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SURFACE-LAYER THICKNESS AND NEAR-SURFACE DIFFUSION OF OXYGEN IN $Y_2O_3$

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Abstract: Oxygen exchange reaction between $Y_2O_3$ and $^{18}O_2$ was monitored with a microbalance. Analyzing data the near-surface diffusion coefficient and the surface-layer thickness were obtained. The near-surface diffusion is 1-4 orders of magnitude faster than the oxygen lattice diffusion in the same system. The surface-layer thickness is similar to the thickness in $m-ZrO_2$ and is slightly larger than that in $NiO$.

I. Introduction

The oxides can be divided into two groups in terms of diffusional characteristics. First group includes $Al_2O_3$, $MgO$, $NiO$, etc. in which the cation lattice diffusion is faster than the anion lattice diffusion. The second group is the oxides in which the anion lattice diffusion is faster than the cation lattice diffusion. This includes $ZrO_2$, $Y_2O_3$, $UO_2$, etc. There are numbers of works\(^1\)-\(^{11}\) on the surface diffusion, $D_{surf}$ and the near-surface diffusion of oxygen, $D_{near}$, in the first system, especially in $Al_2O_3$. There are only few works\(^6\),\(^7\)\(^{12}\) on the surface diffusion in the second group of oxides. Even if the lattice diffusion of oxygen, $D_{lat}$ and the lattice diffusion of yttrium, $D_{Y}$ are included, there are only several works\(^13\)-\(^15\) in $Y_2O_3$. In this work, the near-surface diffusion of oxygen $D_{near}$ and the surface-layer thickness, $\delta$, of $Y_2O_3$ will be reported.

II. Experimental

High purity $Y_2O_3$ powder (99.9%) manufactured by Rare Metallic Co. (Tokyo, Japan) was used.\(^2\) It was calcined at 750°C in air for 18h. The powder of 0.14-0.18g was placed in a platinum crucible in vacuum system and $^{16}O_2$ gas was introduced into the system at the pressure of 6.6kPa. The temperature of the specimen was increased at the rate of 20-100K/min and was held constant at 300-650°C for 5-8h while the specimen's weight was monitored with a microbalance. When the weight change has ceased, it was assumed that the specimen has reached the equilibrium at that condition. It was cooled down to room temperature and the $^{18}O_2$ gas was evacuated. Oxygen enriched with $^{18}O_2$ was introduced into the system (6.6kPa). The temperature of the specimen was increased again at the same rate as before and was kept constant at the temperature where the previous annealing in $^{16}O_2$ was performed. The specimen's weight was monitored continuously. An exchange reaction
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\[ \text{Y}_2\frac{16}{18}\text{O}_3 + (3/2)\frac{18}{18}\text{O}_2 \rightarrow \text{Y}_2\frac{18}{18}\text{O}_3 + (3/2)\frac{16}{16}\text{O}_2 \]  

took place at the surface of the powder and \( ^{18}O \) diffused into the bulk by diffusion. The weight increase due to the reaction (1) is directly related to the diffusion of oxygen in \( \text{Y}_2\text{O}_3 \). The description of the experimental apparatus in detail was seen in elsewhere.

III. Data analysis and Results

Some typical weight changes \( \Delta w \) of the specimen that has been pre-annealed at 750°C were shown in Fig. 1. The weight change that has been observed before the specimen's temperature has reached the diffusional annealing temperature was also included. Time \( t \) in the figure was the time at the diffusional annealing temperature. The weight change at \( t=0 \) is, therefore, not zero.

The shape of the data points in Fig. 1 indicated that the diffusion in the surface layer is contributing to the overall shape of the curve. In order to get a good approximate values of \( D_s \) at each temperature, a straight line was drawn through data points at the small values of time as shown in Figure 1. Sometimes, the data at \( t=0 \) was ignored because it does not fall on a straight line for the reason that has already been discussed. A least square fit to these data gives the value shown in the second row \( (D_i) \) in Table I. With these values the time \( (t_0) \) that has been lost during the period when the temperature of the specimen did not reach the diffusional annealing temperature has been estimated according to the equation:

\[ (D_n t_0)^{1/2} = \frac{n-1}{\sum (D_i t_i)^{1/2}} \]

where \( D \) is the diffusion coefficient at diffusional annealing temperature, \( t=30s, 60s, \) and \( 150s \) for 100, 50, and 20K/min, respectively. If the specimen would be able to be heated instantaneously, \( \Delta w \) at \( t=0 \) would be zero. However, it was not so because the heating rate was finite. We have assumed that the

![Figure 1. Some typical weight gains of \( \text{Y}_2\text{O}_3 \) recorded with a microbalance during the diffusional annealing.](image)
Table I. Time ($t_0$/min) lost during the heating (at three heating rates) to the diffusional annealing temperature. $D_i$ shown in this table are only rough estimation. See the text for the details.

<table>
<thead>
<tr>
<th>$T/°C$</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
<th>600</th>
<th>650</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_i/1\times10^{-16} \text{cm}^2\text{s}^{-1}$</td>
<td>0.049</td>
<td>0.22</td>
<td>0.83</td>
<td>2.5</td>
<td>5.8</td>
<td>15.</td>
<td>32.</td>
<td>60.</td>
<td>110.</td>
<td>180.</td>
</tr>
<tr>
<td>at 100Kmin$^{-1}$</td>
<td>-</td>
<td>0.11</td>
<td>0.29</td>
<td>0.52</td>
<td>0.75</td>
<td>1.11</td>
<td>1.48</td>
<td>1.94</td>
<td>2.54</td>
<td>3.11</td>
</tr>
<tr>
<td>at 50Kmin$^{-1}$</td>
<td>-</td>
<td>0.22</td>
<td>0.58</td>
<td>1.03</td>
<td>1.51</td>
<td>2.22</td>
<td>2.97</td>
<td>3.88</td>
<td>5.08</td>
<td>6.23</td>
</tr>
<tr>
<td>at 20Kmin$^{-1}$</td>
<td>-</td>
<td>0.55</td>
<td>1.45</td>
<td>2.58</td>
<td>3.76</td>
<td>5.55</td>
<td>7.41</td>
<td>9.71</td>
<td>12.71</td>
<td>15.57</td>
</tr>
</tbody>
</table>

![Figure 2. Plots of $M_t/M_\infty$ for $Y_2O_3$. The curves are calculated with the method described in the text.](image)

times such as shown in Table I were lost during the heating; we have added those times to the diffusion time. Then the data were fitted to the solution of Ficks 2nd law for the diffusion in composite spherical solids:inserting approximate values of $D'_i$, $D'$, and $\delta$ into the equation and the values of $(M_t/M_\infty)$ were calculated, where $M_t$ is the total amount of $^{18}O$ in a specimen at time $t$ and $M_\infty$ is the corresponding quantity after an infinite time. By try and error, a set of $D'_i$, $D'$, and $\delta$ that gives a largest values of correlation factor $^{12,15}r^2$ was obtained. Some results of such calculations are shown in Fig. 2 by solid lines. The agreement between the experimental data and the calculated data is good. Consequently the values of $D'_i$, $D'$, and $\delta$ used for the calculation of the solid line was taken to be the $D'_i$, $D'$, and $\delta$ at the experimental condition. The near-surface diffusion of oxygen and the surface-layer thickness were shown in Figures 3 and 4. Also shown in Fig. 3 are the oxygen lattice diffusion coefficient $^{13,14}$ and the yttrium lattice diffusion coefficient. $^{15}$ The surface-layer thicknesses in other systems are included in Fig. 4.
Figure 3. Diffusion coefficients in Y$_2$O$_3$. Data on the diffusion coefficients of Y$_2$O$_3$ reported in the literature are also shown: $D_{1.0}$ and $D_{1.1}$.

Figure 4. Surface-layer thickness in Y$_2$O$_3$. The thicknesses in other oxides are also shown: MgO, Al$_2$O$_3$, Ni$_2$O, and m-ZrO$_2$. 

When the specimen was first annealed at 1300°C for 1.5h, it did not show the presence of $D$. The shape of the curve of $\Delta w$ vs $t^{1/2}$ using the specimen that has been annealed only at 750°C was quite different. This implies that the surface diffusion is not significant in $Y_2O_3$ once the specimen was annealed at higher temperatures.

IV. Discussion

Near-surface diffusion is very fast and takes place within a very short distance. That is why $\Delta w$ that corresponds to surface terminates quickly. When the heating rate is slow, it took long time to reach the temperature of diffusional annealing. Very important parts of the data during the heating may have been lost. Consequently the values of $D$ showed some scatter (Fig. 3). On the other hand, the values of $\delta$ did not show such scatter. The surface-layer thickness is not sensitive to the heating rate. The values of $\delta$ for all the experimental data fall on the same line in Fig. 4. Since the value of $\delta$ corresponds to the knee points in the figure, it seemed that even at the heating rate 20K/min, the information concerning the surface-layer thickness has not been lost.

A least square analysis to all the data shown in Figure 3 resulted in

$$D_{s,0} = 1.38 \times 10^{-12} \exp(-46.3 \text{ kJmol}^{-1}/RT) \text{ cm}^2 \text{s}^{-1}. \quad (3)$$

The activation energy of $D_s$ was 191 and 125kJmol$^{-1}$. The activation energy for $D_{s,0}$ is smaller than that for $D_s$. Similar phenomenon was observed in $\delta$ and $Al_2O_3$. If we follow the discussion made for MgO, the activation energy obtained in this work corresponds to the migration energy of oxygen in the surface layer of $Y_2O_3$. The near-surface diffusion is 1-4 orders of magnitude faster than the lattice diffusion in the temperature range studied. However, they will be almost equal to each other at about 1000°C. This can be seen easily in the curve of $\Delta w$ vs $t^{1/2}$ plot when the experimental temperature is higher than 700°C: the curve is almost straight from $t=0$ to large values of $t$. At these temperatures, $D_{s,0}$ can only be determined.

The least square fit to all the data in Fig. 4 resulted in

$$\delta = 5.79 \times 10^{2} \exp(-29.6 \text{ kJmol}^{-1}/RT) \text{ nm}. \quad (4)$$

The temperature dependence of surface-layer thickness in $Y_2O_3$ is the largest among the data summarized in Fig. 4 which only includes data of static method. The surface-layer thickness in $Y_2O_3$ is very large compared to $\delta$ in $Al_2O_3$ and MgO and it is similar to $\delta$ in $ZrO_2$ and slightly larger than that in NiO.

In the previous papers, we have been assumed that $t$ is unknown and tried to fit the data to find the sets of the values of $D_{s,0}, D_{s,0}^{i}, \delta$ and $t$ that gives the largest value of $\eta$. We always find that the process is time consuming and that $t$ so found was large. Since $t$ should be constant that depends only upon the experimental condition and should not be a variable, the best way to estimate it is to get the approximate value of $D_{s,0}$ as was done in this paper. This is the proper way of estimating the lost time ($t_0$).

V. Conclusion

The near-surface diffusion of oxygen in $Y_2O_3$ was represented by eq. (3) in the temperature range 300-650°C. It was 1-4 orders of magnitude faster than the oxygen lattice diffusion in the system. The surface-layer thickness in $Y_2O_3$ was represented by eq. (4) in the temperature range 300-650°C.
References