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Thermal Barrier Coatings for Aeroengine Applications

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Thermal barrier coatings (TBCs) have been in use in aeroturbine engine hot sections for over 20 years. The initial applications were driven by the need to suppress component degradation caused by excessive thermal gradients in vane airfoils. A TBC is essentially a layered, multimaterial structure that must withstand harsh temperature, environmental, thermal cycling, and stress conditions for an extended number of aircraft takeoffs and landings. A description of the TBC materials systems presently in use is presented, together with a summary of current understanding of materials and failure issues in TBCs.

Introduction

THE demand for improved performance in high-temperature mechanical systems has led to increasingly harsh operating environments, particularly for the components in advanced gas-turbine engines. Future improvements in gas-turbine performance will require even higher operating efficiencies, longer operating lifetimes, and reduced emissions. Achieving these requirements will necessitate still further increases in the gas inlet temperatures and, consequently, the development of structural materials inherently capable of higher temperature performance. Advanced cooling schemes coupled with thermal barrier coatings (TBCs) can enable the current families of superalloy components to meet the materials needs for the engines of tomorrow. Thermal-barrier-coating systems are currently capable of providing metal temperature reductions of up to about 140°C, whereas potential benefits are estimated to be greater than 170°C (Ref. 1). The use of TBCs in combination with cooling schemes has enabled the operation of gas-turbine engines having combustion gas temperatures in excess of 250°C above the melting temperature of the superalloy component (e.g., early stage turbine blades and vanes). Moreover, the use of TBCs at lower operating temperatures reduces the metal temperature, which in turn increases the service life of the component. In fact, current engine design primarily relies on the lifetime extension benefits of TBCs and does not fully exploit the significant performance improvements TBCs are capable of providing. This is because current, state-of-the-art TBCs are not considered "prime reliant" to the extent that they can be used with assurance that failure will not occur. This limitation derives from a number of issues, including the following:

1) TBCs do not provide self-renewing protection. When they spall the thermal protection is lost.

2) TBC service life is subject to scatter that to date has not been adequately taken into account.

3) There are currently no effective methods (e.g., nondestructive evaluation) that can act as quality control and/or monitor for TBCs.

4) Life prediction for TBCs is not as accurate as is needed.

The purpose of this paper is to summarize the current status of advanced TBC systems from a materials science and engineering point of view. More detailed accounts of TBCs can be found, for instance, in the excellent and relatively recent reviews by Peters et al.,[1] Padture et al.,[2] Clarke and Levi,[3] and Evans et al.[4]

Constituents of the TBC System

Commercial advanced TBC systems are typically two-layered structures, consisting of a ceramic top coat and an underlying metallic bond coat. The top coat, which is usually applied either by air plasma spraying (APS) or electron-beam physical vapor deposition (EB-PVD), is most often yttria-stabilized zirconia (YSZ). The properties of YSZ are such that it has a low thermal conductivity, high oxygen permeability, and a relatively high coefficient of thermal expansion. The YSZ top coat is also made "strain tolerant" by depositing a structure that contains numerous pores and/or pathways. The consequently high oxygen permeability of the YSZ top coat imposes the constraint that the metallic bond coat must be resistant to at least oxidation attack. The bond coat is therefore sufficiently rich in aluminum to form a protective, thermally grown oxide (TGO) scale of α-Al_2O_3. In addition to imparting oxidation resistance, the TGO serves to bond the ceramic top coat to the substrate/bond-coat system. Notwithstanding, it is generally found that spallation and/or cracking of the thickening TGO scale is the ultimate failure mechanism of commercial TBCs, particularly EB-PVD TBCs.[5–7]

An example of a TBC system composed of an EB-PVD top coat is shown in Fig. 1 for the case of a blade aerofoil. The approximate thicknesses of the various TBC constituents are indicated in this figure. In general, the adhesion and mechanical integrity of the TGO scale is very dependent upon the composition and structure of the bond coat, which is typically either an MCrAlY overlay (where M=Ni,Co, or both) or a platinum-modified diffusion aluminide (β-NiAl-Pt). The composition and phase constitutions of such bond coats vary. For example, NiCoCrAlY overlay coatings are mainly based on the γ-Ni and β-NiAl phases plus, depending on temperature and coating composition, additional phases such as γ'-Ni_3Al, α-Cr, and σ-(Co,Cr). Both the MCrAlY and NiAl-Pt types of coating were originally developed to enhance long-term oxidation and corrosion protection of turbine components rather than specifically as bond coats. The oxidation resistance provided by these coatings allowed alloy developers to maximize the high-temperature mechanical properties of nickel-base superalloys. The original coatings required a high aluminum content in order to ensure rehealing of the Al_2O_3 scale after repeated spalling during service. In the case of TBC systems, however, Al_2O_3 healing after scale spallation is not an important requirement for ceramic adhesion. This is because

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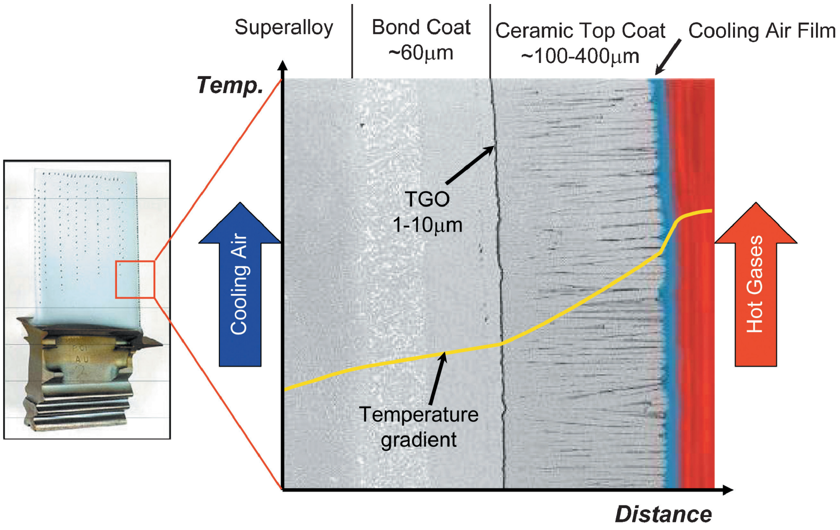


Fig. 1 Example of a cross-sectional image of a TBC system on an aeroturbine blade; the TBC consists of an EB-PVD ceramic top coat. Superimposed on the cross-sectional image is the qualitative variation in the temperature across the TBC. The temperature gradient typically is within the range of about 70–150°C.

the adhesion, and therefore the reliability, of a TBC system is dictated primarily by the first spallation event of the TGO scale. As a consequence, the currently used bond coats, which were originally designed for Al_2O_3 rehealing capability, do not necessarily possess optimum compositions and/or structures for prime reliant TBC systems. Indeed, gaining a more detailed understanding of the interrelationships between bond-coat-scaling behavior and bond-coat composition and structure is integral to the further improvements of TBC durability and reliability. To that end, Rickerby and Wing,[8] Rickerby et al.,[9] and Gleeson and colleagues,[10,11] have recently developed bond coats that have a Pt-modified γ-Ni + γ'-Ni_3Al phase constitution and, hence, are lower in aluminum content and more compatible with the Ni-base superalloy substrate than the established MCrAlY and NiAl-Pt types of coating.

The following discusses in more detail important aspects of the top coat and bond coat in advanced TBC systems.

Ceramic Top Coat

The majority of TBC top coats are ZrO_2 (zirconia) stabilized with 7–8 wt.% Y_2O_3 (yttria). Under equilibrium conditions, yttria at this level enters the zirconia solid solution and stabilizes its tetragonal crystal structure (t-YSZ) above about 1050°C. On cooling and under no mechanical constraints, this t-phase transforms to a mixture monoclinic (m-YSZ) and cubic (c-YSZ) zirconia. The t→m transformation on cooling is martensitic in nature and can result in unwanted cracking of the ceramic as a result of a 4–5% volume change. For kinetic reasons associated with the relatively rapid deposition rate of the top coat, the deposited YSZ typically exists in a closely related but metastable tetragonal-prime (t′) structure rather than the stable tetragonal structure. A significant outcome of this is that the t′-YSZ does not undergo any transformation on cooling, even after an extended number of thermal cycles.[3] Numerous studies have been conducted to identify alternative stabilizers (e.g., MgO, CeO_2, Sc_2O_3, In_2O_3, and CaO) and to develop costabilized (i.e., with Y_2O_3) coatings, but 7–8 wt.% Y_2O_3-stabilized ZrO_2 has consistently been found to be the most suitable for TBC applications.[2,3] The exact reasons for this have yet to be fully elucidated and remain an important topic of current research.

A key physical property of the ceramic top coat is its thermal conductivity (k or λ). In electrical insulators like ZrO_2, heat is transferred by lattice vibrations and radiation. Thus, thermal conductivity can be effectively reduced by increasing phonon (lattice waves) or photon (electromagnetic waves) scattering in the lattice structure of the ceramic. For instance, even increasing the level of Y_2O_3 in ZrO_2 reduces thermal conductivity—but it also decreases the higher temperature stability of the t′ structure. Indeed, much research has quite recently been directed to obtaining novel "low-k" top-coat compositions.[3,12–14] A perceived current deficiency of these novel top coat compositions is decreased resistance to erosion degradation in comparison to the YSZ. Notwithstanding, increased use of low-k top coats is expected.

Table 1 Room-temperature properties of YSZ top coats (after Ref. 14)

	Deposition method	
Property	EB-PVD	APS
Thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$	1.5–1.9	0.8–1.1
Surface roughness, μm	0.5–1	4–10
Adhesion strength, MPa	400	20–40
Young's modulus, GPa	90	200
Erosion rate (normalized to PVD)	1	7

In fully dense form, YSZ has one of the lowest thermal conductivities at elevated temperatures (e.g., ~2.3 $W \cdot m^{-1} K^{-1}$ at 1000°C) of all known ceramics.[15] The thermal conductivity of the YSZ coating is typically less than that of the dense material because of the presence of defects such as cracks and pores in the former. Typical conductivities of EB-PVD YSZ are of the order 1.5–1.9 $W \cdot m^{-1} K^{-1}$ (Ref. 14), which is about a factor of two greater than the 0.8–1.1 $W \cdot m^{-1} K^{-1}$ range found for APS YSZ coatings. This difference is directly attributable to differences in coating microstructures. Specifically, the APS top coating contains microcracks parallel to the coating surface as well as porosity, which are effective in increasing phonon and photon scattering. By contrast, the columnar microstructure of the EB-PVD YSZ top coat is less effective at reducing thermal conductivity.

Sintering of the ceramic top-coat layer during high-temperature exposure is frequently cited as a contributing factor for TBC failure and for increasing thermal conductivity of the top coat during service.[1–4] Ceramic sintering has been shown to occur for both plasma-sprayed and EB-PVD systems and has been shown to be especially significant for high steady-state thermal gradients. For moderately steep thermal gradients, there is evidence to suggest that sintering can magnify the TBC failure modes (Brindley, W. J., personal communication, Rolls-Royce Corp., Indianapolis, IN). For severe gradients it appears that sintering coupled with the thermal stress actually changes the failure mechanism so that spallation occurs within the ceramic, sometimes far from the interface.[16]

The columnar microstructure of EB-PVD top coats confers very high levels of strain compliance in comparison to plasma-sprayed top coats. The EB-PVD top coat systems also generally offer improved adhesion, surface finish, and erosion resistance, all of which are beneficial to engine efficiency and the overall performance of the turbine airfoils.[5,14,17] Table 1 summarizes the typical room-temperature properties of EB-PVD and APS YSZ top coats. The order-of-magnitude lower surface roughness of the EB-PVD YSZ compared to the APS YSZ (see Table 1) remains even after surface finish improvements, with better than 0.75 μm possible for the former.[17] The reduction in engine efficiency loss resulting from a smooth surface finish is particularly important for front stage (i.e., first and second) airfoils, but not as important for later stage airfoils or combustor surfaces. The advantages offered by EB-PVD make this comparatively more expensive process now the standard for depositing YSZ top coats on turbine airfoils. An added and critical advantage of the EB-PVD process is that it deposits the YSZ top coat with minimal closure of the many small (0.25–0.5-mm-diam) cooling holes at the surfaces of the high-pressure turbine airfoils. By contrast, APS process has a much greater tendency to build-up the coating at hole openings and result in their closure.

Metallic Bond Coat

A metallic coating is applied to a superalloy component by one of, or a combination of, two methods. The first method involves enrichment of the component surface by diffusion, that is, a diffusion coating (typically about 40–60 μm thick), and the second method involves the direct, physical deposition of an overlay coating (typically about 100 μm thick). The composition of a diffusion coating is dictated by thermodynamic and kinetic constraints. By contrast, the composition of an overlay coating is dictated essentially only by the composition, or elemental ratio, of the coating source. Consequently, the composition of an overlay coating can be easily varied to specific requirements and hence can often provide superior protection compared to the diffusion coatings. However, in spite of this, the majority of bond coatings that are applied to superalloy components are diffusion coatings. This is caused largely by economic considerations and to the simplicity of the usual diffusion-coating processes.

A common and representative method for applying a diffusion coating is pack cementation, which is a modified chemical vapor deposition process.[18,19] Pack cementation is a relatively cheap batch process, with the inherent ability to coat many components at the same time. In the pack-cementation process, the components to be coated are embedded in a powder mixture containing either a pure or alloyed coating-source material called the master alloy, a halide salt that acts as an activator, and an inert filler material such as Al_2O_3. The purpose of the filler material is to prevent the pack from sintering and to suspend the substrate during coating deposition. Although the codeposition of elements is possible,[20,21] most commercial pack-cementation processes involve the deposition of only one element (i.e., Al, Cr, or Si). Thus, commercial chromium-modified aluminide coatings are usually applied by a two-step pack-cementation procedure in which the components are first pack chromized and then pack aluminized.[19] The modification of aluminide coatings by the addition of greater than about 15 wt.% chromium provides increased resistance to a salt-accelerated form of oxidation known as hot corrosion.[22,23]

Figure 2 shows an example of a platinum-modified, β-NiAl diffusion coating on a Ni-base superalloy. The platinum is in the β solid solution and was added by electroplating a $\sim$6-μm platinum layer onto the superalloy prior to diffusion aluminizing via pack cementation. Platinum is a beneficial alloying addition for reducing Al_2O_3-scale spallation. The structural features and oxidation behavior of the various commercial platinum-aluminide coatings have been discussed by Patnaik et al.[24] and Streiff and Boone.[25] Although it is well established that platinum addition improves the oxidation behavior of β-NiAl based coatings,[24–28] the mechanisms of this beneficial effect are not well understood. Mechanisms that have been proposed include enhanced aluminum diffusion in the β-NiAl (although no measurements have been made) thus allowing for the rapid reformation of an Al_2O_3 scale following spallation[29]; mechanical keying or pegging of the Al_2O_3 scale to the Pt-modified coating[30]; stress relief of the Al_2O_3 scale[31]; exclusion of refractory metals from the outermost zone of the coating[32]; and increased stability of the β phase.[28] Other important factors might be the influence of platinum on the transformation of the Al_2O_3 from its metastable, faster-growing θ structure to its stable, more protective α structure, and the influence of platinum content and distribution on the establishment, growth and adherence of Al_2O_3 scale. Systematic investigations of one or more of these important factors have been recently conducted by a number of investigators.[33–37] For instance, Cadoret et al.[33] reported from the oxidation of $Ni_{50}Al_{50}$ and $Ni_{40}Pt_{10}Al_{50}$ single-crystal alloys at 900 and 1100°C that platinum in fact *slows* the $\theta \rightarrow \alpha$ Al_2O_3 transition, which in turn is beneficial to the relaxation of stresses created by α-Al_2O_3 growth. According to Zhang et al.,[34] a major beneficial effect of platinum addition to the oxidation behavior of NiAl coatings is the elimination of void growth at the TGO scale/coating interface.

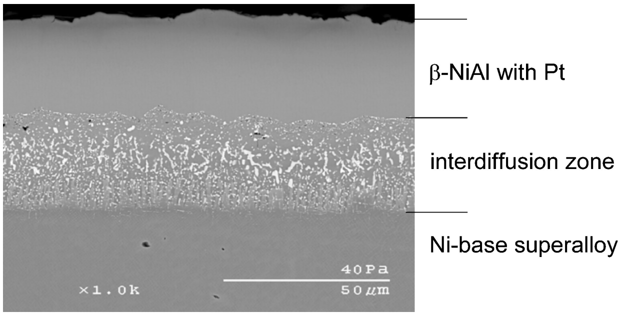


Fig. 2 Cross-sectional secondary electron image of a Pt-modified β-NiAl diffusion bond coating on a Ni-base superalloy.

Overlay metallic coatings for superalloys are often of the NiCrAlY type. The coatings usually contain (in wt.%) 15–25% Cr, 10–15% Al, and 0.2–0.5% Y, and consist of the β-NiAl phase in a solid-solution γ-Ni matrix. Most overlay coatings for gas-turbine applications are currently applied using either EB-PVD or low-pressure plasma spraying (LPPS). The EB-PVD method generally produces higher quality coatings, while LPPS has a cost advantage. Both methods are about two to four times more expensive than the pack-cementation process, but offer much greater variability and control of the coating compositions. The EB-PVD process has been reviewed by Bunshah[38] and the LPPS process by Gill and Tucker.[39]

As indicated in the Introduction, the durability and reliability of advanced TBC systems are critically linked to the oxidation behavior of the bond coat. Ideally, the bond coat should oxidize to form a slow-growing, nonporous, and adherent α-Al_2O_3 scale layer. The ability to promote such ideal TGO formation requires a sound understanding of the influence of bond-coat composition, microstructure, and surface condition at all stages (i.e., very early to long term) of the TGO-formation process. Associated with this are the oxidative effects of minor elements (metal and nonmetal) that with time diffuse into the coating from the substrate during service. Given the importance of the TGO, it is worthwhile to discuss in more detail its formation, growth, and adherence. This is done in the following.

Nature and Stages of TGO Development

There has been much research into the formation and growth of protective α-Al_2O_3 scales.[40–42] Establishment of an Al_2O_3-rich scale requires the alloy to contain more than a critical content of aluminum, which depends on the concentrations of the other alloying elements, the structure of the alloy and the oxidation conditions, particularly temperature and oxygen partial pressure. The critical aluminum content is dictated by kinetic factors and is invariably greater than the content that would be predicted on the basis of local thermodynamic equilibrium. Establishment of an α-Al_2O_3 scale at temperatures below about 1100°C is especially complicated by the fact that there are several transitional Al_2O_3 structures, such as γ, δ, and θ, that form during the transient stage of oxidation. The metastable, transitional Al_2O_3 structures grow at a faster rate than α-Al_2O_3 and often grow as blades or whiskers.[40] The growth of the metastable phases during the transient stage of oxidation can influence considerably the overall amount of oxidation and the subsequent growth of the stable α-Al_2O_3 phase. For example, eventual transformation of metastable θ-Al_2O_3 to the stable α-Al_2O_3 produces an 8–13% volume reduction, which results in apparent tensile stresses in the scale[43] and scale cracking.[44] Hou et al.[45] recently showed using glancing synchrotron X-ray diffraction that a steady-state compressive stress of about 75 MPa at 1100°C is reached after complete transformation of the TGO scale on β-NiAl to α-Al_2O_3. It has been shown empirically that preoxidation of the bond coat to stabilize the α-Al_2O_3 scale significantly improves the lifetime of a TBC system.[46,47]

The effects of minor elements in the alloy on the rates of Al_2O_3 transformation to the stable α structure are unclear; there is, however, evidence to suggest that Cr[48] and Ti[49] can exert an accelerating effect on the transformation. Water vapor and oxygen partial pressure in the atmosphere can also influence the transformation rate and might even either promote[40] or hinder[50] α-Al_2O_3 formation. Moreover, the oxidation behavior of a continuous and adherent α-Al_2O_3 scale does not seem to depend on water vapor content in the oxidizing atmosphere.[51] By contrast, spallation of a moderately adherent α-Al_2O_3-rich scale tends to be exacerbated in the presence of water vapor.[52]

The establishment of a protective TGO scale on an initially "bare" alloy surface during isothermal oxidation can be generally characterized as involving three stages: a transient stage, followed by a steady-state stage, and finally a breakaway stage. Virtually all thermodynamically stable oxides can form during the transient stage, depending on the alloy system, oxidizing atmosphere and temperature. The duration of the transient stage can be seconds or days. The steady-state stage commences when the long-term phase constitution of the scale is established. The breakaway stage corresponds to failure of the steady-state scale and the subsequent formation of less-protective oxides. Clearly, the onset of the breakaway stage for TBC systems should not be an issue, apart from the fact that its occurrence must be prolonged beyond the useful lifetime of the TBC.

The transient stage of oxidation is particularly important in TBC systems because bond coats can be multiphase (i.e., the MCrAlY type), with the different phases often having large differences in aluminum content. Initial high-temperature exposure of these multiphase materials to air typically results in the formation of a transient, heterogeneous scale, consisting of different oxides (e.g., stable and metastable Al_2O_3, Cr_2O_3, $NiCr_2O_4$, etc) nucleating to varying extents on the different phases.[53] (Though less significant, the formation of a heterogeneous, transient-oxide scale will also occur on single-phase coatings.) Eventually, α-Al_2O_3 becomes the dominant oxide in the TGO; however, the stresses resulting from the continuance and/or transformation of the previously established transient oxides can adversely affect the life of the TBC system. Further, the amount and distribution of impurities in the Al_2O_3 that eventually develop can differ between the metallic phases.[54] The variability in α-Al_2O_3 formation behavior with metallic phase constitution and oxidizing conditions is of great importance to the optimization of TBC performance and is a fertile topic for future investigations. This is particularly true considering the introduction of γ-Ni + γ'-Ni_3Al-based bond-coatings.[8–11,14]

Factors Affecting TGO Adherence

Although there is no universally accepted explanation for poor TGO scale adherence, there is a general understanding of the important factors that influence it. Adherence of the TGO scale is primarily affected by the following factors[54]: 1) stresses in the scale that develop during scale growth and those associated with thermal cycling caused by the difference in the thermal expansion between the substrate and the scale; 2) nucleation and growth of physical defects (i.e., voids and microcracks) at the scale/coating interface and/or within the scale; 3) the growth rate of the TGO scale (i.e., the tendency for scale spallation increases with increasing scale thickness); and 4) solubility and interfacial segregation of certain elements, such as S and Ti, in both the metallic and ceramic components. The composition and structure of the bond-coat affect all of these factors. In relation to composition, Barrett[55] statistically analyzed the cyclic oxidation kinetics of 36 commercial aerospace alloys to arrive at phenomenological equations relating spallation behavior to alloy composition. Although these equations are not directly applicable to the bond coats in current TBC systems, they do effectively highlight the sensitivity of scale spallation to alloy composition and, in particular, the apparent interaction between alloying elements.

There is very little doubt that nonmetallic impurities, particularly sulfur, in the bond coat or base alloy are very detrimental to scale adhesion.[34–36,40,41,56,57] Lee et al.[58] reported that with a low sulfur content in the aluminide coating (~0.1–0.2 ppmw) the TGO scale becomes highly resistant to spallation at surfaces within the aluminide grains upon cyclic oxidation at 1150°C. Interestingly, however, the scale that formed over the grain boundaries of the coating spalled. This difference in scale adhesion behavior was attributed to the preferential segregation of heavy alloying elements, such as W, Ta, and Re, from the substrate to the grain boundaries.

Reactive elements such as Y, La, Zr, Ce, and Hf at low concentrations of about 0.005–0.3 wt.% are also highly beneficial for improving scale adhesion of MCrAl and β-NiAl(-Pt) bond-coats, but can be detrimental at concentrations greater than about 1 wt.% because of their tendency to form intermetallic phases that are prone to preferential oxidation.[57,59] Pint et al.[35] recently reported that although the addition of platinum to β-NiAl is beneficial to alumina-scale adhesion it is not as effective as hafnium or zirconium additions. These authors further reported that the addition of 0.05 at.% Hf to a Pt-modified β alloy had the effect of both improving alumina-scale adhesion and decreasing the α-Al_2O_3 growth rate by a factor of 10 compared to the Hf-free alloy. Notwithstanding, the controlled addition of Hf at such a low level to a β bond coat is quite difficult to achieve and, hence, is typically not done in practice because of high yield losses during coating deposition.

Moon and Lee[60] empirically quantified the tendency for a TGO scale to spall during a temperature drop ΔT by the expression

$$\text{tendency to spall} \propto [\zeta(\Delta T)^2/\beta]^m \tag{1}$$

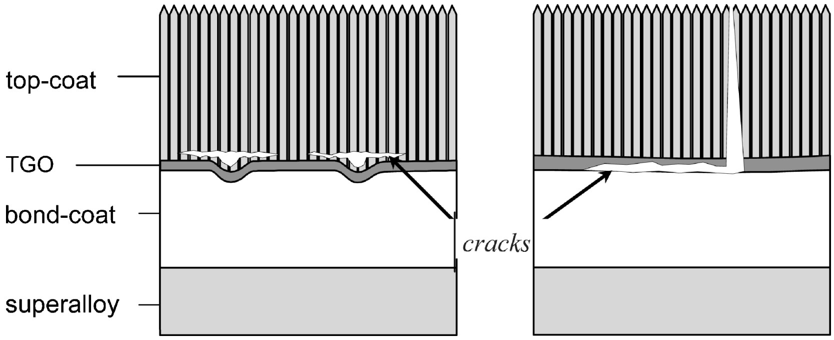
where ζ is the scale thickness before spalling; m is a positive number, which depends on the mechanical properties of the TGO scale; and β is a constant that is dependent upon the strength of adhesion at the alloy/scale interface. The value of β increases with increasing strength of scale adhesion, while m typically varies from unity for a ductile scale to about 4 for a brittle scale. The values of β and m depends on the composition of the scale, which, in turn, depends on the composition of the underlying alloy. In agreement with Eq. (1), Barrett and Lowell[61] concluded from their study of the cyclic oxidation behavior of commercial alloys at 1150°C that the most critical factor in minimizing scale spallation is to keep the TGO scale as thin as possible.

In assessing a given bond-coat system, it is also important to realize that its composition and structure change with time in service caused by both TGO-scale growth and interdiffusion with the substrate. The occurrence of coating/substrate interdiffusion decreases the concentration of aluminum in the coating, thereby reducing the ability of the coating to sustain exclusive Al_2O_3-scale growth, particularly in the event of localized detachment and/or microcracking, and introduces unwanted elements (e.g., sulfur and titanium), which can promote oxide-scale spallation.[62] It is to be expected that as the operating temperature of the turbine increases then so will the extent of coating/substrate interdiffusion.

An additional important concern during the interdiffusion between a coating and a nickel-base superalloy is the formation of topologically close-packed (TCP) phases, such as σ, μ, and R. The morphology of TCP-phase precipitates is typically plate like or needle like, and formation of even a few volume percent TCP phase is considered to be deleterious to the strength and toughness of the coating/alloy system. TCP-phase formation is promoted by deformation and, perhaps more importantly, the presence of refractory metal elements Re, Mo, W, Cr, and Ta.[63] Thus, with the introduction of significantly higher levels of up to 6 wt.% rhenium in the current third-generation superalloys for the purpose of improving creep-rupture strength, TCP-phase formation resulting from coating/substrate interdiffusion is becoming an increasingly important issue.[64,65]

Modes of TBC Failure

Recent studies have collectively started to provide a more complete picture of TBC degradation.[1–4,66–70] The emerging description is a picture of progressive degradation processes that eventually



a) Rumpling

b) Interface delamination

Fig. 3 Schematic representation of TBC failure brought about by a) bond-coat rumpling and b) delamination at the bond-coat/TGO interface.

lead to failure. There are several features, in addition to bond-coat oxidation, that combine to cause failure in TBCs during lab testing and engine service, including the following:

1) Progressive bond-coat rumpling.

2) Fracture caused by a progressive increase in the normal stress across the bond-coat interface acting at bond-coat asperities.

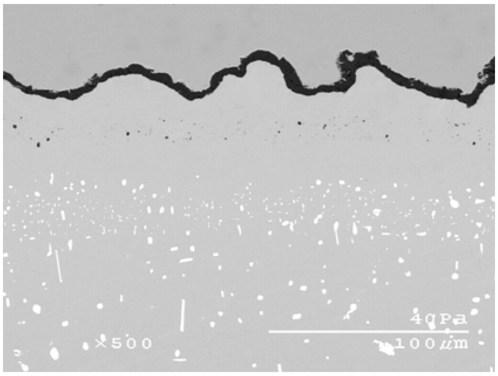
3) Failure caused by a progressive aluminum depletion and formation of oxides other than α-Al_2O_3. This mechanism is rarely observed in practice; however, bond-coat depletion can foster phase changes and changes in its properties that can contribute to the failures modes described in features 1 and 2.

4) Sintering of the ceramic top coat. The first three of these failure features include a strong contribution from bond-coat oxidation and interdiffusion with the substrate.

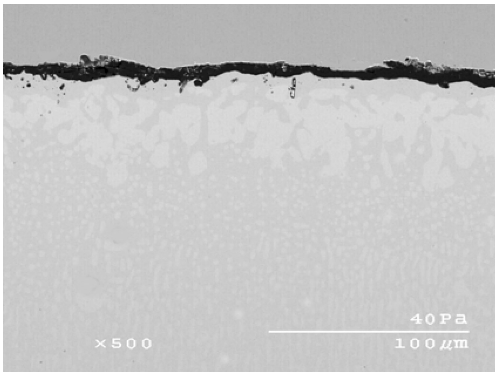
In general, two failure categories can be identified for TBC systems that use a YSZ top coat and considering only thermal cycling conditions. Other mechanisms can arise under isothermal conditions or when the YSZ top coat is replaced by a lower thermal conductivity ceramic, such as $Gd_2Zr_2O_7$ or Y(Gd)SZ, but these will not be discussed in this paper.

The first category is associated with what can be termed *intrinsic mechanisms*, which arise in the absence of large thermal gradients and transients. Intrinsic mechanisms include the modes of failure commonly found when performing furnace cycle tests at typical engine temperatures. They are dominated by the strain misfits within the composite layered assemblage of the top coat, TGO, and bond-coat. As shown schematically in Fig. 3, there are basically two subgroups of intrinsic mechanisms: rumpling (or ratcheting) and interface delamination. The former occurs primarily with NiAl-Pt bond coats, whereas the latter occurs largely in systems with MCrAlY bond coats.[4]

Rumpling is a displacement instability of the TGO/bond-coat region that is manifested as periodic undulations. The extent of rumpling progresses on a cycle-by-cycle basis. Figure 4a shows an example of unconstrained (i.e., no top coat) rumpling of a β-NiAl-Pt bond-coat resulting after 1000 thermal cycles in air, with each cycle consisting of one hour at 1150°C followed by 15 min at ~80°C. The coating was planar at the start of testing and is seen to have become highly undulated after thermal cycling. The progressive development of such undulations can induce cracks that grow during each thermal cycle. These cracks eventually coalesce in some regions, causing the TBC to buckle and spall from the substrate. The failure plane is typically in the TBC just above the TGO.[4] The hot time to failure in this case is dependent on time/temperature history. Models indicate that the extent of rumpling can be decreased by a bond coat with a high creep strength, a top coat with a high stiffness, and a TGO with a low creep strength.[71] In at least partial support of these inferences, Fig. 4b shows that an unconstrained Pt+Hf-modified γ-Ni + γ'-Ni_3Al bond coat retains a relatively planar surface during thermal cycling. The $\gamma + \gamma'$ bond-coat system is expected to have superior high-temperature creep strength compared a β-based system.



a) Pt-modified β-NiAl



b) Pt + Hf-modified γ-Ni + γ'-Ni_3Al

Fig. 4 Cross-sectional secondary electron images of β and $\gamma + \gamma'$ bond coats after 1000 thermal cycles in air, with each cycle consisting on 1 h at 1150°C followed by 15 min at 80°C. No top coat was applied to either of these bond coats. The β bond coat underwent significant rumpling while the $\gamma + \gamma'$ bond coat remained relatively planar.

Recent work by Zimmerman[72] indicates that the occurrence of rumpling is largely dependent upon the β bond coat undergoing a martensitic transformation on cooling coupled with the temperature and compressive stresses in the TGO scale being sufficiently high to allow for creep deformation. A detailed model for the rumpling mechanism that can account for the martensitic transformation has been recently developed by Balint and Hutchinson.[73] However, implementation of a code that embeds this model requires over 20 independent parameters, characterizing several sources of misfit strain between the bond coat, TGO, top coat, and substrate, as well as associated mechanisms of plastic deformation and cracking. The correspondence between measurements and simulations remains to be validated.

A less rigorous treatment based solely on buckling of the top coating as a means to relieve induced compressive stresses provides useful insights on variables influencing top-coat failure. For instance, for a fixed top coat of thickness y and Young's modulus E, the critical compressive stress at which buckling can occur is given by the relation[3]

$$(\sigma/E) = 4.8(y/d_c)^2 \qquad (2)$$

where d_c is the critical crack or flaw size at the base of the top coat and running parallel to the top-coat surface. From this relation it is seen that d_c depends linearly on the top-coat thickness. Further, even for a top coat 100 μm thick the critical crack or flaw size is found to be several millimeters,[3] which is significant and should be detectable by nondestructive evaluation techniques.

In MCrAlY bond-coat systems failure often occurs along the interface between the TGO and bond coat in the absence of any notable rumpling. The durability is apparently similar under cyclic and isothermal conditions.[4,69] The delamination is abrupt (rather than progressive) and occurs when imperfections that penetrate the TGO are generated. The nature of the imperfections and how they evolve with temperature cycling are incompletely understood.

The second category of TBC failure is associated with actual engine operation and, hence, can be termed *extrinsic mechanisms*. These mechanisms are associated with TBC removal induced by the particles ingested into the combustion gas stream. For instance, larger particles can impact the rotating airfoils, causing erosion and foreign object damage (FOD).[4,74] (Use of the term "foreign" in FOD can be misleading, because very often the objects are "domestic" pieces of spalled TBC from the combuster section of the engine.) As shown in Fig. 5, the impacts can induce plastic deformation and densification, as well as cracking and shear bands. The latter causes localized removal of the top coat, which is particularly unwanted. Figure 6 shows an example of erosion damage, which also led to a localized removal of top coat.

The occurrence of erosion and FOD is related to the particle kinetic energy, the temperature of the surface, and the structure and properties of the top coat. Simulations of the velocity evolution as the particles penetrate and arrest reveal connections between the impact conditions, the material, and the nature of the cracking.[74] These connections have indicated that the erosion and FOD thresholds are elevated by enhancing the toughness of the top coat material and by lowering its hot hardness. However, models that provide explicit relations between the impact and the extent of the cracking have yet to be developed.

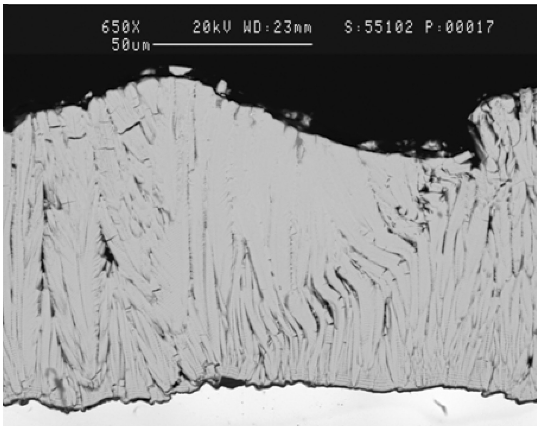


Fig. 5 Cross-sectional secondary electron image of an EB-PVD top coat that has undergone impact damage during engine operation. (Image is courtesy of R. Darolia at General Electric Transportation.

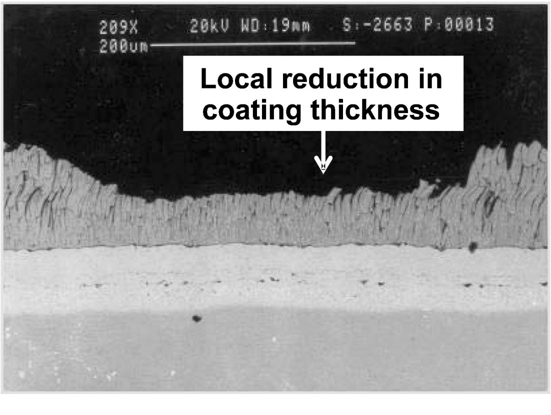


Fig. 6 Cross-sectional secondary electron image of an EB-PVD top coat that has undergone erosion damage during engine operation. (Image is courtesy of R. Darolia at General Electric Transportation.)

In certain cases, smaller particles accumulate on the top-coat surface and melt when sufficiently hot. The melt then penetrates into the top-coat layer, causing its near surface mechanical properties to change (i.e., become more rigid) and enhancing the tendency for spallation during cooling. Mercer et al.[75] termed this mode of degradation as "cold shock delamination," as it occurs during engine shutdown. The primary melt constituents are calcium-magnesium-alumino-silicates (CMAS), with a melting temperature of around 1240°C. A schematic of the degradation caused by CMAS infiltration coupled with cooling is shown in Fig. 7, while an actual example is shown in Fig. 8 (Ref. 75). The in-plane modulus of the CMAS penetrated top-coat layer increases by about a factor 5–10. Such a relatively high modulus of this layer, in conjunction with its moderate toughness, increases its susceptibility to cold shock during engine shutdown. A tentative model has been developed,[75] which predicts that for rapid thermal shock conditions there is a critical thickness of 30 μm of CMAS penetration into the top-coat surface, below which delamination does not occur. To date, there has been no independent validation of this model.

Lifetime Prediction

Previous work examining intrinsic TBC degradation and failure has clearly shown that spallation of the ceramic top coat is a progressive event closely associated with bond-coat oxidation and strongly suspected to be dependent on thermal cycling. In spite of this suspected link to thermal cycling, the main unifying mechanism quantitatively identified to date has been oxidation. Consequently, most models currently in use for life prediction for engines are heavily dependent on oxidation.[76–79] The downside of these models is that they all use simplified empirical descriptions of both oxidation and the relationship between extent of oxidation and spallation. Notwithstanding, oxidation-based models have been shown to work reasonably well for a variety of TBC systems, albeit with varying constants in the Arrhenius description.[76] The likely reason these models can work well is that all oxidation effects on TBC spallation can be related to diffusion-related phenomena, such as TGO growth rate, including variations in rates of transient oxidation; differing rates of diffusion in differing bond-coat and base metal compositions and structures; breakdown of certain "diffusion barrier" phases with time and temperature; and variations in interfacial effects, such as surface segregation of impurities (e.g., sulfur).

Often, however, life prediction based on oxidation alone does a relatively poor job of predicting life, to the extent that models tied to oxidation are typically corrected through an empirical "experience factor" that varies based on the application. The agreement with actual life to within a factor of three for this type of model when predicting outside the experience envelope, and sometimes even within the envelope, is clearly insufficient for TBCs that are to be used in prime reliant mode. Accordingly, more systematic research is needed to better understand TBC degradation and, hence, accurately guide life-prediction models.

There is general agreement that the occurrence of TBC spallation requires both thermal cycling and oxidation.[76,77] Both of these factors have been linked in a general understanding that could be termed "mechanical effects," where the chemical effect of oxidation is a contributor to the mechanical effect of subcritical crack growth during thermal cycling.[80,81] Although mechanical effects can be viewed as a unifying means to understanding spallation, it is clear from virtually all work that oxidation, and the effects related to oxidation, are key intrinsic factors dictating TBC spallation. This appears to be especially true for EB-PVD top coatings, where it is commonly observed that coating life is relatively independent of the number of thermal cycles, but is closely tied to the total time the coating is at high temperature.[67]

Established life-prediction models[76,77] describing TBC failure by thermal fatigue simply account for bond-coat oxidation by introducing a critical TGO thickness. This critical thickness is usually taken

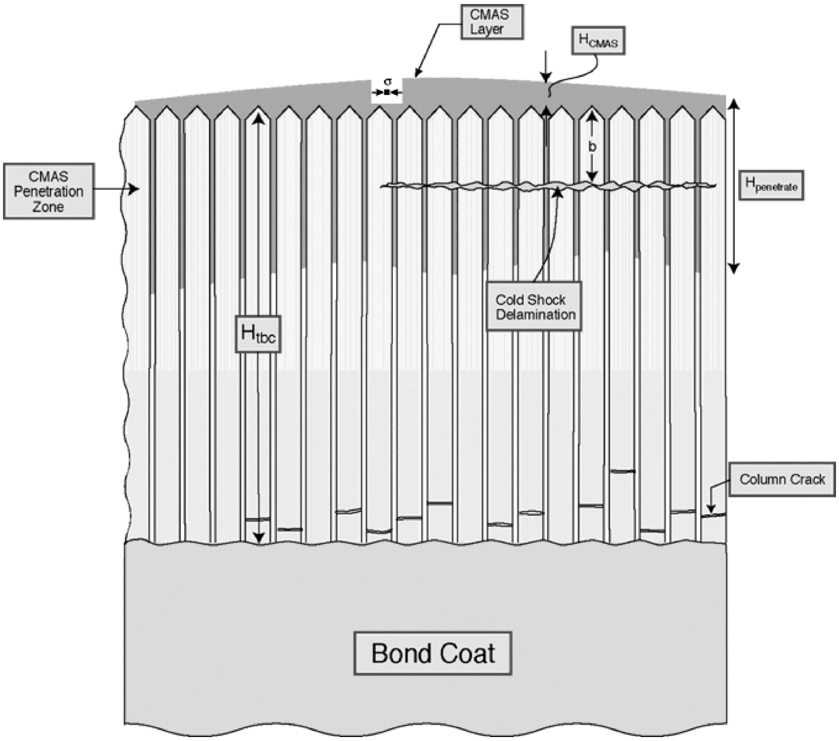


Fig. 7 Schematic of an EB-PVD ceramic top coat undergoing cold shock delamination caused by thermal expansion misfit between the penetrated CMAS and the YSZ top coat. Also shown is cracking at the base of the top coat, which can occur if the energy release rate associated with the stress in the CMAS is sufficiently high.[75]

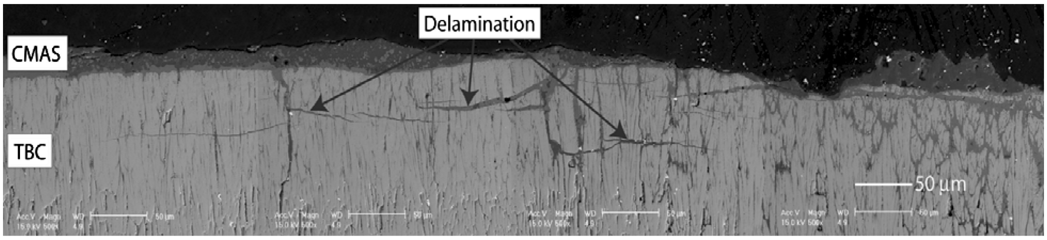


Fig. 8 Delaminations in a CMAS infiltrated top-coat layer found in an engine-tested airfoil.[75]

to be about 10 μm for an APS YSZ coating and 4–7 μm for an EB-PVD coating, and it is assumed that at a thickness greater than the critical value the TGO becomes prone to spallation, thereby deteriorating TBC lifetime. In addition to thickness, the tendency for a TGO to spall during the practical situation of thermal cycling depends on such factors as temperature change (ΔT); minimum temperature during the cycle; severity of thermal transients/gradients; difference in coefficient of thermal expansion (ΔCTE) between the TGO and the bond-coat/substrate system; the mechanical properties of the TGO and the bond coat; and the strength of adhesion at the TGO/bond-coat interface. For a given application, many of these factors are fixed, such as the temperature change and the severity of the thermal transients and gradients. Similarly, some of the properties of the coating system are relatively fixed. For example, the TGO scale is generally considered to be quite stiff and strong, even though the scale structure might vary. Time-dependent factors associated with the scale include its growth rate, adherence, and TGO/bond-coat interfacial structure and composition. Related to these factors are the homogeneity, composition, and structure of the TGO and bond coat, and the presence of physical defects (e.g., voids and microcracks) in the TGO and/or the TGO/bond-coat interface.[54] All of these variables are associated with chemical and structural effects. Traeger et al.[80] recently presented a fracture-mechanics based lifetime model that considers the evolution of spatial stress distributions in the vicinity of the TGO. The model assumes that small cracks form in regions of initial tensile stress at the peaks of the TGO/bond coat and grow into the valleys after stress conversion. However, such a model oversimplifies the situation, as it disregards time- and temperature-dependent chemical and structural changes in the TBC system. Indeed, although mechanical models might be able to describe *why* TBC failure occurs, chemical-based models are required to predict *when* this will occur. The latter types of models are currently not well established.

Summary

Significant advances in understanding the mechanisms governing TBC performance have been achieved over the past decade. It is expected that future advances will be in the areas of 1) new bond-coat compositions to meet higher metal temperature and/or service life capabilities; 2) low-k topcoats with improved resistance to extrinsic degradation mechanisms, such as erosion, FOD, and CMAS attack; 3) improved life-prediction modeling that accounts for time- and temperature-dependent chemical-based phenomena; and 4) the more effective use of sensors and nondestructive evaluation methods for assessing remaining TBC life. Finally, there will remain a strong need for appropriate and cost-effective test methods to understand and assess the thermomechanical and thermochemical behavior of TBC systems and their associated failure mechanisms.

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