U.M.

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report

of

Committee on Examination

This is to certify that we the undersigned, as a committee of the Graduate School, have given Carl Edward Julihn final oral examination for the degree of Master of Arts . We recommend that the degree of Master of Arts be conferred upon the candidate.

Minneapolis, Minnesota

......................191

Samuel L. Hoyt
Chairman

W. H. Hunter

W. H. Emmons

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report

of

Committee on Thesis

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by Carl Edward Julihn for the degree of Master of Arts. They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Arts.

Samuel L. Hoyt.
Chairman

W. H. Hunter

W H Emmons

1918

T H E S I S

Submitted in part fulfillment of the requirements for the A.M. degree at the University of Minnesota, as a result of research conducted under Professor Samuel L. Hoyt in the academic year 1918-19.

THE OCCURRENCE AND DISSOCIATION OF MARTENSITE AND AUSTENITE IN HYPEREUTECTOID STEEL.

by Carl Edward Julihn, E.M.

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THE OCCURRENCE AND DISSOCIATION OF MARTENSITE AND AUSTENITE IN HYPEREUTECTOID STEEL.

by C. E. Julihn, E. M.

Submitted in part fulfillment of the requirements for the A.M. degree at the University of Minnesota, as a result of research conducted under Professor Samuel L. Hoyt in the academic year 1918-19.

THE PROBLEM

In that part of the constitution diagram for the iron-carbon series which lies between the eutectoid composition (0.8% to 0.9% C.) and 2% carbon is a region of exceptional present interest because of the important extension in industrial use of the steels there represented. These hard steels are the accepted materials for the manufacture of springs, but their brittleness constitutes a principal difficulty in their use for cutting tools, such as chisels, etc.

This is due to the presence of martensite as a constituent of the steel. Martensite, though extremely hard, is also brittle. It is, however, a transformation product from austenite, which has very different properties. Austenite has remarkable toughness and deformability, and, when retained as a constituent by quenching from high temperatures, it confers these properties upon the steel.*

*NEW TOOL STEEL - Iron Trade Review, Feb. 27, 1919, p. 576.

Heat treatment of hypereutectoid steels for the development of toughness should therefore have as an object the retention of austenite as a constituent.

It is the purpose of this study to determine, if possible, how this can be accomplished in the case of certain typical steels containing high carbon.

PROJECT OF EXPERIMENTS

Field To Be Covered

In planning a schedule of experiments, it was desired to cover the following points:

A. Conditions affecting the production of pure austenite.
   1. In straight carbon steel.
   2. In steel with appreciable manganese

B. Conditions affecting the production of austenite plus martensite.
   1. In straight carbon steel
   2. In steel with appreciable manganese

C. Effect of reheating on steels containing austenite plus martensite

D. Determination of hardness
   1. Of individual constituents
   2. Of the complex of certain steels

E. Determinations of specific gravities of a suite of reheated specimens containing austenite plus martensite.

Selection of Type Steels

The following steels were selected for the experiment:

I. A standard eutectoid steel.

II. A standard market steel with high carbon and low manganese as follows: C. 1.30%, Mn. 0.26%.

III. A steel to be made in the laboratory to have approximately eutectoid carbon and from 0.6 to 0.7 manganese.

IV. A steel to be made in the laboratory to have approximately eutectoid carbon and about 1% manganese.

V. A steel to be made in the laboratory to have about 1.1% carbon and 1.5% manganese.

VI. A steel to be made in the laboratory to have about 1.75% carbon and 1% manganese.

Plan of Heat Treatment.

The plan of heat treatment included:

1. An observation upon Steel II. of the time effect in the transformation of pearlite, to be accomplished by heating a number of specimens just past the Ac_1. point and quenching them at various time intervals thereafter.

2. Treatment of samples of all six steels by raising specimens to temperatures at various points in the range 800° C. to 1100° C. and quenching them rapidly.

3. Reheating to 100° C., 200° C., 250° C., and 300° C. of at least one selected steel showing austenite plus martensite.

Plan of Microscopic Study.

All the several specimens from the heat treatments to be prepared for examination by the metallographic microscope, to be studied carefully for a determination of constituents and to be photographed in some cases.

Plan for Hardness Determinations.

This to be effected by the schleroscope test for the complex and by scratch test for getting some evidence of the relative hardness of constituents.

Plan for Specific Gravity Determinations.

Specific gravity to be determined in the case of the select retreated steel by weighing in water and in air with a chemical balance sensitive to 0.1 milligram.

PREPARATION OF STEELS

Steels I. and II.

These steels, as previously stated, are standard merchant steels of analyses as shown in summary table following.

Steels III., IV., and V.

These steels were made up from mixtures in proper proportions of Steel II., American Ingot Iron, which contains very little carbon, metallic manganese and Alloy A, an alloy which was prepared with 3% carbon. The mixtures were melted in an Arsem Vacuum Furnace. The steels were forged with a power hammer and quenched.

Steel VI.

This steel was made up directly from American Ingot Iron and carbon, together with metallic manganese. The melt was made in the Arsem Vacuum Furnace. The steel was forged with power hammer, and then quenched.

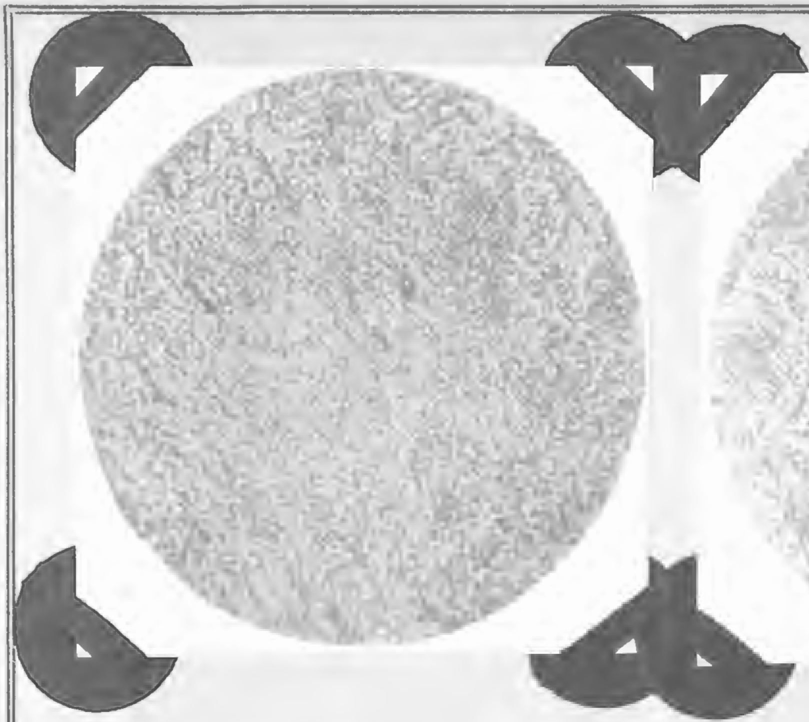
Analyses of Steels Treated.

After the four special steels had been made, all six steels were analyzed with the following results:

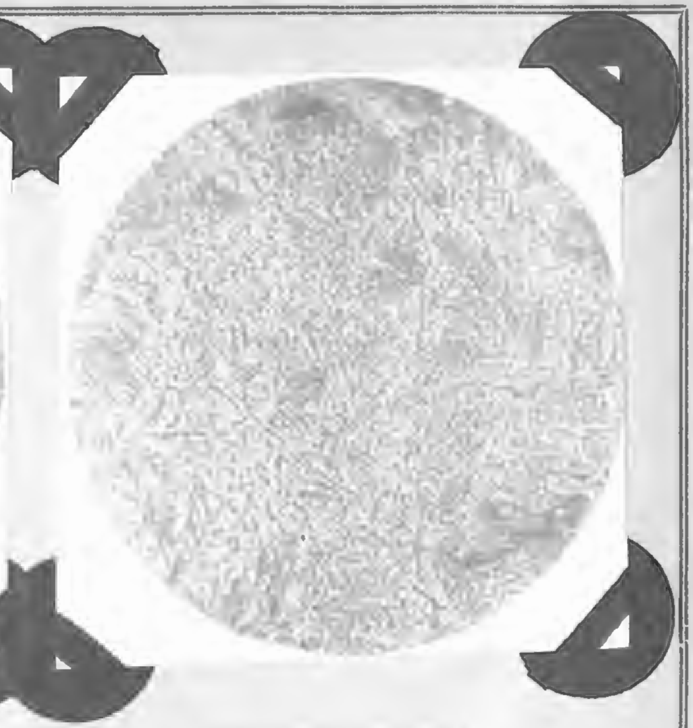
Steel	Analysis				
	C	Mn	Si	S	P
I.	.86	.37	.17	.032	.037
II.	1.30	.26	.25	.025	.01
III.	.862	.648	.20	.02	.008
IV.	.9	.958	.21	.018	.007
V.	1.08	1.445	.20	.019	.009
VI.	1.75	.936	.02	.01	.006

Photomicrographs of the Untreated Steels.

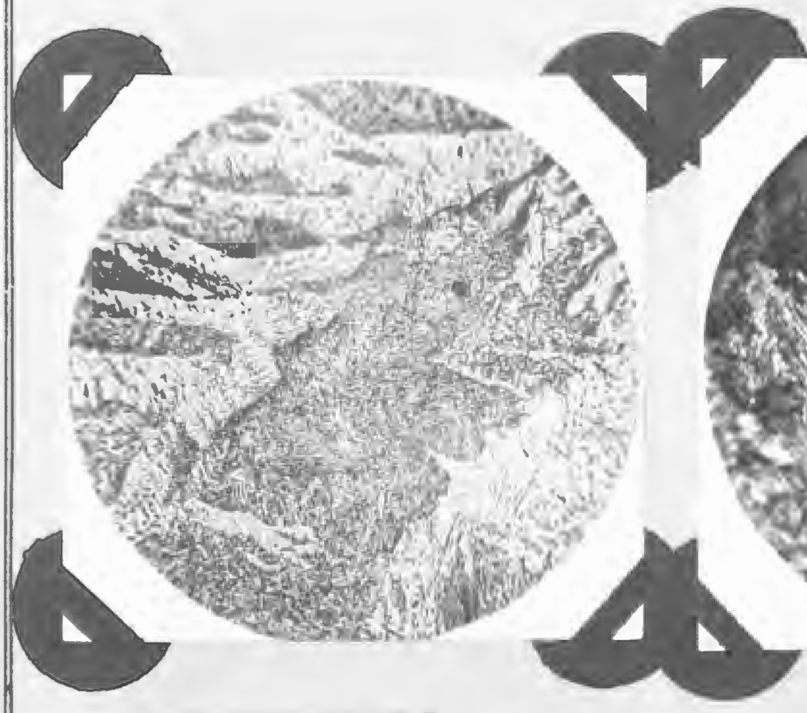
After preparation of metallographic specimens from each untreated steel a microscopic study of them was made and photomicrographs were taken with the following results:



PHOTOMICROGRAPH 1
STEEL I. original
C 0.86% Mn 0.37%
Granular Pearlite



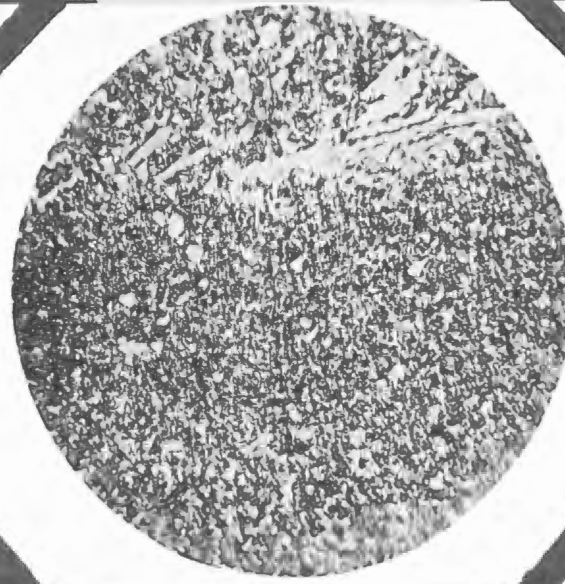
PHOTOMICROGRAPH 2
STEEL II.original
C 1.3% Mn 0.26%
Lamellar and granular pearlite and cementite.



PHOTOMICROGRAPH 3
STEEL III. original
C 0.86% Mn 0.65%
Pearlite and ferrite

PHOTOMICROGRAPH 4
STEEL IV.original
C 0.9% Mn 0.96%
Lamellar pearlite

PHOTOMICROGRAPH 5
STEEL V. original
C 1.08% Mn 1.45%
Troostite and martensite.



PHOTOMICROGRAPH 6
STEEL VI.original
C 1.75% Mn 0.94%
Sorbite with excess of cementite.

In all the above photomicrographs of Series I. the magnification is X 800.

HEAT TREATMENT.

Effect of Time at Ac_{1-2-3} Point in the Transformation of Pearlite.

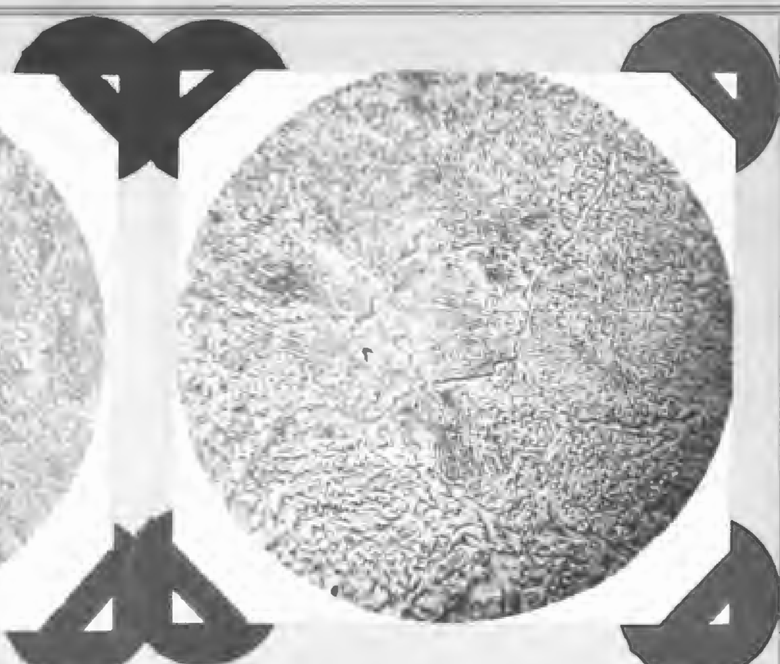
Steel II. was selected for these experiments (C. 1.3%, Mn 0.26).

Nine specimens were slowly heated in an electric furnace to 742° C, just at the end of the transformation point as observed by thermal couple inserted in a blank. One specimen was withdrawn and rapidly quenched in ice water immediately upon the attainment of 742° C. A second specimen was quenched 5 seconds after the temperature was reached. A third was quenched after 10 seconds, a fourth after 25 seconds, a fifth after one minute, and a sixth after two minutes. After the treated specimens had all been polished, etched, and photomicrographed, three of the specimens were retreated as before for periods of five minutes, fifteen minutes, and thirty minutes. These relations may be summarized as follows:

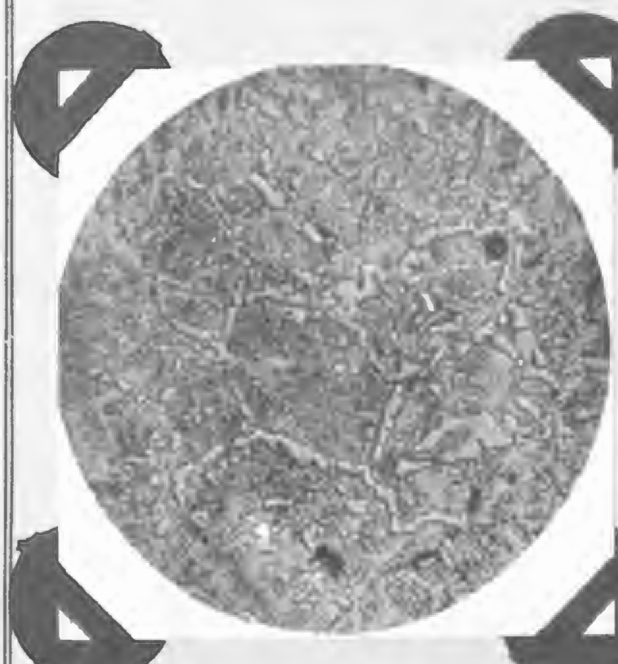
Specimen	Time at 742° C.	
1	0	
2	5 sec.	
3	10 sec.	
4	25 sec.	
12	1 min.	
13	2 min.	
2	5 min.	- retreated
4	15 min.	"
12	30 min.	"

As all of the steels were to receive treatment in the temperature range 800° C. to 1100° C., it was desired in this case to exhibit fully the transformation at 742° C. through which all the steel treated at high temperature must pass. The photomicrographs following show this transformation fairly well. It is apparent that at the stated temperature lamellar pearlite is broken up only slowly, but it has practically disappeared in the last specimen, which was held at 742° C. for thirty minutes. The cementite laminations have been nearly absorbed.

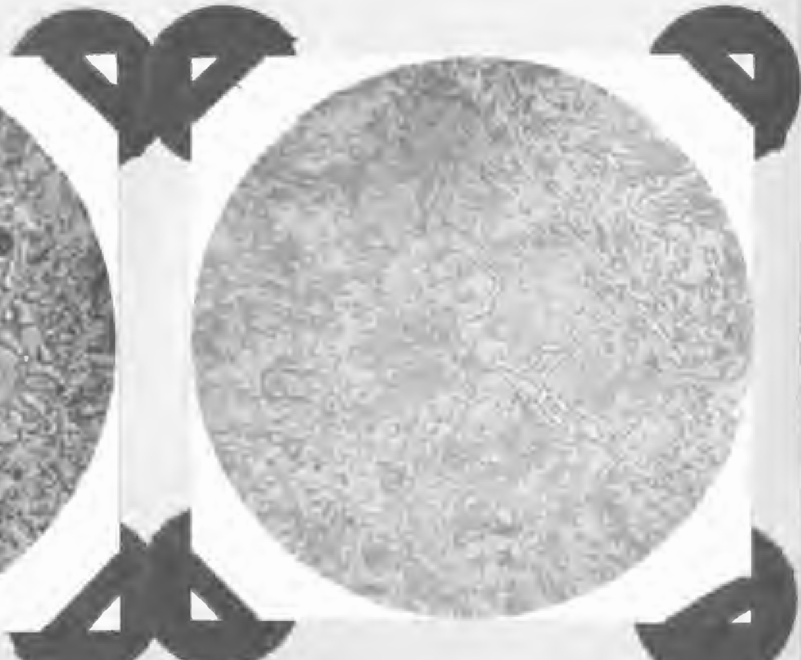
PHOTOMICROGRAPH 7
STEEL II. Heated to 742° C.and immediately quenched in ice water - Pearlite.



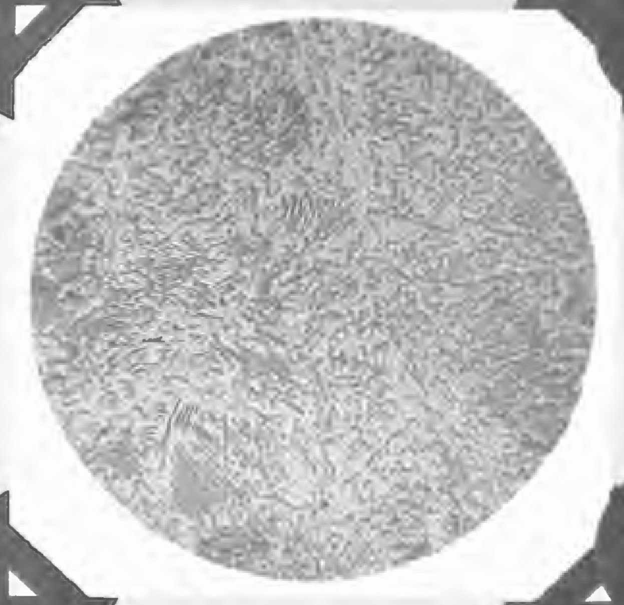
PHOTOMICROGRAPH 8
STEEL II. Held 5 seconds at 742° C. and quenched - Pearlite



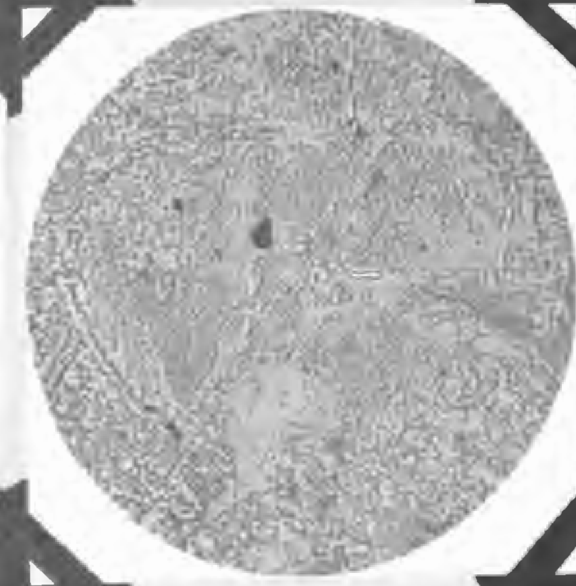
PHOTOMICROGRAPH 9
STEEL II. Held 10 seconds at 742° C. and quenched - Pearlite



PHOTOMICROGRAPH 10
STEEL II. Held 25 seconds at 742° C. and quenched - Lamellar Pearlite breaking up.

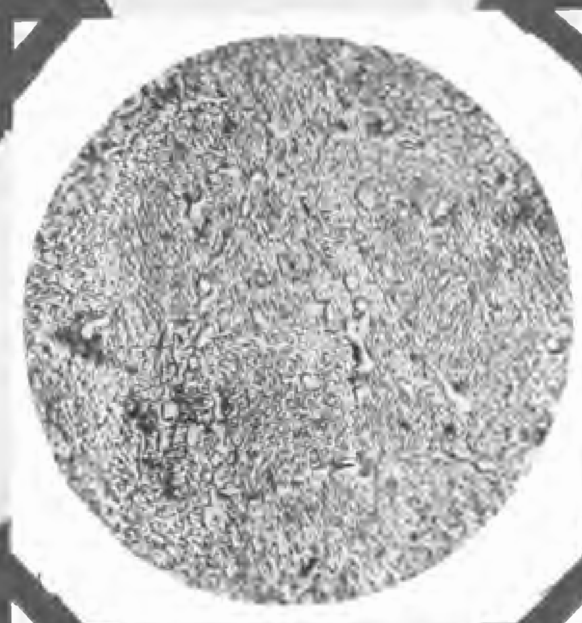


PHOTOMICROGRAPH 11.
STEEL II. Held 1
minute at 742° C.
and quenched -
Pearlite.

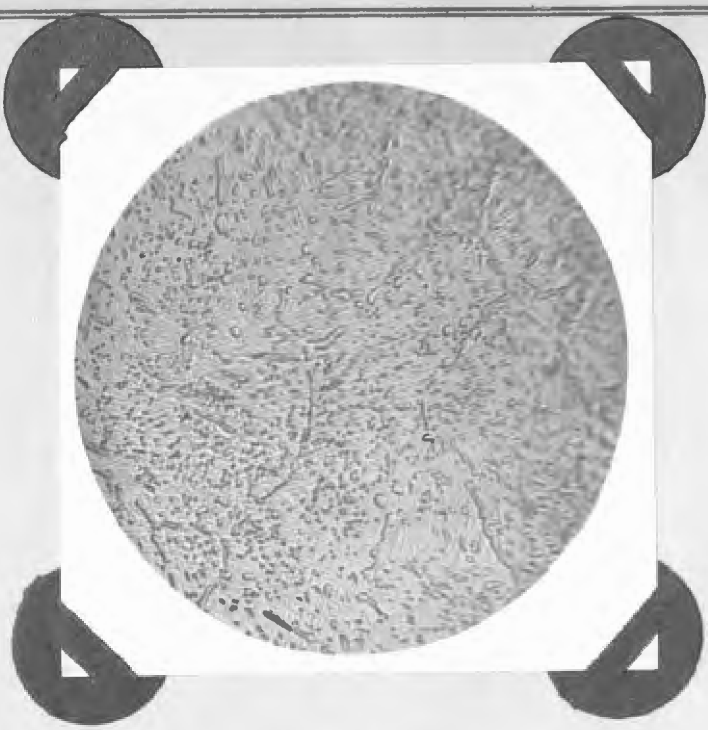


PHOTOMICROGRAPH 12
STEEL II. Held 2
minutes at 742° C.
and quenched.-
Pearlite and some
hardenite.

PHOTOMICROGRAPH 13.
STEEL II. Held 5
minutes at 742° C.
and quenched -
Granular pearlite.



PHOTOMICROGRAPH 14.
STEEL II. Held 15
minutes at 742° C.
and quenched -
Granular pearlite.



PHOTOMICROGRAPH 15.
STEEL II. Held 30
minutes at 742° C.
and quenched -
Cementite lamination
has been nearly ab-
sorbed.

In all the above photomicrographs of Series II. the magnification is X 800.

Effects of Quenching in Temperature Range from 800° C. to 1100° C.

In this series of experiments all the five steels were treated, several specimens of each steel being heated to various temperatures in the range covered and then rapidly quenched in ice water. A vertical, cylindrical electric furnace was used for obtaining the heats. Temperatures were observed by use of a platinum thermal couple which had been carefully calibrated.

Steel I. in Treatment of Series III.

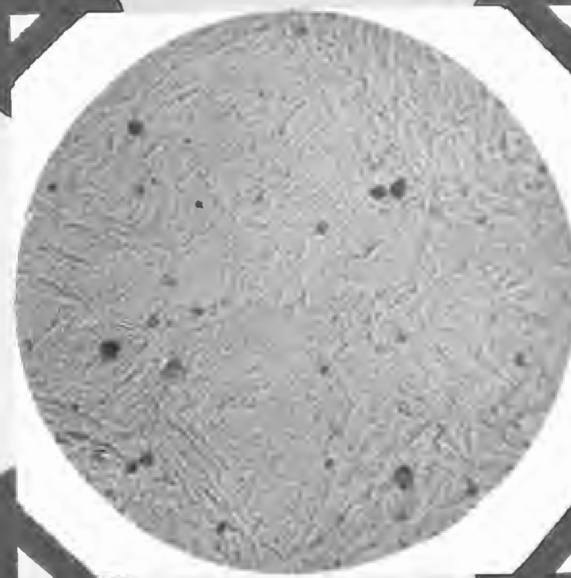
This steel, a commercial eutectoid steel, containing C 0.86%, Mn 0.37%, Si 0.17%, S 0.032%, P 0.037%, is shown untreated in Photomicrograph 1 on page 6.

Specimens were now treated as shown in the following table:

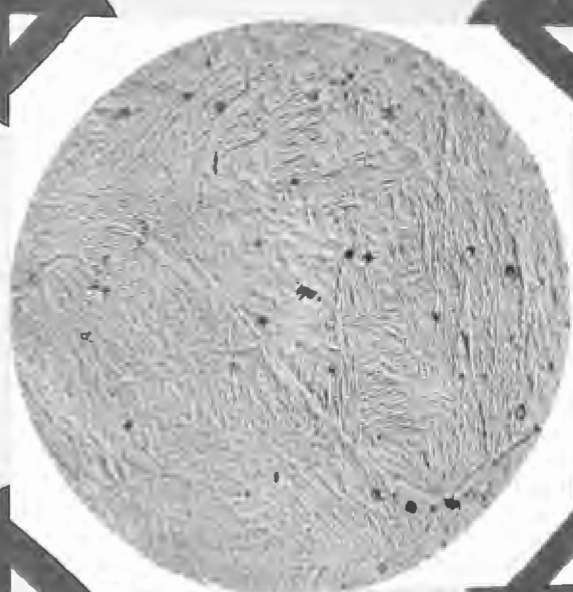
Specimen	Quenching Temperature after being held 15 minutes.
3	800° C.
5	850° C.
1	900° C.
6	950° C.
2	1000° C.
4	1100° C.

The results are exhibited in photomicrographs 16 to 21 inclusive.

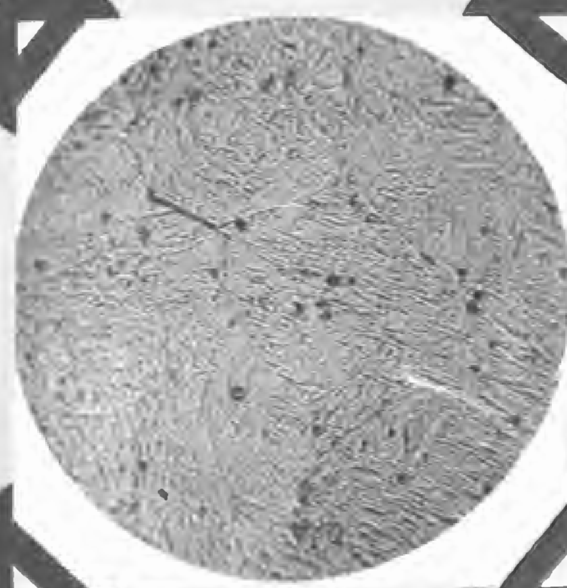
PHOTOMICROGRAPH 16.
STEEL I. held 15
minutes at 800° C.
and quenched.
X 800 - Martensite.



PHOTOMICROGRAPH 17.
STEEL I. held 15
minutes at 850° C.
and quenched.
X 800 - Martensite.

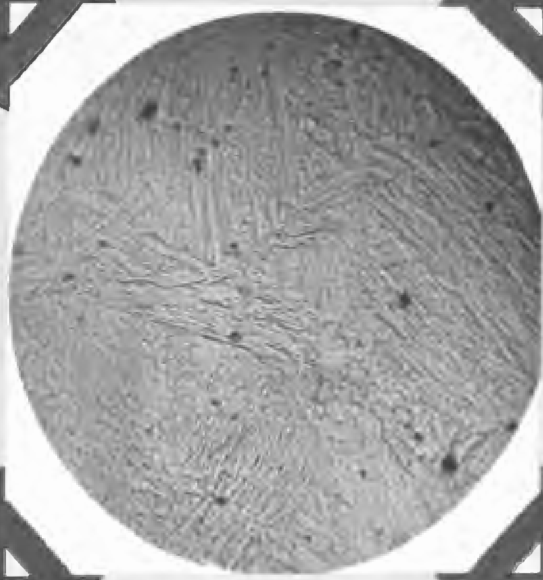


PHOTOMICROGRAPH 18.
STEEL I. held 15
minutes at 900 C.
and quenched.
X 800-Martensite.



PHOTOMICROGRAPH 19.
STEEL I. held 15
minutes at 950° C.
and quenched.
X 800 - Martensite.

PHOTOMICROGRAPH 20.
STEEL I. held 15
minutes at 1000° C.
and quenched.
X 800 - Martensite.



PHOTOMICROGRAPH 21.
STEEL I. held 15
minutes at 1100° C.
and quenched.
X 800 - Martensite.

Discussion of Photomicrographs of Series III.on Steel I.

It appears that Steel I., the eutectoid with low manganese yields no austenite whatever when quenched in the range 800°to 1100° C. as all the above photomicrographs show only martensite. Therefore, this steel is not available for selection and use in the final experiments.

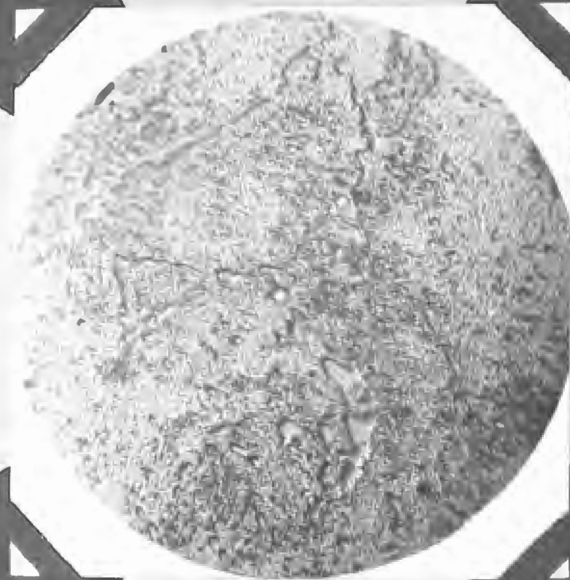
Steel II. in the Treatment of Series IV.

This steel containing C 1.3%, Mn 0.26%, Si 0.25%, S 0.025%, P 0.01%, is shown untreated in Photomicrograph 2, page 6.

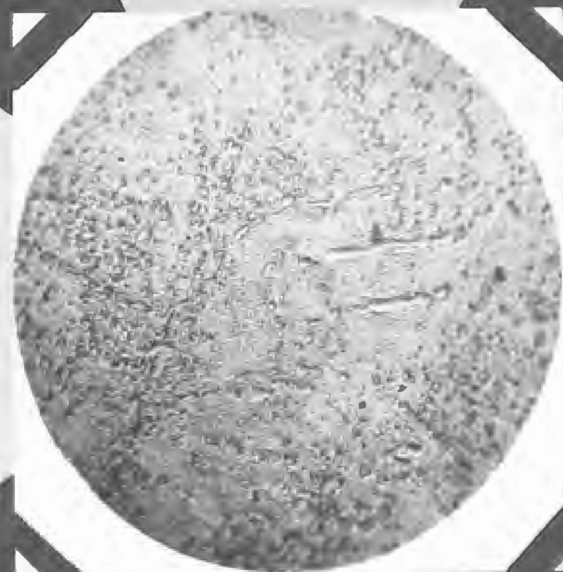
Specimens were now treated as shown in the following table:

Specimen	Quenching Temperature after being held 15 minutes.
10	800° C.
5	850° C.
9	900° C.
7	950° C.
6	1000° C.
8	1100° C.

The results are exhibited in photomicrographs 22 to 27 inclusive.



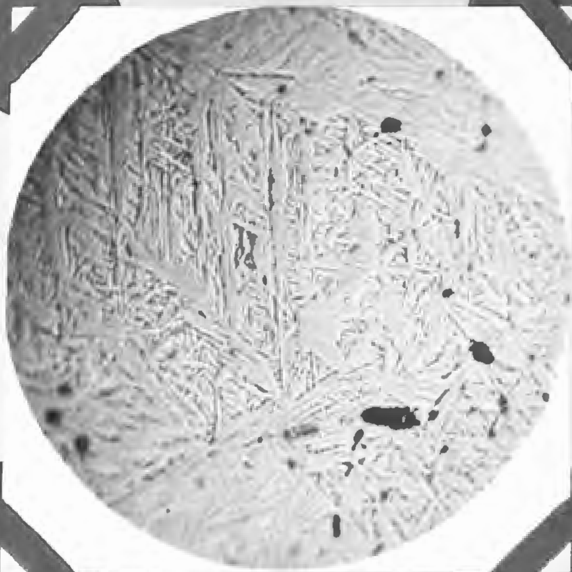
PHOTOMICROGRAPH 22.
STEEL II. held 15
minutes at 800° C.
and quenched.
Martensite and cementite.

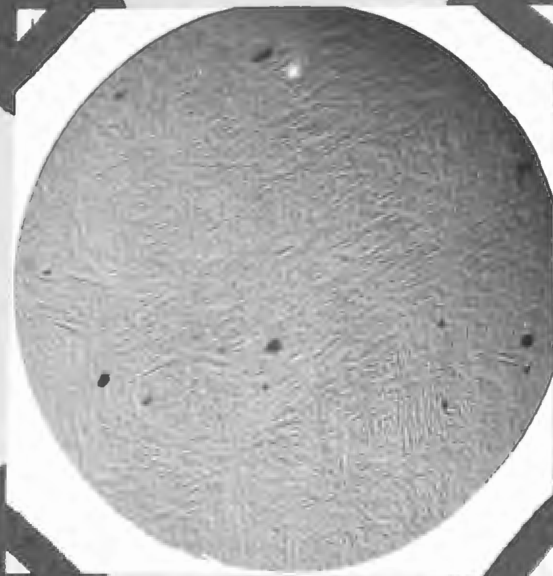


PHOTOMICROGRAPH 23.
STEEL II. held 15
minutes at 850° C.
and quenched.
Martensite and cementite.

PHOTOMICROGRAPH 24.
STEEL II. held 15
minutes at 900° C.
and quenched.
Martensite.

PHOTOMICROGRAPH 25.
STEEL II. held 15
minutes at 950° C.
and quenched.
Martensite.





PHOTOMICROGRAPH 26.
STEEL II. held 15
minutes at 1000° C.
and quenched.
Martensite. Austenite (?)

PHOTOMICROGRAPH 27.
STEEL II. held 15
minutes at 1100° C.
and quenched.
Martensite.

DISCUSSION of Photomicrographs of Series IV. on Steel II.

In the case of Photomicrograph 26 there is a possibility of the existence of some austenite, but on the whole the results in this series offer little encouragement in the range of the lower temperatures at least. While it might be supposed theoretically that some austenite could be obtained in such a steel by quenching from high temperatures, the results actually obtained would not justify the use of this steel for the final experiments of this study.

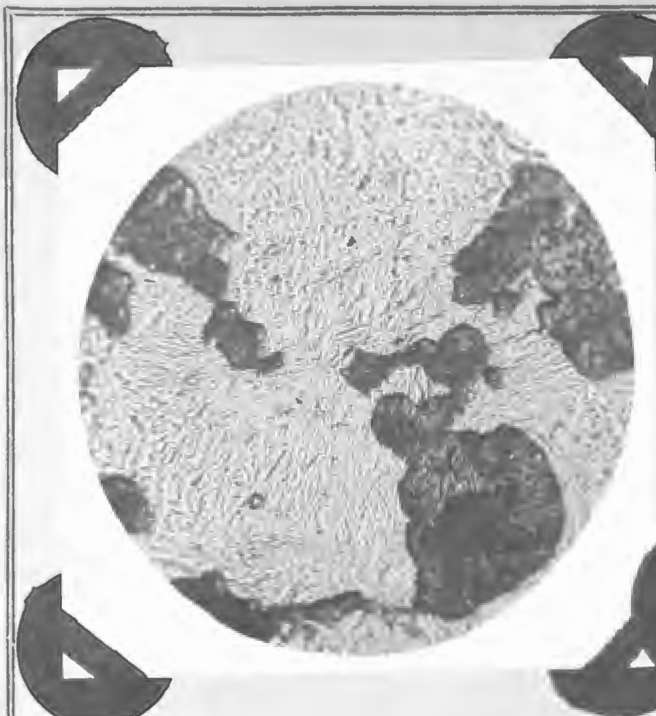
Steel III. in Treatment of Series V.

This steel, containing carbon 0.86, Mn 0.65, Si 0.20, S 0.02, P 0.008, is shown untreated in Photomicrograph 3, on page 6.

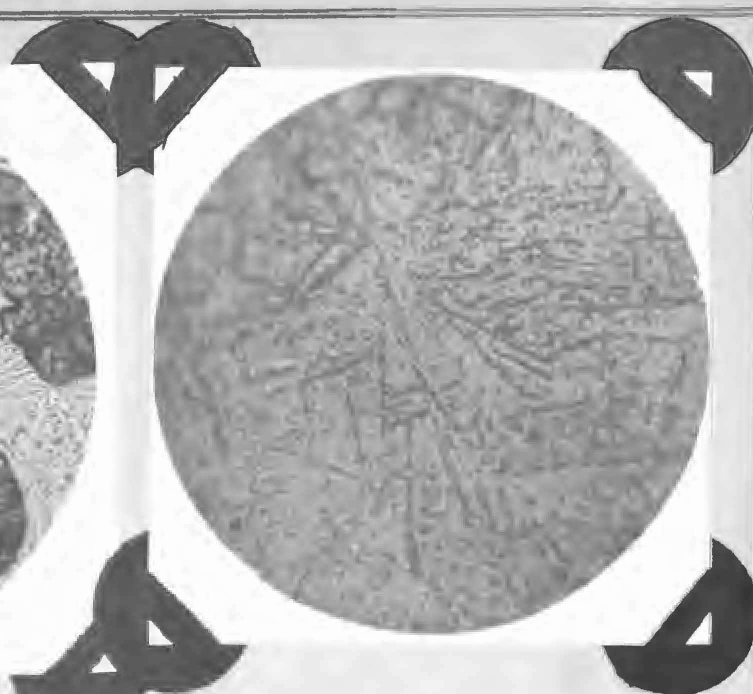
Specimens were now treated as follows:

Specimen	Quenching Temperature after being held 15 minutes.
H	800° C.
L	900° C.
K	1000° C.
I	1100° C.

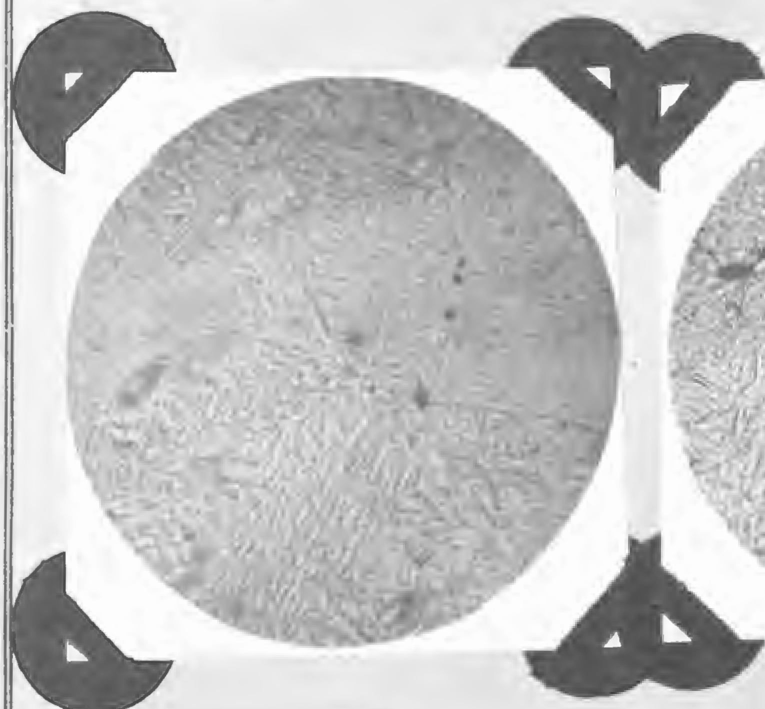
The results are exhibited in Photomicrographs 28 to 31 inclusive.



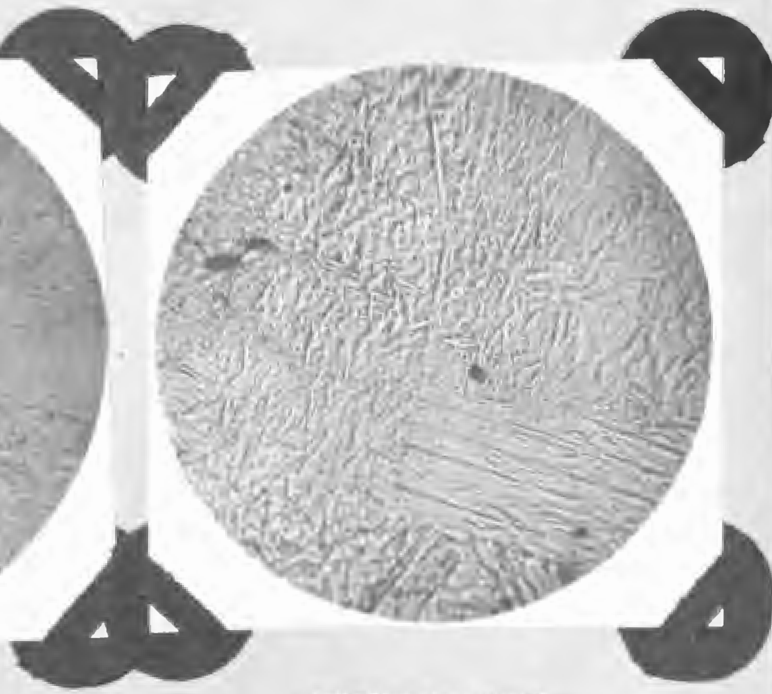
PHOTOMICROGRAPH 28.
Steel III.held 15
minutes at 800° C.
and quenched.
X 800 Martensite plus
Troostite.



PHOTOMICROGRAPH 29.
Steel III. held 15
minutes at 900° C.
and quenched.
X 800 Martensite.



PHOTOMICROGRAPH 30.
Steel III.held 15
minutes at 1000° C.
X 800 Martensite.



PHOTOMICROGRAPH 31.
Steel III.held 15
minutes at 1100° C.
X 800 Martensite.

Discussion of Photomicrographs of Series V. on Steel III.

In this steel also no austenite is obtained by quenching in the range 800° C. to 1100° C. The steel is therefore unavailable for selection and use in the final experiments of this study.

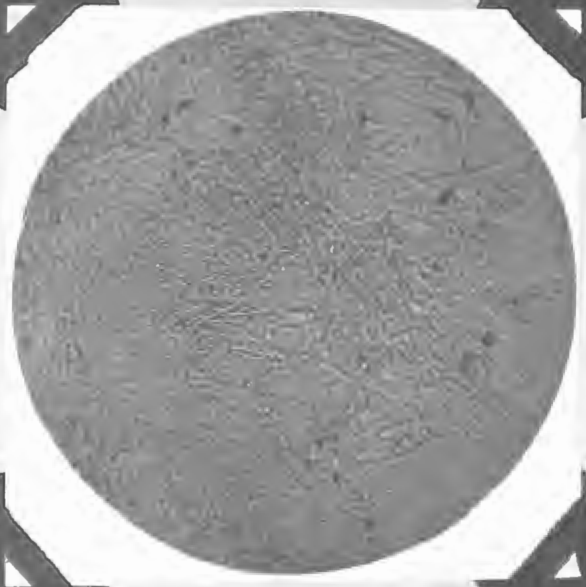
Steel IV in Treatment of Series VI.

This steel, containing C 0.9%, Mn 0.96%, Si 0.21%, S 0.018%, P 0.007%, is shown untreated in Photomicrograph 4, page 6.

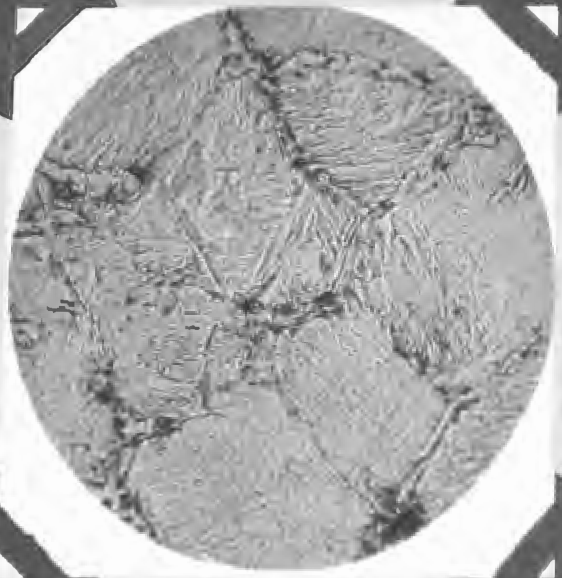
Specimens were now treated as follows:

Specimens	Quenching Temperature after being held 15 minutes.
D	800° C.
G	900° C.
B	1000° C.
C	1100° C.

The results are exhibited in photomicrographs 32 to 35 inclusive.



PHOTOMICROGRAPH 32.
STEEL IV. held 15
minutes at 800° C.
and quenched.
X 800 Martensite.



PHOTOMICROGRAPH 33.
STEEL IV. held 15
minutes at 900° C.
and quenched.
X 800 Martensite.

PHOTOMICROGRAPH 34.
STEEL IV. held 15
minutes at 1000° C.
and quenched.
X 800 Martensite.

PHOTOMICROGRAPH 35.
STEEL IV. held 15
minutes at 1100° C.
and quenched.
X 800 Martensite.

Discussion of Photomicrographs of Series VI. on Steel IV.

Steel IV. quenched in the range 800° to 1100° C. is seen to contain no austenite. It is therefore unavailable for selection and use in the final experiments of this study.

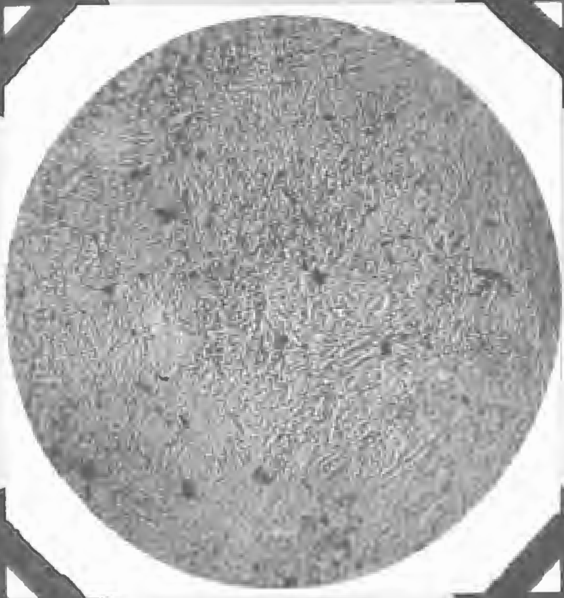
Steel V. in Treatment of Series VII.

This steel containing 1.08% C., 1.45 Mn, Si .20, S .019, P .009 is shown untreated in photomicrograph 5, page 7.

Specimens now treated were as follows:

Specimen	Quenching Temperature after being held 15 minutes.
N	800° C.
P	900° C.
Q	1000° C.
O	1100° C.

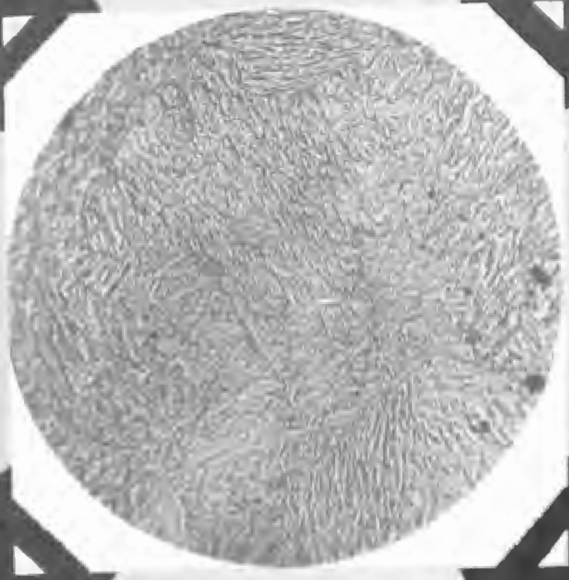
The results are exhibited in photomicrographs 36 to 39 inclusive.



PHOTOMICROGRAPH 36.
STEEL V. held 15
minutes at 800° C.
and quenched.
X 800 Martensite.

PHOTOMICROGRAPH 37.
STEEL V. held 15
minutes at 900° C.
and quenched.
X 800 Martensite.

PHOTOMICROGRAPH 38.
STEEL V. held 15
minutes at 1000° C.
and quenched.
X 800 Martensite.



PHOTOMICROGRAPH 39.
STEEL V. held 15
minutes at 1100° C.
and quenched.
X 800 Martensite.

Discussion of Photomicrographs of Series VII. on Steel V.

Steel V. quenched in the range 800° to 1100° C. is seen to contain little if any austenite. It is therefore unavailable for selection and use in the final experiments of this study.

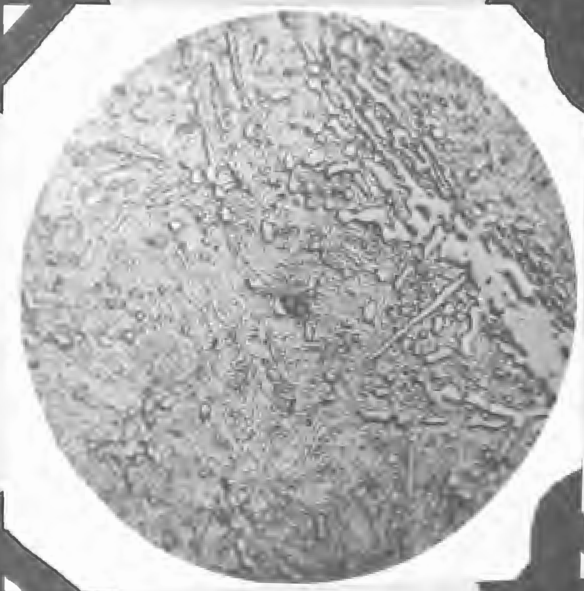
Steel VI. in Treatment of Series VIII.

This steel, containing C 1.75%, Mn 0.94%, Si .02%, S .01%, P. .006%, is shown untreated in photomicrograph 6, on page 7.

Specimens were now treated as follows:

Specimen	Quenching Temperature after being held 15 minutes.
F 1	900° C.
F 4	1000° C.
F 3	1050° C.
F 2	1100° C.

The results are exhibited in photomicrographs 40 to 43 inclusive.



PHOTOMICROGRAPH 40.
STEEL VI. held 15
minutes at 900° C.
and quenched.
X 800 Martensite and
free cementite.

PHOTOMICROGRAPH 41.
STEEL VI. held 15
minutes at 1000° C.
and quenched.
X 800 Martensite and
Austenite.

PHOTOMICROGRAPH 42.
STEEL VI. held 15
minutes at 1050° C
and quenched..
X 800 Martensite and
austenite.

PHOTOMICROGRAPH 43.
STEEL VI. held 15
minutes at 1100° C.
and quenched.
X 800 Martensite and
austenite.

Discussion of Photomicrographs of Series VIII. on Steel VI.

Steel VI. quenched in the range 900° to 1100° C. is seen to contain martensite, plus austenite in the specimens representing quenching at 1000° C., 1050° C., and 1100° C. It is evident, moreover, that the amount of austenite increases at each higher quenching to a maximum at 1100° C. when the martensite is distinctly subordinate.

Steel VI. was therefore considered to be of the type required for selection in regard to further experiments.

Reheating of Steel VI.

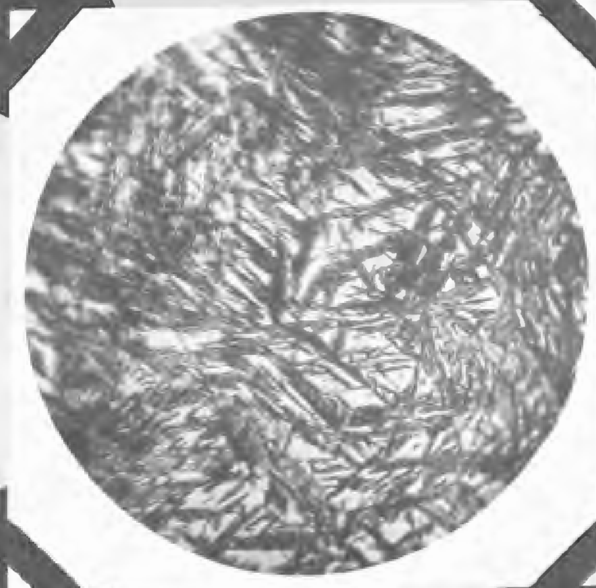
Of the several heat treatments of Steel VI. that at 1050° C. was selected as the most desirable in relative amounts of martensite and austenite for experiments in reheating. Three more specimens were therefore prepared by treatment similar to that given Specimen F 3. This made four specimens which had been heated to 1050° C., held at that temperature 15 minutes, and quenched in ice water.

These specimens were then reheated as follows:

Series IX	Reheated	In	Time held
F 3	100° C.	Water	2 hours
F 5	200° C.	Cottonseed oil	1 hour
F 7	250° C.	Cottonseed oil	3/4 hour
F 6	300° C.	Electric furnace	1/2 hour

The results are shown in photomicrographs 44 to 47 inclusive.

See Photomicrograph 42.



PHOTOMICROGRAPH 44.
STEEL VI. Heated 15 minutes at 1050° C., quenched and reheated 2 hours at 1000° C.
X 800 - Martensite unchanged from original.

PHOTOMICROGRAPH 45.
STEEL VI. Heated 15 minutes at 1050° C., quenched and reheated 1 hour at 200° C.
X 800 - Austenite unaffected. Martensite breaking down into Troostite.

PHOTOMICROGRAPH 46.
STEEL VI. Heated 15 minutes at 1050° C. quenched and reheated 3/4 hour at 250° C.
X 800 - Chiefly Troostite. Martensite gone, but traces of its struture. Remnants of austenite.

PHOTOMICROGRAPH 47.
STEEL VI. Heated 15 minutes at 1050° C., quenched and reheated 1/2 hour at 300° C.
Troostite only.

HARDNESS TESTS.

Hardness of the Complex.

These tests were made with the schleroscope, six tests being averaged in each case. The results were as follows:

Series I. Original Steels.

Steel	Hardness
1	43
2	45
3	59
4	66
5	68

Series II. Steel II. treated at 742° C.

Time Held	Hardness
0 sec.	60
10 sec.	57
2 min.	50
5 min.	54
15 min.	78
30 min.	103

Series III. Steel I. in Range 800° to 1100° C.

Quenching Temperature	Hardness
800	102
850	104
900	105
950	102
1000	98
1100	93

Series IV. Steel II in Range 800° to 1100° C.

Quenching Temperature	Hardness
800	99
850	94
900	91
950	100
1000	99
1100	93

Series V. Steel III in Range 800° C. to 1100° C.

Quenching Temperature	Hardness
800	99
900	93
1000	103
1100	96

Series VI. Steel IV. in Range 800° C. to 1100° C.

Quenching Temperature	Hardness
800	100
900	98
1000	99
1100	92

Series VII. Steel V. in Range 800° C. to 1100° C.

Quenching Temperature	Hardness
800	96
900	92
1000	92
1100	99

Series VIII. Steel VI. in Range 900° C. to 1100° C.

Quenching Temperature	Hardness
900	94
1000	77
1050	85
1100	44

Series IX. Steel VI. Quenched at 1050° C. and Reheated.

Temperature reheating	Hardness
before reheating	85
200	69
250	71
300	82

Hardness of Constituents.

In this it was attempted only to make a rough determination of the hardness of constituents by a microscopic examination of scratches for observing the width of cut in the several constituents. As a result it was found that the same scratch became much less distinct in passing across martensite from austenite, indicating the greater hardness of the former. Less satisfactory results were obtained in comparing the relative hardness of troostite and austenite, but it was fairly evident that the latter was the softer of the two.

SPECIFIC GRAVITY TESTS.

These determinations were made by weighing in air and water with an analytical balance. The results were as follows:

Steel VI.

Quenching Temperature	Specific Gravity
original	7.796
900	7.739
1000	7.825
1050	7.841
1100	7.833

Quenched at 1050° C and reheated to	Specific Gravity
100	7.841
200	7.832
250	7.804
300	7.815

General Discussion and Summary.

Summarizing results as to the necessary composition for obtaining austenite plus martensite as components of the steel after quenching:

Steel VI., containing 1.75% C and 0.94% Mn was the only one which produced the results sought. Steels I., III., IV., and V. are apparently too low in carbon. Steels I., II., and III., are apparently too low in manganese, as that element plays an important part as a brake upon the speed of transformation from austenite to martensite.

While the large proportion of the steels which have yielded negative resplts prevents the setting of definite limits to the field of the composition sought, the work shows, nevertheless, that it is necessary to have within certain limits the correct amount of both carbon and manganese.

As to the heating required piror to quenching, it is shown that the temperature must be high enough to cause the complete absorption of all free cementite by the austenite. This is apparent from an inspection of Photomicrographs 40 and 41. In the former, where free cementite is seen, it is associated only with martensite, while in the latter the same steel, quenched from a higher temperature after complete absorption of the cementite yields austenite plus martensite. This is a direct check upon the first deduction as to the requirement for high carbon in order to get austenite. The cementite seen in Photomicrograph 40, being rich in carbon, has subtracted a considerable amount of that element from the associated austenite. This austenite, being too low in carbon, is completely transformed to martensite on quenching.

This suggests at the same time the existence of an upper limit to the amount of carbon permissible for the production of a tough steel of austenite plus martensite. If the carbon were extremely high martensite plus austenite might be obtained without complete absorption of cementite. This, however, would introduce into the steel a very weak and brittle constituent, which would reduce the toughness and thus defeat the principal object in producing austenite plus martensite.

As to the effects of reheating, it is established by Photomicrograph 45 that in a complex of austenite plus martensite the latter is decomposed into troostite before the austenite. Therefore, by effecting such a transformation an extremely tough steel should be produced as troostite, though hard, is much less brittle than martensite.

A higher drawing temperature also converts the austenite into troostite. This, of course, reduces the toughness as troostite, though less brittle than martensite, is more brittle than austenite.

In conclusion it appears that within the range of the experiments conducted the best results in the constitution of a steel for maximum toughness with considerable hardness are obtained as follows:

Composition - that of Steel VI. C 1.75% Mn 0.94%.

Heat Treatment - 15 minutes at 1050° C followed by rapid quenching in ice water.

Reheating - in cottonseed oil, 1 hour at 200° C.

Result - Austenite with troostite as a transformation from martensite.

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