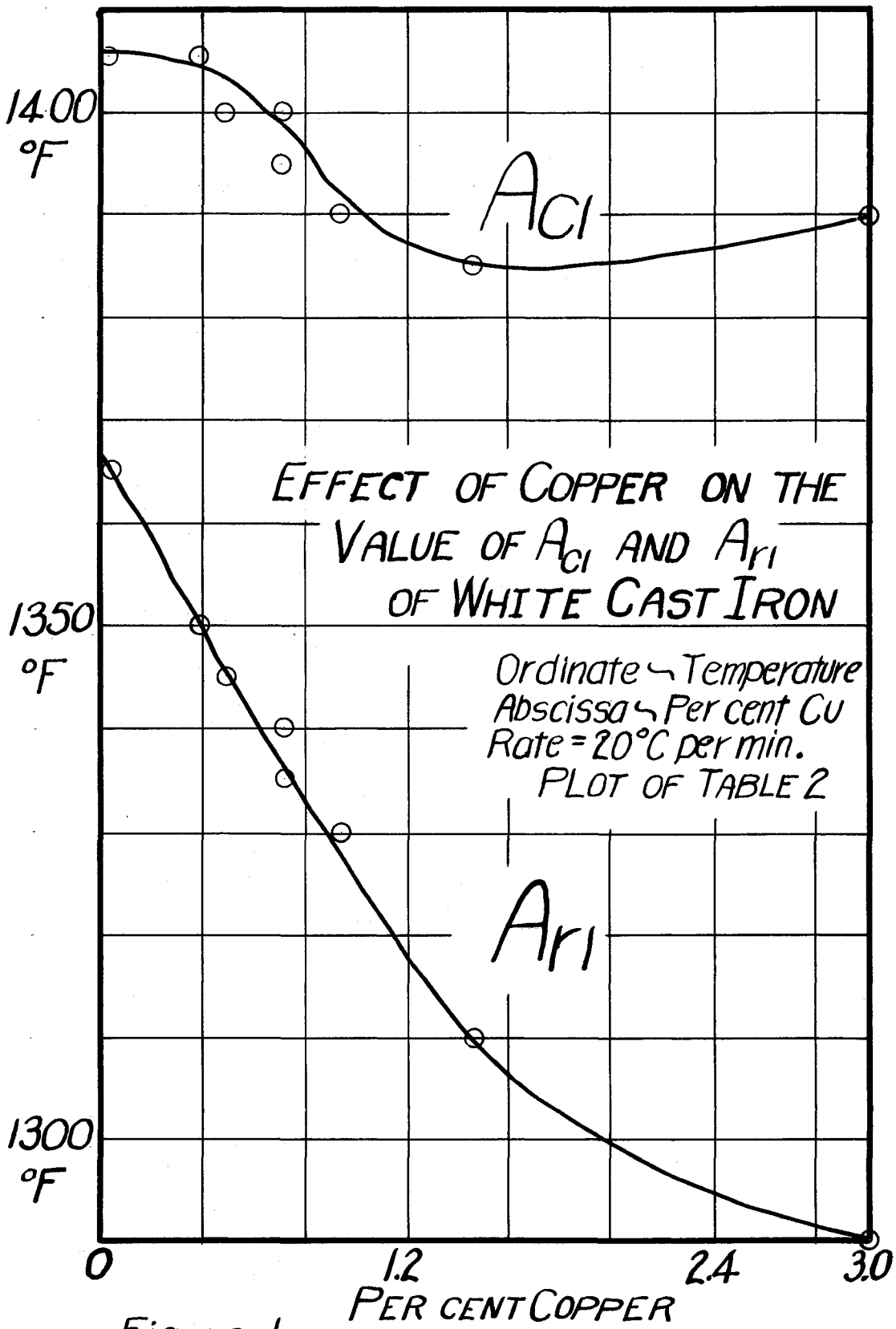

1400 °F
1350 °F
1300 °F
A_{C1}
A_{r1}
EFFECT OF COPPER ON THE VALUE OF A_{C1} AND A_{r1} OF WHITE CAST IRON
Ordinate ~ Temperature
Abscissa ~ Per cent Cu
Rate = 20°C per min.
PLOT OF TABLE 2
0
1.2
2.4
3.0
PER CENT COPPER

Figure 1.

about one-third as much as silicon raises it, and about one-half as much as nickel lowers the transformation temperature.

These results indicate that for white cast iron alloys, that might contain any amount of copper, it would be necessary to finish the two-cycle graphitization process at 1250°-1275°F instead of at 1300°F. This is necessary in order that there may not be any possibility of being above the critical temperature during the last step in malleabilization treatment. From these considerations it was decided to use 1275°F instead of 1300°F as the lower temperature in the trial heat treatment.

F. The Process of the Heat Treatment of White Cast Iron Alloys.

Methods and Apparatus. Any of the desired samples to be heat treated where placed in crucibles made from a capped iron pipe that was 2 inches in diameter and 4 inches long. To minimize oxidation, the samples were surrounded by a packing of coarse gas carbon. Usually these sample-containers were placed in the heat-treating furnace after the furnace had attained the desired temperature. The heat treatment was carried out in a vertic-

al Hump (Leeds and Northrup) electric resistance furnace. Temperature control was maintained through the use of a Leeds and Northrup automatic temperature recorder and regulator. Iron-constantin thermo-couples were used. The thermo-couples and recorder were frequently standardized by means of a standard platinum-rhodium thermo-couple and a student potentiometer. The rate of heating and cooling was controlled by regulating the potential across the resistance terminals. Whenever the sample-containers were removed, they were allowed to cool in the open air. Due to the presence of the carbon, 30 minutes of cooling were necessary before the samples could be handled. A marked sample of each alloy was collectively placed in the pipe sample-container.

The samples were small cylinders formed by breaking the cast bars into one-half to one-inch lengths. After the heat treatment, about one-eighth of an inch was ground off one end of each piece. Then the ground surface was polished and prepared for micro-examination according to Part III, section C.

Heat Treatment. In order to determine the time of decomposition of the free (massive) cementite, the "white-fracture" bars were heated at 1700°F (± 10°F) for two to eight hours. This heating was accomplished by placing one

sample container (containing a piece of each alloy) into the furnace every consecutive hour, until six have been added. After the last set of samples had been in the furnace for one hour, the samples were all cooled in the furnace for another hour, before they were removed. This brought the furnace temperature to 1450°F at the time of removal of the samples. The time of primary heat treatment was then the number of hours at 1700°F plus one hour of cooling.

The polished section of each heat-treated sample was examined for the presence of Fe_3C after etching with sodium picrate. The decomposition of the cementite was considered complete whenever all the massive Fe_3C boundaries had disappeared. The entire polished section was investigated, but any areas of shrink were not included in the examination. The time needed to cause the decomposition of the massive cementite is given in the following table. Photomicrographs (nital etch) of each sample, at the end of the decomposition, are given in the appendix.

The following treatment was used to determine the time necessary at 1275°F to completely graphitize the austinite into ferrite and carbon. Ten iron pipes, containing a piece of each alloy cast iron, were simultaneously placed in the furnace at 1700°F. The samples were main-

tained at 1700°F for ten hours. The furnace was then allowed to cool to 1450°F at the rate of 45°F to 50°F per hour. When temperature of 1450°F was reached the furnace and samples were cooled to 1275°F in ten minutes by opening the furnace. The temperature was maintained at 1275°F while a container was taken out 1,2,3,4,5,6,8, 10,17 hours after the furnace had reached this temperature.

After removing(by grinding) one-eighth inch from the end of each sample the polished sample was etched in 5% nital. The microsection was then examined for the presence of pearlite. The complete disappearance of all but traces of the lamellar pearlite structure was taken as evidence of complete graphitization. Areas of shrink and of marked segregation were omitted in the examination. The samples (number 11 to 14) high in copper etched (in nital) much more rapidly than other samples to a buff matrix that contained a multitude of spots through out the non-grained field. The pearlite in these samples was sorbitic instead of lamellar.

The time needed to complete the graphitization, of the copper bearing cast irons, at 1275°F is given in the following table 3. Photomicrographs of the completely annealed samples are included in the appendix.

IV RESULT OF EXPERIMENTAL HEAT TREATMENT OF WHITE CAST IRON ALLOYED WITH COPPER.

A. General Discussion and Results.

In Table 3 are shown the times necessary to complete the first and second stages of graphitization of the copper-bearing white cast irons. This table lists the time required at 1700°F and 1275°F, and does not include the time (five and one-half hours) consumed in cooling from the high temperature to the low temperature. The total time required for malleablization is the sum of the time at 1700°F and 1275°F plus five and one-half hours. The alloy marked "R" is the commercial white cast iron stock from which the other alloys were made.

A peculiar situation is brought up in reviewing the results of the graphitization tests. Data previously produced in this laboratory and results published by others indicate that the times listed herein for complete graphitization, of commercial white cast iron, are only a fraction of the times usually recorded. The writer has no explanation save that the composition of the cast iron, used in this work, shows a higher carbon and much lower manganese, sulfur and phosphorus than that used by others. There is also the general possibility of the presence of an undetermined chemical or physical factor.

TABLE 3.

TIMES NECESSARY FOR THE GRAPHITIZATION OF THE MASSIVE CEMENTITE AND OF THE EUTECTOID CEMENTITE

Alloy	Weight per cent Cu	C	Si	Time for decomposition of massive cementite at 1700°F	Time for graphitization of eutectoid carbide at 1275°F
11	4.47	2.33	0.81	6 hours	3 hours
12	3.10	2.52	0.84	5 "	3 "
13	2.26	2.49	0.81	5 "	3 "
14	1.94	2.54	0.81	5 "	3 "
15	1.37	2.52	0.82	6 "	3 "
37	1.03	2.60	0.85	7 "	4 "
17	0.76	2.59	0.85	7 "	4 "
18	0.60	2.60	0.84	7 "	4 "
19	0.40	2.60	0.84	7 "	4 "
20	0.17	2.60	0.87	8 "	5 "
21.	0.01	2.63	0.84	8 "	4 "
30	0.94	2.08	0.83	7 "	8 "
37	1.03	2.60	0.85	7 "	4 "
22	0.93	2.84	0.84	6 "	3 "
23	0.92	3.08	0.82	5 "	3 "
31	0.93	2.50	0.68	7 "	6 "
37	1.03	2.60	0.85	7 "	4 "
26	0.91	2.71	0.95	6 "	4 "
27	0.94	2.61	1.07	5 "	4 "
R	0.00	2.51	0.88	8 "	5 "

Note: The samples were cooled from 1700°F to 1450°F in five and one-half hours; from 1450°F to 1275°F in ten minutes.

B. Effect of Varying Copper Content Only.

The table 3 clearly shows that two per cent of copper shortens the total time for complete graphitization about 22%. The time needed to decompose the free carbide is lowered 27.5% by the presence of two per cent copper. The second malleabilization stage is shortened from 4 hours for the white cast iron (0.01% Cu) to 3 hours for the castings containing two per cent copper; this indicates a 25% shortening of the second stage. Above 2 per cent copper, there is no further change of time needed for either the primary or secondary stage. In fact 4.47 per cent copper seems to be deleterious to the decomposition of the free cementite. Furthermore the effect of copper on the malleabilizing process is greater between one and two per cent then from zero to one per cent.

C. Effect of Varying Carbon and Silicon Content for a Given Copper Content.

Carbon and silicon have the same influence in copper-bearing castings as in ordinary white cast iron; that is, the required time for both stages of graphitization is shortened by increasing the carbon or silicon content. Distinctly gray castings were produced (see Part III, section C) by 3.28 per cent carbon in presence of 0.94

per cent copper and 0.85 per cent silicon. Gray castings were also produced by 1.15 per cent silicon in the presence of 2.58 per cent carbon and 0.97 per cent copper. These castings were cast in wet sand flasks. Above 2.50 per cent, the effect of the increase of carbon percentage is three times as great as the same increase in copper content. Similarly, the increase of 0.10 per cent silicon (above .8%) is as effective as an increase of 0.60 per cent copper.

V THE MICROSTRUCTURE OF THE CAST, MASSIVE CEMENTITE-FREE AND GRAPHITIZED ALLOYS.

A. Influence of Composition on Structure.

The dendriditic structure, of the castings alloyed with copper, do not differ greatly from the structure of pure white cast iron. There seems to be less free cementite in the high copper alloys than in those containing just a little. This condition indicates that the eutectoid composition is raised in carbon. High power examination indicates that the cast alloys high in copper seem to contain sorbite or sorbito-pearlite instead of well laminated pearlite.

After the malleabilizing treatment, the high copper

castings show a greater grain refinement of the ferrite than found in ordinary malleable iron. The malleabilized samples containing above one per cent copper yield a ferrite that etches much more readily than pure ferrite, and that seems to contain a multitude of small spots, that are just resolved by a high-power microscope. The copper content does not seems to change the kind and size of temper carbon spots.

B. Photomicrographs of Typical Sections.

Photographs are given, in the Appendix, of typical sections of the various alloys as cast, after decomposition. Alloy 15 has been chosen to serve as an example to show how the process of heat treatment progressed. All photographs are at a magnification of 225 diameters.

VI CONCLUSIONS AND SUMMARY.

1. A study has been made of the influence of copper on the position of the A_{321} point of a white cast iron suitable for malleabilizing. This critical temperature is lowered 45°F (with a marked increase in the temperature hysteresis) by three per cent of copper.

2. The influence of copper on the malleabilizing tendency, of white cast iron, has been studied quantitatively. The times needed to effect the decomposition of the massive-cementite (primary graphitization) and of the pearlite-cementite (secondary graphitization) have been determined for white cast iron containing varying amounts of copper, carbon and silicon. This research indicates that copper shortens the time needed to decompose the carbide in both stages of graphitization.

3. Photomicrographs are included (in an appendix) showing the influence of copper on the structure of the cast, massive cementite-free and malleabilized white cast iron alloys. These pictures indicate the copper promotes grain refinement of the malleabilized alloys, and that copper raises the carbon content of the iron-copper-carbon eutectoid.

VII BIBLIOGRAPHY

1. --Anon. Alloy Cast Iron and High Strength Cast Iron. 1st. Communications New Intern. Assoc. Testing Materials, 1930A, 35-48.

2. --Ballay, M. Recherches sur quelques fontes au nickel et au cuivre.
Revue de Métallurgie, Mémoires, 26, 538-53 (1929).

3. --Bauer, O., Vogel, O. and Holthaus, C. Corrosion Resistance of Structural Steel (with Small Additions of Copper).
Metals and Alloys, 1, 890-2 (1930).

4. --Bauer, O. and Sieglerschmidt, H. Der Einfluss kleiner Zusätze von Kupfer und Nickel auf die Wärmeausdehnung und auf das Wachsen des Gusseisens.
Mitt. deut. Materialprüfungsanstalten, Sonderheft, 9, 63-7 (1929).

5. --Blackwood, P.W. Metallurgical Aspects of Cast Iron.
Trans. Am. Soc. Steel Treating, 13, 1023-38 (1928).

6. --Bremer, E. Composition, Temperature, Time and Control Govern the Short Anneal.
Foundry, 59, 32-4 (1931).

7. --Breuil, P. Cuivre Aciers.
Compt. rend. acad. des sciences, 142, 1421-24 (1906); 143, 377-80 (1906).

8. --Buckholtz, H. and Koster, W. Ueber die Anlasshartung Kupferlegeierten Stahles.
Stahl und Eisen, 50, 687-95 (1930).

9. --Clevenger, G.H. and Ray, B. Influence of Copper on the Physical Properties of Steel.
Trans. Am. Inst. of Min. and Met. Eng., 47, 523-61, 566-8 (1913).

10. --Coleman, W.B. Carbon Characteristics of Copper-bearing Pig Iron.
Am. Inst. Min. and Met. Eng. Tech. Publ., 1927, No. 11, 12-13.

11. --Gilmore, L.E. Effect of Various Elements on Malleable Castings.
Trans. Am. Foundrymens Assoc., 36, 287-92 (1928).

12. --Godefroid, M. La fonte malleable.
Revue fonderie moderne, 23, 243-51 (1929).

13. --Good, R. C. Effects of Alloys in Cast Iron.
Trans. and Bull. Am. Foundrymen's Assoc., 1,
15-28 (1930).

14. --Guertler, W. Influence of Copper on Iron and Steel.
Norges Geol. Undersokelse, #117, 19-25 (1923).

15. --Guillet, L. and Ballay, M. Les Fontes Speciales.
Bulletin De L'Association Technique de Fonderie,
6, 582-97 (1932).

16. --Hague. A. and Turner, T. Influence of Silicon on
Pure Cast Iron.
J. Iron and Steel Inst., 82, 72-93 (1910).

17. --Hamasumi, M. Distribution of Graphite in Cast Iron
and Influence of Other Elements on its Strength.
Sci. Rept. of Tohoku Imp. Univ., Series I, 13, 133-78
(1924).

18. --Hayashi, K. Effect of Copper on the Properties
of Steel. From C. A., 23, 2138 (1929).
Bull. Ordnance, 6, 401-68 (1928). Original not read.

19. --Hayes, A. and Diedericks, W. J. The Mechanism for the
Graphitization of White Cast Iron and its Applica-
tion to the Malleablizing Process.
Iowa State College Eng. Expt. Sta., Bull. #71 (1924).

20. --Hayes, A. and Diedericks, W. J. Malleabilizing Using
Short Annealing Periods.
Trans. Am. Soc. Steel Treating, 6, 491-8 (1924).

21. --Hotari, A. Effect of Copper on Cast Iron.
Bull. College Eng. Kyushu Imp. Univ., 3, 169-80 (1928)
From C. A., 23, 2136 (1929). Original not read.

22. --Hurst, J. E. Metallurgy of Cast Iron, 138-41.
I. Pittman and Sons (1926).

23. --Hurst, J. E. The Influence of Copper in Cast Iron.
Iron and Steel Ind., 5, 319-24, 363-8 (1932).

24. --Ishiwara, I., Yonekura, T. and Ishigaki, T. Ternary Diagram of Iron-Carbon-Copper System. Sci. Rept. Tohoku Imp. Univ., 15, 81-114 (1926).

25. --Kinnear, H. B. One Per Cent Copper Steel has Desirable Properties. Iron Age, 128, 820-24, 898-9 (1931).

26. --Kodama, S. Influence of Copper on Mild Steel. Seitetsu Kenkyu (J. Study of Ferrous Met.), 8, 25-39 (1928).

27. --Musatti, I. and Calbiani, G. Special Steels. From C. A., 25, 3297 (1931). Original not read. Metallurgia Italiana, 22, 649-69 (1930).

28. --Lipin, W. Der Einfluss des Kupfers auf Eisen. Stahl und Eisen, 20, 536-41, 583-90 (1900).

29. --Mikailof, P. B. Resistance to Corrosion of Gray Iron containing Copper. From C. A., 22, 376 (1928).(Original Viestn. Metallspromychl., #9-10, 5-21 (1926). not read)

30. --Nehl, F. Ueber die mechanischen Eigenschaften kupferlegierter Stahle unter besonderer Berucksichtigung der Warmebehandlung. Stahl und Eisen, 50, 678-86 (1930).

31. --Norbury, A. L. Factors Influencing the Hardness of Cast Iron. From C. A., 25, 178 (1931). Die Metallborse, 20, 1939-40 (1930). Original not read.

32. --Norbury, A. L. The Influence of Various Additions on the Properties of Gray Cast Iron. From Metals and Alloys, 3, MA226 (1932). Original not read. Die Metallborse, 21, 240-1 (1931).

33. --Persoz, L. Action of Principle Elements on Steel, Foundry Trade Journal, 40, 181-2 (1929).

34. --Pfannenschmidt, C. The Effect of Copper on Gray Cast Iron. From C. A., 23, 2681 (1929). Die Giesserei, 16, 179-82 (1929). Original not read.

35. --Phillips, M. Malleablizing of White Cast Iron. Mining and Metallurgy, 3, 31-32, January (1922). Original in Am. Inst. Min. and Met. Eng. Trans., No. 1178, 1922, 23 pp.

36. --Reed, E.L. Influence of Special Elements on the Carbon Content of the Iron-Carbon Eutectoid. Trans. Am. Soc. Steel Treating, 20, #2, 115-73 (1932).

37. --Sahmen, R. Eisen-Kupfer-Legierungen. Zeitsch. Anorg. Chem., 57, 1-33 (1908).

38. --Sawamura, H. Influence of Various Elements on the Graphitization of Iron Carbide. Memoirs College of Engr. Kyoto Imp. Univ., 4, 159-260 (1926).

39. --Sawamura, H. Various Methods to Favor the Graphitization of Cast Iron. Proc. World Eng. Cong. Tokyo, 34, 307-57 (1931).

40. --Schwartz, H.A. Recent Progress in Malleable Iron. Metals and Alloys, 2, 143-9 (1931).

41. --Schwartz, H.A. Some Theories of Graphitization. Foundry, 56, 871-3, (1929).

42. --Smalley, O. Effect of Special Elements in Cast Iron. Foundry Trade Journal, 27, 3-6 (1918)

43. --Smith, E.K. and Aufderhaar, H.O. Twenty Alloys of Cast Iron. Iron Age, 126, 1583-7, 1688-93 (1930).

44. --Stogoff, A.F. and Messkin, W.S. Kupferstahl mit hohen Kohlenstoffgehalt. Archiv. für das Eisenhuttenwesen, 2, 331-333 (1928).

45. --Stutzman, M.J. Effect of Nickel upon the Stability of Iron Carbide. Metals and Alloys, 4, 55-8 (1933).

46. --Warwick, C.L. Symposium on Malleable Iron Castings. Proc. Amer. Soc. Testing Mat., 31, Pt. 2, 317-87 (1931).

47. --Wedding, H. Kupfer im Eisen. Stahl und Eisen, 26, 1444-7, 1493-5 (1906).

48. --Wever, F. Ueber den Einfluss von Legierungselementen auf die polymorphen Unwandlungen des Eisens. Mitt. Kaiser-Wilhelm Inst. Eisenforschung zu Dusseldorf, 13, 183-6 (1931).

49. --Wust, F. Ueber die Abhängigkeit der Graphitausscheidung von der Anwesenheit fremdes Elemente im Roheisen. Metallurgie, 3, 169-75, 201-5 (1906).

50. --Schwartz, H.A. and Guiler, G.M. Chemical Elements Inhibiting Graphitization. Trans. Am. Foundrymen's Assoc., 33, 639-45 (1925).

51. --Everest, A.B. Alloy Cast Irons. Foundry Trade Journal, 40, 45-8 (1929).

52. --Kikuta, T. On the Malleable Cast Iron and the Mechanism of its Graphitization. Sci. Rept. of the Tohuku Imp. Univ., 15, #2, 115-55 (1926).

VIII APPENDIX.

Key to symbols under photomicrographs:

A number followed by no other number, or letter, signifies the "as cast" sample of the alloy listed under Part III, section C (Table 1).

When the number (that of the alloy in Table 1) is followed by the letter H or L, the alloy has been heat-treated. A number after the letter H denotes the number of hours heated at the primary annealing temperature (1700°F). The number following L denotes the actual number of hours at the lower annealing temperature (1275°F). For details of the heat-treatment see Part III, section F.

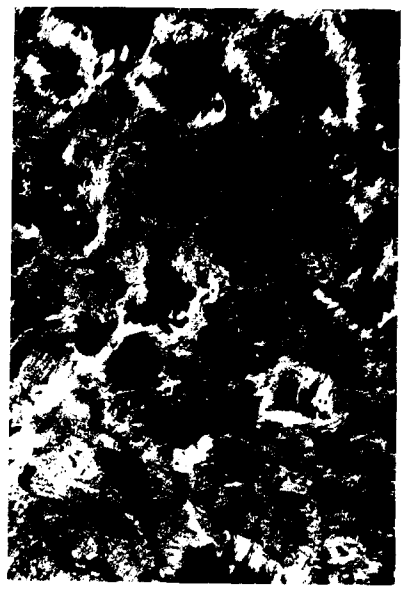
11
Nital Etch 225X

11H6
Nital Etch 225X

11L3
Nital Etch 225X

24
Nital Etch 225X

12
Nital Etch 225X



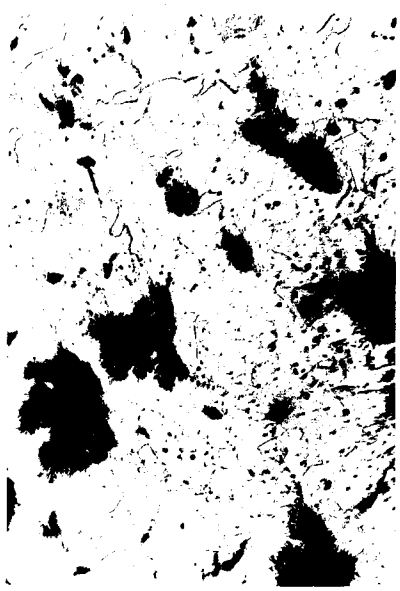
12H5
Nital Etch 225X

12L3
Nital Etch 225X

25
Nital Etch 225X

13
Nital Etch 225X

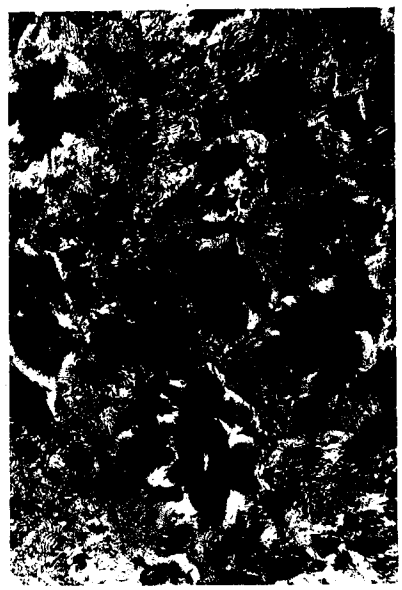
13H5
Nital Etch 225X



13L3
Nital Etch 225X

28
Nital Etch 225X

14
Nital Etch 225X



14H5
Nital Etch 225X

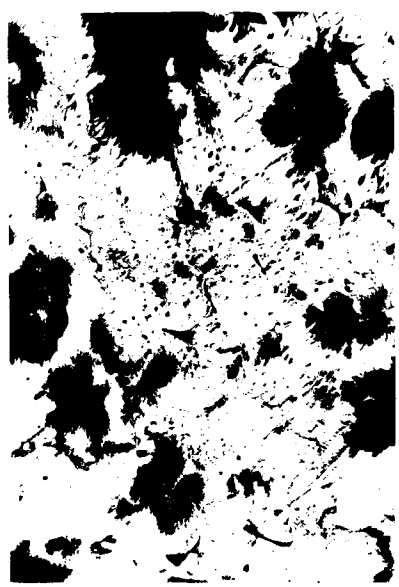
14L3
Nital Etch 225X

29
Nital Etch 225X

15
Nital Etch 225X

15H6
Nital Etch 225X

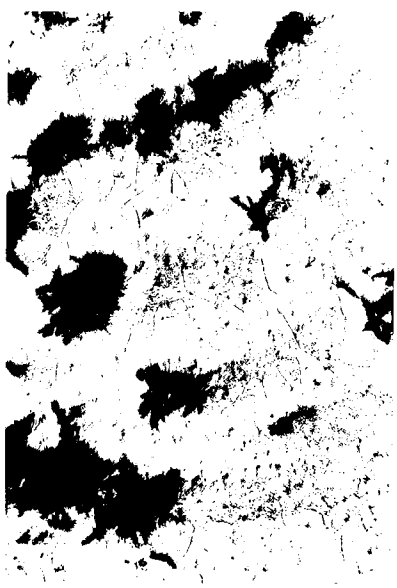
15L3
Nital Etch 225X



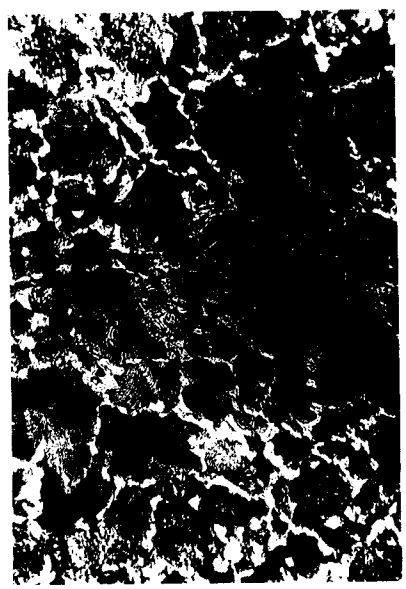
15H3
Picrate Etch 225X

37
Nital Etch 225X

37H7
Nital Etch 225X



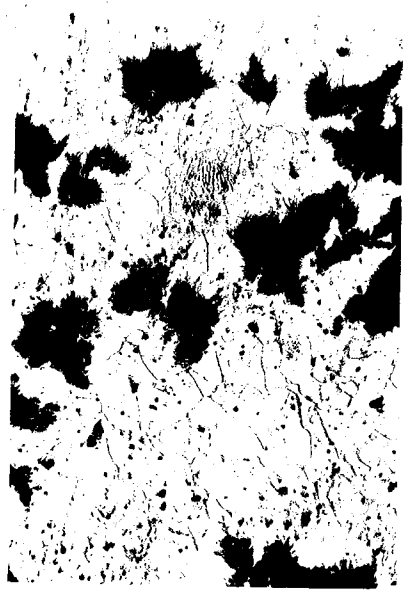
37L4
Nital Etch 225X



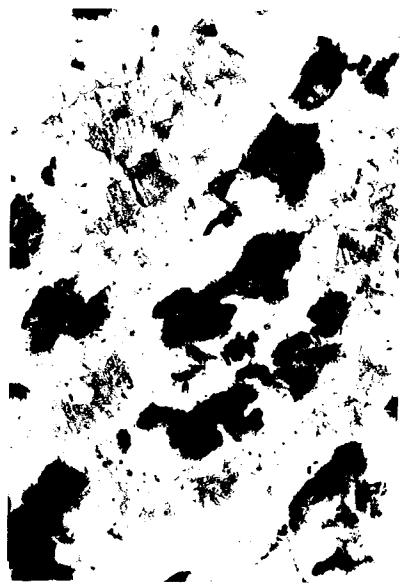
15L0
Nital Etch 225X

17
Nital Etch 225X

17H7
Nital Etch 225X



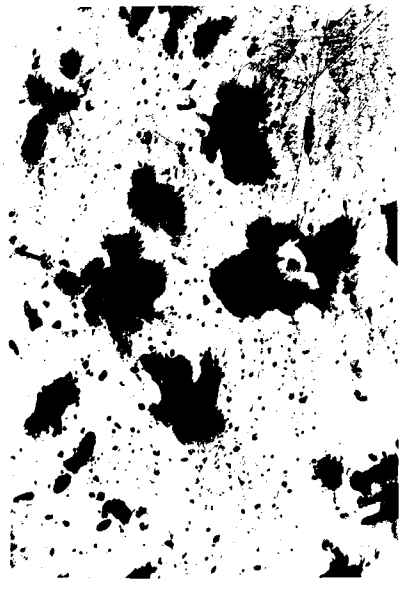
17L4
Nital Etch 225X



15L2
Nital Etch 225X

18
Nital Etch 225X

18H7
Nital Etch 225X

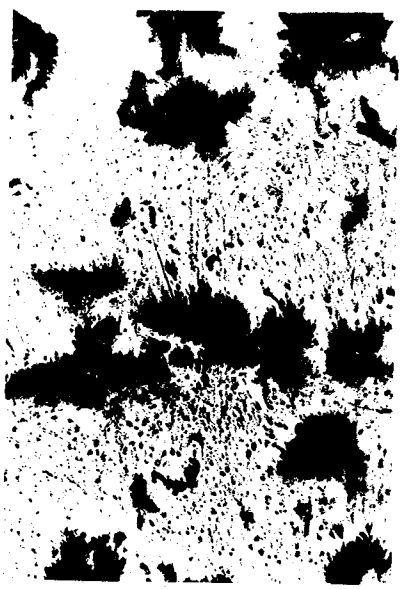


18L4
Nital Etch 225X

R
Nital Etch 225X

19
Nital Etch 325X

19H7
Nital Etch 225X



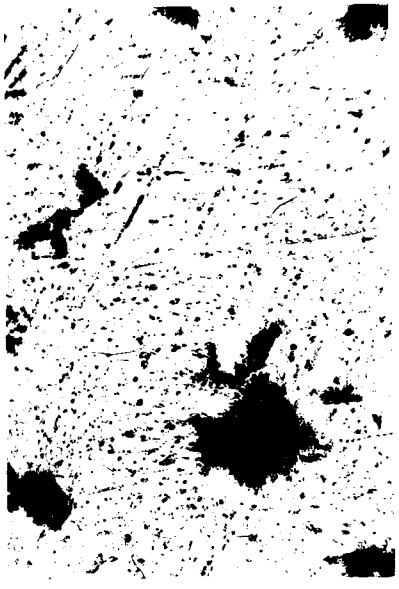
19L4
Nital Etch 225X

RH8
Nital Etch 225X

20
Nital Etch 225X

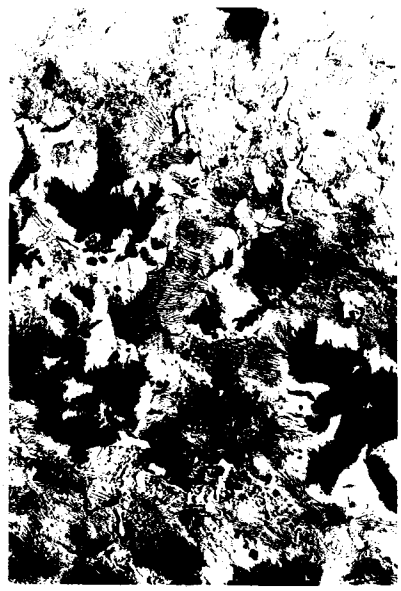
20H8
Nital Etch 225X

20L5
Nital Etch 225X



RL5
Nital Etch 225X

21
Nital Etch 225X



21H8
Nital Etch 225X

21L4
Nital Etch 225X

12L17
Nital Etch 225X

22
Nital Etch 225X

23
Nital Etch 225X

26
Nital Etch 225X

27
Nital Etch 225X

22H6
Nital Etch 225X

23H5
Nital Etch 225X

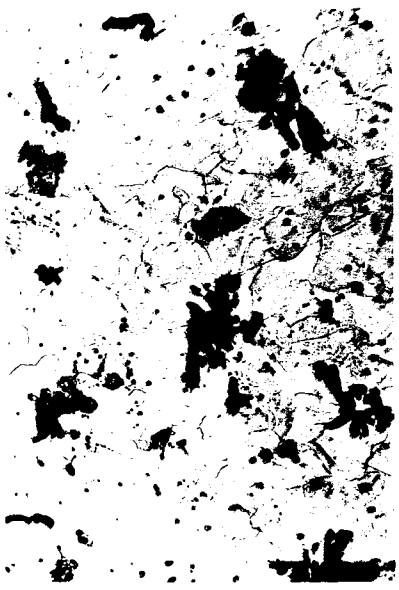
26H6
Nital Etch 225X

27H5
Nital Etch 225X

22L3
Nital Etch 225X

23L3
Nital Etch 225X

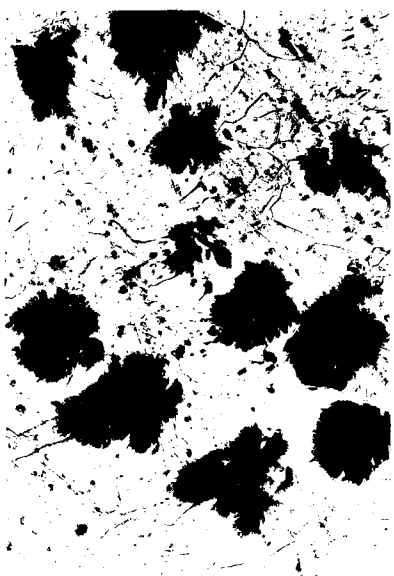
26L4
Nital Etch 225X



27L4
Nital Etch 225X

30
Nital Etch 225X

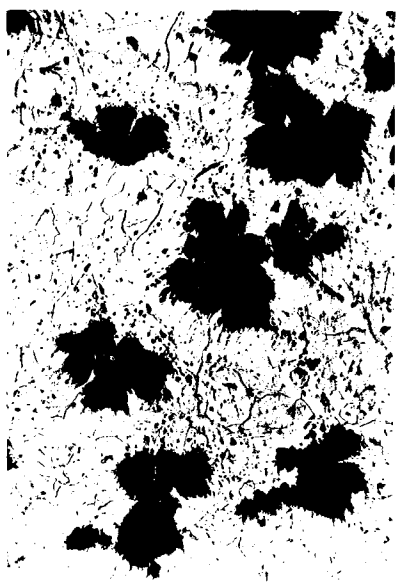
30H7
Nital Etch 225X



30L8
Nital Etch 225X

31
Nital Etch 225X

31H7
Nital Etch 225X



31L6
Nital Etch 225X