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TRANSPORT PHENOMENON OF OXYGEN THROUGH MOLTEN $CaO-SiO_2$ SYSTEM CONTAINING ZINC AND/OR NICKEL OXIDES

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Synopsis: Oxygen transport rate through molten oxides containing p- or n-type semiconductor oxides individually or simultaneously has been observed. Transport mechanism of oxygen through molten oxide containing semiconductor oxide is discussed.

Key words: oxygen, molten oxide, semiconductor, NiO, ZnO, diffusion, temperature, partial pressure

1. Introduction

The authors have developed a thin film penetration method by using an oxygen concentration cell procedure in order to determine the oxygen transport rate through molten oxide. The authors also studied the transport rate through various oxide systems1)-6). Through a series of studies it has been revealed that the oxygen transport rate through molten oxide containing a p-type semiconductor oxide is much higher than that not containing one.

On the other hand Leewis et.al.7) and Pal et.al.8) have reported that the oxygen transport rate is raised when metal wires made of iridium or platinum were thrust into the molten slag phase from the gas phase. The reports by these authors and other researchers have suggested that the transportation of electrons in molten oxide plays an important role in the transportation of oxygen in molten oxide.

An object of research is to reveal if the same oxygen transport phenomenon can be observed in the case of an oxide containing n-type semiconductor. Another object is to reveal the oxygen transport phenomenon in the case of oxides containing both type semiconductors at the same time. Zinc and nickel oxides were preferred as n- and p-type semiconductors, respectively.

The experimental apparatus used in the study is the same as one developed by the authors1). Oxygen transfer rate, P, is defined as Eq. 1.

$$P = QL / S \qquad (1)$$

Where Q is the oxygen transport rate through molten thin oxide film per unit time (mol/s), L is thickness of the molten oxide film (cm) and S is surface area of the film (cm^2), therefore unit of P is mol $O_2 \cdot cm^{-1} \cdot S^{-1}$.

2. Observed Oxygen Transfer Rates

A master oxide is constituted with CaO and SiO_2 of which the molar ratio is 1 to 1. ZnO and NiO are added to the master oxide, individually or at the same time. Experimental temperatures are every 50 ^{o}C between 1450 and 1550 ^{o}C. The relation between the oxygen transport rate, P, and the contents of additive oxides at 1500 ^{o}C is shown in Fig.1 as an example of experimental results.

In the case of a system containing zinc oxide, the rate increases with increases in zinc oxide contents until 20 mol% then the rate decreases with increases in content. Relations between the oxygen transfer rate and the zinc oxide content can be expressed with Eq.2.

$$P = -8.5\times10^{-11} (\text{mol\% ZnO} -22)^2 + 4.2\times10^{-8} \qquad (2)$$

In the case of the system containing nickel oxide, the nickel oxide can dissolve into the master oxide till 12.5 mol%. In the case above 15 mol% NiO, non-dissolved nickel oxide particles are observed in the oxide mixture. On the basis of the above observation, experiments are carried out at less than 12.5 mol % NiO. Relations between the transfer rate and nickel oxide content can be expressed as Eq.3.

$$P = 3.15\times10^{-9} (\text{\% NiO}) \qquad (3)$$

The relations between the oxygen transfer rate and temperature are expressed as Eqs. 4 to 7.

10mol% ZnO - 45 mol% CaO - 45mol% SiO_2 :

$$P = 3.24\times10^{-2} \exp (-50 \times 10^3 / R T) \qquad (4)$$

20mol% ZnO - 40 mol% CaO - 40mol% SiO_2 :

$$P = 6.39\times10^{-2} \exp (-50 \times 10^3 / R T) \qquad (5)$$

30mol% ZnO - 35 mol% CaO - 35mol% SiO_2 :

$$P = 4.36\times10^{-2} \exp (-50 \times 10^3 / R T) \qquad (6)$$

7.6mol% NiO - 46.3mol% CaO - 46.3mol% SiO_2 :

$$P = 3.51\times10^{-2} \exp (-50 \times 10^3 / R T) \qquad (7)$$

where unit of the gas constant, R, is $cal.mol^{-1}.K^{-1}$.

The relation between the oxygen transfer rate and NiO content when NiO is added into the system containing ZnO is shown in Fig.2. The abscissa of Fig.2 shows NiO amount added into 100 mol% of ZnO-CaO-SiO_2 mixture, e.g., 5 mol% NiO on the line of 5 mol% ZnO corresponds to 4.8mol% NiO-4.8mol% ZnO-45.2mol% CaO-45.2mol% SiO_2.

The oxygen transfer rate, in the case of the addition of NiO to the ZnO system, decreases with an increase in NiO content and then it increases with increases in the NiO content. In every case of the system containing ZnO, the transfer rate indicates the minimum value when a ratio of ZnO to NiO reaches 1.65.

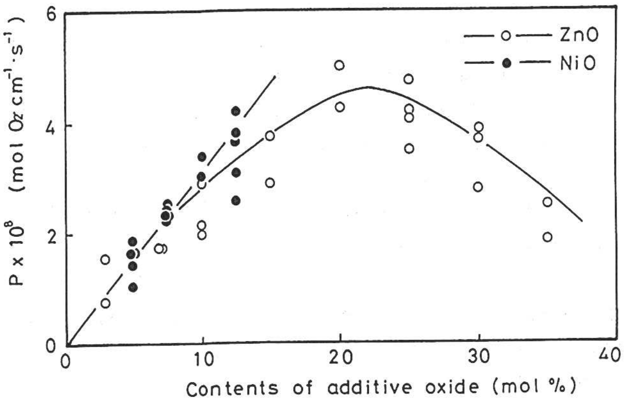

Fig.1 Relation between oxygen transfer and oxide content at 1500^{o}C

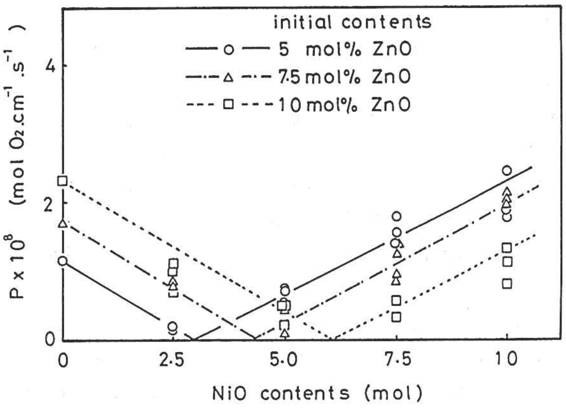

Fig.2 Effect of NiO content on oxygen transfer rate through molten oxide at 1500^{o}.

The effects of oxygen partial pressure at the surface of the molten oxide supplying oxygen on the oxygen transfer rate of the systems containing ZnO or NiO are expressed as Eqs. 8 to 11.

10 mol% ZnO -45 mol% CaO -45 mol% SiO_2:
$P = 2.23\mathrm{x}10^{-8}\ Po_2{}^{-1/4.2}$ (8)
20 mol% ZnO -40 mol% CaO -40 mol% SiO_2:
$P = 4.59\mathrm{x}10^{-8}\ Po_2{}^{1/5.7}$ (9)
30 mol% ZnO -35 mol% CaO -35 mol% SiO_2:
$P = 3.39\mathrm{x}10^{-8}\ Po_2{}^{1/1.6}$ (10)
7.5mol% NiO -4.36 mol% CaO -43.6 mol% SiO_2:
$P = 2.37\mathrm{x}10^{-8}\ Po_2{}^{1/3.6}$ (11)

where the unit of oxygen partial pressure is atm.

Dependencies of the transfer rate on the oxygen partial pressure in the case of a system containing NiO and ZnO at the same time are as follows:

2.4 mol% NiO -9.8 mol% ZnO -43.9 mol% CaO -43.9 mol% SiO_2
$P = 1.0 \times 10^{-8}\ Po_2{}^{-1/3.3}$ (12)
7.0 mol% NiO -4.7 mol% ZnO -44.2 mol% CaO -44.2 mol% SiO_2
$P = 1.6 \times 10^{-8}\ Po_2{}^{1/3.8}$ (13)

3. Discussion on Mechanism of Oxygen Transfer through Molten Oxides

The dissolution reactions of oxygen gas into an oxide mixture containing p- or n-type semiconductor oxides can be expressed as Eqs.14 or 15.

$1/2\ O_2 = O^{-2} + 2\ P^+$ (14)
$1/2\ O_2 + 2\ e^- = O^{-2}$ (15)

Where P^+ and e^- are the positive hole and the excess electron, respectively.

In order to maintain electrical neutrality in the oxide phase, Eqs.16 and 17 are required.

$2\ n_{O^{2-}} = n_{p^+}$ (16)
$2\ n_{O^{2-}} = n_{e^-}$ (17)

where $n_{O^{2-}}$, n_{p^+} and n_{e^-} are numbers of each specie.

When oxygen is transported in the oxide phase by a diffusion relation between the oxygen transfer rate, the diffusion constant and concentration difference can be expressed as Eq.18:

$P = D \quad C = D\ (\ C_{O^{2-}(h)} - C_{O^{2-}(l)}\ )$ (18)

where D is a diffusion coefficient of oxygen anions, C is concentration difference of oxygen anions, $C_{O^{2-}(h)}$ and $C_{O^{2-}(l)}$ are concentrations of oxygen anions at surfaces supplying and releasing oxygen, respectively. When $P_{O2}(h) >> P_{O2}(l)$, the Eq.18 can be expressed approximately as Eq.19:

$P = D \quad C = D\ C_{O^{2-}(h)}$ (19)

Equilibrium constants of reactions expressed with the Eqs.14 and 15 are expressed with Eqs.20 and 21.

$K_{14} = a_{O^{2-}}\ (\ a_{p^+}\ )^2\ /\ Po_2{}^{1/2}$ (20)
$K_{16} = a_{O^{2-}}\ /\ [\ Po_2{}^{1/2}\ (\ a_{e^-})^2\ ]$ (21)

where K_{14} and K_{15} are equilibrium constants, Po_2 is oxygen partial pressure and a is an activity. If it can be assumed that the activity coefficient of oxygen anion, O^{2-}, is constant, a_{e^-} is N_{e^-} and a_{p^+} is N_{p^+}, Eqs. 22 and 23 can be obtained, on the basis of the Eqs.20 and 21:

$N_{O^{2-}} = K'_{14}\ (N_{p^+})^{-2}\ Po_2{}^{1/2}$ (22)
$N_{O^{2-}} = K'_{15}\ (N_{e^-})^2\ Po_2{}^{1/2}$ (23)

where $N_{O^{2-}}$ is molar ratio of oxygen anion, K'_{14} and K'_{15} are constants.

There is a sufficient concentration of O^{2-} to diffuse if $N_{O^{2-}(h)} >> N_{p^+(h)}$ or

$N_{O^{2-}(h)} >> N_{e^{-}(h)}$. However the diffusion flux of O^{2-} is determined with the concentration of the positive hole or excess electron in order to maintain electrical neutrality in the oxide system.

If it can be assumed that $C_{O^{2-}(h)} = \alpha N_{p^{+}(h)}$ or $C_{O^{2-}(h)} = \alpha' N_{e^{-}(h)}$ and $N_{O^{2-}(h)}$ is a constant, Eqs.24 or 25 can be obtained on the basis of the Eqs.19 and 22 or 23, where α and α' are constants.

$$P = K''_{14} P_{O2}{}^{1/4}{}_{(h)} \qquad (24)$$

$$P = K''_{15} P_{O2}{}^{-1/4}{}_{(h)} \qquad (25)$$

where K''_{14} and K''_{15} are constants.

Eq.24 suggests that the oxygen transfer rate is directly proportional to the 1/4 power of the oxygen partial pressure at the surface supplying oxygen, if the concentration of the positive hole is much smaller than that of the oxygen anion in the case of a system containing a p-type semiconductor oxide.

Eq.25 suggests that the oxygen transfer rate is direct proportional to the -1/4 power of the oxygen partial pressure at the surface supplying oxygen if the concentration of the excess electron is much smaller than that of the oxygen anion in the case of a system containing a n-type semiconductor oxide.

On the other hand if $N_{O^{2-}(h)} << N_{p^{+}(h)}$ or $N_{O^{2-}(h)} << N_{e^{-}(h)}$, concentrations of the positive hole or excess electron to diffuse are enough. In this case it can be assumed that $C_{O^{2-}(h)} = \beta N_{O^{2-}}$, and $N_{p^{+}(h)}$ and $N_{e^{-}(h)}$ are constants. Where β is a constant. On the basis of Eqs,19, 22 and 23, Eq.26 can be obtained:

$$P = K''_{26} P_{O_2}{}^{1/2}{}_{(h)} \qquad (26)$$

where K''_{26} is constant.

The Eq.26 suggests that the oxygen transfer rate is directly proportional to the 1/2 power of the oxygen partial pressure at the surface in the case of a higher concentration of the positive hole or excess electrons, regardless of semiconductor type.

It is supported by the experimental results expressed as Eqs.4 to 13 that the estimations are correct.

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