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SOME UNUSUAL FEATURES IN THE MICROSTRUCTURE OF WROUGHT IRON

BY

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Bureau of Standards

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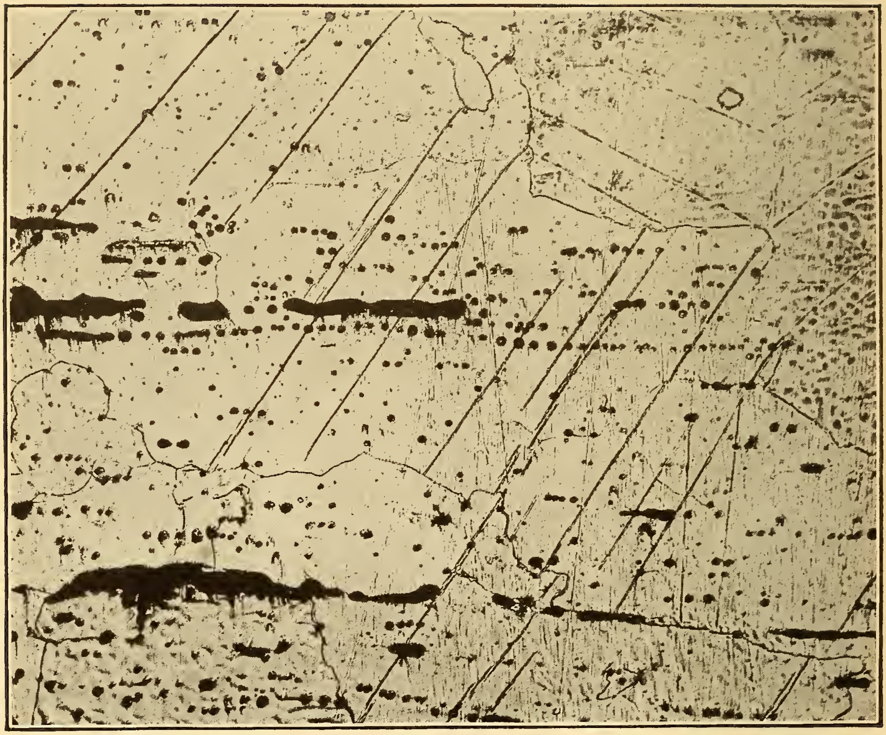

FIG. 1.—*Unusual features in the microstructure of wrought iron*

The dark lines, parallel within any single grain, are the Neumann lines. The mottled appearance of the corner grains indicates the nonhomogeneity of the ferrite due to the unequal distribution of the phosphorus. Specimen: W 1, longitudinal section. Magnification, 100; etching, 10 per cent alcoholic nitric acid.

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By Henry S. Rawdon

CONTENTS

I. INTRODUCTION

The structure of wrought iron as usually described by metallographists and workers in metal is that of a fairly pure iron. Impurities, if present, are usually considered as being in solid solution in the crystals of the ferrite matrix or as forming part of the ever present "slag streaks." Attention is herein directed to one type of these dissolved impurities, to the detection of such impurities, particularly in low-grade irons, and to their possible influence on the physical properties of the metal. The attention of this Bureau was first called to wrought iron of the peculiar and unusual characteristics to be described later, in material which had failed in service and which was submitted for test. The examination was extended to other grades of wrought iron to see whether such features are of common occurrence in this class of material.

II. MICROSTRUCTURE OF WROUGHT IRON

1. USUAL STRUCTURE

The general microstructure of wrought iron is so well known that a detailed description of it here is needless. However, for purposes of reference and comparison, there is shown in Fig. 2*a* the structure of a sample of Swedish iron. This shows the matrix of ferrite crystals in which are embedded the slag threads so characteristic of the puddling process and the subsequent working of the material. The usual commercial product contains varying amounts of the impurities commonly associated with iron and steel, i. e., manganese, phosphorus, silicon, and sulphur, together with small amounts of carbon. Of these, the larger part of the phosphorus and some of the silicon present are held in solid solution in the ferrite, while most of the remaining impurities, other than carbon, exist in the inclosures of slag. Aside from the discontinuities introduced by the slag streaks, the ferrite matrix has the microstructure and appearance of a pure metal. No definite orientation of the various crystals, or grains, is apparent; deep etching of the specimens reveals no intracrystalline (i. e., within the grains) features other than those noted in "pure" metals in general, e. g., etching pits.

2. UNUSUAL FEATURES

The unusual features noted may be best illustrated by a brief description of the structure of the specimen in which they were first observed in abundance. This piece was a wrought-iron eyebar, a tension member of a railway bridge, which after about 30 years of service was modified to suit the increased traffic, after which modification the member failed. The microscopic examination of the metal revealed, in addition to the usual structure of wrought iron, several features so striking as to mark the sample at once as a wrought iron of very unusual properties and composition.

The ferrite crystals presented a peculiar mottled appearance, particularly after prolonged etching with an acid reagent. This etch pattern was not found over the entire surface of the specimen, but was restricted to certain streaks throughout the metal. Particularly was it found associated with crystals unusually large in size. (Fig. 4*a*.) A series of measurements upon those portions of the material in which such etch patterns were developed in abundance showed the crystals to be as large as 0.25 mm by 2 mm. A similar set of measurements upon the crystals of the material of Fig. 2*a* showed the average size to be 0.144 mm by 0.133 mm. The latter set of measurements may be taken as quite characteristic of the grain size of good grades of wrought iron.

The etch pattern referred to above is illustrated in Figs. 1, 2*b*, 3, and 4. By using the copper-chloride etching reagent referred to later (p. 14) these patterns may be developed in a very striking manner. They sometimes consist of broad parallel bands, as seen in cross section, extending across the elongated crystals (Fig. 2*b*) and bearing some resemblance to twinned crystals. More often they present an indefinite mottled appearance of light and dark areas, very similar to the shadows cast by the sunlight streaming through between the leaves of a tree. (Figs. 1 and 3*b*.) The crystals of ordinary wrought iron will not exhibit such etch patterns even after very prolonged etching.

The examination of the metal close up to the fracture which occurred during the service of the material shows that the break occurred through the crystals and parallel to the markings constituting the mottled etch pattern at that point. (Fig. 12*a*.) Many of the crystals close to the face of the fracture show another variety of intracrystalline markings. On casual examination these may be mistaken for scratches left by poor polishing of the material. (Fig. 1.) Closer inspection, however, shows that these markings are parallel to one another within any one crystal and terminate very abruptly at the crystal boundaries. If a slag inclosure lies in the course of one of these markings, the line ends abruptly, reappearing on the other side of the "slag," thus indicating clearly that it is not a scratch. In some crystals a second set, usually not so well developed as the primary ones, is seen. The lines comprising this second set are parallel to one another but form a definite angle with those of the first. Crystals showing markings of this general character in considerable numbers usually present a smoother surface and show less of the shadow-like etch pattern described above than do those crystals in which markings of this class do not occur.

The obvious conclusion is that the nonhomogeneity of the individual crystals as indicated by the mottled etch pattern is to be attributed to some impurity dissolved in the iron but not uniformly diffused throughout the crystal. Robin [1] has called attention to the fact that in ferrite containing considerable phosphorus, e. g., 1 per cent, such a nonhomogeneity may exist. Stead,[2] in his extensive studies of the segregation of phosphorus in iron and steel, makes but very slight reference to this type of intracrystalline variation of structure, which Robin attributes to the nonuniform distribution of phosphorus in the ferrite which forms the body of the crystal. Saklatwalla [3] states that the alloys of iron

[1] Robin, Traité de Metallographie, p. 184.

[2] Jour. Iron and Steel Inst., 140, p. 140; 1915. Stead here summarizes his previous work and gives an extended bibliography of the literature on phosphorus in iron.

[3] Metallurgie, 5, pp. 336, 711; 1908.

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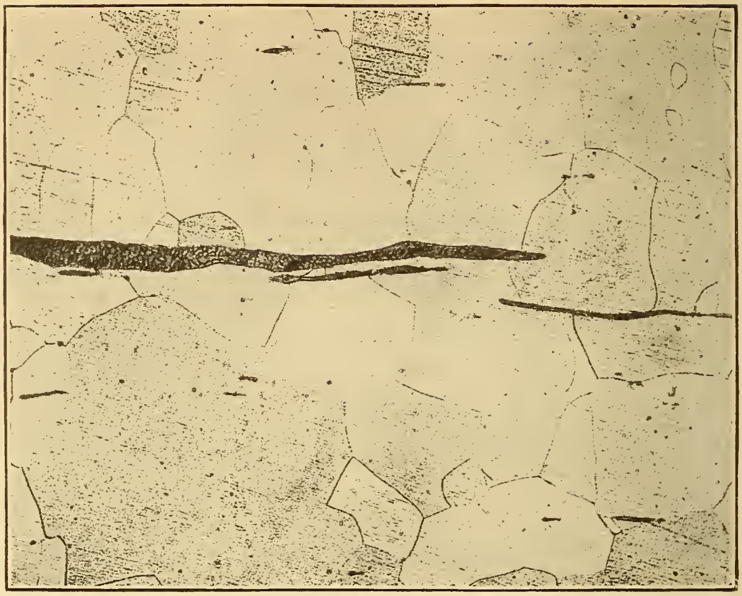

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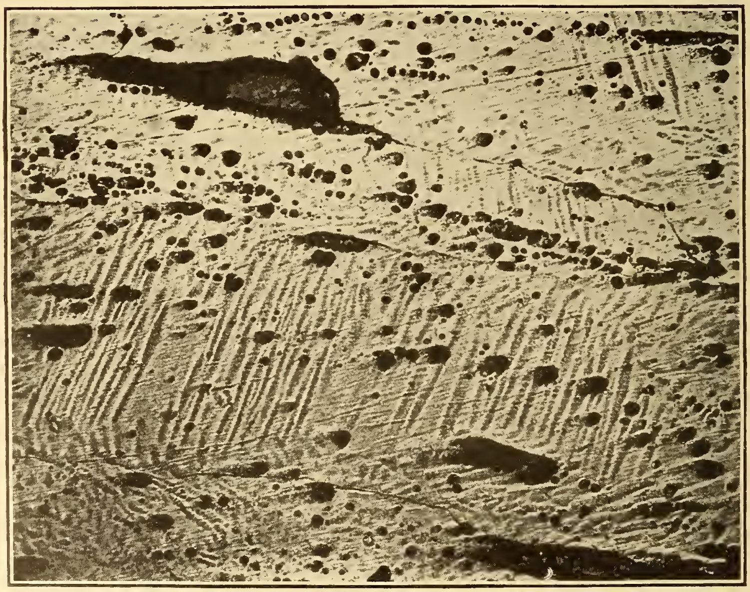

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FIG. 2.—*Usual and unusual microstructure of wrought iron*

(*a*) Microstructure of a longitudinal section of Swedish iron. Magnification, 100; etching, 2 per cent nitric acid.

(*b*) Longitudinal section of specimen W 1, showing the mottled etch pattern occurring as parallel transverse bands within the grains. Magnification, 100; etching, 10 per cent nitric acid.

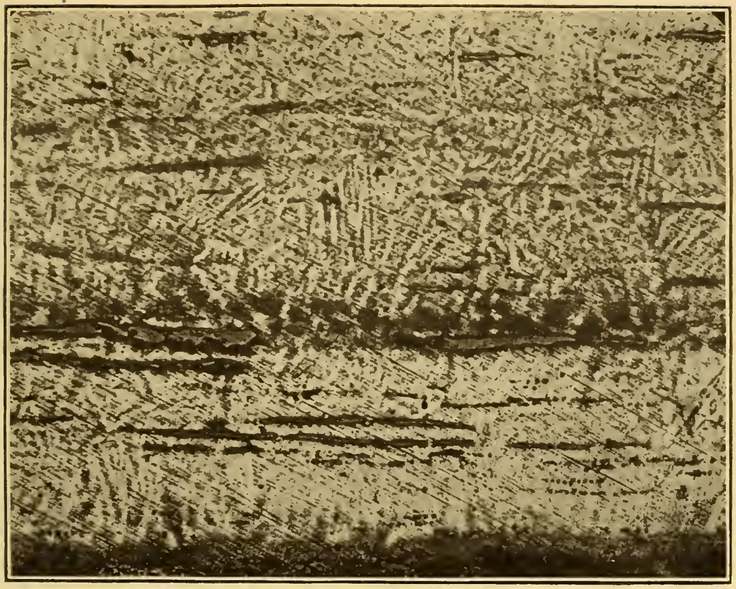

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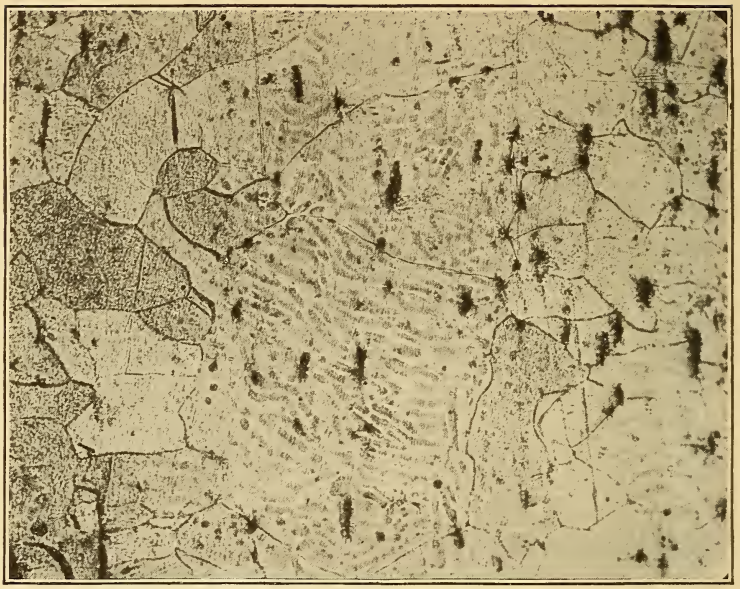
FIG. 3.—*Unusual microstructural features of wrought iron*

(*a*) Specimen W 5, wrought-iron pipe, longitudinal section.
(*b*) Specimen W 4, wrought-iron pipe, longitudinal section.
Etching, alcoholic copper chloride acidulated with hydrochloric acid (Stead's reagent). Magnification 100. The portions shown are from the streaks upon which copper did not deposit.



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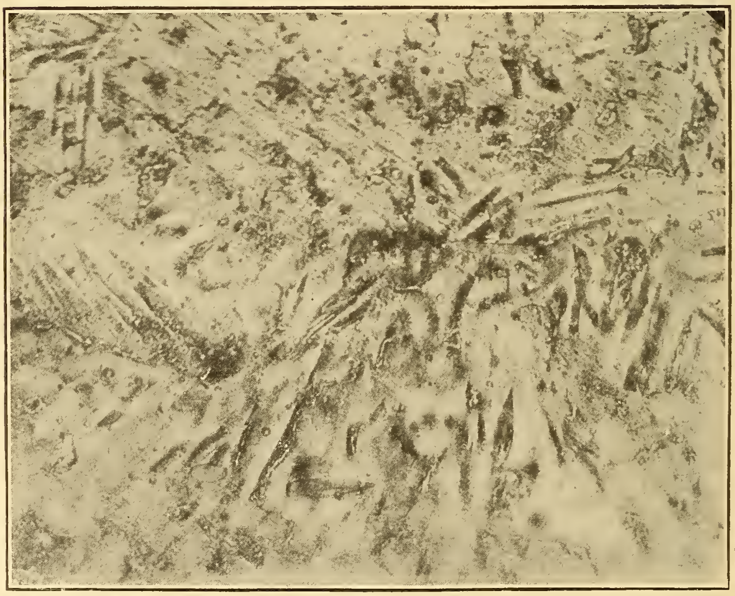

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FIG. 4.—*Unusual microstructural features of wrought iron*

(*a*) Specimen W 1, longitudinal section. The streaks exhibiting the unusual etch-pattern are very often composed of grains which are much larger than the average for the piece. Magnification, 100; etching, 10 per cent nitric acid.

(*b*) Specimen W 22, longitudinal section. Low-carbon steel sometimes exhibits a structure similar to the unusual features in wrought iron. Magnification, 500; etching, Stead's reagent.

and phosphorous are composed of a single constituent up to a concentration of 1.4 per cent of phosphorus, consisting of the solid solution of the phosphorus in the iron. Konstantinow's work [4] deals primarily with the alloys high in phosphorus, and those low in this element receive but scant attention.

III. MATERIALS EXAMINED

The variations from the usual microstructure of wrought iron, first noted in the wrought-iron bridge tension member which failed in service, appeared so striking and unusual in character and have been so meagerly described in the literature on the subject that the examination was extended to other grades of iron. From the accumulated series of wrought-iron specimens which have been submitted to the Bureau of Standards from time to time for examination there were chosen some 37 samples for detailed microscopic examination. Much of this material had been submitted as "unsatisfactory," and one of the purposes of the examination was to see whether such material is characterized by microstructural features similar to those noted above. In the following table are listed the materials used. The examination was made by means of Stead's method of etching,[5] making use of an alcoholic cupric-chloride solution acidulated with hydrochloric acid for etching, by which the segregation of phosphorus is shown by the differential precipitation of copper on the surface of the metal. The precipitation of copper on the areas relatively low in phosphorus is much heavier than on the portions of higher phosphorus content, so that the approximate distribution of this element is rendered visible to macroscopic examination. The "high" and "low" phosphorus streaks thus revealed were then examined microscopically to see whether the unusual mottled etch pattern ocurred in either.

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[4] Zeit. für anorg. Chemie, 66, p. 209; 1910.

[5] Loc. cit.

Description of the Materials Examined

Sample No.	Type of material	Macroscopic appearance after cupric-chloride etching	Microstructure [a]	Per cent of phosphorus
W 1	Wrought-iron eyebar, which failed in service.	No copper deposited, surface becomes brown.	Mottled etch pattern is very prominent over most of the surface.	0.356
W 2	Wrought-iron pipe	Copper deposited uniformly over surface.	No mottled areas seen. The metal is to be classed as steel rather than wrought iron.	
W 3	do	do	do	
W 4	do	Isolated streaks were copper coated; remainder, brown.	Very decided mottled structure in the brown streaks.	
W 5	do	Outer layers slightly copper coated, central ones slightly brown.	Mottled streaks very prominent in central portion.	[b] a, 0.13 [b] b, 0.20
W 6	do	No copper deposited, surface rather brown.	do	
W 7	do	No copper deposited, prominent brown streaks.	Mottled appearance across entire face of the section.	
W 8	do	No copper deposited, brown coloration of surface.	do	[b] a, 0.264 [b] b, 0.271
W 9	Wrought-iron "welding" wire.	Copper deposited over all the section.	No mottled areas seen	0.059
W 10	Wrought-iron (?) bar	do	No mottled areas seen; the material is really a low-carbon steel.	
W 11	Wrought-iron pipe	No copper deposited, central streaks very brown.	Mottled appearance of central streaks very conspicuous.	[b] a, 0.146 [b] b, 0.156
W 12	do	Copper precipitated on outer layers; brown streaks in central part.	No mottled areas found	0.123
W 13	Wrought-iron welding wire.	Uniform precipitation of copper over the section.	do	
W 14	do	Inconspicuous streaks in central portion, otherwise quite uniform precipitation of copper.	do	
W 15	do	do	do	
W 16	Wrought-iron pipe	No copper precipitated, dark central streaks.	Streaks showing the mottled structure abundant across the section.	.16
W 17	Wrought-iron stay bolt	Some light areas showing method of fagotting; precipitation of copper quite uniform.	Very slight trace only of mottled areas.	
W 18	do	do	do	
W 19	Wrought-iron welding wire.	Copper uniformly precipitated over surface.	No trace of mottled structure found.	

[a] Under "microstructure" the presence of streaks showing the mottled structure as illustrated by Figs. 2, 3, and 4 is noted and not a complete description of the microstructure.

[b] "a" indicates the entire cross section of the sample; "b" the central layer approximating 0.3 in W 5 and W 8 and 0.6 in W 11 of the entire cross section.

Description of the Materials Examined—Continued

Sample No.	Type of material	Macroscopic appearance after cupric-chloride etching	Microstructure	Per cent of phosphorus
W 20...	Wrought-iron boiler tube which corroded badly in service.	Copper uniformly precipitated over surface.	No trace of mottled structure found.	0.033
W 21...	.....do.....................	.....do.....................	.....do.....................	....
W 22...	Low-carbon steel pipe......	Central staeaks free from copper.	Mottled structure very evident in central layers.	....
W 23...	Wrought-iron "gooseneck"	Copper deposited quite uniformly over surface.	No mottled areas found; the metal resembles low-carbon steel rather than wrought iron.	.044
W 24...		About 0.7 copper-covered...		.055
W 25...		About 0.1 reddened by copper. Other portions show prominent brown streaks.		.136
W 26...		About 0.9 copper-covered..		.079
W 27...		About 0.7 copper-covered, with outer portion clear.		.059
W 28...		About 0.9 copper-covered..		.073
W 29...		Isolated copper-covered streaks aggregating 0.3 total area; other portions clear or brown.		.112
W 30...	Wrought-iron round stock for forging purposes, chains, etc. All but W 28 and W 34 were reported to give unsatisfactory results in the preliminary tests of the material.	Surface clear with brown streaks, with one small central copper-covered streak.	No mottled areas were found even in those showing but little precipitation of copper, except Nos. 29, 30, and 36, which show a slight trace.	.099
W 31...		Only a few narrow streaks are copper-colored, about 0.1 of area.		.115
W 32...		0.1 copper-covered, remainder clear with brown streaks.		.118
W 33...		One fine streak only, copper-coated, prominent dark streaks in remainder.		.125
W 34...		Less than 0.5 is copper-covered; brown streaks in the clear portion.		.115
W 35...		C.8 to 0.9 of area is copper-covered.		.066
W 35...		0.6 area copper-coated, brown streaks in remainder.		.089
W 37...	Link of wrought-iron chain which failed in service.	No copper deposited; surface was colored brown.	The mottled etch pattern is very prominent throughout.	.27

The results of the examination indicate that the unusual microstructure noted in the failed eyebar, while not to be regarded as a common feature of wrought iron or always associated with iron of inferior grade, is not unique for the single specimen in which it was first observed. It will be noted, however, that such features were found only in material, or portions of such material, which, according to Stead,[6] are to be regarded as relatively high in phosphorus. The results of the analyses for phosphorus of many of the samples examined are given in the preceding table.

IV. NATURE OF UNUSUAL FEATURES OBSERVED

1. COMPARISON WITH IRON-PHOSPHORUS ALLOYS

For purposes of comparison, to make certain that the unusual microstructure observed is indicative of a nonuniform distribution of phosphorus, a series of iron-phosphorus alloys was prepared. The phosphorus content ranged from 0.014 to 0.48 per cent for the series of six alloys which were made. The preparation of an alloy of so volatile an element as phosphorus offers some difficulties, and a brief description of the method employed will be of instructive interest. Electrolytic iron [7] which had been melted in vacuo was used. The iron was machined into cylinders approximately three-fourths inch in length and one-half inch in diameter. The center of the piece was bored out and threaded to receive a threaded plug turned out of the same stock. The desired amount of phosphorus of the yellow variety in the form of sticks was inserted into the cavity, the plug screwed into place, and the whole heated to the melting point of iron in an alundum crucible.

Fig. 6 shows the microstructure of an iron-phosphorus alloy thus prepared containing 0.37 per cent phosphorus. The metal, in solidifying, freezes selectively, i. e., the solid solution which separates first from the melt is relatively low in phosphorus, and the portions successively added are progressively richer in this element. A eutectic consisting of the solution of phosphorus in iron and iron-phosphide, analogous to pearlite in steel, formed out of the portion which solidified last of all. The alloys containing amounts of phosphorus lower than 0.37 per cent showed the same general structure as Fig. 6, minus the eutectic.

The equilibrium diagram based on Konstantinow's work[8] is shown in Fig. 5. According to this, phosphorus is soluble in

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[6] Loc. cit.

[7] Cain, Schramm, and Cleaves, Bureau of Standards Scientific Paper No. 266. Iron prepared as here described was used.

[8] Loc. cit.

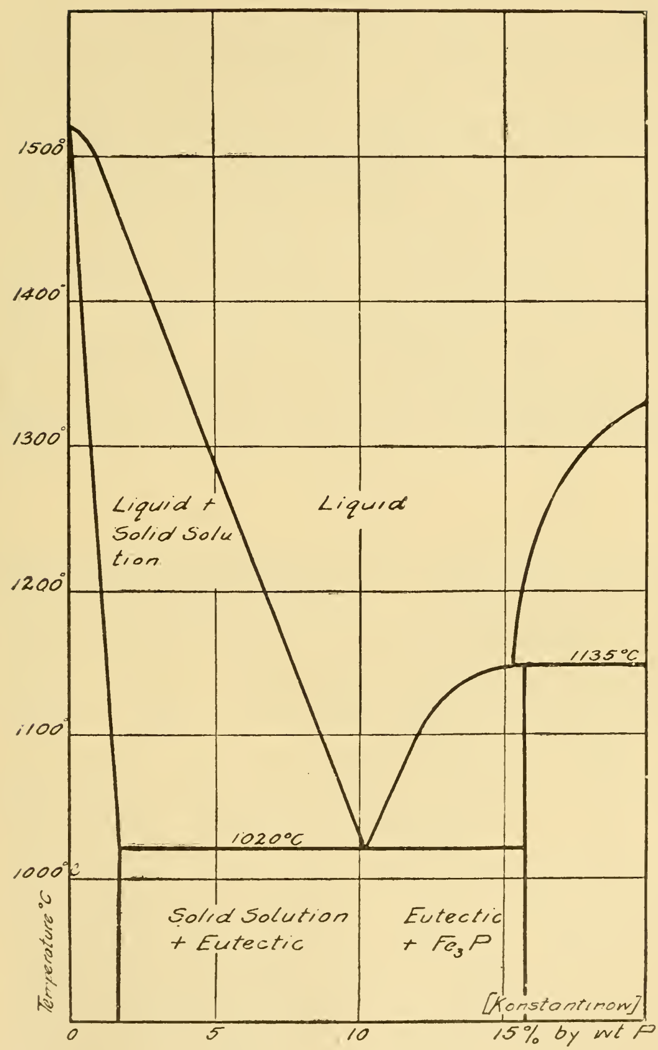


FIG. 5.—*Portion of the constitutional diagram of the iron-phosphorus alloys*

iron up to about 1.7 per cent, when the system is in equilibrium. Two of the alloys as cast, containing 0.37 and 0.48 per cent phosphorus, respectively, though far below the limit of solubility, show the heterogeneous character of those above this limit. This heterogeneity of structure in low phosphorus alloys has not been emphasized by Saklatwalla or Konstantinow in their work on this series. The very slow diffusion of phosphorus in the ferrite is the cause of the heterogeneous structure; a condition very apt to prevail in practice, particularly if the heating and working of the material subsequent to the initial rolling is slighted. On annealing the alloy, the eutectic disappears by the phosphide passing into solution in the ferrite, and if the heating is continued the crystal becomes homogeneous by the diffusion of the phosphorus in solution. Upon etching no pronounced mottled etch pattern now appears, only a coloring, yellow or brown, of the surface is seen (Fig. 7*b*).

The comparison of the structure of the iron-phosphorus alloys with that observed in the wrought irons examined is instructive and very suggestive as to the nature of the markings there seen. The dark bands and spots forming the mottled etch patterns are the portions of the ferrite rich in phosphorus, and each individual crystal in the streaks of the metal showing such mottled appearance is to be regarded not as a simple entity but as a rather complex aggregate. That the different portions of a single ferrite crystal in such portions vary considerably in their properties is to be inferred from the marked variation in composition.

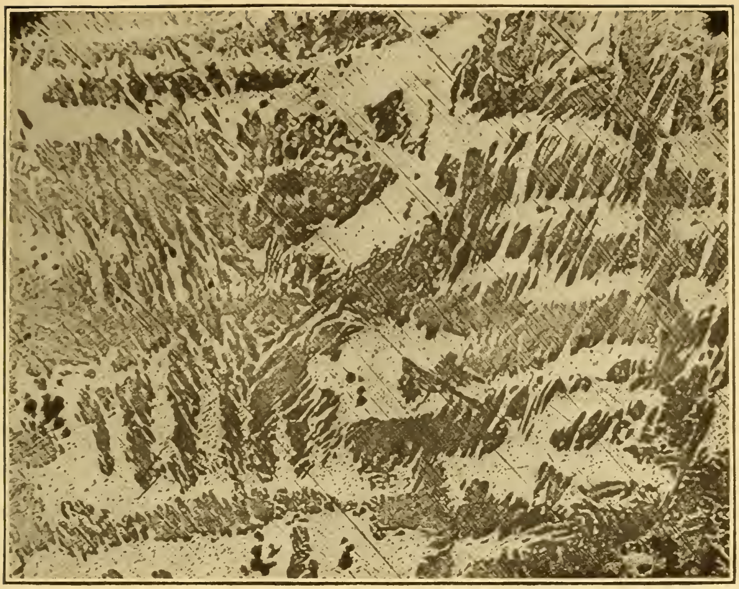
2. CHEMICAL COMPOSITION OF MATERIALS SHOWING SUCH FEATURES

The results of the analyses for phosphorus of many of the materials are listed in the preceding table.

These results show that, though such unusual features of structure as have been described are invariably associated with irons which are rather high in phosphorus, one can not predict with certainty their presence from a knowledge of the average phosphorus content alone. Some of the samples, e. g., W 25, 31, 32, and 33, though comparable with W 11, 12, or 16 in respect to the phosphorus content, showed no traces of these unusual features.

3. ETCHING OF SAMPLES

Upon continued polishing of the specimens before etching, a faint trace of the markings may be seen and recognized by one familiar with this type of iron. This relief polish, however, could



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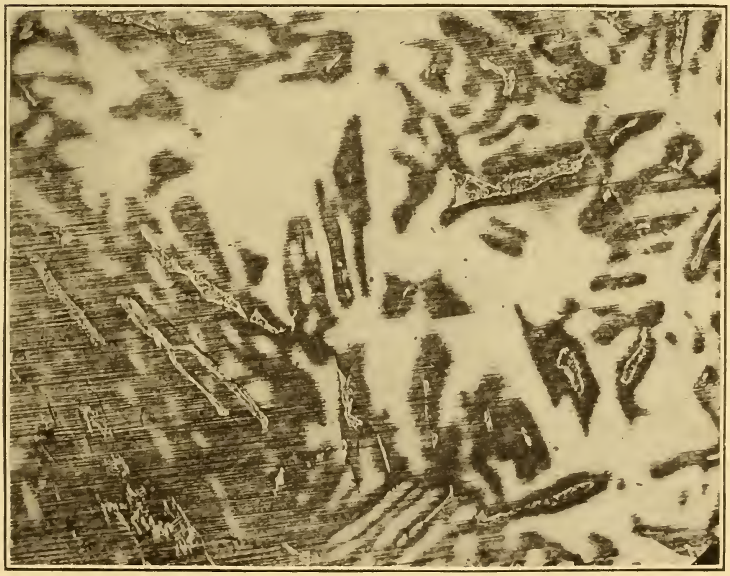

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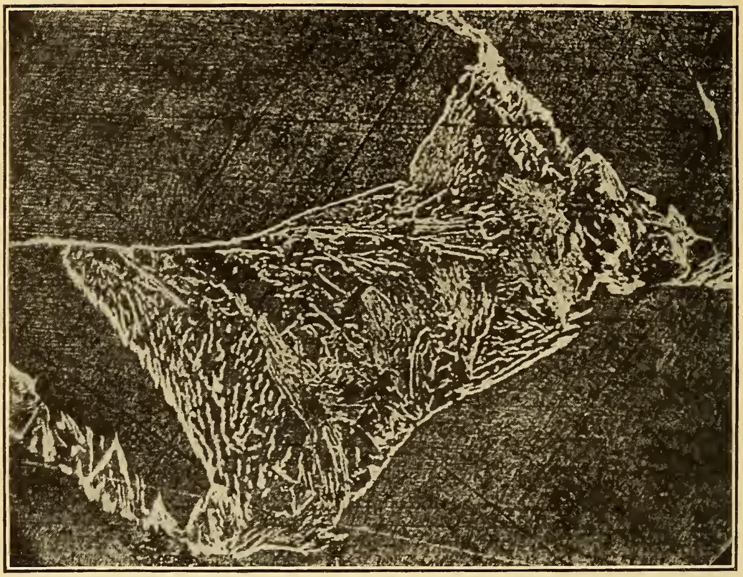
FIG. 6.—*Microstructure of iron-phosphorus alloy*

(*a*) Alloy containing 0.37 per cent phosphorus, in cast condition. Magnification, 25; etching, alcoholic copper chloride acidulated with hydrochloric acid.

(*b*) Same material as *a*. Magnification, 100; same etching.

The dark areas are portions of the ferrite high in phosphorus; *b* shows some of the eutectic as islands in the midst of the dark areas.



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b

FIG. 7.—*Microstructure of iron-phosphorus alloy*

(*a*) Eutectic consisting of iron phosphide and the saturated solid solution of phosphorus in ferrite, from a cast alloy containing 0.37 per cent phosphorus. Magnification, 500.

(*b*) Iron-phosphorus alloy, 0.48 per cent phosphorus after heating 24 hours at 790° C. The eutectic has disappeared by dissolving in the ferrite, although the diffusion of the phosphorus throughout the ferrite is still incomplete. Magnification, 100.

In both cases the ferrite high in phosphorus has been darkened by etching with copper chloride acidulated with hydrochloric acid.

not be developed to a degree to permit successful photographs to be taken. The fact that it can be recognized at all, however, is indicative of the differences in hardness which exist throughout those crystals showing this structure.

By acid etching, preferably using a 5 or even a 10 per cent alcoholic solution of nitric acid, the etch pattern may be satisfactorily developed. The specimen shows to the eye the brown and purple tints similar to those which are often observed when hardened and tempered steels are etched with an acid reagent.

By using the cupric-chloride solution described by Stead[9] the heterogeneous structure may be developed much more strikingly than with acid alone. It was found, however, that the very definite procedure as described by Stead is not necessary; the sample may merely be immersed in an excess of the reagent, as is the usual practice in etching. Ordinarily, when wrought iron is etched with this copper-chloride reagent, it shows the presence of the streaks rich in phosphorus by the deposition of copper on the purer portions, so that the "segregation streaks" appear more lightly colored in contrast to the matrix. On wrought irons high in phosphorus throughout and in the iron-phosphorus alloys of rather high phosphorus content, e. g., 0.37 or 0.48 per cent, such a deposition of copper was not observed even after 15 to 20 minutes' immersion in the etching reagent. The brown tint which results in such cases is very similar in appearance to that obtained with simple acid etching, although the action is more rapid when the copper chloride is used. This coloration has been attributed [10] to a much-retarded deposition of copper. Several samples of the iron-phosphorus alloys and high-phosphorus layers cut out of wrought iron were etched to a pronounced brown by the copper-chloride reagent by immersing for 20 to 40 minutes. The darkened surface layer was dissolved off with nitric acid after thoroughly washing the specimen, and the resulting solution was tested for copper with potassium ferrocyanide after precipitating the dissolved iron with ammonium hydroxide, filtering off the precipitate and acidifying the filtrate with acetic acid. A faint but clearly perceptible test for copper was obtained.

Though the amount of copper precipitated is very slight, the decided increase of contrast in the etched specimen when the acid copper-chloride reagent is used over that obtained with acid alone warrants the conclusion that it is to the copper that the

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[9] Loc. cit. [10] Loc. cit.

more rapid etching action and the striking contrast produced is to be largely attributed.

The areas constituting the mottled etch pattern which are darkened are those relatively high in phosphorus, as is plainly indicated in Figs. 6*b* and 7*a*. The ferrite surrounding the iron-phosphide eutectic and that forming part of the eutectic itself constitute the portions which are most strongly colored and not the less contaminated ferrite which solidified first from the melt. This appears to be in direct opposition to the macroscopic results obtained when a sample of wrought iron is etched, in which case copper is precipitated in relatively large amounts upon the layers low in phosphorus. The precipitation of copper upon the streaks of the comparatively pure material is to be attributed to the electrolytic potential of such material with reference to that of copper. The reverse etching of the metal of high phosphorus content can not be so easily explained upon this basis. The action of the hydrochloric acid alone in the reagent as used will develop the etch pattern, although much more slowly than when the copper chloride is present. A trial of the two solutions showed that by a 12-minute immersion in 1 per cent alcoholic hydrochloric acid a sample of the iron-phosphorus alloy was not etched nearly as satisfactorily as by a 2-minute immersion in the same solution containing copper chloride. The suggestion is offered that metallic copper as such is not deposited, but that there is formed a closely adhering thin film of copper phosphide on the phosphorus-rich portions, and so the result which acid etching alone will produce if enough time is allowed is hastened and intensified. The roughening of the surface by a prolonged acid etching is thus avoided by the use of the copper-chloride solution.

The etching reagent described by Rosenhain and Haughton [11] was tried upon the iron-phosphorus alloys but with unsatisfactory results. It should be noted that if the specimens are mounted in some kind of a matrix for polishing, as is necessary for wires, sections of thin pipe, etc., a matrix of soft alloy or anything of metal must be avoided. The potential difference existing between this metal and the embedded specimen is often so much greater than that between the various portions of the sample under examination as to prevent entirely the differential etching desired.

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[11] Jour. Iron and Steel Inst., No. 1, p. 515; 1914.

4. BEHAVIOR UPON HEATING

The persistence of the unusual intracrystalline structural features upon heating is remarkable. Fig. 9*a* shows the appearance of a specimen of the wrought-iron eyebar previously described after heating it for three hours at approximately 600° C (585°–625°) and then allowing it to cool in the furnace. No apprciable changes have resulted from this treatment. A second sample (Fig. 9*b*) heated for about one and one-half hours at approximately 725° C (718°–735°) and furnace cooled still shows faint traces remaining of the former condition.

Upon heating a sample much higher in phosphorus (W 37) at approximately the same temperature for the same period, i. e., one and one-half hours at 700° C (725°–690°), the structural change which is brought about (Figs. 8 and 10) is very much less than that shown above. Fig. 8*b* shows the structure resulting from heating an iron-phosphorus alloy, 0.37 per cent phosphorus, for 24 hours at approximately 790° C, the specimen being allowed to cool in the furnace. The eutectic has disappeared by solution of the compound, F_3P, in the ferrite, but the nonhomogeneity of structure as shown by the dendritic pattern still persists. This illustrates well the remarkably slow rate of diffusion within the ferrite matrix by which equilibrium is finally attained. The presence of the compound Fe_3P which had separated out from the matrix most probably accounts for the much slower rate of diffusion in these latter cases than was observed in the case of the first wrought-iron samples which were annealed.

The slow rate of diffusion of phosphorus in ferrite has often been remarked, and it is undoubtedly due to this cause that the mottled structure persists and is not entirely wiped out during the manufacture of the wrought iron, i. e., during the heating, rolling, and forging necessary before the wrought iron reaches the finished condition.

V. SUGGESTED SIGNIFICANCE OF UNUSUAL FEATURES OF STRUCTURE

The significance of the unusual features of microstructure described and their possible relation to the service behavior of such material may be suggested. The occurrence of material of this type in two of the samples examined (W 1 and W 37), both of which failed in service and which have the appearance of having failed under the action of alternations or repetitions of stress, sug-

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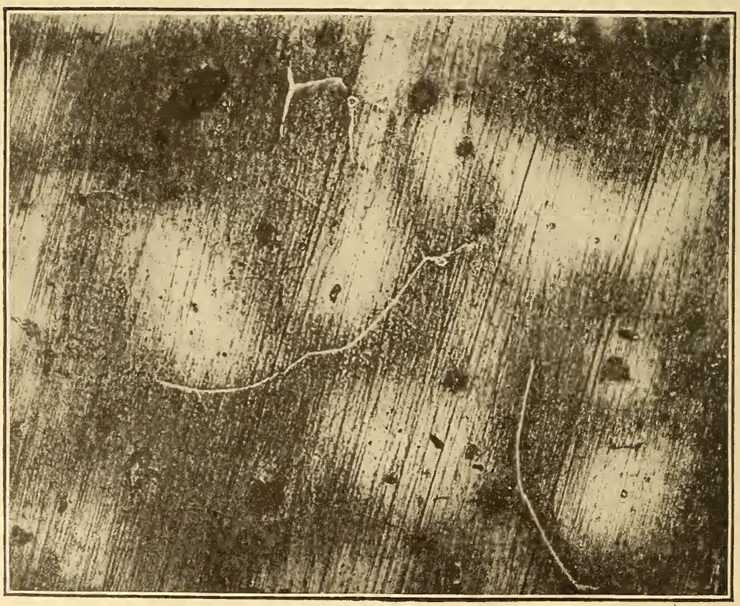

b

FIG. 8.—*High-phosphorus wrought iron*

(*a*) W 37, longitudinal section. In portions of the material, islands of iron phosphide are found; such islands occur in the center of the areas which become brown upon etching. Magnification, 100.

(*b*) Same material as *a*. Magnification, 500. Etching in both cases, alcoholic copper chloride containing hydrochloric acid.

a

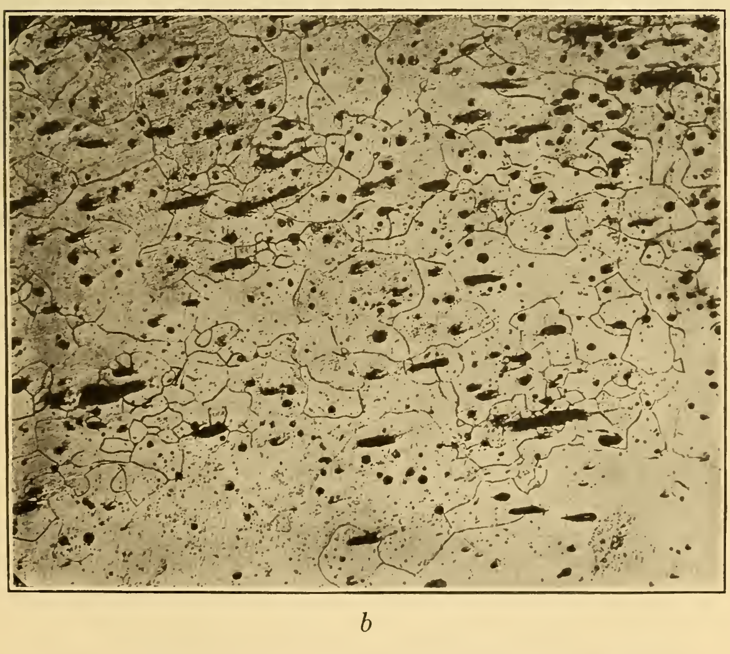

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FIG. 9.—*Effect of annealing upon unusual features in wrought iron*

(*a*) W 1, heated for three hours at 600° C.
(*b*) W 1, heated for one and one-half hours at 725° C.
Magnification, 100; etching, 10 per cent nitric acid.

gests a possible relation between this type of structure and the failure of such material.

The method by which "fatigue" breaks occur in metals by the action of repeated stresses has been clearly and conclusively set forth by Ewing and Humphrey,[12] Rosenhain,[13] and others. The minute back-and-forth slip along certain planes occurring within the crystals if repeated a sufficient number of times becomes

Fig. 10.—*High-phosphorus wrought iron after annealing*

Specimen W 37 after heating one and one-half hours at 700° C. The nonhomogeneity of structure still persists, though the islands of iron phosphide have been dissolved. Magnification, 100; etching, alcoholic copper chloride acidulated with hydrochloric acid.

a permanent displacement, thus initiating an incipient fracture within the crystal. The combined effect of this action within a number of neighboring crystals at some portion of the specimen will be sufficient to cause a real fracture to start at that point if the application of the stresses is continued.

The brittle character of ferrite containing considerable phosphorus is well known. Crystals which show the heterogeneity caused by high and low phosphorus bands in juxtaposition should be much more easily "fatigued" by repeated stresses and show a permanent slip much more quickly than crystals which are more uniform throughout in their structure. In particular this should

[12] Ewing and Humphrey, Phil. Trans. Royal Soc., 200A; 1902.

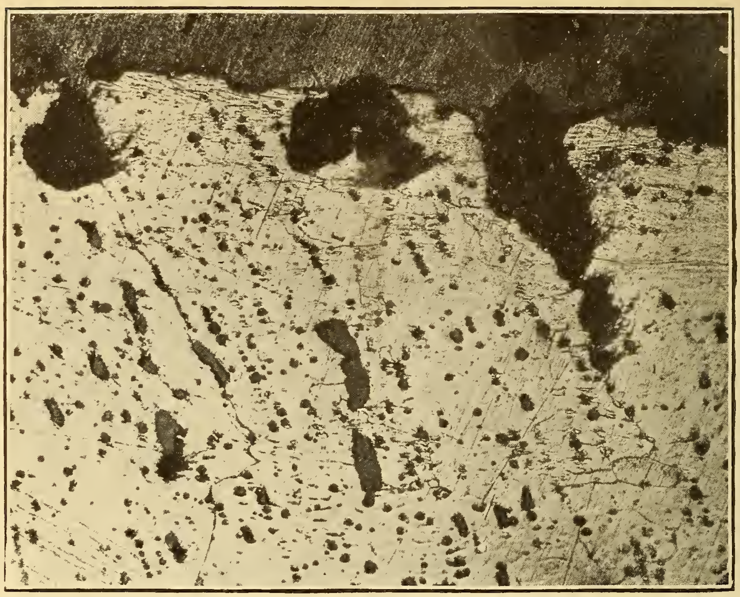
[13] Rosenhain, Introduction to Physical Metallurgy, Chap. VIII.

be true if the bands are transverse to the direction of the stresses acting. The observations upon the fracture of the broken eyebar appear to confirm this. Though the evidence shown by the failed member is only "circumstantial," as is always the case in the examination of "metal failures," still so closely does it correspond to and agree with the results of the work of Ewing and Humphrey that there appears little doubt as to the nature of the fracture.

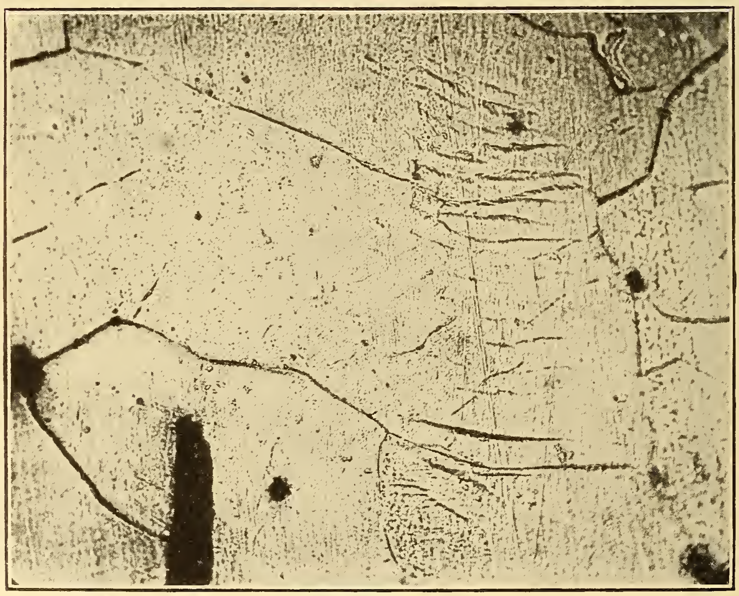
The fact that the face of the fracture followed and its course apparently was determined by the bands within the ferrite crystals has already been referred to (p. 5). Fig. 11*a* shows that the break occurred parallel to the bands of high-phosphorus ferrite which give rise to the peculiar etch pattern. Examination of the metal immediately back of the face of the fracture reveals further evidence. Fig. 11*b* shows the appearance of some of the deepest of the etch bands in the crystals close to the break. These, undoubtedly, represent a stage in which minute transverse cracks, i. e., transverse to the direction of the stresses acting, have opened up within the body of the crystal. The intracrystalline markings obtained by Ewing and Humphrey by subjecting wrought-iron specimens to repeated alternations of stress in the Wöhler test appear in all respects identical with those shown in Fig. 11*b*.

H. H. Campbell[14] quotes the statement that phosphorus up to 0.20 per cent is not injurious in wrought iron. This should be taken, however, as referring to an average content of this amount uniformly diffused throughout the metal. The microsegregation of this element may result in the amount in certain streaks being considerably in excess of this quantity while within the individual crystals of such streaks the nonhomogeneity with respect to phosphorus is still further accentuated. In the material of Fig. 6*b* the ferrite immediately surrounding the eutectic has a phosphorus content of approximately 1.7 per cent or nearly five times the average percentage of phosphorus of the sample. It appears very probable, then, that in such nonhomogeneous crystals as are shown in Figs. 2*b* and 3 the high-phosphorus bands may be as much as four or five times the average of the whole (in the percentage of this element) as determined by chemical analysis. In exceptional cases portions of a sample high in phosphorus may show traces of iron phosphide that has crystallized

[14] Campbell, H. H., The Manufacture and Properties of Steel, p. 91.



a



b

Fig. 11.—*Relation of unusual structural features to the service behavior of the material*

(*a*) Longitudinal section of W 1. The edge of the fracture which occurred is parallel to the bands which constitute the etch pattern here. Magnification, 100.

(*b*) Appearance of very persistent etch lines just back of the fracture in W 1. The specimen has been heated three hours at 600° C. Magnification, 400.

Etching in both cases, 10 per cent nitric acid.

out directly from the melt (Fig. 8, *a* and *b*). The metal at such points has a phosphorus content not far below 1.7 per cent, as is indicated in Fig. 5.

The straight lines, resembling polishing scratches, shown by some of the crystals near the facture (Fig. 1), are the well-known Neumann lines. Such markings are usually considered to be "mechanical" twin crystals, i. e., the twinned position of the metal within each of the narrow zones has been brought about by mechanical causes alone, particularly by shock[15] (Fig. 10). They, in all probability, are the result of shock which finally caused the fracture of the bar. A comparison of these lines with the long narrow bands which often constitute the mottled etch pattern shows immediately that such etch bands can not be attributed to twinning or a similar cause.

Much credit is due to W. L. Christian and W. H. Miltner for the careful and efficient work done in the preparation of the many surfaces necessary in the microscopic study. The help received from L. F. Witmer in the chemical analyses of many of the specimens is also acknowledged.

VI. SUMMARY

1. Wrought irons high in phosphorus sometimes show a peculiar mottled or banded intracrystalline pattern, which, by comparison with alloys of pure iron and phosphorus, is shown to be due to a nonhomogeneous diffusion of the phosphorus.

2. The examination of a wrought-iron member exhibiting such an unusual structure showed that the break which occurred in service bore a definite relation to such banded markings and apparently was largely determined by them.

3. By the nonhomogeneity in the distribution of phosphorus throughout the ferrite crystals the ill effects of phosphorus may be much enhanced.

4. The examination of a series of wrought irons showed that such features are not to be regarded as common or characteristic of all low-grade irons. Many poor grades of iron may be unsuitable for other reasons.

5. A second type of markings is described and illustrated—the well-known Neumann lines—and these are shown to bear no apparent relation to the other variations in structure described.

WASHINGTON, July 15, 1916.

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[15] Howe, H. M., and Levy, A. G. Trans. Am. Soc. Min. Engrs., p. 891; 1915.