FULL PAPER

Effect of chemical composition on mass transfer in $Y_2Ti_2O_7$ under oxygen potential gradient at high temperatures

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The oxygen shielding properties and structural stability of polycrystalline $Y_2Ti_2O_7$ (YT) solid solution wafers, which were cut from a sintered body and served as models for environmental barrier coatings, were evaluated by the oxygen permeation technique at high temperatures. Here, we examined the effect of compositions by using two samples with slightly different Y/Ti molar ratios. The oxygen permeability constants for YT increased dramatically with a slight increment in the Y/Ti molar ratio, and the activation energy for oxygen permeation markedly decreased. Oxygen permeation in the YT was controlled by the diffusion of oxide ions in the crystal. Almost no decomposition of the YT phase occurred due to migration of the constituent cations at high temperatures, indicating high structural stability under an oxygen potential gradient. The crystal structure was identified as the YT-based pyrochlore structure from Rietveld refinements of synchrotron radiation X-ray powder diffraction data, based on information on the composition dependence of the defect concentrations in the crystals estimated by first principles calculations. The diffusion path for oxide ions in the crystal at high temperature was also investigated based on a spatial distribution map described by the bond valence sum method. Finally, the mechanisms for the uptake of oxygen molecules on the YT surface exposed to a high oxygen partial pressure and the subsequent diffusion of oxide ions in the YT crystals were clarified.

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1. Introduction

Environmental barrier coatings (EBCs) for silicon carbide fiber-reinforced silicon carbide ceramic matrix composite (SiC/SiC) components are essential in advanced airplane engines because of their capability for inhibiting oxidation and subsequent volatilization of the protective oxide scale under a high-temperature combustion gas environment.^{1)–3)} In particular, advanced EBCs that exhibit thermal reflectivity are expected to lower the temperature at the interface between the EBC and SiC/SiC substrate. Consequently, oxidative degradation of the SiC/SiC substrate would be drastically suppressed and the amount of cooling air required for the SiC/SiC substrate would also be significantly reduced. A periodic layered structure

consisting of two different oxide materials having a large difference in refractive indices is capable of reflecting thermal radiation energy, as a consequence of interference of electromagnetic waves.^{4),5)} We have previously proposed a periodic layered EBC composed of heat-resistant oxides such as $Y_2Ti_2O_7$ (YT, high index) and Al_2O_3 (low index), for reflection of thermal radiation energy as well as providing a barrier to the oxidation and volatilization.^{6),7)}

Each oxide layer in the EBC is exposed to a large oxygen potential gradient ($d\mu_O$) at elevated temperatures during use, resulting in development of the driving forces for the inward diffusion of oxide ions and outward diffusion of cations in accordance with the Gibbs–Duhem relationship. In general, when only oxide ions are transferred in an oxide film exposed to $d\mu_O$, the film structure is maintained. However, the transfer of cations in the film induces decomposition of the film. This means that the thermal radiation energy reflection function is destroyed by the collapse of the periodic layered EBC. Therefore, it is necessary to clarify the mass transfer in each of the constituent layers to understand and control the structural stability as well as the oxygen shielding function.

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In prior works, we have elucidated the mass transfer processes within the candidate constituent oxides of EBCs by determining the oxygen permeability constants for wafers cut from sintered bodies serving as model EBCs.^{8)–17)} This technique provides accurate evaluation of the intrinsic mass transfer for environmental shielding materials under steady-state conditions where the $d\mu_{\text{O}}$ applied to the wafers and the diffusion length are kept constant. In this technique, the upper and lower surfaces of the wafer are exposed to gases with different oxygen partial pressures (P_{O_2}). While the dissociative adsorption of oxygen molecules will proceed at the higher P_{O_2} surface [the $P_{\text{O}_2}(\text{hi})$ surface], the reverse reaction progresses on the opposite surface with a lower P_{O_2} [the $P_{\text{O}_2}(\text{lo})$ surface]. Therefore, the mass transfer mechanisms through the oxide films comprising the EBC can be simplified and analyzed.

For the case of high-purity polycrystalline Al_2O_3 used in periodic layered EBCs,^{8)–13)} the oxygen permeation proceeded via grain boundary (GB) diffusion of oxide ions from the $P_{\text{O}_2}(\text{hi})$ surface side to the $P_{\text{O}_2}(\text{lo})$ surface side, along with simultaneous GB diffusion of Al ions in the opposite direction. The chemical potentials, GB diffusion coefficients, and fluxes of the ions in Al_2O_3 wafers with an applied $d\mu_{\text{O}}$ were calculated from the oxygen permeability constants. The fluxes of the ions at the outflow side of the wafer were significantly larger than those at the inflow side. Moreover, the electronic transference number near the $P_{\text{O}_2}(\text{hi})$ surface was found to approach unity on application of a $d\mu_{\text{O}}$. For polycrystalline YT, which is another oxide used in periodic layered EBCs, however, the oxygen shielding properties and the mass transfer mechanism at high temperatures are still unknown.

YT is pyrochlore-type oxide (space group $Fd\bar{3}m$) with the general formula $\text{A}_2\text{B}_2\text{O}_7$, and is described as a defective fluorite solid solution,^{18),19)} in which cations form a face-centered cubic lattice and 1/8 of the anions are removed to ensure charge neutrality. Various properties of YT have been investigated with a view to considering possible applications in the fields of photocatalysis,^{20),21)} dielectrics,^{22),23)} and fuel cells.^{24),25)} In addition, since YT has high chemical stability in severe environments, it has attracted attention as a material for safe disposal of actinide-containing nuclear waste,^{26),27)} the reinforcing phase in oxide particle dispersion strengthened steel,^{28),29)} and corrosion-resistant molten-metal containers.^{30),31)}

In general, the electrical characteristics of pyrochlore type oxides are expressed by the diffusion of charged particles in the oxides. Therefore, these characteristics strongly depend on the chemical composition of the oxides and on the surrounding environment to which they are exposed. It goes without saying that the oxygen shielding of EBC materials is also controlled by the movement of charged particles. Hence, we will focus on previous research on the effects of chemical composition and P_{O_2} on the electrical characteristics of YT. The total electrical conductivity of YT in the low P_{O_2} region is dominated by the electrical conductivity, which is proportional to the $-1/4$ power of P_{O_2} , while the ionic conductivity is independent of P_{O_2}

and tends to be predominant in the high P_{O_2} region. Moreover, the change in the type of electrical conduction occurs at higher P_{O_2} as the temperature increases.^{32),33)} At lower temperature, the conduction mechanism for electrons has been experimentally shown to be hopping conduction involving small polarons.^{34),35)} There is no information on the electrical properties or the conduction mechanism for YT at temperatures above 1273 K under application of $d\mu_{\text{O}}$.

In this study, therefore, the oxygen shielding properties and structural stability of polycrystalline YT solid solution wafers, serving as model EBC films, were precisely evaluated by the oxygen permeation technique at high temperatures. In order to clarify the oxygen shielding properties of the YT solid solutions, the characteristics were also compared with that of 10 mol % yttria stabilized zirconia (10YSZ), which is a typical oxide ion conductor. The diffusion coefficients for the oxide ions and the electronic transference numbers were also determined for the YT wafers. Additionally, first-principles calculations based on density functional theory (DFT) were employed to assess the concentrations of point defects over a composition range of YT. The local structure of YT crystals was analyzed by synchrotron X-ray diffraction (XRD). Finally, the effect of the chemical composition on the mass transfer in the YT solid solutions under application of a $d\mu_{\text{O}}$ at high temperatures was investigated based on the combined results.

2. Experimental procedure

2.1 Sample preparation

Raw YT powders were synthesized by ultrasonic spray pyrolysis, which allows for superior control of the product composition, using a precursor solution composed of $\text{Y}(\text{NO}_3)_3$ and TiCl_4 aqueous solution. The Y/Ti molar ratios for the aqueous solutions were controlled to fabricate single-phase YT solid solutions having two compositions, one of which was almost stoichiometric and the other of which was Y-rich. The synthesized raw powders were calcined at 1073 K for 1 h in air. After that, the calcined powders were molded under a uniaxial pressure of 20 MPa and subjected to cold isostatic pressing at 245 MPa. Subsequently, the compact bodies were sintered in air at 1973 K for 5 h. In addition, a polycrystalline 10YSZ sample was also prepared for comparison of the oxygen shielding properties. 10YSZ powder (TZ-10YS, Tosoh ceramics Co., Ltd.) was molded in the same way as the YT samples. The compact body was sintered by two-step sintering. The temperature profile for the first step was heating at 5 K/min to 1523 K, then cooling at 50 K/min to 1323 K, followed by holding for 50 h. The profile for the second step was heating at 5 K/min to 1773 K, followed by holding for 5 h, and finally cooling at 5 K/min to room temperature. The wafer samples were ground and polished to a mirror-like finish to obtain polycrystalline wafer specimens with final dimensions of $\varnothing 11.5$ to $\varnothing 23.5$ mm $\times$ 0.25 mm. **Figure 1** presents an XRD pattern for the YT-1 sample obtained using $\text{Cu-K}\alpha$ radiation. The pattern

Fig. 1. XRD pattern of surface of YT-1 wafer.

Table 1. Chemical composition of samples

	Type	Y/Ti molar ratio	
		YT-1	YT-2
Oxygen permeation test	Bulk	1.006	1.013
Structural characterization	Powder	1.003	1.016

demonstrates the presence of single-phase YT, and YT-2 also exhibited only the YT phase (data not shown). The Y/Ti molar ratios for the YT samples were confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES), and the results are shown in **Table 1**. The near-stoichiometric and Y-rich samples are described as YT-1 and YT-2, respectively. The Y/Ti molar ratios for YT-1 and YT-2 measured by ICP-OES were 1.006 and 1.013, respectively. The relative densities of all samples used for the oxygen permeation tests were found to be more than 98 % of the theoretical densities.

In this study, quenched YT powders were also fabricated for analysis of the crystal structure of the wafer samples during the oxygen permeation tests at high temperatures. The YT raw powders synthesized by the same method as the YT sintered bodies were annealed in a Pt crucible at 1773 K for 5 to 20 h. Subsequently, the crucible including the powder was taken out of the furnace at 1773 K, and quenched in water at room temperature. The compositions of the quenched YT powder samples, which were measured by ICP-OES, were confirmed to be close to those of the corresponding wafer samples. Therefore, the symbols for these powder samples were the same as those used for the wafer samples, indicated in Table 1.

2.2 Oxygen permeation tests

The oxygen permeabilities of the YT wafers were evaluated by a measurement procedure previously used for a series of EBC candidate materials.^{8),9),12)–16)} Each YT wafer was set between two alumina tubes in a furnace. Platinum gaskets were used to create a seal between the wafer and the tubes by loading weights on top of the upper tube. High-purity Ar with oxygen gas at approx. 1 Pa as an impurity was supplied to both sides of the sample at a flow rate of $1.67 \times 10^{-6} \text{ m}^3/\text{s}$. While monitoring P_{O_2} in the upper and lower chambers with an oxygen sensor, a gas-tight seal was achieved by heating at 1893 K. After that, when the monitored value became constant at the measure-

Fig. 2. SIMS- ^{18}O map of cross-section near $P_{O_2}(\text{hi})$ surface of YT-1 wafer exposed to $P_{^{18}O_2}(\text{hi})/P_{^{16}O_2}(\text{lo})$ ratio of $10^4 \text{ Pa}/1 \text{ Pa}$ at 1773 K for 240 s.

ment temperature, the values of P_{O_2} in the upper and lower chambers were measured and used as the background value. The total pressure in each chamber was 10^5 Pa . Then, the wafer was exposed to $d\mu_O$ in the thickness direction by supplying either pure O_2 or Ar with 1 to 30-vol % O_2 to the upper chamber. When the oxygen permeation reached a steady state after a predetermined period of time, P_{O_2} in the lower chamber was measured. The oxygen permeability constant PL [$\text{mol}/(\text{m} \cdot \text{s})$] was calculated from the difference from the background value based on Eq. (1).

$$PL = \frac{C_p \cdot Q \cdot L}{V_{st} \cdot S}, \quad (1)$$

where P is oxygen permeability, L is the wafer thickness, C_p is the concentration of permeated oxygen molecules, Q is the gas flow rate, V_{st} is the standard molar volume of ideal gas, and S is the wafer permeation area.

2.3 Diffusibility of oxide ions

Oxygen permeation experiments with oxygen tracer gas $^{18}O_2$ were also performed to clarify the diffusion paths of oxide ions in the YT wafer. During the permeation test, the YT wafer was exposed to a $P_{^{16}O_2}(\text{hi})/P_{^{16}O_2}(\text{lo})$ of $10^4 \text{ Pa}/1 \text{ Pa}$ at 1773 K for 3 h. Subsequently, the $^{16}O_2$ in the $P_{O_2}(\text{hi})$ chamber was changed to $^{18}O_2$ and maintained for 240 s. Cross-sections of the exposed wafers were cut and ^{18}O mapping of the cross-sections near the $P_{O_2}(\text{hi})$ surfaces were performed by secondary ion mass spectrometry (SIMS, Nano SIMS 50L, CAMECA, France) with a Cs^+ beam diameter of 80 nm. **Figure 2** shows an ^{18}O map of the cross-section for a YT-1 wafer after the treatment. The ^{18}O was distributed almost uniformly both inside the grains and at the GBs, so oxide ions in the YT wafer exhibited lattice diffusion. The lattice diffusion coefficient, D_O , for oxide ions in the YT wafer was determined from the ^{18}O concentration depth profiles. Specifically, in order to obtain clear profiles of the ^{18}O concentration gradient at the same temperature, a measurement temperature of 1473 K was selected. The retention times for YT-1 and YT-2 were set to 3240 and 600 s, respectively. After that, ^{18}O depth profiling was performed by SIMS (IMS-7f,

CAMECA, France). The D_O value for the YT wafers was calculated by a conventional method using Eq. (2).^{15),17)}

$$\frac{C_z - C_s}{C_{bg} - C_s} = \operatorname{erf}\left(\frac{z}{2\sqrt{D_O t}}\right), \quad (2)$$

where z is the penetration depth, t is the measurement time, C_z is the ^{18}O fraction at a depth z , C_s is the ^{18}O fraction at the surface, and C_{bg} is the ^{18}O fraction based on its natural abundance (0.00204).

2.4 First-principles calculations

The concentration of point defects with charge q in a crystalline material, D^q , can be calculated from the defect formation energy via³⁶⁾

$$C(D^q) = N_s(D) \exp\left[-\frac{E_d(D^q)}{kT}\right]. \quad (3)$$

Here, $C(D^q)$, $E_d(D^q)$, and $N_s(D)$ indicate the concentration, the defect formation energy, and the number of sites in the lattice, respectively, associated with D^q defects. The defect formation energy is given by³⁶⁾

$$E_d(D^q) = E_{\text{DFT}}(D^q) - E_{\text{DFT}}(\emptyset) + \sum_{i_{\text{at}}} \Delta N_{i_{\text{at}}}(D) \mu_{i_{\text{at}}} + q\mu_e. \quad (4)$$

Here, $E_{\text{DFT}}(D^q)$ and $E_{\text{DFT}}(\emptyset)$ are the DFT energies for the simulation cells with D^q and without any defects, respectively. $\Delta N_{i_{\text{at}}}(D)$ is the change in the number of atoms of i_{at} species on creating the defect in the host, and $\mu_{i_{\text{at}}}$ is the chemical potential of i_{at} . μ_e is the chemical potential of electrons, which is determined via the charge neutrality condition among the charged defects and electronic carriers, i.e., free electrons and holes, for given values of the atomic chemical potential ($\mu_{i_{\text{at}}}$).

In this work, the oxygen chemical potential was calculated from that for oxygen gas molecules based on the assumption that oxygen atoms in YT equilibrate with an ideal oxygen gas which has two thermodynamic quantities: oxygen partial pressure and temperature. Here, the energy of an oxygen molecule at zero temperature was calculated by DFT, and the NIST-JANAF thermomechanical table³⁷⁾ was referenced to obtain the free energy at a finite temperature. The chemical potentials for Y and Ti atoms were calculated to satisfy the condition that the number of atoms in the YT cell equals the input values. The inputs were determined from a target Y/Ti ratio under the condition that the sum of the numbers of Y and Ti atoms equals the value for the stoichiometric composition. We examined Y/Ti ratios from 0.995 to 1.015.

DFT calculations were performed using the projector augmented wave (PAW) method, as implemented in the VASP code.³⁸⁾ For the exchange–correlation functional, we used the HSE06 hybrid functional.³⁹⁾ The cut-off energy for planewave bases was set to 400 eV for the relaxation of internal parameters only and 550 eV when the lattice constants were also optimized. The defect formation energy expressed by Eq. (3) in charged systems can involve artificial contributions due to interactions between

periodically aligned supercells and unintended electrostatic potential shifts, so the correction of the generalized-FNV scheme^{40),41)} was adopted by using a dielectric constant of 50, which is near the experimental value of 54⁴²⁾ and our calculated value of 50.3 within the GGA-functional framework. The cubic unit cell of the pyrochlore structure was used in the calculations of defect formation energies and the Brillouin zone was sampled by using a $2 \times 2 \times 2$ k -grid mesh.

2.5 Analysis of crystal structure

The crystal structures of the YT solid solutions were accurately analyzed by powder XRD patterns obtained using a synchrotron X-ray diffractometer (PILATUS 100K, DECTRIS Ltd.) with an energy of 16.9 keV, a step size of 0.01° , and an exposure time of 300 s. Diffraction data for CeO_2 were used to correct the wavelength of the synchrotron X-rays. The quenched powders were loaded into a Lindemann glass capillary with a diameter of 0.3 mm. The transmittance of the powder in the capillary was measured to correct for the effect of absorption, and then the corrections were reflected in the structural analysis. Structural parameters were refined by the Rietveld method using RIETAN-FP.⁴³⁾ The crystal structure model employed for the Rietveld analysis was determined based on the chemical composition of the defect concentration in the YT crystal estimated by the first-principles calculations described in section 2.4. The migration route of oxide ions in the crystal was analyzed by bond valence sum (BVS) calculations using the computer program PyAbstantia.⁴⁴⁾ The resulting BVS map was drawn using VESTA.⁴⁵⁾

3. Results and discussion

3.1 Oxygen permeability

The oxygen permeability constant, PL , for YT-1, YT-2, and 10YSZ was measured under a constant $d\mu_O$ with a $P_{O_2}(\text{hi})/P_{O_2}(\text{lo})$ ratio of $10^5 \text{ Pa}/1 \text{ Pa}$ at temperatures ranging from 1273 to 1773 K. **Figure 3** shows the relationship between the PL and the reciprocal of absolute temperature. The PL for YT-1 was almost same as that for 10YSZ at 1773 K, but became smaller than that for 10YSZ at lower temperatures. The $\log(PL)$ values for all samples were proportional to T^{-1} . The PL for YT-2 was significantly larger than those for YT-1 and YSZ, and the slope of the straight line for YT-2 was smaller than that for YT-1. Hence, the PL value for YT was found to greatly increase with only a slight increment in the Y/Ti molar ratio.

Figure 4 shows the PL values for the samples as a functions of $P_{O_2}(\text{hi})$ at 1773 K, at a constant $P_{O_2}(\text{lo})$ of 1 Pa. The larger the $P_{O_2}(\text{hi})$ value on the horizontal axis, the larger the $d\mu_O$ becomes. The PL values for all samples grew proportionally with the $P_{O_2}(\text{hi})$ value on a logarithmic scale. The power constants, n , of YT-1 and YT-2 corresponding to the slopes of these straight lines were 1/6 and 1/4, respectively. The n value for YT-2 was the same as that for 10YSZ. The n value depends on the valence of defects, namely diffusing charged species, generated or annihilated on the $P_{O_2}(\text{hi})$ surface. Therefore, the mass

Fig. 3. Oxygen permeability constants as a function of T^{-1} for YT-1, YT-2 and 10YSZ wafers exposed to $P_{O_2}(hi)/P_{O_2}(lo)$ ratio of $10^5 \text{ Pa}/1 \text{ Pa}$.

Fig. 4. Oxygen permeability constants, PL , for YT-1, YT-2 and 10YSZ wafers as function of $P_{O_2}(hi)$ values at 1773 K, holding $P_{O_2}(lo)$ constant at 1 Pa.

transfer of YT appeared to be drastically changed by only a slight shift in the chemical composition to the Y-rich side.

As an example, **Fig. 5** shows SEM micrographs of $P_{O_2}(hi)$ and $P_{O_2}(lo)$ surfaces and cross-sections of the YT-1 wafer exposed to $P_{O_2}(hi)/P_{O_2}(lo)$ ratio of $10^5 \text{ Pa}/1 \text{ Pa}$ at 1773 K for 10 h. Thermal etching-type equilibrium grooves are observed along the GBs on both surfaces. In addition, energy dispersive X-ray spectroscopy analysis of the cross-sections near both surfaces confirmed that no composition change occurred. Therefore, the decomposition of the YT phase due to migration of the constituent cations was negligible at high temperatures. In other words, the YT solid solutions appeared to maintain structural stability at high temperatures during the application of $d\mu_O$.

Then, the activation energy for oxygen permeation through the YT wafers was determined based on the PL values. The PL values can be expressed by Eq. (5) with $P_{O_2}(hi)$ and $P_{O_2}(lo)$.^{12),15),16)}

$$PL = A_O [P_{O_2}(hi)^n - P_{O_2}(lo)^n] \quad (5)$$

Fig. 5. SEM micrographs of $P_{O_2}(hi)$ and $P_{O_2}(lo)$ surfaces and cross-sections of YT-1 wafer exposed to $P_{O_2}(hi)/P_{O_2}(lo)$ ratio of $10^5 \text{ Pa}/1 \text{ Pa}$ at 1773 K for 10 h.

where A_O is an experimental constant and n is a power constant determined from the P_{O_2} dependence of the PL value shown in Fig. 4. A_O is given by the Arrhenius form of Eq. (6).

$$A_O = A^*_O \exp \left[\frac{-Q(\text{kJ/mol})}{RT} \right] \quad (6)$$

where R is the gas constant, T is the absolute temperature, Q is the activation energy, and A^*_O is the frequency factor.

Figure 6 presents an Arrhenius plot of A_O for each wafer exposed to a $P_{O_2}(hi)/P_{O_2}(lo)$ ratio of $10^5 \text{ Pa}/1 \text{ Pa}$. The A^*_O values for YT-1, YT-2 and 10YSZ were $3.472 \text{ mol} \cdot \text{s}^{-1} \text{ Pa}^{-1/6}$, 2.481×10^{-3} and $1.493 \times 10^{-3} \text{ mol} \cdot \text{s}^{-1} \text{ Pa}^{-1/4}$, respectively. Additionally, the oxygen permeation activation energies for YT-1, YT-2 and 10YSZ were 269, 151 and 172 kJ/mol, respectively. The activation energies for the YT wafers determined in this study were relatively larger than those (103,³²⁾ 79 kJ/mol³³⁾) determined from the electrical conductivity of YT fabricated by the solid-phase method at high temperature. In contrast, the activation energy for 10YSZ was close to the previously reported value (199 kJ/mol⁴⁶⁾).

3.2 Diffusibility of oxide ions

The diffusion coefficient and transport number for oxide ions in YT-1 and YT-2 were determined from the oxygen

Fig. 6. Arrhenius plots of A_O for YT-1, YT-2 and 10YSZ wafers exposed to $P_{O_2}(hi)/P_{O_2}(lo)$ ratio of 10^5 Pa/1 Pa.

permeation data using a conventional technique.^{13),15)} The oxygen permeation constant, P_x , at an arbitrary position, x , in the wafer depth direction is expressed by Eq. (7).

$$P_x = A_O [P_{O_2}(x)^n - P_{O_2}(lo)^n] \quad (7)$$

where $P_{O_2}(x)$ is defined as P_{O_2} in equilibrium with the chemical potential of oxygen at position x . Hence Eq. (8) is derived by combining Eqs. (5) and (7).

$$\frac{x}{L} = \frac{P_{O_2}(x)^n - P_{O_2}(lo)^n}{P_{O_2}(hi)^n - P_{O_2}(lo)^n} \quad (8)$$

Therefore, the $P_{O_2}(x)$ value at an arbitrary position in the film thickness direction can be obtained for a film subjected to a $d\mu_O$ consisting of $P_{O_2}(hi)$ and $P_{O_2}(lo)$. Furthermore, the diffusion coefficient for oxide ions, D_O , can be expressed by Eq. (9).

$$D_O = \frac{nA_O}{C_O \cdot t_e} P_{O_2}(x)^n \quad (9)$$

Here, C_O is the molar concentration of oxide ions per unit volume, and t_e is the electronic transference number. That is, the D_O value at an arbitrary position in the film given by Eq. (9) depends on $P_{O_2}(x)$ and t_e . In this study, t_e for each wafer was assumed to be constant in the film thickness direction.

Figure 7 presents plots of $\text{erf}^{-1}[(C_z - C_s)/(C_{bg} - C_s)]$ as a function of the penetration depth for the YT-1 and YT-2 wafers exposed to a $P_{18O_2}(hi)/P_{16O_2}(lo)$ ratio of 10^4 Pa/1 Pa at 1473 K. The D_O values for oxide ions were determined from the slopes of the straight lines approximated by Eq. (2). The D_O values for oxide ions in YT-1 and YT-2 measured at 1473 K were 1.26×10^{-14} and 8.93×10^{-13} $\text{m}^2 \cdot \text{s}^{-1}$, respectively. This indicated that D_O increased significantly when the chemical composition of YT became slightly Y-rich. **Figure 8** shows the equilibrium partial pressure of oxygen, $P_{O_2}(x)$, as a function of the normalized thickness, x/L , for YT-1 and YT-2 wafers exposed to a $P_{O_2}(hi)/P_{O_2}(lo)$ ratio of 10^4 Pa/1 Pa at 1473 K. The difference in the shape of the curves reflects the difference in the n values. In order to calculate D_O at an arbitrary position

Fig. 7. Plots of $\text{erf}^{-1}[(C_z - C_s)/(C_{bg} - C_s)]$ as function of penetration depth for YT-1 and YT-2 wafers exposed to $P_{18O_2}(hi)/P_{16O_2}(lo)$ of 10^4 Pa/1 Pa at 1473 K.

Fig. 8. Equilibrium partial pressure of oxygen as function of normalized thickness, x/L , for YT-1 and YT-2 wafers exposed to $P_{O_2}(hi)/P_{O_2}(lo)$ of 10^4 Pa/1 Pa at 1473 K.

in the wafer by substituting the $P_{O_2}(x)$ value in Fig. 8 into Eq. (9), the corresponding t_e value is required. If t_e is assumed to be constant in the wafer thickness direction, it can be determined by a curve through the experimental value shown in Fig. 7, calculated using Eq. (9) with the $P_{O_2}(x)$ values. **Figure 9** presents D_O for oxide ions as a function of the normalized thickness, x/L , for YT-1 and YT-2 wafers exposed to a $P_{O_2}(hi)/P_{O_2}(lo)$ ratio of 10^4 Pa/1 Pa at 1473 K. The electronic transference numbers for YT-1 and YT-2 determined from Fig. 9 were 0.70 and 0.33, respectively. The contribution of ionic conductivity was found to be markedly increased by a slight increase in Y content.

3.3 Concentrations of point defects

In order to investigate the stability of point defects in YT using DFT, we examined the following intrinsic point defects: $V_{O(48f)}^{\bullet\bullet}$, $V_{O(8b)}^{\bullet\bullet}$, $O_{(8a)}^{\bullet\bullet}$, $V_{Ti}^{\bullet\bullet}$, $V_Y^{\bullet\bullet}$, $Ti_Y^{\bullet\bullet}$, $Y_{Ti}^{\bullet\bullet}$, and $Ti_{Ti}^{\bullet\bullet}$. The formal charges of ions were assumed to be maintained

Fig. 9. Diffusion coefficients for oxygen as a function of normalized thickness, x/L , for YT-1 and YT-2 wafers exposed to $P_{O_2}(hi)/P_{O_2}(lo)$ of 10^4 Pa/1 Pa at 1473 K, with electronic transference numbers of 0.70 and 0.33, respectively.

Fig. 10. Concentration of point defects in $Y_2Ti_2O_7$ as function of Y/Ti ratio, obtained from DFT calculations at 1600 K under P_{O_2} of 10^4 Pa.

except in the case of Ti'_Ti , which is a small polaron formed by an electron localized on a Ti atom. The obtained concentrations of point defects in YT at 1600 K under P_{O_2} of 10^4 Pa are shown in Fig. 10. The concentrations of $V_{O(8b)}$, $V_{Ti}^{''''}$, $V_Y^{''''}$, free electrons and holes are not displayed in the figure because they are smaller than the lower limit. We summarize the insights gained on the defect chemistry of YT in the following three points:

i) The concentration of the small polaron Ti'_Ti is prominently higher than that of free electrons. The formation of small polaron with trapped electrons in YT has been discussed based on the results of electric conductivity and thermoelectric power measurements.^{33)–35)} In these previous studies, the polarons were considered to form only on oxygen vacancies. In contrast, our calculation results show the possibility of the formation of a self-trapped

polaron (Ti'_Ti) as a source of the small polarons in YT. In our calculations, oxygen vacancies with doubly trapped electrons ($V_{O(48f)}^{\times}$) are also stabilized, and were confirmed to reach a concentration comparable to that of Ti'_Ti depending on the equilibrium conduction. However, these are outside the scope of this paper and omitted here in the interest of brevity.

ii) Y'_Ti and Ti_Y are balanced at compositions near stoichiometry ($Y/Ti \sim 1.0$), which suggests cation mixing as observed in $Yb_{2+x}Ti_{2-x}O_{7-x/2}$ solid solutions,⁴⁷⁾ but the balance is easily upset by a change in Y/Ti ratio. The concentration of Y'_Ti becomes large compared to that of Ti_Y as Y/Ti increases on the Y-rich side and is balanced with $V_{O(48f)}^{\times}$.

iii) $V_{O(48f)}^{\times}$ is predominant over a wide examined range compared to $V_{O(8b)}$. Consequently, oxygen vacancies are considered to be mostly formed at 48f sites during the oxygen permeation tests. We also found that the concentration of $V_{O(48f)}^{\times}$ is appreciably larger than that of $O''_{(8a)}$ for Y-rich conditions ($Y/Ti > 1.0$).

Additionally, we examined the temperature dependence of concentrations of point defects for the O_2 - and Y_2O_3 -rich condition and confirmed that similar tendencies to the above three points were commonly found in the temperature range in which the oxygen permeation tests were performed.

3.4 Analysis of crystal structure

The crystal structure of the quenched YT powders with different Y/Ti ratios, which was believed to be maintained during the oxygen permeation tests at 1773 K, was clarified by synchrotron XRD measurements and subsequent Rietveld analysis. The crystal structure model for the Rietveld analysis was determined based on the defect concentrations estimated by first-principles calculations. As described in section 3.3, the concentration of Y'_Ti increases with increasing Y/Ti ratio, while that of Ti_Y decreases. For the case of the stoichiometric composition of $Y/Ti = 1$, the concentration of these defects is the almost same. Therefore, a condition was set for the occupancy factors for the cation sites under which mixing of cations positioned in 16d and 16c sites can occur. Because the concentration of $V_{O(48f)}^{\times}$ was calculated to be significantly higher than that of $V_{O(8b)}$, the oxygen vacancies were assumed to exist only as $V_{O(48f)}^{\times}$. In addition, when the Y/Ti ratio was greater than 1, the concentration of $O''_{(8a)}$ was extremely low compared with the other defects as shown in Fig. 10. Therefore, it was assumed that $O''_{(8a)}$ was never formed in the quenched powders. Furthermore, the occupancy factors for each site were constrained to maintain both the Y/Ti ratios confirmed by ICP-OES and electrical neutrality.

Figure 11 presents a Rietveld refinement pattern obtained from the YT-1 powder. The experimental pattern is coincident with the calculated one. Table 2 summarizes the structural parameters and reliability indices obtained by Rietveld refinement with the pyrochlore structure (space group $Fd\bar{3}m$). The accuracy of the fitting is

Fig. 11. Rietveld refinement pattern for YT-1. Red crosses and blue lines denote observed and calculated intensities, respectively. Green marks are positions of Bragg reflections. The line at the bottom plots the differences between observed and calculated intensities.

Table 2. Crystallographic parameters and reliability indices for samples

Y/Ti molar ratio	1.003	1.016
Crystallographic parameters		
a (Å)	10.09750(2)	10.09750(2)
ρ_{theo} (g/cm ³)	4.975999	4.981536
x (O _{48f})	0.32812(9)	0.32830(8)
g (Y; 16d)	0.9842(10)	0.9825(9)
g (Y; 16c)	0.0173(10)	0.0254(9)
g (Ti; 16d)	0.0158(10)	0.0175(9)
g (Ti; 16c)	0.9827(10)	0.9746(9)
g (O; 48f)	0.9998(10)	0.9987(9)
g (O; 8a)	0	0
g (O; 8b)	1	1
U (16d) (Å ²)	0.00692(7)	0.00694(6)
U (16c) (Å ²)	0.00559(9)	0.00574(8)
U (48f) (Å ²)	0.00733(25)	0.00693(22)
U (8b) (Å ²)	0.00313(54)	0.00243(48)
Reliability indices		
R_{wp}	5.078	4.177
R_{B}	1.374	1.561
R_{F}	0.918	1.034
S	0.6037	0.4596

sufficient to derive the crystal structure factor from the obtained reliability indices. The lattice constant, the degree of cation mixing, the coordinates of the 48f site, and the isotropic atomic displacement parameter for each site for the quenched powders with different Y/Ti ratios are almost the same.

Figure 12 shows a BVS map for oxide ions in YT-1 viewed along the [100] direction with a quarter of the unit cell. The yellow region is related to the migration route of the oxide ions, which move away from the 8b sites. It is clear that the 48f sites and the vicinity of the 8a sites are the main route for the oxide ions. These tendencies were the same as those for YT-2.

3.5 Mass transfer mechanism

The mass transfer mechanism through the YT will be discussed based on the obtained oxygen permeation data

Fig. 12. BVS map for oxide ion in YT-1 viewed along the [100] direction with quarter unit cell. The isosurface level is 0.4.

and the crystal structure analysis including the defects. The power constants, n , determined from the $d\mu_{\text{O}}$ dependence of the PL values shown in Fig. 4, were related to the uptake reaction of oxygen molecules on the $P_{\text{O}_2}(\text{hi})$ surface. Since n for YT-1 is 1/6, it is presumed that the oxygen molecules were adsorbed and dissociated, followed by being incorporated in the $\text{O}''_{(8a)}$ sites on the $P_{\text{O}_2}(\text{hi})$ surface, according to the reaction in Eq. (10).

The equilibrium constant for Eq. (10) is expressed by Eq. (11).

$$K_{\text{Eq.8}} = \frac{[\text{O}''_{(8a)}]p^2}{P_{\text{O}_2}^{1/2}} \quad (11)$$

Eq. (12) is derived by substituting $p = 2[\text{O}''_{(8a)}]$ into Eq. (11).

$$[\text{O}''_{(8a)}] = \left(\frac{K_{\text{Eq.9}}}{3} \right)^{1/3} P_{\text{O}_2}^{1/6} \propto P_{\text{O}_2}^{1/6} \quad (12)$$

Hence, $[\text{O}''_{(8a)}]$ on the $P_{\text{O}_2}(\text{hi})$ surface is proportional to P_{O_2} to the 1/6-th power. However, when the Y/Ti molar

ratio is 1 or more, $[O''_{(8a)}]$ in the crystal is extremely small compared with $[V_{O(48f)}]$. In other words, the defect species predicted from the oxygen permeation data, in which they mainly contributes to the uptake of oxygen molecules on the $P_{O_2}(hi)$ surface, is different from that estimated from the first-principles calculations in Fig. 10. The reason for this discrepancy is probably related to the fact that the oxygen permeation data were acquired in the steady state, whereas the defect concentrations obtained by the first-principles calculations were estimated by assuming a thermodynamic equilibrium state. That is, because $[V_{O(48f)}]$ is relatively low for compositions close to the stoichiometric composition, inward migration of oxide ions through $V_{O(48f)}$ and the vicinity of $O''_{(8a)}$ inside YT is considered to be slow. Consequently, $V_{O(48f)}$ sites on the $P_{O_2}(hi)$ surface and in its vicinity were saturated immediately by the uptake of oxygen molecules around them during oxygen permeation, so that $O''_{(8a)}$ might act as the main uptake sites.

On the other hand, since n for YT-2 is $1/4$, the incorporation mechanism for oxygen molecules into the $P_{O_2}(hi)$ surface is different from that for YT-1. To order to satisfy the electrical neutrality condition, a large amount of $V_{O(48f)}$ is introduced into the crystal according to Eq. (13) as shown in Fig. 10.

Additionally, since the contribution of ionic conduction in YT-2 was concluded to be clearly larger than that in YT-1 by considering the t_e values determined by the oxygen permeation tests, migration of the oxide ions through $V_{O(48f)}$ sites and the vicinity of $O''_{(8a)}$ was thought to be accelerated by the material being highly Y-rich. As a result, the reactions in Eqs. (10) and (14) can progress simultaneously without annihilation of $V_{O(48f)}$ sites on the $P_{O_2}(hi)$ surface during oxygen permeation. The equilibrium constant for Eq. (14) is expressed by Eq. (15).

$$K_{Eq.12} = \frac{p^2}{P_{O_2}^{1/2} [V_{O(48f)}]} \quad (15)$$

At this point, the relationship in Eq. (16) is defined by satisfying charge neutrality

$$2[V_{O(48f)}] - [Y'_{Ti}] + p - 2[O''_{(8a)}] = 0 \quad (16)$$

$[V_{O(48f)}]$ and $[Y'_{Ti}]$ are much larger than p and $[O''_{(8a)}]$ so the relational expressions of $2[V_{O(48f)}] - [Y'_{Ti}] \simeq 0$ and $p = 2[O''_{(8a)}]$ are established. Moreover, $[V_{O(48f)}]$ can be considered to be independent of the $P_{O_2}(hi)$ value. Eventually, Eq. (17) is derived from Eq. (15). Therefore, $[O''_{(8a)}]$ on the $P_{O_2}(hi)$ surface is proportional to P_{O_2} to the $1/4$ -th power.

$$[O''_{(8a)}] = \frac{1}{2} \{K_{Eq.12} [V_{O(48f)}]\}^{1/2} P_{O_2}^{1/4} \propto P_{O_2}^{1/4} \quad (17)$$

Finally, the oxygen permeation activation energies for YT-1 and YT-2 will be discussed. As described in section 3.4, the U values and the migration route of the oxide ions

in the YT-1 crystal were almost the same as those for YT-2. From these results, the migration route and the corresponding height of the diffusion barrier are believed to be almost the same independent of the chemical composition. Nevertheless, the activation energy for oxygen permeation strongly depends on the composition. This is probably related to the fact that $[V_{O(48f)}]$ for YT-1 increases exponentially with rising temperature, while that for YT-2 is almost constant. Actually, the activation energy difference between YT-1 and YT-2, 118 kJ/mol, is close to the defect formation energy for $V_{O(48f)}$ at 1773 K for the chemical composition of YT-1, 114 kJ/mol, which was estimated by first-principles calculations. Therefore, it is reasonable to conclude that the exponential increase in $[V_{O(48f)}]$ for YT-1 is due to the rise in temperature.

4. Conclusion

The oxygen shielding properties and structural stability of YT solid solutions having slightly different chemical compositions, YT-1 and YT-2, were quantitatively evaluated by the oxygen permeation technique in the temperature range from 1273 to 1773 K. The results showed that the oxygen permeability constants increased significantly with only a slight increase in the Y/Ti molar ratio, and the corresponding activation energy was clearly lowered. Oxygen permeation in both YT samples was controlled by the diffusion of oxide ions in the crystal lattice. The decomposition of the YT phase due to migration of the constituting cations at high temperatures was negligible. Therefore, the YT solid solutions were considered to maintain structural stability at high temperatures during the application of $d\mu_O$.

For YT-1 having a near-stoichiometric composition, oxygen molecules around the $P_{O_2}(hi)$ surface were incorporated into $O''_{(8a)}$ sites on the surface exposed to $d\mu_O$. For YT-2 having an Y-rich composition, they were taken into $V_{O(48f)}$ sites on the surface, for which $[V_{O(48f)}]$ was independent of the $P_{O_2}(hi)$ values, in addition to the $O''_{(8a)}$ sites. Moreover, the migration route for oxide ions in the crystal at high temperature was investigated based on the spatial distribution map described by the BVS method. The crystal structure was identified as the YT-based pyrochlore structure from Rietveld refinement of synchrotron radiation X-ray powder diffraction data, based on information on the composition dependence of the defect concentrations in the crystals estimated by the first principle calculations. The migration route for the oxide ions in the crystals and the corresponding height of the diffusion barrier are thought to be almost the same regardless of the difference in chemical composition. Nevertheless, the activation energy for oxygen permeation strongly depended on the composition. This is probably related to the fact that $[V_{O(48f)}]$ for YT-1 increased exponentially with rising temperature, while that for YT-2 was almost constant.

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