

Understanding Aluminum Oxide Growth in Thermal Barrier Coatings

Berit Hinnemann and Emily A. Carter

Military aircraft jet engines are limited in service lifetime by the failure of thermal barrier coatings (TBCs) that protect the metal from the extreme heat of the combustion gases. We use state-of-the-art electronic structure calculations to study failure mechanisms in atomistic detail. The ultimate goal is to use this knowledge for the design of better TBCs. A TBC consists of several layers, an outer layer of a ceramic heat shield, a middle layer of aluminum oxide, which acts as a corrosion barrier, and a bond coat metal layer, which ensures adhesion of the aluminum oxide and the underlying superalloy (see Figure 1). During service, the aluminum oxide layer grows and ultimately causes delamination and failure of the TBC. The objective of our project is to understand the growth mechanism and how it can be slowed down so that longer TBC lifetimes can be achieved.

Research Objective: A crucial aspect of TBC failure is the growth of the aluminum oxide layer which is located between the bond coat alloy and the heat shield ceramic. As soon as the oxide has reached a thickness of $\sim 3\text{-}10\ \mu\text{m}$, the coating spalls off. It has been shown experimentally that the early transition metal dopants Hf, Y, and Zr slow down the growth of the oxide layer and the suggested explanation is that they block the diffusion of Al ions through the crystal. In this case, the growth presumably occurs by diffusion by inward diffusion of O ions, which is significantly slower. The atomistic details of this mechanism are poorly understood so far, and our objective is to elucidate them using electronic structure calculations. These calculations on realistic yet computationally accessible systems allow us to understand binding and diffusion in atomic detail and in this way to provide information which is not directly accessible for experiments.

Methodology: We use density functional theory as implemented in the Vienna *Ab-initio* Simulation Package (VASP). The ion cores are described by the projector-augmented wave (PAW) method and we use the PBE exchange-correlation functional. Building a structural model of the alumina layer is challenging, as it is polycrystalline and diffusion predominantly occurs along grain boundaries. Thus, we are building model systems of representative grain boundaries and studying diffusion along these defects. As a first approach and "benchmark system," we have studied adsorption and diffusion of Al, O, and Hf on the $\text{Al}_2\text{O}_3(0001)$ surface.

Results and Significance: We find that both Al and Hf bind on the same site on the $\text{Al}_2\text{O}_3(0001)$ surface, but Hf binds significantly more strongly than Al. Their diffusion pathways on the surface are similar, but Hf seems to have a higher diffusion barrier than Al. This suggests that Hf indeed blocks Al diffusion. O absorbs on a different site and also has a different diffusion pathway. This offers an explanation as to how Hf can slow down oxide growth, but not stop it completely. Currently, we are investigating whether these findings hold for diffusion along grain boundaries as well.

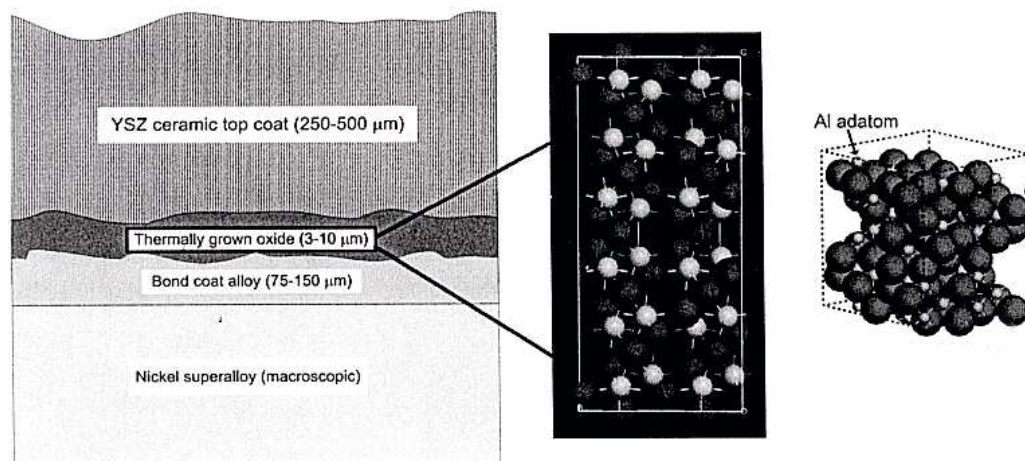


Figure 1. Right: Schematic cross-section of a TBC (not to scale), Middle: Model of the $\Sigma 13$ (1014) grain boundary in $\alpha\text{-Al}_2\text{O}_3$, Left: Model of the $\alpha\text{-Al}_2\text{O}_3(0001)$ surface with an adsorbed Al adatom. Aluminum atoms are shown in gray and oxygen atoms in red.

Author and Contact: Emily A. Carter

Organization: Department of Mechanical and Aerospace Engineering and Program in Applied and Computational Mathematics, Princeton University, Princeton, NJ, 08544-5263

Author: Berit Hinnemann

Organization: Department of Mechanical and Aerospace Engineering, Engineering Quadrangle, Princeton University, Princeton, NJ, 08544-5263

Resources: IBM SPs (*Tempest*) at MHPCC, IBM SPs (*Kraken*) at NAVOCEANO MSRC

Sponsorship: Air Force Office of Scientific Research