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MULLITE BASED THERMAL BARRIER COATINGS AND COATING TECHNIQUES :A REVIEW

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Abstract— **Thermal barrier coatings (TBCs) have beendeveloped to protect metallic and Si-based ceramic components from high temperature environmental attack and thermal stresses in structures and machine components across a wide range of industries and applications.Zirconia-yttria based oxides and (Ba,Sr)Al2Si2O8 (BSAS)/mullite basedsilicates have been used as the coating materials. There are several thermal barriercoating techniques with a objectives of reductionof maintenance costs, increase of the working temperature, reduction of thermal loads, resistance increase to erosion and corrosion and reduction of the high temperature oxidation. Thispaper incorporates a brief review on post researches on several recent activities in the field of modern TBCs, focusing on advanced coating techniques and in addition some advances coatings materials are described.**

Index Terms— thermal barrier coatings, ceramic coating, mullite, APS, EB-PVD.

INTRODUCTION

Thermal barrier coatings were first successfully tested in the turbine section of a research gas turbine engine in the mid-1970s (1). For many decades, the development of TBC remainsan attractive research area due to its applications in various automobiles engines and gas turbines.Thermal Barrier Coatings (TBCs) are surface coatings in which high insulating materials, like ceramics forms the top layer.A thermally grown oxide is sandwiched between top coat and bond coat. This bond coat is bonded to a metal substrate, which is usually metal. This bond coat protects the metal load carrying structure during temperatureexcursions. The application of TBCs can significantly increase the operatingtemperatures up to 1400-1500ºC and increase thermal efficiency. There are many applications, which have benefited from adopting TBC's including aeronautical, aerospace, automotive, nuclear industries, nuclear power plant, heavydutyutilities such as diesel trucks and many other structures.(2,3,4)

Thermal barrier coatings(TBC's) are essential structural components in current and future engineering applications associated with harsh combustion environments or high thermal fluxes. Thermal barrier coating systems (TBCs) are widelyused in modern gas turbine engines to meet increasing demands for greater fuel efficiency, lower NOx emissions, and higher powerand thrust.(5)With continuously increasing demands for significantly higher engine operating temperature and better engine reliability, future EBC systems must be designed for both thermal and environmental protections of the engine components in gas turbine combustion gas environment. In particular, thermal barrier functions of EBC's become a necessity for reducing the engine component thermal loads and chemical reaction rates, thus maintaining required mechanical properties and durability of these components(6).The development of advanced thermal barrier and environmental barrier coatings (TBC's and EBC's) will directly impact the successful use of ceramic components in advanced engine system as in figure 1.

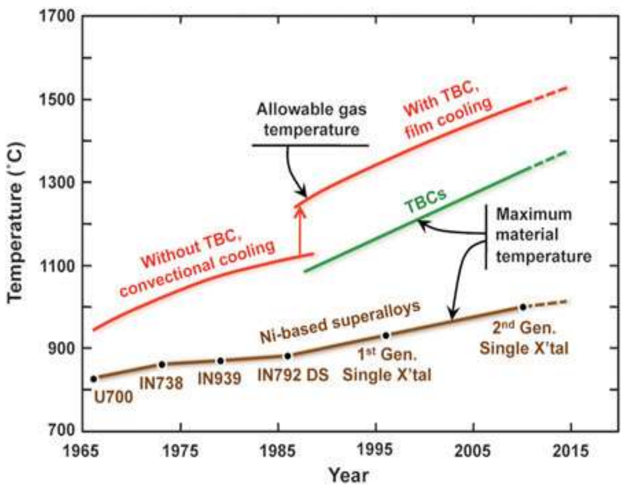

Figure 1 Progression of temperature capabilities of Ni-based super alloys and thermal-barrier coating (TBC) materials over the past 50 years. The red lines indicate progression of maximum allowable gas temperatures in engines, with the large increase gained from employing TBC's(7).

There are four layers in current Thermal barrier coating systems made of different materials with specific properties and functions(as in figure2). These layers are(i) the substrate, (ii) the bond-coat,(iii) the thermally grown oxide (TGO), and(iv) the ceramic top-coat as in figure 2.The bond coat is often a metal and has two major functions. It improves the bonding between the substrate and the topcoat, and it protects the substrate fromcorrosion and oxidation. Two types of bond coats are frequently used, a (platinum) aluminide based one and a so-called MCrAlY with M Ni or Co being(8) The choice of the adequate bond coat depends on the deposition technique used for the topcoat.

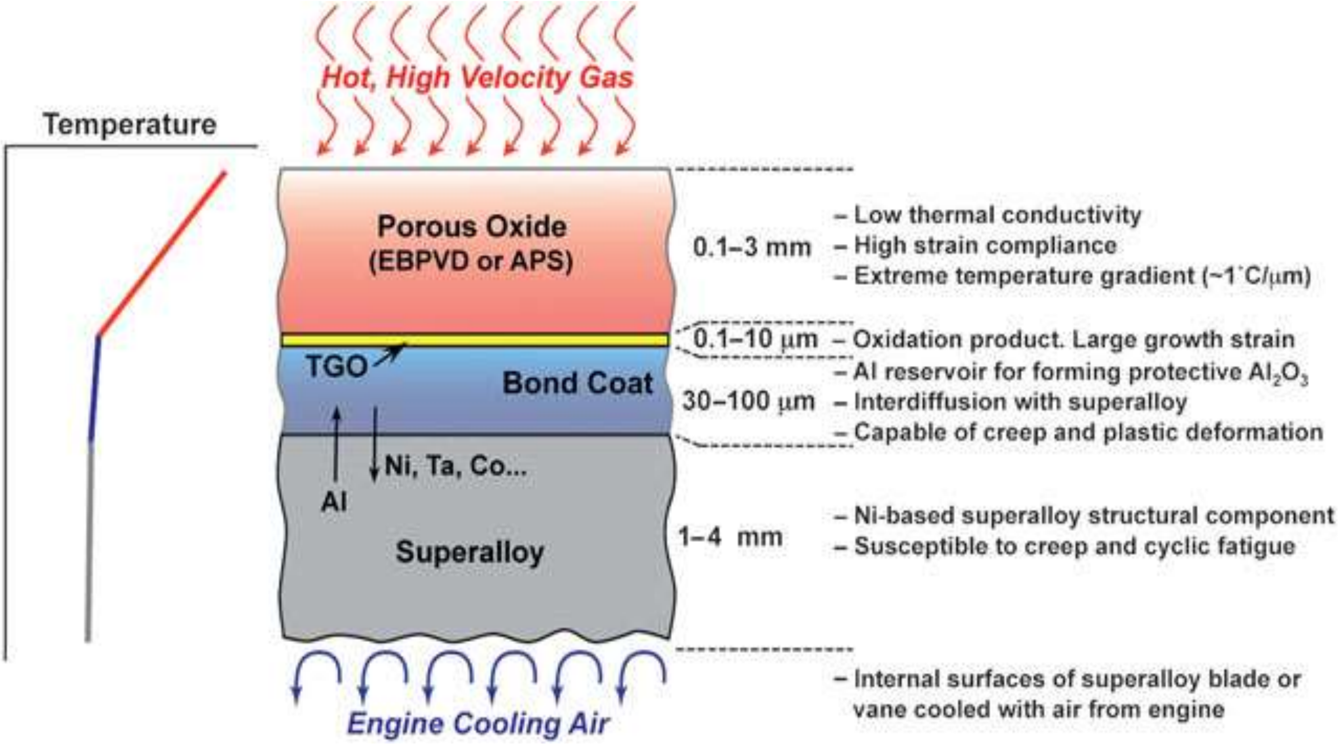

Figure 2 Schematic illustration of the multilayer, multifunctional nature of the thermalbarrier coating system (not to scale). The ceramic topcoat is deposited by electron beamphysical vapor deposition (EBPVD) or air plasma-spraying (APS). Sandwiched betweenthe topcoat and the metallic bond coat is the thermally grown oxide (TGO). Properties/functions and approximate thicknesses of the different layers are indicated (7).

MULLITE

Mullite(3Al2o3.2Sio2) is an attractive engineering ceramic, only stableintermediate phase in the alumina-silica binary system. Due to its harsh formation conditions involving high temperature and low pressure, mullite rarely exists in nature. It emerges at the contact of superheated magma intrusions with Al2O3-rich sediments, as on the Island ofMull (Scotland), where the name mullite comes from (9). Theresulting synthetic mullite composites can be classified into three categories according to the technical routes: sintered-mullite, fused mullite and chemical-mullite (10). It has excellent high-temperature and chemical stabilityat temperature as high as 1500C(ma).In addition, mullite has low thermal conductivity of 0.06 W cm−1 K−1, good thermal shock resistance, coefficient of thermal expansion close to Si-based ceramics(4.7x10-6 for Sic and 5.05 x 10-6 for mullite) showing a great potential as thermal barrier coatings material(11,12). It hasbeen found that mullite coating is superior to ZrO2 protective coating in preventing diesel engine part from crack initiation and propagation during service period (13)

THERMAL BARRIER COATING TECHNIQUES

There are various methods for depositing ceramic coatings on metal substrates. These processes includes flame spray, HVOF, cold spray, Electric arc spray, slurry spray technique (SST).But the Key trends arise from the disparate attributes of EB-PVD and APS coatings**.** (i) air-plasma-spray (APS) deposition, (ii) electronbeamphysical-vapor deposition (EB-PVD).

1. air-plasma-spray (APS) technique

The APS process can obtain high deposition rates and the capability to spray varied geometries. Plasma spraying also allows composition control and can produce coatings with high mechanical strength and durability. In the plasma spraying process, a high intensity arc is operated between a stick-type cathode and a nozzle-shaped water-cooled anode. Gas, introduced along the cathode, is heated by the arc to plasma temperatures and then exits the anode nozzle as a plasma jet. Powder injected into the plasma jet is accelerated and heated to a molten state. As the molten particles in the jet strike the selected substrate, they form splats that build up, particle by particle, into a coating. Among the many spraying parameters, the standoff distance, powder size distribution, power level, and arc gas selection strongly influence the microstructure of coatings.

Two developments in APS technology are particularly notable. The first one is the maturation of the dense, vertically cracked (DVC) TBCs,wherein the incorporation of cracking patterns mimicking the segmentation of the EB-PVD coatings is intended to improve their strain tolerance [14]

2. Electron beam physical-vapor deposition (EB-PVD)technique

Among various vacuum coating methods, electron beam /physical vapor deposition is characterized by the use of a focused high-power electron beam, which melts and evaporates metals as well as ceramics.The high deposition rate results in many cost-effective applications.. EB-PVD TBCs are more durable, but expensive, relative to APS TBCs, and are used primarilyin the most severe applications, such as turbine blades and vanes in aircraft engines.

The most radical innovation in EB-PVD technology is arguably the incorporation of high velocity gas flow to focus the vapor plume, known as ‘‘directed vapor deposition’’ (DVD) [15]. A microwave plasma-enhanced CVD route has also emerged as a viable route to produce YSZ coatings with segmented columnar microstructures at rates competitive with established EB-PVD technology (_4 lm/min) [14]

OVERVIEW OF PAST RESEARCH

In the past decade, many techniques have been described in the literature for the mullite based ceramic’s capability as a thermal barrier coating. There are two main means, mechanical and chemical processes, of applying the material coating to the metal substrate. However, of the two application processes, the mechanical means offer the most robust methods for producing surface coatings in terms of economics, adaptability to large and complex surfaces, different coating and substrate materials. In particular the Electron Beam Physical Vapour Deposition, Powder Flame Spraying, Plasma Thermal Spray and Cold Gas Dynamic Spray Coating techniques are particularly suited for creating environmental barrier coatings. These techniques however, are expensive and impractical for small-scale production.The slurry spray technique (SST) is not as highly utilised as the other techniques and it is desirable to determine whether mullite based ceramics can produce EBC coatings of comparable quality.

K. N. Lee et al (2002) developed state-of-the-art environmental barrier coatings (EBCs) for Si-based ceramics consist of three layers: a silicon bond coat, an intermediate mullite ($3Al_2O_3{\cdot}2SiO_2$) or mullite + BSAS ($(1-x)BaO{\cdot}xSrO{\cdot}Al_2O_3{\cdot}2SiO_2$, $0 \leq x \leq 1$) layer, and a BSAS top coat. Areas of concern for long-term durability are environmental durability, chemical compatibility, volatility, phase stability, and thermal conductivity. Variants of this family of EBC were applied onto monolithic SiC and melt-infiltrated SiC/SiC composites. Reaction between BSAS and silica results in a low-melting (~1300°C) glass, which can cause the spallation of the EBC. At temperatures greater than 1400°C BSAS suffers significant recession via volatilization in water-vapor-containing atmospheres. Both reactions can be EBC life-limiting factors. BSAS undergoes a very sluggish phase transformation (hexagonal celsian to monoclinic celsian), the implications of which are not fully understood at this point.

Li Zhao (2003) developed composite microfiltration membranes combining rugged substrates (both planar and tubular) made of sintered stainless steel powder with the wet powder spraying (WPS) method, in which a sintered titanium dioxide layer is permanently bonded to the porous stainless steel substrates. Through the optimisation of a conventional composition of the Ti02 suspension, the spraying process of the WPS method and the sintering process of the graded structure, stable Ti02 membrane layers are being developed with an average pore size of 0.1 ~µm and a thickness of 20-30 µm. In order to investigate the flow process inside the graded structure, mathematical models were developed to simulate the flow rate both by fluid and gas.

H. Mahdjouba et al (2003) performed a study to determine how the characteristics of spray-dried granules prepared from aqueous yttria doped zirconia slurries can be affected by the spray-drying process parameters: dispersant amount, pH and binder type. First, the colloidal stability of aqueous zirconia suspensions as a function of polyacrylic acid content, pH and binder nature has been investigated in order to establish a stability map. The concentration of dispersant required to stabilise the zirconia suspensions decreases with increasing pH. The addition of a binder may modify the state of dispersion. The stability map makes it possible to define regions of stable (dispersed) and unstable (flocculated) suspensions. Changing the nature of the binder from latex to a hydrosoluble polyvinyl alcohol has an effect on the wall thickness of the hollow granules. The sedimentation volume, which represents the state of dispersion of the suspension, is the major factor controlling the droplet drying mechanism.

M. L. Pines (2004) fabricated graded metal-ceramic composite armour specimens consisting of nickel and alumina through powder processing techniques and pressureless sintering for dynamic mechanical characterization. An approach is employed to control the thermal shrinkage of each microstructure during sintering by varying particle sizes of the two powders. The relationship between porosity and sintered properties was characterized through microhardness measurements, indicating the reinforcing particles are debonded from the matrix and can be treated as additional porosity. Porosity effects were incorporated into constitutive equations for a recently developed finite element sintering model, which was validated through comparison of predicted and experimental shape profiles of graded specimens and through correlation of stress profiles to fracture locations.

X. Wang et al (2005) yttria stabilized zirconia (YSZ) coatings were produced on Fecralloy substrates by a novel slurry method by adopting a 'bricks and mortar' approach. The slurry contained large preformed particles of 10–60 µm, as the 'bricks', and concentrated nano-particle slurry, as the 'mortar'. Green coatings were prepared by spreading the slurry on substrates. Then sintering at 1200°C was carried out to produce coatings with grain size up to 200 nm. The presence of larger preformed particles hindered the shrinkage of the coatings during drying and sintering. It was observed that the mortar could form inter-preformed particle bridging, an underlying mechanism for the formation of cemented preformed particle network. By using different preformed particles, different micro-architectures were obtained and reduced thermal diffusivities were achieved.

P. Roy et al (2005) performed study on the spray drying of ceramic slurries to determine how the characteristics of the spray dried powder can be affected by the process parameters and the sintering of these agglomerated powders viz. yttria partially stabilized zirconia (PSZ) and zirconium silicate. First experiments have been focused on the slurry parameters: dispersant amount, binder type and pH. According to sedimentation tests, stable (dispersed) and unstable (flocculated) suspensions were defined. Changing the nature of the binder from latex to poly vinyl alcohol (PVA) has an effect on the wall thickness of the hollow granules. According to the former results, powders have been elaborated by the spray drying process using several slurries formulations. Finally, the evolution of the morphology of the PSZ spray dried hollow powder after sintering in an oxyacetylene flame or an atmospheric furnace was investigated. When the powder is sintered in a furnace, low shrinkage and approximately no shape variations were noticed, whereas using an oxyacetylene flame tends to density the powder.

P. Nguyen et al. (2007) shows potential of a simple and new techinique of deposition of top layer coating of Yttria Partially Stabilised Zirconia (YSZ) ,called slurry spray technique with a focus on aerospace applications. The objective in the development of this technique was to achieve low cost and quality coating comparable to the existing manufacturing methods, which are often expensive and inapplicable to coat large or curved surfaces. The thermal barrier coating consisted of the Yttria Partially Stabilised Zirconia (YSZ) as the top coat and graded nickel as bond coat with the use of polyvinyl alcohol and terasodium pyrophosphate as the binder and dispersant respectively. This study described the developed technique and presented selected results of thermo-mechanical and fracture testing of the thermal barrier coatings including graded coatings fabricated using this new method.

E. Withey et al (2007) examined using X-ray diffraction, dilatometry, and compression creep the plasma-sprayed stand-alone coatings of 7 wt.% Y2O3-ZrO2 (YSZ), nominally 74 wt.% Al2O3-26 wt.% SiO2 mullite, and a 45:55 volume ratio composite of YSZ to mullite. Creep test were conducted on all three coating types in the as-sprayed condition at stresses from 40-80 MPa and temperatures of 1000° – 1200°C. The linear thermal expansion of YSZ/Mullite composite specimens was 6.4 x 10-6/°C. While the creep behavior of YSZ/mullite composite specimens was between that of pure YSZ and pure mullite specimens for all combinations of temperature and stress tested, the creep response of the composite was more similar to that of pure mullite for all cases tested, consistent with mullite being the continuous phase in the composite.

G. Chen et al (2007) presented the preparation of mullite suspension for electrophoretic deposition (EPD).It was suggested that the successful deposition of mullite coating is closely related to the weight ratio of mullite powder to ethanol solvent, and the concentration of phosphate ester (PE) in ethanol solvent, which is employed to positively charge the mullite particles in suspension. The polyvinyl butyral (PVB) is necessary as binder in the suspension. With increase in the powder: ethanol weight ratio, the content for the PVB in the suspension will also increase in order to make the deposited layer adhere to the substrate. The composition of the mullite suspension was optimised and the process was determined based on the surface quality.

M. J. Garcia-Vergas (2007) presented a study on the short and mid-term corrosion behaviour (100h and 1000h respectively) of different materials (two austenitic and three ferritic steels) with Cr molar fraction of around 20%. The temperature selected for the study was 800°C in both dry and humid air (10% absolute humidity). In situ X-ray diffraction (XRD) was used to measure the oxidation rate and the stresses appearing within the scale during the first 100 h of exposure. One of the problems observed in the use of these materials is Cr migration from the scale formed to the cathode of the cell, which reduces notably the system performance. In order to reduce this problem, two spinal protective coatings were developed. These coatings were developed using Atmospheric Plasma Spray (APS) on several samples of two selected materials. A second contact layer was deposited on the top of the protected layer, using Wet Powder Spray (WPS) in order to favour the contact with the cathode. Short and mid-term corrosion behaviours were characterised, without detecting any Cr migration. The Area Specific Resistance (ASR) of these coated samples was measured, obtaining stable low values.

E. Garcia et al (2009) two powder processing routes Spray Drying (SD) and Flame Spheroidization (FS) were implemented for Mullite and mullite/ZrO2-7wt.%Y2O3 coatings. For each method the particle size, the morphology, and microstructure of the powder particles was determined. In addition, the effect of the heat treatment on the powder crystallinity and microstructure of FS powders was also investigated. To evaluate their suitability as feedstock materials, the powders were plasma sprayed and their in-flight particle characteristics monitored for coatings production. The powder morphology was correlated to the in-flight particle characteristics and splat morphology to gain insight about into the influence of powder characteristics on the coating formation.

F. Bezzi et al (2010) deposited mullite and barium-strontium-aluminosilicate (BSAS) coatings by slurry dip coating on SiC substrates. Slurries were prepared by suspending commercial powders in water or ethanol, using appropriate dispersants. Substrates were dipped into the slurry and subsequently dried and heat treated at high temperature to promote densification. SEM observations were carried out to investigate the microstructure of the obtained coatings and to evaluate crack formation, porosity and adhesion.

J. Guo et al (2010) obtained sodium carboxymethyl cellulose (CMC) porous scaffold using the slurry spray technique as a binder for silicon anodes that demonstrate remarkably improved cycling stability and rate performance. The slurry consisted of 52 wt% Si nano-particles, 12 wt% carbon black, and 36 wt% CMC using water as solvent. The slurry was sprayed onto the heated copper foil, and water evaporated instantly upon contact with the copper foil, thus a porous scaffold electrode was formed.

CONCLUSION

- Properties of mullitelike high-temperature and chemical stability at temperature, low thermal conductivity of 0.06 W cm−1 K−1, good thermal shock resistance, coefficient of thermal expansion makes mullite a prominent contenders for TBC's coatings.
- The published results show that APS and EB-PVD are most valuable techniques for deposition of TBC coatings on substrates.
- Future demand of working in high temperaturesin high speed engines and gas turbines with resistance to corrosion and erosion can be achievedby TBC's.
- However APS,EB-PVD, plasma spray, HVOF, cold spray, Electric arc spray, are generally adopted techniques, but a low cost technique like slurry spray technique (SST)is still tremendous scope for further coating development.
- Mullite based Thermal barrior coatings have strong technological potential and rapid industrial growth is expected over the next decade.

Despite this long and successful history , there has been a great interest among the engineers and scientist in developing new coating materials and researching phenomenon associated with the formation and application of TBC's.

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