THE EFFECT OF WATER VAPOR ON THE CARBURIZATION OF

COMMERCIALLY PURE IRON IN AN ATMOSPHERE

DERIVED FROM NATURAL GAS

by

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PURPOSE

The purpose of this investigation is to determine the effect of water vapor on a carburizing atmosphere derived from natural gas consisting of methane, carbon monoxide, hydrogen, oxygen, ethane, and carbon dioxide on a low carbon steel, and its effect on relative depth of eutectoid zone and free carbon deposition.

INTRODUCTION

The application of controlled gaseous atmospheres in the heat treating and carburizing of steel has made remarkable progress during the past few years. However, there are many variables to be considered, one of which is the moisture content of the atmosphere used. Much is already known regarding the effect of water vapor on carburizing atmospheres, but it is the purpose of this investigation to extend the scope of this information.

Data on heat treating in controlled atmospheres are often so contradictory that definite conclusions cannot be drawn. These variations often can be traced to the chang-

ing moisture content of the gases composing the heat treating atmosphere.

Recent metallurgical literature has evinced the interest of numerous investigators in controlled atmospheres. It is believed that a furtherance of this information will be of interest as applying not only to the operation of case hardening, but also to heat treating processes in general.

Water vapor is susceptible of modifying gas equilibria and has been investigated rather thoroughly by Stansel (14), Guthrie (9), Gillett (8), Cowan (5), Bramley and Jenkings (3), and Austin (1). The nature of their research on this problem has, in general, been mostly qualitative, principally because of the variable conditions which commercial operations inherently have, and there are results showing that moisture seems to cause both an increase and decrease in carburizing rates. Such disagreement represents an enigmatic situation when insufficient data prevent generalization of these curious phenomena. It is the purpose of this investigation, therefore, to make evaluating tests which would give information relative to this effect. This problem becomes very practical when the difficulty in heating with commercial fuels without immunizing from the

attack of water vapor is realized.

A secondary purpose of this investigation was the determination of a procedure and the arrangement of apparatus necessary to carry out the proposed research. Refinements of the equipment and changes in the process are suggested at various points of the discussion.

THEORETICAL DISCUSSION

The Effect of Temperature on Carburization

Carburization takes place when iron is in the allotropic form of gamma iron and is in the presence of a carbonaceous substance which may be either a solid, a liquid, or a gas. This form of iron is not produced until it is heated to a temperature of $700-900^\circ$ C., $1292-1652^\circ$ F., the transition range depending upon the carbon content of the iron. Gillett (8) determined the ideal temperature of carburization to be from $760-941^\circ$ C., $1400-1725^\circ$ F. This degree of heat promotes a high rate of carburization and holds grain growth to a minimum. It is very important that the grain size in the case be small as it decreases the possibility of chipping or exfoliation, and increases

the resistance to wear. Temperature is not as difficult
to control as some of the other factors. However, a dif-
ference of as much as 20 per cent in the depth of case
may be produced by a variation in carburizing temperature
of 25° F. Thus an increase in depth from 0.040-0.050 in-
ches will be obtained on plain carbon steel by increasing
the average temperature from $913-927^{\circ}$ C., $1675-1700^{\circ}$ F.
for a run of approximately four hours. For quantitative
results, it is necessary that a careful and accurate
record be made of the temperature variations in interpre-
ting data of each run.

In the commercial processes using gas, it is very es-
sential that grain growth be retarded and various alloy
steels are excellent for this purpose. For general use,
a steel of the following composition is suggested:

<div style="padding-left:4em;">

carbon   0.10-0.20 per cent

nickel   1.25   per cent

chromium   0.60   per cent

</div>

Each alloying element added is supposed to impart a certain
physical property to the finished product. The carbon con-
tent of the stock is low so that the core of the carburized
material will be soft and ductile and will resist shock.
Nickel tends to retard grain growth at carburizing temper-

atures and also produces a tough core. Chromium, when used alone up to 1.25 per cent, increases the abrasive hardness of the case.

By the addition of these alloying elements, it is said to be possible to make stock for carburizing that is not sensitive to reasonable changes in temperature. Commercially pure iron was used in this investigation due to the lack of information as to the quantitative effect of these various elements on the pyrolysis of the carburizing atmosphere when used in combination.

Pyrolysis of the Carburizing Atmosphere

The gas surrounding the specimens in the carburizing retort is a mixture of CO_2, O_2, CO, H_2, CH_4, C_2H_6, N_2, and water vapor. Pyrolysis data consider only simple mixtures of these gases, therefore, the discussion will deal with parts of the atmosphere. Since methane, CH_4, is the potential carburizing agent of the carburizing process, it will be given the most consideration.

Soot deposition, resulting from the decomposition of methane, has given considerable difficulty and is affected to a marked degree by the amounts of water vapor contained

in the gas. Between 700 and 800° C., 1292 and 1472° F.
methane begins to reduce carbon dioxide with the liberation
of carbon while the formation of carbon monoxide from these
two gases was brisk at 950-1054° C., 1742-1929° F. The
reaction of methane with water vapor at high temperatures
yielded carbon monoxide and hydrogen in the presence of an
excess of water while under other conditions much carbon
was formed.

Methane is much more easily oxidized than hydrogen or
carbon monoxide. Egloff and Schaad (6) found that in
borosilicate tubes at 300-400° C., 572-752° F. methane
combines with oxygen with greater velocity than does hy-
drogen. However, ethane, C_2H_6, burns much more rapidly
than does methane. The ease with which the paraffin
hydrocarbons oxidize increases with their molecular weight.

In considering the reaction of methane with carbon
dioxide, it has been found that reduction of the CO_2 takes
place between 700 and 800° C., 1292 and 1472° F. at which
temperature 0.6 per cent of CO is formed; at 954 and 1054°
C., 1749 and 1929° F., 6.4 per cent and 8.2 per cent car-
bon monoxide were obtained respectively. In each case
carbon was deposited. The decomposition of steam by car-
bon starts at 600° C., 1112° F. and is considerable at

1000° C., 1800° F.

Ethane stands between methane and propane in the ease of thermal decomposition. In the absence of a catalytic agent this breakdown begins at about 485° C., 905° F. and until a temperature of several hundred degrees above this temperature is reached the major reaction is one of dehydrogenation. The products are ethylene, hydrogen, carbon, methane, acetylene, and aromatic hydrocarbons. It is evident, therefore, that the quantity of ethane in the carburizing retort will be decreased since it is operating at a temperature of about 971° C., 1780° F.

Carbon Deposition

On the decomposition of a hydrocarbon atmosphere at an elevated temperature, carbon is deposited. In order that carburization proceeds at a constant rate, it is necessary that the precipitated carbon be of such a character as not to interfere with the gas-metal reaction. If the carbon layer is one of a hard inpenetrable or glazed type, it will prevent further carburization. This type of carbon formation is especially noticed when the moisture content of the gases is low. Such a deposit is perhaps best pictured by considering briefly a condition that was

observed during the experimentation.

Figure 1 shows a chip of carbon which was scraped from the inner walls of the carburizing retort. The nodule or coke-like formation is noticed. Both the specimen and specimen boats were covered with a like deposit. In the final analysis, the iron showed very little carburization.

Figure 1. A coke-like chip showing the condition in the carburizing retort when the gases are dry. X 2.

Carbon deposition is used as one of the steps in commercial gas carburization. The carbon laid down by the decomposed gas is sooty and does not prevent the gas-metal reactions from taking place. The object of soot deposition is to hasten the carburizing rate by causing the formation

of carbon monoxide at the surface of the iron due to the oxidation of the carbon with air under controlled conditions. This controlled procedure has met with commercial favor as to speed and economy.

The character of the surface of the steel has a definite influence on the gas-metal reactions. Jominy (11) states that marked deposition of soot interfers with the rate of carburization. The carbon black that is precipitated is quite inactive and tests have shown that it will not carburize a plain carbon steel in one hour's exposure until a temperature higher than 1260° C., 2300° F. is reached.

Water Vapor and Its Effect on Carburization

Water vapor seems to have a decided influence on carburization. It has been given only a passing mention in the literature. The purpose of this portion of the discussion is to give a summary of the findings of various investigators.

Guthrie and Wozasek (10) found that moisture control is of outstanding importance when using city gas. However, they stated a little moisture was necessary to get rapid

carburization. Austin (1), in discussing controlled at-
mospheres, states that considerable amounts of water vapor
may be present if the gas is thoroughly reducing without
oxidation of the product. Gillett (8) believed that
moisture bearing gases did carburize more rapidly than
dry gases.

Guthrie (9), in an investigation of carburization of
steel with gas, gives findings as to the effect of water
vapor that are of interest. A given operation using 75
cubic feet of mixed coke oven gas and carburetted water
gas at 15 pounds pressure required six to seven hours to
obtain a 1/16 inch case and without any apparent reason
it would require 25 to 30 hours to obtain the same case.
It was later found that the increased duration was due to
the moisture content of the gas. The air, when dried
equivalent to saturation at 0° C., 32° F., cut down the
amount of gas required from 75 to 35 or 40 cubic feet.
This drying caused a precipitation of soot and made the
operation very messy. It was then discovered that if a
minute amount of moisture were introduced into the hot
retort at the beginning of the run the steel article acted
as an inhibitor and prevented the deposition of soot.
Later through experimentation it was found that gas dried

to saturation at $0°$ C., $32°$ F. with water added at the
beginning of the run over a period of about six minutes or
more decreased the formation of soot.

Cowan (5) found that if the gases used for carburiz-
ing were saturated to a dew point of $16°$ C., $60°$ F. and
also $21°$ C., $70°$ F. showed an increase in case depth. He
also states that the results were different from what we
had expected since it was found that with progressive
increase in moisture content there was also an increase
in case depth from 0.096 inch in the dehydrated gas to
0.120 inch in the gas with a dew point of $21°$ C., $70°$ F.

From the various investigators' standpoint, water
vapor has been taken into consideration in explaining un-
predicted effects but very little quantitative work has
been done. This apparent disparity has been the outstand-
ing reason for selecting this problem for research.

Gas Reactions and Equilibria

It has been generally conceded that the carburizing
process usually implies two distinct steps: (a) the for-
mation of a compound between carbon and oxygen, and (b)
the interaction between the latter compound and the iron

of the steel.

In the samples subjected to carburizing, carbon does not exist as such but is found in the form of an iron carbide, Fe_3C. Consequently, the process of carburizing consists of two distinct steps.

1. Formation of iron carbides

2. Absorption of iron carbide by the steel

Both processes require a high temperature for their completion although the formation of iron carbide can be accomplished at temperatures below the critical range. An allotropic form of iron, alpha, is in existence below the critical temperature and has but a very limited solubility for the carbides. Gamma iron, another allotropic form of iron found at temperatures above the critical range, can hold in solution as much as 1.7-1.8 per cent carbon. On subsequent cooling to room temperature, iron carbide is liberated and is found as either structurally free or as part of pearlite.

The active carburizing gas is considered to be carbon monoxide. It is derived from the partial combustion of the hydrocarbon gas by the oxygen from the air and it gives carbon to iron according to the reaction,

1. $2CO + 3Fe - Fe_3C + CO_2$
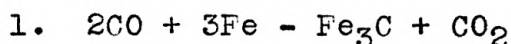
the resulting Fe_3C being dissolved in gamma iron. The CO_2 reacts with the carbon or the methane which is present in the following way:

(a) $CO_2 + C - 2CO$

(b) $CO_2 + CH_4 - 2CO + 2H_2$
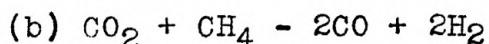
Thus, the carbon monoxide is regenerated and the cycle of reaction goes on repeating itself during the whole time that carburization takes place (13).

The atmosphere used in this investigation was derived from natural gas which is largely composed of methane. Therefore, the discussion of equilibrium and reactions following will deal mainly with this constituent.

In controlling the quantities of gas and air in the active zone of the carburizing furnace, there are several phenomena which have to be taken into consideration. Among these factors of influence are initial composition of the fuel gas, rate of gas flow, temperature of the precombustion and cracking chamber, effect of catalysts, degree of dehydration of the gas before entering the carburizing retort, and the temperature of the carburizing atmosphere.

If the gas and air ratios are kept constant, various reactions under static conditions will reach an equilibrium. There are three ratios which must be considered in carburi-

zation when using a gaseous atmosphere. The CO_2/CO represents a ratio which, if large, will cause decarburization and the formation of scale. If very small, both actions will be reversed in an intermediate range as shown by Stansel's curves (14) and carburization and scaling may occur simultaneously (figure 2). This value may range from 0.03-0.70, the temperatures being 900-680° C., 1650-1270° F. If the CH_4/H_2 ratio is large, carburization will take place. If very small, this action will be reversed. The equilibrium values range from 0.02-0.16 at temperatures of 900-700° C., 1650-1290° F. A very important equilibrium in determining gaseous reactions is the H_2O/H_2 ratio. If this ratio is large, the surface of the steel will be oxidized when small reduction will take place. These ratios vary from 0.33-0.58, the temperatures being 900-600° C., 1650-1112° F.

Methane during thermal decomposition produces both hydrogen and carbon. This reaction goes to equilibrium with the quantities of hydrogen and methane which can exist together in the presence of the carbon in the steel. In carburization, it is necessary to avoid a change in the carbon content of the steel due to these reactions.

$$CH_4 - C + 2H_2$$

$$Fe_3C + 2H_2 - CH_4 + 3Fe$$
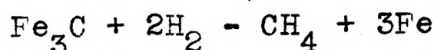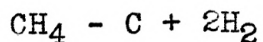
At any given temperature, at equilibrium with carbon in steel in the system, methane-hydrogen and vapor carbon in steel, the partial pressure of the carbon vapor is equal to the vapor pressure of carbon in the steel. This vapor pressure varies with the degree of the carbon saturation of the steel and for any given temperature is the maximum at carbon saturation, i. e., for carbon saturation the vapor pressure of graphite. The equilibrium ratio of hydrogen and methane with reference to carbon in steel is as follows:

$$\frac{K_t}{p_c} = n_t = \frac{(p_{H_2})^2}{p_{CH_4}}$$

for temperature t

K_t = the dissociation constant for methane

p_{H_2} = the partial pressure of hydrogen

p_c = the partial pressure of vapor carbon

p_{CH_4} = the partial pressure of methane

n_t = equilibrium constant characteristic of the degree of saturation of the steel for the above system

If water vapor is present in a hydrogen atmosphere, it reacts with the methane in the system, thus lowering the methane content and thereby promoting decarburization.

Various reactions which take place during carburization have been made in a chart form and are shown in table 1.

Table 1. Reactions of Furnace Gases with Fe, Fe_3C, Oxides of Fe, and Individual Interactions – Krogh (12).[3]

Symbol:	O_2	CO	CO_2	H_2	CH_4	H_2O
Fe	:Oxide	:Carb.	:Oxide	: X	:Carb.	:Oxide
Fe_3C	:Decarb.	: X	:Decarb.	:Decarb.	: X	: X
FeO Fe_2O_3 Fe_3O_4	:Oxide	:Reduc.	: X	:Reduc.	: X	: X
O_2	: X	:CO_2	: X	:H_2O	:CO & H_2O	: X
CO	:CO_2	: X	: X	: X	: X	: X
CO_2	: X	: X	: X	:CO & H_2O	: X	: X
H_2	:H_2O	: X	:CO & H_2O	: X	: X	: X
CH_4	:CO & H_2O	: X	: X	: X	: X	: X
H_2O	: X	:CO_2 & H_2	: X	: X	: X	: X
N_2	: X	: X	: X	: X	: X	: X
C	:CO	: X	:CO	:CH_4	: X	: X
Decomposes into	: X	:C & O_2	:CO & O_2	: X	:C & H_2	:H_2 & O_2

Stansel (14) has collected equilibrium data of the various gases composing a carburizing atmosphere and his findings are shown in figure 2. These data were based on equilibrium with austenite saturated with carbon at a given temperature. The curves show that in an atmosphere high in water vapor the oxidizing tendency is balanced by hydrogen at 649° C., 1200° F. but with a H_2O/H_2 ratio of 0.50 on cooling below that temperature will result in oxidation. It is very essential that the proportions of water vapor must be strictly limited when steel is to be cooled in the furnace. Any ratio of CO_2/CO that is not oxidizing at a high temperature will continue to be non-oxidizing at any lower temperature though it may be decarburizing or carburizing. The graph shows that water vapor or CO_2 unbalanced by a reducing gas will be oxidizing at any heat treating temperature.
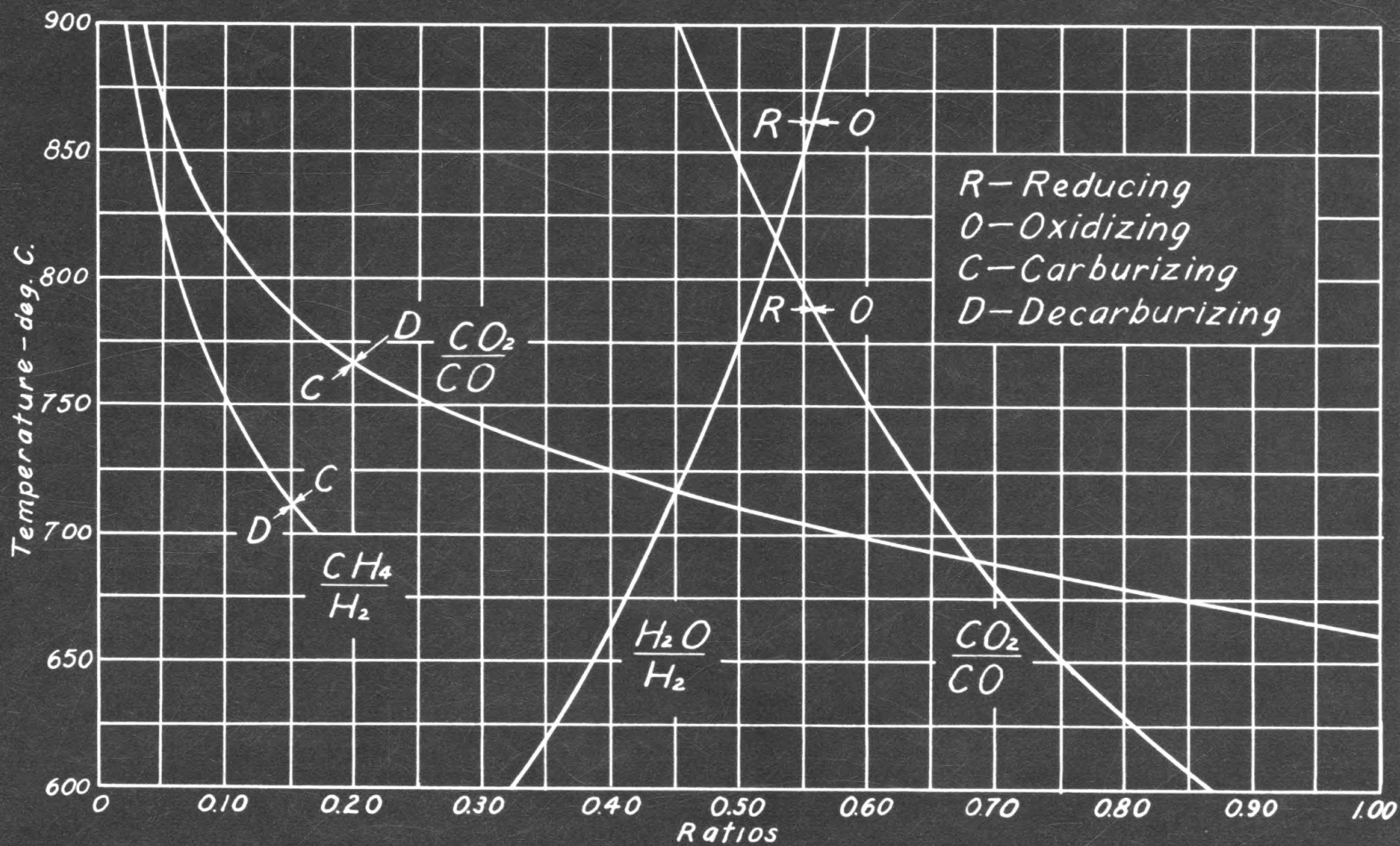
Fig. 2 Equilibrium Ratios for the CH_4-H_2 ; CO_2-CO; and H_2O-H_2 Reactions, in Contact with Iron-Carbon Alloys Saturated with Carbon at the Temperature in Question.   Stansel.

In scaling, the effect of the H_2, H_2O, CO, CO_2 mixtures can be deduced from the CO_2/CO ratio alone since the total equilibrium is expressed by the ratio $\frac{(H_2O) \, (CO)}{(H_2) \, (CO_2)}$ of the water gas constant so if a non-scaling CO_2/CO ratio is chosen, the H_2O/H_2 ratio in equilibrium with it will also be non-scaling. Egloff, Schaad and Lowery (7) have tabulated the data determined by Shenck, Krageloh, Eisenstecken and Klas.

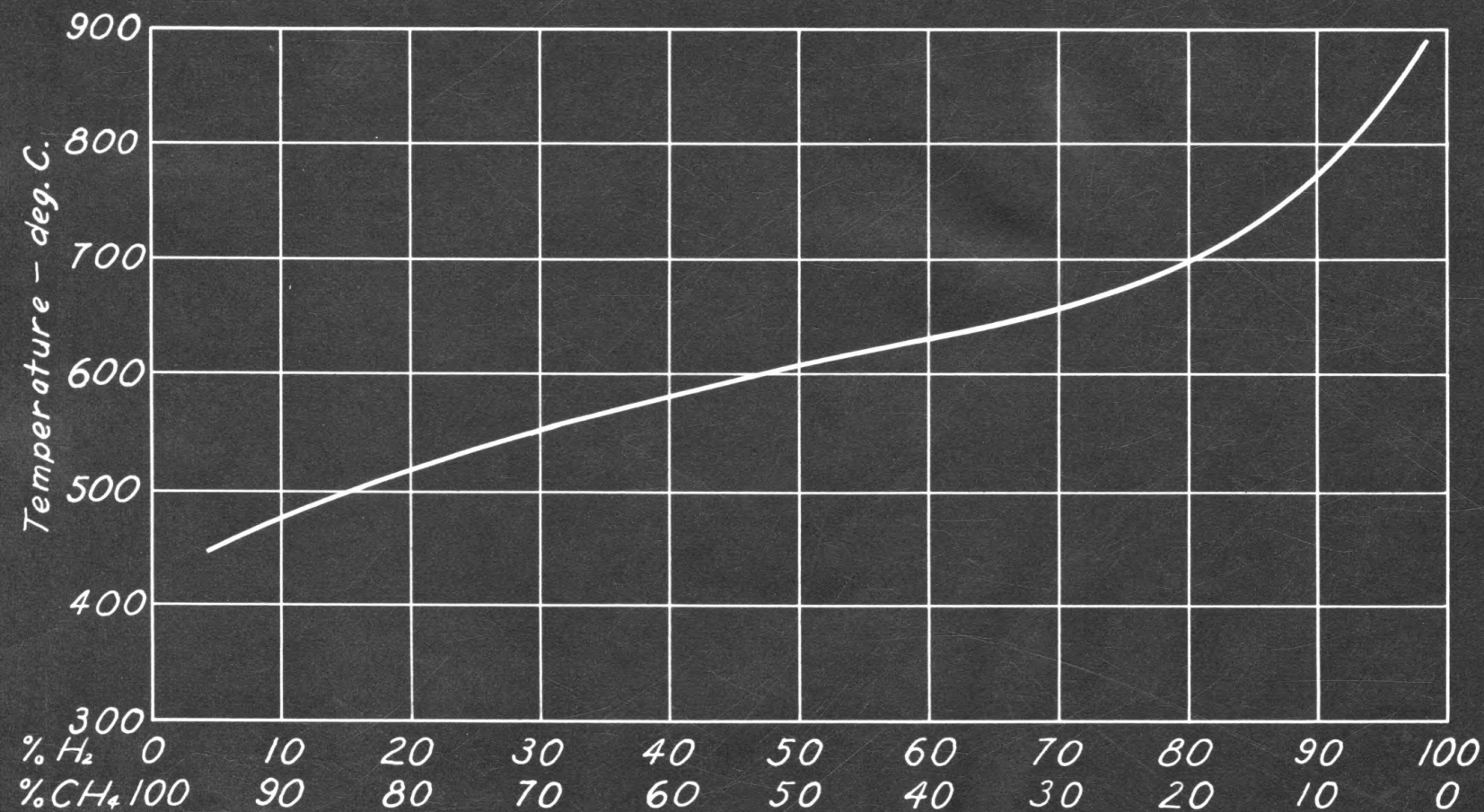A graph of these data is shown in figure 3 for the decomposition of methane.

Fig. 3 Shows the Equilibra of Methane in the Presence of Iron. $3Fe + CH_4 \rightleftarrows Fe_3C + 2H_2$. Data by Schenck, Krageloh, Eisenstecken, and Klas.

EXPERIMENTAL PROCEDURE

Apparatus

A full view of the apparatus is shown in figure 4.
Beginning at the left of the photograph mounted on the wall
is a Brown temperature recording pyrometer. This instru-
ment recorded temperature variations of both the partial
combustion and carburizing furnaces. In the background on
the table is a motor driven rotary disc gas meter (See also
figure 5, A). Next to the meter is a potentiometer which
was used to check the accuracy of the thermocouples from
time to time. The three furnaces and the electrolytic cell
are shown more in detail in figure 5 and their functional
role is explained subsequently. A Sargent 20 cubic foot
model wet test meter was used to check the total volume
of gas flowing through the furnaces. Temperature control
of the natural gas combustion and carburizing furnaces was
maintained by the two rheostats shown in the right back-
ground, mounted on the wall.

At the extreme right of the photograph (figure 4) is
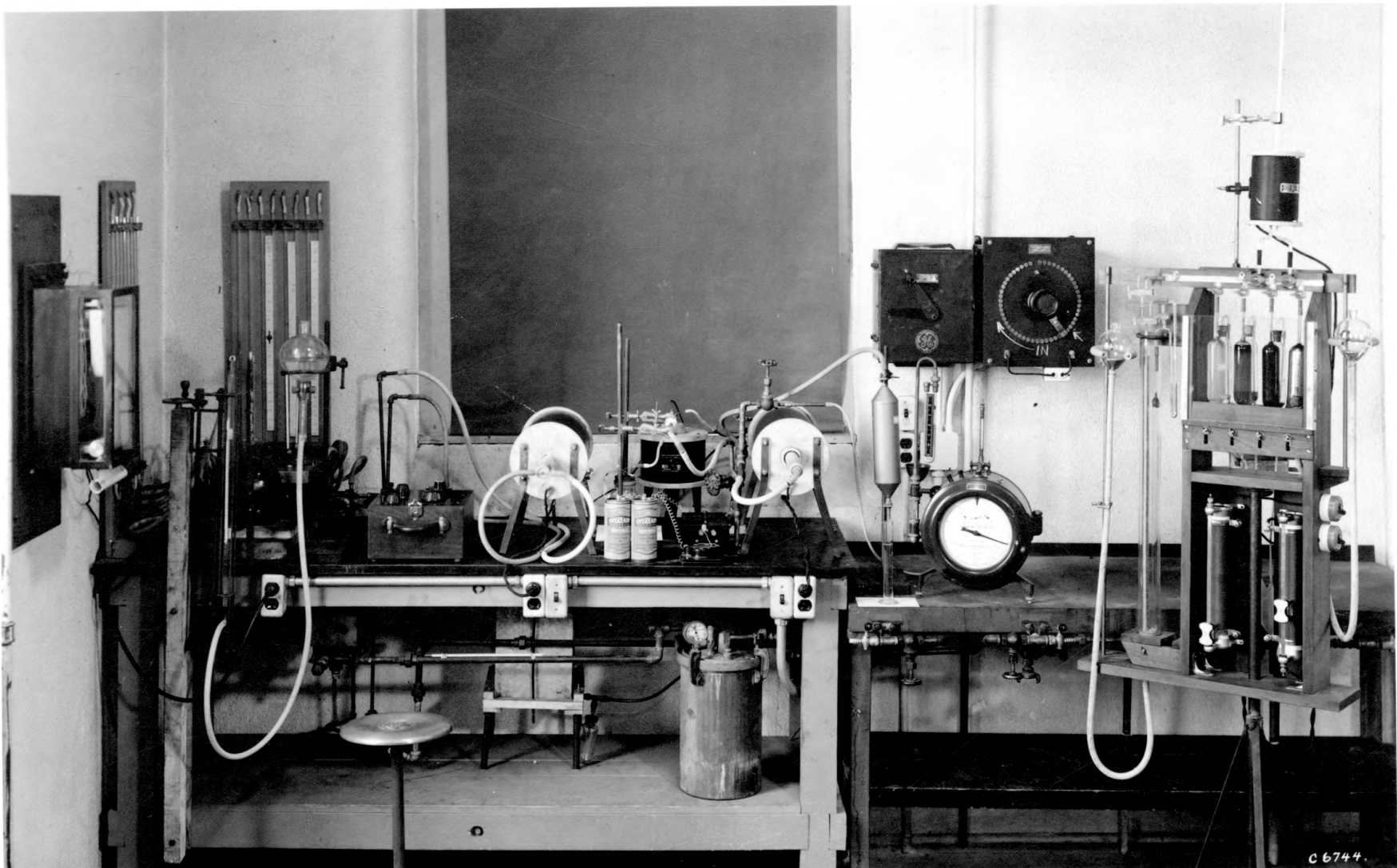a Bureau of Mines gas analyzer built for the purpose of de-

Figure 4. Shows a full view of the carburizing apparatus.

termining the composition of the carburizing atmospheres.

Figure 6 shows the combustion furnace (B) where natural gas was partially burnt with air. The products of this combusion were CO_2, CO, H_2, H_2O, and C. This mixture was used to dilute the natural gas to prevent carbon deposition in the carburizing retort.

An electrolytic cell (D) was found to be a convenient way of adding minute quantities of water at a constant rate to the carburizing gases. This cell consisted of a glass container in which was sealed a dilute solution of sulphuric acid and submerged in this solution were two platinum electrodes. Current flow through this circuit was controlled by a rheostat (F), thus by varying the current, as read on the milliameter (G), the amount of hydrogen and oxygen evolved could be changed.

The electrolytic hydrogen and oxygen were mixed with raw and cracked gas and the whole mixture was passed through a calcium chloride drying tube (C) to remove any water carried over by electrolysis. A combination of these two elements to form water was accomplished by allowing the gases to flow through a tube of granular CuO which was held at a temperature of 300° C., 580° F. by a fractional combustion furnace (E). At this temperature all the H_2 in

a CH_4-H_2 mixture can be burned to water without any of the CH_4 being decomposed. The velocity of the gases was kept high enough so that precipitation of moisture on the exit of the CuO tube was prevented.

Moisture addition was measured by electrochemical equivalent calculations from the milliameter reading.

It might be anticipated that water would, by evaporation, be carried over by the hydrogen and oxygen but a check on this point was made by weighing the cell before and after experimentation. The loss in weight was about two or three per cent greater than that calculated by equivalence from the milliameter readings (2). This small error, as stated by Austin, was not considered significant and the actual milliameter readings were used in calculating the amount of water added to the gas mixtures.

After moisture had been added to the gas mixture, it was passed into the furnace (H) where carburization took place. Both furnaces (B and H) have a 220 volt-650 watt capacity. The water synthesis furnace (E) is a Hoskins Multiple unit type having 110 volt-400 watt capacity.

The sample tube (I) is filled with a saturated solution of sodium chloride and a measured amount of this solution was taken off in the graduated cylinder (J) at fif-
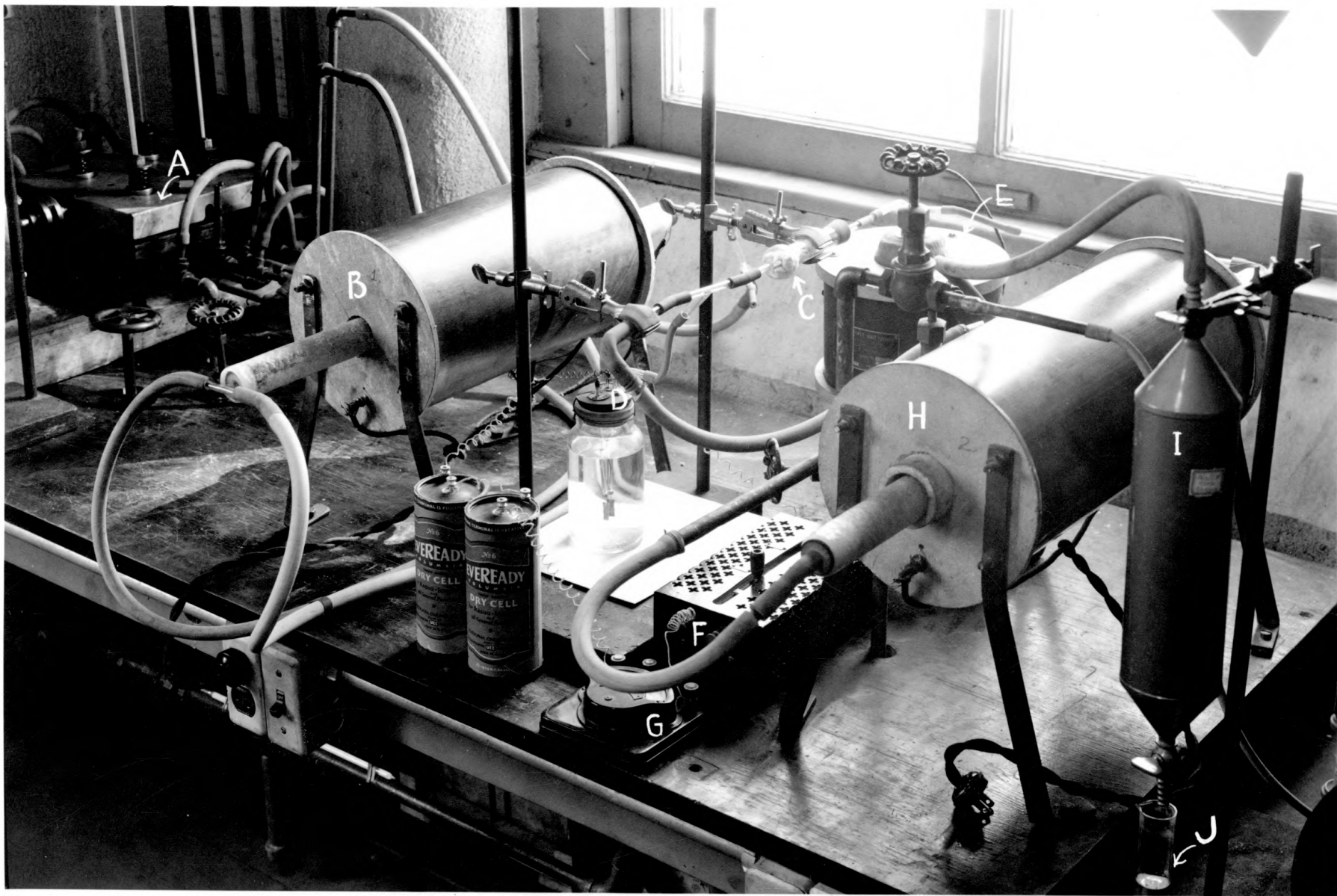
Figure 5. Detailed photograph of apparatus.

teen minute intervals during the four-hour period. By this method, a cumulative sample of the whole run was obtained.

Carburizing

This research problem was divided into two parts. To determine the effect of various dry air-gas mixtures and the effect of moist air-gas mixtures upon the carburizing process.

In the first, the gases were dried thoroughly by passing them through a water condenser, then over anhydrous calcium chloride and finally, before passing into the carburizing retort, bubbled through concentrated sulphuric acid.

In order to eliminate the effects of alloying elements a simple low carbon steel of high purity was selected. The steel used was Armco iron. The high purity of this material is well substantiated by the fact that the Bureau of Standards has chosen it for a "standard sample" of ingot iron. A typical analysis of Armco ingot iron is as follows: C (combustion) 0.012, Mn 0.017, P 0.005, S 0.025, Si Trace, Fe by difference 99.941 per cent.

After determining the air-gas ratios and temperatures to be used the procedure was as follows: A mixture of air

and natural gas was passed into a steel retort tube which
was heated by a small resistance wound electric furnace.
The temperature in this furnace was held practically con-
stant at 815° C., 1500° F. These gases had previously
been measured in a rotating disc type gas meter. In
passing through this combustion furnace, the gases were
decomposed to CO, CO_2, H_2, H_2O, and C. A slight excess of
oxygen was allowed to pass on with this mixture.

It was necessary that all the water be removed from
this cracked gas so it was next passed into a water cooled
condenser. The gases were then mixed with raw natural gas
in such proportions that carbon was not precipitated on
the sample or retort walls of the carburizing furnace.
After mixing the cracked gas and raw gas, they were then
passed over anhydrous calcium chloride to remove all final
traces of moisture. The gases were then passed into the
carburizing retort where the two samples were maintained
at a temperature of 971° C., 1780° ± 10°. Various lengths
of time were tried to determine the proper period which
would give evidence of carburization under the poorest con-
ditions. Four hours were found to give a thin case even
under only slightly carburizing conditions.

Several changes were made in the apparatus for running

the second series of specimens. Fused silica tubes of one inch inside diameter were substituted for both retort tubes as it was found that the iron acted catalytically upon the gases and gave varying results. The temperature of decomposition for CH_4 varies with experimental conditions. In contact with substances of little or no catalytic action, CH_4 has been reported to undergo change at between 650-700° C., 1202-1292° F.

Methane in silica bulbs has been found to decompose at 638° C., 1261° F. Catalysts reduce the decomposition temperature. In the presence of palladium, there is decomposition at 250° C., 482° F., with nickel at 320° C., 608° F., and with iron at 350° C., 662° F.

A variation of the moisture content of the carburizing atmosphere was used in the second series. This variance of moisture was carried out as described previously by an electrolytic method.

Moisture variations were made to both extremes from carburizing to decarburizing conditions. In this manner, the effect of moisture on the rate of carburization was studied.

After the samples had been subjected to the prescribed atmosphere for four hours, they were then allowed

to cool in the furnace with both inlet and exit valves
closed to reduce the oxidation on cooling to a minimum.
This slow cooling produced an annealed condition which made
it possible to identify the zones of various carbon content
by metallographic procedure as later described.

Methods of Analysis

It was necessary to determine with analytical accu-
racy the action taking place during the various phases of
the carburizing process. In order to check the amounts of
moisture in the gaseous atmosphere, a vanier bulb was used
on the exit of the carburizing furnace. The moisture was
absorbed in sulphuric acid and the gain in weight repre-
sented the actual amount of moisture passing over the
samples.

A Bureau of Mines type of gas analyzer was built in
order that the complex mixture composing the carburizing
atmosphere could be accurately determined.

The individual components of the cumulative gaseous
mixture consisting of CO_2, O_2, CO, H_2, CH_4, C_2H_6 and N_2
were determined as follows: A solution of potassium hy-
droxide was used to absorb the CO_2. Oxygen was absorbed in

an alkaline pyrogallate solution. In determining the CO and H_2, fractional combustion methods were used. The mixture of gases was passed slowly over CuO, the temperature of which was 300° C., 580° F. The CO in the mixture was oxidized to CO_2 and the H_2 to H_2O. Hydrogen was measured by the contraction in volume and the CO_2 absorbed in the KOH solution, this being a measure of the CO. Part of the residue was taken for the analysis of CH_4, C_2H_6 and N_2. This portion was passed slowly into the slow combustion pipette containing a measured amount of oxygen. The contraction in volume, due to the formation of H_2O, was measured and the residual sample passed into the KOH pipette to measure the CO_2 formed by slow combustion. This procedure seemed to give a very good criterion relative to the action that had taken place in the carburizing retort.

The method of analysis of the steel specimens consisted mainly of a microscopical study and micrographs of each coupon to record the depth of case.

For determining the microstructure of the specimens after being subjected to these atmospheres, the following steps were used. Due to the fact that the carbon enters all surfaces, it was necessary to saw the sample in half in order that a representative cross section may be observed.

It is very essential that the edges of the sample remain as they were originally, so, for protection, the half sample was mounted in a plastic moulding material, Tennite, and then polished to a final stage using levigated alumina. The samples which were photographed to show the depth of case were not carried to these finer stages of polishing as it is unnecessary to show the detailed structure.

Photomicrographs were made of all samples used and a magnification of 25 diameters was found to show the depth of case nicely. The same procedure of polishing and mounting was followed with the second series of samples, the only difference being that they were polished before and after carburization and carefully weighed to one-tenth of a milligram to check a gain or loss in weight. This polishing consisted in rubbing the samples by hand with 320 mesh alumina until a lustrous surface was obtained.

Since there has been considerable discussion as to the technique of determining the depth of case, the suggestions, as outlined by the American Society for Metals (4), were considered. Case depth, as given by this authority, is that portion of a carburized, nitrided, or cyanided iron base alloy article in which the carbon or nitrogen content has been substantially increased. It is seen that

this definition is quite inadequate to use as a basis for determining the case depth in a quantitative manner.

Various methods suggested by the American Society for Metals for the actual measurement of case depth are as follows:

1. Scale measurement of ordinary fracture

2. Scale measurement of blued fractures

3. Scale measurement of ordinary fracture which has been dipped in acid

4. Scale measurement of polished cross sections
    a. Blued
    b. Etched

5. Microscopic measurement of highly polished cross sections etched in standard reagents

6. File or drill through from the core at right angles to the case until the hardness of the case resists further cutting or abrasion. Measurement of the remaining hard case is taken as the depth of case

7. Machine off successive amounts of surface from soft carburized work. Analyze the results of depth based on the individual's conception as to the amount of carbon which can be considered case

8. Weigh the parts to be carburized before and after carburization and compute the added carbon and depth of case

9. Magnetic analysis

10. Taper grind hardened work so that some unit of linear measurement of surface represents a known depth from the original surface, and test each unit of linear surface by some practical form of hardness test

In this research, method 5 was used to determine case depth. All samples were etched to a degree where the structure was no longer discernable. This procedure made the line of demarcation between the case and core easily distinguished when magnified at 25 diameters.

Gas Carburizing Data Comparison Sheet
Data Arranged in Order of Increasing Moisture Additions

Specimen Number	Meter Differentials (Raw Gas)	Air	Crack Gas	Time in Hours	Average Temp. deg.F of Carburizing Furnace	Average Temp. deg.F of Combustion Furnace	Average Depth of Case Hyper-zone in m.m.	Weight Gain of Sample in Grams	Weight of H_2O Added in Grams	CO_2	Ill.	O_2	CO	H_2	CH_4	C_2H_6	N_2	Volume of Gas Used in Cubic Inchs	Carbon Deposition
1	14	8.75	16	4	1785	1500	1.05	0.0488	0.000	0.23	0	1.23	4.81	32.00	31.41	0.00	30.32	675	Coke Formation
2	14	8.75	16	4	1785	1500	1.25	0.0878	0.000	0.00	0	1.02	4.41	30.41	29.87	0.00	34.69	930	Coke Formation
3	14	8.75	16	4	1785	1500	1.58	0.0737	0.008	0.21	0	3.84	0.82	17.64	33.11	0.00	44.38	1025	Slight
4	14	8.75	16	4	1785	1500	0.45	0.0385	0.008	0.22	0	3.21	5.20	18.21	33.61	0.00	39.55	1120	Heavy Soot
5	14	8.75	16	4	1785	1500	0.71	0.0526	0.015	0.84	0	1.82	6.21	26.63	33.21	0.00	31.29	868	Slight
6	14	8.75	16	4	1785	1500	0.95	0.0722	0.017	0.23	0	2.03	2.00	29.43	38.28	0.00	28.08	1073	Thread Formation
7	14	8.75	16	4	1760	1500	0.45	0.0226	0.018	0.57	0	1.60	6.81	20.90	33.52	0.00	36.60	1138	Soot on Upper Side
8	14	8.75	16	4	1785	1500	0.75	0.0257	0.018	0.63	0	1.42	7.41	21.20	34.93	5.81	28.60	1193	Soot on Under Side
9	14	8.75	16	4	1785	1500	0.00	0.0123	0.035	0.00	0	3.00	4.82	16.43	40.82	0.00	34.95	1206	Flakey Glazed Type
10	14	8.75	16	4	1785	1500	0.92	0.0628	0.053	0.42	0	3.63	2.60	29.21	41.64	0.00	22.60	1130	Slight
11	14	8.75	16	4	1785	1500	0.48	0.0678	0.148	0.00	0	1.63	2.40	30.00	38.92	0.00	27.05	594	Slight
12	14	8.75	16	4	1785	1500	0.15	0.0036	0.168	0.41	0	1.43	5.20	25.00	65.00	0.00	2.96	1198	Slight
13	14	8.75	16	4	1785	1500	0.48	0.0190	0.232	0.00	0	0.41	6.62	25.61	62.00	0.00	5.36	1270	Slight

Data Arranged in Order of Increasing Case Depth

Specimen Number	Meter Differentials (Raw Gas)	Air	Crack Gas	Time in Hours	Average Temp. deg.F of Carburizing Furnace	Average Temp. deg.F of Combustion Furnace	Average Depth of Case Hyper-zone in m.m.	Weight Gain of Sample in Grams	Weight of H_2O Added in Grams	CO_2	Ill.	O_2	CO	H_2	CH_4	C_2H_6	N_2	Volume of Gas Used in Cubic Inchs	Carbon Deposition
9	14	8.75	16	4	1785	1500	0.00	0.0123	0.035	0.00	0	3.00	4.82	16.43	40.82	0.00	34.95	1206	Flakey Glazed Type
12	14	8.75	16	4	1785	1500	0.15	0.0036	0.168	0.41	0	1.43	5.20	25.00	65.00	0.00	2.96	1198	Slight
4	14	8.75	16	4	1785	1500	0.45	0.0385	0.008	0.22	0	3.21	5.20	18.21	33.61	0.00	39.55	1120	Heavy Soot
7	14	8.75	16	4	1760	1500	0.45	0.0226	0.018	0.57	0	1.60	6.81	20.90	33.52	0.00	36.60	1138	Soot on upper side
13	14	8.75	16	4	1785	1500	0.48	0.0190	0.232	0.00	0	0.41	6.62	25.61	62.00	0.00	5.36	1270	Slight
11	14	8.75	16	4	1785	1500	0.48	0.0678	0.148	0.00	0	1.63	2.40	30.00	38.92	0.00	27.05	594	Slight
5	14	8.75	16	4	1785	1500	0.71	0.0526	0.015	0.84	0	1.82	6.21	26.63	33.21	0.00	31.29	868	Slight
8	14	8.75	16	4	1785	1500	0.75	0.0257	0.018	0.63	0	1.42	7.41	21.20	34.93	5.81	28.60	1193	Soot on under side
10	14	8.75	16	4	1785	1500	0.92	0.0628	0.053	0.42	0	3.63	2.60	29.21	41.64	0.00	22.60	1130	Slight
6	14	8.75	16	4	1785	1500	0.95	0.0722	0.017	0.23	0	2.03	2.00	29.43	38.23	0.00	28.08	1073	Thread Formation
1	14	8.75	16	4	1785	1500	1.05	0.0488	0.000	0.23	0	1.23	4.81	32.00	31.40	0.00	30.32	675	Coke Formation
2	14	8.75	16	4	1785	1500	1.25	0.0878	0.000	0.00	0	1.02	4.41	30.41	29.87	0.00	34.69	930	Coke Formation
3	14	8.75	16	4	1785	1500	1.58	0.0737	0.008	0.21	0	3.84	0.82	17.64	33.11	0.00	44.38	1025	Slight

MICROGRAPHS

One specimen representative of each run was photographed at twenty-five diameters after being polished and then etched with a four per cent nitric acid in alcohol solution. Micrographs that represent the most typical conditions are shown as figures 6 to 11. These illustrations show the relative depth of case with reference to the moisture added to the carburizing atmosphere. Each specimen was also studied under the microscope to determine the detailed structure before over etching to show case depth.

Figure 6. Micrograph of carburized specimen
No. 1. Depth of case, 1.05 mm. Water added,
none. Etched with four per cent nitric acid
in alcohol. X 25.

Figure 7. Micrograph of carburized specimen
No. 4. Depth of case, 0.45 mm. Water added,
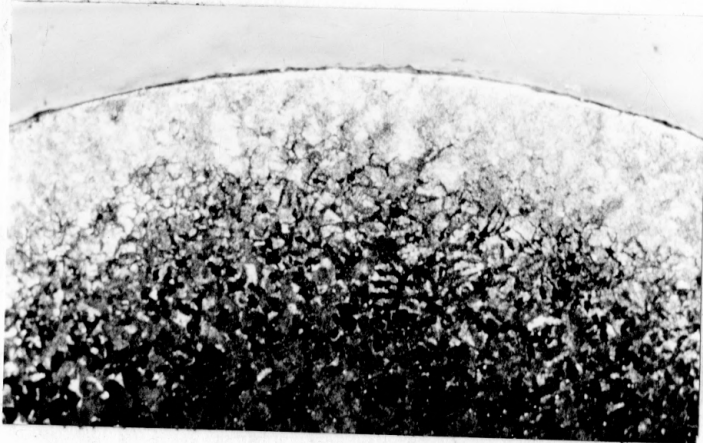0.008 gms. Etched with four per cent nitric
acid in alcohol. X 25.
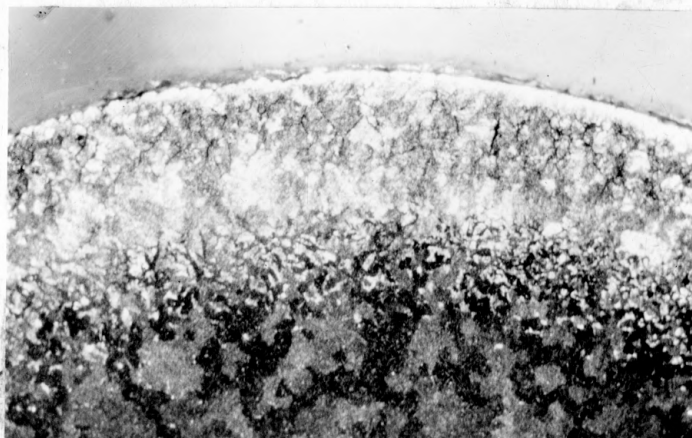
Figure 6
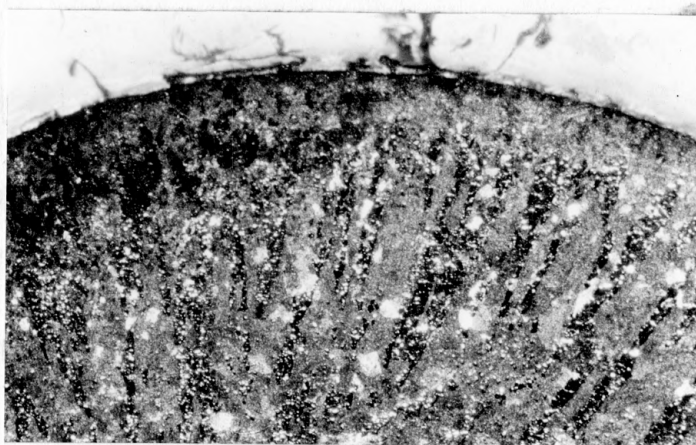
Figure 7

Figure 8. Micrograph of carburized specimen
No. 6. Depth of case, 0.95 mm. Water added,
0.017 gms. Etched with four per cent nitric
acid in alcohol. X 25.

Figure 9. Micrograph of carburized specimen
No. 10. Depth of case, 0.92 mm. Water added,
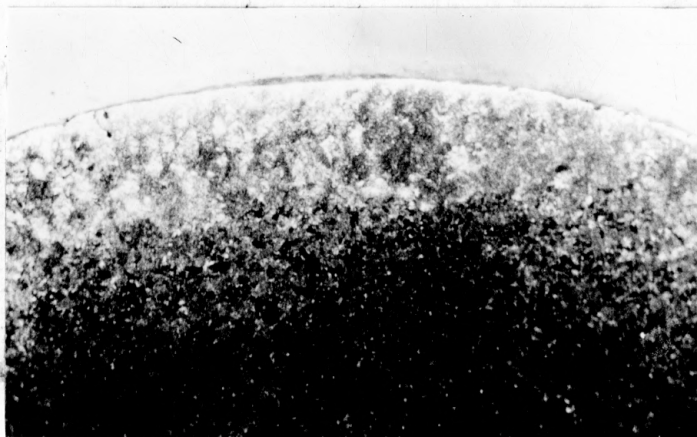0.053 gms. Etched with four per cent nitric
acid in alcohol. X 25.

Figure 8

Figure 9

Figure 10. Micrograph of carburized specimen
No. 11. Depth of case, 0.48 mm. Water added,
0.148 gms. Etched with four per cent nitric
acid in alcohol. X 25.

Figure 11. Micrograph of carburized specimen
No. 13. Depth of case, 0.48 mm. Water added,
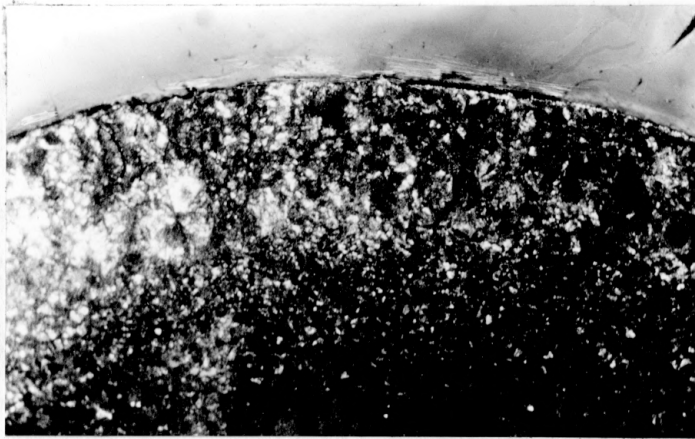0.232 gms. Etched with four per cent nitric
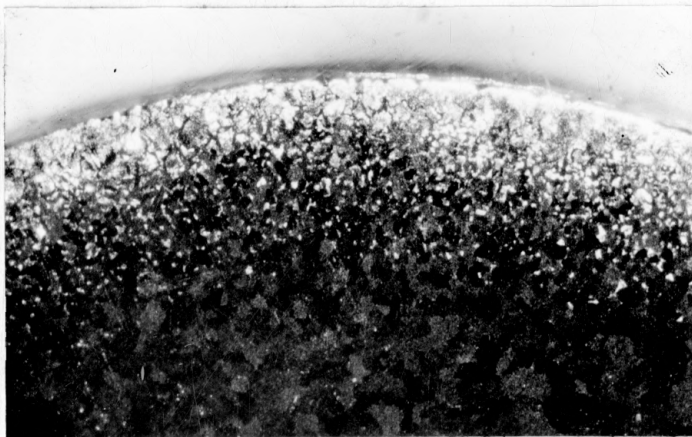acid in alcohol. X 25.

Figure 10

Figure 11

SUMMARY AND CONCLUSIONS

From this investigation, these data indicate that in order to have a carburizing reaction the presence of a pervious type of carbon is necessary. By varying the amounts of water vapor in the atmospheres, different types of carbon deposits were produced. Dry atmospheres deposited a coke-like layer over the retort and specimens. This deposit could be a penetrable or impenetrable type. In either case, carburization was spotty and uneven. Atmospheres used with specimens 3 and 6 inclusive, in which the water additions ranged from 0.008 to 0.017 gram, showed even case formation and a small amount of soft soot. Moisture contents above 0.017 showed slightly less average case increase. The maximum water added for any one run was 0.232 gram. The average volume of gas passing over the specimens was 1,033 cubic inches.

Moisture seems to prevent excessive carbon deposition but does not proportionally affect the rate of carburization. The tabular arrangement of these data, according to moisture and case depth, shows generalized effects of the

various conditions.

It is believed that a procedure has been determined whereby decisive data could be obtained on various factors pertaining to gas carburizing.

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