MICROSTRUCTURE OF IRON AND MILD STEEL AT HIGH TEMPERATURES

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I. INTRODUCTION

The method of demonstrating the structure which exists in any particular metal or alloy at high temperatures by etching a polished sample while it is being heated at the desired temperature is quite familiar to metallographists. The usual method of procedure[1] is to heat the specimen previously polished for microscopic examination in a neutral atmosphere (hydrogen or nitrogen) to the desired temperature, then to admit the etching gas (chlorine, hydrochloric acid, or similar gas) for a few seconds, and after flushing out the etching gas with the neutral one, and finally to cool the specimen in the neutral atmosphere. The etch pattern produced by etching at any definite temperature is usually taken as a record of the microstructure which prevailed at that temperature. It has been pointed out frequently that changes in composition of the surface metal occur during the preliminary heating in the neutral atmosphere, so that the appearance produced by the etching at high temperature may not be truly representative of the condition of the interior of the specimens. To overcome this uncertainty the heating has at times been done in vacuo,[2] the etching gas admitted when the desired temperature was reached, and then pumped out; the specimen then cooled in vacuo.

[1] N. Gutowsky, Uber die Structur des Stahlen bei hohen Temperaturen, Metallurgie, 6, p. 743; 1909. H. Hanemann, Etching at High Temperatures, Inter. Zeit. Metallographie, 3, p. 176.

[2] N. Tschischewsky and N. Schulgin, Jour. Iron and Steel Inst., 95, p. 189; 1917.

150058°—20

The work of Rosenhain, Humphrey, and other workers [3] demonstrates that surface changes in the steel occur, however, even when the specimens are heated in vacuo. Such changes in themselves are sufficiently pronounced so as to record in the changed appearance of the surface the microstructure which prevailed at the temperature at which the change took place. The surface configuration or pattern thus produced, to which various names, "heat relief," "heat etching," and "vacuum etching," have been applied, has been explained by Rosenhain as due to volatilization of the surface metal. This is more pronounced along the crystal boundaries than over the face of the crystal itself. The change in composition of the layer immediately adjacent to the surface of a steel sample, when heated in vacuo or in a neutral atmosphere, has also usually been attributed to volatilization. Howe [4] has offered an entirely new and striking explanation for this phenomenon. His explanation is to the effect that the change in composition of the surface layer is local only, the average composition of the specimen does not change. Upon cooling a sample of steel from a high temperature the free constituent (ferrite or cementite, as the case may be) is expelled to the outside of the mother austenite crystal, and thus to the surface of the specimen in the case of the crystals which form the exterior. By repeated heatings, the layer of expelled ferrite (in the case of low-carbon steel) is augmented until the specimen has the appearance of being decarburized at the surface.

The series of examinations described below were made with the aim of showing to what extent the change in composition of the surface layer, which usually accompanies heating in vacuo, affects the results of any tests which may be made to reveal the microstructure existing at high temperatures. The results also throw some additional light upon the nature of the composition change of the surface layer, and also the formation of the surface pattern, by which the microstructure is revealed by means of "heat-relief" etching.

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[3] W. Rosenhain and J. C. W. Humfrey, The Crystalline Structure of Iron at High Temperature; Collected Researches, National Phys. Lab., Teddington, 6, p. 189. W. Rosenhain and J. C. W. Humfrey, The Tenacity, Deformation, and Fracture of Soft Steel at High Temperatures, Jour. Iron and Steel Inst., 87, pp. 219–315; 1913. J. C. W. Humfrey, The Intercrystalline Fracture of Iron and Steel, Collected Researches, National Phys. Lab., Teddington, 10, p. 113, 1913; also Iron and Steel Inst., Carnegie Scol. Memoir, 4, 1912. W. Rosenhain and D. Ewen, Intercrystalline Cohesion in Metals, Collected Researches, National Phys. Lab., Teddington, 10, p. 91, 1913; also from Jour. Inst. Metals, 8, No. 2; 1912. Adolphe Krool, The Crystallography of the Iron-Carbon System, Jour. Iron and Steel Inst., 81, p. 304; 1910.

[4] H. M. Howe, The Position of Ae_3 in Carbon-Iron Alloys, Discussion, Trans. Am. Inst. Min. Engrs., 47, p. 659; 1913.

II. METHOD OF REVEALING STRUCTURAL CHANGES OCCURRING AT HIGH TEMPERATURES

Pure iron and low-carbon steel were chosen as typical materials to demonstrate how heat etching may be used to show the structural changes which occur in these metals upon heating. Both of these materials show pronounced changes in structure accompanying some of the transformations which occur upon heating. The normal structure of each is very familiar; also the microstructure existing at high temperature has been demonstrated by means of the etching method.

I. PURE IRON

A remelted electrolytic iron of the following composition was used: Carbon 0.03 per cent, sulphur 0.002 per cent, and silicon 0.009 per cent. By thermal analysis, the material was shown to have the following thermal characteristics: Ac_2, 768° C; Ac_3, 910° C; Ar_3, 900° C; Ar_2, 768° C. The specimens, which were of the size used for thermal analysis (approximately 3 g), were mounted on the end of the platinum platinum-rhodium thermocouple and heated in the evacuated tube of a differentially heated furnace of the Rosenhain type.[5] The following temperatures were used:

950° C. ..... above A_3
880° C. ..... between A_2 and A_3
700° C. ..... below Ac_1 (of steels)

In each case the specimen was held for approximately 30 minutes at the maximum temperature and then cooled in the evacuated furnace at an approximate rate of 0.15° per second by moving the specimen to the cold end of the tube. The surface of the specimens, after heating, showed no evidence of oxidation. In most cases, particularly those heated to the highest temperatures, the surface had a slightly roughened or matt appearance.

In Fig. 1 is shown the surface pattern produced by heating the iron above the Ac_3 transformation. Two distinct patterns are to be seen superimposed one upon the other. One of the patterns is similar in appearance to that of pure iron, as ordinarily etched at room temperature; the other network contains numerous straight lines, and many of the inclosed "grains" have the appearance of twinned crystals. This is clearly shown in Fig. 1*a*. The two long, narrow crystals are the twinned layers of a much larger

[5] H. Scott and J. R. Freeman, Bull. Am. Inst. Min. and Met. Engs., 152, p. 1429: description of the furnace and auxiliary apparatus is given.

crystal, the boundaries of which can be faintly seen. Another network, outlining a second system of grains, is superimposed upon the twinned crystals. Fig. 1*b* shows similar features.

The network which delineates the straight-sided polyhedral twinned crystals is a record of the structure of the γ iron; that is, the form existing above the A_3 transformation. The second network belongs to the crystal structure which prevails below this transformation, as is shown in specimens heated to a temperature below A_3. Only one network is developed in such a case; this is identical with the second pattern of specimens heated above A_3. The specimen shown in Fig. 2 illustrates this, and also shows that no characteristic crystal form corresponds to the so-called β range. The appearance is the same as that of specimens heated at a temperature well below A_2 (Fig. 3), and also of samples polished and etched under ordinary conditions. This observation confirms that of Rosenhain and Humfrey[6] in this respect.

In Fig. 3 is shown the surface of a polished specimen heated to 700° C. The network outlining the arrangement of the crystals showed faintly even at this relatively low temperature.

The surface of freshly heated specimens often has a "matt finish" appearance, and when viewed at an oblique angle is seen to be considerably roughened. The volatilization which occurs at high temperature, as shown in Fig. 1*a*, accounts partly for the matt finish. It will be noted that the volatilization develops rather well-defined "etching pits" on the surface, by means of which the structural orientation within the twin crystals relative to the mother crystal is plainly shown. The roughened appearance is due largely to a buckling of the surface of the individual crystals. Fig. 4, which shows a section perpendicular to the polished surface which was exposed to the heat, demonstrates the distortion which occurs; the boundary—that is, the trace of the polished flat surface—originally rectilinear, now consists of a series of undulations. Specimens heated to a temperature a little below A_3 show an irregular branching network within the grains themselves (Fig. 2*b*). This is often seen in pure iron after ordinary etching, for microscopic examination particularly, if the sample has been strongly heated previously; for example, specimens which have been heated several times for thermal analysis curves. Whether this bears any relation to the β change has not yet been determined.

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[6] Loc. cit. See note 3.

a

b

FIG. 1.—*Microstructure of pure iron above the A_3 transformation*

Both micrographs show the surface appearance of the same material, a specimen of which was heated for 30 minutes at 950° C. Two networks, indicative of two different crystalline arrangements, are to be seen. The one showing the twinned crystals is the structure prevailing above A_3; the other, superimposed upon the first, corresponds to the structure at lower temperatures. Magnification, 500 diameters; "heat-etched"

a

b

FIG. 2.—*Microstructure of pure iron between the A_2 and A_3 transformations*

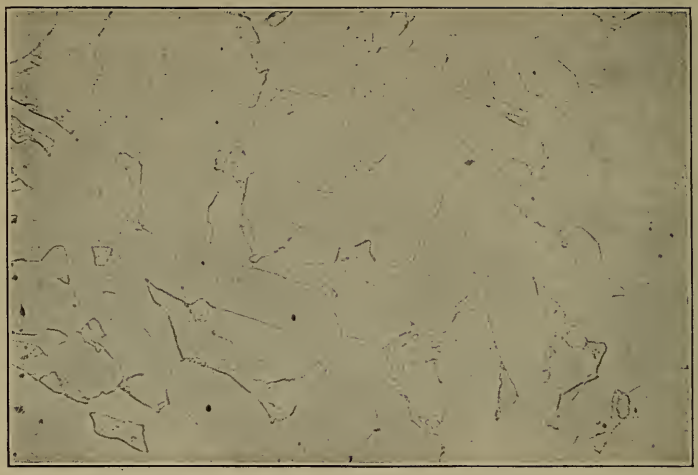
The polished specimen, represented by the two micrographs, was heated 30 minutes at 880° C, i. e., just below A_3. The appearance of the previously polished surface reveals the structure, which is of the same type as that prevailing at ordinary temperatures. The excessive volatilization at the margins of the grains has clearly developed the boundaries. Magnification, 500 diameters; "heat-etched"

FIG. 3.—*Microstructure of pure iron below the transformation temperatures*

A polished specimen of the material was heated for 30 minutes at 700° C. The volatilization at the grain boundaries, though slight, has been sufficient to reveal the structure, which is of the same type as that existing between A_2 and A_3. Magnification, 500 diameters; "heat-etched"

FIG. 4.—*Microstructure of pure iron at high temperatures*

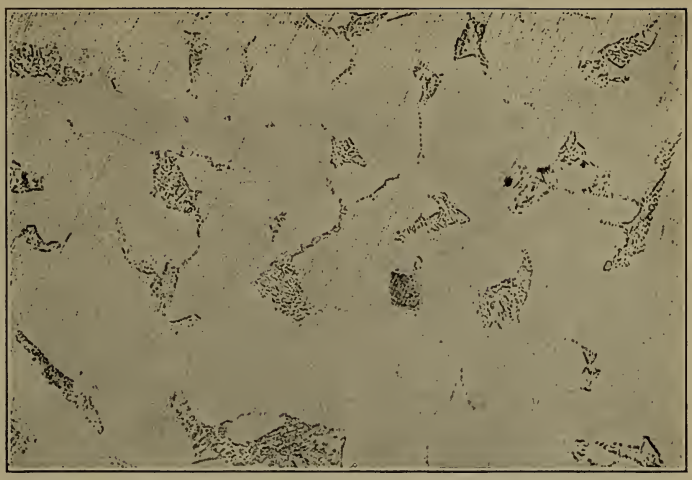
The micrograph shows a section perpendicular to the polished and "heat-etched" surface of Fig. 1. A layer of electrolytic copper was deposited to preserve the edge during the polishing of the specimen. The originally rectilinear edge has been changed into a series of undulations by the volume changes at the transformation temperature. Magnification, 500 diameters; etching, 2 per cent alcoholic nitric acid



(*a*) The polished specimen was heat-etched by heating it for 30 minutes at 700° C

(*b*) The polished specimen was distorted sufficiently to show slip-bands and then heat-etched as in (*a*). The slip-bands still persist

FIG. 5.—*Microstructure of low-carbon steel just below the* A_1 *transformation. Magnification, 100 diameters*



(*a*) The material of Fig. 5*a* was slightly polished to remove the effects of heat-etching and etched with 2 per cent alcoholic nitric acid. The material shows the normal structure for this class of steel

(*b*) A specimen similar to Fig. 5*a* was etched with 2 per cent alcoholic nitric acid directly after being heat-etched. The surfaces etch and darken immediately

FIG. 6.—*Microstructure of low-carbon steel just below the* A_1 *transformation. Magnification, 100 diameters in both cases*

(*a*) Magnification, 100 diameters. Both ferrite and pearlite are clearly shown.

(*b*) Magnification, 500 diameters. The boundaries of the ferrite grains extend through the pearlite islands

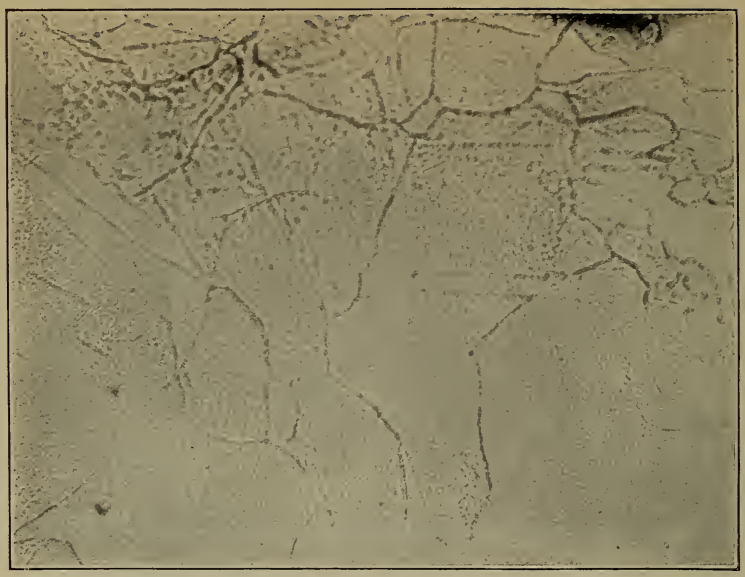
FIG. 7.—*Microstructure of low-carbon steel just above the A_1 transformation*

The polished specimen was heat-etched by heating 30 minutes at 760° C

(*a*) The specimen of Fig. 7*a* was slightly polished and etched. The surface metal is pure ferrite

(*b*) Section of the specimen shown in (*a*), taken perpendicular to the heat-etched surface. A layer of electrolytic copper was deposited to protect the edge during polishing. The pearlite has been removed from the surface metal, by the heating, for a considerable depth

FIG. 8.—*Microstructure of low-carbon steel previously heated just above the A_1 transformation. Etched with 2 per cent alcoholic nitric acid. Magnification, 100 diameters*



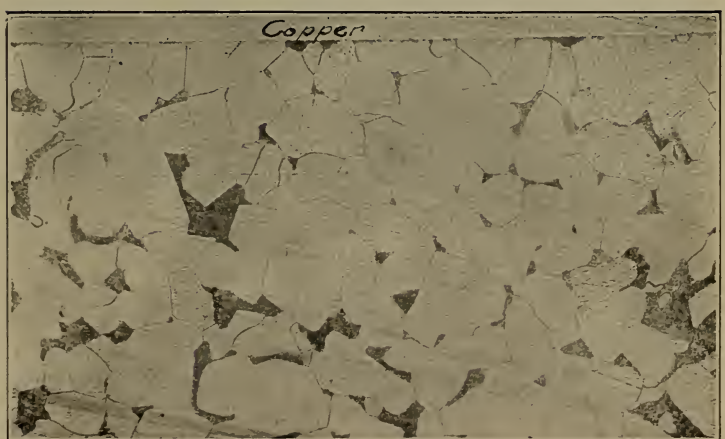
(*a*) The polished specimen was heat-etched by heating 30 minutes at 950° C. Two patterns corresponding to the α and the γ forms (compare Fig. 1) are to be seen

(*b*) The polished specimen was etched with 2 per cent nitric acid before heating at 1000° C for 30 minutes. The original pearlite pattern shown by the first etching has persisted throughout the heating. Upon this two other patterns similar to those in (*a*) above, have been superimposed

FIG. 9.—*Microstructure of low-carbon steel above the A_3 transformation. Magnification, 500 diameters*

(*a*) Heated for 30 minutes above the A_1 transformation (760° C)

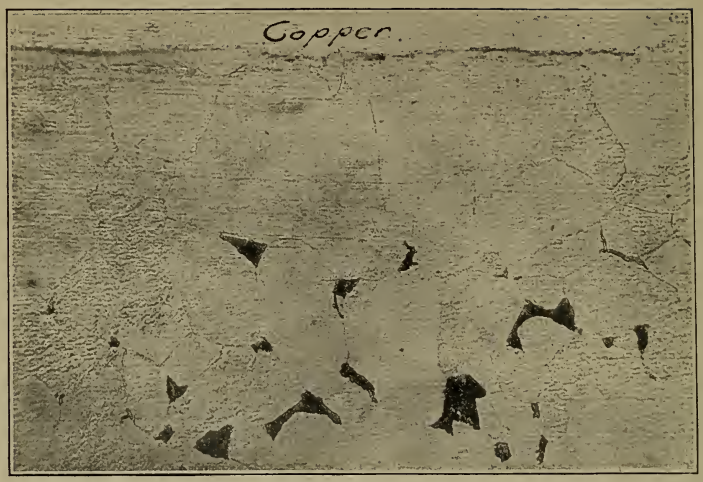
(*b*) Heated for 30 minutes just below the A_3 transformation (820° C)



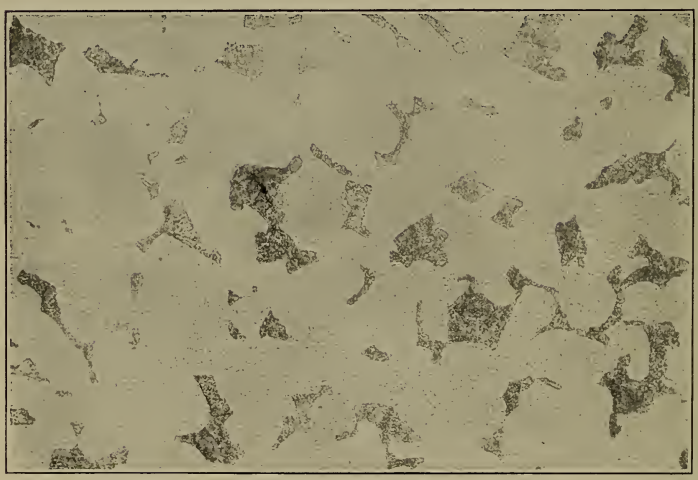
(*c*) Heated for 30 minutes above the A_3 transformation (890° C)

FIG. 10.—*Surface changes produced in low-carbon steel by heating in vacuo*

In each case a section perpendicular to a surface which had been heat-etched was taken. Magnification, 100 diameters; etching, 2 per cent alcoholic nitric acid.



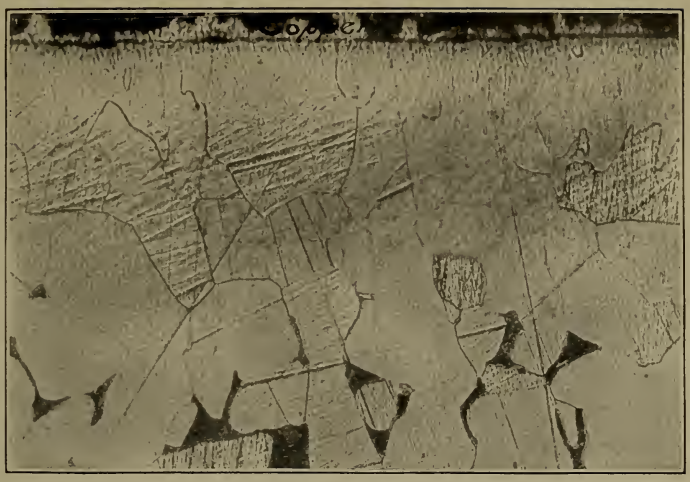
(*a*) Carbonless surface layer.



(*b*) The average structure at the center of the specimen

FIG. 11.—*Surface changes produced in low-carbon steel by heating above the A_3 transformation temperature*

A polished specimen was heated continuously for four hours above the A_3 transformation temperature. The heat-etched surface was then protected with a deposit of electrolytic copper, and the specimen sectioned perpendicularly to this face. Magnification, 500 diameters; etching, 2 per cent alcoholic nitric acid



(*a*) Carbonless surface layer

(*b*) Average structure of the central portion

FIG. 12.—*Surface changes produced in low-carbon steel by heating above the A_3 transformation temperature*

The specimen was used for a series of thermal curves and was heated four times above the A_3 transformation temperature; the total period above this temperature was four hours. The specimen was treated as for Fig. 13, with which this figure should be compared. Magnification, 500 diameters; etching, 2 per cent alcoholic nitric acid

(*a*) The average surface condition is shown. The cementite envelopes disappear at some distance below the surface. In the original condition of the specimen they extended to the surface. Cementite has been removed from the surface

(*b*) In a few exceptional spots a thin white (probably ferrite) layer formed at the surface. Etching with hot sodium picrate showed that this layer was not cementite

FIG. 13.—*Surface changes produced in high-carbon steel by heating in vacuo above the A_3 transformation temperature*

The specimen was prepared in a manner similar to those of Fig. 12. Magnification, 500 diameters; etching, 2 per cent alcoholic nitric acid

2. LOW-CARBON STEEL.

A synthetic low-carbon steel[7] of the following composition was used as representative of this class of material: Carbon, 0.18 per cent; silicon, 0.007 per cent. The steel has the following thermal characteristics: Ac_1, 738° C; Ac_2, 769° C; Ac_3, 840° C; Ar_3, 792° C; Ar_2, 769° C; Ar_1, 700° C. The specimens, which were first polished ready for microscopic examination, were heated in vacuo in the same manner as the pure iron; the sample was held in each case, approximately 30 minutes, at the maximum temperature. The specimens were heated to the following temperatures:

950° C. ..... above Ac_3
760° C. ..... above Ac_1
700° C. ..... below Ac_1

Fig. 5 shows the appearance of a specimen heated to 700° C; that is, just below the transformation Ac_1. Even at this temperature the heat relief has been sufficient to clearly indicate the islands of pearlite. In Fig. 5*b* is shown the appearance of a specimen which, after polishing, was distorted enough to develop slip bands and then heated to 700° C. The slight roughening of the surface due to the slipping still persists at this temperature and shows that no marked volatilization has occurred at the surface.

Fig. 6*a* shows the specimen of Fig. 5*a* after it was polished slightly to remove the effects of the heat relief and then etched. The material has the usual appearance of low-carbon steel. When the specimen is etched directly after heating—that is, without any supplementary polishing—the surface darkens almost immediately and gives the appearance shown in Fig. 6*b*. A similarly pronounced darkening of ferrite upon etching is often observed when a specimen is finished on a polishing wheel which has been allowed to become quite free from water so that the surface heats considerably. Upon heating a polished specimen of this material above the Ac_1 transformation the surface takes on the appearance shown in Fig. 7*a*, which is very similar to that produced by heating below Ac_1. The position of the preexisting pearlite islands is clearly indicated. It will be noted that the network which marks the boundaries of the ferrite crystals is now continuous through the pearlite areas instead of around them. This is best seen at a higher magnification as in Fig. 7*b*. When the surface is etched after heating—that is, without any polishing—the appearance is the same as is shown in Fig. 6*b*. However, when the surface is slightly

[7] An alloy of iron and carbon prepared according to the method given in Scientific Papers No. 266 was used.

polished and then etched, no darkening results, nor is there left any trace of the pattern developed by heat relief. The material which constitutes the surface is pure ferrite (Fig. 8*a*); all the pearlite has been removed to a considerable depth, as is shown in Fig. 8*b*, which shows a section of the specimen perpendicular to the polished face. The normal appearance of the material is shown in the lower portion of the micrograph. The boundary between the outer, or carbonless, metal and the inner normal material is very clearly defined. The change from the outer zone to the unchanged metal of the interior is very abrupt and not a gradual one.

In Fig. 9*a* is shown the pattern developed by heat relief on the polished surface by heating above the Ac_3 transformation. The more clearly defined network corresponding to the γ condition is superimposed upon a less distinct one which shows the characteristic outlines of the α crystals. In Fig. 9*b* this is more plainly seen. The polished specimen in this instance was etched to reveal its initial structure and then heated at 1000° C for 30 minutes; that is, well above the temperature of the Ac_3 change. The roughening of the surface corresponding to the islands of pearlite, shown by the initial etching, still persists. Upon this pattern two others are superimposed; these show, respectively, the crystalline condition above Ac_3 upon heating and below Ac_3 on cooling. The twin crystal (Fig. 9*b*), which had its origin when the steel was in the γ state, is seen to cut through the preexisting islands of pearlite and to bear no relation to them. It should be borne in mind, however, that the carbide has been removed from the surface material, probably before the change to the γ state is brought about, as has been described above.

III. NATURE AND EXTENT OF THE SURFACE CHANGES UPON HEATING

The magnitude of the change (apparently decarburization) which occurs in some samples (Fig. 8) makes the explanation offered by Howe [8] appear to be an inadequate one. In order to clearly show the nature of the change and to test out the explanation, a series of specimens of the low-carbon steel previously used were heated in vacuo for equal periods at the following temperatures:

760° C	above Ac_1,	for 30 minutes
820° C	just below Ac_3,	for 30 minutes
880° C	above Ac_3,	for 30 minutes

[8] Loc. cit. See note 4.

The specimens were cooled in the furnace at the same rate as the previous ones. In each case the carbonless layer varies considerably in thickness on the same specimen; the maximum thickness of this changed layer in specimens heated at the three temperatures given above is shown in Fig. 10. In the specimen heated at the lowest temperature, the decarburized layer is more pronounced than in those heated for the same period at higher temperatures. This is not to be attributed to a greater loss of carbon at the lower temperature, but rather to an increased rate of diffusion of carbide in iron at higher temperatures, by which any change at the surface due to loss of carbon is masked by a replenishment from the interior by diffusion.

In Fig. 11 is shown the condition at the surface and near the center of a specimen (the material is the low-carbon steel previously used) heated continuously for four hours above Ac_3, 990° C was the maximum temperature. The structure of a sample of the same material used for a series of four thermal curves, and which was above the Ac_3 temperature for a total of four hours, is shown in Fig. 12. The thickness of the changed surface layer of the sample heated intermittently is somewhat greater than that of the specimen heated continuously for four hours above the Ac_3 transformation temperature. The carbon content of the interior, as estimated from the structure, is slightly less in the specimen heated continuously, however, than in second one. This apparently contradictory behavior of the specimen most strongly heated is to be interpreted as further evidence of the part played by diffusion in masking the change which occurs at the surface. By comparing Figs. 10*a* and 11*a* it will be noted that a much more pronounced change is produced in the surface metal for a short period at the lower temperature (30 minutes at 760° C) than by prolonged heating at a higher one (240 minutes at 990° C). Whether this difference in the rate of diffusion is one due entirely to temperature or partially to the allotropic condition of the iron, α or γ, can only be conjectured.

In Fig. 13*a*, is shown the surface change induced in a high-carbon steel by heating four times in vacuo to a temperature above the Ac_3 transformation (950° C). The steel was of the following composition: Carbon, 1.28 per cent; manganese, 0.23 per cent; phosphorus, 0.017 per cent; sulphur, 0.017 per cent; silicon, 0.23 per cent. The cementite grain envelopes do not extend entirely to the surface as they did originally, but gradually diminish in thick-

ness and disappear at some distance below the surface. In no case was an accumulation of cementite found, as Howe's explanation requires. In a few areas a very thin layer of ferrite was found to have formed, as is shown in Fig. 13*b*. The conclusion is evidently warranted that the change of structure of the surface metal heated in vacuo represents loss of carbon.

IV. INTERPRETATION OF RESULTS

The question may very properly be asked as to what extent the indications of the etchings, used to reveal the structure of steel at high temperature, are vitiated by the changes of composition which occur in the surface metal upon heating. The experimental results discussed in the previous sections show that no decarburization below the temperature of A_1 transformation can be detected. This is due to the physical form in which the carbon exists. Not until the carbon (as carbide) is in the state of a solid solution in the iron—that is, above A_1—is there any appreciable change in the exposed surface metal. Below the A_1 transformation the carbon occurs in the form of a definite crystalline compound, and the loss upon heating may be entirely neglected.

A very marked change, however, occurs upon heating a specimen just above the A_1 transformation. The carbon passes from the form of crystalline cementite to a solution (of cementite) in the iron. In this form it quite readily volatilizes from the surface, so that a pronounced carbonless layer is soon formed in specimens (low-carbon steels) that are held for periods no greater than 30 minutes at this temperature. The method of heat etching, however, serves to record the structure both before and after the change has taken place. The pronounced differential expansion of pearlite and ferrite at the A_1 transformation will account partially for this. The fact that at temperatures below A_1 the structure is clearly revealed by heat etching, however, shows that this is not the sole cause, but that the slight general volatilization which occurs, together with the slight differences in the rate of thermal expansion of pearlitic steel and iron (ferrite) are sufficient to record clearly and definitely the structure of the metal. The volatilization of iron is pronounced enough at the crystal boundaries to clearly show them. Across the face of the crystals, however, there is very little loss, as is shown by the persistence of slip bands upon heating. That the ferrite is changed somewhat, however, is shown by its increased tendency toward oxidation.

Upon slight etching with nitric acid, a very pronounced oxide film readily forms, so that the ferrite is colored very dark.

Specimens which are heated to temperatures higher than the A_1 transformation show a carbonless layer which becomes less pronounced as the temperature is increased. This is properly to be attributed to the increased rate of diffusion of carbide in iron, by which the change at the surface is masked. The results obtained by etching specimens at the higher temperatures (heat etching or otherwise) are more truly indicative, therefore, of the structure of the interior than those at lower temperatures; for example, just above A_1. That the loss of iron by volatilization across the face of the crystals is very slight, even at high temperatures, is shown by the persistence of the slight roughening due to preliminary etching throughout the entire period of heating. The loss by volatilization is of a magnitude sufficient to show the crystalline structure by the production of "etching pits;" at the crystal boundaries the loss is much greater. In addition the carbide is removed to a very appreciable depth on all the exposed faces of the specimen.

V. SUMMARY

1. When polished metal specimens are heated in vacuo, a record of the structure which exists at the particular temperature used is inscribed on the polished surface of the specimen. This record consists of a slight roughening due to volatilization and to a slight buckling of the surface due to the volume change which forms part of the transformation. The terms "heat relief," "heat etching," and "vacuum etching" have been applied to this means for developing the microstructure.

2. By means of heat relief the structure of iron and steel at high temperatures is readily revealed. This is a much simpler method than high-temperature etching, often used. It appears probable that much of the effect usually attributed to etching at high temperature is due to the heating itself.

3. An appreciable change of composition and structure of the surface metal occurs in steel upon heating. This is very pronounced just above the A_1 transformation, and becomes less so upon heating to higher temperatures due to the increased rate of diffusion of carbon (as carbide) in iron, with increase of temperature. The structure revealed on the surface by heat relief or by high-temperature etching is less representative of the interior at

temperatures just above the A_1 transformation than at any other temperatures.

4. The change in composition of the surface layer of steel heated in vacuo to high temperatures is to be explained as due to volatilization of the carbide. No appreciable change takes place until the carbide enters into solid solution in the iron, that is, above the A_1 transformation.

5. The volatilization of iron from the surface, upon heating, is very slight. Polished specimens of iron and steel, etched before being heated, retain the slight roughening due to the etching even after pronounced heating. The volatilization of ferrite at the crystal boundaries is much more pronounced than across the face of the crystal.

WASHINGTON, July 14, 1919.