

# Determination of Oxygen in Cast Iron\*

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## Synopsis

Recently, the determination of oxygen in cast iron has been required and it is important to determine not only the total amount of oxygen but also the oxygen in each oxide. The non-metallic inclusion method is usually used for determining each oxide in cast iron, which, however, is tedious and not reliable. Hence, the fractional vacuum fusion method was studied, and it was found that by using a tin-bath, FeO could be extracted at 1050°C, MnO at 1150°C, SiO<sub>2</sub> at 1450°C and Al<sub>2</sub>O<sub>3</sub> at 1750°C by this simple method. For comparison, samples of the same cast iron were also analyzed by the hot nitric acid method, the chlorine method and the electrolytic method, and satisfactory results were obtained by the fractional vacuum fusion method in comparison with the case of the non-metallic inclusion method.

## I. Introduction

The quantitative determination of oxygen in cast iron has recently been required in order to improve the quality of steel. As the research on this matter such as strong cast iron proceeds, it is necessary to determine not only the whole quantity of oxygen, but also the individual quantity of oxygen in oxidized substances.

In the present author's laboratory, the so-called non-metallic inclusion methods such as chlorine method, electrolytic method and hot nitric acid method etc. have been developed and put into use to determine the individual quantity of the oxidized substances, although much trouble and time are required for these methods and reliable results are hardly obtained in the case of cast iron as compared with ordinary steel. Therefore, the present authors have turned their attention to the fractional vacuum fusion method<sup>(1)</sup> which has not yet been verified in Japan. Compared this method with the non-metallic inclusion method, the former has been found more preferable than the latter, especially in the sense that satisfactory results could be obtained without requiring much time.

## II. Experimental results

### 1. Apparatus

The apparatus was the same as that used for gas analysis in metals,<sup>(2)</sup> the

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\* The 939th report of the Research Institute for Iron, Steel and Other Metals. Published in Japanese in the Journal of the Iron and Steel Institute of Japan, **42** (1957), 49.

(1) L. Reeve, A. I. M. E., **113** (1934), 90.

J. G. Thompson, H. C. Vacher and H. A. Bright, A. I. M. E., **125** (1937), 258.

T. Swinden, W. W. Stevenson and G. E. Speight, I. & S. I., Sp. Rep., **25** (1939), 65.

(2) H. Gotô and S. Suzuki, J. of the Japan Institute of Metals, **19** (1955), 89.; Sci. Rep. RITU, **A8** (1956), 25.

schematic diagram of which is shown in Fig. 1. A high frequency induction furnace of vacuum bulb system (frequency is 800 KC and out put power is 5 KW) was used for heating source, and the vacuum furnace was made of transparent quartz tube of 70 mm in diameter. A graphite cylinder was hung down with molybdenum wire of 1 mm in diameter from the transparent quartz funnel in

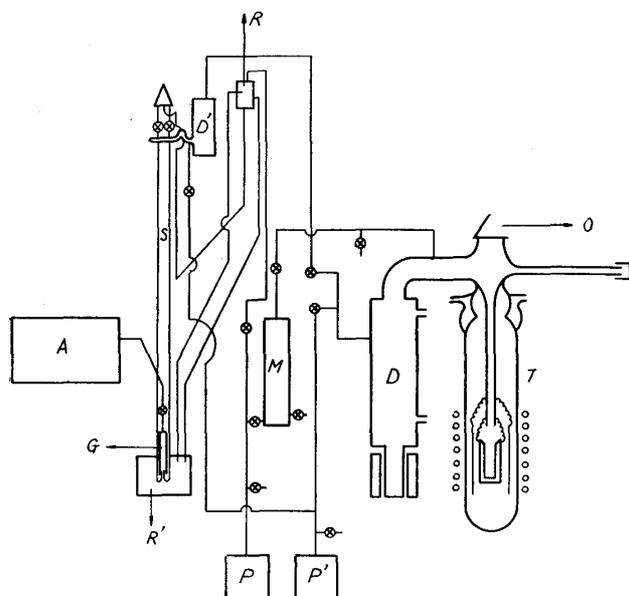


Fig. 1. Schematic diagram of gas analysis apparatus.

- T. Reaction tube
- D. Four stage mercury diffusion pump
- D'. Two stage mercury diffusion pump
- S. Mercury dropping pump
- A. Orsat type micro-gas analysis apparatus
- M. Mc'leod guage
- O. Optical pyrometer
- P, P'. Rotary pump
- G. Gas volume
- R, R'. Mercury reservoir

ed by a mercury dropping pump under atmospheric pressure. Just in front of the mercury dropping pump was placed a two-stage mercury diffusion pump so as to decrease a dead space. The gas collected under normal pressure was determined with usual Orsat type micro-gas analyzing apparatus.

## 2. Analytical procedure

According to L. Reeve's<sup>(1)</sup> work, FeO could be completely reduced at 1050°C and the reduction of MnO was readily carried out at temperature 1050~1150°C. On the other hand, to reduce SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> needed respectively 1300°C and 1570°C or higher temperature. So, after temperature was raised high sufficiently to withdraw all the gas in the graphite crucible as in the ordinary vacuum fusion method, the temperature was fallen below 1000°C and about 20~30 grams of metallic tin was thrown in. The temperature was then gradually raised up to 1750°C and the blank value should be kept at this temperature below 0.1 ml for 30 minutes. In the next step, it was kept at 1050°C and cast iron sample was thrown into melt.

the tube, inside of which was placed a graphite crucible. Fine quality graphite containing less than 0.1 per cent ash was used. Molybdenum plate was hung down outside the graphite cylinder as a heat shielding plate. The same plate was also put on the upper part of the crucible. The vacuum furnace was efficiently air-cooled from outside by a blower. The furnace was connected directly with a four-stage mercury diffusion pump through a glass tube of 50 mm in diameter to quicken the extraction of gas. This is supposed to have a good effect on preventing the gas adsorbing action of tin which volatilizes on the wall of the reaction tube during the analysis. The gas extracted out by the mercury diffusion pump was then collect-

This was done to reduce and extract FeO. In the same way, MnO was extracted at 1150°C, SiO<sub>2</sub> at 1400°C, and finally Al<sub>2</sub>O<sub>3</sub> at 1750°C. The amount of oxygen was determined quantitatively in each case.

### 3. Analytical results and the comparison with non-metallic inclusion method

The results of the analysis of the same sample by several methods such as

Table 1. Kamaishi pig iron A.

C 2.55 %, Si 2.05 %, Mn 0.46 %, Ti 0.22 %, P 0.150 %

Oxide	Fractional vacuum fusion method (%)		Electrolytic method (%)		Chlorination method (%)	
	FeO	0.008	0.009	0.014	0.025	0.028
MnO	0.005	0.004	0.001	0.001	0.004	0.005
SiO <sub>2</sub>	0.008	0.007	0.009	0.009	0.006	0.010
Al <sub>2</sub> O <sub>3</sub>	0.013	0.014	0.008	0.006	0.008	0.009
Total oxygen	0.013	0.013	0.012	0.014	0.014	0.018

Table 2. Muroran pig iron A.

C 2.67 %, Si 1.70 %, Mn 0.52 %, Ti 0.29 %, P 0.162 %

Oxide	Fractional vacuum fusion method (%)		Electrolytic method (%)		Chlorination method (%)	
	FeO	0.012	0.008	0.008	0.012	0.025
MnO	0.003	0.008	0.001	0.001	0.005	0.002
SiO <sub>2</sub>	0.008	0.008	0.007	0.007	0.010	0.008
Al <sub>2</sub> O <sub>3</sub>	0.013	0.012	0.006	0.007	0.010	0.012
Total oxygen	0.013	0.014	0.009	0.010	0.017	0.014

Table 3. Muroran pig iron C.

C 2.31 %, Si 1.83 %, Mn 0.53 %, Ti 0.29 %, P 0.171 %

Oxide	Fractional vacuum fusion method (%)		Electrolytic method (%)		Chlorination method (%)	
	FeO	0.006	0.007	0.006	0.008	0.027
MnO	0.010	0.008	0.006	0.008	0.003	0.004
SiO <sub>2</sub>	0.009	0.009	0.006	0.008	0.010	0.008
Al <sub>2</sub> O <sub>3</sub>	0.006	0.006	0.006	0.007	0.004	0.004
Total oxygen	0.010	0.011	0.008	0.009	0.013	0.014

Table 4. Synthetic iron.

C 3.25 %, Si 1.44 %, Mn 0.31 %, P 0.012 %, S 0.016 %

Oxide	Fractional vacuum fusion method (%)		Electrolytic method (%)		Chlorination method (%)		Hot nitric acid method (%)	
	FeO	0.037	0.031	0.037	0.044	0.052	0.036	0.001
MnO	0.016	0.033	0.0002	0.0005	0.005	0.009	0.0002	0.0003
SiO <sub>2</sub>	0.010	0.010	0.009	0.008	0.007	0.008	0.008	0.010
Al <sub>2</sub> O <sub>3</sub>	0.023	0.022	0.023	0.027	0.027	0.024	0.008	0.023
Total oxygen	0.028	0.030	0.024	0.027	0.029	0.026	0.008	0.017

Table 5 Synthetic iron.

C 3.25 %, Si 1.44 %, Mn 0.31 %, P 0.012 %, S 0.012 %

Oxide	Fractional vacuum fusion method (%)	Electrolytic method (%)		Chlorination method (%)	Hot nitric acid method (%)	
FeO	0.0016	0.0019	0.0015	0.0083	0.0014	0.0010
MnO	0.0007	0.0005	0.0006	0.0006	0.00003	0.00002
SiO <sub>2</sub>	0.0018	0.0036	0.0034	0.0037	0.0039	0.0032
Al <sub>2</sub> O <sub>3</sub>	0.0021	0.0012	0.0013	0.0021	0.0010	0.0007
Total oxygen	0.0026	0.0030	0.0029	0.0053	0.0029	0.0024

chlorine method, hot nitric acid method, electrolytic method and fractional vacuum fusion method are shown in Tables 1~5. It was believed that chlorine method was not suitable for the analysis of FeO and MnO when pig iron was used, because high values were unusually obtained. However, a new method was proposed, in which after the sample was chlorinated the residue was washed thoroughly with 5 per cent ammonium citrate solution until no reaction of iron was observed, then it was treated with 100 ml of 5 per cent sodium carbonate solution at 80°C and finally washed again with 5 per cent ammonium citrate solution and warm water. Next, this residue was boiled in 30 ml of concentrated hydrochloric acid for 10 minutes and the same amount of water was added to it. After the solution was boiled for 20 minutes it was filtered off. The amounts of FeO and MnO were calculated from these of iron and manganese in the filtrate. SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were obtained from the total amount of silicon and aluminium in the residue and filtrate. By using this method, high values usually obtained by some other methods could be avoided. The results of chlorine method shown in tables were obtained by the above methods.

Considering from the result shown above, the electrolytic method would give a low value for MnO as previously mentioned, and in some pig iron samples chlorine method would give a high value for FeO even by the above-mentioned procedure. Although there are still much to be studied, an almost satisfactory value of MnO may be obtained by this method. A correction for the value of FeO by the amount of its phosphate was not made when the electrolytic method was used, because there were some doubts about its composition, and the value for phosphorus in the electrolytic residue was found too small.

As the Kamaishi cast iron and the Muroran cast iron A and C contained titanium, it was presumed that TiO<sub>2</sub> naturally existed. However, TiO<sub>2</sub> could not be determined by using chlorine and electrolytic method, since TiO<sub>2</sub> was decomposed by the graphite in chlorine method and almost all of titanium was determined by the hydrolysis of titanium in electrolytic method. Another attempt to extract fractionally TiO<sub>2</sub> at 1350~1550°C using fractional vacuum fusion method was tried but in vain. Therefore, as seen in the table, the amount of TiO<sub>2</sub> was not determined at all in the case of chlorine and electrolytic method. The actual whole quantity of oxygen must be much higher, and in the case of fractional vacuum

fusion method it was presumed that the value of  $\text{Al}_2\text{O}_3$  included that of  $\text{TiO}_2$ . So, if the sample was exactly the same, it would be likely that the value of  $\text{TiO}_2$  should be obtained from the difference in the values of  $\text{Al}_2\text{O}_3$  obtained by the two methods. But actually it might not be used because of some undesirable factors such as segregations of the oxide in the sample. The most important question in the fractional vacuum fusion method lies in that tin vaporizes and condenses on the wall of reaction tube and adsorbs the extracting gas. However, this phenomenon was not observed so much in the present experiment, because the total amount of oxygen in the same sample as that determined at  $1800^\circ\text{C}$  without tin-bath was almost the same as that in the case of fractional vacuum fusion method.

#### 4. Time required for analysis

This method usually required 30~60 minutes for the reduction and extraction of FeO and MnO, and 30~45 minutes for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . So, the total extraction time would be 2~3.5 hours. It was found that much more time was needed for this method as compared with that required for the whole amount of oxygen. However, for the quantitative determination of each oxide, this method is considered better in the point of time required and in the reliability than some previous methods. But there is some room for studying the quality of tin used in this case, since it takes much time for the extraction of gas contained in tin metal.

### Summary

- (1) The fractional vacuum fusion method for the determination of oxygen in cast iron was studied by the use of tin-bath.
- (2) It was found that FeO could be extracted at  $1050^\circ\text{C}$ , MnO at  $1150^\circ\text{C}$ ,  $\text{SiO}_2$  at  $1450^\circ\text{C}$  and  $\text{Al}_2\text{O}_3$  at  $1750^\circ\text{C}$  by this simple method, but  $\text{TiO}_2$  could not be extracted separably.
- (3) The chlorine method was developed for the determination of pig iron and the same cast iron samples were analyzed by the fractional vacuum fusion method, the hot nitric acid method, the proposed chlorine method and the electrolytic method.
- (4) Satisfactory results were obtained both by the fractional vacuum fusion method and by the proposed chlorine method in comparison with the case of the usual non-metallic inclusion method.

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