Dec. 7, 1943. G. DERGE 2,336,075

METHOD FOR THE RAPID DIRECT ANALYSIS OF OXYGEN IN STEEL

Filed May 13, 1941

Fig. 1.

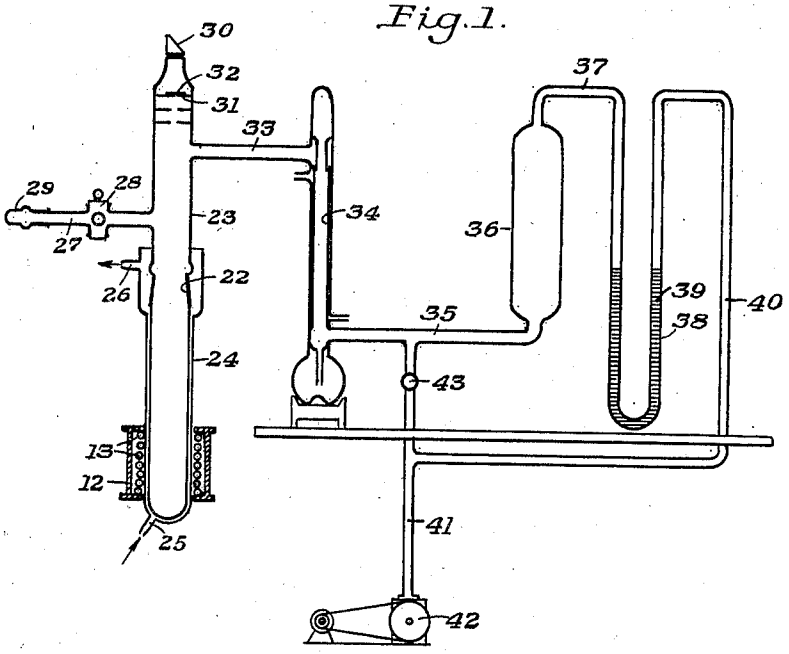


Fig. 2

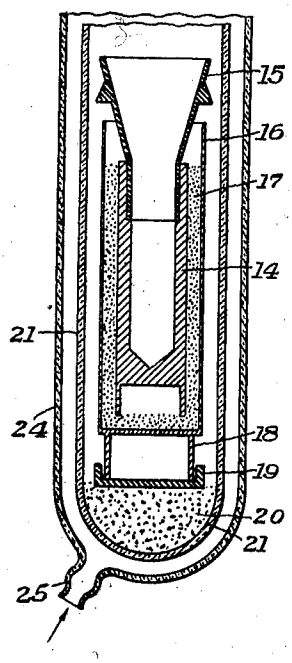


Fig. 3.

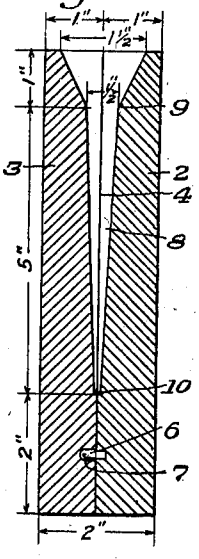
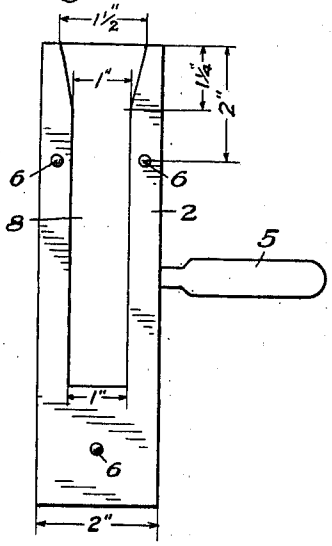


Fig. 4.



INVENTOR
Gerhard Derge
by
Stebbins and Blenko.
His Attys.

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METHOD FOR THE RAPID DIRECT ANALYSIS OF OXYGEN IN STEEL

Gerhard Derge, Aspinwall, Pa., assignor to Carnegie Institute of Technology, Pittsburgh, Pa., a corporation of Pennsylvania

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6 Claims. (Cl. 23—230)

This invention relates to method and apparatus for the rapid direct analysis of oxygen in steel. The invention is suitable for use in the control of industrial steel making operations such as the open hearth, Bessemer and electric furnaces whenever a value for the oxygen content of the steel or iron bath is desired, especially near the end of the heat, when the proper deoxidation treatment must be determined.

In steel making practice, the elimination of carbon, phosphorus, sulphur, silicon and manganese from the iron is an oxidation process and the oxidation is generally described as being brought about by FeO dissolved in the molten iron. However, the oxygen is probably also present in other forms than FeO and is very likely also associated with other elements such as silicon and manganese. When the desired composition in regard to these elements has been attained, the steelmaker should know the amount of FeO present. A certain minimum amount of FeO is required for those grades known as rimming steels. In other types known as semi-killed and killed steels, the FeO must be reduced to definite amounts by deoxidation with other elements, such as aluminum. The amount of FeO in the finished steel will thus vary with the grade of steel and the method of manufacture, but in all cases it is required that the FeO content be known and accurately controlled, if the steel is to be of the desired quality.

In current practice, the amount of FeO in the steel must be estimated by indirect methods which depend upon the operator's experience and the analysis for other elements in the slag or metal. The equilibrium between these elements and FeO in the metal are often displaced by variations in various operating factors, or they may not always be attained to the same degree, or they may be of such a nature as to be of little value in certain composition ranges. It is, therefore, desirable to eliminate these uncertainties by providing some direct rapid method of analysis for FeO in the steel. In order to be of value, this method must be sufficiently rapid so that it can be made while the heat is in the furnace or in the ladle in order that after the analysis is made the working of the heat may be adjusted accordingly or that a deoxidizer may be added to the steel while it is still molten and in accordance with the test. The method hereinafter more fully described is such that the total oxygen in the steel may be analyzed within about five minutes under favorable conditions and accordingly the heat may be worked and finished as indicated by the test.

Although rapid methods are now known for analyzing carbon in steel so that the carbon can be adjusted while the bath is still in a molten condition, no rapid methods are now available for analyzing for oxygen, so that deoxidizers can be added to the steel while it is still in molten condition to thereby produce deoxidation of the steel to the desired extent. The present methods for analyzing for oxygen in the steel are complicated and take too long a time to be of use in controlling the working and finishing of the heat and they are also less accurate than is desired. A vacuum fusion method is known which can be used in the laboratory to analyze for oxygen, hydrogen and nitrogen but this method and the apparatus used in carrying out the analysis are complicated and the analysis takes several hours to perform. Thus it is of no value in analyzing a steel for oxygen within a short period of time such that a deoxidizer may be added to the steel bath in accordance with the test. The time of testing is so long that the steel bath would have changed radically in composition or the steel making process would have ended before the analysis was completed.

Another method of analyzing for oxygen in steel is the bomb method in which aluminum is placed in a cast iron bomb provided with a thin metal cover and the bomb is placed in the steel bath. The thin metal cover melts, the steel flows into the bomb and the iron oxide in the steel converts the aluminum into alumina. The bomb is removed from the bath and the contents of the bomb are analyzed for alumina from which the content of FeO in the steel can be determined. The alumina may be determined by a turbidity method which involves treating the steel with acid and measuring the turbidity of the solution. Another method is to subject the steel containing alumina to a vacuum fusion treatment to determine the oxygen in the steel. There are several objections to this bomb method in which aluminum is converted into alumina by the FeO in the steel. Experiments indicate that the conversion of the oxygen in the steel to alumina is not complete. Thus the sample does not truly represent the steel in the bath. Another objection is that if the contents of the bomb are subjected to a vacuum fusion treatment a relatively high temperature such as of the order of about 1600° C. is required, in order to reduce the alumina. As contrasted with this, where according to the present invention the vacuum fu-

sion method is carried out on a sample in which the oxygen has not been converted to alumina, the reduction may be accomplished at a considerably lower temperature, for example at about 1400° C., and is also more rapid. In addition, the analysis of oxygen in steel by a method which involves formation of alumina from aluminum and the subsequent determination of the amount of alumina involves a long period of time, so that this method is not suitable for making a rapid determination in order that the analysis may be of use in the working and finishing of the heat.

In accordance with the present invention, I provide a rapid method of analyzing for total oxygen in the steel without resort to the intermediate step of converting aluminum into alumina and without employing a complicated vacuum fusion method which required a long time to perform.

In the accompanying drawing, which illustrates preferred forms of apparatus which may be used in carrying out the method,

Fig. 1 is a front elevation of a simple form of vacuum fusion apparatus;

Fig. 2 is a vertical longitudinal section through the crucible assembly;

Fig. 3 is a vertical longitudinal section through a split mold used in obtaining the sample which is to be analyzed in the apparatus shown in Fig. 1; and

Fig. 4 is a front elevation of one of the parts of the mold shown in Fig. 3.

Referring now more particularly to the accompanying drawing, the method and apparatus may be conveniently described in two sections, each of which are important:

A. Sampling
B. Analysis

The sampling of the steel will be described first. The steel bath which is to be analyzed for oxygen is sampled with a small well-slagged spoon of the type in common use for taking carbometer samples. This sample is frozen as rapidly as possible by pouring it into a small split, wedge mold made of copper or other material having high heat conductance. The object of rapidly freezing the sample is to stop as quickly as possible the reaction between the FeO and carbon in the steel. Evolution of CO is particularly rapid in the freezing range, so the sample must be solidified as rapidly as possible. If the chilling of a sample is not very rapid, it allows the reaction between FeO and carbon to continue, thereby forming carbon monoxide which escapes from the mold. Thereby some of the FeO in the steel bath is lost in making the test piece, so that the analysis of the test piece does not accurately indicate the content of FeO in the steel bath.

A preferred form of mold for obtaining the sample is shown in Figs. 3 and 4, on which the dimensions of the mold have been indicated. This mold is made of copper which rapidly chills the sample. The mold is a split mold made in two sections 2 and 3 split along the vertical line 4, each of the sections being provided with a handle part 5. One of the mold sections is provided with dowel pins 6 which fit into corresponding recesses 7 in the other mold section. It will be noted that the mold when the sections are assembled is square in horizontal cross section and has a width of about 2", a thickness of about 2" and an overall height of about 8". The mold cavity 8 is about 5" in height, is about 1" in width and tapers from a thickness of about ½" at the top 9 to a fairly sharp edge 10 at the bottom. The dimensions of this mold have been determined by experiment to be satisfactory in obtaining a proper sample and although the dimensions may be varied somewhat, they are to a certain extent critical. In any case, the material of which the mold is made and its dimensions including the dimensions of the mold cavity should be such as to rapidly chill at least the lower portion of the sample adjacent the edge 10 so quickly that the reaction between FeO and carbon is quickly stopped. The sample will contain a large cavity or "pipe" and it is important that this be left in the sample and that no attempt be made to eliminate it by adding additional metal. An attempt to eliminate this cavity by pouring additional metal prevents the rapid chilling of the sample required to stop the reaction between the FeO and carbon. The lower part of the sample will have a bright or only very slightly tarnished surface which shows that the chilling of the sample has been extremely rapid so as to prevent the formation of temper colors. A portion of from 10 to 20 grams is cut or broken off of the bottom part of the sample, is weighed and is placed in the analytical apparatus shown in Fig. 1.

Referring now more particularly to Figs. 1 and 2, the construction of the apparatus and the method of analyzing the sample for total oxygen is as follows:

An induction furnace 12 having coils 13 surrounds a crucible assembly which is illustrated more in detail in Fig. 2. The sample to be analyzed for oxygen is introduced into a graphite crucible 14 which is provided adjacent its top with a graphite funnel 15 for aiding introduction of the sample into the crucible as more particularly explained hereinafter. A slotted graphite shield or thimble 16 is spaced from and surrounds the crucible, the space between the crucible and shield being filled with graphite turnings 17 acting as heat insulation material. The bottom of the shield 16 has a depending base 18 which rests on an alundum supporting base 19, so as to space the thimble 16 from the alundum supporting base. The supporting base 19 rests on 40–60 mesh magnesium oxide designated by the reference numeral 20, which acts as a heat insulator and is contained in a glazed quartz tube 21 spaced from the thimble 16. The upper end 22 of the quartz tube has a tapered ground joint connection with the lower end of the heat resistant glass furnace head 23 as shown in Fig. 1. The joint is made vacuum-tight by wax or other sealing material. A water cooling jacket 24 made of heat resistant glass surrounds the crucible assembly and the joint 22, cooling water being introduced through an inlet 25 and passing out through an outlet 26.

An important feature of the crucible assembly is the use of the graphite thimble or shield 16 in conjunction with the graphite turnings 17 and the graphite crucible 14. It has been customary in the past to place graphite turnings or other particle form of graphite between a graphite crucible and an aluminum oxide shield or thimble 16. There is a considerable tendency at the high temperatures employed for the powdered graphite to react with the aluminum oxide thimble reducing the aluminum oxide and forming carbon monoxide. This reaction may produce a hot spot in which the reaction is pronounced, there-

by developing enough carbon monoxide to give an inaccurate analysis of the oxygen in the steel. By using a graphite thimble to retain the graphite powder or turnings according to the present invention, reaction between the graphite powder and aluminum oxide to form carbon monoxide is avoided.

As shown in Fig. 1, the furnace head 23 has a side arm 27 provided with a stop cock 28. The side arm 27, through which the sample to be analyzed is introduced, is provided with a cap 29. The furnace head is fitted at the top with a prism 30 through which temperature may be taken with an optical pyrometer. Within the furnace head and below the prism there is located a copper radiation shield 31 designed to prevent metallic vapors from condensing on the prism. A sighting hole through the shield is opened and closed by a magnetically operated steel door 32.

The head 23 is connected by an arm 33 to a mercury pump 34 of any usual or desired construction which will produce a high vacuum in the system. A tube 35 leads from the mercury pump to a gas reservoir 36 of known volume, which in turn leads by a tube 37 to a manometer 38 for measuring the pressure in the system. This manometer may be filled with butyl phthalate 39 or other suitable liquid. A tube 40 connects the manometer to a tube 41 connected to an oil forepump 42. The tube 41 also is connected to the tube 35 and is provided with a valve 43.

Preliminary to carrying out the analysis, the equipment must be baked out by heating the crucible above the normal operating temperature of about 1400° C. This baking may be carried out at a temperature of about 1800° C. for approximately 3 hours, until the gas evolved at the operating temperature becomes negligible. During this preliminary evacuation of the system, the forepump 42 is employed as well as the mercury pump 34. The steel sample to be analyzed is then placed in the arm 27 after closing the stop cock 28 and removing the cap 29. The cap is then replaced and the stop cock opened. The valve 43 leading to the forepump 42 is then closed but the mercury pump 34 is continued in operation. The sample is moved along the arm 27 by a magnet moved along the outside of the arm and the sample drops into the crucible 14, being guided in its descent by the funnel 15. The crucible is heated to a temperature of about 1350–1600° C., preferably about 1400° C., during the vacuum fusion treatment. It is desirable to have previously put into the crucible a mixture of tin and iron which makes the melting of the sample and elimination of gases more rapid. Manganese in the sample vaporizes at the temperature of extraction and condenses on the cooler portions of the furnace and head. The presence of tin in this condensed layer prevents or minimizes the absorption of gases by the manganese. A small amount of tin is preferably added before each successive analysis is made.

The carbon dissolved in the molten metal will react with the various forms of oxygen in the sample to form carbon monoxide which is evolved along with nitrogen and hydrogen and collects in the reservoir 36 where its pressure is measured. The total volume of the nitrogen and hydrogen will be nearly constant from sample to sample in any regular steel practice. Also the volume of nitrogen and hydrogen is very small compared to the volume of carbon monoxide. For example, a typical open hearth steel may contain about

	Per cent by weight
FeO	0.266
H_2	0.0019
N_2	0.0006

Therefore, knowing the volume of the reservoir 36 and the pressure and temperature of the gas, the amount of oxygen or FeO in the sample can be readily determined in accordance with the formula $PV=NRT$ in which

P=Pressure in atmospheres
V=Volume in cc.
N=No. of mols of gas
R=Gas constant
T=Absolute temperature

Since each of the factors except N is known, the equation may be solved for N (the number of mols of gas). In any regular steel making practice, such for example as the open hearth, Bessemer or electric furnace, it can be ascertained by previous experiments what approximate proportions of nitrogen and hydrogen the steel contains and this correction factor can be applied to determine the number of mols of carbon monoxide which were evolved from the steel sample by the vacuum fusion analysis. Thus assume that having read the pressure as indicated by the manometer and having solved for N in the equation $PV=NRT$, N is found to have a value of 0.00044, which is the mols of total gas. Assume that the steel which was analyzed was open hearth steel and that from previous experiments it is known that in such steels the hydrogen is about 5%, the nitrogen about 3% and the oxygen equivalent to about 92% of carbon monoxide based on the volume of the total of these gases (nitrogen, hydrogen and carbon monoxide). The number of mols of carbon monoxide is, therefore, 0.00041. This corresponds to 0.00041 mol FeO or 0.03 gram FeO. Assuming that the steel sample weighed 10 grams, this would mean that the FeO in the sample amounted to 0.3%.

Of course, it will not be necessary in each individual analysis to figure out the percentage of FeO from the gas pressure as indicated by the manometer. These calculations can be figured out previously and a table or graph can be prepared showing the relationship between the pressure as indicated by the manometer and the percentage of FeO in the steel sample. In preparing the tables or graphs, different correction factors may be used which have been found from previous experience to apply to the particular type of steel making practice by which the sample was prepared. In this manner, it is only necessary to subject the sample to a vacuum fusion treatment, read the pressure as given by the manometer and refer to a chart or graph to obtain the approximate amount of FeO or oxygen in the steel bath. A deoxidizer or deoxidizers may then be added to the bath in accordance with the analysis.

The invention provides a rapid method for analyzing for total oxygen in a steel or iron bath without the necessity of converting aluminum into aluminum oxide by the oxygen of the bath. The vacuum fusion method may be carried out rapidly because no attempt is made in the particular analysis under consideration to analyze for hydrogen and nitrogen but only for carbon monoxide. Since the amounts of hydrogen and nitrogen are very small as compared with the

amount of carbon monoxide, and since the amounts of hydrogen and nitrogen contained in a steel made by any regular steel making practice can be determined beforehand, the use of a correction factor for the hydrogen and nitrogen does not introduce a serious error into the method of analysis for oxygen.

The present method is so rapid that a sample may be taken from the steel bath, the analysis for oxygen made and a deoxidizer added while the bath is still in a molten condition. So far as I am aware, no other method is known for sampling and analyzing steel for oxygen with sufficient rapidity so that deoxidizer can be added to the steel in controlled amount while the bath is still in molten condition.

The invention has been particularly described in connection with the sampling and analyzing of steel for oxygen. The copper mold or a mold of other metal of high heat conductivity or the rapid method of chilling the molten steel sample may, however, be used in obtaining a sample of steel for analyzing for hydrogen. An important feature of the present invention is the very rapid chilling of the molten steel so as to prevent loss of the element for which the steel is to be analyzed during its solidification.

Although I have illustrated and described a preferred apparatus and method, it is to be understood that the invention may be otherwise embodied or practiced within the scope of the following claims.

I claim:

1. A rapid method of analyzing oxygen in a steel bath, which comprises chilling a molten sample of the steel so rapidly as to stop the reaction between carbon and iron oxide, subjecting the chilled sample to a vacuum fusion treatment in which the total evolved gases are collected in a known volume reservoir and measuring the total pressure of said gases.

2. A rapid method of analyzing oxygen in a steel bath, which comprises chilling a molten sample of the steel so rapidly as to stop the reaction between carbon and iron oxide, subjecting the chilled sample to a vacuum fusion treatment in which the total evolved gases are collected in a known volume reservoir and from the measurement of total pressure only of said gases determining the amount of oxygen in the steel, whereby the treatment of the steel bath from which the sample is taken can be controlled in accordance with the results of the test.

3. A rapid method of analyzing oxygen in a steel bath, which comprises chilling a molten sample of the steel so rapidly as to stop the reaction between carbon and iron oxide, subjecting the chilled sample to a vacuum fusion treatment in which the total evolved gases are collected in a known volume reservoir, measuring the total pressure of said gases and applying a previously determined correction factor to compensate for other gases in determining the oxygen in the steel from said pressure measurement, whereby the treatment of the steel bath from which the sample is taken can be controlled in accordance with the results of the test.

4. A rapid method of analyzing oxygen in a steel bath, which comprises chilling a molten sample of the steel so rapidly as to stop the reaction between carbon and iron oxide, subjecting the chilled sample to a vacuum fusion treatment in which the total evolved gases are collected in a known volume reservoir and measuring the total pressure of said gases, stopping the analysis without separating the evolved gases from each other, and from the measurement of total pressure of said gases determining the amount of oxygen in the steel, whereby the treatment of the steel bath from which the sample is taken can be controlled in accordance with the results of the test.

5. A rapid method of analyzing oxygen in a steel bath, which comprises chilling a molten sample of the steel so rapidly as to stop the reaction between carbon and iron oxide by forming a wedge shaped piece of steel by contact of the molten steel with walls of high heat conductivity, and subjecting at least a portion of the chilled sample to a vacuum fusion treatment in which the total evolved gases are collected in a known volume reservoir, measuring the total pressure of said gases, and from the measurement of total pressure only of said gases determining the amount of oxygen in the steel, whereby the treatment of the steel bath from which the sample is taken can be controlled in accordance with the results of the test.

6. A rapid method of analyzing oxygen in a steel bath, which comprises chilling a molten sample of the steel so rapidly as to stop the reaction between carbon and iron oxide by pouring it into a copper mold having a wedge shaped cavity, subjecting the lower portion of the wedge to a vacuum fusion treatment in which the total evolved gases are collected in a known volume reservoir measuring the total pressure only of said gases, and from the measurement of total pressure of said gases determining the amount of oxygen in the steel, whereby the treatment of the steel bath from which the sample is taken can be controlled in accordance with the results of the test.

GERHARD DERGE