Determination of Oxygen in Metals by Argon Carrier-Fusion Coulometric Titration Method

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Synopsis

The automatic coulometric titration apparatus was tentatively used for the determination of oxygen in metals by the argon carrier-fusion method. The whole procedure was very rapid to complete the analysis and the blank value was very small with little variation. Each analysis of various kinds of iron and steel sample could be made within 3 to 5 minutes with high precision and accuracy. The determination of oxygen in ferromanganese, titanium, and Zircalloy was also examined and a statisfactory result was obtained by the use of a tin bath for ferromanganese, and an iron-tin bath for titanium and Zircalloy. Oxygen in ferrochromium was determined at high analytical temperatures.

I. Introduction

The inert gas-carrier fusion method using argon is being increasingly applied to the determination of oxygen in iron, steel, and other metals because the method does not require high vacuum and the procedure is simple.[1]~[5] The carbon monoxide formed by this procedure is carried by argon gas and oxidized by iodine pentoxide, and then its amounts is determined by the condensation-vaporization method[1]~[5] or by electrical conductivity.[2][3][4] The condensation-vaporization method is rather complicated in that the use of liquid oxygen and the removal of moisture are required, and the observation of gas extraction process is not possible. In the method using electric conductivity, the effect of temperature variation is so serious that a great care must be taken and the measured values of electric conductivity have to be corrected with a standard sample. The coulometric titration method used in the present investigation is quite insensitive to temperature variation and the amount of oxygen can be obtained from the coulombic quantity. Further, the method enables one to observe time-integral change of the extraction of oxygen from the sample as carbon monoxide and to complete the reaction.

In the present series of experiments, the automatic coulometric titration apparatus, manufactured by the Kokusai Denki Co. and designed especially for oxygen analysis, was used for the oxygen analysis in iron, steel, iron alloys,

* The **1219th** report of the Research Institute for Iron, Steel and Other Metals. Read at the Meeting of The Iron and Steel Institute of Japan, 1964.
(1) W.G. Smiley, Anal. Chem., **27** (1955), 1098.
(2) P. Elbling and G.W. Goward, ibid., **32** (1960), 1610.
(3) C.V. Banks, J.W. O'Laughlin and G.J. Kumin, ibid., **32** (1960), 1613.
(4) S. Kollman and F. Collier, ibid., **32** (1960), 1616.
(5) H. Gotô, S. Ikeda, T. Shimanuki and A. Ônuma, J. Japan Inst. Metals, **27** (1963), 558.

Zircalloy, and titanium metal.   It was found that this method was of high precision and accuracy in the determination of oxygen in these metals and was also a rapid method since the determination was completed within 5 minutes after charging the sample.

II. Apparatus

Analytical apparatus is illustrated in Fig. 1, in which Nos. 5 to 7 show the fusion-reaction part.   The sample is fused in a graphite crucible 22 mm in outside diameter, 16 mm in internal diameter, 30 mm in depth, and 5 mm in thickness of
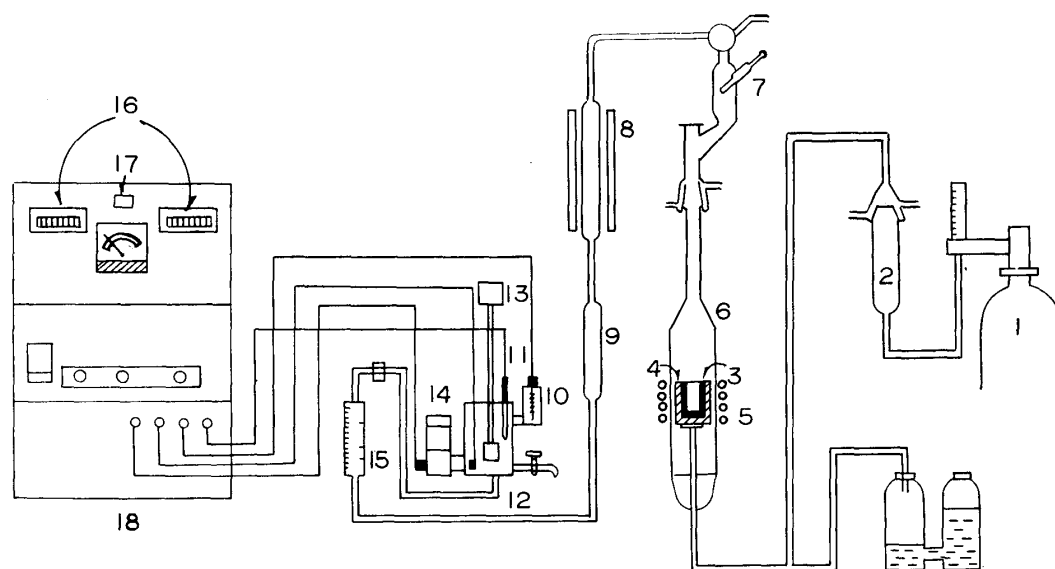

Fig. 1.   Inert gas fusion-coulometric titration apparatus for the determination of oxygen.

(1) Argon   (2) Sponge titanium for purification of Ar.   (3) Graphite crucible   (4) Quartz crucible   (5) High frequency electric furnace   (6) Quartz reaction tube   (7) Holder for sample inlet   (8) I_2O_5 (9) $Na_2S_2O_3$ 10) AgCl indicator electrode   (11) Glass electrode   (12) Cathode chamber   (13) Stirrer   (14) Anode chamber   (15) Flow regulater   (16) Pulse counter   (17) Pilot lamp   (18) Automatic coulometer

the bottom.   The graphite crucible is placed in a quartz crucible and the interspace between them is filled with 200 mesh high purity graphite powder for spectral analysis, as a heat insulater.   A high purity argon gas is used after being purified by passing through titanium sponge preheated to about 500°C (No. 3 in Fig. 1). Carbon monoxide gas formed by the reaction of the sample is oxidized by iodine pentoxide heated to about 150° (No. 9 in Fig. 1).   The liberated iodine is absorbed in the solid sodium thiosulfate (No. 10 in Fig. 1) and the carbon dioxide generated is led to the cathodic chamber of the electrolytic cell (No. 12).   The catholyte is a mixture of 5% barium perchlorate and 2% isopropyl alcohol adjusted to a definite pH.   When carbon dioxide is absorbed in this solution, the reaction

$$Ba^{2+} + CO_2 + H_2O \rightarrow BaCO_3 + 2H^+$$
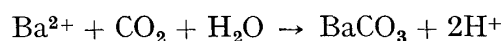
takes place and pH of the solution changes. Electrolysis of the solution is carried out in order to put the pH back in the present value. The pilot lamp (No. 17 in Fig. 1) indicates the end-point of the reaction and the amount of oxygen is calculated from the quantity of electricity (coulombs used) according to Faraday's rule. The electrolysis is carried out by the pulse current and the quantity of electricity per pulse in this instrument is equal to 6×10^{-3} coulomb, which corresponds to 0.5×10^{-6} g of oxygen. Total amount of oxygen determined as CO_2 is indicated by the digital counter (No. 16), that is, 1 count is equal to 0.00005 % of oxygen per gram of sample. A stopper is connected with the pH-meter, which prevents incomplete absorption of a large quantity of carbon dioxide when the oxygen content is too great.

III. Analytical conditions

Conditions for analysis, such as the temperature of the reaction, the time for degasification, and the flow rate of argon gas were first examined. Degassing for over 30 minutes at 2400°C at the argon flow rate of 500 ml/min gave blank values of $1 \sim 2$ μg/min at the analytical temperature and this value was found to be almost unchanged after analyses of a large number of samples. The analytical temperature was different with different kinds of metal sample, i.e., around 1900°C for iron and steel samples, $2000 \sim 2100$°C for high-melting metals like titanium, and below 1700°C for samples containing a large quantity of manganese. Argon flow rate of $150 \sim 400$ ml/min had no effect on the absorption of carbon dioxide in catholyte but samples with a large content of oxygen were found to result in incomplete absorption of carbon dioxide because the action of the stopper controlling the introduction of carbon dioxide into the catholyte was not in time when the argon flow was too large. Therefore, the flow rate of argon was made constant at 200 ml/min.

IV. Analytical results

1. Iron and steel

The metal was polished and cleaned by the usual method and $1 \sim 3$ g of the sample accurately weighed was placed on the inlet cock (No. 8 in Fig. 1) and introduced into the apparatus. After about 30 seconds the sample was allowed to drop into the graphite crucible heated to the analytical temperature. After the reaction, carbon monoxide evolved was oxidized and the amount was measured by the coulometric titration. Periodical change of pulsed counts for electrolysis at this stage is shown in Fig. 2.

As shown in Fig. 2, pulse counts per minutes increased rapidly in 2 to 3 minutes, after charging the sample, and in about 5 minutes reached the value of blank test before charging the sample. Then the blank values during the analysis were subtracted from the total count and the quantity of oxygen was calculated. As shown in Table 1, there is no difference between this value and that of oxygen calculated from the number of counts at the time the pilot lamp goes up, without

subtracting the blank value. Therefore, it is quite practicable to estimate the amount of oxygen from the total count obtained at the time the pilot lamp goes up. Results of repeated experiments with pure iron and carbon steel are given in
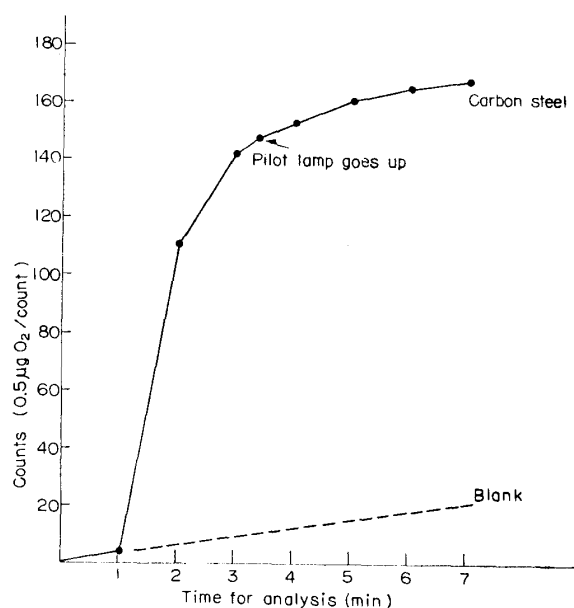

Fig. 2.   Counting-time curve for the coulometric titration of oxygen in steel.

Table 1.   Determination of oxygen by the coulometric titration

Sample	Sample taken (g)	The pilot lamp goes up			The extraction finished		
		required time (sec)	count number	oxygen* (%) determined	required time (sec)	count number	oxygen(%)** determined
Carbon steel	1.3236	230	567	0.0214	420	585	0.0213
	1.2636	225	490	0.0194	420	507	0.0193
	1.2979	230	496	0.0191	420	514	0.0190
Pure iron	2.0358	260	982	0.0240	420	998	0.0238
	2.0355	260	980	0.0240	420	997	0.0238
	2.0865	270	1119	0.0268	480	1140	0.0267
	2.0691	290	1065	0.0257	420	1076	0.0255

* Calculated without subtraction of blank value.
** Calculated after subtraction of blank value.

Table 2, and those for various kinds of iron and steel samples are given in Table 3. It can be seen from these tables that the present method is of a high precision, and that the values are in good agreement with those obtained by the vacuum-fusion method.   Samples containing a large amount of nickel and chromium were analyzed at 2000~2100°C.

2.   Ferromanganese and ferrochromium

There have been several reports on the difficulty of carrying out the determination of oxygen in samples containing a large quantity of manganese by the vacuum-

fusion method.[6][7] In the case of argon carrier method, the effect of manganese is considered to be less than that in the vacuum-fusion method.   In the earlier report from this laboratory the determination of oxygen in manganese metal by the condensation-vaporization method has been described,[8] and so an investigation

Table 2. Determination of oxygen in iron and steel (1).

Sample	Oxygen determined (%)			Mean value (%)	Oxygen determined by V.F.* (%)
Pure iron (1)	0.0026	0.0024	0.0028	0.0028 $\sigma \% = 9.3$	0.0028
	0.0030	0.0029	0.0031		
Pure iron (2)	0.0208	0.0191	0.0188	0.0203 $\sigma \% = 5.11$	0.0189
	0.0210	0.0210	0.0210		
Pure iron (3)	0.0231	0.0248	0.0222	0.0229 $\sigma \% = 6.06$	0.0211
	0.0216				
Carbon steel (1)	0.0223	0.0234	0.0238	0.0236 $\sigma \% = 2.75$	0.0258
	0.0238	0.0236	0.0244		
Carbon steel (2)	0.0435	0.0413	0.0418	0.0426 $\sigma \% = 3.56$	0.0437
	0.0442	0.0439	0.0407		
Carbon steel (3)	0.0262	0.0274	0.0251	0.0258 $\sigma \% = 3.58$	0.0254
	0.0247	0.0261	0.0254		
Carbon steel (4)	0.0201	0.0205	0.0216	0.0215 $\sigma \% = 5.30$	0.0206
	0.0216	0.0234	0.0221		

* V.F.;   Vacuum fusion method

Table 3. Determination of oxygen in iron and steel (2).

Sample	Oxygen determined (%)		Mean value (%)	Oxygen determied by V.F. (%)
Pure iron	0.0067	0.0065	0.0066	0.0065
Mild steel	0.0068	0.0070	0.0069	0.0071
High resisting alloyed steel (1)	0.0043 0.0040	0.0041	0.0040 0.0041	0.0044
High resisting alloyed steel (2)	0.0043 0.0040	0.0041	0.0042	0.0040
Stainless steel	0.0092	0.0088	0.0090	

Analytical temperature; 1900~2000°C

was made of the feasibility of the present method for the determination of oxygen in ferromagnanese.   Approximately well-corresponding values were obtained with this metal by the analysis at 1700°C, using tin with 10 times the amount of sample,

(6)   H.A. Sloman, J. Inst. Metals, 70 (1946), 391.
(7)   Y. Matoba and S. Banya, Japan Analyst, 5 (1956), 171.
(8)   H. Gotô, S. Ikeda and A. Ônuma, ibid., 13 (1964), 880.

and charging the sample after completion of the degassing of the tin bath. This result is shown in Table 4.

With samples containing a large amount of chromium, a continuous determination was found to give increasingly lower value due to the viscosity of chromium but it was found from the analysis of ferrochromium samples that good reproducible values could be obtained by making use of iron bath at 1800°C and by the analysis at 2000°C without the iron bath. These results are given in Table 5.

Table 4. Determination of oxygen in ferromanganese by
tin bath extraction.

Sample	Sample taken (g)	tin added (g)	Oxygen determined (%)	Mean value
Mc-Fe-Mn A	0.7021	7.0	0.012	
	0.4689	5.0	0.014	
	0.5011	5.0	0.010	
	0.4532	5.0	0.011	0.012
Hc-Fe-Mn	0.3610	5.0	0.146	
	0.2860	3.0	0.128	
	0.2840	4.0	0.138	
	0.3701	4.0	0.128	
	0.3959	4.0	0.122	0.132

Analytical temperature; 1650~1700°C

Table 5. Determination of oxygen in ferrochromium.

Analytical temperature °C	Oxygen determined (%)			Mean value (%)	Oxygen determined (%)*	
1800	0.045	0.039	0.041		0.048	0.051
	0.040	0.036	0.036	0.039		
1900~2000	0.050	0.050	0.048		0.048	0.047
	0.046	0.048	0.047	0.048		
2000~2100	0.047	0.048	0.048			
	0.049	0.047	0.050	0.048		

* Iron bath was used.
Sample taken; 0.5~1.5 g

3. Titanium and Zircalloy

The determination of oxygen in high-melting metals like titanium and zirconium is being carried out by making use of a platinum bath in recent years. [2][9][10][11] This is because when iron bath is used, the retention of iron in a graphite crucible for too long time at high temperatures results in the reduction of the fluidity of the bath, which makes the reaction of the sample upon graphite difficult and tends to give lower determination values. However, platinum is to expensive and is not suitable for routine analyses. In argon carrier-coulometric titration, there is no fear of bumping at the time of sample charging at very high

(9) D.H. Wilkens and J.E. Fleischer, Anal. Chim. Acta, **15** (1956), 334.

(10) W.P. Hansen, M.W. Mallett and M.J. Trgechak, Anal. Chem., **31** (1959), 1237.

(11) K. Shimazaki, S. Shindô and K. Hosoda, Japan Analyst, **9** (1960), 494.

temperatures, as often takes place in the vacuum-fusion method, iron used for the bath can be charged in the graphite crucible at a constant temperature, and the state of gas extraction can be observed. Consequently, the time for degassing of the bath can be minimized and so iron can be used most effectively as a metal bath. Therefore, the determination of oxygen in titanium and Zircalloy samples was tried by making use of iron bath and iron-tin bath. It was found, however, that the oxygen values determined have a tendency to become lower by continuous determination on using iron as a bath. By the use of iron-tin bath, in which fresh iron and tin were used for every sample, and in which the sample was immediately charged after degassing the bath, a satisfactory result could be obtained, as shown in Table 6. These analytical values agree well with those obtained in other laboratories by the vacuum fusion method using platinum bath.

Table 6. Determination of oxygen in titanium
and Zircalloy by iron-tin bath extraction.

Sample	Oxygen determined (%)			Mean value (%)	Oxygen determined by Pt-bath*
Titanium A	0.072	0.071	0.068		
	0.070	0.070	0.068	0.070	0.071
Titanium B	0.091	0.095	0.089		
	0.093	0.092	0.096	0.093	0.098
Titanium C	0.194	0.192	0.191		
	0.185	0.188	0.188	0.189	0.172
Zircalloy	0.093	0.095	0.095		
	0.094	0.097	0.095	0.095	0.093

* Vacuum fusion method
Sample taken; 0.15~0.25 g
4.5 g of iron and 2.0 g of tin were added to each sample.
Analytical temperature; 2000~2100°C

Summary

The analysis of oxygen in metals by the argon carrier-fusion method is very simple in procedure and the result can be obtained rapidly. The use of an automatic coulometric titration apparatus together with this method was found to give practically constant blank values and the reaction of the sample was completed in a short time. This method was therefore used to determine oxygen in iron, steel, several iron alloys, titanium, and Zircalloy, and the following results were obtained.

(1) Good precision and accuracy were obtained with pure iron and special steel samples by analysis at 1800~2100°C.

(2) In the analysis of ferromanganese, the use tin of 10 times the amount of sample prevented vaporization of manganese and inhibited gas adsorption, and continuous analyses were possible with one crucible. With ferrochromium, the determination of oxygen was possible by raising the analytical temperature.

(3)   With titanium and Zircalloy, the determination of oxygen was found to give values agreeing well with those obtained by the use of a platinum bath by carrying out the proposed method with iron-tin bath.