

1928

I. The causes of incomplete graphitization near the surface when white cast iron is malleableized, II. The production and prevention of embrittlements in malleable castings by heat treatments below the critical range

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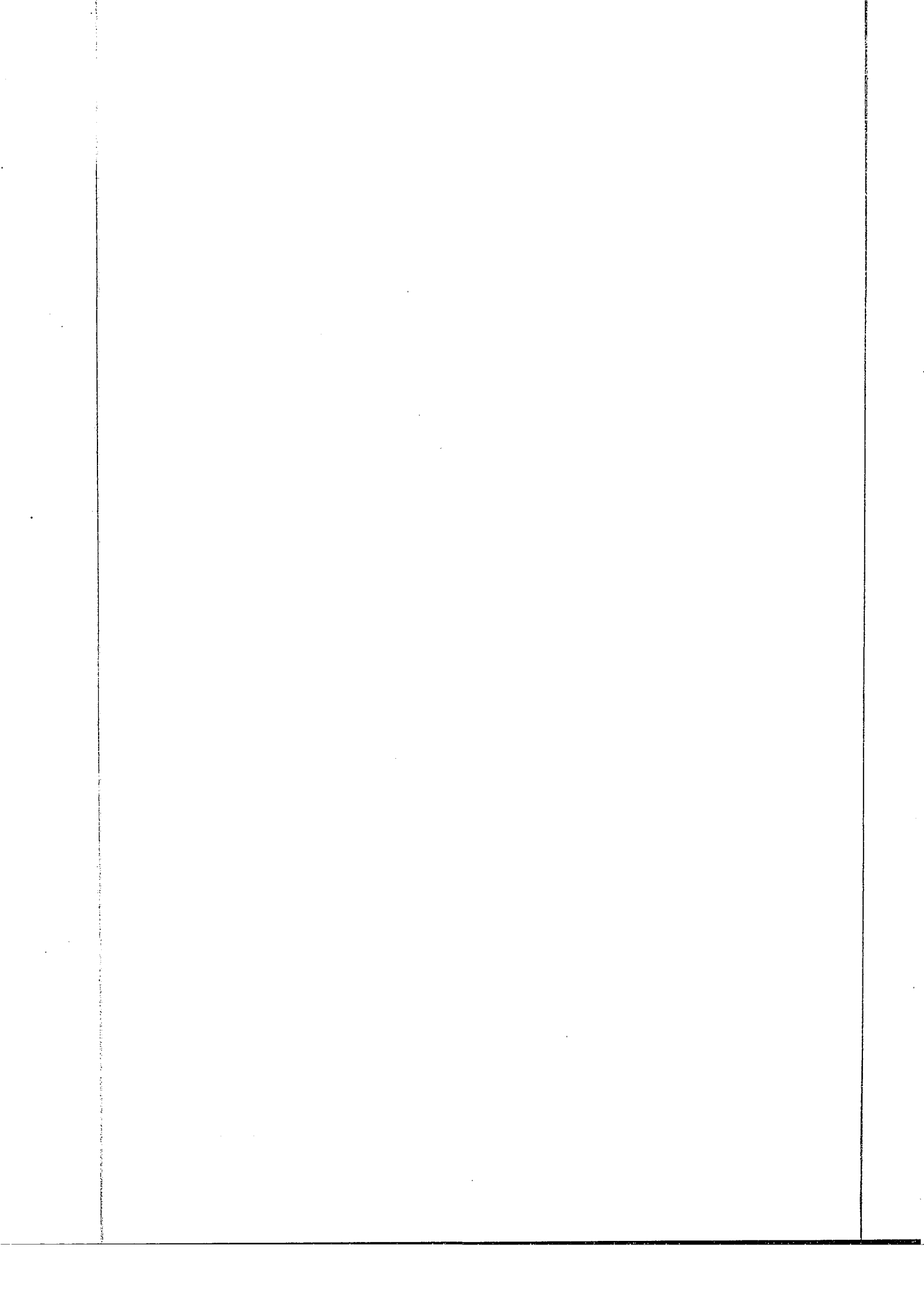
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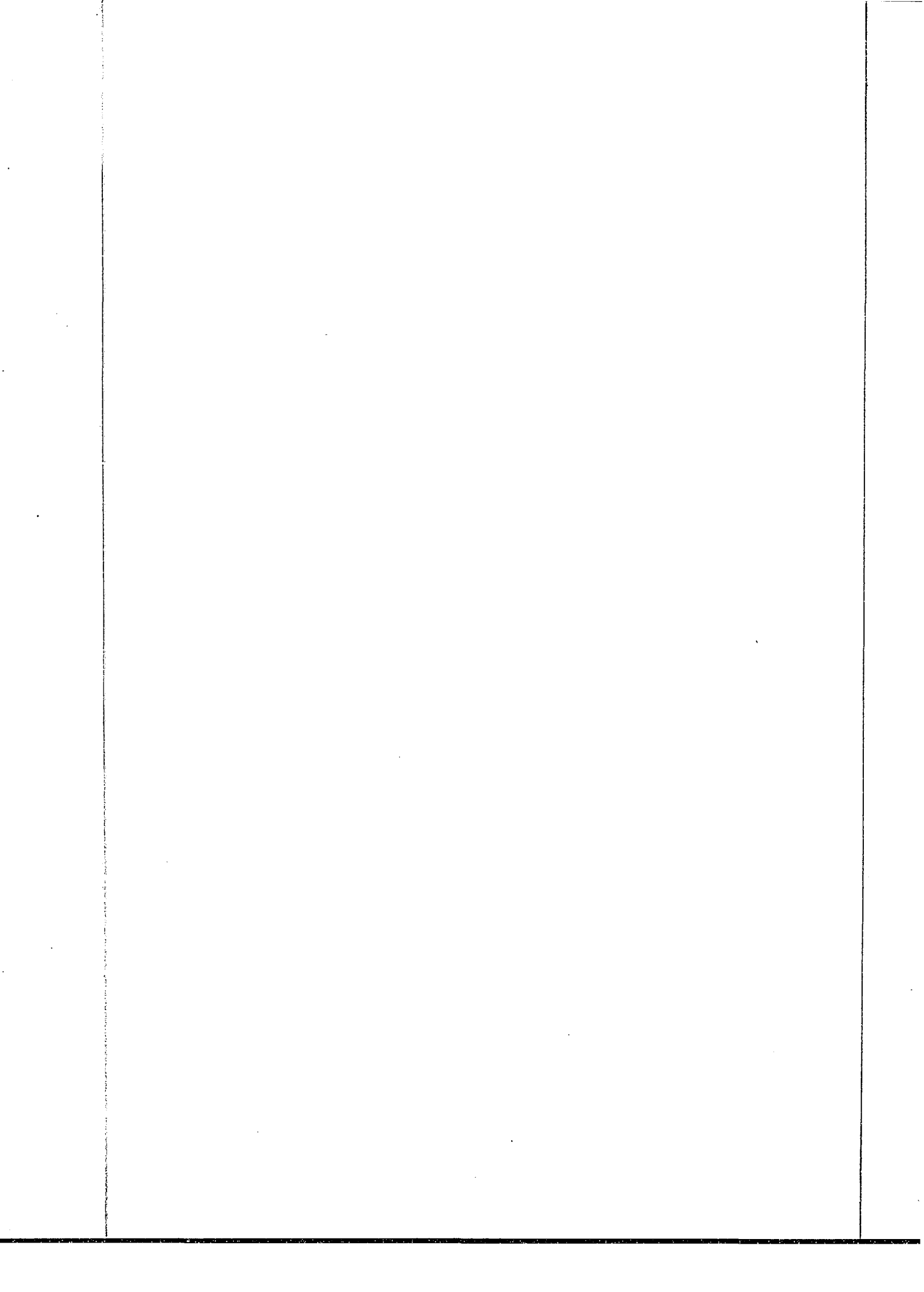
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- I. THE CAUSES OF INCOMPLETE GRAPHITIZATION NEAR THE SURFACE
WHEN WHITE CAST IRON IS MALLEABLEIZED
- II. THE PRODUCTION AND PREVENTION OF EMBRITTELEMENTS IN MALLEABLE
CASTINGS BY HEAT TREATMENTS BELOW THE CRITICAL RANGE

A Thesis Submitted
to the Graduate Faculty in Candidacy
for the Degree of

DOCTOR OF PHILOSOPHY

by

Hyrum Edward Flanders

Major Subject: Physical Chemistry

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I - THE CAUSES OF INCOMPLETE GRAPHITIZATION NEAR THE SURFACE WHEN WHITE CAST IRON IS MALLEABLEIZED

INTRODUCTION

No systematic study of the incomplete graphitization near the surface of white cast iron, which frequently occurs during the process of graphitization, has been made. It was because of the need of such a study that this work was attempted. It was thought that such a study would develop certain principles which might be used in preventing this difficulty.

This incomplete condition is represented by a thin band of combined carbon existing as pearlite and varying in composition up to eutectoid or even hypereutectoid. It is usually distinctly hypoeutectoid. It is situated parallel to the surface and varies in depth according to conditions. There is usually a band of ferrite between this pearlitic portion and the surface but such is not necessarily the case. Inside the pearlitic area are the ferrite and carbon spots of the normal malleable iron. Due to the appearance of this structure, it has been given different names chief of which is "picture frame" which will be its name in this paper.

Due to the fact that the pearlitic layer is distinctly harder than the ferrite portions irregularities occur in the machining operation that hinder greatly the high speed process. Its effect is also felt in other ways. This incomplete graphitization is then a serious consideration in malleable cast iron production and is the cause of great loss of yield in the product.

HISTORICAL

The formation of picture frame has long been recognized. Its presence was for a long time detected by the nature of the fracture and various causes of these fractures were assigned. With the advent of the microscope into metallurgical control a closer acquaintance with picture frame was had.

In spite of the long recognition of this trouble there is but little discussion of any value in the literature. E. Touceda has done much to direct attention to a specialized study of this problem, but he was more interested in a practical result than in a theoretical discussion of the difficulty. His first study considers primarily the nature of the fracture. (1) He refers to it here as "skin formation." In a later paper, (2) he mentions picture frame. In this article he says, "Very frequently certain low silicon, carbon, manganese compositions will yield what are known as picture frame fractures." Typical ones were produced by him in bars containing: Si, 0.54%; P, 0.162%; S, 0.053%; Mn, 0.108%; C, 2.01%. (This would be an extremely slow graphitizing alloy.) He found that the pearlitic portion generally corresponded to a combined carbon composition of 0.35% C. to 0.45% C. Quoting further, he said, "If the sulphur in the hard iron is unduly high and particularly if not well balanced by manganese the castings will almost invariably show a picture frame on the fracture, and especially is this true if the temperature of anneal is too high and not well balanced by sulphur the same result will follow. There are some compositions that unquestionably have frame producing tendencies.

These compositions will not produce a frame when annealed in an atmosphere which is not oxidizing." Surface structure of the white cast iron has no effect as was shown by his experiments. "It is the belief of the writer that whether there will be a pearlitic ring or not depends upon the rate of surface decarbonization as compared with the rate at which a dissociation of the cementite takes place. When conditions are such that there will exist a region between the decarbonized surface border and the core that will have a carbon content of about 0.90%, equilibrium seems to be established in this region and if carbon passes from this region to the decarbonized border it is replenished by carbon from the core."

By reheating a series of eight specimens he found that the picture frame fracture was found to be deeper each time and was deepest and widest in the sample heated eight times. In each anneal the total carbon decreased. Again quoting, "The matter can be summed as follows: if conditions are such that a region containing 0.90% or less carbon is formed this region while permitting carbon to migrate or diffuse through it will at the same time be incapable of having its carbon precipitated. Under proper conditions the region can alter its position and increase in extent. For such a region to have a start it is essential that there be a very substantial difference in carbon content in the two parts of the section."

Oberhoffer and Welter (3), (4), studied the effect of sulphur and manganese in the formation of picture frame. It was definitely shown by analyses and photomicrographs that an accumulation of sulphur due to furnace conditions takes place in the outer portions of the castings being

graphitized. It was also shown that when a low sulphur alloy is treated in an atmosphere containing sulphur that this element was absorbed to increase the sulphur content. On the other hand excessively high sulphur contents may be reduced during treatment. The presence of oxides were also shown in the surface decarburized portions.

Oberhoffer and Zingg (5), made a study of equilibrium conditions in furnace gases and suggested equations for the decarburization of iron. High silicon content was found to increase the amount of skin and scale over that formed at lower concentrations.

Bean (6), divided fractures in which picture frame was present into two classes: First, a stable pearlite near the surface resulting from abnormal compositions. This pearlite is incapable of graphitization. Second, "amealing" or "cooling" rim pearlite not necessarily stable. This is the result of a "rate of cooling at the critical point being so high as to arrest the graphitization in that portion of the casting where decarburization had already rendered graphitization somewhat difficult." The pearlite formed through this cause can be made to graphitize by longer treatment provided abnormal compositions do not enter into its formation.

EXPERIMENTAL

It was shown quite conclusively in a portion of this research omitted from this thesis that oxidation is one of the factors in picture frame formation. Considerable thought was then given to the various constituents in the white cast iron which might be affected. The simplest conclusion was that some of the silicon existing in the casting as solid solution

might be oxidized to silicon dioxide during the graphitization process. This would remove part of the silicon from activity in promoting graphitization and the process would therefore be slower. Since the oxidation of this silicon would be greatest at the surface the lowest concentration of silicon existing in the solid solution would be there. As the interior of the alloy is reached the amount of silicon dioxide would decrease. There would thus arise a silicon gradient causing a gradually increasing rate of graphitization toward the central portions of the casting. The decarburized portion was considered to be due to the direct oxidation of carbon by the exterior gases.

To test these ideas test bars of both white cast iron and malleable cast iron were put into cylindrical shape so that concentric shells could be machined off the bars and analyzed after these had been heat treated. These shells were one half millimeter thick. They were analyzed for silicon and silicon dioxide by a method given by E. Britzke (7).

In this method total silicon is determined in the usual way and the silicon dioxide is found by passing dry chlorine gas over the samples to be analyzed. These samples were placed in porcelain boats which were put in a three quarter inch quartz tube thirty inches long through which the chlorine gas was passed. The chlorine was purified by passing it through dry calcium chloride, sulphuric acid and carbon which was placed in the quartz tube in such a way as to be heated to the temperature of the samples. This was to remove any oxygen in the gas. We used a twenty inch tubular electric furnace which was made for this work. The samples were heated to about 900° C. but most of the action had ceased before a dull red heat was reached.

The residue consisting of carbon and silicon dioxide was put into a platinum crucible and weighed. After any carbon was burned off it was weighed again. This loss in weight represented an approximate carbon determination. The remaining residue was treated with hydrofluoric acid to give the weight of silicon dioxide which was present in the shell of the test bar. The method proved to be very difficult and checks were present in every analytical test to make sure of the conditions. Five boats were generally run two or three of which were samples to be analyzed. The least variation from ideal conditions destroyed the value of the result.

The test bars used in these tests had the following analysis:

C, 2.40%; Si, 0.98%; P, 0.19%; Mn, 0.23%; S, 0.05%.

The experiments are summarized under the tests enumerated below.

TEST NO. 1

A cylindrical bar of malleable cast iron (No A₃₀) was put in a three inch iron pipe nearly filled with fine graphite and closed at both ends by means of caps. Another cylindrical bar (No A₃₂) was put in the open hump furnace together with the above three inch pipe and its contents. The furnace was closed and holes covered with insulation. The heat treatment given was:

Heated to 1750° F in three hours and held 18 hours
1750° F to 1400° F in 6-1/2 hours
1400° F to 1200° F in 7-1/2 hours
1200° F to 1000° F in 13 hours
Cooled in furnace

The bar No A₃₀ showed no indication of oxidation. The analysis of the concentric shells is given in Table 1. Bar No A₃₂ showed excessive oxidation and its shells analyzed as given in Table 2.

TABLE 1

ANALYSIS OF SHELLS OF BAR NO A₃₀

ANALYSIS FOR CARBON

TEST	SHELL NO.					
	Surface					Interior
	1	2	3	4	5	6
1		2.33	2.42	2.36	1.92	
2	1.92	2.03				
3	1.86	2.10	2.24	2.31	2.41	
4	1.90	2.26	2.35	2.33	2.62	
5	1.71	3.03	2.12	2.80	2.70	
AVERAGE	1.85	2.18	2.29	2.53	2.41	

ANALYSIS FOR Si as Si O₂

TEST	SHELL NO.					
	Surface					Interior
	1	2	3	4	5	
1	0.05	0.03	0.04	0.02	0.01	
2	0.06	0.01	0.01	0.01	0.01	
3	0.06	0.05	0.07	0.03	0.01	
4	0.03	0.00				
5	0.06	0.05				
6	0.15	0.07	0.01	0.00	0.01	
AVERAGE	0.07	0.03	0.03	0.02	0.01	

TABLE 2

ANALYSIS OF SHELLS OF BAR A32

ANALYSIS FOR CARBON

TEST NO.	SHELL NO.					Remarks
	Surface	1	2	3	4	
1	0.00	0.25	0.70	1.18	1.77	In 1 oxides present
2	0.03	0.15	0.60	1.03	1.33	In 2 attempted to pick from oxides
AVERAGE	0.01	0.20	0.70	1.10	1.55	

ANALYSIS FOR Si as Si O₂

TEST NO.	SHELL NO.					Remarks
	Surface	1	2	3	4	
1	2.58	0.141	0.03	0.04	0.04	Same as above
2	0.56	0.08	0.01	0.00	0.00	
AVERAGE		0.11	0.02	0.02	0.02	

TEST NO. 2

For the purpose of finding the result of a long treatment at a high temperature with carbon monoxide and carbon dioxide acting under conditions which are not oxidizing a cylindrical bar of malleable cast iron (No A₃₃) was put in a three inch iron pipe filled with graphite and closed at both ends as in Test No. 1. This was held for about fifty hours at 1750° F to 1800° F and cooled in the furnace. Upon removal a slight indication of oxidation on the surface was present. The analysis of the

shells is recorded in Table 3.

TABLE 3
ANALYSIS OF SHELLS OF BAR A₃₃
ANALYSIS FOR CARBON

TEST NO.	SHELL NO.					
	Surface	1	2	3	4	Interior
1	1.35	1.26	1.47	1.41	1.52	
2	1.65	1.23	1.57	1.71	1.81	
3	1.38	0.87	1.34	1.98	1.64	
4	1.38	1.42	1.32	1.58	1.36	
AVERAGE	1.44	1.19	1.42	1.67	1.56	

ANALYSIS FOR Si as Si O₂

TEST NO.	SHELL NO.					
	Surface	1	2	3	4	Interior
1	0.19	0.03	0.05	0.02	0.02	
2				0.02	0.02	
3	0.35	0.08	0.05	0.07	0.03	
4	0.25	0.08	0.04	0.02	0.01	
AVERAGE	0.23	0.06	0.03	0.03	0.02	

TEST NO. 3

A malleable cast iron bar (No A₃₄) was packed as in Test No. 2 and heated for 44 hours at 1400° F to 1475° F then cooled in 9 hours from 1475° F to 1300° F. This was followed by seven hours cooling to 800° F. The bar showed considerable oxidation due chiefly to furnace conditions. After removing these oxides the shells analyzed as given in Table 4.

TABLE 4

ANALYSIS OF SHELLS OF BAR A₃₄

ANALYSIS FOR CARBON

TEST NO. :	SHELL NO.				
	Surface	1	2	3	Interior:
1	0.12	0.16	0.23	0.83	0.97
2	0.06	0.22	0.20	0.41	0.90
3	0.06	0.10	0.16	0.36	0.70
4	0.12	0.26	0.22	0.72	1.04
AVERAGE	0.09	0.18	0.20	0.58	0.90

ANALYSIS FOR Si as Si O₂

TEST NO. :	SHELL NO.				
	Surface	1	2	3	Interior:
1	0.40	0.01	0.01	0.01	0.
2	0.02	0.01	0.00	0.00	0.00
3	0.01	0.00	0.01	0.01	0.01
4	0.03	0.00	0.00	0.00	0.01
AVERAGE	0.02	0.01	0.01	0.01	0.01

TEST NO. 4

Mr. G. C. Scott (8) was doing experimental work at this time so a cylindrical bar (No A₃₇) was given a heat treatment under a pressure of sixty pounds per square inch the gases being an equilibrium mixture of carbon monoxide and carbon dioxide. The results are given in Table 5.

TABLE 5

ANALYSIS OF SHELLS OF BAR NO A37

	SHELL NO.				
	Surface		Interior		
	1	2	3	4	5
% C	0.39	1.77	1.92	1.56	
% Si as					
Si O ₂	0.10	0.04	0.04	0.03	

A summary of the results given above and of others of a similar nature is given in Table No. 6.

TABLE 6

TABULATED RESULTS OF ANALYSES OF CONCENTRIC SHELLS

	SHELL NO										Remarks	
	Surface							Interior				
	1	2	3	4	5	6	7	8	9			
	% Si	% Si	% Si	% Si	% Si	% Si	% C	% C	% C	% C	% C	% Si
	as	as	as	as	as	as	as	as	as	as	as	as
	SiO ₂	SiO ₂	SiO ₂	SiO ₂	SiO ₂	SiO ₂	SiO ₂	SiO ₂	SiO ₂	SiO ₂	SiO ₂	SiO ₂
Bar No A30	1.85	0.07	2.18	0.03	2.29	0.03	2.33	0.02	2.41	0.01		Average of 5
Bar No A32	0.03	0.56	0.30	0.11	0.70	0.02	1.10	0.02	1.55	0.02		Oxides present in 1st shell
Bar No A33	1.44	0.25	1.19	0.06	1.42	0.03	1.67	0.03	1.56	0.02		
Bar No A34	0.06	0.11	0.11	0.00	0.13	0.01	0.39	0.00	0.56	0.00		
Bar No A37	0.39	0.10	1.77	0.04	1.92	0.04	1.56	0.03				Miscellaneous
Bar No A51	0.56	0.22	0.71	0.01	0.92	0.00	0.52	0.01	1.06	0.00		
Bar No A52	0.26	0.14	0.50	0.01	0.78	0.00	0.51	0.02	1.02	0.00		

From the results of the tests just recorded it can be seen that the oxidation of silicon in the surface portions of the white cast iron as it graphitizes is not an important factor in causing "picture frame."

Analysis of the concentric shells of bar No A₃₃ for phosphorus gave the following results:

Shell No.	1	2	3	4	5
% Phosphorus	0.216	0.234	0.247	0.234	0.219

This was a little higher than the average analysis of the bar which was 0.19% phosphorus. It has been shown that sulphur will accumulate in the surface portions of the piece as it is being graphitized if sulphur is present in the furnace gases. Any study of sulphur must include a parallel study of manganese due to the close relationship of these elements in iron alloys. The presence of a carbon gradient is distinctly visible in any malleable iron piece. This study then at this point become a study of the effects of the different constituents present in white cast iron, on the graphitization rate, when the carbon is at different concentrations.

It was accordingly decided to make alloys that had but one of the constituents variant while the amount of carbon was held at different values. This should give the effect of the different constituents under different carbon concentrations. To make these alloys proved to be a task that required much labor and material before a technique and method were developed that would give desirable constancy in the compositions.

The alloys were made in an Ajax induction furnace. The coil was cylindrical in shape, four inches in diameter, ten inches deep. Inside this coil was placed a four inch asbestos shell as a protection to the coil. Different sizes of cylindrical carbon crucibles made from Acheson

graphite were centrally located in the furnace and vitrefax (an impure magnesium oxide) screened between ten and thirty mesh was put between this and the asbestos shell. This screened material proved to be the best insulation we could find. Since the chief function of the graphite crucible put in the furnace in this way was to hold the insulation it was sometimes made with a very thin wall to give a larger capacity.

Refractory linings were made in another graphite crucible of such a size as to fit loosely in the furnace as prepared above. These were also made of Acheson graphite. The lining was of finely powdered vitrefax (60 mesh) which was chosen after trial because of its greater strength over linings made of pure magnesium oxide. Some loose vitrefax was put in the bottom of the graphite crucible and a tapered carbon rod or a piece of glass tubing of the proper size was centrally located in the crucible. "Vitrefax" was then filled around the rod or glass tubing and packed by means of pounding on the table adding more vitrefax as that around the rod settled. When sufficient was in, the rod or tube was carefully removed and an unbroken lining resulted. This was put in the furnace and heated to about 1800° C or until it fumed profusely. After slow cooling a very dense hard crucible lining slightly smaller than its container, so that it could be easily removed, resulted.

The thickness of its walls could be easily regulated. These linings were always used in a graphite container as a protection to the furnace and also as a means of lifting out of the furnace. Above 1600° C these linings get quite fragile and hard to handle when full of molten iron. When the depth of the molten alloy exceeded three inches the refractory crucible was very apt to crack and allow the contents to be contaminated with an excess of carbon.

All the alloys reported in this research were made by melting about 800 grams of a mixture of white cast iron and ARMCO Ingot Iron together with enough ferro-phosphorus, ferro-manganese, ferro-silicon, and iron sulphide to approach the desired composition. This 800 grams of melted alloy was poured into four smaller crucibles which had been heated to about 900° C to avoid cracking. Each of these portions was again melted and carbon additions made. They were then poured into dry sand moulds and allowed to cool. The chemical composition of the alloys together with the heat treatment number and the results are given in the following Table 8.

TABLE 8

ANALYSIS OF SAMPLES USED IN TESTING GRAPHITIZATION RATES WITH INDICATED HEAT TREATMENT AND RESULTS

SAMPLE:	:	:	:	:	:	Heat Treat-	% Graphi-
N	% Si	% Mn	% S	% P	% C	ment No	tization :
114 A	:1.03	:0.249	:0.03	:0.191	:1.70	:	: 44 :
114 B	:1.03	:0.244	:0.041	:0.188	:2.08	:	: :
114 C	:1.00	:0.240	:	:0.192	:2.30	4	: 57 :
114 D	:0.95	:0.228	:0.045	:0.205	:2.53	:	: 70 :
:	:	:	:	:	:	:	: :
122 A	:1.056	:	:0.022	:0.218	:1.84	:	: 29 :
122 B	:0.985	:	:0.033	:0.199	:2.24	4	: 75 :
122 C	:0.985	:	:0.021	:0.192	:2.88	:	: 29 :
122 D	:0.946	:	:0.027	:0.184	:3.35	:	: 100 :
:	:	:	:	:	:	:	: :
139 A	:	:	:	:	:	:	: 57 :
139 B	:	:	:	:	:	:	: 89 :
139 C	:	DUPLICATE OF 142's				:	: 92 :
139 D	:	:	:	:	:	:	: :
:	:	:	:	:	:	:	: :
142 A	:0.76	:0.154	:0.053	:0.17	:	1	:See No. :
142 B	:0.74	:0.153	:0.054	:0.165	:	:	: 139's :
142 C	:0.77	:0.155	:0.057	:0.155	:	:	: :
142 D	:0.76	:0.157	:0.044	:0.165	:	x	: :
:	:	:	:	:	:	:	: :
161 A	:0.71	:0.13	:0.073	:0.21	:1.65	:	: 20.5 :
161 B	:0.71	:0.12	:0.070	:0.20	:2.13	1	: 49.2 :
161 C	:0.68	:0.13	:0.075	:0.18	:2.28	:	: 64.3 :
161 D	:0.69	:0.13	:0.074	:0.19	:2.47	:	: 68.6 :

(Continued on next page)

SAMPLE:	:	:	:	:	:	:	Heat Treat-	:% Graphi-	:
N	:	% Si:	% Mn:	% S :	% P :	% C :	ment No	tization :	:
166 A	:	1.022:	0.218:	0.042:	0.201:	:	:	70	59 :
166 B	:	1.026:	0.202:	0.044:	0.198:	See	:	:	55 :
166 C	:	0.968:	0.193:	0.046:	0.199:	Fig. 1A:	2	:	70 :
166 D	:	0.983:	0.196:	0.046:	0.188:	:	:	76	:
168 A	:	0.883:	0.235:	0.042:	0.283:	:	3 2	:	74 32 :
168 B	:	0.845:	0.220:	0.046:	0.260:	See	:	:	49 23 :
168 C	:	0.790:	0.209:	0.046:	0.255:	Fig. 1B:	:	:	44 :
168 D	:	0.823:	0.214:	0.041:	0.270:	:	:	:	55 18 :
:	:	:	:	:	:	:	:	:	:

The results are recorded by means of a term "percentage graphitization" which is defined as

$$\frac{\text{area of ferrite}}{\text{area of (ferrite + pearlite)}} \times 100$$

The heat treatment was such as only to allow partial action below the eutectoid temperature (1420° F). This was done by holding at about 1300° F to 1350° F and removing all the members of any one set at a chosen time usually found by previous experiment. The samples were

polished, etched and the relative areas of pearlite, carbon and ferrite counted by means of a set of squares placed on the microscopic image focussed on a ground glass. The positions of these observations was taken in a definite way over the surface of the sample and at least ten images recorded for a result. It is thought that the above method of recording gives a very good picture of the state of the sample during the process of the action below the lower critical point.

HEAT TREATMENT NO. 1

Heated to 1825° F in 2-1/2 hours
Cooled to 1725° F in 1 hour
Cooled to 1705° F in 75 hours
Cooled to 1400° F in 16 hours
Held between 1400° F and 1340° F - 3-1/2 hours

HEAT TREATMENT NO. 2

Heated to 1760° F in 2 hours
Held 1760° F to 1700° F for 110 hours
Cooled 1700° F to 1365° F in 9 hours
On removal these did not show a desirable structure for comparison so they were again put in the furnace and held at 1500° F for 1 hour.
Cooled to 1420° F in 2 hours
Cooled to 1240° F in 12 hours

HEAT TREATMENT NO. 3

Heated to 1700° F and held 10 hours
Cooled to 1430° F in 3-1/2 hours
Cooled to 1250° F in 5-1/2 hours

HEAT TREATMENT NO. 4

Heated to 1700° F and held between 1675° F and 1750° F for 42 hours
Cooled from 1675° F to 1475° F in 6-1/2 hours
Held 1475° F for 2 hours
Cooled 1480° F to 1355° F in 6 hours

In the heat treatment of the samples it was found necessary to hold some of them for a long time at the high temperature (1650° F to 1800° F)

in order to complete the absorption of the free cementite. High sulphur together with low manganese was the worst condition met with. High manganese with a low sulphur increased the time necessary greatly. Low silicon made the time longer. The effect of phosphorus was not so pronounced but seemed to be of the opposite nature. In all cases it took longer for the absorption of the carbon in the high carbon samples.

In two sets of alloys, one giving different manganese contents and the other different sulphur contents, there was a definite minimum time requirement at the high temperature indicating that there is a manganese and sulphur ratio deviations from which makes the graphitization slower. This was also found to be true in the graphitization below the eutectoid temperature. Whether or not this ratio of manganese to sulphur that gives the shortest time is a constant for various compositions of either constituent was not investigated.

A series of experiments reported in a published article (9), were based on the concept of a manganese sulphur ratio that gives faster graphitizing material. Sulphur was added to high manganese alloys to improve them and manganese was added to high sulphur alloys for the same purpose.

Quantitative data obtained in this laboratory under the direction of Dr. Anson Hayes further showing the effects of chemical composition on graphitization rates are given in Tables 9, 10, and 11.

TABLE 9

EFFECT OF MANGANESE OF DIFFERENT COMPOSITIONS ON GRAPHITIZING TIME BELOW Ar₁

ALLOY	% C	% Si	% P	% Mn	% S	TIME
1	2.45	0.97	0.10	0.048	0.063	740
2	2.40	0.93	0.15	0.067	0.059	36
3	2.45	0.92	0.11	0.102	0.06	26
4	2.52	0.98	0.144	0.163	0.061	12
5	2.48	0.94	0.15	0.19	0.055	12
6	2.45	0.96	0.135	0.266	0.058	12

TABLE 10

EFFECT OF MANGANESE OF DIFFERENT COMPOSITIONS ON GRAPHITIZING TIME BELOW Ar₁

ALLOY	% C	% Si	% P	% Mn	% S	TIME
1	2.50	0.87	0.14	0.115	0.16	Incomplete
2	2.53	1.11	0.14	0.215	0.16	718
3	2.48	1.11	0.14	0.306	0.158	13
4	2.54	1.11	0.14	0.392	0.159	11
5	2.54	1.10	0.139	0.443	0.159	11
6	2.51	1.10	0.141	0.535	0.162	13

TABLE 11

EFFECT OF MANGANESE OF DIFFERENT COMPOSITIONS ON GRAPHITIZING TIME BELOW Ar₁

ALLOY	% C	% Si	% P	% Mn	% S	TIME
1	2.48	0.84	0.134	0.091	0.132	
2	2.48	0.85	0.132	0.175	0.130	39
3	2.47	0.83	0.135	0.209	0.136	36-1/2
4	2.46	0.84	0.134	0.306	0.132	33
5	2.45	0.85	0.131	0.406	0.129	30-1/2
6	2.49	0.85	0.133	0.478	0.126	32-1/2
7	2.53	0.83	0.132	0.662	0.133	35

During the progress of this research problem there was reported a similar investigation by Kikuta (12). In this work the effect of the various elements on rates of graphitization of white cast iron were studied by means of a dilatometer. This method had the distinct advantage in that the progress of the action could be watched and a definite time result easily attained. Graphitization was divided into two parts - the absorption of the free cementite at the high temperature (1700° F - 1800° F) being called the first stage and the precipitation of carbon below A_{r_1} being called the second stage. His results give quantitative confirmation to results of necessity of a more qualitative nature found in this research. His data however were got from a different point of view and only two carbon compositions (2.00% C and 2.50% C) were studied consistently. The second stage of graphitization was only studied with the alloys shown in Table 12. It can be seen that there are only two alloys in which the carbon is very different from 2.50% (14 and 32) and the difference in these is only in the silicon. The graphitizing times (25 and 7-1/2 hours) show distinctly the effect of carbon at 710° C. Probably a better comparison is with No. 14 and 25 which show graphitizing times of 25 hours and 12 hours respectively. The effect of silicon on this time requirement is very plain from the data.

ALLOYS STUDIED BY KIKUTA (12) WITH REFERENCE
TO THE SECOND STAGE OF GRAPHITIZATION AT 710° C

SAMPLE	% C	% Si	% Mn	% S	% P	Time of graphiti- zation at 710° C
14	2.09	1.22	0.24	0.023	0.122	25 hours
21	2.45	0.86	0.19	0.029	0.115	25 hours
24	2.42	1.07	0.17	0.028	0.134	16 hours
25	2.53	1.21	0.17	0.031	0.137	12 hours
26	2.42	1.35	0.16	0.023	0.132	9 hours
27	2.39	1.51	0.16	0.029	0.127	6 hours
28	2.41	1.64	0.19	0.028	0.129	5-1/2 hours
32	2.84	1.23	0.17	0.021	0.095	7-1/2 hours
40	2.51	1.15	0.46	0.033	0.127	24 at 700
41	2.61	1.20	1.02	0.033	0.130	43 at 690
46	2.45	1.24	0.26	0.007	0.061	6 hours 20 min.
47	2.62	1.15	0.22	0.026	0.126	10 at 710° C
48	2.50	1.14	0.22	0.051	0.121	15 hours
49	2.54	1.14	0.22	0.066	0.128	23 hours
50	2.45	1.15	0.22	0.072	0.120	22 + x
56	2.54	1.13	0.22	0.027	0.212	11 hours
58	2.40	1.14	0.22	0.039	0.451	9 hours
60	2.41	1.06	0.20	0.059	0.792	10 + x
:	:	:	:	:	:	:

DISCUSSION

The outstanding fact developed in the time studies of graphitization indicate that a carbon gradient resulting from the removal of carbon from the surface portions of the castings is one of the causes of picture frame. In commercial practice the carbon is removed completely in the ferrite rim and carbon nuclei are absent in the pearlitic portion. The absence of these carbon nuclei is one reason for slow graphitization in this portion.

We have also seen the effects of the various compositions of the constituents manganese and sulphur on the rates of graphitization of alloys of the same carbon content the promotion of picture frame by the absorption of sulphur from the furnace gases is then very plain. Aggravated conditions

of this type however will give rise to the class of picture frame caused by stable pearlite as outlined by Bean (6). To remove this pearlite decarburization must take place. In some of our tests of commercial samples such conditions have been met.

It is highly improbable that any gradient of impurities will form such that the high concentrations of them will be at the surface of white cast iron. The impurities, especially phosphorus and sulphur, tend to accumulate in the last solidifying liquid. Proper attention to sinkheads and the avoidance of shrink in the castings eliminates considerable of these impurities by having this last solidification take place in the sinkhead. The accumulation of phosphorus and sulphur in the surface portions as has been shown must then result from conditions arising during the annealing operation.

In the case of phosphorus a reason for its higher concentration near the surface can be based on the fact that phosphorus tends to separate itself from the carbon containing portions of the piece. As the surface is decarburized phosphorus diffuses to these carbon free areas. Phosphorus however has no decided effect on the rate of the action at 1300° F until its concentration gets considerably greater than that ordinarily present in the malleable cast iron.

The accumulation of sulphur in the surface portions has been explained above from the work of Oberhoffer and Welter (3), (4).

It may be said that certain compositions have greater picture frame tendencies than others. In some cases we have met picture frame pearlite after extended time treatment at 1300° F while in others the tendency must be recognized in the partially graphitized piece. Except in the extreme

case the pearlite will always decompose if given time. It is not permissible to consider the furnace gases responsible for all picture frame but when compositions are not ideal, or particularly when the manganese sulphur ratio is off, picture frame formation becomes more of a problem. With a manganese composition that is near the lower limit necessary to neutralize the sulphur when this too is low, the castings are particularly sensitive to sulphur content in the furnace gases since the absorption of sulphur under these conditions retards the graphitization rate very much and picture frame results. Any slowly graphitizing casting has a marked tendency toward picture frame.

As a result of work not given in this thesis other causes of picture frame have been found and it is hoped that these can be given consideration at some future date.

SUMMARY AND CONCLUSION

It is shown in this paper that picture frame in malleable castings is due to:

- FIRST -- A carbon gradient which results from the oxidation of the carbon present in the casting by the furnace gases.
- SECOND - The absorption of sulphur from the furnace gases causing a high sulphur content in the surface portions and a resulting slow action at 1300° F in these portions, and
- THIRD -- Alloys whose composition causes it to be a slowly acting one.
- FOURTH - When the picture frame is not due to "stable" pearlite it may be removed by further annealing.

FIFTH -- Oxidation is a primary cause of picture frame but other causes acting in connection with this must be considered before a true picture of the process of its formation is had.

LITERATURE CITED

- (1) Touceda, E. - Phosphorus Limit in Malleable Castings. Foundry, 43: 446 - 9. 1915.
- (2) Touceda, E. - Research Work on Malleable Iron. Mech. Eng., 41: 593 - 600. 1919.
- (3) Oberhoffer, P. und Welter, J. - Beitrag zur Kenntnis des Temperprozesses. Stahl und Eisen, 43: 105 - 110. 1923.
- (4) Oberhoffer, P. und Welter, J. - Beitrag zur Kenntnis des Temperprozesses. Stahl und Eisen, 43: 301 - 7. 1923.
- (5) Oberhoffer, P. und Zingg, E. - Ueber die Schalenbildung beim Temperprozess. Stahl und Eisen, 44: 1197 - 1200. 1924.
- (6) Bean, W. R., Highriter, H. W. and Davenport, E. S. Explain the Structures of Malleable. Foundry, 49: 557 - 6. 1921.
- (7) Britzke, E. - Uber die Trennung der Kieselsaure von Silicium und Kohlenstoff. Chem. Zeit., 33: 1098 - 9. 1909.
- (8) Hayes, A. and Scott, G. C. The Catalysis of the Graphitization of White Cast Iron by the Use of Carbon Monoxide Carbon Dioxide Mixtures When Applied Under Pressure. Trans. Am. Foundrymen's Assoc., 33: 575 - 93. 1925.
- (9) Hayes, A. and Flanders, H. E. One of the Causes of Variations in Rates of Graphitization of White Cast Iron. Trans. Am. Foundrymen's Assoc., 33: 634 - 7. 1925.
- (10) Hayes, A. and Gray, M. P. - Information on Graphitizing Time. Private Communication.

- (11) Yemanidjian, M. K. - On the High Sulphur - Manganese White Cast Iron Alloys and Their Rates of Graphitization - Unpublished Thesis. Library Iowa State College, Ames, Iowa. 1928.
- (12) Kikuta, T. - On the Malleable Cast Iron and the Mechanism of Its Graphitization. Sci. Repts. Tohoku Imp. Univ., 15: 115 - 55. 1926.

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II - THE PRODUCTION AND PREVENTION OF EMBRITTLEMENT IN MALLEABLE CASTINGS BY HEAT TREATMENTS BELOW THE CRITICAL RANGE

INTRODUCTION

Many malleable castings are used under conditions in which there is no wear, and to prevent their deterioration through corrosion, coatings are applied. Probably the cheapest and best method of applying a durable coating is by galvanizing with zinc in the "hot dip" process. The process consists in immersing the castings for a short time in the molten zinc, the temperature of which is kept near 840° F. to 850° F. in order to keep the zinc in the fluid condition.

Difficulties that have not yet been explained arise as a result of this galvanizing process. Perfectly normal malleable castings when subjected to this galvanizing treatment often result in material very brittle in nature and of a very inferior quality. This paper is a discussion of work done in seeking information about these difficulties.

HISTORICAL

In discussing the brittle condition caused by galvanizing malleable castings Bean (13) says:

"A large number of specimens have been examined carefully under the microscope without as yet having discovered any definite change in microstructure accompanying the presence of such a white fracture."

A micrograph of a galvanized specimen which possessed normal fracture

before galvanizing showing that from all appearances the microstructure is identical with that of normal annealed malleable cast iron was given by Bean.

A normal fracture of malleable cast iron is a black fracture, the casting being ductile and not brittle. A white fracture results when a brittle malleable casting is broken. In the black fracture the rupture is through the grains of the material and in a white fracture it is along the grain surfaces.

Experimental work of a more direct nature than that of Bean was carried out by L. H. Marshall (14) with the results indicated in figure 2. These results were obtained by immersing the normal malleable castings in an oil or lead bath heated to the desired temperature. They were held in the bath three minutes and then quenched. The analysis of his alloys was:

Alloy	% C.		% Si.	% P.	% Mn.	% S.
	C.	G.				
A	2.10	2.00	0.80	0.20	0.26	0.075
B	2.55	2.10	0.91	0.18	0.25	0.051
C	2.90	2.85	0.64	0.17	0.58	0.072

His results were obtained on a notched sample of a definite size by means of an impact machine in which the energy necessary to break the sample could be recorded.

EXPERIMENTAL

Due to the absence of any impact testing machine such as that used by Marshall we started testing brittleness with a vice and hammer. It was

soon noted that there were all stages of white and black fracture between the two limits. As the piece became increasingly brittle the white fracture, beginning on the compression side, would increase in width and finally cover both tension and compression sides. We then considered that in the transition stage between malleable (black fracture) and brittle (white fracture) that the proportion of the two kinds of fracture is a measure of the transition state. From the almost perfect consistency of every result taken in this manner it must be admitted that such is at least partially true. That such a simple test is so fruitful seems to indicate a very pronounced condition in the piece that is as yet unexplained.

The samples used in these tests were cut from normal malleable cast iron test wedges. No attempt in any test was given to the selection of any portion of the wedges for testing. Nor was any attempt made to cut the pieces in definite sizes. The only requirement was that the sample be small enough to be breakable in the vice. This limited the thickness to about one quarter inch and the method of cutting left them one inch long. The wedges were cut in a crosswise manner and the samples always broken between the sawed surfaces so that one was a compression side and the other a tension side.

The analyses of the alloys together with their identification number are given in table 13. These were furnished by the Iowa Malleable Company.

TABLE 13
ANALYSES OF ALLOYS USED IN EMBRITTLEMENT STUDY

Alloy No.	% P.	% Si.
1	0.157	0.70
2	0.157	1.02
3	0.159	0.95
4	0.211	0.90
5	0.218	0.78

:	6	:	0.184	:	1.08	:
:	7	:	0.219	:	1.03	:
:	8	:	0.175	:	0.97	:
:	10	:	0.178	:	0.77	:

TEST NO. 1

The purpose of the first test was to find the temperature range in which embrittlement would take place. Accordingly a member of each of the nine alloys was put in seven piles in the ten inch hump furnace.

The heat treatment follows:

Heated to 400° F. in 1 hour.
Held at 400° F. to 425° F. 1-1/2 hours.

Set 1 removed and quenched.

Heated to 585° F. in 1 hour.
Held at 585° F. to 605° F. 1/2 hour.

Set 2 removed and quenched.

Heated to 790° F. in 1/2 hour.
Held at 790° F. to 805° F. 1/2 hour.

Set 3 removed and quenched.

Heated to 995° F. in 1/2 hour.
Held at 995° F. to 1010° F. 1/2 hour.

Set 4 removed and quenched.

Heated to 1215° F. in 1/2 hour.
Held at 1215° F. to 1190° F. 1/2 hour.

Set 5 removed and quenched.
Set 6 removed and air cooled.
Set 7 cooled in furnace.

The results of these treatments are shown in table 14.

TABLE 14
RESULTS OF TEST NO. 1 IN TERMS OF FRACTIONAL WHITE FRACTURE

Alloy No.	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6	Set 7
1	0.10	0.25	0.80	0.20	0.00	0.00	0.00
2	0.25	0.33	0.67	0.33	0.00	0.00	0.20
3	0.25	0.20	0.75	0.20	0.00	0.00	0.00
4	0.40	0.40	1.00	0.40	0.00	0.00	0.20
5	0.10	0.25	1.00	0.25	0.00	0.00	0.00
6	0.10	0.60	1.00	0.25	0.00	0.00	0.20
7	0.60	0.90	1.00	1.00	0.00	0.00	0.10
8	0.35	0.20	0.75	0.35	0.00	0.00	0.00
10	0.10	0.25	0.67	0.25	0.00	0.00	0.00

TEST NO. 2

In the process of malleable cast iron manufacture the action that takes place below the lower critical point is not complete in practice until a temperature as low as 1250° F. is sometimes reached. This depends on the rate of cooling in this temperature region and the graphitizing rate of the castings themselves. It was therefore desirable to know what the effect of different methods of cooling from 1200° F. to 1250° F. would have on embrittlement rate. Accordingly the three sets (5, 6, & 7) given the heat treatments as shown in test No. 1 were heated to 800° F. Set 6 was held one hour. One portion was quenched and another cooled in the furnace. Sets 5 & 7 were quenched. The results are summarized in table 15.

TABLE 15
RESULTS OF TEST NO. 2 IN TERMS OF FRACTIONAL PART WHITE FRACTURE

		: Set 6 heated to ; : 800° F. for one ; : hour and cooled ; : in		: Set 5 heated to ; : 800° F. for 16 ; : hours and cooled ; : in		: Set 7 heated to ; : 800° F. for 16 ; : hours and cooled ; : in	
Alloy No.	Water	Furnace	:	Water	:	Water	:
1	0.33	0.00	:	0.10	:	1.00	:
2	0.40	0.33	:	0.33	:	1.00	:
3	0.25	0.10	:	0.33	:	1.00	:
4	0.50	0.50	:	0.90	:	1.00	:
5	0.50	0.10	:	0.90	:	1.00	:
6	0.25	0.25	:	0.15	:	1.00	:
7	0.50	0.20	:	1.00	:	1.00	:
8	0.33	0.33	:	0.90	:	1.00	:
10	0.33	0.10	:	0.50	:	1.00	:

TEST NO. 3

The purpose of this test was similar to that in test No. 2. The samples, however, were heated above the critical range and re-cooled to again graphitize them so that their complete history would be better known. They were therefore heated to 1500° F. to 1550° F. for 2 hours, cooled to 1300° F. in 1 hour, cooled to 1250° F. in 10 hours, and held at 1250° F. for 5 hours.

One set (No. 8) was quenched and the other (No. 9) was cooled in the furnace. Tests on these samples showed a little more brittleness in the furnace cooled pieces. Portions of each set were heated to 800° F. and held 45 minutes and quenched. The results of the test are shown in table 16.

TABLE 16
RESULTS OF TEST NO. 3 IN TERMS OF FRACTIONAL WHITE FRACTURE

Sample No.	Remalleableized and cooled from 1250° F. in	Water cooled from 1250° F. Reheated to 800° F. & cooled in	Furnace cooled from 1250° F. Reheated to 800° F. for 45 minutes & cooled in	Water cooled from 1250° F. Reheated to 800° F. for 26 hrs. & cooled in	Furnace cooled from 1250° F. Reheated to 800° F. for 26 hrs. & cooled in	Water cooled from 1250° F. Reheated to 800° F. for 26 hrs. & cooled in
1	0.10	0.25	1.00	0.25	0.95	
2	0.00	0.20	1.00	0.50	0.75	
3	0.33	0.33	1.00	0.67	1.00	
4	0.20	0.33	1.00	1.00	1.00	
5	0.00	0.50	1.00	0.33	0.90	
6	0.10	0.17	1.00	0.95	1.00	
7	0.25	0.25	1.00	1.00	1.00	
8		0.10	1.00	0.95	1.00	
10	0.10	0.33	0.95	0.60	1.00	

TEST NO. 4

For the purpose of watching the samples during cooling, some samples were given the following heat treatments:

Heated to 1550° F. and held 3 hours.

Cooled to 1320° F. in 6-1/2 hours.

Held at 1320° F. to 1290° F. for 11 hours.

Cooled to 1000° F. and set 162 taken out and cooled in container.

(Hessian crucible)

Cooled to 800° F. in 4 hours and set 163 removed and cooled in container.

Cooled to 600° F. in 5 hours and set 164 removed and cooled in container.

Cooled to 400° F. in 6 hours and set 165 removed and cooled in container.

Cooled to 200° F. when set 166 was removed.

The results are shown in table 17.

TABLE 17
RESULTS OF TEST NO. 4 IN TERMS OF FRACTIONAL WHITE FRACTURE

: REMA LLEABLEIZED AND SLOWLY						
Alloy : COOLED TO --						
:						
No.	1000° F.	800° F.	600° F.	400° F.	200° F.	:
1	0.00	0.00	0.20	0.00	0.00	:
2	0.35	0.00	0.33	0.40	0.33	:
3	0.16	0.33	0.33	0.33	0.00	:
4	0.25	0.50	0.50	0.50	0.50	:
5	0.25	0.33	0.50	0.67	0.33	:
6	0.00	0.50	0.50	0.50	0.40	:
7	0.25	0.67	0.60	0.50	0.40	:
8	0.25	0.60	0.50	0.33	0.40	:
10	0.25	0.33	0.35	0.33	0.00	:
:	:	:	:	:	:	:

TEST NO. 5

Convinced by this time that there is some sort of an equilibrium state characteristic of each temperature and composition, it was decided to approach this equilibrium if possible from perfectly brittle material. Accordingly 3 sets of samples (171, 172, 173) were heated at 800° F. for 19 hours and quenched. Set 171 was broken as a check after this quenching. Set 172 was heated to 250° F. for 13 hours and quenched. Set 173 was held at 400° F. for 23 hours and quenched. The results are in table 18.

TABLE 18
RESULTS OF TEST NO. 5 IN TERMS OF FRACTIONAL WHITE FRACTURE

Alloy No.	171	173	172
	800° F.	400° F.	250° F.
1	1.00	0.33	0.40
2	1.00	0.40	0.40
3	1.00	0.50	0.50
4	1.00	0.90	1.00
5	1.00	0.40	1.00
6	1.00	0.50	0.90
7	1.00	1.00	1.00
8	1.00	0.67	1.00
10	1.00	0.67	0.75

TEST NO. 6

This was intended to be a long time study of the conditions produced at each temperature using 50° F. intervals and due to lack of time it was not completed. The samples were held for 16 to 24 hours at each temperature. This time interval was to be increased to one or two weeks at the lower temperatures. Even the above time gave a reversal in a point or two as can be seen from the curves of figure 5. The results are tabulated in table 19.

RESULTS OF TEST NO. 6 IN TERMS OF FRACTIONAL WHITE FRACTURE

TABLE 19

Alloy No.	1150°F	1100°F	1050°F	1000°F	950°F	900°F	850°F	800°F	750°F	700°F	650°F	Nearly 1 week 2500 F.
1	0.20	0.25	0.33	0.67	0.80	0.80	0.67	0.33	0.60	0.25	0.12	0.60
2	0.40	0.67	0.85	1.00	1.00	1.00	1.00	1.00	0.95	0.75	0.33	0.60
3	0.20	0.50	0.67	0.90	1.00	1.00	1.00	1.00	0.95	0.60	0.25	0.00
4	0.10	0.50	0.90	1.00	1.00	1.00	1.00	1.00	1.00	0.98	0.95	0.50
5	0.50	0.50	0.95	0.80	1.00	1.00	1.00	1.00	1.00	0.50	0.50	0.50
6	0.33	0.10	0.10	0.95	1.00	1.00	1.00	1.00	1.00	0.90	0.33	0.25
7	0.90	0.90	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.60
8	0.25	0.50	0.67	1.00	1.00	1.00	1.00	1.00	1.00	0.75	0.60	0.50
10	0.25	0.40	0.50	0.80	1.00	1.00	1.00	0.60	0.75	0.60	0.60	0.16

TEST NO. 7

It appeared from the results so far that both phosphorus and silicon were playing parts in causing embrittlement. Two groups of alloys were found that had quite different silicon contents with phosphorus as a variant. The first set was made by Mr. Foulle and the second by Mr. Barlow. These alloys analyzed as shown in table 20.

TABLE 20
ANALYSIS OF ALLOYS USED IN TEST NO. 7

Sample No. :	% C. :	% Si. :	% P. :	% Mn. :	% S.
F1 :	2.25 :	1.10 :	0.073 :	0.184 :	0.053
F2 :	2.30 :	1.02 :	0.099 :	0.170 :	0.051
F3 :	2.25 :	1.08 :	0.153 :	0.170 :	0.052
F4 :	2.24 :	1.01 :	0.174 :	0.169 :	0.057
F5 :	2.26 :	1.01 :	0.259 :	0.164 :	0.050
1-1 :	1.88 :	1.15 :	0.051 :	0.222 :	0.063
1-2 :	1.88 :	1.22 :	0.076 :	0.223 :	0.064
1-3 :	1.99 :	1.21 :	0.129 :	0.208 :	0.066
1-4 :	2.17 :	1.20 :	0.143 :	0.201 :	0.065
1-5 :	1.92 :	1.25 :	0.186 :	0.205 :	0.064
1-6 :	1.87 :	1.22 :	0.212 :	0.223 :	0.063

One set of samples was held at 800° F. for 1-1/4 hours and another for 2 days. Another set was heated to 1300° F. and cooled to 200° F. in 30 hours and then reheated to 850° F. and held for 1 hour and quenched in water. These results are in table 21.

TABLE 21
RESULTS OF TEST NO. 7 IN TERMS OF FRACTIONAL WHITE FRACTURE

Sample No.	: Heated to : 800° F. and : held 1-1/4 : hours. Quenched : in water	: Heated to : 800° F. and : held 2 days : and quenched : in water	: Heated to 1300° F. cooled to : 200° F. in 50 hours. Reheated : to 850° F. and held 1 hour. : Quenched in water
F1	: 0.00	: 0.10	: 0.33
F2	: 0.10	: 0.00	: 0.00
F3	: 0.10	: 0.00	: 0.20
F4	: 0.00	: 0.00	: 0.20
F5	: 0.10	: 0.20	: 0.80
1-1	: 0.10	: 0.10	: 0.00
1-2	: 0.20	: 0.00	: 0.25
1-3	: 0.10	: 0.00	: 0.33
1-4	: 0.20	: 0.50	: 1.00
1-5	: 0.50	: 0.60	: 1.00
1-6	: 0.95	: 1.00	: 1.00

DISCUSSION

We have in figure 3 the results of heating normal malleable cast iron alloys of different compositions to different temperatures below the critical range for about one half hour. This graph plainly shows the greatest effects on those samples heated to 800° F.

In table No. 15 we have the effect of heating common malleable castings to 1200° F. to 1250° F. and cooling in various ways on the embrittlement properties produced at 600° F. and 800° F. The results are of the same nature when the temperature (1200° F. - 1250° F.) is approached as in the normal process of malleableizing as is shown in table No. 16. The value of

quenching from 1200° F. is clearly shown. The facts given here have been used as a basis for the production of very high quality malleable cast iron, resistant to embrittlement in galvanizing and effecting a savings in cost of production by permitting the removal from the annealing furnace as soon as convenient after the action below the lower critical point is completed.

In explanation of the effects of different cooling rates it is thought that while the castings are cooling slowly from 1200° F. to low temperatures that they change their state at least partially toward that which is characteristic for each temperature through which they cool. This gives the castings partial embrittlement and much less action is necessary in the embrittlement range to produce the white fracture than is necessary when they were cooled rapidly either by quenching in water or in an air blast.

In reading the curves of figure 4 it must not be thought that they indicate a greater embrittlement at 400° F. than at 800° F. (e. g. alloy No. 5) but that it has approached this value while passing through the embrittlement range. Recovery from embrittlement at 400° F. or lower is quite slow but it does take place. This is shown in table 18. In case of alloy No. 7 the embrittlement range extends below 400° F. and there is no recovery at 400° F. There is, however, at 250° F. These statements are in agreement with the long time heat treatments recorded in table 19 and figure 5.

In reviewing the graphs one can plainly see the distinct difference of

alloy No. 7. This alloy has a composition that is high in both silicon and phosphorus. Alloy No. 6 with high silicon and rather high phosphorus is nearest to alloy No. 7 on figure 3, but the results of alloys No. 4, 5, & 6 allow of no differentiation. It appears that either silicon or phosphorus may be the cause of embrittlement. In either case the presence of the other causes a spread in the embrittlement range.

In table 20, figure 6 are shown the effects of phosphorus variations in two series of alloys each with a different but fairly constant silicon content. These alloys showed the effects of the initial cooling rate to a marked degree. If the difference in results in the two sets of alloys is due to composition it is again plain that silicon is a very important factor in embrittlement.

The curves in figure 5 are arranged in groups of constant phosphorus content. Silicon is different in each member of a group and its increasing concentration in each group increases the embrittlement range. The action of phosphorus and silicon are then mutual.

SUMMARY AND CONCLUSION

It may be said then that

First:

The embrittlement is produced to the greatest extent at temperatures near 800° F.

Second:

All ordinary malleable compositions become brittle at this temperature if held for a sufficient time.

Third:

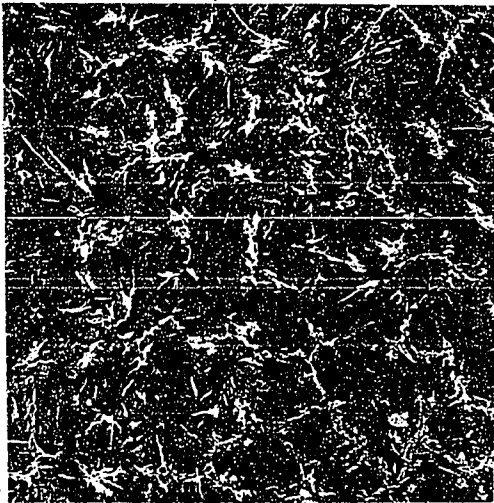
That silicon and phosphorus mutually affect the embrittlement properties.

Fourth:

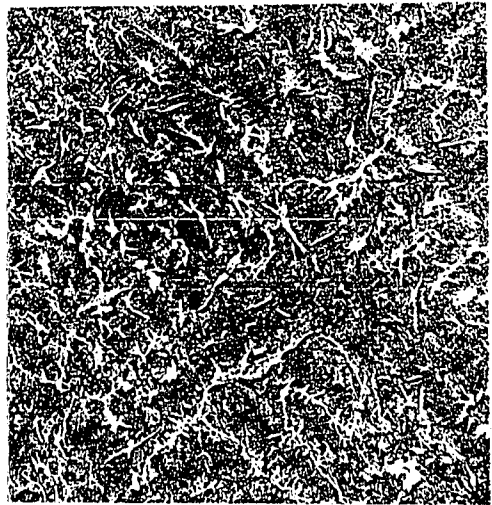
That a rapid cool from a temperature just below the critical range greatly reduces the tendency toward embrittlement and this fact can be used in prevention of embrittlement in the "hot dip" galvanizing process.

LITERATURE CITED

13. Bean, W. R. Highriter, H. W., and Davenport, E. S. Explain the structures of Malleable. Foundry, 49: 557 - 6. 1921.
14. Marshall, L. H. - Embrittlement of Malleable Cast Iron Resulting from Heat Treatment. U. S. Bureau of Standards. Tech. Paper No. 245. 1923.



166a



166b

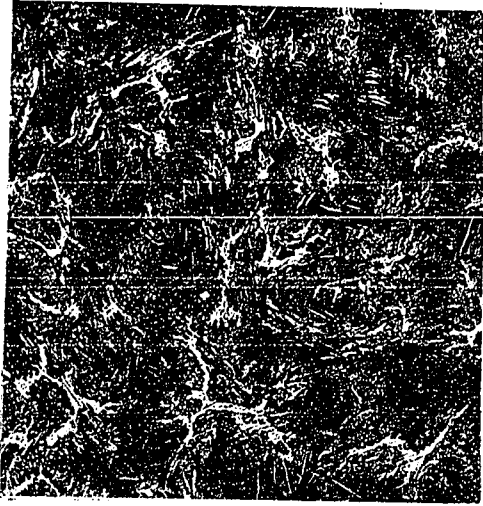


166c

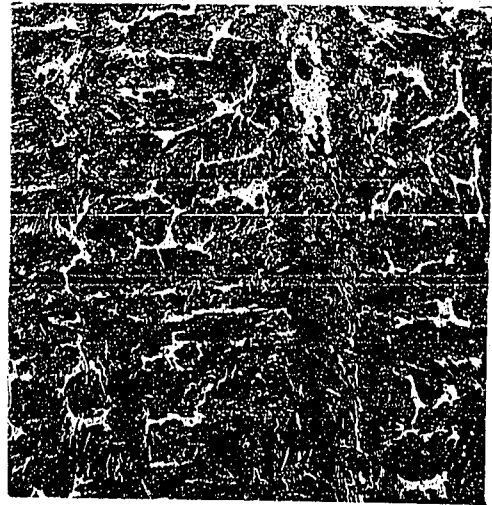


166d

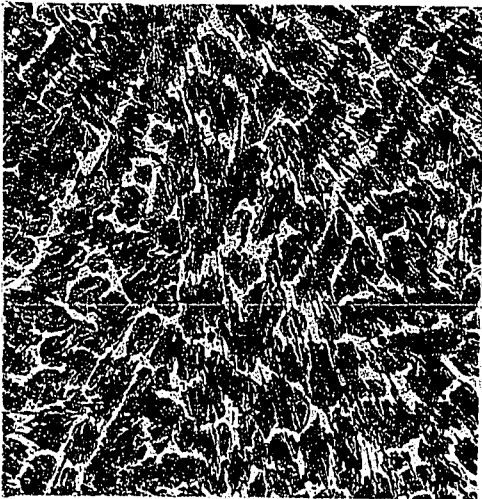
Figure 1A. This shows the structures of the alloys of series 166 together with the different carbon concentrations.



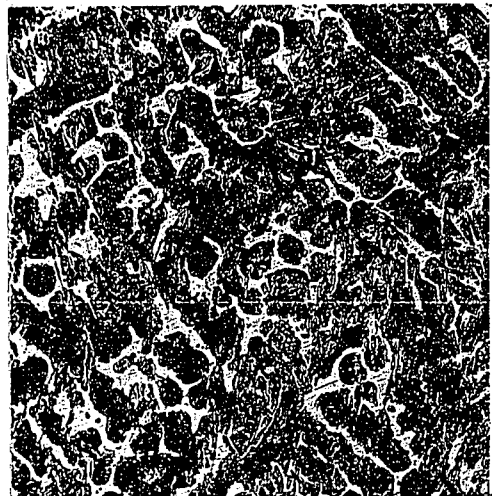
168a



168b



168c



168d

Figure 1B. This shows the structures of the alloys of series 168 together with the different carbon concentrations.

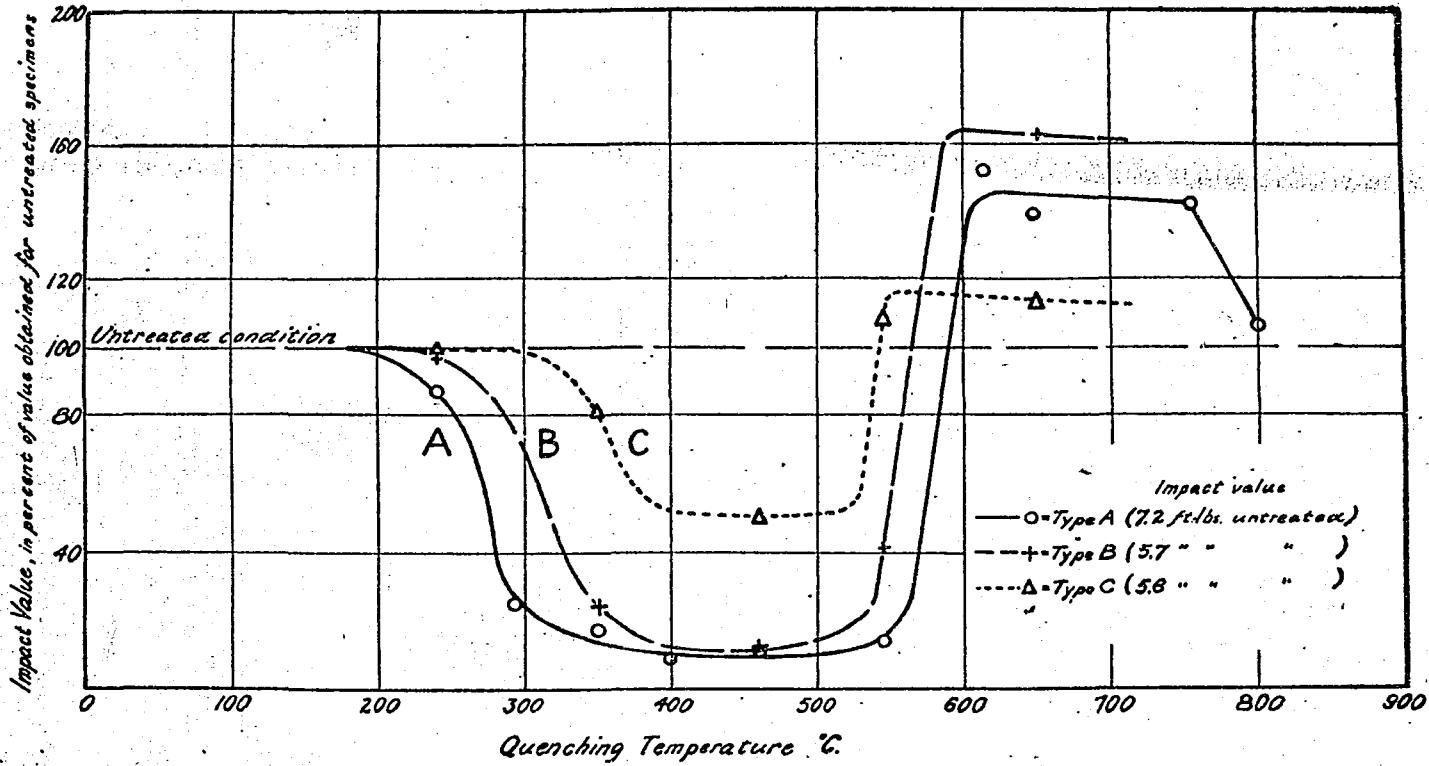


FIG. 2.—Effect of heat treatment on the impact resistance of malleable cast iron.

Figure 2

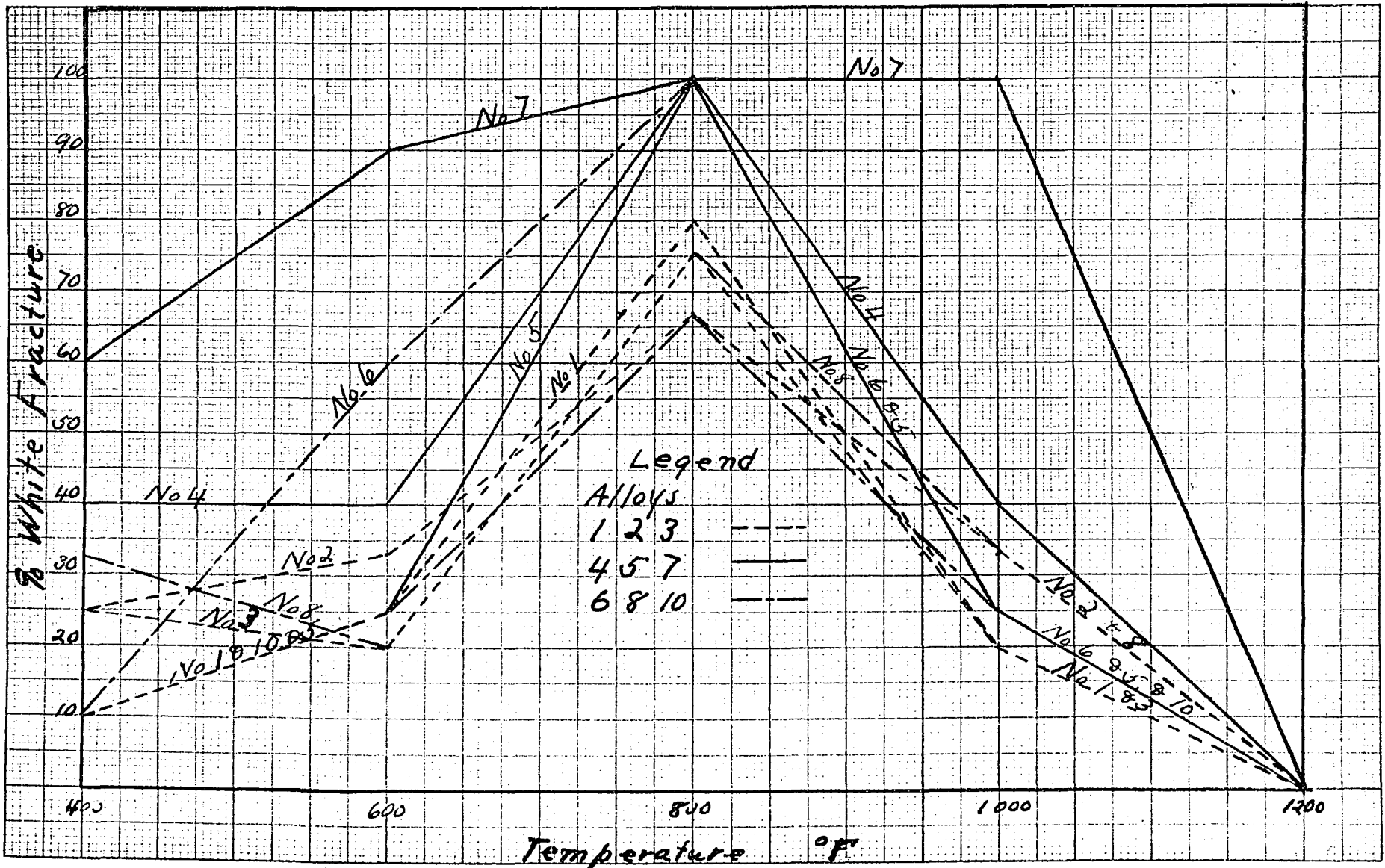


Figure 3

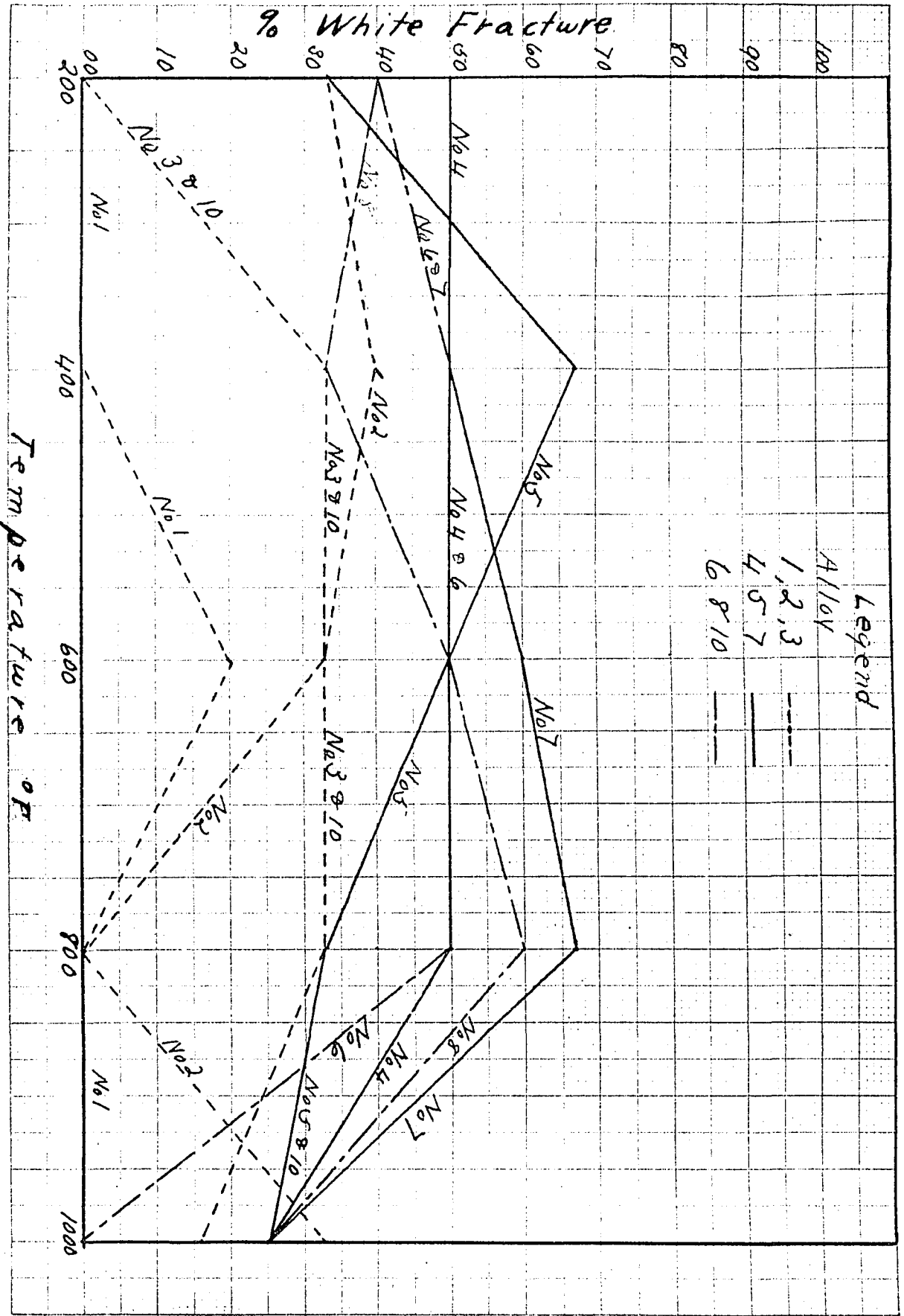


Figure A

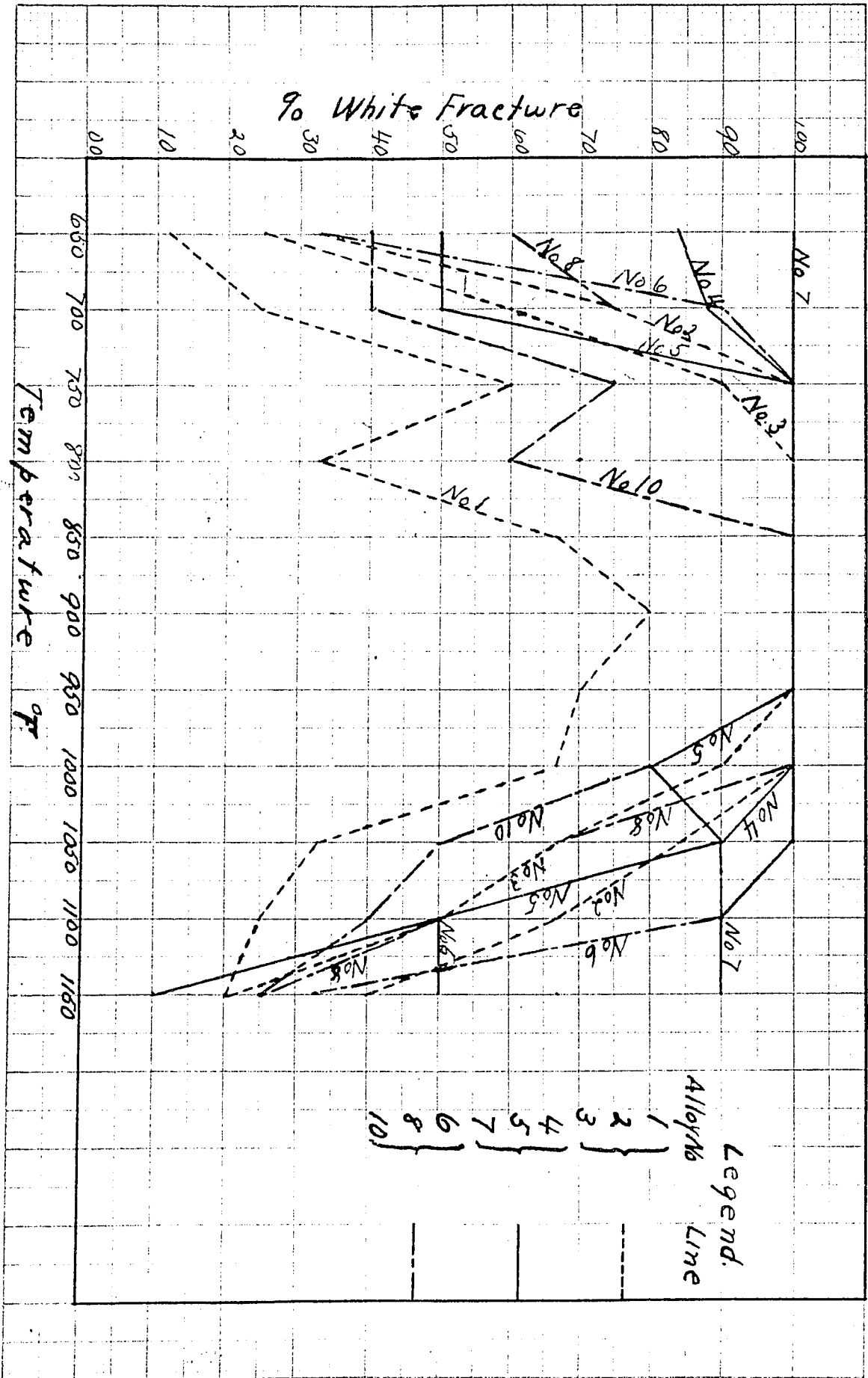


Figure 5

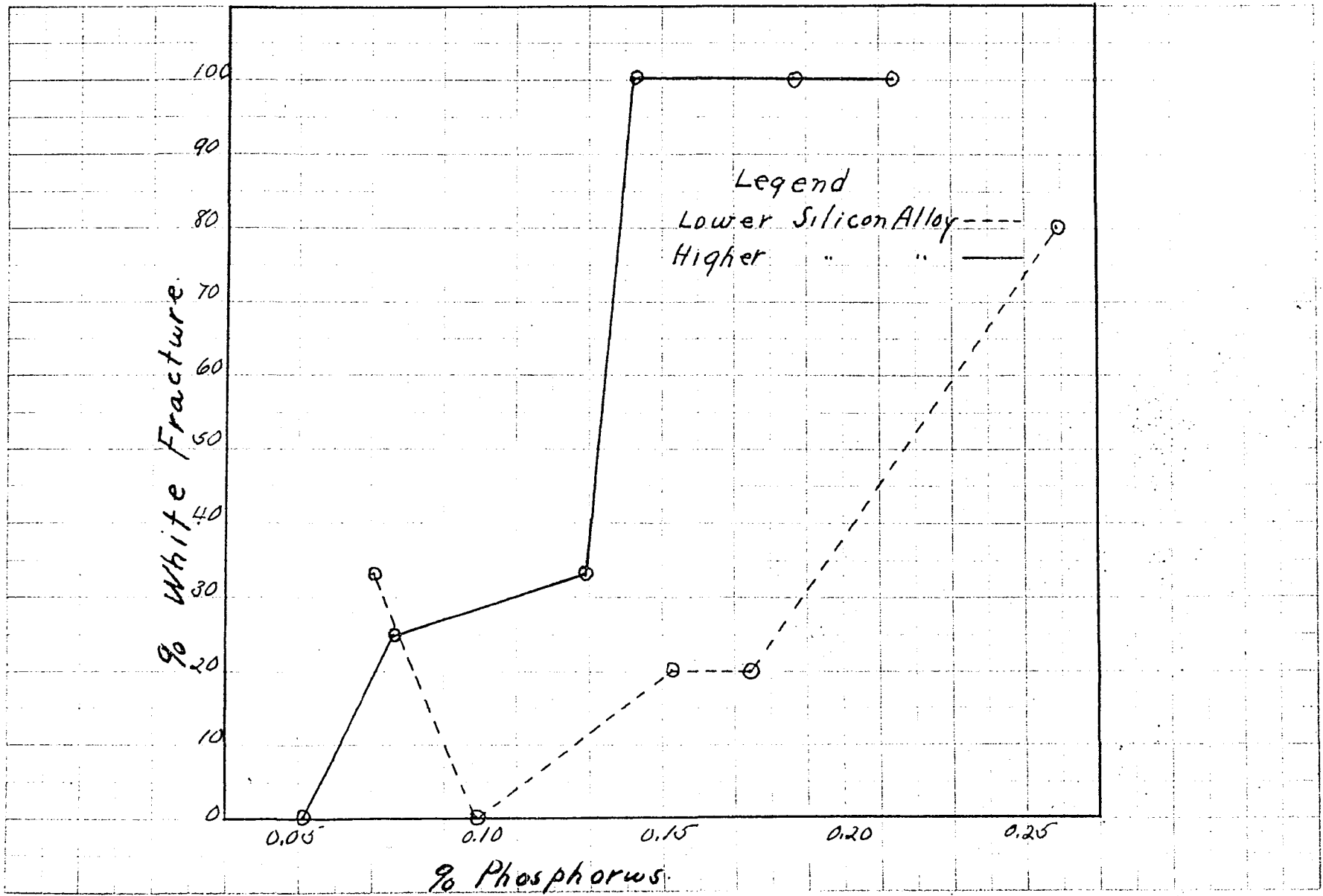


Figure 6