

Control of Mass Transfer along Grain Boundaries in α -Alumina under Oxygen Potential Gradients at High Temperatures

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Alumina-forming alloys are widely used in hot-section components of gas turbine engines, and have an important influence on the durability of thermal barrier coatings (TBCs). Although these coatings have excellent thermal barrier characteristics, and prevent large temperature increases in the alloys, they are effectively transparent to oxygen diffusion from the atmosphere, so that the underlying metal becomes oxidized. This thermally grown oxide (TGO) thickens with time, eventually reaching a critical thickness at which spallation occurs. In general, the TGO is composed of polycrystalline α -alumina, and its growth is regulated by solid-state diffusion of oxygen and aluminum along grain boundaries (GBs) in the alumina layer in response to their respective chemical potential gradients. Thus, the durability of hot-section components is expected to be determined by the amount of such mass transport that occurs.

Small quantities of oxygen-reactive elements, such as Y, Zr and Hf, are often added to alumina-forming alloys in order to improve their oxidation resistance. These elements segregate at GBs in growing alumina scales during the oxidation process, and are thought to suppress mass transfer along the GBs, as well as to improve scale adhesion under thermal cycling conditions. This study focuses on control of oxygen and aluminum GB diffusion in alumina by such segregated dopants.

In previous studies [1-2], polycrystalline α -alumina wafers were used to represent the TGO layer in TBCs, and their permeability to oxygen was measured using a zirconia oxygen sensor. Because the wafers were highly resistant to oxygen permeation, the experiments were carried out at temperatures above 1773 K, in order to accelerate mass transfer. An oxygen partial-pressure difference, expressed as $\Delta P_{O_2} = P_{O_2}(\text{hi}) - P_{O_2}(\text{lo})$, was applied across the wafers. At such high temperatures, oxygen permeation occurred by GB diffusion of oxygen from the $P_{O_2}(\text{hi})$ surface to the $P_{O_2}(\text{lo})$ surface, along with simultaneous GB diffusion of aluminum in the opposite direction, similar to the case for mass transfer through alumina scales. It was found that the oxygen and aluminum fluxes at the outflow side of the wafer were significantly larger than those at the inflow side [1]. The narrow bandgap of incoherent GB suggests to be responsible for the switching behavior of the main diffusion species [3].

The effect of GB segregation of Hf or the rare-earth elements such as Y and Lu on mass transport has also been previously investigated for a large ΔP_{O_2} at temperatures above 1773 K [1]. Very interestingly, Hf and the rare-earth elements were found to selectively reduce the diffusivity of aluminum and oxygen, respectively. The reduction in oxygen diffusivity was found to be similar for Y and Lu. In all cases, the reduction in diffusivity was not associated with a change in the activation energy for diffusion, given by the Arrhenius equation, but was instead due to a change in the frequency factor.

In the present study, to further improve the oxygen shielding capability of

alumina layers, the effect of Hf and Lu dopants on GB diffusion of aluminum and oxygen was investigated for alumina wafers exposed to a large ΔP_{O_2} at high temperature. While past research was limited to the effect of a single type of dopant, the present study also considers a Hf and Lu co-doped single wafer, and a bilayer wafer containing adjacent Hf- and Lu-doped layers exposed to different P_{O_2} gradients.

Figure 1 shows the calculated oxygen and aluminum flux profiles in different wafers exposed to $P_{O_2}(\text{hi})$ and $P_{O_2}(\text{lo})$ partial pressures of 10^5 and 10^{-8} Pa, respectively, at a temperature of 1873 K. The calculation procedure has been described in detail elsewhere [2]. The dotted lines in the figure indicate the summation of the oxygen and aluminum fluxes; this is constant because it represents the steady-state oxygen permeation. For the bilayer wafer with the Lu-doped layer at the $P_{O_2}(\text{lo})$ side, the maximum fluxes at the outflow sides, which control the mass transfer, are only about one-third of those for the undoped wafer.

However, for the bilayer wafer with the Lu-doped layer at the $P_{O_2}(\text{hi})$ side, the maximum fluxes are similar to those for the undoped sample. The sum of the integrated fluxes with respect to the sample thickness is equal to four times the oxygen permeability constant. The calculated oxygen permeability constants were found to be in good agreement with the experimental values obtained from the oxygen permeation tests. On the other hand, for the co-doped wafer, the oxygen permeability (data not shown) was higher than that for the undoped wafer because of the formation of Lu-stabilized HfO_2 particles at the GBs, which acted as extremely fast oxygen diffusion paths. These results demonstrate that a suitable choice of dopant configuration, taking into account the nature of the diffusing species and the role of the dopants, allows optimization of the high-temperature oxygen shielding capability of alumina.

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References

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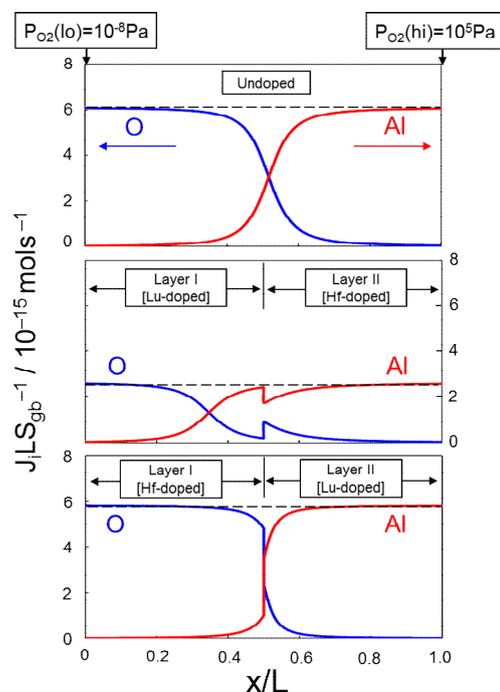


FIG. 1. Oxygen and aluminum flux profiles in samples exposed to $P_{O_2}(\text{hi})$ and $P_{O_2}(\text{lo})$ partial pressures of 10^5 and 10^{-8} Pa, respectively, at a temperature of 1873 K.