

## Studies on Gas Analysis in Metallic Titanium

著者	GOTO Hidehiro, SUZUKI Shin, ONUMA Akira
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	8
page range	24-30
year	1956
URL	<a href="http://hdl.handle.net/10097/26749">http://hdl.handle.net/10097/26749</a>

# Studies on Gas Analysis in Metallic Titanium\*

Hidehiro GOTÔ, Shin SUZUKI and Akira ÔNUMA

*The Research Institute for Iron, Steel and Other Metals*

(Received December 12, 1955)

## Synopsis

Determination of hydrogen, oxygen and nitrogen in metallic titanium was studied by the vacuum fusion method and the chlorination method. By the vacuum fusion method, hydrogen and oxygen were completely extracted and could be determined at 1850~1900°C by using iron bath, but nitrogen was not extracted. By the chlorination method, oxygen could be determined at 300°C in a stream of mixed gases of chlorine at 5 ml/min and nitrogen at 20~30 ml/min. These results agreed well with those by the vacuum fusion method.

## I. Introduction

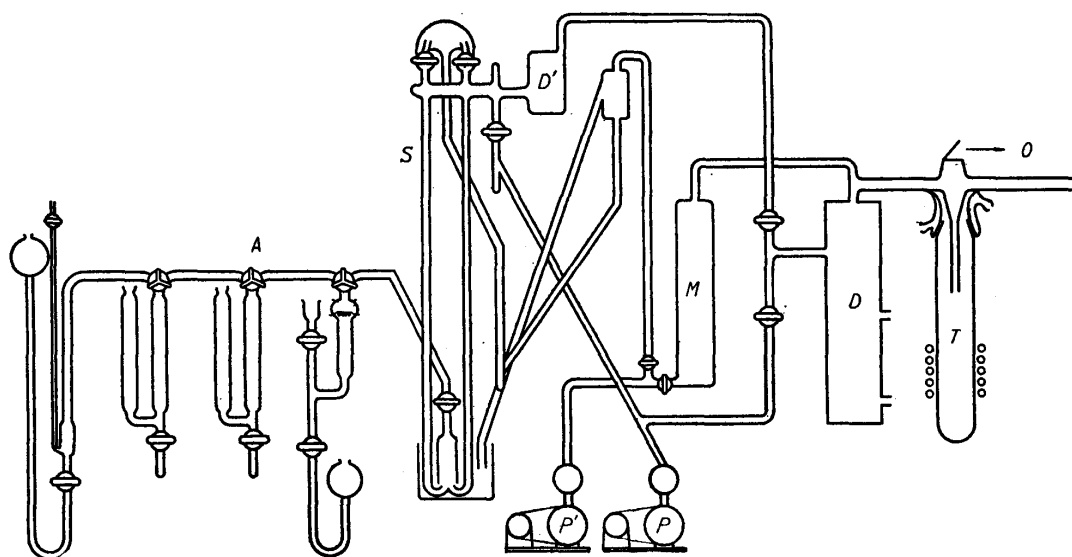
Recently, as the production of metallic titanium increases, the method for the determination of a very small amount of the impurities contained in the metallic titanium has been studied. Compared with iron and steel, metallic titanium extremely easily absorbs gases which greatly affect the hardness and other mechanical properties of titanium, and so the accurate and rapid analysis of these gases are required. The present authors studied the analyses of oxygen and other gases occluded in metallic titanium by the vacuum fusion method and chlorination method, and obtained satisfactory results.

## II. Vacuum fusion method

### 1. Apparatus

The gas analysis apparatus for iron and steel was used without modification. The apparatus is diagrammatically shown in Fig. 1. A vacuum tube, high-frequency electric induction furnace (800 KC) of 5 kW is used, with a vacuum furnace of clear quartz tube of about 70 mm in diameter, and a large graphite crucible or a clear quartz crucible is suspended from the quartz funnel in this furnace using molybdenum wire and a small graphite crucible is placed in it, and graphite granule is filled between two crucibles. The ash of graphite is less than 0.1 per cent. Molybdenum plates are suspended around the graphite cylinder to act as heat close plate, and also placed above the crucible. This vacuum furnace is air-cooled from outside by a fan and is connected through a glass tube, 50 mm in diameter, to a metallic four-stage mercury diffusion pump, in order to increase the velocity of gas exhaust. This was assumed to be effective in preventing reabsorption of the extracted gas by titanium which had volatilized onto the wall of the reaction tube. The gas extracted by the mercury diffusion pump is collected under an ordinary

\* The 824th report of the Research Institute for Iron, Steel and Other Metals. Reported in the Journal of the Japan Institute of Metals, **19** (1955), 89.



- T : Reaction tube  
 D : Four stage mercury diffusion pump  
 D' : Two stage mercury diffusion pump  
 S : Mercury dropping pump  
 A : Orsat type gas micro analysis apparatus  
 M : Mc'Leod gauge  
 O : Optical pyrometer  
 P, P' : Rotary pump

Fig. 1. Schematic diagram of gas analysis apparatus.

pressure by the mercury dropping pump. Glass two-stage mercury diffusion pump is placed directly before the dropping pump in order to decrease the dead space. The gas collected under ordinary pressure is determined by the Orsat type gas microanalysis apparatus.

## 2. Analytical procedures

Some studies have been reported regarding gas analysis in metallic titanium by the vacuum fusion method<sup>(1)</sup>. Most of them employed a tin or tin-iron bath at 1800~1900°C. The heat of formation of the titanium dioxide is 218.1 kcal/mole, being between those of 191.0 kcal/mole for silicon dioxide and 375.8 kcal/mole for aluminium oxide. In the case of gas analysis of iron and steel, the sample de-oxidized with aluminium is completely reduced and extracted at 1700°C, and so titanium dioxide should naturally be reduced at around this temperature. In the case of metallic titanium, the extraction of the gas is difficult at about 1700°C. This seems to be due to the fact that the melting point of titanium (1800°C) is higher than that of steel, and that the carbon in steel is extremely activated that these oxides are very easily reduced in the case of iron and steel. The raising of the extraction temperature to effect complete reduction of titanium dioxide would cause volatilization of titanium and the volatilized titanium would reabsorb the extracted gas. In the case of iron and steel, a tin bath is often employed in order

(1) G. Derge, *J. Metals*, **1** (1949), 31; D. I. Walter, *Anal. Chem.*, **22** (1950), 297; H. A. Sloman and Harvey, *J. Inst. Metals*, **80** (1952), 391; W. M. Albrecht and M. W. Mallett, *Anal. Chem.*, **26** (1954), 401.

to lower the melting point and facilitate extraction of gas. The use of a tin bath was tried in the present series of experiments, but, even with the Kahlbaum analytical grade tin, the amount of gases occluded in tin was extremely high and the lowering of the blank values in 5 g of tin on heating to above 1700°C was still incomplete after several hours. Further, this temperature was still too low to analyze the gas and the use of a tin bath seemed to result in no advantage; hence, an iron bath instead used. In this case, 10~15 g of iron was heated in the graphite crucible to the analysis temperature and the molten iron is thereby saturated with carbon, which effects not only the reduction of titanium dioxide but also the lowering of the fusion temperature. If iron used has not be deoxidized with aluminium, the lowering of the blank value can be effected by heating it at 1900°C for 30 minutes.

The analytical procedures were as follows: Iron, 10~15 g, was dropped into the graphite crucible, preliminarily heated to the analysis temperature and fused to drive out the gas occluded in iron completely. The heating was continued until the blank value fell to below 0.1 ml during 30 min, and the gas collected was discarded. Then the temperature was lowered to 1500°C, titanium sample was dropped in, and the temperature was raised to that of analysis. The gas extraction was made until the pressure inside the furnace became the same as that before the addition of the sample. The gas thus extracted was analyzed as usually for carbon mono-oxide, carbon dioxide, hydrogen and nitrogen by the Orsat gas analyzer.

### 3. Analytical results

The sample was prepared from titanium sponge obtained by the Kroll method, which was fused and rolled into a sheet of about 2 mm in thickness. Its analytical values are shown in Table 1.

Table 1. Determination of oxygen and hydrogen by the vacuum fusion method.

Exp. No.	Sample taken (g)	Temp. (°C)	Pressure in furnace ( $10^{-4}$ mmHg)	Time extracted (min)	O <sub>2</sub> found (%)	H <sub>2</sub> found (%)
1	0.0918	1650	2	60	0.07	0.03
2	0.0718	"	"	70	0.08	0.05
3	0.0998	"	"	50	0.01	0.04
4	0.0718	"	"	40	0.04	0.02
5	0.0645	1750	"	30	0.02	0.05
6	0.0837	"	"	45	0.06	0.03
7	0.1128	1800	"	105	0.12	0.05
8	0.2433	1850	0.5	60	0.28	0.62
9	0.1740	"	2	50	0.40	0.62
10	0.4723	"	2	110	0.36	0.33
11	0.3110	1900	4	40	0.30	0.46
12	0.4198	"	"	50	0.33	0.21
13	0.3507	"	"	50	0.33	0.71

Titanium carbide should be formed at 1650°C, and so the extraction was first carried out at this temperature, but the extractions of oxygen and hydrogen were found to be insufficient. The same occurred at 1750°C, and the raising the

temperature to 1800°C effected some improvements, though still insufficient of the extraction. At 1850~1900°C, the extraction finally became complete. The reason why such a high temperature is necessary for the extraction of hydrogen is still unknown, but, as shown in Table 2, the determination of the extract at various temperatures indicates that such a high temperature as required for the extraction of oxygen is also necessary for hydrogen. Regarding the extraction of nitrogen, the chemical analysis indicated the presence of 0.02 per cent of nitrogen, but it could not be extracted at all by the present method or, if extracted, the values were so scattered and so low that they could not be trusted.

Table 2. Results of the extracted oxygen and hydrogen at various temperatures by the vacuum fusion method.

Exp. No.	Sample taken (g)	Temp. (°C)	Pressure in furnace (10 <sup>-4</sup> mmHg)	Time extracted (min)	O <sub>2</sub> found (%)	H <sub>2</sub> found (%)
14	0.1639	1750	0.1	30	0.05	0.21
		1800	1	60	0.19	0.07
		1850	1	40	0.07	0.37
Total					0.31	0.65

### III. Chlorination method

Chlorination method is often used for the analysis of oxygen in iron and steel, and Corbett<sup>(2)</sup> has already attempted this method to analyze oxygen in metallic titanium. Since this method is simple without using the expensive apparatus as in the vacuum fusion method, some experiments were carried out by this method with the same sample as those used in the fusion method in order to ascertain the oxygen values obtained by the vacuum fusion method.

#### 1. Apparatus

The apparatus was almost the same as that used for the analyses of iron and steel, as shown in Fig. 2. Special precaution was taken to prevent the hydrolysis of titanium tetrachloride formed, and an ice-cooled trap was directly connected with the reaction tube in order to prevent the escape of titanium tetrachloride which might close the gas passage by hydrolysis.

#### 2. Analytical procedures

The sample was placed in a clear quartz boat, placed in the reaction tube and nitrogen was passed through the apparatus to replace the air with nitrogen from the tube filled with sugar carbon heated to about 950°C. Then chlorine was passed into the apparatus and the temperature of the reaction tube was raised gradually to the required temperature, thereby metallic titanium being chlorinated. After the chlorination was finished, nitrogen was passed through the apparatus to remove chlorine remained in it, the quartz boat was taken out, and the amount of titanium in the residue was analyzed to calculate the amount of oxygen.

(2) J. A. Corbett, *Analyst*, **76** (1951), 652.

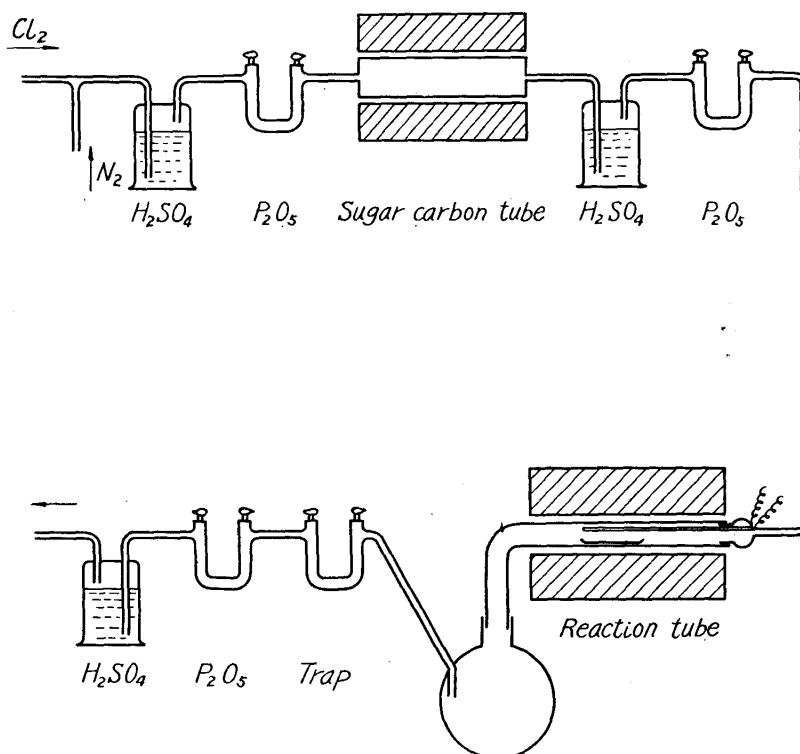


Fig. 2. Schematic diagram of chlorination apparatus.

### 3. Analytical results

The analytical results obtained by the foregoing procedures are listed in Table 3. Corbett<sup>(2)</sup> has obtained satisfactory results by carrying out the chlorination by the passage of chlorine at 400°C at a flow rate of 5~15 l/hr. In the present series of experiments, the flow rate was about 30 ml/min, as in the case

Table 3. Determination of oxygen by the chlorine method.

Exp. No.	Sample taken (g)	Flow rate (ml/min)	Reaction temp. (°C)	Reaction time (hr)	O <sub>2</sub> found (%)
1	1.1013	30	280~320	3	0.10
2	1.2363	"	"	2	0.04
3	1.0667	>50	80	4.5	0
4	1.1154	"	"	4.5	0
5	1.2704	2~3	250~300	2.5	0.34
6	0.3987	"	280~350	5.0	0.38
7	0.5703	"	350~450	2.3	0.22
8	0.5990	"	"	3.0	0.21
9	1.1138	"	250~300	2.0	0.13
10	1.0063	"	"	"	0.16
11	0.6339	"	350~400	3.0	0.85
12	0.6685	"	"	4.0	0.52
13	0.2995	{ Cl <sub>2</sub> 5 { N <sub>2</sub> 20~30	300~350	4.0	0.32
14	0.4983		"	"	0.34
15	0.6554		"	"	0.32

of iron and steel samples, but the oxygen values were extremely low and scattered, as indicated by the Experiment Nos. 1 and 2. During these reactions, it was observed that the temperature indicator needle made a sudden move and that, while the reaction seemed to begin originally at 290°C from the surface of the sample, there was a sudden reddening of the sample above this point and sometimes showed incandescence. This is assumed to be due to the fact that the chlorination of titanium is an extremely violent reaction, its reaction heat causing chlorination of titanium dioxide. The reaction was therefore carried out with a more rapid flow rate with Experiment Nos. 3 and 4. In these experiments, the reaction began when the temperature of the reaction tube reached about 80°C, reacted vigorously, and there was no residue as may be seen from the table. From these results, the flow rate of chlorine was made extremely slow in Experiment Nos. 5 and 6, and the reaction was allowed to proceed very gradually, by which the values agreed well with those obtained by vacuum fusion method. It was found that the raising of the reaction temperature to 450°C resulted in the chlorination of titanium dioxide and the low values such as shown in Experiment Nos. 7 and 8 were obtained. Even at this slow rate, a part of the metal reddened occasionally and gave low values as in Nos. 9 and 10. In the case in which such reddening did not occur, the values were extremely high, as shown in Nos. 11 and 12. This is assumed to be due to the fact that titanium chloride remains as it was in the boat by the extreme slow rate of the flow of chlorine.

In order to remove these foregoing defects and to obtain accurate oxygen values, a gas mixture of chlorine and nitrogen was passed through the reaction tube. As shown by the values in Experiment Nos. 13, 14 and 15, it was found that values agreeing fairly satisfactorily with those by the vacuum fusion method were obtained by chlorination with a gas mixture of 5 ml/min of chlorine and 20~30 ml/min of nitrogen at 300~350°C. Corbett<sup>(2)</sup> reported that titanium carbide in metallic titanium reacted upon titanium dioxide during chlorination and that titanium nitride was also chlorinated. In the present series of experiments, however, nitrogen was determined from the reaction residue and titanium nitride did not seem to have been chlorinated. These facts, however, were not further examined since the samples were limited to one kind and, because the sample contained 0.01 per cent of total carbon and 0.02 per cent of nitrogen, it seemed that the effect of segregation in the sample was greater.

### Summary

- (1) The gases in metallic titanium were analyzed by the vacuum fusion and chlorination methods.
- (2) In the vacuum fusion method, iron bath was used. Both oxygen and hydrogen were completely extracted at 1850~1900°C and were determinable, but nitrogen could not be determined.

(3) By the chlorination method, oxygen could be determined by chlorination with a mixture of 5 ml/min of chlorine and 20~30 ml/min of nitrogen at 300~350°C, and the results obtained by this method agreed with those by the vacuum fusion method.