

Jing Zhang · Yeon-Gil Jung *Editors*

Advanced Ceramic and Metallic Coating and Thin Film Materials for Energy and Environmental Applications

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Preface

The field of research into advanced metallic and ceramic thin film materials for energy and environmental applications has been rapidly moving forward. This book provides the latest information of the developments in the field. It also gives the perspective of future research. This book collects the contributions by several established worldwide researchers from academia, industry, and a government research laboratory. The book covers the fundamental mechanisms, processing, and applications of advanced thin film and coating materials.

The book covers a broad range of topics related to thin film and coating materials, including overview of advanced ceramic and metallic coatings, surface modification, magnetic materials, thermoelectric materials, solar energy materials, solid oxide fuel cells, coatings in solid-phase microextraction process, and modeling and simulation of thin film materials.

This book is primarily aimed at researchers in thin film and coating fields in both academia and industry. It can be used as a reference book for graduate and undergraduate students in materials science and mechanical engineering.

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Chapter 1

Overview of Advanced Ceramic and Metallic Coating for Energy and Environmental Applications

Zhe Lu, Yeon-Gil Jung, and Jing Zhang

1.1 Introduction

Advanced ceramics have gradually become an important part as the new and key materials in developing modern technologies, affecting the advancement and progress in industries. A series of excellent properties in advanced ceramics, specifically fine structure, such as superior strength and hardness, wear-resisting, corrosion resistance, high temperature resistant, conductive, insulation, magnetic, pervious to light, piezoelectric, ferroelectric, acousto-optic, semiconductor and superconductor, and biological compatibility are widely used in national defense, chemical industry, metallurgy, electronics, machinery, aviation, spaceflight, biomedicine, etc. Also, the development of advanced ceramics is a new growth point of national economy, and its status—research, application, and development, embodies a country as an important symbol of comprehensive strength of national economy. At present, the worldwide advanced ceramic technology is rapidly progressing, its application area is expanding, and the stable growth trend in market is obvious.

The United States and Japan are leading the development and application of advanced ceramics. The United States National Aeronautics and Space Agency (NASA) is in the development of structural ceramics and a processing technology is

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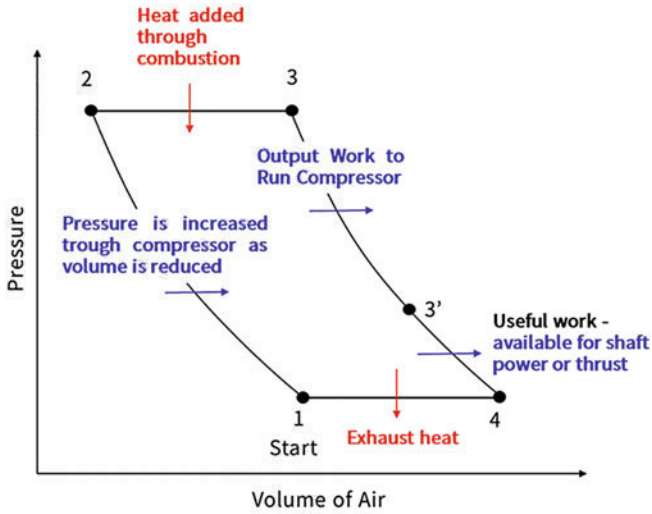
to implement a massive research and development program, focusing on the key closed-loop implementation of aircraft engine, engine ceramic replacement, at the same time of nanostructured ceramic coatings, biological medicine, and photoelectric ceramic research and industrialization on funding [1]. There are ten big plans, like America's "brittle material design" and so on. One of federal plans is "the advanced material and equipment," with cost up to \$2–\$2.5 billion in a year for materials research and the construction, in order to improve its international competitiveness. The advanced ceramics in Japan, related to the advanced manufacturing equipment and excellent product stability, are also gradually becoming the leader of the international market, especially in functional ceramics areas including thermal, pressure sensitive, magnetic susceptibility, gas sensor, photosensitive monopoly in the international market gradually [2]. One of Nippon Provincial fine ceramics production research and development plans is "moonlight"; one of items is the development of 300 MW gas turbine [3]. In addition, the EU countries, especially Germany and France, have carried on the key researches in the field of structural ceramics, mainly concentrated in the power generation equipment, new energy materials and ceramic components of engine, etc. The European Union, including Germany, France, Britain, and other countries, are adopting some corresponding measures to the development of new materials, such as "eureka program" [4]. The United States department of ceramic industry statistics shows that average annual growth rate in advanced ceramics market is about 12% in the United States, Japan, and the European Union—Annual average growth rates of EU, United States, and Japan are 15–18%, about 9.9%, and about 7.2%, respectively [5].

This chapter is aimed at providing a comprehensive review of two major coating materials, i.e., thermal barrier coating and environmental barrier coating. The historical evolution and latest advancement of the materials are presented. Suggested future development is also provided.

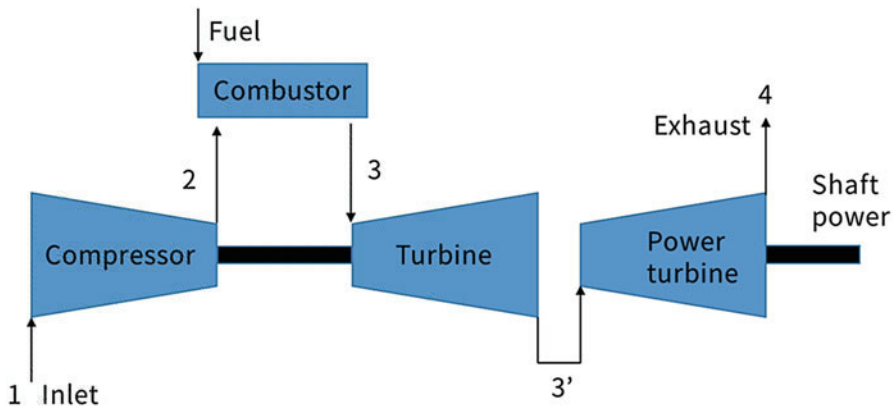
1.2 Thermal Barrier Coating (TBC)

1.2.1 Overview of TBC

The gas turbine cycle usually describes the relationship between air volume (V) and pressure (P) in the system. The Brayton cycle (1876) called as a simple cycle of gas turbine is a representation of the properties of a fixed amount of air as it passed through a gas turbine in operation (Fig. 1.1a). These same points are also marked in the engine schematic in Fig. 1.1b. The useful work (from 3' to 4 in Fig. 1.1a) is the energy available to cause output shaft power for a land-based gas turbine (for power generation), or thrust for jet aircraft. Unlike the aircraft engine, land-based gas turbine added other equipments to increase efficiency and/or the output of a unit such as regeneration, intercooling, and reheating. The regeneration involves in the installation of heat exchanger to heat the exhaust gas before entering combustor. Thus, this regenerated process increases the efficiency by 5–6%. The intercooler is a heat exchanger that cools compressed gas during the compressing process.



(a)



(b)

Fig. 1.1 Brayton cycle diagram: (a) pressure–volume diagram for a unit mass of working fluid and (b) gas turbine schematic showing relative points

In the system consisting of a high and low pressure unit, the intercooler is mounted between them and reduces the necessary work for compressing in the high pressure compressor. The reheating located between high pressure turbine and low pressure turbine can be used to “reheat” the flow. The combined cycle gas turbine (CCGT) power plant combined with gas turbine and steam turbine achieves greater efficiency with using the exhaust gas of gas turbine to steam turbine heat resource. Actually efficiency values have obtained as high as 52–58% with CCGT [6]—now days the

efficiency is increasing to 62%. As gas turbine engine is designed to meet demands for higher power or lower specific fuel consumption, the engine must accommodate: (1) increased mass airflow, (2) increased pressure ratio, (3) increased maximum allowable turbine inlet and outlet temperature, and (4) improved efficiency of the compressor and turbine sections [7]. Several technical progresses have been achieved to satisfy these demands, and one of them is thermal barrier coating (TBC).

Numerous types of coating are applying to protect structural engineering materials from corrosion, erosion, wear, etc., providing more hardness, lubricant and thermal insulation. Especially, TBCs are the most complexity structure due to high operating temperature and high rotating speed of aircraft and industrial gas turbine engines. TBCs have been used since 1970s (jet engine for aircraft) and 1980s (gas turbine for power generation) to protect the metallic parts in hot section components of gas turbine engine. TBCs comprise (1) a substrate, (2) a metallic bond coat, (3) a TGO (thermally grown oxide), and (4) a ceramic top coat, which can improve durability and efficiency in the gas turbine as insulating turbine and combustor engine components from the hot gas stream (Fig. 1.2). Demands for advanced TBC systems for enhanced performance and longer lifetime have continuously been emerging at higher operating temperature [8, 9].

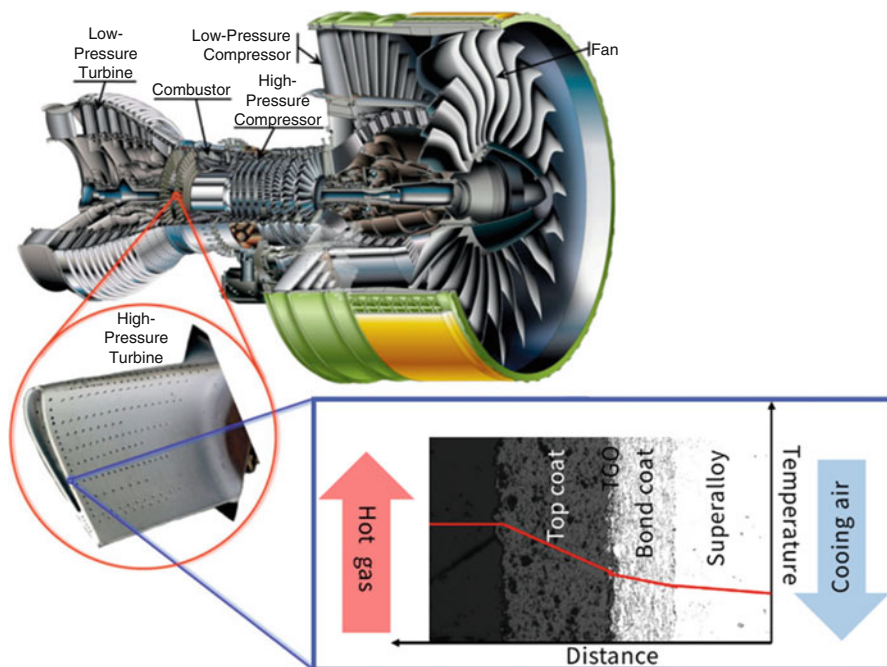


Fig. 1.2 Cutaway view of Engine Alliance GP7200 aircraft engine and photograph of a turbine blade with TBC from the high-pressure hot section of an engine, and microstructure image of TBCs (Engine image courtesy of Engine Alliance, turbine blade photograph courtesy of YXLON) [10]

Over the past 60 years, the development of high temperature engineering alloys has been a primary driver of increased operating temperatures in gas turbine engines [11]. The temperatures that turbine blades are exposed to can be close to the melting point of superalloys. Therefore, TBCs are extensively employed in high temperature components of gas turbine engines, such as turbine blade, turbine vane, and combustion, to increase the turbine inlet temperature, hence increasing the efficiency and performance of gas turbine engines [12]. TBCs can be considered a four-layered material system as mentioned above, consisting of the following aspects: (1) a substrate of the nickel- or cobalt-based superalloy, (2) an oxidation-resistant metallic bond coat of MCrAlY formed by the air plasma spray (APS), vacuum plasma spray (VPS), low-pressure plasma spray (LPPS), and high velocity oxy-fuel (HVOF) methods, (3) TGO layer, typically α -Al₂O₃ or spinel structure oxide, formed during heat treatment or in service, and (4) a ceramic top coat of 6–8% (mass %) yttria (Y₂O₃)-stabilized zirconia (ZrO₂: 6–8 YSZ) deposited by either APS or electron beam-physical vapor deposition (EB–PVD) processes [13, 14]. APS, twin wire-arc spraying, and HVOF spraying are the most popular deposition processes from an economic point of view and involve many small particles being accelerated by the high-power plasma or combustion flow to form a coating layer. It is well known that many new techniques, such as solution-precursor plasma spraying (SPPS) and EB–PVD, have exhibited an increasing potential in improving the thermal durability of TBC systems [15–17].

The common processes used to deposit the ceramic top coat are APS and EB–PVD. The EB–PVD method has been developed to enhance adhesive strength and improve strain resistance. The APS method with its economic benefits is still preferred commercially, in contrast to the use of the complex and expensive EB–PVD [8, 18, 19], although it has a relatively low strain tolerance compared with coatings prepared by more advanced coating methods. The bond coat plays an important role in ensuring structural effectiveness and affording extra adhesion of the top coat to the substrate. Many techniques, such as LPPS, APS, high-frequency pulse detonation, and HVOF, have been applied to form the bond coat [20–23]. The APS process is widely used to create the bond coat in a TBC system because of its economic benefits. However, to meet the requirement in increasing working temperature and improving fuel efficiency in gas turbines and diesel engines, the HVOF process is employed for the bond coat. Unfortunately, the oxidation environment required for the HVOF process may affect the subsequent oxidation properties of the top coat, which are important in the applied high-temperature working environments. A dense bond coat without oxide formation during spraying can be deposited by LPPS or VPS [24, 25]. Therefore, the bond coat prepared by LPPS or VPS has been employed in the most advanced TBCs [26–29], although their wide application is limited because of their high costs.

Numerous factors have to be considered in practical applications of TBCs, including high melting point, thermal stability, low thermal conductivity, chemical inertness, thermal expansion match and good adhesion with the metallic substrate, low sintering rate, and thermo-mechanical properties [30, 31]. Among them, the thermal stability or durability in high-temperature environments, especially in

cyclic thermal exposure, is essential factor to improve the reliability and lifetime performance of TBC system, and the thermal durability of TBC system is closely related with its microstructure. There are three ways to enhance TBC performance, specially focused on the lowering of thermal conductivity of TBC system: (1) studying about coating materials with a low thermal conductivity, (2) controlling the porosity in TBC, and (3) increasing the thickness of TBC. The effects of porosity and material on thermal conductivity of TBC have been reported, indicating that thermal conductivity is strongly dependent on the porosity and material composition [32]. When the thicknesses of TBCs using APS are greater than 1.5 mm, the TBCs spontaneously fail during preparation or service [27, 28, 33–35], which makes other coatings or processes preferable, such as a dense vertical crack (DVC) TBC, gradient or high-porosity coatings, and SPPS process [15, 35, 36].

1.2.2 Current Research Status of TBC

1.2.2.1 Research Background

The industrial development of TBCs started in the 1950s with the manufacture of the first enamel coatings for military engine components [37]. In the 1960s the first flame sprayed ceramic layers with NiAl bond coats were used in commercial aero engines [38]. The science and technology of TBCs have advanced considerably since reports of the first test on turbine blades in a research engine in 1976. Today, TBCs are flying in revenue service in a low risk location within the turbine section of certain gas turbine engines [39]. To improve combustion efficiency and reduce fuel consumption, the operation temperature of gas turbine engines is increased as high as 1600 °C. A high operation temperature requires the use of many advanced structural materials, extensive cooling of components, and adoption of various coatings. Currently, single crystal Ni-based superalloys have been employed to the environment with a maximum temperature of approximately 1100 °C. Therefore, more temperature gain can be obtained by developing TBCs [40, 41].

1.2.2.2 TBC Materials

Demands for higher operating temperature and more efficiency in gas turbines were originally met with the development of superalloys. However, the addition demand to increase the operating temperature has been continuously requesting and it has been achieving with evolution of cooling technology and TBCs that are used to protect hot section components, especially in blade and vane. The hot section components in a gas turbine engine are subjected to serve mechanical, chemical, and thermal stresses. Hence, requirements demanded in TBC materials are (1) high

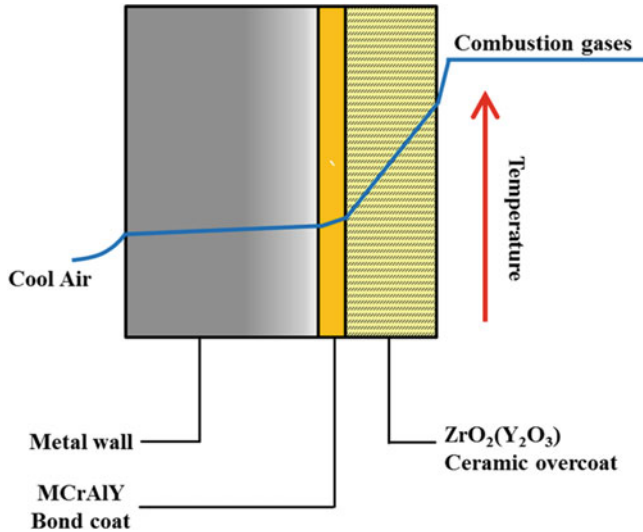


Fig. 1.3 A schematic diagram showing the temperature reduction provided by TBC

melting point, (2) no phase transformation under temperature changes, (3) low thermal conductivity, (4) chemical inertness, (5) high coefficient of thermal expansion (CTE), (6) bonding strength, and (7) high sintering resistance [41].

1.2.2.3 Structure of TBC

The typical TBC system can be considered as a four-layered material system as mentioned above [13, 14]. The insulation top coat of usually 6–8YSZ is deposited either using APS or EB–PVD process. The bond coat protects the substrates from oxidative and corrosive attacks and improves the bonding between the top coat and the substrate. The top coat has a significantly lower thermal conductivity than the metallic substrate and it is possible to establish a large temperature drop (general reduce of 100–150 °C) across the top coat by applying an internal cooling inside the components as shown in Fig. 1.3.

1.2.3 Material Selection for TBC

Material selection guidelines are desirable in identifying and developing alternative materials for higher temperature capability of TBCs in protective and insulative coatings on hot section components of gas turbines and their applications, like blade, vane, and combustion chamber, resulting in improving turbine efficiency and increasing service temperature [42, 43]. Some relate to candidate materials that

exhibit particularly low values of thermal conductivity at high temperatures and others relate to thermodynamic stability in contact with the TGO formed between the bond and top coats [44, 45]. First, a thermally protective TBC with a low thermal conductivity is required to maximize the thermal drop across the top coat. Also, the top coat is likely to have a CTE that differs from the component (substrate or bond coat) to which it is applied. Therefore, the top coat should have a high in-plane compliance to accommodate the thermal expansion mismatch between the bond and top coats, and/or between the coating layer and the underlying superalloy-based substrate. In addition, it must be able to retain the thermal and mechanical properties and its low thermal conductivity during prolonged environmental exposure [46, 47].

1.2.3.1 Ceramic Material for Top Coat

The selection of TBC materials for top coat is restricted by some basic requirements as mentioned above: (1) high melting point, (2) no phase transformation between room temperature and operation temperature, (3) low thermal conductivity, (4) chemical inertness, (5) thermal expansion match with metallic substrate, (6) good adherence to metallic substrate, and (7) sintering resistance at operation temperature [37, 41, 48–51]. The number of materials that can be used as TBCs is very limited. So far, only a few materials have been found to basically satisfy these requirements [31, 52].

The applications of pure ZrO_2 are restricted because it shows polymorphism. It is monoclinic (*m*) at room temperature and changes to tetragonal phase (*t*) from above 1100 °C, as shown in Fig. 1.4 [53]. This involves a large change in the volume (4–5%) and causes extensive cracking. Hence ZrO_2 has a low thermal shock resistivity. The addition of some oxides results in stabilizing the cubic phase and the creation of one oxygen vacancy, as shown in Fig. 1.5. However, YSZ is a mixture of ZrO_2 polymorphs, a cubic phase (*c*) and a metastable tetragonal ZrO_2 phase (*t'*) obtained with specific amount of stabilizer. Hence YSZ is also called tetragonal zirconia polycrystal (TZP). This has one of the lowest thermal conductivity ($\sim 2.3 \text{ W m}^{-1} \text{ K}^{-1}$ at 1000 °C for fully dense material) due to its high concentration of point defects (oxygen vacancies and substitutional solute atoms), which scatter heat-conducting phonons (lattice wave) [54]. YSZ also has a high CTE ($\sim 11 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), which helps to alleviate arising stress between the top coat and the bond coat ($\sim 14 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$). YSZ has relatively the low density ($\sim 6.4 \text{ kg m}^{-3}$), which is critical for parasitic weight consideration in high speed rotating engine component [55]. The hardness ($\sim 14 \text{ GPa}$) of YSZ can also have the resistance to erosion and foreign material impact [8].

The amount of yttrium is an important parameter since it has an influence on the grain size, the temperature of the martensitic transformation, strength, and degradation behavior, especially in humid environment [7]. In practice, a Y_2O_3 concentration in the range of 6–8 wt.% is generally used since this composition maximizes spallation life due to the formation of the “non-transformable” metastable tetragonal YSZ phase (*t'*), which is remarkably resistant and does not undergo the

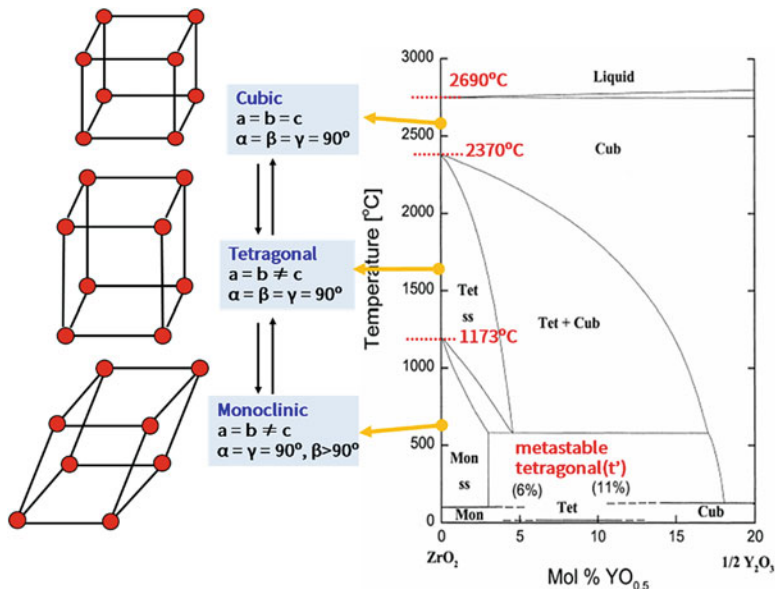
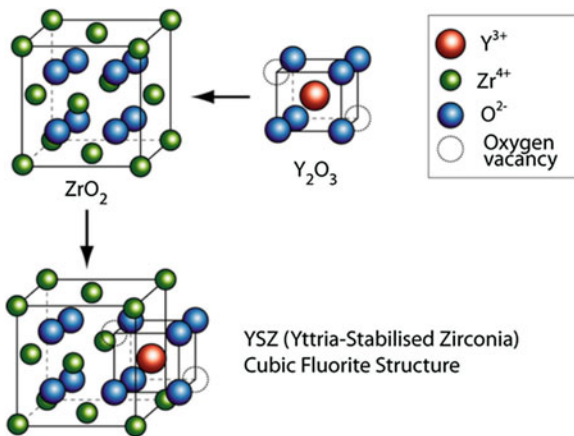


Fig. 1.4 Phase diagram of yttria-stabilized zirconia (YSZ) [53]

Fig. 1.5 YSZ crystal structure with oxygen vacancy



transformation to the monoclinic phase under stresses [56, 57]. However, the metastable tetragonal YSZ phase (t') undergoes a phase separation by diffusion when aged at temperatures greater than 1200 °C, which can allow the $t \rightarrow m$ transformation upon cooling. From a crystallographic point of view, the ratio of the cell parameters can be used to distinguish between the two tetragonal phases, t and t' : the ratio $c/a\sqrt{2}$ tends to 1.010 for the t' cell parameters while it is superior to 1.010 for the t phase [58]. The 7–8 YSZ is the most widely studied and used as TBC material in high-temperature applications such as diesel engines and gas turbines,

and reports about this material are numerous [59]. The TBCs prepared with by 7–8 YSZ have been proved to be more resistant against the corrosion of Na_2SO_4 and V_2O_5 than the ZrO_2 coating stabilized by CaO or MgO [31, 60].

1.2.3.2 Intermetallic Material for Bond Coat

The bond coat provides environmental resistance, oxidation and corrosion protection, adherence, and chemical and mechanical stability between the top coat and the superalloy substrate. Due to the high oxygen penetrability of the external top coat, the oxidation protection of substrate is imposed to the bond coat. This metallic coating is engineered to ideally ensure the formation of a slow-growing, uniform, and defect-free $\alpha\text{-Al}_2\text{O}_3$ scale (TGO) that acts as an oxygen diffusion barrier for the substrate. Thus, a sufficient aluminum reservoir is a necessary constituent of the coating chemical composition. Therefore, the bond coat is one of the most important components of the TBC system, and that is very decisive in determining TBC's durability [61, 62].

The bond coat provides a rough surface for the mechanical bonding of top coat, protects the underlying substrate against the high-temperature oxidation corrosion, and reduces the CTE mismatch between the substrate and the top coat. The bond coat is an oxidation resistant metallic layer, 75–300 μm in thickness, and it essentially dictates the spallation failure of the TBC. The bond coat is typically made of intermetallic alloys and deposited by using the APS or HVOF process. Other types of bond coat are made of aluminides of Ni and/or Pt, which are deposited electroplating in conjunction with diffusion aluminizing or chemical vapor deposition. In a minority of cases, the bond coat consists of more than one layer, having a different chemical/phase composition [63–65]. But due to their lack of oxidation and corrosion resistances, these materials are protected by nickel aluminides or MCrAlY (where M = Co, Ni or Co/Ni) coatings. NiCoCrAlYTa presents a very good corrosion resistance and is used as a standalone coating or as a bond coat in TBC systems [65–67]. The usual ways of coating preparation are physical vapor deposition (PVD), LPPS, VPS, APS, or HVOF spraying, and finally electrolytic deposition methods are also applied [68–70].

The high temperature microstructure of MCrAlY coating is mainly composed of two phases: $\gamma\text{-Ni}$ provides ductility and $\beta\text{-NiAl}$ provides Al-reservoir for the oxidation resistance. The proper contents of Cr and Al in the metallic bond coat are adjusted to provide an adjustment between oxidation and corrosion resistance. The concentrations of Cr and Al typically vary between 15–25 wt.% and 10–15 wt.%, respectively. The quantities of Cr in the alloy reduce the necessary amount of Al for exclusive alumina formation scale [71]. Co improves the ductility and the corrosion resistance because of increasing solubility of Cr in the γ -matrix phase, reducing the tendency to form brittle phase such as $\gamma'\text{-Ni}_3\text{Al}$ and $\alpha\text{-Cr}$. Furthermore Co reduces the stacking fault energy (SFE, a measure of the mobility of dislocations inside the material), since SFEs for Ni and Co are 300 mJ/m^2 and 25 mJ/m^2 , respectively, and thus improves the creep resistance of the MCrAlY [72]. Some

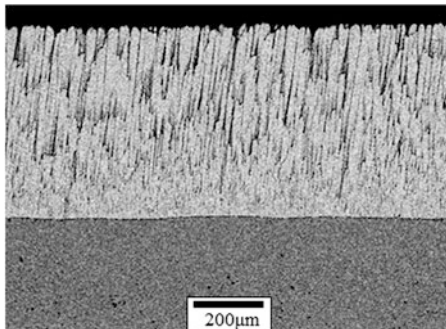
commercial MCrAlY coatings could include Re, amount of 1–3 wt.%, for improving the oxide scale adherence, thermomechanical fatigue resistance, and retardation of inter diffusion with substrate [73, 74]. Ta reacts with the upward diffusing carbon and titanium from the substrate, and thus, prevents their inclusion in the oxide scale. Ta-contained MCrAlY coating improves creep resistance and yield strength [75]. Ti diffusion from the substrate causes TGO to degrade the adherence of alumina oxide by forming TiO_2 [76]. The reactive elements are usually added to the bond coat to mainly improve the oxide scale adherence. Comparing with the oxides of other main elements (Ni, Co, Cr.), the oxide of Al, alumina ($\alpha\text{-Al}_2\text{O}_3$, TGO) has a lower formation energy, and is always the chosen oxide to form a continuous and dense scale against high-temperature oxidation in MCrAlY coatings.

1.2.4 Fabrication Method of TBC

The widely used TBCs for various applications can be classified into two categories as diffusion coating and overlay coating [77, 78]. The diffusion coating process is a thermally activated high temperature oxidation/corrosion/wear resistance coating for iron-, nickel-, cobalt-based metals in severe operating conditions. It provides a chemically bonded, tenacious coating which acts as a diffusion barrier against oxygen and other elements into the substrate [79, 80]. Diffusion coating has the superior oxidation, corrosion, and erosion resistance for the base metal up to 1150 °C without spallation, providing highly reliable substrate for critical components. It is commonly used for gas turbine engine components, such as blades, vanes, cases, seals in power generation, pump impellers, and valve gates in diesel applications. The overlay coatings are mostly deposited by using PVD and APS techniques [81–83]. The PVD describes a variety of vacuum deposition methods used to deposit thin films by the condensation of a vaporized form of the desired film material onto the surfaces of various work pieces [84, 85]. The PVD coatings show sometimes harder and more corrosion resistant than coatings applied by the electroplating process. Most coatings have high temperature and good impact strength, excellent abrasion resistance and are so durable that protective top coats are almost never necessary [86, 87].

The thermal spraying techniques are a kind of coating process in which melted (or heated) materials are sprayed onto a surface. The thermal spraying techniques are widely used for coating the materials such as metallic, ceramic, polymeric, and cermet. Thermal spraying can provide thick coatings (approx. thickness range is 20 μm to several mm, depending on the process and feedstock), over a large area at high deposition rate as compared to other coating processes such as electroplating and vapor deposition. They are fed in powder or wire form, heated to a molten or semi-molten state, and then accelerated toward substrates in the form of micrometer-size particles. Combustion or electrical arc discharge is usually used as the source of energy for thermal spraying. Resulting coatings are made by the

Fig. 1.6 Typical microstructure of top coat prepared by EB-PVD



accumulation of numerous sprayed particles. The surface may not heat up significantly, allowing the coating of flammable substances.

1.2.4.1 EB-PVD Process

The EB-PVD method has been developed to obtain a good microstructure, enhance adhesive strength, and improve strain resistance. The EB-PVD TBCs have been used in production since 1989. The TBCs produced by EB-PVD have a columnar microstructure with elongated inter-columnar pores that become predominantly aligned perpendicular to the plane of the coating as its thickness increases [54]. A typical microstructure for an EB-PVD is shown in Fig. 1.6, exhibiting a columnar structure with a gap between the columns that extend from the interface between the bond and top coats to the surface. The columnar structure, with a certain space between the individual columns, can improve the strain tolerance, resulting in good thermal durability under service conditions. Usually, the fine intra-columnar pores contribute a moderate reduction in thermal conductivity as they are generally inclined to the heat flow. Even though the EB-PVD TBC (which are currently being used in jet aircraft engines) usually exhibits higher durability, extending its lifetime performance, the lower deposition rate and higher cost of the EB-PVD process limits its application [88]. In addition, when the material composition is complicated, the process is more difficult due to the element's vapor pressure. The performance of EB-PVD TBC has been studied extensively for several decades and a new technology and an advanced TBC are still proposed [89, 90].

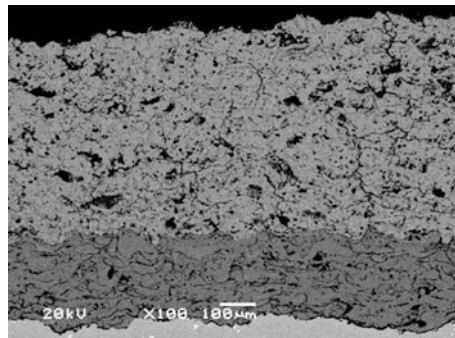
1.2.4.2 APS Process

Plasma spraying is the most commonly used method for depositing TBCs and has been used since 1950s to protect hot section components of gas turbine engines [91–93]. In plasma spraying process, the material to be deposited (feedstock)—typically as a powder, sometimes as a liquid, suspension or wire—is introduced into the plasma jet, emanating from a plasma torch. In the jet, where the temperature is on

the order of $15,000\text{ }^{\circ}\text{C}$, the material is melted and propelled toward a substrate. The molten droplets flatten, rapidly solidify, and form a deposit. Commonly, the deposits remain adherent to the substrate as coatings; free-standing parts can also be produced by removing the substrate. There are a large number of technological parameters that influence the interaction of the particles with the plasma jet and the substrate, and therefore the deposit properties. These parameters include feedstock type, plasma gas composition and flow rate, energy input, torch offset distance, substrate cooling, etc. [94–96].

In recent decades, the development of advanced coatings and processing methods has been a field of active research in TBCs. Many new techniques, such as SPPS, electrostatic spray assisted vapor deposition, electron beam-directed vapor deposition (EB–DVD), and EB–PVD, have been used to create advanced TBCs [97, 98]. Economical coating methodologies that enable a high degree of control over the coating morphology are desired in land-based gas turbines. The APS process, with its economic benefits, is still preferred commercially, because of the relatively low cost and simple process compared with advanced coating methods, such as EB–PVD and EB–DVD [99–101]. The APS process also has its own advantages in producing the large and complex-shaped TBCs. Numerous factors have to be considered in practical applications of TBCs, such as thermal durability, thermal conductivity, chemical inertness, CTEs, and thermomechanical properties. Among them, the thermal durability in cyclic thermal exposure is an essential factor for the reliability and lifetime performance of APS–TBC system, which is closely related to its microstructure. In addition, there are many ways to enhance TBC performance, such as controlling the porosity of TBC, employing materials with a low thermal conductivity, and increasing the thickness of TBC [102, 103]. The TBCs prepared by APS method present a strong damage tolerance under the most severe operating conditions, even when a high number of defects are present, such as pores and microcracks. The typical microstructure (cross-sectional microstructure) with horizontal “splat” boundaries/cracks, pores, and unmelted powders in the top coat is shown in Fig. 1.7, in which both coats, the bond and top coats, are prepared by using APS process. The bond coat indicates a general microstructure prepared by using APS process with oxide layer, and some pores and unmelted powders.

Fig. 1.7 Typical microstructure of TBC system prepared by APS

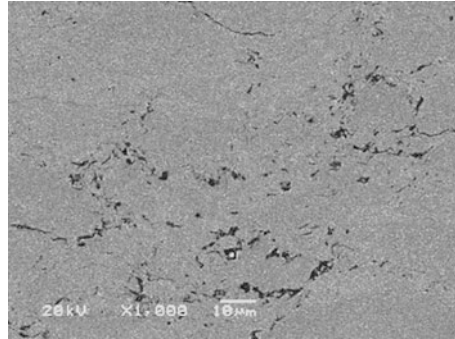


1.2.4.3 HVOF Process

A thermal spray process utilizing the combustion of gases such as hydrogen or a liquid fuel such as kerosene has been developed in 1980s, which is HVOF process. The HVOF spraying is commonly used for its versatility to deposit dense metallic/alloy and cermet coatings. By these HVOF process features the coating generally near bulk density and low residual tensile stress, in most case, compressive stress, which enable to product thicker coating than other processes (e.g., cold spray, arc coating, flame coating, plasma spray). Fuel and oxygen mix and atomize within the combustion area under conditions that monitor the correct combustion mode and pressure. There are two distinct differences between conventional flame spray and HVOF. HVOF utilizes a confined combustion and an extended nozzle to heat and accelerate the powdered coating material [104, 105]. Typical HVOF devices operate at hypersonic gas velocities, i.e., greater than MACH 5. The extreme velocities provide kinetic energy which help to produce coatings that are very dense and very well adhered in the as-sprayed condition (some of which exceed 83 MPa, or 12,000 psi). The HVOF process efficiently combusts oxygen and a gaseous or liquid fuel to produce high kinetic energy with controlled heat input. Depending on user requirements, both gas fuel (propylene, propane, hydrogen, or natural gas) and liquid fuel (kerosene) can be used. The coating material, in powder form, is introduced into and uniformly heated by the hot gas stream to a molten or semi-molten condition [106–108]. The flame and powder are accelerated by a converging and diverging nozzle (air cap) to produce supersonic gas and particle velocities, which propel the powder particles toward the substrate to be coated.

As a result, the injected particles flatten plastically and they impact on the surface of substrate. For this reason, coating microstructure shows homogeneous and fine granular structure. Coating formed by high velocity particle impact of spray particles on the substrate in solid state provides the compressive residual stress state. This is very beneficial about lifetime of coated components under dynamical load. Additionally, the actual flame temperature can be affected by the ratio between combustible and oxygen flow rate. And the choice of the combustible must also be taken under consideration of the required supply pressure that should be higher than the combustion chamber pressure (modern guns can exceed 1 MPa). More recently, HVOF coatings due to its low cost and high quality deposits have a similar oxidation rates with VPS coatings at high temperature, being sometimes even lower than this one [105, 108]. The bond coat prepared by HVOF process has outstanding characteristics, even above other thermal spray processes, that include high density, high bonding strength, optimum hardness, improved toughness, thicker coating thickness, beneficial residual stress, and superior corrosion resistance [109, 110]. A typical microstructure of the bond coat prepared by HVOF process is shown in Fig. 1.8.

Fig. 1.8 Typical microstructure of bond coat prepared by HVOF



1.2.4.4 LPPS Process

The LPPS process, also known as VPS, has been employed at higher chamber pressure than 2 kPa during the coating operation. However the chamber is usually evacuated to nearly 1 Pa before it is flooded with an inert gas to the required working pressure. The LPPS process is a low velocity and high temperature spraying process that is performed in a near-vacuum argon atmosphere. The LPPS and VPS processes are two different designations for the same process. The “flame” (no fire is actually involved in the process) is high temperature plasma and the spraying is performed in a low-pressure argon atmosphere. This process enables materials, so-called MCrAlYs, which are sensitive to oxidation to be sprayed [111, 112]. The coating features high density (porosities of coatings are less than 1 or 2%), homogeneous and oxide-free microstructure on the bond coat. The surface roughness is strongly dependent on the particle size used for the spraying. Normally, a relatively high degree of roughness is created and the surface will be smoothed by a shot peening and/or polishing process after coating production. The LPPS process is the preferred metallic coating technology for single airfoil components. It is also used for the production of metallic anti-corrosion coatings [20, 113, 114].

The bond coats of TBCs are typically manufactured using the APS and HVOF processes. The predominant drawback of these techniques is that their inherent high temperatures inevitably lead to changes in the coating microstructure, namely oxide inclusions. The MCrAlY bond coats prepared using the APS and HVOF processes show oxide contents of 1.8 and 0.94 wt.%, respectively, which are attributed to the oxidation during spraying [96, 115–117]. A dense bond coat without oxide formation during spraying can be deposited by VPS process. Significantly, the oxide content in the bond coat prepared by LPPS process is about 0.16%, which is lower than bond coats prepared by the APS and HVOF processes [118]. A typical microstructure of the bond coat prepared by LPPS process is shown in Fig. 1.9, indicating that there is less oxide content compared with those of the APS and HVOF processes shown in Figs 1.7 and 1.8, respectively.

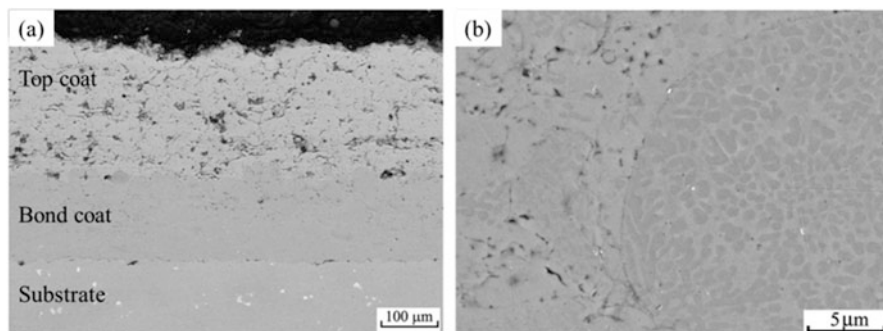


Fig. 1.9 Typical microstructure of TBC with bond coat prepared by LPPS: (a) overall microstructure and (b) bond coat microstructure

1.2.5 Advanced Thermal Barrier Coatings

1.2.5.1 Rare-Earth Oxides

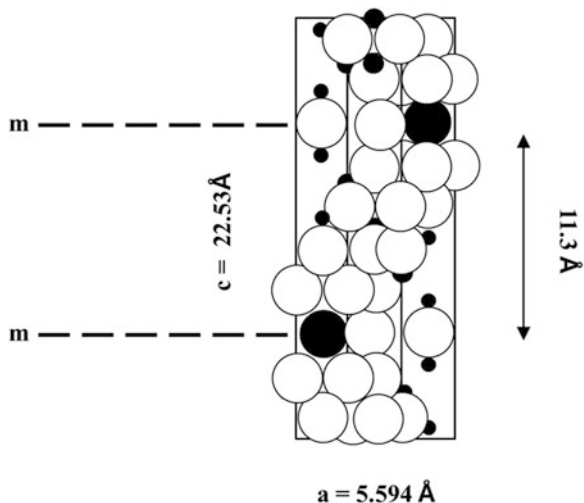
Advanced TBCs with low conductivity and high thermal stability have been developed using a multi-component oxide defect-clustering approach. The advanced coatings are designed by incorporating multi-component, paired-cluster rare-earth oxide dopants into conventional ZrO_2 and hafnia- Y_2O_3 oxide systems [119]. As the atomic radius of rare-earth oxide dopants is increased with a certain range, the thermal diffusivity can be reduced due to the addition of expansion distorted. TBCs with advanced multi-component and low conductivity oxide have been developed based on an oxide defect-clustering design approach and using a laser high-heat-flux thermal conductivity technique. The laser test approach emphasizes real-time monitoring of the coating conductivity at high temperatures in order to assess the overall coating thermal conductivity performance under engine-like heat-flux and thermal gradient conditions. Although the advanced coatings with oxide cluster follow a similar trend as the pseudo-binary ZrO_2 - Y_2O_3 coatings in the furnace cyclic behavior where the cyclic lifetime of coating generally decreases with increasing the total dopant concentration, the oxide cluster coatings show a promise to have significantly better cyclic durability (comparable to that of zirconia-4.55 mol% Y_2O_3) than the binary ZrO_2 - Y_2O_3 coatings with equivalent dopant concentrations [118]. Under the NASA Ultra-Efficient Engine Technology (UEET) program, the durability of the advanced low conductivity coatings was evaluated using cyclic furnace tests. In terms of performance the rare-earth oxide dopants into conventional ZrO_2 and hafnia- Y_2O_3 oxide systems provide superior low conductivity, longer cycling lifetime performance and higher stability compared to the current YSZ coatings at high temperature. Through advanced coating system design, optimized dopant and composition, and improved processing technology, it can be expected in the future that the cycling lifetime performance of the coating will be more extended.

1.2.5.2 Lanthanum Hexaaluminate (LHA)

Lanthanum hexaaluminate (LHA) with a magnetoplumbite structure is a promising competitor to Y-PSZ as a TBC, since most ZrO_2 coating's lifetime performance significantly decreases, including undesired densification at temperatures exceeding $1100^\circ C$. The microstructure of calcined lanthanum hexaaluminate powders and thermally sprayed coatings show a platelet structure [120]. Due to its high melting point, high thermal expansion, low thermal conductivity, excellent longtime sintering resistance, and structural stability up to $1800^\circ C$, these materials have also been found advantageous for TBC applications. The nominal composition is $(La, Nd) MA_{11}O_{19}$ where M could be Mg, Mn to Zn, Cr, Sm [121]. Also the addition of Li has been proven to be advantageous [122]. Among these, the most interesting one is $LaMgAl_{11}O_{19}$ which has been extensively investigated in terms of its thermophysical properties and processing issues during air plasma spraying [123–126]. The plasma sprayed coating is partly amorphous in the as-sprayed condition due to the rapid quenching from the molten state. Upon an initial heat treatment recrystallization occurs over the temperature range from 800 to $1200^\circ C$ which is marked by a large decrease in the volume of the free-standing coatings [125].

It characterizes that the magnetic structure is highly charged lanthanum cation located in an oxygen position of a hexagonal close-packed oxygen ions. Ion diffusion strongly inhibits perpendicular to the crystallographic c-axis, thereby obstructs the densification by sintering. Compared to Y-PSZ, the LHA shows similar thermophysical properties, outstanding structural and thermochemical stability. LHA crystallizes in the magnetoplumbite structure, a super lattice of the spinel structure as shown in Fig. 1.10. In contrast to the oxygen ion conducting ZrO_2 , LHA permits operating temperatures above $1300^\circ C$ because of its thermal stability and electrically insulating properties.

Fig. 1.10 Crystallographic unit cell of lanthanum hexaaluminate (LHA)



1.2.5.3 $\text{La}_2\text{Ce}_2\text{O}_7$ (LC)

$\text{La}_2\text{Ce}_2\text{O}_7$ (LC) is proposed as a promising TBC material which is the solid solution. CeO_2 has higher CTE and lower thermal conductivity than YSZ, and the addition of CeO_2 into YSZ coating is supposed to be effective for the improvement of thermal cycling lifetime performance. Remarkable improvement of thermal shock tolerability could be attained by the addition of CeO_2 into YSZ [127–129]. The CeO_2 -doped coating has a better thermal shock resistance because mainly: (1) there is little phase transformation between the monoclinic and tetragonal phase in the $\text{CeO}_2 + \text{YSZ}$ coating [130], (2) stress generated by bond coat oxidation is smaller in the $\text{CeO}_2 + \text{YSZ}$ coating due to better thermal insulation, and (3) the CTE of $\text{CeO}_2 + \text{YSZ}$ coating is larger than that of YSZ coating. However, the addition of CeO_2 has some negative effects, such as the decrease of hardness and stoichiometry change of the coating due to the vaporization of CeO_2 [127], reduction of CeO_2 into Ce_2O_3 , and accelerated sintering rate of the coating [131, 132]. Some previous investigations declare that the LC solid solutions with more CeO_2 content than LC have higher CTEs below 400 °C—it should be effective to reduce the stress induced by the CTE mismatch between the substrate and the top coat in the low temperature range. Obviously the LC is used as an outer layer due to its lower thermal conductivity and good phase stability at high temperatures compared to YSZ. However, the CTE of LZ suddenly reduces at low temperature range (200–350°C).

1.2.5.4 Graded TBC

Commonly TBCs include a metal layer (substrate) and a ceramic layer (top coat)—the substrate has a high thermal conductivity, toughness, and ductility properties, and the top coat has high hardness, wear resistance, corrosion, and high temperature resistance performance. However, the CTE, the elastic modulus, and other properties between the top coat and the substrate provide with a great diversity, and there exists an obvious interface. Therefore, the bond layer (coat) alleviates the thermal expansion mismatch between the top coat and the substrate, and improves high temperature oxidation resistance performance. TBC structure is divided into three types: (a) double layer system, (b) multilayer system, and (c) graded system, which are shown in Fig. 1.11. Among them, the double layer system mainly composed of the top coat and the bond coat has a simple structure and mature technology advantages. However, the CTE and elastic modulus of the top coat and the bond coat have the deviation in temperature during thermal cycling easy to delaminate.

Therefore, in order to release the physical properties mismatch at the interface, the multilayer system has been developed which is mainly composed of substrate, heat insulation multilayer, Al_2O_3 anti-oxidation layer, and the top coat. Compared with the double layer system, the multilayer system can reduce the growth rate of the oxide (TGO) layer and improve the oxidation resistance of the coating, but the

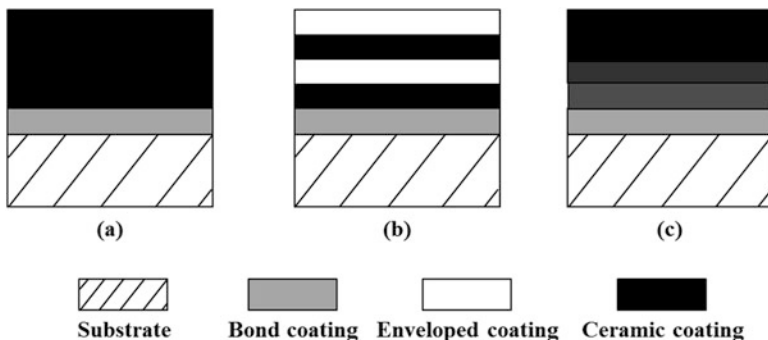


Fig. 1.11 Three kinds of TBC structure: (a) normal structure, (b) layered structure, and (c) graded structure

sophisticated technological process and performance poorly in thermal shock resistance restrict application in the field of aero engine areas. As a consequence, the graded system design in order to further improve the mechanical properties and high temperature oxidation resistance of TBCs can reduce the residual stress and effectively prevent delamination of the coating by changing chemical composition, organization structure, and mechanical properties with coating thickness along the direction of the gradient changes.

1.3 Environmental Barrier Coating (EBC)

1.3.1 Overview of EBC

One key barrier to the application of advanced silicon-based ceramics and composites for hot section structural components in gas turbines is their lack of environmental durability. A new class of coating, environmental barrier coating (EBC), has been developed in the 90s to protect Si-based ceramics and ceramic composites from the degradation by water vapor, even though silicon-based ceramics exhibit excellent oxidation resistance in clean and dry oxygen environments, by forming a slow-growing and dense silica scale [133, 134]. Oxide coatings are a promising approach to provide environmental protection for advanced heat engine components because oxides are in general more resistant than silicon-based ceramics to corrosive environments [135].

There are several key issues that must be considered in selecting coating materials [136, 137]. Figure 1.12 schematically shows the key issues. Firstly, the coating must possess the ability to resist reaction with aggressive environments, as well as low oxygen permeability to limit the transport of oxygen. Secondly, the coating must possess CTE close to that of the substrate material to prevent delamination or racking due to CTE mismatch. Thirdly, the coating must maintain a stable

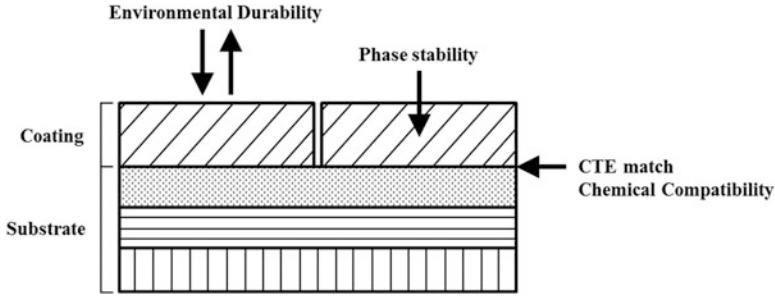


Fig. 1.12 Key issues in selecting coating materials for EBCs

phase under thermal exposure. Phase transformation typically accompanies a volumetric change, disrupting the integrity of the coating. Fourthly, the coating must be chemically compatible with the substrate to avoid detrimental chemical interaction [138]. Early coatings work focused on protecting Si-based ceramics from molten salt corrosion. Mullite has attracted interest as a coating for Si-based ceramics mainly because of its close CTE match with SiC.

1.3.2 Development of EBC

The first generation water vapor-resistant EBC was developed by combining the crystalline mullite coating with an Y_2O_3 -stabilized ZrO_2 (YSZ, ZrO_2 -8 wt.% Y_2O_3) top coat [139, 140]. In the first generation EBC, the mullite bond coat provided adherence, while the YSZ top coat provided protection from water vapor. The relatively high silica activity in mullite and the resulting selective volatilization of silica cause rapid recession of mullite in water vapor, necessitating the top coat for a water vapor resistant. YSZ was a logical candidate for the top coat because it had been successfully used as the TBC for metallic components in gas turbine engines, indicating its durability in water vapor. The first generation EBC could provide protection from water vapor for several 100 h at $1300^\circ C$. In longer exposures, however, water vapor eventually penetrated through cracks in the EBC and attacked the Si-based substrate, leading to coating delamination [141].

The second generation EBC, with substantially improved performance compared with the first generation EBC, was developed in the NASA High Speed Research-Enabling Propulsion Materials (HSR-EPM) program in joint research by NASA, General Electric, and Pratt and Whitney [142]. The new EBC consists of three layers: a silicon bond coat, a mullite or a mullite + BSAS ($(1-x) BaO \cdot x SrO \cdot Al_2O_3 \cdot 2SiO_2$, $0 \leq x \leq 1$) intermediate coat, and a BSAS top coat [143]. The second generation EBC has some durability issues that limit their use temperature and lifetime performance. One key issue is the volatilization of the BSAS top coat in high velocity combustion environments. A projection based on a silica volatility model in conjunction with BSAS volatility data from high steam

low velocity environments indicates a BSAS recession of 70 μm after 1000 h at 1400 $^{\circ}\text{C}$, 6 atm total pressure, and 24 m/s gas velocity [141]. Actual gas turbines operate at significantly higher pressures and gas velocities, increasing the projected recession to much higher levels. In fact the EBC on solar turbine engines suffered significant BSAS recession in some areas after the 14,000 h test [144]. Another key durability issue is the chemical reaction between BSAS and SiO_2 formed on the Si bond coat by oxidation. The reaction between BSAS and SiO_2 generates a low-melting (1300 $^{\circ}\text{C}$) glass that causes EBC degradation and premature failure at temperatures above 1300 $^{\circ}\text{C}$ [141]. Therefore, under the gas turbines working environments, the corrosion resistance in water vapor of the top coat becomes particularly important.

Owing to the existed deficiencies of the second generation EBC, hence the NASA research center concentrated on a new top coat that can be substituted for the BSAS. Research has been undertaken at the NASA Glenn Research Center under the support of the Ultra Efficient Engine Technology (UEET) program to develop EBCs that can withstand a 1482 $^{\circ}\text{C}$ (2700 $^{\circ}\text{F}$) surface temperature and sustain 1316 $^{\circ}\text{C}$ (2400 $^{\circ}\text{F}$) EBC/substrate temperature over thousands of hours. Figure 1.13 shows plasma-sprayed Si/mullite +20 wt.% BSAS/BSAS on SiC/SiC composite after 1000 h at 1316 $^{\circ}\text{C}$ (1 h cycles) in 90% H_2O -balance O_2 [138]. The purpose of the third-generation EBC was substituted for original BSAS, showing a multilayer system. It has the key attributes for a successful EBC, such as a low silica activity, a low CTE, and a low modulus (~ 100 GPa for dense BSAS). The low silica activity provides stability in water vapor, while the low CTE and low modulus provide low thermal stresses. The EPM (Enabling Propulsions Materials) EBCs exhibit dramatically improved durability compared to the mullite/YSZ EBC [145]. The EBC maintains excellent adherence and crack resistance. New coating system preserves favorable thermal stability at 1500 $^{\circ}\text{C}$ which have been required. In addition, which have remarkable chemical and mechanical with the mullite/mullite + BSAS inter-layer.

Fig. 1.13 Plasma-sprayed Si/mullite +20 wt.% BSAS/BSAS on a SiC/SiC composite coupon after 1000 h at 1316 $^{\circ}\text{C}$ (1-h cycles) in 90% H_2O -balance O_2 [138]

