MICROSTRUCTURAL CHARACTERISTICS OF HIGH-PURITY ALLOYS OF IRON AND CARBON

By Thomas G. Digges

ABSTRACT

A study was made of the microstructural characteristics of slowly cooled high-purity alloys of iron and carbon of hypereutectoid composition and of the influence of certain impurities (oxygen, aluminum, and hydrogen) on the structures of the slowly cooled alloys. The alloys were prepared from 17 irons, varying in degrees of purity, by carburizing in a mixture of hydrogen and benzene vapor. The structure of the carburized irons of highest purity, free from aluminum and with a total of less than 0.009 percent of identifiable impurities, contained free ferrite in the hypereutectoid zone. If oxygen were responsible for this structural feature, then a minute amount was sufficient and as effective as larger quantities. Aluminum in excess of about 0.001 percent prevented the formation of free ferrite, and alumina was not the factor responsible for its formation in these alloys. The hydrogen dissolved in the irons during carburization had no detectable effect on the divorcement of ferrite. The experimental results indicate that a structure containing free ferrite is characteristic of very high purity alloys of iron and carbon of hypereutectoid composition that have been slowly cooled from the austenitic condition.

CONTENTS

I. INTRODUCTION

The existence of free ferrite adjacent to coalesced masses of cementite in the hypereutectoid zone of carburized specimens from certain heats of plain carbon steel was reported in 1922 by McQuaid and Ehn [1].[1] Steels showing this lack of perfection in the crystallization of pearlite after carburizing were designated as "abnormal." Such steels usually have relatively fine-grained austenite at the carburizing

[1] The figures in brackets refer to the literature references at the end of this paper.

temperature. In "normal" steels the austenitic grain size usually is relatively large, and, after slowly cooling from the carburizing temperature, the pearlite extends continuously to thin envelopes of cementite in the hypereutectoid zone. In McQuaid and Ehn's practice, the surfaces of the normal steels were completely hardened whereas the surfaces of the abnormal steels frequently contained soft spots after the quenching treatment. Abnormality was attributed to the presence of oxides, either in solution or as submicroscopic particles.

The choice of the words "normal" and "abnormal" to designate the differences in structure and hardenability of these carburizing steels appeared to be reasonable and suited to this specific use. The terms are clear to all when they are restricted to their original application, namely to plain carbon steels of the carburizing type, but confusion results when the terms are applied to other grades of alloys and steels. This nomenclature has been the concern of many metallurgists, as shown by the comments of Epstein and Rawdon [2], Davenport and Bain [3], and others. To eliminate confusion in the present report, the terms "normal" and "abnormal" will be retained only for reference to previous investigations. The structures produced in the slowly cooled alloys may be completely identified by representative micrographs and by naming all the constituents therein observed, such as free ferrite, massive cementite, or cementite and pearlite. The structure containing free ferrite (divorced ferrite) corresponds to that previously designated as abnormal.

The present study was made primarily to determine the influence of small amounts of impurities, particularly oxygen, aluminum, and hydrogen, in different irons, on the structures produced by oxygen-free carburizing followed by cooling slowly and at a constant rate through the transformation range.

II. PREVIOUS INVESTIGATIONS

McQuaid and Ehn's work with commercial steels was followed by numerous investigations carried out by carburizing both commercial steels and high-purity irons. A survey of some of the publications on this subject shows wide differences in opinion regarding the factors responsible for normality and abnormality. In 1928 Epstein and Rawdon [2] pointed out that many cases of abnormality in commercial steels seemed to be associated with the use of aluminum for deoxidizing, although abnormal steels could be produced in other ways. Nothing arose during their experiments to disprove Ehn's theory that abnormality was due ordinarily to the presence of oxides, perhaps dissolved but more probably undissolved. Several years later, Grossman [4] was of the opinion that abnormality was due to oxygen dissolved during carburization.

In 1932 Duftschmid and Houdremont [5] reported the presence of abnormal structures at the surfaces of electrolytic and carbonyl irons after carburizing. They contended that a prerequisite to abnormal structure was a rapid rate of crystallization, which occurred when the Ar_1 transformation took place at a very high temperature. The regions of highest purity were believed to be responsible for abnormality in carburized structures.

In 1932 Bain [6] reported the results of carburizing experiments with a variety of irons obtained from widely different sources. These irons developed abnormal structures in pack-carburizing and, with one exception, in oxygen-free carburizing. The exception was a hydrogen-treated iron which was almost entirely normal after carburizing in pure hydrogen and hydrocarbon. This iron contained 0.005 percent of carbon, 0.003 percent of sulfur, 0.028 percent of manganese, 0.004 percent of phosphorus, 0.0012 percent of silicon, 0.003 percent of oxygen, and 0.0001 percent of nitrogen. With other irons containing aluminum in excess of 0.4 percent, normal structures were produced by carburizing in hydrocarbon and abnormal structures were developed in the outer portion of the hypereutectoid zone by pack-carburizing. Bain at that time was of the opinion that pure oxygen-free iron (perhaps with hydrogen in solution) would be normal after oxygen-free carburizing, and that dissolved oxygen lowered the critical point (Ae_1) and at the same time provided the high reaction rate and high carbon-diffusivity responsible for abnormality. To secure a normal structure by the standard McQuaid-Ehn procedure required the presence of an element such as silicon or aluminum, which contributed to deep hardening, or at least materially reduced oxygen solubility. However, in 1934, Davenport and Bain [3] were of the opinion that carburized high-purity iron was abnormal.

In 1937 Brophy and Parker [7] reported the results of carburizing experiments with irons containing 0.001, 0.01, 0.1, and 1 percent of aluminum. Normal structures were produced in the cases of all the irons when carburized in a mixture of hydrogen and benzene vapor and abnormal structures when pack-carburized. They concluded that extremely small amounts of aluminum were sufficient to cause abnormality if oxygen was available. However, in the discussion McMullan pointed out that normality or abnormality in steel was a function of composition and cooling rate and that any of the common steels might have their apparent normality or abnormality greatly changed by varying the rate of cooling from the carburizing temperature. Aluminum by itself increases normality and grain size; but when both aluminum and oxygen were present in the right amounts, the steel was fine-grained, and hence might show an abnormal structure after carburizing. McQuaid was of the opinion that Brophy and Parker's results would have been more conclusive had a definite hypereutectoid case been obtained in both methods of carburizing and that the presence of hydrogen might have affected the final structure obtained by carburizing in hydrogen-benzene atmosphere.

In 1938, Derge, Kommel, and Mehl [8], reported the results of carburizing experiments with irons containing aluminum or silicon. All the irons had abnormal structures after pack-carburizing, and normal structures after carburizing in oxygen-free hydrocarbon vapor. This was interpreted as indicating that abnormality under these conditions was due to dissolved oxygen obtained from the carburizing gas rather than to aluminum, Al_2O_3, or oxides already existing in the metal. In the discussion, McQuaid reported that his results indicated that steels carburized in hydrogen-hydrocarbon atmospheres were normal due to the presence of hydrogen and not to the absence of oxygen and that silicon, with or without the presence of aluminum, was an important factor that affected the results obtained after carburizing.

The present writer, in discussing the paper by Derge and coworkers, submitted micrographs showing that abnormal structures were obtained in specimens of iron (total identifiable impurities less than 0.031 percent) which were carburized to contents of 1.01, 1.14, and 1.21 percent of carbon, respectively, in oxygen-free hydrocarbon vapor, homogenized, and subsequently heated at 1,700° F in vacuo and slowly cooled in vacuo. Analyses of duplicate specimens indicated that there was no change in the oxygen content of the specimen (0.003 percent) during the carburizing treatment, and it was difficult to believe that oxygen could have been picked up anywhere in the cycle, to cause the abnormal structures. Derge, however, suggested that oxygen might have entered the specimen during the vacuum treatments and cited experiments by Wells in which abnormal structures never were obtained when specimens of comparable purity were carburized in pure, oxygen-free hydrocarbon mixtures. In his closure, Derge expressed the opinion that the whole question of abnormality, in general, is one of relative rates, which may be influenced by a great many factors.

A review of the literature shows that abnormality has been attributed to:

1. Oxides, perhaps dissolved but more probably undissolved.
2. Alumina.
3. Oxygen dissolved during carburization.
4. Oxygen in solid solution in the original material.
5. High Ar_1 temperature.
6. High purity.
7. High carbon diffusivity.
8. High transformation rate (rapid rate of recrystallization).
9. Fine grain size.
10. Aluminum in small amounts, if oxygen is present.

Normality has been attributed to:

1. Aluminum.
2. Hydrogen.
3. Silicon.
4. Coarse grain size.
5. Low transformation rate.
6. Alloying elements of the deep-hardening type.
7. Alloying elements which reduce oxygen solubility.

Obviously some of the items listed as influencing either normality or abnormality are interrelated. It is now generally recognized that normality and abnormality are functions of composition and cooling rate.

III. MATERIALS AND EXPERIMENTAL PROCEDURE

Specimens from 17 irons were used in the present investigation. These irons were prepared by different methods and some differences existed in the identifiable impurities, as listed in table 1. The irons of highest purity, designated 1, 2, 5, 6, 11, 15, and 18, respectively, were prepared by Thompson and Cleaves, as described in detail in a previous report [9]. The procedure consisted essentially in converting purified iron oxide to sponge iron, followed by melting in a vacuum, treating with hydrogen while molten, and solidifying in a vacuum.

TABLE 1.—*Impurities determined in the irons*

Iron No.	Element (percentage by weight)																	
	Mn	P	S	Si	Cr	Al	Cu	Ni	Co	Ca	Pb	Mg	Be	Ge	O_2[2]	N_2	H_2	Total identifiable[3]
BEFORE CARBURIZING																		
1	ND[1]	------	0.002	0.001	ND	ND	<0.002	ND	ND	ND	ND	ND	<0.001	ND	0.002_2	0.000_1	0.000_1	$<0.009_2$
2	ND	<0.0005	.002	.001	ND	ND	<.002	ND	ND	ND	ND	ND	<.001	ND	$.001_2$	$.002_2$	$.002_2$	$<.008_4$
5	ND	------	.001	.003	ND	<0.001	<.002	ND	ND	ND	ND	ND	ND	ND	$.004_9$	$.002_2$	$.002_2$	$<.012_3$
6	ND	------	.001	.001	ND	ND	<.002	ND	ND	ND	ND	ND	<.001	ND	$.005_4$	$.002_2$	$.002_3$	$<.011_5$
11	ND	------	.001	ND	ND	ND	<.002	ND	ND	ND	ND	ND	ND	ND	$.005_4$	$.002_2$	$.000_1$	$<.009_7$
15	ND	------	.001	ND	ND	<.001	<.002	ND	ND	ND	ND	ND	ND	ND	$.002_8$	$.006_6$	$.002_2$	$<.008_4$
18	ND	------	.001	ND	ND	ND	<.002	ND	ND	ND	ND	ND	ND	ND	$.004_3$	$.000_1$	$.002_2$	$<.008_2$
J[4]	0.013	ND	$.000_2$	.003	.0005	ND	.013	0.006	ND	ND	ND	ND	ND	ND	.001	.003	$.000_5$	<.045
D[5]	.002	<.001	.004	.002	ND	ND	<.001	.007	.007	<.001	<.001	<.001	ND	ND	.003	$.000_2$	$.000_1$	<.031
AFTER CARBURIZING[6]																		
A[7]	<0.001	------	------	<0.001	0.002	ND	0.003	0.02	<0.01	------	------	------	ND	------	0.010 to .017	------	0.000_1	------
B	<.001	------	------	<.001	.003	ND	.002	.02	<.01	ND	ND	ND	FT[1]	T[1]	$.007_5$	$.000_7$	$.000_2$	------
C	<.001	------	------	<.001	<.001	.1	<.001	.06	<.01	ND	ND	ND	T	ND	$.002_1$	$.000_4$	$.000_2$	------
E	<.001	------	------	.008	.003	.025	.003	.02	<.01	ND	ND	ND	FT	T	.002 to .005	$.000_3$	$.000_2$	------
F[7]	<.001	------	------	<.001	<.001	.1 to .2	.001	.06	<.01	ND	ND	ND	T	ND	$.001_5$	ND		------
G[7]	<.001	------	------	.015	.002	<.005	.002	.01	<.01	ND	ND	ND	FT	ND	$.001_6$	$.000_2$	$.000_2$	------
H[7]	<.001	------	------	.004	.002	.3	.003	.01	<.01	ND	ND	ND	W[1]	ND	$.002_8$	$.000_3$	$.000_3$	------
I[7]	<.001	------	------	.015	<.001	.2	.001	.01	<.01	ND	ND	ND	T	T	$.001_8$	ND	$.000_2$	------

[1] ND means not detected; T means trace; FT means faint trace; W means weak.
[2] Includes surface oxygen.
[3] Carbon was not included.
[4] This iron also contained 0.004 percent of Mo and traces of V and Sn.
[5] Some of the values reported were obtained on specimen after carburizing.
[6] Values for Mn were obtained by chemical analysis on specimens that were not carburized. Values reported for all of the other elements except gases for the irons after carburizing were determined by spectrochemical analysis.
[7] Values for gases obtained on specimens that were not carburized.

Chemical analyses were made by H. A. Bright, J. L. Hague, and W. H. Jukkola; spectrochemical analyses by B. F. Scribner and H. R. Mullin; and vacuum fusion analyses by V. C. F. Holm.

Iron J was carbonyl iron subsequently treated with hydrogen. The remaining irons were prepared from different lots of electrolytic iron melted and solidified in a vacuum. In some of the latter melts, a small amount of carbon was added to deoxidize the iron, and to iron I sufficient carbon was added (in the form of an iron-carbon alloy) to produce a carbon content of 1.12 percent in the final product.

The impurities, other than carbon, that were identified by spectrochemical and chemical methods, and the gas content, as determined by the vacuum-fusion method, are listed in table 1. The arc spectrum for each iron, except A, was examined for the sensitive lines of Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cb, Cd, Co, Cr, Cu, Ga, Ge, Hf, Hg, In, Ir, Mg, Mn, Mo, Na, Ni, Os, Pb, Pd, Pt, Re, Rh, Ru, Sb, Si, Sn, Ta, Th, Ti, U, V, W, Zn, and Zr. The sensitive lines of Ce, K, Li, Sc, Sr, Tl, and Y were sought in the spectra of all the irons of highest purity and of iron D. The elements identified, other than iron and carbon, are given in the table. The aluminum which is present as an impurity in some of the irons was obtained principally from the alumina crucibles used in preparing these particular heats.

The impurities were determined either on specimens from the original ingots or on specimens after the carburizing treatment, and the specimens used for carburizing were not necessarily taken from the same part of the ingot as the specimens used for analyses. However, in some instances, determinations of manganese, silicon, oxygen, nitrogen, and hydrogen were made on the same iron before and after carburizing, and the results, summarized in table 2, show that there was no appreciable change in these impurities incident to the carburizing treatment.

TABLE 2.—Impurities determined in irons before and after carburizing in a mixture of hydrogen and benzene vapor

Iron No.	Condition [1]	Impurities (percentage by weight)				
		Mn	Si	O_2	N_2	H_2
2	Before carburizing	ND [2]	0.001	0.001$_2$	0.000$_2$	0.000$_2$
2	After carburizing	ND	ND	.002$_6$	.000$_3$	.000$_2$
5	Before carburizing	ND	.003	.004$_9$	.000$_2$	.000$_2$
5	After carburizing	ND	<.001			
15	Before carburizing	ND	ND	.002$_3$	.000$_6$	.000$_2$
15	After carburizing	ND	ND			
B	Before carburizing			.007$_5$	.000$_7$	.000$_4$
B	After carburizing			.007$_5$	.000$_7$	.000$_3$
B	____do		<.001	.007$_3$	.000$_7$	.000$_3$
C	Before carburizing			.003	.000$_2$	.000$_2$
C	After carburizing		<.001	.002$_1$	.000$_4$	.000$_3$
D	Before carburizing	.002	.002	.004$_4$	.000$_3$	.000$_2$
D	After carburizing		<.001	.003$_2$	.000$_5$	.000$_1$
E	Before carburizing			.003$_8$	.000$_3$	.000$_2$
E	After carburizing		.008	.004$_1$	.000$_3$	.000$_3$
E	____do			.002	ND	.000$_2$
E	____do			.002$_2$	.000$_2$	.000$_2$
E	____do			.005	.000$_3$	.000$_2$

[1] For each iron, the different specimens were not always from the same part of the original ingot.
[2] ND means not detected.

Specimens of the different irons, usually between 0.04 and 0.05 in. in thickness, were carburized at about 1,700° F for 3 hours in

a mixture of hydrogen and benzene vapor, followed by cooling in this atmosphere through the Ar_1 transformation at approximately 4° F/min. Time in the carburizing temperature range was sufficient to produce a hypereutectoid zone throughout the cross section of the specimen. The benzene used was thiophene-free and conformed to American Chemical Society specifications. The hydrogen was purified and dried by passing in succession through Ascarite, silica gel heated to 1,300 to 1,350° F, magnesium perchlorate, and phosphorus pentoxide. The dry hydrogen next passed through the benzene and then into the quartz tube, where the specimens were suspended vertically by a wire of high-purity iron or iron-carbon alloy. The hydrogen finally passed into the air at the exit end of the train. The quartz tube was contained within an electrically heated furnace. The hot junction of a Chromel-Alumel thermocouple was located outside of the carburizing chamber, between the quartz tube and the furnace tube, in the uniformly heated zone.

The gas flow was not accurately determined or maintained constant during the carburization of the various irons, but the average flow was believed to be about 100 ml/min. The vapor not used in carburizing was burned at the exit end of the train.

The specimens were cleaned by washing in xylene or benzene and were then suspended in the cold zone of the quartz tube near the outlet. The tube was thoroughly flushed with the mixture of hydrogen and benzene vapor before lowering the specimens from the cold zone to the uniformly hot or carburizing zone.

Measurements of the austenitic grain size of the carburized specimens were made by the method described by Jeffries [10] and by comparison with the grain-size chart of the American Society for Testing Materials [11].

IV. STRUCTURES OF THE CARBURIZED IRONS

The structures obtained by carburizing the various irons at 1,700 °F for 3 hours in the hydrogen-benzene atmosphere followed by cooling in this atmosphere through the Ar_1 transformation at 4° F/min are summarized in table 3 and figures 1 to 6.

It is well known that the rate of cooling through the thermal critical range influences the divorcement of ferrite in hypereutectoid steels. Rejection of free ferrite could be entirely prevented in the present iron-carbon alloys by cooling at sufficiently high rates from the temperature used in carburizing. As pointed out by Davenport and Bain [3], cooling rates of 4° to 5° F/min are considered satisfactory for obtaining consistent results in normality studies. Obviously, the relative amounts of free ferrite in the alloys might have been different had the cooling rates differed widely from that used.

The impurities present in alloys of iron and carbon may be without effect or may act either to increase or to decrease the transformation rate of austenite or the diffusivity of carbon in the temperature range of the Ar_1 transformation and accordingly influence the divorcement of ferrite in the final structures. Since in this study it was difficult to isolate the effect of an individual impurity, it must be borne in mind that the structure produced in any alloy may have resulted from the combined effects of all of its impurities.

TABLE 3.—*Structure and austenitic grain size of iron-carbon alloys*

[Specimens were carburized at 1,700° F$ for 3 hours in a hydrogen-benzene atmosphere and cooled in this atmosphere through the Ar_1 transformation at 4° F/min]

No.	Iron — Base	Iron — Deoxidizer	Iron — Fabrication	Treatment with hydrogen after solidification	Al	$O_2{}^2$	N_2	H_2	Total identified	Average number of grains per square inch at ×100	ASTM No.	Structure and remarks
1	Sponge	Hydrogen	As cast	None	ND [1]	0.002	0.0001	0.0001	<0.010	0.5	0	Free ferrite, massive cementite network, and pearlite, as shown in fig. 1 (A).
2	do	do	do	do	ND	.001	.0002	.0002	<.009	1.0	1	Free ferrite, massive cementite network, and pearlite, as shown in fig. 6 (A and B).
5	do	do	do	do	<0.001	.005	.0002	.0002	<.013	0.2	−1	Very small amount of free ferrite, cementite network, and pearlite as shown in fig 1 (D). Mixed size with some very large austenitic grains.
6	do	do	do	do	ND	.005	.0002	.0002	<.012	0.8	1	Free ferrite, massive cementite network, and pearlite, as shown in fig. 5 (A).
11	do	do	do	2,000° F for 1 hour and water quenched.	ND	.005	.0002	.0001	<.010	1.6	2	Free ferrite, massive cementite network, and pearlite, as shown in fig. 5 (B).
15	do	do	Hot and cold worked.	None	<0.001	.003	.0006	.0002	<.009	0.6	0	Free ferrite, massive cementite network, and pearlite, as shown in fig. 1 (C). Mixed size austenitic grains.
18	do	do	As cast	do	ND	.004	.0001	.0002	<.009	0.6	0	Free ferrite, massive cementite network, and pearlite, as shown in fig. 1 (B).
A	Electrolytic	None	do	do	ND	.010 to .017		.0001		1.1	1	Free ferrite, massive cementite network, and pearlite, as shown in fig. 5 (C). Some elongated austenitic grains.
A	do	do	do	2,000° F for 1 hour and water quenched.						1.0	1	Free ferrite, massive cementite network, and pearlite, as shown in fig. 5 (D).
B	do	do	do	None	ND	.007	.0007	.0003		0.9	1	Free ferrite, massive cementite network, and pearlite, as shown in fig. 2 (B). Elongated austenitic grains.
C	do	do	do	do	0.1	.002	.0004	.0002		2.6	2	Cementite network and pearlite, as shown in fig. 3 (A).
D	do	do	Hot and cold worked.	do	ND	.003	.0005	.0001	<.031	5.6	3	Free ferrite, cementite network, and pearlite, as shown in fig. 2 (A).
E	do	Carbon	As cast	do	0.025	.004	.0003	.0002		5.0	3	Cementite network and pearlite with a very small amount of free ferrite in some areas, as shown in fig. 2 (D). Mixed size austenitic grains.

F	do	do	do	do	.1 to .2	.001	ND			6.5	4	Cementite network and pearlite, as shown in fig. 3 (B). Marked difference in austenitic grain size. Some No. −2 grains.
G	do	do	Hot- and cold-worked.	do	<0.005	.002	.0002	.0002		0.9	1	Cementite network and pearlite, as shown in in fig. 2 (C). Marked difference in austenitic grain size. Some No. −2 grains.
H	do	do	As cast	do	0.3	.003	.0003	.0003		9.5	4	Cementite network and pearlite, as shown in fig. 3 (C).
H	do	do	do	2,000° F for 1 hour and water quenched.						7.6	4	Cementite network and pearlite similar to fig. 3 (C). Some elongated austenitic grains.
H	do	do	Hot- and cold-worked.	do						2.8	2	Cementite network and pearlite similar to fig. 3 (C).
H	do	do	do	None		.002	.0004	.0002		1.0	1	Cementite network and pearlite, as shown in fig. 3 (D). Some elongated austenitic grains.
I	do	do	As cast (1.12% C).	do	0.2	.002	ND	.0002		2.1	2	Cementite network and pearlite, as shown in fig. 4 (D). Mixed size austenitic grains.
J	Carbonyl	Not melted	Hot-worked	Treated. Exact treatment unknown.	ND	.001	.003	.0005	<.045	0.3	−1	Small amount of free ferrite, cementite, and pearlite. Cementite principally in plates. Only a few austenitic grains delineated by cementite.

[1] ND means not detected.
[2] Includes surface oxygen.

1. INFLUENCE OF IMPURITIES

(a) OXYGEN

The aluminum-free irons of highest purity (total identifiable impurities less than 0.012 percent), with oxygen content ranging from about 0.001 to 0.005 percent, had appreciable amounts of free ferrite in the final structures, as illustrated in figure 1, A and B. However, this difference in oxygen content had no detectable effect on the amount of free ferrite. If oxygen, either in the form of oxides or more probably in solution, was responsible for this structural condition then a minute amount of the element evidently was sufficient and as effective as larger amounts. Furthermore, in the aluminum-free irons of intermediate purity (B and D, table 1) more free ferrite was obtained in the carburized structure of the iron containing 0.003 percent of oxygen (fig. 2, A) than in the iron containing 0.007 percent of oxygen (fig. 2, B).

Oxygen contents of about 0.001 percent as determined by the vacuum-fusion method represent a close approximation to oxygen-free material. The vacuum-fusion method determines the total oxygen content, that is, the film of oxides on the surface of the specimen as well as the oxygen in the interior of the specimen. Evidence has been obtained indicating that the surface film on certain specimens amounts to about 0.001 percent. For these reasons vacuum-fusion determinations of less than 0.001 percent of oxygen are seldom obtained, even for the most carefully deoxidized material.

The oxygen content, from 0.001 to 0.007 percent, could not be correlated with the divorcement of free ferrite in the final structure of these alloys, which were free from aluminum but some of which contained appreciable amounts of other impurities. A structure containing free ferrite is characteristic of very high-purity alloys of iron and carbon of hypereutectoid composition, with very low oxygen content, that have been cooled slowly from the austenitic condition through the thermal critical range.

(b) ALUMINUM AND ALUMINA

The carburized structures of all of the irons which were free from aluminum contained free ferrite. All of the irons which contained more than 0.001 percent of aluminum had carburized structures that were practically free from ferrite.

Of the two carburized irons that contained a trace of aluminum (less than 0.001 percent), number 15 had an appreciable amount of free ferrite in the hypereutectoid zone (fig. 1, C) and number 5 had only a small amount of free ferrite (fig. 1, D). The values obtained by analyses indicated that sufficient oxygen was available in each of these carburized irons (0.003 and 0.005 percent of oxygen, respectively) to combine with all of the aluminum to form alumina, provided the greater portion of the oxygen reacted in this manner. Thus it appears probable that both alloys were free from metallic aluminum and each had approximately the same amount of alumina. Evidently the differences in amounts of free ferrite in the final structures were not due to differences in metallic aluminum or alumina. A noteworthy feature is that, when a trace of aluminum was present, the carburized specimens from the iron with lower oxygen content had the greater
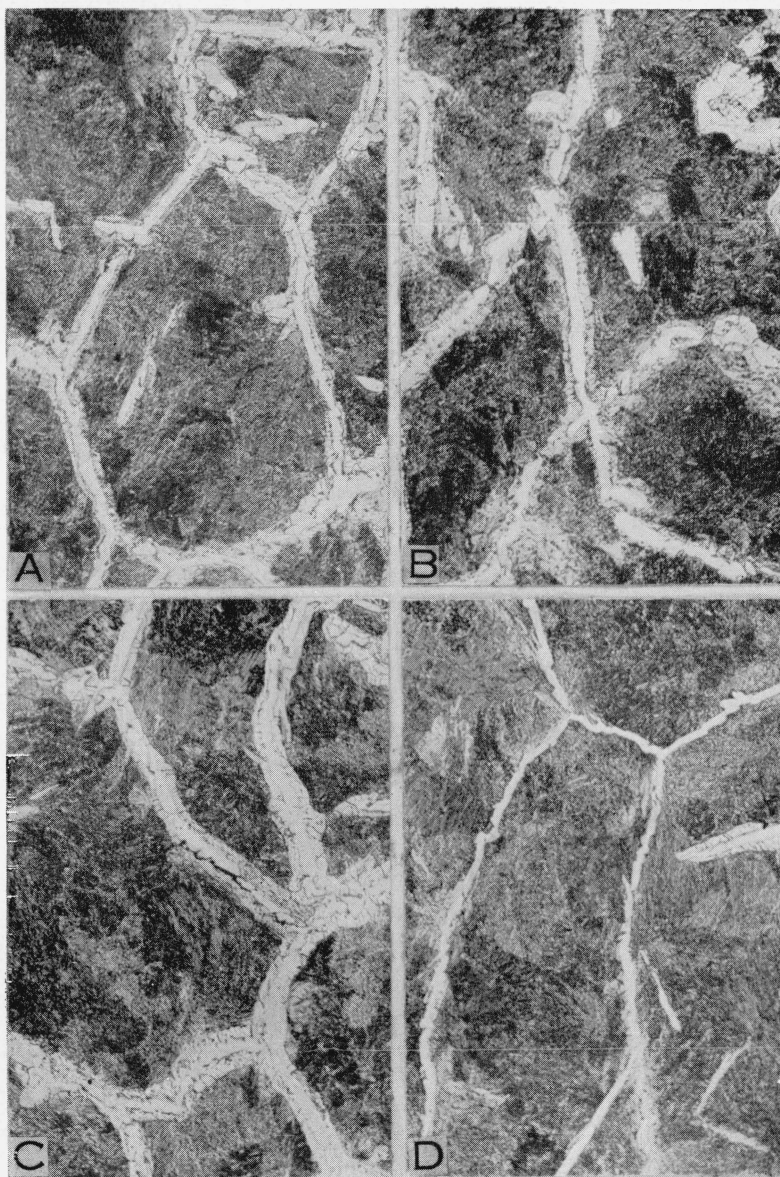
FIGURE 1.—*Structure of high-purity irons after carburizing.*

A, Iron 1, with 0.002 percent of O_2, no Al, and <0.010 percent of total identifiable impurities; *B*, Iron 18, with 0.004 percent of O_2, no Al, and <0.009 percent of total identifiable impurities; *C*, Iron 15, with 0.003 percent of O_2, <0.001 percent of Al, and <0.009 percent of total identifiable impurities; *D*, Iron 5, with 0.005 percent of O_2, <0.001 percent of Al, and <0.013 percent of total identifiable impurities.   Etched with 1-percent nital.   ×100.
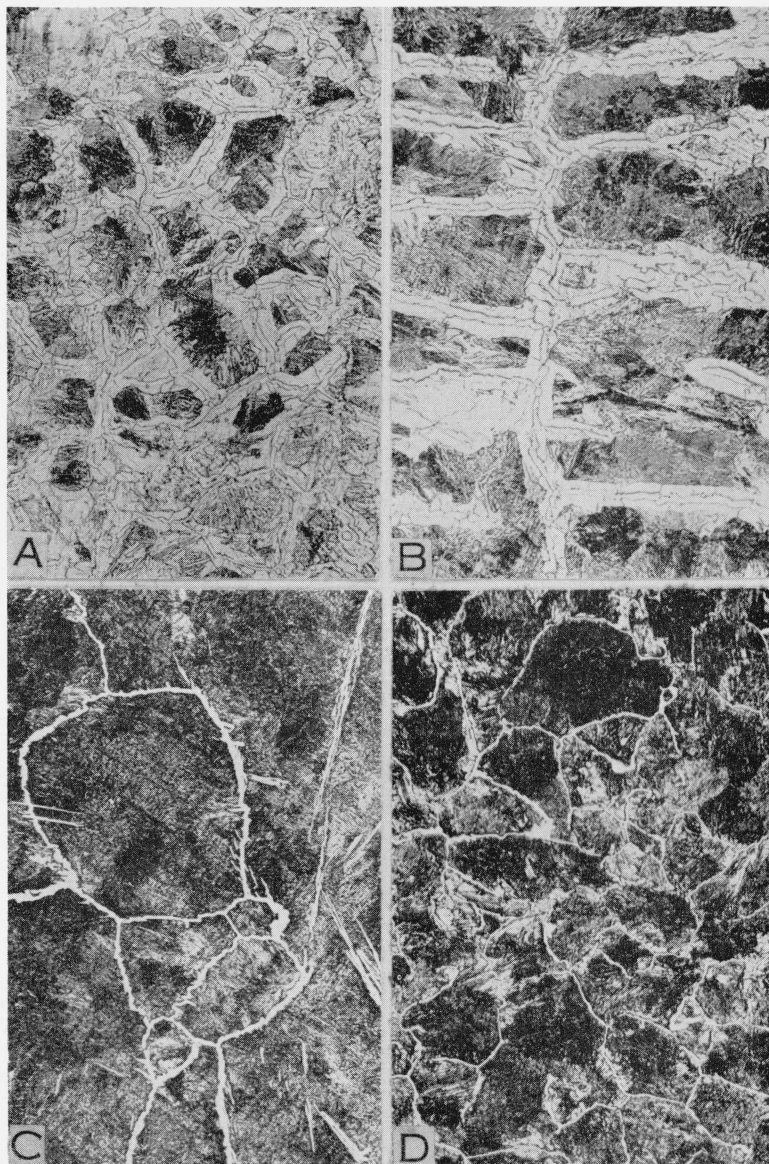
FIGURE 2.—*Structure of intermediate-purity irons after carburizing.*

A, Iron *D*, with 0.003 percent of O_2 and no Al; *B*, Iron *B*, with 0.007 percent of O_2 and no Al; *C*, Iron *G*, with 0.002 percent of O_2 and <0.005 percent of Al; *D*, Iron *E*, with 0.004 percent of O_2 and 0.025 percent of Al. Etched with 1-percent nital. ×100. Irons *D* and *G* were hot- and cold-worked prior to carburizing, whereas irons *B* and *E* were as cast.
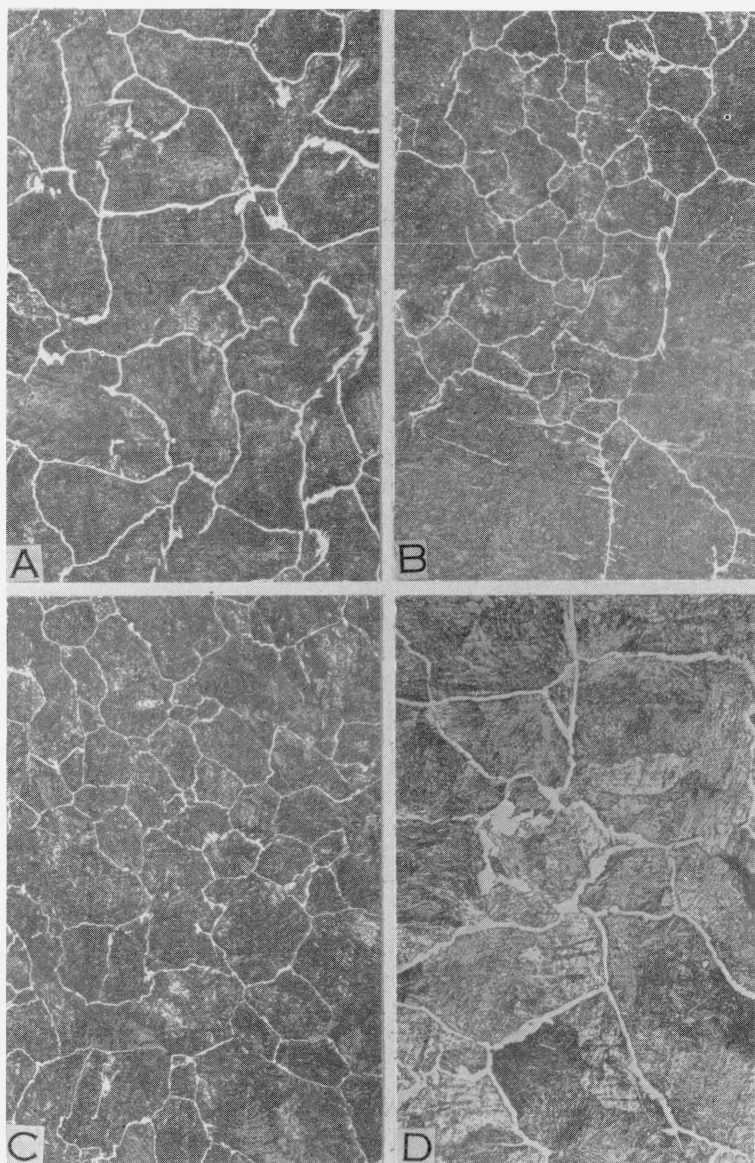
FIGURE 3.—*Structure of irons containing aluminum after carburizing.*

A, Iron C, with 0.002 percent of O_2 and 0.1 percent of Al; initial structure as cast; B, Iron F, with 0.001 percent of O_2 and 0.1 to 0.2 percent of Al; initial structure as cast; C, Iron H, with 0.003 percent of O_2 and 0.3 percent of Al; initial structure as cast; D, Iron H, with 0.002 percent of O_2 and 0.3 percent of Al; initial structure as hot- and cold-worked. Etched with 1-percent nital. ×100.
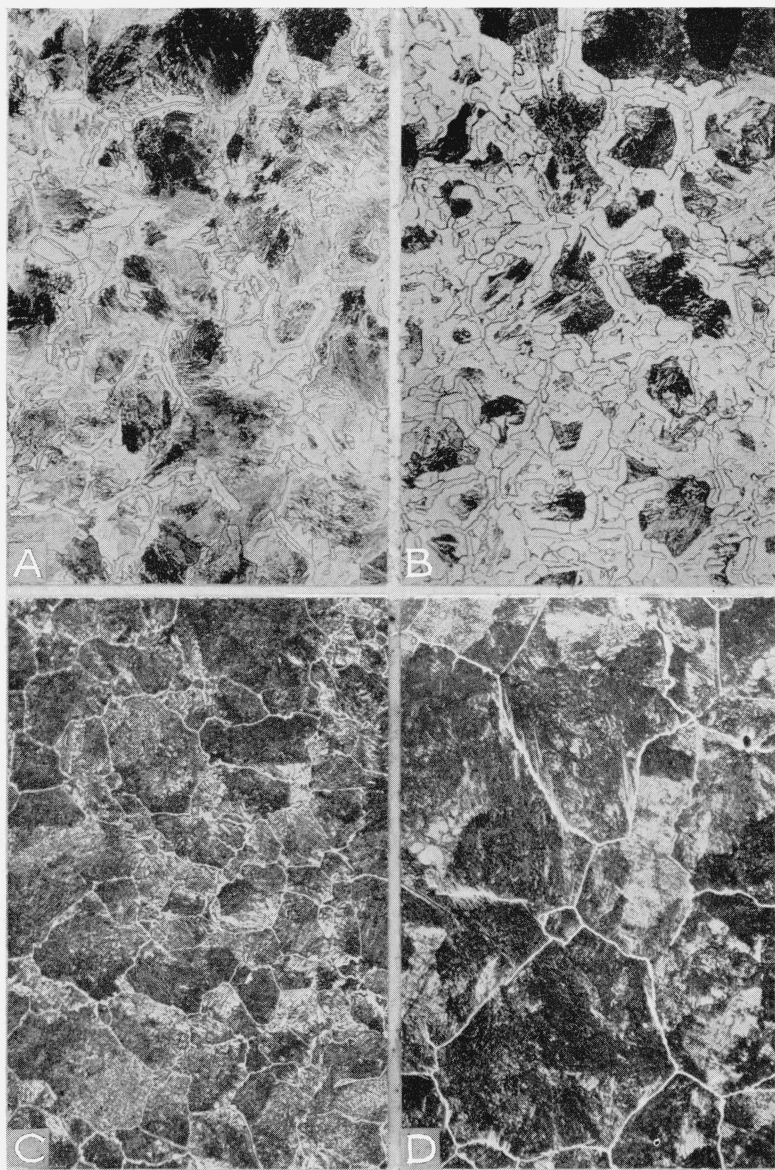
FIGURE 4.—*Structure of iron-carbon alloys after annealing in vacuo or as carburized.*

A, 1.01 percent of C, prepared from iron *D*, after annealing in vacuo; *B*, 1.21 percent of C, prepared from iron *D*, after annealing in vacuo; *C*, 1.12 percent of C, prepared from iron-carbon alloy *I*, after annealing in vacuo; *D*, Iron-carbon alloy *I*, after carburizing. The annealing treatment consisted of heating in vacuo at 1,700° F for 1 hour and cooling through the *Ar₁* transformation at 4° F/min. Etched with 1-percent nital. ×100.

amount of free ferrite, a fact which is contrary to the prevailing opinion.

The carburized structure of iron G with less than 0.005 percent of aluminum (0.015 percent of silicon) was essentially free from ferrite (fig. 2 C) and that of iron E with 0.025 percent of aluminum (0.008 percent of silicon) contained only a small amount of free ferrite in some areas (fig. 2, D). The relatively high silicon content was perhaps a factor in preventing the formation of ferrite in these alloys, especially in the one with the lower aluminum content. However, the carburized structures (fig. 3) of the irons with aluminum ranging from 0.1 to 0.3 percent (silicon from trace to 0.004 percent) contained no free ferrite. It should be pointed out that the two alloys with a trace of silicon also contained relatively high nickel (0.06 percent), but the amount of nickel in the other alloy (0.01 percent) was only slightly higher than that of the aluminum-free alloy of figure 2 (A) (0.007 percent of nickel), which contained a large amount of free ferrite.

The values for oxygen ranged from approximately 0.001 to 0.005 percent in the alloys containing aluminum and, as already stated, from 0.001 to 0.007 percent in the aluminum-free alloys which contained appreciable amounts of free ferrite in the final structures. In the alloys of low aluminum content, the aluminum should be present almost entirely as the oxide (alumina) and, while the alloys of high aluminum content also contained alumina, the greater portion should be present as the metal. It is generally believed that alumina increases the decomposition rate of austenite to ferrite and carbide by acting as centers for transformation, whereas metallic aluminum enters into solid solution in the austenite and thereby decreases its transformation rate. The present results show that aluminum in excess of about 0.001 percent inhibits the divorcement of ferrite and that alumina was not the factor responsible for its formation in these hypereutectoid alloys.

(c) HYDROGEN

Carburized and homogenized specimens prepared from iron D [12] containing 1.01 and 1.21 percent of carbon, were annealed in an atmosphere of dry hydrogen at 1,700° F for 1 hour and cooled through the Ar_1 transformation at 4° F/min. Other specimens of the same alloys, with the same initial structure of fine pearlite, were given a similar thermal treatment in vacuo. During the time of cooling from the annealing temperature through the transformation range, the former specimens were saturated with hydrogen whereas the specimens annealed in vacuo were relatively free from hydrogen. The surfaces of the specimens annealed in hydrogen were decarburized, but a hypereutectoid zone was retained in the center of some of the specimens. The hypereutectoid zones contained free ferrite and had a structure similar to that of the vacuum-annealed specimens shown in figure 4 (A and B). Furthermore, the amount of free ferrite obtained in the latter specimens was of the same order of magnitude as that of specimens of the same iron D carburized at 1,700° F in a mixture of hydrogen and benzene vapor and cooled at a similar rate directly from the carburizing temperature in an atmosphere containing hydrogen (see fig. 2, A). Thus this structural feature of free ferrite in slowly cooled hypereutectoid alloys was produced with equal facility either

by cooling directly from the carburizing temperature or by subsequently annealing in vacuo or in hydrogen.

The structure of alloy I (containing 1.12 percent of carbon as cast) after the annealing treatment in vacuo (fig. 4, C), and the structure of the same alloy after the carburizing treatment (fig. 4, D), consisted of cementite network and pearlite. A marked increase in austenitic grain size resulted from the carburizing treatment in which the specimen was held at 1,700° F for 3 hours in an atmosphere containing hydrogen. Free ferrite was not produced in the structure of alloy I either by annealing in hydrogen or in vacuo.

Specimens from several different irons were treated in dry hydrogen at approximately 2,000° F and quenched in water (table 3). Although the time at high temperature was sufficient for the hydrogen to diffuse throughout the cross section of the specimens, it was not sufficient to cause an appreciable reduction in the oxygen content, as shown by determinations made on similarly treated specimens. The hydrogen content of the specimens immediately after quenching varied; the maximum value was about 0.0005 percent. The hydrogen was extracted by heating at about 1,500° F for 6 to 15 minutes [13] before carburizing in the hydrogen-benzene atmosphere in the usual manner. The structures produced by carburizing untreated high-purity iron 6 and hydrogen-treated iron 11 of equivalent purity, and untreated and hydrogen-treated iron A, are shown in figure 5. Free ferrite was present in all of these specimens, and no difference in the amount of free ferrite was obtained as a result of the hydrogen treatment (compare fig. 5, A, with fig. 5, B, and fig. 5, C, with fig. 5, D).

These results show that hydrogen had no influence on the final structures obtained in the slowly cooled alloys.

2. INFLUENCE OF TOTAL IMPURITIES

The results summarized in table 3 show, in general, that the irons of highest purity (total identifiable impurities less than about 0.010 percent) had structures containing free ferrite in the hypereutectoid zone after carburizing and slowly cooling in an oxygen-free atmosphere. However, the carburized structure of iron 5 (total impurities less than 0.013 percent) contained only a relatively small amount of free ferrite (fig. 1, D) as compared with the carburized structure (fig. 1, C) of iron 15 (total impurities less than 0.009 percent). Since specimens from these two irons were carburized at the same time, the different amounts of free ferrite in the final structures must be attributed to differences in composition and not to the carburizing conditions. As shown in table 1, the identifiable impurities for the original ingots of irons 5 and 15 differed mainly in silicon (0.003 percent and nil, respectively) and oxygen (0.005 and 0.003 percent, respectively), but these differences are of doubtful significance because of the uncertainty of analytical determinations of this order of magnitude. Spectrochemical analysis showed that no definite change in the amounts of impurities occurred during the carburizing treatment, and it has already been shown that the carburizing treatment did not change appreciably the amounts of the gaseous elements. It is difficult, therefore, to explain satisfactorily the observed differences in the percentages of free ferrite on the basis of such minute variations in these detectable impurities.
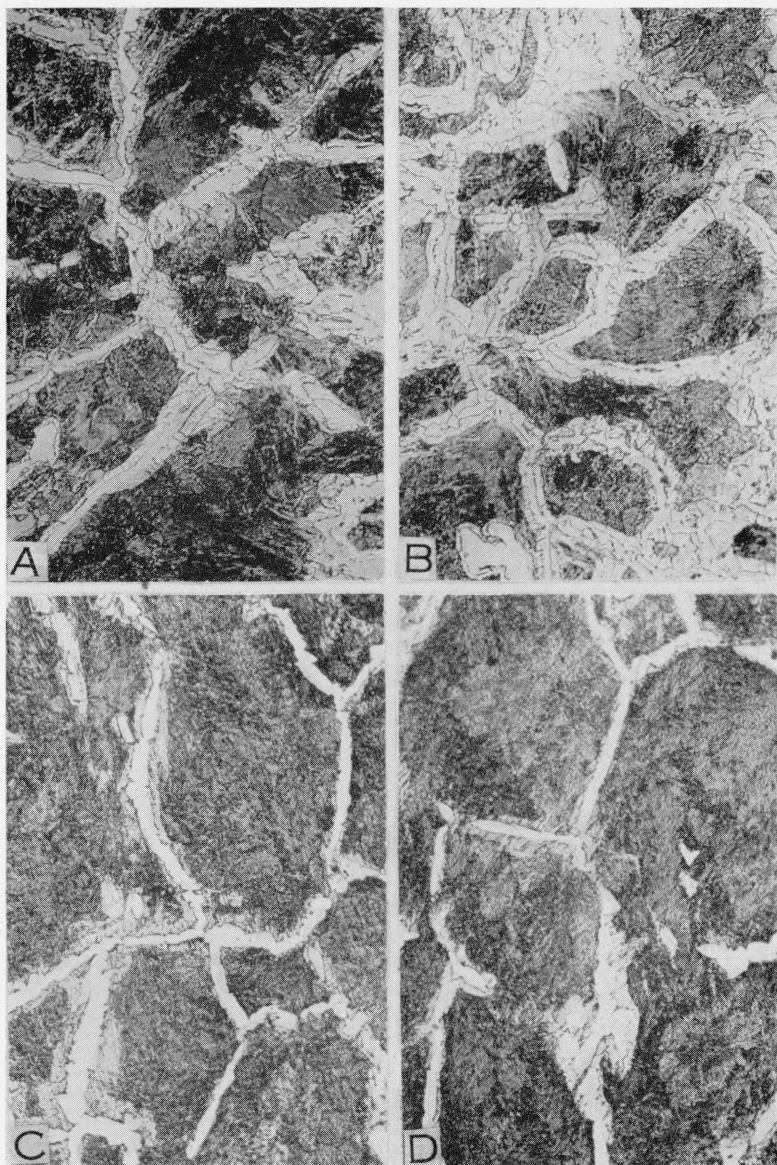
FIGURE 5.—*Structure of irons after carburizing.*

A, Iron 6, not treated with hydrogen before carburizing; *B*, Iron 11, treated with hydrogen before carburizing; *C*, Iron *A*, not treated with hydrogen before carburizing; *D*, Iron *A*, treated with hydrogen before carburizing. The hydrogen treatment consisted of heating specimens of the irons as cast in dry hydrogen at 2,000° F for 1 hour and quenching in water. Etched with 1-percent nital. ×100.
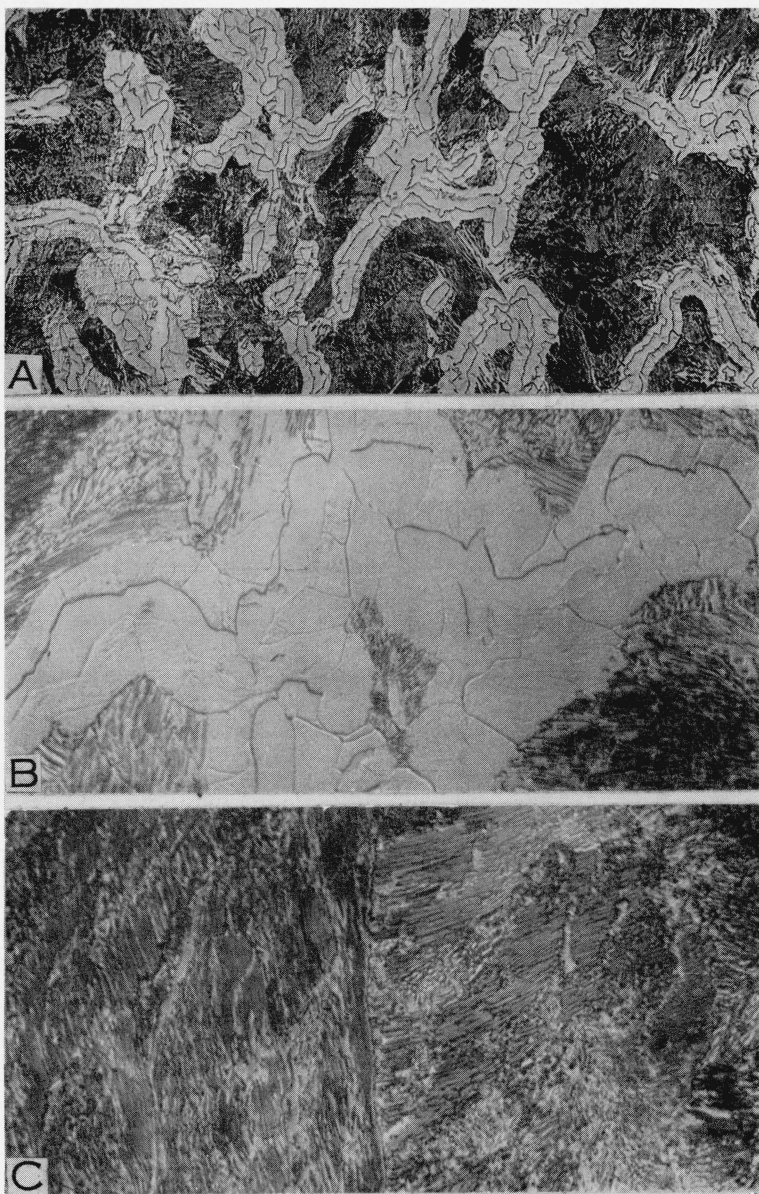
FIGURE 6.—*Structure of the hypereutectoid and eutectoid zones produced in high-purity iron by carburizing.*

A, Iron 2, hypereutectoid zone, ×100.   B, Iron 2, hypereutectoid zone, ×500.   C, Iron 2, eutectoid zone, ×500.   Etched with 1-percent nital.

Different amounts of free ferrite were obtained in the carburized structures of the irons of intermediate purity (0.03 to 0.05 percent of identifiable impurities), whereas the carburized structures were essentially free from ferrite for the irons of relatively low purity (appreciable amounts of aluminum).

These results show that the presence of free ferrite in the hypereutectoid zone of very high-purity alloys of iron and carbon is characteristic of the structures obtained after slowly cooling from the carburizing temperature. As the amounts of impurities are increased, the final structures obtained in the alloys by slowly cooling after carburizing may or may not contain free ferrite in the hypereutectoid zone, depending on whether the added impurities are of the type which increase or decrease the reaction rate of austenite or the diffusivity of carbon in the Ar_1 transformation range.

3. INFLUENCE OF OTHER FACTORS

(a) CARBON

Divorcement of ferrite was not observed in the eutectoid zone of any of the carburized specimens. As illustrated in figure 6, the presence of a proeutectoid constituent (carbide in this case) in austenite appears to be essential for the production of free ferrite in the structure of iron-carbon alloys cooled at 4° F/min through the thermal critical range. With slowly cooled alloys of eutectoid content, the austenite transformed entirely to pearlite (fig. 6, *C*). However, variations may exist in the carbon content in excess of the eutectoid without appreciably influencing the amount of free ferrite in the final structure of the slowly cooled alloys, as illustrated in figure 4 (*A* and *B*).

(b) ANNEALING TREATMENT

It has already been pointed out that carburized and homogenized specimens containing 1.01 and 1.21 percent of carbon (prepared from iron *D*) and subsequently annealed in a vacuum had approximately the same amount of free ferrite in the final structures (fig. 4, *A* and *B*) as specimens of the same iron carburized to produce a hypereutectoid alloy in the hydrogen-benzene atmosphere, followed by cooling in this atmosphere at the same rate (fig. 2, *A*).

No increase in oxygen content of the iron-carbon alloys occurred during the time of annealing in vacuo, as shown by the values obtained for oxygen as follows:

Iron or alloy designation	Condition	Oxygen (percentage by weight)
D	As carburized	0.003
D	As carburized and annealed	.003
I	As cast (1.12 percent of C)	.002
I	As cast and annealed	.001

The structural feature consisting of free ferrite in slowly cooled hypereutectoid alloys was produced with equal facility either by cooling directly from the carburizing temperature or by subsequently annealing in vacuo.

(c) INITIAL STRUCTURE

For most of the irons, the structure prior to carburizing was that of the cast metal. In several irons, however, the initial structure was that obtained by hot- and cold-working the cast metal, and the carbonyl iron had been hot-worked after sintering. As shown by the results summarized in table 3, figure 2 (*A* and *B*), and figure 3 (*C* and *D*), the amount of free ferrite obtained in the carburized structure was independent of the initial structure of the irons, whether as cast or as hot- and cold-worked.

4. INFLUENCE OF AUSTENITIC GRAIN SIZE

In a previous report [14] it was shown that the austenitic grain size affected the rate of decomposition of austenite in the Ar' temperature range of high-purity alloys of iron and carbon. The critical cooling rate progressively decreased (hardenability increased) as the austenitic grain size increased in alloys containing 0.80 to 0.85 percent of carbon. Davenport, Grange, and Hafsten [15] recently reported that with an increase in austenitic grain size the isothermal transformation of austenite in an SAE 4140 steel was retarded in the temperature levels (about 1,050° F and above) where soft lamellar structures form.

The grain sizes established in the various irons by carburizing at 1,700° F were determined, and the results are summarized in table 3. Variations existed in the average size of the austenitic grains, and in some cases grains of mixed sizes were obtained in the same alloy; but no correlation was found between austenitic grain size and divorcement of ferrite in the final structures of the slowly cooled hypereutectoid alloys. For example, two of the alloys which had structures free from ferrite had average American Society for Testing Materials grain number 4 (fig. 3, *C*) and grain number 1 (fig. 2, *C*, mixed-size grains containing some No. −2), whereas two other alloys with approximately the same average grain sizes had structures containing appreciable amounts of free ferrite (fig. 2, *A*, and 6, *A*, respectively). An interesting feature is the large austenitic grains and a structure containing free ferrite which was obtained in the alloys of highest purity, as shown in figure 1.

V. SUMMARY

Seventeen irons, varying in degrees of purity, were carburized in a mixture of hydrogen and benzene vapor at 1,700° F for 3 hours followed by cooling in this atmosphere through the transformation range at 4° F/min. The time at the carburizing temperature was sufficient to produce hypereutectoid zones in all of the irons.

The presence of free ferrite in the hypereutectoid zones is characteristic of the structures obtained in irons of very high purity under these conditions. As the amounts of impurities in the irons are increased, the final structures obtained after carburizing may or may not contain free ferrite in the hypereutectoid zone, depending upon whether the added impurities are of the type which increase or decrease the reaction rate of austenite or the diffusivity of carbon in the Ar_1 transformation range. Differences in oxygen content from about 0.001 to 0.007 percent could not be correlated with the amount of free ferrite in

the final structure of the alloys. Some of the irons represent a close approximation to oxygen-free material. The precise role of oxygen in the development of ferrite in the final structure is not entirely clear. However, if oxygen were responsible for this structural feature in the hypereutectoid alloys of highest purity, then a minute amount was sufficient and as effective as larger amounts.

The carburized structures of all the irons which were free from aluminum contained free ferrite. Aluminum in excess of about 0.001 percent inhibits the formation of free ferrite in the hypereutectoid zone, and alumina was not the factor responsible for its formation.

The presence of hydrogen in the carburizing and annealing atmospheres had no detectable effect on the formation of free ferrite.

Free ferrite was not detected in the eutectoid zone of any of the alloys. However, variations might exist in amounts of proeutectoid carbide without markedly affecting the formation of free ferrite on slowly cooling from the austenitic condition.

Free ferrite in hypereutectoid alloys was produced with equal facility either by cooling directly from the carburizing temperature or by annealing in vacuo. The initial structures of the irons, either as cast or after working, had no effect on the formation of free ferrite in the final structures.

The average grain size established in carburizing the various irons at 1,700° F ranged from American Society for Testing Materials grain number 4 to —1, but there existed no correlation between austenitic grain size and the formation of free ferrite. A noteworthy feature was the large austenitic grains of the alloys of highest purity which contained relatively large amounts of free ferrite.

VI. REFERENCES

[1] H. W. McQuaid and E. W. Ehn, *Effect of quality of steel on case-carburizing results*, Trans. Am. Inst. Mining Met. Engrs., Iron and Steel Division, **67**, 341 (1922).

[2] S. Epstein and H. S. Rawdon, *Steel for case hardening—normal and abnormal steel*, BS J. Research **1**, 423 (1928) RP14.

[3] E. S. Davenport and E. C. Bain, *General relations between grain size and hardenability and the normality of steels*, Trans. Am. Soc. Metals **22**, 879 (1934).

[4] M. A. Grossman, *Oxygen in steel*, Trans. Am. Soc. Steel Treating **18**, 601 (1930).

[5] F. Duftschmid and E. Houdremont, *Purest steels develop soft spots if carburized and quenched*, Metal Progress **21**, 30 (1932).

[6] E. C. Bain, *Factors affecting the inherent hardenability of steel*, Trans. Am. Soc. Steel Treating **20**, 385 (1932).

[7] G. R. Brophy and E. R. Parker, *Influence of aluminum on the normality of steel*, Trans. Am. Soc. Metals **25**, 315 (1937).

[8] G. Derge, A. R. Kommel, and R. F. Mehl, *Some factors influencing austenitic grain size in high purity steels*, Trans. Am. Soc. Metals **26**, 153 (1938).

[9] J. G. Thompson and H. E. Cleaves, *Preparation of high-purity iron*, J. Research NBS **23**, 163 (1939) RP1226.

[10] Zay Jeffries, Am. Soc. Testing Materials, Standards, pt. 1, Metals, Designation E 2–36 (Note 2), p. 763 (1936).

[11] Standard grain size chart for classification of steels, Am. Soc. Testing Materials, Standards, pt. 1, Metals, Designation E 19–33, p. 761 (1936).

[12] T. G. Digges, *Effect of carbon on the hardenability of high-purity iron-carbon alloys*, Trans. Am. Soc. Metals **26**, 408 (1938). Also, *Effect of carbon on the critical cooling rate of high-purity iron-carbon alloys and plain carbon steels*, J. Research NBS **20**, 571 (1938) RP1092.

[13] V. C. F. Holm and J. G. Thompson, *Determinations of hydrogen in ferrous materials by vacuum extraction at 800° C and by vacuum fusion*, J. Research NBS **26**, 245 (1941) RP1373.

[14] T. G. Digges, *Influence of austenitic grain size on the critical cooling rate of high-purity iron-carbon alloys*, J. Research NBS **24**, 723 (1940) RP1308.

[15] E. S. Davenport, R. A. Grange, and R. J. Hafsten, *Influence of austenite grain size upon isothermal transformation behavior of S. A. E. 4140 steel*, Metals Tech. **8** (1941) TP1276.

WASHINGTON, April 29, 1941.