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The determination of the effect of manganese and sulfur on the malleablization of white cast iron

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THE DETERMINATION OF THE EFFECT OF MANGANESE
AND SULFUR ON THE MALLEABILIZATION OF
WHITE CAST IRON

BY

Arnold P. Hoelscher

A Thesis Submitted to the Graduate Faculty
for the Degree of

¹⁶⁷
DOCTOR OF PHILOSOPHY

Major Subject Physical Chemistry

Approved

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Dean of Graduate College

Iowa State College
1930

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I. INTRODUCTION

This work was begun in order to obtain data on the effect of manganese and sulfur on the rates of malleablization or graphitization of white cast iron. Two basic compositions were chosen, one of about 2.40% carbon and 1.0% silicon, and the other 2.10% carbon and 1.10 - 1.15% silicon. In both cases the phosphorus was maintained at about 0.15%. The attempt was made to keep the sulfur at a low and constant amount. The variable element was manganese, which was started from a low value and increased at definite intervals. This experimental program was followed as near as it was possible. Although the heat treating results are somewhat of a qualitative nature, they are indicative of the result that was sought at the beginning.

II. HISTORICAL

Probably one of the earliest references that was made in regard to the effect of manganese and sulfur on white cast iron was that of Hammer. Schwartz (9) quotes Hammer to the effect that there exists, "A chemical ratio as between carbon and silicon, and manganese and sulphur." In 1875 Hammer established his laboratory which was one of the first in the industry.

Schwartz (9) states that to form manganese sulfide a slight excess of manganese over the theoretical amount is necessary. He also mentions that the only harmful effect sulfur will have is to prevent complete graphitization.

Hayes and Flanders (4) from their results of studying a number of samples of white iron concluded that sulfur has a very harmful influence on the rates of graphitization and that a small amount of manganese corrected the difficulty. They also found that a little sulfur corrected a high manganese iron.

Schwartz and Guiler (10) say, "It is of common knowledge, also, that the presence of sulphur or manganese in abnormal amounts will greatly retard or prevent anneal in the malleable industry."

Flanders (1) while working with material for complete absorption of free cementite found that the worst condition met was a high sulfur value with low manganese. A low sulfur combination also increased considerably the time of graphitiza-

tion. He also found that a definite minimum time exists for the graphitization of a well balanced manganese sulfur combination.

Yemenidijan (13) concluded that the best percentage of manganese to balance the effect of sulfur on the rates of graphitization could be expressed by the equation, $Mn = 2S + 0.15$. Apparently, this constant (0.15) is lower for higher values of silicon. His results of alloy series numbers 2 and 3 are shown in tables I and II, respectively. These tables follow.

TABLE I (a)
PERCENT CHEMICAL ANALYSIS

Number of Sample	C	Si	P	Mn	S
1	2.48	0.84	0.134	0.091	0.132
2	2.48	0.85	0.132	0.175	0.130
3	2.47	0.83	0.135	0.209	0.136
4	2.46	0.84	0.134	0.306	0.132
5	2.45	0.85	0.131	0.406	0.129
6	2.49	0.85	0.133	0.478	0.126
7	2.53	0.83	0.132	0.662	0.133

TABLE I (b)
HEAT TREATMENT

Number of Sample	Time at 1700° F.	Time at 1300° F.
1	44+ hours	—
2	22 hours	39 hours
3	22 hours	36 1/2 hours
4	19 hours	33 hours
5	19 hours	30 1/2 hours
6	19 hours	32 1/2 hours
7	18 hours	35 hours

TABLE II (a)

PERCENT CHEMICAL ANALYSIS

Number of Sample	C	Si	P	Mn	S
1	2.50	0.87	0.142	0.115	0.160
2	2.52	1.11	0.140	0.215	0.159
3	2.48	1.11	0.141	0.306	0.158
4	2.54	1.11	0.140	0.393	0.159
5	2.54	1.10	0.139	0.443	0.159
6	2.51	1.10	0.141	0.535	0.162

TABLE II (b)

HEAT TREATMENT

Number of Sample	Time at 1700° F.	Time at 1300° F.
1	38+ hours	—
2	10 hours	18+ hours
3	9 hours	13 hours
4	9 hours	11 hours
5	9 hours	11 1/2 hours
6	9 hours	13 1/2 hours

TABLE III

RESULTS DERIVED FROM TABLES I AND II

<u>Number of Sample</u>	<u>Mn,S Ratio</u>	<u>Mn - 2S</u>	<u>Total Time for Annealing</u>
1	1-1.5	-0.173	44+x hours
2	1.3-1	-0.085	61 hours
3	1.5-1	-0.063	59 1/2 hrs.
4	2.3-1	0.042	52 hours
5	3.2-1	0.148	49 1/2 hrs.
6	3.8-1	0.226	51 1/2 hrs.
7	4.7-1	0.396	53 hours
1	1-1.4	-0.205	38+x hours
2	1.4-1	-0.103	28+x hours
3	1.9-1	0.010	22 hours
4	2.4-1	0.075	20 hours
5	2.8-1	0.125	20 1/2 hrs.
6	3.3-1	0.211	22 1/2 hrs.

Kikuta's ⁽⁵⁾ conclusions in regard to manganese and sulfur were that the former should be limited to 0.5% and the latter to 0.06% for good results in annealing. An excess of either one hinders malleablization especially in the second stage. Table IV which follows gives alloys studied by Kikuta and the results of time at the first (925° C.) and second (710° C.) stages of graphitization.

TABLE IV (a)
CHEMICAL ANALYSIS

Number of Sample	% C	% Si	% Mn	% S	% P
14	2.09	1.22	0.24	0.025	0.122
21	2.45	0.86	0.19	0.029	0.115
24	2.42	1.07	0.17	0.028	0.134
30	2.51	1.15	0.46	0.033	0.127
47	2.62	1.15	0.22	0.026	0.126
48	2.50	1.14	0.22	0.051	0.121
49	2.54	1.14	0.22	0.066	0.128
50	2.45	1.15	0.22	0.072	0.120
56	2.54	1.13	0.22	0.027	0.212
58	2.40	1.14	0.22	0.039	0.451
60	2.41	1.06	0.20	0.059	0.792

TABLE IV (b)
TIME OF GRAPHITIZATION

Number of Sample	925° C	710° C
14	6 1/2 hours	25 hours
21	9 hours	25 hours
24	5 1/2 hours	16 hours
30	5 1/2 hours	24 hrs. (at 700° C)
47	5 hours	10 hours
48	6 hours	15 hours
49	7 hours	23 hours
50	7 1/2 hours	22+x hours
56	6 hours	11 hours
58	4 hours	9 hours
60	2 2/3 hours	10+x hours

TABLE V

RESULTS DERIVED FROM TABLE IV

<u>Number of Sample</u>	<u>Mn,S Ratio</u>	<u>Mn - 2S</u>	<u>Total Time for Annealing</u>
14	9.6-1	0.190	31 1/2 hrs.
21	6.5-1	0.132	34 hours
24	6.1-1	0.114	21 1/2 hrs.
30	14.0-1	0.394	29 1/2 hrs.
47	8.5-1	0.268	15 hours
48	4.3-1	0.118	21 hours
49	3.3-1	0.088	30 hours
50	3.1-1	0.076	29 1/2+x hrs.
56	8.2-1	0.166	17 hours
58	5.6-1	0.142	13 hours
60	3.4-1	0.082	12 2/3+x hrs.

Gilmore (2) showed that the minimum for the ratio, Mn/S , should be 1.7. He recommended for good practice $Mn = 1.7 \times S + 0.1$ for those cases where the sulfur ranges from 0.0% to 0.15%. He applied this relation to air furnace, open hearth and electric furnace operation. The relation for manganese and sulfur in cupola iron is the same in regard to the minimum, but for recommended practice in this case it is, $Mn = 1.7 \times S + 0.20$. The added constant is higher because the sulfur is higher, namely, from 0.15% to 0.30%, and also because of greater variations in both manganese and sulfur. Gilmore concluded that whenever the manganese sulfur (ratio) falls below the limit 1.7, the material can not be made into good malleable iron.

Smith (11) drew the following conclusions in regard to sulfur in the production of malleable cast iron (white heart), first, "Sulphur is not removed during the ordinary annealing process", and second, "When the exterior of the casting is oxidized, sulphur tends to segregate into the unoxidized portions."

Norbury (8) quoted Evans and Peace as follows, "The manganese must be in sufficient quantity to neutralize whatever quantity of sulphur is present. The amount is not, however, the theoretical requirement to form manganese sulphide, i. e., 1.72 times the sulphur content, but is in excess of this. Ac-

tual practise has established that the excess required increases with the sulphur content. With 0.04 percent sulphur the excess required is in the neighbourhood of 0.20 percent manganese. If the excess is more than 0.25 percent, the manganese retards graphitisation. Norbury in his study of gray iron showed two photographs in which a small area of iron sulfide was enclosed within a much larger area of cementite. He suggested that this cementite was not graphitized because of iron sulfide. The field surrounding the cementite was pearlitic.

Levy (6) annealed (a) iron free from sulfur, (b) iron containing 0.2% sulfur, and (c) iron containing 0.80% sulfur at 1000° C. in a gas muffle furnace for a period of sixty hours. He found areas of free cementite still persisting in the 0.2% and also in the 0.8% sulfur iron. In the iron free from sulfur, the cementite was absorbed sometime between ten and thirty hours at 1000° C.

Levy (7) concluded that the sulfur acts mechanically and physically so that the conditions which favor the breakdown of cementite are opposed, physically, by the lowering of melting points and by surface tension, mechanically, by the formation of sulfide films which envelope the cementite crystals. These envelopes, according to Levy, may also hinder the expansion which accompanies the graphite formation. In regard to manganese Levy observed that for the quantities usually found in cast iron, manganese tends to form carbides which are

very stable.

Hatfield (3), in his work on the influence of sulfur on iron carbide in the presence of silicon, found that, (a) the sulfur increased the stability of the cementite at the higher temperatures; (b) the small amount of sulfur associated with the carbide is probably the cause of the stability of the latter; (c) the action of sulfur is chemical in nature, which is not in accord with Levy's idea; (d) the effect of silicon was to neutralize the detrimental action of the sulfur; and (e) manganese neutralizes the action of the sulfur.

Stead (12) while working with gray irons determined that sulfur crystallized with the carbide. This was determined by analyzing the carbide residue which was obtained from treatment of the iron with a 10% hydrochloric acid solution.

III. EXPERIMENTAL PROCEDURE AND DATA

A. Preparation of Alloys

The materials used in the preparation of these alloys consisted of Armco iron, graphite, ferro-silicon (46% silicon), ferro-manganese (46% manganese), ferro-phosphorus (25% phosphorus), and ferrous sulfide (50% sulfur).

About 5000 grams of Armco iron were melted in a small Flumbago crucible by means of a 35 kv - a. Ajax Northrup electric furnace. The graphite, ferro-silicon, ferro-phosphorus, and ferrous sulfide were then added in quantities to give white iron compositions. Immediately after these additions were made the melt was stirred with an Armco rod. The molten metal was poured into bars of convenient size by using sand molds. This was the basic stock of the material. The basic stock was then remelted and ferro-manganese added to produce the desired percentage of manganese. Any corrections in composition were made at this remelting. The bars on the remelt were poured in individual sand molds in 12 inch lengths having 5/8 inch diameter. A pouring temperature of 2400° - 2500°F. was used as determined by a Leeds and Northrup optical pyrometer. The sand molds had been allowed to dry at room temperature for a period of 48 - 50 hours. After pouring the remelt, the sand mold was allowed to stand 30 minutes before breaking it. The fracture of the bars in all cases was white. Many

bars, however, had an area of shrink in the middle.

The only deviation in the pouring of these alloys was in the making of numbers 70, 71, 72 and 73, 74, 75. In these cases each set of three was made by melting about 3000 grams of Armco iron and directly making the necessary additions for the composition desired.

B. Chemical Analysis of Alloys

The analytical methods used for the determination of the chemical compositions were those recommended by the American Society for Testing Materials. Check and blank determinations were made in all cases. The carbon determination was made by direct combustion in oxygen, Ascarite being used as the absorbent. The silicon method used was that of nitro-sulphuric acid dehydration. The manganese method used was the sodium bismuthate. Sulfur was determined by the barium sulfate precipitation method. For phosphorus, the alkali-acid titration method was used.

TABLE A
CHEMICAL ANALYSIS

No. Sample	% C	% Si	% Mn	% S	% P
6	2.11	0.99	0.006	0.040	0.14
9	2.06	1.06	0.012	0.057	0.14
15	2.08	1.07	0.033	0.046	0.14
16	2.10	1.11	0.034	0.058	0.15
17	2.11	1.11	0.036	0.054	0.16
8	2.07	1.08	0.066	0.053	0.14
24	2.16	1.13	0.063	0.043	0.16
26	2.10	1.14	0.061	0.038	0.13
31	2.13	1.14	0.087	0.043	0.14
32	2.12	1.10	0.098	0.043	0.13
14	2.09	1.07	0.104	0.053	0.14
41	2.08	1.15	0.143	0.050	0.16
40	2.08	1.16	0.149	0.040	0.15
42	2.08	1.14	0.156	0.040	0.16
43	2.10	1.11	0.155	0.045	0.15
45	2.10	1.16	0.188	0.056	0.16
68	2.08	1.13	0.180	0.033	0.14
69	2.07	1.15	0.171	0.020	0.14
44	2.09	1.11	0.218	0.035	0.16
55	2.09	1.07	0.220	0.037	0.16
73	2.16	1.10	0.358	0.041	0.16
74	2.17	1.00	0.350	0.040	0.15
75	2.17	1.06	0.361	0.040	0.15
64	2.12	1.15	0.388	0.038	0.14
65	2.12	1.10	0.397	0.036	0.14
66	2.12	1.10	0.385	0.035	0.14
67	2.11	1.09	0.397	0.038	0.12

TABLE B
CHEMICAL ANALYSIS

No. Sample	% C	% Si	% Mn	% S	% P
1	2.39	1.04	0.007	0.055	0.16
2	2.38	1.01	0.006	0.044	0.16
3	2.41	1.06	0.031	0.051	0.18
7	2.37	1.00	0.030	0.055	0.16
12	2.40	0.97	0.043	0.058	0.16
18	2.41	0.97	0.038	0.047	0.14
16	2.41	0.92	0.098	0.055	0.15
20	2.40	1.02	0.083	0.051	0.14
21	2.38	1.03	0.079	0.042	0.16
22	2.43	1.04	0.093	0.040	0.16
27	2.37	1.03	0.089	0.020	0.16
28	2.39	1.02	0.098	0.023	0.15
29	2.40	1.02	0.084	0.023	0.13
30	2.35	1.02	0.085	0.023	0.14
33	2.38	0.96	0.120	0.056	0.14
35	2.43	0.95	0.111	0.060	0.15
36	2.38	1.01	0.126	0.053	0.15
38	2.41	0.98	0.129	0.054	0.14
46	2.36	1.03	0.225	0.033	0.16
70	2.43	1.01	0.254	0.040	0.13
71	2.45	0.99	0.244	0.042	0.15
72	2.44	1.00	0.247	0.049	0.15
47	2.38	1.09	0.274	0.042	0.16
48	2.37	1.09	0.271	0.028	0.14
49	2.39	1.08	0.270	0.033	0.15
50	2.42	1.09	0.273	0.031	0.18
51	2.38	1.09	0.374	0.032	0.17
52	2.38	1.10	0.372	0.033	0.16
53	2.37	1.07	0.337	0.040	0.16
54	2.34	1.08	0.356	0.040	0.17

C. Heat Treatment of Alloys

Samples of about one to two inches in length of the various alloys were placed in a Hump annealing furnace which had previously been brought to a temperature of 1700° F. (926° C.). The time required to bring samples to 1700° F. (926° C.) depended on the number of samples which were entered and this time was not included in the total time at 1700° F., or the first stage of graphitization. In order to avoid as much decarburization as possible the samples were packed with graphite in small iron or carbon containers. In spite of this precaution and that of keeping the furnace chamber as air tight as possible, considerable decarburization occurred. The time required for complete removal of free cementite was determined by withdrawing samples at various time intervals. The presence or absence of free cementite was checked by first grinding sufficiently an area of a sample, in order to avoid any surface defects, and then carefully polishing this area. The polished samples were etched with a 5% solution of nitric acid in ethyl alcohol and viewed at a magnification of about a hundred times. The nitric acid etch was removed by polishing and the samples etched with sodium picrate solution. This served as a check on the nitric acid etch. In each case the entire polished surface was investigated microscopically, areas of shrink not being included in the examination. Whenever free cementite remained,

the samples were returned to the furnace at 1700° F. (926° C.) for more annealing.

After the total time for completion of the first stage of graphitization at 1700° F. (926° C.) had been determined, the samples were again placed in the containers and packed with carbon as before. The samples were then placed in the furnace and heated to 1700° F. (926° C.). The power was turned off and the samples were allowed to cool in the furnace to 1300° F. (704° C.). This temperature was maintained for a sufficient time to break down the pearlite. The time necessary for the complete removal of the pearlite was determined by taking out the samples at various intervals and checking microscopically the progress of the second stage of graphitization. If the pearlite was not broken down, the samples were returned to the annealing furnace at 1300° F. (704° C.) for another period. In some cases it was necessary to repeat this procedure several times. With a number of the samples this procedure was abandoned because it appeared that the time required would be of a long duration and of little value in this investigation.

Upon removal from the furnace the samples were allowed to cool to room temperature in the container; this required usually less than an hour.

Because of the fact that decarburization had occurred and also because of the nature of the compositions, picture frame

was encountered, and this was removed by more annealing at the lower temperature, 1300° F. (704° C.).

The temperature of the annealing furnace was controlled and recorded by a Leeds and Northrup Recorder. This temperature was frequently checked by a portable pyrometer indicator which in turn had been checked by a Leeds and Northrup Student Potentiometer (new model) and found satisfactory. Iron - constantan thermocouples were used and frequent replacements were necessary due to the oxidation of the iron.

TABLE C

FIRST STAGE OF GRAPHITIZATION 1700° F. (926° C.)

Number of Sample	Incomplete at	Almost Complete at	Complete at
6	71 hours	_____	_____
9	71 hours	_____	_____
15	41 hours	43 hours	51 hours
16	_____	_____	20 hours
17	22 hours	_____	24 hours
8	20 hours	_____	24 hours
24	20 hours	_____	24 hours
26	7 hours	_____	9 hours
31	7 hours	_____	9 hours
32	22 hours	_____	24 hours
14	20 hours	24 hours	30 hours
41	5 hours	_____	6 hours
40	6 hours	_____	7 hours
42	_____	6 hours	8 hours
43	10 hours	_____	12 hours
45	5 hours	_____	6 hours
68	_____	6 hours	8 hours
69	_____	6 hours	7 hours
44	5 hours	_____	6 hours
55	4 hours	5 hours	6 hours
73	5 hours	_____	6 hours
74	5 hours	_____	6 hours
75	4 hours	5 hours	6 hours
64	8 hours	_____	12 hours
65	_____	4 hours	5 hours
66	_____	6 hours	8 hours
67	4 hours	_____	5 hours

TABLE D

FIRST STAGE OF GRAPHITIZATION 1700° F. (926° C.)

Number of Sample	Incomplete at	Almost Complete at	Complete at
1	49 hours	_____	51 hours
2	49 hours	_____	51 hours
3	26 hours	_____	44 hours
7	26 hours	_____	44 hours
12	20 hours	_____	22 hours
18	30 hours	_____	44 hours
10	36 hours	_____	41 hours
20	_____	18 hours	20 hours
21	28 hours	_____	30 hours
22	_____	_____	15 hours
27	_____	_____	6 hours
28	6 hours	_____	7 hours
29	6 hours	7 hours	9 hours
30	6 hours	_____	7 hours
33	_____	6 hours	7 hours
35	6 hours	_____	7 hours
36	_____	5 hours	7 hours
38	_____	_____	20 hours
46	6 hours	8 hours	10 hours
70	5 hours	6 hours	7 hours
71	5 hours	_____	6 hours
72	5 hours	6 hours	7 hours
47	10 hours	_____	12 hours
48	4 hours	5 hours	6 hours
49	_____	6 hours	7 hours
50	_____	6 hours	7 hours
51	10 hours		12 hours
52	6 hours		7 hours
53	6 hours		7 hours
54	6 hours		8 hours

TABLE E

SECOND STAGE OF GRAPHITIZATION 1300° F. (704° C.)

Number of Sample:	:Incomplete: at	:Complete but :Picture Frame:	:Complete:Hours to Remove :Picture Frame	:Hours to Remove :Picture Frame
6	—	—	—	—
9	—	—	—	—
15	50 hours	—	—	—
16	80 Hours	—	—	—
17				
8	80 hours	—	—	—
24	80 hours			
26	60 hours	—	80 hours	—
31	60 hours	70 hours	80 hours	10
32	—	—	30 hours	—
14	80 hours			
41	—	15 hours	18 hours	3
40	12 hours	15 hours	25 hours	10
42	—	15 hours	25 hours	10
43	15 hours	25 hours	30 hours	5
45	20 hours	24 hours	30 hours	6
68	—	15 hours	25 hours	10
69	24 hours	30 hours	40 hours	10
44	12 hours	15 hours	25 hours	10
55	20 hours	—	30 hours	—
73	22 1/2hrs.	30 hours	35 hours	5
74	12 hours	—	30 hours	—
75	22 1/2hrs.	30 hours	35 hours	5
64	24 hours	31 1/2hrs.	40 hours	8 1/2
65	30 hours	—	40 hours	—
66	15 hours	25 hours	30 hours	5
67	20 hours	30 hours	40 hours	10

TABLE F

SECOND STAGE OF GRAPHITIZATION 1300° F. (704° C.)

Number : Incomplete:Complete but :Complete:Hours to Remove
of Sample: at :Picture Frame: :Picture Frame

Number of Sample	Incomplete at	Complete but Picture Frame	Complete Picture Frame	Hours to Remove Picture Frame
1				
2				
3	80 hours	_____	_____	_____
7	80 hours	_____	_____	_____
12	80 hours	_____	_____	_____
18	80 hours	_____	_____	_____
10				
20	30 hours	_____	35 hours	_____
21		_____	30 hours	_____
22	22 hours	29 1/2 hours to 39 1/2 hours	_____	10 1/2
27	20 hours	22 1/2 hours	30 hours	7 1/2
28	20 hours	22 1/2 hours	35 hours	12 1/2
29	22 hours	24 hours	40 hours	16
30	20 hours	22 1/2-40hrs	_____	17 1/2
33	29 1/2hrs	_____	34 1/2hrs	_____
35	12 hours	_____	15 hours	_____
36	10 hours	12 hours	18 hours	6
38	20 hours	25 hours	35 hours	10
46	_____	15 hours	25 hours	10
70	12 hours	15 hours	22 hours	7
71	12 hours	15 hours	22 hours	7
72	12 hours	15 hours	22 1/2hrs	7 1/2
47	_____	15 hours	25 hours	10
48	22 hours	25 hours	30 hours	5
49	22 hours	24 hours	30 hours	6
50	_____	15 hours	25 hours	10
51	_____	25 hours	30 hours	5
52	25 hours	_____	30 hours	5
53	12 hours	15 hours	40 hours	25
54	15 hours	25 hours	30 hours	5

TABLE G
TOTAL TIME FOR MALLEABILIZATION

Number of Sample	Hours at 1700°	Hours at 1300°	Total Hours
6	71	—	—
9	71	—	—
15	51	50+x	101+x
16	20	80+x	100+x
17	24	—	—
8	24	80+x	104+x
24	24	80+x	104+x
26	9	80	89
31	9	80	89
32	24	30	54
14	30	80+x	110+x
41	6	18	24
40	7	25	32
42	8	25	33
43	12	30	42
45	6	30	36
68	8	25	33
69	7	40	47
44	6	25	31
45	6	30	36
73	6	35	41
74	6	30	36
75	6	35	41
64	12	40	52
65	5	40	45
66	8	30	38
67	5	40	45

TABLE H

TOTAL TIME FOR MALLEABILIZATION

Number of Sample	Hours at 1700°	Hours at 1300°	Total Hours
1	51	—	—
2	51	—	—
3	44	80+x	124+x
7	44	80+x	124+x
12	22	80+x	102+x
18	44	80+x	124+x
10	41	—	—
20	20	35	55
21	30	30	60
22	15	39 1/2+x	54 1/2+x
27	6	30	36
28	7	35	42
29	9	40	49
30	7	40+x	47+x
33	7	34 1/2	41 1/2
35	7	15	22
36	7	18	25
38	20	35	55
46	10	25	35
70	7	22	29
71	6	22	28
72	7	22 1/2	29 1/2
47	12	25	37
48	6	30	36
49	7	30	37
50	7	25	32
51	12	30	42
52	7	30	37
53	7	40	47
54	8	30	38

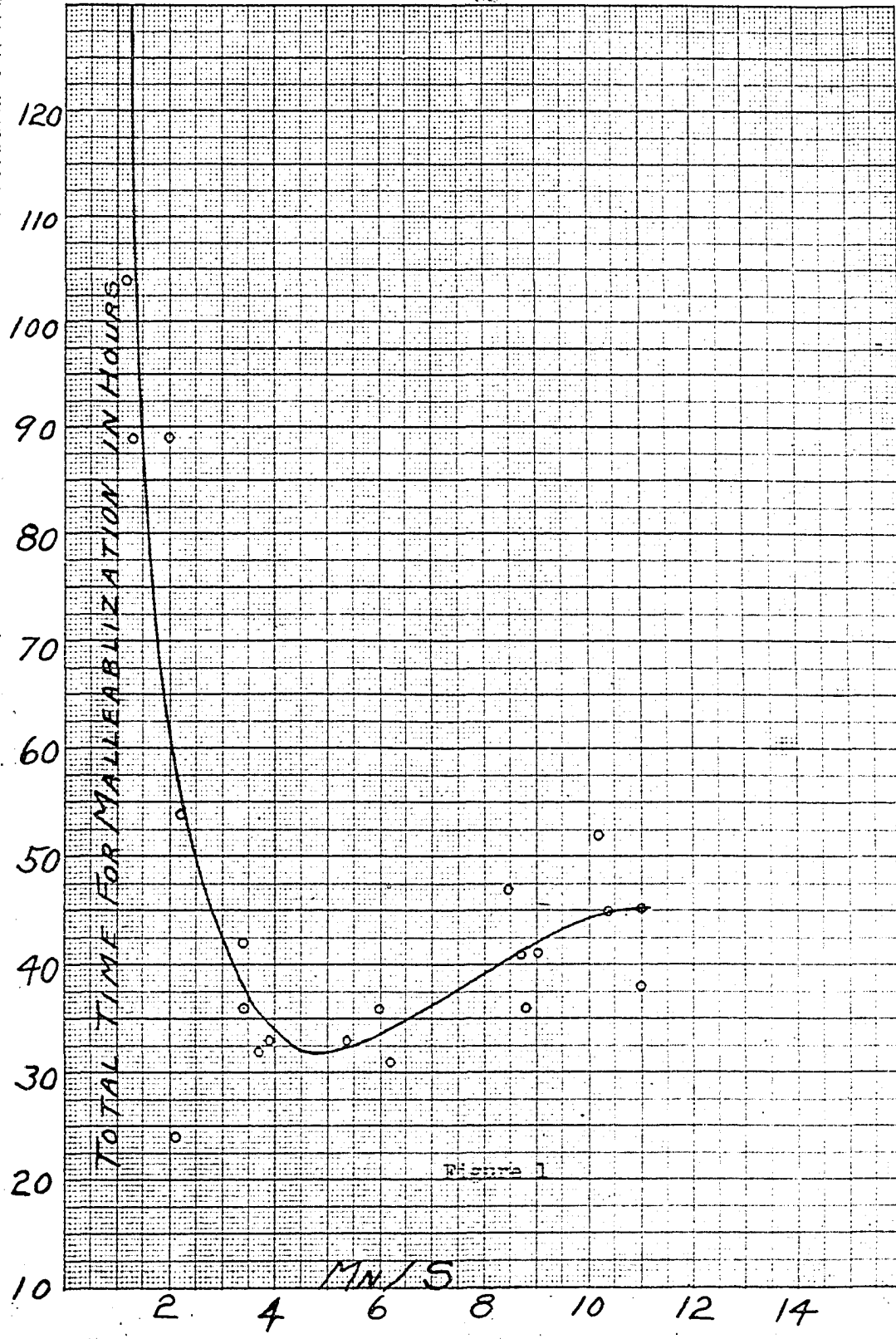
TABLE I
MANGANESE SULFUR RELATIONS

Number of Sample	Mn, S Ratio	Mn - 2S
6	1-7	-0.074
9	1-5	-0.102
15	1-1.3	-0.059
16	1-1.7	-0.082
17	1-1.5	-0.072
8	1.2-1	-0.040
24	1.5-1	-0.023
26	1.3-1	-0.015
31	2.0-1	0.001
32	2.2-1	0.012
14	2.0-1	-0.002
41	2.1-1	0.043
40	3.7-1	0.069
42	3.9-1	0.076
43	3.4-1	0.065
45	3.4-1	0.076
68	5.4-1	0.114
69	8.5-1	0.131
44	6.2-1	0.148
55	6.0-1	0.146
73	8.7-1	0.276
74	8.8-1	0.270
75	9.0-1	0.281
64	10.2-1	0.312
65	11.0-1	0.325
66	11.0-1	0.315
67	10.4-1	0.321

TABLE J

MANGANESE SULFUR RELATIONS

Number of Sample	Mn, S Ratio	Mn - 2S
1	1-8	-0.103
2	1-7.3	-0.082
3	1-1.7	-0.071
7	1-1.8	-0.080
12	1-1.4	-0.073
18	1-1.2	-0.056
10	1.8-1	-0.012
20	1.6-1	-0.019
21	1.9-1	-0.005
22	2.3-1	0.013
27	4.4-1	0.049
28	4.3-1	0.052
29	3.7-1	0.038
30	3.8-1	0.039
33	2.1-1	0.008
35	1.9-1	-0.009
36	2.3-1	0.020
38	2.4-1	0.021
46	6.8-1	0.159
70	6.4-1	0.174
71	5.8-1	0.160
72	5.0-1	0.149
47	6.5-1	0.190
48	9.6-1	0.215
49	8.2-1	0.204
50	8.8-1	0.211
51	11.7-1	0.310
52	11.6-1	0.306
53	8.4-1	0.257
54	8.9-1	0.276



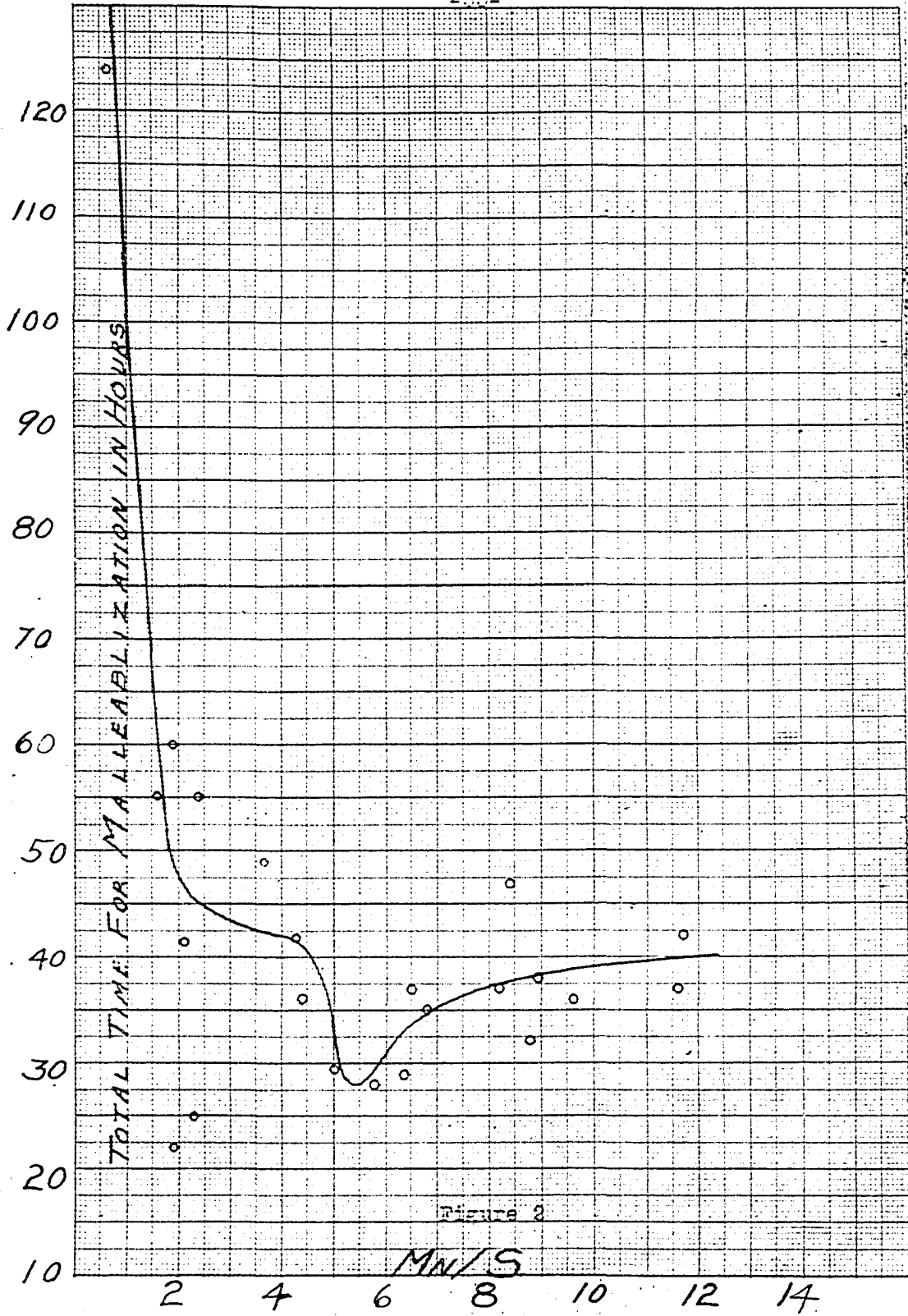


Figure 2

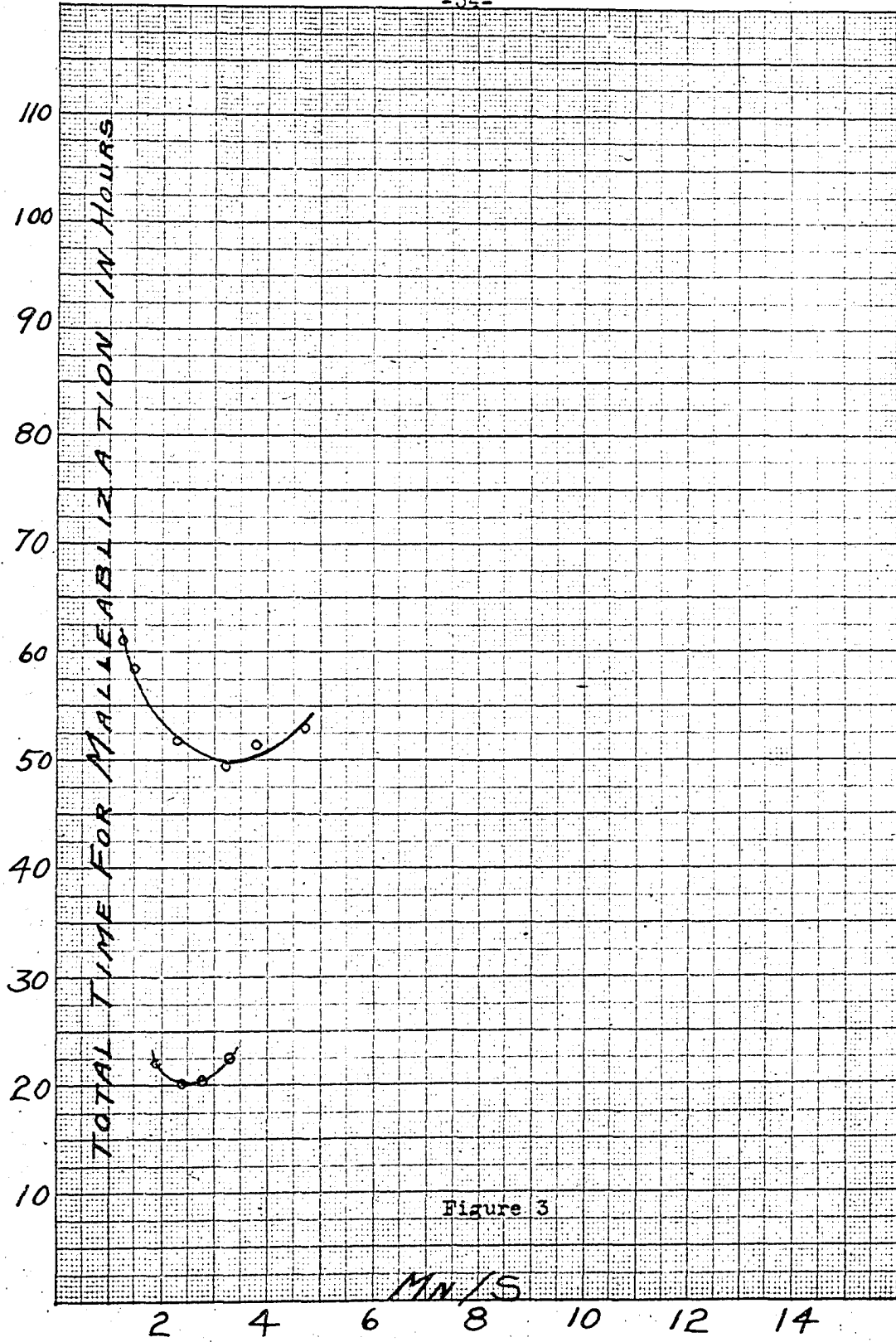
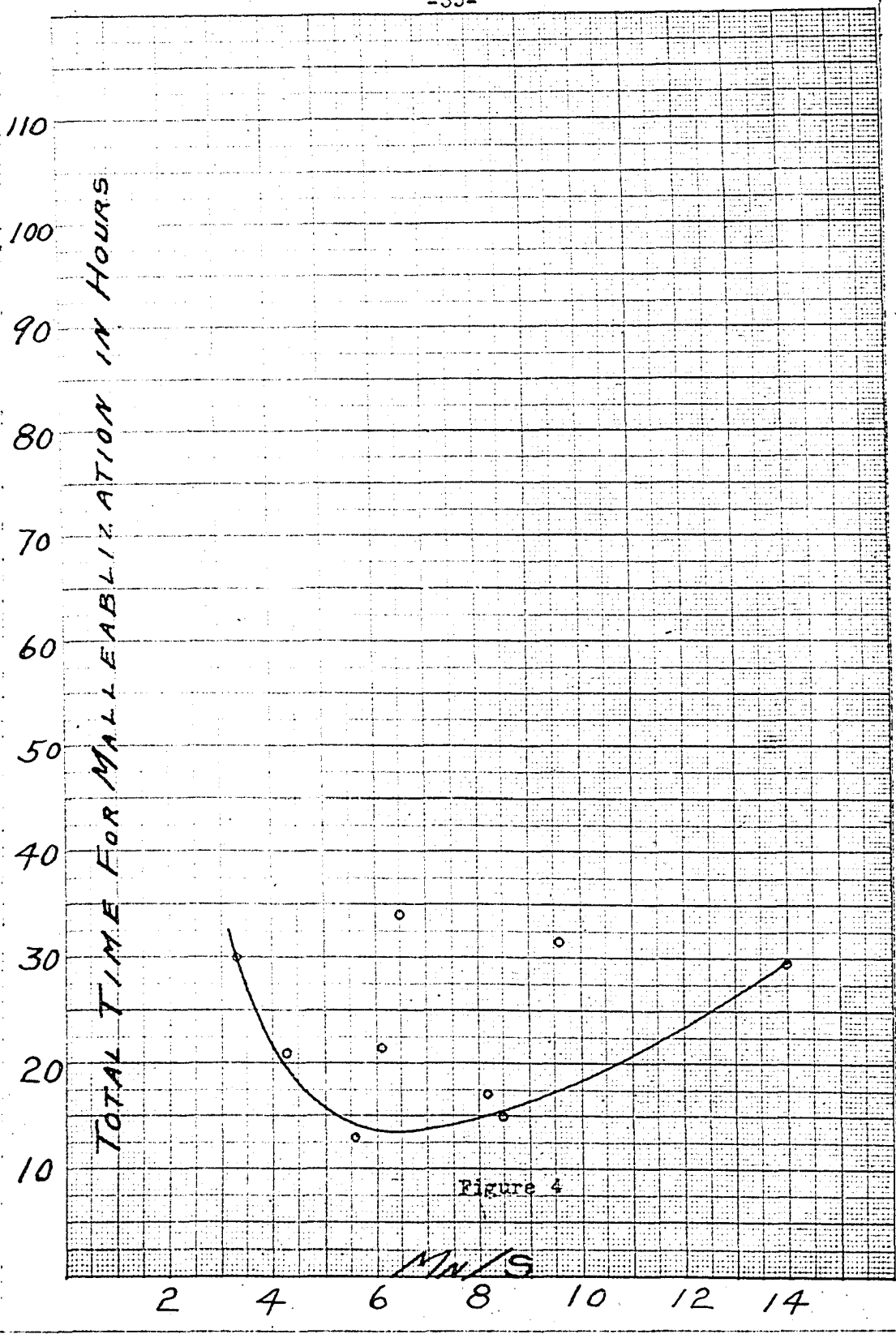


Figure 3



D. Photographing of Alloys

A number of the samples were photographed to show their structure, as cast, during the progress of the graphitization, and upon completion of the same. Such magnifications were used as would show the detail of the structure to the best advantage.



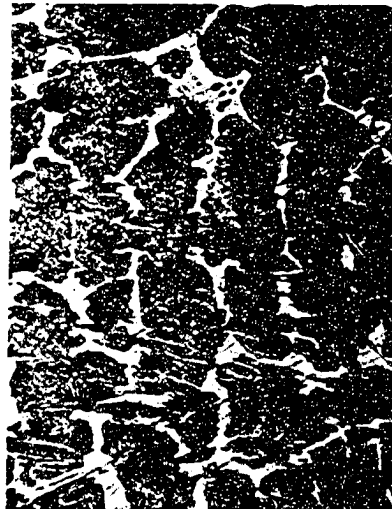
Alloy 1.
Structure as cast.
Nitric acid etched. 240X.



Alloy 6.
Structure as cast.
Nitric acid etched. 240X.



Alloy 35.
Structure as cast.
Nitric acid etched. 240X.



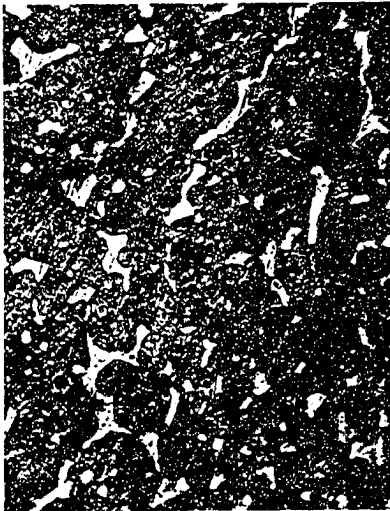
Alloy 44.
Structure as cast.
Nitric acid etched. 240X.



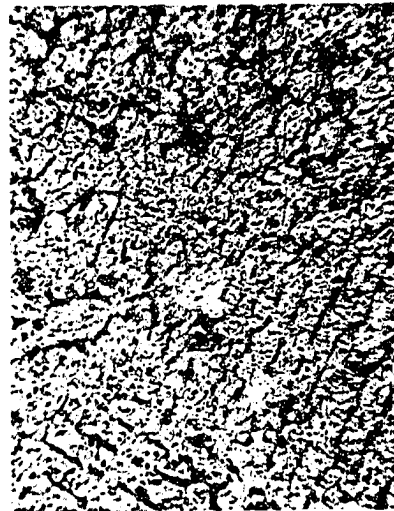
Alloy 65.
Structure as cast.
Nitric acid etched. 240X.



Alloy 69.
Structure as cast.
Nitric acid etched. 240X.



Alloy 6.
Annealed at 1700°F. (926°C.)
for 71 hours.
Nitric acid etched. 240X.



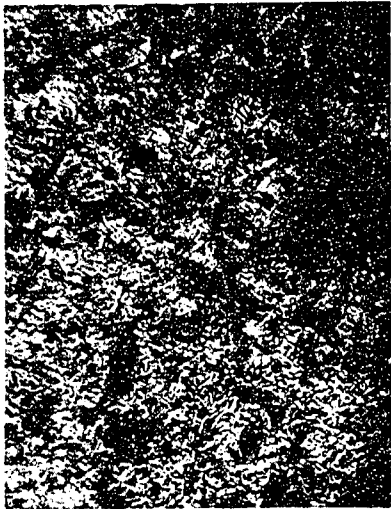
Alloy 6.
Annealed at 1700°F. (926°C.)
for 49 hours.
Sodium picrate etched. 100X.



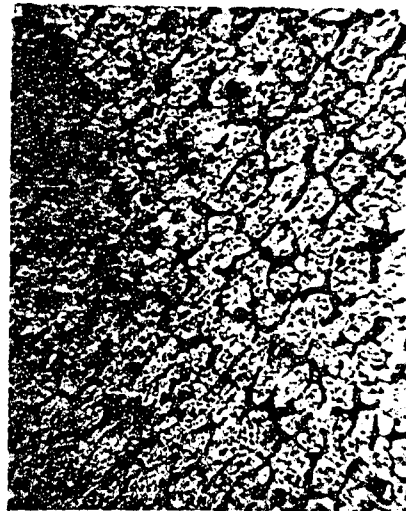
Alloy 71.
Annealed at 1700°F. (926°C.)
for 5 hours.
Nitric acid etched. 240X.



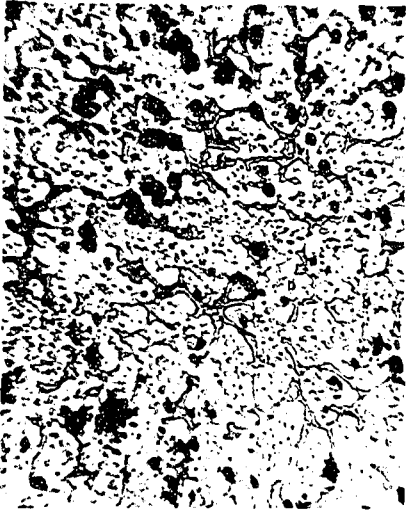
Alloy 71.
Annealed at 1700°F. (926°C.)
for 6 hours.
Nitric acid etched. 240X.



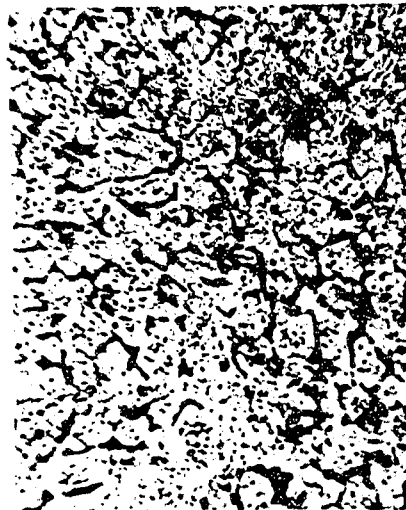
Alloy 22.
Annealed at 1700°F. (926°C.)
for 15 hours.
Nitric acid etched. 240X.



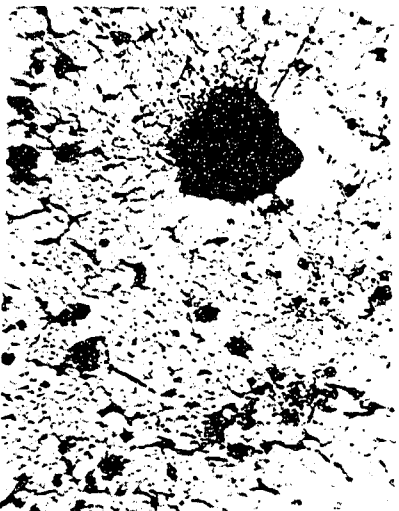
Alloy 1.
Annealed at 1700°F. (926°C.)
for 49 hours.
Sodium picrate etched. 100X.



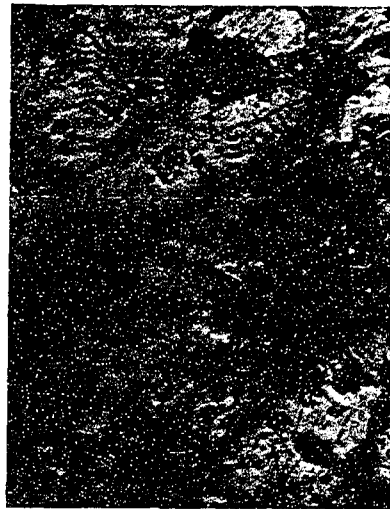
Alloy 2.
Annealed at 1700°F. (926°C.)
for 49 hours.
Sodium picrate etched. 100X.



Alloy 9.
Annealed at 1700°F. (926°C.)
for 49 hours.
Sodium picrate etched. 100X.



Alloy 15.
Annealed at 1700°F. (926°C.)
for 49 hours.
Sodium picrate etched. 100X.



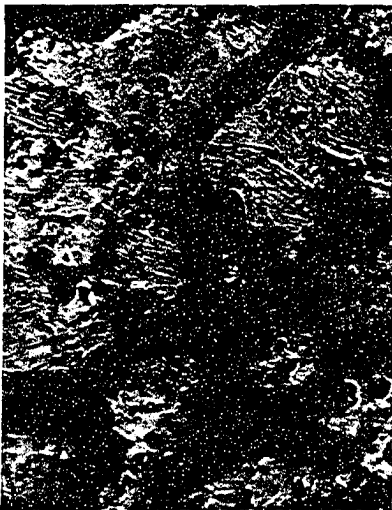
Alloy 15.
Annealed at 1700°F. (926°C.)
for 49 hours.
Sodium picrate etched. 725X.



Alloy 1.
Annealed at 1700°F. (926°C.)
for 49 hours.
Sodium picrate etched. 725X.



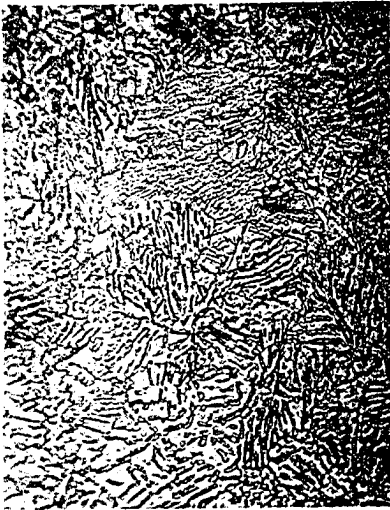
Alloy 2.
Annealed at 1700°F. (926°C.)
for 49 hours.
Sodium picrate etched. 725X.



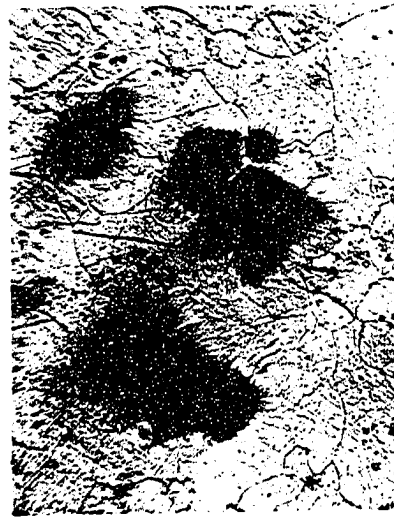
Alloy 6.
Annealed at 1700°F. (926°C.)
for 49 hours.
Sodium picrate etched. 725X.



Alloy 9.
Annealed at 1700°F. (926°C.)
for 49 hours.
Sodium picrate etched. 725X.



Alloy 26.
Annealed at 1300°F. (704°C.)
for 80 hours.
Nitric acid etched. 105X.



Alloy 24.
Annealed at 1300°F. (704°C.)
for 80 hours.
Nitric acid etched. 240X.



Alloy 46.
Annealed at 1300°F. (704°C.)
for 15 hours.
Nitric acid etched. 105X.



Alloy 46.
Annealed at 1300°F. (704°C.)
for 15 hours. Picture frame.
Nitric acid etched. 105X.

IV. DISCUSSION OF RESULTS

In considering what has been designated as the 2.10% carbon series, tables A, C, E, G, I, pages 19, 24, 26, 28, 30, respectively, there are two samples 6 and 9 in which the free cementite has not been removed even at 71 hours at 1700° F. (926° C.). Therefore, complete data were not obtained for the first stage of graphitization and consequently no data at all for the second stage.

Samples 8, 15, 16 and 24 were completed at the first stage of graphitization. In each case, the total time consumed was 100 or more hours. The Mn/S was 0.93, and the Mn - 2S was -0.051. A minimum time of 24 hours for complete graphitization was found for sample 41, whose Mn/S was 2.1, and Mn - 2S was 0.043%.

Considering samples 40, 41, 42, 44, 68, there was an average total time of 30.6 hours, an average Mn/S of 4.26, and an average Mn - 2S of 0.09%.

For the maximum manganese percentage there may be considered samples 64, 65, 66, and 67, whose average total time for malleablization was 45 hours. In this case, the average Mn/S was 10.65 and the Mn - 2S average was 0.308.

From these results it can be seen that the total time for malleablization passes through a minimum at a Mn/S of 4.6, Figure 1, page 32. This minimum corresponds to what is called a well balanced manganese to sulfur ratio.

In similar manner the 2.40% carbon series, Tables B, D, F, H, J, pages 20, 25, 27, 29, 31, respectively, may be reviewed. In this group, those alloys which stand out as the most resistant to malleablization are numbers 3, 7, 12, and 18. From Table J, page 31, it can be seen that the average Mn/S was 0.66, the Mn - 2S value was -0.07%. In this case the total time of heat treating averaged 118.5 hours after which the annealing was discontinued. A minimum total time of 25.7 hours was found for samples 35, 36, 70, 71, 72. The average value for Mn/S was 4.28, and for Mn - 2S was 0.128%. In considering, however, samples 70, 71, and 72, a value of 5.73 was obtained for Mn/S, and for Mn - 2S a result of 0.16%. The average total time of annealing was 28.8 hours.

Referring to Tables H and J, pages 29 and 31, respectively, for the higher manganese composition, it was found that the average total time for malleablization was 41 hours, the average Mn/S was 10.15 and the average value for Mn - 2S was 0.287%. Again, the total time for malleablization passes through a minimum at a Mn/S of 5.4, Figure 2, page 33.

By a comparison of the two series a similarity was found in that the total time passes through a minimum as the Mn/S increases. These results are shown graphically in Figures 1 and 2, pages 32 and 33, respectively. They are in fair agreement with the results obtained by Yemenidjian (13) who worked with a higher sulfur composition of white cast iron.

His results are graphed on page 34, Figure 3. Somewhat better agreement is obtained with the results of Kikuta (5), whose results are shown graphically on page 35, Figure 4; this is probably accounted for by the closer agreement of the manganese and sulfur composition.

For samples 1, 2, 10 and 17, no data were reported for the second stage of graphitization because anomalous results were obtained. Since these abnormalities presented, in themselves, a problem, it was decided to leave them for a future and more extensive investigation and study.

The manganese sulfur ratios were arranged in groups having nearly the same numerical values, and these values averaged. In each of these groups, the corresponding total hours of malleablization were averaged. Figures 1 and 2, pages 32 and 33, respectively, show the curves obtained by plotting these averaged values. This gave representative curves of the values plotted and due consideration to those values which were irregular.

V. CONCLUSION

It has been found in this investigation that in both the 2.10% and 2.40% carbon series, the total time for mal-leablization passes through a minimum as the manganese sulfur ratio increases.

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