THE DETERMINATION OF THE PERCENT OF CARBON IN STEEL BY MEANS OF THE MICROSCOPE

> Thesis by Henry Eveleth Publow 1919



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THE DETERMINATION OF THE PERCENT OF CARBON IN STEEL BY MEANS OF THE MICROSCOPE



A THESIS

Submitted to the Faculty of the MICHIGAN AGRICULTURAL COLLEGE

by

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THESIS

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INTEORUCTION

Two decades ago, the science of metallography was almost unknown, altho in many other lines of investigation, the microscope had become a necessity. It is only within the last few years that its value in this direction has been recognized. In spite of many drawbacks, the work has made remarkable progress, particularly during the late war.

This work was undertaken with the thought in mind, that if the microscope could be used in this work for roughly approximatemenalyses, it might also be used for more exact work. If the solution theory, as advanced at present is correct, then it would be necessary only to overcome the mechanical difficulties, in order that we might have an accurate method for determining carbon, by this means, within a degree good enough for commercial specifications, or even closer. In addition, the analyst can get a glimpse of the physical make up of the metal, which is impossible in a chemical enalysis by combustion, as here the first requirement is the destruction of the existing structure.

In the first chapter, the author has endeavored to give a brief summary of the solution theory and the application of the phase rule to it, in so for as it applies

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to metals and their alloys. This conception of it has been taken from the works of Howe, Fay, Saueveur, and others, who have done much for the advancement of the science.

In chapter two, by simple mathematical calculations and the application of the solution theory, the relationexisting between the components and constituents of slowly cooled steels is discussed. Here it is shown that, that relationship is very definite and exact, and that if the various constituents cannot be measured, it is due to mechanical difficulties.

Chapters three and four deal with the apparatus and the actual data collected. It will be seen that the results obtained justify the effort. Before any of the work was written up, the method was tried in the lalyatory by the authors classes. The results obtained were very good, the main flifficulty for the beginning student being the estimation of the areas covered by the various constituents. This, after a little pratice was overcome.

If the author, has by this work, added a mite to the great fund of knowledge being gathered to-gether along these lines, he will feel amply repaid.

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CHAPTER I

In the year 1878, Willard Gibbs, at that time Professor of Physics in Yale University, enunciated the Phase Rule, one of the most notable contributions ever made to physical chemistry. Altho the rule applies to every system of materials with which we come in contact, it is particularly useful in helping us to interpret the constitution of the metallic alloys.

The phase rule deals with the equilibrium of systems and is generally expressed as follows-

 $\mathbf{F} = \mathbf{C} + \mathbf{2} - \mathbf{P}$

Showing the relation existing between the degrees of freedom (F), the number of components (C), and the number of phases (P), As these different factors are capable of various definitions, the following are given as applying to the rule.

First-

We will consider a system in equilibrium when it is both physically and chemically at rest, that is there is no molecular motion, neither are there any compounds being broken up, or being formed. We have two main types of substances, namely, homogenous and heterogenous, and alloys of metals exist in both conditions. Howe suggested that we call the homogenous alloys, "metarals," because of the close resemblance between their constitution and those of rocks, while the term "aggregate" is used by Saueveur to designate heterogenous alloys.

Second-

There are three independent variables which may affect

the equilibrium of a system, namely-

1 - Pressure

2 - Temperature

3 - Concentration

If we can vary one or more of these conditions without causing a chemical or physical change, then the system is said to be in stable equilibrium, but if the variation of one of the conditions causes a change, then the system is said to be in unstable equilibrium. Often a system will fail to undergo a transformation when the change is due, in this case it is said to be in a metastable condition of equilibrium.

Third-

By degrees of freedom, we mean the number of the three variables, temperature, pressure and concentration, which may be changed without disturbing the equilibrium. If the system has no degrees of freedom it is said to be "unvariant", and if it has one degrees of freedom it is said to be Bunivariant", while if it has two degrees of freedom it is said to be "bivariant".

Fourth-

By phase is meant the homogenous physically distinguishable and mechanically separable constituents of a system.

Fifth-

By components, we mean those constituents, the concentration of which can undergo independent variation in the different phases. Howe gives a clearer definition, "those free elements and compounds which in the nature of the case are undecomposable under the conditions, and thus play the part of elements. It is sometimes difficult to determine the number of components in a system , unless the following rule is applied.

As the components of a system, there are to be taken the smallest number of independently variable constituents, by means of which the composition of each phase participating in the states of equilibrium can be expressed in the form of a chemical equation. In the the case of alloys, such difficulty does not arise, as the components are always the constituent metals, or some simple compound.

When dealing with alloys, the influence of pressure is generally neglected, because of the fact that they are so feebly volatile, and are thus subject to atmospheric pressure. If the pressure is eliminated, we necessarily reduce by one the degrees of freedom, so that the rule becomes-

$$F = C + 1 - P$$

This limits the number of possible phases, for an alloy in equilibrium, made up of X metals cannot have more than X phases. If it $n \in X+1$ phases, the rule becomes-

$$F = X + 1 - (X-1) = 0$$

and the alloy would not be in stable equilibrium, on the other ham if the alloy had X-1 phases then-

$$F = X + 1 - (X-1) = 2$$

and the alloy would have the maximum number of degrees of freedom.

PHASE RULE APPLIED TO ALLOYS

In general the metallic elements may exist in either a liquid or solid state, and the study of what occurs as they pass from one state to another, brings in the application of the phase rule. We know that if a pure metal in the liquid state is gradually cooled to a solid state, at the temperature at which the change takes place there is an evolution of heat. If we are measuring the drop in in temperature by means of a suitable pyrometer and plotting a curve, using time and temperature as the coordinates, the curve would look like that given in Figure 1, Plate 1. The portion BC of the curve shows where the change of state occus there being an evolution of heat. As there is only one metal, there can be only one component, but three phases are possible, (1) liquid metal, (2) solid metal, (3) alotropic forms of the so solid metal. In Figure 1, Plate 1, above the point T, we have all liquid, therefor one phases and the rule becomes-

F = 2 - 1 = 1

That is the system is univariant, therefore we can alter its tem temperature within wide limits without disturbing its equilibrium. At the temperature T, we find crystals forming in the liquid, thus we have two phases present and the rule reads-

F = 2 - 2 = 0

and the system is unvariant. If we either raise or lower the temperature, we will cause the disappearance of one phase of the other. Below T, the system is entirely solid, that is the number of phases is again one, and we have-

F = 2 - 1 = 1

the system being univariant.

Now let us turn to binary alloys. That is, those alloys which are made up of two metals. In this case we have two components and the phase rule reads-

$$F = 2 + 1 - P \quad \text{or } 3 - P$$

First let us examine the cooling curves of a binary alloy. Here we have three cases-

(1) - Alloys soluble in each other when both hot and cold.



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(2) - Alloys soluble in each other when hot, but insoluble in each other when solid.

(3) - Alloys soluble in each other when hot, and partially soluble in each other when cold.

Let us briefly examine case 1. A typical cooling curve of such an alloy is shown in Figure 2. Plate 1. As the alloy cools from A to B, we have a steady drop in the curve. When the point B is reached at a temperature T, instead of getting an evolution of heat enough to hold the temperature constant, there is a slowing up only, the alloy gradually becoming solid, but not entirley so till C is reached at a temperature T'. From C to D we have a normal cooling curve. From this it is shown that between C and B, there is a gradual precipitation of crystals and not a sudden one as in the case of a pure metal. Figure 3, Plate 1, we have the cooling curves of a series of alloys of the same two metals, varying from 100 % of A to 100 % of B. At a, the curve is similar to the one in 1, a',a",a'", are similar to that in Figure 2, and at a"" the same as Figure 1. If we connect b, b', b", b"", b"", and b, c', c", c"", b"", we will get a curve that can be used for any alloy of the metals A and B. However in this case we are attempting to pot both time and composition along the same line. Let us eliminate the time factor, ploting b's and c's directly under each other. Our curve then is shown by Figure 4, Plate 2. From this curve we can study the mechanism of solidification. Above acb everything is liquid and below adb everything is solid, while within the area acbd we have the transformation of one state to the other. If everything above acb is liquid we have but one phase and

F = 3 - 1 = 2

Which simply means that both the concentration and the temperature of the liquid may be changed within wide limits without disturbing the equilibrium of the system, or which in this case means solidification. The same rule applies below adb, except that here both temperature and concentration may be changed without causing the alloy to melt. Within the area acbd, we have two phases present, liquid and solid and the system is univariant, that is only the temper-

ature or the concentration may be varied arbitrarily. In Figure 4, plate 2, let us consider an alloy of the composition R. As the alloy cools to the poin y! crystals begin to precipitatite out, the composition of which at the temperature y^* , is shown by the point x^* . If the point x' does not show the composition of the crystal, then some other point on the line y'x' must show it. Let us suppose that the composition lies somewhere to the left of x', then it lies within the area acbd and the crystal itself must be a part liquid which is impossible, while if it lies to the right of x^* it must have become solid at a higher temperature than y'. Therefore it must have a composition shown by the point x'. As the temperature slowly drops the composition of the crystals change from x^{\dagger} , to $x^{\dagger \pi}$, while the composition of the liquid bath shifts from y' to y'", and the last drop to solidify has the composition y'",. If the alloy is gradually cooled below adb, difusion will gradually takes place in the solid solution, so that all the crystals will have the composition R', In other words within the area a c b d, if we vary the temperature, the concentration will vary accordingly, or if the concentration be varied the temperature will change.

Case 2-

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If we have a molten alloy falling under this case and





plot the cooling curve, it will take the form given in Figure 5, Plate 2. Here we have two parts to the curve where solidification takes place, namely BC and CD. Also we find that no matter what the percentage of each constituent the line CD always falls at the same temperature.

Case 3-

This is simply a combination of case 1 and 2. That is metal A will hold some of metal B in solution and B will hold some of A in solution. If we plot the cooling curves of a series of alloys of both A and B, omitting the time factor, we get Figure 6, **p**late 2. It will be seen that at the point b, or the eutectic we have a percentage of each metal where solidification takes place instantly. At this point we have two phases in the solid state, consisting of two solid solutions, and also one liquid phase.

Taking an alloy of a composition R, above a b c, we have all liquid, therefore one phase and 2 degrees of freedom. When the temperature L is reached, solidification begins. This means two phases within the area a b e, and the system is univariant. The first crystals that form are solid solutions of A and B having a composition S. If we shift the temperature to S'L', the composition of the crystals change to S', and the composition of the liquid bath becomes L'. If we lower the temperature to eb the composition of the liquid becomes b, but below eb, everything is solid, therefore we get sudden precipitation of the liquid whose composition is denoted by the point b. The structural composition of the solid material would consist of crystals of the solid solution of B in A, these being well formed, if the cooling took place slowly, and an aggregate of finely divided solutions of B in A and A in B, the compositions of each being shown by point G and H. However we still have just two phases, therefore the system is univariant.

As the iron-carbon alloys belong to the class of binary alloys, the constituents of which are partially soluble in each other when cold, let us examine their fusibility curves, and apply the phase rule to them, In this case we have several allotropic changes as well as changes of state. These forms can be grouped under nine heads as follows-

(1) - Liquid iron
(2) - Liquid Fe₃C
(3) - Solid solution of Fe₃C in Gamma iron
(4) - Solid gamma iron
(5) - Solid beta iron
(5) - Solid beta iron (ferrtie)
(7) - Solid alpha iron (ferrtie)
(7) - Solid solution of C or Fe₃C in beta iron
(8) - Solid Fe₃C (cementite)
(9) - Graphite

Figure 7, Plate 3, gives the cooling curves of the iron-carbon alloys as far as 4 % C. Let us apply the phase rule to it. Above the liquidus, we have only one liquid phase, and consequently 2 degrees of freedom for

F = 3 - 1 = 2

Within the area LSE, we have two phases, namely liquid solution plus solid solution (austenite) and therefore only one degree of freedom.

Within the area LAHDS, we have but one phase, a solid solution and here the system is bivariant. As we reach the point the point D, the system becomes non-variant, for here we have





austemite ferrite, and cementite as the three phases. In the area DSS'F we have two phases, namely austenite and cementite and the system is univariant. Within the region ABH we have beta iron and austentite and the system is univariant, while in the region BCDH, there are also two phases, namely austenite and alpha iron, the system still remaining univariant while finaly below CDF, there are several possible cases.

Case 1 - The cementite formed during the solidification and cooling remains unchanged and we have a univariant system the phases being ferrite and cementite. The system is however in a metastable condition. This is the condition of the slowly cooled steels of commerce.

Case 2 - The cementite has been completely changed over to ferrite and graphite, giving a condition of stable equilibrium.

Case 3 - The cementite has been partly decomposed into graphite, thus giving three phases, and therefore a nonvariant system, this being the condition of the slowly cooled gray cast iron of commerce.

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CHAPTER II

We find that in dealing with metals, particularly in the solid state, the time factor in cooling plays an important part in our final structure. If we wish to obtain material from which we can pick out the different components, by means of a medium powered microscope, it is necessary that we allow the metal to change its state slow enough, that the different components have time to adjust their crystals. At the same time, we cannot allow two long a period on account of the expense involved. As this work deals only with carbon steels, I will outline briefly the results produced upon the metal by different rates of cooling.

When a pisce of steel is in the region LSDHA Figure 7, Plate 3, it is composed wholly of austenilte and is in the solid state. As it passes thru the upper critical range, there is a change of state, from one phase to two and at the point D, we have three phases present. On account of the material being in the solid state, diffusion takes place much more slowly, thus requiring a longer time for the reaction to complete itself. This means then that we have a change in cypstaline structure. If the steel is allowed to gradually approach AHD, and gradually pass thru the transformation points sufficient time will elapse so that the new structure will be fairly perfectly formed into its basic structural constituents. On the other hand, if the time is greatly shortened, then the crystals will not have time to reform

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before the metal becomes so cold that movement is impossible or at least almost infinitely retarded, and we have a structure from which the components cannot be easily picked. However this may increase the value of the metal from a commercial standpoint for certain uses. I have attempted to show this in Figures 8,9, and 10, Plate 4.

Let us take for instance a steel whose composition is R, Figure 11, Plate 4a, nemely 0.5 % C. As we cool it to 1, the first change from the solid solution takes place, ferrite being thrown out from the crystals of austenite, thus making the remaining sustenite richer in Fe₃C. If these ferrite crystals are allowed to grow gradually, they will get a chance to form a fairly definite structure, but if we suddenly stop this growth, by cooling the whole mass suddenly, then they will be too fine to distinguish clearly by the usual means. Ont the other hand if the growth proceeds at a normal rate, more ferrite will be thrown down, and segregate in large crystals, till we reach the line CD, when there will be a sudden precipitation of the extectoid mixture of 1 part cementite and 7 parts of ferrite, forming a fine sggregate. Figure 12, Blate 4b, shows this taking place in five steps, first sustenite crystals, lastly ferrite and pearlite. As the range of temperature becomes smaller, where precipitation can take place, that is as we approach the eutectoid point from either direction, the cooling thru this range must be more gradual if good results are to be obtained. However some pearlite is likely to be caught in very thin films between the ferrite, even with the slowest cooling possible.












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If a definite relationship can be established between the percentages of these constituents and the percent of Carbon present, we will have a simple and accurate method of determining the percent of carbon. Commercial carbon steels are never pure alloys of iron and carbon, and the smount of the imputities affects both the critical points and the position of the eutectoid point. However the amount of impurities is limited by the specifications under which the steel is purchased, and for carbon steels of fair grade, the amount allowed will not introduce enough error to cause any trouble.

In the case of hypo-eutectoid steels the relationship between the structural and chemical composition as regards carbon, may be found as follows-

We know that the whole mass is composed of ferrite and pearlite, therefore-

F + P = 100

Where F = the percent of ferrite and P = the percent of pearlite. Also all the carbon is contained in the pearlite, therefore.

$E/100 \times P = 0$

Where E = the percent of carbon in the pearlite and 0 = the percent of carbon in the steel. Also as the carbon is present in the shape of Fe₃C, by molecular weights Fe₃C contains 6.67 % C. We do not however know the exact position of the eutectic point, but simply that it lies very close to 0.85 % C, the exact position depending upon the chemical composition and the heat treatment the **petce** has received. Assuming that it is 0.85 % C, we have

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 $6.67/100 \times \% C = 0.85$

% C = 100/6 67 x 0.85 = 12.74

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or the ratio of cementite to ferrite in the pearlite is about 1 to 7, which places the eutectoid point at $0.834 \ \%$ C. From this we can easily calculate the structural composition of a hypo-eutectoid steel. The total cementite will be = to 15C and there is eight times as much pearlite as cementite, we will have the total pearlite = total cementite time 8 or P will equal 120 C. Figure 13, Plate 5, gives the results of plotting the percent of pearlite for any percent of carbon. In the case of hyper-eutectoid steels we have only free cementite and pearlite and here

P + Cm = 100

also $\frac{5}{100} P + 6.67/100 Cm = C$

as all the ferrite is contained in the pearlite, and therefore the total ferrite = F = 7/3 P.

 or
 % P = 8/7 F, but F = 100 - Cm

 therefore
 P = 3/7(100 - total Cm)

 but
 Cm = 15 C

 substituting
 P = 8/7(100-150)

 or
 P = 114 - 17 C,

These values are also to be found in Figure 13. Plate 5, as well as the corresponding values for cementite, total and free. From Figure 13, we can therefore determine the percentage of the structural constituents. For instance, a steel containing 1.2 % C, contains 82 % P and 18 % Cm, while a steel containing 0.5 % C, has 40 % F and 60 % P.

On the other hand we can reverse the use of the diagram. That is if we know the percentage of the structural constituents, we can determine the percent of Carbon. For





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example, a steel containing $30 \ \%$ of P and $70 \ \%$ of !F, contains 0.25 % C. In order to make the reading of the diagram more simple Figure 14, Plate 6, has been drawn. Here the pearlite is given in one continous line, as are also the other constituents, in order that the reading may be more easily done.

Thus we have a clearly established relationship existing between the structural components and the percent of carbon present. The only remaining difficulty is to measure the percentages of the structural constituents simply and accurately. If this can be done, we will have a method of determining the carbon content, which will be a great aid in checking the chemical composition as determined by the combustion method, if indeed it does not tell us far more than the latter.





OHAPIER III

In order that a clear understanding may be had of the methods used in the following work, a short description is given below of the apparatus used. None was used except such as might be found in any fairly well equipped lagratory. The sample to be tested was polished in the usual menner, using 65F alundum on broad cloth for the final polishing. The specimens were etched with a 5 % solution of HNO, in $C_{2}H_{5}OH$. Two types of microscopes were used. The first will bear description, as it was reconstructed from a regular instrument. In fact this one was used for all the work, the regular metallurgical microscope not being delivered till late in the spring term. This latter machine was a Bausch and Lomb regular COM with a mechanical stage and all the necessary attachments. This was mounted upon a camera made by the same firm, light being furnished by a new type arc, with an aspheric condenser. This outfit is shown in figure 19, Plate 27. A picture of the homemade apparatus is given in Figure 16, Page 27. The microscope was fitted with a Leitz dark field illuninator, the substage removed and in its place was substituted an electro magnet, capable of movement in two directions by means of slow motion acrews. Light was furnished by a Leitz Lilliput are lamp, fitted with a bulls eye condenser. The lamp and microscope were mounted upon a board and the image thrown against a clear glass, fitted into a sketching board, supported by a nickeled rod, the board being capable THE NEW MICROSCOPE did not come till

MAY 19, 1919.





FIGURE 16 . BOTH OUTFITS MOUNTED ON THE SAME BASE.

METALLURGICAL LAB. M.A.C.



FIGURE 17 SAME AS ABOVE, SHOWING DETAILS.

of movement on the rod, and also horizontally around it. The tracing paper was slipped under suitable clips on the board and the image traced off. This formed a convenient and easy meyhod of sketching the structure of the petce. It was found that a magnification of between 100 and 200 diameters, was great enough, if the sample had been given proper treatment, so that the various constituents could be easily distinguished, and the outlines of the crystals traced with a sharp pencil.

There are several factors, which will, if not taken care of, produce results far from right.

Case 1- Improper heat treatment.

(A) Too rapid cooling.

(B) The temperature not being carried above the upper critical point.

Case 2 - Improper etching and polishing of the surface.

- (A) Over etching
- (B) Spoiled etching solution
- (C) Improper drying of the specimen
- (D) Poor polishing

Case 1 - (A)

If we cool too rapidly, we will get a structure is which shows that the ferrite, if it is a low carbon steel, and the cementite, if it is a high carbon steel, are thrown out suddenly, with the result that the crystals become jagged and sharp and poorly formed. This is shown in Figure 18,Page 30 and in Figure 19,Page 30. These pictures show a medium and a low carbon steel. Both were cooled, by simply removing the pieces from the furnace and allowing them to cool in air. The temperature of the furnace being About 1700 degrees F.



Magnification of each about x 120 The effect of under heating is shown in Figure 20, this being the same sample as Figure 18, but the temperature at which the sample was treated was about 1000 degrees F. It will be noted that the structure of the passe is the same as that of the specimen when reacived, this being shown in Figure 21.



Heated to 1000 deg. F As received Magnification x 120

Case 2 - (A)(B)(C) If we allow the specimen to remain in the etching bath for a long period of time, as the action of this bath is one of **corros** on, the mere outline of the crystals will not show, but the different crystals themselves will be eaten away, causing blacking of the surface in spots and areas will appear pearlitic, which are really ferrite. The actual error introduced will be shown later on. If the etching solution has been used a number of times, it will contain iron salts in sufficient quanity to produce deposits upon the surface, which will give a very different structure than the real one. This will also introduce error, Then if the specimen is not dried rapidly, films of oxide will deposit, which will spoil the surface for carbon determinations.

(D) If just the carbon content is desired, then the surface need not be entirely free from scratches, all tho very few should be present. If we desire to keep a per& menant record of the sample in the form of a photograph , then the surface must be free from scratches.

In some of thes work we wished to know the actual size of the crystals, and also the distance covered by the drawing. The method used, while not the most accurate, gave good results and was very simple. The draw slide from a slide rule was inserted under the microscope, instead of the specimen, and the instrument focused on the log scale. As the divisions came to a sharp point, even at 200 diametes the distance could be accuratly measured between points, and this distance measured a minot the actual scale. The number of times preater, the distance between points that

one division of the log scale would give the magnification. If this was found to be 160, then by a simple calculation one inch of screen represents 1/160 of an inch on the specimen or **B**.0062". One square inch of the screen then means **0**.0000000 sq.in. of specimen surface. The cross section paper used contains 20 lines per inch, therefore 400 areas per sq.in. If a crystal covers 50 areas on the section paper, the actual crystal covers **0**,0000000 times **0**.125 = **0**.0000043 sq.in of surface.

CHAPTER IV

Keeping in mind the errors which can easily occur, I wished to formulate a method if possible, by which the carbon content of a given sample might be determined by an examination of its structure thru the microscope. This method must be simple enough to be used by the students, and at the same time the results obtained must check combustions run on the same sample.

First six typical samples were selected. These were of Carpenter steel of very good quality, and gave a range of carbon from low to 1.2 %. The samples were numbered as follows- A,D,E,F,G,H. The above samples were analysed by direct combustion. The absorbing medium being Bakers Soda Lime for Combustions and consisting of

NaOH =
$$37 \%$$

Ca(OH)₂ = 45%
H₂O = 15%

Filings were taken from several bars at various places and well mixed, so that the results obtained would be general as far as possible.

The results obtained are shown in Table 1, Page 34, This analysis falls within the limits usually required. Then by the methods previously described the carbon percentage was determined.

Accordingly a plece was cut at random from one of the bars, marked sample A, treated and tested.

No. of Sample	% C Trial 1	% C Trial 2	% C Average
A	0.16	0.18	0 .17
D	0.28	0.31	0.30
E	0.64	0 67	0.65
F	0.78	0.80	0.79
G	0.88	0.90	0 89
Н	1.19	1.21	1.20

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Table 1

The average percent of carbon was taken as the standard value for checking the microscopical analysis.

Three pieces were cut from A and marked A-1, A-2, A-3. A-1 and A-2, were heated to 1700 degrees F. A-2 wes conted in the air A-1, slowly cooled in the furnace thru a period of 24 hours. During the first 6 hours the temperature dropped from 1700 to 1200, during the remainder of the time to 75 degrees. The sample was then cut in Lo, so that the interior might be worked with, where no decarburizing effects had taken place. After cutting A-1, the surface was filed and enough filings obtained to run a combustion. This giving the chemical composition of the steel as close to the structure examined as possible. The specimens were polished, etched with 5 % HNO₃ and examined. The structure of A-2 was sketched upon cross section paper, within a two inch circle. Three different points upon the surface were taken , average structure being selected. Plate 7, Page 36, gives the original drawings under figures A-1-1, A-1-2, A-1-3. In table II will be found the results of the three determinations together with the results obtained by the combustion method. Figure 22 Page 37, gives a photograph of the specimen.

After polishing and etching, Sample A-2, was examined and a photograph is given under Figure 25, Page 37. It will be seen that the crystals are distorted, and over& lap eachother in such a manner that it would be impossible to sketch them accuratly.

The method of determining any given area of crystals was as follows. The number of squares within the area were counted, and as each square wass passed, a slight mark was placed upon it with the pencil. The counts were made in series of 199 at a time.









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Sample A-1 Heated to 1700 F Cooled in the furnace

Figure 22

Figure 23

Sample A-2 Heated to 1700 F Cooled in air.

Figure 25

Figure 24



Sample A-3 Heated to 1500 F Cooled in the furnace



Sample C-1 Heated to 1700 F Cooled in air.

Sample No.	Heated to	Cooled in	Area of Pearlite	Area of Circle	% P	% C	ダ C Combus, T1-T2-Av
A-1-1	1700	Furnace	221	12 50	18	0.15	
A-1-2	1700	n n	198	1250	16	0.13	.161817
A-1-3	1700	11 11	204	1250	16	0,13	

From the above table it can be seen that the areas had a maxium variation of 23 areas out of 221 or about 10 %. But for 0.1 % C it requires about 150 areas, and in the 150 there would be a maxium variation of 15, or this would be equivalent to 0.01 % C. Our chemical analysis came only within 0.02 %, giving an average of 0.17 %, while the average by the physical method was 0.143 %, or 0.027 % below that obtained by the chemical analysis made, and given in table 1.

The next piece A-3, was treated as follows. Heated to 1500 F and cooled in the furnace. This treatment took the piece only a little way above the critical point. The sample was polished and etched in the same manner as A-1, and the results are given in Plate 7, Page 36. The areas of the different points are given in Figures A-3-1, A-3-2, and A-3-3., Figure 24, Page 37, gives a photograph of A-3.

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II

TABLE

From the photographs of the different samples taken fro bar A, it can be seen that slow furnace cooling is necessary, and that for low carbon steels the maximum temperature should be above the upper critical point. That temperatures between 1500 and 1700 F, will give good results if the cooling be slow enough.

Next samples D,E,G,H were given the same treatment as bar A, and the results are shown in Table 3. The sys tem of numbering the different pieces is the same as given for sample A. That is the letter stands for the bar number, the first figure for the piece taken from the bar, and the second number for the area of the piece.

It will be noted on examining this data, that in nearly every case the 5 pf carbon by this method fell a little below that obtained by the combustion method. Also that this difference was very nearly constant except around the eutectic point. At this point, and for a little way on each side of it, it is impossible, even with the slowest treatment, which could be economically given, to distinguish either free ferrite or free cementite. I believe the reason that the microscopial analysis ran a little below the chemical was due to the fact, that in the mechanism of solidification some of the pearlite is caught between the ferrite grains and thus lies in such fine films that it can not be measured at the magnification used. In the case of high carbon steels, the cementite areas were counted, and the same held true here. If we give each sample the same heat treatment, for like carbon content, we will get about the same error.

Sample No.	Heated to	l Co	oled in	Area of Pearlit e	Area of Circle	₿ P	ب ر	C T1	% ombu T2	ls. Ave.
A-1-1	1700	Fur	nace	221	1250	18	0.15			
A-1-2	17 00	Ħ	n	198	1250	16	0.14	, 16	. 19	.17
A-1-3	1700	n	Ħ	204	1250	16	0.14			
Average	e						ن 1 4غ			. 17
A-3-1	1500	Fur	nace	222	1250	18	0.15			
A-3-2	1500	n	n	233	1250	19	0.16	. 1ó	. 1 9	. 17
A-3-3	1500	Ħ	n	218	1250	16	0.14			
Average	9						0.15			
D-1-1	1700	Fur	nace	452	1200	36	0.30			
D-1-2	1700	8	n	415	1250	33	0.28	.28	.31	.30
D -1-3	1700	n	n	458	1250	37	0.31			
Average	2						0.296			. <u>z</u> o
E-1-1	1700	Fur	nace	975	1250	78	0.65			
E-1-2	17 00	11	n	978	1250	78	0 .65	.64	.67	.66
E-1-3-	1700	n	Π	96 8	1250	7 7	0.64			
Average	2						0.646			.6C
F-1-1	1700	Fur	nac e	1141	1250	91	0.76			
F-1-2	1700	n	n	1143	1250	91	J.76	.78	.80	• 7 9
F-1-3	17 00	n	n	1151	1250	92	0.77			
Avernge	9						0.763	,		. 79

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III

TABLE

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Table 3, con't.
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G-1-1 1700 Furnace 1250 100 0.83 all G-1-2 n Ħ 0.83 .00 .9J .89 1700 all 1250 100 G-1-3 1700 n 0.83 " 811 1250 100 Average 0.83 69 H-1-1 1700 Furnace 1174 1250 94 1.18 H-1-2 1700 n 1184 1250 95 1.13 1.18 1.21 1.2 H-1-3 1700 n n 1.17 1172 1250 94 1.16 Average 1.2

The original tracings may be found on the following Plates.

Sample A,- Plate 7, Page 36 Sample D,- Plate 9, Page 42 Sample E,- Plate 10, Page 43 Sample F,- Plate 10 Page 43 Sample G,- Plate 11, Page 44 Sample M,- Plate 11, Page 44













The results given in Table 3, I have plotted on Plate 12, Bage 46. Not using the average value for the difference, but the maximum and minimum, for each sample. and thus obtaining a curve which broadens out at the points where error occurs. The true pearlite curve is also given, as taken from Plates 4 and 5. It will be noticed in table 3, that sample H was heated to 1930 F instead of 1700 F. This was so it could be taken above the Acm line in order to get complete precipitation of the cementite.

On Pages 47 and 48, may be found photographs of the various samples, showing the increase in the amount of pearlite present up to the eutectoid point and the cementite surrounding the grains in the high carbon steel.

In order to use the curve given in Plate 12, proc proceed as follows-

Determine the area of pearlite at three different points on the surface of the metal. Two values for the percent of carbon will be found for each percent of struck ctural constituents. This will give six values in all. Take the average of the six. If the percent of pearlite runs over 50, count the other constituent and subtract from 1250, or whatever the total area of the drawing happens to be.

Now the reverse of what has been given was tried. The carbon content of several samples was determined in this manner, and the result checked by the combustion method. The results are given in table 4. Page 49. Each of the samples will be taken up in detail.







Low carbon Steel, about 0.2 % X 200 Heated to 1700 F, and cooled in the furnace.



Medium Carbon steel, about 0.5 %. \$ 170 Heated to 1700 F, cooled in the furnace



Eutectoid Steel, about 0.88 % C, X 150 Heated to 1700 F, cooled in the Furnace



High Carbon Steel, about 1.2 %, X 150 Heated to 1900 F, cooled in the furnace. .

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Sample No,	Heated to	Area of Circle	Ar ea P	of % P	Min	% (አ.ጠ. 1) (.A⊽€	% C	Differen e e	
B-1-1	1700	1250	376	30	.26	.27	06	.25 .2 7	••	
B -1- 2	1700	1250	36 7	29	.25	.26	.20	.20	.90	
B 1-3	1700	1250	165	15	.14	.16		Area on edge sample	of	
B-3-1	1500	1250	355	2 8	.24	.25	•1.	SAME AS D-	22	
B-3-2	1500	1250	3 35	27	.23	.25	• 6 4	٠	.02	
B -3-3	1 5 00	1250	175	14	. 13	.16		Area on edge sumple	01	
C-1-1	1700	1250	69 2	55	.47	.48	.48	.36 .39	•••	
0-1-2	1700	1250	541	44	.38	•39	-0	. ₂ 6	. 12	
0-1-3	1700	1250	552	44	37	•39	. 38		.99	
S -1- 1	1700	1250	168	13	.13	.15				
S-1-2	1700	1250	162	13	13	.15	. 14	.12 .15	01	
S-1-≶	1700	1250	166	13	. 13	.15		. 12	.01	
AT 1- 1	1700	1250	427	34	.28	.30				
AT-1-2	1700	1250	385	31	.27	.28	.27	Edge of case	hardened	
AT-1-3	1700	1250	405	32	.28	.29		be 1. 2	of boad 5 5 0	

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Case (1) Sample B

The sample was heated to 1700 F and cooled in the furnace for 24 hours. The specimen was then sawed in two and the anterior examined. The structure is shown in Plate 8, Page 51 Figures B-1-1 and B-1-2, were portions of the surface, taken on the enterior of the surface, and , and these results check the combustion determination very closely. In Figure B-1-3, we have a determination which does not check. This drawing was made on the very edge of the sample and shows that the prolonged heating in an oxidizing atmosphere, caused a decarburization of the exterior of the sample.

Case (2) Sample B

This was off the same bar as the above sample, but as will be seen on the data sheet, the sample was only heated to 1500F instead of 1700 F. In this case the crystaline structure is not as well defined, the crystals not having had as much time to grow, and are therefore somewhat smaller. In the case of B-3-3, and B-3-2, the results check pretty well. Good enough for commercial analysis at least. Figure B-3-3, again shows the effect of prolonged heating on the carbon content.

Case (3) Sample C

This sample was taken from the forge shop stock from some material which had been giving trouble. It was su supposed to be about 0.6 % C. Some of the bars would harden alfright, others would not. Some of the bars seemed to harden better in the center than on the ends. The sample tested was taken from the end of one of the bars. Figure C-1-2 and C-1-3, show the true content of the bar. C-1-1





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gives a much higher percentage than the other two. This sample was taken to show the effect of overetching, and shows that a mistake in this direction can be made very easily. The other drawings check the carbon content as determined by the combustion method. C-1-1 and C-1-2-3are found on Plate 9, Page 42.

Case (4) Sample \$

This sample came from the Gier Pressed Steel Co. After proper treatment, the drawings of the sample were made and are given on Plate 13, Page 53. Here care was used in all three areas examined to get characteristic portions of the surface. The results obtained in Figures S-1-1, S-1-2, S-1-3, check very closely with the carbon content found by the combustion method. In this particular test, The actual time consumed in the operation. after the sample was taken from the furnace was 18 minutes. While the time taken for the combustion was 20 minutes. This shows that the time consumed is just about the same for either method.

Case (5) Sample AT

This sample came from the Reo Motor Co. It was taken on the edge of a piece of case hardened material. The case was supposed to be about 1.2 % C, but it would not harden when quenched. On examination, as will be seen from Figures AT-1-1, AT-1-2, AT -1-3, Plate 13, Page 53, the carbon content of the case did not exceed 0.27 %. It was found that the trouble was due to faulty pyrometers, and that the temperature was not high enough. The sample suggested to the author that here a case might present it self, where the method of determining the D of C, might be of value. It is impossible





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 $= e_{ij} e_{i$

Sample of low carbon steel showing the effect of different rates of cooling on

the structure of the specimen.

Sample as received X 150



Slowly cooled in the furnace X 150



Cooled in air X 150



Quenched in water X 150

to determine the carbon content of the case by the combustion method. for if it is only 1/16 of and inch deep, we could not be sure that our filings did not have some of the softer material. Yet if this method worked, the Carbon content could be determined at any depth in the case with esseand accuracy.

Consequently 4 specimens of case hardened material were obtained, these being hereafter designated as samples AT,HT,HS,HR. Sample AT has already been described. Sample HR, was found to be cased to 0.52~% C. The other two were found to run to sutsciold composition. On Page 56 and 57 are shown photographs of these different specimens.

Plate 14, Page 58, gives a drawing of a section of sample HT. This drawing is a good deal larger than the image thrown upon the screen, and was obtained by carefully moving the paper and the piece in unison. Altho this requires very careful work, and takes a little experience, the results justy the effort. Here the specimen was magnified 160) and onthe drawing the actual depth of case has been scaled off. It will be seen that the eutectoid composition extends in 0.0103 ". The chart at the bottom of the plate gives the carbon content for each half inch of depth on the drawing or for each 0.0031" of actual metal.

Plate 16, Page 59, shows the case of sample *\$ HS-1-1. Great care was used in making the drawing, and the case had been so put in, that we might have a gradual



Sample AT X 50 Slowly cooled from 1700 F Outside of case

Sample AT X 100



Sample HS X 50 Slowly cooled from 1700 F

Sample HT X 50 Slowly cooled from 1700 F.







1.14 . 1.11 A.14 . . 1.11

R

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4 1.0

increase in the percent of carbon from the center out.

This is also shown in sample NR, here we again have the effect of decarburizing action. and on first examination it appeared as if the exterior of the case might run as high as 1.4 % C. But section N and O only had pearlitic areas of 529 and 443 out of 600. This would have made the carbon content run up above the limit for steel. Yet it looked as though a very high case had been obtained.

This type of examination gives one a very good clue as to what has happened to the passe, an until r the heat to which the passe was carried with the carbarizing anterial used was proper.

The last sample tried was a high carbon steel, which was supposed to be of subschold composition. However the total area of pearlite was below 100 %, and considerable commutite showed up. This gave an average analyis for the specimen will be found on Plate 17, Page 62, Figures HU-1-1, HU-1-2- HU-1-3.

Tables 5 and 6, give the results for samples HR and MS. These will be found on pages 64 and 65.









TABLE	v

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Section	Area of Peorlite	Arca oi Circle	5 % P	デ C Min. Max.	ූ් C Average
A	62	600	10	.115 .125	. 12
В	84	600	14	.135 .165	.15
С	134	േഠ	22	.200 .210	.21
D	138	600	25	.200 .220	.22
Е	214	600	36	.305 .320	.31
F	280	600	47	.400 .410	.41
G	<u> </u>	60 0	64	.540 .550	. 75
Н	412	60 0	69	.585 .59 0	.50
I	495	600	82	.690 .705	70
K	533	600	3 7	.750 .750	.74
L	570	600	9 7	.800 .900	.85
М	58 0	600	9 7	.80 0 .90 0	.85
IJ	52 9	600	87	.730 .750	.74
0	443	600	74	.625 .6 35	.63



TABLE	V	
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Section	Area of Perrlite	Area of Circle	% P	f C Min. Max.	0 % Averaje
A	62	600	10	.115 .125	. 12
В	84	600	14	.155 .165	.15
C	134	60 0	22	.200 .210	.21
D	138	60 0	25	.002 .200	.22
E	214	600	<u>36</u>	.305 .320	. 31
F	280	600	47	.400 .410	.41
G	<u>335</u>	60 0	64	.540 .550	• <u>5</u> 5
Н	412	୧୦୦	69	.585 .590	.58
I	495	600	82	.690 .705	70
K	533	600	ි7	.750 .750	.74
L	570	63 0	9 7	069. 063.	.85
Μ	580	600	97	.80 0 .90 0	.85
N	52 9	600	ଞ 7	.730 .750	.74
0	443	600	74	.625 .6 35	.63

TABLE VI

Sample HS

Section	Area of Pearlite	Area of Section	% P	% € MinMax.	% C Average
A	53	80 0	7	.080 .105	.09
В	63	80.)	8	.090 .110	.10
С	95	800	12	.120 .135	.13
D	132	80 0	17	.155 .165	. 16
E	165	800	21	.190 .205	.20
F	194	800	24	.210 .215	.21
G	201	800	25	.220 .230	.23
н	273	800	34	.290 .300	.30
I	338	800	42	.360 .370	.37
К	374	800	47	.400 .410	.41
L	417	800	52	.440 .450	.45
М	430	800	54	.460 .470	.47
N	48 7	200	60	.510 .520	.52

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Showing cases of different carbon content.



Photograph showing the effect of improper polishing and etching of the specimen.

Conclusion-

The author hopes that by this work he has given a glimpse into a field of analytical work which at present is almost untrodden. The results obtaimed compare favorably with those obtained by chemical means. In the case of material such as case hardened we can get results which it would be impossible to get by the combustion method. For the combustion would give only the average carbon content, which of course would be useless.

The entire work may be summed up in a few brief paragraphs. We know that the amount of pearlite im a slowly cooled steel is proportional to the carbon content, and as steel is an alloy of iron and carbon, whose cooling curves have been accurately determined, and also as it is an alloy, the cooling of which can be easily controlled, it is possible by proper heat treatment to cause nearly complete separation of the ferrite and pearlite in hypo-eutectoid and the pearlite and cementite in hypor-eutectoid steel. This statement does not apply to alloy steels. Also by using proper magnification, these differnet constituents may be fairly well traced off and measured. The error introduced is low and fairly constant, so that a correction curve may be plotted, which will give results that check the carbon determinations by the combustion method very closely.

In the range from 0.79 to 0.90 % C, it will be noted that the constituent of which there is very little present can not be calculated, so that within this range our error amounts to 0.06 %. However this gives results as close as most specifications read within this range. On the whole a mistake is less likely by this method, for here we bring out physical structure, and thus the chemical constituents, while a chemical analysis calls for the complete destruction of the sample, and if some constant error should creep in, it is likely that it would not be detected.

In order to get good results, the following points should be observed:#

- (1) The specimen should be heated to a least
 1700 F, and slowly cooled in the furnace.
 Steels above 1.0 %, can be heated to 1900
 F, with better results.
- (2) The specimen must be properly polished and etched. For slowly cooled steels, a 5 %
 HNO3 in C2H5OH, gives good results.
- (3) The different areas traced must be representative of the whole piece, and not of

 a particular point, unless we wish to examine that particular area.
- (4) A magnification of between 100 and 200 Xhigh enough for a properly treated sample.

 (5) - The tracing and measuring of the constituents must be carefully done, and the correction curve used to determine the percent of carbon. Count the area of the constituent which is less than 50 %.

All the negatives used in this work in the making of the photographs are on file in the author's laboratory at M.A C.

Preformed in the Metallurgical Laboratory at The Michigan Agricultural College

May 1919.

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