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THE EFFECTS OF MOLYBDENUM AND CHROMIUM ON THE MALLEABLIZATION OF WHITE CAST IRON

By

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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

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The writer takes this means of expressing his sincere thanks to Dr. W.H.Jennings who suggested and directed this investigation for his assistance and encouragement during the progress of the work and in the preparation of this thesis.

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I. INTRODUCTION

During the last decade the qualities demanded in cast irons have continually become more exacting and severe. The manufacturer has been called upon to produce a material with definite improvements in many physical properties such as tensile strength, toughness, ductility, hardness and machinability. Some progress has been made by the judicious use of certain alloying elements and the lowering of the time required for the annealing cycle.

During 1923-1924 an intensive program was initiated in this laboratory under the direction of Professor Anson Hayes with the view of a thorough investigation of the various factors that were involved in the production of malleable iron from white cast iron by a shortened annealing cycle. But following the initial work of Hayes and Diederichs (1), Hayes and Flanders (2) and Hayes, Henderson and Bessmer (3), it became evident that a complete study of the physical factors and the chemical factors that affect graphitization was essential. Since that time these investigations have continued under the direction of Professor Hayes and through his successor, Professor W.H.Jennings, Jr.

In spite of the mass of contributions to the literature of cast iron, very little definite information is available concerning the effect of some of the elements on the rates of decomposition of iron carbide, Fe_3C, in the preparation of malleable iron from commercial white cast iron with its lower silicon and carbon content as compared to the gray cast variety. This is particularily applicable to molybdenum where most of the information concerns gray cast iron.

The purpose of the investigation, reported in this paper, was to study the effects of molybdenum, chromium and various combinations of these two elements on the decomposition of iron carbide, Fe_3C, in white cast iron.

II. REVIEW OF THE LITERATURE

A. General Effect of Added Elements on Graphitization and Physical Properties.

It is sometimes difficult to draw definite conclusions concerning the effect of special elements on the properties of any form of cast iron. This is due to the many factors that must be considered as affecting the final condition of the product. Cast iron cannot be considered as a simple alloy of iron and carbon. It is probably a conglomerate, not of simple alloys and solutions, but of elements, compounds and solid solutions. The properties of cast iron are influenced by many factors and one of the most important of these factors is the effect of the addition of special elements in small quantities.

In 1925 Schwartz and Guiler (4) reported the results of an investigation of the effects of thirty-four different elements on the graphitization of cast iron. They report the following elements as showing positive deleterious effect on the process of malleablization:

Antimony
Boron
Cerium°
Chromium
Molybdenum
Selenium
Tellurium
Tin

°Including Lanthanum, Neodymium and Praesodymium.

In view of the fact that these data are only qualitative, no critical conclusions may be drawn from their study.

Probably the most recent work on the effect of alloying elements on the rates of graphitization is the report of Smith and Aufderhaar (5) in 1930 on their investigation of gray cast iron. The following conclusions may be drawn from a study of their results:

Aluminum produces a softening effect up to 0.1 per cent. From 0.1 to 0.5 per cent there is a continual separation of free graphite. Above 0.5 per cent there is a decrease of graphite and at 0.75 per cent there is a definite conversion of the gray type into white iron.

Arsenic shows no inhibiting effect up to 0.1 per cent.

Boron, as high as 0.4 per cent, produces an increased hardness and at 0.8 per cent the casting becomes very brittle.

Calcium has no effect up to 0.2 per cent.

Chromium, in any amount, increases the carbide content and therefore decreases graphitization and increases hardness and shrinkage. Above 0.5 per cent the increased carbide content results in pronounced machining difficulties. Some additions of nickel or silicon may serve to decrease these harmful effects.

Cobalt shows little positive effect up to 2 per cent.

Copper shows only a slight effect on graphitization up to 2 per cent but increases the tensile strength and Brinnell hardness to a slight extent. The corrosion resisting properties are improved, showing a maximum effect at 1 per cent copper content.

Molybdenum acts as a strengthener and hardener of gray cast iron. The tensile strength is increased up to 1.55 per cent. The rates of graphitization are lowered.

Nickel produces a general improvement and very good results are obtained by a combination of nickel and chromium. Tensile strength is increased and the casting becomes more machinable and resistant to high temperatures. The presence of nickel serves to partially counteract the harmful effects of chromium on the graphitization process.

Silicon is present in all cast irons, usually from 1.0 to 2.5 per cent. Five per cent silicon produces a very brittle casting which is quite resistant to corrosion. It is of interest to note that a percentage of 9 to 10 per cent gives a product which corrodes very readily. At 11 to 14 per cent the resistance to corrosion is again noted and this property reaches a maximum at 14.5 to 17.0 per cent of silicon. The presence of silicon promotes the graphitization.

Vanadium in the amount of 1 per cent produces a 60 per cent increase in tensile strength and increases the Brinnell hardness. This element shows a deleterious effect upon graphitization. It favors carbide formation.

Piwowarsky (6) made a study of the effect of various elements by employing a Swedish Cast Iron base with 4.01 per cent total carbon. Three series, according to the silicon content, were prepared for study.

Series I	Series II	Series III
1 per cent silicon.	1.75 per cent silicon.	2.75 per cent silicon.

Piwowarsky summarizes his results as follows:

Aluminum (0.2 to 0.8 per cent) increases the bending strength and impact value 25 per cent in Series I and II but only slightly in Series III. Hardness and resistance to compression decreases in all series. The graphite particles are somewhat refined.

Titanium behaves similar to aluminum by favoring graphite formation in a refined form. This element probably produces non-metallic compounds in the cast iron.

Nickel (0.5 to 1.0 per cent) resulted in an improvement of mechanical properties as much as 20 to 30 per cent. This may be due in part to the formation of solid solutions. Graphitization is promoted.

Chromium produces no appreciable improvements in mechanical properties when used alone. But when combined with nickel it improves the mechanical properties as much as 60 to 80 per cent in some cases. In Series I the most optimum results were obtained with 0.5 per cent chromium and 0.2 per cent nickel. In Series II and III the best results were obtained by increasing the nickel content to 0.4 - 0.8 per cent.

Vanadium favors carbide formation and increases the hardness, bending strength, toughness, density and resistance to wear. The improvement started suddenly with a 0.5 per cent vanadium content and was more pronounced in Series I and II than in Series III.

Tungsten improves all the mechanical properties. This fact is probably due to a series of solid solutions of tungsten ferrite. The most beneficial results were obtained with a tungsten content of 0.5 per cent.

Molybdenum produces a similar influence to that of tungsten. This may be initially noted at a content of about 0.5 per cent molybdenum. Graphitization is inhibited to an appreciable extent but not completely stopped.

Manganese, sulfur and phosphorus, in the amounts as found in the technical iron that was used, produced favorable effects on the properties of the base material, and in their presence, nickel and chromium had a greater effect than on pure iron. Phosphorus, above 0.7 to 1.0 per cent, indicated a deleterious effect on the castings. Sulfur, in the absence of manganese, gave injurious results to the properties of the cast iron.

Everest (7) has offered a summary of the effects of the most commonly available elements on the decomposition of iron carbide as follows:

Group I

Promotes Graphitization.

Silicon
Aluminum
Nickel
Phosphorus
(below 0.8 per cent)

Group II

Either Retards the Rate or Completely Stops Graphitization.

Manganese
Sulfur
Chromium
Molybdenum
Tungsten
Tantalum
Selenium
Tellurium
Tin
Antimony
Titanium
Vanadium
Phosphorus
(above 0.8 per cent)

Copper apparently produces no effect either way up to 2 per cent.

Many of these conclusions have been confirmed in a general way by the following investigators:

A.P.Hoelscher (8), on the effect of manganese and sulfur on the rate of graphitization in white cast iron.

M.J.Stutzman (9), on the effect of nickel on the graphitization rates in white cast iron.

C.D.Foulke (10), on the effect of chromium on the rates of graphitization of white cast iron with a variable silicon content.

F.L.Coonan (11), on the effect of molybdenum in the decomposition of iron carbide in cast iron of a composition comparable to that demanded for the white variety.

Franz Roll (12), on the influence of various elements on the stability of iron carbide in cast iron.

R.C.Good (13), on the general effect of various elements on the stability of cementite in cast iron.

Jean Challansonnet (14) reports the effects of nickel in combination with vanadium and with molybdenum. His results confirm those that have been previously noted.

One of the most informative contributions to the literature of cast iron is a general resume of the known facts concerning this substance as reported in a general article by G.M.Enos (15).

B. Phase Diagrams of Iron-Molybdenum-Carbon Systems.

A search of the literature has failed to reveal any information concerning the nature of the binary equilibrium diagram for carbon and molybdenum nor is any mention made of the possible ternary diagram for the iron-molybdenum-carbon system.

The most recent information concerning the iron-molybdenum system is the diagram proposed by Takei and Murakami (16). This diagram is reproduced in Figure 1 on page 12. This diagram was obtained by microscopic investigation, the electric resistance method and by dilatomeric and magnetic analysis. In this system, two

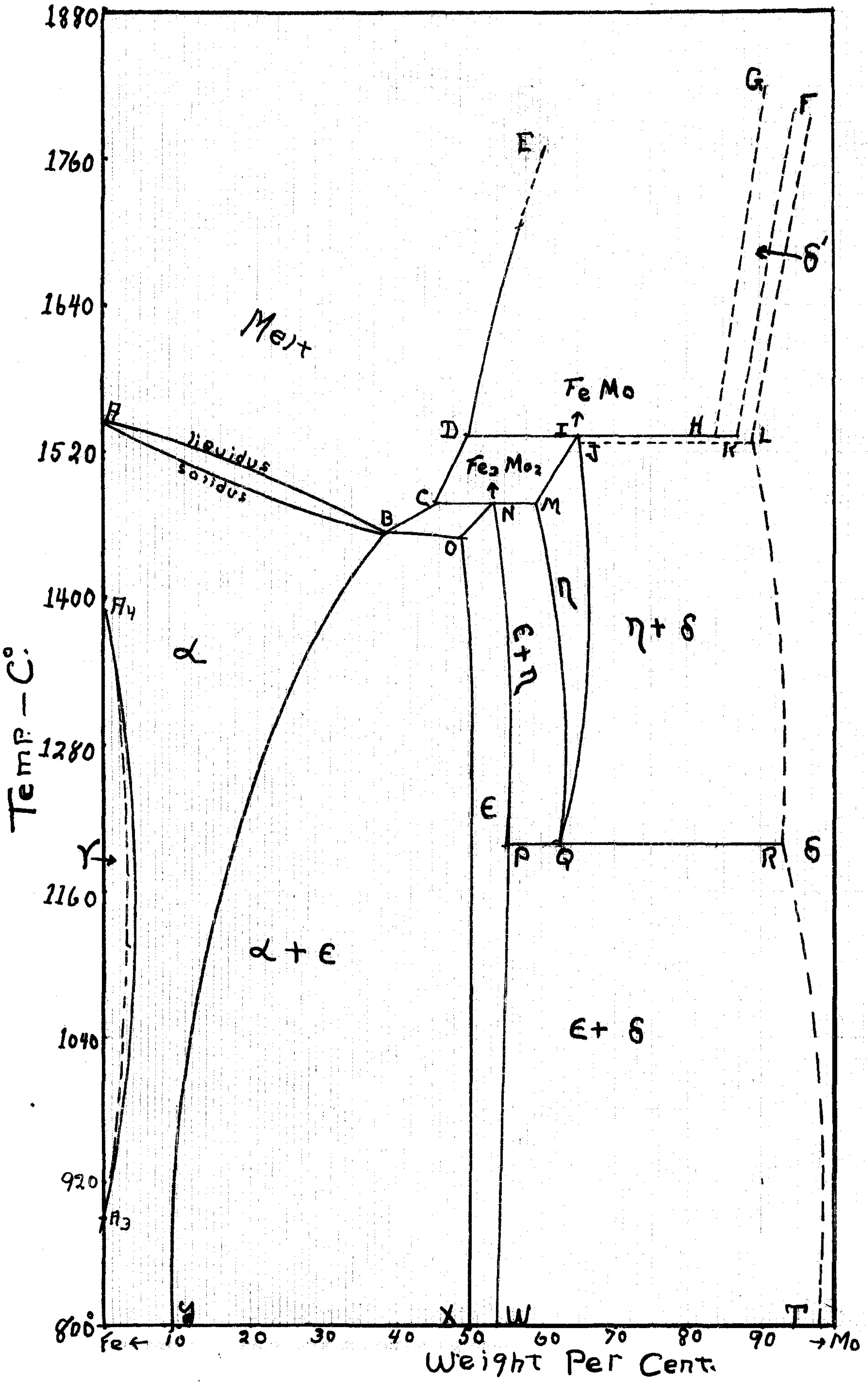

1880
1760
1640
1520
1400
1280
1160
1040
920
800°
Temp – C°
Melt
E
G
F
δ'
Fe Mo
A
D
I
H
J
K
L
liquidus
solidus
Fe3 Mo2
C
N
M
B
O
A4
α
η
η + δ
ε + η
ε
P
Q
R
δ
γ
α + ε
ε + δ
A3
y
X
W
T
Fe ←
10
20
30
40
50
60
70
80
90
→ Mo
Weight Per Cent

FIGURE I

intermetallic phases exist, epsilon (ϵ) and eta (η), consisting of the compounds Fe_3Mo_2 and FeMo respectively. These phases are formed by peritectic reactions, melt + eta = epsilon, and melt + delta' (δ') = eta. The former forms a eutectic with alpha iron, dissolving molybdenum at 1440°C in the range of composition of about 38 to 50 per cent of molybdenum. The latter decomposes to the epsilon phase and molybdenum dissolves iron at about 1180°C. The solubility of molybdenum in alpha iron is about 38 per cent at 1440°C and decreases to 6 per cent at room temperature. The A_2 point of the alpha solid solution is slightly lowered as the molybdenum content increases, while the A_3 point rapidly rises to 3 per cent of molybdenum. In alloys containing more than 63 per cent of molybdenum, a eutectoid is found, consisting of the eta-phase and molybdenum dissolving in iron. Thus this diagram shows six solid phases, viz., alpha (α), gamma (γ), epsilon (ϵ), eta (η), delta (δ) and delta' (δ').

The iron-molybdenum diagram of W.P.Sykes (17) is very similar to the one just described, the most important difference being in its failure to despict the formation of the eta-phase, FeMo. While a complete consideration of the entire iron-molybdenum diagram would be of theoretical interest, the present investigation is only concerned with molybdenum percentages no higher than 5 per cent. This covers only the alpha and gamma field and a portion of the liquid field.

C. Cast Irons Containing Molybdenum and Chromium.

1. Molybdenum.

E.K.Smith and Aufderhaar (18) prepared forty melts using a gray cast iron base and a molybdenum content of 0.65, 1.77 and 3.10 per cent. Increasing molybdenum content showed a tendency for decreasing graphitic carbon and approached the carbon condition of white cast iron. No carefully studied annealing tests were made. They found that the Brinnell hardness was increased with an increasing molybdenum content. The tensile strength was also increased but with decreasing properties of good machinability.

Musatti and Calbiani (19) made a complete study of the effects of molybdenum on the properties of malleable iron. This was prepared from a special cast iron with a carbon content near that usually found in white cast iron but with a silicon content from two to three times greater than that of the usual white cast variety. While it is of interest to note that they obtained an improvement of the physical properties through the addition of molybdenum, no definite conclusions may be drawn in connection with the ultimate results of the investigation that are reported in this paper.

The work of Coonan (11) approaches nearer to the field of investigation, that is reported in this paper, than any other report that is available. However, Coonan's work is incomplete and covers a molybdenum content no higher than 1 per cent. He annealed sample bars, with a molybdenum content ranging from zero to 1 per cent, for an overall period of 140 hours at a temperature of 1550°F. This included the time of heating and cooling. No information is given concerning the rate of cooling nor the time at the maximum temperature. The cast iron contained from 2.30 to 2.80 per cent carbon and from 0.60 to 0.80 per cent silicon. The physical properties, as reported in Coonan's paper, are reproduced below in Table I.

TABLE I

Sample No.	Per Cent Mo	Yield Point lbs/sq. in.	Tensile Strength lbs/sq. in:	Elongation in 2 inch per cent.
1	0.00	31600	44200	7.5
2	0.25	35100	48500	8.0
3	0.50	35100	54300	8.5
4	0.75	40200	58300	8.0
5	1.00	44000	60000	7.0

There is a decided increase in yield point and in tensile strength but the ductility reaches a maximum with 0.5 per cent molybdenum and decreases again as the molybdenum content is increased to 1 per cent.

Coonan failed to determine the conditions for the destruction of the pearlitic portion of his alloys and all his specimens which contain molybdenum show the presence of pearlite. His conclusion that molybdenum retards the decomposition of cementite into temper carbon is justified from an examination of the photomicrographs that are exhibited.

Murakami and Takei (29) report that molybdenum lowers the critical points as a result of their study of some special molybdenum steels. However, their results were quite dependent upon the rate of cooling and the maximum heating temperature.

Smith and Aufderhaar (18), while working with alloys of an approximate gray iron composition, report that there is a tendency for molybdenum to convert the graphite into a nodular form and to refine the pearlitic structure approaching a pearlite-sorbite composition. They attribute this action to the presence of molybdenum in the form of a solid solution in ferrite. The material is toughened and the grain growth is inhibited. The increased hardness is not due to carbide formation but to this solid solution.

So in general, we may expect that molybdenum will increase the toughness, tensile strength and the hardness of cast irons. It inhibits the decomposition of iron carbide but tends to convert flaky carbon into nodular form. The grain structures of pearlite and ferrite are refined through the presence of molybdenum.

2. Chromium.

A general resume of the iron-chromium cast irons, as well as the constitutional diagrams of the iron-chromium-carbon alloys, has been given by Foulke (11) in his report of an investigation concerning the effect of chromium on the decomposition of iron carbide with varying silicon content but with a carbon content comparable to that usually found in white cast iron. Foulke states in his conclusions that chromium produces a marked stabilizing effect on the combined carbon both in the eutectoid and in the massive cementite. This conclusion is reached from the abnormally long time that is required for the graphitization of white cast iron containing chromium up to 0.5 per cent.

Chromium seems to show a tendency for carbide formation. This is indicated from the report of Raffo and Sambucety (21) on the separation and identification of a double carbide of chromium and iron in a colloidal state. They ascribe the probable formula as Fe_4C_3,Cr_3C_2.

In general, chromium may be considered to impart hardness and brittleness to malleable iron through its stabilizing effect upon the carbide content.

D. Physical Factors Which Affect Rates of Graphitization.

The mechanism and velocity of graphitization is vitally affected by a number of critical physical factors such as the pouring temperature, rate of cooling in the moulds, prequenching treatment and the temperature and time of annealing.

Kikuta (22) has made a study of the effects of the temperature of pouring upon the rate of graphitization during the primary stage for a cast iron containing 2.70 per cent carbon and 0.98 per cent silicon. He found that a higher pouring temperature produced a casting that required a longer period to complete the primary stage of graphitization than does a casting poured at a lower temperature. The pouring temperature used varied from 1300°C to 1550°C. Kikuta furthur shows that a hot mould produces an alloy in which both the primary and secondary stages of graphitization are slower than when cast in a cold mould. The temperatures employed ranged from that of green sand at room temperature to a temperature of 1000°C. This alloy contained 2.17 per cent carbon and 1.07 per cent silicon.

Using an alloy containing 2.72 per cent carbon and 1.29 per cent silicon, Kikuta (22) studied the effect of annealing temperatures on both the primary and secondary stages of graphitization. For the primary stage, using a temperature range from 870.5 to 970.5°C, it was found that the higher temperature produced a more rapid rate of graphitization. The secondary stage was studied between the temperatures of 650 and 730°C and the graphitization was more complete with the higher temperature.

These results of Kikuta as well as those of Hayes and Flanders (2) and White (23) indicate that the logarithm of the time required at the high temperature for the graphitization of the free carbide, when plotted against the temperature, produces a straight line.

Moldenke (24) states that the recent discovery of the ability of cast iron, melted under the ordinary conditions of super-heating, to retain minute particles of graphite in suspension, indicates the probability of their action as nuclei for the subsequent growth to large crystals of graphite as the molten metal freezes. If this molten metal is given a furthur heating up to 1540 to 1650°C, these suspended particles of graphite will all be dissolved. The metal may then be cooled to the point of solidification with no nuclei favoring the formation of large graphite crystals. The metal may actually sub-cool below the ordinary freezing temperature and, in setting, precipitate the graphite in a very fine form with resultant increased strength and other good physical properties.

Schwartz, Johnson and Junge (25) have suggested the improvement of the properties of malleable iron from white cast iron by a prequenching before the process of malleablization is completed. They state that this treatment will accelerate the migration of carbon because of the greatly increased number of graphite nuclei with accompanying decrease in migratory distances.

III. EXPERIMENTAL METHODS AND DATA.

A. Materials Used.

The materials employed in the preparation of the alloys used in this investigation are listed as follows:

1. Ferro-chrome, containing an average of 72.7 per cent of chromium as reported by the manufacturer's analysis.

2. Ferro-molybdenum, showing the following analysis:

TABLE II

	Weight Per Cent		
	I	II	III
Molybdenum	63.18	62.73	62.91
Carbon	1.13	1.13	1.12

3. Commercial white cast iron test bars with the following composition:

TABLE III

	Weight Per Cent	
	I	II
Carbon	2.58	2.63
Silicon	0.780	0.782
Manganese	0.19	0.21
Sulfur	0.034	0.032
Phosphorus	0.1538	0.1553

4. Ferro-silicon, containing 46 per cent silicon as reported by C.D.Foulke.
5. Crushed and powdered graphite.

The analytical methods employed were, in general, those that have been recommended and approved by The American Society for Testing Materials. Some alterations were made, particularilly in the case of sulfur where the iron was removed by precipitation with sodium carbonate solution before the sulfur was precipitated with barium chloride solution as barium sulfate in an acid medium.

The carbon determination was made by direct combustion of the sample in a stream of oxygen, using an Ascarite tower as the absorbent. The sodium bismuthate method was used for the manganese. The alkalai-acid titration method was used for phosphorus and the nitric-sulfuric acid dehydration method was employed for the determination of the silicon. When available, Bureau of Standard samples were analyzed in conjunction with the other analyses to serve as a check on the accuracy of the determination.

B. Preparation of the Alloys.

The alloys were prepared from the commercial white cast iron as a base. Calculated amounts of ferro-molybdenum or ferro-chrome were added to give the desired compositions. About 5000 grams of the white cast iron were melted in a Plumbago crucible by means of a 35 kv. Ajax Northup electric induction furnace. After the iron had become molten the calculated quantities of ferro-molybdenum or ferro-chrome were added and the melt was thoroughly agitated with an Armco iron rod. Shortly before the pouring, small amounts of powdered graphite and ferro-silicon, equivalent to about 0.1 per cent of the total melt, were added to the melt to compensate for any burning out of these two elements. The molten material was again stirred with an armco rod and immediately poured into moulding sand to produce bars of approximately 5/8 inch in diameter. The bars were allowed to cool to near room temperature before breaking open the moulds. The pouring temperature, as determined by a Leeds and Northup optical pyrometer, was between 1300 and 1370°C.

After cooling the bars were broken into convenient sizes of approximately one inch in length. One specimen of about six inches in length was reserved from each melt for chemical analysis. The one inch pieces were reserved for subsequent heat treatment and microscopical examination. The fracture was from gray-white to white and many specimens showed a slight segregation towards the center of the piece.

C. Chemical Composition of the Alloys.

The composition of the molybdenum alloys is given in Table IV on page 22. Table V shows the approximate composition of the chromium and the chromium-molybdenum alloys.

The molybdenum was determined gravimetrically as lead molybdate. The other constituents were determined by the same methods as were employed for the commercial cast iron.

No analysis was made of the chromium and the chromium-molybdenum alloys as it was found early in the investigation that graphitization was completely stopped in those alloys containing chromium.

It was felt to be a waste of time to make a routine analysis of the chromium containing alloys in which there was no graphitization up to 406 hours at 932°C.

TABLE IV

Molybdenum Alloys.

Melt No.	Weight Per Cent.					
	Mo	C	Si	Mn	S	P
S-1-1	0.921 0.922	2.79 2.78	0.780 0.782	0.21 0.20	0.031 0.035	0.1482 0.1490
S-12-1	0.934 0.929	2.63 2.70	0.762 0.770	0.18 0.20	- - - -	0.1491 0.1497
S-6-2	1.84 1.86	2.51 2.52	0.792 0.820	0.19 0.21	0.036 0.038	0.1506 0.1510
S-11-2	1.85 1.86	2.62 2.63	0.857 0.862	0.17 0.20	- - - -	0.1500 0.1504
S-7-3	3.17 2.98	2.63 2.63	0.657 0.630	0.18 0.19	0.038 0.036	0.1491 0.1506
S-13-4	4.09 4.11	2.55 2.61	0.650 0.649	0.22 0.19	0.034 0.036	0.1485 0.1490
S-14-5	4.95 4.96	2.58 2.63	0.610 0.620	0.21 0.19	0.033 0.032	0.1502 0.1510

Samples of the molybdenum series, the chromium series and the chromium-molybdenum series were found to be extremely hard as cast. A great deal of difficulty was experienced in preparing them for the chemical analysis.

In Table V, page 23, are shown the calculated amounts of molybdenum and chromium as determined from the weight of ferro-molybdenum and ferro-chrome that was added to the white cast iron base in the preparation of the chromium and the chromium-molybdenum alloys.

TABLE V

Chromium and Chromium-Molybdenum Alloys.

Melt No.	Calculated Weight Per Cent			
	Cr	Mo	C	Remarks
X-1	5	5	2.5	
X-2	3	5	2.5	
X-3	1	5	2.5	
X-4	5	3	2.5	
X-5	3	3	2.5	
X-6	1	3	2.5	
X-7	5	1	2.5	
X-8	3	1	2.5	
X-9	1	1	2.5	See Figure XII-c
X-10	3	3	2.5	Remelt of X-5. No Si added.
X-11	3	5	2.5	Remelt of X-1 + X-2. 6 gms Ferro-silicon added
X-12	1	5	2.5	Remelt of X-2 + X-3. 6 gms Ferro-silicon added
X-13	1	0	2.5	See Figure XII-a
X-14	3	0	2.5	
X-15	5	0	2.5	

The fractures of the samples from the above series were gray to white with a slightly greater tendency towards gray than those of the series containing only molybdenum.

D. Heat Treatment.

As previously stated, the purpose of this investigation was to determine the effect of molybdenum, from one to five per cent compositions, and chromium covering the same range of compositions, together with combined compositions of molybdenum and chromium from one to five per cent of each element, upon the rates of graphitization after a predetermined heat treatment.

The heat treatment was made in a hump annealing furnace. The temperature of this furnace was controlled and recorded by a Leeds and Northup Automatic Recorder. Iron-Constantan thermocouples were employed and these were replaced every twenty-four hours at the 932°C range and every forty-eight hours at the lower range of 704°C. The temperatures were frequently checked by a Leeds and Northup Student Potentiometer. The samples under treatment were packed in 2 x 8 inch iron gas pipes, capped at one end, or in small Plumbago crucibles. Gas carbon of about 20 mesh was employed as the packing material. This was to partially check the decarburization of the samples that were held at the elevated temperatures for long periods. In spite of these precautions, appreciable decarburization was seen at the surface of the samples.

In the preliminary study the samples were removed from the furnace to the air and allowed to cool in the carbon pack. In the final treatments the samples were allowed to cool in the furnace to a temperature of 450°C before removing to the air for the cooling to to room temperature.

Furthur consideration of the chromium containing alloys may be disposed of at this point with the statement that no decomposition of cementite, either primary or secondary stages, occurred after 406 hours at 932°C and 257 hours at 704°C. These conclusions are confirmed by reference to the photomicrographs as shown in Figures XII-a,b,c,d and XIII-a,b. The remainder of this report will be devoted to the consideration of those alloys which contain only the molybdenum as the element added to the white cast iron base.

A preliminary series of heat treatments was made by placing in the furnace seven containers, each consisting of a specimen of the commercial white cast iron and of each melt of different molybdenum composition. The furnace was allowed to attain a temperature of 932°C before the containers were introduced. Counting from the time that the furnace again reached 932°C after the samples were introduced, a container was removed at the following intervals:

1/2 hour. 10 hours. 48 hours.

74 hours. 100 hours. 202 hours.

257 hours.

Upon removal at the stated intervals the samples were ground down on the rough emery wheel to a depth of 1/8 to 3/16 inch to remove abnormal surface conditions. The samples were then polished and examined microscopically in both the unetched and etched condition. The etching was done by emersion of the polished surface of the samples in an ethyl alcohol-nitric acid mixture (5 per cent of concentrated nitric acid by volume) for such a length of time that would show the structure of the metal to the best advantage. The molybdenum alloys usually required from thirty to fifty seconds to obtain the best results. The approximate time required for the primary stage of graphitization at 932°C for each molybdenum composition was thus determined.

With the approximate time found, the above procedure was repeated until the exact time required (+ or - 5 hours) was determined for complete graphitization of the massive cementite for each composition at the elevated temperature of 932°C. In order to avoid any discrepancies, at least four samples of each composition were given the predetermined treatment at 932°C.

The next step in the investigation was to determine the time required for the second stage of graphitization or the complete decomposition of the pearlite structure at 704°C. A similar procedure was followed as was done in determining the time required for the primary stage at 932°C. The samples, which had previously been given the required treatment at 932°C, were placed in the furnace at 932°C and held at this temperature for one-half hour. The furnace was then allowed to cool at a controlled rate of 18.5°C per hour until a temperature of 704°C had been reached. This temperature was then maintained and samples were removed at approximately twenty-four hour intervals and examined microscopically to determine the progress of the graphitization in the second stage. When the proper time for each composition was definitely determined all specimens were returned to the furnace at proper intervals to insure that all samples of the same composition would have the same time at 704°C. When the required time had elapsed, the furnace was cooled under control from 704°C to 450°C at a rate of 6.8°C per hour. The samples were then removed from the furnace and allowed to cool to room temperature in the carbon pack.

Table VI gives a complete summary of the heat treatment for representative samples of each melt of varying molybdenum content.

TABLE VI

Melt No.	Sample No.	Total Hrs. at 932°C.	Total Hrs. at 704°C.	Photograph Shown in Figure:-
S-1-1	32	65	76	- - -
S-1-1	70	75	98	- - -
S-12-1	14	80	99	- - -
S-12-1	33	65	125	- - -
S-1-1	51	74	124	III-b,c,d.
S-1-1	13	80	126	- - -
S-12-1	52	74	0	II-d.
S-12-1	105	202	0	- - -
S-1-1	87	100	0	III-a
S-6-2	34	89	160	- - -
S-11-2	35	89	160	V-b,c,d.
S-11-2	71	103	122	- - -
S-6-2	15	104	147	- - -
S-6-2	88	100	149	- - -
S-6-2	53	101	148	- - -
S-11-2	54	101	172	- - -
S-11-2	16	104	0	- - -
S-11-2	106	202	0	- - -
S-7-3	17	153	223	- - -
S-7-3	72	151	196	VII-b,c,d.
S-7-3	89	155	197	- - -
S-7-3	55	153	174	- - -
S-13-4	90	203	174	- - -
S-13-4	18	205	198	- - -
S-13-4	73	200	198	- - -
S-13-4	56	201	223	- - -
S-13-4	108	202	247	IX-b,c,d.
S-14-5	57	252	198	- - -
S-14-5	91	252	223	- - -
S-14-5	74	252	247	XI-b,c,d.
S-14-5	109	257	247	- - -
Cast Fe	C-92B	65	100	XII-c,d. XIV-a
Cast Fe	C-110B	202	148	- - -
Cast Fe	C-92I	70	0	- - -
Cast Fe	C-110I	229	0	- - -

After undergoing the above treatment, the samples were then ready for the final microscopical examination and photographic study. Those that were photographed for permanent record are indicated in the above table by reference to the proper figure.

In each case the samples listed in the preceeding table were cooled from 932°C to 704°C at the rate of 18.5°C per hour and were cooled from 704°C to 450°C at the rate of 6.8°C per hour. They were then removed from the furnace and allowed to air cool in the carbon pack.

Table VII shows the heat treatment that was given a few representative samples at 932°C only. The time indicated is the approximate number of hours required for the primary stage of the graphitization. These samples were all removed from the furnace at 932°C and allowed to air cool in the gas carbon pack.

TABLE VII

Melt No.	Sample No.	Total Hrs. at 932°C	Photograph Shown in Figure:-
S-12-1	14	80	II-c
S-11-2	16	104	IV-b
S-7-3	55	153	VI-c
S-13-4	18	205	VIII-c
S-14-5	109	257	X-c

TABLE VIII

Melt No.	Sample No.	Total Hrs. at 932°C	Photograph Shown in Figure:-
S-12-1	52	74	- - -
S-6-2	53	74	IV-c,d.
S-7-3	55	74	VI-d
S-13-4	56	74	VIII-d
S-1-1	87	100	- - -
S-6-2	88	100	V-a
S-7-3	89	100	VII-a
S-13-4	90	100	IX-a
S-14-5	91	100	XI-a

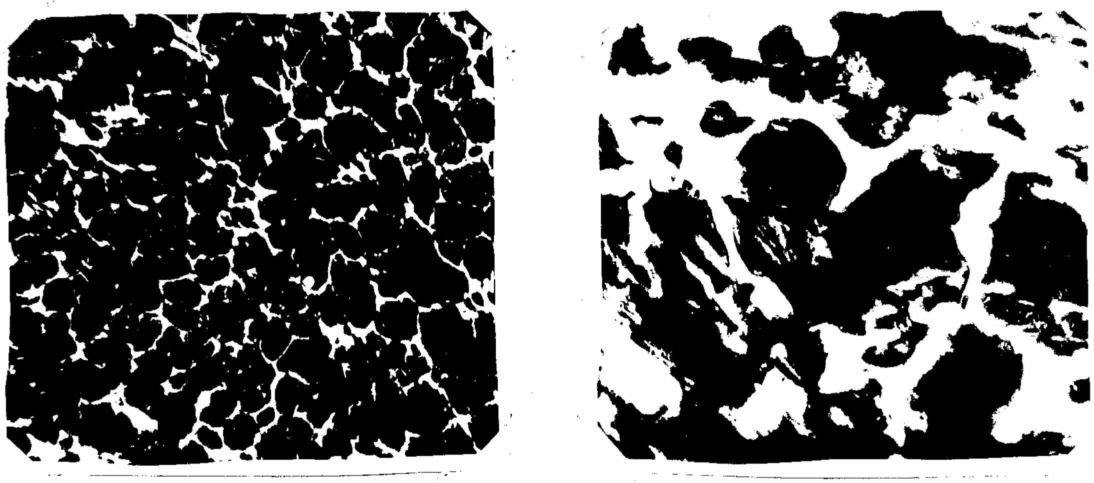
In Table VIII, above, is given a summary of heat treatment of a few representative samples at 932°C for 74 and 100 hours. These are offered to illustrate some of the intermediate stages of heat treatments. These samples were removed from the furnace at 932°C and allowed to air cool in the carbon pack.

E. Photographic Study.

A photographic record of the results obtained in this investigation is presented in Figures II to XIV, pages 30 to 42, inclusive. No attempt has been made to present a photograph of every sample prepared and studied. Only representative photographs are presented as are needed to show the structure of the alloys as cast and during the progress and completion of the two stages of graphitization. Such magnifications have been used as would show the details of the structure of the alloys to the best advantage. Photographs of the completely graphitized white cast iron are presented as a basis of comparison.

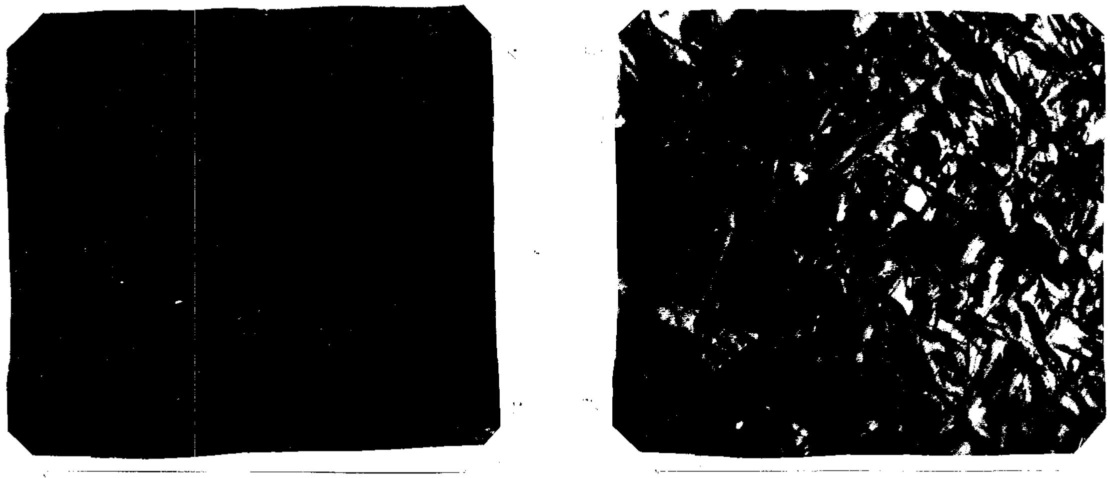
In order to conserve space, the following abbreviations are employed under each photograph:

1. The letter H, following the number of hours, indicates a temperature of 932°C (+ or - 6°C).
2. The letter A, following the number of hours, indicates a temperature of 704°C (+ or - 6°C).
3. Unless otherwise indicated, all photographs represent samples that have been etched in ethyl alcohol-nitric acid etching solution.
4. All compositions for molybdenum are given to the nearest whole number.



(a) Mo = 1 per cent. 125 X.
As Cast

(b) Mo = 1 per cent. 350 X.
As Cast



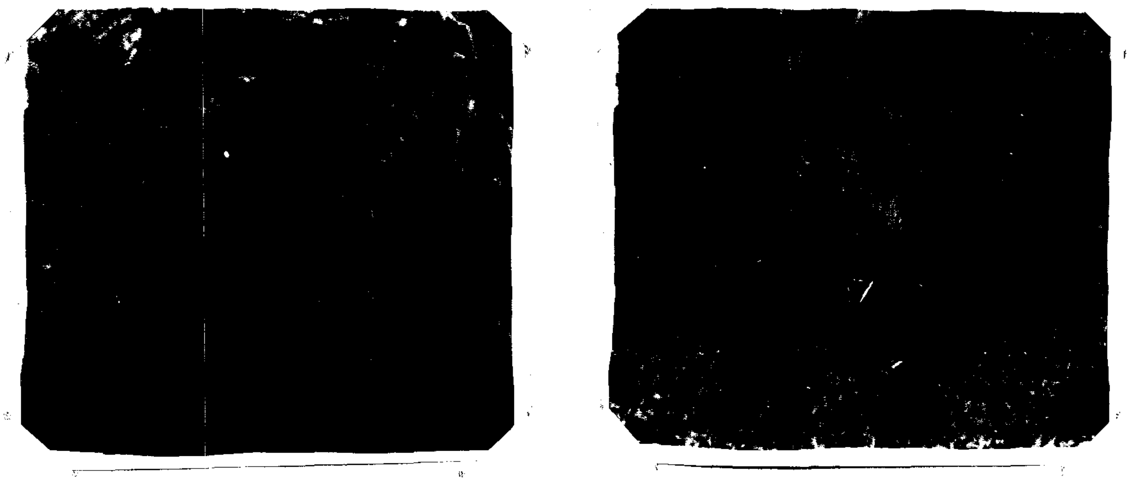
(c) Mo = 1 per cent. 350 X.
80 Hrs. at H

Sample No. 14

(d) Mo = 1 per cent. 550 X.
74 Hrs. at H

Sample No. 52

FIGURE II

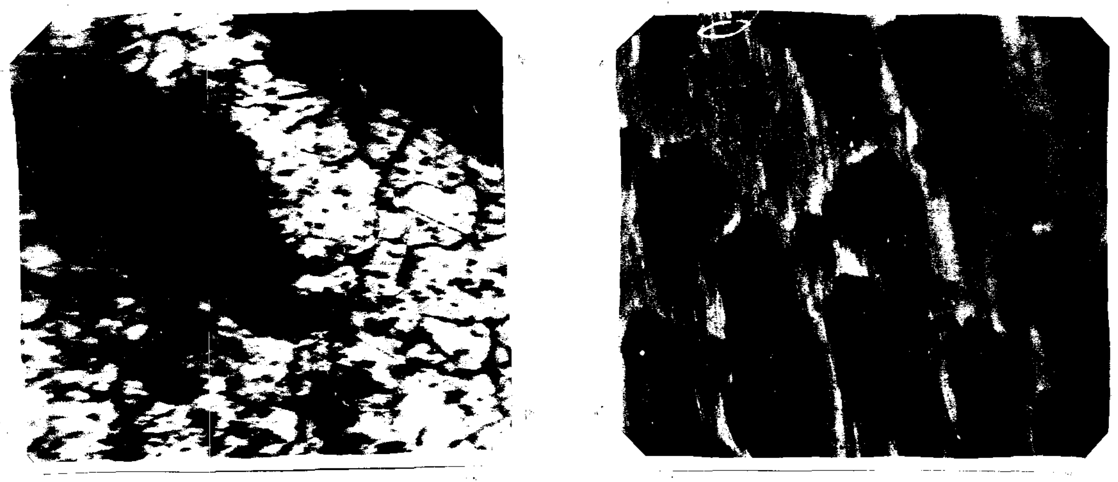


(a) Mo = 1 per cent. 550 X.
100 Hrs. at H

Sample No. 87

(b) Mo = 1 per cent. 150 X.
74 Hrs. at H
124 Hrs. at A

Sample No. 51



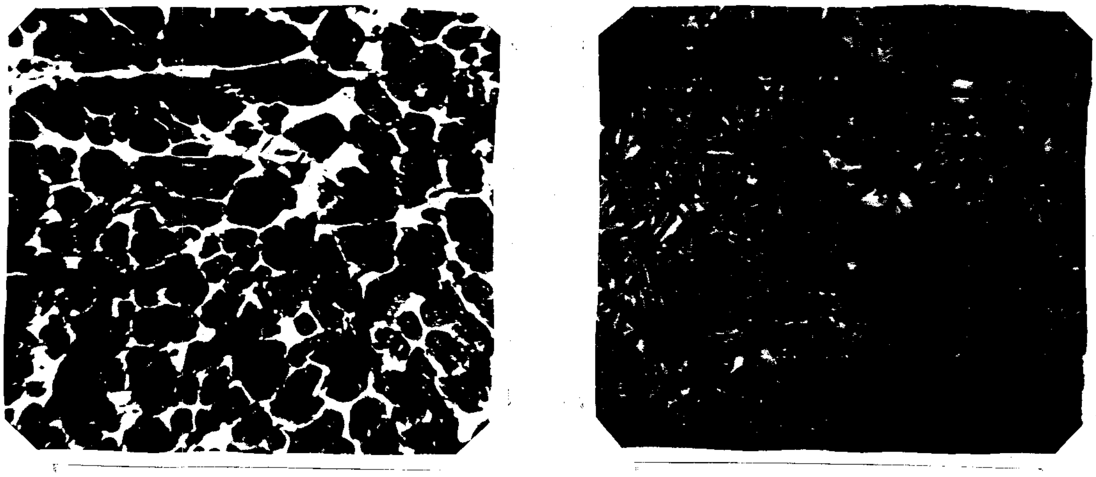
(c) Mo = 1 per cent. 350 X.
74 Hrs. at H
124 Hrs. at A

Sample No. 51

(d) Mo = 1 per cent. 80 X
74 Hrs. at H
124 Hrs. at A
UNETCHED

Sample No. 51

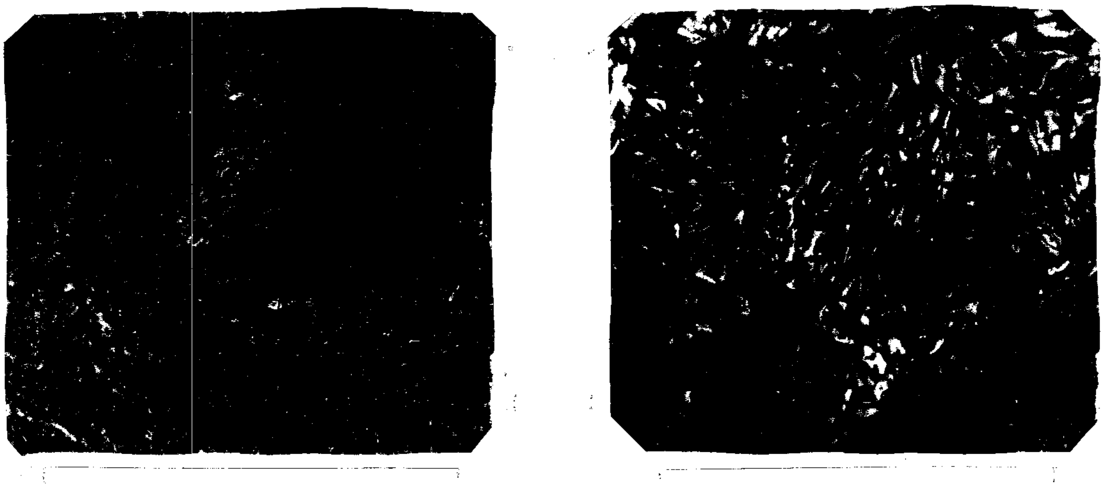
FIGURE III



(a) Mo = 2 per cent. 125 X.
As Cast

(b) Mo = 2 per cent. 350 X.
104 Hrs. at H

Sample No. 16



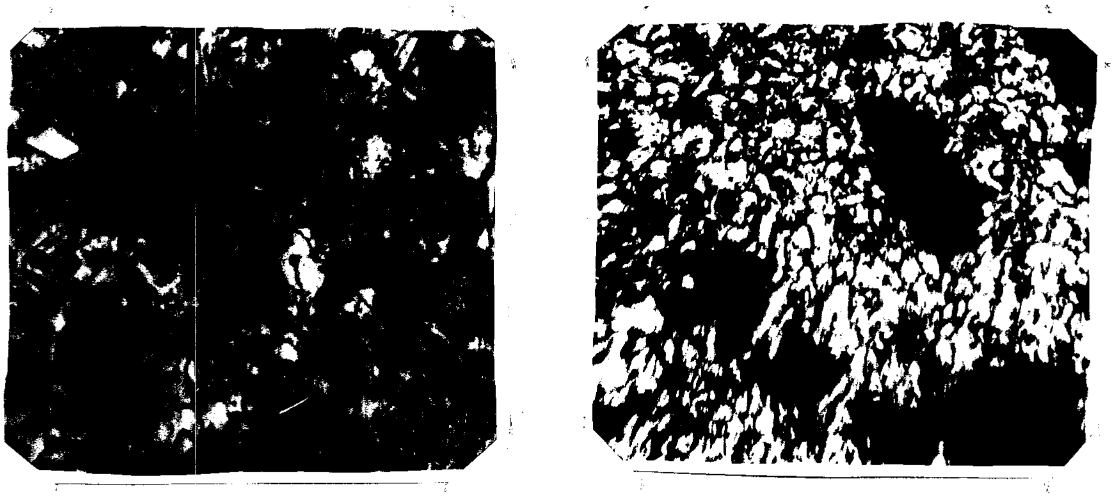
(c) Mo = 2 per cent. 350 X.
74 Hrs. at H

Sample No. 53

(d) Mo = 2 per cent. 550 X.
74 Hrs. at H

Sample No. 53

FIGURE IV

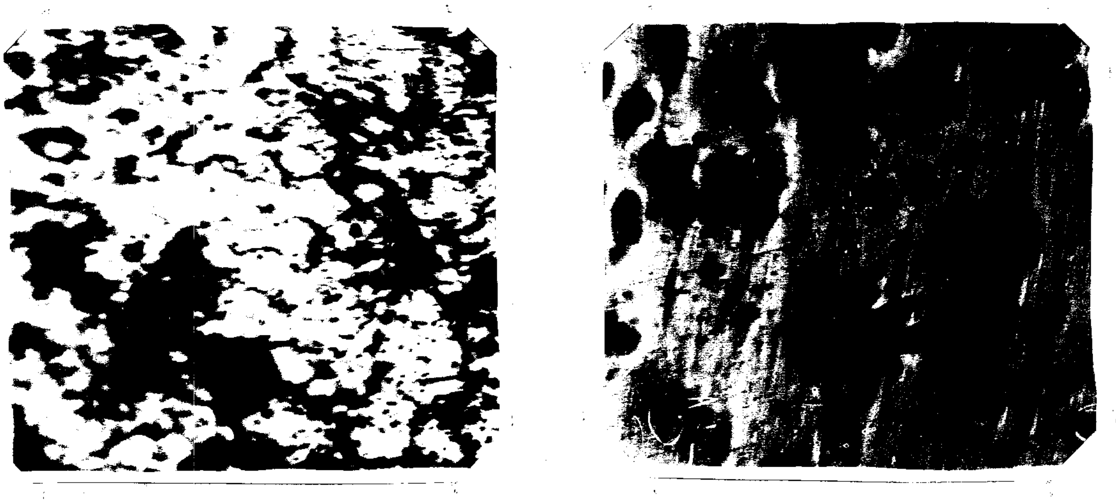


(a) Mo = 2 per cent. 550 X.
100 Hrs. at H

Sample No. 88

(b) Mo = 2 per cent. 150 X.
89 Hrs. at H
163 Hrs. at A

Sample No. 35



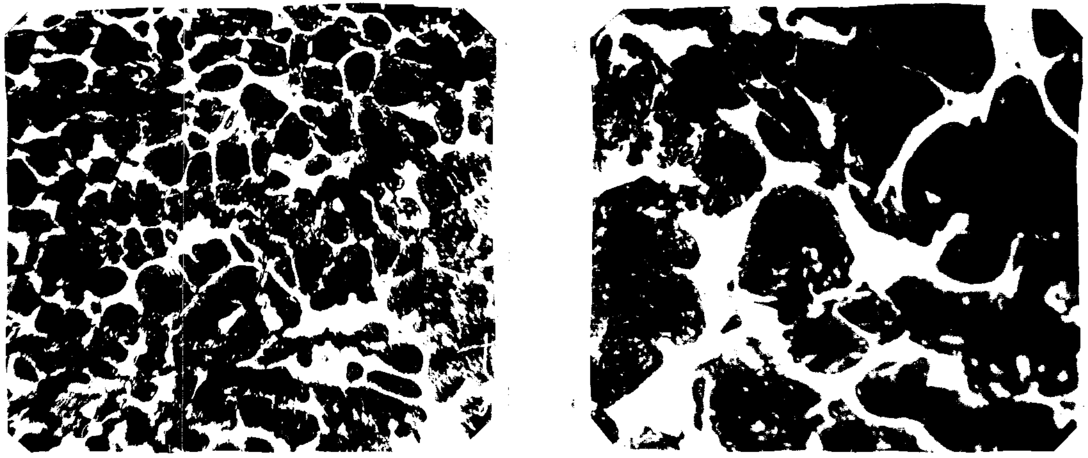
(c) Mo = 2 per cent. 350 X.
89 Hrs. at H
163 Hrs. at A

Sample No. 35

(d) Mo = 2 per cent. 80 X.
89 Hrs. at H
163 Hrs. at A
UNETCHED

Sample No. 35

FIGURE V



(a) Mo = 3 per cent. 125 X.
As Cast

(b) Mo = 3 per cent. 350 X.
As Cast

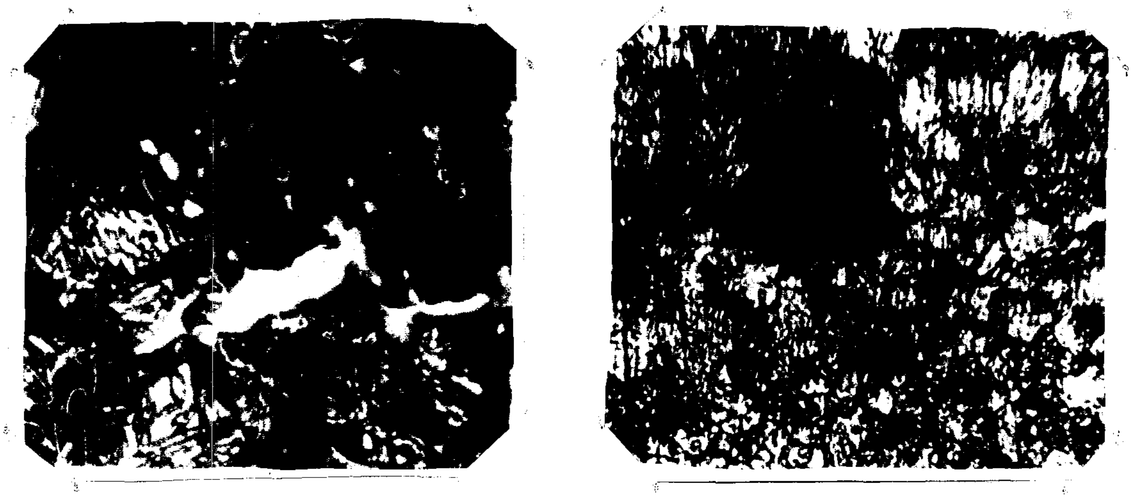
(c) Mo = 3 per cent. 350 X.
153 Hrs. at H

Sample No. 55

(d) Mo = 3 per cent. 550X.
74 Hrs. at H

Sample No. 55

FIGURE VI

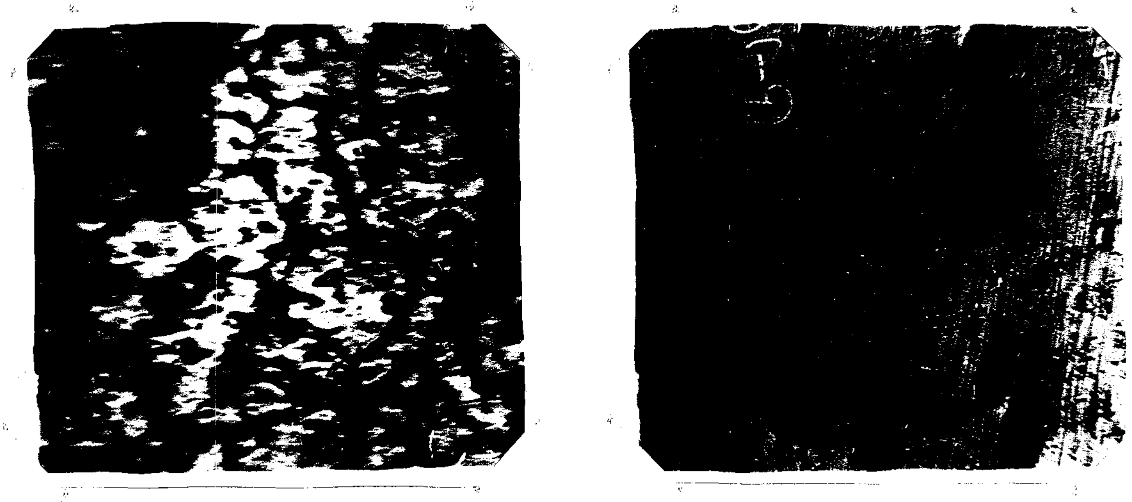


(a) Mo = 3 per cent. 550 X.
100 Hrs. at H

Sample No. 89

(b) Mo = 3 per cent. 150 X.
151 Hrs. at H
196 Hrs. at A

Sample No. 72



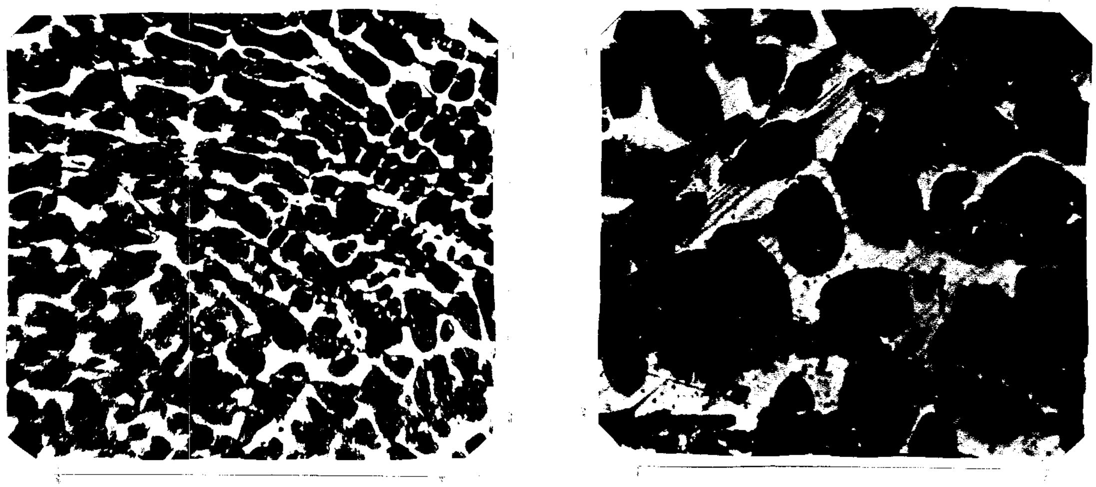
(c) Mo = 3 per cent. 350 X.
151 Hrs. at H
196 Hrs. at A

Sample No. 72

(d) Mo = 3 per cent. 80 X.
151 Hrs. at H
196 Hrs. at A
UNETCHED

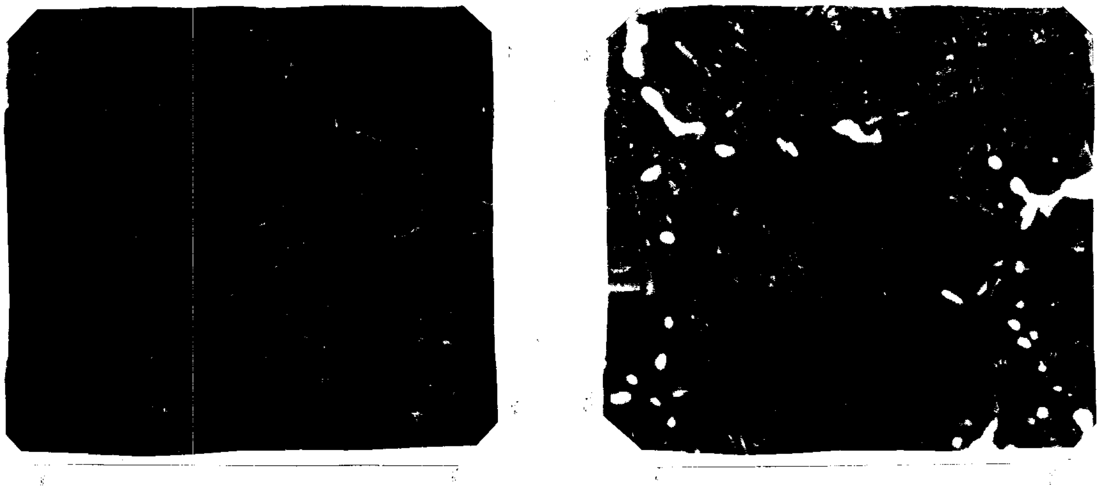
Sample No. 72

FIGURE VII



(a) Mo = 4 per cent. 125 X.
As Cast

(b) Mo = 4 per cent. 350 X.
As Cast



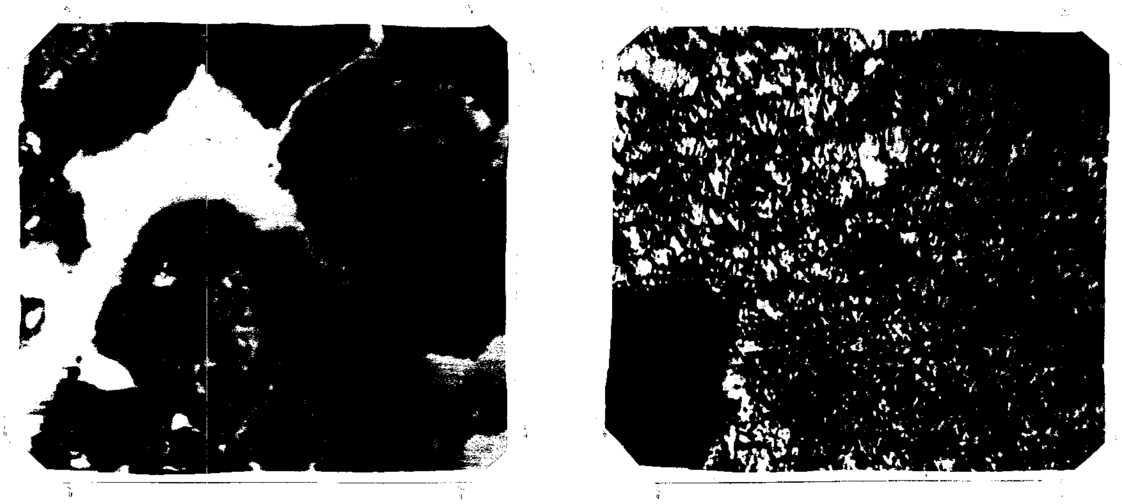
(c) Mo = 4 per cent. 350 X.
205 Hrs. at H

Sample No. 18

(d) Mo = 4 per cent. 550 X.
74 Hrs. at H

Sample No. 56

FIGURE VIII

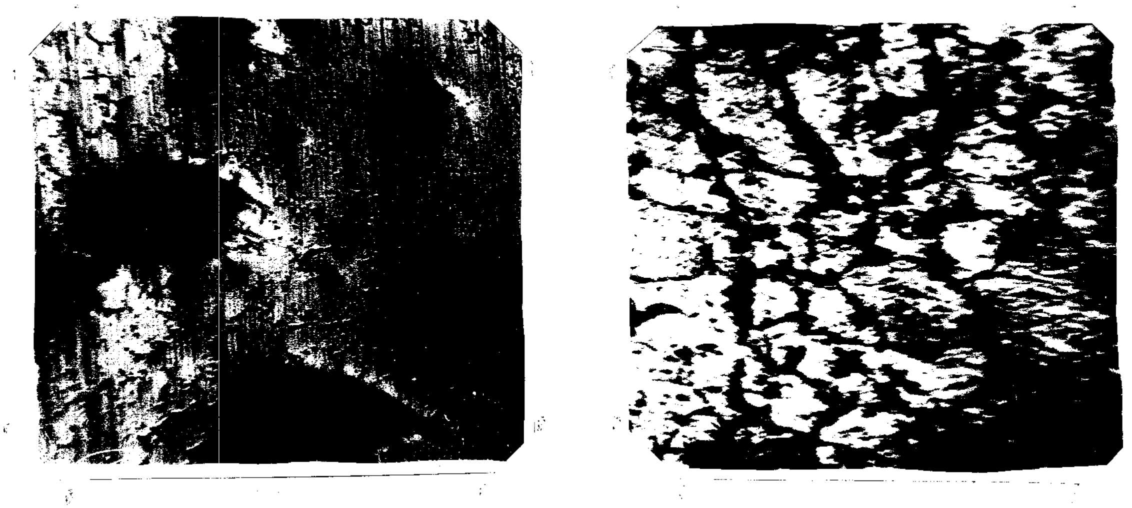


(a) Mo = 4 per cent. 550 X.
100 Hrs. at H

Sample No. 90

(b) Mo = 4 per cent. 150 X.
202 Hrs. at H
247 Hrs. at A

Sample No. 108



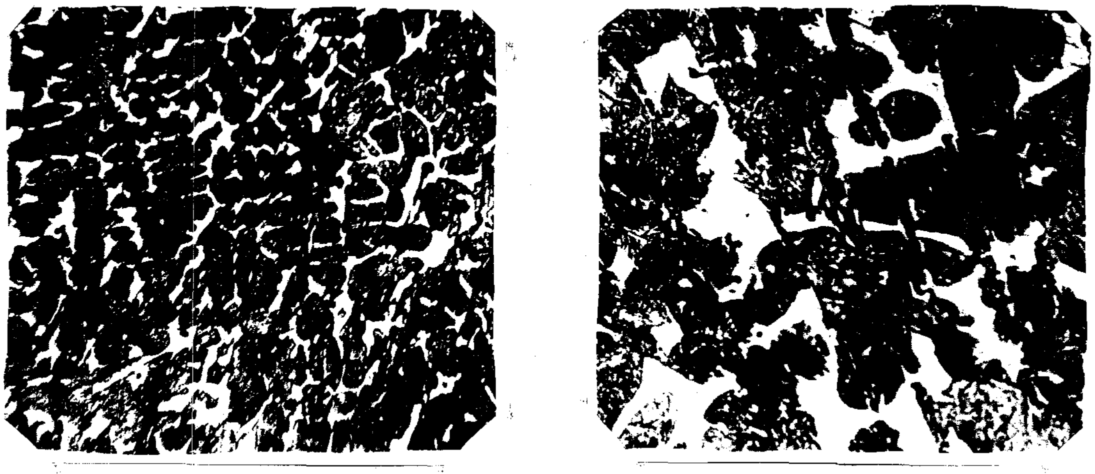
(c) Mo = 4 per cent. 80 X.
202 Hrs. at H
247 Hrs. at A
UNETCHED

Sample No. 108

(d) Mo = 4 per cent. 350 X.
202 Hrs. at H
247 Hrs. at A

Sample No. 108

FIGURE IX



(a) Mo = 5 per cent. 125 X.
As Cast

(b) Mo = 5 per cent. 350 X.
As Cast

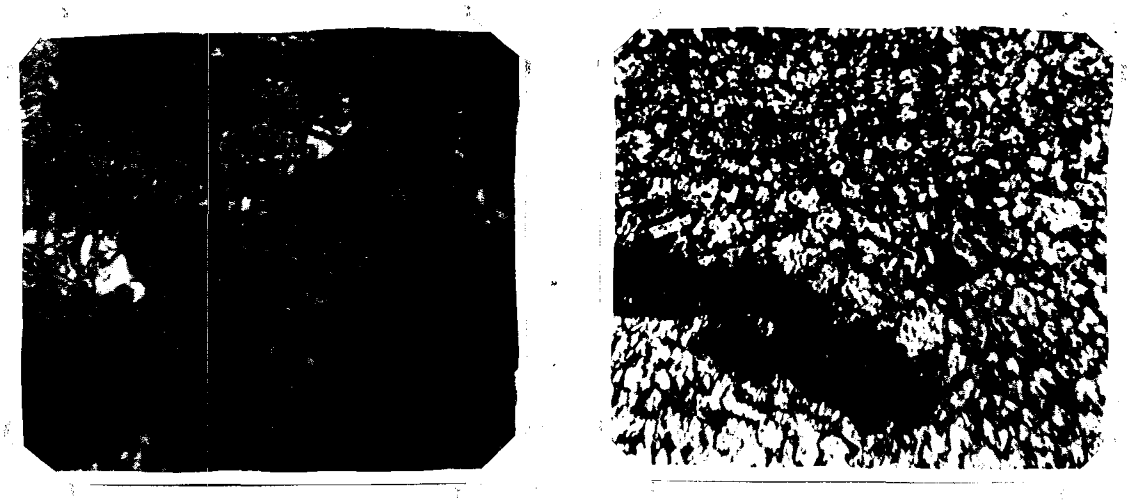
(c) Mo = 5 per cent. 350 X.
257 Hrs. at H

Sample 109

(d) Mo = 5 per cent. 550 X.
74 Hrs. at H

Sample 57

FIGURE X

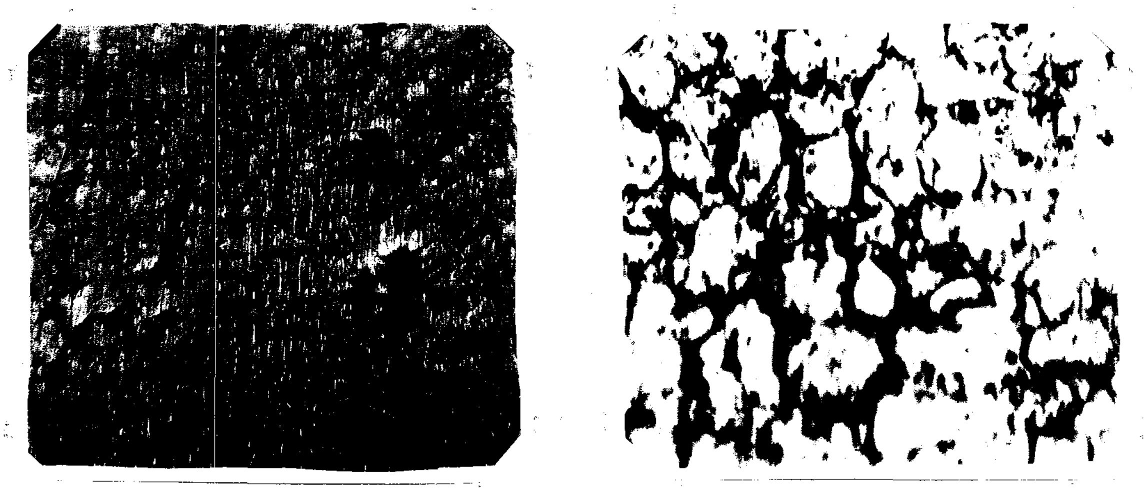


(a) Mo = 5 per cent. 550 X.
100 Hrs. at H

Sample No. 91

(b) Mo = 5 per cent. 150 X.
252 Hrs. at H
247 Hrs. at A

Sample No. 74



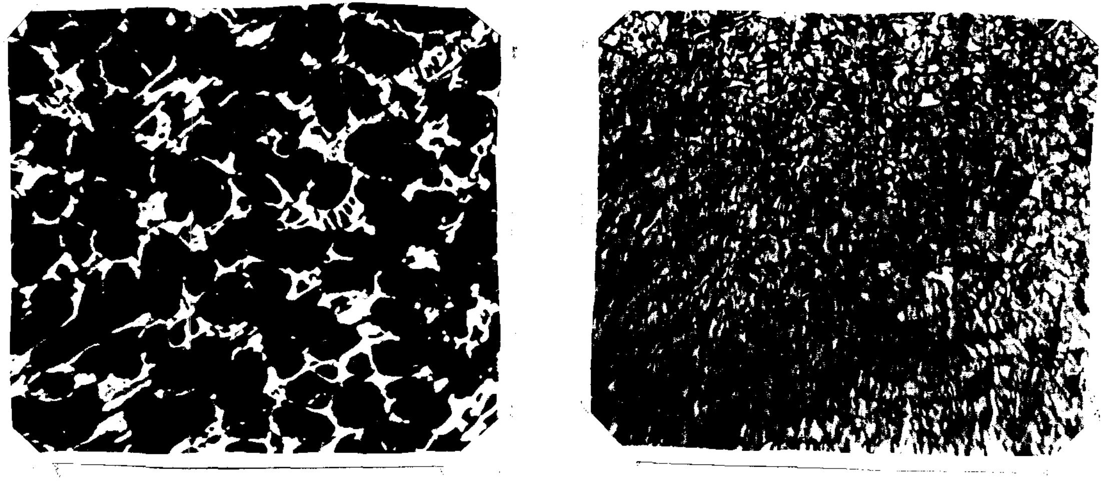
(c) Mo = 5 per cent. 80 X.
252 Hrs. at H
247 Hrs. at A
UNETCHED

Sample No. 74

(d) Mo = 5 per cent. 350 X.
252 Hrs. at H
247 Hrs. at A

Sample No. 74

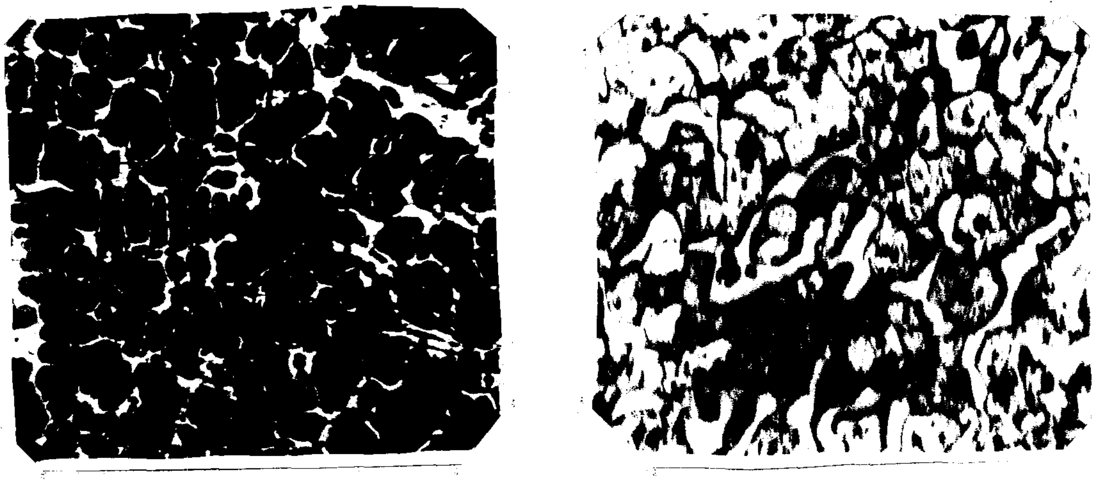
FIGURE XI



(a) Cr = 1 per cent. 150 X.
Mo = 0 per cent. As Cast

(b) Cr = 1 per cent. 150 X.
Mo = 0 per cent.
406 Hrs. at H
257 Hrs. at A

Sample No. 102

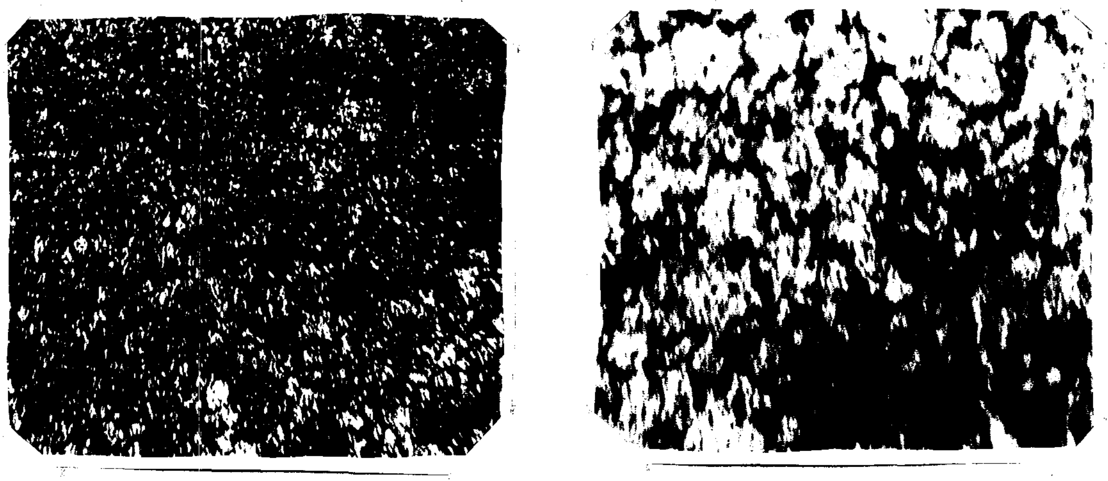


(c) Cr = 1 per cent. 150 X.
Mo = 1 per cent. As Cast

(d) Cr = 1 per cent. 350 X.
Mo = 0 per cent.
406 Hrs. at H
257 Hrs. at A

Sample No. 102

FIGURE XII

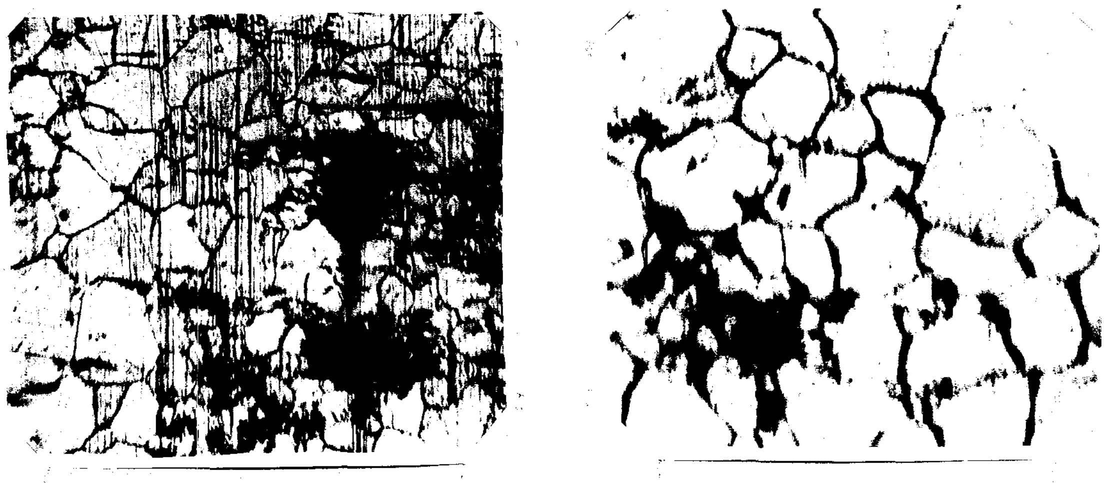


(a) Cr = 1 per cent. 150 X.
Mo = 1 per cent.
406 Hrs. at H
257 Hrs. at A

Sample No. 98

(b) Cr = 1 per cent. 350 X.
Mo = 1 per cent.
406 Hrs. at H
257 Hrs. at A

Sample No. 98



(c) Commercial Cast. 150 X.
65 Hrs. at H
100 Hrs. at A

Sample No. C-92-B

(d) Commercial Cast. 350 X.
65 Hrs. at H
100 Hrs. at A

Sample No. C-92-B

FIGURE XIII

(a) Commercial Cast. 80 X.
65 Hrs. at H
100 Hrs. at A
UNETCHED

Sample No. C-92-B

FIGURE XIV

. . . .

The photographs given in Figures XII-a,b,c,d and XIII-a,b are given in order to confirm the the conclusions that graphitization does not occur in those alloys that contain chromium, even as low as 1 per cent.

Some difficulty was experienced in obtaining clear and sharp photographs for those samples that required a high magnification. However, these high magnifications were necessary in some cases because of the fine grain structure imparted to the alloys by the addition of molybdenum.

IV. DISCUSSION OF RESULTS.

A. Practical Considerations.

The most optimum time required for the completion of the primary and secondary stages of graphitization is given below in Table X. The amounts of molybdenum and chromium are given in round numbers.

TABLE X.

Alloy No.	Weight Per Cent.		Time for Complete Graphitization	
	Mo	Cr	At 932°C	At 704°C
S-1-1	1.00	0	75 to 80 hrs.	125 hrs.
S-12-1	1.00	0	75 to 80 hrs.	125 hrs.
S-6-2	2.00	0	90 to 100 hrs.	160 to 165 hrs.
S-11-2	2.00	0	90 to 100 hrs.	160 to 165 hrs.
S-7-3	3.00	0	150 to 155 hrs.	195 to 200 hrs.
S-13-4	4.00	0	200 to 205 hrs.	245 to 250 hrs.
S-14-5	5.00	0	Incomp. 255 hrs.	Incomp. 250 hrs.
Com. Cast	0	0	60 to 65 hrs.	100 to 105 hrs.
X-9	1.00	1.00	None at 406 hrs.	None at 255 hrs.
X-13	0	1.00	None at 406 hrs.	None at 255 hrs.

An accuracy no closer than plus or minus six hours is claimed for these results. These are well within the limits of experimental error that are characteristic of an investigation of this type.

In Figures XV and XVI, pages 45 and 46 respectively, are shown three curves. Curve 1, Figure XV, is the result of plotting the magnitude of the molybdenum compositions against the number of hours required for complete graphitization at 932°C. Curve 2 of Figure XV is the result for the same procedure at 704°C. The values for the commercial cast iron are taken for the zero molybdenum composition.

In Table XI, below, are tabulated the results obtained for each molybdenum composition by dividing the time for the secondary stage of graphitization at 704°C by the time required for the primary stage at 932°C.

TABLE XI.

Per Cent Mo.	Ratio: Time at 704°C/Time at 932°C
0.00	1.67
1.00	1.67
2.00	1.60
3.00	1.33
4.00	1.19
5.00	Indeterminate

The curve obtained by plotting these values is illustrated in Figure XVI on page 46. All the values fall very nearly on a smooth curve with the exception of that for three per cent molybdenum.

The curves illustrated in Figures XV and XVI give evidence in support of the conclusions that the rates of graphitization, both the primary and secondary stages, are in an inverse ratio to the percentage of molybdenum present in the alloys.

One of the most striking features of these molybdenum cast irons is the apparent refinement of the grain structure of the

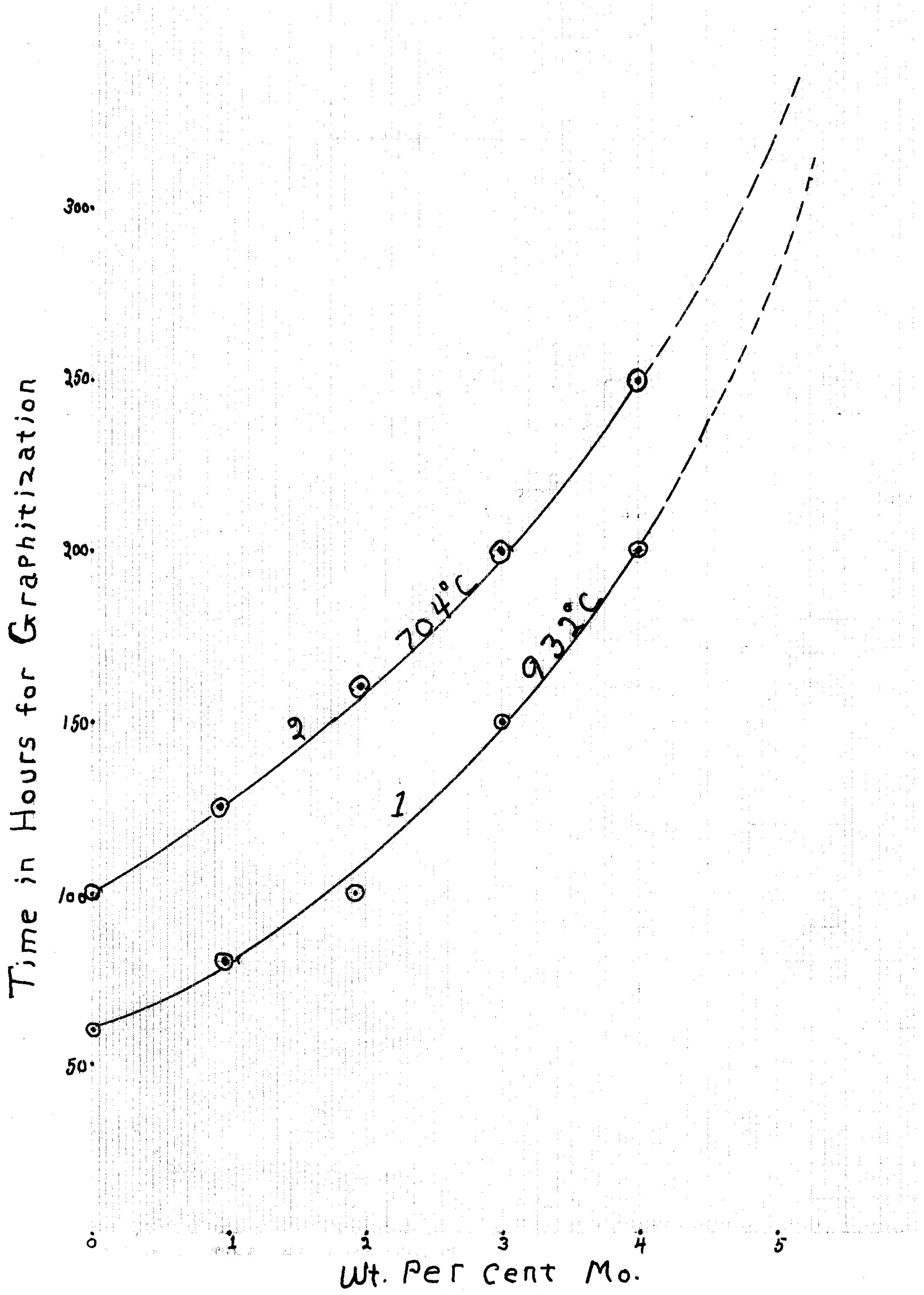

Time in Hours for Graphitization
300
250
200
150
100
50
0
1
2
3
4
5
Wt. Per Cent Mo.
2
704°C
1
932°C

FIGURE XV

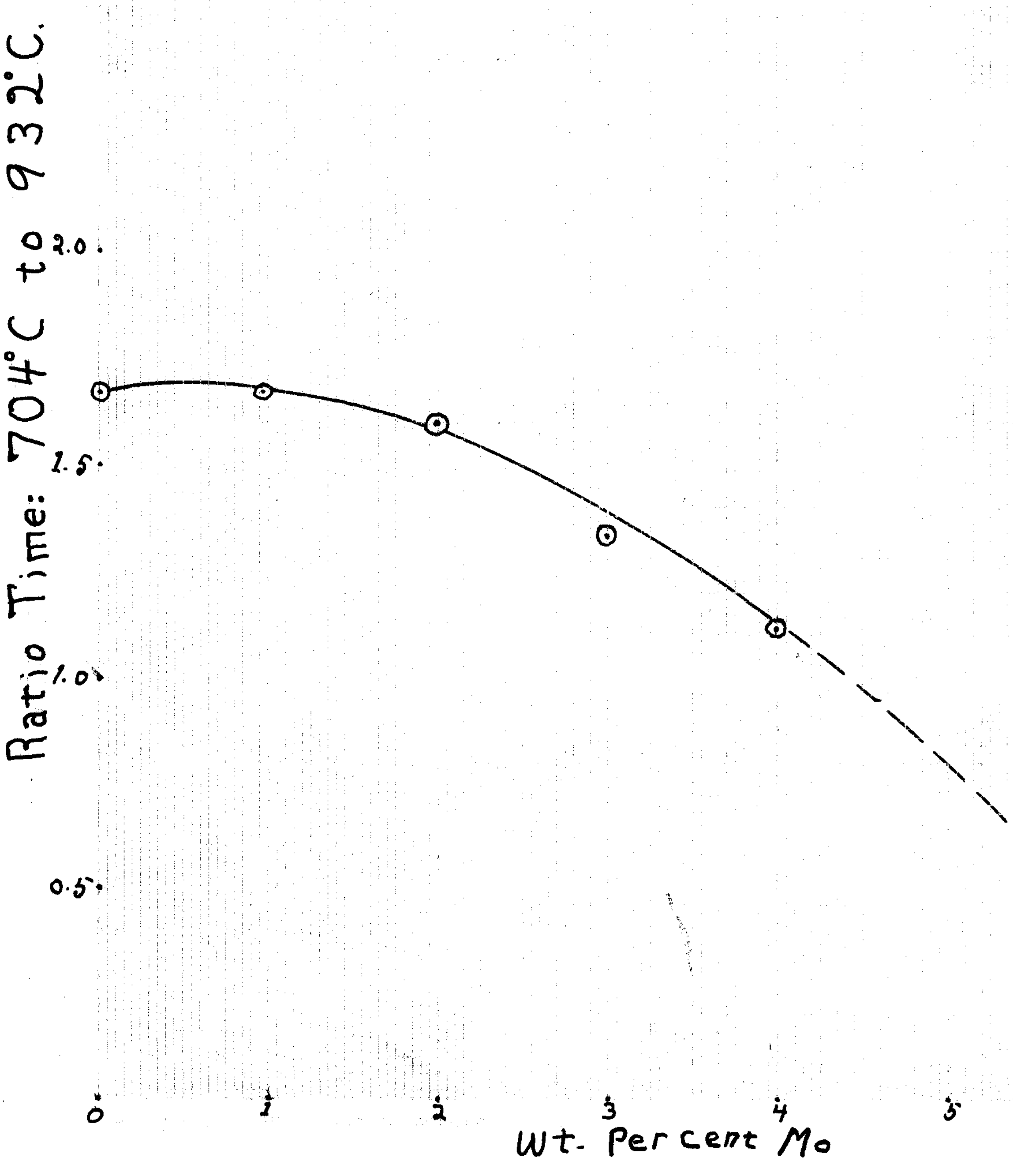


FIGURE XVI

completely graphitized specimens as compared to the commercial white cast iron which has been converted to the same conditions. This is shown quite clearly by reference to Figures III-b, V-b, VII-b, IX-b and XIII-c, the latter being the commercial cast iron. This small grain structure is a contributing cause to the toughness and greater tensile strength of the molybdenum containing alloys. This type of grain structure also results in greater hardness in comparison to the product from the commercial white cast iron.

Because no information of practical value would be obtained, no heat treatment for the secondary stage of graphitization at 704°C was carried out beyond 255 hours. For this interval the decomposition of the pearlite was quite incomplete for the five per cent molybdenum alloy. This would indicate that the slope of curve 2 in Figure XV approaches infinity as the molybdenum content is increased beyond five per cent. While a 255 hour heat treatment for the five per cent alloy at 932°C brings more positive results for the primary stage than was found for the secondary stage at 704°C, yet the decomposition of the massive cementite is quite incomplete. This may be confirmed by reference to Figures X-c and XI-b,d.

The time required for the alloys from one to four per cent molybdenum may be seen by reference to Figures III-b,c,d, V-b,c,d, VII-b,c,d and IX-b,c,d. The a-parts of Figures VII and IX show much massive cementite that remains undecomposed. Small amounts of this cementite also remains at the end of 100 hours at 932°C for the one and two per cent molybdenum content. This is shown in Figures III-a and V-a. Figures XIII-c,b and XIV-a show a completely malleablized specimen of the commercial white cast iron that was employed as a base in the preparation of the molybdenum alloys. The larger grain structure, in comparison to the molybdenum alloys, may be especially noted.

For observations of the incomplete graphitization of the primary stage, reference may be made to Figures IV-a,b, VI-d, VII-a, VIII-d, IX-a, X-d and XI-a. Figures XII-b,d and XIII-a,b show the absence of graphitization for those samples which contain chromium.

The structures of the alloys as cast are pictured in Figures II-a,b, IV-a, VI-a,b, VIII-a,b, X-a,b and XII-a,c. These all show quite similar structure with the exception that the massive cementite fields appear to be divided into a greater number of smaller areas as the molybdenum content increases.

While these alloys were very hard and tough as cast, the hardness was partially destroyed by holding samples at 932°C for one hour and air cooling in the carbon pack. However, these properties could be improved by quenching in cold water rather than cooling in the air. A martinsitic structure seemed to predominate.

B. Some Theoretical Considerations.

The question may arise as to the probability of predicting the effect of elements in general and of molybdenum and chromium in particular upon the graphitization of white cast iron. Several theories have been proposed. However, we may safely assume the following fundamental chemical equation for the graphitization process:

$$(1) \quad Fe_3C \rightleftarrows 3Fe + C$$

For actual operating conditions involved in the graphitization of white cast iron, the following modified form of the general free energy may be applied:

$$(2) \; -\Delta F = RT \left(\ln K - \ln \frac{(a'_C)\,(a'_{Fe})^3}{(a'_{Fe_3C})} \right)$$

In the pure iron-carbon alloys, the activities of the carbon, iron and iron carbide may be assumed to be unity and the second term in equation (2) becomes zero. However, different conditions would result should an added element affect the activity of the iron or the iron carbide. The activity of the free carbon is generally assumed to be independent of the alloying elements.

When silicon is added to an iron-carbon alloy, such as white cast iron, the silicon is dissolved in the iron to form a solid solution. The activity of the iron becomes less than unity and $-\Delta F$ becomes more positive. The decomposition of Fe_3C is favored according to equation (2). This is in accord with experimental evidence, whereby silicon promotes the graphitization of white cast iron.

Chromium shows a marked tendency for carbide formation. In the development of the chromium-carbon phase diagram, Ruff and Foehr (26) have shown the formation of at least three carbides of chromium, viz., Cr_5C_2, Cr_4C_3 and Cr_3C_2. Moissan (27) has shown the existence of an additional carbide, Cr_4C. The existence of Cr_7C_3 has been shown by the X-ray studies of Westgren and Phragmen (28). Evidence of the formation of a double carbide of iron and chromium, Fe_4C_3,Cr_3C_3, has been offered by Raffo and Sambucety (21).

With this information available, we would expect that if chromium is added to white cast iron the activity of the Fe_3C would be lowered below unity. This would result in $-\Delta F$, for equation (2), becoming less positive. The tendency for the decomposition of the iron carbide, according to equation (1), would be less and the reaction should eventually proceed to the left and favor the formation of the carbide when $-\Delta F$ has become negative. This prediction is in accord with the results found in this investigation and the results as reported by Foulke (10).

In general, those elements which form solid solutions with the iron have been found to promote graphitization, due to the lowering of the activity of the iron according to the explanation just given. The elements that show a tendency for carbide formation are known to inhibit or completely stop the mechanism of graphitization.

This paper has shown that molybdenum decreases the rate of the graphitization process. However, it is not completely stopped until the molybdenum content exceeds five per cent. According to Takei and Murakami (16), iron and molybdenum form solid solutions within the ranges employed in this problem for pure iron-molybdenum alloys. But from the results found in this investigation, it seems that the molybdenum for the most part is associated with the carbide. Little is known concerning the compounds of molybdenum and carbon except the report of Neuburger (29) on the existence of a carbide, Mo_2C. The literature offers no information concerning the possible ternary compounds of iron-molybdenum-carbon.

If the molybdenum is wholly or in part associated with the carbide, $-\Delta F$ would become less positive and the tendency for the decomposition of the Fe_3C, according to equation (1), would be less. This mechanism has been confirmed by the experimental results that have been obtained in this investigation.

V. CONCLUSIONS AND SUMMARY.

1. A study has been made of the quantitative effect of molybdenum upon the decomposition of iron carbide in the malleablization process for white cast iron. Molybdenum contents from one to five per cent were employed.

2. It has been shown that the rates of graphitization for both secondary and primary stages definitely decrease with an increase of the molybdenum content. The secondary stage is practically negligible for the five per cent molybdenum alloy over a time interval of 255 hours.

3. Definite time requirements for the primary and secondary stages of graphitization have been determined for each molybdenum composition. These results are shown in tables in their proper sequence.

4. It has been shown that the presence of molybdenum results in a positive refinement of the grain structure.

5. No attempt has been made to correlate the physical properties of the alloys with the chemical composition except the observations that were made during the breaking, grinding and polishing of the samples. Such observations have led to the belief that molybdenum imparts increased hardness, toughness and tensile strength to the malleablized iron.

6. The effect of chromium, alone and in combination with molybdenum, upon the rates for the decomposition of iron carbide in white cast iron has been determined. It has been found that the graphitization is completely stopped in all alloys containing chromium from one to five per cent.

7. Photographs have been included to show the effects of molybdenum, chromium and molybdenum-chromium combinations.

8. The general free energy equation has been applied in the theoretical prediction of the effects of selected elements on the rates of graphitization of commercial white cast iron. Experimental evidence offers confirmation to these theoretical predictions.

9. A general review of the literature, as applied to the effects of various elements on graphitization rates, has been given. A comprehensive bibliography is appended.

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