Chapter 1

Introduction

1.1 The Gas Turbine Engine

The Gas turbine is an internal combustion engine that converts available heat energy into useful mechanical energy. Gas turbines are optimised to produce thrust force from the combustion exhaust gases to propel the passenger and armed flights [1, 2]. Figure 1.1 shows the main parts of the jet engine that includes cold and hot sections. The cold section of the jet engine has air inlet and compressor section, which receives air from atmosphere and compressed into high pressure.

The hot section of the jet engine consists of combustor chamber, gas turbine and exhaust nozzle. The high pressure air received from compressor is mixed with atomised fuel and then allowed to burn inside the combustion chamber. The combustion gases are allowed to expand through turbine by adiabatically to extract the energy. During adiabatic expansion through turbine blades, the gaseous energy is converted into useful mechanical rotational energy. The energy extracted combustion gases are exhausted through the nozzle and provides thrust to the jet, which moves the jet in forward direction.

The thermal efficiency of gas turbine is dependent with the hot gas inlet temperature. A higher the temperature is resulted in higher efficiency. But there is a limitation to increase the gas temperature to a unlimited level due to the melting point of superalloys, which are used to build the gas turbine. The melting point of super alloy is in the range of 1150 -1300 °C. Hence, the use of cooling system or protective coatings are suggested to protect the component from heat and to increase the component life. Figure 1.2 shows exploded view of commercial aircraft jet engine.
Fig. 1.1 Schematic cross sectional view of Jet Engine shows major components of cold and hot sections [Ref. 1]

Fig. 1.2 A Sketch of an aircraft gas turbine engine, the combustor and turbine structural components are protected by thermal barrier coatings (TBCs) [Ref. 1]
1.2 Gas Turbine Materials

The temperature and pressure of the turbine cycle determines the thermal efficiency of the turbine. The higher turbine entry temperature (TET) of hot gases results in higher thermal efficiency. Hence, the development of more efficient gas turbine relies on high temperature-high creep strength gas turbine materials, protective and thermal barrier coatings (TBCs). Among these, TBC are widely accepted system to increase the TET as well as the themodynamical efficiency [5].

The gas turbine components such as combustor, rotor, stator and nozzle guide vanes can be affected by high temperature creep, vibrational stress, hot corrosion, oxidation and erosion degradation mechanisms [6]. Hence, the alloy development for these components is the critical task and requires more attention. Different design criteria can be adopted for material selection to gas turbine. Light weight material and composites may be suitable choice for low pressure initial stage compressors, however, second stage compressors requires high pressure, temperature and creep resistant materials.

Combustor and turbine blade assembly are also subjected to high temperature creep and vibrational stresses. The material for combustor should have higher thermal stability at microstructural level and thermal conductivity as well as thermal expansion co-efficient must be low to keep the originality of the component size and shape. Apart from the thermal and vibrational stress, centrifugal stress is also exists in turbine blades at higher temperature, which can cause thermal fatigue. Superalloys, and in particular nickel based superalloys that are often used at the hottest parts of
turbine engines due to their excellent high temperature properties. Today, more than 50% of the weight of modern aero-gas turbine engines comes from superalloys.

The higher strength of nickel based super alloys were realized at the cost of poor oxidation and high temperature hot corrosion resistance. Hence, hot corrosion and oxidation resistance can be provided by the metallic surface coatings developed by diffusion or thermal spray processes. Further, heat protection for the metallic substrate can be provided by overlay porous natured coatings.

Thermal barrier coating (TBC) is a system, which consists of substrate, metallic bond coat and ceramic topcoat. Intermediate metallic bond coat provides oxidation resistance to the substrate and sufficient bond strength of the ceramic topcoat to the substrate. Ceramic topcoat protects the metallic component from high temperature. Figure 1.3 shows the increased temperature capability of gas turbine components made of nickel based super alloy combined with thermal barrier coatings. It can be concluded that TBCs can increase the TET temperature, thus improved turbine efficiency can be achieved.

Various protective coatings have been applied to the jet engine components (Fig. 1.4) to prevent erosion wear, fretting wear, abrasive wear [7]. Clearance control coatings are also applied to keep the dimensional stability of the rotating components in gas turbine. The thickness of the bond coat in TBCs can be varied from 20-150 μm, depending upon the application and processing route. The prerequisite for the metallic bond coat should protect the substrate by forming a dense $\alpha$-Al$_2$O$_3$ layer over its surface. Most of the bond coat materials contain a sufficient amount of aluminium to form this dense oxide layer.
Fig. 1.3 Temperature capabilities of Nickel based superalloy and TBC system [Ref. 9]

Fig. 1.4 Various parts of gas turbine applied with protective coatings [Ref. 10]

Aluminum oxide dense layer in TBCs can be called as thermally grown oxide (TGO), can be seen adjacent to the ceramic top coat. TGO form slowly and should be thermodynamically compatible with the ceramic thermal barrier at a given high temperature. The bond coat-TGO interface adhesion can be degraded by any
deleterious refractory elements coming out from the substrate. For that bond coat should act as a diffusion sink as well as chemical reservoir for thermally grown oxide formation.

Among the possible thermal insulating ceramic materials, Yttria stabilized zirconia (YSZ) is a favourable material for temperature reduction. Pure zirconia shows cubic phase structure at temperatures above 2370 °C. A tetragonal phase structure has been observed in the temperature range of 1170 °C-2370 °C. Again, it transforms into tetragonal phase to monoclinic phase below 1170 °C, accompanied by a volume increase of 5% [8]. Transformation of tetragonal phase to monoclinic is diffusionless martensitic formation that makes the zirconia in to a very brittle and cracked material. This makes zirconia in its pure form is unsuitable for thermal barrier coatings. In order to prevent this phase transformation in zirconia, it can be alloyed with oxide stabilizers such as CaO, MgO, CeO₂, ScO₂, Y₂O₃, etc., Now researchers have been focused towards the low thermal conductivity and high coefficient thermal expansion candidate materials for future TBCs.

Rare earth oxide (REO) doped zirconates show promising results for TBC applications. Most of the REO doped zirconate have very high melting points, favourable thermal expansion coefficients and low thermal conduction properties. [9]. Hence, the present study motivates to prepare a rare earth oxide based TBC system that could endure more thermal cycling life. The present work aims to compare the commercially available yttria stabilized zirconia (YSZ) thermal barrier top coat ceramic material to our laboratory prepared thermal barrier candidate material lanthanum zirconate (LZ) in terms of microstructure, mechanical properties, thermal properties and thermal cycling performance.
1.3 Thermal Barrier Coating (TBC) Systems

The temperature reduction capability of the TBC system can be evaluated by using the following steady state thermal conduction equation,

\[ \Delta T = \frac{1}{kA} \Delta x \frac{dQ}{dt} \]  

(1.1)

Where, \( k \) is the conductivity, \( A \) is the cross-sectional area, \( \Delta x \) is the coating thickness, \( dQ/dt \) is the heat flux across the area. TBC system consisting ceramic topcoat provides better insulation against the high heat flux [11]. However, metals and alloys could not be considered for the heat insulation as the thermal conductivity of the metals and alloys increases with increasing temperature. Figure 1.5 shows the typical TBC system employed on turbine blade.

TBCs are widely used in higher operating temperatures to protect the metallic structures in gas turbine. In 1970’s, Air Plasma Sprayed (APS) magnesia stabilised zirconia based TBCs were developed to protect gas turbine combustion chamber walls with a NiCr or NiAl bond coat. After the extensive research carried out by NASA and the Original Equipment Manufacturers (OEMs), presently used 6-8 wt% YSZ on MCrAlY bond coats have been identified as a potential system for more highly thermally loaded parts like vane airfoils and vane platforms.

Electron beam physical vapour deposition (EBPVD) TBCs can be coated on turbine blade aerofoils (Fig. 1.2) because of its higher strain tolerance, better adhesion to the substrate and aerodynamically smooth surfaces. Though, the APS coatings are cheaper and have lower thermal conductivity than the EBPVD coatings, the aforementioned benefits attracts EBPVD TBCs for severe environments. However, for vanes and combustion chamber walls APS TBCs (Fig. 1.6) still perform adequately and relatively low production costs.
Fig. 1.5 Turbine blade coated with TBC system

Fig. 1.6 Combustor liner coated with APS TBC [Ref. 1]
1.3.1 Nickel based super alloys

The materials used for gas turbine components are expected to operate at high pressure and high temperature environment. To meet the above said requirements nickel based super alloys have been developed from group VIII A elements. These alloys can withstand at elevated temperature mechanical stresses and has higher surface dimensional stability. Therefore nickel based super alloys are widely used in land, marine and aerospace gas turbine application. Wrought Ni-Cr alloys to directionally solidified and single crystal are the recent developments of nickel based super alloy. Addition of Al and Ti can increase the higher temperature operating capability of nickel based super alloy and capable to work up to its 0.8 melting point [12].

1.3.2 Bond coat

To meet the functional requirements of the bond coat in gas turbine, it should be manufactured with the desired composition. Bond coat manufacturing processes can be divided into two ways: diffusion coatings and overlay coatings. Diffusion coatings can be performed in two ways such as vapor phase aluminizing (VPA) and chemical vapor deposition (CVD) processes. In both cases, components to be coated is kept in a high temperature retort, need not to be placed in a pack.

Aluminium bearing vapors transported to the retort through the inert gas medium. Through the interdiffusion process, bond coat structure evolves at high temperature environment. The product of interdiffusion between the superalloy and aluminium source is called aluminide coatings (Fig. 1. 7 (a)), but there is a chance of phase changes or elemental migration that are detrimental effect to the coatings performance.
Though, the aluminide coatings protects the gas turbine components from oxidation, the effectiveness of the coatings under cyclic thermal loading is poor due to the constant depletion of Al in the aluminide coating leads to reduced oxidation resistance. Hence, researchers have modified aluminide coatings by adding reactive elements such as Ce, Y, Cr, Pd, Pt, Rh, Hf and Ir to improve higher temperature oxidation resistance of the jet engine components such as vanes and blades.

Among the investigated materials, Pt in the aluminide bond coats enhances turbine components high temperature oxidation resistance by forming protective oxide adhesion scale during high temperature exposure. Addition of Pt is believed to be reduce the segregation of the harmful elements such as S in the bond coat and also induces the formation of peg in the protective oxide scale thereby improved adhesion to the coated substrate [14]. Though, the Pt-alunidide coating (Fig. 1. 7 (b)) offers excellent oxidation resistance and cost effective, this process should be specifically designed for various super alloy compositions to avoid the brittle phase formation and fast growing secondary reaction zone (SRZ), find alternative process to deposit the bond coats [15].

Overlay coatings offer flexibility to tailor the coating composition to the required thickness (50-200 μm). There are number of processes exists to manufacture the MCrAlY bond coats with different density and low oxide content. High quality MCrAlY coatings to be produced by EBPVD, but this process costly one and requires maintenance. An alternative to EBPVD, low pressure plasma spray (LPPS) developed to produce oxide free dense coatings (Fig. 1. 7 (c)). But the cost associated with LPPS to manufacture coating is huge that requires vacuum chamber [17].
(a) Aluminized bond coat [Ref. 13]  (b) Pt-aluminized bond coat [Ref. 16]

(c) Vacuum plasma sprayed NiCrAlY bond coat [Ref. 17]  (d) Atmospheric plasma sprayed NiCrAlY bond coat [Ref. 17]

(e) High velocity oxy fuel sprayed CoNiCrAlY bond coat [Ref. 18]

Fig. 1.7 Microstructure of bond coats produced by different manufacturing processes
To overcome these difficulties, atmospheric deposition processes has emerged as a low cost alternative to EBPVD and LPPS processes. Presently, atmospheric plasma spray (APS), high velocity oxy-fuel (HVOF) have been used to deposit MCrAlY at higher deposition rate. APS deposits (Fig. 1.7 (d)) contains significant amount of pores and oxides, whereas HVOF deposits have low porosity and nearly oxide free coating structure [18]. (Fig. 1.7(e)). The trend enables the atmospheric deposition of dense coatings with limited oxidation of the most reactive elements. To attain this some new processes like cold gas dynamic spraying (cold spray) and activated combustion high-velocity air fuel (HVAF) spraying emerged recently.

1.3.3 Top coat

6–8 wt% (3.4–4.5 mol%) Y₂O₃ partially stabilized zirconia is a widely used ceramic topcoat material to protect the hot section components. But, it experiences phase instability at high temperature for long term exposure. This provides the opportunity to identify new materials for TBC applications with high phase stability.

Presently, researchers have tried to identify the low thermal conductivity with high thermal expansion coefficient candidate material for TBC applications. Figure 1.8 shows the thermal conductivity of emerging thermal barrier coating materials. Numerous ceramic materials were analysed for the TBC application that includes A₂B₂O₇ (A₂=Gd, La, Y, Sm, Nd; B₂=Hf, Ti, Zr), etc.

Researchers have attempted to explore the possibilities of rare earth zirconates having a general formula A₂B₂O₇ (where Re is a rare earth element) as TBC material due to its lower thermal conductivity than yttria stabilized zirconia.
(a) Temperature dependent  
(b) Temperature independent

Fig. 1.8 Thermal conductivities of proposed materials for TBC’s applications [Ref. 19]

Fig. 1.9 Effect of A and B cation ionic radius on thermal conductivity for pyrochlore $\text{A}_2\text{B}_2\text{O}_7$ [Ref. 19]
Table 1.1 Important thermo physical and mechanical properties of A₂B₂O₇ and YSZ TBC materials [Ref. 8, 11]

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal conductivity at 700 °C (W m⁻¹K⁻¹)</th>
<th>Thermal expansion coefficient (10⁻⁶/°C)</th>
<th>Elastic modulus (GPa)</th>
<th>Hardness (GPa)</th>
<th>Density (g/cc)</th>
<th>Maximum operating temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd₂Zr₂O₇</td>
<td>1.6</td>
<td>11.6</td>
<td>205</td>
<td>10</td>
<td>7.0 pyrochlore</td>
<td>1575</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.9 fluorite</td>
<td></td>
</tr>
<tr>
<td>Nd₂Zr₂O₇</td>
<td>1.6</td>
<td>-</td>
<td>219</td>
<td>10</td>
<td>6.4</td>
<td>2300</td>
</tr>
<tr>
<td>Sm₂Zr₂O₇</td>
<td>1.5</td>
<td>10.8</td>
<td>231</td>
<td>11</td>
<td>6.7</td>
<td>2200</td>
</tr>
<tr>
<td>La₂Zr₂O₇</td>
<td>1.56</td>
<td>9.1</td>
<td>175</td>
<td>10.54</td>
<td>6.05</td>
<td>2573</td>
</tr>
<tr>
<td>7 YSZ</td>
<td>2.3</td>
<td>11</td>
<td>250</td>
<td>14</td>
<td>6.1</td>
<td>1425</td>
</tr>
</tbody>
</table>

Figure 1.9 shows the thermal conductivity simulation results of pyrochlore family. Pyrochlore structure can stable up to its melting point. It is observed that increasing radii of B cations in the pyrochlore structure reduces thermal conductivity. However, increasing A-cation radii shows only marginal effect. Thermal conductivity of the YSZ has been reduced by substituting Y³⁺ into the Zr⁴⁺ sites. Both the Zr⁴⁺ and Y³⁺ have similar atomic mass that creates point defect in the structure there by enhanced phonon scattering reduces thermal conductivity [19]. Table 1.1 shows the thermo physical and mechanical properties of A₂B₂O₇ (A₂=Gd, Sm, Nd, La, Y; B₂=Hf, Ti, Zr) and YSZ TBC materials.

Rare earth oxides can replace yttria that can further reduce the thermal conductivity of zirconia. Two or more oxides can be co-doped into zirconia to further
reduce the thermal conductivity. One must be trivalent oxide such as Gd₂O₃ or Yb₂O₃ and the other should be pentavalent oxide such as Nb₂O₅ or Ta₂O₅. By co-doping, Yb-Ta co-doped zirconia has shown reduced thermal conductivity of 1.4 W m⁻¹ K⁻¹ at 900°C (7YSZ-2.2 W m⁻¹ K⁻¹).

![Graph showing thermal expansion coefficient vs. temperature for various materials](image)

**Fig. 1.10** Linear thermal expansion co-efficient of various A₂B₂O₇ TBC materials compared with 8YSZ [Ref. 20]

Although thermal conductivity of ceramic materials is the key factor for TBCs, it should be thermo-mechanically compatible with the substrate and bond coat. TBCs experience thermal stress due to different thermal expansion mismatch of substrate, bond coat and top coat (superalloy substrate-16×10⁶ K⁻¹; NiCrAlY-17.5×10⁶ K⁻¹; YSZ-10.7×10⁶ K⁻¹ at 1273 K). Figure 1.10 shows the coefficient of thermal expansion enhancement of TBCs top coat zirconia based ceramic materials by doping similar atomic radii cations in zirconia. It is believed that these materials reduces thermal expansion mismatch between the adjacent layers that will definitely increases the thermal cycling life [20].

**1.4 Thermal Spraying of Protective Coating**

By thermal spraying process, Wide range of materials can be deposited irrespective of substrate or feedstock material. Thermal spraying offers flexibility to
tailor the coating characteristics from low density to high density, gradual compositional variations from substrate interface to top of the coating surface. Apart from this, thermally spray coated components can be repaired easily by repairing coating without disturbing underlying metallic components. Present modern equipment requires thermal, corrosion, wear resistance and electrical protective coatings [21].

Thermal spraying process mainly classified based on the available heat energy utilized to melt the feedstock. They are combustion spraying and electric arc spraying. Flame spraying, high velocity oxyfuel spraying, detonation gun spraying process comes under the combustion spraying. Wire arc and plasma spraying are evident of electric arc spraying category. Feedstock can be fed in the form of either powder or rod to the heat source to develop the coating. Depending upon the enthalpy available in the process, the feedstock is propelled towards the substrate in either molten or semi molten condition. The accelerated molten particles impinges over the substrate and deform plastically to form the coating as layers (Fig. 1.11).

The enthalpy in the flame and gas velocity determines the materials to be melted in the process. The high enthalpy plasma spray melts the higher melting point ceramics for thermal protection and bio-ceramic applications. Higher gas velocity and medium enthalpy HVOF process are utilised to deposit tungsten carbide coatings for wear protection without decomposing.

1.4.1 Present Techniques for TBC Deposition

The layered microstructure of APS coatings are build up by impinging molten particle by particle over the previously deposited splats on the substrate as shown in Fig. 1.12. APS coatings have a non-homogeneous, layered structure, consisting of splats with a pancake-like shape.
Fig. 1.11 Schematic diagram of thermal spray coating deposition [Ref. 21]

Fig. 1.12 Plasma spray deposition of ceramic coatings [Ref. 22]
Porosity of plasma sprayed coating may be advantageous for low thermal conductivity TBCs. Porosity of coatings can be varied from 4-28 % by properly optimising the plasma spray parameters. Fine cracks between splats and voids are usual forms of porosity. The mechanical properties of plasma sprayed coatings such as microhardness and elastic modulus are usually lower than bulk ceramics. For example plasma sprayed YSZ coatings show 5-50 GPa of elastic modulus whereas 250 GPa for bulk zirconia. The lower elastic modulus of plasma spray coatings can accommodate the stress, which is developed during the service [22].

Recently, dense vertically cracked APS coatings are gaining importance to tolerate the strain caused by the thermal expansion mismatch between the bond coat and ceramic topcoat. APS ceramic coatings are applied in aircraft engine components such as stator vanes and combustors.

Excellent strain tolerance offered by the EBPVD TBCs attracts the modern advanced gas turbines. A vertical columnar fine-grained microstructure provide the mechanical compliance to the TBCs (Fig. 1.13). EBPVD coatings exhibit thermal conductivity in the range of 1.5-2.2 W/m K, whereas APS coating shows a lower value of 1.0-1.2W/m K for the same chemical composition of 6-8YSZ coatings [22]. Although APS coatings reduce the thermal conduction at initial stages, prolonged exposure of APS YSZ coatings experience sintering of topcoat that increases thermal conductivity of coating at later stages. Further, horizontally cracked APS coatings show less spallation resistance than the EBPVD TBC. Hence, higher spallation resistance of EBPVD TBCS promotes use in severe parts in aircraft engine components such as blades, vanes, etc. EBPVD TBCs are more durable but cost is also high.
Fig. 1.13 EB PVD coating process: (a – d) SEM images of EB-PVD coatings showing column tips [Ref. 22]

Fig. 1.14 A summary of the various mechanisms that can cause spalling of the TBC on turbine airfoils [Ref. 23]
1.5 Failure Modes and Microstructural Changes

Testing and evaluation of TBCs in a service environment is a major challenging task because actual TBC system operate in an extremely harsh, oxidative and corrosive high temperature environment. Apart from this within the TBCs, there are possibilities of interdiffusion between the layers and microstructural changes led to thermal assisted mechanical loading.

Sintering of 6-8 wt% YSZ also has detrimental effect to the coating system as it increases both the thermal conductivity and elastic modulus. Increasing thermal conductivity reflects on bond coat oxidation that promotes thermally grown oxide (TGO) formation which reflects on the durability of the TBCs under thermal cycle load. Degradation in the actual TBC systems cannot be predicted by laboratory level experiments. Hence, it is important to develop the evaluation methods to understand failure of the TBCs in a working environment through sensors and non-destructive testing procedures that includes infrared imaging, Raman spectroscopy, thermography, impedance spectroscopy, acoustic emission, and luminescence sensing [23].

Some of the failure mechanisms in YSZ TBC coatings developed by APS have been identified from the literature and shown in Fig. 1.14. Interface cracking between the bond coat and TGO, Vertical and horizontal cracks within the ceramic topcoat, Coalescence of micro cracks leading to spallation near TGO thickness are evident from the figure. Some of the ways to impede the inevitable TBC spallation are reduced growth kinetics of TGO, improved toughness of the topcoat with modified microstructure, improved strain tolerance of the top coat, reduced roughness between the bond coat and thermally grown oxide interface (Fig. 1.14).
A double ceramic layer, with an overlay La$_2$Zr$_2$O$_7$ layer over YSZ has shown to improve the overall performance, compared to single layered YSZ coating [24]. Transferred arc plasma (TAP) melting is a low cost and simple technique which can be effectively used to prepare thermal spray grade lanthanum zirconate powder from commercially available lanthanum oxide (La$_2$O$_3$) and zirconium oxide (ZrO$_2$) [25].

1.6 Brief Outline of the Thesis

The thesis contains nine chapters. The first chapter presents the details of ceramic materials and its applications, plasma spray deposition and thermal barrier coatings. A comprehensive literature review is presented in the second chapter. Scope and objectives of the present investigation are presented in the third chapter and the detailed experimental procedures used in this investigation is illustrated in the fourth chapter. The results and discussion of the experimental works are presented in chapters V to VIII. Fifth chapter deals with plasma spray deposition of YSZ. Sixth chapter deals with preparation and plasma spray deposition of lanthanum zirconate powder. Effect of thermal spray processes on microstructure, mechanical and thermal properties of NiCrAlY coating are analyzed in seventh chapter. Eighth chapter deals with effect of powder material on coating properties such as microstructure, mechanical and thermal properties. The important conclusions of the present investigation are presented in chapter nine.