The Tracer Diffusivity of Oxygen in Wustite and Cobaltous Oxide

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The tracer diffusivity of oxygen in Fe_{1-x}O and CoO has been determined from measurements of the depth profile of ^{18}O by secondary ion mass spectrometry. The tracer diffusivity in Fe_{1-x}O was evaluated, by taking into account the surface reaction of oxygen, as $D/\text{m}^2 \cdot \text{s}^{-1} = (1.17 \pm 0.78) \times 10^{-1} \exp [-(375 \pm 23 \text{ kJ/mol})/RT]$ between 1093 and 1455 K for $p_{\text{CO}_2}/p_{\text{CO}} = 1.00$. The tracer diffusivity in Fe_{1-x}O increased with increasing x . The surface reaction rate constant was expressed as $K/\text{m} \cdot \text{s}^{-1} = (48.3 \pm 27.5) \exp [-(293 \pm 14 \text{ kJ/mol})/RT]$. The tracer diffusivity in CoO was estimated, by taking account of evaporation of CoO , as $D/\text{m}^2 \cdot \text{s}^{-1} = (8.76 \pm 5.67) \times 10^{-8} \exp [-(287 \pm 18 \text{ kJ/mol})/RT]$ between 1273 and 1573 K for $p_{\text{O}_2} = 21.3 \text{ kPa}$ (0.21 atm). The evaporation rate was expressed as $V/\text{m} \cdot \text{s}^{-1} = (2.65 \pm 1.59) \times 10^{-5} \exp [-(167 \pm 16 \text{ kJ/mol})/RT]$.

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I. Introduction

Wustite (Fe_{1-x}O) has a large deviation from stoichiometry, depending on p_{O_2} . No measurements have been reported on the tracer diffusivity of oxygen in Fe_{1-x}O . The tracer diffusivity in cobaltous oxide (CoO), on the other hand, has been measured near 1 atm (10^5 Pa) p_{O_2} . While the defect structure of CoO has been well established by thermogravimetry⁽¹⁾ and electrical conductivity measurements⁽¹⁾⁽²⁾ in a wide range of oxygen gas pressures, the p_{O_2} dependence of the diffusivities of oxygen in CoO has not been established.

Mass spectrometric measurement of the gas phase has been commonly used for determining the tracer diffusivity of oxygen at near atmospheric pressures. However, only a few studies at low p_{O_2} have been reported using this method. The oxygen tracer diffusivity in Fe_3O_4 has been measured with gas mixture of $\text{H}_2\text{--H}_2\text{O}$ ⁽³⁾, and other measurements were made by changing the total pressure of pure O_2 gas from 10^{-3} atm (0.10 kPa) to 1 atm (101 kPa)⁽⁴⁾ or by using pure CO_2 gas⁽⁵⁾. It becomes necessary to establish new techniques to measure the diffusivity of oxygen in oxides at

low p_{O_2} , in order to investigate those oxides which exist only under low p_{O_2} , such as Fe_{1-x}O , or over a wide range of oxygen pressures.

In the present work, we have developed a gas sealed capsule method, in which oxide samples are diffusion annealed in a CO--CO_2 gas mixture containing ^{18}O and are analyzed to get the ^{18}O concentration profile by secondary ion mass spectrometry (SIMS). The SIMS technique has previously been successfully applied to the tracer diffusion of oxygen in rutile⁽⁶⁾ and sulfur in calcium sulfide⁽⁷⁾.

II. Experimental Procedure

1. Materials

Materials used in this study were a single crystal boule of cobaltous oxide prepared by the Verneuil method, and sheets of oxidized wustite. The single crystal boule was supplied by Murakami Eng. Co. Ltd. (Yokohama, Japan), and had a purity of at least 99.9%. A qualitative analysis by SIMS showed that the CoO crystal contained impurities such as Al, Si, Ti, and Na and that the relative intensities of secondary ion did not change with diffusion annealing. The CoO boule was either sliced by a diamond cutting wheel or cleaved along (100) plane to give specimens about $5 \text{ mm} \times 5 \text{ mm} \times 1 \text{ mm}$ in size. Fe_{1-x}O sheets were made from and Fe rod (Johnson and Matthey Co.), which contained 0.03% C, 0.01% O, 0.01% N, 3 ppm

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Mn, 1 ppm Cu, and residuals (Mg, Ag, Ca) less than 1 ppm. This rod was cold-rolled and sliced to a sheet about 10 mm × 40 mm × 1 mm in size, and then oxidized in a recrystallized alumina tube under CO–CO₂ mixture. The Fe_{1-x}O sheet specimens thus obtained were polycrystalline with grain diameters ranging from 3 to 4 mm.

Oxygen gas and carbon dioxide gas, both containing 20 at% ¹⁸O, were supplied from British Oxygen Co. Ltd. (London, England).

Fe_{1-x}O and CoO sheet specimens were polished with abrasive paper (#280–1200), diamond paste (3 μm), and Al₂O₃ polishing powder (0.5 μm), and were pre-annealed for homogenization either in dried air, dried pure natural O₂ gas, or CO–CO₂ gas mixture at the same temperature and the same CO₂/CO ratio as in the diffusion annealing, but for a longer than the diffusion time. The pre-annealing time was long enough to attain a homogeneous composition throughout the samples after quenching with Ar gas. The samples of wustite were then chemically polished in concentrated phosphoric acid to remove the contaminated surface layer.

2. Experimental procedure of diffusion

The CoO diffusion annealing was done in a closed chamber apparatus⁽⁶⁾, the CoO sample covered with a platinum mesh holder being placed in a recrystallized alumina protecting tube within a quartz chamber. After evacuating the closed chamber to 10⁻¹ Pa, ¹⁸O₂ gas was introduced into the chamber to 21.3 kPa (0.21 atm), and then, a pre-heated furnace was

moved to cover the chamber. The chamber temperature was monitored by a Pt–13%Rh–Pt thermocouple, and the oxygen gas pressure was monitored and adjusted from time to time. At the end of the diffusion annealing, the furnace was removed, and the chamber was quenched by pouring water over it. The experimental conditions for the CoO samples are summarized in Table 1.

The diffusion annealing for all the Fe_{1-x}O samples was carried out in gas sealed quartz capsules⁽⁷⁾, in which the Fe_{1-x}O sheets were enclosed. A washed quartz tube of 26.5 mmID containing four separately placed samples in a platinum mesh holder was evacuated for at least 3.6 ks (1 h), and a mixture of C¹⁸O₂ gas and C¹⁶O gas were then introduced into the quartz tube. After 1.8 ks (30 min), during which the gas mixture was homogenized, four 100 mm long capsules were sealed off, each containing one sample and all with the same gas composition. The total pressure in the capsules at room temperature was so determined that it could be 101 kPa (1 atm) at the highest annealing temperature of four samples. The capsules were then placed in an annealing furnace, and at the end of the diffusion annealing, they were quenched in water. The experimental conditions for Fe_{1-x}O samples are summarized in Table 2.

3. Depth profiling method

The depth profiles of ¹⁸O and ¹⁶O in the diffusion annealed samples were obtained by measuring the intensity of negative singly charged ions with a Hitachi ion micro-analyzer

Table 1 Conditions for homogenization and diffusion annealing and determined diffusivities of CoO.

Sample No.	Temp.	Pre-ann. time	P _{O2}	Diff-ann. time	Tracer diffusivity	Evaporation rate
	K	10 ⁴ s	Pa	10 ⁴ s	m ² /s	m/s
1– 1	1323	9.36	81.1	8.64	4.51 × 10 ⁻¹⁹	3.64 × 10 ⁻¹⁰
5	1473	43.3	21.3	8.22	5.35 × 10 ⁻¹⁸	3.04 × 10 ⁻¹¹
6	1573	37.8	21.3	3.51	2.94 × 10 ⁻¹⁷	1.07 × 10 ⁻¹⁰
11	1273	92.5	21.3	14.0	2.20 × 10 ⁻¹⁹	4.91 × 10 ⁻¹⁰
20	1516	12.6	21.3	1.90	1.32 × 10 ⁻¹⁷	4.42 × 10 ⁻¹¹
23	1408	7.73	21.3	8.65	2.30 × 10 ⁻¹⁸	1.80 × 10 ⁻¹¹
24	1298	7.95	21.3	4.22	1.67 × 10 ⁻¹⁹	5.15 × 10 ⁻¹²
30	1408	10.5	21.3	4.33	1.66 × 10 ⁻¹⁸	1.15 × 10 ⁻¹¹

Table 2 Conditions for homogenization and diffusion annealing and determined diffusivities of Fe_{1-x}O .

Sample No.	Temp. K	Pre-ann. time 10^4 s	$p_{\text{CO}_2}/p_{\text{CO}}$	p_{O_2} Pa	x in Fe_{1-x}O	Dif.-ann. time 10^3 s	C_s/C_g	Tracer diffusivity m^2/s	Reaction rate constant m/s
2-7	1290	15.2	2.74	1.20×10^{-8}	0.104	10.8	0.828	3.72×10^{-16}	1.75×10^{-10}
8	1455	15.1	2.74	4.70×10^{-6}	0.110	1.86	0.893	7.51×10^{-15}	2.30×10^{-9}
10	1290	7.91	1.00	1.59×10^{-9}	0.074	10.8	0.750	5.64×10^{-17}	5.95×10^{-11}
11	1455	7.95	1.00	6.26×10^{-7}	0.080	1.86	0.825	3.04×10^{-15}	1.20×10^{-9}
12	1455	7.95	1.00	6.26×10^{-7}	0.080	1.86	0.885	5.84×10^{-15}	2.01×10^{-9}
13	1093	6.41	1.74	3.66×10^{-13}	0.093	112.0	0.618	5.98×10^{-18}	4.38×10^{-12}
15	1290	6.38	1.74	4.85×10^{-9}	0.094	10.8	0.708	1.05×10^{-16}	7.19×10^{-11}
16	1290	6.38	1.74	4.85×10^{-9}	0.094	10.8	0.721	2.70×10^{-16}	1.18×10^{-10}
17	1455	6.40	1.74	1.90×10^{-6}	0.097	1.86	0.753	1.00×10^{-14}	1.86×10^{-9}
18	1455	6.40	1.74	1.90×10^{-6}	0.097	7.20	0.708	7.22×10^{-15}	7.04×10^{-10}
21	1290	8.17	0.562	5.05×10^{-10}	0.059	10.8	1.00	5.63×10^{-16}	—*
22	1455	8.13	0.562	1.98×10^{-7}	0.064	1.86	1.00	5.11×10^{-15}	—*
23-1	1193	9.85	1.00	2.20×10^{-11}	0.060	39.7	0.690	3.79×10^{-18}	6.69×10^{-12}
23-2	1193	9.85	1.00	2.20×10^{-11}	0.060	39.7	0.675	6.89×10^{-18}	8.97×10^{-12}
28	1455	13.2	5.62	1.99×10^{-5}	0.125	1.86	0.817	1.81×10^{-14}	2.78×10^{-9}

* K value was too large to estimate.

(IMA).

The conditions of the IMA were in general the same as those in a previous report⁽⁶⁾. After each analysis, the diameter and the depth of the ion etched crater were measured with a surface profilometer. Flat bottomed craters were obtained, typical crater profiles for Fe_{1-x}O and CoO being shown in Fig. 1.

III. Results

Typical measurements of the depth profile of the oxygen isotopes in CoO and Fe_{1-x}O are shown in Figs. 2 and 3, respectively. C_g and C_0 are the initial concentration of ^{18}O in the gas phase and in the solid phase, respectively, and C is the concentration of ^{18}O in the solid at depth x , and C_s is the concentration of ^{18}O at surface of the solid phase ($x=0$). The initial concentration (C_0) is considered to be the sum of the concentration of naturally occurring ^{18}O and the background in the IMA analysis. In this study, the ^{18}O concentration in a region far from the diffusion penetration was very close to the natural ^{18}O concentra-

(a) CoO sample No. 1-30

(b) Fe_{1-x}O sample No. 2-17

Fig. 1 Profilometric measurements of sputtered craters.

Fig. 2 Measured concentration profiles of ^{18}O in CoO . Solid line shows the theoretical curve of eq. (A-4) from calculated D and V .

Fig. 3 Measured concentration profiles of ^{18}O in Fe_{1-x}O . Solid line shows the theoretical curve of eq. (A-3) from calculated D and K .

tion (0.204 at %).

The distance from the surface in Figs. 2 and 3 was calculated from the sputter time and the sputter rate, the latter being determined from profilometer measurements of the crater depth.

In the case of CoO , evaporation from the surface could not be ignored, for deposition of CoO on the Al_2O_3 protecting tube were clearly observed after each diffusion annealing, and in addition, the inverse error function plot of $(C - C_0)/(C_s - C_0)$ along with eq. (A-1) was not linear but convex upward. The diffusivities were, therefore, calculated by eq. (A-4), in which the evaporation effect was taken into account.

The values of D calculated from eq. (A-4) are plotted against the reciprocal temperature

Fig. 4 Arrhenius plot of tracer diffusivities of oxygen in single crystalline CoO and polycrystalline Fe_{1-x}O .

in Fig. 4. The equation of best fit for the measured D values for $p_{\text{O}_2} = 21$ kPa (0.21 atm) can be expressed as

$$D/\text{m}^2 \cdot \text{s}^{-1} = (8.76 \pm 5.67) \times 10^{-8} \times \exp [-(287 \pm 18 \text{ kJ/mol})/RT],$$

where R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and T is the temperature in K. The D values are listed in Table 1. The surface evaporation rate constant was simultaneously obtained, and listed in Table 1. The V values are plotted against the reciprocal temperature in Fig. 5, and can be expressed as

$$V/\text{m} \cdot \text{s}^{-1} = (2.65 \pm 1.59) \times 10^{-5} \times \exp [-(167 \pm 16 \text{ kJ/mol})/RT].$$

For Fe_{1-x}O , the surface ^{18}O composition was different from that of the gas phase. This indicates that ^{18}O transfer from the gas phase to the solid phase was controlled not only by diffusion in the solid but also by an oxygen surface exchange reaction.

Fig. 5 Arrhenius plot of surface reaction rate constants K for Fe_{1-x}O and evaporation rate constants V for CoO.

The values of D and K for Fe_{1-x}O were determined from eq. (A-3) by the least squares method, and are listed in Table 2. The calculated values of D and K are plotted against the reciprocal temperature in Figs. 4 and 5, respectively. The equation of best fit for the measured D values for Fe_{1-x}O and $p_{\text{CO}_2}/p_{\text{CO}} = 1.00$ can be expressed as

$$D/\text{m}^2 \cdot \text{s}^{-1} = (1.17 \pm 0.78) \times 10^{-1} \times \exp [-(375 \pm 23 \text{ kJ/mol})/RT].$$

The surface reaction constant can be expressed as

$$K/\text{m} \cdot \text{s}^{-1} = (48.7 \pm 27.5) \times \exp [-(293 \pm 14 \text{ kJ/mol})/RT].$$

In Fig. 6, the D values at 1455 K are plotted against the composition x in Fe_{1-x}O . The values of x were estimated from the CO_2/CO ratio⁽⁸⁾⁻⁽¹⁰⁾ at this temperature.

For CoO samples diffusion-annealed by the

Fig. 6 Dependence of tracer diffusivity of oxygen on composition x in Fe_{1-x}O .

sealed capsule method in a C^{18}O – C^{16}O gas mixture with a CO_2/CO ratio ranging from 10 to 50, the Ar^+ ion-bombarded surface was positively charged. The built-up charge was eliminated by the electron spray method⁽⁷⁾, but the intensity of the positive ions, including ^{18}O and ^{16}O , was too small and the errors too great to calculate the D value.

IV. Discussion

For some CoO samples, the surface concentration of ^{18}O was slightly smaller than the initial concentration of the gas, indicating that the gas composition changed to a similar degree. For the D calculation using eq. (A-4), however, the surface composition (C_s) was assumed to be unchanged. This assumption caused a small relative error in the calculated D value, i.e. 10%, in comparison with the further assumption that C_s be $0.848 C_b$, based on the minimum value of C_s .

Regarding oxygen tracer diffusivities in CoO, three studies have been reported. One is a measurement at $p_{\text{O}_2}=0.13$ atm (13 kPa) at 1273 K by Thompson⁽¹¹⁾, using the mass spectrometric analysis of the gas phase. His data are 10^5 times larger than the present one. Another is a report of Holt⁽¹²⁾, who used the proton activation technique at $p_{\text{O}_2}=0.17$ atm (17 kPa) at 1673 K, giving a slightly larger value than the present data. The third report is by Chen and

Jackson⁽¹³⁾, who measured the change in the gas phase composition due to the uptake of ^{18}O into the CoO at $p_{\text{O}_2}=0.21$ atm (21 kPa) between 1448 and 1833 K. Their data, shown in Fig. 4, are greater by nearly one order of magnitude than the present data. This large discrepancy is considered to be due to the evaporation having been ignored in Chen and Jackson's report. The apparent amount of ^{18}O take-up in their mass spectrometric method is considered to include the amount taken up by evaporated CoO as well as that which diffused into solid CoO sample. Taking this evaporation effect into account, their D values become smaller and closer to the present values.

The calculated evaporation rate constants of CoO in this work were rather fast, ranging from 4.0×10^{-12} to 3.0×10^{-11} m/s, compared with the value of NiO due to Dubois⁽¹⁴⁾, about 10^{-14} (m/s) at 1600 K. The apparent activation energy for evaporation of CoO in the present study was calculated to be 167 kJ/mol, which was small compared with the reported value of the activation energy of evaporation, 440 kJ/mol⁽¹⁵⁾. This result indicates that the present evaporation condition was intermediate between free evaporation in a small chamber and equilibrium evaporation.

The D value of sample No. 1–1 for $p_{\text{O}_2}=81$ kPa (0.80 atm) is apparently higher than that expected from the best fit equation for $p_{\text{O}_2}=21$ kPa (0.21 atm) shown in Fig. 4. This result is in good agreement with Seltzer *et al.*'s report⁽¹⁶⁾ that the steady state creep rate increases with increasing p_{O_2} . A similar dependence of the oxygen diffusivity has been reported for NiO by O'Keefe and Moore⁽¹⁷⁾.

The measurements for Fe_{1-x}O show larger scatter than those for CoO. Two reasons for this are possible. One is the anisotropy effect of the crystal structure on diffusion and sputtering. The crystal orientation of the diffusion direction varied from one sample to another, since the Fe_{1-x}O samples were polycrystalline and generally only one grain was analyzed in the IMA analysis. The anisotropy in diffusion is caused by the difference in the diffusion direction, but the error due to this effect would be small compared with that due to sputtering. The most probable source of error is considered

to be the anisotropy in sputtering. Two grains were simultaneously analyzed for sample Nos. 2–8, 12, 15, and 22, and the difference in the sputtering rate between the two grains caused a difference in the crater depth as large as $1.2\ \mu\text{m}$. The average of the two depths was used, giving rise to an error ($\pm 20\%$) in the evaluation of the diffusivity. The second possible reason, in the case of the polycrystalline Fe_{1-x}O samples, is enhanced diffusion along the grain boundaries, though, in this study, only one grain boundary was contained in the sputtered area and the area altered by grain boundary diffusion was negligibly small compared with the sputtered area (1 mm diam.).

There has been as yet no study of oxygen diffusion in Fe_{1-x}O . Ilschner, Reppich, and Riecke⁽¹⁸⁾ measured the steady state creep rate by a compression technique from 1273 to 1573 K. Their conclusion was that the mechanism of high temperature creep is the flow of oxygen vacancies between dislocations. Their results are in excellent agreement with the present ones in their activation energy being 326 kJ/mol for creep under constant composition x and the present value being 375 kJ/mol for the tracer diffusion of oxygen under a constant CO_2/CO ratio of 1.00.

The composition dependence of D in Fe_{1-x}O shown in Fig. 6 is expressed as

$$\log(D/\text{m}^2 \cdot \text{s}^{-1}) = 1.92 \log x - 12.1.$$

The slope for the steady state creep rate, due to Ilschner *et al.*, is compared with the present results in Fig. 6. Both the “diffusion” and the “creep” slopes are very close, indicating that the creep rate is determined by diffusion of oxygen. In view of the p_{O_2} or the composition dependence of D shown in Fig. 6, the simple vacancy mechanism can not be considered to operate on diffusion of oxygen in Fe_{1-x}O . This is because, if so, the diffusivity should decrease with increasing x or p_{O_2} .

The most plausible mechanism in Fe_{1-x}O , therefore, seem to be the interstitialcy diffusion via cation vacancy proposed by Howng and Wagner, Jr.⁽¹⁹⁾ for the diffusion of sulfur in NiO . This model may be simply expressed as⁽²⁰⁾

$$D = a_0 \gamma N_{\text{V}}^{\text{Fe}} N_{\text{I}}^{\text{O}},$$

where a_0 is the jump distance, γ is a geometrical factor, $N_{\text{V}}^{\text{Fe}} (= 2x)$ is the number of Fe vacancies, and N_{I}^{O} is the number of oxygen atoms diffusing via octahedral iron vacancies. Since N_{I}^{O} is considered to depend linearly on the number of Fe vacancies, the last equation is related to x as $D \propto x^2$, or $\log D \propto 2 \log x$. This relation is in good agreement with the present data in Fig. 6.

The activation enthalpy for diffusion in CoO and Fe_{1-x}O in the present study has been compared with other oxygen diffusivities in oxides with NaCl type structure. The enthalpy for MgO was reported to be 261⁽²³⁾ and 344⁽²⁴⁾ kJ/mol, and for CoO 397 kJ/mol⁽¹³⁾. The value for NiO was reported as 241⁽¹⁷⁾ and 538⁽¹⁴⁾ kJ/mol. The present values for CoO and Fe_{1-x}O were 287 and 375 kJ/mol (for $p_{\text{CO}_2}/p_{\text{CO}} = 1.00$), respectively, and are in intermediate between the other values.

V. Summary

The tracer diffusivity of oxygen in Fe_{1-x}O and CoO was estimated by the SIMS method. For Fe_{1-x}O , the diffusivity was calculated by taking into account the surface exchange reaction. The diffusivity was increased with increasing deviation from stoichiometry, x , and the mechanism for oxygen diffusion was suggested as an interstitialcy mechanism. The diffusivity of oxygen in CoO was calculated by taking into account the evaporation of CoO from surface, and was compared with reported values.

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Appendix

The solution of Fick's second law for semi-infinite media under constant surface concentration is solved as⁽²⁰⁾

$$(C - C_0)/(C_s - C_0) = \operatorname{erfc}(x/2\sqrt{Dt}), \quad (\text{A-1})$$

where C is the isotope concentration at time t and depth x , C_s is the concentration at the surface, C_0 is the initial concentration in solid, and D is the diffusivity.

When C_s varies with time due to surface exchange reaction, if the reaction is assumed to be of the first order, the boundary condition for diffusion at the solid surface is

$$-D(dC/dr)_{at r=0} = K(C_0 - C_s), \quad (\text{A-2})$$

where K is the rate constant of the exchange reaction. The solution of Fick's second law for this boundary condition is⁽²¹⁾

$$\begin{aligned} (C - C_0)/(C_g - C_0) = & \operatorname{erfc}(x/2\sqrt{Dt}) \\ & - \exp(hx + h^2Dt) \\ & \times \operatorname{erfc}(x/2\sqrt{Dt} + h\sqrt{Dt}), \end{aligned} \quad (\text{A-3})$$

where C_g is the ^{18}O concentration in the gas phase and $h = K/D$. This equation was used for the calculation of D in Fe_{1-x}O .

When the evaporation is of significance, eq. (A-1) can be modified to be⁽²²⁾

$$\begin{aligned} (C - C_0)/(C_s - C_0) = & 1/2 \\ = & \left[\operatorname{erfc}\left(\frac{x + Vt}{2\sqrt{Dt}}\right) + \exp\left(-\frac{Vx}{D}\right) \operatorname{erfc}\left(\frac{x - Vt}{2\sqrt{Dt}}\right) \right], \end{aligned} \quad (\text{A-4})$$

where V is the evaporation rate constant (m/s). This equation was used to obtain the D values in CoO .