Nov. 24, 1959 H. L. SNAVELY 2,914,434

METHOD FOR CONTROLLING ATMOSPHERES WHILE HEAT TREATING STEEL

Filed April 11, 1956 2 Sheets-Sheet 1

FIG. 1

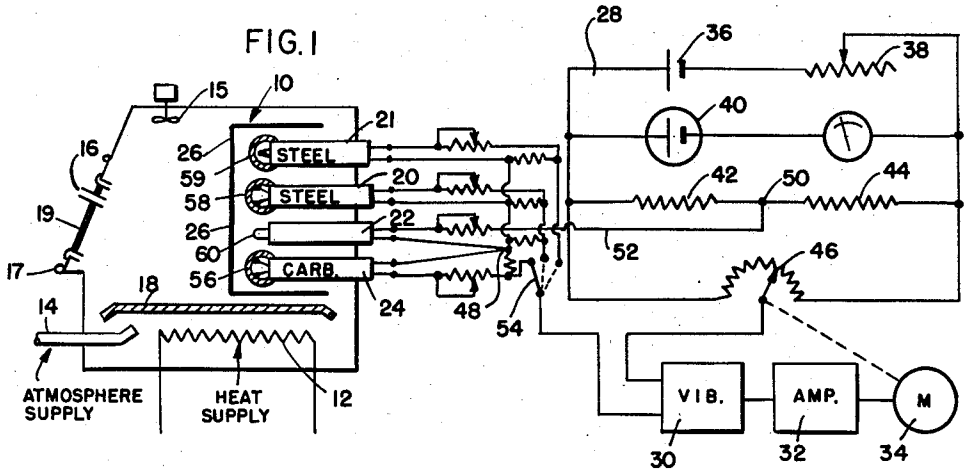

FIG. 2

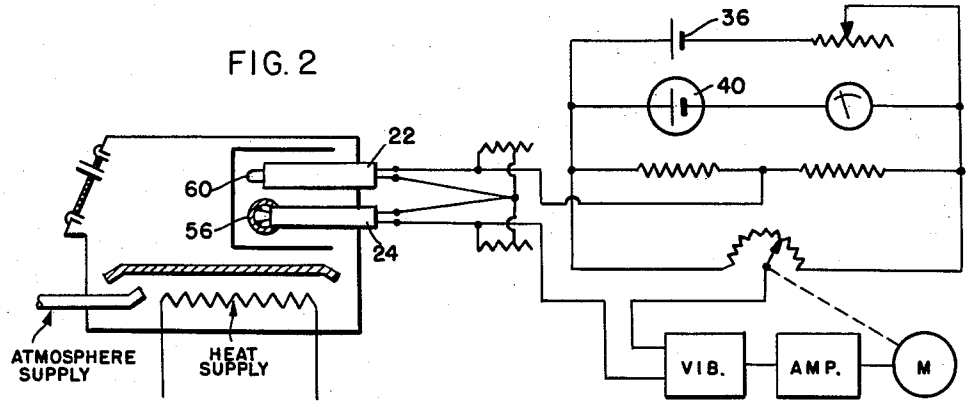

FIG. 3

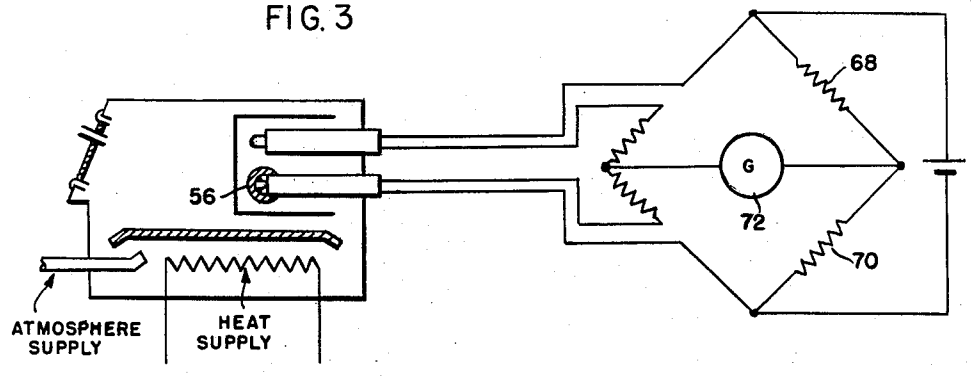

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FIG. 4

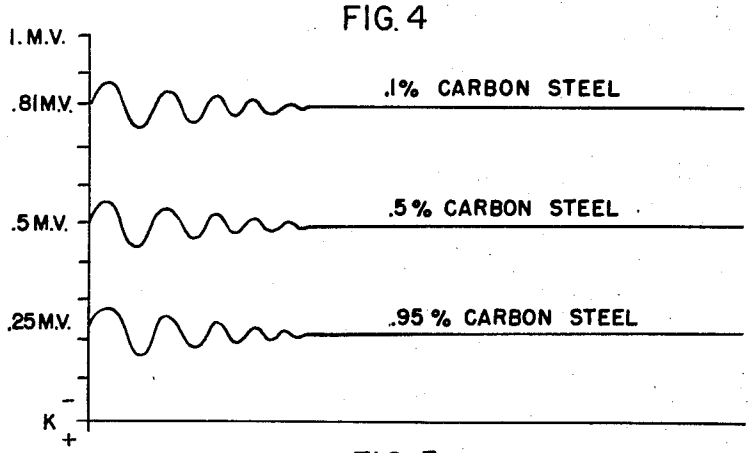


FIG. 5

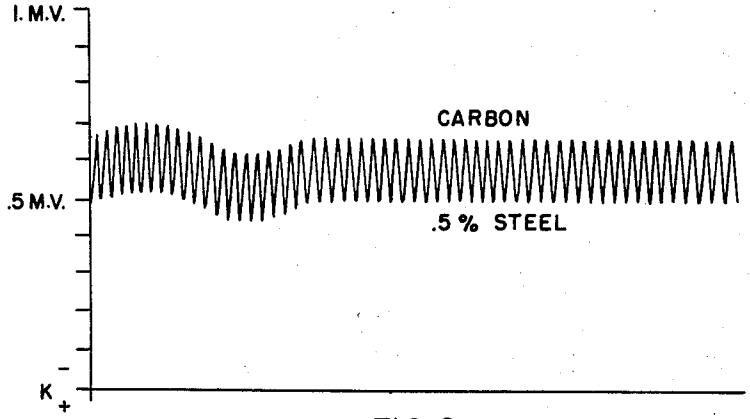
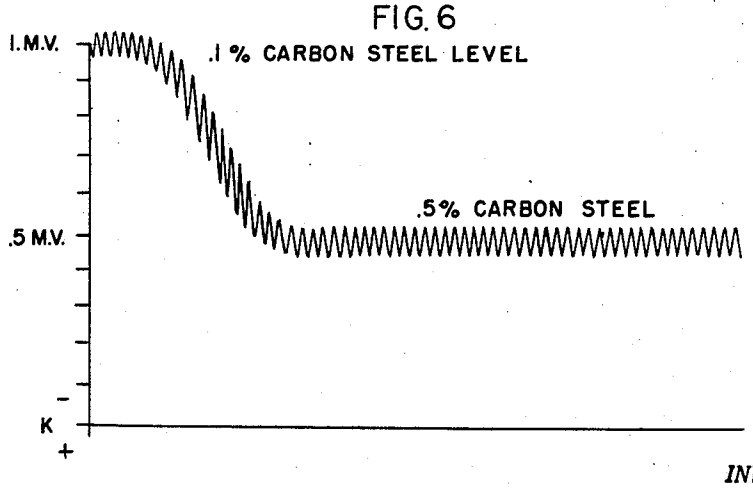


FIG. 6



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METHOD FOR CONTROLLING ATMOSPHERES WHILE HEAT TREATING STEEL

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4 Claims. (Cl. 148—16)

This invention relates to the heat-treatment of metals such as those containing iron and carbon and more particularly relates to the measuring and control of chemical reactions occurring in heat-treating processes; the relative equilibrium conditions of an atmosphere with respect to various pieces of metal where carbon content is to be controlled or changed; and the composition of particular pieces of metal with respect to the percentage of carbon therein.

In the heat-treating of metals either a significant chemical (gas-metal) reaction is not taking place in a particular carbon bearing atmosphere, which state can be referred to as a state of gas-metal equilibrium, or a chemical reaction is taking place in either one of two ways: either carbon is being taken on or given up by the metal.

The significant chemical reaction taking place is reversible and seldom does a perfect equilibrium exist that is maintained for any long lengths of time. In processing metals, it is very important that the reaction does not reverse, and also very important that a reaction desired is not overstressed if the metals being treated are to remain bright and not be either pitted or covered with scale. The more closely the effective equilibrium of an atmosphere can be determined, the brighter the heat-treat finish, the greater the saving in expensive gases and generator equipment, and the faster and the more surely a batch of metal pieces can be heat-treated without any parts being damaged. Moreover, shut-down times for cleaning heat-treat furnaces are eliminated because the furnace also runs clean and bright, and higher temperatures for faster reactions can be employed with utmost safety to the parts.

The solution of the problem is not easy because metals having different carbon content have gas-metal equilibrium conditions which are different; and to change the carbon content of metal various degrees in as little time as possible, the effective equilibrium of the atmosphere should be varied for acceptable overemphasis during heat-treat.

The atmospheres involved in these chemical reactions can be controlled by varying the proportions of suitable gases, hereafter identified further as a carrier gas of determined hydrogen content and a hydrocarbon gas such as natural gas which has a high percentage of methane and is generally referred to as enriching gas. With respect to any particular piece of metal, the carrier and the enriching gas can be varied to effect the removal of carbon therefrom, the addition of carbon thereto, or neutralization of any reaction in which the application of heat for hardening is the sole purpose of the heat-treat. In controlling these mixtures, the effective equilibrium point, sometimes referred to merely as the equilibrium of the atmosphere, must be known so that close and careful control can be had.

Temperature plays an important part in providing and determining a given status of equilibrium. Thus, to have an absolute empirical determination of equilibrium under the temperature conditions in a heat-treat furnace itself

is most desirable but difficult. Moreover, an apparent equilibrium can become something different merely with slight addition of H_2O in the system.

Also, for the better understanding of the invention in the reaction where $C+CO_2 \leftrightharpoons 2CO$, it is interesting to note that an increase in temperature promotes the formation of more carbon monoxide with a corresponding change in the value of equilibrium constant, i.e., the effective equilibrium, and with a drop in temperature less carbon monoxide is formed; and with hydrogen present, the water content is increased. The quality of atmosphere within a furnace thus can and does vary from point to point and consequently, the analysis of the products of the reaction by withdrawal and analytic methods is not only slow and tedious but is characterized by uncertainty and wide margins of error. So also of dew point tests which are substantially indicative of the temperature at a particular point in the furnace at a particular time. There are variations in dew point because of variation in moisture entrained in the gas introduced, and of variations in temperature due to leaks, and of gas quality, et cetera.

With this in mind, a primary object of the invention is to provide a method and apparatus for determining the effective equilibrium points of chemical reactions incident to heat-treating quickly and in the furnace itself at the temperatures existing in the furnace.

One thing further is to be noted with respect to the significant chemical reaction occurring. In every chemical change there is either absorption of heat, an endothermic reaction, or an evolution of heat, which is termed an exothermic reaction. The heat of reaction is usually included in a chemical equation as:

$$CO_2+C \leftrightharpoons 2CO—41.3 \text{ kilogram calories}$$

Therefore, for every gram-molecule of carbon dioxide converted to carbon monoxide, 41.3 kilogram calories are absorbed. Similarly, the same amount of heat is evolved when two gram-molecules of carbon monoxide break down to carbon dioxide and carbon. This evolution or absorption of heat is irrepressible and can be measured even at the elevated temperatures employed in conventional heat-treating furnaces. In an exothermic reaction the temperature of the material undergoing this reaction will always exceed the ambient temperature, and likewise in an endothermic reaction the temperature of the material will always be less than the ambient temperature. In instances where an equilibrium exists, the temperatures will coincide.

According to the present invention, a sample of an ingredient of a reaction, such as carbon, is located in the furnace and its temperature as present in the furnace atmosphere is measured and compared to the sensible temperature present at that time instant in the furnace. The differential between the two temperatures indicates that a reaction is taking place and also a measure of the heat of reaction occurring in sample.

However, I have found that the complexity of the chemical reactions in a furnace at a particular time produces heat for different reasons and from diverse reactions too complicated to compute or factor out with accuracy. The temperature difference between the sample and the furnace may, however, be calibrated to indicate empirically the prevalence of a particular reaction and its effect on the carbon sample. For example, in the heat-treating of steel there are changes, at various temperatures, in the ratio of carburizing gases to decarburizing gases. These changes cannot be determined with accuracy with present apparatus as to their total effect on the carbon content of the charge at a particular time. It has been found that greater control can be obtained over carburization and decarburization when the atmosphere is endo-

thermic. Therefore, the curves of temperature differentials for various gas mixtures will all be on the side of endothermic reaction. The carbon sample will run cooler than the ambient temperature of the furnace proportionately to the degree of the reaction.

The present invention also contemplates the use of a work sample identical with the metal to be treated. Continuous measurements may be made of the heat of reaction of this sample, and comparison made not only with the sensible furnace temperature which will be referred to as the ambient temperature but also with the heat of reaction of the carbon sample. The differential between ambient and steel sample temperatures will tell whether a reaction is occurring that is either endothermic or exothermic, or neutral. The differential between the ambient and carbon sample temperatures, as mentioned, will identify the status of the atmosphere. When the two differentials are brought to a reliable constant, then either the atmosphere has been changed to equilibrium for the steel sample, or the steel has changed to equilibrium for the atmosphere.

The present invention also contemplates the use of a trial sample identical with the steel composition to which a work piece is to be changed by the heat-treat if carbon is to be added or removed. The differential between ambient and trial sample temperatures determines how far off the atmosphere is with respect to equilibrium for the trial sample and indicates what differential is to be expected when the work sample has attained the change desired with a given atmosphere condition.

Comparison between the carbon differential and the trial piece differential will determine the carbon content of the trial piece when the two differentials are constant with respect to a scale employed to record same against previously determined known values. Also a comparison between the same differentials will be a warning of increased or decreased water content in the atmosphere which would not primarily effect the carbon differential reading.

A further object of the invention is to accurately and quickly read the heat of reaction occurring or likely to occur with a particular charge of work pieces to be heat-treated.

Another object of the invention is to provide apparatus for determining the requisite atmosphere for chemical equilibrium or for accomplishing chemical changes in a furnace charge of work pieces to be treated.

Other and further objects, advantages and features of the present invention will be apparent to those skilled in the art from the following description, taken in conjunction with the accompanying drawings in which similar reference characters relate to similar parts and in which:

Fig. 1 is a diagrammatic view of an indicating and control apparatus made in accordance with the present invention;

Fig. 2 is a diagrammatic view of a modified form of the invention shown in Fig. 1;

Fig. 3 is a diagrammatic view of another modified form of the invention shown in Fig. 1;

Figs. 4, 5 and 6 are graphs showing the operating characteristics of the apparatus of Figs. 1 and 2.

It is contemplated that the method of the present invention may be carried out utilizing only a carbon sample to determine carbon equilibrium levels for steels of various different percentages. According to this form of the present method a carbon sample is placed in a furnace along with a predetermined low rate of carrier gas which may be of the endothermic type having approximately 39% hydrogen and 21% carbon monoxide. This gas is wildly carburizing. At the same time hydrocarbon gas, such as natural gas, containing a large percentage of methane is fed into the furnace. Preferably, the volume of carrier gas is slightly greater than that of the hydrocarbon gas. By using limited quantities of carrier gas and hydrocarbon gas and having the volume of carrier gas slightly exceed the volume of hydrocarbon gas, applicant has found that the carburization process with its diffusion of the charge may be controlled accurately and that a proper atmosphere for bright heat-treating can be reached without inadvertent decarburization of the charge or undesired carburization.

A steel sample of unknown carbon content may be placed in the furnace and the furnace heated to within a range of 1400° F. to 1700° F. The temperature within the carbon sample will vary according to complex chemical reactions occurring between the sample and the constituents of the atmosphere at this heat range. The difference in temperatures between the carbon sample and the interior of the furnace may be detected by a pyrometer of the potentiometer or the resistance type. The ratio of gases may be varied so that this heat differential is uniform. When the heat differential is uniform a definite carbon change will occur in the steel sample. A low carbon steel sample may be carburized to an intermediate degree and a relatively high carbon steel may be decarburized to a certain extent. These changes may be measured by removing the steel samples from the furnace and weighing them to determine the differences in weight, if any.

By the same procedure, steel samples of known carbon content may be tested to determine the gas ratio necessary to obtain equilibrium for particular carbon levels. These levels are represented by definite temperature differences from the carbon sample differential and may be charted. When it is desired to carburize a particular charge to a certain percentage carbon content the charge is placed in the furnace and the gas ratio adjusted until the heat differential of the carbon sample is at a level corresponding to the desired carbon content of the charge.

For bright heat-treating a neutral atmosphere is required. This may be obtained in a charge of known carbon content merely by adjusting the gas ratio so that the temperature differential of the carbon sample assumes a level in parallelism with the level of equilibrium of the particular charge. For convenience, a continuous indication may be made of the carbon sample differential and the chart may be calibrated to indicate the equilibrium levels of steels of various carbon contents.

Decarburization of a charge to a certain level may be obtained by adjusting the atmosphere until the carbon differential line follows a predetermined line on the calibrated chart.

In another form of the present method, a charge may be brought to a predetermined carbon content by placing in the furnace, in addition to the carbon sample, a steel trial sample of the degree of carburization desired. The temperature differential between the carbon sample and the interior of the furnace and between the trial sample and the interior of the furnace are then alternately measured. By this arrangement, a check may be had on the equilibrium level of the steel sample selected. By following the method above set forth, the ratio of gases in the atmosphere may be varied so that the desired degree of carburization is obtained in the charge. The heat differential of the carbon sample is charted along with the heat differential of the steel sample and the lines charted for these values will assume a parallel relation when equilibrium for that trial sample is reached. The value of this checking device is that atmosphere fluctuations due to changes in gas quality can be observed and anticipated. An observation of the chart will indicate the atmosphere correction required.

In making adjustments of the atmosphere, I have found that contrary to prevailing opinion, highest carbon content equilibrium for the atmosphere is attained by lessening both the gas and the carrier gas, particularly the carrier gas as distinguished from flooding the furnace with gas without lowering the carrier gas. Sooting conditions prevalent are eliminated and also pitting of work pieces due to excessive water content.

The invention is primarily directed to a method and apparatus for measuring by means of sensitive thermocouples for calibrated resistance elements the temperature differential between the temperature of a carbon sample in a heat furnace and the ambient temperature of the atmosphere in the furnace. The equilibrium point of the carbon may be obtained by varying the atmosphere to obtain a uniform temperature differential. The equilibrium points of various steel samples of different carbon contents may be calibrated by the same method or empirically. These equilibrium points assume a definite thermal relation with respect to the equilibrium of the carbon sample. Differential readings of steel samples on one side or the other of the equilibrium point indicates that either carburization or decarburization is occurring for the steel samples.

With reference now to the drawings and more particularly to Fig. 1, a furnace **10** is provided with a source of heat such as an electrical resistance unit **12**, an atmosphere inlet **14**, an atmosphere outlet **16**, and a shield **18** for diffusion of the atmosphere and the heat throughout the furnace and a flame curtain fuel source below the charge door **19**. Preferably a fan **15** maintains homogeneity in the furnace atmosphere.

A plurality of thermocouples **20**, **21**, **22** and **24** are mounted within the furnace in contact with the atmosphere but shielded against irregular radiation conditions therein by a barrier **26**. These thermocouples are connected to a recording potentiometer **28** of the voltage opposition type and having a vibrator **30** for conversion of minute direct current to alternating current which is amplified by means of an amplifier **32** for operation of a reversible combined balancing and chart motor **34**.

The potentiometer **28** includes a battery **36**, a rheostat **38**, a standard cell **40**, fixed resistances **42** and **44** desirably of constantan or the like for uniformity under varying temperature conditions, and a slide wire **46**. The junctions of each of the thermocouples **22** and **24** are desirably of chromelconstantan and each have a conductor joined at **48**. The ambient temperature thermocouple **22** is connected at **50** by means of a conductor **52** to a point between the fixed resistances **42** and **44**. The thermocouples **20**, **21** and **24** are alternately connected to the potentiometer **28** by means of a rotary switch **54**. The junction of the thermocouple **24** is embedded in a cap **56** of pure carbon while the junctions of the thermocouples **20** and **21** are covered by steel samples **58** and **59** of desired carbon contents.

When the switch **54** is in the position shown the temperature differential between the carbon sample **56** and junction **60** of the thermocouple **22** is indicated by the voltage differential between these thermocouples. The current variations pass through the vibrator **30** and the amplifier **32** for rotation of the motor **34** in one direction or the other depending upon the direction of the current. When the switch **54** is the position shown in dotted lines the temperature differentials between the interior of the furnace, as recorded by the junction **60**, and the steel samples **58** or **59**, is indicated. Preferably before being covered by their respective caps or samples, the thermocouples are all balanced to identical electrical constants by variable series resistors **61** and shunts **63** of approximately 500 ohms to "zero in" the system and its components.

In Fig. 2 is shown a modified form of the present apparatus in which the thermocouple **20** and the switch **54** is eliminated. In this form of the invention there is recorded the difference in temperature between the carbon sample **56** and the interior of the furnace, as indicated by the junction **60**. As pointed out above, this differential indicates an equilibrium level under existing atmosphere conditions within the furnace.

The difference in temperature between the carbon sample **56** and the interior of the furnace may also be measured by the difference in resistance of resistors placed in the furnace in lieu of the thermocouples of the forms of the invention shown in Figs. 1 and 2. These resistors are equal in value and are connected to a Wheatstone bridge **66** having known resistances **68** and **70** and a galvanometer **72** for indicating differences in resistance of the resistors, and consequently, the difference in temperature between the resistor exposed to the atmosphere in the furnace and the resistor embedded in the carbon sample **56**. The values obtained by this resistor method may be calibrated with heat levels obtained by the potentiometer method above described.

Example I

A sample of steel AISI C 1010 is placed in the furnace at 1600° F. along with a carbon sample. The temperature difference of the carbon sample and the interior of the furnace corresponds to a .83 mv. reading on the potentiometer. The steel sample was weighed before insertion and the balance indicated that it weighed 4.00601 gr. After exposure for a period of ½ hour to carrier gas alone the sample showed a gain of only .00014 gr. This low gain indicates that the furnace was practically at equilibrium for this particular carbon steel.

Example II

A sample of AISI C 1050 steel is substituted for the steel of Example I and exposed to an atmosphere of a minimum amount of carrier gas along with .5 cu. ft. of hydrocarbon gas at 1600° F. for a period of ½ hour. During this period the temperature differential is indicated by a .5 mv. reading on the recording potentiometer. A loss of only .00109 gr. is recorded which is close to equilibrium for a .5% carbon steel at this temperature.

Example III

An AISI C 1095 steel sample was substituted for the steel sample of Example II and a 3 mv. reading is obtained on the recording potentiometer. The volume of hydrocarbon gas is increased to 1.5 cu. ft. for a period of time and a gain of .00130 gr. is indicated. Since the volume of hydrocarbon gas is in excess of that required for equilibrium conditions, this volume is gradually reduced until the carbon content reaches an equilibrium with the steel.

Example IV

A sample of steel AISI C 1018 is placed in the furnace at 1500° F. along with a carbon sample and a charge of C 1010. The atmosphere is adjusted so 6 c.f.h. of enriching gas and 2.6 c.f.h. of carrier gas are flowing into the furnace. After a period of ½ hour the charge is removed and is found to have gained .00007 gr. per square centimeter of surface area. During this period the steel sample differential and the carbon sample differential are substantially equal at .81 mv. on the recording potentiometer. Thus, at equilibrium for C 1018 steel a small gain is indicated in the C 1010 charge.

Example V

A sample of steel AISI C 1050 is placed in the furnace at 1500° F. along with a carbon sample and a charge of steel C 1053. The atmosphere is adjusted so that 2 c.f.h. of enriching gas and 3.5 c.f.h. of carrier gas are flowing into the furnace. After a half hour of operation the charge is removed and is found to have gained .000001 gross per square centimeter of surface area. During this period the steel sample differential and the carbon sample differential are substantially equal at .5 mv. on the recording potentiometer. Thus at equilibrium for C 1050 steel the charge of C 1053 is in substantial equilibrium.

Example VI

A sample of steel AISI C 1095 is placed in the furnace at 1500° F. along with a carbon sample and a charge of C 1099 steel. The atmosphere is adjusted so that there is no flow of enriching gas and a flow of only .5 c.f.h. of

carrier gas. After a half hour of operation the charge is removed and is found to have lost .00019 gr. per square centimeter. During this period the steel sample differential and the carbon sample differential are substantially the same at .25 mv. on the recording potentiometer.

Referring now to Fig. 4, there is shown in this figure a graph in which the horizontal line K indicates an ideal equilibrium point for the reactions to which the carbon sample is subjected. K is also the point where all the thermocouples are "zeroed in." In actual practice, this equilibrium level is seldom reached in an endothermic atmosphere. In this type of atmosphere the temperature of the carbon sample is below the temperature of the furnace as indicated by the negative readings on the graph. In a heavily hydrocarbon atmosphere, of course, a level on the plus side will be obtained, and this will be a carburizing atmosphere. According to the present invention, an endothermic atmosphere is introduced into the furnace and after initial adjustment of the atmosphere it is found that the heat level of the carbon assumes a definite line. Using only the carbon sample method, as illustrated by the apparatus of Fig. 2, steel samples of known content may be placed in the furnace and the atmosphere ratio necessary for their heat levels to follow a straight line are absorbed. These levels may be charted as shown so that a carbon sample of unknown carbon content may be placed in the furnace and the atmosphere may be varied so that they assume one of the equilibrium levels shown.

Fig. 5 shows curves obtained by the method of the apparatus of Fig. 1. These curves indicate that placing a charge in the furnace in which a steel sample of .5% carbon, for instance, will assume a certain equilibrium level, and that the carbon sample will do likewise. These curves indicate that the charge will be carburized to the carbon content of the steel sample connected to the thermocouple, or if the charge is at that level no carburization or decarburization will take place. These curves can be with or without the differential recording of what is happening with the work sample thermocouple, it being appreciated that the work sample if used should be approximately twice the thickness of the depth to which carburization or decarburization is to be accomplished in the work pieces.

Fig. 6 indicates that a charge of .1% carbon steel may be carburized to the value of .5% by alternately charting the heat levels of the carbon and a steel sample of .5% carbon which is connected to the thermocouple. It is found that, with suitable variations in the gas ratio, the heat level of the carbon will remain substantially the same while the heat differential of the .5% sample will follow a line substantially identical to that shown in Fig. 5. Since an equilibrium condition for .5% steel is indicated at a particular atmosphere the carbon content of the chart will rise to this extent.

By the present apparatus and method, applicant is able to determine the carbon potential of a heat-treat atmosphere with accuracy. This has not been heretofore possible. In addition, applicant is able to determine the carbon content of a steel sample or charge without the need for chemical processing. According to the present method, the carbon potential existing in the furnace at any particular time may be measured and its effect on metals may be calculated. The present method and apparatus may be utilized for a wide variety of gas-metal reactions and it is not intended that the scope of this invention be limited to the testing of steel heat-treating atmospheres.

It will be apparent that this invention may be embodied in devices which differ in many respects and details from the particular embodiment disclosed. All modifications which do not go beyond the scope of the invention will readily suggest themselves to those skilled in the art. It is, therefore, not intended that the invention be limited to the exact construction shown and described, but only to the inventive concept as defined in the appended claims.

I claim:

1. A method for controlling the carbon potential of a prepared heat-treating atmosphere to obtain a charge of predetermined carbon content comprising the steps of placing a steel sample of known carbon content in a furnace, raising the temperature of the furnace to within heat-treating range, introducing endothermic carrier gas at a predetermined low rate, introducing hydrocarbon gas at a predetermined low rate, measuring the temperature difference between the steel sample and the interior of the furnace, varying the ratio of carrier gas to hydrocarbon gas until the temperature difference is uniform whereby the carbon content of the charge equals the carbon content of the sample.

2. A method for controlling the carbon potential of a heat-treating atmosphere to obtain a charge of predetermined carbon content comprising the steps of placing a steel sample of known carbon content in a furnace, raising the temperature to within heat-treating range, introducing endothermic carrier gas at a predetermined low rate, introducing hydrocarbon gas at a predetermined low rate, measuring the temperature difference between the steel sample and the interior of the furnace, varying the rate of flow of the gases until equilibrium is reached at a particular temperature differential, placing suceeding samples of known but different carbon contents in the furnace, measuring the temperature differential between the latter samples and the interior of the furnace, varying the rates of flow of the gases until equilibrium is reached for each sample, placing a charge of unknown carbon content in the furnace and varying the rates of flow of the gases corresponding to the rates of flow established as appropriate by the sample bearing the carbon content desired in the furnace charge until the equilibrium level of a steel of a desired carbon content is reached.

3. A method for heat-treating steel in a neutral atmosphere comprising the steps of placing a steel sample of known carbon content in a furnace, raising the temperature to within heat-treating range, introducing endothermic carrier gas at a predetermined low rate, introducing hydrocarbon gas at a predetermined low rate, measuring the temperature difference between the steel sample and the interior of the furnace, varying the rate of flow of the gases until equilibrium is reached at a particular temperature differential, placing succeeding samples of known but different carbon contents in the furnace, measuring the temperature differential between the latter samples and the interior of the furnace, varying the rates of flow of the gases until equilibrium is reached for each sample, charting the temperature levels that are characteristic of the equilibrium levels of the several samples, placing in the furnace a charge corresponding in carbon content to one of the equilibrium levels, and exposing the charge to the heat level of the furnace for a sufficient period of time to effect heat-treating, whereby the charge is neither oxidized, carburized or decarburized.

4. A method for determining the carbon potential of a carbon correction atmosphere comprising the steps of placing a carbon sample and a steel sample of known carbon content and a charge of unknown carbon content in a furnace, raising the heat level of the furnace to operating temperature, introducing a carrier gas at a predetermined low rate, concurrently introducing a hydrocarbon gas at a predetermined low rate, alternately measuring the temperature differential between the carbon sample and the interior of the furnace and the temperature differential between the steel sample and the interior of the furnace, varying the rates of flow of the gases until equilibrium temperature differential between the sample and the furnace for the steel sample is reached

and equilibrium temperature differential of the carbon sample is achieved.

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