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Automatic Micro-Analytical Apparatus for Gases in Metals*

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Abstract

This study relates to mechanisms of automatic micro-analysis for gases in metals by the vacuum fusion method. Determination of extracted gases is automatically performed by recording the changes of pressure of gases gathered in a constant volume by a diffusion pump (heating current is constant) after eliminating each gas from others. We thought out a rotary McLeod gauge, which has stretched resistance-platinum string in its capillary so as to enable us to measure electrically and to record automatically the pressures of gases as an electric current in the course of analysis. The rotary McLeod gauge is automatically rotated. The automatic selection of paths of gases, where the reactions of eliminating gases take place, are controlled with solenoid mercury cuts by time-switches on a rotary drum. The time necessary to determining O_2 and N_2 in a metal sample is less than 30 minutes including the time of extracting gases.

I. Introduction

It is well known that even a small amount of gas has remarkable inflences on mechanical as well as electric properties of metals. As the method for analysing the gases, the vacuum fusion process is generally used. Oxygen in metal is extracted as the forms of CO and CO_2 from the heated graphite crucible. The determination of the extracted gases is performed by the vacuometric method which is to measure the content of gases such as CO_2, CO, H_2 and N_2 respectively by observing the changes of pressure in a constant volume after eliminating each constituent. In order to make this apparatus work automatically, we devised a rotary McLeod manometer so as to enable us to record the pressure of gas in the process of analysis. Each step of reaction of eliminating gas from others is automatically controlled by selecting paths of gases with magnetic solenoid mercury cuts conducted with time-switches on a rotary drum. Another characteristic of this apparatus is the small energy of the high frequency oscillater.

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II, Apparatus

This apparatus consists of high frequency furnace, magnetic solenoid mercury cuts and recording manometer.

1) High frequency furnace

Size of oscillator with transformer : 60×50×95cm
Oscillting tube : TC1513 (equal to 450CL of U. S. A.)
Rectifying tube ; 4H72 (equal to 872A of U. S. A.) two tubes.
Frequency : 20 MC
Source : 100V (or 200V)
Input of anode of oscillating tube ; 1.65KW
Output of anode of oscillating tube : Ca. 1KW
Anode voltage : 3KV
Diameter of pipe coil : 4mm
Height of the coil : 30mm
Inside diameter of the coil : 51mm
Highest temperature : 1950°C (In case of using two oscillating tubes, total energy of anode input becomes 3.3KW and highest temperature is 2300°C.)

Graphite crucible : 10mmϕ×40mm (inside), 14mmϕ×43mm (outside), boiled in 6N-HCl for 3 days and washed. Ten crucibles are treated at one time in a flask with cooler above the flask.

Graphite powder : 200 mesh (thicknss of layer 7mm)

Graphite cylinder for heat shield; 28mmϕ×50mm (inside) 32mmϕ×53mm (outside) with vertical slits (6 direcsions, width of the slit 1mm). Graphite cylinder is hanged with molybdnum wires in a quarz tube (outside diameter 50mm).

The gases evolved from the sample melt in the graphite crucible by the high frequency induction heating are extracted and carried by the mercury diffusion pump.

2) Automatic selection of paths of gases.

In order to establish automatic selection of paths of gases, thirteen automatic cuts[1)2)] (detail construction Fig. 2) are set in the apparatus. Each solenoid has 3200 turns of wire of 0.2mm diameter. The current transmitted in the solenoid is about 0.5 amperes. Too much current such as more than 1 ampere made the solenoid warm and broke the glass. And the current of 0.5 amperes is not enough to rise the cap in mercury cut, so we put an O. P. magnet ring (Oxide powder permanent magnet) on the solenoid to help the lifting power of the solenoid. Dimension of the O. P. magnet is indicated in Fig. 2, and the value of (B·H)max. of this magnet is 1.3·2.0×10^6 Gaus·Örsted.

1) Farkas A., Melville H. W.: Experimental Methods in Gas Reaction (1939) p. 62
2) Horton W. S., Brady J.: Anal. Chem. 25, 1891 (1953)

When current is transmitted, this mercury cut is open. When current is stop-

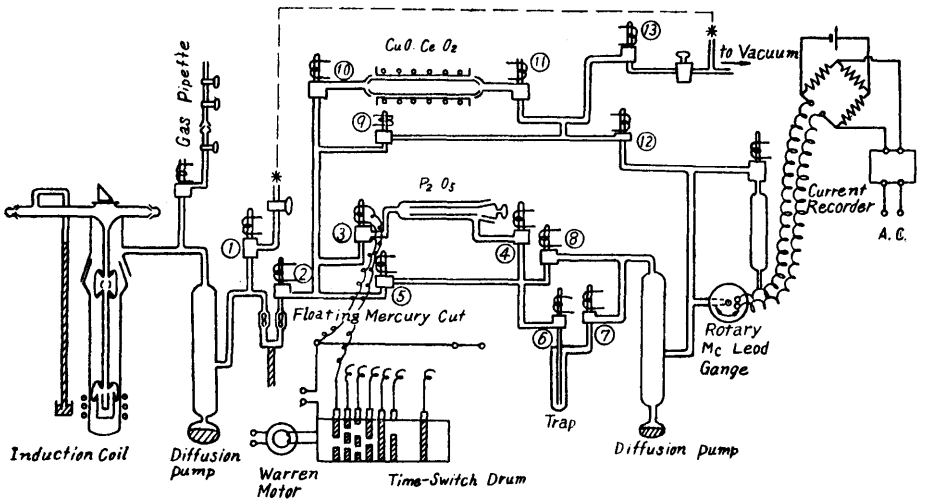

Fig. 1 Schematic Diagram of Automatic Micro-Analytical Apparatus for Gases in Metals.

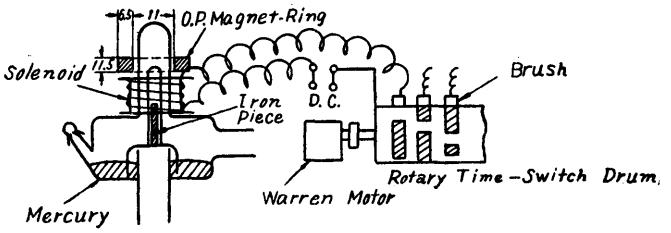

Fig. 2 Automatic Solenoid Mercury Cut.

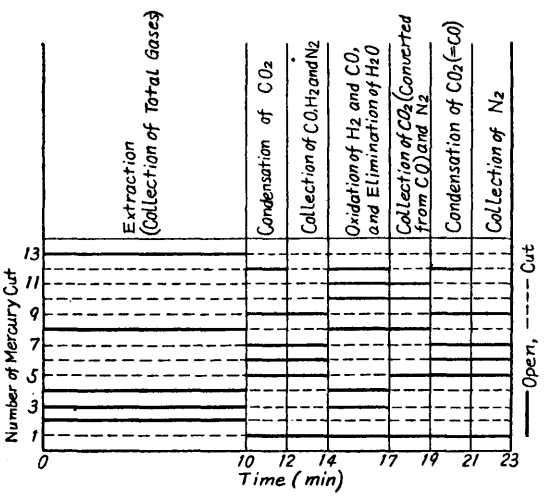

Fig. 3 Worknig Diagram of Autmatic Mercury Cut

ped, this cut is shut. Opening and shutting of these mercury cuts are controlled by the time-switches which are constructed with brushes and locally cop-per-covered rotary drum. This drum is rotated by a small Syn-chronous motor used for elec-tric clock. The drum is design-ed with copper plates so as to controll the course of analysis such as extracting gases, con-densation of CO_2, oxidation and elimination of H_2 and CO.

The working diagram of the automatic mercury cuts are illustrated in Fig. 3.

3) Recording manometer

Among many sensitive manometers, only McLeod, diaphragm manometer and Knudsen gauge do not vary with the kinds of gas. We improved a rotary McLeod gauge [3] so as to be able to record the pressures. It has a stretched resistance-platinum string in its capillary and pressure is obtaied by measuring difference

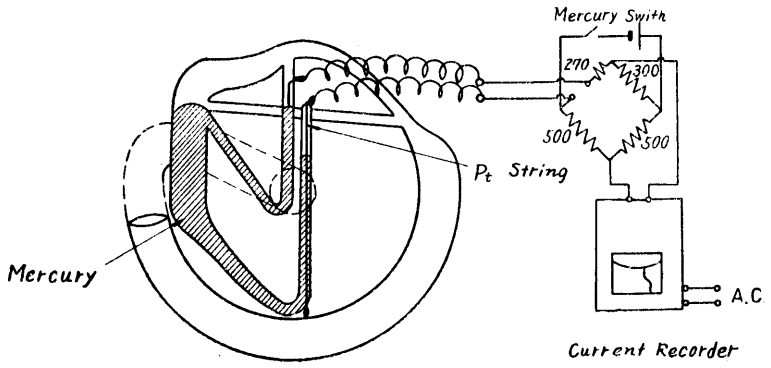

Fig. 4 Resistance-Type Recordiug Rotary Mc Leod Gauge

of mercury height i. e. the resistance of platinum string (Fig. 4). This resistance is led to the Wheat-Stone bridge, and recorded by a commercial microrecorder as a microcurrent. The full resistance of the platinum string is 30.00 ohm. and the resistances of the bridge are shown in Fig. 4.

The relation between pressure and resistance of McLeod gauge is obtained as Fig. 5. The rotary McLeod gauge is revolved by a small commutator motor which is controlled by the rotation controller. The rotary controller consists of two parts, the direction selecter and the electric brake switches, and regulator the circular motion of the rotary McLeod gauge.

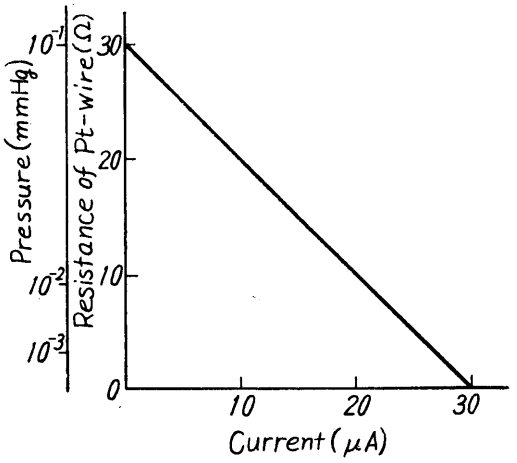

Fig. 5 Relation between Pressure and Current of the Recorder

The McLeod gauge is revolved to right and left periodically (every 5 seconds) and stop for a while (Ca. 5 seconds, for the purpose of keeping time for the delay of needle pointing of the recorder) in the recording state. So the direction and the time of rotation of the McLeod gauge are governed by a relay, the direction selector, which is made up of copper brushes and copper rails winding upon the surface

3) Axelbank M.: Rev. Sci. Instr. **21**, 511 (1950)

of the cylinder. For the purpose, the cylinder of the relay is connected with a warren motor which is used for electric clock.

Although the signals from the direction selector are pretty correct, they are not sufficient to control the McLeod gauge as to stop always at the exactly same situation because of the repeated additions of small differences causing by inertia and friction of the revolving system. For the sake of avoiding this error, the authors have attempted to set up the electric brake switches which work by self-switching of the McLeod gauge. The circuit diagrams of these schemes are illustrated in Fig. 6. A, B, C and D are the brushes. When the McLeod rotates (direction **AC**) to the point p, the brake switches contact on S_2 and T_2 respectively and then McLeod begins to rotate to the direction **BD**. As soon as this rotation (direction **BD**) begins, the contacts on S_2 and T_2 are separated by a spring near the point Q, and when the rotation comes to the point Q, the brake switch contacts on R_1 and then the rotation begins to the direction **AC**.

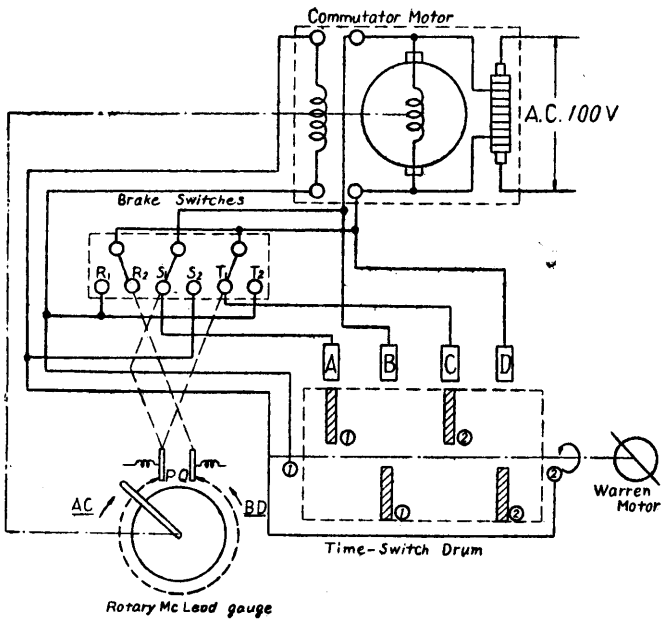

Fig. 6 Schematic Circuit Diagram of Rotation Controller of McLeod gauge.

It is also designed that only when the McLeod stands vertically and the platinum string is put into the circuit of the bridge by the contact of mercury in the McLeod, the current is transmitted from the cell into the bridge circuit by another mercury switch, which is connected at the same axis of the rotation of the McLeod.

III. Analysis of Gases

1) Preparation

As written in the item of furnace, owing to the washing graphite cruibles in boiled hydrochloric acid solution and distilled water we could start the analysis at the blank value of extracted gases of 0.004cc/hr.

Samples are small cylinders and their weight is about 0.3g each. Their surfaces are polished and washed with benzene and alcohol and put in the apparatus.

2) Analysis

The samples are dropped into the heated crucible one by one, by a magnet.

As is written above, thirteen mercury cuts are automatically controlled by the time switches on the drum and the time for extracting gases from a sample is designed to be 10 minutes. But we can change the time for extracting gases according to the kind of sample.

Oxygen in metal reacts with carbon in iron melt and produces CO and CO_2 gases.

Nitrogen combined as nitrides in metal sample as isolated as N_2 gas.

Hydrogen occluded in metal is isolated as H_2 gas by heating and extracting. In case of steel sample, however, as the size of sample analysed by this apparatus is rather small, there remains very little hydrogen, owing to the spontaneous out-diffusion of hydrogen from the specimen. Therefore the analysed value of hydrogen cannot represent the true value of hydrogen content. Becanse the out-diffusing velocity of hydrogen from a steel cylinder is in inverse ratio to the square of the diameter of the specimen.

The above reactions are discussed in detail by Sloman [4].

The Total gases are extracted by a diffusion pump and gathered in a constant volume (354 cc) by another diffusion pump (heating current is 2.5 amperes constant) and total amount of gases extracted is recorded in the course of gathering gases.

Then the mercury cuts are opened and gases are circulated (for 2 min.) and meanwhile CO_2 gas is condensed into the trap by liquid air and after shutting the merury cut above the McLeod, other gases (CO, H_2, N_2) are gathered (for 2 min.) and recorded.

Then the gases are circulated via the oxidizing tube which contains $CuO-CeO_2$ regent. Preparation of $CuO-CeO_2$ is performed as written by Walter [5]. For the temperature for oxidizing CO and H_2, we preferred 500°C †. At this temperature we could oxidize these gases in three minutes during the circulation of the gases. Meantime the produced water vapor is catched by P_2O_5 tube and hydrogen is determined by the difference of the pressures in the same volume. Adding a trap, cooled by dryice, at the neibour of the P_2O_5 tube, we could obtain more accurate results. Instead of these, however, use of magnesium perchlorate will be best, we think.

Then the remaining gases (CO_2 converted from CO, and O_2) are gathered (for 2 min.) and recorded. The gases are again circulated via the trap of liquid air and CO_2 are eliminated (for 2 min.). At last the remained gas, considered to be

4) Slaman H. A., Harvey C.A., J. Inst. Metals 71, 391 (1945)

5) Walter D. J.: Anal. Chem. 22, 297 (1950)

† Oxygen vapour pressure of CuO is not so high at 500°, and the reaction velocity of oxidation is very quick. So three minutes is enough for oxidizing CO and H_2.

nitrogen, is gathered and recorded (for 2 min.). CO and N_2 is determined as such. And oxygen in metal sample is determined by the summation of amounts of CO_2 and CO $\times \frac{1}{2}$.

The time for extracting gases is 10 minutes and the time for analysing all constituents is 13 minutes. So total time for one sample is 23 minutes.

In case of gaseous sample, we shall be able to analyse four constituents in it within 15 minuses by this apparatus.

3) Results

Gases in a Ni—Cr—steel sample (C 0.29, Si 0.25, Mn 0.42, P 0.018, S 0.011, Cr 0.81, Ni 2.75% respectiuelp) is analysed and the results are as follows

No. of Sample	O_2 wt%	N_2 wt%	Temqerature of Analysis, °C
1	0.00443	0.00312	1600
2	0.00414	0.00433	1600
3	0.00428	0.00417	1600
4	0.00415	0.00321	1600
5	0.00412	0.00527	1650
Mean	0.00422	0.00402	
Mean value by the 19th subcommittee for special steel in Japan	0.0043	0.0043	1500—1900

IV. Conclusion

The authors succeeded to assemble an apparatus available for analysing gases in metals. By this device the results are recorded automatically through out the whole process of analysis, reducing all the troubles and errors which might be introduced when managed with hands.

Further we are now planning to set a diaphragm micro-manometer instead of the rotary McLeod gauge. We think this diaphragm manometer is simpler in mechanism than the rotary McLeod manometer.

Acknowoledgement

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