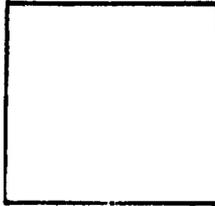


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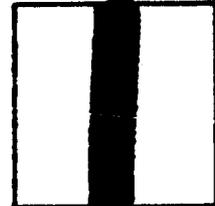
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REPORT NO. 15471

NOTES ON THE RELATIONS BETWEEN THE MICRO-STRUCTURE
OF A HYPER-EUTECTOID PLAIN CARBON STEEL AND
ITS CRYSTAL STRUCTURE AS SHOWN BY
THE X-RAY SPECTROMETER

By

BERNARD H. ZORNIG
Major, Ordnance Department, U.S.A.

Submitted in Partial Fulfillment of the Requirements

FOR THE DEGREE OF

MASTER OF SCIENCE

from the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

1923

WATERTOWN ARSENAL

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INTRODUCTION.

A study of the available literature dealing with the crystal structure of the constituents and structures recognized to exist in the iron-carbon alloys shows that most of our knowledge on the subject is based on separate experiments conducted from time to time in different laboratories by different investigators using very often quite different apparatus. Conclusions have some times been based upon small differences in measurements, which measurements were not easy to make, and which were subject to errors which are difficult to correct. It appears that additional information regarding the crystal structure of the transformation stages in the iron-carbon alloys and regarding the manner in which the transformations take place may be obtained by series of X-ray diffraction patterns produced by specimens differing from each other by changes in, as nearly as possible, but one variable; the photographs of the diffraction patterns to be taken under uniform conditions, in the same apparatus, and in a manner which will eliminate as many of the known sources of possible error as is practicable.

The research program of the Laboratories of the Watertown Arsenal includes the production of a number of such series of diffraction patterns. The attempt of the writer, working in these laboratories, to produce one such series is herein described. This series is intended to show the relations existing between crystal structure and micro-structure in a hyper-eutectoid plain carbon steel.

DESCRIPTION OF APPARATUS.

The X-ray spectrometer used in these experiments was the standard X-ray Diffraction Apparatus manufactured by the General Electric Company, and described by Wheeler P. Davey in the Journal of the Optical Society of America, Vol. V. No. 6. Nov. 1921. In order to adapt this apparatus to take specimens of the shape found to be best suited to this work, one of the cassettes was slightly modified as described later.

DESCRIPTION OF SPECIMENS.

The use of individual crystals as specimens was obviously impossible so there remained three general forms of specimens to choose from, namely: the powdered material mounted in tubes or in films of amorphous materials, (3 & 4) the material drawn or otherwise formed into fine wire, (3) or narrow flat surfaces of the material such as the edges of ribbons.⁽¹⁾ Of these, the last form was chosen because it permitted the use of specimens which could be easily heat treated and in which the surface layer of the diffracting

(1) D.W. McKeehan: Jour. Franklin Inst. Vol. 12 (1922) 231.

crystals could readily be examined microscopically. Figure I shows the shape and approximate size of the specimens used, and Figure II indicates the method of mounting them in the spectrometer.

The specimens were prepared from a piece of 1.50" (3.805 cm.) diameter, round, hot rolled bar stock. This was carefully forged down into several strips about 0.187" (.475 cm.) by 0.875" (2.22 cm.) by 14" (35.5 cm.) in size. These strips were reduced by grinding to a section of 0.085" (0.215 cm.) by 0.75" (1.9 cm.), care being taken to remove about the same amount of material from opposite sides. They were then cut into lengths of about 1.25" (3.17 cm.). Each of these lengths was finished by grinding to the shape and size shown in Figure I.

This method, it is believed, insures uniformity in the chemical composition of all the specimens to well within the limits required for this work.

Drillings, taken from the tonghold (about 1" (2.54 cm.) square in section) which had been left on one of the forged strips, were analyzed to obtain the chemical composition of the specimens. This is given in Table I.

Table I.

Chemical Composition of Specimens.

Constituent	Percent by Weight	Atomic Percent	Remarks
Carbon	1.110	4.96	
Manganese	0.330	0.32	
Silicon	0.200	0.38	
Sulphur	0.021	0.04	
Phosphorus	0.008	0.02	
Nickel	0.350	0.30	
Chromium	0.090	0.09	
Iron	97.891	93.89	By difference
Iron Carbide (Fe ₃ C)	16.6		Calculated, assum- ing all the carbon present is combined with iron in the form of Fe ₃ C.

The specimens were next heat treated as shown in Table II.

Table II.

Heat Treatment of Specimens

Specimen Number	First Treatment		Second Treatment		Third Treatment	
	Heated to	How Held at Temperature	Heated to	How Held at Temperature	Heated to	How Held at Temperature
1	950°C	30 Min. Furnaces				
2	950°C	30 Min. Mercury				
3	950°C	30 Min. Oil*	300°C	10 Min. Water*		
4	950°C	30 Min. Oil*	800°C	10 Min. Oil*		
5	950°C	30 Min. Oil*	800°C	10 Min. Water*	185°C	30 Min. Air*
6	950°C	30 Min. Oil*	800°C	10 Min. Water*	275°C	30 Min. Air*
7	950°C	30 Min. Oil*	800°C	10 Min. Water*	375°C	30 Min. Air*
8	950°C	30 Min. Oil*	800°C	10 Min. Water*	475°C	30 Min. Air*
9	950°C	30 Min. Oil*	800°C	10 Min. Water*	575°C	30 Min. Air*
10	950°C	30 Min. Oil*	800°C	10 Min. Water*	675°C	30 Min. Air*

** Footnotes on next page.

*Details of cooling methods were as follows:

- Furnace - Cooled in the furnace with power shut off.
- Mercury - Quenched in mercury bath surrounded by ice and brine bath.
- Water - Quenched in water bath at room temperature.
- Oil - Quenched in bath of "Houghton's #2 Soluble Quenching Oil" at room temperature.
- Air - Cooled in the atmosphere while supported on a piece of asbestos board.

To prevent, as much as possible, the decarburizing of the surface, all specimens while being heated to the 800° and 950° temperatures were immersed in a bath of "Meltite" contained in a clay assayer's crucible. All specimens, except #1 and #2, were heated to the 800° and 950° temperatures together in the same furnace.

After heat treatment the diffracting surface, A-A (Figure I), of each specimen was polished, etched, and examined microscopically. In every case a slight amount of surface decarburization was found. The decarburized surface layer was carefully removed from the top and sides of the specimen by hand, using a fine file, or where the specimens were very hard, a slow moving grindstone well covered with water. The removal of surface metal was in each case continued until the whole of the surface A-A (Figure I) showed, after polishing and etching, a uniform structure upon microscopic examination. The width of the diffracting surfaces was at this time brought to $0.7 \text{ m/m} \pm 0.05 \text{ m/m}$.

Photo-micrographs were made of the prepared surfaces at magnifications of 100 and 2000 diameters. The etching reagent used in all cases was a 2% solution of nitric acid in alcohol. The photo-micrographs taken at

a magnification of 2000 diameters are intended to show the details of the structure existing in the specimen.

Method of Taking X-ray Diffraction Patterns:

For the taking of the X-ray diffraction patterns the specimens were mounted, two at a time, in the modified cassette as shown in Figure III. The modification of the cassette consisted only of the addition of the special specimen holder which is shown in the photograph and whose operation and construction is so obvious as to need no further description. In mounting the specimen in the holder, care was taken to line up accurately the diffracting surfaces especially with respect to their tops and the edges away from the source of the X-rays. In this way it is possible to produce on the same photographic film under identical conditions the diffraction patterns of two specimens whose crystal structures are to be compared.

The standard exposure selected was 1000 milli-

(2)
ampere hours. This exposure was not obtained in all cases mainly because of trouble with the diffraction apparatus.

In taking the X-ray diffraction patterns, specimen Number 1 was used as the "control" or standard comparison specimen. It was selected for this purpose because it has the typical structure of annealed material. In it, according to accepted theories, all or nearly all the carbon is combined with iron in the form of the carbide, Fe_3C , and the crystals of the carbide and the remaining iron are in equilibrium. This specimen was "standardized" by comparing its diffraction pattern with that from a specimen of annealed electrolytic iron whose composition as determined by chemical analysis was:

Carbon	0.02%
Manganese	Nil
Silicon	Nil
Sulphur	0.003%
Phosphorus	0.003%

(2) In this laboratory exposures are, for the sake of convenience, expressed in milli-ampere-hours. The exposure is found by multiplying the average tube current in milli-amperes by the length of exposure in hours.

The diffraction patterns of the remaining specimens were each taken on the same photographic film with the pattern of the annealed specimen.

Data obtained.

The X-ray diffraction patterns taken are listed in Table III, and are shown, as well as it was found possible to reproduce them by photographic means, in the accompanying illustrations. The photo-micrographs showing the structure of the specimens which produced the diffraction patterns are also shown in the illustrations.

Table III.

Showing arrangement of X-ray diffraction patterns

Film No.	Specimen No.	Description	Approximate exposure in milli-ampere-hours
1	A	Electrolytic Iron, not annealed	1000
	B	Electrolytic Iron, annealed	
2	B	Electrolytic Iron, annealed	1000
	1	1.11 Carbon Steel, annealed	
3	1	1.11 Carbon Steel, annealed	1000
	2	1.11 Carbon Steel, martensitic with trace of austenitic	
4	1	1.11 Carbon Steel, annealed	980
	3	1.11 Carbon Steel, martensitic	
5	1	1.11 Carbon Steel, annealed	1000
	4	1.11 Carbon Steel, martensitic	
6	1	1.11 Carbon Steel, annealed	980
	5	1.11 Carbon Steel, martensitic with trace of troostitic	
7	1	1.11 Carbon Steel, annealed	925
	6	1.11 Carbon Steel, troostitic with trace of martensitic	
8	1	1.11 Carbon Steel, annealed	1000
		1.11 Carbon Steel, troostitic	
9	1	1.11 Carbon Steel, annealed	890
	8	1.11 Carbon Steel, troostitic with trace of sorbitic	
10	1	1.11 Carbon Steel, annealed	850
	9	1.11 Carbon Steel, sorbitic	
11	1	1.11 Carbon Steel, annealed	1000
	10	1.11 Carbon Steel, sorbitic showing beginning of spheroidizing of cementite.	

Where it is thought necessary the lines in the several diffraction patterns have been marked to indicate the part of the crystal structure which produced them. The lines produced by the iron crystals have been identified by comparing the interplanar distances computed from measurement of the diffraction patterns with the interplanar distances calculated from the space lattice of α iron as determined by Hull⁽³⁾ and that of γ iron as determined by Westgren.⁽⁴⁾ The iron carbide lines have been identified by comparison of their location on the diffraction pattern with the location of the lines in the iron carbide pattern as reported by Westgren⁽⁵⁾ and Phragmen and with other data regarding the iron carbide pattern which has been obtained at the Watertown Arsenal in connection with another research but this has not yet been published.

Discussion of data.

On film Number 1 are produced the diffraction patterns from two specimens of electrolytic iron. Specimen A contains the metal as it was deposited from the electrolyte, and specimen B contains the metal

(3) Hull, W.W: Physical Review, Vol. X, No.6 (1917) 661

(4) Westgren, Arne: Jour. Iron & Steel Institute (British) Vol. C.III. No. 1, 1921, 303.

(5) Westgren and Phragmen: Jour. Iron & Steel Inst. (British) Vol. CV. No. 1, (1922) 241.

annealed. Some of the lines of both patterns show dense spots which on close examination appear to be very flat ellipses. Such spots have been shown by McKeehan⁽⁶⁾ to be images of the source of X-rays produced by the presence, in the specimens, of large crystals with uniformly oriented lattices.

Film No. 2 shows that the diffraction pattern produced by specimen No. 1 contains without displacement all the lines found in the pattern produced by specimen B. The lines in the pattern produced by specimen No. 1, however, show no dense spots similar to those found in some of the lines in the pattern produced by specimen B which were described in the preceding paragraph. In addition to the lines found in the pattern produced by specimen B, the pattern produced by specimen No. 1 contains a number of comparatively faint but clear outlines which have been identified, in the manner already described, as belonging to the pattern of crystals of the iron carbide, Fe_3C . These diffraction patterns then show that the annealed specimen (No. 1) which has a typical pearlite and cementite micro-structure consists of a mixture of normal α iron and iron carbide (Fe_3C) crystals.

(6) L.W. McKeehan: Jour. of the Franklin Institute Vol. 194. (1922) 87.

The patterns produced by specimens No. 2, 3, 4 and 5 are particularly interesting. First because of the absence from them of all the lines pertaining to the carbide, Fe_3C , pattern, and second, because of the presence in them of lines pertaining to both the α and γ iron patterns. The pattern to which the various lines pertain is indicated on the photographic reproductions.

In the pattern produced by specimen No. 2 there is room for doubt as to whether the lines which have been indicated as having been produced by the $100^{(2)}$ (second order spectrum) and 331 planes of the γ iron crystals might not have been produced by the 310 and 111 planes, of the α iron crystals, the corresponding interplanar distances in the case of the γ iron crystals being 0.903 \AA and 0.828 \AA and in the case of the α iron crystals 0.904 \AA and 0.825 \AA respectively. A close examination of the photograph, however, shows that the line identified as having been formed by the $100^{(2)}$ plane of the γ iron crystals is somewhat further to the right than the line known to have been formed by the 310 planes of α iron in the pattern, on the same film, produced by sample No. 1. Furthermore, in the pattern produced by specimens No.

3, 4 and 5, in which specimens it is known that the austenite is successively more completely transformed, the line shifts successively further to the left and becomes weaker until in the pattern produced by specimen No. 4 it is almost exactly in coincidence with the line in the pattern produced by specimen No. 1 which line is known to have been produced by the 310 planes of the α iron crystals. In the pattern produced by specimen No. 5 this line has gained considerable in strength and has shifted still further to the left until it occupies a position with respect to the corresponding line in the pattern from specimen No. 1 which is occupied by all other lines of the α iron pattern in the diffraction pattern produced by specimen No. 5. For these reasons this line is identified as pertaining to the γ iron in the patterns produced from specimens No. 2 and 3, and to the α iron in the patterns produced by specimens No. 4 and 5. Similarly, the line in the pattern produced by specimen No. 2 which is identified as having been produced by the 331 planes of the γ iron crystals, will on close examination be found to be displaced a little to the left of the line in the pattern from specimen No. 1 which line is known to have been produced by the 111 planes of α iron

crystals. In the pattern from specimens No. 3 and 4 this line is not distinguishable at all and in the pattern from specimen No. 5 it appears in the proper position to identify it as having been produced by the 111 planes of the α iron crystals.

In the pattern from specimen No. 2 there is also a plainly distinguishable line just to the left of the line produced by the 211 planes of the α iron crystals. This line does not belong to the typical patterns of either the α or γ iron crystals and its presence is still unaccounted for.

In Table III is shown the number of lines pertaining to the typical patterns of α and γ iron crystals which are found in the diffraction patterns from specimens No. 2, 3, 4 and 5.

Table III

Specimen producing pattern	Number of lines visible in pattern:			Total	Remarks
	pertaining to α iron	pertaining to γ iron			
No. 2	5	7	13	One not identified.	
No. 3	5	4	9		
No. 4	6	3	9		
No. 5	8	1	9		

All the lines in these diffraction patterns are more or less diffused and broadened, and are less dense than corresponding lines in the pattern produced by specimen No. 1 which appears alongside. The broadening of the lines pertaining to the γ iron pattern extends about the same distance from each side of their normal position while the broadening of the lines pertaining to the α iron pattern in most cases extends to the left of their normal position.

The comparative density of a line, other things being equal, will of course depend on the amount of the material, producing the line, which is present in the specimen. Broadening and diffusing of lines has been shown by Scherrer⁽⁷⁾ to be produced in proportion as the size of the diffracting crystals becomes smaller. The broadening of the lines from this cause should extend practically equally in both directions from the normal position of the line in the pattern. Diffusion and broadening of lines might also be produced if the space lattices in some or all of the crystals were slightly distorted or varied slightly in dimensions, the distortion or variation in size being so small that the line produced by one size or shape of space lattice overlapped

(7) Gottinger Nachrichten, Sitzg., 26, Jul. 1, 1918;
R. Zsigmondy, Kolloid Chemie, 3 Aufl., Leipzig,
1920, page 387.

the line produced by the next size of shape. In this case the extent of the broadening of the line and the direction in which it extended from the normal position of the line should give some indication of the manner in which the space lattices differed from each other.

These considerations, however, have not as yet enabled the writer to definitely explain the behavior of all the lines in these diffraction patterns. It is thought that their behavior will probably be found to be closely associated with the mechanism of transformation of the δ iron crystals to α iron crystals. For the present, it can only be said that the phenomenon probably indicates the presence in the specimen of crystals of very small size, or having slightly distorted, enlarged or contracted space lattices, probably all.

The photo-micrographs of specimens No. 2 to 5 inclusive show that in micro-structure they cover very well the martensitic range, No. 2 at one extreme, being martensitic with some indication of the austenitic and No. 5, at the other extreme, being martensitic with an indication of the troostitic.

It is evident, therefore, that the martensitic structure indicates the presence, in the specimen, of a mixture of α and β iron crystals, the proportion of β iron crystals decreasing and the proportion of α iron crystals increasing as the structure changes from the austenitic toward the troostitic. The space lattices of the iron crystals probably suffer little, if any, distortion or change in dimensions as long as any of these crystals exist. The β iron crystals, however, are evidently very minute and probably somewhat distorted, gradually increasing in size and becoming more nearly normal in space lattice form or dimensions as the troostitic structure is approached. The failure of any of the lines of the iron carbide (Fe_3C) pattern to appear in these diffraction patterns cannot be taken as conclusive evidence that the compound does not exist in these structures. It might be present in such small crystals as to cause the lines of its pattern which are rather weak anyway, to be so diffused as to be indistinguishable from the darkening of the photographic film which is caused by the general (white) X-radiation from the specimens.

The photo-micrographs of specimens No. 6, 7 and 8 show that they have a troostitic structure, with a

trace of the martensitic in specimen No. 6 and a trace of the sorbitic in specimen No. 8. The diffraction patterns produced by these specimens contain only lines pertaining to the α iron crystals. These lines are still somewhat diffused and widened, the widening extending toward the left end of the pattern, and decreasing in amount as the structure of the specimen approaches the sorbitic. The presence, in specimen No. 6, of a trace of the martensitic micro-structure would lead to the suspicion that some of the iron in that specimen was still in the γ form. The absence of lines pertaining to the γ iron from the patterns produced by this specimen does not preclude the possibility of this actually being the case. It is quite conceivable that some γ iron crystals remain but are so small in size and so few in number that the lines produced by them are so weak as to be indistinguishable. The failure to find in their diffraction patterns any of the lines of the iron-carbide pattern again does not give definite proof that the compound is not present, either in small amounts or in the form of very minute crystals.

In specimens No. 9 the micro-structure is shown to be sorbitic. The diffraction pattern produced by it contains not only all the lines of the κ iron pattern

but also some faint lines of the iron-carbide pattern. The lines of the α iron pattern are seen, by comparison with the corresponding lines in the pattern from specimen No. 1 which is shown as the same photographic film to be but very little over their normal width, indicating that the α iron crystals in the two specimens are of the same order of magnitude as the crystals in specimen No. 9. The presence of some of the lines of the iron carbide pattern shows conclusively that in this specimen there are present crystals of the compound in appreciable number and of appreciable size.

The microscope shows specimen No. 10 to still have a sorbitic structure but also that the iron carbide crystals have at least begun to collect in irregular shaped globular masses in the matrix of more or less pure ferrite. The diffraction pattern produced by this specimen is practically a duplicate of the pattern produced by specimen No. 1 on the same photographic film, with the exception that the lines pertaining to the iron carbide pattern are not as strong in the former as in the latter. The only difference between the conditions of the material in specimens No. 1 and 10, which has been indicated, is in the distribution of the iron-carbide crystals in the matrix and possibly in their size.

Summary

The evidence discussed above shows that, at ordinary temperatures, in plain carbon steels of hyper-eutectoid composition, the crystal structure, as shown by the X-ray spectrometer, varies through a continuous series from that existing when the metal has been very rapidly cooled from a temperature in or above the critical range to that existing when the cooling has been very slow from a temperature above the critical range.

Typical micro-structures are developed in such steels depending upon the portion of this series to which the crystal structure existing in them belongs. These typical micro-structures have long been recognized and the range of the crystal structures which each indicates has been shown to be as follows:

1. The martensitic micro-structure indicates the existence of a mixture of α and γ iron crystals, the proportion of γ iron crystals decreasing and the proportion of α iron crystals increasing as the structure approaches the troostitic. The space lattices of the γ iron crystals apparently do not suffer much, if any, distortion as long as any of these crystals exist. The space lattices of the α iron crystals however are

probably somewhat distorted, the distortion decreasing as the troostitic structure is approached.

2. The troostitic structure represents a condition in which iron crystals are present only in the α form. The space lattices of these crystals are also probably somewhat distorted, but to a lesser extent than in the martensitic structures. As the structure approaches the sorbitic this distortion of the space lattices decreases.

3. In the condition denoted by the sorbitic structures, there exists a mixture of α iron and very minute iron-carbide crystals. The probable distortion of the space lattices of the α iron crystals disappearing and the size of the iron carbide crystals growing as the micro-structure approaches the pearlitic.

4. In the alloys having the pearlite and cementite structures there is a mixture of perfectly formed α iron and iron carbide crystals.

The X-ray diffraction patterns of this series do not definitely indicate the disposition of the carbon atoms in the martensitic and troostitic micro-structures. They do not positively show the presence of iron carbide crystals nor do they produce evidence that very minute crystals of the compound do not exist.

Acknowledgment

The experimental work described above was performed in the laboratories of the Watertown Arsenal. For permission to work in those laboratories the writer wishes to express his appreciation to Colonel T.C. Dickson, Ordnance Department, United States Army, Commanding Officer of that Arsenal. In the laborious and often difficult work of preparing the specimens the advice and encouragement of Dr. F. C. Langenberg, Director of Laboratories at the Watertown Arsenal, was of the greatest value. The production of satisfactory spectrograms was made easy by the advice, assistance and cooperation of Dr. H.H. Lester, Physicist in charge of X-ray Laboratory at the Watertown Arsenal.