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2,932,558

HYDROGEN ANALYSIS

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Application February 5, 1958, Serial No. 713,456

7 Claims. (Cl. 23—230)

The present invention relates to industrial quantitative chemical analysis, and particularly to a method and apparatus for the accurate and rapid determination of the hydrogen content, both in the free and in the combined form, in various materials including metals such as titanium, zirconium and metal hydrides for instance.

In the manufacture and refining of certain metals—titanium is an example—it is substantially impossible to prevent the inclusion of some hydrides such as TiH_2 for instance.

For almost all purposes titanium hydride has a deleterious effect upon the physical values of titanium, and therefore it is considered good practice, and in most instances necessary, to subject samples of refined titanium to analytical procedures to determine whether or not the titanium hydride content is below some allowable maximum. The methods in use for this determination are, in general, rather slow, complex and quite expensive, or the capital investment required for equipment is high.

In the past, some attempt has been made to determine hydrogen in titanium, zirconium or metal hydrides by burning a sample of the material to be tested in oxygen, and collecting the water vapor and determining the hydrogen content of the sample on the basis of the amount of water resulting from the combustion. So far as I am aware, all attempts to determine hydrogen in this manner are based upon the use of rather cumbersome equipment including the use of heavy furnaces which are slow to bring to proper operating temperature.

The present method depends for its operation upon this combustion phenomenon, but novel means are used for bringing about and regulating the combustion and the water recovery so that results throughout an extremely wide range of materials and concentrations are reproducible within an extremely small margin of error.

It is thus one of the objects of the present invention to provide a novel analytical method for the determination of hydrogen in metals and hydrogen in hydrides in test samples.

An additional object of the present invention is to provide improved apparatus for testing analytical samples for hydrogen in metals and hydrides which gives precise results at low cost and in minimum time, and which does not include a moisture blank in the result.

Another object is to provide novel apparatus and a novel method of procedure for burning titanium, zirconium, and similar metals and their hydrides, and other hydrogen containing materials in such fashion that the method of procedure may be largely standardized regardless of the material being tested.

Yet another object is to provide novel apparatus of the above character which makes use of radio frequency induction heating and which does not ordinarily require the use of the usual accelerator substances, such as tin for instance, in order to insure complete combustion.

Yet another object is to provide improved apparatus for carrying out the above set forth method in which

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the major structure is essentially the same as that described for the determination of carbon in U.S. patent application Serial No. 226,017.

Other objects and advantages will become apparent from the following description of a preferred embodiment of my invention.

In the drawings, in which similar characters of reference refer to similar parts throughout the several views,

Fig. 1 is a somewhat diagrammatic representation of the apparatus which forms the subject matter of the present invention and which is capable of practicing the method of the present invention; and

Fig. 2 is a longitudinal medial sectional view drawn to larger scale and taken through a portion of the apparatus so as to illustrate the construction thereof in greater detail, this view being taken in the direction of the arrows substantially along the line 2—2 of Fig. 1.

In the drawings, the tube at 10 provides an inlet connection for oxygen. In use, this tube, therefore, is connected through the usual reducing valve and on-off valve to an ordinary oxygen cylinder. From the tube 10, oxygen passes into the train indicated at 12. This train may be of conventional construction and needs no specific description. Its purpose is simply to pass the oxygen through hygroscopic agents which remove any water or water vapor which may be present as a contaminant in the oxygen; also SO_2 and CO_2 are removed and flow rate is measured. From the water absorbing train at 12, the oxygen passes through a tube 14 to a small catalytic tube heated by a furnace 16 which is energized through its mounts 17 and is arranged to pass the oxygen through a heated mass of copper oxide. The action in this hot catalytic mass is to cause any free hydrogen present in the oxygen to combine with the oxygen, thereby effecting conversion of hydrogen or hydrogen compounds to water or water vapor. From the furnace 16 the stream of oxygen, with a trace of water vapor therein, passes through a flexible tube 18 to a second small water absorbing canister at 20. The gas stream leaves the canister 20 by way of the metal tube 22, and at this point in the system is free of hydrogen and water vapor.

The tubes 10, 14 and 18 may be formed of the usual flexible rubber or plastics substances, but I prefer that the tube at 22 be made of metal. This is because it becomes hot enough to give up hydrogen and water to the gas stream if made of organic substances containing hydrogen and would thus introduce a high result in the determination.

The apparatus at 24 provides a high frequency induction furnace and accessory equipment, and is substantially similar to that forming the subject matter of the previously referred to patent application. This apparatus is so arranged that a high frequency power circuit mounted behind the panel 26 supplies energy to an induction coil 28 which surrounds a tube 30 formed of substantially fused quartz, or high silica content glasses which may be considered as essentially artificial fused quartz. This tube is therefore extremely resistant to thermal shock and high temperatures.

The coil 28 and the tube 30 are enclosed within a cage 32 which protects these elements and eliminates the possibility of the operator being burned. The bottom of the cage has an opening through which a vitreous ceramic or equivalent pedestal 34 can be raised so that its upper end is within the lower portion of the field of the coil 28. This pedestal 34 is supported at the upper end of a rod or plunger 36 which slides vertically within a tube 38. The tube has a vertical slot 40 therein with an offset portion at the top indicated at 42. A horizontal arm or lever 44 projects through the slot 40—42, and, at its inner end, is hinged to a transverse pin (not shown) at about the center of the rod 36. The

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free end of the lever 44 carries a counterbalance weight 46.

In use, with the lever 44 at the lower end of the slot 40, a crucible or other apparatus can be placed upon the upper end of the pedestal 34, after which raising the lever 44 to the top of the slot and swinging it sideways into the offset portion 42 raises the pedestal 34 to its uppermost position. When the lever 44 is released, the weight 46 will swing downwardly slightly, thereby wedging the stem 36 upwardly a small amount. This acts to seal the structure surrounding the pedestal 34 to the enclosing tube 30 at its lower end so as to prevent leakage.

The metal tube 22 leading from the water removing canister at 20 is connected at its upper end to a fitting 48 on the stem 36. This fitting and a passage 50 within the stem provide a flow path for the oxygen through to the base of the pedestal 34. From the base of the pedestal, oxygen flows upwardly through the annular space between the pedestal 34 and the enclosing quartz tube 30.

The upper end of the quartz tube 30 is of reduced diameter, as at 52, and this small diameter portion passes through the top of the cage 32. Its upper end is equipped with a ball-type ground glass quick disconnecting fitting 54 adapted for connection to a complementary socket 56 formed at the lower end of a glass tube 58. The tube 58 is bent to the right as shown in Fig. 1, and thence downwardly where it is equipped with another quick disconnect socket 60 fitted to a ball 62 at the upper end of a tube 64 leading into a furnace 66 for heating a catalyst within the tube 64. This assembly may be considered as identical with that at 16. From the furnace 66, the lower end 68 of the tube 64 leads downwardly to a ball-type fitting 70. This fitting is adapted for connection to a socket fitting 72 which acts as the inlet to a U tube or other removable water absorber 74. The outlet of the U tube is connected by a piece of rubber or plastics tubing to a water removing exhaust fitting 76 having its remote end open to the atmosphere. The fitting 76 prevents water from entering the absorber 74 if atmospheric air is sucked back into the apparatus through the outlet opening.

The U tube 74 and the water removing exhaust fitting 76 may have any of several well known water absorbents therein, these or similar materials also being used in the canister 20 and the train at 12. The ball and socket fittings used throughout as quick disconnects are of standard type and need no special description. In use, they are held together by spring clips or other devices so as to effect a seal and prevent separation, these clips being omitted in the present semi-diagrammatic showing since their use is well understood.

The portion of the tube 58 directly above the upper end 52 of the combustion chamber forming tube 30 is equipped with a short branch 78 which is inclined somewhat upwardly and is equipped with a socket fitting 80 at its end. A short tube 82 has a ball fitting 84 at one end seated in the socket 80, and the remote end of this tube is closed as is shown at 86. The tube 82 is free to swivel in a vertical plane so that the end remote from the fitting 80—84 may be positioned either well below or well above the fitting 80—84.

Preferably, as shown, an electric heating tape 96 should be wound around the tube 68 between the catalytic furnace 66 and the fitting 70, around the tube 58, and around the branch tube 82. The temperature of this heating element, and hence the temperature of the tubes heated thereby is controlled by an autotransformer 88 having a control knob 89.

A small vitrified ceramic crucible 90 is adapted to rest upon the upper end of the pedestal 34 so as to be raised therewith into the tube 30 so as to repose within the field of the induction coil 28. This crucible supports a sleeve or chimney 92 which rests upon its upper edge.

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The sleeve is cylindrical and extends upwardly so as to touch, or substantially touch, the shoulder formed where the large diameter portion of the tube 30 is joined to the small diameter portion 52. Preferably, as shown, the passage 94 through the upper portion of the tube 30 should be slightly smaller in diameter than the passage through the sleeve 92, and the sleeve passage should, in turn, be slightly smaller in diameter than the mouth of the crucible 90.

The above described apparatus is used for hydrogen determination as follows. For the first of several determinations, it is necessary to blank the instrument and bring the water absorbent bulb 74 to constant weight. This is done as follows: The catalytic furnaces 16 and 66 and the tape 96 are energized and brought to proper temperature. It will be appreciated that the temperature of the tape 96 should be such that the temperature of all of the tubing heated thereby is maintained above the temperature at which moisture will condense from the products of combustion.

The oxygen supply is turned on so that oxygen flows into the connection at 10, thereby flushing out the apparatus. The rate is not critical, about 400 mls./min. is satisfactory for the apparatus shown. A crucible 90 then receives a charge of powdered iron, approximately three grams is sufficient, and the charged crucible with the sleeve 96 supported thereon is then placed upon the pedestal 34 and elevated into position.

The radio frequency power circuit is then turned on to energize the coil 28 so as to heat the charge of iron in the crucible until it ignites and burns slowly. After five minutes or so, a water absorbent U tube or other water absorber 74 is attached to the fitting 70 so that the gas stream flows therethrough. Periodically this U tube is removed and weighed until it arrives at a constant weight indicating that no more water is passing thereinto from the system. Once the system has arrived at a constant weight for the U tube 74, the system is ready for a hydrogen determination. In this connection it should be noted that this blanking or standardizing procedure is necessary only when placing the apparatus into operation for the first time after a considerable rest. Thereafter each determination will serve in effect as the blanking cycle for the next determination.

Once the apparatus has been blanked, a determination is made as follows: A sample to be analyzed is cut, broken, or ground into pieces which will fit into the side tube 82, these pieces being washed (in carbon tetrachloride, for instance), weighed, and placed within the loading tube. The tube is then attached at the fitting 84—80 in such position that the closed end 86 is low. The size of the sample is not critical, but in general, as in most analytical processes, is determined largely by the concentration of the substance to be measured so as to make the final result easy to read. With apparatus of the type shown of reasonable size, appropriate sample sizes may range from 1 gram for concentrations of 0.1% H to 0.01% H, up to 10 grams for hydrogen concentrations below 0.005% H.

After the sample to be analysed has been loaded into the tube 82 and this tube has been attached to the remaining portion of the apparatus, a crucible 90 receives a charge of powdered iron, and this crucible together with the sleeve 92 thereon is elevated into position. No attention need be given to the catalytic furnaces 16 and 66, nor to the heating tape 96, since they remain energized throughout the period the apparatus is in use, and it will be assumed therefore that they are still energized following the blanking determination.

When the crucible has been elevated into place with the oxygen stream flowing through the apparatus, the induction heating coil 28 is energized so as to cause slow combustion of the powdered iron within the crucible. After the iron has melted and has been burning for a few minutes, an absorbent U tube 74 is attached to the

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fitting 70. After the U tube has been in place for a minute or so, it is detached and weighed to determine whether or not there has been a gain in weight due to water absorption. Ordinarily, experience with the apparatus will soon enable the operator to omit this last step, since he will know that all the water has been removed from the powdered iron and the apparatus swept clean within a certain time interval, and therefore by waiting for a period somewhat longer than this interval before attaching the U tube 74, he will know that all the water has been removed from the apparatus.

In any event, once the weight of the U tube 74 has stabilized and this weight is recorded, and while the coil 28 remains energized and the iron within the crucible continues to burn slowly, the free end of the side-arm 82 is elevated so as to dump the sample therein into the tube 58 through which it falls by way of the sleeve 92 into the crucible 90. Shortly after it falls into the pool of burning iron, the sample will catch fire and burn, the rate of combustion of the sample being determined by its composition. For example, titanium samples usually burn very rapidly in a manner that might well be characterized as a flash. On the other hand, certain metal hydrides burn quite slowly. For this reason, an autotransformer 100 is used in the oscillator circuit to facilitate control of the energy supplied to the crucible charge, since less outside energy is needed for samples which burn easily.

In any event, after combustion has been completed, the oxygen is allowed to continue to flow for a matter of five minutes or so, after which the U tube is detached and weighed to determine the gain in weight.

The percent of hydrogen in the sample equals the gain in weight of the U tube in grams, times 11.2, divided by the weight of the sample in grams.

In actual practice it is preferred to use two U tubes or other water absorbers 74 so that the operator can be weighing one to determine its final weight after one determination (also its weight for the start of the next determination) while the other tube is connected to the apparatus in a water absorbing position. At the end of each determination, the two tubes are interchanged in a manner which will be well understood by those familiar with the use of almost any type of gravimetric apparatus.

The water removing exit tube at 76 has been found to be advisable because there are conditions under which there may be a backflow due to a slight rarefaction within the apparatus, such that for a short period of time room air may be drawn in through the exit fitting 76 and thence into the U tube 74. Use of the exhaust desiccating bulb 76 prevents water from being absorbed in the U tube 74 under conditions where this reverse flow may take place.

Extensive use of the melted and burning iron bath apparatus and process, as above described, demonstrates that 100% recovery of hydrogen, both in the free and in the combined form, can be expected from a determination. Furthermore, the precision or sensitivity of the determination has been found to be controlled almost entirely by the sensitivity of the balance used for weighing the U tubes 74.

From the above description of a preferred embodiment of my invention it will be appreciated that changes may be made therein without departing either from the spirit or scope of the invention, and that therefore the scope of the invention is to be measured within the scope of the accompanying claims.

Having described my invention, what I claim as new and useful and desire to secure by Letters Patent of the United States is:

1. A hydrogen analyzer comprising a source of oxygen, passage forming means forming a gas passage connected to said source, said passage including in order from said source, means for removing water and traces of hydrogen from the oxygen flowing from said source,

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means providing a combustion chamber, a crucible in said combustion chamber having a charge of combustible metal therein, a means for reacting hydrogen with oxygen to produce water, a water measuring device, a water absorbing device connected to the outlet of said water measuring device, an induction heating coil disposed outside said combustion chamber and adapted to provide an induction heating field within said crucible to ignite the crucible charge to provide a pool of burning metal, means for heating said gas passage from said combustion chamber to said water measuring device to prevent water condensation therein, means forming a receptacle for a sample to be analyzed, means forming a gate connecting said receptacle to said combustion chamber for dumping said sample from said receptacle into said combustion chamber in a position such that said sample falls into said crucible and said gate being operable to dump said sample while said pool of metal is burning.

2. A hydrogen analyzer comprising a source of oxygen, passage forming means forming an oxygen passage connected to said source, said passage including in order from said source, means for removing water and hydrogen from an oxygen stream passing therethrough, means providing a combustion chamber, means for reacting hydrogen with oxygen to produce water, a removable gravimetric water absorbing device, an induction heating coil disposed outside said combustion chamber and adapted to provide an induction heating field within said combustion chamber, means for inserting a crucible charged with a quantity of combustible metal into said combustion chamber within said induction heating field to form a pool of burning metal, means for heating said passage forming means from said combustion chamber to said gravimetric water absorbing device to prevent water condensation therein, means forming a receptacle for a sample to be analyzed, said receptacle being adapted to dump the contents thereof into said crucible after said combustible metal has formed said burning pool.

3. A hydrogen analyzer comprising a source of oxygen, passage forming means forming an oxygen passage connected to said source, said passage including in order from said source, means for removing water, means for reacting traces of hydrogen with oxygen to produce water, a second water removing means, means providing a combustion chamber, a crucible in said combustion chamber containing a charge of a combustible metal, a second means for reacting hydrogen with oxygen to produce water, a removable gravimetric water absorbing device, a fourth removable water absorbing device connected to the outlet of said gravimetric water absorbing device, an induction heating coil disposed outside said combustion chamber and adapted to heat the combustible metal in said crucible to the ignition temperature to form a pool of burning metal, means for heating said passage forming means from said combustion chamber to said gravimetric water absorbing device to prevent water condensation therein, means forming a receptacle for a sample to be analyzed, means forming a gate connecting said receptacle to said combustion chamber for dumping said sample from said receptacle into said combustion chamber in a position such that said sample falls into said crucible and said gate being operable to dump said sample while said pool of metal is burning.

4. The method for determining the hydrogen content of analytical samples of metals and metal hydrides which comprises, providing an induction heated crucible within a closed combustion chamber, flowing oxygen from which water and hydrogen have been removed through said combustion chamber, heating a quantity of iron in the crucible to form a pool of melted and burning iron, dumping a sample to be analyzed into the pool of burning iron after all water vapor and hydrogen have been swept clear of the burning iron, collecting the water resulting from combustion of the sample in the burning iron pool, and calculating the hydrogen content of the sample on the

basis of the assumption that the hydrogen in the water collected represents 100% of the hydrogen originally in the sample.

5. The method for determining the hydrogen content of analytical samples of metals and metal hydrides which comprises, providing an induction heated crucible within a closed combustion chamber, flowing oxygen from which water and hydrogen have been removed through said combustion chamber, heating a quantity of a combustible metal in the crucible in the oxygen atmosphere to form a pool of melted and burning metal, sweeping all water vapor and hydrogen clear of the burning metal and subsequently while the metal in the pool is still burning, dumping a sample to be analyzed through an air lock into the combustion chamber in a position above the pool of burning metal so that said sample falls into the pool of burning metal, collecting the water resulting from combustion of the sample in the burning pool, and calculating the hydrogen content of the sample on the basis of the assumption that the hydrogen in the water collected represents 100% of the hydrogen originally in the sample.

6. The method of determining the hydrogen content of analytical samples of metals and metal hydrides which comprises providing in a closed combustion chamber a pool of burning metal from which water and hydrogen have been removed, passing oxygen from which water and hydrogen have been removed through the chamber to support combustion of the metal, dumping a sample to be analyzed into the pool of burning metal without opening the combustion chamber, collecting water resulting from combustion of the sample in the pool, and calculating the hydrogen content of the sample on the basis of the assumption that the hydrogen in the water

collected represents 100% of the hydrogen originally in the sample.

7. The method of determining the hydrogen content of analytical samples of metals and metal hydrides which comprises providing in a closed combustion chamber a pool of burning metal from which water and hydrogen have been removed, passing oxygen free of water and hydrogen through the chamber to support combustion of the metal, dumping a sample to be analyzed into the combustion chamber through an air lock in a position such that the sample falls into the pool of burning metal without opening the combustion chamber to the atmosphere, collecting water resulting from combustion of the sample in the metal pool, and calculating the hydrogen content of the sample on the basis of the assumption that the hydrogen in the water collected represents 100% of the hydrogen originally in the sample.

References Cited in the file of this patent

UNITED STATES PATENTS

1,515,237	Yensen	Nov. 11, 1924
2,332,943	Sobers	Oct. 26, 1943
2,686,211	Cargill	Aug. 10, 1954
2,754,178	Mack	July 10, 1956
2,809,100	Krasl	Oct. 8, 1957
2,836,482	Dreher	May 27, 1958

OTHER REFERENCES

- Brun et al.: "Anal. Chem.," 8, 315, 316 (1936).
 Natelson et al.: "Anal. Chem.," 10, 609-12 (1938).
 Renoll: "Anal. Chem.," 9, 566, 567 (1937).
 Booth et al.: "Analyst," 82, 50-51 (1957).