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 Editorial

Interface science of thermal barrier coatings

Theodore M. Besmann

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The drive for greater efficiency in propulsion and industrial/power production machinery has pushed metallurgists to develop ever better alloys and taken existing metallic components to their reliability threshold. Nowhere is that better illustrated than in gas turbine engine materials. The nickel-based superalloys currently in use for the most demanding areas of the engines melt at 1,230–1,315 °C and yet see combustion environments ~1,600 °C. The result is that these components require thermal protection to avoid failure from phenomena such as melting, creep, oxidation, thermal fatigue, and so on [1]. The stakes are high as the equipment must remain reliable for thousands of take-offs and landings for aircraft turbine engines, and at least 40,000 h of operation in power generating land-based gas turbines [2, 3]. The most critical items that see both the greatest temperatures and experience the highest stresses are the hot-section components, particularly the high pressure turbine blades. Two strategies have been adopted to help the superalloy turbine blades survive the demanding environment: active air cooling and ceramic thermal protection coatings, which together can reduce metal surface temperatures by >300 °C [2]. The combination of turbine blade external film cooling and internal air cooling requires an exceptionally complex structure with flow passages and sets of small holes in the blades where air bled from a matching stage of the compressor is directed through the blade and over the surface. Stecura [4] was among the first to describe a successful coating system, and today's ceramic insulating layer alone is credited with reducing metal temperatures as much as 165 °C [1, 5].

T. M. Besmann (✉)
Materials Science and Technology Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6063, USA
e-mail: besmanntm@ornl.gov

Given their substantially different thermo-mechanical properties, it has been a considerable challenge to successfully retain a ceramic coating on a metal substrate. Yet thermal barrier coatings (TBCs) on turbine components, and particularly turbine blades, are now standard for most systems. The current thermal barrier coating consists of two applied layers. The first is a metallic bond coating that protects the substrate alloy from oxidation followed by a top coat of the thermally insulating ceramic layer. The aluminum-containing bond coat is designed to grow a third layer at high temperatures, which is an adherent alumina 1–10 μm in thickness that is a barrier to oxygen diffusion, thus resulting in a three layer system. Care is taken so that single-phase, defect-free α-alumina, which has a very low oxygen diffusivity, is formed as the "thermally grown oxide" (TGO) on the bond coat. Air plasma spray (APS) or electron-beam physical vapor deposition (EB-PVD) is used to deposit the insulating layer, typically 100–400 μm of 7–8% yttria-stabilized zirconia (YSZ) and, more recently, $Gd_2Zr_2O_7$ is beginning to be used. Between the presence of some porosity and the material's inherent very low thermal conductivity, this ceramic layer provides an excellent high-temperature thermal insulator. In this system, the TGO is particularly important given the high mobility of oxygen in YSZ and the possible through-thickness porosity of the layer.

Despite the great care taken in preparing the various layers on the substrate alloy, i.e., bond coat, TGO, and YSZ, the inevitable stresses that result from thermal cycling material layers with such differing properties of thermal expansion and modulus lead to eventual coating failure. Figure 1 shows an as-prepared coated turbine blade and a blade that has seen considerable service, exhibiting regions where the coating has spalled off. For more than two decades, there has been intense study of the

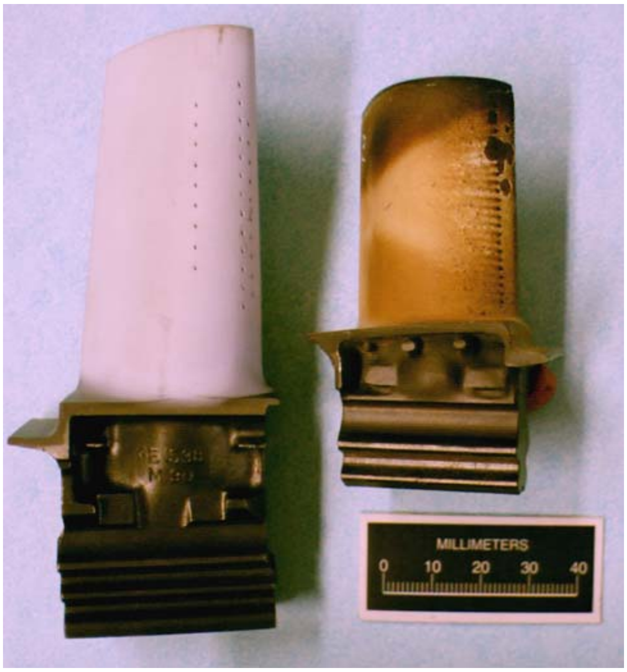

Fig. 1 Aircraft turbine blades as coated (*white*) and after significant hours of service where areas of coating can be seen to have spalled off (Courtesy GE Aircraft Engines)

phenomena thought to control adhesion of the ceramic layers. What appears to be phenomenologically understood is that some contaminants reduce metal–ceramic adhesion, and that specific dopants/additives can improve behavior. Miller [6] at NASA was one of the first to identify bond coat oxidation as the primary cause of TBC failure [5, 7]. The modes of failure include delamination cracks in the YSZ layer just above the TGO, cracking within the TGO, and failure at the TGO–bond coat interface [5, 8, 9].

Recent years have seen very significant progress in understanding material constituents that influence failure behavior [10]. Even sulfur contents at the parts-per-million level in the materials are seen to migrate to metal–ceramic interfaces and weaken them [11]. The additions of elements such as platinum to the bond coat help to more quickly form a better, purer protective α-alumina scale, slowing interdiffusion between the bond coat and superalloy [12], although that was not necessarily observed in the work of Zhang et al. [13]. The effects of phase changes and creep in the TGO has also been seen as a significant contributor to failure, causing substantial increases in residual stress [3, 14]. Yttrium and hafnium in the superalloy substrate and/or bond coating are seen to improve TGO adhesion by segregating to the metal–alumina interface and encouraging the formation of desired oxide microstructure at the interface, which appear to increase the toughness of the bond coat–TGO attachment [8]. Platinum reduces the detrimental effect of sulfur on adhesion through a third element effect [15], while yttrium and hafnium also apparently bind sulfur and additionally mitigate its effect [10]. These and other phenomena have resulted in development of complex superalloys and bond coats, including MCrAlYX where M is nickel and cobalt, and X can be Hf and Si, to both optimize the mechanical and expansion behavior of the bond coat and TGO and control the effects of contaminants.

The set of papers that make up this Special Issue on the Interface Science of Thermal Barrier Coatings plumb the frontier of understanding of the behavior of these systems where the critical ceramic and metal layers meet. Wolfgang Braue of the Materials Research Institute of the German Aerospace Center takes a practical look at the factors affecting TBCs on actual engine hardware. These include typical infiltration of environmental $CaSO_4$ and the complex calcia–magnesia–alumino–silicate (CMAS) materials and he relates that to phase compatibilities in pseudoternary oxides systems. Pint and More at Oak Ridge National Laboratory report on in-depth, high resolution characterization of the alumina interfaces in TBCs, determining that interstitial elements in the substrate influence diffusion of cation dopants (e.g., yttrium and hafnium), and their potential ultimate effect on performance. The Group for High-Temperature Corrosion at the Forschungszentrum Juelich has investigated the effect on lifetime of TGO formation on TBCs with MCrAlY bond coats looking at microstructure, geometrical and processing effects, particularly coating roughness and thickness (paper by Naumenko et al.). They also interestingly contrast EB-PVD and APS coatings as to the effect of surface structure on coating stability.

Compositional factors affecting alumina-scale formation are explored by Gleeson and coworkers from the University of Pittsburgh and Hokkaido University. They see the beneficial role platinum plays as a non-reactive addition that decreases the aluminum activity in the bond coat alloy, which in turn serves to kinetically promote the early-stage establishment of an alumina scale. Hou of the University of California, Berkeley has explored segregation behavior at the TGO–bond coat interface as it relates to sulfur and other elements. The chemistry at these interfaces is revealed by Auger spectroscopy, and the results correlated with a scratch width on the surface of the oxidized sample and the extent of spallation. Thery, Poulain, and coworkers at ONERA, the French Aerospace Laboratory, adopted an experimental approach to determine adhesion energy between the bond coat and the topcoat YSZ layer using a modified four-point bending test for different bond coat compositions. An energetic model of spallation was developed to predict failure.

Fundamental, first-principles techniques have been applied by Jiang and Smith at the University of California, Santa Barbara to determine the effects of bond coat additive platinum on adhesion between it and the TGO α-alumina. Density functional theory (DFT) was used to compute the interactions of hafnium or platinum with sulfur in bulk nickel at elevated temperatures. They determined that the thermodynamically preferred interface is aluminum rich. For that interface, they found that hafnium strengthens adhesion by pinning sulfur, while platinum does not directly enhance interface bonding although it can block sulfur from segregating as a result of it being an energetically preferred segregant. Milas and Carter at Princeton University also used DFT, however, this time to investigate grain boundary sliding in α-alumina. They found that the segregation of a number of metallic dopants increases the barrier to grain boundary sliding, affecting creep activation energies in alumina and supporting the idea that the phenomenon plays a dominant role in the creep of the TGO.

More energy efficient designs await thermal barrier coatings that are less costly and have longer life. While today's TBCs can provide the insulating capacity desired, the lack of adequate reliability force the operation of systems to lower temperatures to avoid catastrophic failure due to extensive coating spallation. It is to overcome this limitation that the type of intensive studies and development of fundamental understanding represented by these contributions to the Special Issue on Interface Science in Thermal Barrier Coatings is focused. While much work to understand and mitigate the various phenomena affecting TBC performance remains to be done, we are now well positioned with the tools, talent, and approaches to eventually achieve the ultimate goal of having prime reliant thermal barrier coatings that will boost propulsion and energy systems' capability and efficiency.

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