Oxygen Permeability of Y$_2$SiO$_5$

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The oxygen permeation through a wafer of Y$_2$SiO$_5$ has been measured in the temperature range from 1973 to 2033 K and the oxygen permeability constant of Y$_2$SiO$_5$ has been determined, because Y$_2$SiO$_5$ is favorable for the outer layer of our proposed oxidation protection double layered coating on C/C composites. We presented a data reduction, which can separate lattice diffusion through the wafer from other contributions. The experimental data are in agreement with previous data reported in the literature for Ca stabilized zirconia and alumina in a maximum error of 10$^{-12}$ kg/(m-s). The oxygen permeability constant of Y$_2$SiO$_5$ at 1973 K is 10$^{-10}$ kg/(m-s). A 100µm-thick Y$_2$SiO$_5$ outer layer would extend a life time of a 100µm-thick SiC inner layer up to 70 hours, assuming that the SiC layer is consumed by oxygen permeated through the Y$_2$SiO$_5$ layer. The mechanism of the oxygen transport is discussed in accordance with the activation energy of the oxygen permeation and relationship between the oxygen permeability constants and oxygen partial pressure. Experimental results indicate that vacancy diffusion is dominant below 1913 K and interstitial diffusion is dominant above 1913 K. It is estimated that there is a mechanism to switch vacancy diffusion to interstitial diffusion with increasing temperature, because interstitial diffusion should not be active at higher temperature.

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1. Introduction

Carbon/carbon (C/C) composites are attractive for high temperature applications such as re-entry vehicles and space planes. Most of these applications have to consider oxidizing atmospheres, thus C/C composites need oxidation resistant coatings. SiC is a reliable coating material due to formation of a stable SiO$_2$ film on SiC below 1773 K, but the use at higher temperature is limited by vaporization of SiO$_2$ by SiO formation and detrimental interfacial reaction between SiO$_2$ and SiC. Therefore, the development of a high-performance oxidation resistant coating on C/C composites is required. Especially it is important for H-II Orbiting Plane-Experimental (HOPE-X), because the surface temperature of the nose cone and the leading edge of HOPE-X is estimated to reach 1973 K during the re-entry.

One approach for developing oxidation resistant coatings is to apply an outer erosion resistant layer to SiC coating. It was found that Y$_2$SiO$_5$ has favorable properties for the outer erosion resistant layer$^{1,2}$, a high melting point, a same thermal expansion coefficient as that of the SiC inner layer$^3$ and a low vaporization rate. Adding to these properties, low oxygen permeability is important for the outer layer, but the oxygen permeability for Y$_2$SiO$_5$ at high temperature is not clear. The aim of the study is to determine the oxygen permeability of Y$_2$SiO$_5$ in order to evaluate its applicability as the outer protection shield.

Two methods to determine oxygen permeabilities at high temperature have been proposed. Criscione et al. measured the oxygen permeated from outside containing oxygen to inside vacuum through a induction-heated tubular specimen by a mass spectrometer$^4$ and determined the oxygen permeabil-

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sities and crystal structure of specimens are shown in Table 1. Y$_2$SiO$_5$ specimens consists mostly Y$_2$SiO$_5$ phase with a little Y$_2$O$_3$ phase.

2.2 Apparatus and experimental procedure

The oxygen permeability was measured with a specially designed apparatus shown in Fig. 1 with a reference to previous work.\textsuperscript{5} Test wafers between the end of weight-loaded high-purity Al$_2$O$_3$ tubes (Nikkato, SSA-S) were sealed with platinum gaskets. These Al$_2$O$_3$ tubes provided two opposing chambers, an upper chamber containing a mixture of argon and oxygen and a bottom chamber containing high-purity argon (O$_2 < 0.2$ vol ppm). The two chamber imposed an oxygen potential gradient across the test wafer. An alignment tube prevented misalignment of the upper tube and the specimen as shown in Fig. 2. An outer shroud tube helped to reduce oxygen diffusion from the outside. Oxygen permeated across the test wafer was swept up by high-purity argon flow and carried to an oxygen sensor (Toray Engineering Co. Ltd., LC-750L), which allows a minimum oxygen concentration of 0.1 vol ppm to be detected. This assembly was positioned within a vertical molybdenum heater furnace. Measurement procedure was as follows: (1) heating up the test wafer up to 1973 K, (2) loading the weights to seal, (3) introducing argon-oxygen mixture into the upper chamber and high-purity argon into the bottom chamber at 1.67 x 10$^{-6}$ m$^3$/s and keeping for 36 ks ~ 500 ks, estimated from $I^2/3D$, to attain a stable state, (4) measuring the oxygen concentration in the bottom chamber under thermal cycles between 1273 K and 2023 K at a rate below 6.67 K/s.

2.3 Data conversion

In this section firstly we introduce a basic theory about oxygen permeation through a membrane and then extend it to a description containing the oxygen penetration by gas diffusion. The oxygen permeability constant $P_l$ is defined as the product of the oxygen permeation rate per unit area $P$ and the thickness of the coating $t$ under difference of oxygen partial pressure of 2.1 x 10$^4$ Pa between each side of the coating.\textsuperscript{4} Oxygen permeation consists of three process, namely dissolving into a coating, diffusing through the coating and degassing from the coating. If the diffusion is the rate-determining step, oxygen defect formation at each surface is in equilibrium and the concentration of oxygen defects is given by the oxygen partial pressure.

Consider the case of uni-directional diffusion under constant temperature $T$ and constant oxygen partial pressure $p_1$(O$_2$) and $p_2$(O$_2$) at each surface, oxygen flux $P$ through a plane of unit area is written as

$$P = -D \frac{\partial C}{\partial x} = -D \frac{k p_2^n(O_2) - k p_1^n(O_2)}{l}$$

(1)

where $\partial C/\partial x$ is a gradient of oxygen defect concentration, $D$ oxygen diffusion coefficient and $k$ equilibrium constant. The exponent $n$ depends on the oxygen defect reaction on the surface. Under the condition of $p_1(O_2) \gg p_2(O_2)$, the oxygen permeability constant $P_l$ can be written as

$$P_l = Dk p_1^n(O_2)$$

(2)
Table 2  Composition, densities, thicknesses and diffusion parameters of reference specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Composition</th>
<th>Density, ρ/kg · m⁻³</th>
<th>Thickness, l/mm</th>
<th>Diffusion coefficient at 1973 K, D/m²·s⁻¹</th>
<th>ρ²/3D/ks</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSZ</td>
<td>94 mass% ZrO₂</td>
<td>5500</td>
<td>1.00</td>
<td>2.3 × 10⁻¹¹</td>
<td>15</td>
<td>ZR-11, Nikkato</td>
</tr>
<tr>
<td>AL-1</td>
<td>99.5 mass% A1₂O₃</td>
<td>3900</td>
<td>1.00</td>
<td>6.6 × 10⁻¹³</td>
<td>505</td>
<td>SSA-S, Nikkato</td>
</tr>
<tr>
<td>AL-2</td>
<td>99.5 mass% A1₂O₃</td>
<td>3900</td>
<td>0.50</td>
<td>6.6 × 10⁻¹⁵</td>
<td>126</td>
<td>SSA-S, Nikkato</td>
</tr>
</tbody>
</table>

$D$ and $k$ are functions of temperature as follows,

$$D = D_0 \exp \left( -\frac{E_d}{RT} \right)$$

$$k = k_0 \exp \left( -\frac{E_s}{RT} \right)$$

where $E_d$ is the activation energy for diffusion and $E_s$ is the activation energy for the oxygen defect reaction on the surface. Substituting eqs. (3) and (4) in eq. (2) and neglecting $E_s$ because of $E_d \gg E_s$ in general, we obtain

$$Pl = D_0 k_0 P_i^{n}(O_2) \exp \left( -\frac{E_d}{RT} \right)$$

$n$ can be 1/6 or 1, depending upon the type of defect interactions; $n$ would be 1/6 for oxygen vacancies and 1 for molecular oxygen.

If a test wafer is dense and oxygen penetrated from openings at connections is negligible, the observed oxygen concentration in the bottom chamber would be due to oxygen permeation by lattice diffusion through the wafer. Therefore, it is given by the following expression.

$$C_p = \frac{PV_0 S}{QMO_2} = c_0 \exp \left( -\frac{E_d}{RT} \right)$$

where $C_p$ is measured oxygen concentration of carrier gas, $V_0$ standard molar volume of ideal gas, $S$ the area of the wafer, $Q$ flow rate of the carrier gas, $MO_2$ molar weight of oxygen.

For a thin Y₂SiO₅ wafer which might have open pores and cracks, however, the measured oxygen concentration contains not only oxygen permeated through the wafer by lattice diffusion but also oxygen penetrated by gas diffusion through openings at connections and cracks in the wafer. Therefore it is necessary to separate the contribution of oxygen permeation by lattice diffusion through the wafer from the other contributions. We propose a data conversion by specific temperature dependence of the each contribution.

The oxygen penetration paths for gas diffusion is considered to consist of two kinds of paths, one is cold paths through openings at connections outside the furnace and the other is hot paths through cracks in the wafer inside the furnace. The contribution of oxygen penetration through cold paths to oxygen concentration $C_c$ is independent on the temperature and we can give it a constant.

$$C_c = c_1$$

The contribution of oxygen penetration through hot paths to oxygen concentration $C_h$ is proportional to the gas diffusion coefficient of oxygen $D_h$ which is a function of temperature. According to gas dynamics, $D_h$ is written approximately by

$$D_h = \frac{1}{3} \langle v \rangle \lambda$$

where $\langle v \rangle$ is the average speed of oxygen molecular and $\lambda$ the mean free path of the molecular. The temperature dependence of $\langle v \rangle$ and $\lambda$ is respectively expressed as follows,

$$\langle v \rangle \propto T^{1/2}$$

$$\lambda \propto T$$

With the width of the cracks $r$, the temperature dependence of the contributions are given as follows.

$$C_{h1} = c_2 T^{1/2} \quad \text{for } r < \lambda$$

$$C_{h2} = c_3 T^{3/2} \quad \text{for } r > \lambda$$

Therefore theoretical oxygen concentration in the bottom chamber $C_t$ which contains all contributions can be expressed by

$$C_t = C_p + C_c + C_{h1} + C_{h2} = c_0 \exp(-E_d/RT) + c_1 + c_2 T^{1/2} + c_3 T^{3/2}$$

Observed oxygen concentrations were treated by least-square fitting for obtaining the parameter in eq. (13). The oxygen permeability constant was determined by substitution of $c_0$ and $E_d$ into eq. (6).

In order to check the performance of the apparatus, the oxygen permeabilities of Ca stabilized ZrO₂ (CSZ) and high-

![Fig. 3 Temperature dependence of oxygen content in the bottom chamber for AL-1.](image-url)
purity Al₂O₃ (AL-1, AL-2) was measured. Composition, density, thickness and diffusion parameter of the specimens are shown in Table 2. The measured oxygen concentration-temperature curve for AL-1 is shown in Fig. 3. Figure 3 indicates that theoretical curve expressed by eq. (13) fits the experimental data. The oxygen permeability constant derived from the measured oxygen concentration is shown in Fig. 4. The error bars in Fig. 4 correspond to the scattering in the measured values. The oxygen permeabilities of CSZ are in good agreement with the data reported by Criscione et al.4 but as for AL-1 and AL-2, the experimental data exhibited positive deviation from the data reported by Courtright and Prater.6 Volk and Meszaros7 in the lower temperature region. It is due to the experimental error which relatively increase with decreasing temperature. The measured oxygen concentrations for AL-1 and AL-2 are in error by 1 vol ppm, which correspond to oxygen permeability constant of 4 × 10⁻¹² kg/(m-s) and 7 × 10⁻¹² kg/(m-s) respectively. It can be concluded that the accuracy of the oxygen permeability measurement was better than 10⁻¹¹ kg/(m-s).

3. Results

The measurements were performed 1 to 3 times for a same specimen without cooling the specimen down to room temperature. Figures 5 to 7 shows the temperature dependence of the oxygen concentration in the bottom chamber for YSO-1, YSO-2 and YSO-3. The plots for YSO-2 and YSO-3 exhibited negative deviations from exponential curves above 1913 K. The data points below 1913 K were subjected to least-squares fitting by the eq. (13), to obtain the parameters. The data above 1913 K have not only deviation from an exponential curve but also poor reproducibility, even decrease with temperature increasing in contrast to an excellent reproducibility of the oxygen permeability below 1913 K. Table 3 shows the fitting parameters derived from the results. The fitting parameter c₃ were omitted in Table 3, because C₉₂ were negligible in comparison with C₉₁. The parameter c₀ corresponds to the amount of leakage from connections and have a minimum of 11.4 vol ppm. The parameter Eₐ corresponds to the activation energy of diffusion and are in the range from 227 to 349 kJ/mol. Subtracting Cₐ and C₉₁ from observed values and substituting the obtained values into eq. (6), we obtained the oxygen permeability constants of Y₂SiO₅. Figure 8 shows the oxygen permeability constants with literature data of refractory oxides.5,6 The error bars correspond to the scatter in the obtained values.

Figure 9 shows variation of oxygen permeability constant with oxygen partial pressure in the upper chamber at 2013 and 1983 K. In both case, the oxygen permeability constants are proportional to oxygen partial pressure in the upper chamber.

The cross-section of the specimens YSO-2 before and after the oxygen permeability measurement are shown in Fig. 10.
<table>
<thead>
<tr>
<th>Specimen</th>
<th>c₀ (vol ppm)</th>
<th>c₁ (vol ppm)</th>
<th>Eₐ/kJ · mol⁻¹</th>
<th>c₂/vol ppm T¹/²</th>
<th>R</th>
<th>T/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSO-1</td>
<td>run1 230</td>
<td>3.8 × 10⁹</td>
<td>290</td>
<td>5.013</td>
<td>0.99948</td>
<td>1653–1973</td>
</tr>
<tr>
<td></td>
<td>run1 11</td>
<td>3.5 × 10⁸</td>
<td>239</td>
<td>0.004</td>
<td>0.99984</td>
<td>1333–1893</td>
</tr>
<tr>
<td>YSO-2</td>
<td>run2 11</td>
<td>1.5 × 10⁸</td>
<td>227</td>
<td>0.005</td>
<td>0.99984</td>
<td>1333–1893</td>
</tr>
<tr>
<td></td>
<td>run3 12</td>
<td>2.5 × 10⁸</td>
<td>235</td>
<td>0.101</td>
<td>0.99937</td>
<td>1323–1903</td>
</tr>
<tr>
<td>YSO-3</td>
<td>run1 335</td>
<td>8.9 × 10¹²</td>
<td>327</td>
<td>15.159</td>
<td>0.99965</td>
<td>1363–1913</td>
</tr>
<tr>
<td></td>
<td>run2 312</td>
<td>3.2 × 10¹¹</td>
<td>349</td>
<td>15.254</td>
<td>0.99963</td>
<td>1303–1913</td>
</tr>
</tbody>
</table>

Fig. 7  Temperature dependence of oxygen content in the bottom chamber for YSO-3.

Fig. 8  Oxygen permeability constants of Y₂SiO₅ and Y₂O₃ (thick lines) with literature data of refractory oxides⁴⁻⁶ (thin lines). The error bars correspond to the scatter in obtained values.

Fig. 9  Variation of oxygen permeability constants of YSO-2 and YSO-3 with oxygen content in the upper chamber.

The specimens were subjected to energy dispersive X-ray analysis following the measurement. The concentration profiles in the cross-section indicate that demixing took place and it led to an enrichment of Y₂O₃ at the higher oxygen potential side (the upper side) and an enrichment of SiO₂ at the opposite side. The demixing is considered to be due to an oxygen potential gradient across the wafer as reported by Laqua and Schmalzried.⁸ According to the report, the chemical potential of AO in multicomponent oxide AₓB₁₋ₓO, in which D₀ ≪ Dₐ, Dₓ, given by

\[ d\mu_{AO} = \frac{(1 - x)(\beta - 1)}{x + (1 - x)\beta} d\mu_O \]  

where \( \beta \) stands for \( D_A / D_B \). In the case of \( Y_2SiO_5 \), \( d\mu_{Y_2O_3} \) is negative therefore \( \beta < 1 \). The order of the diffusion constants is given by

\[ D_0 \ll D_{Si} < D_x \]  

4. Discussion

Oxygen transport properties of a material are ultimately related to the presence of defects and the crystal structure. \( Y_2SiO_5\) (B-type) consists of one-dimensional \( Y^{3+} - O^{2–} \) chains and isolated \( SiO_4 \)-tetrahedrons.⁹ There are two possible mechanisms for oxygen transport in \( Y_2SiO_5 \). One is vacancy mechanism where vacancies at \( O^{-} \) sites in the \( Y^{3+} - O^{2–} \) chains may play dominant role. Another is inter-
Table 4 Activation energies of oxygen permeation through $\text{Y}_2\text{SiO}_5$, $\text{Y}_2\text{O}_3$ and $\text{SiO}_2$.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$E_a$/kJ·mol$^{-1}$</th>
<th>Mechanism</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Y}_2\text{SiO}_5$</td>
<td>227–349*</td>
<td></td>
<td>Oxygen permeability</td>
<td>Current work</td>
</tr>
<tr>
<td>$\text{Y}_2\text{O}_3$</td>
<td>306**</td>
<td></td>
<td>Oxygen permeability</td>
<td>Current work</td>
</tr>
<tr>
<td>$\text{Y}_2\text{O}_3$</td>
<td>233</td>
<td></td>
<td>Oxygen permeability</td>
<td>6)</td>
</tr>
<tr>
<td>$\text{Y}_2\text{O}_3$</td>
<td>160</td>
<td>Vacancy</td>
<td>Conductivity</td>
<td>10)</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>82–121</td>
<td>Interstitial</td>
<td>SIMS</td>
<td>11)</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>234–298</td>
<td>Vacancy</td>
<td>SIMS</td>
<td>11)</td>
</tr>
</tbody>
</table>

*: 1303 K-1913 K  **: 1673 K-1953 K

Fig. 10 Concentration profiles of Y, Si and O for YSO-2 (a) before and (b) after the oxygen permeability measurement.

The interstitial diffusion of molecular oxygen as observed in silicates glasses. Table 4 shows comparison of the activation energy of oxygen permeation through $\text{Y}_2\text{SiO}_5$, $\text{Y}_2\text{O}_3$, and $\text{SiO}_2$. The activation energy of $\text{Y}_2\text{SiO}_5$ is close to that of vacancy diffusion and much higher than that of interstitial diffusion of molecular oxygen. Therefore it is considered that vacancy diffusion is dominant in oxygen transport through $\text{Y}_2\text{SiO}_5$ below 1913 K.

On the contrary, the proportional relationship between the oxygen permeability of $\text{Y}_2\text{SiO}_5$ and oxygen partial pressure above 1913 K indicates that interstitial diffusion is more active in the condition than vacancy diffusion. Assuming that both oxygen diffusion mechanisms are active in the whole temperature range, vacancy mechanism should be more dominant at higher temperature because its activation energy is higher than the other. Consequently the Arrhenius plot of oxygen permeability constants should have positive deviation at higher temperature. The results, however, disagree with the assumption mentioned above. Therefore it is estimated that there is a mechanism to switch vacancy diffusion to interstitial diffusion at 1913 K with increasing temperature.

A criterion of oxygen permeability of oxidation resistant coating on C/C composites was proposed by Sheehan. According to his criterion, if it is assumed that thickness of
a coating is 50 μm, a 2% weight loss will occur in a C/C composite in 10 hours with a coating permeability of about 10^{-10} kg/(m·s) and this is upper bound. On the other hand, Courtright proposed that it needs oxygen permeability of 10^{-11} kg/(m·s) for life time of 1000 hours, if oxygen permeated through a coating form CO₂ with the substrate which allows a recession of 100 μm.⁶

In our proposed coating system, a recession of an inner SiC layer will occur, assuming that oxygen diffuse inward through the outer Y₂SiO₅ layer and oxidation products diffuse outward through the Y₂SiO₅ layer. The oxidation reaction is given by

\[ \text{SiC(s)} + \text{O}_2(g) \rightarrow \text{SiO(g)} + \text{CO(g)} \]  

(16)

It is estimated that the surface temperature of HOPE-X reaches 1973 K for 1100s during the re-entry.¹³,¹⁴ The oxygen permeability constant of Y₂SiO₅ is 1 × 10^{-10} kg/(m·s) at 1973 K as shown in Fig. 8. A recession rate of a SiC layer with an outer Y₂SiO₅ layer thickness of 100 μm will be 1.4 μm/h, which corresponds to a life time of about 70 hours for a 100 μm-thick SiC layer. It is concluded that the oxygen permeability constant of Y₂SiO₅ is low enough to protect SiC layer against oxidation during the re-entry of HOPE-X.

5. Conclusions

We have measured oxygen permeated through wafers of Y₂SiO₅ in the temperature range from 1273 to 2033 K to determine the oxygen permeability constant. The oxygen permeability constant of Y₂SiO₅ at 1973 K is 10^{-10} kg/(m·s). A 100 μm-thick Y₂SiO₅ outer layer can serve a life time of about 70 hours for our proposed oxidation protection double layered coating, on the assumption that an inner SiC inner layer is consumed by oxygen coming through the Y₂SiO₅ outer layer. The activation energy of the oxygen permeation below 1913 K in ranges from 227 to 349 kJ/mol. The fact indicates that vacancy mechanism is dominant in the oxygen transport through Y₂SiO₅. On the contrary, the proportional relationship between the oxygen permeability constants and oxygen partial pressure above 1913 K indicates interstitial diffusion is dominate. It is estimated that there is a mechanism to switch vacancy diffusion to interstitial diffusion with increasing temperature.

REFERENCES