

Advanced Nanoceramic Thermal Barrier Coating Systems

Yi Qu*

Department of Queen Mary University of London Engineering School, NPU, 710000 Xi'an China

Abstract. With the continuous development of aerospace propulsion technologies and gas turbines, there always exists high demand for the stability and performance assurance of thermal barrier coatings under extreme high-temperature conditions. Current researches have indicated that traditional thermal barrier coating systems have shown significant issues during long-time service including sintering densification, phase instability, and environmental degradation such as those based on yttria-stabilised zirconia. So nanostructured and nanoceramic thermal barrier coatings have progressively emerged as a crucial research and environment direction for enhancing thermal protection performance because their unique size effects and tunable microstructural characteristics have played a significant influence. This research focuses on the current state of development for nanostructured thermal barrier coatings, providing an objective analysis of the performance and production processes of coatings across different material systems. It particularly aims to explain the relationship between preparation process, microstructure, and performance and it will provide guidance for the further development of material systems and production processes for advanced thermal barrier coatings.

1 Introduction

Gas turbines and aerospace propulsion systems are commonly required to operate at high temperatures in order to improve efficiency. In many applications, the temperature of hot-section components is now close to, or even exceeds, the limits of existing thermal protection systems. Under these conditions, thermal barrier coatings (TBCs) must provide not only effective thermal insulation, but also stable microstructures and reliable long-term performance.

A typical TBC system is composed of several functional layers. These usually include a nickel-based superalloy substrate that provides structural support, an MCrAlY (M = Ni and/or Co) bond coat that improves coating adhesion and provides oxidation and corrosion resistance, a thermally grown oxide (TGO) layer formed during high-temperature exposure, and a ceramic top coat (TC) that acts as the main thermal insulation layer. Through the combined function of these layers, the metallic substrate can be effectively protected under severe service conditions [1].

* Corresponding author: Jp2023304225@qmul.ac.uk

Most conventional TBC systems use yttria-stabilized zirconia (YSZ) as the ceramic top coat, and this material has been applied in turbine and aerospace components for many years. YSZ is commonly chosen because it offers low thermal conductivity, acceptable thermal expansion compatibility with metallic substrates, and relatively good fracture toughness compared with many other ceramics. Nevertheless, under ultra-high-temperature conditions, YSZ-based coatings still exhibit several inherent limitations. Sintering-induced densification, phase instability, and corrosion caused by calcium – magnesium – alumino – silicate (CMAS) gradually degrade coating performance, particularly during long-term thermal cycling in complex service environments.

Because of these limitations, nanostructured and nanoceramic thermal barrier coatings have been explored as alternative thermal protection materials. Compared with traditional micro-scale coatings, nanostructured TBCs show clear size effects and adjustable microstructural features. Many studies have confirmed that they can significantly improve thermal insulation, damage tolerance, and thermal shock resistance. At the same time, increasing research efforts have focused on material design, advanced fabrication techniques, and microstructural control strategies. However, existing studies are still scattered, and a systematic review of the relationships between processing, microstructure, and performance, as well as long-term failure behavior, is still needed.

Therefore, this review summarizes and analyzes recent progress in nanostructured and nanoceramic thermal barrier coatings, focusing on material systems, fabrication technologies, microstructural control strategies, thermal protection performance, and failure mechanisms. The aim is to establish a clear structure – performance – service relationship and provide guidance for the rational design of next-generation TBC systems.

As gas turbines and aerospace engines continue to pursue higher thermal efficiency, the stability and service life of TBC systems under extreme temperatures have become increasingly important. In this context, nanostructured thermal barrier coatings have become a major research focus because they allow heat transfer behavior, mechanical deformation, and microstructural evolution to be adjusted at the microscopic scale. Current research can generally be divided into two categories. One focuses on nanostructured coatings based on traditional YSZ, aiming to extend its service temperature range and thermal cycling resistance through microstructural refinement and defect control. The other explores advanced ceramic materials such as high-entropy oxides, perovskite oxides, and alumina, which rely on their unique crystal structures and high-temperature properties to overcome the performance limits of YSZ and meet the demands of next-generation extreme service environments.

2 Nanostructured YSZ-based thermal barrier coating systems

2.1 Advantages and limitations of nanostructured YSZ coatings

YSZ has long been used as the standard ceramic top coat material for gas turbines, mainly because it shows a good balance of properties under high-temperature conditions [2]. YSZ has a high melting point, low thermal conductivity, good thermal expansion compatibility, and a stabilized phase structure. The high-temperature tetragonal phase of ZrO_2 is usually stabilized by adding 6–8 wt.% Y_2O_3 . As a stabilizer, Y_2O_3 introduces a large number of oxygen vacancies and point defects. These defects distort the crystal lattice and increase the number of phonon scattering centers, which shortens the phonon mean free path. Since heat transfer in ceramics is mainly carried by phonons, a shorter phonon path leads to lower thermal conductivity [3].

In addition, the moderate density and controllable microstructure of YSZ make it easier to form insulation structures with both dense regions and pores during thermal spraying. Because of its good fracture toughness, low thermal conductivity, and thermal expansion compatibility with metallic substrates, YSZ has been widely regarded as the benchmark material for TBC applications. With the introduction of nanostructure concepts, conventional micron-scale YSZ coatings have been further refined to the nanoscale, leading to significant changes in microstructural morphology and defect distribution.

Typical nanostructured YSZ coatings show a bimodal microstructure consisting of fully molten regions and semi-molten regions that retain some nanoparticles. This structure contains a high density of nanograin boundaries, nanopores, and fine microcracks, which together form a system with strong phonon scattering ability and good strain accommodation. Grain refinement increases the number of interfaces, which enhances phonon scattering and further reduces heat transfer. So nanoscale pores and microcracks provide space for stress relaxation and it enables the coating to better accommodate thermal expansion and contraction during rapid thermal cycling and it also reduces the risk of large crack propagation [4].

Despite there are many performance advantages of nanostructured YSZ coatings, The sintering also will happen under extreme conditions such as high temperatures. With the increase in service use, this leads to pore shrinkage and grain growth and it will diminish the original insulating properties and increasing thermal conductivity. Furthermore, both toughness and strain tolerance decline accordingly. Consequently, YSZ coatings still face significant challenges in maintaining the structural stability of nanomaterials under extreme high-temperature conditions.

2.1 Processing optimization of nanostructured YSZ coatings

2.1.1 Atmospheric plasma spraying (APS)

The preparation of nanostructured YSZ coatings like APS. This method enables the formation of a layered structure characterised by stacked sputtered particles. Not all particles are fully molten upon reaching the substrate. That's because the APS process has an extremely high cooling rates during the APS process. So some nanoscale features and submicron pores can be preserved inside the coating. These features are generally considered beneficial for lowering thermal conductivity and for providing a certain degree of stress relaxation. However, it should also be noted that defects located at splat boundaries are relatively unstable at high temperature. During long-term exposure, these defects tend to sinter, which leads to a gradual increase in coating density [5].

2.1.2 Electron beam physical vapor deposition (EB-PVD)

Coatings produced by EB-PVD show a different type of microstructure. Instead of a lamellar structure, EB-PVD coatings are composed of columnar grains that are aligned in a preferred direction. Small gaps exist between neighboring columns, and these gaps allow the coating to deform more easily during thermal cycling. For this reason, EB-PVD coatings usually show good strain tolerance. On the other hand, the presence of columnar grains also means that heat can be transported more easily along the columns, and the thermal conductivity of EB-PVD coatings is therefore often higher than that of APS coatings [6].

2.1.3 High-power impulse magnetron sputtering (HiPIMS)

Magnetron sputtering methods have also been applied to the preparation of nanostructured YSZ coatings. Among them, HiPIMS has attracted attention in recent years. In HiPIMS, a highly ionized particle flux is generated, and strong ion bombardment occurs at the growing surface. These conditions can promote atomic rearrangement during deposition and lead to relatively dense coatings with refined grain structures. In many studies, HiPIMS-deposited coatings show slower sintering behavior and more stable interfaces, and some improvement in mechanical properties has also been reported [7].

The influence of the deposition process is not limited to surface morphology. Changes in pore shape, grain boundary distribution, and defect stability are all closely related to the deposition conditions. So the deposition method selected for a given coating system has a strong impact on its overall behavior during service, especially at elevated temperatures. In fact, nanostructured YSZ coatings are still attractive for thermal barrier applications. Their advantages in thermal insulation, thermal shock resistance, and strain tolerance are well recognized, and this explains why they are still used in many industrial systems. However, there are still some limitations. Phase instability, sensitivity to sintering, and susceptibility to calcium - magnesium - alumino - silicate (CMAS) corrosion continue to limit their performance when the service temperature reaches the range of 1300 - 1500 °C. These issues provide the main motivation for exploring alternative ceramic coating systems.

3 Advanced ceramic nanostructured thermal barrier coating systems

When YSZ coatings are used at increasingly high temperatures, their intrinsic limitations become more evident. For this reason, a number of alternative ceramic material systems have been investigated in recent years. These systems include rare-earth zirconates, hafnates, perovskite oxides, and high-entropy oxides. In comparison with conventional YSZ, many of these ceramics show lower lattice thermal conductivity, improved phase stability, and better resistance to CMAS corrosion. Owing to these characteristics, they are often discussed as potential candidates for thermal barrier coatings intended for higher-temperature service.

3.1 High-Entropy Oxide (HEO) thermal barrier coating systems

High-entropy oxides constitute a class of multicomponent ceramic materials in which five or more metallic cations occupy the same lattice sites in a random manner. Unlike conventional ceramics dominated by a single metallic cation as the primary element, hydrogen-oxygen alloys (HEOs) feature chemically disordered lattice structures and pronounced lattice distortion. These characteristics exert a significant influence on their thermal and mechanical behaviour.

3.1.1 Advantages and limitations of HEO microstructures

When several different cations are put into the same lattice randomly, HEOs will end up with a distorted, uneven crystal structure. It will decrease the efficiency of phonon conduction within materials. Complex disordered crystal structures lead to more frequent phonon collisions so that phonons lose their original efficient propagation pathways and it will hinder heat transfer. So these materials are frequently regarded as effective insulators owing to their relatively low thermal conductivity.

The second significant advantage of HEOs is about their unique configurational entropy. Multiple elements randomly occupy lattice sites, which will increase the system's entropy. Under extreme high-temperature conditions, this rise in system entropy can decrease Gibbs free energy and it will also facilitate the maintenance of stability in the solid solution state. In fact, HEOs coatings exhibit substantially reduced grain growth and pore closure rates when exposed to temperatures of approximately 1200 – 1500° C. Although sintering still happens, the growth rate remains obviously slow so that it will maintain thermal properties in a relatively stable state over long-time periods. Complex chemical lattice structures typically exhibit superior oxidation resistance. In certain cases, this property enhances tolerance to CMAS attack [1].

Any attempt at coating fabrication involves trade-offs. While utilize the advantages of high-entropy designs, it is necessary to consider the costs of their processing and the complexity of their technical requirements. HEOs contain multiple metal cations, and these elements often behave differently during processing. During coating deposition, variations in vapour pressure, diffusion rates, and chemical reactivity become critically important. For instance, in thermal spraying processes, if certain elements evaporate earlier than others or are randomly distributed unevenly, the coating composition may deviate from the intended high-entropy state, leading to the formation of secondary phases or partial phase separation [8].

The preparation of HEO coatings need stringently control of processing conditions due to the sensitivity of their multi-element systems. Energy input, deposition atmosphere, and deposition rate must be maintained within relatively narrow, precise ranges. Even much small variations can influence the final microstructure and composition and it will make it challenging to maintain consistent quality. This issue remains one of the primary obstacles to large-scale industrial application [3]. Mechanical considerations must be addressed. The presence of nanoscale particles and high defect densities can enhance performance but it will simultaneously introduce structural vulnerabilities. Besides, Grain boundaries often serve as crack initiation sites. If the number of grain boundaries is too big, it may cause localised strain concentration which will potentially promote brittle behaviour. Under repeated thermal cycling or high-stress conditions, these factors may accelerate crack propagation and shorten the coating's service life. So although it enables HEOs with attractive properties, it also introduces significant processing challenges and reliability risks [9].

3.1.2 Fabrication methods for HEO coatings

Controlling composition during coating preparation is extremely important because HEOs contain many different elements. In theory, all elements should melt, move, and deposit at the same time to form a uniform solid solution. Actually, this is not easy to achieve. Traditional thermal spraying methods work under extreme temperature conditions such as APS or HVOF. Hence, multi-component powders often do not melt uniformly, and some elements may behave differently from others during deposition. This situation can easily lead to compositional variations in the coating, which limits the suitability of these methods for fabricating high-quality HEO coatings.

Compared with thermal spraying, high-power impulse magnetron sputtering (HiPIMS) provides better control over the deposition process. The plasma generated during HiPIMS contains a high fraction of ionized species, and the strong ion bombardment helps promote atomic mixing and the formation of dense microstructures. In this way, grain size and pore structure can be controlled more effectively, and a more uniform solid solution can be obtained. So HiPIMS is often considered a more suitable technique for preparing HEO-based thermal barrier coatings, especially in laboratory-scale studies.

3.2 Perovskite oxide thermal barrier coating systems

Perovskite oxides usually refer to ceramic materials with an ABO_3 crystal structure, where the A-site and B-site can be occupied by different cations and they are varying ionic sizes and valence states. So their crystal structure is more flexible, and many physical and chemical properties can be adjusted by changing the composition. This wide compositional range makes perovskite oxides a material system that has been considered for thermal barrier coating applications.

3.2.1 Advantages and limitations of perovskite microstructures

Perovskite oxides are often discussed in thermal barrier coating research because their crystal structure can be modified through compositional changes. Replacing the A-site or B-site cations makes it possible to change lattice size, lattice distortion, and the number of oxygen vacancies. When cations with different sizes or valence states are led into, the ideal lattice arrangement is disturbed. So lattice distortion and local structural variations appear. At the same time, oxygen vacancies also appear together. These changes make it more difficult for phonons to move through the lattice, which can lead to the decrease of thermal conductivity.

Changing the A/B-site composition also affects lattice dimensions and can slightly adjust the thermal expansion coefficient. Local distortion and defects give the material some room to respond to thermal stress through small-scale deformation. This helps ease thermal mismatch between the coating and the substrate. In the truth, this indicates that the thermophysical properties of perovskite oxides can be adjusted to some extent by selecting suitable chemical compositions [10].

Perovskite oxides also have some problems. Their phase stability at high temperatures is always lower than that of YSZ or rare-earth zirconates. When the temperature rises above about 1200 °C, decomposition, phase changes, or reactions with CMAS or oxide substrates may occur. Their fracture toughness is also limited, and their performance under long-term thermal cycling is often not ideal. Because of these issues, perovskite oxides are not often applied as independent top coats in extreme environments. Actually, they are commonly applied as functional layers or transition layers in composite coating systems.

3.2.2 Fabrication methods for perovskite oxide coatings

Perovskite oxides' fabrication requires careful control of processing conditions. That's because perovskite oxides are sensitive to composition loss and structural instability. High-temperature deposition processes may cause decomposition, evaporation of volatile species, or undesired phase transformations, which degrade coating quality. Pulsed laser deposition (PLD) offers good composition transfer and enables non-equilibrium growth. Using PLD, ABO_3 coatings with controlled composition and crystallographic orientation can be deposited at relatively low substrate temperatures, reducing the risk of elemental segregation and structural degradation. As a result, PLD is widely used in fundamental studies of perovskite oxide thermal barrier coatings.

3.3 Alumina and related oxide thermal barrier coating systems

Alumina and related oxides represent a group of ceramic materials with high melting points and good chemical stability. Among them, Al_2O_3 is the most extensively studied. In thermal barrier coating systems, alumina-based materials are typically applied as functional layers rather than as the main thermal insulation layer.

3.3.1 Advantages and limitations of alumina microstructures

Alumina (Al_2O_3) is frequently used in coating systems because of its high hardness, good wear resistance, and chemical stability. The α - Al_2O_3 phase has a stable crystal structure and exhibits excellent oxidation resistance at high temperatures. Alumina also shows strong resistance to CMAS attack, molten salts, and particle erosion, which improves the environmental durability of multilayer coating systems.

However, alumina is not well suited as a thermal insulation material. Although α - Al_2O_3 is thermodynamically stable, its high melting point makes it difficult to deposit thick α -phase coatings using conventional deposition techniques. In real coating processes, alumina rarely forms the α phase right away. In many cases, γ - or δ - Al_2O_3 appears first. These metastable phases often stay in the coating during early use and may convert to the α phase only after exposure to high temperatures in a long time. Such a phase transformation is typically linked with small volume changes and the build-up of local stresses. Over time, this stress can make the coating more likely to develop microcracks.

Another issue is about thermal properties. Alumina conducts heat much more easily than typical thermal barrier materials such as YSZ or rare-earth zirconates. At the same time, its thermal expansion coefficient is much lower than that of metallic substrates. When the coating experiences repeated heating and cooling, this mismatch can create additional stress. Over repeated thermal cycles, this situation makes alumina coatings more prone to cracking and. Even in some cases, it may lead to delamination.

Alumina is generally not used as the main thermal insulation layer in TBC systems due to those limitations but it is more commonly applied as a sealing layer, an erosion-resistant layer, or a protective outer layer. In these roles, its chemical stability and hardness can still play a useful part in improving the overall durability of the coating system [11].

3.3.2 Fabrication methods for alumina-based coatings

Advanced ceramic systems often perform more stably at high temperatures than conventional YSZ coatings, and they also have ability to resist chemical degradation more effectively, especially when the demanding temperature is over about 1300 °C. However, this does not indicate that these materials are perfect. In fact, issues such as limited fracture toughness and poor thermal expansion matching with metallic substrates are still commonly observed. Hence, advanced ceramics are rarely used as single-layer coatings in real applications but multilayer or composite coating structures are usually preferred. By combining different ceramic materials within a single coating system, it is possible to balance thermal insulation performance, mechanical compliance, and long-term service stability.

4 Conclusion

As gas turbines and aerospace propulsion systems operate at higher efficiencies and temperatures, thermal barrier coatings must maintain stability and reliability under more demanding service conditions. Traditional YSZ-based TBC systems have shown stable and well-balanced performance in many engineering applications. However, under harsh service conditions, their phase stability, sintering resistance, and environmental durability gradually decrease, which limits further use at very high temperatures. For this reason, nanostructural design and advanced ceramic materials are often studied as ways to improve TBC performance.

Many studies indicate that introducing nanoscale grains, pores, and multi-level interfaces can improve the thermal insulation performance, strain tolerance, and thermal shock resistance of YSZ-based coatings, and can also extend their service temperature range to

some extent. However, these structural modifications cannot fully prevent performance degradation of YSZ at high temperatures. As a result, relying only on nanostructure control is not enough to meet the long-term stability requirements of applications operating at very high temperatures.

Compared with YSZ, advanced ceramic systems such as high-entropy oxides, perovskite oxides, and alumina offer different advantages in crystal structure, thermal conductivity control, and chemical stability. However, these materials often have poor thermal expansion matching, limited fracture toughness, and strict processing requirements, which make large-scale engineering application difficult. Many studies suggest that advanced ceramics are more suitable as functional layers in multilayer or composite TBC systems rather than as direct replacements for YSZ top coats.

In general, the performance of thermal barrier coatings is not determined only by the initial material or microstructure. Instead, it results from the combined influence of processing methods, microstructural evolution, and failure behavior during service. While nanostructures can improve initial thermal insulation and strain accommodation, they may also introduce new degradation paths. For this reason, future TBC design needs to pay more attention to microstructural stability and evolution during long-term high-temperature service, rather than only initial performance.

Further development of thermal barrier coatings is expected to rely more on combinations of different materials and multilayer structures. Greater attention should be paid to long-term structural stability and process reliability. Combining experimental studies with simple computational analysis can help better understand coating behavior during service and support their use at higher temperatures and in more complex environments.

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