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Emission Spectrographic Determination of Oxygen in Steel by a D.C. Carbon Arc Method*

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Synopsis

The oxygen content in steel could be determined by a spectrographic method. A d.c. carbon arc discharge was used to extract oxygen as carbon monoxide from the sample. The intensity ratio of OI 7771.9Å/ArI 8006.2Å was a function of the argon pressure in the excitation chamber, the current value and the oxygen content. The oxygen concentration in the range from 0.008 to 0.1 weight per cent could be determined from a variant coefficient of 7～12 per cent.

I. Introduction

The determination of oxygen in iron and steel has hitherto been carried out mainly by the vacuum fusion and the argon gas carrier fusion methods⁽¹⁾. For the determination of oxygen in iron and steel by emission spectroscopy, the conditions have been established when a d.c. arc and Shimadzu Ebert-type grating spectrometer were used. Fassel and his co-workers attempted the determination of oxygen in various metals by using a JACO spectrometer, with ArI 7891.1Å as the internal standard line⁽²⁻⁵⁾. With domestic infrared photographic plate using the Shimadzu GE-340 Ebert-type spectrometer, the spectral line of ArI 7891.1Å could not be observed, and accordingly, the spectral line of ArI at 8006.2Å (13.16 eV) was used as the internal standard in the present series of experiments.

II. Apparatus

Light source:	Shimadzu's high-precision electric discharge supply; d.c. arc, max. current 35 A output.
Spectrometer:	Shimadzu spectrophotometer GE-340. Grating, 1200 lines/mm. Degree of dispersion, 2.5 Å/mm (primary). Blaze wave length, 5000 Å.

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* The **1241st** report of the Research Institute for Iron, Steel and Other Metals.

(1) H. Gotô, S. Ikeda, A. Ônuma and T. Shimanuki, J. Japan Inst. Met., **27** (1963), 558.
(2) V.A. Fassel and R.W. Tabeling, Spectrochim. Acta, **8** (1956), 201.
(3) V.A. Fassel and L.L. Altpeter, Spectrochim. Acta, **16** (1960), 443.
(4) V.A. Fassel and W.A. Gordon, Anal. Chem., **30** (1958), 179.
(5) F.M. Evens and V.A. Fassel, Anal. Chem., **33** (1961), 1056.

Photometer: Shimadzu projection-type microphotometer PD-20.

An excitation chamber was constructed in the laboratory by improving on the one used by Fassel and others. It is an air-tight chamber of 150-cc capacity consisting of a quartz tube 35 mm in internal diameter 65 mm in height and 3 mm in thickness, and a water-cooled electrode holder made of stainless steel.

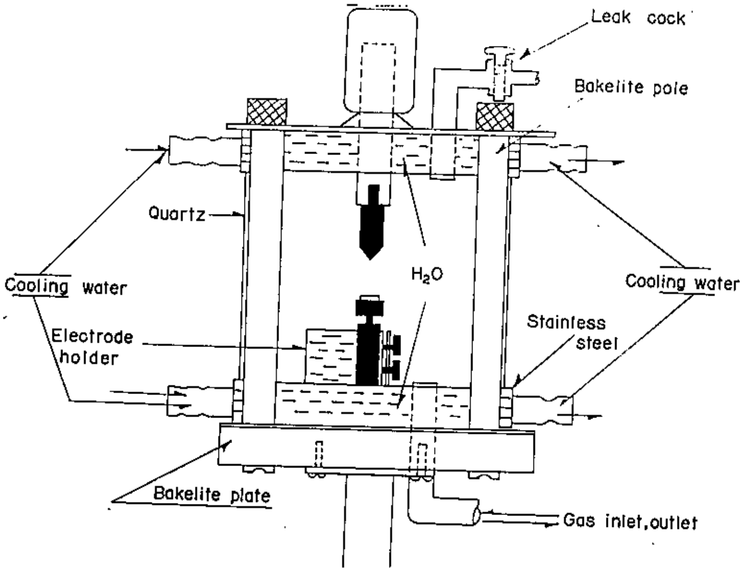

Fig. 1. Excitation chamber.

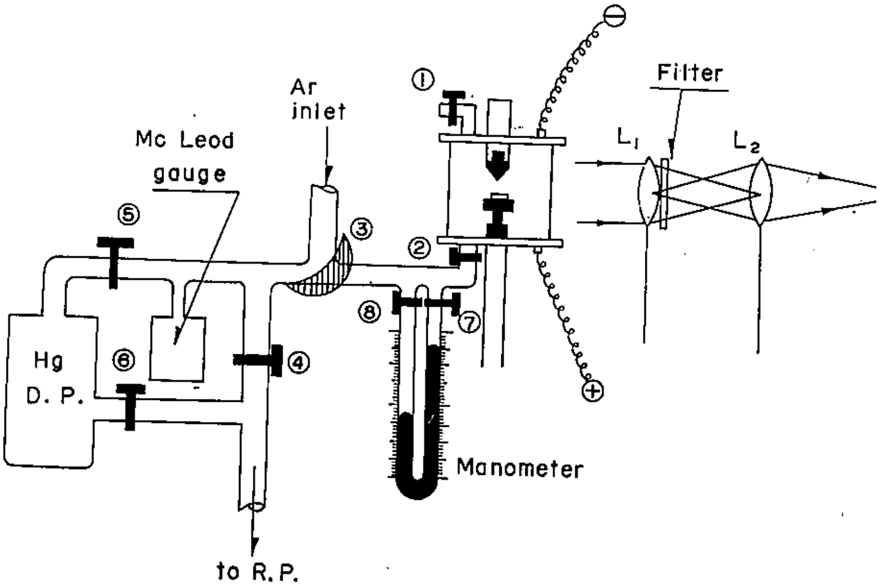

Fig. 2. High vacuum and gas-handling system.

A schematic diagram of the chamber is shown in Fig. 1.

Fig. 2 shows the vacuum system that may also be used as argon gas filling system. Vacuum of 2×10^{-3}mm Hg can be created by a rotary pump (capacity: 100 L/min) and this is brought to a vacuum of 10^{-4}mm by a mercury diffusion pump.

Anode: Hitachi graphite electrode of regular grade, 8 mm in diameter, finished to the dimensions shown in Fig. 3.

Counter-electrode: Hitachi graphite electrode of regular grade, 6.15 mm in diameter.

Photographic plate: Konishi Sakura infrared plate 750

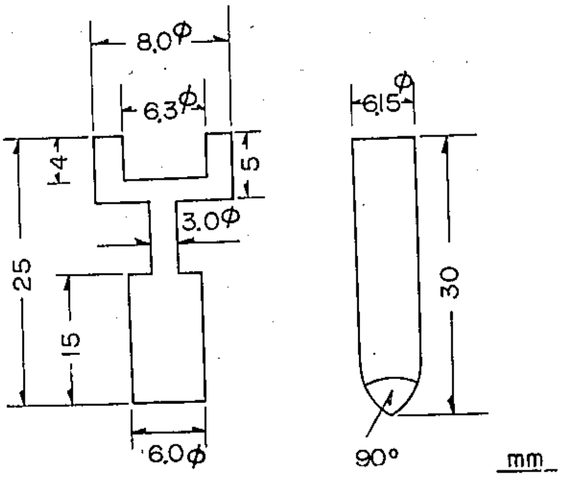

Fig. 3. Graphite electrode geometry.

III. Experimental and result

1. Experimental method

In order to lessen the blank values in the determination of oxygen, the excitation chamber and the electrodes were degassed in the following manner.

An auxiliary carbon electrode was placed on the electrode holder in the excitation chamber and air inside the chamber was drawn off with vacuum pump for over 3 minutes. The glass cock (3) in Fig. 2 was turned to allow argon gas to fill the chamber, the pressure was held at 160~200 mmHg, and then the cocks (2) and (3) (in Fig. 2) were closed, and arc discharge was made for 5 seconds with a current of 34.5 A to effect degassing. This procedure was repeated twice, gas was drawn out for 3 minutes, and argon gas was filled to the same pressure as before. Then d.c. arc discharge was made for 2 minutes with a current of 24.5 A, and finally gas was drawn out for 10 minutes to complete degassing procedure.

The excitation chamber is brought to ordinary atmosphere for the insertion of sample, and the sample was always inserted in a stream of argon gas at a flow rate of about 6 L/min. After the completion of degassing procedure, the upper lid was opened with caution so as not to touch the internal wall of the chamber and the lid was closed after the insertion of sample, followed by turning the glass cock (3) (in Fig. 2), air was drawn out further for about 10 minutes to obtain a vacuum of over 10^{-4}mm Hg. After this, the cock (3) (in Fig. 2) was turned to send in the argon gas to adjust the pressure inside the excitation chamber to a constant, and the cocks (1) and (2) (in Fig. 2) were closed. Excitation discharge was then carried out and the photograph was taken. The same procedure was carried out for each of the samples. During this period cooling water was allowed to flow slowly.

2. Selection of internal standard

Fassel and others used ArI 7891.1Å as the internal standard and carried out the determination of oxygen with 0I 7771.9Å/ArI 7891.1Å as the analytical line pair. With the spectrometer used in the present experiment and a domestic infrared plate (Sakura 750), the argon spectral line of ArI 7891.1Å was not observed as shown in Fig. 4. When the Eastman Kodak plate (I-N) was used as in the case of Fassel and others, ArI 7891.1Å appeared under the same conditions as the above. Therefore, the disappearance of this line on the domestic Sakura plate (750) was assumed to be due to the low photosensitivity of this plate. Therefore, instead of ArI 7891.1Å, the argon spectral line of ArI 8006.2Å (13.16 eV) was adopted since it had excitation voltage close to that of the oxygen spectral line of 0I 7771.9Å (10.73 eV), and a line pair of 0I 7771.9Å/ArI 8006.2Å was adopted.

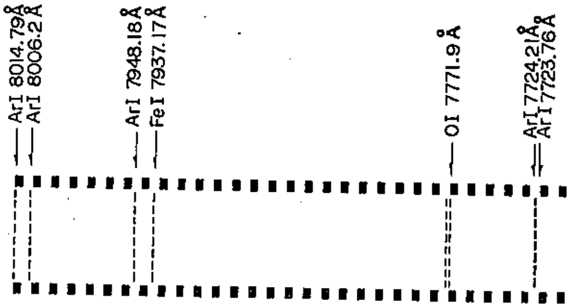

Fig. 4. Spectral lines of argon and oxygen observed at the wave length between 7700Å and 8000Å

3. Intensity ratio—current curve of oxygen and argon spectral lines

Mild steel was used as the sample. D.c. arc discharge was carried out under the conditions of 200 V, capacitance of 60 μF, argon pressure of 400 and 600 mm Hg, and exposure time of 180 seconds. The intensity ratio of the oxygen to the argon spectral line was calculated and the spectral intensity ratio — current curve was examined. As shown in Fig. 5, the relationship between the spectral intensity ratio and the arcing current at 400 and 600 mm Hg showed that the oxygen-argon ratio

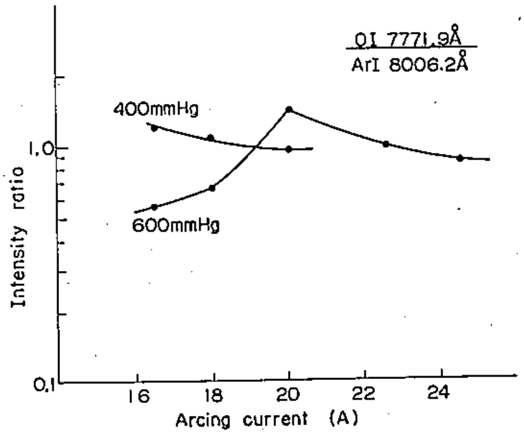

Fig. 5. Relationship between intensity ratio and arcing current.

decreased with increasing current in the case of 400 mm Hg, while in the case of 600 mm Hg pressure, the intensity ratio became maximum when 20 A was used. Consequently, 600 mm Hg argon pressure and 20 A were used in subsequent experiments.

4. Intensity ratio — time curve of oxygen and argon spectral lines

Mild steel was used as the sample and the intensity ratio of the oxygen to the argon spectral line was examined under the condition of d.c. arc discharge V of 200 V, C of 60 μF, and L of 50 μH, with argon gas pressure of 600 mm Hg at the current of 16.5, 18.0, 20.0, 22.5, and 24.5 A by the stepwise sector method, and

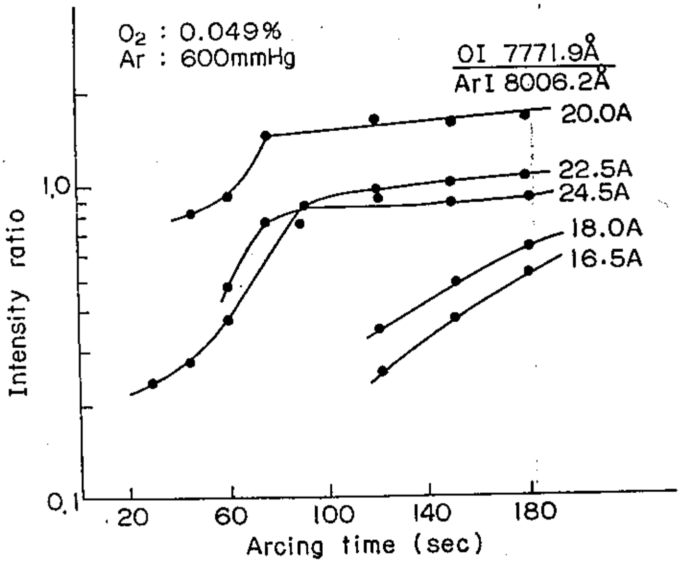

Fig. 6. Relations between intensity ratio and arcing time at 600 mmHg argon pressure.

the time — spectral intensity ratio relation at various conditions was examined as shown in Fig. 6. As will be clear from Figs. 5 and 6, the maximum intensity ratio is obtained when the argon pressure is 600 mm Hg and the current is 20.0 A, and the sensitivity is satisfactory. A preliminary discharge of 120 seconds seemed to be sufficient. Consequently, in subsequent experiments, analytical conditions were determined, as shown in Table 1, under the condition of d.c. arc discharge at 200 V, capacitance of 60 μF, current of 20 A, and argon gas pressure of 600 mm Hg. The samples were cut into the length of about 5 mm out of a rod of 6 mm diameter so as to weigh about 1 g. The cut surfaces of the sample were made smooth with a metal file, finished with No. 02 emery paper, and finally washed with petroleum benzine or ether.

Table 1. Experimental conditions.

Sample 1 g (Diameter 6 mm, Length 5 mm)		
Argon gas-pressure 600 mmHg		
Degassing	34.5 A	5 second
	34.5 A	5 second
	24.5 A	120 second
Prearc time	11 A	15 second
	20 A	105 second
Exposure time	20 A	120 second
Analytical-gap	6 mm	
Emulsion	Sakura infra-red plate	
Filter	FT 101	
Wave length	7100～8300 Å (1st. order)	
Slit width	0.05 mm	
Development	4 minutes at 21°C in FD-31	
Line pair	OI 7771.9 Å/ArI 8006.2Å	

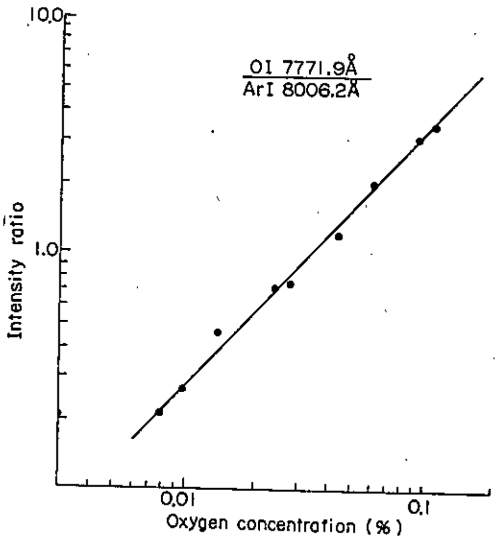

Fig. 7. Working curve for the determination of oxygen in iron and steel.

5. Preparation of a calibration curve

Under the conditions shown in Table 1, mild steel sample whose oxygen content had already been determined by the argon gas carrier fusion method was submitted to d.c. arc discharge and a calibration curve was prepared. As shown in Fig. 7, a straight line was obtained for the oxygen content between 0.008 and 0.1%.

6. Analysis of experimental samples

Several kinds of electrolytic iron, mild steel, and aluminium-killed and silicon-killed steel samples were submitted to the analyses under the conditions given in Table 1. These results were compared with that obtained by the argon gas carrier fusion method and a satisfactory agreement was observed as shown in Table 2.

The accuracy of the present method was examined by repeating the analysis five times each with two samples to obtain the standard deviation and, as shown in Table 3, the coefficient of variation was 7.3% at oxygen concentration of 0.06% and 11.7% at the concentration of 0.02%.

Table 2. Analytical results.

Samples		Results by Ar gas carrier fusion method	Results by proposed method
Mild steel	a	0.11 (%)	0.11 (%)
〃	b	0.059	0.060
〃	c	0.024	0.026
〃	d	0.014	0.017
〃	e	0.013	0.010
Electrolytic iron		0.040 (%)	0.040 (%)
Si-killed steel	a	0.11 (%)	0.11 (%)
〃	b	0.13	0.18
Al-killed steel	a	0.014 (%)	0.012 (%)
〃	b	0.0075	0.0085

Table 3. Precision of analytical results.

Results by Ar gas carrier fusion method	Results by proposed method	Average	Standard deviation	Coefficient of variation
0.057 (%)	0.059 (%) 0.056 0.048 0.054 0.056	0.055 (%)	0.004	7.3 (%)
0.022 (%)	0.023 0.022 0.020 0.027 0.021	0.023 (%)	0.0027	11.7 (%)

IV. Discussion

Fassel and others made experiments by using a JACO 3.4-meter Ebert-type spectrometer with a grating of blaze wave-length 13000Å and a photographic plate of Kodak 1-N. The spectral lines usually used for analyses of iron, steel, and other metals are in the range of 2000 to 5000Å, a grating of 13000Å being not generally used. In the present series of experiments, Shimadzu 3.4-meter Ebert type spectrometer with a grating of blaze wave-length of 5000Å and a domestic photographic plate were used to examine their adaptability and possibility. The Sakura infrared plate 750 was not sensitive to the ArI 7891.1Å used by Fassel and others, but it was found that oxygen in iron and steel can be determined with sufficient accuracy by using this domestic Sakura 750 infrared plate with the argon spectral line of ArI 8006.2Å at the excitation voltage close to that of 0I 7771.9Å as the internal standard line and 0I 7771.9Å/ArI 8006.2Å as the analtyical line pair.. A comparative examination was also made on the depth of the hole for auxiliary carbon electrode (anode) of 3 and 4 mm but there was no large difference in the analytical values.

Summary

(1) Determination of oxygen in iron and steel was examined by the d.c. arc discharge using Ebert type spectrophotometer with a grating of blaze wave-length of 5000Å and a closed excitation chamber with a quartz window.

(2) Optimum analytical conditions were determined from the time-spectral intensity curves as voltage of 200 V, capacitance of 60 μF, current of 20.0 A, preliminary discharge of 120 seconds, exposure of 120 seconds, and argon gas pressure of 600 mm Hg.

(3) Analytical line pair of 0I 7771.9Å/ArI 8006.2Å was adopted.

(4) Calibration curve showed linear relationship between oxygen concentration and oxygen-argon spectral line intensity ratio in the range of 0.008~0.1% oxygen content.

(5) Analytical values obtained with aluminium-killed and silicon-killed steel, mild steel, and electrolytic iron as the experimental sample agreed well with those found by the argon gas carrier fusion method. Coefficient of variation of the present method was 7~12%.