Effect of Dopants on Mutual Grain-boundary Transport of Aluminum and Oxygen in Polycrystalline Al$_2$O$_3$

Satoshi Kitaoka[1], Tsuneaki Matsudaira[1], Masashi Wada[1], Tadashi Hamanaka[2], Takeharu Kato[2]

[1]Materials Research and Development Laboratory, [2]Nanostructures Research Laboratory,
Japan Fine Ceramics Center, Nagoya 456-8587, Japan

Alumina-forming alloys are widely used for hot-section components such as thermal barrier coatings that can withstand high temperatures and oxidizing environments. Their excellent high-temperature performances appear to be due to the formation of an alumina scale, which acts as a protective layer by inhibiting further oxidation. To save energy and reduce the use of alloys containing rare elements, it is highly desirable to further improve the high-temperature durability of such components. In this regard, suppressing mass transfer through the alumina scale is expected to markedly enhance the alloy durability. When these alloys are oxidized through the alumina scale under high oxygen partial pressures (P$_{O2}$) (such as in air), the scale is subjected to a steep oxygen potential gradient (ΔP$_{O2}$) in the opposite direction to that of the aluminum potential gradient. Thus, scales grow on the alloys by inward grain boundary (GB) diffusion of oxygen and outward GB diffusion of aluminum, producing GB ridges on the scale surfaces.

To clarify the GB transport mechanism, oxygen permeation through polycrystalline alumina wafers exposed to various ΔP$_{O2}$ at high temperatures was measured with each surface of the wafer deliberately subjected to a different P$_{O2}$ value [1]–[3]. When a ΔP$_{O2}$ is generated by a combination of high P$_{O2}$ values, oxygen permeates mainly via GB diffusion of aluminum from the lower to the higher P$_{O2}$ surface, resulting in the formation of GB ridges on the higher P$_{O2}$ surface. Conversely, under a ΔP$_{O2}$ generated by low P$_{O2}$ values, oxygen permeation occurs by GB diffusion of oxygen from the higher to the lower P$_{O2}$ surface. Thus, the GB diffusion coefficients of aluminum and oxygen could be estimated from oxygen permeability constants measured under various ΔP$_{O2}$, for which either aluminum or oxygen mainly diffused through the GBs [1].

The alloys typically contain small quantities of oxygen-reactive elements (REs) (e.g., hafnium and lutetium). They segregate at the GBs in growing alumina scales formed by alloy oxidation. This improves the oxidation resistance of the alloy. Under ΔP$_{O2}$ for which either aluminum or oxygen primarily diffuses through the GBs in RE-doped alumina wafers, hafnium and lutetium were found to selectively reduce the aluminum and oxygen mobilities, respectively [2].

When aluminum and oxygen interdiffused in undoped polycrystalline alumina wafers subjected to a steep ΔP$_{O2}$, these ions migrated without any acceleration or inhibition due to the interdiffusion, in accordance with the Gibbs–Duhem equation ($2d\mu_{Al} + 3d\mu_{O} = 0$) [3]. Furthermore, we estimated mass-transfer parameters such as the chemical potentials, the GB diffusion coefficients, and the aluminum and oxygen fluxes as a function of depth. These parameters varied significantly with depth. However, it is unclear how their depth profiles were altered by RE dopants segregated at the GBs, which reduce the mobility of either aluminum or oxygen. This study investigates the effect of dopants on the mutual GB transfer of aluminum and oxygen.

The materials used in this study were undoped, lutetium-doped, and hafnium-doped polycrystalline alumina. The total concentration of doped cations was fixed at 0.2 mol%. Wafers with dimensions of $\phi 23.5 \times 0.25$ mm were cut from sintered bodies and polished to a mirror finish. All wafers had relative densities that were >99% of the theoretical density. The methods used to measure the oxygen permeability constants and to calculate the mass-transfer parameters of aluminum and oxygen have been described in detail in Refs. 1 and 3.

Figure 1 shows distributions of the mass-transfer parameters of aluminum and oxygen as a function of depth x for 1923 K and $P_{O2}(II)/P_{O2}(I) = 10^5$ Pa/10^{-8} Pa. In this figure, μ_i is the chemical potential, D_{gb} is the GB diffusion coefficient, δ is the GB width, J_i is the flux, L is the wafer thickness, and S_{gb} is the GB density of the alumina wafers at 1923 K. The arrows in the figure indicate the transport directions of aluminum and oxygen. For undoped alumina, μ_O of the wafer decreases with decreasing x/L; it exhibits an inverse relationship with μ_{Al} in conformity with the Gibbs–Duhem equation. $D_{gb}\delta$ of oxygen increases with decreasing x/L, whereas that of aluminum decreases with decreasing x/L. Consequently, the aluminum and oxygen fluxes at the inflow side are significantly smaller than those at the outflow side.

When the oxygen mobility is reduced to 0.3 that of undoped alumina by lutetium doping [2], $D_{gb}\delta$ and flux of oxygen are reduced. The aluminum flux near the outflow side also decreases because the driving force ($d\mu_i/dx$) for aluminum near the same side decreases. The void formation mechanism in the alumina scales is thought to be related to depth profiles of the mass-transfer parameters.
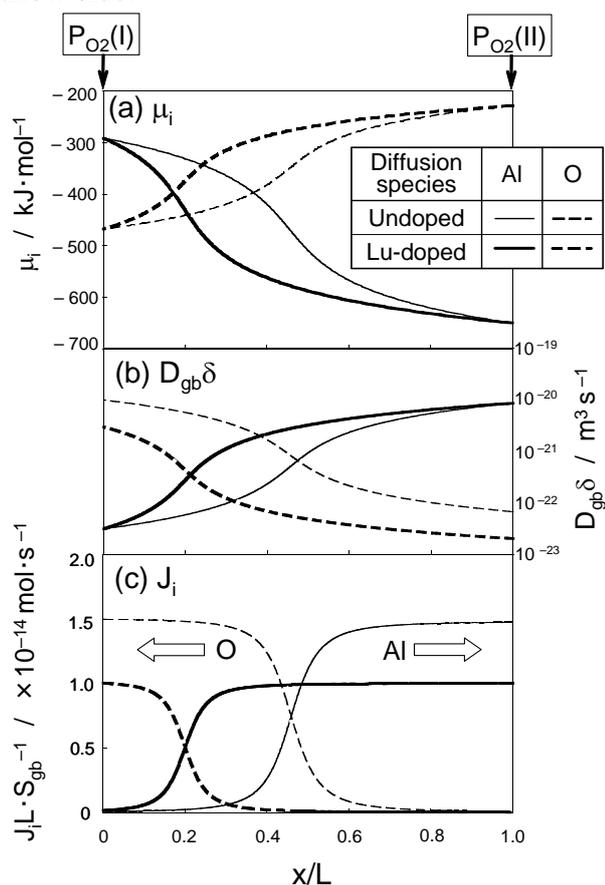
FIG. 1. Distributions of the mass-transfer parameters for aluminum and oxygen in alumina wafers at 1923 K and $P_{O2}(II)/P_{O2}(I) = 10^5$ Pa/10^{-8} Pa.

References
[1] S. Kitaoka, et al., Mater. Trans., 50 (2009) 1023.
[2] T. Matsudaira, et al., Acta Mater., 58 (2010) 1544; ibid., 59 (2011) 5440.
[3] M. Wada, et al., J. Ceram. Soc. Jpn., 119 (2011) 832