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# Oxygen permeability in cation-doped polycrystalline alumina under oxygen potential gradients at high temperatures

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## Abstract

The oxygen permeability through the grain boundaries of Hf- and/or Lu-doped polycrystalline alumina wafers that were exposed to oxygen potential gradients generated by combinations of different oxygen partial pressures ($P_{O_2}$) was investigated at temperatures up to 1923 K. Hf doping decreased the mobility of Al grain-boundary diffusion from the lower $P_{O_2}$ surface side to the higher $P_{O_2}$ surface side to half that of undoped samples, but did not influence oxygen diffusion through the grain boundaries. Lu doping had the opposite effect. It is thought that the ability of a dopant to inhibit the mobility of either Al or oxygen would strongly depend on the atomic structural environment in the vicinity of dopant segregated at the grain boundaries. However, the oxygen permeability was increased by co-doping with Lu and Hf under all the oxygen potential gradients investigated, although the corresponding power constants were maintained.

*Keywords:* Alumina; Oxygen permeation; Oxygen potential gradient; Diffusion; Grain boundary

## 1. Introduction

Alumina-forming alloys are widely used in hot-section components such as thermal-barrier coating systems [1]. The durability of these components is generally controlled by the barrier's performance with respect to oxygen permeation through the grain boundaries in the polycrystalline alumina scale formed on the alloy surfaces, which are exposed to steep oxygen potential gradients. These alloys typically contain small quantities of oxygen-reactive elements (REs) (e.g., Y, La, and Zr) to improve their oxidation resistance. These REs segregate to grain boundaries in growing alumina scales during oxidation of the alloys, which are thought to suppress both inward diffusion of oxygen and outward diffusion of Al [2,3]. The obvious difficulty is that it is not known what the diffusing species along the grain boundaries in the scales might be. Nevertheless, the REs are believed to inhibit scale growth by effectively blocking the outward grain-boundary diffusion of Al due to an ionic-size mismatch, since the ionic sizes of the REs are larger than that of $Al^{3+}$ [3]. However, it was found that during long-duration, high-temperature oxidation, REs that segregated to grain boundaries diffused toward the scale surfaces together with Al, resulting in the precipitation of RE-rich particles on the surfaces [3]. This casts doubt on the conjecture that REs will always be able to control the movement of Al. The coexistence of various REs further complicates the interpretation of experimental results.

On the other hand, it is well known that the segregation of rare-earth (e.g., Y, Lu, Tm, and Eu) and group IV (Zr, Hf) elements at the grain boundaries of alumina can significantly retard oxygen grain-boundary diffusivity, resulting in suppression of creep deformation, and final-stage sintering under homogeneous environments without any oxygen potential gradients [4–9]. The retardation of these mass transfers is thought to be related to (i) ionic size of the doping elements, (ii) bond strength between cation and oxygen, (iii) oxygen coordination number of the dopants segregated at grain boundaries.

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It has been suggested that in the ionic size effect, the grain-boundary environment is changed by "site-blocking" critical oxygen diffusion pathways due to the ionic size mismatch of the large dopants segregated at the grain boundaries [10–15]. For example, the ionic radii of rare-earth and group IV elements with the corresponding ionic valence for an oxygen coordination number of 6 are, respectively, 0.90, 0.86, 0.72, and 0.71 Å for $Y^{3+}$, $Lu^{3+}$, $Zr^{4+}$, and $Hf^{4+}$, all much larger than the 0.51 Å reported in the literature for $Al^{3+}$ [16]. Therefore, the ionic size effect for rare-earth elements is speculated to be larger than that for group IV elements. Cho et al. [12] have investigated the steady-state creep rate of various singly doped aluminas from 1473 to 1623 K, where larger dopants such as Y, Nd, and La effectively decreased the creep rate compared with the smaller dopant, Zr.

With respect to the bond strength effect, Yoshida et al. [5] demonstrated that the creep resistance of polycrystalline alumina can be improved by doping elements that increase the bonding strength between Al and oxygen near a dopant substituted for Al in $Al_2O_3$, for which the product of the Al and oxygen net charges decreased in the order Lu- or Y-doped > Zr-doped > undoped alumina, as determined by first-principles molecular orbital calculations. On the other hand, Buban et al. [17] reported for Y as a dopant segregated at the $\Sigma 31$ grain boundary of an alumina bicrystal that the increase in the bond strength between Y and oxygen toward a more covalent bond was responsible for the improvement in creep resistance, according to Z-contrast images obtained by scanning transmission electron microscopy (STEM) of the bicrystal and charge density maps generated by first-principles ab initio calculations using the Vienna Ab Initio Simulation Package (VASP).

Buban et al. [17] pointed out that, in addition to the increase in bonding strength, the improvement in creep resistance was presumably also related to the increase of the oxygen coordination number for Y segregated at the grain boundaries [17]. In theoretical modeling and STEM energy-loss near-edge structure (ELNES) studies of a near $\Sigma 11$ grain boundary in a non-doped polycrystalline alumina, the oxygen coordination number of some Al was reported to be reduced to four, compared with six in perfect $Al_2O_3$ [18–20]. This reduction is likely to distort cation arrangements in the grain boundaries. The atomic structural environment of grain boundaries in Y- or Zr-doped polycrystalline alumina was investigated through extended X-ray absorption fine structure (EXAFS) measurements, where the oxygen coordination numbers for Y and Zr segregated at the grain boundaries were 4.2 and 5.0, respectively [11]. The oxygen coordination numbers for the dopants were evidently higher than that for Al in non-doped alumina. An increase in the oxygen coordination numbers of the dopants, namely an increase in the bond numbers at the grain boundaries, likely retards the mass transfer through the grain boundaries. However, despite these vigorous investigations, it has remained unclear which inhibition parameters, viz., the ionic-size mismatch, bonding strength and oxygen coordination number, effectively controlled the diffusion of Al, oxygen, or both.

We have evaluated the oxygen permeability of undoped and Lu-doped polycrystalline alumina wafers, which were exposed to oxygen potential gradients ($\Delta P_{O_2}$) at high temperatures, with each surface of the wafer deliberately subjected to different oxygen partial pressures ($P_{O_2}$) [21–24]. The main diffusion species during oxygen permeation through the alumina grain boundaries were found to depend on the $P_{O_2}$ that created the oxygen potential gradients. Under a $\Delta P_{O_2}$ generated by low $P_{O_2}$ values, where oxygen permeation occurred by oxygen diffusion from regions of higher to lower $P_{O_2}$, segregated Lu at the grain boundaries suppressed only the mobility of oxygen in the wafers, owing to a reduction in the effective area of grain boundary diffusion, without affecting the oxygen permeation mechanism. By contrast, under oxygen potential gradients generated by high $P_{O_2}$ values, where oxygen permeation proceeded by Al diffusion from regions of lower to higher $P_{O_2}$, Lu had little effect on Al diffusion and migrated with Al, resulting in precipitation and growth of $Al_5Lu_3O_{12}$ particles on the higher $P_{O_2}$ surface [24]. The effective retardation of the oxygen grain boundary diffusivity by Lu-doping is thought to be caused by grain-boundary strengthening due to the bonding strength between Al and oxygen and by site-blocking due to the ionic-size mismatch. The influence of Lu-doping on the diffusion of Al along the grain boundaries was small, presumably because of the generation of a large number of Al vacancies at the grain boundaries under $\Delta P_{O_2}$, which may reduce such inhibition parameter effects. Furthermore, because Al vacancy formation decreases the oxygen coordination number of Al near the grain boundaries, the Al grain boundary diffusivity is thought to be strongly affected by the change in the oxygen coordination number of Al. To date, there have been no theoretical or experimental reports on the oxygen coordination number of Lu segregated at the grain boundaries. However, Lu belongs to the same homologous series in the periodic table as Y. The core levels of $Lu^{3+}$ are completely filled with electrons like those of $Y^{3+}$, and their cationic radii are comparable. The excess doping of these cations into alumina leads to the precipitation of complex oxides with a garnet structure at high temperatures. Thus, it is believed that the characteristics of grain boundaries with segregated Lu would be similar to those of grain boundaries with segregated Y, and the oxygen coordination number of Lu at the grain boundaries may be slightly larger than those of Al.

The mass transfer behavior through grain boundaries in alumina was systematically investigated using four types of alumina bicrystal wafers at high temperatures [25]. In the bicrystal wafers, which were exposed to a constant $\Delta P_{O_2}$, Al mainly diffused through the single grain boundary, resulting in the growth of a grain boundary ridge on the surface exposed at the higher $P_{O_2}$ side due to alumina formation. The grain boundary diffusion coefficients of Al estimated from the volume of the grain boundary ridges