Structural Stability Design of Mullite under Oxygen Potential Gradients at High Temperatures

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Environmental barrier coatings (EBCs) can play a key role in enabling SiC fiber-reinforced SiC matrix (SiCf/SiCm) composites to be applied as advanced hot-section components in airplane engines, as a means of realizing exceptional fuel efficiency. An EBC must exhibit superior oxygen/water vapor shielding and thermomechanical durability under severe combustion environments. Thus, a multilayered structure is generally applied when designing EBCs to achieve enhanced performance through the use of layers with individual characteristic functions [1]. Fully dense oxide layers naturally provide excellent gas shielding when exposed to a large oxygen potential gradient (dO) at high temperatures. This results in the inward diffusion of oxygen and outward diffusion of cations, according to the Gibbs-Duhem relationship. It should be noted that cation transport induces decomposition of the oxides and a collapse of the layered EBC structure. Therefore, to develop robust EBCs with excellent gas shielding, it is very important to elucidate and control the mass transfer within EBCs.

Mullite is considered here as a potential oxygen shielding material, based on previous investigations on the application of mullite as a protective film against the oxidation of SiCf/SiCm [2], and because its thermal expansion coefficient is close to that of SiCf/SiCm. However, the existing quantitative information on the oxygen shielding and mass transfer mechanisms of mullite is insufficient. In particular, there are no data regarding oxygen diffusion through this material under various dO conditions, despite the widespread use of mullite. Therefore, to clarify the mass transfer mechanism, we have evaluated oxygen permeation through polycrystalline mullite wafers that served as a model for an EBC layer. The wafers were exposed to dO at temperatures greater than the assumed used temperature of 1673 K, with each surface of the wafer deliberately subjected to a different PO2 (PO2(hi)>>PO2(lo)) [3]. The oxygen permeability of mullite was found to be controlled by the interdiffusion of oxygen and Al along the grain boundaries (GBs) under dO, whereas the contribution to oxygen permeation from the GB diffusion of Si was negligibly small. The difference in the cation diffusivity was determined to be responsible for the decomposition of mullite in the vicinity of the PO2(lo) surface. Furthermore, the oxygen permeability constant and the breakdown of oxygen and Al diffusion could be determined at an arbitrary temperature and dO.

In the present study, the structural stability of a model EBC sample was evaluated at the applied temperature of 1673 K and approaches to enhance the stability of the structure were proposed. Mullite coated on a Si substrate was used as the test sample because Si is often used as a bond coat between mullite and underlying SiCf/SiCm layers. FIG. 1 shows cross-sectional scanning electron microscopy (SEM) and bright-field scanning transmission electron microscopy (BF-STEM) images of the sample interface after annealing at 1673 K and PO2=10⁵ Pa for 10 h. A damaged layer...
was formed near the interface on the mullite side, which consisted mainly of alumina and Si with partially amorphous silica segregated at the GBs slightly further from the interface. As soon as the amount of Al solid solution in the mullite layer near the interface exceeded the limit determined by the outward diffusion of Al, mullite in the vicinity of the interface was decomposed to Si-rich mullite and silica. The oxygen chemical potential ($\mu_O$) at the interface was too low, so that some of these oxides were reduced to form Si and alumina, and the released oxygen was probably dissolved in the lower Si substrate. Voids that formed in the damaged region may have been simultaneously filled by the outward diffusion of Si from the lower substrate. FIG. 2 shows the oxygen permeability constant and the breakdown of oxygen and Al diffusion in the mullite layer as a function of the $P_{O_2}(hi)/P_{O_2}(lo)$ ratio at 1673 K. $P_{O_2}(lo)$ is a constant of $6 \times 10^{15}$ Pa, where both Si and silica are assumed to coexist thermodynamically. This implies that the $P_{O_2}(hi)/P_{O_2}(lo)$ ratio across the mullite layer in FIG. 1 is probably larger than that at the broken line in FIG. 2. It is noteworthy that the total permeability constant and the contribution of oxygen diffusion are not significantly affected by a decrease in the $P_{O_2}(hi)$ values, whereas the contribution of Al diffusion is remarkably reduced. Therefore, structural stabilization of the mullite layer can be achieved by reducing the influence of Al diffusion. As a first approach, an upper layer with a moderate oxygen shielding function is set on the mullite layer. The Al and oxygen fluxes at the outflow sides in the mullite layer are significantly larger than those at the inflow side, in accordance with dominant Al transport at the $P_{O_2}(hi)$ side and dominant oxygen transport at the $P_{O_2}(lo)$ side. Therefore, if the upper layer decreases the $P_{O_2}$ at the interface below $10^{-9}$ Pa, the Al flux in the mullite layer will be significantly reduced, which results in an improvement of the structural stability of the mullite layer. Another approach is to set a lower layer with an Al-reservoir function. Thus, even if the outward diffusion of Al occurs in the mullite layer, the underlying bond layer containing Al can supply Al to the Al-deficient zone in the mullite layer.

References