

Effect of Doping Elements on Mass Transfer in Alumina Ceramics under Oxygen Potential Gradients at Ultra-High Temperatures

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Alumina-forming alloys are widely used in hot section components such as thermal barrier coating systems under high operating temperatures in oxidizing environments. The excellent high-temperature performance of these alloys is due to the formation of alumina scale on the alloy surface, which acts as a protective layer against further oxidation. To save energy and reduce the usage of alloys containing rare elements, however, it is highly desirable to further improve the high-temperature durability of such components. In this regard, suppressing mass-transfer through the alumina scale should have a pronounced effect on the durability of the alloys. The alloys contain small quantities of oxygen-reactive elements (REs) (e.g., Y, La, Ti, Zr, and Hf), which improve their oxidation-resistance. These REs segregate at grain boundaries in growing alumina scales during oxidation of the alloys. 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 aluminum due to ionic size misfit, since the ionic sizes of the REs are larger than that of Al^{3+} [1,2]. However, during long-duration, high-temperature oxidation, REs segregated at grain boundaries were found to diffuse toward the scale surfaces together with aluminum, resulting in the precipitation of RE-rich particles on the surfaces [2]. This casts doubt on the ability of the REs to effectively control the movement of aluminum. The coexistence of various REs further complicates the interpretation of the experimental results.

The effectiveness of polycrystalline Al_2O_3 as a barrier to oxygen permeation has been estimated by measuring oxygen permeation through grain boundaries in Al_2O_3 wafers exposed to oxygen potential gradients at high temperatures, with each surface of the wafer deliberately subjected to different oxygen partial pressures (P_{O_2}) [3,4]. When the potential gradients are produced by a combination of high P_{O_2} values, oxygen permeates mainly via grain boundary diffusion of aluminum from the lower to the higher P_{O_2} surface, resulting in the formation of grain boundary ridges on the higher P_{O_2} surface. Conversely, under an oxygen potential gradient generated by a combination of low P_{O_2} values, oxygen permeation occurs by grain boundary diffusion of oxygen from the higher to the lower P_{O_2} surface. The primary diffusing species clearly depends on the oxygen potential gradient. This phenomenon will be useful in elucidating the degree to which the migration of oxygen and aluminum is affected by REs segregated at grain boundaries.

In this study, the effect of Lu and/or Hf doping on oxygen permeability in polycrystalline Al_2O_3 wafers exposed to steep oxygen potential gradients was evaluated at high temperatures to investigate the complex mass-transfer phenomena through the scale. It is well-known that Lu doping can significantly improve creep resistance in polycrystalline Al_2O_3 , and that Hf doping modifies the oxidation resistance of the alloys. Therefore, these elements are expected to effectively retard mass-transfer in Al_2O_3

under oxygen potential gradients.

The materials used in this study were undoped, LuO_{1.5} doped, and/or HfO₂ doped polycrystalline Al₂O₃. The total amount of doped cation was fixed at 0.2 mol%. Wafers with dimensions of $\phi 23.5 \times 0.25$ mm were cut from sintered bodies, and then polished to a mirror finish. The relative density of all wafers was >99% of the theoretical density. Each wafer was set between two alumina tubes in a furnace using Pt gaskets to create a seal between the wafer and the tubes. A gas-tight seal was achieved in both chambers by heating to 1893-1973 K. Ar gas was introduced to the lower chamber of the specimen, and Ar/O₂ or Ar/H₂ mixtures were supplied to the upper chamber, imposing an oxygen gradient across the wafer. P_{O₂} in the lower chamber was held constant, on the order of 1 Pa. The oxygen permeation of each wafer was evaluated at 1923 K. The methods used for measurement of the oxygen permeability constants, and the subsequent estimation of grain boundary diffusion coefficients for aluminum and oxygen ($D_{gb}\delta$) were previously described in detail [3,4].

Figure 1 shows $D_{gb}\delta$ of aluminum and oxygen in polycrystalline Al₂O₃ as a function of the equilibrium P_{O₂} in the upper chamber at 1923 K. When the wafer was subjected to potential gradients caused by a P_{O₂} below 10⁻³ Pa, Lu doping decreased the mobility of oxygen by a factor of about 3, compared to the undoped case. In contrast, under oxygen potential gradients generated by P_{O₂} values above 10³ Pa, Lu doping did not directly influence aluminum migration, and the doped Lu moved to the higher P_{O₂} surfaces together with aluminum, resulting in the development of grain boundary ridges and the simultaneous precipitation and growth of Al₅Lu₃O₁₂ particles at the grain boundaries. On the contrary, Hf doping suppressed the mobility of aluminum, but did not affect the migration of oxygen. It is noteworthy that each dopant retarded the migration of either aluminum or oxygen ions, but not both. Unfortunately, the $D_{gb}\delta$ values of aluminum and oxygen in Lu and Hf co-doped Al₂O₃ are the same as those in undoped Al₂O₃. Because a reaction product such as cubic-HfO₂ existed in the co-doped Al₂O₃, the strong chemical affinity between Lu and Hf ions through oxygen may be responsible for the absence of retardation in co-doped samples.

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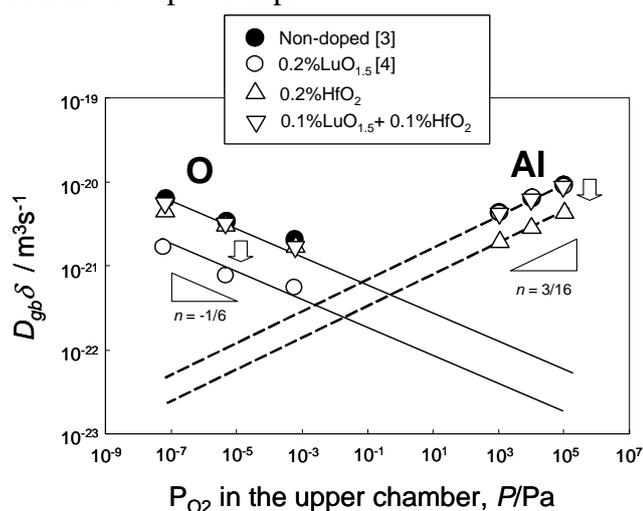


Fig. 1 $D_{gb}\delta$ of aluminum and oxygen in polycrystalline Al₂O₃ as a function of the equilibrium partial pressure of oxygen in the upper chamber at 1923 K.