Analysis of Oxygen-18 in Solid Oxides by Spark Source Mass Spectrometry

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スパーク放電形質量分析計による固体酸化物中の酸素-18 の分析

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In order to clarify the mechanism of solid state reaction involving solid oxides, it is often necessary to know a part oxygen plays in it. Three kinds of radioisotopes of oxygen are unsuitable for tracers, since they all have too short half-lives. Then the stable isotope, ^{17}O or ^{18}O , must be used for the study of the solid state reaction. J.B. Holt¹⁾ studied the formation of CoAl_2O_4 from CoO and Al_2O_3 using oxides enriched in ^{18}O . In his study ^{18}O was detected by making use of the $^{18}\text{O}(\text{p}, \text{n})^{18}\text{F}$ nuclear reaction and autoradiography. However, mass spectrometry is a more direct method of detecting the stable isotope, so we attempted to apply the spark source mass spectrometry to the analysis of ^{18}O in solid oxides.

The instrument we used in this experiment was a Japan Electron Optics Laboratory JMS-01B double focusing mass spectrometer. In the case of the application of the instrument to oxide insulators such as MgO and Al_2O_3 , some devices were needed in the method of spark excitation. In general, powdered insulators are mixed with high-purity graphite powder and then pressed into a mould to form electrodes. But this technique is unsuitable for the analysis of oxygen, since graphite powder is apt to adsorb moisture. Besides, for the purpose of the analysis it is preferable that a single crystal or a sintered specimen is analyzed as it is in a state of a lump. After some trials, such method was adopted successfully that a solid specimen was wound around by high-purity gold wire with 0.3 mm diameter and attached to a sample holder, and a pointed gold wire with 1 mm diameter was set as a counter-electrode. This specimen-electrode configuration is similar to that reported by M. Desjardins and others²⁾, and the photograph of our configuration is shown in Fig. 1.

Fig. 1. Specimen-electrode configuration for spark excitation.

In the next place the influence of water adsorbed on the surface of the specimen becomes into question. The mass of ^{18}O , 17.9992 amu, is very close to that of $^1\text{H}_2^{16}\text{O}$, 18.0106 amu. These mass spectra are separated sufficiently by the improvement of the resolution through regulation of the instrument. But oxygen, a constituent of water, possibly affects a result, so it is necessary to remove the water adsorbed on the surface of the specimen as much as possible. As a result of many experiments the procedure described below was adopted: An electric heater was set in the BeO insulator that supported the sample holder on the ion source chamber. After the specimen was attached to the sample holder and the ion source chamber was evacuated, the specimen was heated for 30 minutes by use of the heater. Though the temperature of the specimen was not measured, it was estimated to be between 200°C and 300°C , while a vacuum of $\approx 10^{-7}$ mmHg was maintained. The spark excitation was started after the specimen and the ion source chamber were cooled enough. Fig. 2. shows mass spectra of MgO detected on Ilford Q2 photoplate. The spectrum of $^1\text{H}_2^{16}\text{O}$ is recognized to disappear after the use of the

Fig. 2. Partial mass spectra of MgO : (a) before the use of the heater, (b) after the use of the heater.

Table 1. Exposure ratios at equal densities.

Run No.	Exposure ratio	
	$\frac{q(^{16}\text{O}^+)^*}{q(^{18}\text{O}^+)}$	$\frac{q(^{24}\text{Mg}^+)**}{q(^{18}\text{O}^+)}$
1	6.8×10^{-2}	6.4×10^{-2}
2	6.3×10^{-2}	1.0×10^{-1}
3	6.6×10^{-2}	1.2×10^{-1}
4	6.0×10^{-2}	1.3×10^{-1}
Average	6.4×10^{-2}	1.0×10^{-1}

* The natural abundance of ^{16}O is 99.759%.** The natural abundance of ^{24}Mg is 78.70%.

heater.

The results of the analysis of ^{18}O in normal MgO and ^{18}O -enriched MgO are described below as an example. Mg^{18}O was prepared by the following reactions :

carried out at 850°C for 6 hours,

carried out at 1000°C in argon atmosphere. The concentration of ^{18}O in ^{18}O -enriched water used in this experiment was 8.6 atom %.

The quantitative analysis was performed by taking consecutive exposures based on monitored charges q as shown in Table 1. At the time of spark excitations, ions are generated from not only the specimen but also the gold wire. Therefore it is suitable to compare the density of the spectrum of ^{18}O with that of a main component. About ^{18}O -enriched MgO, the exposure ratios giving equal density of a standard ion spectrum, a spectrum of $^{16}\text{O}^+$ or $^{24}\text{Mg}^+$, to $^{18}\text{O}^+$ spectrum were determined with a microdensitometer. The results are shown in Table 1. Table 1 shows $^{16}\text{O}^+$ is preferable to $^{24}\text{Mg}^+$ as a standard from the view point of reproducibility. The inverse ratio of exposure of $^{18}\text{O}^+$ spectrum to that of $^{16}\text{O}^+$ spectrum is considered to be equal to the ratio of concentration of ^{18}O to that of ^{16}O , since the sensitivities of those two spectra are regarded to be equal. In this manner the concentrations of ^{18}O in normal MgO and ^{18}O -enriched MgO were

Table 2. Determination of ^{18}O in MgO.

Specimen	Conc. of ^{18}O (atom %)
Normal MgO	0.21
^{18}O -enriched MgO	6.0

Table 3. Dimensions of excitation craters.

Specimen	Monitor charge (coulomb)	Diameter (μ)	Depth (μ)
Single-crystalline	1×10^{-10}	≈ 500	≈ 10
MgO	1×10^{-11}	≈ 200	< 5
Polycrystalline	1×10^{-10}	≈ 700	≈ 20
MgO	1×10^{-11}	≈ 300	≈ 5

determined as shown in Table 2. The value obtained about normal MgO is consistent with the natural abundance of ^{18}O , 0.204 atom %.

At the time of spark excitation, craters were produced on the specimen surface. The diameters and depths of craters were measured by the microscopy as shown in Table 3. Therefore it is possible to maintain the depth of sampling within the order of 5μ by shifting a spark point at every spark excitation of 1×10^{-11} coulombs.

The rate of self-diffusion of oxygen in solid oxides is frequently required in the study of solid state reaction, sintering, electric properties of oxides etc. Nearly all investigations of oxygen self-diffusion in solid oxides have been performed by the gaseous exchange method. This method precludes the experimental determination of the ^{18}O distribution in the oxide and is insufficient to clarify the mechanism of oxygen diffusion. Therefore, the analysis method stated in this note will be applied validly to determine the ^{18}O diffusion profile in the solid oxide.

References

- 1) J.B. Holt, UCRL-12396 (1965)
- 2) M. Desjardins and J.P. Williams, *J. Am. Ceram. Soc.* 51 (5) 296-97 (1968).

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