Oxygen Permeability and Morphological Stability of Alumina Ceramics under O2 Potential Gradients at Ultra-High Temperatures

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Environmental barrier coatings (EBCs) for gas turbine engines have been developed to protect the hot-section components of non-oxide materials in combustion environments. Higher performance of EBCs contributes to achieve higher operating efficiencies, lower emissions and long-term durability. In a combustion gas at ultra-high temperatures, EBC layers are required to exhibit excellent heat resistivity, corrosion resistance, and gas barrier property in addition to depress demixing of EBCs under steep oxygen potential gradients. Polycrystalline Al2O3 is one of promising candidate materials for EBC layers because of its excellent thermal stability. However, there are few studies on the gas permeability of Al2O3 under the oxygen potential gradients at high temperatures and no morphological stability has been reported. On the other hand, it has been shown that conduction mechanism of single crystal Al2O3 at elevated temperatures depends on O2 partial pressure (Po2): p-type conduction related to hole and aluminum vacancy is controlled in oxidizing atmospheres and n-type conduction related to electron and oxygen vacancy is dominant in reducing atmospheres [1]. However, it is not clarified that a similar relation holds for gas permeation mechanism of polycrystalline Al2O3 under oxygen potential gradients at high temperatures. It has been reported that doping with rare earth oxides is effective in improving creep resistance of polycrystalline Al2O3 [2], while it has been uncertain which diffusivity of the aluminum and oxygen ions the dopants segregated at the grain boundaries control. However, if ionic species diffused fastest at the grain boundaries are dependent on Po2 in a similar manner as the electrical conduction of single crystal Al2O3, it may become possible to specify the ionic species which are affected by the dopants. In this study, the gas permeation properties and morphological stability of Al2O3 was evaluated under a potential gradient of oxidizing gases at ultra-high temperatures.

Single crystal and pressureless sintered polycrystalline Al2O₃ were used. A thin disk specimen was set between two alumina tubes in a furnace and platinum gaskets were used to create a seal between the specimen and the alumina tubes. High purity Ar gas was initially supplied into both upper and lower chambers with heating up the furnace. After a gas-tight seal was formed and equilibrium was reached, Po2 of lower chamber was measured to determine a background value. Then, Ar-O2 or Ar-H2 gas mixtures were introduced into the upper chamber, followed by measuring Po2 of lower chamber. The O2 permeability constant (Pl) was calculated using the difference between Po2 measured under the oxygen potential gradient and that of the background. Surface morphologies after the tests were evaluated from the electron micrographs.

O2 permeability constant of the polycrystalline Al2O3 under oxygen potential gradient between O2 (Po2 = 10⁵ Pa) and Ar (= 2 Pa) at 1973 K was determined as 6.2×10⁻¹⁰ mol/(m·s) in good agreement with the previous high purity Al2O3’s data. In contrast, that of the single crystal Al2O3 was under the detection limit. The O2 permeation of the polycrystalline Al2O3 is attributed to the grain boundary diffusion of the oxygen.

Fig. 1 shows O2 permeability constant of the polycrystalline Al2O3 as a function of Po2 of the upper chamber. Po2 differences between the upper and lower chambers are sufficiently large, and therefore the O2 permeability constant is proportional to the Po2ⁿ. At higher Po2 region, the O2 permeability constant is proportional to the Po2⁻³/₁₆. The following reaction is expected to occur and therefore p-type conduction is dominant.

\[ 1/2O₂ → O²⁺ + 2/3VₐO²⁻ + 2h \quad (p-type) \] (1)

On the other hand, at lower Po2 region, the Po2 dependence of O2 permeability constant was expressed as Pl \( \propto \) Po2⁻¹/₁₀ and the estimated reaction is as follows.

\[ O²⁺ + 1/2O₂ + Vₒ²⁺ + 2e \quad (n-type) \] (2)

Fig. 2 shows SEM images of tilted surfaces for the polycrystalline Al₂O₃ which were exposed to the O₂ potential gradients between O₂ and Ar. At higher Po2 side, the grain boundaries rise,
forming ridges. On the opposite side of lower $P_{O_2}$, deep grooves are formed at the grain boundaries. In higher $P_{O_2}$ region, $O_2$ permeation occurs as a result of the migration of aluminum ions through aluminum vacancies. Such reaction mainly occurs at the grain boundaries and few oxygen ions diffuse into the lattice. These morphological changes may be act as the origin of spalling of EBCs.

Fig. 3 shows SEM micrographs of $Al_2O_3$ which were exposed to the oxygen potential gradients between $P_{O_2}$ reduced Ar ($= 0.9$ Pa) and Ar-2% H$_2$ ($= 6 \times 10^{-8}$ Pa). Equilibrium grooves are formed at the grain boundaries on both $P_{O_2}$ sides. In lower $P_{O_2}$ region, it is thought that $O_2$ permeation occurs by the migration of oxygen ions through oxygen vacancies.

In summary, mechanism of grain boundary diffusion in high purity polycrystalline $Al_2O_3$ depending on $P_{O_2}$ is as same as that of lattice diffusion in single crystal, while the mobility of diffusion species at the grain boundaries is significantly larger than that of grain. On the other hand, significant surface morphological changes of $Al_2O_3$ are occurred under the oxygen potential gradients of p-type region. Therefore, when alumina is applied as an EBC, it is preferable to use under the conditions of the n-type region.

The dopant effects will be also presented at the conference.

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References

FIG. 1. $P_{O_2}$ dependence of $O_2$ permeability constants of polycrystalline $Al_2O_3$ at 1923 K

FIG. 2. SEM images of polycrystalline $Al_2O_3$ which were exposed to $O_2$ potential gradients between (a) $P_{O_2} = 10^5$ Pa and (b) $P_{O_2} = 2$ Pa at 1973 K

FIG. 3 SEM images of polycrystalline $Al_2O_3$ which were exposed to $O_2$ potential gradients between (a) $P_{O_2} = 0.9$ Pa and (b) $P_{O_2} = 6 \times 10^{-8}$ Pa at 1973 K