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THERMAL BARRIER COATINGS (TBCs): A BRIEF OVERVIEW

Maria BOGDAN[1], Ildiko PETER[2]

[1]University of Medicine, Pharmacy, Science and Technology" G.E. Palade" of Târgu Mureş

Nicolae Iorga Street, no. 1, 540088, Mureş County, Romania

[1]maria.bogdan@umfst.ro
[2]ildiko.peter@umfst.ro

Abstract

This review provides a concise summary of the current state of thermal barrier coatings (TBCs), based on reviewing literature from the past few years and supplemented by personal insights. It synthesizes a collection of technical information regarding the role of TBCs, their application domains, structure, materials, coating processes and failure mechanisms. Despite their successful use in performant applications over the past decades, TBCs remain a focus for advanced industries such as aerospace, power generation, machine building and automotive. The materials used in TBCs are grouped by their chemical formulas and main constituents and the most common coating techniques are discussed. Key failure mechanisms like delamination, spallation, erosion and corrosion are examined. Future research directions include encouraging experimental testing, developing new materials and methods to reduce heat diffusion at the atomic level.

Key words: thermal barrier coatings (TBCs), high-temperature performance, advanced ceramics, thermal protection, yttria stabilized zirconia (YSZ)

1. Introduction

From an engineering perspective it is well known that advanced industries demand exceptionally high standards for the quality and precision of components found in various assemblies. Often, this results in significant costs due to the use of special materials and manufacturing requirements. Therefore, implementing effective solutions to extend the lifespan and maintain the performance of these components is crucial. Harsh operating environments can drastically shorten the lifespan of components and diminish the overall efficiency of the systems, which is undesirable primarily due to economic reasons. Consequently, continuous improvements are being pursued to address these challenges [1, 2].

Thermal stress resulting from cyclic or sudden exposure to extreme temperatures or thermal variations is commonly encountered in aerospace, energy, automotive and industrial applications. Over time, with the development of specialized materials, such as superalloys, methods to protect these materials in demanding thermal environments have also evolved.

The foundational studies on TBCs trace back to the late 1940s, with the first favorable tests in jet engines, marking the beginning of what would become a pivotal advancement in materials engineering. These coatings serve as robust defensive systems against thermal degradation, featuring a multilayer structure. The functionality of the coatings is ensured by a ceramic insulating layer with low thermal conductivity, capable of reflecting a significant amount of heat. Typically, an intermediate layer is applied between this outer layer and the substrate of the protected component to enhance adhesion and mediate thermal behavior. Upon exposure to high temperatures, a thin oxide layer forms at the interface between the ceramic and the bond layer. This coating system thereby ensures greater durability and enhanced efficiency of the systems it protects [3].

2. Application fields

The application of TBCs can be found in a wide variety of contexts, ranging from specialized sectors such as aerospace, maritime and heavy industry, to more common areas encountered in everyday life, such as the automotive sector.

Figure 1 provides a detailed illustration of the primary fields where TBCs are utilized, highlighting their diverse applications and significance.

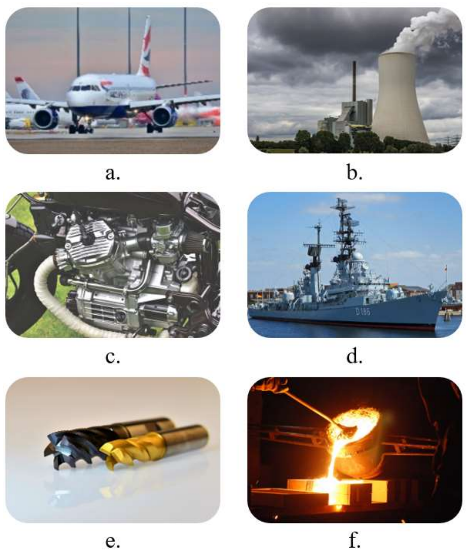

Fig. 1: Application areas of TBCs
(a.Aeronautical/ Aerospace; b.Power generation; c.Automotive; d.Naval industry; e.Tooling; f.Metalurgy) [4]

The *aeronautic and aerospace fields* employ TBCs as protective methods for components found in the propulsion systems of aircrafts, including turbines of airplanes and helicopters, as well as rocket engines and other spacecraft propulsion systems. In the case of rockets, the propulsion system components are exposed to extreme temperatures, ranging from -240°C in cryogenic fuel systems to 3200°C in the combustion area [5]. In modern gas turbines, the surface temperatures of components can frequently exceed 1500°C, often surpassing the melting point of the alloys from which they are made [6].

Power generation applications share similar requirements with aircraft turbines, though depending on their complexity and size, they may require a longer lifespan for the coatings due to costs and maintenance challenges involved.

The *automotive industry* utilizes TBCs to reduce harmful emissions from internal combustion engines, improve performance and protect some components of combustion chambers. Despite the mentioned benefits, TBCs have to be applied judiciously because excessively high temperatures in the combustion chamber due to thermal insulation can lead to increased NOx emissions in diesel engines [7]. In spark-ignition engines, it can lead to premature ignition of the fuel-air mixture, a phenomenon known as knocking [8].

In the *naval industry*, the use of TBCs may not be as prominent. However, they find application in engines used for propulsion, as well as methods of protection against corrosion in the marine environment [9].

In the *field of machine building technology*, some of the most relevant applications include the design and manufacture of cutting tools and foundry equipment. For the first mentioned application, materials used in coatings include nitrides, carbides, borides and oxides, which enhance wear resistance and extend lifespan by dissipating the heat from the exterior of the tool body. Additionally, there is an effort to develop coatings that besides providing thermal protection, also offer self-hardening, self-healing or self-lubrication functions [10]. In foundries, beyond using coatings for thermal protection of equipment exposed to high temperatures in melting environments, special refractory coatings are applied to molds or cores. These coatings aim to minimize the porosity, reduce the physicochemical reactions between the molten metal and the mold material and even improve the surface quality of the cast parts [11].

3. Structural Design of TBCs

As previously mentioned, TBCs are multilayered systems created by stacking various materials with distinct and complementary properties and roles. The classic structure of a TBC is shown in Figure 2.

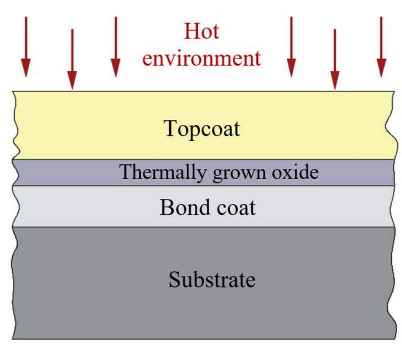

Fig. 2: Structure of TBCs

The *substrate* is the material from which the component is made, serving a structural role and bearing mechanical loads. It forms the base for the deposition of the other layers. Typically, superalloys are used due to their superior mechanical properties and resistance to extreme temperatures. The *bond coat* (BC) is a metallic layer applied specifically to enhance the adhesion between layers, primarily acting to mediate the thermal expansion between the substrate and the external ceramic material. The most common chemical composition of this layer is MCrAlX (M = Ni and/or Co; X = Zr, Y, Hf and/or Si). Different compositions are used based on the desired properties. Nickel (Ni) is effective against oxidation, while Cobalt (Co) offers superior resistance to hot corrosion. The *thermally grown oxide* (TGO) layer develops as a result of exposing the coating to high temperatures, leading to the oxidation of reactive elements in the BC. This oxide layer needs to be thin (≤ 10 μm) and continuous to effectively act as a protective film against the oxidation of the substrate. Based on the composition of the BC, various oxides can form, with common types including chromia, spinel, nickel oxide and silica. Notably, alumina (Al_2O_3), particularly α-Al_2O_3 phase, is the most important due to its stability. This phase forms through a sequence of transformations, as shown in Equation 1 [12].

$$\gamma\text{-}Al_2O_3 \xrightarrow{750^\circ C} \delta\text{-}Al_2O_3 \xrightarrow{900^\circ C} \theta\text{-}Al_2O_3 \xrightarrow{1000^\circ C} \alpha\text{-}Al_2O_3 \quad (1)$$

The *topcoat* (TC) is typically made of ceramics, featuring low thermal conductivity and low coefficient of thermal expansion (CTE). These properties minimize heat transfer from the external environment to the substrate [13].

4. Common topcoat materials

Given the broad spectrum of applications and the ongoing need for innovation, the materials used in TBCs have evolved into numerous and complex compositions that are challenging to describe. In a previous paper [14] that extensively addressed these coatings, a detailed classification of the materials used was conducted. Summarizing the aspects discussed in the paper, the materials can be classified based on their chemical form and composition, as shown in Figure 3 and Figure 4.

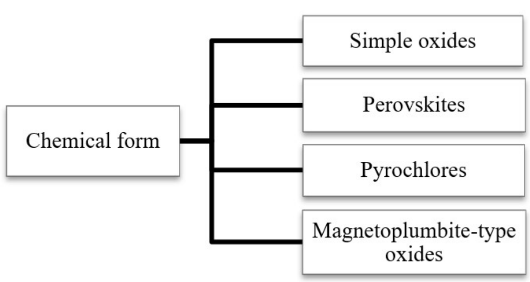

Fig. 3: The chemical form of topcoat materials

The general chemical formula for oxides is A_xO_y (A - metal), perovskite materials have the general formula ABO_3 (A, B - two distinct ions), pyrochlore is identified by the formula $A_2B_2O_7$ (A - cations with +3, sometimes +2 valence, B - cations with +4 or +5 valence), while the oxides of magnetoplumbite type have formula $LnMA_{11}O_{19}$ (Ln - lanthanides from La to Gd; M - Mg, Mn, Cr, Sm and Zn; A - Al or Fe).

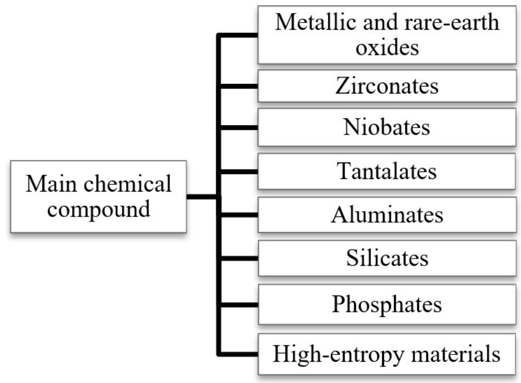

Fig. 4: Classification by main chemical compound of TC

Simple oxides like alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2) or chromia (Cr_2O_3) are rarely used as TC materials in their pure form. Typically, they are combined with other elements such as rare earths to create structures that offer greater thermal protection and enhanced mechanical and chemical resistance.

Zirconates can include a wide range of chemical combinations, among which Yttria-Stabilized Zirconia (YSZ/ Y_2O_3-ZrO_2) is the most common. Depending on the proportions of its constituents, this coating exhibits excellent protective performance up to temperatures that do not exceed 1100-1200°C.

Niobates and tantalates are materials that contain niobium (Ni) and tantalum (Ta) in combinations with other elements, typically rare earths. They offer advantages due to their high melting points. However, their chemical compositions must be carefully formulated to optimize the CTE.

While some aluminates can maintain phase stability up to 1600°C, with promising thermal conductivity and good CTE, silicates and phosphates are less commonly used due to less favorable coefficients. However, they can serve as effective environmental barriers.

High entropy materials are characterized by their chemical complexity, incorporating more than five different elements. In these structures, the emergence of a high degree of disorder that includes defects is favored. Such structure significantly lowers the materials' thermal conductivity.

5. Coating methods

Coating methods also include a wide range of techniques, ranging from basic methods such as plating to more advanced techniques involving complex and expensive equipment for nano-scale coatings. Among the most common processes are Air Plasma Spray (APS), Electron Beam - Physical Vapor Deposition (EB-PVD) and Suspension Plasma Spray (SPS) [15].

APS is one of the most cost-effective coating processes, utilizing simple equipment with a high coverage efficiency, making it suitable for coating large parts. The resulting structure is lamellar ("splats"), with micro-cracks along the coating. This structure is less durable and prone to spalling. For better adhesion, the BC surface needs to be roughened.

EB-PVD is the most expensive process widely used, primarily due to the equipment which includes an electron beam generator and a vacuum chamber. The resulting structure is columnar with a long lifespan. It features cracks perpendicular to the substrate, which helps limit the propagation of parallel cracks that could lead to delamination. Additionally, it helps to match the CTEs of the outer layers with that of the substrate.

SPS represents an alternative in structure to APS and a cost-effective option compared to EB-PVD. This process can produce columnar or cauliflower-like structures that are much more porous and finer, with good strain tolerance and low thermal conductivity, all at a relatively low cost.

6. Failure of TBCs

Failure refers to the loss of coating functionality when the TC loses adhesion and detaches, exposing the inner layers to harmful conditions. Failure is preceded by degradation, which involves progressive changes in the TBC that reduce its efficiency. Understanding and monitoring these processes are crucial for the effective design and use of TBCs [14]. Some of the most common mechanisms that lead to the failure of TBCs are as follows.

The growth of thermally grown oxide is influenced by exposure conditions to heat and the constituent elements of the BC. The growth rate decreases over time due to the accumulation of oxides that hinder oxygen diffusion. Excessive growth (exceeding 5-10 µm) causes adhesion problems due to the accumulated stress in the coating, leading to delamination and spalling [16].

Delamination occurs when layers of the TBC separate due to cracks propagating parallel to the surface, either at the edges (edge delamination) or within the coating (buckling delamination). *Spallation* involves layers peeling off due to cracks running transversely through the coating. Typically, delamination precedes spallation [17].

Aluminum depletion is a chemical failure where the Al content in the BC decreases during high-temperature operation, leading to spallation. This occurs when available Al in the BC is consumed through oxidation, reducing its concentration below the level required to sustain α-Al_2O_3 formation. Consequently, other elements (such as Cr, Ni and Co) react with O_2, forming bulkier and more brittle oxides called spinels, which increase stress in the TGO [18].

Impurities, including chemical elements such as sulfur, can reduce TBC layer adhesion, causing spalling. *Sulfur segregation* at the BC/ TGO interface within voids formed during alumina formation is particularly problematic. Sulfur can come from raw materials used in coating, turbine or engine fuels or environmental pollution during operation [19].

Foreign object damage is a critical issue for aircraft, where hard foreign objects larger than 100 µm (such as sand, rocks and birds) can enter open turbines and damage the TBC or entire components. These particles, heated by the combustion environment and propelled by the blades, can fragment into projectiles, causing significant damage to jet engine blades or nozzle guide vanes [20].

Erosion refers to the physical wear caused by the impact of solid or semi-melted particles on the TBC surface, which over time compromises its durability. Particles smaller than 2 µm have a minimal effect, those between 10-20 µm primarily affect the back of the airfoil and particles larger than 40 µm compromise the leading edges of the blades [21].

Corrosion is a chemical process of deterioration where the TBC interacts with reactive substances such as oxides, salts or gases present in the environment. These aggressive compounds, which deposit on the surface of components can come from sources like low-quality fuel, pollution or foreign object damage [20]. Corrosion frequently occurs due to molten silicates such as calcium-magnesium-alumino-silicate (CMAS; CaO-MgO-Al2O3-SiO2). Formed from dust, sand and volcanic ash, CMAS adheres to turbine components when temperatures exceed 1100°C, creating a glassy layer [22].

7. Research perspectives

Based on the review of the specialized literature, several promising research directions have been identified as less studied and could represent valuable opportunities. Developing coatings for fifth and sixth-generation superalloys in the context of increasing turbine operating temperatures beyond 1700°C is one such direction [23]. Exploring simple rare earth combinations with high disorder structures or with chemical inhomogeneities could match or surpass the performance of high-entropy materials with numerous chemical elements in their composition [24]. Studying residual stress in TBC-coated elements and investigating stress relief methods derived from heat treatment science are also crucial. Additionally, examining heat transfer at the atomic scale , both theoretically and experimentally, can help discover new methods to reduce thermal coefficients.

8. Conclusions

This study provides a concise analysis of TBCs applied to metallic materials. It describes and discusses their application domains, coating design, materials and techniques used, as well as the mechanisms involved in TBC failure. Extending the temperature ranges in applications such as power generation to enhance system efficiency remains essential, making the protection of equipment in thermally aggressive environments with TBCs crucial. On the other hand, in machining processes, reducing temperatures is desired, but the necessary machining parameters for productivity and surface quality generate intense heat, where TBCs help direct this heat. The materials used range from simple oxides to rare earth combinations and high-entropy materials, processed through methods such as APS, EB-PVD or SPS, depending on application needs. Some potential research directions identified include nanometric-level studies and the integration with heat treatment techniques to reduce stress in coatings.

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