A STUDY OF THE FORMATION OF CEMENTITE IN STEEL

THESIS FOR THE DEGREE OF M. S.

John E. Wilson

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Cementite
Steel

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A STUDY OF THE FORMATION
of
CEMENTITE IN STEEL.

THESIS

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Failed! Time after time allotments of similar types of steel treated under identical conditions have provokingly failed to live up to tested requirements. Wire of a standard composition treated in the most approved manner to give the required results has discouragingly failed when put to use. Such failure when detected are translated into huge losses for both the consumer and the manufacturer. Industry has bent every effort to localize the indicators of the so-called abnormal steel. Yet the steel being discussed, exhibiting such failures is not abnormal as the word is usually understood. Specimens that have stood up under static tests have failed miserably under dynamic tests. Steel which should display certain potentialities has failed to even fulfil minimum specifications. Steel of identical quality and workmanship still fails.

It has been noticed that such failures occur particularly in steel of low carbon content; steel of which the highest degree of ductility is required. Such processes as stamping and the drawing of wire have demanded such ductility of steel and have likewise been confronted by this failure of steel. Naturally, every effort has been expended to overcome it, but the problem still remains. The author's attention was first turned to this problem by the failure of some specimens of steel when stamped into spokes and timeing gear covers. Two specimens, supposedly the same, (the difference being that the one had failed, the other had stamped perfectly) were immediately subjected to a microscopical examination. The cause for the failure was soon evident. The specimens were not identical. The one that had failed showed a banded pearlitic structure. Naturally, further tests were not made on the two samples of unidentical nature.

Experimental work done in the past offered a clue towards the solution of the igma. Low carbon steel in some cases when examined under an oil immersion lens revealed a thin film around the ferrite grains.

Undoubtedly if this film consisted of cementite it would affect materially the ductility of the specimen when tested. This being true the effort to solve the problem resolves itself for the time being into a study of this film surrounding the ferrite grains, its formation and its subsequent effect upon steel.

That this film is cementite can be readily seen by examining the micrographs of some steel S. A. E. 1040, following a slow cool from 1850°F[*] (Fig's. 1-7). The cementite apparently flows from the cementitic areas in the pearlite into the grain boundaries. It would be difficult in the light of the evidence offered to suggest that all the boundaries surrounding the ferrite grains consist of cementite. Rather it seems more probable that some of the boundaries are composed of cementite, especially in the case of the lower carbon steels. Attention is called to the difference in the free cementite formed in the grain boundaries of the low carbon steel. There is the large masses of the cementite similar to that noticed in the right half of Figure 1. Further, there are large distinct cementitic grain boundaries formed directly between the pearlitic areas. (Fig's. 2 & 3) And lastly there are cementitic grain boundaries seemingly eminating from the pearlitic areas and surrounding the ferrite grains. (Fig's. 1, 4, 6, & 7)

In an effort to study the formation of cementite in the grain boundaries in the following proceedure was carried out: Six pieces of 20% carbon steel (A_1 2 & 3 and D_1 2 & 3) cut from the same bar, were placed in two bombs[*2], heated in an electric furnace to 1850°F for one hour; all six were then furnace cooled to 1675°F; No's. D 1, 2, & 3, were removed from the furnace and allowed to cool in the bomb; No's. A 1, 2, & 3 were cooled slowly to

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[*] The specimen was heated in a Hoskins automatically controlled electric furnace at 1850°F for one hour, cooled in the furnace to 1320°F, more slowly cooled at the rate of a drop of 20°F every 10 minutes to 1250°F, and then furnace cooled to room temperature.

[*2] The bombs consisted of one inch steel pipes six inches long sealed at each end.

Fig. 1

Mag. 2160 X

Fig. 2

Mag. 2160 X

Fig. 3

Mag. 2160 X

Fig. 4

Mag. 2160 X

Fig. 5

Mag. 2160 X

Fig. 6

Mag. 2160 X

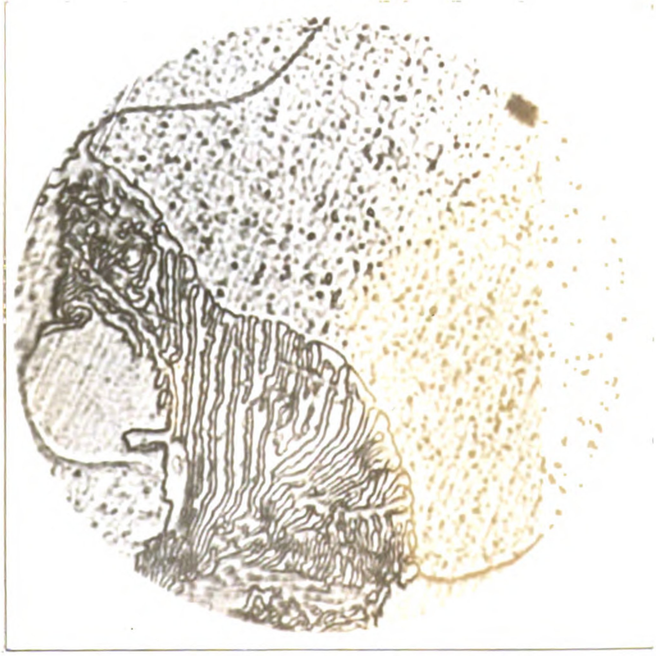


Fig. 7

Mag. 2160 X

1175°F, at the rate of a drop of 20° every 10 minutes, from which point they were furnace cooled to room temperature. Both $A_{2\&3}$ and $D_{2\&3}$ were heated to 1260°F held for one hour and water quenched. A_3 and D_3 were then heated to 1260°F held for one hour and water quenched.

In order to afford a check on the work the experiment was repeated, giving the treatment formerly given to the A series to the D series, and giving to the A series that which was given to the D.

It is apparent from the photomicrographs (Fig's. 8 & 9, corresponding to A_1 and D_1) that the size of the pearlitic areas increases, while the number decreases, as the time consumed in passing thru the lower critical is lengthened. Likewise the size of the lamellae, both in length and breadth, increases with an increase in time. Comparing the structures formed after the two rates of cooling as exemplified in steels numbered A_1 (Fig's. 10 & 11) and D_1 (Fig. 12), it is observed that there is in the slower cooled steel, A_1, a margin of cementite around the most of the pearlitic areas and that the film surrounding the ferrite grains evidently contains a greater amount of cementite. Whereas in A_1 the pearlite seems to fill an entire grain (whether it is an austenite grain or not, is difficult to say) the pearlite in D_1 the more rapidly cooled piece seems to start from the grain boundaries. It is true that there are some cases noticed in which the pearlite is entirely isolated from the grain boundaries but for the most part the first stages of the pearlitic formation seems to center around the grain boundaries as seen in Figure 7. Attention is called to the apparent fact that in the more rapidly cooled piece, very little cementite existed in the boundaries surrounding the ferrite grains. The cementite that was present was there as free isolated cementite in the boundaries or else as a cementite grain boundary between two pearlitic areas.

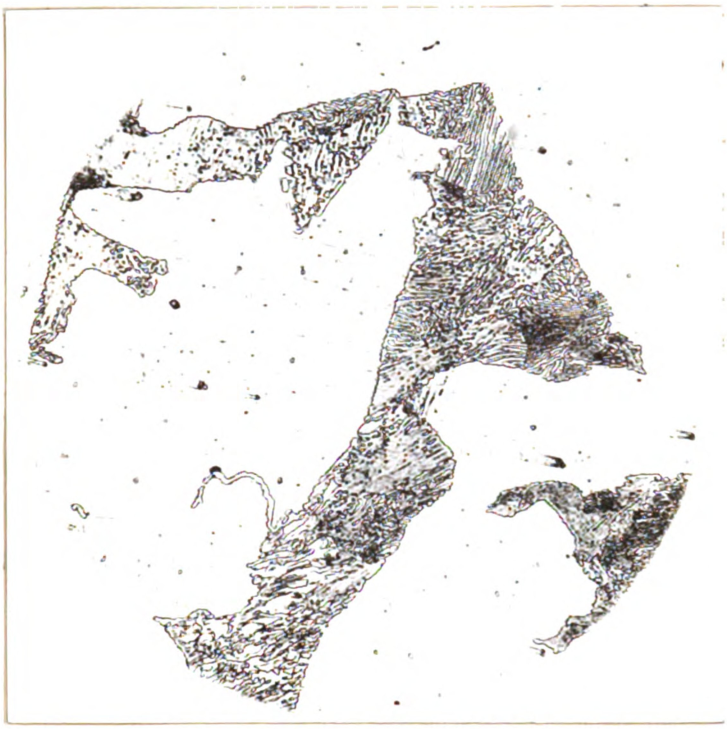
The size of the pearlitic grains in A_2, the slow cooled steel following

Fig 8

Mag. 450 X

Fig. 9

Mag. 450 X



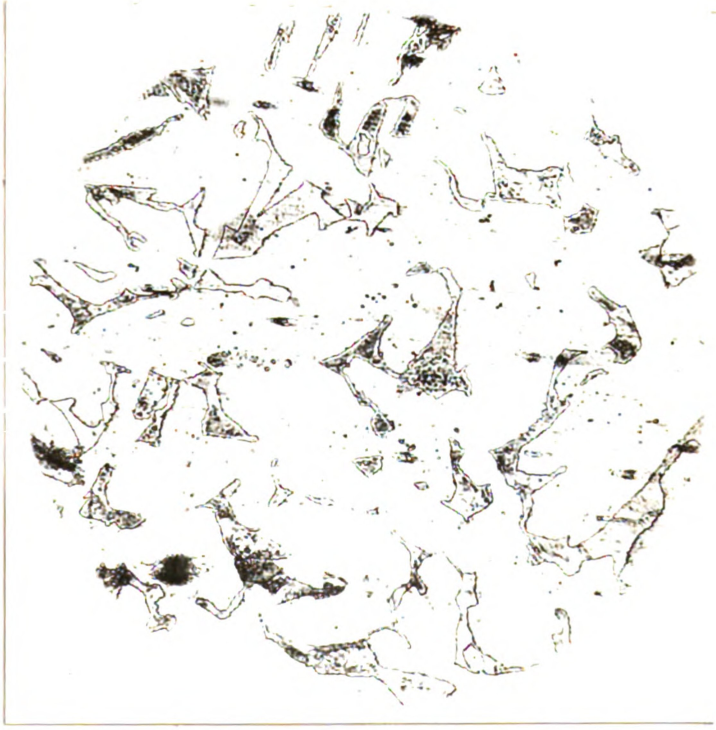
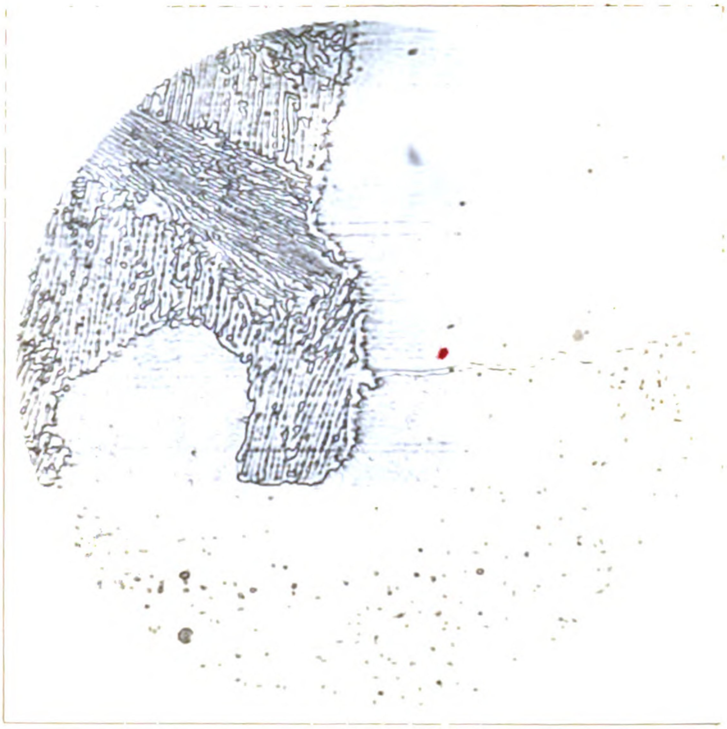


Fig. 10

Mag. 1905 X

Fig. 11

Mag. 1905 X



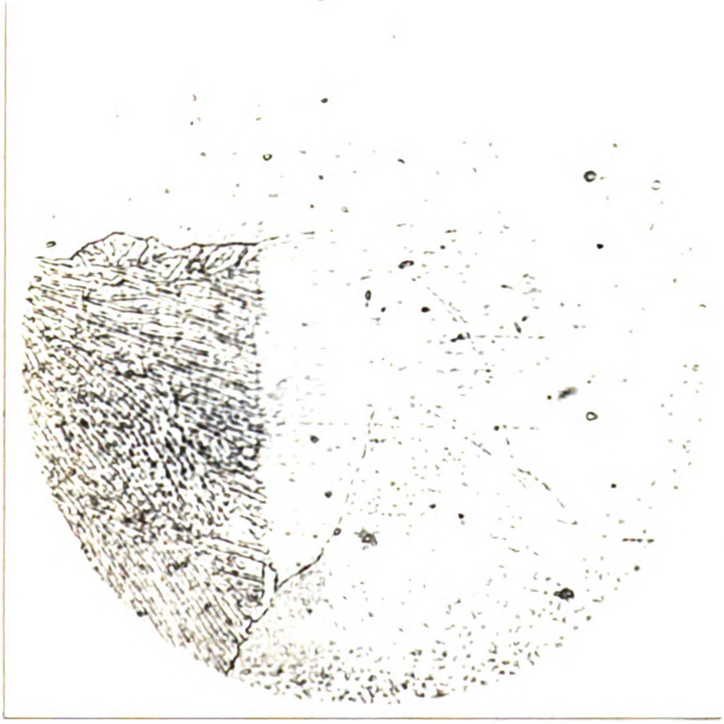
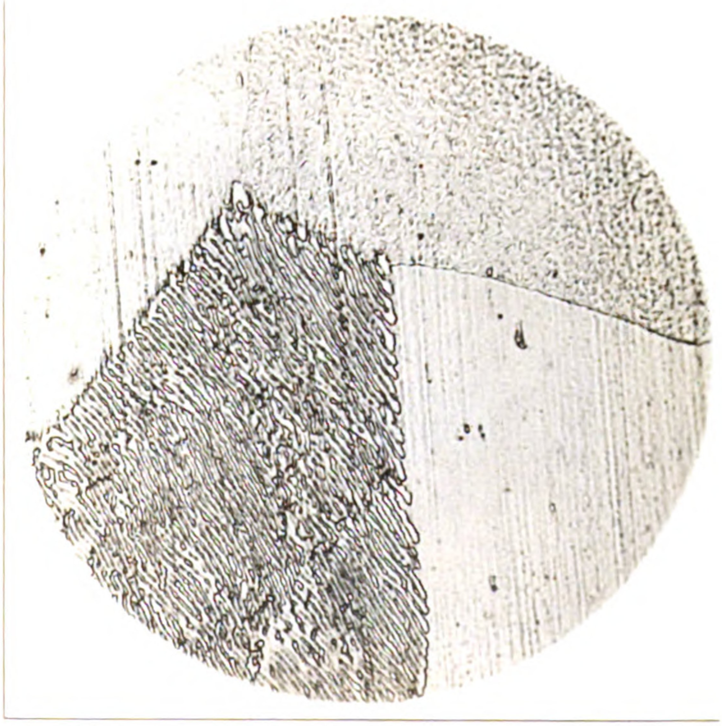


Fig. 12

Mag. 1905 X

Fig. 13

Mag. 1905 X



the first water quench, seems to be little affected. However, there is a noticeable less of cementite in the pearlitic areas; the margins in some cases have disappeared and the lamellae have become thinner. Markedly enough, the ferrite has become much disturbed, not being as clean as formerly. The grain boundaries have not increased in size. (Fig. 13)

From the structure in D_2, the more rapidly cooled piece after the first water quench, it is evident that the pearlite is beginning to ballup, not markedly but enough to cause a breaking up of the pearlitic formation. The grain boundaries evidently have become a little larger thru this treatment. (Fig. 14)

In A_3, the slow cooled steel after the second quench, the pearlite in most cases has started to break up; the lamellar structure where it still exists has become much thinner. Noticably, the cementite particles have started to spherodize in the grain boundaries, not necessarily near the pearlitic areas. (Fig. 15)

In D_3, the more rapidly cooled piece after the second quench, the pearlite is very much broken up. There was not however, the same spherodizing of cementite in the grain boundaries as in A_3. Yet the grain boundaries surrounding the ferrite were larger than in D_1. (Fig 16)

The hardness of the pieces treated above is shown in table I.

Specimen	Rockwell Hardness No. "B" Scale
~~A~~ A_1	25.8
A_2	41.6
A_3	39.2
D_1	45.3
D_2	46.8
D_3	41

The results obtained by reversing the specimens used in the experiment

Fig. 14

Mag. 1905 X

Fig. 15

Mag. 1905 X

Fig. 10

Mag. 1905 X

show the carbon content to be the same. In every case the observations seemed to check those made previously.

The hardness of the pieces after reversing the treatment is shown below in Table II.

Specimen	Rockwell Hardness of No. "B" Scale
A_1	74
A_2	73.6
A_3	71
D_1	62.3
D_2	72.2
D_3	71

The hardness of the slower cooled piece in each case was much less. However it is noticed after quenching from below the lower critical, that it compared very favorable with the more rapidly cooled piece.

Thus far attention has been centered on the cementitic formations which follow the change from gamma to alpha iron with a lowering of temperature. In the absence of gamma iron, the effect of heat treatment at a temperature just below the lower critical produces very different results. If the treatment is continued long enough, a spheroidal structure is obtained, especially if the structure so treated is in a fine condition. Apparently following a spheroidal structure is obtained, especially if the structure so treated is in a fine condition. Apparently following a spheredizing treatment, the cementite particles exist as isolated spheroids. If this is true, cementite cannot have precepitated to the grain boundaries upon the transformation from gamma to alpha iron, although proof of their existence in the grain boundaries would not preclude that they were deposited there in their entirety at the time of transformation. Rather, in the face of the work done previously it would seem probable that a small amount would be precepetated at the grain boundaries following the transformation the amount increasing by migration with time. However, ordinary examination of the structure of spherodized low carbon steel does not reveal any grain boundary. In order to clarify the situation and if possible, throw a little more light upon this type of cementitic formation, the following experiment was carried out: a sample of .40% carbon steel was heated to 1850°F in a Hoskin's automatically controlled electric furnace and held for one hour, air cooled, reheated to 1850°F and air cooled again. The piece was then heated to 1250°F for fifteen hours and allowed to cool slowly. Following the cooling the sample was etched for 2 seconds, 3 seconds, 4 seconds, and 10 seconds, with four percent nital solution.

In Figures 17 and 18, the 2 second etch was very light. So light in fact, that a photomicrograph poor in detail was obtained. Even at that one can observe order about the arrangment of the spheroids. They seem to be in some cases, laid down in strings. With a little deeper etch, 3 seconds, a clearer detail of this line like arrangment is seen at low magnification, (19) while at a higher magnification a faint line is seen to run from one to another of these spheroids. (20) The structure obtained with a 4 second etch is shown in Figures 21 and 22, very similiar to the three second etch. With a 10 second etch at low magnification dark lines are seen to distinctly connect some of the spheroids together. (Fig. 23) While at a higher magnification it is evident that the spheroids are connected by channels of cementite--grain boundaries of cementite if one so wishes to call them that. (Fig. 24 & 25) Upon closer examination it can be noticed in either Figure 24 or 25 that the cementite actually runs from the spheroids into the grain boundaries.

Whether all the spheroids are connected together in the same manner is beyond the scope of the paper, although there seems to be some indication

Fig. 17

Mag. 580 X

Fig. 18

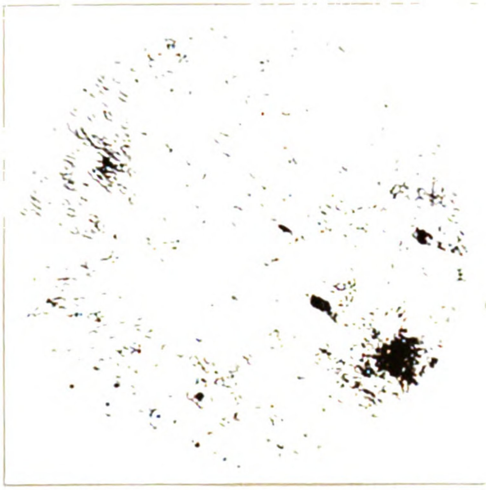
Mag. 2300 X

Fig. 19

Mag. 580 X

Fig. 20

Mag. 2300 X



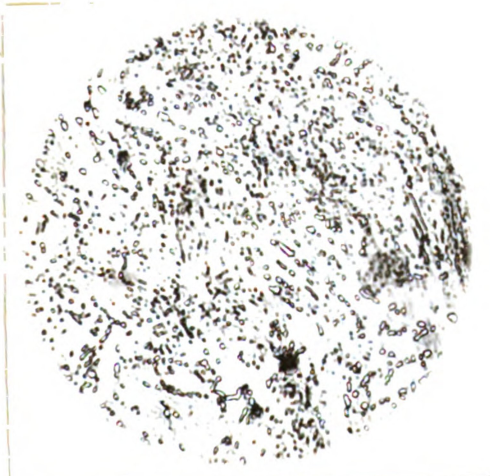


Fig. 21

Mag. 580 X

Fig. 22

Mag. 2300 X

Fig. 23

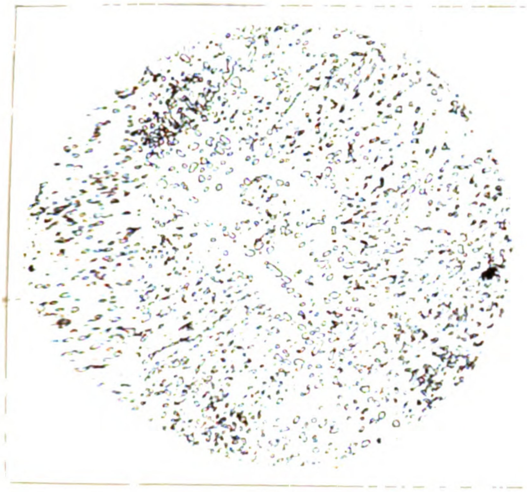
Mag. 580 X

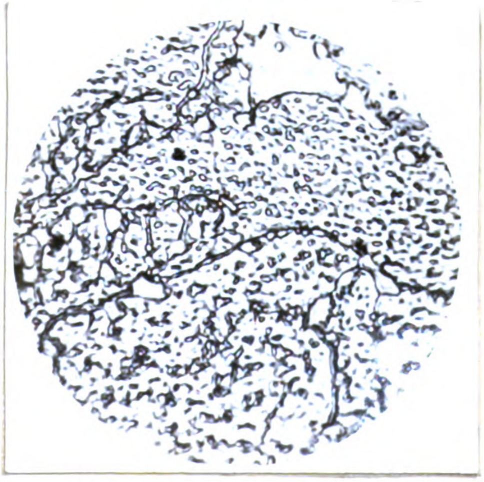
Fig. 24

Mag. 2200 X

Fig. 25

Mag. 2200 X





they may be. The pertenent point to be gained is that in further observation of spheroidal structure in low carbon steel, these cementitic grain boundaries must be considered, at least mentally.

From the results obtained in spheroidizing, the force of cohesion is one that must be contended with. That it exists at the time of the cementitic formation is undoubtedly true. But the force of cohesion comes into predominance when a migration of the cementite becomes possible in the absence of a precipitating constituent such as gamma iron--more briefly, when the steel is heated to a point just below the A_1 point. Yet considering the time envolved, the force must be small. However, if sufficient time is allowed, the question arises; will the cementite "ball-up" further in grain boundaries, and will the grain boundaries themselves, tend to "ball-up"? Before actually developing the experiment, the fact that the amount of cementite present may alter the circumstances enough to alter the results, must be considered. Thus, another variant is introduced into the experiment, which is as follows: three types of steel (.20% carbon, .40% carbon, and eutectoid) were considered. The eutectoid steel was received in a spheroidal condition. The .20% carbon and the .40% carbon steel were heated to 1850°F, air-cooled, reheated to 1850°F, and air-cooled to place the specimens in a fine condition. The three steels in this condition were then placed in the furnace and heated to 1250°F. From time to time the pieces were taken out and examined, and photomicrographs were made. When the .40% carbon steel had been subjected to the treatment for 209 hours and the .20% carbon and the euctectoid steel for 228 hours, the samples were removed.

The structures considered in the experiment are shown in figures 26-76. An observation chart is shown. (Table IV)

TABLE IV

FIG. NO.	SAMPLE AND HEAT TREATMENT	OBSERVATION NOTES
26-27	S.A.E. 1040 after double air cool from 1850°F.	Structure is very fine previous to spheroidizing treatment.
28-29	S.A.E. 1040 after 15 hrs. at 1250°F.	There is a tendency to spheroidize. However, the spheroids are angular. No movement to the ferrite gap. Only a few lamellae left.
30-31	S.A.E. 1040 after 24.5 hrs. at 1250°F.	Advancement of spheroidizing process. Note inter-cementite connections.
32-33	S.A.E. 1040 after 36.5 hrs. at 1250°F.	The spheroids are small and have lost their angular nature.
34-35 36-37	S.A.E. 1040 after 46.5 hrs. at 1250°F.	There is not much diffusion. The cementite seems to be lengthening out.
38	S.A.E. 1040 after 57 hrs. 50 min. at 1250°F.	Lengthing of the cementite particles.
39-40	S.A.E. 1040 after 62 hrs. 50 min. at 1250°F.	The cementite seems to be lengthening inte parallel rods.
41-42	Tool steel about Eutectoid composition after 72 hrs. 1250°F. Structure spheroidal to start.	The spheroids are larger. There are a few indications of the spheroids lengthening out.
43-44	S.A.E. 1020 after a double air quench from 1850°F. followed by a heat at 1250°F. for 72 hrs.	Fig. 35 shows the connection between cementite particles. Fig. 36 shows cementite in the grain boundary as a result of mass action or surface tension.
45-46	S.A.E. 1040 after 72 hrs. at 1250°F.	Parallelism of the cementite is noticeable. The grain boundaries still exist.
47	S.A.E. 1040 after a spheroidizing treatment at 1250°F. for 15 hrs.	A typical example of spheroidized plain carbon steel.
48-53	S.A.E. 1040 after 76 hrs. at 1250°F.	Margins have coalesced-lamellae appear to run from the margins. Fig. 52 & 53 show cementite in the grain boundary and also the appearance of cementite in the ferrite grain.
54-55	S.A.E. 1040 after 89 hrs. 30 min. at 1250°F.	Fig. 54 shows the development of the parallel structure. Fig. 55 illustrates cementite in the grain boundaries.

TABLE IV (con't)

FIG. NO.	SAMPLE AND HEAT TREATMENT	OBSERVATION NOTES
56-57	S.A. E. 1040 after 98 hrs. 45 min. at 1250°F.	The length of the cementite particles seems to increase.
58-59	S.A.E. 1040 after 110 hrs. 10 min. at 1250°F.	A smearing action of polishing seems to predominate. However, the relative increase in size is evident.
60-61	S.A.E. 1040 after 119 hrs. 20 min. at 1250°F.	Fig. 60 shows an example of the parallel cementite rods or plates. Fig. 61 illustrates this same point and also the lengthening of the cementite.
62	S.A.E. 1040 after 132 hrs. 35 min.	Illustrates the development of parallelism in the cementite particles.
63-65	S.A.E. 1040 after 148 hrs. at 1250°F.	Shows spheroids in the grain boundaries and cementite in the ferrite.
66	S.A.E. 1040 after 135 hrs. at 1250°F.	Shows long development of cementite chain.
67	S.A.E. 1040 after 148 hrs. at 1250°F.	Due to the cementite and grain boundary has apparently increased in size.
68-69	S.A.E. 1040 after 152 hrs. 50 min. at 1250°F.	The development of a lamenated cementite together with partial coalescence is noticed.
70-71	S.A.E. 1040 after 209 hrs. at 1250°F.	Development of the cementite lamellae. Fig. 71 shows colascence of lamellae with spheroids in the grain boundary.
72-73	As recieved spheroidal eutectoid tool steel after 238 hrs. 30 min. at 1250°F.	A little development ofthe laminated structure is noticeable but it is exceptional.
74-75	S.A.E. 1020 after 238 hrs. 30 min. at 1250°F.	Evidentually all the cementite has migrated to the grain boundary.

Fig. 26

Mag. 950 X

Fig. 27

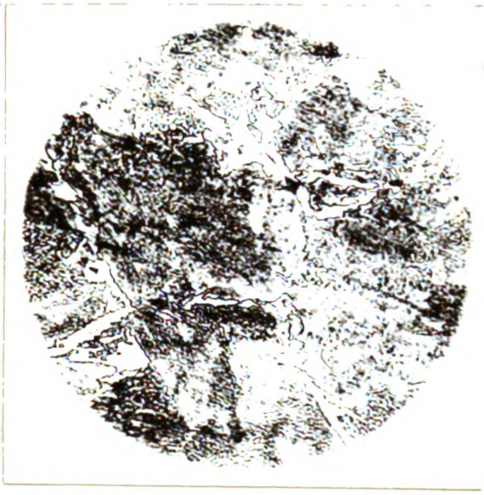
Mag. 1905 X

Fig. 28

Mag. 955 X

Fig. 29

Mag. 1905 X



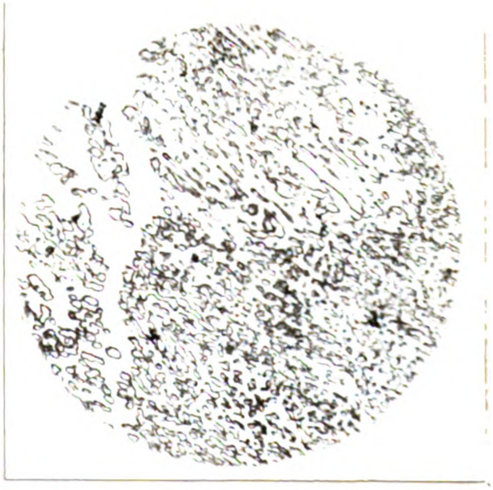


Fig. 30

Mag. 1905 X

Fig. 31

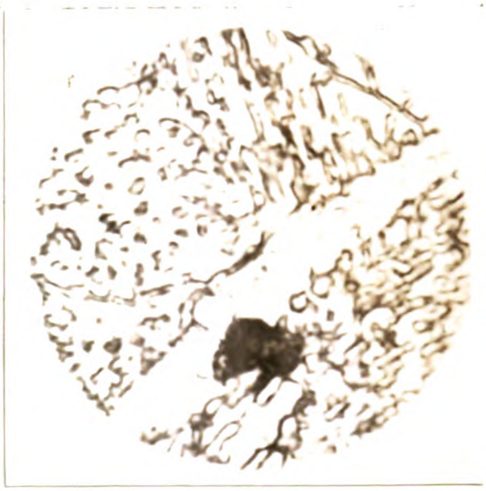
Mag. 3075 X

Fig. 32

Mag. 1910 X

Fig. 33

Mag. 1910 X



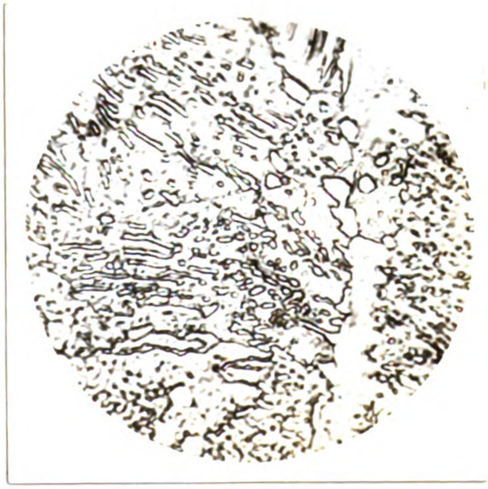


Fig. 34

Mag. 1905 X

Fig. 35

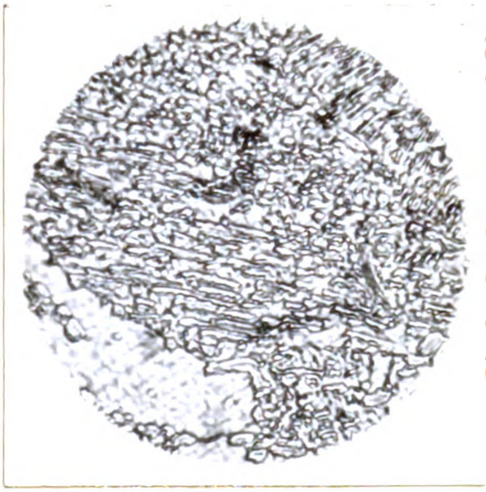
Mag. 1905 X

Fig. 36

Mag. 2460 X

Fig. 37

Mag. 950 X



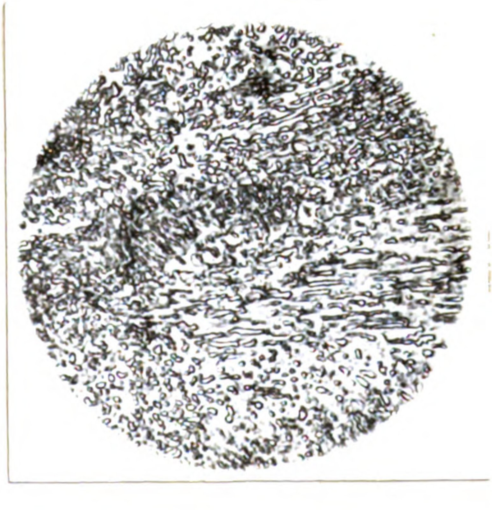


Fig. 38

Mag. 19o5 X

Fig. 39

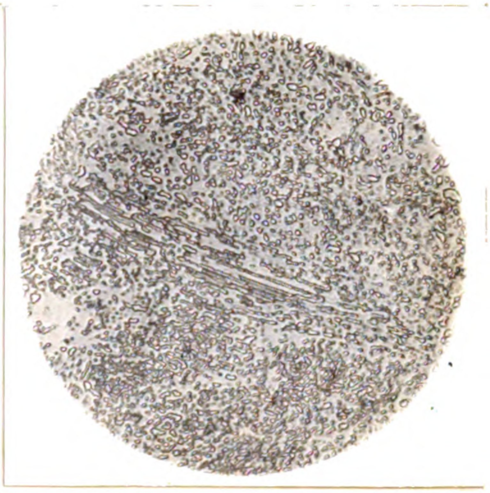
Mag. 800 X

Fig. 40

Mag. 1600 X

Fig. 41

Mag. 1905 X



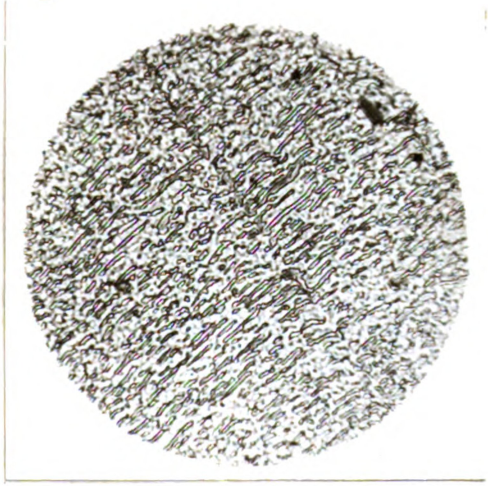


Fig. 42

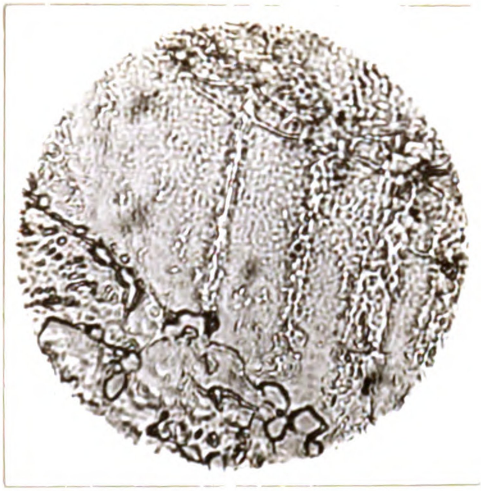
Mag. 1905 X

Fig. 43

Mag. 1905 X

Fig. 44

Mag. 1905 X



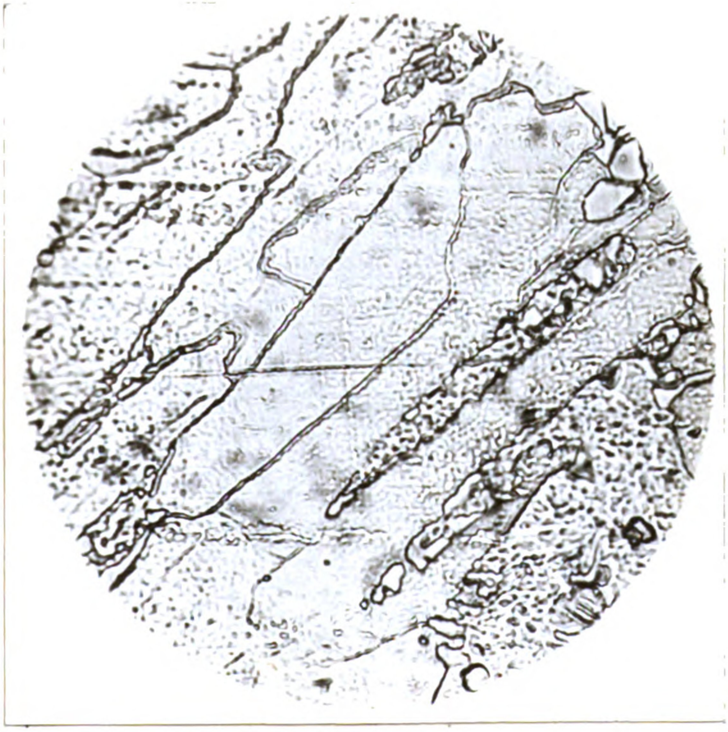


Fig. 45

Mag. 1905 X

Fig. 46

Mag. 950 X

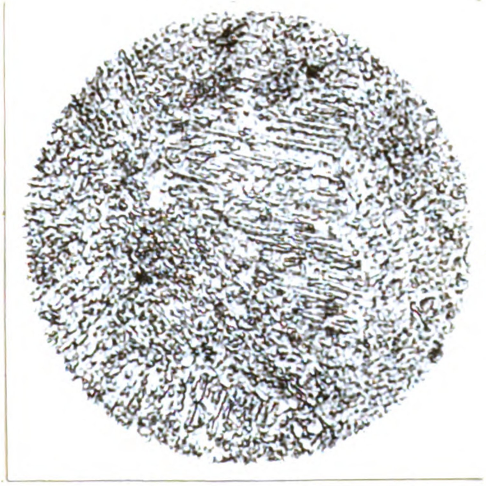


Fig. 50

Mag. 1880 X

Fig. 49

Mag. 2040 X

Fig. 47

Mag. 580 X

Fig. 48

Mag. 870 X




Fig. 51

Mag. 1910 X

Fig. 52

Mag. 1905 X

Fig. 53

Mag. 1905 X

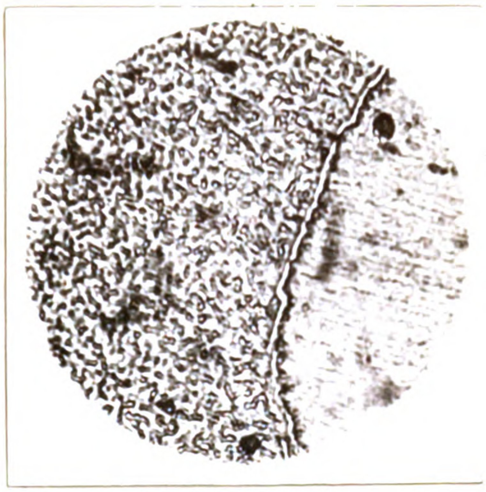


Fig. 54

Mag. 1905 X

Fig. 55

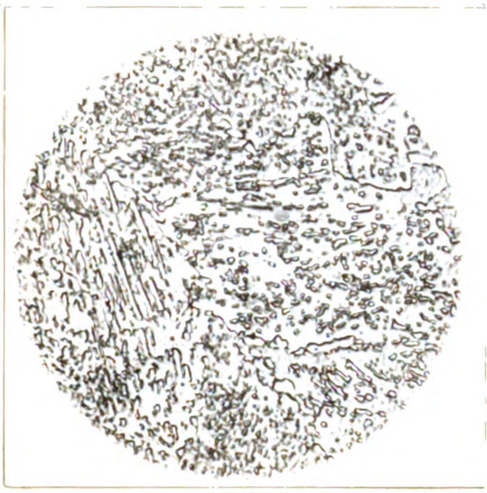
Mag. 1905 X

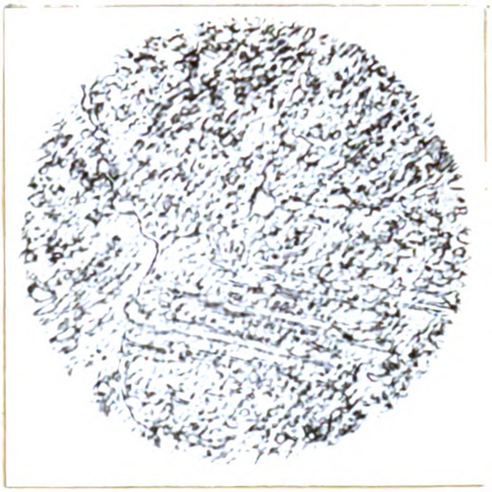
Fig. 56

Mag. 950 X

Fig. 57

Mag. 1905 X





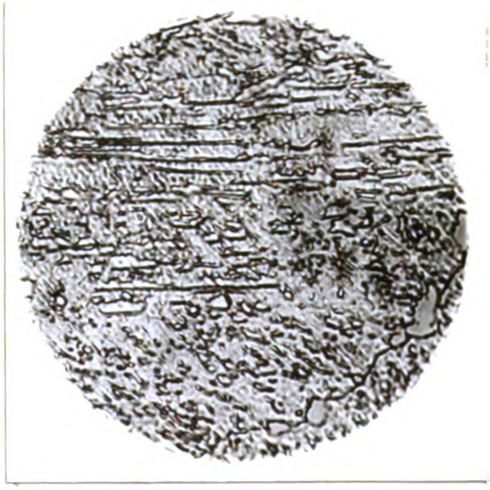


Fig. 58

Mag. 1905 X

Fig. 59

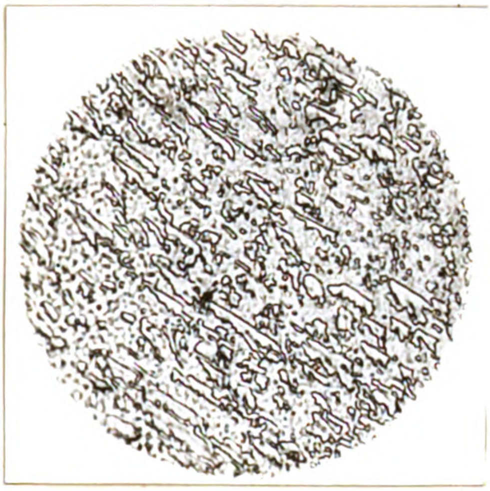
Mag. 1905 X

Fig. 60

Mag. 950 X

Fig. 61

Mag. 1905 X



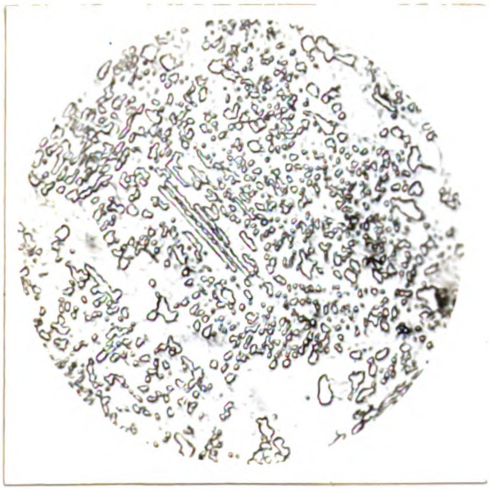


Fig. 62

Mag. 950 X

Fig. 63

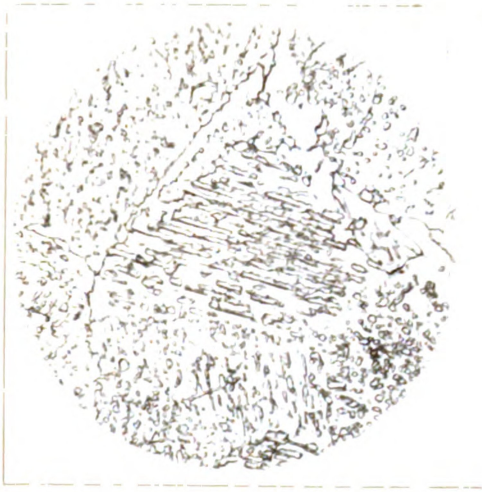
Mag. 1905 X

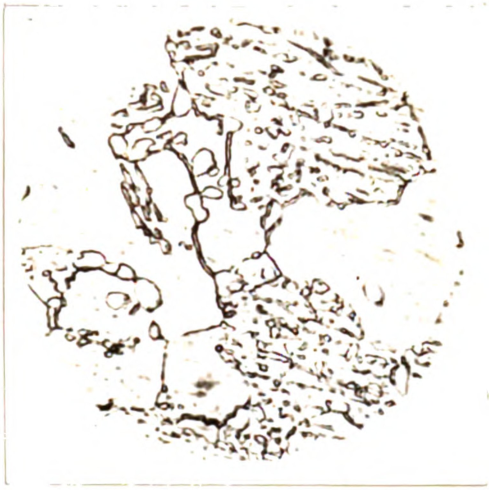
Fig. 64

Mag. 1905 X

Fig. 65

Mag. 1905 X





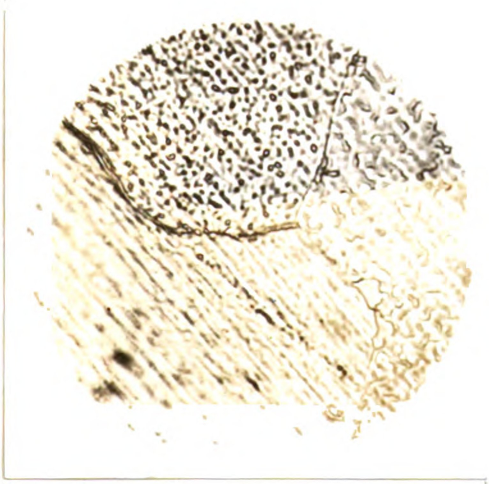


Fig. 67

Mag. 1905 X

Fig. 66

Mag. 1905 X

Fig. 68

Mag. 950 X

Fig. 69

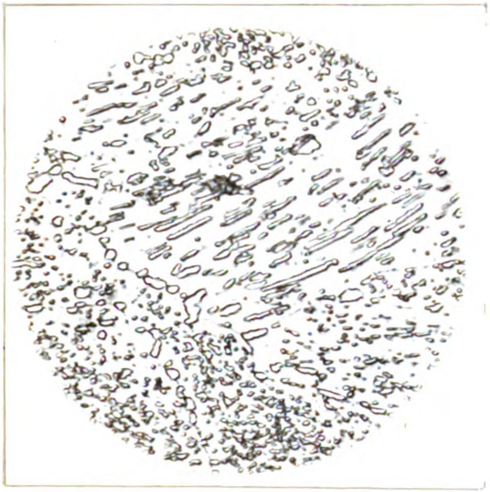
Mag. 1905 X

Fig. 70

Mag. 950 X

Fig. 71

Mag. 1905 X



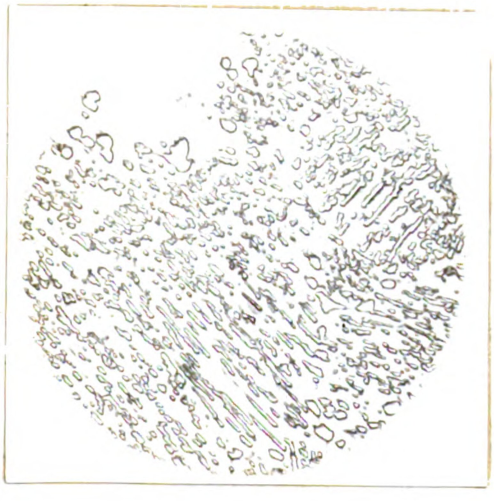


Fig. 72

Mag. 3175 X

Fig. 73

Mag. 1905 X

Fig. 76

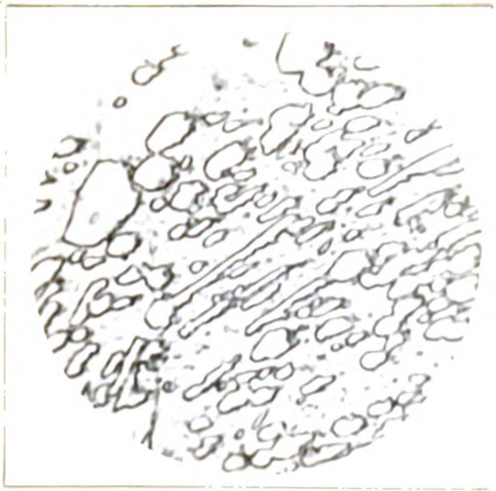
Mag. 950 X

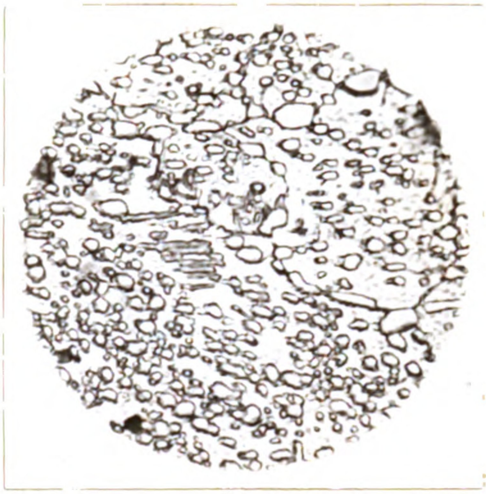
Fig. 74

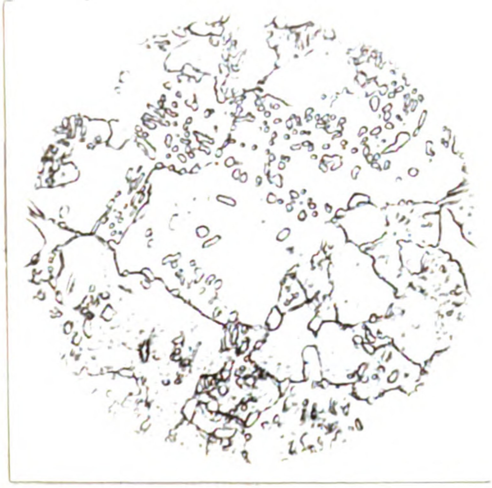
Mag. 950 X

Fig. 75

Mag. 1905 X







It may be generalized from the data obtained in this last experiment, that in low carboned steels, in particular, cementite is precipitated to the grain boundaries after a long heat treatment below the lower critical. Further, that in steels ether of eutectoid nature, cementite tends to migrate to the grain boundaries. The speed with which cementite or the carbon migrates at a temperature just below A_{r1} depends largely upon the amounts considered. This is evident by the fact that after 238 hours, the spheroids remained as such in eutectoid steel. Whereas with low carbonsteel, as has been shown, migration takes place quite rapidly.

It has been the firm conviction of most authorities that cementite is very hard and brittle. Sauveur sums up the general thought predominate from the time of Howe to the present, by saying that, "Cementite is an extremely hard substance, being in fact the hardest of all the constituents occuring in iron and steel, harder even than hardened, high carbon steel." Howe states that it is harder than glass and nearly as brittle. As it scratches feldspar and not quartz, it is generally assigned to rank of 6.5 (Mohs scale of hardness). Others have endeavored to determine the exact hardness, indicating such hardness as high as 8.20 Brinell as the true value. Yet the writer has found evidence upon different occasions which would indicate that cementite, or such as we know it, is not always hard. If the hardness of cementite does vary, then the cementitic structures likewise varying, will affect the steel. In the same fashion the cementic structures which are being studied should vary.

In order to determine the hardness of the cementitic formation, a micro character hardness machine was first used. However, it was soon evident that such a device could not serve the purpose. The resulting scratch was much too large. So that any relative difference that might exist between the small formation was completely nullified by the large force brought into play at the point of the diamond used to scratch the specimen. In an effort to overcome this difficulty, various methods were devised. Finally, the following was used to determine the relative hardness*: the sample to be tested was polished in such a manner that unetched, the scratches ran in one direction only; the scratches did not go so deep that they could not be removed by the etchant; the sample was scratched at a 90° angle to the polishing scratches, the scratch being of the same magnitude as the formation considered. (*The hardness obtained by this method is one of abrasion. The results of course can not substitute for the other forms but a difference in the abrasive hardness must indicate a difference in the constituent causing the hardness. Further, the author is trying to show a relative difference between the various forms of cementite and not an absolute hardness of cementite.) The method of hardness scratching is carried out by saturating some broadcloth with pure metnyl alcohal following an impregnation with a few grains of Levigated Alumina powder. The sample is then placed, etched surface downward, on the cloth, and moved firmly about an inch and a half across the surface. The sharp grains, held as they are, act as the diamond point, cutting deeply into the soft material and lightly into the hard. Care must be used when scratching low carbon steel, for the etched surface is destroyed very easily. In the case of low carbon steel it was found that cheese cloth, used a few times previously, would scratch the surface of the specimen when rubbed across it and to aid in dyying. In this work impurities which might cause miscellaneous scratches must be removed or eliminated after etching. In order to avoid any extra scratching that might arise from drying with a cloth, after washing with a fast stream of water, the samples were immersed in xyol and then methyl alcohol (must be pure or a film is left on the surface) and allowed to dry in the air.

The specimens of steel tested in the above manner contained .40%, .79%-.80%, .90%, .99%, and a 1.20% of carbon, in both the normal and spheroidal forms. Of these it is interesting to note that of the two, the spheroidal form was harder to scratch, two and sometimes three scratching operations being necessary to obtain scratches of the same magnitude as the formations.

Considering in detail the spheroidal structures for the five different steels, shown in Figures 77-81, it can be seen that the scratch rides over or around the cementitic spheroids in almost every case, despite the difference in carbon content. (The photomicrographs shown in Figure 77 was taken from a .79-.80% carbon steel, Figure 78 from a .40% carbon steel, Figure 79 from eutectoid steel, Figure 80 from a .99% carbon steel, and Figure 81 from a 1.20% carbon steel.) There were a few cases where the scratch cut through the spheroid, but this was an exception. (See Figure 79) Undoubtedly, the cementite is a hard constituent; yet let us turn our attention to the steels when the cementite is in a laminated condition.

Figure 82 shows a scratch about the size of the lamellae it is cutting. Close examination reveals that the lamellae are bent in some cases, not all being cleanly cut. Such is contrary to current expectations. If the lamellae are brittle, protruding plates or rods, they would shatter when the fine point of the alumina grain comes in contact with it. In Figure 83, showing a .77-.80% carbon steel, the cementitic lamillae did not crack or shatter, but were bent downward. Likewise in both the .99% carbon steel (Figure 84) and the 1.20% carbon steel, (Figure 85) the lamellae were not shattered, cracked or ridden over,--they were bent. A constituent almost as brittle as glass bent through a 45 to 90° angle! More startling than that is the fact that the scratch while ploughing thru the cementite in pearlitic areas, rode over the cementite in the grain boundaries of the high carbon steel (Figure 85). This same variation between the cementite in the grain boundaries and the pearlitic areas was noticed in the low carbon steel.

Evidently the hardness of cementite must vary.

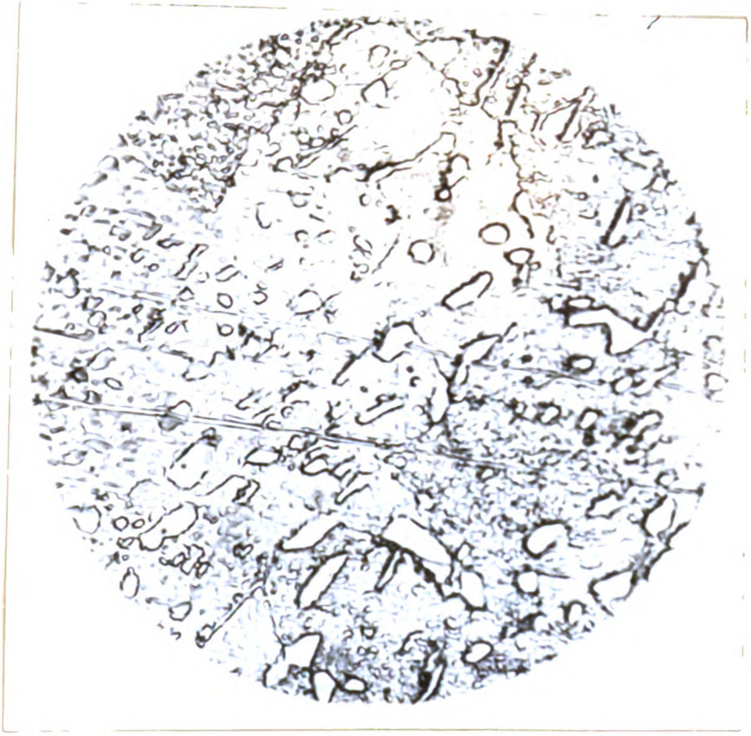
With a large difference existing between the cementite in the grain

Fig. 77

Mag. 1905 X

Fig. 78

Mag. 1905 X



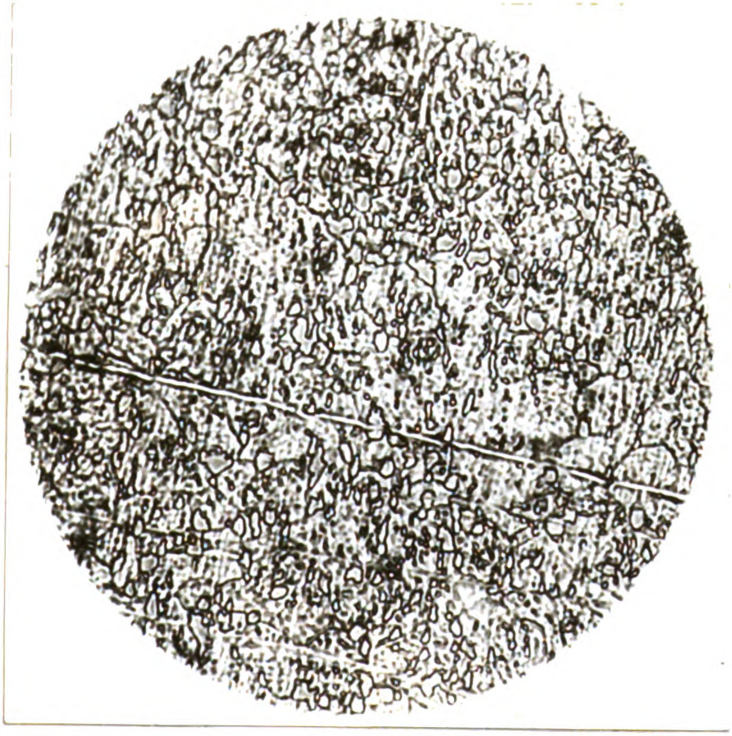
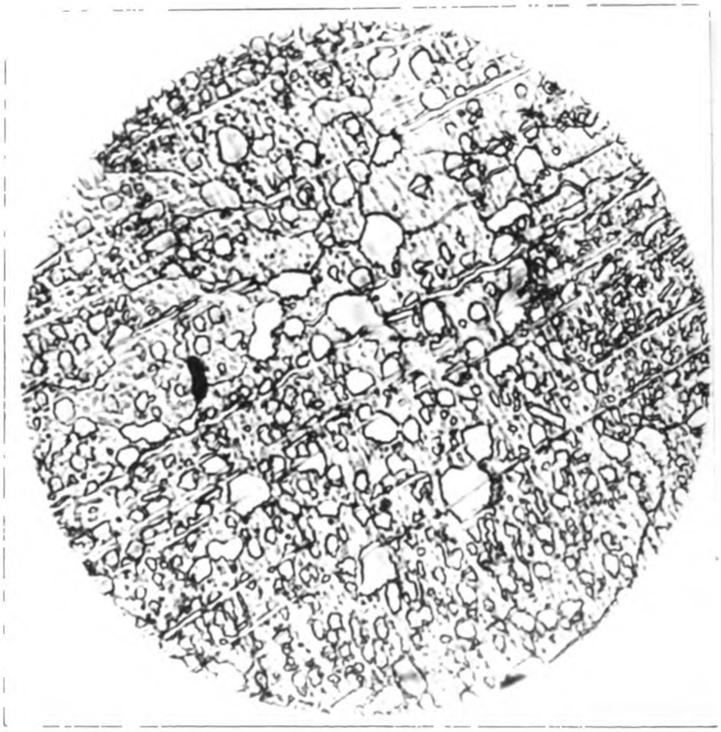


Fig. 79

Mag. 1905 X

Fig. 80

Mag. 1905 X



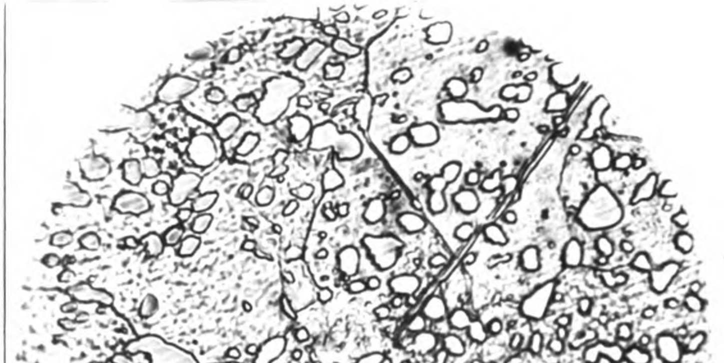


Fig. 81

Mag. 1905 X

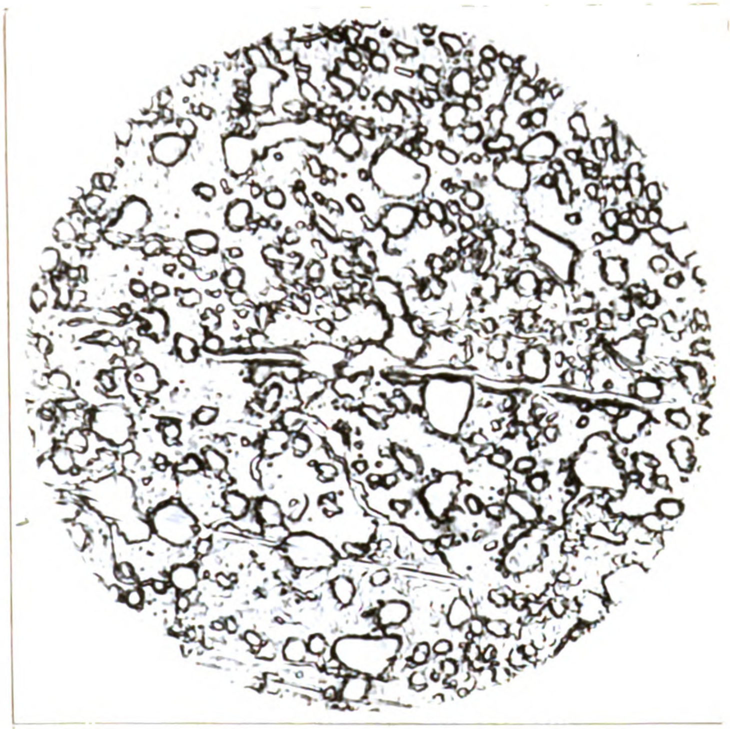


Fig. 82

Mag. 1905 X

Fig. 83

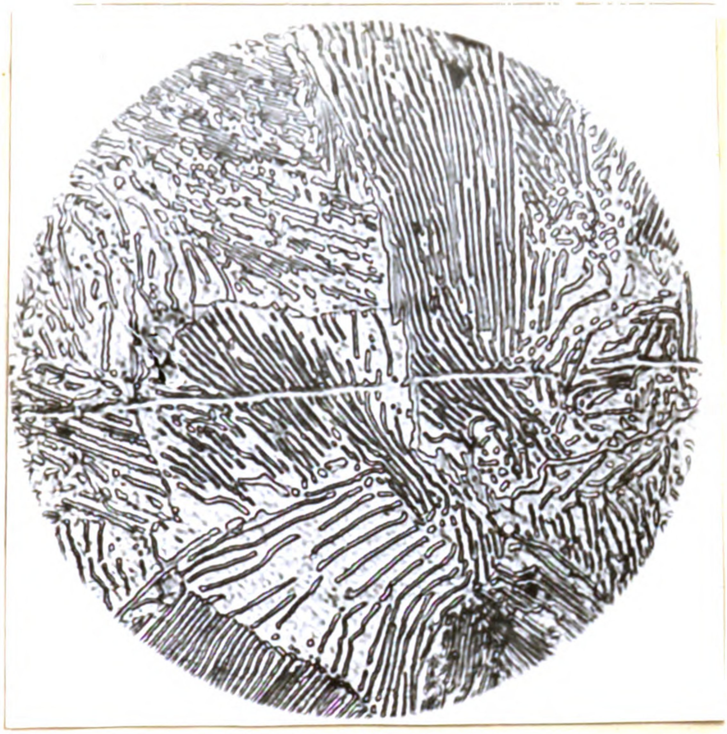
Mag. 1905 X

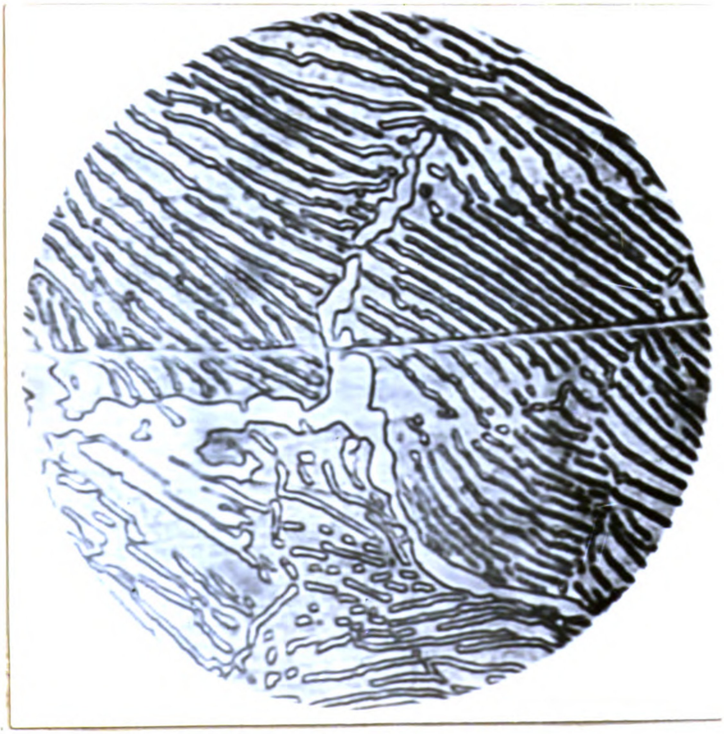
Fig. 84

Mag. 1905 X

Fig. 85

Mag. 2980 X





boundaries and that in the pearlite, there must be some noticeable effect upon the ductile properties of steels depending upon the location of the cementite. In order to determine the exact effect these cementite formations have upon the ductility of low carbon steel, specimens of 5 inch round, .20% carbon, cold rolled steel were prepared in the regular manner for the Izod impact tests. All the pieces were heated in the furnace to 1850°F for one hour. They were then cooled to 1675°F. Series B was cooled rapidly through the A_{r3}-Ar_1 range, but slow enough to obtain pearlite. Series A was cooled slowly through the same range taking at least two hours to cool to 1175, cooled in the furnace to room temperature. A_2 and B_2 were then heated to 1260°F and held for one hour, after which they were water quenched. A_2 and D_2 were heated to 1260°F for one hour and water quenched again. Impact tests were then made following a microscopical examination. The results are shown in Table V.

SUMMARY OF EXPERIMENTAL FACTS

TABLE V

Izod Impact values		Rockwell Hardness No. "B" Scale
A_1	26.5	69.6
B_1	46	78.6
A_2	44	77
B_2	47	77.6

1. The size of the pearlitic areas increases with the time consumed upon passing through the critical ranges $A_{r1} - A_{r3}$.
2. The formation of the cementite and the cementite in the grain boundaries between the pearlitic areas is related to the speed with which the piece passes through the critical ranges.
3. The amount of cementitic precipitation at the grain boundaries surrounding the ferrite grain increases with the time consummed upon

passing through the transformation range.

4. The hardness of very slowly cooled steel can be made to increase by heating to a point just below the lower critical and quenching.
5. Continued heating at a point below the lower critical decreases the hardening qualities slightly, following a quench.
6. There are spheroids of cementite precipitated in the grain boundary of low carbon spheroidal steel.
7. The readiness with which cementite (temperature at a point just below the lower critical) migrates to the grain boundaries in the presence of alpha iron is governed by the amount of carbon present.
8. The hardness of cementite varies. This variation is most noticeable between the cementite in grain boundaries and that in the pearlitic areas.
9. That brittleness of a sample cooled rapidly (slow enough to form pearlite) through the critical range is less than one cooled very slowly.

DISCUSSION

Undoubtedly an explanation should be forthcoming. Yet the auther hesitates to depart radically from the generally accepted theories to expalin the facts found in the expermental work. In so far as possible, concurrent theories predominating at the present will be used as a basis. However, the facts for the most part are in themselves radical. Not that they are new; rather they have been over-looked or assumed in the past. In order to explain them it will be necessary to deviate from the general thought a little.

At the outset cognizance is made of the idea advanced by some, that the structure obtained by etching is not the true structure. Those who advance this theory believe that the structure obtained by etching is the result of a chemical action which might indeed justify their conclusions. However, since the same basic structures should give the same final structure with the same etch, and since the work presented here maybe compared with the past, the theoretical idea that the structures viewed are not the true structures will be set aside.

Perhaps in considering a possible explanation for the formation of the cementitic film, it might be well to review briefly the phenomena, as it is generally understood, that takes place as a specimen of steel is slowly cooled.

Above the upper critical, hypoeutectoid steel consists of austenite, generally regarded as a solid solution of carbon or iron carbide in gamma iron, which is crystalline in nature. At a sufficiently high temperature (1850°F as was used in the experiment) the austenite grains will be homogenious, altho the composition may vary from grain to grain. As the temperature is lowered to below the upper critical, alpha iron begins to form. This newly formed ferrite has a certain amount of cementite retained mechanically within it, which since it is more soluble, in gamma iron, migrates upon slow cooling from the alpha iron. It is believed that above the lower critical cementite is soluble in alpha iron to a certain extent, so that not all the cementite will pass over to the austenite. At any definate temperature equilibrium is quickly established between the cementite in gamma iron and that in the alpha iron. As the temperature is lowered more alpha ferrite is formed which will leave a smaller amount of gamma ferrite. Necessarily because the carbide is more soluble in gamma iron, it will become increasingly rich in the carbide as the temperature is lowered. However, if equilibrium is to be established at a lower temperature, assuming that the partition constant to remain constant, then more and more carbide will be contained in the alpha ferrite. Finally, a point will be reached where the ferrite becomes supersaturated and small carbide particles will commence to

precipitate from the solution. (The solubility of iron carbid in alpha ferrite is never great and must become increasingly less as the temperature is lowered.) According to J. H. Whitely*, this precipitation will occur in the regions of A_{r1}.

Before reaching the lower critical the effect of various cooling rates upon the formation of alpha ferrite should be considered. In this discussion the cooling rate is never considered as being rapid enough to form any other structure than normal pearlite. The work of H. C. H. Carpenter and J. M. Robertson throws some light upon this point*. Upon slow cooling, alpha ferrite startes to precipitate at the grain boundaries. Not entirely around the austenite grain at once, for due to physical differences, heat is not radiated equally. Once the precipitation has started the formation of the alpha ferrite crystal increases in size as in the formation of crystals from liquid solution upon cooling over a long period of time. As the rate of cooling is increased the formation of alpha ferrite takes place at more numerous centers, thus giving rise to smaller crystals. If the speed is increased still further, ferrite can be found to form in the austenitic areas, tending to break it up. This viewpoint opens up an explanation of the plate-like formations of cementite, for according to Carpenter and Robertson, "large masses of residual austenite always transforms to pearlite, but small films may, under certain conditions, give rise to cementite. This is formed when the particles of residual austentite are very thin. Under these conditions, all the carbon in the austenite transforms to the plate of cementite and the ferrite adds itself to the existing crystals."

*1 Coalescence of Pearlite, Journal Iron and Steel Institution No. 2, pp. 147, Sept. '29.

*2 Formation of Ferrite from Austenite, Journal of Institute of Iron & Steel, No. 1, pp. 363, '31.

"For the formation of cementitic films , however, it is necessary for all the carbon in the particles of residual austenite to form cementite about one center. This requires time for the necessary diffusion to take place, and the faster cooling the greater the tendency for the cementite to form at a number of points, thus giving pearlite."

Undoubtedly for such an explanation of cementitic films, the conditions are narrow, for the rate of cooling must be rapid enough to cause the splitting up of the austenite grain and it must be slow enough to provide for diffusion to take place. From their work it is apparent that they did not consider the formation of a fine cementitic film around the ferrite grain. Nor did they consider the effect of passing thru the A_{r_1} upon the formation of the film.

To continue the discussion, at a point just above the lower critical two phases exist in equilibrium, austenite and ferrite. Whether there is a distinct boundary seperating the two is a Moot question. Theory and some evidence would indicate that there is, altho to the present time no proof of its existence has been made in every case. It remains for better technique or better equipment to answer this question. At the A_{r_1} the austenite remaining changes to pearlite. This change according to J. H. Whitely* takes place over a range of temperatures. The initial pearlitic formation takes place at the grain boundary when cementite starts to precipitate there. (Figure 7) The cause for such a precipitation may be due to inoculation of the supersaturated solution of gamma ferrite with minute cementitic particles precipitated from the surrounding supersaturated solution of alpha ferrite or it may be due to nuclei of impurities situated in the grain boundaries causing the precipitation. Following the theory advanced by Whitely, the alpha ferrite becomes supersaturated with carbide with respect to the cementite.

* Coalescence of Pearlite, Journal of Iron and Steel Institute, No. 2 pp. 147, September '29.

With the result that the carbide is precipitated on the lamillae of the pearlite at the expense of the gamma iron solution. With continued depostion of cementite upon very slow cooling there will be little chance for many new nuclei to form, thus explaining the difference in structures obtained (Figure's 8 & 9) upon continued slow cooling thru the transition stage. The margins of the lamillae meet and coalesce, and eventually, over a long enough peroid of time, the cementite would coalesce into a mass, which would account for the plate-like formation in the grain boundaries. The cementite in the grain boundaries between the pearlitic areas can be accounted for by either the precipitation at the grain boundary of a cementitic section which later developed, the usual lamenated extensions at either end; or by the growth in the grain boundary after the pearlitic area has developed and the margins have begun to form. Since the prominant structures have been found in specimens that have cooled rapidly, it is assumed that the former view is correct. Such an assumption does not obliterate the possibility that the latter may take place in slowly cooled steels.

Stead offers another similar explanation for the large plates of cementite which form in the grain boundaries. In describing the effect he states, "the series of knob-like extremities were not there when they came out of solution, and only became bulbous by coalescence and segregation at some temperature below the critical point. Had favorable conditions for the movement been allowed to continue for a much longer time, the lamenations would have segregated to such a thickness that they would have joined together to form a solid enveloping ring of massive cementite and possible segregated into a large mass."*

To the present time most men in this field have turned their attention to the cementitic segregation and inter-pearlitic formations which have

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* Journal of the Society of Chemical Industry, 1903 Volume XXXII

already been discussed. E. A. Atkins* was one of the first to notice the formation of cementite around the grains of ferrite. He first noticed this thru his work done on wire drawing. Altho the exact cause for the phenomena was not exactly clear to him, it seems as if the "cementite segregates formed after annealing (cold drawn wire) always shows up at the grain boundary." According to him he concluded that, "the formation of cementite in mild steel appears to be due to the change in grain size taking place below the lower critical point Ac_1 -- as the pearlite from which the cementite is formed is in an elongated form, it must therefore have travelled by a process of solid diffusion to the reformed ferrite boundaries. The cementite appears to accumulate at these points, and segregate as films partially surrounding the grains owing to the fact that the condition of temperature necessary for eutectoid formation are not present." His concluding statement would seem to indicate his further belief that the formation of cementite in the grain boundaries is in some manner connected with a change in grain size. "The slow heating and cooling associated with pot annealing is particularly favorable for changes in grain sizes, and, even if the temperature obtained exceeds the A_{r1} point and pearlite seperates, the subsequent slow cooling is often sufficient to cause alterations in grain size and formation of cementite."

Later, in the same year, Whitley published a paper, innocent of Atkin's work, indicating the formation of cementite in the grain boundaries.*2 To illustrate his point, a sample was cooled slowly from elevated temperature to room temperature; reheated to 1260°F, held for one hour and quenched in water; the piece was again reheated to 1260°F, held for one hour and quenched again. Upon examination of the last piece, according to him, spheroids of

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* Journal of Iron & Steel Institute, No. 1, p 443, 1927

*2 Journal of Iron & Steel Institute, No. 2, 1927

cementite appeared in the grain boundaries while there had been none in the first sample. He explained this by saying that upon heating to 1260°F the carbon by rapid migration proceeded to go to the grain boundary where it appeared as spheroids.

The work of both these men has thrown a great deal of light upon the precipitation of cementite in the grain boundaries. However, it is the author's belief that certain points have been overlooked which are necessary for a clearer understanding of the problem. Before considering these let us turn our attention to the solubility of cementite in the alpha ferrite. Indeed the previous theoretical discussion would lead one to conclude that, on slow cooling at least, alpha ferrite may contain some cementite in solution below the A_{r1}. To what temperature the carbon is soluble in alpha ferrite, is still ill-defined. However, experimental work done recently may clarify the point a little and at least indicate the solubility of carbon in ferrite. Sauveur stated in 1925,[1] that in ordinary steels alpha ferrite contained as much as .06% carbon in solution. During the same year [illegible] published a paper[2] indicating that between .04 to .05% was present. Two years later Tamura published an account of his work[3] indicating that alpha ferrite contained .034% carbon in alpha at the A_1 point. Whitley verified this the same year by stating that he had found from his experiments, that a slow cooled specimen contained only .01% cementite in solution. Upon heating there was very little change until a temperature of 6 30°C was reached at which point a little more was dissolved. At 720° C, the amount of cementite that was taken into solution reached .03%

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[1] Journal of Iron & Steel Institute, 1925, No.2, P 313

[2] "The Physical Chemistry of Steel Making Processes", Transactions of the Farady Society, 1925 Vol. XXI P 272

[3] Journal of Iron & Steel Institute, No.1, 1927 P 747

With this in mind it is reasonable to suppose the carbon becoming less soluble upon slowly cooling is precipitated at the grain boundaries as seen in Figures 10 and 11. Evidently this precipitation takes place slowly for in the specimen cooled more rapidly than that referred to above, but slow enough to obtain pearlite, there was no appreciable amount of cementite to be found in the grain boundaries. (Figure 12) Moreover, assuming the general accepted theory to be true, taht a fine dispersion of cementite increases the hardness, we are led to believe upon examining the hardness values presented in Table I, that carbide particles in the more rapidly slow cooled pieces are mechanically held in the ferrite grains. As if to verify further, it was noticed after reheating to 1260°F, holding for an hour and quenching, that the hardness of the piece equalled that of the more rapidly slow cooled piece. Evidently carbide particles redissolved into the ferrite and were held in the ferrite grains. Peculiarly enough, there did not seem to be much change in the size of the grain boundaries. (Figures 10, 11, and 13) Yet there was a marked decrease in margins surrounding the pearlitic areas, which would indicate that the carbide came from there. The reason for a preferential dissolving of the cementite from the pearlitic areas is unanswerable for no further experimentation was carried out along this line. It is entirely possible that a phenomena of equalization was taking place between the cementite in the pearlitic areas and that in the grain boundaries. A discussion a little latter should make plain the reason for this belief.

Reheating after the first quench should favor the precipitation of the cementite particles. However, the physical nature of the ferrite grains would act as an obstructing agent at low temperatures. As the temperature increased it has been indicated that the solubility increased, a marked effect taking place in the neighborhood of 6 30°F. This would account, theoretically, at least, for a precipitation of the particles at the grain

boundaries if the specimen is held for a long period of time below 6 30°C (1150°F). However, an ordinary heat to 1260°F would not permit such a phenomena to take place. The alpha ferrite would become fairly well saturated with carbide, but no appreciable precipitation would take place. The effect of such a treatment upon the cementite in both the pearlitic areas and the grain boundaries would be to cause coalescence. (Figure 15) In the light of this it would be expected that there would be little or no spherodizing in the fine grain boundaries of the rapidly cooled piece in such a short space of time, because of the small amount of cementite present. With sufficient time at a temperature below A_{r_1}, the amount of cementite in the grain boundaries will increase because migration by means of the saturated alpha solution will take place between the pearlitic areas and the grain boundaries. This is born out by observation. Upon continued heating just below the critical there is a slow migration of cementite from pearlite to the grain boundaries. Undoubtedly, the first formations to appear are spheroids but with a longer heat treatment the boundaries fill out as in Figure 59.

Atkins, as stated previously, indicated the formation of cementite in the grain boundaries of cold drawn wire after annealing for long periods of time. Although he did not know exactly what to attribute the cause, believing that it was connected in some manner to a change in grain size, he recognized the formation. Considering the formations in the light of the foregoing discussion it must have been due to precipitation phenomena following a long annealing and cooling process.

J. H. Whitely on the other hand indicated that the cementite formed in the grain boundaries as spheroids. He recognized the fact that cementite is soluble in alpha ferrite as his previous statements would indicate. Apparently he overlooked the fact that upon slow cooling, cementite dissolved in the alpha ferrite, may be precipitated at the grain boundaries, altho he admits he has found that the solubility of cementite in alpha iron at 720°C (1328°F) is .03%, while in a slow cooled specimen it is .01%. The result is that he is faced with the task, for which he has been severly criticized, of contending that at one time alpha ferrite at a point just below the lower critical will dissolve cementite and at another precipitate it. Further, to back up this contenetion he reaches the conclusion that the carbon or carbide particles are able to diffuse at a rapid rate through the alpha iron without passing into solution. It is entirely possible that cementite particles in the pearlitic area may pass to the grain boundaries by going into solution as clearly demonstrated by the previous experiment illustrating the effect of a long heat treatment upon low carbon steel, but this cannot be accomplished in a shor t time. Evidently he is aware of this and unfortunately resorts to the seemingly impossible explanations to fit in a few of his facts.

Considering the time necessary to spherodize a sample, it is not surprizing to find cementite in the grain boundaries of low carbon steels upon etching, In considering some working explanation it must be remembered that the amount of the two constituents have a marked effect upon the formation of the grain boundaries. At the outset, after air quenching, it is assumed that the cementite is well distributed throughout the individual grain. Quite natually it is to be expected also that, following the rapid cool, as in the case of the rapid slow cool, the ferrite is saturated with cementite. Heating the specimen at a point just below the lower critical would not faver the dissolving of any more cementite in the saturated ferrite. However, it does promote deposition and coalescence between the nuclei scattered in the grain boundaries and the grains. After continued heating, spheroids begin to appear. From the work carried out precipitation does not apparently occur along the grain boundaries until after the spheroids have been well formed. The equiblibrium between the carbide nuclei in the ferrite and the pearlite is undoubtedly suseptiable to reajustment upon reheating to a temperature below A_{r_1} that will allow such a process to take place. Carbon is deposited upon nuclei in certain localities from the ferrite solution. This enables the solution to take up more carbide at the expense of the smaller nuclei.

With time the forces of the two components, cementite and ferrite, show a decided effect. In what manner this takes place, the writer is admitedly at a loss to explain. Yet from experiments it is evident that with increasingly larger amounts of carbon up to the eutectoid ratio, the constituents tend to balance each other. This is brought to attention, markedly by etching a sample of eutectoid steel subjected to a spherodising treatment for 238 hours, a peroid of time in which under the same conditions, the cementite of a .20% carbon steel was precipitated entirely at the grain boundaries. (Figures 74 & 75) After a deep etch, a fine localised condition which apparently was a grain boundary was noticed. To be sure there was a localised stringing out of the cementite particles (Figures 72 & 73) yet it had not reached the proportions that it might be considered to envelope a grain of ferrite. With a lowering of the carbon content the carbide is apparently forced to the grain boundary as if the mass action of the excessive ferrite was to "squeeze" the cementite to the grain boundaries. Some investigators believe that it is a matter of surface tension that causes the formation of cementite at the grain boundary. Whatever the force is that causes carbide to precipitate at the boundary, we may assume that the migration takes place at the expense of the spheroids, similar to the migration from nuclei to nuclei.

If cementite is a definite compound expressed by the formula Fe_3C, then an explanation of a difference in hardness obtained in the experiment, becomes an impossibility. On the other hand, if the basis for assuming that the formula Fe_3C is weak then perhaps another line of reasoning is opened. Indeed, such seems to be the case. In 1885 Cloëx[1] described the recovery of pure carbide and following mathematical calculations based upon the per cent carbon and ferrite present, he concluded the constituent carbide to have the formula Fe_3C. However, E. D. Campbell indicated by chemical analysis that there was more than one carbide present in plain carbon steel. He even went so far as to indicate that in annealed steel the mean molecular weight of the hydrocarbons evolved, hence, presummably of the carbides from which the hydrocarbons are devived decreases as the percentage of carbon increases; that carbides existing in hypereuctectoid steel have a greater molecular weight than those in the hypeutictoid, and that in a given steel the mean molecular weight of hardened steel is lower for the same steel annealed. There are many metallurgists who never took kindly to Campbell's findings. Some believe that hydrocarbons are not indicators of chemical combinations, but of a physical relationship. Rejecting the idea that cementite is a definite compound Fe_3C, two methods of explanation are available; first, that cementite consists of varying numbers of carbides and secondly, that cementite is a solid solution.

Should cementite consist of varying amounts of carbides, then two angles of approach are available. The one would hinge around the idea advanced by Jefferies[2] that in austenite, carbon exists as a free atom in gamma iron. As carbon steel austenite cools slowly from above the critical temperature range, it transforms into alpha iron and the iron carbide. The carbide is supposed to form from the atoms of carbon and the atoms of iron after changing from gamma to the alpha state. The formations

[1] Journal of Iron & Steel Institute 1914

[2] Transaction by ie SST. March 1928

and crystallization undoubtedly takes place simultaneously. Yet suppose more than carbide is formed. It is reasonable that upon formation, coincident with diffusion of the carbon atom, that it would be precipitated. If, on the other hand, the carbides existed in the austentic condition as molecules, they would also be precipitated upon reformation following the transformation from gamma to alpha iron. This would account for a difference in hardness, but upon closer inspection, especially in the hypereutectoid steels, it becomes a very weak explanation. As the upper critical was passed upon cooling in high carbon steels, cementite was precipitated out of solution. As the temperature was lowered still further, more cementite was precipitated from the solution. This action necessarily becomes a straight line function of the temperature. To date general observation of the formation of cementite in the grain boundaries seems to bear this out. Yet at this point the idea of the formation of several carbides becomes untenable. If the carbides are already formed, their precipitation would follow individual functions depending on each carbide. If they are graded in this respect, their composit result may produce an effect similar to that obtained if one carbide exists. However, this raises a great many objections which would make it desirable to abandon the idea. In the same manner it must be believed that a graded effect exists should the carbides be formed after they are thrown out of solution. As before the veracity of such an idea becomes doubtful. Until sufficient evidence would point to the conclusion that such a gradional formation takes place, it too, should be held with mental reservations.

The solid solution theory, offers a little more sound explanation. To aide in this explanation a solid solution will be considered as being an association of substances, homogenous throughout, the proportions of

whose components can be altered gradually without the production of abrupt changes in the properties of the same. In such a solution, the exact arrangement of the carbon atom in respect to ferrite atoms is not definitely known. The general assumption is that the arrangement is a physical orientation of one or more carbon atoms in the space lattice of the system. Upon cooling below the upper critical the cementite, rich in carbon, would be precipitated (Hypereutectoid steel). Each successive precipitates becoming leaner in carbon until the lower critical was reached. The lamillae forming in the pearlite would necessarily be leaner than those found in the grain boundaries, thus supporting the experimental results.

Concerning the precipitation of cementite in low carbon steel, assuming cementite to be a solid solution, it may be said that the same process takes place as in the higher carbon steel. It is to be expected that a reajustment of the carbides in both the gamma iron and the alpha ferrite takes place continually upon cooling through the transformation ranges. Cementite rich in carbon will, after all the austenite has transformed, tend to be situated in the alpha ferrite. Necessarily this precipitate in the grain boundaries will be a little harder than that in the lamellae. This is born out by observation which indicates the grain boundary is a little harder than the cementitic lamellae in the pearlite. Experimental evidence also supports the foregoing explanation, that the cementite in the pearlite (not reajusted) is of varying hardnesses.

Short Discussion of the First Paragraph, Ferrite Brittleness

Without a doubt a great deal of the ferrite brittleness found in steel can be traced to the effects of a long heat treatment just below the lower critical. This heat treatment as has been pointed out may consist of

a very slow cool through the range below the lower critical or a prolonged annealing operation below the lower critical. It has been assumed in the past that the slower the cooling operation or the longer the annealing operation, the less brittle the heat treated specimen will be. However, as has been shown, prolonged cooling or lengthy anneals below the lower critical promote the precipitation of cementite in the boundaries surrounding the ferrite grains. Consequently, with a disregard for exactness in heat the treatment below the lower critical, it is not to be wondered that, while identical heat treatments are given to heats of steel above the lower critical, they may very below the A_1 point. Therefore, if the heat treatment is finished at the lower critical, ferrite brittleness can be expected in different steels having the same composition and heat treatment. In any case, it may be concluded that more consideration must be given to the phenomena that occurs below the A_1 while heat treating.

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BIBLIOGRAPHY

Atikins, E. A.

The Drawing of Steel Wire and Its Relation to Qualities of Steel.

Journal Iron & Steel Institute 1927 No.I p443

Campbell, E. D.

Contribution to the Theory of Hardening and the Constitution of Steel.

Jounral Iron & Steel Institute 1914

Carpenter, H. C. H. & Robertson

Formation of Ferrite from Austenite

Journal Iron & Steel Institute 1931 No.III p35

Cleox

Comptes Rendus Vol.85 p1103

Hatfield

The Physical Chemistry of Steel Making Processes

Transactions of the Farady Society 1925 Vol. 21 p272

Howe, H. M.

The Metallurgy of Steel

N. Y. 1892

Howe, H. M. & Levy A. G.

The Life History of Pro Eutectoid Cementite

Proc. Int. Assoc. Testing Materials 2(13) II

Jefferies, Z.

A contribution tothe Theory of Hardening and the Constitution of Steel

Transaction by A. S. S.T. March 1928

Koster, W.

Influence of Heat Treatment below A_1 Point on the Properties of

Bib. con't.

Technical Iron

Arch. Ersenhuttenew 2, 503--22 (1928-29)

MacPherran, R. S. & Harper, J. F.

Spheroidized Cementite in Hyproectectoid Steel

Transactions of A.S.S.T. 6 341-74 (1924)

Sauveur, A.

The Austenitic-Pearlitic Transformation

A. S. S. T. 17 199 Feb. 1930

The Metallography and Heat Treatment of Iron & Steel

Cambridge, Mass. 1926

Dendertic Segration in Iron-carbon Alloys

Journal Iron & Steel Institute 1925 No. II P313

Stead, J. E.

The Segregatory or Migratory Habit of Solids in Alloys and in Steel Below the Critical Points.

Journal Society of Chem. Institute 1903 Vol. 22 p30

Tamaru, K.

The Hardness of Different Structures in Steel

Sci. Papers Inst. Phy. Chem. Research 5, 25-44 (1926)

Notes on Pseudo-Twinning in Ferrite and on the Solubility of Carbon in Alpha-iron at the A_1 point.

Journal Iron & Steel Inst. 1927 No. I p747

Walldow, E.

Investigation of the Mechanism of the Solution of Cementite in Carbon steels and the Influence of the Hetrogenity of the Metal

Journal Iron & Steel Inst. Sept. 1930

Solution of Cementite in Carbon Steel Engineering 131, 27-30 1931

Whitley, J. H.

The Solution of Cementite in Alpha Iron & its precipitation
J. Iron & Steel Institute. 1922 No.I p354

Whitley, J. H.

Globular Pearlite

Journal Iron and Steel Institute 1922 No.I p339

Coalescence of Pearlite

Journal Iron & Steel Inst. No.II p147 Sept. '29

Diffusion of Cementite

Journal Iron & Steel Institute 1927 NoII p293