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The Determination of Oxygen in Metals with High Melting Points by the Inert Gas Fusion Method: A Silicon Fusion Technique

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The determination of oxygen in metals with high melting points is important for the development of metallurgy. This paper will describe a very simplified apparatus and a procedure which gives precise results almost without a blank test. A silicon fusion technique developed by the present authors is used instead of the platinum bath method for the purpose of decomposing oxides in metals. It enables us to determine oxygen in a small quantity of a sample by the use of a highly-sensitive gas chromatograph. The amount of oxygen in the purified tantalum and niobium was determined within a standard deviation of 0.0038%. The precision established in tests of titanium samples containing 0.074% of oxygen was 0.0018%; this observed value is in good agreement with that obtained by the vacuum fusion method.

The precise determination of the oxygen content in metals with high melting points is important for the development of metallurgy. Many authors[1-5] have described complicated high-vacuum equipment and have obtained precise results by means of the platinum bath method, but for practical use some points may be improved at small expense.

Recently, various attempts, such as that using

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the inert gas fusion method[9-12] without vacuum equipment and that using the neutron activation analysis method,[6-8] have been made to simplify the determination. Concerning the coulometric determination of oxygen in zirconium and zircaloy, Elbling and Goward[10] showed that Smiley's[9] platinum bath technique in a vacuum fusion method was applicable in the case of an inert gas fusion method. In other recent investigations, Holt and Goodspeed[12] have reported the simultaneous manometrical determination of oxygen and nitrogen in metals, while Evens and Fassel[13] have described a d.c. carbon-arc fusion method using gas chromatography for the determination of oxygen and nitrogen in steels.

This paper will describe a very simplified apparatus, a silicon fusion technique and a highly-sensitive method of gas chromatographic analysis. This method enables us to carry out the determination of oxygen in metals with high melting points almost entirely without a blank test; the agreement of this result with that obtained by the platinum bath method is satisfactory.

Experimental

Apparatus.—The apparatus was similar in principle to that already described[14] by the present authors. It consisted of gas extraction, collection, and measurement apparatus. The fusion products were transferred from the extraction system by means of an argon stream, and the concentration of this carbon monoxide was measured by the gas chromatograph.

A schematic diagram of the apparatus is given in Fig. 1. A high frequency induction furnace, Kokusai Denki combustion unit, Model HFT-7a, was used for the analyses of carbon and sulfur. The furnace assembly is shown in Fig. 2. A graphite crucible in the thimble was placed in a transparent silica tube, A, by controling the screw, G, attached to the pedestal, E. As the furnace was small, a special thimble was used instead of the silica thimble and graphite powder conventionally used; this new method has been found to be convenient and practical. The tube, D, was connected with a ground joint (a ball-shaped joint; 18 mm. in spherical diameter and with a 9 mm. bore) to the upper side of the silica tube, A, using a little Daifloil 50 grease and a spring clamp, I. The lower side was sealed by a metal cup, H, and a ring packing of silicone rubber. Purified argon, containing 0.0001% oxygen, 0.0005% nitrogen and 0.01 ml./l. water, was fed from a gas cylinder through a reducing valve, a needle valve, and a reference tube of the thermal conductivity cell, N. The gas was dried by passing it through columns of activated alumina, I, and phosphorus pentoxide, J. The fusion products were then transferred through a hard vinylon tube (3 mm. in diameter) to the concentration column.

Gas Chromatography. — The chromatographic column was built in a copper tube 1.5 m. long and 4 mm. in diameter. It was packed with Molecular Sieve 5A of 30—60 mesh. The column was maintained at 75°C, and the argon flow rate was 50 ml./min. The recorder had a sensitivity of 1.5 mV. at the full scale, as was determined by using a pre-amplifier; for a thermal conductivity cell of the gas chromatograph, the bridge current was adjusted to 150 mamp.

The concentration column, F, was a copper tube 50 cm. long and 4 mm. in diameter; it was packed with activated charcoal of 30—60 mesh. This column was capable of concentrating carbon monoxide in about 7 min. under ordinary conditions, with a flow rate of the argon carrier gas of 50 ml./min. at about −10°C. The concentrated gas was eluted from this column within one minute by warming it to 130°C.

Fusion Technique.—In the silicon fusion technique developed by the present authors, the platinum bath was not used. This technique was, however, found

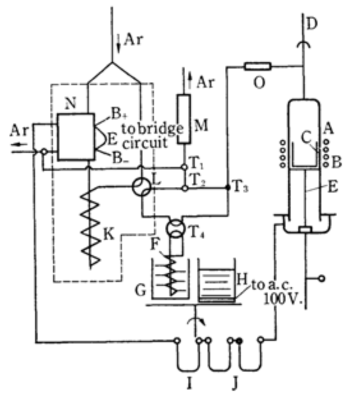

Fig. 1. Schematic diagram of apparatus.
A Transparent silica tube
B H-F coil
C Thimble and graphite crucible
D Entrance
E Pedestal
F Precolumn for collection of carbon monoxide
G Saline-ice solution
H Hot potash bath
I Activated alumina
J Phosphorus pen-oxide
K G. C. column
L Gas sampling cock
M Flow meter
N Thermal conductivity cell
O Silica gel tube
T_1 T_2 T_3, Greased cocks, T_3 By-pass cock

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9) W. G. Smiley, *Anal. Chem.*, **27**, 1098 (1955).
10) P. Elbling and G. W. Goward, ibid., **32**, 1610 (1960).
11) T. A. Sullivan, B. J. Boyle, A. J. Mackie and R. A. Plott, *U. S. Bur. Mines. Rept. Invest.*, **No. 5834**, 30 (1961).
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13) F. M. Evens and V. A. Fassel, ibid., **35**, 1444 (1963).
14) J. Kashima and T. Yamazaki, *Rept. of the Castings Research Lab., Waseda Univ.* (*Tokyo*), **13**, 15 (1962).

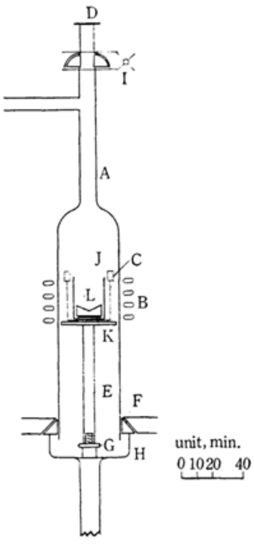

Fig. 2. Furnace assembly.
- A Transparent silica tube
- B H-F working coil
- C Leco crucible No. 528-30 and sleeve
- D Window of flat clear silica plate
- E Silica pedestal
- F Silicon ring packing
- G Screw
- H Metal cup
- I Spring clump
- J Degussit AL23 crucible
- K Sintered alumina disk
- L Graphite crucible

to give just as good results as those obtained with the platinum bath technique.

Procedure.—The concentration column was pretreated at about 130°C. by passing the argon carrier gas through it at a flow rate of 50 ml./min. for about 30 min.

The sample (approximately 20 mg.), after the surface contamination had been removed, was weighed into a capsule (10—20 mg.) made of tin foil. The capsule was then introduced into a degassed graphite crucible, together with a piece of silicon (100—150 mg.), via the entrance, D. After air had been expelled from the extraction system by an argon flow for 30 sec., the concentration column was connected to the silica tube. This concentration column was dipped into a Dewar flask filled with a saline-ice solution. The inert gas fusion was started, and the fusion products were transferred into the column. A fusion time of about 3 min. was needed in order to decompose the oxides in the sample perfectly. The flow was then continued for about 5 more min., when only a trace of the gas remained. After the column had been separated from the extraction system by turning the cocks, T_2, T_3 and T_4, the column was warmed by dipping it into the boiling bath, H. It was then connected to the chromatographic column, K, by turning the gas sampling cock, L, and the concentrated gas was measured chromatographically. Typical chromatograms are shown in Fig. 3.

The carbon monoxide content was obtained from a

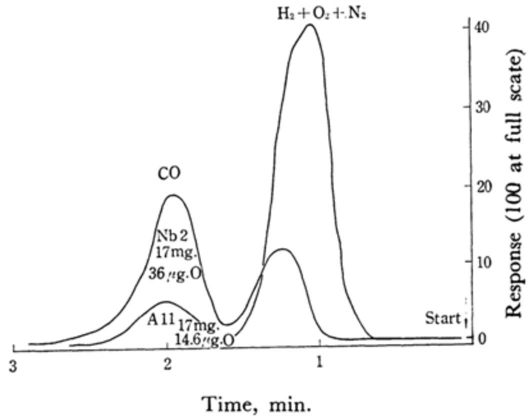

Fig. 3. Typical chromatograms of the gases collected.

peak area measured either by a planimeter or by the conventional approximate method. The oxygen content was obtained by means of the following equation;

$$\text{Oxygen, \%} = (a_t - a_b)/w \cdot K$$

where a_t: the area of the chromatogram of carbon monoxide (in sq. mm.) for the sample; a_b: the area of the chromatogram of carbon monoxide (in sq. mm.) for the blank test; w: the sample weight (in mg.); and K: the constant (0.014 μg. oxygen per sq. mm.). K was determined by using standard carbon monoxide. The standard gas is of a special grade (99.999%) which may be used for the calibration of gas chromatography or mass spectrometry. The calibration was carried out with gas samples containing 3.0—50.0 μg. of oxygen, which was introduced into the sampling cell (1.0 ml.) manometrically by the use of a silicone oil gauge (sp. gr. 0.987, at the temperature of 15°C). For simple calibration, it is also possible to use known steel samples as a secondary standard.

Results and Discussion

The accuracy of this method was tested with titanium samples. The results are compared with those obtained by other authors in Tables I and II. It was found that this method gives a good reproducibility. The determined values are in good agreement with the AED values of 0.085(A7) and of 0.103(B7) respectively for the samples of A11 and B21. The average value of the sample, B, which was obtained by ten co-operating laboratories using the vacuum fusion method was 0.098.

This method can be used for the determination of the amounts of oxygen in tantalum, niobium, molybdenum and tungsten. The results are summarized in Table III.

In order to degas the graphite crucible used in the experiment, it was necessary to heat it above 1800°C for about 10 min. In the case of the silicon fusion technique using 100—150 mg. of the metallic silicon, the time of heating was reduced (3—5 min.). The graphite-SiC crucible obtained by the above treatment was heated at about 2000°C for 30 sec. before the experiment. If the fusion of the sample is completed within 3 min., the value obtained by the blank test is only about 0.3 μg. oxygen; this value is negligible.

Table I. Comparison of oxygen values found by vacuum fusion, argon fusion and neutron activation analysis methods

Methods	Co-operating laboratory*	Titanium sample designation	Oxygen wt.%
Vacuum fusion	D.I.C.	A5	0.078_5
		B11	0.103
		2-1-2-(1)	0.067_7
Argon fusion	R.I.I.	A9	0.070
		B15	0.091
		2-1-4-(2)	0.055
Neutron activation analysis	A.E.D.	A7	0.085
		B7	0.103
		2-1-1-(1)	0.066

* D.I.C. = Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo.
R.I.I. = Research Institute of Iron, Steel and Other Metals, Tohoku University.
A.E.D. = Atomic Energy Department, Central Research Laboratory, Tokyo Shibaura Electric Co., Ltd.

The silicon fusion technique is effective in decomposing oxides in metals in the following ways; (1) metals with high melting points (tungsten,

Table II. Precision of simplified method (titanium)

Sample designation	Oxygen wt.%		Standard deviation, %
A11 (Sheet)	0.0864		
	0.0883		
	0.0871		
	0.0805		
	0.0880		
	0.0882		
	0.0852		
	0.0867		
	Mean 0.086_3	0.087*	0.002_2
B21 (Sheet)	0.106		
	0.096		
	0.092		
	0.091		
	0.103		
	Mean 0.097_9	0.0109*	0.006_6
2-1-5-(2) (Rod)	0.0728		
	0.0741		
	0.0736		
	0.0756		
	0.0774		
	Mean 0.074_9	0.077*	0.001_8

* Values obtained by platinum bath technique.

Table III. Oxygen content in high-melting-point metals

Material	No. of determinations	Oxygen, wt.% simplified method		Vacuum fusion method	Std. Dev.. %	Figulation of sample
		Si bath	Pt bath			
Tantalum-1	5		0.15_3	0.20	0.02_0	Powder
Tantalum-2	4	0.067_1		0.075	0.002_4	Powder
Tantalum-3	6	0.036_2		0.030	0.004_5	Powder
Niobium-1	5		0.095_5		0.004_5	Powder
Niobium-2	5		0.21_5		0.02_3	Powder
Niobium-3	4		0.33_8		0.03_6	Powder
Molybdenum	8	0.11_5			0.01_5	Wire
Tungsten	6	0.069_0			0.01_7	Wire

Table IV. X-ray analyses of metal residue in crucible used at silicon bath*1 technique

Material	Weight, mg.	Peak height (at chart responce)*3			
		SiK_α	2θ*4	Metals K_α	2θ*4
Titanium (sheet)	30	1.5	108°-15′	0.2	30°-15′
Molybdenum (wire)	20	0.6		0.4	20-15
Zircalloy (rod)	65	2.0		6.0 (Zr)	22-30
Tungsten (wire)	16	0.3		trace ($WL_{\alpha1}$)	42-15
Zircalloy (rod)*2	40	—		3.9 (Zr)	22-30
Titanium (sheet)*2	40	—		0.05	36-15
Niobium (powder)	30	0.3		0.8	21-20
Tantalum (powder)	40	0.7		trace	

*1 Approximately 100 mg. of pure silicon was added.
*2 Without silicon
*3 Recorders indication is ten at full scale
*4 Goniometer position
Instrumental conditions: crystal topaz LiF or EDDT; 50 kV. 50 mamp., base line 2.5 V., counter high voltage S. C. 890 V.; rate meter 2×10^5; time constant 0.5 sec.; Norelco

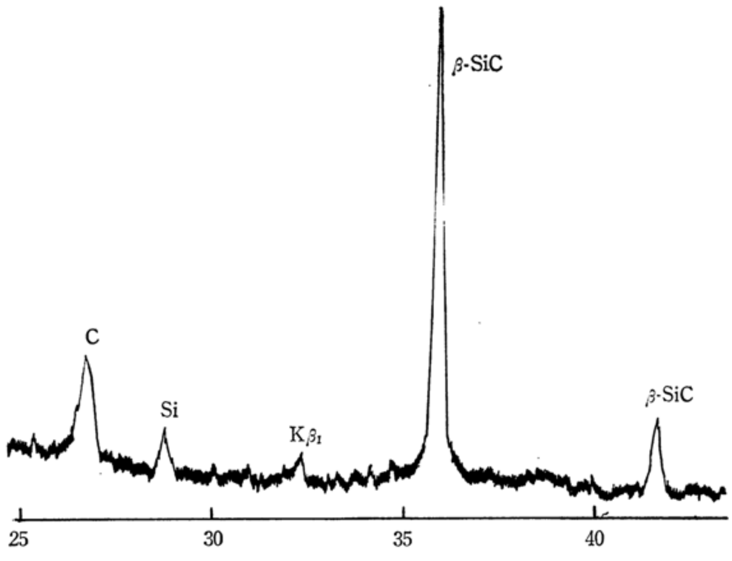

Fig. 4. Fluorescent X-ray spectroscopic observation of crucible wall used silicon bath technique.

molybdenum, tantalum, etc.) are very fusible at high temperatures in a large quantity of liquid silicon, because the Si-MSi_2 eutectics which are formed in the 78—95 wt.% range of silicon have melting points of 1300—1400°C (2) at very high temperatures (>1800°C), silicon and silicon-rich alloys penetrate into the crucible within one minute to form carbides. Six-hundred milligram of liquid silicon or 400 mg. of liquid silicon alloys (containing 50—100 mg. of metals) can be penetrate into a graphite crucible (about 2.5 g.) (3) semiconductor grade silicon or pure silicon (99.8—99.9 wt.% silicon containing 0.0005 wt.% of oxygen) can be used, because metals with high melting points contain large amounts of oxygen.

In the graphite-SiC crucible, the free silicon was found by a chemical method to be 1.24 wt.%. A fluorescent X-ray diffraction diagram of this crucible is given in Fig. 4. The metals contained in the crucible could be detected by studying the intensity of the sharp peak of the X-ray diagram; the intensity readings are summarized in Table IV. It was found that all of the metals combined to form carbides. By this fusion technique the oxide contained in the sample was almost decomposed when the sample was in the form of a filament, wire, powder, or a thin sheet.

The reactive metals, such as titanium, tantalum and niobium powders, fuse quickly and scatter from the crucible upon the addition of silicon; this produces erratic results. These metals must be treated with tin foil; when they are so treated, the duration of fusion increases from 20 sec. to about 50 sec. without scattering.

In the case of tantalum and niobium powder which contain more than 0.1 wt.% oxygen, the value of deviation increases slightly, as is shown in Table III. When the quantity of the sample is small, the analytical results will also be affected by the segregation of oxygen.