

Concept of Functionally Graded Materials for Advanced Thermal Barrier Coating Applications

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This feature article explores the concept of creating functionally graded metal-ceramic composite microstructures for thermal barrier coatings used in gas-turbine applications. From a thermomechanical perspective, this concept offers the possibility of significantly improving the life and reliability of thermal barrier coatings. However, prior research reveals that progress has been somewhat limited because of the oxidative instability exhibited by some metal-ceramic composite microstructures. The present study addresses some of the materials criteria and research issues associated with preparing chemically stable, yet mechanically durable, graded metal-ceramic microstructures for realistic application environments.

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I. Introduction

DURING the past several decades, the gas-turbine community has made considerable progress in using ceramic coatings to protect metals from high-temperature turbine environments. These ceramic coatings, commonly referred to as thermal barrier coatings (TBCs), are currently used, in conjunction with air cooling, to prolong the life of metallic "hot-section" turbine components in revenue-generating aircraft engine services.¹ The use of TBCs also offers the possibility of increasing turbine inlet temperatures and, consequently, of improving the thermodynamic efficiency of gas turbines used in aircraft and land-based applications.² However, in practice, such benefits have not been realized yet, largely because the performance of currently available TBCs is considered as not sufficiently reliable and predictable for use as a "prime reliant" material. In other words, current TBC systems are conservatively designed to avoid situations where the ceramic layer (or a portion of the layer) may prematurely spall off, possibly causing the catastrophic failure of the underlying metallic components.

Nevertheless, from a materials perspective, TBC technology is currently considered as a viable near-term solution for the development of more-efficient aircraft engines and land-based gas turbines.³ Some of the major technical issues associated with the development of reliable TBCs are (i) processing



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improvements from both performance and economic standpoints, (ii) understanding the failure mechanisms of current TBCs in simulated and actual turbine environments, and (iii) developing characterization and test methods to measure and understand the time-, temperature-, and environment-dependent characteristics of TBCs for reliable life prediction. However, with the anticipation of the ultimate limitations associated with conventional TBCs, it also seems necessary to explore the possibility of incorporating novel materials concepts in future coating design. In particular, this study addresses the concept of functionally graded materials (FGMs) by reviewing prior work and reporting some confirmatory experimental results.

II. Conventional Thermal Barrier Coatings

(1) Design Philosophy

Most TBCs are structurally as well as functionally complex and, therefore, should be considered and studied as a materials system. For example, a state-of-the-art TBC system used in aircraft engines typically consists of a 125–250 μm thermally insulating ceramic layer and a 50–125 μm metallic bond coat layer between the ceramic layer and the metal component surface. Y_2O_3 -stabilized ZrO_2 (YSZ) is most commonly used as the ceramic layer because of its low thermal conductivity and relatively high coefficient of thermal expansion (CTE) for a ceramic (Table I). The role of the metallic bond coat is to protect the substrate from high-temperature oxidation because the transport of oxygen through the YSZ layer, via ionic diffusion and/or through microcracks or connected porosity, is relatively fast at typical turbine temperatures.

In the early stage of TBC development, ZrO_2 coatings partially stabilized with 6%–8% Y_2O_3 prepared by air plasma spray (APS) were found to be suitable for TBC applications.¹⁰ It also was observed that the incorporation of a controlled amount of porosity resulted in improved spallation behavior.¹¹ This behavior was attributed to the fact that the incorporation of microstructural defects, such as porosity and microcracks, into the APS coating effectively increased the apparent compliance of the coatings. This approach of using a compliant YSZ layer has been practiced as an effective means of accommodating the strains developed between the ceramic coating and metallic substrate due to their mismatch in material properties.

In another significant development,^{11,12} electron-beam physical vapor deposition (EBPVD) was used to produce a coating microstructure that consisted of YSZ columns (several micrometers in diameter) that were preferentially oriented perpendicular to the substrate surface (Fig. 1). The spallation life of the EBPVD coating was found to be superior to that of air-plasma-sprayed coatings by some investigators.¹² This result was attributed to the ability of the YSZ columns in the EBPVD coating to become physically separated or segmented during thermal cycling and, therefore, to accommodate residual and thermal stresses. This type of microstructure was observed to be unique to the EBPVD process. Dinwiddie et al.¹⁴ showed that the thermal conductivity of the as-deposited EBPVD coating was higher than that of the as-sprayed APS coating (-1.5

$\text{vs } -0.8 \text{ W}/(\text{m}\cdot\text{K})$ at 1000°C) but was much less susceptible to degradation by thermal aging. The EBPVD coating was reported to be particularly useful for protecting rotating turbine components in commercial aircraft applications.¹

Thus, from a practical standpoint, the conventional approach for accommodating the material mismatch between the ceramic coating and metallic substrate is to make the ceramic layer compliant by incorporating structural defects, such as microcracks and porosity as well as vertically segmented columns. However, in terms of achieving long-term durability, several major problems are associated with the presence of these microstructural features. As an example, the sintering of the microstructural defects with increased temperature or prolonged time exposure becomes an important issue, which may result in an increase in thermal conductivity¹⁴ and a decrease in coating compliance. Also, these microstructural features provide rapid diffusion paths for oxygen and other corrosive species.

(2) Failure Modes

Simulated and actual aircraft engine tests have shown that state-of-the-art TBCs typically exhibit wide failure distributions and also experience a variety of failure modes ranging from particulate-induced erosion, to salt-induced hot corrosion, to high-temperature oxidation, to thermal–mechanical fatigue.² However, from a more fundamental point of view, the instability at the metal–ceramic interface can be considered as the most critical factor that limits the ultimate performance of current TBCs. This bimaterial interface, inevitably required for bonding the ceramic coating and metallic surface, is the major source of time-, temperature-, and environment-dependent property changes as well as failures.

The YSZ coating prepared by APS tends to fail by the spallation of the YSZ layer near the interface between the bond coat and the ceramic layer but mostly within the ceramic layer.^{10,15,16} The time-to-failure depends on many factors, but the two most dominant parameters are the oxidation of the bond coat and the number of thermal cycles. The ultimate failure of the EBPVD coating also is due to the spallation of the ceramic layer. However, its exact failure location is clearly different from that observed for the APS coating. As shown in Fig. 1, the EBPVD coating fails at the interface between the bond coat surface and its Al_2O_3 scale.^{12,17} As in the case of the APS coating, the life of the EBPVD coating mainly depends on oxidation and thermal cycles.¹²

In both APS and EBPVD systems, a thin Al_2O_3 scale forms on the surface of the bond coat upon exposure to oxidative environments because of rapid transport of oxygen through the YSZ layer. Because Al_2O_3 is relatively impermeable to oxygen, further oxidation of the bond coat is retarded once a continuous scale is formed. This scale formation, therefore, actually provides protection to the metallic substrate from high-temperature oxidation. Therefore, the overall performance of a TBC not only depends on the ceramic layer itself but also is dictated by its bond coat and, more precisely, the nature of the metal–oxide interface that develops upon oxidation. This is particularly true for the EBPVD YSZ layer that appears to be sufficiently compliant so that the coating fails not within the ceramic layer, but at the scale–bond coat interface. Also, for the EBPVD system,

Table I. Selected Properties of Potential Coating Materials*

Material	Linear CTE ($\times 10^{-6} \text{ K}^{-1}$)	Elastic modulus (GPa)	Thermal conductivity ($\text{W}/(\text{m}\cdot\text{K})$)	Oxygen diffusivity at 1000°C (m^2/s)
YSZ (partially stabilized)	8.9–10.6	205	–2 at 1127°C	$10^{-11\ddagger}$
Al_2O_3	7.2–8.6	380–434	5.8 at 1127°C	10^{-21}
$3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ (mullite)	5.7	145	3.3 at 1127°C	10^{-18}
TiO_2	9.4	283	3.3 at 1127°C	10^{-17}
$\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$	3	70	~1 at 1000°C	

*Measured for dense, bulk materials. Compiled from Refs. 4–9. Apparent properties of these materials, if prepared by APS and EBPVD, are expected to be widely different from the tabulated values. Also, this type of materials assessment always suffers from the lack of high-temperature properties and uncertainties in reported values, depending on specimen preparation, impurity levels, measurement methods, etc. Nevertheless, this type of assessment provides a starting basis. [†]For ZrO_2 .

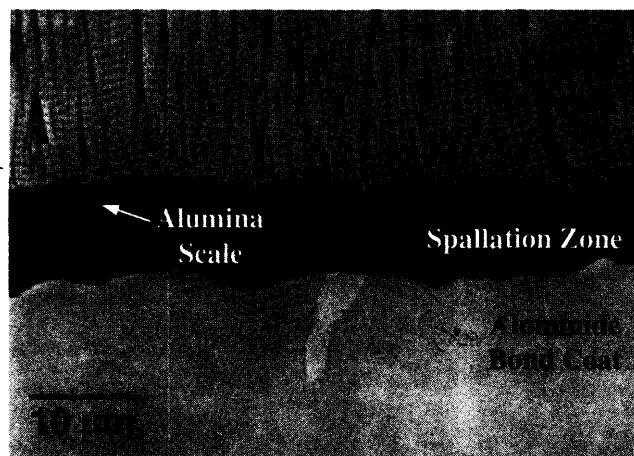


Fig. 1. Cross-section of an EBPVD YSZ coating deposited on a superalloy substrate coated with an aluminide bond coat after exposure to oxidative environments. Micrograph shows that the EBPVD coating fails by debonding at the interface between the Al_2O_3 scale and the bond coat surface. (Micrograph courtesy of Ben Nagaraj, General Electric Aircraft Engines.)

the effects of substrate materials can be considerable because of the diffusion of some alloying elements as well as impurities to the metal–scale interface. Therefore, to a large extent, the development of more-reliable EBPVD TBCs necessitates a new generation of bond coat materials, which substantially improve the adhesion of the metal–scale interface.

(3) Scale Formation and Adhesion

Currently, nickel and platinum aluminide coatings prepared by gas-phase pack or chemical vapor deposition (CVD)¹⁸ and vacuum-plasma-sprayed (VPS) MCrAlY (where M = Ni, Co, CoNi, or NiCo) coatings¹ are used as bond coats for most TBC applications. The protection mechanism provided by these types of Al_2O_3 -forming coatings recently has been described by Birks *et al.*¹⁹ Upon oxidation, a continuous α - Al_2O_3 scale, consisting of equiaxed grains, grows on the surface of the bond coat after a brief transient growth period. Eventually, a columnar grain microstructure develops. At this stage, the transport of oxygen mainly occurs along grain boundaries between the oxide columns. Also, the formation of small voids (as large as several micrometers) has been observed underneath the scale at the metal surface as a result of interactive morphological and diffusional mechanisms. The ability of the bond coat to continue to support the growth of the Al_2O_3 scale depends on the activity and the total amount of aluminum available in the coating. However, during use, the aluminum reservoir of the bond coat is depleted by consumption by the Al_2O_3 scale growth and by diffusion into the alloy substrate. When the aluminum level of the bond coat falls below at which Al_2O_3 cannot be formed preferentially, faster growing oxides of the other constituents of the bond coat will form. Then, the adhesion of the TBC can be significantly degraded. Another factor is that the continuing growth of the otherwise protective Al_2O_3 scale at the bond coat–YSZ interface is a source of increasing strain.

When a bond coat is used without a ceramic top coat (as in the case of many aircraft and land-based gas turbines operating today), the Al_2O_3 scale tends to spall off during thermal cycling, and, subsequently, a new oxide scale forms on the coating surface. This cycle of scale formation and spallation continues at the expense of the sacrificial metallic coating layer, which can be refurbished or repaired at regular maintenance intervals. However, when the aluminide or MCrAlY coating is used as a bond coat for a TBC layer, even local scale spallation can initiate coating failure. Therefore, scale formation, which is essential for the oxidation protection of the base metal, is an important issue to consider in TBC design.

From a mechanical point of view, the driving force for scale spallation is the development of residual and thermal stresses at the interface between the oxide scale and the metal surface. The scale becomes severely strained with temperature cycling and increased scale thickness because of the large differences in material properties, such as CTE and Young's modulus. In a qualitative sense, when the level of these stresses exceeds the bond strength of the bimaterial interface, the scale and metal surfaces are debonded. From the standpoint of fracture mechanics, it is important to consider factors that affect crack initiation and propagation along this metal–scale interface. For example, the presence of small voids at the metal–scale interface can contribute to spalling by reducing the resistance of crack propagation.²⁰

Scale adherence can be improved by several methods. First, the addition of small amounts of so-called reactive elements—such as yttrium, hafnium, and zirconium—to superalloys and coatings can significantly improve scale adhesion.^{21–23} Second, the removal of sulfur impurities to below sub-ppm levels also increases scale adhesion because sulfur tends to segregate and weaken the bonding between the metal and scale.^{21,22} A low level of sulfur also is observed to reduce the degree of void formation at the metal–scale interface.¹⁹ In a conceptual sense, these approaches can be viewed as an avenue to increase the work of adhesion at the metal–scale interface. The concepts of adding reactive elements or removing sulfur impurities have been used or are being pursued by modifying current casting and coating procedures.

III. Functionally Graded Thermal Barrier Coatings

The basic thesis behind the FGM concept is that, by appropriately combining two or more materials, the functionality of a particular material system can be tailored and extended beyond what is possible with nongraded material systems.²⁴ For various applications, the FGM approach has been explored to mitigate some of the major problems associated with the development of a sharp interface at the join of two dissimilar materials. For structural applications, compositionally and/or microstructurally graded interfaces, if properly designed and prepared, can be more resistant to crack initiation and propagation.²⁵ Also, in principle, the graded interfaces can be useful for lowering peak stresses and eliminating stress singularities at certain crack-sensitive locations because of the gradual changes in material properties, such as CTE and Young's modulus, through the graded interface region.²⁵ Although the FGM concept itself is rather intuitive and simple to comprehend, there are many technical challenges associated with measuring and estimating physical and mechanical properties of graded materials and, therefore, validating their potential benefits.^{26–28}

(1) Examples of Functionally Graded Thermal Barrier Coatings

In the past, not surprisingly, the FGM concept has been pursued as a means for managing residual stresses and to replace the sharp YSZ–MCrAlY interface encountered in the APS TBC system. However, demonstrating this FGM concept generally has been difficult because the graded regions containing YSZ and MCrAlY as ceramic and metallic constituents tend to become unstable upon exposure to oxidative environments. As an example, Fig. 2 shows a typical graded microstructure containing YSZ and NiCoCrAlY, which was created using APS equipment configured with a single plasma torch with separate YSZ and NiCoCrAlY powder feeders. As recently reviewed by Sampath *et al.*,²⁹ similar graded microstructures have been produced by various plasma spray techniques. Some selected properties of the graded materials, such as hardness and elastic modulus, have been measured.²⁹ Also, several studies^{30,31} have been conducted to address the measurement and estimation of the physical and mechanical properties of this type of graded materials. The graded microstructure

shown in Fig. 2 was prepared on a Mar-M-247 substrate ($-2\text{ cm} \times -2\text{ cm}$) as an abradable seal. Note that, in the turbine section, abradable seals are used to help minimize the gas leakage through the gap between the tips of the rotating blades and the turbine shroud.^{1,32} Typically, abradable seals are much thicker than the TBCs used for vanes or airfoils. Although the temperature requirements for abradable seals are not generally as demanding as those for the coatings used for airfoils, there are other structural criteria, such as abradability, to consider. To some extent, abradable seal applications have been targeted as a test vehicle to validate the usefulness of the FGM coating concept because of the relatively lower temperature requirements as well as the need for a greater thickness (i.e., -4 mm) that allows more gradual compositional grading profiles. Figure 3 shows the compositional change of the NiCoCrAlY and YSZ phases measured as a function of coating thickness, using a digital image analyzer interfaced with an optical microscope. The seal consists of a 0.13 mm NiCoCrAlY layer, a 2.54 mm region graded with NiCoCrAlY and YSZ, and a 1.27 mm pure-YSZ layer.

(2) Failure Mechanism of Graded MCrAlY + YSZ TBCs

The stability of the graded seal shown in Fig. 2 was tested at 1000°C in air in a resistance-heated tube furnace. The temperature of the seal was measured using an optical pyrometer. The seal spalled within the graded region after an isothermal treatment of 100 h. The lateral dimension of the spalled piece was increased relative to that of the remaining substrate, which was attributed to the volume expansion caused by the oxidation of the metallic phase. A similar spallation behavior was observed after 242 h of oxidation at 1000°C . Figure 4 shows that spallation occurred within the graded region -0.5 mm , measured from the initial substrate surface. Metallographic and X-ray diffraction (XRD) analyses indicated that most of the metallic phase in the spalled region was oxidized. However, the seal

structure remaining on the substrate was not extensively oxidized although some localized penetrations were evident. Also, preferential oxidation of the metallic phase occurred near the substrate interface, where it intersected with the free edges of the seal specimen. Because of the crude nature of this oxidation experiment, it was not possible to resolve the relative contributions to the observed spallation behavior from the oxidation of the graded region versus that of the free edges. However, in the context of the present study, the critical issue to be emphasized was the oxidative instability of the graded microstructure of this particular coating design, which contained YSZ and NiCoCrAlY as composite constituents.

Similar observations were reported previously by other investigators. The work of Eaton and Novak⁴ showed that graded YSZ + CoCrAlY coating microstructures were not stable in high-temperature oxidizing environments. In that study, a set of free-standing metal-ceramic composite samples was prepared by APS for oxidation testing. CoCrAlY was used as the metallic constituent (about 12 vol%). Upon oxidation at 1093°C , it was observed that the size and weight of the YSZ + CoCrAlY composite samples significantly increased as a result of the oxidation of the metallic phase in the YSZ matrix. Tiwari *et al.*³³ also observed similar behavior with free-standing APS composites containing NiCrAl and YSZ. In comparison to pure NiCrAl free-standing APS samples, the weight gain of the NiCrAl + YSZ composite samples after oxidation at 600° and 800°C was -3 times higher. The increased oxidation observed for the metal + ceramic composite samples was attributed to several reasons by Tiwari *et al.* The presence of numerous metal-ceramic interfaces in the composite samples provided short-circuit paths for oxygen diffusion. Also, the rapid diffusivity of oxygen through YSZ, with an increased metallic surface area available through the dispersion in the YSZ matrix, increased the oxidation of the metallic phase. For similar reasons, Miller³⁴ recommended that plasma spray coatings with an

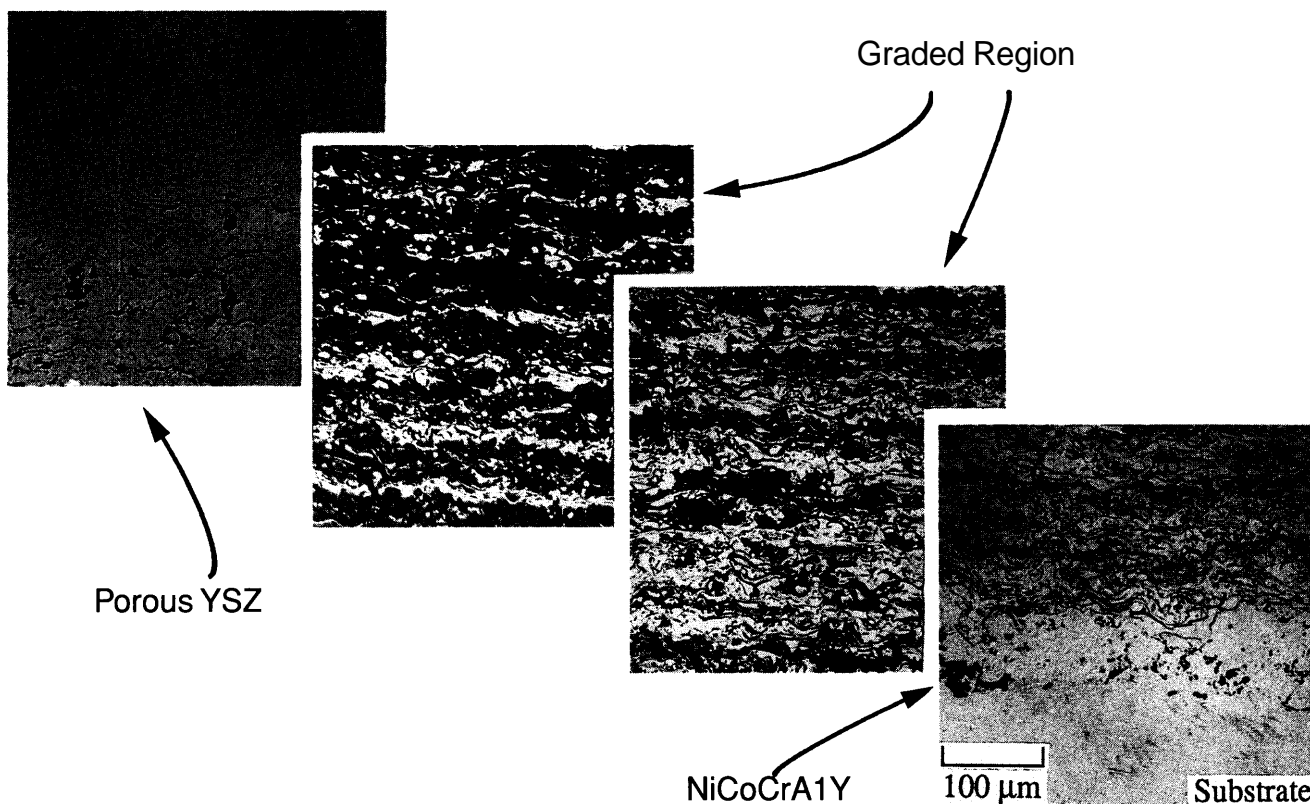


Fig. 2. Typical APS-FGM microstructure containing NiCoCrAlY and YSZ as metallic and ceramic constituents, respectively. This FGM microstructure was prepared on a Mar-M-247 superalloy substrate for use as an abradable seal. Lighter area is the metallic phase, and the darker area is the ceramic phase. Graded microstructure was created using an APS apparatus configured with a single plasma torch with separate YSZ and NiCoCrAlY powder feeders.

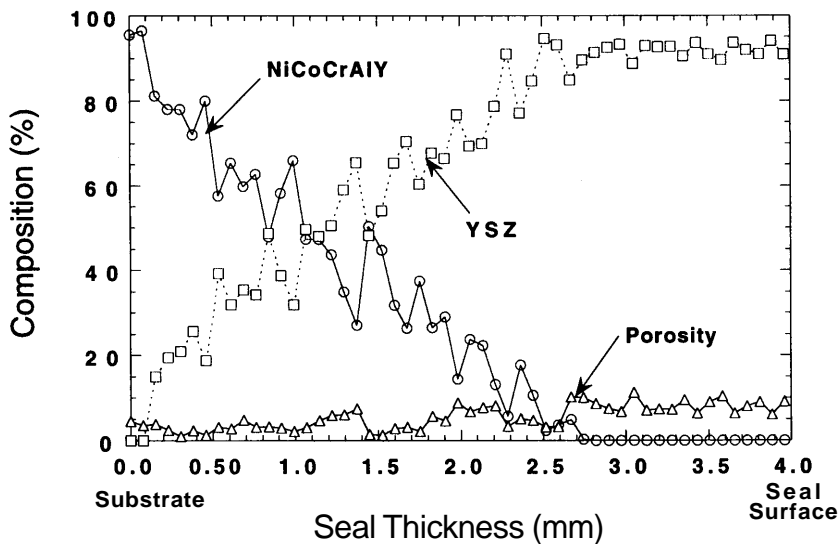


Fig. 3. Compositional change measured as a function of seal thickness using a digital image analyzer interfaced with an optical microscope. For the analysis, 52 digital scans were made at 75 μm thickness intervals along the polished cross section of the APS-FGM seal structure. Lamellar microstructural features developed during spraying (see Fig. 2) were responsible for relatively large fluctuations in the composition profiles observed in the graded region. Level of splat boundaries, which were created between molten particles during spraying, was estimated to be $-8.42\% \pm 1.5\%$ in the outer YSZ layer without considering any particle pullouts during polishing. Compositional contribution from the splat boundaries was added arbitrarily to the YSZ phase. In the graded region, the presence of the splat boundaries was not quantified because the splat boundaries and ceramic phase could not be distinguished clearly during the image analysis.

interface region graded with MCrAlY and YSZ are inappropriate because of oxidation of the graded region at temperatures $>800^\circ\text{C}$.

Despite the oxidation problems associated with using YSZ as a ceramic constituent, most FGM TBC work reported in the literature has been performed on the APS YSZ + MCrAlY material system.³⁵⁻⁴¹ Successful oxidation test results generally have not been reported for this material system except for the work of Mendelson *et al.*⁴¹ They have reported that the cyclic life of a dual-graded TBC containing a graded YSZ-MCrAlY interface and a laser-glazed top surface was longer than that of conventional two-layer TBCs. Also, for the lower-temperature situations ($<600^\circ\text{C}$) encountered in diesel-engine environments, the concept of using step-graded interfaces containing MCrAlY and YSZ appears to be an effective means of managing residual and thermal stresses.⁴²

These observations suggest that YSZ is not an ideal ceramic for preparing TBCs with a graded metal-ceramic region

because YSZ rapidly conducts oxygen at elevated temperatures. Also, the strain-tolerant microstructure of the APS coating allows rapid oxygen diffusion. Therefore, the major lesson from prior research is that, when a FGM system is being considered for a TBC application, thermochemical as well as thermo-mechanical compatibilities between the proposed metallic and ceramic constituents should be examined. Also, their synergistic interactions with the surrounding environment should be considered.

(3) Alternative Thermal Barrier Materials

In recognition of the failure modes observed for state-of-the-art TBCs and the results with YSZ + MCrAlY FGM TBCs, an "ideal" TBC material can be envisioned. This coating material should be a thermally insulating ceramic. Also, the coating needs to be intrinsically resistant to oxygen diffusion (including diffusion along grain boundaries) and to be free of microstructural defect features, such as porosity and microcracks. At the

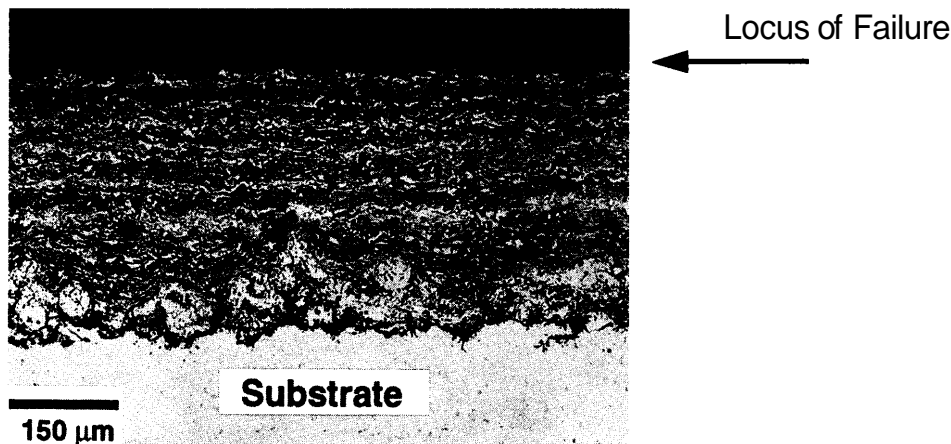


Fig. 4. FGM seal failed by spallation after isothermal oxidation at 1000°C for 242 h in air. This optical micrograph shows that the spallation took place within the graded region—500 μm , measured from the initial substrate surface.

same time, the ceramic coating must be chemically and mechanically compatible with its bond coat and substrate as well as with turbine atmospheres. Meanwhile, the concept of grading can be used to manage stresses and to increase the toughness of its metal–ceramic interfacial region.

In a practical sense, it appears that no single ceramic material is likely to meet this complex set of criteria. Even if such a material exists, another important issue is whether strain-tolerant ceramic microstructures will continue to be needed at the expense of oxidation performance. To illustrate this point, a new class of ceramic materials, commonly referred to as NZPs, can be considered as a possible alternative material to YSZ. NZPs are named after their parent composition ($\text{NaZr}_2\text{P}_3\text{O}_{12}$).^{43,44} As compared in Table I, the thermal conductivity of these materials ($\sim 1 \text{ W}/(\text{m}\cdot\text{K})$ for slip-cast $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$)⁵ is essentially lower than that reported for dense, fully or partially stabilized YSZ ceramics ($\sim 2 \text{ W}/(\text{m}\cdot\text{K})$).⁶ Young's modulus of the NZP materials also is rather low for a ceramic ($\sim 70 \text{ GPa}$),⁴⁴ which is another desired characteristic relating to coating compliance. The melting point of NZPs is typically $>1800^\circ\text{C}$. Because of their crystal structure, oxygen diffusivity in NZPs (both ionic and electronic) is expected to be relatively low, although it has not been measured accurately.⁴⁵ Furthermore, one of the NZP compositions, $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$, has been found to be resistant to corrosion induced by Na_2SO_4 .⁴⁶ However, the CTE of NZPs is very low (see Table I), particularly in comparison to nickel-based superalloys. Also, their stability in turbine environments (e.g., possible dissociation into gaseous species containing phosphorus) and compatibility with respect to the nickel-based alloys are highly questionable. Recently, $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$ was air plasma sprayed onto a nickel-based superalloy with a MCrAlY bond coat.⁴⁷ Preliminary isothermal oxidation test results suggest that this particular NZP material reacts substantially with the bond coat at 1000°C in air after 100 h. This observation suggests that, although the $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$ material has some desirable characteristics, its use as a direct substitute for YSZ is unlikely.

(4) Rationale for Multilayered Functionally Graded Thermal Barrier Coatings

Exploring alternative thermal barrier materials is expected to be a difficult, time-consuming, and uncertain task because of the complex materials criteria imposed on candidate materials. Probably a more pragmatic approach to this challenge is to incorporate additional layers in the coating structure to satisfy the multiple functionality required for more oxidation resistant, yet mechanically durable TBCs, as schematically illustrated in

Fig. 5. One plausible example of this multilayer approach is to incorporate an oxygen barrier layer that is sandwiched between the thermal barrier layer and metallic surface. The role of this interlayer, which can be functionally graded, is to retard oxygen transport to the metal surface as well as to avoid the formation of a sharp metal–ceramic interface.

(5) Oxygen Barrier Materials and Required Morphology

Table I lists several ceramic materials for consideration as an oxygen barrier material. ZrO_2 -based materials (i.e., stabilized with CeO_2 , MgO , SrO , etc.) are not included in Table I because most of them are good electrolytes and, thus, oxygen conductors. Table I shows that Al_2O_3 and mullite exhibit low oxygen diffusivity at 1000°C , but their thermal conductivity is higher than that of YSZ. Other properties, such as CTE and elastic modulus, also should be considered because these properties determine the level of residual and thermal stresses in the coating and substrate. As a qualitative approximation, the in-plane residual stress of the coating (σ) due to temperature changes or gradients is expected to be proportional to the magnitude of the CTE mismatch between the substrate and coating materials ($\Delta\alpha$) and inversely proportional to the compliance of the coating (C); i.e., $\sigma \propto \Delta\alpha/C$. The compliance of a dense coating depends on its intrinsic elastic modulus as well as microstructure. From this simple approximation, it can be argued that a dense mullite coating deposited on a superalloy substrate generates less residual stress than a dense Al_2O_3 coating because the low modulus of mullite compensates for its low CTE value. However, mullite's oxygen diffusivity is expected to be higher than that of Al_2O_3 .

Eaton and Novak observed that Al_2O_3 , mullite, and MgAl_2O_4 composites mixed with a metallic phase (CoCrAlY) exhibited superior oxidative stability to YSZ + CoCrAlY composite specimens. The observed oxidation behavior was explained mainly by the relatively low rate of oxygen diffusion through these oxides. The use of Al_2O_3 as a ceramic constituent for preparing a graded abrasion seal structure recently was reported by DeMasi-Marcin and Gupta.¹ In this application, an abrasion seal was graded in multiple steps to provide smooth transitions going from a metallic bond coat, to Al_2O_3 , to fully stabilized YSZ, to partially stabilized YSZ. Recently, Rumaner et al.⁴⁸ reported that an APS coating graded with MCrAlY and mullite (or Al_2O_3) was much more crack and oxidation resistant than conventional dual-layered MCrAlY/YSZ TBCs, but at the expense of increased thermal conductivity. Therefore, from a standpoint of matching CTE, providing thermal resistance, and obtaining strain-tolerant microstructures, Al_2O_3 or mullite is

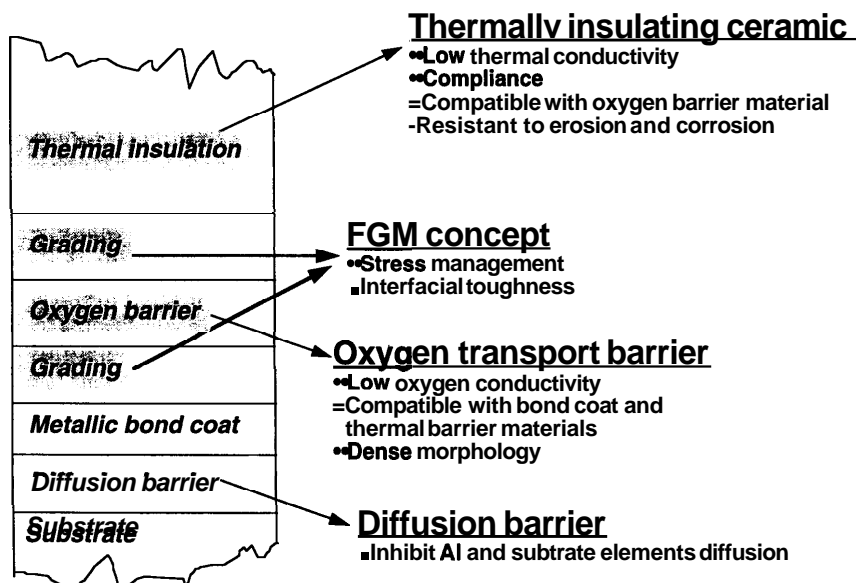


Fig. 5. Materials criteria for designing a functionally graded, multilayer coating system for thermal insulation as well as oxidation resistance.

same time, the ceramic coating must be chemically and mechanically compatible with its bond coat and substrate as well as with turbine atmospheres. Meanwhile, the concept of grading can be used to manage stresses and to increase the toughness of its metal–ceramic interfacial region.

In a practical sense, it appears that no single ceramic material is likely to meet this complex set of criteria. Even if such a material exists, another important issue is whether strain-tolerant ceramic microstructures will continue to be needed at the expense of oxidation performance. To illustrate this point, a new class of ceramic materials, commonly referred to as NZPs, can be considered as a possible alternative material to YSZ. NZPs are named after their parent composition ($\text{NaZr}_2\text{P}_3\text{O}_{12}$).^{43,44} As compared in Table I, the thermal conductivity of these materials ($-1 \text{ W}/(\text{m}\cdot\text{K})$) for slip-cast $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$ ⁵ is essentially lower than that reported for dense, fully or partially stabilized YSZ ceramics ($-2 \text{ W}/(\text{m}\cdot\text{K})$).⁶ Young's modulus of the NZP materials also is rather low for a ceramic (-70 GPa),⁴⁴ which is another desired characteristic relating to coating compliance. The melting point of NZPs is typically $>1800^\circ\text{C}$. Because of their crystal structure, oxygen diffusivity in NZPs (both ionic and electronic) is expected to be relatively low, although it has not been measured accurately.⁴⁵ Furthermore, one of the NZP compositions, $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$, has been found to be resistant to corrosion induced by Na_2SO_4 .⁴⁶ However, the CTE of NZPs is very low (see Table I), particularly in comparison to nickel-based superalloys. Also, their stability in turbine environments (e.g., possible dissociation into gaseous species containing phosphorus) and compatibility with respect to the nickel-based alloys are highly questionable. Recently, $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$ was air plasma sprayed onto a nickel-based superalloy with a MCrAlY bond coat.⁴⁷ Preliminary isothermal oxidation test results suggest that this particular NZP material reacts substantially with the bond coat at 1000°C in air after 100 h. This observation suggests that, although the $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$ material has some desirable characteristics, its use as a direct substitute for YSZ is unlikely.

(4) Rationale for Multilayered Functionally Graded Thermal Barrier Coatings

Exploring alternative thermal barrier materials is expected to be a difficult, time-consuming, and uncertain task because of the complex materials criteria imposed on candidate materials. Probably a more pragmatic approach to this challenge is to incorporate additional layers in the coating structure to satisfy the multiple functionality required for more oxidation resistant, yet mechanically durable TBCs, as schematically illustrated in

Fig. 5. One plausible example of this multilayer approach is to incorporate an oxygen barrier layer that is sandwiched between the thermal barrier layer and metallic surface. The role of this interlayer, which can be functionally graded, is to retard oxygen transport to the metal surface as well as to avoid the formation of a sharp metal–ceramic interface.

(5) Oxygen Barrier Materials and Required Morphology

Table I lists several ceramic materials for consideration as an oxygen barrier material. ZrO_2 -based materials (i.e., stabilized with CeO_2 , MgO , SrO , etc.) are not included in Table I because most of them are good electrolytes and, thus, oxygen conductors. Table I shows that Al_2O_3 and mullite exhibit low oxygen diffusivity at 1000°C , but their thermal conductivity is higher than that of YSZ. Other properties, such as CTE and elastic modulus, also should be considered because these properties determine the level of residual and thermal stresses in the coating and substrate. As a qualitative approximation, the in-plane residual stress of the coating (σ) due to temperature changes or gradients is expected to be proportional to the magnitude of the CTE mismatch between the substrate and coating materials ($\Delta\alpha$) and inversely proportional to the compliance of the coating (C); i.e., $\sigma \propto \Delta\alpha/C$. The compliance of a dense coating depends on its intrinsic elastic modulus as well as microstructure. From this simple approximation, it can be argued that a dense mullite coating deposited on a superalloy substrate generates less residual stress than a dense Al_2O_3 coating because the low modulus of mullite compensates for its low CTE value. However, mullite's oxygen diffusivity is expected to be higher than that of Al_2O_3 .

Eaton and Novak observed that Al_2O_3 , mullite, and MgAl_2O_4 composites mixed with a metallic phase (CoCrAlY) exhibited superior oxidative stability to YSZ + CoCrAlY composite specimens. The observed oxidation behavior was explained mainly by the relatively low rate of oxygen diffusion through these oxides. The use of Al_2O_3 as a ceramic constituent for preparing a graded abrasion seal structure recently was reported by DeMasi-Marcin and Gupta.¹ In this application, an abrasion seal was graded in multiple steps to provide smooth transitions going from a metallic bond coat, to Al_2O_3 , to fully stabilized YSZ, to partially stabilized YSZ. Recently, Rumaner et al.⁴⁸ reported that an APS coating graded with MCrAlY and mullite (or Al_2O_3) was much more crack and oxidation resistant than conventional dual-layered MCrAlY/YSZ TBCs, but at the expense of increased thermal conductivity. Therefore, from a standpoint of matching CTE, providing thermal resistance, and obtaining strain-tolerant microstructures, Al_2O_3 or mullite is

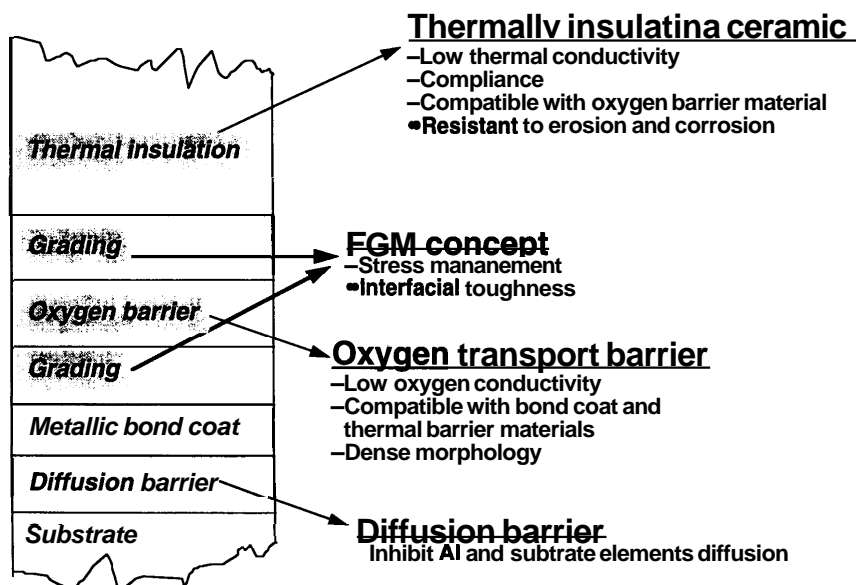


Fig. 5. Materials criteria for designing a functionally graded, multilayer coating system for thermal insulation as well as oxidation resistance.

less desirable than YSZ. However, because of its ability to resist rapid oxygen diffusion, the use of Al_2O_3 or mullite as an oxygen barrier in the intermediate region of a TBC structure can be effective.

The morphology of such an oxygen barrier layer also was expected to be important. For example, Strangman⁴⁹ reported that the presence of a 1 μm thick $\alpha\text{-Al}_2\text{O}_3$ interlayer (not graded) prepared by CVD increased the burner-rig life of a TBC consisting of EBPVD YSZ and VPS MCrAlY from 15–35 h to 95–143 h at 1150°C with 30 min cycles. The increased oxidation life was attributed to the dense morphological quality and high chemical purity of the $\alpha\text{-Al}_2\text{O}_3$ layer prepared by CVD, which is an atomistic growth process. Also, Sun *et al.*⁵⁰ reported that the presence of a 4 μm thick CVD $\alpha\text{-Al}_2\text{O}_3$ interlayer between the APS YSZ layer and VPS MCrAlY bond coat layer increased cyclic oxidation life. The rate of bond coat oxidation was reduced by the presence of the $\alpha\text{-Al}_2\text{O}_3$ layer. Furthermore, in the case of the $\alpha\text{-Al}_2\text{O}_3$ interlayer, the formation of spinels, i.e., $\text{Ni}(\text{Cr},\text{Al})_2\text{O}_4$, was not observed at the scale–YSZ interface. This suggested that the initial mechanism for bond coat oxidation was altered because of the presence of the $\alpha\text{-Al}_2\text{O}_3$ interlayer. These studies by Strangman and Sun *et al.* suggest that, in terms of improving oxidation behavior, the morphological quality and chemical purity of the interlayer are as critical as the thickness and grading of the interlayer. More recently, Lee *et al.*⁵¹ showed that an aluminide coating dispersed and graded with small $\alpha\text{-Al}_2\text{O}_3$ particles could be created by CVD. The potential merit of such a graded interfacial structure is currently being investigated.

IV. Research Needs

The results described in this study suggest that progress in the development of useful FGM TBC systems generally has been limited by the selective, high-temperature oxidation of a metallic phase when it is mixed and graded with the most commonly used ceramic material, YSZ. This instability is attributed to both the high oxygen conductivity of YSZ at elevated temperatures and the presence of extended metal–ceramic interfaces, as well as microstructural defects, such as microcracks and porosity, in the graded phase, which allow rapid oxygen transport. These observations also illustrate that developing a realistic FGM coating system has to be approached from a system consideration to satisfy the uncompromising set of thermomechanical and thermochemical requirements. Therefore, although TBC applications have been targeted by many investigators as the most immediate place for the demonstration of the FGM concept, this study indicates that it is still a challenging task.

From this perspective, it seems that the first step toward validating the FGM TBC concept should be to investigate the design and creation of a coating structure possessing a multiple number of metal–ceramic as well as ceramic–ceramic interface regions to achieve the desired combination of thermal resistance, mechanical compliance, and oxidation resistance. It is projected that, when these coating constraints are appropriately dealt with, the FGM concept then can be fully utilized for managing peak stresses and increasing interfacial toughness. As an example, some prior work indicates that the incorporation of an oxygen barrier layer between the metallic bond coat surface and YSZ layer appears to be a promising system to be further explored. The role of this oxygen barrier layer is to retard oxygen transport to the metal surface. Also, in principle, such a layer can be microstructurally and compositionally graded to avoid the formation of a sharp metal–ceramic interface. The selection criteria for such an oxygen barrier material should be based on intrinsic material properties, such as oxygen diffusivity, CTE, and modulus as well as on the type of morphology that can be created by a particular processing method.

Once the selection of candidate materials and synthesis methods is completed for a multilayer TBC system, it would be a good starting point to conduct thermomechanical modeling,

processing experiments, extensive characterization, and property measurements. This type of comprehensive work is required to appropriately design and test the validity of the proposed multilayer FGM concept. Ultimately, the long-term thermochemical stability of FGM microstructures also should be addressed.

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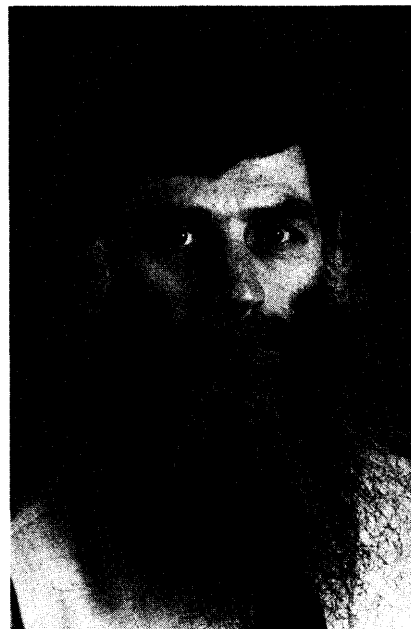


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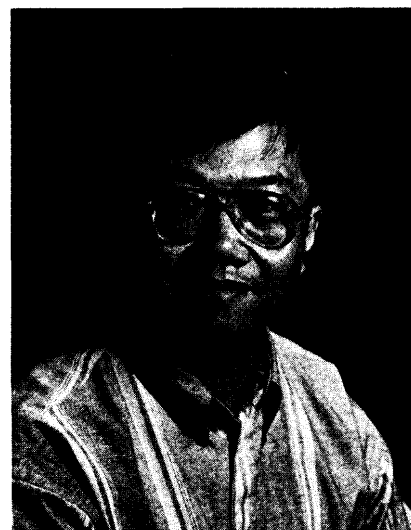
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