

## Determination of Oxygen in Metallic Manganese by Argon-Carrier Fusion Method

著者	GOTO Hidehiro, IKEDA Shigero, ONUMA Akira
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	17/18
page range	237-242
year	1965
URL	<a href="http://hdl.handle.net/10097/27253">http://hdl.handle.net/10097/27253</a>

# Determination of Oxygen in Metallic Manganese by Argon-Carrier Fusion Method\*

Hidehiro GOTÔ, Shigerô IKEDA and Akira ÔNUMA

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

(Received July 28, 1965)

## Synopsis

Determination of oxygen in metallic manganese, which is considered to be difficult by the conventional vacuum fusion method, was attempted by the argon-carrier fusion method. The gettering effect of manganese was found to be inhibited by using a fresh bath, containing tin 15~20 times the amount of sample, for each run and by carrying out the analysis at  $1650 \pm 30^\circ\text{C}$ . Analyses of several kinds of metallic manganese sample under these conditions gave well-reproducible results. Recovery of oxygen was determined to be 95~110% by the addition of a definite amount of manganese oxide to these samples, showing that the gettering effect of manganese is inhibited completely.

## I. Introduction

The determination of oxygen by the vacuum fusion method has been widely used, not only for iron and steel but also for alloys and non-ferrous metals. In some of these metals containing a large amount of manganese, the vaporization of manganese is large and the vapor forms a film on the wall of the reaction tube. This tends to adsorb the gas produced and to result in lower determination values. For these reasons, many studies have been made of a permissible limit of manganese. This limit must be checked with each instrument but the progress of instrumentation has raised the upper limit of this permissible range. According to Sloman<sup>(1)</sup>, the determination of oxygen can be made in samples containing around 12% of manganese. In this case, the analytical temperature is below  $1550^\circ\text{C}$ , and only the determination value of the first charged sample is reliable. In the vacuum fusion method, the vaporization of manganese is active even at a comparatively low temperature and the effect of adsorption is likely to become very conspicuous. On the other hand, in the inert gas fusion method the fusion would be carried out in an inert gas at ordinary pressure, and accordingly, such an effect would be rather small. Previous experiments on the determination of oxygen in ferromanganese by the argon-carrier fusion capillary-trap condensation method has shown that the analysis of oxygen is possible even in iron and steel samples containing a high manganese<sup>(2)</sup>. In the present study, this point was examined with oxygen in metallic manganese and a satisfactory result was obtained.

---

\* The 1208th report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in the Japan Analyst, **13** (1946), 880.

(1) H. S. Sloman, J. Inst. Metals, **71** (1946), 391.

(2) H. Gotô, S. Ikeda and A. Ônuma, J. Japan Inst. Met., **27** (1963), 558.

## II. Apparatus

The argon-carrier fusion capillary-trap condensation apparatus<sup>(2)</sup> made in this Institute was used.

## III. Experimental results

The effect of manganese is decreased by the addition of chromium, nickel or tin<sup>(3)</sup>. Tin is said to be an effective metal-bath having anti-gettering action but the use of a large quantity of it in the vacuum fusion method is said to give an adverse effect because of strong vaporization of tin, though its rate depends on analytical conditions. However, such a bad effect is not likely to take place at the inert-gas-carrier fusion method and the use of tin seems to be effective, because of its low melting point, formation of fluid alloy at low temperatures and of its anti-gettering action. Therefore, examinations were made of the effect of a tin-bath.

### 1. Analytical procedure

As in the case of iron and steel samples, degassing was carried out at 2400°C at the flow rate of argon of 500 ml/min for 0.5~1 hour. The blank value was measured at argon flow rate of 250 ml/min for 10 minutes after lowering the temperature to the analytical temperature. When the blank value became to show around 3  $\mu\text{g}/\text{min}$  and sufficient degassing was obtained, the analyses were carried out. The samples used were electrolytic manganese plate, broken into convenient sizes and washed with benzene. Tin used for the bath was a product of Junsei Kagaku, first grade.

### 2. Relationship between manganese content in the tin-bath and value of oxygen determined.

#### (i) Analysis at 1500~1550°C

It has been said that the analytical temperature of high-manganese samples by vacuum fusion method should be below 1550°C<sup>(4)</sup>. The analysis of metallic manganese was, therefore, carried out at 1500~1550°C. A tin-bath was prepared with a definite quantity of tin, which was degassed, and the manganese sample was then added to it to determine the amount of oxygen in the sample. The result is shown in Table 1. It was found that when the manganese sample was added to the tin-bath consecutively, the determined values tended to come out lower at and after the second charge. When tin was added to the bath with the sample, there was still a tendency to give rise to lowering value though not rapidly.

#### (ii) Analysis at 1650°C

The same experiment was carried out at a higher temperature of 1650 $\pm$ 30°C because the effect of volatilization at the inert-gas-carrier fusion method seemed small even at higher temperatures and because of a rapid and complete extraction of oxygen by the increase of reaction rate. This result, as shown in Table 2, indicated that the determination values became lower when the manganese content

(3) S.L. Hoyt and M.A. Schell, Trans. AIME, **125** (1937), 328.

Table 1. Results of oxygen determination at 1500~1550°C

Sample	Sample taken (g)	Sn added (g)	Mn in Sn (%)	Oxygen determined (%)
Electrolytic manganese No. 1	0.4892	10	4.9	0.089
	0.4544		9.4	0.026
	0.3333		12.8	0.029
	0.5141		17.9	0.009
Electrolytic manganese No. 2	0.4130	10	4.1	0.078
	0.3635		7.8	0.087
	0.3713	3	7.6	0.062
	0.4420		8.0	0.063
Electrolytic manganese No. 3	0.3247	10	3.2	0.080
	0.3723	4	4.9	0.069
	0.2366	4	5.8	0.056

Table 2. Results of oxygen determination at 1650±30°C

Sample	Sample taken (g)	Sn added (g)	Mn in Sn (%)	Oxygen determined (%)
Electrolytic manganese No. 1	0.3425	10	3.4	0.090
	0.4325		7.7	0.100
	0.2160		9.8	0.078
	0.3882		13.6	0.067
	0.5378		19.0	0.063
	0.4085	10	4.1	0.095
	0.3464	10	3.8	0.088
	0.2940		5.3	0.075
	0.3796	8	5.0	0.100
	0.2615		4.1	0.105
	0.3419	7	4.4	0.102
	0.3556		5.9	0.078
Electrolytic manganese No. 2	0.4206	9	4.7	0.119
	0.3925	6	5.4	0.122
	0.3252	4	7.1	0.120
	0.2145	5	5.7	0.123
	0.4240	7	5.8	0.116
	0.4915	5	9.8	0.099
	0.4542		9.5	0.095
	0.4376		9.2	0.102
	0.4126		9.4	0.081
	Electrolytic manganese No. 3	0.3425	5	6.9
0.3040		4	7.2	0.084
0.3714		5	7.3	0.081
0.3137		4	7.4	0.076
0.2952		4	7.1	0.079
0.3270		4	8.5	0.066
0.3628			8	4.5
0.4426		9	4.7	0.081

in the tin-bath was above 9% and also below 8% when fresh tin was not added to the bath. When fresh tin was added with each charge and manganese content in the tin-bath was kept below 8%, determination values highest and the analysis gave approximately agreed values.

(iii) Analysis at 1750~1800°C

The same analytical procedure carried out at a still higher temperature of 1750~1800°C gave the results shown in Table 3. The value of oxygen determined

Table 3. Results of oxygen determination at 1750~1800°C

Sample	Sample taken (g)	Sn added (g)	Mn in Sn (%)	Oxygen determined (%)
Electrolytic manganese No.2	0.3675	11	3.3	0.126
	0.3231		6.3	0.099
	0.3172	5	6.3	0.086
	0.3332		8.3	0.065
	0.3020	5	7.8	0.063
	0.4145	8	5.3	0.119
	0.3957	7	5.4	0.081
	0.4310	8	5.4	0.075

on the first charge was approximately the same as that obtained at  $1650 \pm 30^\circ\text{C}$  but subsequent values became gradually lower even with supplementation of tin with every charge of the sample.

### 3. Suitable conditions for the analysis

The above-mentioned preliminary tests show that the analysis at 1500~1550°C gives lower values because of insufficient reaction, while that at 1750~1800°C gives a high value at the first charge but the values begin to decrease at and after the second charge, even if tin is added with each charge to the bath, showing that the gettering effect of manganese appears markedly at this temperature. Supplementation of tin to the bath with each sample was found to give a correct and approximately constant value, provided the manganese content in the tin-bath was kept below 8%. These experimental results suggest that there is still no exact explanation of the mechanism of gas adsorption at the time of manganese volatilization, but it seems that this is not a mere adsorption on the vaporized film, i.e., a static adsorption, but a chemical adsorption in the course of vaporization. Addition of tin with each sample charge at an appropriate analytical temperature to make a fresh tin-bath is likely to make the anti-gettering action of tin more effective, and this is probably the reason for reproducible results.

Based on these experimental results, analytical conditions for the determination of oxygen in metallic manganese were determined as follows: Analytical temperature of  $1650 \pm 30^\circ\text{C}$  was used. Tin, 15~20 times the amount of the sample, was added to the graphite crucible to make a tin-bath which was first degassed, and then the manganese sample was added to it. This was submitted to the

determination at the argon flow rate of 250 ml/min for 10 minutes. When the analysis was to be continued, fresh tin was supplemented to maintain the manganese content of the bath to around 5~8%. Oxygen was determined in several kinds of electrolytic manganese under these conditions, and well-agreeing values were obtained as shown in Table 4.

Table 4. Results of oxygen determination in metallic manganese

Sample	Sample taken (g)	Mn in Sn (%)	Oxygen determined (%)
Electrolytic manganese	0.5640	4.0	0.103
	0.3972	4.0	0.107
	0.5647	5.6	0.107
	0.2894	7.5	0.102
Dehydrogenated electrolytic manganese	0.3464	3.8	0.088
	0.4928	8.0	0.086
	0.5218	5.2	0.086
Nitridated electrolytic manganese	0.3646	7.0	0.093
	0.3512	8.0	0.089
	0.3581	7.3	0.090

#### 4. Recovery of oxygen from manganese oxide

Although approximately agreeing values were obtained by consecutive determination of oxygen in metallic manganese under the above-mentioned conditions, it was still uncertain whether these were correct because of the absence of standard samples. For this reason, the recovery of oxygen was examined by its determination under the same conditions using the sample containing manganese oxide added. Manganese oxide, with manganese content of 69.63% by chemical analysis, was accurately weighed, and embedded in the iron-bath prepared by degassing in argon atmosphere. This sample was submitted to the same analysis as for iron and steel samples and the values of oxygen, obtained after subtracting the blank value for iron-bath, were 29.98, 29.71, and 29.93%. A definite quantity of this oxide sample was weighed accurately, wrapped in iron foil, and further wrapped in iron foil with separately weighed metallic manganese sample. This wrapped sample was placed in a vacuum desiccator and after evacuation argon gas was sent in it to replace air inside the iron foil with argon gas. Immediately before its analysis, this sample was allowed to stand inside the charge cock for 5 minutes. Direct addition of the sample into the tin-bath at 1650°C gave a recovery of around 70%. This was probably due to the fact that the oxide was only wrapped in a thin iron foil and its direct addition to the high-temperature crucible caused a sudden reduction reaction of the oxide and resulted in a partial loss of finely powdered manganese oxide with sudden evolution of carbon monoxide. The sample was therefore added after lowering the temperature of the crucible below 800°C by switching off the heating current for 3

Table 5. Recovery of oxygen in manganese oxide

Sample taken (g)	Oxygen in sample ( $\mu\text{g}$ )	Manganese oxide***		Oxygen determined ( $\mu\text{g}$ )	Oxygen in manganese oxide	
		Added (mg)	Cal.oxygen ( $\mu\text{g}$ )		Recovered ( $\mu\text{g}$ )	Recovery (%)
0.3053*	305	3.35	1001	1330	1025	102.4
0.3109*	311	5.06	1512	1747	1436	95.0
0.4220**	385	5.58	1668	2267	1882	112.8
0.4310**	374	4.67	1396	1715	1341	96.1
0.3570**	312	4.28	1279	1684	1372	107.3
0.3166**	271	3.32	992	1266	995	100.3

\*Electrolytic manganese 0% = 0.100

\*\*Dehydrogenated electrolytic manganese 0% = 0.087

\*\*\*0% = 29.89

minutes and then the temperature was again raised to 1650°C. The amount of tin in the bath and other conditions were all the same as before. As shown in Table 5, oxygen in the oxide was almost completely recovered and the effect of gas adsorption by volatilized manganese seems to be inhibited completely under these conditions. It appears from these results that oxygen in metallic manganese is completely extracted and determined by the present method.

### Summary

The determination of oxygen in metallic manganese, considered to be difficult by the conventional vacuum fusion method, was attempted by the argon-carrier fusion method. It was found that the gettering effect of manganese is completely suppressed by the addition of fresh tin to the bath with every charge of the sample to maintain the manganese content of the bath below 8%, and to keep the analytical temperature at  $1650 \pm 30^\circ\text{C}$ . Several kinds of manganese sample were analyzed under these conditions and reproducible results were obtained. The determination of oxygen was also carried out under the same conditions with samples containing manganese oxide added. The recovery of oxygen was 95~110%, and this suggested that the gettering effect of manganese was completely suppressed. Based on these experiments, a method was established for the determination of oxygen in metallic manganese, using argon-carrier fusion method.