April 6, 1965 F. R. COE 3,176,500

MEASUREMENT OF GASES IN METALS

Filed April 20, 1961 2 Sheets-Sheet 1

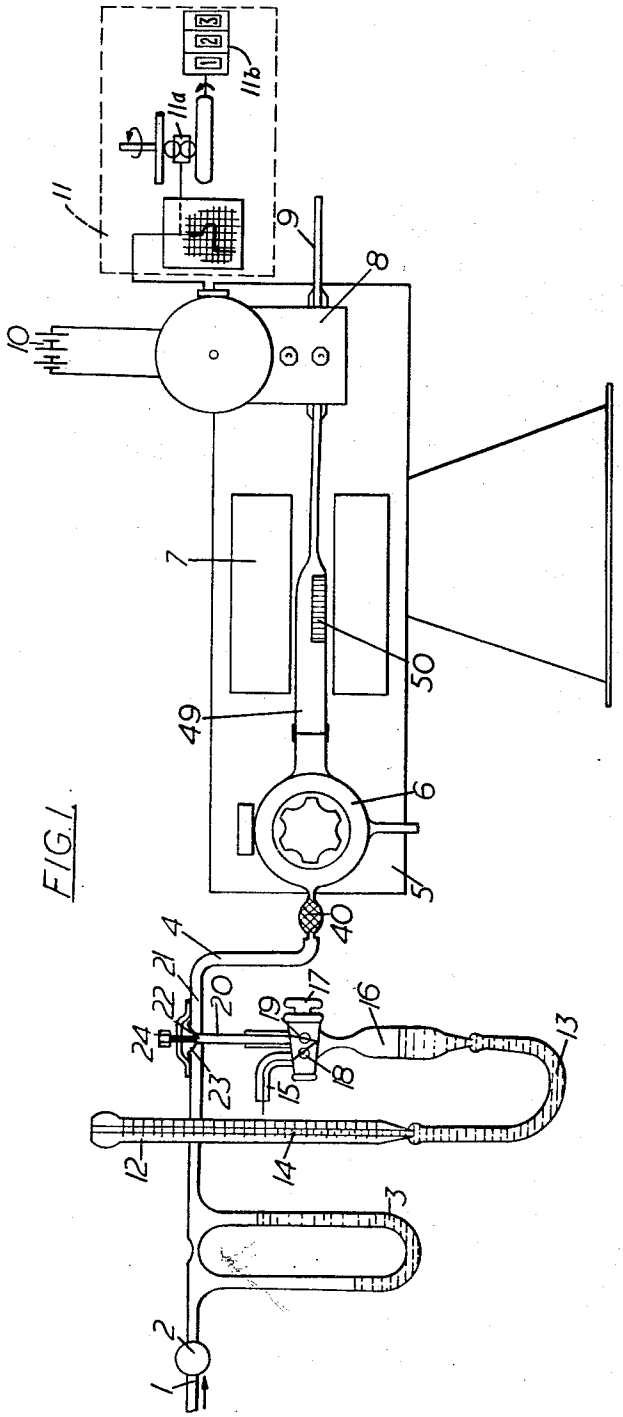


FIG. 1

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FIG. 2

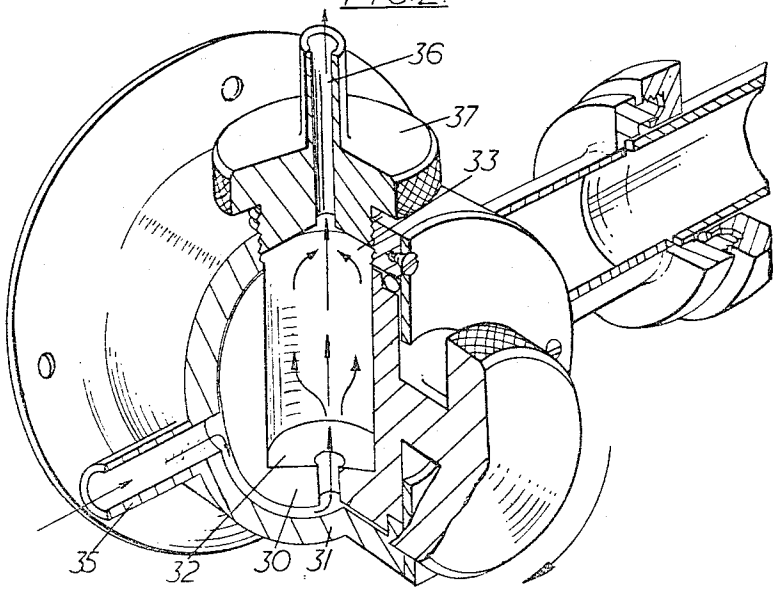
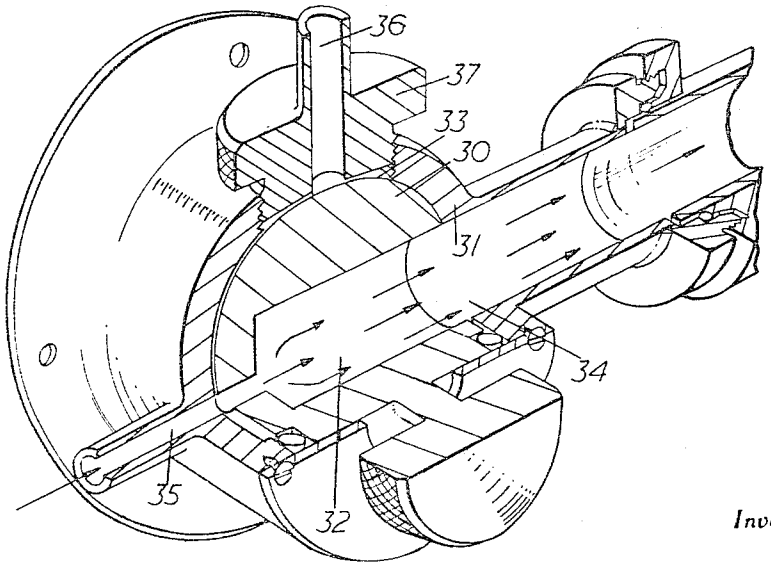


FIG. 3



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MEASUREMENT OF GASES IN METALS

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4 Claims. (Cl. 73—19)

This invention relates to improvements in apparatus for determining the amount of gas in a metal.

A usual method of determining the amount of hydrogen in steel, for example, comprises heating a sample of the steel to approximately 600–700° C. in a vacuum chamber and analysing the gas evolved in a low pressure system. The equipment used in this method is costly and skilled operators are required. Another method of measuring the hydrogen content of steel which has been suggested comprises providing a constantly recirculating stream of nitrogen in the chamber and noting the change in thermal conductivity produced by the mixing of the evolved hydrogen with the nitrogen. This system requires pumps for circulating the nitrogen and necessarily involves the use of a large volume of gas with the result that the final hydrogen concentration is too small to produce a great enough change in the thermal conductivity of the gas for the volume of the evolved hydrogen to be determined with accuracy. Another disadvantage of this last method is the time required for steady conditions to be attained and the fact that the time occupied by a determination is yet further increased because it is necessary to flush the whole apparatus with carrier gas before and after each determination. In a further known method the hydrogen evolved by the sample of steel at 650° C. is swept away by an inert carrier gas such as nitrogen, oxidised to water by a heated catalyst and determined by titration with Karl Fischer reagent. This method, however, does not enable accurate determinations to be made particularly when the volumes of hydrogen evolved are small, partly due to presence of moisture in the system from sources other than the oxidation of the hydrogen evolved by the steel and partly due to difficulty in determining the end point of the Karl Fischer titrations at these low levels.

According to the present invention, apparatus is provided comprising a loading device for introducing the specimen, accompanied by only a negligible amount of air, into an oven which is provided with means for heating the specimen to cause it to evolve its occluded gas; a carrier gas inlet for connection to a carrier gas source; means for guiding a moving stream of carrier gas from the inlet over the heated specimen; means for measuring the thermal conductivity of the mixture of carrier gas and evolved gas leaving the specimen and thus providing an indication of the amount of evolved gas in the mixture, and a gas outlet through which the mixture is released after passing the measuring means.

In the preferred form of the apparatus the loading device includes a loading chamber which is normally in communication with the oven but which can be cut off from the oven during loading to prevent air entering the oven. This device may be provided with a gas inlet and outlet through which carrier gas is passed after loading to flush the air out of the loading chamber and replace it with carrier gas before the loading chamber is again connected to the oven. The flushing of the loading chamber does not take long when compared with the flushing of the whole circulatory system previously described and the amount of occluded hydrogen lost during this process has been found to be negligible. A drying agent is also included in the apparatus to dry the stream of gas entering the sample loading device because variations in the moisture content of the gas mixture would tend to cause variations in thermal conductivity which would be indicated as variations in the amount of evolved gas.

A convenient method of measuring the thermal conductivity of the gas mixture is to pass it through a Katharometer cell which is a well known method of obtaining values of thermal conductivity to a high degree of accuracy. The amount of gas evolved may be evaluated by causing an output signal from the Katharometer cell to drive a digital counter, for example, which has previously been calibrated by the injection of known quantity of the gas under investigation into the carrier gas stream. When the gas evolved by the specimen has a comparatively high thermal conductivity (for example, hydrogen) and the carrier gas has a low conductivity (for example, argon which has the lowest conductivity of available inert gases) 5 gm. samples yielding only .05 ml. of hydrogen at N.T.P. at the 1 ml./100 gm. level may be used, and the estimated precision of the determination is ± .002 ml. of hydrogen at N.T.P. or ± .04 ml./100 gm. With a typical apparatus according to the invention a determination can be completed much more quickly than was possible using known methods and, moreover, little skill is required on the part of the operator and expensive, fragile vacuum apparatus or pumps are not required.

In order that the invention may be more easily understood, an apparatus embodying it will now be described, by way of example, with reference to the accompanying drawings in which:

FIGURE 1 is a diagrammatic representation of an apparatus embodying the invention; and

FIGURES 2 and 3 are enlarged views of a detail of FIGURE 1 in the positions occupied during the loading of the specimen and during the evaluation process, respectively.

Referring first to FIGURE 1, argon of a high degree of purity is supplied to the system through the inlet tube 1, a fine control needle valve 2, and a calibrated mercury U-tube flow-meter 3. A length of flexible neoprene tubing 4 then carries the gas past a small quantity of drying agent 40 to a pivoted board 5 on which is mounted a sample loading lock 6 (to be described later), a small furnace 7 operating at approximately 650° C. and the Katharometer cell-block 8. From the cell 8 the argon passes through a short length of narrow bore tubing 9 to waste.

A constant current is supplied to the cell 8 from the battery 10 and the output from a bridge circuit included in the cell-block is taken to a single point electronic recorder 11. The signal applied to the recorder 11 the magnitude of which is thus dependent on the thermal conductivity of the mixture of gases passing through the Katharometer cell operates as an automatic integrator 11*a* which is included in the recorder 11, and which operates a counter 11*b* which displays a number representative of the total amount of evolved gas present in the carrier gas stream. In one convenient form of integrator the signal from the Katharometer cell 8 is used to drive a roller so that the speed of rotation of the roller is directly proportional to the strength of the signal. The number of revolutions of the roller is then counted by a digital counter and the reading of the counter is displayed. The signal from the Katharometer cell is also used to describe a trace on a chart to provide a permanent record of the form of variation of the signal. If desired the area under the trace could be integrated using a planimeter after the test is completed and the chart removed from the apparatus.

In order to calibrate the system it is necessary to inject small volumes of hydrogen into the argon stream before the mixture enters the furnace and to correlate these with readings from the recorder. For this purpose a small hydrogen burette **12** is included in the apparatus. An inlet tube **15** is provided for introducing hydrogen under pressure into an enclosed space **16** above one arm of a U-shaped column of mercury **13** the other arm of which is contained in a graduate tube **14**. The first arm is provided with a tap **17** with two channels **18** and **19** the first of which enables the hydrogen to be introduced from the inlet tube **15** into the reservoir **16** above the mercury and the second of which connects the hydrogen reservoir **16** to a stainless steel outlet tube **20**. This outlet tube **20** opens into a copper tube **21** which is a continuation of the inlet tube **1** through which the argon carrier gas is introduced into the apparatus. The opening **22** of the stainless steel tube **20** is controlled by a neoprene pad **23** acted on by a closing screw **24**. When the burette tap **17** is opened and the outlet tube **20** is connected with the reservoir **16**, controllable amounts of hydrogen can be injected into the argon stream by opening the stainless steel tube **20** at **22** by releasing the screw **24**. The volume of hydrogen introduced can be calculated at N.T.P. from the change in height of the column of mercury in the graduated arm **14** of the burette.

Readings registered by the counter when a series of known volumes of hydrogen are injected into the argon stream are noted and plotted against the hydrogen volumes to obtain a calibration curve for the apparatus. The temperature of the furnace appears to have no effect on the response of the Katharometer cell **8** or the calibration curve. Variation of the flow-rate of the carrier gas does not affect the zero stability of the detector but resolution of the apparatus becomes greater at higher flow rates. This is evidenced by an increase in the resolution of the peaks traced on a chart by the recording pen when hydrogen is mixed with the carrier gas passing the Katharometer cell **8** and results in smaller peak areas, a steeper gradient to the calibration curve and a consequent loss of sensitivity (when expressed at ml./cm.^{2}). An increase of chart speed counteracts this lose to some extent but it is clearly desirable to maintain a constant carrier gas flow-rate and chart speed.

Traces of air accidentally admitted to the system would produce peaks very similar to those due to hydrogen and therefore in the preferred form of the apparatus special loading means (shown in greater detail in FIGURES 2 and 3) are included to prevent air entering. The loading lock **6** consists of a cylindrical brass block **30** free to rotate through 90° inside a closely fitting hollow brass cylinder **31**. The centre block **30** is drilled to form a bore **32** to accommodate the sample **50**. A stoppered loading port **33**, a connection to the furnace **34** and gas inlet port **35** are provided on the outer cylinder and a gas outlet port **36** is provided through the centre of the stopper **37** which closes the the loading port **33**. The sample **50** is loaded when the bore **32** in the block **30** is open to the loading port **33** as shown in FIGURE 2, the stopper **37** is replaced, and the argon flows in through the gas inlet **35** and sweeps any entrained air away to waste through the outlet **36** in the center of the stopper as indicated by the arrows in FIGURE 2, the connection **34** to the furnace being closed by the brass cylinder block in this position. The brass cylinder block **30** containing the sample is then rotated through 90° to the position shown in FIGURE 3 when the bore **32** then faces the tube **34** to the furnace so that the sample **50** is free to slide along the silica tube **49** into the furnace **7** when the board **5** is tilted in a clockwise direction, as seen in FIGURE 1. This rotation of the cylinder block **30** also places the carrier gas inlet **35** in communication with the furnace connection **34**. The whole operation occupies about 30 seconds, and no "air wave" appears on the recorder, nor

is the zero of the recorder affected. For unloading, the operations are repeated in reverse and when not in use the cylindrical centre block **30** is kept in the position shown in FIGURE 3.

A drying train including anhydrone (magnesium perchlorate) for example, is inserted into the gas flow path at **40** before the sample loading device **6** because the use of the flexible neoprene tubing **14** to allow the board **5** to be tilted permits traces of moisture to diffuse through into the carrier gas stream which would break down and pass on hydrogen to the Katharometer cell if it were allowed to come into contact with the hot steel sample.

Although the apparatus described is designed to measure the amount of hydrogen evolved when a steel specimen is heated, analysis of the evolved gas may be necessary in which case a molecular sieve column could be inserted into the apparatus to separate the components prior to their analysis with the Katharometer cell **8**. The thermal conductivities of other gases which might be encountered are all approximately one-tenth of that of hydrogen.

I claim:

1. Apparatus for use with a thermal conductivity measuring device in determining the amount of occluded gas in a metal specimen comprising: a heating chamber and means for heating a specimen in the heating chamber to cause the specimen to evolve its occluded gas; outlet passage means adapted to connect said heating chamber to a device for measuring the thermal conductivity of a gas; loading means and a passage connecting said loading means with said heating chamber, said loading means comprising a housing and a body which is rotatable within said housing between a loading position and a discharge position and which includes a loading chamber, said housing having a first aperture for the introduction of a specimen into said loading chamber in the loading position of said body and a second aperture connected through said passage to said heating chamber for the discharge of said specimen into said passage after the rotation of said body into its discharge position, said loading chamber being isolated from said outlet passage means when said body is in said loading position and isolated from the atmosphere when said body is in said discharge position; said apparatus further comprising means for moving said loading chamber and said passage in a first sense to permit said specimen to slide under gravity from said body when in its discharge position to said heating chamber and in a second sense to return said specimen to said chamber for removal when the determination has been carried out; means for supplying a stream of carrier gas to said loading chamber whereby when said body is in said loading position carrier gas is flushed through said loading chamber and when said body is in said discharge position the carrier gas is guided over the heated specimen, and then, carrying occluded gas, is guided through said outlet passage means.

2. Apparatus according to claim 1 in which said housing is provided with a removable stopper having a passage therethrough, the stopper partially closing said first aperture in said housing after introduction of the specimen into said loading chamber, and said passage therethrough constituting a discharge path to atmosphere for gas flushed through said loading chamber when said body is in said loading position.

3. Apparatus according to claim 1, including calibration means for introducing measured quantities of gas into the carrier gas stream, comprising an injection tube extending into the carrier stream upstream of said outlet passage means; means for normally sealing the injection tube from the carrier gas stream; a reservoir of calibration gas; means for replenishing said reservoir; means for selectively connecting said reservoir of calibration gas to said injection tube and to said replenishing means; means for measuring the volume of gas in said reservoir, and means for unsealing said injection tube when said res-

ervoir is connected to said injection tube and calibration is required, so that calibration gas is admitted into the stream of carrier gas, and for resealing said injection tube when a predetermined volume of calibration gas has been admitted into the carrier gas stream.

4. Apparatus for use with a thermal conductivity measuring device in determining the amount of occluded gas in a metal specimen comprising: a heating chamber and means for heating a specimen in the heating chamber to cause the specimen to evolve its occluded gas; outlet passage means adapted to connect said heating chamber to a device for measuring the thermal conductivity of a gas; loading means, and a passage connecting said loading means with said heating chamber, said loading means comprising a housing and a body which is rotatable within said housing between a loading position and a discharge position and which includes a loading chamber, said housing having a first aperture for the introduction of a specimen into said loading chamber in the loading position of said body and a second aperture connected through said passage to said heating chamber for the discharge of said specimen into said passage after the rotation of said body into its discharge position, said loading chamber being isolated from said outlet passage means when said body is in said loading position and isolated from the atmosphere when said body is in said discharge position; said apparatus further comprising movable means for selectively positioning said loading chamber, said passage and said heating chamber at different vertical levels relative to each other so as selectively to cause said specimen to move from said loading chamber to said heating chamber

or from said heating chamber to said loading chamber; means for supplying a stream of carrier gas to said loading chamber whereby when said body is in said loading position carrier gas is flushed through said loading chamber and when said body is in said discharge position the carrier gas is guided over the heated specimen, and then, carrying occluded gas, is guided through said outlet passage means.

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