Design of Thermal Barrier Coatings
A modelling approach
Mohit Gupta
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A modelling approach

Mohit Gupta
TIDIGARE AVHANDLINGAR

1. THOMAS WINMAN Transforming information into practical actions
   A study of professional knowledge in the use of electronic patient
   records in health care practice, 2012
2. PEIGANG LI Cold lap information in Gas Metal Arc Welding of steel
   An experimental study of micro-lack of fusion defects, 2013
3. NICHOLAS CURRY Design of Thermal Barrier Coatings, 2014
4. JEROEN DE BACKER Feedback Control of Robotic Friction Stir Welding, 2014
Dedicated to my beloved parents

Smt. (Late) Raj Kumari Gupta and Shri Ram Niwas Gupta
Acknowledgements

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Mohit Gupta

14th December 2014, Trollhättan
Populärvetenskaplig Sammanfattning

Nyckelord: Kraftgenererande gasturbiner; Gasturbiner för flygmotorer; Termiska värmebarriärskikt; mikrostruktur; Värmeledningsförmåga; Termiskt tillväxt oxid; Termisk utmattning livslägd; Modellering; design


Målet med detta avhandlingsarbete var att utforma ett optimerat TBC system med bättre värmeisolering och längre livslägd än de som används industriellt idag. Simulerings teknik användes i första hand för att uppnå detta mål. Arbetet genomfördes i två steg. Det första steget var att undersöka samband mellan beläggningarnas mikrostruktur och termomekaniska egenskaper, och att utnyttja dessa samband för att utforma en mer optimerad struktur. Detta steg utfördes genom att i första hand styra defekternas storlek och omfattning i toppskiktet. Det andra steget var att undersöka samband mellan ytstrukturen hos den tillväxande oxid (TGO skiktet) och spänningarna som bildas i gränszonen mellan bindskiktet och toppskiktet på grund av denna oxid, och att utnyttja dessa samband för att utforma ett skiktsysten med längre livslägd.

Abstract

Title: Design of Thermal Barrier Coatings – A modelling approach

Keywords: Thermal barrier coatings; Microstructure; Thermal conductivity; Young’s modulus; Interface roughness; Thermally grown oxide; Lifetime; Finite element modelling; Design

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Atmospheric plasma sprayed (APS) thermal barrier coatings (TBCs) are commonly used for thermal protection of components in modern gas turbine application such as power generation, marine and aero engines. TBC is a duplex material system consisting of an insulating ceramic topcoat layer and an intermetallic bondcoat layer. TBC microstructures are highly heterogeneous, consisting of defects such as pores and cracks of different sizes which determine the coating’s final thermal and mechanical properties, and the service lives of the coatings. Failure in APS TBCs is mainly associated with the thermo-mechanical stresses developing due to the thermally grown oxide (TGO) layer growth at the topcoat-bondcoat interface and thermal expansion mismatch during thermal cycling. The interface roughness has been shown to play a major role in the development of these induced stresses and lifetime of TBCs.

The objective of this thesis work was two-fold for one purpose: to design an optimised TBC to be used for next generation gas turbines. The first objective was to investigate the relationships between coating microstructure and thermal-mechanical properties of topcoats, and to utilise these relationships to design an optimised morphology of the topcoat microstructure. The second objective was to investigate the relationships between topcoat-bondcoat interface roughness, TGO growth and lifetime of TBCs, and to utilise these relationships to design an optimal interface. Simulation technique was used to achieve these objectives. Important microstructural parameters influencing the performance of topcoats were identified and coatings with the feasible identified microstructural parameters were designed, modelled and experimentally verified. It was shown that large globular pores with connected cracks inherited within the topcoat microstructure significantly enhanced TBC performance. Real topcoat-bondcoat interface topographies were used to calculate the induced stresses and a diffusion based TGO growth model was developed to assess the lifetime. The modelling results were compared with existing theories published in previous works and experiments. It was shown that the modelling approach developed in this work could be used as a powerful tool to design new coatings and interfaces as well as to achieve high performance optimised morphologies.
Appended Publications

In all papers, the co-authors participated in both the basic ideas behind the papers as well as writing the manuscripts. The modelling work in all papers was done by M. Gupta except Paper G where the code development for oxide growth model in ANSYS Fluent was done by U. Sand at EDR Medeso, Västerås. In Paper E, all experimental work was done by M. Gupta except the bilayer curvature measurements.

**Paper A.** Relationships between Coating Microstructure and Thermal Conductivity in Thermal Barrier Coatings – A Modelling Approach  
- I. Tano, M. Gupta, N. Curry, P. Nylén, and J. Wigren


**Paper B.** Design of Low Thermal Conductivity Thermal Barrier Coatings by Finite Element Modelling  
- M. Gupta, and P. Nylén


**Paper C.** Design of Next Generation Thermal Barrier Coatings — Experiments and Modelling  
- M. Gupta, N. Curry, P. Nylén, N. Markocsan, and R. Vaßen


**Paper D.** A Modelling Approach to Design of Microstructures in Thermal Barrier Coatings  
- M. Gupta, P. Nylén, and J. Wigren


**Paper E.** An Experimental Study of Microstructure-Property Relationships in Thermal Barrier Coatings  
- M. Gupta, G. Dwivedi, P. Nylén, A. Vackel and S. Sampath

Paper F.  Influence of Topcoat-Bondcoat Interface Roughness on Stresses and Lifetime in Thermal Barrier Coatings  
- M. Gupta, K. Skogsberg, and P. Nylén 

Paper G.  A Diffusion-based Oxide Layer Growth Model using Real Interface Roughness in Thermal Barrier Coatings for Lifetime Assessment  
- M. Gupta, R. Eriksson, U. Sand, and P. Nylén 
Surface & Coatings Technology, Accepted, in press

Paper H.  Stress and Cracking during Chromia-Spinel-NiO Cluster Formation in Thermal Barrier Coating Systems  
- R. Eriksson, M. Gupta, E. Broitman, P. Jonnalagadda, P. Nylén, and R. L. Peng 
Journal of Thermal Spray Technology, Submitted
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>2D</td>
<td>Two-Dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-Dimensional</td>
</tr>
<tr>
<td>APS</td>
<td>Atmospheric Plasma Sprayed</td>
</tr>
<tr>
<td>CMAS</td>
<td>Calcium-Magnesium-Alumino-Silicate</td>
</tr>
<tr>
<td>CSN</td>
<td>Chromia, Spinel and Nickel oxide</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of Thermal Expansion</td>
</tr>
<tr>
<td>DoE</td>
<td>Design of Experiments</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EB-PVD</td>
<td>Electron Beam – Physical Vapour Deposition</td>
</tr>
<tr>
<td>ECP</td>
<td>Ex-situ Coating Property</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FDM</td>
<td>Finite Difference Method</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Method</td>
</tr>
<tr>
<td>FOD</td>
<td>Foreign Object Damage</td>
</tr>
<tr>
<td>HVOF</td>
<td>High Velocity Oxy-Fuel</td>
</tr>
<tr>
<td>LOM</td>
<td>Light Optical Microscopy</td>
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<tr>
<td>LFA</td>
<td>Laser Flash Analysis</td>
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<tr>
<td>LPPS</td>
<td>Low Pressure Plasma Spraying</td>
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<tr>
<td>Micro-CT</td>
<td>Micro-Computed Tomography</td>
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<tr>
<td>MIP</td>
<td>Mercury Intrusion Porosimetry</td>
</tr>
<tr>
<td>OOF</td>
<td>Object Oriented Finite element analysis</td>
</tr>
<tr>
<td>PS-PVD</td>
<td>Plasma Spray – Physical Vapour Deposition</td>
</tr>
<tr>
<td>RQ</td>
<td>Research Question</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>SANS</td>
<td>Small-Angle Neutron Scattering</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SPPS</td>
<td>Solution Precursor Plasma Spraying</td>
</tr>
<tr>
<td>SPS</td>
<td>Suspension Plasma Spraying</td>
</tr>
<tr>
<td>TBC</td>
<td>Thermal Barrier Coatings</td>
</tr>
<tr>
<td>TCF</td>
<td>Thermal Cyclic Fatigue</td>
</tr>
<tr>
<td>TGO</td>
<td>Thermally Grown Oxide</td>
</tr>
<tr>
<td>VPS</td>
<td>Vacuum Plasma Spraying</td>
</tr>
<tr>
<td>XMT</td>
<td>X-ray Micro-Tomography</td>
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<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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<td>YSZ</td>
<td>Yttria Stabilised Zirconia</td>
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**Paper H.** Stresses and Cracking during Chromia-Spinel-NiO Cluster Formation in Thermal Barrier Coating Systems
1 Introduction

Thermal barrier coating systems (TBCs) are widely used in modern gas turbine engines in power generation, marine and aero-engine applications to lower the metal surface temperature in combustor and turbine section hardware. Application of TBCs can provide increased engine performance/thrust by allowing higher gas temperatures or reduced cooling air flow, and/or increased lifetime of turbine blades by decreasing metal temperatures. TBC is a duplex material system consisting of an insulating ceramic topcoat layer and an intermetallic bondcoat layer. It is designed to serve the purpose of protecting gas turbine components from the severe thermal environment, thus improving the efficiency and at the same time decrease unwanted emissions. Turbine entry gas temperatures can be higher than 1500 K with TBCs providing a temperature drop of even higher than 200 K across them (Ref 1). TBCs were first successfully tested in the turbine section of a research gas turbine engine in the mid-1970s (Ref 2).

Improvement in the performance of TBCs remains a key objective for further development of gas turbine applications. A key objective for such applications is to maximize the temperature drop across the topcoat, thus allowing higher turbine entry temperatures and thus, higher engine efficiencies. This comes with the requirement that the thermal conductivity of the ceramic topcoat should be minimized and also that the value should remain low during prolonged exposure to service conditions. In addition to this, longer lifetime of TBCs compared to the state-of-the-art is of huge demand in the industry. In case of land-based gas turbines, a lifetime of around 40,000 hours is desired. Therefore substantial research efforts are made in these areas as TBCs have become an integral component of most gas turbines and are a major factor affecting engine efficiency and durability.

The coating microstructures in TBC applications are highly heterogeneous, consisting of defects such as pores and cracks of different sizes. The density, size and morphology of these defects determine the coating’s final thermal and mechanical properties, and the service lives of the coatings (Ref 3-6). To achieve a low thermal conductivity and high stain tolerant TBC with a sufficiently long lifetime, an optimization between the distribution of pores and cracks is
required, thus making it essential to have a fundamental understanding of microstructure-property relationships in TBCs to produce a desired coating.

Failure in atmospheric plasma sprayed (APS) TBCs during thermal cyclic loading is often within the topcoat near the interface, which is a result of thermo-mechanical stresses developing due to thermally grown oxide (TGO) layer growth and thermal expansion mismatch during thermal cycling. These stresses induce the propagation of pre-existing cracks in as-sprayed state near the interface finally leading to cracks long enough to cause spallation of the topcoat (Ref 7-14). The interface roughness, although essential in plasma-sprayed TBCs for effective bonding between topcoat and bondcoat, creates locations of high stress concentration. Therefore, understanding of fundamental relationships between interface roughness and induced stresses, as well as their influence on lifetime of TBCs is of high relevance.

The traditional methodology to optimise the coating microstructure is by undertaking an experimental approach. In this approach, certain set spray parameters are chosen based on prior experience with the equipment and process, or as is the case quite often, spray parameters from a factorial design experiments are chosen. Thereafter, coatings are deposited using these parameters and evaluated by different testing methods. This procedure could be iterated until the specified performance parameters are obtained. As it might be apparent, this experimental approach is extremely time consuming and expensive, apart from the drawback that it does not enhance our knowledge of quantitative microstructure-property relationships.

Therefore, derivation of microstructure-property relationships by simulation would be an advantage. Simulation approach, apart from being time-saving and cost-effective, is highly useful for establishment of quantitative microstructure-property relationships. New coating designs can be developed and analysed with the help of simulation in a much easier manner compared to the experimental approach. Another advantage of using simulation is that the individual effects of microstructural features (such as defects, roughness profiles, etc.) could be artificially separated and analysed to study their effect on properties of TBCs independently which is not possible by experimental methods. However, it must be noted here that the relationships between process parameters and microstructure have to be established via an experimental approach (Ref 4, 6). A simulation approach is schematically described in figure 1 showing the steps required to achieve a high performance TBC requiring low thermal conductivity and long lifetime. It should be noted that the microstructural parameters for modelling are obtained through the link with experimental spray parameters during the optimisation routine via process maps as described further in section 3.4.
Figure 1. A schematic block diagram showing the steps required to obtain a high performance TBC.
2 Objective

The aim of this work was to design an optimised TBC which exhibits low thermal conductivity, high strain tolerance and long lifetime compared to the state-of-the-art coatings used today industrially for gas turbine applications. Simulation technique was the primarily utilised tool in this work.

The objective of the research work performed in this study can be described by the following research questions (RQs):

1. What are the fundamental relationships between TBC topcoat microstructure and thermal-mechanical properties of TBCs, and how can these relationships be utilised to design an optimised microstructure resulting in low thermal conductivity and long lifetime of TBCs?
2. What are the fundamental relationships between topcoat-bondcoat interface roughness, TGO growth and lifetime of TBCs, and how can these relationships be utilised to design an optimal interface resulting in long lifetime of TBCs?

![Figure 2. A schematic illustrating the relationships between TBC characteristics and properties. The effect of changing chemistry is not included.](image)

A schematic illustrating the relationships between TBC properties and characteristics as well as highlighting the RQs is shown in figure 2.
2.1 Scope and Limitations

The present study is general in itself as it is based on analysis of microstructure images and roughness profiles, and is not dependent on material or equipment used to fabricate them. However, other factors might have to be considered if this study is applied to other materials or coating applications.

The limitations in this work can be broadly divided in the following categories:

(i) Process

The study was limited to APS for topcoats and mainly High velocity oxy-fuel (HVOF) spraying for bondcoats using powder feedstock. The effect of varying bondcoat spray parameters on bondcoat microstructure and surface roughness was not considered.

(ii) Material

Only one topcoat material, namely zirconia, was used with different stabilisers such as yttria and dysprosia. NiCoCrAlY was used as the only bondcoat material.

(iii) Experimental evaluation techniques

The experimental analysis performed in this work was limited to the scope of the used technique. Microstructure was evaluated with light optical microscopy (LOM) and scanning electron microscope (SEM) which could be incapable of detecting all fine pores and cracks present in the microstructure. Lifetime testing was limited to TCF testing.

(iv) Modelling

The effect of changing chemistry was not considered in this work. The microstructure considered in this work consisted of only the defect morphology. The thermal-mechanical properties modelled in this work were thermal conductivity and Young’s modulus. Lifetime assessment considered in the modelling work was based on thermal cyclic fatigue (TCF) testing.

Most of the material properties used in the modelling work were considered to be temperature independent even though the properties could change significantly over the wide range of temperature considered. As the focus was set on qualitative analysis rather than on predicting exact values, this assumption
was considered to be valid in this case. The effect of radiation was not considered when predicting thermal conductivity as it can be assumed to be scattered due to the porous microstructure.

Two-dimensional (2D) domain was considered in several models used to determine coating properties which could affect the final values, though it can be used effectively for comparative purposes. Virtually designed microstructures were limited by the scope of the software used. Focus was placed on the individual influence of microstructural features on the final properties of the coating.

The effect of coating thickness was not considered in the stress analysis model. The failure mechanism considered in the modelling work was limited to spallation of coating due to thermo-mechanical stresses; other failure mechanisms such as erosion, etc. were not considered.
3 Background

3.1 Thermal Spraying

Thermal spraying is a branch of surface engineering processes in which metallic or non-metallic coating material (in powder, wire or rod form) is heated to a molten or semi-molten state, and then propelled towards a prepared surface by either process gas or atomization jets. These particles adhere to the surface and build-up to form a coating. The workpiece on which the coating is deposited, or the substrate, remains unmelted.

The credit for inventing thermal spraying process belongs to M. U. Schoop (Zurich, Switzerland) (Ref 15) who, along with his associates, developed equipment and techniques for producing coatings using molten and powder metals in early 1900s. The process was initially called ‘Metallization’. In 1908, Schoop patented the electric arc spray process. In 1939, Reinecke introduced the first plasma spraying process. Advancements in thermal spray equipment technology saw much higher pace after 1950s. Different variations of thermal spray technique exist today, such flame spraying, HVOF, APS and vacuum plasma spraying (VPS), etc.

A major advantage of thermal spraying is that it can be used to deposit a wide variety of materials without a significant heat input. In theory, any material that melts without decomposing can be used for spraying without any undue distortion of the part. A major disadvantage is that thermal spraying is a ‘line of sight’ process, although new processes such as plasma spray-physical vapour deposition (PS-PVD) allow even shadowed areas to be coated (Ref 16).

3.1.1 Atmospheric plasma spraying

Plasma is an electrically conductive gas containing charged particles. When a gas is excited to high energy levels, atoms loose hold of some of their electrons and become ionised producing plasma containing electrically charged particles (ions and electrons) with temperatures ranging up to 20,000 K. The plasma generated for plasma spray process usually incorporates one or a mixture of argon, helium, nitrogen, and hydrogen. The advantage of plasma flame is that it supplies large
amounts of energy through dissociation of molecular gases to atomic gases and ionisation.

Figure 3. A photograph taken during atmospheric plasma spraying process

A typical plasma spray process can be described in the following steps-

- First, a gas flow mixture (H₂, N₂, Ar) is introduced between a water-cooled copper anode and a tungsten cathode.
- A high intensity DC electric arc passes between cathode and anode and is ionised to form a plasma to reach extreme temperatures.
- The coating material in the form a fine powder conveyed by carrier gas (usually argon) is introduced into the plasma plume formed due to the flow gases via an external powder port and is heated to the molten state.
- The compressed gas propels the molten particles towards the substrate with particle velocities ranging from 200-800 m/s.

Figure 3 shows a photograph taken during the plasma spray process showing the different components of the spraying unit.

Materials suitable for plasma spraying include zinc, aluminium, copper alloys, tin, molybdenum, some steels, and numerous ceramic materials (Ref 15). The
advantage of using plasma spray process compared to combustion processes is that it can spray materials with very high melting points (refractory metals like tungsten and ceramics like zirconia). On the other hand, it has relatively high cost and increases the process complexity.

In some cases, it could be advantageous to perform plasma spray process under controlled environment under low pressure or vacuum, correspondingly termed as low pressure plasma spraying (LPPS) or VPS. The use of controlled environment could improve the coating quality due to reduced oxidation while spraying. However, these processes increase the costs for the set-up equipment as well as processing times, thus leading to significantly enhanced overall costs.

### 3.1.2 High velocity oxy-fuel spraying

In HVOF spraying, a mixture of a fuel gas (such as hydrogen, propane, or propylene) and oxygen is ignited in a combustion chamber at high pressures and the combustion gases are accelerated through a long de Laval (convergent-divergent) nozzle to generate a supersonic jet with very high particle speeds. This spray process generates extremely dense and well bonded coatings.

The coatings usually sprayed by HVOF process are hard cermets like WC/Co or Cr₂C₃/NiCr or MCrAlY (M = Ni and/or Co) applied as bondcoats to aircraft turbine blades (Ref 15). The advantage of using HVOF, apart from being suitable for making dense coatings, is that the coatings contain few oxides due to the low process temperature making it very attractive for TBC bondcoat applications.

### 3.1.3 Liquid feedstock plasma spraying

The limitation of minimum particles size which could be used for APS led to the development of plasma spray technology based on using liquid feedstock, mainly in the form of suspension or solution, correspondingly known as suspension plasma spraying (SPS) or solution precursor plasma spraying (SPPS). Since powders below 5 µm in size are difficult to feed and inject into the plasma torch, nanostructured coatings are obtained by dispersing/dissolving nano or sub-micrometric powder in a liquid media to create a suspension/solution respectively and using it as a feedstock (Ref 17). Suspensions are either based on water or an organic solvent in the form of alcohol which is typically ethanol. Solutions are typically made of nitrates or chlorides which are oxidised during the spray process forming an oxide particle that forms the coating (Ref 17).
3.2 Thermal barrier coatings

A typical TBC (schematically shown in figure 4) consists of an intermediate metallic bondcoat and a ceramic topcoat that provides the temperature drop across the coating. In addition to a low thermal conductivity, topcoats should also have phase stability during long term high-temperature exposure and thermal cycling. The present state-of-the-art topcoat material is a 6-8 wt.% yttria-stabilized zirconia (YSZ) ceramic applied usually with plasma spray on a bondcoat of NiCoCrAlY (Ref 15). YSZ has a low thermal conductivity compared to other ceramics such as alumina. Also, it is durable and chemically stable with a high melting point which makes it a good choice. Further benefits of this material are discussed in detail in section 3.5.1.

The ceramic top layer is typically applied by APS, electron beam-physical vapour deposition (EB-PVD) or SPS. Figure 5 summarizes a simplified comparison of APS, EB-PVD and SPS TBCs. The main purpose of the topcoat is to provide thermal protection. In addition, it should be susceptible to the thermo-mechanical stresses arising during the operating conditions.

The bondcoat provides improved bonding strength between the substrate and the topcoat. It also reduces the interface stresses arising due to the difference in coefficients of thermal expansion (CTEs) of ceramic topcoats and metallic substrates. As at high temperatures the porous ceramic topcoat is transparent to the flow of oxygen and the exhaust gases, an aluminium-enriched bondcoat composition is used to provide a slow growing, adherent aluminium oxide film known as TGO. TGO layer provides oxidation protection to the substrate as alumina has very low diffusion coefficients for both oxygen and metal ions.

**Figure 4. A typical thermal barrier coating system**

<table>
<thead>
<tr>
<th>Material</th>
<th>Layer (thickness)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-8% Y$_2$O$_3$-stabilized ZrO$_2$</td>
<td>Topcoat (~500 μm)</td>
<td>thermal insulation</td>
</tr>
<tr>
<td>MCrAlY [M=Ni or Co]</td>
<td>Bondcoat (~200 μm)</td>
<td>bonding of topcoat, oxidation protection</td>
</tr>
<tr>
<td>Ni-base superalloy</td>
<td>Substrate</td>
<td></td>
</tr>
</tbody>
</table>
3.3 Coating formation

Plasma sprayed coatings are built up particle by particle. Each individual molten or semi-molten particle impacts the substrate surface and flattens, adheres and solidifies to form a lamellae structure called splot. Unmelted particles are bounced back from the substrate reducing the deposition efficiency of the coating. When a spherical liquid droplet strikes a flat surface with a high impact velocity, it tries to flatten to a disc but the radially flowing thin sheet of liquid becomes unstable and disintegrates at the edges to form small droplets. This process is interrupted by rapid solidification in the case of plasma spray as the substrate is well below the melting point of the droplet, with a cooling rate as high as $10^6$ K s$^{-1}$ (Ref 18). Major part of the heat energy from the particle is transferred to the substrate by conduction and the solidification starts at the interface between the particle and the substrate. Heat transfer due to convection and radiation makes a small contribution at the conditions of plasma spray process (Ref 4).

Small voids exist between the splats, which can be formed due to incomplete bonding between splats owing to lack of adhesion, relaxation of the residual stresses mainly during the rapid cooling of the splot, or trapped gases. The real area of contact between splats is around 20% (Ref 18), due to which the properties of the coatings, such as mechanical, thermal and electrical properties, are very different compared to the sprayed bulk material. The major factors influencing the structure of a coating are the temperature, velocity and size distribution of the incident particles, apart from substrate temperature and roughness (Ref 19).
3.4 Process parameters

Plasma spray process is influenced by a number of process parameters. The dependence of microstructure on so many parameters has also been an enigma in terms of process control. A vast number of parameters need to be monitored and controlled, and several others are very difficult to control, such as electrode wear, humidity in surrounding air and fluctuations in controllable parameters. Several studies have been performed in the past emphasizing on examination of process-structure-property relationships based on process maps to overcome this drawback to some extent (Ref 4, 5, 20, 21). These process maps, however, are restricted to the specific spray gun, powder and all other parameters, except the ones varied to conduct the study, which makes implementation of the process maps from one gun to another rather difficult. Some of the process parameters in plasma spraying are presented in figure 6. The parameters indicated in red were altered as variables during this work.

![Diagram of plasma spray process parameters](image)

Figure 6. Plasma spray process parameters. The parameters indicated in red were altered as variables during this work.
3.5 Coating materials for TBCs

3.5.1 Topcoat

The ceramic topcoat provides thermal insulation to the substrate underneath. Some of the basic properties to be exhibited by the material used as topcoat are (i) low thermal conductivity, (ii) high melting point, (iii) phase stability, etc. The material most widely used as topcoat is 6-8 wt.% YSZ due to its low thermal conductivity, relatively high CTE and adequate toughness (Ref 22). Apart from YSZ, other ceramics which are used as TBC materials are mullite, Al₂O₃, TiO₂, CeO₂ + YSZ, La₂Zr₂O₇, pyrochlores, perovskites, etc. (Ref 23).

![Phase diagram for the zirconia-yttria system](Ref 25)

Figure 7. Phase diagram for the zirconia-yttria system (Ref 25)

Zirconia-ceramics are one of the very few non-metallic materials which have good mechanical properties as well as electrical properties, apart from having low thermal conductivity. These properties are exhibited due to the particular crystal structure of ZrO₂, which is principally a fluorite type lattice. Pure ZrO₂
has a monoclinic crystal structure at room temperature and undergoes phase transformations to tetragonal (at 1197°C) and cubic (at 2300°C) at increasing temperatures with a melting point of about 2700°C (Ref 23, 24). Figure 7 shows the phase diagram for the zirconia-yttria system. The Zr$^{4+}$-ions in the cubic-ZrO$_2$ have very low coefficients of diffusion as they are very immobile which gives ZrO$_2$ a very high melting point and good resistance to both acids and alkalis. On the other hand, the O$^{2-}$-ions are mobile due to the presence of vacancies, which makes the cubic phase ion conducting and thus providing it good electrical properties. The main sources of ZrO$_2$ in nature are zircon (ZrSiO$_4$) and baddeleyite. Apart from TBCs, ZrO$_2$ has widespread applications in fuel cells, jewellery (cubic- ZrO$_2$), oxygen sensors, electronics, etc.

The volume expansion which occurs due to the phase transformation from cubic ($c$) to tetragonal ($t$) to monoclinic ($m$) phases causes large stresses which will produce cracks in pure ZrO$_2$ upon cooling from high temperature. Thus, several oxides are added to stabilize the tetragonal and/or cubic ZrO$_2$ phases like yttria (Y$_2$O$_3$), ceria (Ce$_2$O$_3$), magnesium oxide (MgO), calcium oxide (CaO) etc. Specific additions of cations like Y$^{3+}$, Ca$^{2+}$ into the ZrO$_2$ lattice causes them to occupy the Zr$^{4+}$-positions in the lattice which results in the formation of anion vacancies in order to maintain the charge equilibrium.

YSZ is preferred to CaO or MgO stabilized zirconia for TBCs as YSZ coatings have been proved to be more resistant against corrosion (Ref 23). Also, YSZ coatings exhibit highest degree of resistance to coating failure due to spallation and an excellent thermal stability (Ref 26). Its major disadvantage is the limited operating temperature ($<1473$ K) for long-term application (Ref 23). At higher temperatures, the metastable $t'$-tetragonal phase, which is the main phase present at the room temperature, transforms first to tetragonal and cubic ($t + c$) phase and then to monoclinic ($m$) phase during cooling, which results in volume contraction, and consequently, formation of cracks in the coating (Ref 23). Also, as the YSZ coatings possess high concentration of vacancies, they facilitate oxygen transport at high temperatures which results in the oxidation of the bondcoat. This leads to the failure of TBCs due to spallation of the ceramic. The latter problem is solved by inducing the formation of oxidation resistant TGO layer between the topcoat and bondcoat by using alloys based on NiAl with various additions such as Cr, Co, Pt, Y and Hf as bondcoat material (Ref 22).

### 3.5.2 Bondcoat

The bondcoat provides oxidation protection of the substrate and improved adhesion of the topcoat. Some of the basic requirements from a bondcoat
material are (i) resistance to inter-diffusion with the substrate, (ii) high creep strength with suitable ductility, etc.

The typically used thermal sprayed bondcoat materials consist of a variety of MCrAlX alloys, where M=Ni and/or Co and X=Y, Hf, and/or Si (Ref 27). Nickel is added to enhance oxidation resistance while cobalt for corrosion resistance (Ref 28). Aluminium is added to bondcoat to act as a local aluminium reservoir to provide a slow growing TGO α-alumina during service conditions to provide oxidation protection. Alumina is preferred to other oxides due to its low thermal diffusivity and better adherence (Ref 29). Chromium is added to enhance oxidation and corrosion resistance (Ref 30). Yttrium is added to provide protection from sulphur diffusion into the coating by acting as a gettering site and promoting formation of alumina as well as its adhesion (Ref 29).

3.5.3 Thermally grown oxides

The oxidation of bondcoat in service conditions results in the formation of a TGO layer near the topcoat-bondcoat interface. The major oxide formed due to the oxidation of a typically used MCrAlY bondcoat is alumina. Other oxides which are usually formed are chromia ((Cr,Al)₂O₃), spinel (Ni(Cr,Al)₂O₄), nickel oxide (NiO), silica, etc. (Ref 31). Chromia, spinel and nickel oxide are usually abbreviated as CSN in literature. The oxidation of bondcoat has been recognised as one of the major causes for TBC failure (Ref 10, 31); it will be discussed in detail in section 4.5.
4 Characteristics of TBCs

The characteristics of TBCs are very different to that of the bulk material. Apart from the presence of several defects present in plasma sprayed coatings, the splat interfaces present in coatings are rough, resulting in multiple contact points ranging from micrometre to nanometre scale. These contact points can have very different bonding characteristics. These features have a significant implication on the macro-scale properties of TBCs.

4.1 Microstructure

As discussed earlier, the microstructure of APS ceramic coatings is significantly influenced by the process parameters. This influence results in a complex microstructure with various forms of porous features. Common features present in a ceramic coating are presented in figure 8. This image of coating cross-section has been taken by a SEM using backscattered electron detector mode which is a common technique used for analysing the microstructures in TBCs.

![Figure 8. SEM micrograph illustrating common features present in APS coating microstructures](image-url)
As it can be observed in figure 8, the microstructure consists mainly of large porous features, commonly referred to as globular pores, or simply pores, and several long and narrow porous features, commonly referred to as delaminations and cracks. They are also called interlamellar (delaminations, horizontally oriented) and intralamellar (vertical cracks or those non-horizontally oriented). It could be difficult to differentiate between delaminations and cracks, especially at lower magnifications, and so they are quite often simply referred to as cracks. Some fine scale porosity and partially melted particles can be also noticed in the microstructure image.

Globular pores are formed due to incomplete packing of the deposited particles or due to defects in the structure. This effect is magnified in the case of the low energy spray parameters since in that case the particles are unmelted/partially melted and so they do not flatten out adequately on impact. Delaminations are formed due to incomplete bonding between consecutively deposited particles, usually during successive passes of the spray gun. Cracks are formed due to the stresses developed within the coating when the sprayed particles cool down. The rapid cooling of particles results in large shrinkage which induces tensile stresses as the underlying material tries to prevent the shrinkage. These tensile stresses are released by the formation of cracks in the coating. Under appropriate spray conditions, vertical cracks in the coating can propagate to form long cracks orthogonal to the surface known as segmentation cracks. One such microstructure image is shown in figure 9.

**Figure 9.** Microstructure image showing vertical cracks in the coating
The individual splats have a typical columnar grain structure caused by the directional solidification of the particles. This structure can be typically observed in a fracture surface of the coating as shown in figure 10. It can be observed that the columnar grains grow as usual along the direction of heat flow from top to bottom (Ref 32). The grain structure and size depends on the processing conditions of the particles during spraying, and can vary significantly during service conditions which could affect the coating properties (Ref 28).

![Microstructure Image](image)

**Figure 10.** A microstructure image showing the fracture surface of the coating in as-sprayed condition *(Courtesy of Nicholas Curry)*

Thermal-mechanical properties and lifetime of TBCs depend mainly on the various microstructural features present in the topcoat. A thermal sprayed YSZ coating has a thermal conductivity around 0.5-1 W m⁻¹K⁻¹, as compared to the thermal conductivity of 2.5 Wm⁻¹K⁻¹ for bulk material (Ref 4). A large amount of pores and cracks perpendicular to the heat flow will provide better insulation properties to the coating (Ref 33). On the other hand, these horizontal cracks might propagate due to the thermal and mechanical stresses during operating conditions and eventually lead to failure of the coating by spallation (Ref 4). Segmentation cracks increase the flexibility of the coating as they help in relaxing the residual stresses within the coating (Ref 1). Again, on the other
hand, these vertical cracks enhance the thermal conductivity of the coating as they allow the flow of high temperature gases thus increasing the heat transfer to the substrate (Ref 1). To achieve a low thermal conductivity and high stain tolerant TBC with a sufficiently long life time, an optimization of microstructural features is required.

4.2 Heat transfer mechanism

4.2.1 General theory

The theory of heat transfer in crystalline solids is described very well in literature (Ref 34). It has been briefly reviewed in other sources as well (Ref 1, 35-37).

Heat energy can be transferred by three mechanisms in crystalline solids—electrons, lattice waves (phonons) and electromagnetic waves (photons) (Ref 35). The total thermal conductivity $\kappa$, which is the sum of the three components, can be expressed in general form as (Ref 35)-

$$\kappa = \frac{1}{3} \sum_{j=1}^{N} C_{p,j} \nu_j l_j$$  \hspace{1cm} (Eq. 1)

where $C_p$ is the specific heat at constant pressure, $N$ is the total number of energy carriers, $\nu$ is the velocity of a given carrier (group velocity if the carrier is a wave), and $l$ is the corresponding mean free path.

The electrons are capable of transferring energy only when they are free of interactions with the crystal lattice. This type of electrons is present only in metals and partly in metal alloys, especially at high temperatures. The electronic thermal conductivity part $\kappa_e$ is proportional to the product of the temperature and the electron mean free path, with $\nu_e$ being independent of temperature (Ref 35). The electron mean free path has two parts- residual mean free path, which is related to the scattering of electrons by defects, and intrinsic mean free path, which is related to the scattering of electrons by lattice vibrations. The residual mean free path is independent of temperature while intrinsic mean free path is directly proportional to temperature. At low temperatures, the electrons are mainly scattered by the defects, while as the temperature increases, the scattering mechanism by the phonons becomes more and more dominant. Therefore, the electronic component of thermal conductivity is proportional to temperature at low temperatures, becoming less dependent as temperature increases, and finally becoming independent of it at high temperatures (Ref 35).
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Lattice thermal conduction, or heat energy transport by phonons, occurs in all type of solids, with the phenomenon being dominant in alloys at low temperatures and in ceramics. At low temperatures ($T$), the component of thermal conductivity related to heat transport by phonons, $\kappa_{ph}$, may be represented by an exponential term $\exp(T^*/T)$, whereas it is inversely proportional to temperature at high temperatures (Ref 35). Here $T^*$ is the characteristic temperature of the material which is generally proportional to the Debye temperature. $\kappa_{ph}$ may also be expressed as (Ref 37)-

$$\kappa_{ph} = \frac{1}{3} \int C_v \rho \nu l_p$$  \hspace{1cm} (Eq. 2)

where $C_v$ is the specific heat at constant volume, $\rho$ is the density, and $l_p$ is the mean free path for scattering of phonons.

Heat energy transport by photon conduction (radiation) occurs especially at high temperatures in materials transparent to infrared radiation such as ceramics (over 1200-1500 K) and glasses (over 900 K) (Ref 35). The radiative component of the thermal conductivity, $\kappa_r$, can be expressed as (Ref 37)-

$$\kappa_r = \frac{16}{3} \sigma_s n^2 l_l T^3$$  \hspace{1cm} (Eq. 3)

where $n$ is the refractive index and $l_l$ the mean free path for photon scattering (defined as the path length over which the intensity of radiation will reduce by a factor of $1/e$), and $\sigma_s$ is the Stefan-Boltzmann constant.

In real crystal structures, scattering of phonons occurs due to their interaction with lattice imperfections in the ideal lattice, like vacancies, dislocations, grain boundaries, atoms of different masses and other phonons. Phonon scattering may also occur due to ions and atoms of different ionic radius as they distort the bond length locally, and thus, elastic strain fields might be present in the lattice. The phonon mean free path $l_p$ is defined as (Ref 37)-

$$\frac{1}{l_p} = \frac{1}{l_i} + \frac{1}{l_{vac}} + \frac{1}{l_{gb}} + \frac{1}{l_{strain}}$$  \hspace{1cm} (Eq. 4)

where $l_i$, $l_{vac}$, $l_{gb}$ and $l_{strain}$ are mean free path associated with interstitials, vacancies, grain boundaries and lattice strain, respectively. The intrinsic lattice structure and the strain fields mainly affect the phonon mean free path in conventional materials, with the grain boundary term having the least effect.

Thermal conduction in gases depends on the molecular mean free path, $\lambda$, of the gases. $\lambda$ is a function of temperature and pressure $P$, and is proportional to $T/P$ for ideal gas behaviour (Ref 1). The thermal conductivity of a gas, $\kappa_g$, in a constrained channel of length $d_c$ can be expressed as (Ref 1, 38)-

23
\[ \kappa_g = \frac{\kappa_g^0}{1 + BT/(d_vP)} \]  
(Eq. 5)

where \( \kappa_g^0 \) is the normal (unconstrained) conductivity of the gas at the temperature concerned, and \( B \) is a constant which depends on the gas type and the properties of the interacting solid surface (Ref 1).

### 4.2.2 Application to TBCs

In a real engine environment, TBCs protecting the substrate receive radiation which can be classified into following two categories– far-field and near-field radiation (Ref 36). Figure 11 shows the temperature distribution across a typical TBC system during service conditions from the hot gases in the combustor to the substrate.

**Figure 11.** Temperature distribution during typical service conditions across a typical thermal barrier coating system

Far-field radiation comes from the combustion gases which are at temperatures around 2000°C, having a spectral distribution same as that of a black body at that temperature. This far-field radiation makes a small contribution as the hot combustion gases have finite thickness and limited opacity and thus have
reduced emissivity, which results in the far-field radiation being reduced by a geometrical factor.

Near-field radiation comes due to the layer of cooler gas, at around 1200°C, which is adjacent to the topcoat. The topcoat ceramic surface, which is at a similar temperature as this gas layer, emits radiation which can pass through the partially transparent ceramic topcoat to the metallic bondcoat and the substrate. This near-field radiation contributes to the thermal conductivity of the ceramic and can affect it significantly at elevated temperatures (Ref 36).

The three important factors influencing the heat conduction in typical thermal sprayed coatings are the dimensions of the grains, the impurities and the porosity (Ref 35).

The grain dimensions depend on the solidification conditions of sprayed liquid droplets, which depends mainly on spraying technique, cooling of the substrate and the thickness of the sprayed coating (particles solidifying on previously deposited layers have lower solidification rates and thus larger grain sizes) (Ref 35). In case of oxides, however, the grain size might influence the phonon mean free path only at low temperatures, with the crystal structure being the major factor influencing mean free path rather than the grain size (Ref 35).

The typical impurities present in plasma sprayed coatings are, besides oxides, the copper and tungsten particles coming from the electrodes of the torch, and the sand blasted particles at the interface between coating and substrate. The effect of these impurities on thermal properties of coatings can be ignored if the electrodes are cleaned systematically and the substrate is cleaned after sand blasting (Ref 35).

The thermal conductivity of gas inside a pore is close to that of free gas if the dimensions of the pore are much larger than the mean free path \((L < 10\lambda)\), but it can fall significantly below the free gas value for even moderately fine structures \((L < \sim 1 \mu m)\) (Ref 1). Both pore thickness and gas pressure can affect the pore conductivity significantly, as well as the temperature (Ref 38). Convective heat transfer within the pores can be neglected for plasma-sprayed TBCs, as it is only likely to be significant if the pores are large \((L > \sim 10 \text{ mm})\) (Ref 1). Also, convective heat transfer through the porosity network can also be neglected, even though most porosity in TBCs is normally inter-connected (Ref 1).

As zirconia based ceramics are electronic insulators with electrical conductivity occurring only at high temperatures by oxygen ion diffusion, there is no contribution to thermal conductivity due to electrons. Thus heat transfer in
zirconia takes place only by lattice vibrations (phonons) or radiation (photons) (Ref 37). Adding yttria to zirconia modifies the lattice structure locally by introducing ion vacancies and generating local strain fields due to the incorporation of large dopant atoms, which results in lower intrinsic mean free path due to enhanced scattering of phonons and thus, reduced thermal conductivity (Ref 37). The radiative heat transfer part in zirconia-based plasma-sprayed TBCs becomes significant only at temperatures above ~1500 K, and thus was neglected in the present modelling work (Ref 1). The contribution from radiation depends on the radiation scattering length, which increases as the grain and pore structure coarsens and inter-splat contact area increases as well as the coating thickness increases (Ref 1, 39).

4.3 Mechanical behaviour

4.3.1 Stress formation

The residual stresses in APS coatings in the as-sprayed condition arise due to two main factors (Ref 40, 41):

(i) **Quenching**: These stresses arise due to the rapid solidification of single particles during spraying while their contraction is restricted by the adherence to the substrate. Due to the temperature difference between the substrate and the particles, tensile stresses are generated in the particles known as quenching stresses.

(ii) **Thermal mismatch**: These stresses arise due to mismatch in CTE of the coating and the substrate during cooling after spraying. As ceramic topcoats have much lower CTE than the metallic substrates, the CTE mismatch results in compressive stresses in the coating as the substrate shrinks more during cooling.

The stress state in the coating is due to the combination of the above two factors leading to stress generation in APS coatings. In addition, several other factors could also attribute to the final stress state in the coating, such as temperature gradients during and after deposition, stress relaxation processes (plastic deformation, cracking, etc.), phase transformations, chemistry changes, etc. (Ref 41). In general, topcoats in TBCs have low residual stresses in as-sprayed condition mainly due to the brittle nature of the ceramic which results in stress relaxation (Ref 42).

The stress state in TBCs during service conditions changes as the TGO layer is gradually formed; this phenomenon is discussed in detail in section 4.5.
4.3.2 Young’s modulus

The mechanical properties of thermal sprayed coatings are highly dependent on the microstructure as it is significantly different to that of conventionally processed materials. The elastic modulus or Young’s modulus and Poisson’s ratio are the basic parameters associated with mechanical behaviour of materials from an engineering context.

Young’s modulus is the most commonly used parameter in industry for TBCs to describe their mechanical behaviour. It determines the coating’s response under a state of tension or compression. Young’s modulus is required to evaluate the parameters describing the material mechanics in TBCs such as thermal stress, residual stress, etc.

Most of the studies on mechanical properties of TBCs have been based on evaluating Young’s modulus and elastic anisotropy at low stresses, apart from studies investigating hardness, creep behaviour etc. It has been observed that ceramics show up to three to ten times lower stiffness constants than the corresponding well sintered materials (Ref 43). Different Young’s moduli in different directions parallel and perpendicular to the surface have also been observed. This anisotropy is attributed to the preferred orientation of the planar defects present in the topcoat, which affects the local compliance substantially and results in a lower value of measured Young’s modulus (Ref 44). Analytical models have been also developed which explain this behaviour (Ref 43, 45). Similar behaviour in tension and compression was assumed in these models.

The evaluation of modulus provides indication of the coating integrity, porosity and bonding quality between splats. It also provides an idea of the thermal stress developed in the coating during operation since the modulus is roughly proportional to the induced thermal stresses (Ref 46).

4.3.3 Nonlinear properties

Recent developments have shown that ceramic coatings exhibit anelastic mechanical response (Ref 47, 48). Their behaviour both in tension and compression is strongly nonlinear. In general, increasing tensile stress results in a lower value of coating modulus (Ref 49). Generally, anelastic responses arise due to two factors: phase transformation or geometrical condition (Ref 48). Since YSZ coatings usually exhibit a stable tetragonal structure during the whole range of operating temperature, phase transformations should not occur. Thus the anelasticity should be due to the geometrical aspects of the coating.
The nonlinearity seems to be driven by unique microstructural features present in the TBCs, specifically micro-cracks and weak splat interfaces. The opening and closing of cracks and sliding of sprayed lamellae over each other gives rise to a nonlinear response. The apparent stiffness decreases with increasing tensile stress as the cracks faces open apart, while it increases with increasing compressive stress as the cracks faces are closed together. The frictional sliding of unbonded interfaces between the splats results in dissipated energy during the loading-unloading cycle thus giving rise to hysteresis.

The anelastic response of a APS YSZ coating during the bilayer curvature measurements using ex-situ coating property (ECP) sensor is shown in figure 12 (Ref 32); the measurement set-up details are discussed further in section 6.3. The coating, initially under a state of compression after deposition, is heated from room temperature to a certain temperature (stress transition from state A to B in figure 12). Due to the difference in CTE between substrate and coating materials, thermal mismatch stresses arise which result in the change of stress state in the coating from compression to tension during heating and then back to compression as the system is cooled down to the start temperature. Nonlinear behaviour of the coating during both heating and cooling part of the cycle can be clearly noticed, as well as the hysteresis in the stress-strain curve. It should be remarked here that the results exhibit nearly complete elastic recovery indicating anelastic response.

![Plasma Sprayed YSZ Coating](image)

**Figure 12.** Anelastic response of APS YSZ coating during bilayer curvature measurements (Ref 32)
4.4 Interface roughness

4.4.1 Roughness relationship with lifetime

Surface roughness is an essential requirement for an APS coating to adhere to the substrate (bondcoat in case of TBCs) on which it is sprayed. Mechanical anchoring is believed to be one of the key mechanisms responsible for adherence of the coating, which would be enhanced by higher surface roughness (Ref 50). If the roughness is too low, the coating adhesion will not be adequate. On the other hand, if the roughness is too high, large thermo-mechanical stresses would be induced on the topcoat, especially due to TGO growth, and the coating could spall off. Additionally, local aluminium depletion could occur near the local protrusions within the bondcoat close to the topcoat-bondcoat interface. This could result in formation of the fast-growing detrimental spinel oxides, and thus even higher stresses. Daroonparvar et al. showed this phenomenon experimentally where Ni infiltrated through the micro-cracks across the Al₂O₃ layer leading to the formation of mixed oxides (CSN) which formed protrusions in the TGO that initiate failure mechanisms of the topcoat (Ref 51). Thus an optimised surface roughness is required for achieving a TBC with long lifetime. Fauchais et al. have shown that the height of surface roughness hills must be about one-third to one half of the mean splat diameter for good adhesion of APS coatings (Ref 17). The ideal level of bondcoat roughness for APS topcoats for good adhesion of the coating is believed to be in the range $Ra = 6-12 \, \mu m$ (Ref 28). The bondcoat roughness could be influenced by the spray parameters as well the bondcoat powder feedstock size and size distribution (Ref 52-54).

Topcoat-bondcoat interface roughness is one of the important parameters which determine the lifetime of a TBC. Eriksson et al. studied this effect by considering four specimens with same chemistry but with different bondcoat roughness. It was observed that increasing $Ra$ resulted in a higher TCF lifetime (Ref 55). These results were in agreement with a detailed modelling work done earlier by Vassen et al. where it was concluded that lower roughness results in longer cracks near the topcoat-bondcoat interface, which would imply earlier failure (Ref 54). However, in another recent work done by Curry et al., two samples with same chemistry as well as similar $Ra$ were found to have significantly different lifetimes, which was understood to be due to the presence of different topographical features (Ref 56). These results show that the traditionally used $Ra$ is not sufficient to characterise the coatings and more sophisticated procedures should be used which could characterise the three-dimensional (3D) surface profile in a more precise way.
4.4.2 Stress inversion theory

A theory for crack propagation mechanism for APS TBCs has been proposed in earlier works, namely ‘stress inversion’ theory explained by using a simplified sinusoidal wave profile to represent the topcoat-bondcoat interface (Ref 54, 57, 58). According to the proposed theory, in the initial as-sprayed state without a TGO layer, tensile stresses exist in the hills while compressive stresses exist in the valleys within the topcoat near the topcoat-bondcoat interface as shown in figure 13(a). This stress state is inverted as the TGO layer grows during thermal cyclic loading as shown in figure 13(b). Thus, a crack starts from the hill and propagates to the adjacent valley as the TGO is formed joining the corresponding crack from other side eventually leading to the spallation of the topcoat as schematically illustrated by the dashed line in figure 13. The thickness of the TGO when the stress inversion takes place depends on several factors such as the loading conditions, geometry, and material (Ref 10, 59).

This effect which occurs due to different CTEs of different layers in the TBC could be explained by considering the bondcoat hill as small cylinder surrounded by a concentric cylindrical shell representing the topcoat and topcoat profile as small cylinder surrounded by a concentric cylindrical shell representing the bondcoat for the bondcoat valley (Ref 54). In the as-sprayed state, the metallic bondcoat contracts more due to higher CTE than the ceramic topcoat which leads to tensile stresses in the topcoat near the hills and compressive stresses near the valleys. After the TGO layer forms, the stress state can be understood by replacing the bondcoat by TGO in the concentric cylindrical shell model. Since the TGO is even more stiff (lower CTE) than
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topcoat, compressive stresses are now introduced in the topcoat near the hills and tensile stresses near the valleys. This explanation has been verified with the help of finite element modelling in several works (Ref 58, 60).

The stress inversion theory has been observed to follow the trend in earlier works when the time to stress inversion was compared to the experimental lifetime of TBCs. A 2D sinusoidal profile representing the topcoat-bondcoat interface roughness was used in finite element models by Vassen et al. to evaluate the residual stresses developed in TBCs and it was observed that the time to stress inversion was shorter for samples which failed earlier in experiments (Ref 54).

4.5 Oxide formation

As soon as the TBC is put into operating conditions, the bondcoat starts to undergo oxidation due to the exposure to high temperatures. The YSZ topcoat used typically in a TBC is transparent to oxygen due to two effects: (i) zirconia is transparent to oxygen flow due to the presence of vacancies, and (ii) the interconnected porosity network present within the topcoat allows free flow of oxygen (air). Therefore, the bondcoat metallic alloy is designed to act as a local aluminium reservoir allowing the formation of slow growing $\alpha$-alumina which could provide oxidation resistance to the substrate. Alumina is the primary and most stable oxide formed for a NiCoCrAlY bondcoat during operation (Ref 61). This is due to the fact that alumina has a lower formation energy than the other main element such as Ni, Co and Cr present in the bondcoat (Ref 30). The formation energy of alumina ($\Delta G^\circ$) is given by the following relationship:

$$\Delta G^\circ = R.T.\ln(a_{Al^{4/3}}P_{O_2})$$

(Refs. 30)

where $R$ is the gas constant, $T$ is the temperature in Kelvin, $a_{Al}$ is the activity of aluminium and $P_{O_2}$ is the partial pressure of oxygen. The activity of aluminium depends on the bondcoat composition.

The alumina layer is supposed to suppress the formation of other detrimental oxides during the extended thermal exposure in service thus improving lifetime of the TBC. However, other oxides such as CSN are formed at a later stage due to microstructural defects such as cracks present within the alumina layer and depletion of alumina within the bondcoat depending on several factors such as the composition of the bondcoat and the operating conditions as described by Eq. 6.
The oxide formation process at high temperatures typically during TCF testing is usually categorised in three stages (Ref 12, 30):

(i) **Transient stage:** In this stage, oxides form at a rapid rate. Almost all of the alloying element present in the bondcoat can be oxidised during this stage, the variety mainly dependent on the chemical composition and microstructure of the coating. This stage is typically very short; in the range of less than one hour for Ni-Cr-Al alloys above 1000 °C (Ref 62).

(ii) **Steady stage:** In this stage, alumina grows in a continuous and dense form linearly which acts as a protective layer. The alumina layer could be cracked or spalled off due to thermo-mechanical stresses and reformed (Ref 30).

(iii) **Acceleration stage:** When the aluminium content in the bondcoat becomes lower than a critical level, other mixed oxides such as CSN start to form aggressively leading eventually to failure.

In case of alumina, the oxide growth is believed to be mainly driven due to two parallel diffusion mechanisms: inward diffusion of oxygen, mostly along grain boundaries, towards the TGO-bondcoat interface and outward diffusion of aluminium along the already formed alumina particles towards the topcoat-TGO interface (Ref 61). However, it is generally accepted that the inward growth of alumina is the pre-dominant step and the reaction occurs primarily at the bondcoat-TGO interface (Ref 8, 63).

The growth of the TGO layer causes stress in the TBC both due to swelling of TGO resulting in ‘growth stresses’ as well as stresses generated due to the mismatch in CTEs between the different layers in the TBC. The growth stresses are usually relaxed quite quickly due to the high creep rates in the ceramic topcoat layer at elevated temperatures (Ref 10). However, the thermal mismatch stresses, generated especially near the topcoat-bondcoat interface when the TBC is cooled, could be detrimental and result in formation of cracks and/or elongation of pre-existing cracks near the topcoat-bondcoat interface which could eventually lead to failure (Ref 10).

The growth of mixed oxides is highly disadvantageous for a TBC as these oxides grow at a rapid rate and have an associated volume expansion which could result in very high growth stresses leading to spallation and thus, failure. It has been shown that these oxides form protrusions in the TGO which could initiate failure mechanisms of the topcoat (Ref 51). Bulky mixed oxide clusters may form from individual splats which are cut off from the rest of the bondcoat and quickly oxidise as they run out of aluminium. It has been observed in previous work that these oxide clusters are prone to cracking and CSN nucleated cracks.
would assist the crack coalescence process leading to the formation of large cracks that could result in spallation and thus failure (Ref 12). Eriksson et al. observed a significant reduction in TCF lifetime of TBCs which formed more CSN (Ref 55).

4.6 Failure mechanisms

Failure mechanisms in TBCs are very complex and are usually a mixture of several mechanisms. The primary failure method is spallation of the coating due to a fracture in the ceramic layer and/or the TGO layer. These types of failures occur if either the local stresses increase, the material strength decreases or a combination of the two. The stress can increase due to mismatch in CTE, temperature gradient and TGO formation. The changes in stress distribution induce the propagation of pre-existing cracks near the interface finally leading to cracks long enough to cause spallation of the topcoat. The formation of mixed oxides can significantly enhance the crack propagation and coalescence as discussed in detail in section 4.5. The topcoat could become more brittle due to sintering at high temperatures and/or propagation of cracks, while the bondcoat could become more brittle due to depletion of aluminium which would lead to growth of more brittle oxides.

Some of the other failure mechanisms of a TBC are: (i) damage induced by particle impact, such as erosion and foreign object damage (FOD), (ii) cracks formed due to the penetration of deposits of calcium-magnesium-alumino-silicate (CMAS) formed due to ingress of sand and dust present in the atmosphere into the turbine engine (Ref 64, 65).
5 Modelling of properties of TBCs

Since the macroscopic properties of TBCs are highly dependent on their microscopic structure, modelling of properties of TBCs consists of a representation of the present porosity dispersed within a solid phase. Several studies have been performed in the past using both analytical and numerical models for evaluating thermal-mechanical properties of TBCs; a few of them are discussed below.

5.1 Thermal conductivity

5.1.1 Analytical models

Since the end of 19th century, several analytical models have been developed for determining the thermal conductivity of multiphase solids, especially in porous materials. Brief reviews of such works have been done earlier (Ref 35, 38, 66-69). Most of these models consisted of randomly distributed non-interacting pores or ellipsoids, or periodic structures. The first model developed by Maxwell-Eucken was given as (Ref 35):

\[
\frac{k_{tot}}{k_d} = \frac{1-P}{1+0.5P}
\]

(Eq. 7)

where \(k_{tot}\) is the thermal conductivity of porous material, \(k_d\) is the thermal conductivity of dense material and \(P\) is the fraction of porosity; assuming that the thermal conductivity of pores \(k_p\) is small compared to \(k_d\). More recently, another model was developed by Klemens given as (Ref 70):

\[
\frac{k_{tot}}{k_d} = 1 - \frac{4}{3}P
\]

(Eq. 8)

Hasselman (Ref 33) developed a model which calculated the effect of cracks of various orientations on the thermal conductivity of solid materials. He concluded that maximum thermal insulation is obtained with cracks perpendicular to the direction of heat flow while cracks parallel to the direction of heat flow have no effect on thermal conductivity.
In this work, focus is placed on models based on plasma sprayed coatings.

The first analytical model for predicting thermal conductivity of plasma sprayed coatings was proposed by McPherson (Ref 71) which involved regions of good and poor contact between lamellae where the regions of poor contact act as thermal resistances. The model can be given as (Ref 71):

\[
\frac{\kappa_{\text{tot}}}{\kappa_d} = \frac{2f\delta}{\pi a}
\]  

(Eq. 9)

where \( f \) is the fraction of ‘true contact’, \( \delta \) is the lamellae thickness and \( a \) is the radius of individual contact areas. Li et al. (Ref 72) further developed this model and proposed quantitative structural parameters to characterize the deposit lamellar structure instead of porosity content, the most important parameter being the bonding ratio at the interfaces between lamellae. Thus, they incorporated the thermal resistance of the lamellae into the model. Boire-Lavigne et al. (Ref 73) also included the oxide layer resistance in the contact areas in the model. They used this analogy to determine the thermal diffusivity of plasma-sprayed tungsten based coatings, where the geometrical parameters were calculated from an image analysis procedure.

Bjorneklett et al. (Ref 74) compared experimental values of thermal diffusivity for ZrO\(_2\)-7% Y\(_2\)O\(_3\) and Al\(_2\)O\(_3\)-3% TiO\(_2\) plasma sprayed coatings with analytical models based on effective medium theories. Models representing three different microstructures were considered - a continuous ceramic with dispersed pores, a continuous ceramic matrix with continuously interconnected pores, and dispersed ceramic loosely bonded together. It was shown in this work that last two microstructure models conformed better to the theoretical values compared to the first one. This implied that the thermal conductivity model consisting of an agglomerate of ceramic particles behaves similar to reality compared to a solid ceramic sheet with pores. This behaviour is also in agreement with the formation process of a plasma sprayed coating.

Sevostianov et al. (Ref 75) developed a model which gave an explicit relation between the anisotropic thermal conductivities and the microstructure parameters of plasma sprayed TBCs. The microstructure was assumed to be composed of two families of penny-shaped cracks - horizontal and vertical. The orientational scatter was also accounted for in the model by an appropriate orientation distribution function. The effective conductivity was dependent mainly on the crack densities and their orientational scatters, and the overall porosity \( P \) played only a secondary role (Ref 75). The thermal conductivity in the direction perpendicular to the substrate was given by the expression (Ref 75):
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\[
\frac{\kappa_{\text{tot}}}{\kappa_d} = 1 - \frac{8\alpha_v}{3(1-P)}
\] (Eq. 10)

where \(\alpha_v\) is the component of crack density tensor in the direction perpendicular to the substrate that incorporates the crack densities of both pore families and their orientational scatters. An explicit correlation between elastic and conductive properties, dependent only on the elastic and conductive properties of the bulk material, was also derived later (Ref 45). The simplified expression is given as (Ref 76):

\[
\frac{E_d-E_{\text{tot}}}{E_{\text{tot}}} \approx 2.14 \frac{\kappa_{\text{tot}}-\kappa_d}{\kappa_d}
\] (Eq. 11)

where \(E_d\) is the Young’s modulus of bulk material and \(E_{\text{tot}}\) is the Young’s modulus in the direction normal to the substrate. More accurate correlations for the two cases of ideally parallel and randomly oriented cracks were also given later, which indicated that the actual cross-property factor would be slightly lower than the one in the last equation (Ref 77). Eq. 10 and Eq. 11 were also verified on YSZ coatings by using the image analysis data from photomicrographs of the coatings and comparing the predicted values to experimental values which were in good agreement (Ref 77).

Lu et al. (Ref 78) made a model which included different kind of pore morphologies- randomly oriented pores, aligned but spatially random pores, periodic pores and zigzag pores, with distributed pore shapes. Finite element method (FEM) was used to compute the conductivity related to zigzag pores. They applied the model on TBCs made by EB-PVD.

Golosnoy et al. (Ref 38) developed an analytical model which comprised of solid layers separated by thin, periodically bridged, gas-filled voids. The model was based on dividing the material into two independent zones- one characterized by unidirectional serial heat flow occurring through lamellae and pores, and the other by channelled conduction through the bridges between the lamellae. Radiative heat transfer and the effect of gas pressure inside the pores were also included in the model, and thermal conductivity was computed over a range of temperatures. Cipitria et al. (Ref 79) used this geometrical model to develop a sintering model based on application of the variational principle to diffusional phenomena. It also accounted for the effects of surface diffusion, grain boundary diffusion and grain growth. Good agreement was found between these two models and experimental results.
5.1.2 Numerical models

Hollis (Ref 80) developed a model using FEM to compute the thermal conductivity of VPS and APS tungsten coatings. The domain of the model was a 2D image recorded using SEM. The image was thresholded based on the grey scale level in the micrographs. The dark phase represented the pores while the light phase represented tungsten. A finite element mesh was created over the image. It was observed that VPS coatings were well represented by the 2D model while APS coatings were not due to their complex microstructure (Ref 80). A method to compensate for 3D pore structure effects was also proposed by choosing the maximum effective pore length (MEPL) for APS coatings, and sectioning and shifting the model prior to performing the node temperature calculation (Ref 80).

A finite difference method based approach was given by Dorvaux et al. (Ref 66) by developing software for the computation of the thermal conductivity of porous coatings from binary images of real material cross sections. This approach takes account of the complex morphology of the ceramic. It was used to determine the contribution of each pore family (globular pores, cracks etc.) to thermal insulating capabilities with the help of image analysis. It was concluded that major heat insulation is provided by the cracks oriented perpendicular to the heat flow direction (Ref 66). This approach was used later as an alternative to diffusivity measurements for ranking coatings according to their heat insulation capacity with regard to the morphology (Ref 81). It was also used to study the relationship between sintering effects and thermal conductivity increase, and to study the effect of pressure on thermal conductivity of TBCs (Ref 82). This approach was associated to a morphology generator to develop the software TbtcooL (ONERA, France) for building a predictive tool which can be used to generate plasma sprayed TBC like morphology. This tool has been discussed in detail in section 5.6.

Bartsch et al. (Ref 83) compared the results from finite-difference (TbtcooL) and finite-element simulations for determining the thermal response from binary images of EB-PVD TBC microstructures. It was observed that the results are more accurate with decreasing mesh size, and when the calculated section area of the microstructure image is larger. The finite-element codes resulted in higher conductivity values compared to finite-difference codes, for same sections and similar mesh width. It was concluded that finite-difference codes take less computer memory for calculations for larger models (Ref 83).

Kulkarni et al. (Ref 84) used small-angle neutron scattering (SANS) to study the effect of material feedstock characteristics (powder morphology) on the properties of plasma sprayed YSZ coatings. A 2D finite element model
representing the coating microstructure was built from the volumetrically averaged information available from the SANS data. The voids were divided into three families- interlamellar pores (assumed to hexagonal in shape), intrasplat cracks and globular or irregular pores. Aspect ratios were assumed for each void family and the volume fractions, mean pore dimensions and orientations were taken from anisotropic multiple SANS (MSANS) data. The predicted thermal conductivity was higher than the experimentally measured values due to lack of information on the splat boundaries and pore size distribution (Ref 84).

Tan et al. (Ref 85) used processed SEM images of coating microstructure to generate a 2D finite element mesh and predict the effective thermal conductivity using a commercial finite-element code for YSZ, molybdenum and NiAl coatings. It was observed that the modelling procedure was not sensitive to slight changes in the threshold level of the images. For YSZ coatings, the predicted thermal conductivity values were higher than the values measured by laser flash analysis (LFA), but they still followed the same trends, for both before and after annealing the coatings (Ref 85).

Liu et al. (Ref 86) developed a 3D finite element model which included spherical pores and unmelted particles, and ellipsoidal cracks, each inside a unit cell. The unmelted particles were assumed to be completely debonded from the substrate. The unit cell model was used to predict the thermal insulation behaviour of different features on YSZ plasma sprayed coatings.

Qunbo et al. (Ref 87) used digital image processing to create a finite element mesh over a real microstructure image to predict the thermo-mechanical properties of TBCs, and concluded that transverse cracks in the coating are most significant for thermal insulation.

### 5.2 Young’s modulus

#### 5.2.1 Analytical models

Li et al. (Ref 88) developed an idealized model for estimating Young’s modulus of thermal sprayed ceramic coatings consisting of the stacking of few micrometres thick lamellae using circular plate bending theory. Two components of elastic strain of the coating under tensile stress were considered in the model, one related to the localized elastic strain at the regions of contact area between lamellae, and the other related to the elastic bending of the lamellae between bonded regions. It was shown that the bending component
becomes significant only when the percentage bonding ratio between lamellae becomes less than 40%.

Sevostianov et al. (Ref 45) developed a model for Young’s modulus as a function of microstructural parameters similar to the one described in section 5.1.1 for thermal conductivity and proposed an equation as given below:

\[
E_{tot} = E_d \left[ 1 + \frac{8(4-\nu_0)(1-\nu_0^2)}{3(2-\nu_0)} \frac{\alpha_p}{1-p} \right]^{-1}
\]  
(Eq. 12)

where \( \nu_0 \) is the Poisson’s ratio of the material; other parameters are defined the same as in earlier equations.

Azarni et al. (Ref 89) investigated APS deposited alloy 625 coatings and compared the Young’s modulus measured by uniaxial tension test to several analytical models available for predicting Young’s modulus of porous materials and a finite element modelling technique OOF (discussed in section 5.5.2). A significant difference was observed between the predicted values by analytical models and experimentally measured values of the elastic modulus.

### 5.2.2 Numerical models

Michlik et al. (Ref 90) used a FEM approach using a finite element package OOF pre-processor to generate the mesh and employ an in-house developed solver using extended finite element method (XFEM). The XFEM approach accounted for the existence of cracks in TBCs which enabled to study the effect of sintering of coating on elastic modulus.

Amsellem et al. (Ref 91, 92) used both 2D and 3D analyses of APS microstructures to determine Young’s modulus of the coatings. 2D finite element meshes were created from SEM images of microstructures while 3D microstructures were obtained using X-ray microtomography (XMT). The limitations of both 2D and 3D modelling approaches were discussed and it was concluded that the 2D approach was suitable for characterizing mechanical properties due to the low resolution of XMT (Ref 91). 3D approach was assessed to be beneficial for studying the shape and orientation of pores as well as to simulate the stress concentration in the coating.

Apart from the numerical techniques discussed above, another finite element technique which has been used extensively to determine the thermal-mechanical properties of APS coatings is OOF, as described in section 5.5.2.
5.3 Interface roughness

The influence of topcoat-bondcoat interface roughness on thermo-mechanical stresses is of high relevance for understanding the failure mechanisms as well as assessing the lifetime of TBCs. Analysing the effect of interface roughness on stresses could be a tedious and extremely complicated task to perform experimentally. Therefore numerical modelling techniques are commonly used to understand these fundamental relationships. In most of the earlier works, a 2D or 3D sinusoidal wave profile has been chosen as a simplification to represent the topcoat-bondcoat interface (Ref 58-61, 93-104) to analyse the stress distribution in TBCs.

A crack propagation model was proposed by Bäker (Ref 59), Ranjbar-Far et al. (Ref 95) and Bialas (Ref 99) to analyse the stress distribution in TBCs by using a 2D wave profile to represent the topcoat-bondcoat interface. Ranjbar-Far et al. used uniform as well as non-uniform amplitudes to represent the wave profile and an inhomogeneous topcoat layer with an artificial lamellar structure. It was concluded that the cracking depends mainly on the interface morphology and the thickness of TGO layer.

Failure mechanisms were analysed by Evans (Ref 7) with the help of a 2D finite element model representing the interface as 2D sine wave profile. Lifetime prediction models were made by Vaßen et al. (Ref 10), Wei et al. (Ref 94), Brodin et al. (Ref 102) and He et al. (Ref 104) based on the growth of delamination cracks using a 2D sine wave profile for modeling the interface. The lifetime model by Vaßen et al. was based on the stress distribution analysis model developed by Ahrens et al. (Ref 60).

Kyaw et al. (Ref 93) used a 2D sine wave profile to represent the interface and incorporated temperature-dependency of material properties and sintering of topcoat in the finite element model. Qi et al. (Ref 96) used a 2D sine wave profile to represent the interface and attributed the stress distribution to the interface roughness and thermal mismatch. Asghari et al. (Ref 97) used a 2D semicircular profile to represent the interface with a nonlinear material model for topcoat implementing the effect of sintering. Hermosilla et al. (Ref 98) and Busso et al. (Ref 61) developed a couple microstructural-mechanical model using a 2D wave profile to represent the interface. The TGO growth was determined by a diffusion model in these studies.

Bednarz (Ref 100) did an extensive work in this field by using a 2D profile with different shapes such as sinusoidal, semicircular and elliptical. The major conclusion of this work was that the most significant parameters affecting the stress development during thermal cycling are time dependent material
properties of topcoat and TGO, TGO growth behavior and interface roughness. Jinnestrand et al. (Ref 58) developed a model using a 3D sine wave profile to represent the interface to analyze the stress distribution.

Ghafouri-Azar et al. (Ref 105) and Klusemann et al. (Ref 106) made a 2D model to analyze the residual stresses in tungsten carbide-cobalt (WC-Co) coatings sprayed by HVOF method. Micrograph images were used to define the coating as well as substrate geometry for the finite element model including the coating-substrate interface.

As it could be observed from the above references, the general research trend in the modelling approach in this field has been to develop the material models for individual layers and simulation conditions so as to represent the real simulation conditions in a more precise way (Ref 93). However, a simplified roughness profile might not lead to precise predictions as it does not incorporate the complex surface topography created during thermal spraying.

In a recent work by Nordhorn et al., finite element analyses of realistic 3D models captured using laser microscopy and multiple 2D models based on different interface approximation functions were performed to predict the thermally induced stress fields (Ref 107). The objective was to simulate the 3D reference stress fields using 2D models so as to reduce the required computational time to assess the stress fields. It was concluded in this work that the 3D model was too complex with respect to the geometric interface features to be replaced by a single 2D approximating function. However, the 2D models could correctly reflect essential TGO growth related features such as stress inversion.

5.4 Oxide formation

Visualisation of TGO growth in-situ by experimental methods is highly non-trivial. One of the destructive ways of capturing the TGO growth by experiments is to treat several samples of the same coating for different operating times until failure and then inspecting the cross-sectional microstructure. However, in this case the TGO growth cannot be analysed at the same location in the TBC sample as the area inspected will differ between the samples and may not contain the exactly same surface topography. A non-destructive way could be to perform Micro-computed tomography (Micro-CT) on a sample in several stages over the sample’s lifetime. This technique, apart from being extremely expensive and time-consuming, can be performed usually only on a very small sample with relatively low resolution. Thermography has
been successfully performed in the past to analyse the crack growth during lifetime testing, but a low resolution is obtained with this technique (Ref 108). High temperature X-ray diffraction (XRD) was used by Czech et al. to determine the thickness of TGO in-situ under isothermal conditions by measuring the intensity curves, but the TGO profile could not be detected with this technique (Ref 109).

As apparent from the above discussion, modelling of TGO formation would be highly beneficial since using experimental methods would be highly challenging. The conventional way of modelling TGO growth \( (d_{\text{TGO}}) \) as a function of time \( (t) \) and temperature \( (T) \) is described a parabolic growth law given as (Ref 10):

\[
d_{\text{TGO}} = A_{\text{TGO}} \cdot t^p \cdot \exp\left(-\frac{E_{\text{TGO}}}{k_BT}\right) \quad \text{(Eq. 13)}
\]

where \( A_{\text{TGO}} \) is TGO growth coefficient, \( p \) is TGO growth exponent, \( E_{\text{TGO}} \) is TGO growth activation energy and \( k_B \) is the Boltzmann constant. However, this parabolic growth law does not include the effect of bondcoat roughness on TGO formation. TGO growth models based on diffusion could thus provide a better reflection of the reality.

A few studies have been performed earlier to model the TGO layer formation based on diffusion of species. A multi-scale continuum mechanics approach based on a coupled diffusion-constitutive framework was implemented by Busso et al. to study the local stresses induced in TBCs using a parametric unit cell finite element model (Ref 61). A numerical model describing the TGO growth by an oxygen diffusion-reaction model was developed by Hille et al. to perform an analysis of a representative TBC system subjected to a thermal cycling process and to make a parametric study for different fracture strengths of the topcoat to determine its influence on the durability of a TBC system (Ref 8). A one-dimensional oxidation–diffusion model considering both surface oxidation and coating–substrate interdiffusion as well as aluminium depletion during operating conditions was developed by Yuan et al. to predict the lifetime of TBCs (Ref 110). A diffusion-reaction of aluminium and oxygen to form TGO in TBCs was studied through an analytical model by Osorio et al. and the results were compared to experiments to evaluate the TGO growth rate (Ref 111). However, all of the models discussed above did not incorporate the inherent TBC microstructure or the topcoat-bondcoat interface topography.

Apart from achieving fundamental understanding of the TGO growth phenomena, the development of TGO in-situ during thermal cyclic loading conditions needs to be implemented in a diffusion based model in order to evaluate stresses developed due to TGO formation. The following general
assumptions based on above references could be made for developing such model:

1. TGO growth occurs only during the dwell phase of the TCF testing.
2. The bondcoat mainly consists of aluminium and the TGO formed consists of pure alumina for a NiCoCrAlY bondcoat. Formation of other oxides can be neglected.
3. The reaction rate of aluminium and oxygen to form alumina is very high compared to the diffusion rates of the constituents.
4. The diffusion rate of oxygen within the topcoat can be considered to be very high since zirconia is transparent to oxygen flow as discussed in section 4.5.

5.5 Finite element modelling

The over-simplification of porosity description in the analytical models limits the predictive capacity and the certainty for the complex interconnected porous structures. Numerical schemes seem to be more promising in such cases as they involve a material structure which is close to the real structure (Ref 66, 89). In cases where the spatial geometry is too complex for the usage of analytical models, numerical modelling such as FEM or finite difference method (FDM) is beneficial.

Two important issues must be considered for numerical modelling of complex micro structural features present in APS coatings. First, the model sample volume must be large enough to contain sufficient micro structural details and hence represent the average property of the sample. Second, fine details of the micro structural features have to be captured within the model volume so that the actual properties are estimated precisely.

5.5.1 Basics of FEM and FDM

Both FEM and FDM are numerical approximation techniques to solve a set of equations which are typically not easily solvable analytically, for example due to complicated irregular geometry, complex material composition, etc. In both methods, the geometry is fractioned in small basic units, the problem is set-up individually in each basic unit, and then solved together to calculate the result. Only lines/squares/cubes can be used as basic units in FDM, while arbitrarily shaped basic units can be used in FEM thus enabling better and less complex description of the geometry. The FEM hence requires less computational power.
and has a better accuracy than FDM. In addition, FEM is more suitable as an adaptive method since it easily facilitates for local refinements of the solution.

FEM is applied to most engineering problems either by writing a custom made finite element program using softwares such as Matlab (MathWorks Inc., MA, USA) or by using an already developed commercial finite element program. Commercial finite element tools have a variety of built in features for modelling different engineering problems but the cost associated with purchasing these tools and learning the way how to use them is usually high. Custom made finite element programs might have a small cost initially but they handle a small variety of problems at a time and are less flexible. The solution of a finite element problem involves the construction a matrix equation of type $AX = B$ where $A$ is the stiffness matrix, $X$ is the vector containing all the unknowns and $B$ is the vector that depends on the boundary condition.

### 5.5.2 Image based finite element model

The possibility to determine a material’s macroscopic properties based on its microstructure is of great importance to material science. The object oriented finite element analysis (OOF) code, developed at the Center for Computational and Theoretical Materials Science (CTCMS) at US National Institute of Standards and Technology (NIST), enables complex two dimensional microstructures to be modelled using images of the actual microstructures. Its current version, OOF2, is available as public domain software (Ref 112). This technique has been employed extensively in recent years to simulate thermo-mechanical properties of APS coatings.

Wang et al. (Ref 113) compared the models based on SANS and OOF for predicting thermal conductivity of plasma sprayed YSZ coatings. The effect of splat boundaries on thermal conductivity was also discussed, and it was concluded that splat interfaces account for 25-60% of the total reduction in conductivity, with larger values for higher splat interface density coatings (Ref 113).

Jadhav et al. (Ref 114) used OOF and an analytical model to predict thermal conductivity of APS and SPPS coatings and compared them to the experimental values measured by LFA. It was concluded that OOF model fitted better with experimental values compared to the analytical model and it captured the effect of real microstructures on the thermal conductivities more accurately (Ref 114). The model was also used later to determine residual stresses in SPPS TBCs (Ref 115). The low value of predicted residual stresses depicted that the TBC microstructures produced by SPPS were strain-tolerant.
Bolot et al. (Ref 116) predicted thermal conductivity of AlSi/polyester coatings with two different numerical codes- TS2C (based on finite differences) and OOF. Some discrepancies between the values obtained were observed, why the code was developed further by changing the discretization method which gave better results (Ref 117).

5.5.2.1 Modelling procedure

OOF is very efficient in capturing the actual microscopic images and generating the required finite element meshes based on the colours present in the image (Ref 118, 119). Though it is limited to 2D images, it can be very useful in determining macroscopic properties of materials consisting of more than one phase.

The model geometry information for analysis is obtained from the microstructure image which is used as an input. Different phases/features present in the microstructure image are then grouped based on their colour and/or contrast. Each group of pixels can be assigned a specific material property. The microstructure images are usually represented in grayscale. Even though OOF2 offers several tools for creating pixel groups of a grayscale image, it is simpler to modify the image before using it in OOF2. For example, if there are two phases present in the image, the image can be converted into binary format by thresholding to reduce the number of hues, thus making it more suitable for an automatic and repetitive method as shown in figure 14.

![Figure 14](image)

**Figure 14.** A small portion of a microstructure image in (a) the original grayscale and (b) binary format.

Rough skeletons are first generated on the image using an adaptive meshing routine. The skeleton is a grid that adapts to all pixel groups boundaries present in the image. Initially individual elements may contain pixels corresponding to different individual phases. During the meshing procedure, the elements are
refined and the nodes are moved so that the material interfaces are well defined. Based on the boundaries of the defined pixel groups present in the image, the skeleton is refined to capture the irregular boundaries marking the different phases of the microstructure. Finer elements are automatically generated near the interfaces to account for higher gradients.

There are several skeleton modifying options in OOF2, many dependent on the two types of “energies” of the elements; shape energy and homogeneity energy (Ref 61). The total energy \(E\) of an element is calculated with the following equation:

\[
E = \alpha_h \cdot E_{\text{hom}} + (1-\alpha_h) \cdot E_{\text{shape}} \quad (\text{Eq. 14})
\]

where \(E_{\text{hom}}\) is the definition of the homogeneity energy, \(E_{\text{shape}}\) is the definition of the shape energy and \(\alpha_h\) is an adjustable parameter between 0 and 1. A high value of \(\alpha_h\) is used when the priority is the homogeneity of elements, i.e. it is more important that the element nodes match the image boundaries rather than keeping a good shape.

![Skeleton modification process](image)

**Figure 15.** A skeleton modification process in the FE software OOF based on the image in Figure 14(b).

An example of a skeleton modification process is shown in figure 15. Figure 15(a) shows an initial skeleton, without any consideration to the image boundaries. This skeleton is generated in the first step based on the maximum
element size defined by the user. Figure 15(b) shows the skeleton after a number of Anneal iterations have been performed. The Anneal routine moves nodes randomly and accepts moves according to a given criterion (Ref 89). In figure 15(c) the Refine method has been used, which splits elements into smaller pieces to make the skeleton correspond better to the boundaries (Ref 89). In figure 15(d) and figure 15(e) several additional skeleton modifying steps, e.g. Rationalize, have been used in order to further optimise the skeleton. The Rationalize option fixes badly shaped elements by modifying them and adjacent elements or by removing them completely (Ref 119).

During the skeleton creation process, OOF2 displays a homogeneity index showing the average homogeneity level of all elements. This value should increase during the process, as the skeleton gets finer and more adapted to the boundaries. A high value of homogeneity index is desired which would imply that the different pixel groups are well defined by the created mesh. If the index reaches 1, all elements are 100% homogenous.

When the meshing procedure is completed, the elements are assigned the property of the material with the dominant pixel group present in each element to generate the final mesh. Once the mesh is created, the equation system and boundary conditions are defined over the model.

The main quality concern in OOF is capturing the required microstructural details present in the images. Since the fine details of phases/features present in the image depend on the quality of image, SEM images are preferred over optical microscope images. Lower resolution images also result in higher errors due to inefficient discretization of the image during the thresholding procedure. Dorvaux et al. and Tan et al. have discussed the uncertainties arising due to the effects of image threshold level, image location across the sample cross-section, and image magnification and size on the final results (Ref 66, 85). These factors must be kept in mind when using OOF for predicting macroscopic material properties. In general, an image covering a large area of cross-section with high resolution should be used. Several images acquired across the sample cross-section must be used so as to reduce the errors induced due to the effect of local features on predicted properties.

The quality of mesh generated over the group of pixels representing the different phases present in the microstructure image also has a major influence on the modelling results. It is found that minimizing the maximum scale of element size is crucial in addition to setting a small minimum element size. Figure 16 shows the finite element mesh generated with coarse and fine element sizes. The red and white areas represent the two phases (pixel groups) present in the image. As shown in figure 16, the mesh with fine element is capable of
capturing the small microstructural details which are missed out in the coarse mesh, since the material property for an element is assigned on the basis of the dominant pixel group present in that element. Thus, a finer mesh is required for higher accuracy of the predicted results.

![Finite element mesh with different element maximum and minimum sizes.](image)

It can be clearly noticed that the mesh in (b) is able to capture much finer details compared to (a).

An advantage of using OOF2 is that the meshes created in OOF2 can be saved and exported in different file formats, which enables the use of OOF2 meshes in other finite element software applications, such as ANSYS Workbench (ANSYS Inc., USA), etc. This is highly beneficial when more tedious calculations are necessary and/or additional simulation options are required. Another advantage is that once the meshing procedure is optimised for one of the microstructure images for a sample, the entire procedure can be automated. This can be done by saving the input instructions in a script form and changing only the text referring to input image file for other images for the sample. Thus, errors induced due to the operator can be reduced.

### 5.5.2.2 Property evaluation

Once a finite element mesh has been created over the microstructure image, a simple set-up could be made to evaluate properties such as thermal conductivity and Young’s modulus using the mesh as shown in figure 17.
Thermal conductivity ($\lambda$) can be evaluated by setting up a temperature difference ($\Delta T$) across the top and bottom boundaries while keeping the other boundaries insulated to calculate the heat flux ($\frac{dQ_y}{dt}$) and then using the steady-state heat equation in 2D domain given as:

$$\frac{dQ_y}{dt} = \lambda \cdot A_y \left( \frac{\Delta T}{L_y} \right) \quad \text{(Eq. 15)}$$

where $A_y$ is the cross-sectional area perpendicular to the $y$-axis and $L_y$ is the thickness of the model domain along the $y$-axis as shown in figure 17.

Similarly Young’s modulus ($E$) can be evaluated by setting up a prescribed deformation ($\delta_x$) along $x$-direction to calculate the average stress ($\sigma_x$) across the model and then using the stress-strain equation given as:

$$\sigma_x = E \left( \frac{\delta_x}{L_x} \right) \quad \text{(Eq. 16)}$$

where $L_x$ is the thickness of the model domain along the $x$-axis as shown in figure 17.

Since the area representing the image is only a small fraction of the total cross-sectional area of the coating and the microstructural features might vary significantly from one part of the coating to the other, a number of images need to be analysed to achieve a statistical significance.

### 5.6 Artificial coating morphology generator

Tbctool software was developed by ONERA, France within the Brite Euram HITS project (Project BE96-3226 HITS, task 1.4). It is an interactive computer program which was created especially for TBC development. As mentioned
earlier, it has been used in the past to predict thermal conductivity of TBCs based on FDM. However, the major advantage of Tbcctool is that it can be used as a predictive tool for generating plasma sprayed TBC like morphology. The software generates randomized microstructure images based on several pre-defined criterion. Figure 18 shows an artificially generated microstructure image using Tbcctool simulating a plasma sprayed coating morphology. The generation process is described in detail in the reference manual for Tbcctool (Ref 120) and is described only briefly here.

The generation process is divided into four major sequences which are executed step by step: spheroids or globular pores generation, linked cracks or cracks connected to globular pores, free cracks, and dust or fine scale pores. Each sequence has several parameters which can be defined using a statistical distribution function. The function can be defined using analytical distribution laws such as Uniform, Normal, Log Normal or Custom, or tabulated laws with numerical definition. This statistical or probabilistic definition of parameters creates the randomness in the generation process. However, it must be kept in mind that these sequences can end up in an infinite loop, if too strict constraints are imposed on the generation parameters.

![Artificial image created using Tbcctool morphology generator simulating a plasma sprayed coating morphology](image)

**Figure 18.** An artificial image created using Tbcctool morphology generator simulating a plasma sprayed coating morphology

In the spheroids generation process, first the amount of spheroidal porosity needs to be defined. After that, the software chooses a set of particles from the ‘particles library’ on the basis of other specifications such as particle area, elongation, orientation and compactness, so that the total area of the particles
chosen becomes larger than the amount of defined spheroidal porosity level. The particles library, which consists of thousands of particles or globular pores, is incorporated within the software. This particle library was developed by extracting features from the actual microscopic images of several APS coatings. Then the software assigns random positions to the set of chosen particles in the field on the basis of other specifications such as overlapping rejection probability and minimum distance between particles.

The linked cracks sequence is divided into three sub-sequences: main or primary cracks, secondary cracks and segment cracks. Figure 19 shows the different linked crack families. The primary cracks start from the spheroids and the secondary cracks start from the primary cracks, while the segment cracks may start from spheroids and/or other cracks. First the amount of linked cracks porosity, and the fractions of main linked cracks and secondary linked cracks need to be defined. All the cracks start from ‘seeds’, which are generated according to various specifications such as seed birth probability and seed fraction. All cracks are built according to several parameters related to crack shape (like shape pulsation and shape damping) and crack size (like crack length and crack thickness).

![Figure 19. Different crack families in Tbcctool (Ref 120)](image)

The free cracks generation sequence is very similar to the segment cracks generation process described above, the difference being in the nature of the seeds used. The dust generation sequence is the simplest one with amount of dust porosity specified being generated on the basis of dust distance specified so that there is no overlapping of particles.
MODELLING OF PROPERTIES OF TBCS

The main limitation of Tbc tool morphology generator is that it uses geometric methods which are not directly related to the process physics. This means that the morphology generation parameters are somewhat arbitrarily related to the actual process parameters. The generation procedure widely uses random sub-processes which are difficult to optimize all together and might not have a physical significance. This limitation can also be used as an advantage since new coating morphologies can be fabricated virtually and explored for further analysis. However, in this case, the input parameters need to be linked to process parameters to ensure that the generated morphology is possible to achieve experimentally as well. Another limitation is the finite size of the particles library, so all types of particles cannot be generated using Tbc tool, especially if one considers new coating materials. Comparisons between real and artificially generated microstructures, and the methodology to design an optimised microstructure using Tbc tool have been discussed in detail in Paper B and Paper C.
6 Experimental methods

6.1 Microstructure characterisation

Various techniques have been used in the past for qualitative and/or quantitative analysis of microstructure of TBCs. Mercury intrusion porosimetry (MIP) enables measurement of total porosity for open pores and the evaluation of pore size distribution over a wide range (Ref 121, 122). SANS can obtain statistical results for small scale defects as well as orientation information (Ref 84, 113, 123). Image analysis is a robust, reliable and inexpensive method to characterise TBC microstructures from cross-section images which can be used to obtain information about porosity, pores and cracks distribution and orientation, etc. (Ref 124). The commonly used techniques to capture microstructure cross-section images of TBCs are LOM and SEM.

During the image analysis procedure, several images are taken along the coating cross-section in order to capture the variation in the microstructure. These images are then converted to binary format by thresholding using an image analysis software such as Aphelion (ADCIS, France), ImageJ (National Institutes of Health, USA), etc. The images have to be taken carefully at a certain magnification so as to capture the relevant coating microstructure details. High magnification images result in a loss of global coating information, while too low magnification images are unable to capture small-scale details present in the microstructure. Other factors which could affect the image analysis results are threshold level, microscope effects (such as image brightness and contrast, operating mode, etc.), coating location where the image has been taken, etc. (Ref 124).

6.2 Thermal conductivity measurements

The most widely accepted method for evaluating thermal conductivity of TBCs is LFA technique (Ref 125). The state-of-the-art measurement set-up is shown in figure 20.
In this method, a laser pulse is shot at the substrate face of the sample and the resulting temperature increase is measured at other face of the sample with an infrared detector. The signal is then normalised and the thermal diffusivity is calculated using an equation based on one of the existing models. One such equation is as follows:

\[ \alpha = \frac{(0.1388L^2)}{t_{(0.5)}} \]  

(Eq. 17)

where \( \alpha \) is thermal diffusivity, \( L \) is the thickness of the sample and \( t_{(0.5)} \) is the time taken for the rear face of the sample to reach a half of its maximum rise. Thermal conductivity \( (K) \) can then be calculated if the density (\( \varrho \)) and specific heat capacity (\( C_p \)) of the coating are known using the following relation:

\[ K = \alpha \cdot C_p \cdot \varrho \]  

(Eq. 18)
Samples are normally coated with a thin layer of graphite or gold before the measurements. Since zirconia is translucent to light in the wavelength of the laser, the presence of graphite layer is essential to prevent the laser pulse from travelling through the ceramic layer.

Density can be measured using one of the several existing methods such as Archimedes displacement, mercury porosimetry and gas absorption methods. These measurements are based on the assumption that all porous features present in the coating are interconnected, which is not true in every case. An indirect approach for evaluating density could be to measure the porosity level from image analysis of microstructure cross-section images and then calculating the density based on the density of bulk material. Usually, the density evaluated using image analysis method is lower than the mercury porosimetry method, which could be attributed to the effect of unconnected or sealed porosity detected by the image analysis method. Specific heat capacity data of the coatings can be used from existing databases, though it is recommended to measure it for each coating material using differential scanning calorimetry (DSC) for accuracy.

Thermal conductivity is measured either on free-standing ceramic coating which can be peeled off from the substrate, or on the complete TBC system. In the latter case, thermal conductivity of topcoat is calculated afterwards by measuring the thicknesses of individual layers and thermal conductivity values of only the substrate and substrate sprayed with bondcoat. Thicknesses are measured from microstructure cross-section images using an optical microscope. Measurement of thickness can be difficult due to high roughness of the interfaces in TBC systems, and can result in high errors in final measurements since thermal diffusivity is proportional to the square of thickness (Ref 125).

LFA technique is essentially non-contact and the equipment is available commercially from several companies. A major drawback is that only small flat samples can be used for measurement and thus, measurement on a real component is not possible.

### 6.3 Young’s modulus measurements

Traditional techniques used for measuring Young’s modulus of APS topcoats are micro-indentation, four-point bending, etc. Another technique which has been developed in recent years is bi-layer curvature measurements. The ECP sensor which consists of noncontact displacement lasers and thermocouples to monitor the displacement and temperature simultaneously at the back of the
sample during a heating and cooling cycle is used for these measurements (Ref 42). The bilayer curvature measurement set-up is shown in figure 21.

![Figure 21. The bilayer curvature measurement set-up using the ex-situ coating property sensor (Courtesy of ReliaCoat Technologies, NY, USA)](image)

The techniques used to measure Young’s modulus of TBCs can be classified in three categories (Ref 126):

(i) **Mechanical loading methods**: These techniques are based on the direct measurement of the deformation of the test material upon application of an external force. Examples include bending tests of coating system or a freestanding coating, tensile or compression tests, and indentation tests.

(ii) **Resonance vibration methods**: These techniques are based on the principle that the resonance frequency of a material depends on its elastic modulus of the material. Examples include acoustic emission techniques (Ref 127).

(iii) **Pulse-echo methods**: These techniques are based on the principle that the velocity of sound in a material depends on the elastic modulus of the material. Examples include laser-induced ultrasonic techniques (Ref 128).

It has been observed in earlier work that the modulus value highly depend on the technique used to evaluate it and it could be different even if the test specimens are identical between different techniques (Ref 129). This effect, which is related to the local variations of the microstructure within the coating, could be explained by the scale of the testing technique which ranges from microscopic (nano-indentation) to mesoscopic (micro-indentation) and
macscopic (bending tests, ultrasonic testing) dimensions (Ref 129). Therefore, elastic modulus needs to be considered as an engineering value for quantifying and ranking coating systems rather than as a fundamental property.

6.4 Roughness measurements

The traditional technique to measure surface roughness is to use a surface profilometer. Surface profilometer is a contact technique which determines the profile of a surface by dragging a stylus along it. The equipment is able to output the 2D roughness parameters such as $R_a$, $R_q$, $R_z$, etc. This technique is cheap and very simple to use.

Table 1. Some of the ISO 25178 feature parameters calculated for HVOF and APS bondcoat samples

<table>
<thead>
<tr>
<th>Parameter (units)</th>
<th>Parameter description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spd (1/mm$^2$)</td>
<td>Density of hills (number of hills per unit area)</td>
</tr>
<tr>
<td>Spc (1/mm)</td>
<td>Arithmetic mean hill curvature (arithmetic mean of the principle curvatures of hills within a definition area)</td>
</tr>
<tr>
<td>Sha (mm$^2$)</td>
<td>Mean hill area (average area of the hills connected to the edge at a particular height)</td>
</tr>
</tbody>
</table>

However, recent works have shown the 2D surface roughness parameters might not be sufficient to characterise a coating (Ref 56). Other techniques such as white light interferometry and laser stripe projection could be useful to analyse these coatings. The major advantages of using these techniques are: (i) a 3D profile could be captured with these techniques which could provide better visualisation of the surface features, (ii) very low resolution can be obtained with these techniques; for example, the vertical resolution obtained with interferometry is in the range of nanometres, (iii) the newly formulated ISO 25178 parameters could be measured and calculated with the help of these techniques thus enabling to characterise the 3D profile quantitatively. The
disadvantages of using these techniques are that they are very expensive and the data analysis could be a complex procedure.

The feature parameters are a new family of parameters which has been integrated in the ISO 25178 standard. Feature parameters are derived by creating segmentation motifs over a surface which makes it possible to identify specific areas such as hills and valleys. Some of the ISO feature parameters are given in Table 1. Quantifying the density, size and shape of the hills and valleys of the bondcoat surface could be highly beneficial to assess the stresses characteristics near the topcoat-bondcoat interface.

Figure 22. (a) Bondcoat surface profiles captured using white light interferometry technique, and (b) Segmentation motifs captured using stripe projection technique.
Figure 22(a) shows a surface profile of a bondcoat sample captured using white light interferometry. The figure shows the presence of large hills over the surface which are suspected to be partially melted/unmelted particles formed during the spray process. Figure 22(b) shows segmentation motifs captured using stripe projection technique for the same sample. The presence of the hills over the surface could be quantitatively analysed with the help of this image.

### 6.5 Lifetime testing

Assessing the lifetime of TBCs is a challenging task since testing them in real environments is very time consuming and expensive. Accelerated and simplified tests are used to reduce testing times by exposing the TBCs to harsher environments than reality. Due to the over-simplification of testing methods, there can be large discrepancies between the performance in testing and operating conditions. Nevertheless, the lifetime tests provide a fair idea of the coating behaviour and can be used to judge different coatings. Common methods for testing the lifetime of TBCs are TCF and thermal shock tests. Both these methods are well practiced in industry.

*Figure 23. Samples during TCF testing showing spallation of a few samples*
In TCF tests, the samples are typically first heated in a furnace at high temperatures around 1100ºC for one hour and then cooled down for ten minutes using compressed air to approximately 100ºC. These two steps are repeated until failure. The criterion for failure is deemed to be more than 20% visible spallation of the coating. A visual record of the samples surface is made at the end of each cycle using a webcam which is used later for calculating the number of cycles to failure. Figure 23 shows one such photograph taken during the testing where it can be seen that a few of the samples have the topcoats spalled off while a few are still intact.

Thermal shock testing simulates the rapid heating and cooling experienced by coatings during service. As the name suggests, the coatings are heated up to a specified temperature and then cooled down rapidly with air or by dipping them into water. Burner rig test is a common way of testing thermal shock behaviour. In this test, samples are heated on the coating face with a combustion burner flame and then cooled down with compressed air. Samples are cooled on the back face with water or air to set up a thermal gradient within the TBC system. A typical cycling time for burner rig tests is five minutes heating and two minutes cooling.

![Image of topcoat-bondcoat interface after failure showing the TGO growth](Figure 24.png)

**Figure 24.** Topcoat-bondcoat interface after failure showing the TGO growth

Figure 24 shows a microstructure cross-section image of part of the topcoat-bondcoat interface after failure during TCF test. The topcoat zirconia layer was sprayed by APS while the bondcoat NiCoCrAlY layer was sprayed by HVOF.
EXPERIMENTAL METHODS

technique. The dark grey layer in the image between the topcoat and bondcoat consists of TGO formed during the test.

Both TCF and thermal shock testing methods have their own limitations. TCF tests have the benefit that they provide information about sintering of topcoat, TGO growth in TBC system and the topcoat’s ability to sustain the induced stresses due to TGO growth and thermal mismatch. In this way, results obtained from TCF tests are highly dependent on the bondcoat material and structure. The major limitation of TCF tests is the time taken for the tests to be completed, since it can take more than a month to obtain lifetime results. Another limitation is that since the samples are normally maintained in an isothermal heating environment, a thermal gradient is not present in the TBC system which is present in service conditions. Homogeneous temperature state can lead to higher stresses and thus lower lifetime than reality (Ref 130). Thermal shock tests induce large thermal stresses in the topcoat-bondcoat interface and they are mainly dependent on the strain tolerance of topcoats. There is little time in these tests for any significant effect of bondcoat oxidation or sintering of topcoats on coating lifetime. Though thermal shock tests are much faster as they normally take less than a week to be completed, they have a disadvantage that they are much more severe than reality. An alternative testing method which involves a combination of TCF and thermal shock tests was suggested in an earlier work for better representation of actual engine conditions (Ref 131).
7 Summary of Appended Publications

**Paper A.** Relationships between Coating Microstructure and Thermal Conductivity in Thermal Barrier Coatings – A Modelling Approach


In **Paper A**, a combination of a statistical model and a finite element model was used to evaluate and verify the relationship between microstructural defects and thermal conductivity. First, a statistical model was used as ‘screening’ method to determine the most important microstructural features affecting thermal conductivity. The results from this model indicated that pores and cracks in contact have a major influence over thermal insulation properties compared to free cracks and free pores. The OOF model based on microstructure images obtained using SEM was utilised in the next step to validate these results. These tentative results indicated that this modelling approach can be used to evaluate and verify relationships between microstructural defects and thermal conductivity.

**Paper B.** Design of Low Thermal Conductivity Thermal Barrier Coatings by Finite Element Modelling

(Surface Modifications Technologies XXIV, Sep 7-9, 2010 (Dresden), ed. by T.S. Sudarshan, E. Beyer and L.-M. Berger, 2011, p. 353-365)

In **Paper B**, the finite element model developed in **Paper A** was combined with a plasma-sprayed TBC like morphology generator (TbcTool) to enable the development of low thermal conductivity coatings by simulation. The coating morphology generator was used to generate artificial microstructure images using the input parameters determined from image analysis of real microstructure images obtained using SEM. These artificially generated images were used as an input to the finite element model to predict thermal conductivity. The artificially generated images were verified by two methods. First, by comparing their image analysis data with SEM images, and second, by comparing the predicted thermal conductivity values with the predicted thermal conductivity values from SEM images and the thermal conductivity values obtained from LFA experiments. It was observed that the finite element model
ranked the coating systems the same way in terms of thermal conductivity as the experimental values. Also, same ranking was observed for the artificial images generated. These tentative results indicated that the images generated by the coating morphology generator were similar to the real coatings.

**Paper C. Design of Next Generation Thermal Barrier Coatings — Experiments and Modelling**

*(Surface & Coatings Technology, 2013, 220, p. 20-26)*

In **Paper C**, a combined empirical and numerical approach was used to enable the development of high performance coatings, i.e. coatings with low thermal conductivity and long lifetime. Different morphologies of ceramic topcoat were evaluated, including dual layer systems and polymer porosity formers. Dysprosia stabilised zirconia was studied as a topcoat material along with the state-of-the-art YSZ. Thermal conductivity of coatings was measured by LFA and lifetime was assessed by TCF testing. The finite element model utilised in **Paper A** and **Paper B** was developed further to evaluate thermal-mechanical material behaviour of the coatings. The finite element model was combined with an artificial coating morphology generator (Tbctool) to design the morphology of the coating through establishment of relationships between microstructure, thermal conductivity and Young’s modulus. It was shown that the combined empirical and numerical approach can be used as an effective tool for designing high performance coatings. The results showed that large globular pores and connected cracks inherited within the coating microstructure result in a coating with best performance.

**Paper D. A Modelling Approach to Design of Microstructures in Thermal Barrier Coatings**


In **Paper D**, the finite element model developed in **Paper A** and **Paper B** was used to investigate fundamental relationships between microstructure and thermal-mechanical properties, and obtain an optimised coating microstructure. A design of experiments (DoE) was conducted by varying selected spray parameters and finite element model was used to predict thermal conductivity and Young’s modulus. The lowest thermal conductivity and Young’s modulus were shown by a coating exhibiting large globular pores with connected cracks inherited within the microstructure. For the purpose of verifying the modelling results, this microstructure was sprayed along with a reference coating with a new spray gun, and thermal conductivity and thermo-cyclic fatigue lifetime were measured. The coating with large globular pores with connected cracks
performed better compared to the reference coating sprayed with standard settings before optimisation, which verified the modelling results obtained in the first part of this work.

**Paper E.** *An Experimental Study of Microstructure-Property Relationships in Thermal Barrier Coatings*


In **Paper E**, an experimental approach was undertaken to explore process-microstructure property relationships with existing links to TCF lifetime in TBCs. A study evaluating the three crucial functional parameters in TBCs—thermal properties, mechanical properties and lifetime, was performed and relationships between process parameters, microstructure and coating properties were established. A DoE was conducted for this purpose with current, spray distance and powder feed rate as the varied spray parameters. An alternative route for fabricating high porosity microstructures with large globular pores and connected cracks inherited within the microstructure was provided. This type of microstructure exhibited the best performance in this study which was in accordance with earlier work presented in **Paper C** and **Paper D**. A relationship between the nonlinear degree derived from ECP bilayer curvature measurements and TCF lifetime based on *a priori* established microstructure analysis was proposed which may enable a predictive capability for coating response. It was, however, observed that there are two microstructure regimes for which this relationship holds—porous and vertically-cracked. The results indicated that ECP bilayer curvature measurements along with microstructure examinations can be used to optimise topcoat microstructures for TBCs.

**Paper F.** *Influence of Topcoat-Bondcoat Interface Roughness on Stresses and Lifetime in Thermal Barrier Coatings*


In **Paper F**, finite element modelling was used to study the residual stress profile in the topcoat-bondcoat interface using real surface topographies. The differences in functional performance between APS and HVOF bondcoat samples observed in earlier work were evaluated with both 2D and 3D simulations. Both 2D and 3D simulations were shown to verify the previously formulated stress inversion theory established using simplified sinusoidal curves. It was observed that the stress inversion from compressive to tensile stresses occurred earlier in the topcoat-bondcoat interface for the HVOF samples which could be a reason for an earlier failure in lifetime testing. It was remarked that unmelted particles present on the HVOF bondcoat surface could increase the
overall stresses in the topcoat which could also contribute to earlier failure in lifetime testing. It was concluded that the modelling approach using real topographies can be a tool to attain valuable insight into the stress distribution in topcoat-bondcoat interfaces. The results indicated that optimisation of bondcoat roughness can be realised through this technique.

**Paper G. A Diffusion-based Oxide Layer Growth Model using Real Interface Roughness in Thermal Barrier Coatings for Lifetime Assessment**

*Surface & Coatings Technology, Accepted, in press*

In **Paper G**, a 2D TGO growth model based on aluminium and oxygen diffusion-reaction equations was presented consisting of real topcoat-bondcoat interface profiles extracted from cross-sectional micrographs. The model was first validated by comparing the TGO profiles artificially created by the model to cross-sectional micrographs taken from specimens at failure. It was observed that the generated TGO profiles were able to capture the essence of the actual TGO growth during operational conditions of TBCs. Thereafter, TGO profiles generated at different stages of TGO growth were extracted from the TGO growth model and used in the stress analysis model developed in **Paper F** to evaluate the thermo-mechanical stresses within the topcoat near the topcoat-bondcoat interface. Three experimental specimens with same chemistry but different interface roughness were studied using this modelling approach. The time to stress inversion was analysed for the three specimens and it was observed that same ranking was achieved when compared to the lifetimes measured experimentally. The combination of the two models described in this work presented an effective approach to assess the stress behaviour and lifetime of TBCs in a comparative way. The TGO growth model consisting of real interface topography can be used as an effective tool to visualise the TGO growth in-situ which could be otherwise a non-trivial task if performed experimentally.


*Journal of Thermal Spray Technology, Submitted*

In **Paper H**, an attempt was made to understand the driving force for cracking of CSN clusters and their role in TBC spallation in a better way. First, nanoindentation was performed on a CSN cluster in a TBC sample to map the Young's modulus of the various oxides included in CSN clusters. A finite element analysis was then performed using the established Young’s moduli and the exact geometry of the CSN cluster derived from micrographs using the
model developed in *Paper F*. Several stages of the CSN cluster formation process, as well as the volumetric increase associated with the oxidation of the last Ni-rich core, were modelled. It was concluded that crack formation in the oxide clusters can occur due to the induced tensile stresses during cooling in the NiO core owing to high CTE of NiO. The stresses introduced due to the oxidation of the Ni core were observed to relax fast enough at high temperature. Silica particles in the cluster could possibly assist cracking due to the CTE mismatch.
8 Conclusions

An automated procedure was developed using finite element modelling to predict thermal conductivity and Young’s modulus of TBC topcoats. By comparing the predicted values with the experimental results, it was shown that finite element modelling approach utilising real microstructure images can be used as powerful tool to predict and derive microstructure-property relationships.

It was shown that coating morphologies with similar microstructural features as the real microstructure images taken using SEM can be artificially generated by using an artificial coating morphology generator.

Presence of large globular pores with connected cracks inherited within the coating microstructure was shown to significantly enhance the performance of TBCs. Low thermal conductivity, low Young’s modulus and high lifetime were exhibited by these coatings. This relationship was derived by designing the microstructure using the combination of finite element modelling and artificial coating morphology generator, and then verified experimentally.

The stress inversion theory established using simplified sinusoidal curves was verified by both 2D and 3D simulations using real topographies. It was shown that the modelling approach using real topographies can be a useful tool to attain insight into the stress distribution in topcoat-bondcoat interfaces. It was shown that the time to stress inversion can be used as an indicator to assess coating lifetime. The results indicated that an optimal bondcoat topography could be designed through this technique.

The diffusion-based TGO growth model consisting of real interface topography developed in this work can be used as an effective tool to visualise the TGO growth in-situ which could be otherwise a non-trivial task if performed experimentally. The combination of the TGO growth and stress analysis models developed in this work could be used as an effective approach to assess the stress behaviour and lifetime of TBCs in a comparative way. Based on the fundamental knowledge gained from these models about the relationships between topcoat-bondcoat interface roughness, TGO growth and lifetime of TBCs, the models need to be developed further to realise an optimised interface design.
The finite element model based on analysing real microstructure images was successfully implemented to achieve fundamental understanding of the phenomena of stress development and cracking during mixed oxide cluster formation in TBCs. It was concluded that the major reason for cracking was the large CTE between NiO and other oxides formed during thermal cycling.

Thus, it can be concluded that the modelling approach developed in this work could be used as a powerful tool to design new coatings as well as to achieve optimised microstructures as well as topographies which could significantly enhance the performance of TBCs.

### 8.1 Future work

Further work in this field could be to develop the TGO growth model from 2D to 3D as it would provide a global view of TGO growth as well as enable to perform stress analysis in 3D. The inclusion of aluminium depletion and mixed oxides in the TGO growth model in the future would be highly valuable.

In recent years, coatings produced by SPS/SPPS are becoming of major interest. The analysis of failure mechanisms as well as application of the models developed in this work to SPS/SPPS coatings could be another possibility in the future.
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Design of Thermal Barrier Coatings

A modelling approach

Thermal barrier coatings (TBCs) are used for thermal protection of components in modern gas turbine applications such as power generation and aero engines. TBC is a duplex material system consisting of an insulating ceramic topcoat layer and an intermetallic bondcoat layer. Improvement in performance of TBCs will lead to more efficient and durable engines thus decreasing harmful emissions.

In this work, important microstructural parameters influencing the performance of TBC topcoats were identified, modelled and experimentally verified. Real topcoat-bondcoat interface topographies were used in a model to predict induced stresses and a diffusion based oxide growth model was developed to assess the lifetime. It was shown that the modelling approach described in this work can be used as a powerful tool to design new coatings and interfaces as well as to achieve optimised microstructures.

Mohit Gupta

Mohit comes from Lucknow in India and received his bachelor’s degree in mechanical engineering from Indian Institute of Technology Kanpur, India in 2009. He received his master’s degree in mechanical engineering from University West in 2010. His research interests are finite element modelling, plasma spraying and solid oxide fuel cells.