Chapter 11

Grain Boundary Engineering of Alumina Ceramics

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Abstract Oxygen permeability through alumina wafers was evaluated at high temperatures up to 1923 K to elucidate the mass-transfer mechanisms of polycrystalline alumina and serve as a model for protective alumina film formed on heat-resistant alloys. Oxygen permeation proceeded via grain boundary (GB) diffusion of oxygen from the higher oxygen partial pressure (P_{O_2}) surface side to the lower P_{O_2} surface side, along with the simultaneous GB diffusion of aluminum in the opposite direction to maintain the Gibbs–Duhem relationship. Oxygen GB diffusion coefficients in the vicinity of the $P_{O_2}(\text{hi})$ surface were lower than those of oxygen GB self-diffusion without an oxygen potential gradient ($d\mu_O$). When $d\mu_O$ was applied to the wafer, the oxygen and aluminum fluxes at the outflow side of the wafer were significantly larger than those at the inflow side. Ln (Y and Lu) and Hf segregation at the GBs selectively reduced the diffusivity of oxygen and aluminum, respectively. Thus, the mesoscopic arrangements of segregating dopants, which were selected by taking into consideration the behavior of the diffusion species and the role of dopants, enabled the alumina film to have enhanced oxygen shielding capability and structural stability at high temperatures. Furthermore, the GB diffusion data derived from the oxygen permeation experiments were compared to those for alumina scale formed by the so-called two-stage oxidation of alumina-forming alloys.

Keywords Alumina • Grain boundary • Oxygen permeation
Diffusion • High temperature

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11.1 Introduction

Polycrystalline α -alumina scale can play a key role to enable heat-resistant alloys that include aluminum to be applied as hot section components of airplane engines, gas turbines, and heat treatment furnaces in combustion environments. The α -alumina scale acts as a protective film against further oxidation of the alloys at high temperatures. Growth of the alumina scale is determined by the solid-state diffusion of both oxygen and aluminum along the grain boundaries (GBs) in response to their respective chemical potentials. Thus, it is expected that the durability of hot section components would be determined by the mass transport of oxygen and aluminum through the scale.

For scale growth by inward oxygen GB diffusion, the annihilation and production of oxygen vacancies proceed at the scale-gas and scale-metal interfaces by reactions (11.1) and (11.2), respectively [1]:

Scale growth also occurs by outward aluminum GB diffusion. Aluminum vacancies are produced at the scale-gas interface by reaction (11.3) and are annihilated at the scale-metal interface by reaction (11.4) [1]:

Although these reactions are expressed with holes or electrons on opposite sides, the concentrations of electrons (n) and holes (p) are related by another equilibrium constant [2]:

$$K_i = n \times p \quad (11.5)$$

When the alloys are oxidized through alumina scale under high oxygen partial pressures (P_{O_2}) (such as in air), i.e., when they are subjected to a steep oxygen potential gradient ($d\mu_O$), the outward GB diffusion of aluminum produces new alumina on the GB surface of the scale, which results in the formation of GB ridges [3]. However, such ridges do not form in a low- P_{O_2} environment, such as in a purified argon flow, where oxidation of the alloys could proceed thermodynamically [3]. The mass-transfer mechanisms in the scale appear to be strongly dependent on the extent of $d\mu_O$ to which the scale is exposed.

There have been many studies on oxygen GB diffusion in polycrystalline alumina using either secondary ion mass spectroscopy (SIMS) [4–7] or nuclear reaction analysis (NRA) [8] to determine depth profiles of ^{18}O (oxygen tracer) after high temperature exchange with ^{18}O -enriched oxygen. The oxygen diffusion

coefficients of single GBs were recently determined by a SIMS- ^{18}O line profiling technique at each GB near the surface of an alumina cross section [1]. The activation energies reported for the oxygen GB diffusion in the scale tend to be larger than those for the corresponding self-diffusion data. Thus, the application of a $\text{d}\mu_{\text{O}}$ suggests there is some influence on the oxygen GB diffusivity. However, there has been only one report [1] of GB self-diffusion coefficients for aluminum in alumina in the absence of a $\text{d}\mu_{\text{O}}$ and no data with application of a $\text{d}\mu_{\text{O}}$. One of the likely reasons for this is the lack of an appropriate radioactive tracer, such as ^{26}Al with a very low specific activity and an extremely long half-life of 7.2×10^5 years, which makes it very difficult to perform radiotracer diffusion experiments. Consequently, for the mutual GB diffusion of both oxygen and aluminum in alumina during application of a $\text{d}\mu_{\text{O}}$, it has yet to be clarified whether or not these ions migrate with a synergistic effect.

Alumina-forming alloys typically contain small quantities of oxygen-reactive elements (REs) (e.g., Y, La, Zr, and Hf) to improve their oxidation resistance. The REs segregate to GBs during alumina scale growth by oxidation of the alloys [9]. The REs have been considered to primarily decrease the aluminum GB diffusivity with respect to the oxygen diffusivity, according to ^{18}O depth profiling in scale after two-stage oxidation experiments [10–13]. In addition, the REs are considered to inhibit scale growth by effectively blocking the GB diffusion of aluminum due to an ionic-size mismatch because the ionic sizes of the REs are larger than that of Al^{3+} . However, the GB segregated REs diffused toward the scale surface together with aluminum during high-temperature oxidation for long periods, which resulted in the precipitation of RE-rich particles on the surface [9]. The addition of 0.05 at% Hf to a Fe–Cr–Al alloy was more effective for a reduction of the scale growth rate during oxidation of the alloy at 1427 K than a similar amount of Y-dopant [14]. Thus, Hf^{4+} is more effective than Y^{3+} , although the ionic radius of Hf^{4+} is midway between those of Al^{3+} and Y^{3+} . Therefore, there is little correlation between the ionic radius and suppressed scale growth [14]. The localized changes in the bonding strength between oxygen and aluminum or oxygen coordination of these segregated cations [15] may be related to these phenomena.

Both oxygen and aluminum not only interdiffuse along the GBs in growing scale, but their migration is simultaneously affected by various factors, such as $\text{d}\mu_{\text{O}}$, the REs, impurities, and the diffusion length. Therefore, it is extremely difficult to quantitatively determine the degree of influence for individual factors that influence the movement of each diffusion species. The oxygen permeability technique with polycrystalline α -alumina wafer, which served as a model scale, is thus expected to be very useful to accurately evaluate mass-transfer through the wafers because the $\text{d}\mu_{\text{O}}$ applied to the wafers and the diffusion length are constant [16–24].

In this study, the mass-transfer mechanisms along the GBs in α -alumina are investigated using the oxygen permeation technique with $^{18}\text{O}_2$ at high temperatures. This is followed by further improvement of the oxygen shielding capability and structural stability of alumina on the basis of the flux distribution analysis. Finally, the mass-transfer through the actual scales is discussed by comparing the diffusion data determined from oxygen permeation trials with literature values for the scales.

11.2 Experimental Procedures

11.2.1 Oxygen Permeability Measurements

Polycrystalline alumina wafer specimens with or without REs such as Ln (Lu, Y) and Hf, which were cut from the sintered bodies and polished to a mirror-like finish, served as a model scale for the measurement of oxygen permeability constants using a technique described in detail elsewhere [16–24]. Ln doping was expected to effectively retard mass-transfer in alumina under application of a $\Delta\mu_{\text{O}}$ because Ln can significantly improve high-temperature GB creep resistance in polycrystalline alumina [25–27]. For the single RE-doped samples, a portion of the dopant was segregated at the GBs, and the remaining dopant was precipitated mainly at GBs as crystalline phases containing the dopant, which were identified as $\text{Al}_5\text{Ln}_3\text{O}_{12}$ and monoclinic- HfO_2 (m- HfO_2). Furthermore, mass-transfer along single GBs in two types of non-doped alumina bicrystal wafers was also evaluated by the oxygen permeation technique to clarify the correlation between the mass-transfer along each GB and the GB structural characteristics [18].

Figure 11.1 shows a schematic diagram of the oxygen permeability apparatus [23]. Each wafer specimen was placed between two alumina tubes under an Ar gas flow in a furnace, with Pt gaskets to create a seal between the wafer and the tubes.

Fig. 11.1 Schematic diagram of the oxygen permeability apparatus [23]

The P_{O_2} , included as an impurity in the Ar gas, was monitored at the outlets of the upper and lower chambers that enclosed the wafer and the alumina tubes using a zirconia oxygen sensor at 973 K. The partial pressure of water vapor (P_{H_2O}), another impurity in the Ar gas, was measured at room temperature using an optical dew point sensor. A gas-tight seal was achieved in both chambers by heating to 1893–1923 K, after which the wafer was kept at temperatures above 1773 K for 3 h in Ar at a flow rate of $1.67 \times 10^{-6} \text{ m}^3/\text{s}^1$ for measurement of the oxygen permeability constants. Either Ar or Ar containing 1 vol% H_2 were subsequently introduced into both chambers at the same temperature.

Once the P_{O_2} and P_{H_2O} values were constant, an equilibrium state was reached, and these were taken as background levels. Other gases with different P_{O_2} , such as pure O_2 and Ar gas containing either 0.01–10 vol% O_2 or 0.01–1 vol% H_2 , were then introduced into one of the chambers, which caused the wafer to be subjected to a steep $d\mu_O$. The partial pressure of H_2 was measured at room temperature using gas chromatography. The oxygen permeation flux was considered to have reached a steady state when the monitored values of P_{O_2} , P_{H_2O} , and P_{H_2} at the outlets became constant. The P_{O_2} in each chamber at a high testing temperature, with the wafer subjected to a $d\mu_O$, was calculated thermodynamically from the P_{O_2} measured at 973 K, or from the P_{H_2O} and P_{H_2} measured at room temperature. High purity polycrystalline alumina has excellent oxygen shielding properties; therefore, oxygen permeability measurements using a zirconia oxygen sensor must be conducted at high temperatures to accelerate the mass-transfer in the alumina wafers and aid in the detection of small amounts of oxygen molecules that permeate through the wafers. Oxygen permeation was detected for all polycrystalline wafers but not for a single-crystal wafer; therefore, permeation was considered to occur preferentially along the GBs with a strong dependence on the GB density S_{gb} (i.e., the grain size) of the wafers. Therefore, the oxygen permeability constant was calculated using:

$$\frac{PL}{S_{gb}} = \frac{C_p \cdot Q \cdot L}{V_{st} \cdot S \cdot S_{gb}}, \quad (11.6)$$

where P is the oxygen permeability, L is the wafer thickness, C_p is the concentration of permeated oxygen (P_{O_2}/P_T , where P_T = total pressure), Q is the flow rate of the test gases, V_{st} is the standard molar volume of an ideal gas, and S is the permeation area of the wafer. S_{gb} values were determined by image analysis of the wafer surface microstructures after the oxygen permeation tests using scanning electron microscopy (SEM). The S_{gb} values of the bicrystal wafers were reduced by a factor of 10^5 compared with the polycrystalline alumina wafers; therefore, the amount of permeated oxygen could not be detected because it was below the lower detection limit of the oxygen sensor. The mass-transfer along each GB, especially aluminum diffusivity, was evaluated by measuring the surface profiles around the GB on both surfaces of the bicrystal wafer using atomic force microscopy (AFM) [18].

11.2.2 Determination of Oxygen GB Diffusion Coefficients for Each GB

The oxygen diffusion coefficients near the high- P_{O_2} surface were determined using a SIMS- ^{18}O line profiling technique at each GB [1, 24, 28, 29]. First, ^{18}O mapping of a wafer cross section was performed using SIMS with a beam diameter of 50 nm. The oxygen GB diffusion coefficient was then determined for individual GBs using Eq. (11.7) [30]:

$$D_{gb}\delta = 1.322\sqrt{\frac{D_L}{t}}\left(-\frac{\partial(\ln(C_y - C_{bg}))}{\partial y^{6/5}}\right)^{-5/3}, \quad (11.7)$$

where y is the penetration depth along each GB, t is the exposure time, D_L is the lattice diffusion coefficient for oxygen in sapphire, and C_y and C_{bg} are the respective fractions of ^{18}O at the penetration distance along each GB and the natural abundance (0.00204). D_L is also likely to depend on μ_O in the wafer, similar to the GB diffusion coefficient of Eq. (11.17). However, D_L was assumed to be constant at 5×10^{-20} m²/s at 1873 K [6] because μ_O was almost constant in the immediate vicinity of the $P_{O_2}(\text{hi})$ surface [21, 22]. The oxygen GB diffusion coefficients were determined from Eq. (11.7) within the range that corresponded to the normalized positions of the wafer, x/L . The β values (defined as $\delta(D_{gb}/D_L^{-1})/2(D_L t)^{1/2}$) for the oxygen GB diffusion coefficients must be sufficiently large ($\beta > 10$) to allow the use of Eq. (11.7). In the present work, all β values were larger than 100 and thus met the requirement.

11.3 Results and Discussion

11.3.1 Oxygen Permeation

Figure 11.2 shows the effect of the steady-state P_{O_2} in the upper chamber on the oxygen permeability constants of non-doped and RE-doped samples [16, 17, 19, 23]. P_{O_2} in the lower chamber was held constant at approximately 1 Pa. When a $d\mu_O$ is formed by the combination of P_{O_2} less than 10^{-3} Pa and P_{O_2} of ca. 1 Pa (low P_{O_2} region), the oxygen permeability constants decreased with an increase in P_{O_2} for all the samples. The oxygen permeability constants for the Hf-doped sample were comparable to those for the non-doped sample, whereas those for the Lu- and Y-doped samples were approximately one-third of those for the other samples. In the low P_{O_2} region, all curve slopes corresponded to similar power constants of $n = -1/6$. For all the samples exposed to the low P_{O_2} region, GB grooves were observed on both surfaces with a similar morphology to that formed by conventional thermal etching. The absence of GB ridges on the higher- P_{O_2} ($P_{O_2}(\text{hi})$) surface suggests that aluminum migration played a small role in oxygen permeation. Therefore, the power

Fig. 11.2 Effect of equilibrium P_{O_2} in the upper chamber on the oxygen permeability constants of polycrystalline alumina at 1923 K. The open symbols indicate the data for specimens exposed to a $d\mu_O$ that resulted from a P_{O_2} of 1 Pa in the lower chamber and a P_{O_2} in the upper chamber [23]

constant is applicable to the defect surface reaction given in Eq. (11.1) on the $P_{O_2}(\text{hi})$ surface, and the reverse reaction proceeds on the opposite, lower- P_{O_2} ($P_{O_2}(\text{lo})$) surface ($P_{O_2}(\text{hi}) \gg P_{O_2}(\text{lo})$).

In contrast, when a $d\mu_O$ was generated by a combination of P_{O_2} above 10^3 Pa and a P_{O_2} of ca. 1 Pa (high P_{O_2} region), the oxygen permeability constants increased with P_{O_2} for all the wafers. The oxygen permeability constants for the Hf-doped sample were about half of those of the non-doped, Lu-doped, and Yu-doped samples. All the slopes under high P_{O_2} ($>10^3$ Pa) are comparable to each other and correspond to a power constant of $n = 3/16$, which suggests that the defect surface reaction given in Eq. (11.3) progresses on the $P_{O_2}(\text{hi})$ surface side (formation of new alumina), while the reverse reaction occurs on the $P_{O_2}(\text{lo})$ surface side (decomposition of alumina). In this case, GB ridges with heights of a few micrometers were observed on the $P_{O_2}(\text{hi})$ surface, while deep crevices were formed at the GBs on the $P_{O_2}(\text{lo})$ surface, as shown in Fig. 11.3. This result supports the participation of the defect surface reaction given by Eq. (11.3). In contrast, co-doping with both Lu and Hf increased the oxygen permeation for both P_{O_2} regions and the corresponding power constants were maintained [19]. The formation of cubic-HfO₂ particles segregated at the GBs, which contain a large amount of oxygen vacancies due to a Lu solid solution, was considered to make it difficult to suppress oxygen permeation by co-doping.

Oxygen permeation is known to be controlled by the GB diffusion of oxygen and aluminum. According to the GB disconnection model, [1, 2, 31] oxygen vacancies are created by the reverse reaction of Eq. (11.1) at $P_{O_2}(\text{lo})$ surface ledges and migrate by surface diffusion to the closest GBs, where they are annihilated at jogs on disconnections to form positively charged jogs. The oxygen GB disconnections, which carry some of the free space and all of the positive charge of the oxygen vacancies, migrate toward the $P_{O_2}(\text{hi})$ surface. The charged jogs on the oxygen GB disconnections just below the $P_{O_2}(\text{hi})$ surface then reform oxygen vacancies that migrate to surface ledges and are annihilated according to the reaction in Eq. (11.1).

Fig. 11.3 SEM micrographs of the surfaces and cross sections of non-doped alumina exposed to $P_{O_2}(hi)/P_{O_2}(lo) = 10^5 \text{ Pa}/1 \text{ Pa}$ at 1923 K for 10 h: **a** $P_{O_2}(hi)$ surface side and **b** $P_{O_2}(lo)$ surface side [20]

In contrast, aluminum vacancies are formed at the $P_{O_2}(hi)$ surface ledges by the reaction given in Eq. (11.3) and migrate to nearby GBs via surface diffusion. Annihilation of the aluminum vacancies at jogs on GB disconnections causes the formation of negatively charged jogs. The aluminum GB disconnections migrate toward the $P_{O_2}(lo)$ surface. The aluminum vacancies are then reconstituted just beneath the $P_{O_2}(lo)$ surface and undergo surface diffusion to the closest surface ledges, where they are annihilated by the reverse reaction of Eq. (11.3). Thus, the migration of aluminum GB disconnections means that aluminum diffuses from the $P_{O_2}(lo)$ to $P_{O_2}(hi)$ sides, which results in the formation of ridges near the GBs on the $P_{O_2}(hi)$ surface.

The oxygen permeability constants for each P_{O_2} region can be expressed in terms of Eqs. (11.8) and (11.9) [20–23].

For the low P_{O_2} region (oxygen GB diffusion),

$$\frac{A_O}{S_{gb}} \left(P_{O_2}(hi)^{-1/6} - P_{O_2}(lo)^{-1/6} \right) = \frac{4PL}{S_{gb}}, \quad (11.8)$$

and for the high P_{O_2} region (aluminum GB diffusion),

$$\frac{A_{Al}}{S_{gb}} \left(P_{O_2}(hi)^{3/16} - P_{O_2}(lo)^{3/16} \right) = \frac{4PL}{S_{gb}}. \quad (11.9)$$

Table 11.1 Frequency factors and activation energies for GB diffusion in alumina [21, 22]

Samples	$A_i^* \cdot S_{gb}^{-1} \text{ (mol s}^{-1} \text{ Pa}^{-n}\text{)}$		$Q_i \text{ (kJ mol}^{-1}\text{)}$	
	Oxygen ($\times 10^{-4}$)	Aluminum	Oxygen	Aluminum
Non-doped	15.49	23.14	467	604
Ln*-doped	4.547	23.14	467	604
Hf-doped	15.49	11.34	467	604

*Y or Lu

At temperatures above 1773 K, A_O and A_{Al} are normalized according to S_{gb} and are given by the following Arrhenius equation for non-doped, Ln-doped, and Hf-doped alumina, for which the concentration of each dopant was 0.2 cation% [21–23]:

$$\frac{|A_i|}{S_{gb}} = \frac{A_i^*}{S_{gb}} \exp\left(\frac{-Q_i}{RT}\right), \quad (11.10)$$

where $A_i^* \cdot S_{gb}^{-1}$ and Q_i are the frequency factor and activation energy for oxygen and aluminum GB diffusion, respectively. Table 11.1 provides a summary of $A_i^* S_{gb}^{-1}$ and Q_i [21–23].

Alumina scale formed on alloys is exposed to an extremely large $d\mu_O$, and scale growth proceeds by the interdiffusion of both oxygen and aluminum along the GBs. Accordingly, oxygen permeability constants were also measured at high temperatures under a $d\mu_O$ at which mutual GB diffusion proceeded in the samples. Figure 11.4 shows the oxygen permeability constants for the non-doped alumina as a function of $P_{O_2}(\text{hi})/P_{O_2}(\text{lo})$ at 1923 K, in which $P_{O_2}(\text{lo})$ was constant at 8×10^{-8} Pa. Lines a and b indicate the oxygen permeability constants related to the diffusion of aluminum and oxygen, respectively. Each line was calculated from Eqs. (11.8)–(11.10) with the values listed in Table 11.1. Line c is a sum of lines a and b, which is given by Eq. (11.11):

$$\frac{A_O}{S_{gb}} \left(P_{O_2}(\text{hi})^{-1/6} - P_{O_2}(\text{lo})^{-1/6} \right) + \frac{A_{Al}}{S_{gb}} \left(P_{O_2}(\text{hi})^{3/16} - P_{O_2}(\text{lo})^{3/16} \right) = \frac{4PL}{S_{gb}}. \quad (11.11)$$

The measured oxygen permeability constants were coincident with line c. Therefore, the experimental constants in Table 11.1 determined for either oxygen or Al diffusion are applicable to that with a large $d\mu_O$, where both oxygen and Al interdiffuse without any synergistic effect, which satisfies the Gibbs–Duhem equation. The contribution of aluminum GB diffusion to the oxygen permeation through non-doped alumina increases with the $P_{O_2}(\text{hi})/P_{O_2}(\text{lo})$ ratio.

Figure 11.5 shows an SEM micrograph of the $P_{O_2}(\text{hi})$ surface and cross section of non-doped alumina exposed to $P_{O_2}(\text{hi})/P_{O_2}(\text{lo}) = 10^5 \text{ Pa}/8 \times 10^{-8} \text{ Pa}$ at 1923 K for 10 h, which corresponds to the condition shown by the arrow in Fig. 11.4 [20].

Fig. 11.4 Oxygen permeability constants for non-doped alumina as a function of $P_{O_2}(\text{hi})/P_{O_2}(\text{lo})$ at 1923 K, where $P_{O_2}(\text{lo})$ is a constant of 8×10^{-8} Pa at 1923 K. Lines a, b, and c indicate the contributions related to the GB diffusion of oxygen, aluminum, and their summation, respectively. Each line was calculated from Eqs. (11.8), (11.9), and (11.11). The arrow corresponds to the exposure condition from Fig. 11.5 [20]

Fig. 11.5 SEM micrograph of the $P_{O_2}(\text{hi})$ surface and cross section of the non-doped alumina exposed to $P_{O_2}(\text{hi})/P_{O_2}(\text{lo}) = 10^5$ Pa/ 8×10^{-8} Pa at 1923 K for 10 h [20]

The $P_{O_2}(\text{hi})$ surface shown in Fig. 11.5 was exposed to the same $P_{O_2}(\text{hi})$ in Fig. 11.3a; the amount of oxygen permeation related to the diffusion of aluminum is predicted to be close to that in Fig. 11.3a, according to Eq. (11.11). This suggests that the corresponding morphology of the $P_{O_2}(\text{hi})$ surfaces would be similar to each other. However, the formation of GB ridges on the $P_{O_2}(\text{hi})$ surface is significantly accelerated by the increase of the μ_{O} , especially at multi-junctions of the surface. The large μ_{O} may locally accelerate aluminum diffusivity near the GBs on the $P_{O_2}(\text{hi})$ surface.

Figure 11.6 shows a SIMS- ^{18}O map of a cross section in the vicinity of the $P_{O_2}(\text{hi})$ surface of an alumina wafer exposed to $P_{18O_2}(\text{hi})/P_{16O_2}(\text{lo}) = 10^4$ Pa/ 10^{-8} Pa at 1873 K for 1 h. The triangular marks indicate the position of the $P_{O_2}(\text{hi})$

Fig. 11.6 SIMS- ^{18}O map of the cross section in the vicinity of $\text{P}_{\text{O}_2}(\text{hi})$ surface of alumina wafer exposed to $\text{P}_{16\text{O}_2}(\text{hi})/\text{P}_{16\text{O}_2}(\text{lo}) = 10^4$ Pa/ 10^{-8} Pa at 1873 K for 9 h, and subsequent replacement of the $^{16}\text{O}_2$ at the $\text{P}_{\text{O}_2}(\text{hi})$ side to the same partial pressure of the $^{18}\text{O}_2$ side for 1 h. The GBs used to determine the GB diffusion coefficients for oxide ions are surrounded by ellipses in the map. The arrowheads indicate the position of the $\text{P}_{\text{O}_2}(\text{hi})$ surface [24]

surface. ^{18}O was concentrated along the GBs from the $\text{P}_{\text{O}_2}(\text{hi})$ surface to a depth of approximately 20 μm . A strongly concentrated region with a width of approximately 1 μm extended to a depth of approximately 5 μm in the vicinity of the $\text{P}_{\text{O}_2}(\text{hi})$ surface. During oxygen permeation, ambient O_2 molecules were considered to dissociatively adsorb over the entire $\text{P}_{\text{O}_2}(\text{hi})$ surface, and then immediately diffuse to the surface GBs. As a result, some reacted at the $\text{P}_{\text{O}_2}(\text{hi})$ surface GBs with aluminum diffusing along the GBs from the $\text{P}_{\text{O}_2}(\text{lo})$ side to the $\text{P}_{\text{O}_2}(\text{hi})$ side to form GB ridges of new alumina, and the remaining oxygen diffused inward along the GBs [24]. The oxygen GB diffusion coefficients were measured from the ^{18}O line profiles along the GBs surrounded by ellipses in Fig. 11.6. The average value of the oxygen GB diffusion coefficient was determined to be 9.1×10^{-23} m/s.

11.3.2 GB Diffusion Under Oxygen Potential Gradients

The charged particle fluxes of oxygen and aluminum for oxygen permeation through the wafer, and from the spatial coordinate $x = 0$ to $x = L$, which correspond to the $\text{P}_{\text{O}_2}(\text{lo})$ and $\text{P}_{\text{O}_2}(\text{hi})$ surfaces, can be expressed in terms of the oxygen permeability constants [20–23]:

$$\int_0^L \frac{J_{\text{TO}}}{S_{\text{gb}}} dx = \int_0^L \frac{(J_{\text{O}} + J_{\text{Al}})}{S_{\text{gb}}} dx = \frac{4PL}{S_{\text{gb}}}, \quad (11.12)$$

where J_{TO} is the total flux of oxygen permeation through the wafer. J_{O} and J_{Al} correspond to the fluxes of oxygen and aluminum, respectively. The oxygen permeability constant at an arbitrary position x , along the depth direction of the wafer P_x , is given by Eq. (11.13):

$$\int_0^x \frac{J_{TO}}{S_{gb}} dx = \int_0^x \frac{(J_O + J_{Al})}{S_{gb}} dx = \frac{4Px}{S_{gb}}, \quad (11.13)$$

where $P_{O_2}(x)$ is the O_2 partial pressure in equilibrium with the chemical potential of oxygen at x . Combining Eqs. (11.12) and (11.13) gives Eq. (11.14):

$$\frac{x}{L} = \frac{\frac{A_{Al}}{S_{gb}} (P_{O_2}(x)^{3/16} - P_{O_2}(lo)^{3/16}) + \frac{A_O}{S_{gb}} (P_{O_2}(x)^{-1/6} - P_{O_2}(lo)^{-1/6})}{\frac{A_{Al}}{S_{gb}} (P_{O_2}(hi)^{3/16} - P_{O_2}(lo)^{3/16}) + \frac{A_O}{S_{gb}} (P_{O_2}(hi)^{-1/6} - P_{O_2}(lo)^{-1/6})} \quad (11.14)$$

The chemical potentials of oxygen (μ_O) and aluminum (μ_{Al}) are given by:

$$\mu_O = \frac{\mu_{O_2}^\circ + RT \ln P_{O_2}}{2}, \quad (11.15)$$

$$\mu_{Al} = \frac{2\mu_{Al_2O_3}^\circ - 3(\mu_{O_2}^\circ + RT \ln P_{O_2})}{4}, \quad (11.16)$$

where $\mu_{O_2}^\circ$ and $\mu_{Al_2O_3}^\circ$ are the standard chemical potential energies per mole of molecular O_2 and pure alumina, respectively, R is the gas constant, and T is the absolute temperature. Thus, μ_O and μ_{Al} at x can be determined using Eqs. (11.15) and (11.16) with the $P_{O_2}(x)$ values calculated from Eq. (11.14). The GB diffusion coefficients of oxygen and aluminum at x can be calculated using Eqs. (11.17) and (11.18) with the corresponding $P_{O_2}(x)$.

$$D_O \delta = \frac{1}{6C_O \cdot t_{e'}} \frac{|A_O|}{S_{gb}} P_{O_2}^{-1/6}, \quad (11.17)$$

$$D_{Al} \delta = \frac{1}{12C_{Al} \cdot t_{e'}} \frac{A_{Al}}{S_{gb}} P_{O_2}^{3/16}, \quad (11.18)$$

where δ is the GB width. C_O and C_{Al} , the molar concentrations of the species per unit volume of alumina, are 1.168×10^5 and $7.787 \times 10^4 \text{ mol/m}^3$, respectively. The experimental parameters $|A_O|$ and A_{Al} are related to the mobility of oxygen and aluminum, respectively. $t_{e'}$ is the electronic transference number, which was comparatively close to unity, as determined using Eq. (11.17) with the average value of the oxygen GB diffusion coefficients measured by the SIMS- ^{18}O line profiling technique. That for alumina scale formed by the oxidation of β -NiAl alloy under high P_{O_2} at 1373 K was reported to be approximately 0.9 [32]. Hence, in this study, the alumina subjected to $d\mu_O$ is assumed to be an electronic conductor, i.e., $t_{e'} = 1$.

Fig. 11.7 Distributions of P_{O_2} , chemical potentials, and GB diffusion coefficients for oxygen and aluminum in a non-doped alumina wafer exposed to $P_{O_2}(hi)/P_{O_2}(lo) = 10^5 \text{ Pa}/10^{-8} \text{ Pa}$ at 1873 K [23]

Figure 11.7 shows distributions of P_{O_2} , chemical potentials, and GB diffusion coefficients for oxygen and aluminum in a non-doped alumina wafer exposed to $P_{O_2}(hi)/P_{O_2}(lo) = 10^5 \text{ Pa}/10^{-8} \text{ Pa}$ at 1873 K. The P_{O_2} plot is a sigmoid curve. μ_O increases with x/L in an inverse relationship to μ_{Al} , in accordance with the Gibbs–Duhem equation. The oxygen GB diffusion coefficient decreases with an increase in x/L , while the aluminum GB diffusion coefficient increases. As a result,

the aluminum diffusion coefficient is larger than the oxygen diffusion coefficient near the $P_{O_2}(\text{hi})$ surface, which is the opposite relationship to that near the $P_{O_2}(\text{lo})$ surface.

The evaluation of mass-transfer through the GBs in alumina bicrystals, in which the character of the GBs can be arbitrarily controlled, is a very powerful method used to elucidate the fundamental mechanisms of GB phenomena such as creep and diffusion [5, 15]. The measured oxygen GB diffusion coefficients were strongly dependent on the atomic-scale GB structures. However, the effect of the atomic-scale GB structures on the GB diffusion of aluminum has not yet been clarified for the reasons discussed in the Introduction. Figure 11.8 shows a schematic diagram of the fabricated bicrystal alumina wafers and AFM images of the surfaces of bicrystal alumina wafers ($\Sigma 13$ and $\Sigma 31$) exposed to $P_{O_2}(\text{hi})/P_{O_2}(\text{lo}) = 10^5 \text{ Pa}/1 \text{ Pa}$ at 1923 K for 10 h. The morphology of the surface profiles is strongly dependent upon the GB characteristics [18]. For the wafer with a relatively low GB coherence such as $\Sigma 31$ (Fig. 11.8), a ridge was formed along the GB on the $P_{O_2}(\text{hi})$ surface and a deep GB ditch was observed on the opposite $P_{O_2}(\text{lo})$ surface due to the migration of aluminum through the GBs from the $P_{O_2}(\text{lo})$ surface to the $P_{O_2}(\text{hi})$ surface. On the other hand, for the $\Sigma 13$ bicrystal wafer with high GB coherence, there is a shallow groove along the GBs on both surfaces, as shown in Fig. 11.8, similar to grooves formed by conventional thermal etching. There was neither a GB ridge on the $P_{O_2}(\text{hi})$ surface nor a ditch on the $P_{O_2}(\text{lo})$ surface. Therefore, the migration of aluminum through the $\Sigma 13$ wafer does not occur to any significant extent under the present experimental conditions. The GB diffusion coefficient of aluminum was determined from the volume of GB ridges observed on the $P_{O_2}(\text{hi})$ surface. The aluminum GB diffusion coefficient for the $\Sigma 13$ GB ($1.1 \times 10^{-20} \text{ m}^3/\text{s}$) was similar to that for a

Fig. 11.8 Schematic diagram of the fabricated bicrystal alumina wafers and AFM images of the surfaces of bicrystal alumina wafers ($\Sigma 13$ and $\Sigma 31$) exposed to $P_{O_2}(\text{hi})/P_{O_2}(\text{lo}) = 10^5 \text{ Pa}/1 \text{ Pa}$ at 1923 K for 10 h

polycrystalline wafer ($8.5 \times 10^{-21} \text{ m}^3/\text{s}$). They had a tendency to be proportional to the GB energies and the mean bond lengths between oxygen and aluminum around the GB [18]. Mass-transfer during oxygen permeation is considered to progress preferentially along GBs with relatively low GB coherence.

Ogawa et al. investigated the switching behavior (P_{O_2} -dependence) of the dominant diffusion species by quantum mechanical density functional theory (DFT) calculation of the formation energies for charged oxygen and aluminum vacancies [33]. The electronic structure of the $\Sigma 31$ bicrystal revealed significant narrowing of the band gap to approximately 60% of that for a single crystal ($E_g^B = 9.1 \text{ eV}$). Figure 11.9 shows the effect of P_{O_2} on the Fermi levels and formation energies of oxygen and aluminum vacancies at 1923 K for relative band gaps of 1.0 and 0.6 compared to that for the single crystal. Although the defect formation energies and the Fermi levels at the GB are not directly calculated, they exhibit different behavior for wide band gap and narrow band gap structures. For a wide band gap, the aluminum vacancies and holes are dominant, regardless of P_{O_2} . However, a switchover in the formation energies of the two types of vacancies appears for a significantly narrow band gap. This suggests that GBs with low coherence in polycrystalline alumina, i.e., narrow band gap structures, is the origin of oxygen diffusion. In this case, the Fermi level at the $P_{\text{O}_2}(\text{lo})$ side is only slightly higher than that at the $P_{\text{O}_2}(\text{hi})$ side (+0.17 eV). This may support the assumption of the constant of t_e in alumina subjected to a $d\mu_{\text{O}}$.

Fig. 11.9 Effect of P_{O_2} on
a Fermi levels and
b formation energies of
oxygen and aluminum
vacancies at 1923 K for
relative band gaps of 1.0 and
0.6 eV compared to that for a
single crystal ($E_g^B = 9.1 \text{ eV}$)
[23]

11.3.3 Design of Oxygen Shielding Capability and Structural Stability

The fluxes of oxygen and aluminum normalized according to L/S_{gb} at position x/L are given by:

$$\frac{J_{O}L}{S_{gb}} = 2 \left(\frac{C_O \cdot t_e \cdot D_O \delta}{RT} \right) \frac{\partial \mu_O}{\partial (x/L)}, \quad (11.19)$$

$$\frac{J_{Al}L}{S_{gb}} = -3 \left(\frac{C_{Al} \cdot t_e \cdot D_{Al} \delta}{RT} \right) \frac{\partial \mu_{Al}}{\partial (x/L)}. \quad (11.20)$$

Thus, each flux can be determined from Eqs. (11.19) and (11.20) with the calculated GB diffusion coefficients and differentials of the chemical potentials at x/L . In this study, t_e is assumed to be unity. Figure 11.10a shows that for non-doped alumina, the oxygen and aluminum fluxes at the outflow side are significantly larger than those at the inflow side. In this case, oxygen permeation from the diffusion of oxygen is comparable to that of aluminum. The dotted line in Fig. 11.10a represents the summation of both the fluxes and corresponds to the oxygen permeation in the steady state

As listed in Table 11.1, Lu-doping decreases only the frequency factor of oxygen to one-third of that for a non-doped alumina layer, while Hf-doping decreases only the frequency factor of aluminum by half. For the bilayer sample, as shown in Fig. 11.10b, in which a Ln-doped layer is exposed to the lower P_{O_2} side and an Hf-doped layer is exposed to the higher P_{O_2} side, and where each layer has the same thickness, the sum of both fluxes is decreased, i.e., the oxygen shielding capability and structural stability of the alumina bilayer are increased. However, when the bilayer structure is reversed, as shown in Fig. 11.10c, the summation of both fluxes is similar to that for the non-doped single layer. The integrated values of each flux with respect to the thickness of all the layers were consistent with four times the actual oxygen permeation data [22]. Therefore, these results suggest that to improve oxygen shielding and structural stability by the alumina bilayer, it is very important to achieve an optimal dopant arrangement that takes into consideration the behavior of the diffusion species and the role of the dopants within the layers.

11.3.4 Mass-Transfer in Alumina Scale

The approaches developed to elucidate mass-transfer in alumina during oxygen permeation experiments were extended to an analysis of the interdiffusion mechanisms in actual scale exposed to lower temperatures [23]. The GB diffusion coefficients of oxygen and aluminum are dependent on P_{O_2} ; therefore, a comparison

Fig. 11.10 Distributions of oxygen and aluminum fluxes in specimens exposed to $P_{O_2}(hi)/P_{O_2}(lo) = 10^5 \text{ Pa}/10^{-8} \text{ Pa}$ at 1873 K:

a non-doped sample, **b**, **c** double layered samples consisting of Ln-doped and Hf-doped layers. The dashed lines indicate the summation of both the oxygen and aluminum fluxes [23]

with the oxygen permeation data and those values obtained from ^{18}O depth profiling in the scale after two-stage oxidation experiments [6, 7] is required to estimate the P_{O_2} value, in equilibrium with μ_{O} in the depth profiling zone. The activation energy for the oxygen GB diffusion coefficients from the oxygen permeation trials is close to that in scale. It is thus postulated that Eqs. (11.10) and (11.17) are

applicable for alumina scale. The activation energies for oxygen in the scale are also assumed to be the same as those obtained from the oxygen permeation experiments, as listed in Table 11.1, regardless of whether the alumina scale was doped with Y or not.

Consequently, P_{O_2} and A_{O^*}/S_{gb} in Eqs. (11.10) and (11.17) for scale can be determined by solving the simultaneous equations using the profiling position (x/L) and the corresponding oxygen GB diffusion coefficients.

The oxygen GB diffusion data for Y-doped scale formed on ODS-MA956 alloy [6] was determined at an x/L of approximately 0.88–0.96; however, there was no description of the measurement ranges for other types of scales [7]. Thus, these ranges for all the scales in this study are assumed to be equal to that for Y-doped scale [6], which adopts the middle value ($x/L = 0.92$) of the measurement range because such a depth profiling is generally performed in a zone just near the scale surface. As a result, P_{O_2} and A_{O^*}/S_{gb} for scale formed on the RE-free alloy at 1373 K, i.e., non-doped scale, are 1.6×10^{-17} Pa and $13.94 \times 10^{-4} \text{ mol s}^{-1} \text{ Pa}^{-1/6}$, respectively. The calculated A_{O^*}/S_{gb} value is almost equal to that determined from the oxygen permeation experiments, as given in Table 11.1.

Figure 11.11 shows Arrhenius plots of the GB diffusion coefficients for oxygen, together with data from the literature [6, 7]. Table 11.2 summarizes the measurement conditions and activation energies for the GB diffusion data in Fig. 11.11. The dashed line a, which is determined by substitution of $P_{O_2} = 1.6 \times 10^{-17}$ Pa in

Fig. 11.11 Arrhenius plots of the GB diffusion coefficients for oxygen, together with data from the literature [6, 7]

Table 11.2 Summary of measurement conditions and activation energies for the oxygen GB diffusion data in Fig. 11.11

	Lines	Samples	Methods	P _{O2} (Pa)	Q _i (kJ mol ⁻¹)
This work	a	Non-doped	Oxygen permeation	2×10^{-17}	467
	b	Ln*-doped		7×10^{-13}	
Chevalier et al. [7]	c	“Non-doped” scale formed on Fe–20Cr–5Al	Isotopic tracer (SIMS)	–	323
	d	“Y-doped” scale formed on Fe–20Cr–5Al–0.1Y		–	–
Messaoudi et al. [6]	e	“Y-doped” scale formed on ODS-MA956	Isotopic tracer (SIMS)	–	391

*Y or Lu

Eq. (11.17), when extrapolated to lower temperature is consistent with that reported for scale (line c). Thus, the oxygen GB diffusion mechanism for non-doped alumina is considered to be independent of temperature. The oxygen GB diffusion coefficients for Y-doped scale (point d and line e) is approximately $1/10^4$ of that for the non-doped scale (line c) shown in Fig. 11.11.

P_{O2} and A_O*/S_{gb} for the Y-doped scale were also calculated at 1373 K using a similar method to that for the non-doped scale, and were determined as 6.7×10^{-13} Pa and 2.175×10^{-6} mol s⁻¹ Pa^{-1/6}, respectively. Therefore, the significant retardation of oxygen GB diffusivity due to Y-doping is probably related to a decrease of A_O*/S_{gb} and an increase of μ_O in the vicinity of the scale surface, which results in a decrease of the driving forces for both oxygen and aluminum diffusion according to the Gibbs–Duhem relationship. Line b in Fig. 11.11 at P_{O2} = 6.7×10^{-13} Pa, when extrapolated to a lower temperature, is significantly deviated from the data for the Y-doped scale (d and e in Fig. 11.11), despite the almost identical activation energies. The magnitude of the reduction in oxygen diffusivity due to the presence of Y suggests a discontinuous decrease with an increase in temperature. A similar phenomenon was reported for the evolution of a bimodal Y-doped alumina structure by characterization of the grain growth of both normal and unimpinged abnormal grains as a function of time [34]. The discontinuous change of the GB mobility at approximately 1773 K is considered to be caused by transition of the GB structures, i.e., so-called complexion to produce an equilibrium interfacial state. However, the corresponding activation energies were constant during the complexion transition, so that there may be other possible causes for this phenomenon. This requires further examination of the discontinuity with respect to the temperature dependence of the GB diffusivity.

11.4 Conclusions

The oxygen permeability of polycrystalline alumina wafers, with and without RE dopants such as Ln (Y, Lu) and Hf, served as model alumina scale for evaluation under a $\Delta\mu_{\text{O}}$ at temperatures up to 1923 K. Oxygen permeation occurred by the GB diffusion of oxygen from the $\text{P}_{\text{O}_2}(\text{hi})$ surface side to the $\text{P}_{\text{O}_2}(\text{lo})$ surface side, while simultaneous GB diffusion of aluminum proceeded in the opposite direction. A bilayer wafer with a Ln-doped layer on the $\text{P}_{\text{O}_2}(\text{lo})$ side and a Hf-doped layer on the $\text{P}_{\text{O}_2}(\text{hi})$ side decreased the oxygen permeability. When the sign of $\Delta\mu_{\text{O}}$ was reversed, the wafer did not exhibit a decrease in oxygen permeability and instead exhibited behavior similar to that of a non-doped wafer. Furthermore, the approaches developed to elucidate the mass-transfer in alumina during oxygen permeation experiments were extended to analysis of the interdiffusion mechanisms in actual scale exposed to lower temperatures. Y segregated at the GBs in the scale was considered to decrease the oxygen frequency factor and the driving forces for both oxygen and aluminum diffusion in the vicinity of the $\text{P}_{\text{O}_2}(\text{hi})$ surface.

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