Microstructure and Thermal Conductivity of Liquid Feedstock Plasma Sprayed Thermal Barrier Coatings

Ashish Ganvir
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Ashish Ganvir
Dedicated to my family
Acknowledgements

It is with immense gratitude that I acknowledge the financial support provided by the Västra Götalandsregionen, Sweden, to accomplish this research work. This research work was performed at the Production Technology Center (PTC), Trollhättan as a part of the thermal spray research group at University West, Trollhättan, Sweden.

First and foremost, I wish to thank my supervisors Assoc. Prof. Nicolaie Markocsan and Prof. Per Nylen for the continuous support in my PhD study, for their patience and immense knowledge. Their guidance helped me in all the time of research and writing of this thesis. I could not have imagined having better supervisors for my PhD study. It's a privilege to be your student and I wish I keep learning from you both. Thank you for always motivating me to do this research!

My sincere thanks also go to Dr. Nicholas Curry and Mr. Stefan Björklund for their immense help with spraying and sharing their vital knowledge to enhance my practical skills. It's been a pleasure to work with you both!

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I would like to thank all friends and colleagues at PTC for making these days so enjoyable. It's been a great fun to be around you. Lucky to have you all!

Finally, I would like to thank my family: my parents and to my brother and sisters for supporting me spiritually throughout this period.

Ashish Ganvir
12th of February 2016, Trollhättan
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12th of February 2016, Trollhättan
Populärvetenskaplig Sammanfattning

Nyckelord:
Mikrostruktur; Termiska barriärbeläggningar; Axialmatning; Plasmasprutning; Höghastighetsflamsprutning; Lösningsbaserad sprutning, suspensionssprutning; Porositet; Värmeledningsförmåga

Titel: Mikrostruktur och värmeledningsförmåga hos suspensionssprutade termiska värmebarriärbeläggningar

Termiska värmebarriärbeläggningar (TBC) används i stor utsträckning på gasturbinkomponenter för att åstadkomma termisk isolering och oxidationsskydd. TBCs, i kombination med avancerad kylning, möjliggör högre förbränningstemperaturer i gasturbinen även över smälttemperaturen för metalliska material. Det finns ett ständigt behov, främst av miljöskäl, för att både minska bränsleförbrukning och emissioner och att öka förbränningstemperaturen vilket kräver nya typer av TBC-lösningar.

Genom att använda en suspension vid termisk sprutning, kan nya typer av TBC framställas. Suspensionsplasmasprutning och lösningsbaserad plasmasprutning är exempel på tekniker som kan användas. Dessa tillvägagångssätt, som är alternativ till den konventionella tekniken med tillsatsmaterial i fast form, röner ett allt större forskningsintresse: Anledningen till det stora forskningsintresset är möjligheten att producera beläggningar med överlägsna funktionella egenskaper.

Syftet med detta avhandlingsarbete var att undersöka samband mellan processparametrar, beläggningarnas mikrostruktur, och beläggningarnas värmeledningsförmåga för termisk sprutade värmebarriärbeläggningar där tillsatsmaterialet införs i lågan i flytande form. Ett ytterligare syfte var att utnyttja denna kunskap för att producera en värmebarriärbeläggning med lägre värmeledningsförmåga jämfört med state-of-the-art inom industrin idag, det vill säga då tillsatsmaterialet tillförs i fast form. Olika spruttekniker såsom suspensionssprutning med plasma, lösningsbaserad sprutning med plasma, suspension med höghastighetsflamsprutning undersöktes och jämfördes med plasmasprutning där tillsatsmaterialet införts i fast form.

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Title: Microstructure and Thermal Conductivity of Liquid Feedstock Plasma Sprayed Thermal Barrier Coatings

Thermal barrier coating (TBC) systems are widely used on gas turbine components to provide thermal insulation and oxidation protection. TBCs, in combination with advanced cooling, can enable the gas turbine to operate at significantly higher temperatures even above the melting temperature of the metallic materials. There is a permanent need, mainly for environmental reasons, to increase the combustion turbine temperature, hence new TBC solutions are needed.

By using a liquid feedstock in thermal spraying, new types of TBCs can be produced. Suspension plasma/flame or solution precursor plasma spraying are examples of techniques that can be utilized for liquid feedstock thermal spraying. This approach of using suspension and solution feedstock, which is an alternative to the conventional solid powder feedstock spraying, is gaining increasing research interest, since it has been shown to be capable of producing coatings with superior coating performance.

The objective of this research work was to explore relationships between process parameters, coating microstructure, thermal diffusivity and thermal conductivity in liquid feedstock thermal sprayed TBCs. A further aim was to utilize this knowledge to produce a TBC with lower thermal diffusivity and lower thermal conductivity compared to state-of-the-art in industry today, i.e., solid feedstock plasma spraying. Different spraying techniques, suspension high velocity oxy fuel, solution precursor plasma and suspension plasma spraying (with axial and radial feeding) were explored and compared with solid feedstock plasma spraying.

A variety of microstructures, such as highly porous, vertically cracked and columnar, were obtained. It was shown that there are strong relationships between the microstructures and the thermal properties of the coatings. Specifically, axial suspension plasma spraying was shown as a very promising technique to produce various microstructures as well as low thermal diffusivity and low thermal conductivity coatings.

Keywords: Microstructure, Thermal Barrier Coating; Axial Injection; Suspension Plasma Spraying; Suspension High Velocity Oxy Fuel Spraying; Solution Precursor Plasma Spraying; Porosity; Thermal Diffusivity; Thermal Conductivity

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List of Appended Publications

**Paper A.**
Characterization of Thermal Barrier Coatings produced by various thermal spray techniques using solid powder, suspension and solution precursor feedstock material
Ashish Ganvir, Nicholas Curry, G. Sivakumar, Nicolaie Markocsan
International Journal of Applied Ceramic Technology, online, DOI: 10.1111/ijac.12472, Sept. 2015
As the main Author, Ashish Ganvir has performed all the experimental characterization, analyzed all the results, designed the structure of the article and had the main responsibility in writing the article. Co-authors contributed in formulating concepts and ideas, planning the project, spraying and article editing. In addition, Nicholas Curry also contributed in writing the article.

**Paper B.**
Comparative study of suspension plasma sprayed and suspension high velocity oxy-fuel sprayed YSZ thermal barrier coatings
Ashish Ganvir, Nicholas Curry, Nicolaie Markocsan, Per Nylén and F.-L. Toma
As the main Author, Ashish Ganvir has performed all the experimental characterization, analyzed all the results, designed the structure of the article and had the main responsibility in writing the article. Co-authors contributed in formulating concepts and ideas, planning the project, spraying and article editing.

**Paper C.**
Characterization of microstructure and thermal properties of YSZ coatings obtained by axial suspension plasma spraying (ASPS)
Ashish Ganvir, Nicholas Curry, Stefan Björklund, Nicolaie Markocsan, Per Nylén
As the main Author, Ashish Ganvir has performed all the experimental characterization, analyzed all the results, designed the structure of the article and had the main responsibility in writing the article. Co-authors contributed in formulating concepts and ideas, planning the project, spraying and article editing.
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LIST OF APPENDED PUBLICATIONS

Paper D. Influence of microstructure on thermal properties of axial suspension plasma sprayed YSZ thermal barrier coatings
Ashish Ganvir, Nicholas Curry, Nicolaie Markocsan, Per Nylén, Shrikant Joshi, Monika Vilemova, Zdenek Pala

As the main Author, Ashish Ganvir has performed all the experimental characterization except mercury intrusion porosimetry (MIP) and x-ray diffraction (XRD), analyzed all the results, designed the structure of the article and had the main responsibility in writing the article. Co-authors contributed in formulating concepts and ideas, planning the project, spraying and article editing. MIP and XRD were carried out by co-authors Monika Vilemova and Zdenek Pala respectively.
Table of Content

Acknowledgements ................................................................. V
Populärvetenskaplig Sammanfattning ....................................... VII
Abstract .................................................................................. IX
List of Appended Publications ................................................ XI
Table of Content ..................................................................... XIII
Abbreviations / Nomenclature ................................................. XV

1 Introduction ........................................................................ 1
  1.1 Thesis outline ............................................................... 1
  1.2 Objective and research questions .................................... 1
  1.3 Scope and limitations .................................................... 2

2 Background ......................................................................... 5
  2.1 Thermal Barrier Coating (TBC) system ......................... 6
     2.1.1 Bond coat (BC) ...................................................... 7
     2.1.2 Thermally grown oxide (TGO) ............................... 7
     2.1.3 Ceramic top coat .................................................. 8
  2.2 Thermal spraying of a TBC system ............................... 10
     2.2.1 Atmospheric plasma spraying (APS) ....................... 12
     2.2.2 Liquid feedstock spraying ..................................... 14
     2.2.3 Process characteristics of SPS ............................... 17

3 Characteristics of TBC ....................................................... 27
  3.1 Microstructure ............................................................. 27
     3.1.1 Solid powder feedstock APS sprayed coatings ......... 27
     3.1.2 Liquid feedstock thermal sprayed coatings ............. 28
  3.2 Porosity ...................................................................... 30
  3.3 Thermal conductivity .................................................... 32
     3.3.1 Heat transfer in conventional APS sprayed TBCs ....... 32
     3.3.2 Comparison of heat transfer in conventional APS and liquid feedstock plasma/flame sprayed TBCs .... 33

4 TBC characterization techniques ......................................... 35
## TABLE OF CONTENT

4.1 Microstructure evaluation of the TBC .......................... 35

4.2 Porosity measurement .................................................. 36

4.3 Evaluation of thermal conductivity ................................. 37

4.4 Evaluation of thermal-cyclic fatigue lifetime .................... 39

5 Microstructure and its effect on the thermal conductivity of a TBC system ................................................................. 41

6 Conclusions ........................................................................ 45

7 Future work ........................................................................ 47

References ............................................................................. 49

8 Summary of appended publications ................................. 57

APPENDED PUBLICATIONS .................................................. 59
Abbreviations / Nomenclature

APS: Atmospheric Plasma Spraying
ASPS: Axial Suspension Plasma Spraying
BC: Bond Coat
CSN: Chromia, Spinel and Nickel oxide
CTE: Coefficient of Thermal Expansion
D_{50}: Median size (diameter) of a particle in a certain particle size distribution.
DSC: Differential Scanning Calorimetry
EB-PVD: Electron Beam Physical Vapor Deposition
HVAF: High Velocity Air Fuel
HVOF: High Velocity Oxy Fuel
HVSFS: High Velocity Suspension Flame Spraying
IGTs: Industrial Gas Turbines
LFA: Laser Flash Analysis
MIP: Mercury Intrusion Porosimetry
OM: Optical Microscopy
SEM: Scanning Electron Microscopy
S-HVOF: Suspension-High Velocity Oxy Fuel
SPPS: Solution Precursor Plasma Spraying
SPS: Suspension Plasma Spraying
TBC: Thermal Barrier Coating
TCF: Thermal-Cyclic Fatigue
ABBREVIATIONS / NOMENCLATURE

TGO: Thermally Grown Oxide
XRD: X-ray Diffraction
YSZ: Yttria Stabilized Zirconia

1 Introduction

A brief introduction to the outline of this thesis, objective of this work and research questions are presented in this chapter. Additionally, the scope and limitations of this thesis work are also described in brief.

1.1 Thesis outline

This thesis is organized in eight chapters. The coverage in each chapter is briefly summarized below:

Chapter 1 provides a brief outline of the thesis, discusses the objective, research questions and also the scope and limitations of the research work. Chapter 2 provides a detailed background of the overall motivation behind this research and why the research work is important to the scientific society, specifically to the thermal spray community. Additionally, this chapter also provides a brief description of a thermal barrier coating (TBC) system and its deposition and, further, outlines the advantages of spraying a liquid feedstock instead of a solid powder feedstock. Process characteristics of suspension plasma spraying (SPS) and the theory behind coating formation in SPS of TBCs are also discussed in chapter 2.

Chapter 3 presents the main characteristics of the TBCs in general and the main focus is on microstructure, porosity, thermal diffusivity and thermal conductivity.

Chapter 4 describes the characterization techniques utilized to investigate the TBCs produced in this work.

In chapter 5 the various routes which can be followed to obtain a low thermal conductivity TBC are presented. In addition, this chapter also briefly discusses various microstructural features and their effect on thermal diffusivity and conductivity.

Chapter 6 provides the conclusions of this thesis.

Finally, the future work for this research and summary of all the journal papers included in this thesis are given in chapter 7 and 8 respectively.

1.2 Objective and research questions

The objective of this research work was to explore relationships between process parameters, coating microstructure, thermal diffusivity and thermal conductivity in liquid feedstock thermal sprayed TBCs. A further aim was to utilize this...


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1.2 Objective and research questions

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knowledge to produce a TBC with lower thermal diffusivity and lower thermal conductivity compared to state-of-the-art in industry today.

The work was accomplished by trying to answer the following research questions:

1. Can the TBC microstructure be significantly changed by varying the spray techniques and process parameters in liquid feedstock thermal spraying, and if so, which spraying technique seems as the most feasible?
2. How do different microstructural features influence the thermal properties of the coating in liquid feedstock thermal spraying?
3. Can the thermal diffusivity and thermal conductivity be reduced by using a liquid feedstock instead of a solid feedstock in plasma spraying, and if so, why?

1.3 Scope and limitations

The work was focused on studying the coating microstructure and understanding the influence of various microstructural features on thermal properties of an yttria stabilised zirconia (YSZ) which is also sometimes referred as yttria partially stabilised zirconia TBC. Certain limitations should be considered if the results are to be applied to other coating materials, spraying techniques or coating applications and these can be briefly summarized as follows:

i. Coating applications

The work was focused on TBCs for industrial gas turbines (IGTs) and aero engine turbines. However, the screening study revealed that varying microstructural features and porosity could also result in coating microstructures, which could be applicable for various applications ranging from solid oxide fuel cells to heat shields in space shuttles. These microstructures need to be further investigated for each of the respective application's point of view.

ii. Coating functional properties

For a TBC, lifetime and thermal conductivity are the two most crucial properties. The current study solely focused on understanding the latter, however, lifetime needs to be separately investigated.

iii. Material

Only one ceramic top coat material, namely 4 mol. % YSZ was used in various forms (powder/suspension/solution precursor). For bond coat a material of a composition NiCoCrAlY was used and for substrate Hastalloy® X (Ni-based
super alloy). However, use of other alternative ceramic top coat materials such as gadolinium zirconate or dysprosia stabilized zirconia etc. also need to be further investigated, to understand their role in further improving the thermal properties of TBCs.

iv. Spraying techniques

The spraying of bond coats was limited to atmospheric plasma spray (APS) and high velocity air fuel (HVAF). For top coats, different thermal spray techniques were explored; such as APS, solution precursor plasma spray (SPPS), suspension-high velocity oxy fuel (S-HVOF), radial injection suspension plasma spray (SPS), and axial injection suspension plasma spray (ASPS). Electron beam physical vapor deposition (EB-PVD), which is a commonly used coating technology for top coats, was not explored in this research. However, it was of interest to explore the potential to produce similar coating microstructures by SPS. Whether or not the inter-relationships between microstructural features and thermal properties derived in the present study are valid in case of EB-PVD needs to be separately investigated.

v. Coating characterization techniques

Coating characterization performed in this study was limited by the characterization techniques available. Use of high resolution microscopy to observe very fine scale pores and/or grains and grain boundaries would provide better insights to further refine the correlations between coating microstructure and thermal properties.

Image analysis, water impregnation and mercury intrusion porosimetry (MIP) were used to analyse the overall porosity and pore size distribution. All these techniques have limitations. Water impregnation and MIP can only measure the open pores (pores which can be accessible by water or mercury). Image analysis can reveal both open and closed pores, but is sensitive to sample preparation. The above constraints should be borne in mind while utilizing the results of the present study, although the broad qualitative trends involving porosity are expected to remain valid.

Laser flash analysis (LFA), which was utilised for thermal diffusivity measurements, is prone to uncertainty in measurements when used at temperatures over 1000°C due to the transparent nature of zirconia to wavelengths of laser light used in the LFA experiment.
Background

Over the past 40 years, the gas turbine industry has extensively used TBCs in various sectors, such as power generation and aero engines [1], [2]. The hot sections in gas turbines include the combustor, turbine blades and vanes, and the afterburner which can be seen in Figure 1 (the parts in red and orange).

Figure 1: Schematic of gas turbine RM-12 aero engine [courtesy: GKN Aerospace]

In today's aero engines the hot gas temperature exceeds by more than 250 °C the softening point of the metallic structure of the turbine material, which usually is a Ni-based super-alloy [1], [2]. This requires extensive cooling, which reduces the thermal efficiency of the engine [3]–[5]. Thermodynamics suggest that the efficiency of gas turbine engines can be increased by increasing the combustion temperature [3]. However increase in combustion temperature is limited by the inherent temperature capability of the Ni-based super-alloys used in gas turbine engines. There is a desire to always increase combustion temperature to achieve higher gas turbine engine efficiencies [3]. TBCs play a key role in enabling this [1], [2]. Enhancing their insulating capability and augmenting their durability is a continuous challenge.

Due to its thermal insulation properties there is a transient temperature drop across the TBC in-service conditions. This drop allows higher turbine entry temperatures and hence, higher engine efficiency [1]–[3]. The extent of temperature drop can be increased either by lowering the thermal conductivity of the ceramic top coat or by increasing the top coat thickness. For the sake of understanding, 'ceramic top coat' from now onwards will be denoted as 'TBC'.

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conditions. The thickness of the TBC is mainly limited by the risk of spallation. Thicker coating thus results in lower lifetime, due to the increased residual stresses in the coating [6]. Hence, reduction in thermal conductivity remains the most feasible option.

In general, thermal conductivity in a TBC can be reduced if a low thermal conductivity TBC material is used. However, this is limited by the availability of the materials that fulfil the necessary requirements of a TBC, e.g. low thermal conductivity, high thermal expansion matching with the metallic bond coat, good thermal and or phase stability at elevated temperatures, good mechanical properties etc. Although there has been significant progress in developing new TBC materials, the most used material so far is YSZ, a ceramic [7] that was introduced in the late '70s [8]. Another possible route of reducing the thermal conductivity is, by changing the microstructure of the deposited TBC [9], [10], since the microstructure, i.e. microstructural features such as pores and cracks strongly affect the thermal properties of the TBC.

Presence of various microstructural features in different microstructures of TBCs, such as pores and cracks of different shape, size and orientation [5], [11]–[13], make these microstructures significantly different from each other. Its these microstructural features, as previously stated, can significantly influence the heat transfer through the coating [5], [10], [13]. Higher total porosity can for instance significantly reduce the effective thermal conductivity of the TBC [13], [14].

Other important characteristics of a TBC than having a low thermal conductivity are, excellent thermal cyclic durability, phase stability at higher temperatures for longer exposure, and low cost (this is a relative factor and it is not as big driver as the performance is). Depending on the application, a balance between these four properties is needed. For example, aero engine turbines operate at peak power for shorter periods during take-off and landing, hence experiences relatively frequent thermal-cycling, whereas industrial gas turbines (IGTs) run typically for longer duration at constant temperature and hence experiences significantly less frequent thermal-cycling.

### 2.1 Thermal Barrier Coating (TBC) system

There are three primary constituents in a TBC system as shown in Figure 2: (1) a metallic bond coat (BC) approximately 200 µm thick [15]; (2) a thermally grown oxide (TGO) which grows from 0 µm to 10 µm [16], [17], during the in-service life between the ceramic top coat and the BC, and (3) the ceramic top coat (TBC) of around 300 µm to 1 mm [18], which acts as a main thermal insulation layer. The BC and the TBC coatings can be deposited/sprayed using various coating
technologies. The important thing to note here is that the TGO is a layer, which is generated due to the oxidation of the BC during the in-service life of the TBC system. The different layers are described in the following subsections.

<table>
<thead>
<tr>
<th>Material Used</th>
<th>TBC System</th>
<th>Function/Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typically YSZ</td>
<td>Ceramic Top coat (TBC)</td>
<td>Thermal insulation</td>
</tr>
<tr>
<td>Mainly Al₂O₃</td>
<td>Thermally grown oxide (TGO)</td>
<td>Oxidation barrier</td>
</tr>
<tr>
<td>MCrAlX</td>
<td>Bond Coat (BC)</td>
<td>Bonding &amp; Oxidation protection</td>
</tr>
<tr>
<td>Ni based super alloy</td>
<td>Substrate</td>
<td>Thermo-mechanical loading</td>
</tr>
</tbody>
</table>

Figure 2: Schematic of TBC system showing each layer, its material and applications

2.1.1 Bond coat (BC)

The BC is the first layer that is deposited on the Ni-based superalloy material substrate. The purpose of this coating is to protect the substrate from oxidation and/or high temperature corrosion and to provide the necessary bonding of the ceramic to the substrate material. Also, it helps in reducing the interface stresses due to the mismatch in coefficients of thermal expansion (CTE) between the TBC and the substrate material.

These BC can be divided in two categories, diffusion (Pt-modified Aluminides) and overlay (MCrAlX-type) coatings [19]. Overlay coatings are typically used in thermal sprayed TBC system (a TBC system can also be deposited by other techniques than thermal spray, such as physical vapor deposition etc.). In overlay coatings, M is commonly Ni, Co, Fe or a combination of these and X is an oxygen-active element, for example Y, Si, Ta, Hf [20]. Usually a mixture of Nickel and Cobalt based coatings are widely used.

2.1.2 Thermally grown oxide (TGO)

The second layer in a TBC system is the TGO layer (see Figure 2). When a TBC system is under operating conditions (during the in-service life), a TGO
layer is formed between the TBC and a BC at the metal – ceramic interface [16], [21]. This layer is formed due to the oxidation of the BC. The porous ceramic TBC allows oxygen to diffuse to the metallic BC, which results in the oxidation of the BC. Even if the ceramic TBC were fully dense, the high ionic diffusivity of oxygen in the ZrO$_2$-based ceramic TBC renders it ‘oxygen transparent’, that’s why oxidation still is an issue.

The TGO plays an important role in TBCs performance: Failure in TBCs is initiated, at or near the TGO, mostly between the TGO and the BC [22]–[24]. The growth of a TGO layer causes stresses during in-service in a TBC system, due to the difference in CTEs of different layers in a TBC system. These stresses will initiate cracks or cause a crack growth in a TBC, which finally causes failure of the TBC system. Thus, controlling the growth of this oxide is a critical issue to increase the lifetime of the TBC system.

It should be noted that several oxides are formed due to the oxidation of the BC, which typically are Cobalt, Chrome, Aluminium alloys, such as Chromia ((Cr, Al)$_2$O$_3$), Spinel (Ni(Cr, Al)$_2$O$_4$), Nickel oxide (NiO), Silica, and Alumina [22]. Chromia, Spinel and Nickel oxides are usually referred as CSN in the literature.

2.1.3 Ceramic top coat

The last layer is the ceramic top coat or TBC (see Figure 2). The main purpose of this layer is to provide the thermal insulation to the substrate.

The choice of a material for the ceramic TBC layer is determined by some basic requirements such as: high melting point, no phase transformation between room temperature and the operating temperature, low thermal conductivity, chemical inertness, a thermal expansion match with the metallic substrate, good mechanical properties and good adherence to the metallic bond coat [10], [25]. Over the years of development of TBCs, YSZ has become the most widely used commercial material because of its superior thermal and functional performances compared to other ceramics [1], [2]. It has been shown [8] that by stabilising zirconia with 3-4 mol. % or 6-8 wt.% of yttria a superior coating can be created; 3-4 mol.% YSZ was shown to have high thermal expansion coefficient, low thermal conductivity (2.25 W m$^{-1}$K$^{-1}$) in bulk form), good mechanical properties and good phase stability up to 1200°C [26], [27]. Other ceramics which can be used as TBC materials are mullite, Al$_2$O$_3$, TiO$_2$, CeO$_2$+YSZ, La$_3$Zr$_2$O$_7$, pyrochlores, perovskites, etc. [27].

Zirconia (ZrO$_2$) has three allotropic crystal structures, i.e. monoclinic, tetragonal and cubic. The monoclinic phase is stable below 1197°C but transforms to tetragonal above this temperature; the tetragonal phase is stable between 1197°C
and 2300°C; above 2300°C tetragonal transforms to cubic, which then is stable up to 2700°C, the melting point of zirconia. This phase transformation is illustrated below:

\[
\text{Monoclinic} \quad 1197°C \quad \leftrightarrow \quad \text{tetragonal} \quad 2300°C \quad \leftrightarrow \quad \text{cubic} \quad 2700°C \quad \leftrightarrow \quad \text{liquid}
\]

As the structural phases have different volumes, transformations from one to another are detrimental for the performance of a TBC as it induces cracks due to the corresponding volume change and thus promotes failure of the coating [28]. The largest volume change is from tetragonal to monoclinic (4.5% volume expansion) and moreover it happens at temperatures which are in the range of the in-service temperature of a gas turbine. Thus, an external stabilizer e.g. yttria (Y₂O₃), ceria (Ce₂O₃), magnesium oxide (MgO), calcium oxide (CaO) is added to stabilize a desired phase in the material.

Figure 3 explains the effect of yttria content on the stability of the phases present within the YSZ. The addition of yttria in zirconia is critical and it is important to have the content of Y₂O₃ approximately between 3-4 mol.% in order to obtain a non-transformable tetragonal (T') phase (in figure 3, it is shown as 6-11 mol. % since it is 0.5 (Y₂O₃)), which is very resistant to the transformation. Below 3-4 mol. % Y₂O₃ content a transformable tetragonal (T) phase is formed, which may undergo phase transformation as explained above.

As it can be seen from the phase diagram (see Figure 3), at higher temperatures, even the metastable non-transformable tetragonal (T') phase, undergoes a phase separation by diffusion, when aged at temperatures greater than 1200°C. This can allow the tetragonal to monoclinic (T → M) transformation upon cooling. This transformation, as explained earlier, induces cracks, which then may lead to the failure of the coating. Hence, YSZ becomes an ideal material for applications only up to operating temperature less than 1200°C [7]. Addition of higher contents of yttria could completely stabilize the high temperature phases, but the mechanical properties (toughness, erosion resistance) are also altered, so that the in-service requirements and life-time are negatively affected [2], [28].
2.2 Thermal spraying of a TBC system

Thermal spraying [18] is a technique used to deposit a coating on various structures; in which metallic or non-metallic coating feedstock material, in the
form of rod, powder, wire, suspension or solution, is fed into a spray ‘gun’ by a controlled feed system. This feedstock material is heated by electrical (plasma or arc) or chemical (combustion flame) means and then accelerated by the hot gas/plasma jet towards the substrate. Accelerated feedstock material then impinges the substrate in the form of molten or semi-molten state droplets, which upon impact form a pancake shape so called splat and adheres to the substrate by rapid solidification and quenching.

This coating technology, which is a branch of surface engineering is considered as one of the production technology methods. This method is used not only for repairing, rebuilding, and retrofitting machine components but also for restoring original dimensions or applying protective metal layers to various infrastructures, such as bridges, turbines etc. [18], [29].

A major advantage of thermal spraying is that it can be used to produce a coating without a significant heat transfer to the substrate. This avoids thermal distortion and possible damage to the substrate. The major disadvantage of thermal spraying is that it is a ‘line of sight’ process, which makes complex geometry components difficult to spray. Plasma spray physical vapor deposition is a recently introduced process by which shadowed areas can also be coated [30].

For spraying a TBC system several thermal spraying techniques are available. The BC is usually sprayed by plasma spraying or high velocity oxy-fuel (HVOF) and more recently by high velocity air-fuel (HVAF) spraying [31].

BC needs to be dense (no porosity), to serve its purpose in the TBC system, that is to minimize the oxygen penetration to the substrate. Due to the high jet velocity involved in the HVAF process (typically around 1200 m/s), a very dense coating can be produced [32].

Feedstock material in HVAF is mostly in the form of powder, and is injected axially into the flame at the nozzle exit. The feedstock material is then partially or fully melted and accelerated towards the substrate. With a very high impact the particles then form a splat, subsequent splat deposition over each other at high velocity lead to the dense coating formation [32].

The TBC is usually sprayed by plasma spraying since this process inherently has enough thermal energy to enable melting of the ceramic powder during the short-residence time typical of thermal spray processes. EB-PVD process is also commercially used for TBC deposition as it can produce strain tolerant TBCs. In the next subsections, deposition of the TBC layer using various plasma spray processes and feedstock materials used in this study are described.
2.2.1 Atmospheric plasma spraying (APS)

The APS is the conventional technique to deposit TBCs. In this process a plasma is used at atmospheric conditions to spray the feedstock material. Due to the high temperature in the plasma, which can exceed 20000°C [29], and thus the high thermal energy of the plasma jet can melt easily any type of feedstock material.

![Figure 4: Schematic of conventional powder atmospheric plasma spraying process](image)

The basic principle of this technique consist of melting a consumable (most often powder of size 10 µm to 100 µm [33]) and projecting it as molten or semi molten particles onto the substrate as can be seen in Figure 4. The modern plasma spraying process uses a direct current electric arc, to generate a stream of high temperature ionized plasma from one or a mixture of inert gases (Ar, He, H₂, N₂), which acts as the spraying heat source. The coating material, in powder form, is conveyed by a carrier gas (typically Argon) stream into the plasma jet, where it is heated and propelled with a typical particle velocity of 200-300 m/s towards the substrate [29]. The accelerated molten or semi molten particle strikes the substrate and under its impact to the substrate forms a splat. Subsequent deposition of splats over each other leads to the formation of a coating, see Figure 5. The generated splat can be in a size range of few tens to few hundreds of micrometre in diameter and few micrometre thick [33], depending on the spraying conditions or particle size used during spraying.

The formed splats upon impact, shrink and solidify and can form a void or pore in between the two splats. Additionally, a splat may also have gases trapped in it, which can also lead to the formation of a pore within the splat, when the splat is solidified upon cooling.
To generate a desired coating microstructure by plasma spraying, several process parameters need to be controlled, which are explained through the schematic shown in Figure 5. This figure can be generalized for almost all types of plasma spraying techniques with certain changes depending on the specification of the technique. In general, these process parameters can be categorized as: injector and feedstock parameters, spray gun parameters, robot fixture parameters, substrate and plasma jet parameters. The desired microstructure that forms during powder spraying is controlled by the complete history of powder material used; from production, to in-flight conditions to final impact on the substrate leading to the formation of splats.

The size of the particles is very important as it is a major factor influencing the microstructure of the coating and hence its functional properties [34], [35]. Many advantages were found, if the coatings were deposited using fine (submicron and nano-size) powder particles, which are explained in detail in the following subsubsection.

2.2.1.1 Fine powder feedstock

Spraying fine powder particles result in achieving smaller splats (few tens of nm to few hundreds of nm) compared to conventional powder splats (few tens of µm to few hundreds of µm), thus making it possible to obtain coatings with fine
structure. These fine structured coatings are characterized by their fine microstructural features present in the coating microstructure such as fine pores/cracks, fine grains etc. Any nanostructured (or nano-crystalline) material is characterized by a microstructural length or a grain size of 1 nm – 100 nm, whereas submicron structured material is characterized by nearly 0.1 µm to 0.3 µm of its grain size [36].

Such fine structured coatings have shown to have advantages over conventional coatings such as lower thermal diffusivity and thermal conductivity at room temperature [23] as well as at higher temperatures up to 1200°C [37], [38]. The sub-micrometric and nanometric microstructural features have been shown to lower the thermal conductivity [39]. Furthermore, these fine structured coatings have also shown to be better in thermal shock resistance, thermal-cyclic fatigue (TCF) lifetime and a better CTE match [37], [40].

It is difficult to spray fine solid powder feedstock (20 nm to 5 µm) using a standard APS equipment. This is because, these fine particles do not have a good flow-ability and also can’t achieve enough momentum to penetrate the high velocity plasma stream [41]. Spraying fine powder particles may also be an environmental issue i.e. a health problem.

For both health reasons as well as to avoid particle agglomeration during storage and feeding into the spray equipment, a liquid feedstock can be used [42]. The liquid injection method can increase the momentum of the feedstock particles, aiding penetration of fine particles into the thermal jet core. Details about a liquid feedstock spraying are provided in the next subsection.

### 2.2.2 Liquid feedstock spraying

In liquid feedstock spraying, fine powder particles are mixed with a fluid to form a liquid (suspension or solution), which then is injected into the plasma/flame either by atomization or by a liquid stream [43], [44]. In Figure 4, instead of solid powder particles one can imagine a stream of liquid or atomized (break-up of liquid stream into smaller droplets) liquid droplets to be injected into the plasma plume.

Examples of thermal spray processes that can use liquid feedstock are SPPS, S-HVOF, SPS and ASPS [43]–[48], where a liquid in the form of suspension or solution, instead of direct solid powder, is used as a feedstock material.
2.2.2.1 Suspension versus Solution

Suspensions are prepared by mixing submicron or nano-sized solute (ceramic powder) particles in a solvent (water or alcohol (mainly ethanol)). A serious issue with suspensions is, it settles down with time, which if not properly re-mixed before spraying, can influence the coating microstructure and properties. To overcome this problem, some additional elements can be added such as dispersant agents, which can prevent agglomeration of the particles or settling down of the suspension [43]. Proper stirring is required for the suspensions during the spray in order to minimize the settling problem. Also, pumping of suspensions from the storage tank to the plasma torch should be made in a way to generate as stable flow as possible. Any fluctuations may cause a non-homogenized coating structure.

Solutions are a homogeneous mixture of a solute (precursor material) and a solvent, and unlike suspensions no solid particles exist in it. In Figure 6, a droplet of suspension with many fine solid particles and a droplet of homogenized solution are shown. Typically the solutions are salts of respective ceramic powders, such as nitrates, chlorides, acetates, iso-prop oxides and other combinations [43].

Figure 6: Schematic of a suspension and a solution precursor droplet
2.2.2.2 Solution Precursor Plasma Spraying (SPPS)

A recent development in liquid feedstock spraying is the SPPS process, where a liquid in the form of a salt solution of a respective ceramic powder is injected into the plasma. A ceramic salt solution (nitrate or chloride) is fed into the plasma jet, where, the salt is oxidized in-flight forming an oxide particle. Under a rapid heating the solution droplet evaporates and the solid oxide particles in contact with the plasma, are melted and subsequently deposited onto the substrate [49]. Deposition of fine, melted particles then leads to a fine structured coating.

An advantage of SPPS over conventional APS technique is that it can produce a strain tolerant vertically cracked microstructure with low thermal conductivity, due to vertical cracks (cracks normal to the substrate) and the submicron and nano-sized interconnected porosity [50]. However, a limitation of this technique is currently the deposition efficiency due to the difficulty in spraying high molarity solutions.

2.2.2.3 Suspension - High Velocity Oxy Fuel (S-HVOF)

Another possibility in liquid feedstock spraying is the high velocity suspension flame spraying (HVSFS), which is a modification of the conventional HVOF thermal spraying process. This is also referred as S-HVOF spraying [47]. Here, the liquid is in the form of a suspension of a respective ceramic powder.

S-HVOF was developed with the aim of spraying submicron or nanoparticles suspensions with hypersonic speed to deposit thin and very dense coatings. Suspension injection in this process usually is done axially i.e. in same direction as the spray direction [45].

The process parameters which can influence the final coating structures in this process are different from plasma spraying. Examples of important parameters that can be controlled in order to obtain a desired microstructure are [45]:

- Suspension nozzle shape and geometry: In HVSFS, shape and exit nozzle diameter plays a crucial role as it decides the shape of the exiting suspension spray jet.
- Combustion fuel type: Different fuels have different burning characteristics, which can influence the flame temperature and hence the particle temperature. Combustion fuels such as propane, ethane, acetylene etc. can be used.
- Total gas flow: Gas flow can influence the flame velocity and hence the particle velocity. That is higher total gas flow rate can result in higher particle velocity.
Due to the high particle velocity involved in this process (typically around 400 m/s to 600 m/s [29]) the coatings are expected to be denser than the conventional APS and the SPPS coatings.

### 2.2.2.4 Suspension Plasma Spraying (SPS)

Another spraying process by which a liquid feedstock can be sprayed is the SPS [43], [44], [51]. Alike in S-HVOF, submicron or nano-sized powder particles are dispersed in a solvent, typically water or alcohol, in a certain chemical ratio to form a liquid (in this case a suspension). This suspension then is injected into the plasma plume. The suspension then undergoes atomization to form very fine droplets, where each droplet consists of extremely fine solid powder particles individually or in agglomerated form. The liquid from the droplet evaporates quickly and the fine powder particles can undergo sintering, partially or fully melting and may form agglomerates. Then, they subsequently get deposited with a heavy impact on the substrate to form a fine structured coating [43].

The major drive for SPS comes from the possibility to develop coatings with a unique strain tolerant columnar microstructure similar to EB-PVD. SPS coatings have shown to have a similar columnar structure as of EB-PVD, but with a lower thermal conductivity [52]. Columnar coatings with a lower thermal conductivity are demanding in gas turbine industry due to their inherent strain tolerant nature, which enhances the lifetime of the coating.

Even though, SPS has shown a great interest of research for producing TBCs for gas turbine applications, the complexity involved in the process as such, makes it a very difficult process. This process can be described by understanding the detailed process characteristics, which are explained in detail in the next following subsection.

### 2.2.3 Process characteristics of SPS

Similar to the conventional plasma spray process, coating microstructure and coating properties depend on the various process parameters. In fact, in this case the process becomes even more complex due to the chemistry of the suspension and very fine powder particles involved. All the process parameters schematically shown in Figure 5 are also important in SPS. However, some extra parameters, which are also important in this process and can have significant influence on the coating microstructure and properties, are discussed below in the following subsubsections.
2.2.3.1 *Type of solvent: Water versus Alcohol*

As explained in former subsection, suspensions can either be water based, alcohol (mainly ethanol) based or a mixture of water and alcohol based. Both water and alcohol have some advantages over each other, but also have few limitations. The water based suspension is cheaper than the alcohol based suspension. But, the heat required to vaporize ethanol is one-third of that of water, which leads to more usage of power during spray in case of water based suspensions [53]. Also, it was found that the deposition efficiency and the ratio of the coating mass to the powder mass sprayed towards the substrate doubled, when switching from a water-based YSZ suspension to an ethanol-based YSZ suspension [54]. Properties such as viscosity and surface tension of the suspension are also important and depend on the type of solvent used, which can play crucial role in SPS coating formation, as further discussed in 2.2.3.5 and 2.2.3.6. Water based suspensions has higher surface tension than ethanol based suspensions, due to the higher surface tension of water than ethanol [43], [55]. However, viscosity of the suspension is not significantly altered by changing the solvent but by changing the solid load (amount of powder in suspension) and solute particle size [43], [55], [56].

2.2.3.2 *Initial powder size of the solute particles mixed with the solvent*

It is believed that, in conventional solid powder feedstock APS coatings, the scale of microstructural features present in a coating microstructure may depend upon the initial powder particle size. However, unlike APS, initial powder particle size of the respective solute ceramic powder may not necessarily have a direct influence on the microstructure and the microstructural features in SPS TBCs [57]. Initial powder particle size can be denoted as the median size or D50, which is a median diameter of a powder particle in a certain particle size distribution and it signifies that half of the population lies below this size. As discussed earlier, typical fine powder particles used in SPS are shielded by the solvent fluid around them, which forms a suspension droplet as shown in Figure 6. Unlike APS, upon injection, it is this droplet which is in direct contact with the plasma and not the powder particles. This droplet consisting several of those fine powder particles undergoes a thermal treatment in the plasma, which is discussed in the next following subsubsections. Due to this thermal treatment the initial powder particle size may indirectly influence the microstructure, which is also discussed in 2.2.3.5 (in-flight conditions).
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2.2.3.3 Injection of suspension

Proper injection of a suspension is as important as other process parameters discussed so far, to obtain the desired coating microstructure. This is because, in SPS, droplet formation has a great influence in the microstructure formation which will be discussed in a subsubsubsection 2.2.3.6.

Injection of the suspension can be influenced by following two factors:

1. Injector type
   a. Mechanical injector
   b. Atomizing injectors
2. Injection type
   a. Radial injection
   b. Axial injection

Injectors can be of two types, either a mechanical injector or an atomizing injector. In a mechanical injector, which is also called a stream injector, a stream of suspension is injected into the plasma jet. In this case, the plasma jet itself performs the step of stream break-up into small droplets. However, in an atomizing injector, the suspension stream is first atomized (broke-up) into smaller droplets and then injected into the plasma jet.

Injections can also be of two types either radial injection or axial injection. Both injection types are explained in detail in the next subsubsection.

2.2.3.4 Axial injection versus radial injection

Depending on the various spray gun systems, the liquid or solid feedstock is injected into the energetic plasma jet either radially or axially. The term ‘radial injection’ means injecting the feedstock material perpendicular to the plasma flow. ‘Axial injection’ means injecting the feedstock material in the same direction as the flow of plasma. This is explained schematically in Figure 7.

If the feedstock material is injected radially, it may have a strong effect on the thermal treatment of the droplets (in case of liquid feedstock) or particles (in case of solid feedstock) during the in-flight. Different droplet/particle sizes gives different momentum of the droplets/particles when they enter the plasma stream and hence their trajectories will be different. For example, very small droplets/particles may not penetrate the plasma at all or pass only through the periphery. Optimum sized droplets/particles may enter the core of the plasma and get fully treated. However, larger droplets/particles may completely pass through the plasma resulting on the substrates as un-molten particles (overspray)
due to insufficient thermal treatment. Entering different zones of the plasma plume as well as different dwell times (the total time a particle spends in a plasma/flame jet) lead to different heat treatment and acceleration of the particles/droplets towards the substrate which leads to a more heterogeneous microstructure. This is explained schematically in Figure 7 (a).

Axial injection on the other hand can overcome this problem, as there is no issue of trajectory involved due to the parallel injection of feedstock material to the spray direction. As can be seen from Figure 7 (b) that, instead of an individual droplet/particle trajectories, dispersion of droplets/particles undergo the uniform treatment during the in-flight in the plasma.

2.2.3.5 In-flight conditions

Assuming a stable flow of suspension upon injection in the plasma jet, suspension droplets may undergo various stages before final deposition during its in-flight (see Figure 8). These are, injection of suspension, atomization of suspension, vaporization of solvent from the suspension droplet, agglomeration of the fine
solid particles in the suspension droplet, melting of solid particles and finally deposition on the substrate in the form of fine splats.

![Diagram of various stages of a suspension droplet during in-flight](image)

**Figure 8:** Schematic of various stages of a suspension droplet during the in-flight, from an injection of the suspension to the final deposition on the substrate

1) **Stage 1: Injection**

The first stage is the injection of the suspension, and depending on where the suspension stream is injected, either in the core of the plasma plume, which is extremely hot, or the periphery which is colder, it will be treated differently during in-flight [58].

In general, bigger droplets injected into the periphery or cold regions of the plasma jet may form hollow spherical particles on the substrate. Smaller droplets injected directly into the hot core of the plasma jet may form solid particles which then experiences melting and solidification, and deposit on the substrate as splats. These splats are similar to the molten splat structure of the conventional powder feedstock APS process, except that these splats are around ten times smaller. Moderate droplets passing through the moderately hot volume of the jet may form half-melted spherical particles.

2) **Stage 2: Atomization**

The second stage is the atomization of the suspension, which occurs once the suspension stream is in contact with the plasma after injection. Size of droplets and hence the final coating structure directly depends on atomization of the suspension. The following factors can influence the atomization:

1. Plasma drag force
2. Surface tension of the suspension
3. Viscosity of the suspension

Fazilleau et al. have derived a relation between these parameters and the atomized droplet size [59], as shown below:

$$d_d = \frac{8 \sigma}{C_D \rho u^2}$$  \hspace{1cm} \text{(1)}

where $d_d$ (m) is the droplet diameter produced due to atomization, $\sigma$ (N/m) is the surface tension of the suspension, $C_D$ (unit less) is the drag coefficient, whereas $\rho$ (kg/m$^3$) and $u$ (m/s) are density and stream velocity of the plasma respectively.

From the above equation, it can be seen that, to obtain a smaller droplet, a lower surface tension and a higher plasma drag force, which depends on plasma density and velocity, is needed. Also, the viscosity of a suspension, which is not discussed in this equation influences the atomization. Lower viscosity favours atomization of the suspension [55].

Plasma drag force can be controlled directly from the plasma gun hardware, plasma gas compositions, flow rate and the arc current. Whereas, surface tension is hard to control as such and depends on the solvent used. Water has much higher surface tension than ethanol, which then makes difficult to atomize the suspension. Viscosity, on the other hand can be altered and modified by altering the suspension solid load and solute particle size [43], [55].

3) Stage 3: Evaporation of the solvent

In this stage, the atomized droplets are rapidly heated up and the solvent from the atomised droplets vaporizes. Vaporization of the suspension during the in-flight stage undergoes with thermal energy absorption from the plasma plume which thus gets cooler. Cooler plasma may result in insufficient melting of the solid particles. Hence, a suspension plasma spraying needs more energy or power during spraying than conventional powder spraying. Also, the droplets are accelerated concurrently with the vaporization stage.

4) Stage 4: Agglomeration of the solute particles

The solute particles (initial powder particles of certain $D_{50}$ mixed with the solvent as discussed in 2.2.3.2) of respective ceramic powder used in the suspension are usually very fine. These fine particles have a tendency to undergo agglomeration or sintering. This may lose the original characteristics of fine particles, since they are no more fine but agglomerated and larger. This is also one of the reason that the initial powder particle size ($D_{50}$) may not directly influence the microstructure. However, larger initial particle size ($D_{50}$) means that the atomized droplet
BACKGROUND

(containing some agglomerated fine particles) contains larger solid particles’ mass, which will undergo melting in the next stage.

5) Stage 5: Melting of the solid particles

Complete vaporization and some agglomeration leads the agglomerated fine solid powder particles in direct contact with the plasma, which are heated and melted. The molten particle may consists of few of the initial powder particles of certain D_{50}, which were agglomerated in the previous stage and which may result in slightly larger solid mass in the molten particle than the initial powder particle mass. This then explains, the fine microstructural features may not necessarily, a direct result from the fine initial powder particles in the suspension started with. Instead, it is this molten particle (of different size and mass (typically larger and heavier) than the initial powder particle), which decides the splat size and hence the other microstructural features in the coating. The degree of heating so as melting depends again on the overall power level of the spray process and also the plasma gas composition [60]. The heating of a particle also depends on the spray distance, usually in SPS the spray distance is kept shorter than the conventional APS. This is because of the very fine size of the powder particles involved in SPS; which needs less time to be melted. The small size also means that the particles are cooled faster, hence a shorter spray distance is necessary.

6) Stage 6: Deposition of the particles

In the final stage, the molten or semimolten agglomerated solid particles in the form of a molten particle (larger and heavier than the initial powder particle) end up on the substrates with a heavy impact to generate fine splats. The way the molten particle impact the substrate is presented in 2.2.3.6. Subsequent deposition of these splats then leads to a coating of a certain thickness depending on the spraying conditions and the application.

2.2.3.6 Coating formation in SPS

Coating build up in suspension plasma sprayed coatings is completely different to that in conventional APS powder sprayed coatings. Coating formation in SPS is understood to be related to the generation of very fine droplets due to the atomization or fragmentation of suspension after injection and resulting small in-flight particles once the solvent has evaporated [61]. The trajectory of the particles smaller than 5 μm can be affected by plasma stream in the boundary layer close to the substrate and deposit at shallow angles on surface asperities leading to shadowing effect [61], which is shown schematically in Figure 9. This is because of the low momentum of these smaller particles, which can be influenced by the drag of the plasma stream in the boundary layer close to the substrate. This can
be seen in Figure 10 where, Berghaus et al. simulated the influence of plasma direction changes on particle velocities [61].

![Diagram showing plasma flow and particle velocities](image)

**Figure 9: Schematic showing the shadowing effect on the substrate asperity of particles with different sizes**

Based on the above concepts VanEvery et al. has proposed three major possible types of coating microstructures in SPS [62]. If the droplet size after the fragmentation is extremely small (< 1 µm), the shadowing effect is larger, which can generate a columnar type structure. Droplets having higher momentum (> 1 µm) but still small enough (< 5 µm) to be affected by the plasma flow can form a structure with some porosity bands within the columns which can be termed as feathery columnar structure. Finally, droplets with much higher momentum can have a direct impact on the substrate with a very little influence of a plasma drag. This may result in to a lamellar (similar to the conventional powder sprayed APS process) or vertically cracked structure.
In such a lamellar structure, the presence of micro cracks can form the vertical crack as the splats overlaps during the coating growth. Vassen et al., however, have shown that driving force for vertical crack growth in SPS coating is the higher tensile stresses present in the coating [48]. The increased tensile stresses in the SPS coating are due to the presence of less micro cracks than in APS. Minimized micro cracks can then increase tensile stresses in the SPS coating.
Characteristics of TBC

Examples of important characteristics of a TBC are the microstructure, porosity, thermal conductivity and lifetime. The first three, which are in the scope of this research work are discussed in detail in this chapter.

3.1 Microstructure

If there is something which can explain most about the final properties and performance of a thermal spray coating, then it is the coating’s microstructure. Changes in coating microstructure result in changes in coating properties, thus it is important to understand its formation and how various microstructural features influence the coating performances. In this section a typical APS microstructure and a liquid feedstock plasma sprayed coating microstructure are discussed respectively.

3.1.1 Solid powder feedstock APS sprayed coatings

Typical solid feedstock APS coating’s microstructure have a lamellar structure as shown in Figure 11. The coating is built-up by subsequent deposition of splats with sizes in the range of tens to hundreds of µm in diameter and few to tens of µm in height, which finally form lamellar structured coating. The lamellar structured coating is heterogeneous and has a lot of microstructural features such as pores, cracks and delaminations of various sizes. They are important characteristic of the coating, since they strongly influence the coating properties. Delaminations and cracks are formed in the coating due to the insufficient bonding of splats to the surface and cooling of splats respectively. Fine scale pores are formed due to the gas bubbles between splats or gas voids within powder particles. Globular pores on the other hand, are formed due to low temperature or velocity parameters.

All these features contribute to the overall porosity of the coating which influence the thermal insulation of the coating. The role of these various microstructural features on thermal properties, will be discussed in the latter section in detail. Mechanical and functional properties such as coating’s stiffness, cyclic lifetime etc. are also influenced by these features, which is beyond the scope of this work.
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3.1.2 Liquid feedstock thermal sprayed coatings

Liquid feedstock thermal spray as explained in chapter 2, can give a wide variety of coating microstructures. On a macro-scale these coatings exhibit different microstructures with features such as: vertical cracks, spacing between columns (inter-columnar spacing), inter-pass porosity bands, branching cracks etc.; whereas at a micro-scale, coatings show features such as fine pores (interconnected or independent). Based on the microstructure at a macro-scale these coating structures can be mainly categorized as follows:

1. Vertically cracked structure
2. Highly Porous structure
3. Columnar structure
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1. Vertically cracked structure
2. Highly Porous structure
3. Columnar structure

These structures are shown in Figure 12. Depending on a specific combination of numerous factors such as feedstock material (suspension or solution), spray technique and spray parameters etc., which are discussed in chapter 2, any of the particular structure or a structure similar to these can be obtained.

As explained above, these coatings also look different at micro-scale, as can be seen in Figure 13. It can be observed from the figure that the coating also has pores in the submicron and nano range.
Porosity is one of the microstructural features present in a coating. In liquid feedstock plasma sprayed coatings as explained above, all the different microstructural features, both at large scale and small scale, can be counted as total porosity content of the coating. These pores are nothing but empty voids filled with a free gas or air at ambient conditions. Porosity can be open when the pores are interconnected (accessible by a fluid if injected externally) or closed when they are isolated from each other (non-accessible by a fluid from outside the coating). The definition of open porosity and closed porosity may vary depending on the usage of the porosity term in various applications, but in case of thermal barrier coatings it is dealt with a fluid accessibility in pores.

- Open porosity: Vertical cracks, spacing between adjacent columns (inter-columnar spacing), inter-pass porosity bands which are typically connected with the vertical cracks or inter-columnar spacing. Also, in some cases there can be branching cracks, cracks which originate at the
vertical cracks or inter-columnar spacing and grow parallel to the substrate. All microstructural features mentioned above are considered as open porosity.

- Closed porosity: Smaller and larger scaled pores which are independently present in the coating, independent clustered pores which are connected with each other but not with any of the features shown in the open porosity so that an external fluid cannot reach them. Also, in some cases, fine cracks which are present in the coating but not connected with any of the features shown in the open porosity.

Figure 14: Simplified schematic of typical liquid feedstock plasma sprayed TBC microstructure, showing all possible features which can be counted in as total porosity

All these features are shown in a schematic of typical liquid feedstock plasma sprayed coating in Figure 14. All these features can significantly affect the thermal insulation nature of the coating. Vertical cracks or inter-columnar spacing are through the thickness of the TBC. These through thickness cracks if present in large number (higher vertical crack density in the coating) can increase the overall thermal conductivity of the coatings [63], [64]. However, branching cracks and inter-pass porosity bands are perpendicular (or close to perpendicular) to the direction of heat flow within the coating and hence can act as a significant thermal barrier within the coating [64], [65]. Other fine features such as cracks and pores also help in decreasing the overall thermal conductivity of the coating. This is
because of the much lower thermal conductivity of these features (containing air) compared to the bulk material (in this work 4 mol. % YSZ).

The above mentioned features also have significant effect on the mechanical and functional properties of these coatings which is beyond the scope of this work.

### 3.3 Thermal conductivity

Thermal conductivity is another important property of a TBC, which drives the overall performance of a TBC system on a gas turbine. Thermal conductivity is a measure of a heat conduction through the top ceramic coating or TBC. The lower the thermal conductivity of a TBC is, the better the thermal insulator it is. Hence, it is important to understand possible modes of heat transfer in a TBC and henceforth to understand how to lower the thermal conductivity of a TBC system. Since, the work was focused on 4 mol. % YSZ TBCs, in brief, different possible modes of heat transfer in 4 mol. % YSZ TBCs and their thermal conductivity, both for conventional and liquid feedstock plasma sprayed TBCs are discussed.

#### 3.3.1 Heat transfer in conventional APS sprayed TBCs

Golosnoy et al. [66] explained several possible contributing modes of heat transfer in conventional APS 4 mol. % YSZ TBCs, which influences the overall thermal conductivity of the TBC system. These are

- conduction through the solid YSZ,
- conduction through the gases in pores,
- radiative heat transfer, and
- some contribution from convection if the segmented cracks are present.

At ambient (room conditions) temperature and pressure, conductive heat transfer through solid YSZ is largely predominant followed by conduction through the gases in pores [66]. Radiative heat transfer is significant only at higher temperatures (greater than 1000K) [66]. Convection plays partial role if ceramic top coats in the TBC system have thick or wide and through vertical cracks or segmented cracks [66]. This is because these segmented cracks can allow the hot gases to pass through the coating easily hence increasing the overall thermal conductivity of the TBC system [63], [64].

For the bulk , 4 mol. % tetragonal YSZ coating, the thermal conductivity at ambient conditions is \(\sim 2.25 \text{ W m}^{-1}\text{K}^{-1}\), which is due to the phonon conduction [67]. In reality, since the coating is not fully dense and consists of many microstructural features such as pores and cracks the overall thermal conductivity...
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3.3.2 Comparison of heat transfer in conventional APS and liquid feedstock plasma/flame sprayed TBCs
Similar to conventional TBCs, all the modes of heat transfer, which contribute for thermal conductivity, are also valid for 4 mol. % YSZ liquid plasma/flame sprayed TBCs. However, because of the presence of different microstructural features, these coatings can conduct heat through both solid YSZ as well as gases in pores compare to APS coatings in a significantly different manner. As in conventional APS, radiation heat transfer can be neglected at ambient conditions but, conduction through solid YSZ and gases in pores can have significant different influence on thermal conductivity, due to the different microstructure of these coatings compared to conventional APS coatings. As presented in the sections 3.1 and 3.2 liquid feedstock plasma/flame sprayed coatings may have a microstructure with considerable higher content of very fine (<1 μm) submicron or nano-sized porosity.

Due to the presence of fine (<1 μm) submicron or nano-sized microstructural features in these coatings [68], [69], phonon scattering enhances, which then helps in lowering the overall thermal conductivity [66], [67]. Also, since the pores present in such coatings are in submicron or nano range, conductivity in the gas within the pores can also be significantly lower than in conventional APS coatings
(see the discussion in the previous section) [66], [67]. However, presence of segmented cracks or inter-columnar spacing can increase the thermal conductivity, if they are large or wide enough to allow convection through them [63], [64], [66], [67].
4 TBC characterization techniques

Many characterization techniques are available to analyse TBCs [11], [12], [70]–[73], however, only those which are within the scope of this work are presented in this chapter. Figure 15 describes in brief different types of characterization techniques used in this work.

4.1 Microstructure evaluation of the TBC

Microstructures of TBC in a TBC system, in general were studied in this work using scanning electron (SEM) and optical microscopy (OM). Phase analysis was performed using X-ray diffraction (XRD). In case of liquid feedstock sprayed coatings, due to the fine scaled features present in the microstructure, a high resolution SEM was needed to get a thorough understanding of all the features.

Prior to the microstructure study in a microscope it is very important to prepare the samples using proper metallographic techniques. Typically sample preparation of TBCs involve cutting, mounting in a low viscosity epoxy resin, grinding and polishing the samples manually or using semi-automated machine. Thus standard procedure is presented in detail elsewhere [70].
4.2 Porosity measurement

Measuring the porosity in a liquid feedstock plasma/flame sprayed coating is a big challenge due to the presence of different scaled porosities, starting from micrometric vertical cracks to submicron and nano-sized pores. Hence, porosity analysis was done using three different techniques. Open porosity measurement was done using water impregnation (Archimedean porosimetry) and mercury intrusion porosimetry (MIP). Also, SEM image analysis was carried out to determine the content of both closed and open porosity in the coating.

In Archimedean porosimetry a free standing ceramic coating is immersed in water and kept there under vacuum for certain time (around 5 minutes) to force the water into the pores. Both, wet (immersed coating) weight and dry (as-sprayed coating) weight are measured by an electronic weighing machine. Weight difference of wet and dry coating is then calculated, which gives a measure of the coating porosity and hence the density. Detailed explanation can be found in the appended Papers A and B.

Unlike water in Archimedean porosimetry technique, mercury is intruded into the coating in MIP. Similar to water impregnation, a free standing ceramic coating is kept under vacuum in a capillary tube and the mercury is forced by using an external pressure, which can then fill the coating pores. MIP is based on the premise that a non-wetting liquid (one having a contact angle greater than 90°) will only intrude capillaries under pressure [74]. A detailed explanation of the MIP technique and the equipment is provided in Paper C. The pore size distribution is determined from the volume intruded at each pressure increment; whereas the total porosity content is determined from the total volume intruded.

The conventional way of analysing porosity of TBCs is using image analysis on an established number of SEM micrographs of coatings cross-section. The analysis involves converting a SEM greyscale image into a binary image (black and white) using any image analysis software (ImageJ, Aphelion etc.) with proper thresholding for determining the boundary between bulk and pore. Finally, the fraction of white (pores) portion relative to the black (bulk material) portion of the binary image of a given SEM greyscale micrograph gives a porosity content in that particular image. Average of the porosity of all the images then gives the net porosity content of the coating.

Since liquid feedstock plasma/flame sprayed coatings showed porosity at varied scale (micrometric, submicron, and nano pores); two different magnifications were utilized for analysis, x1000 and x10000 in this work. These two magnifications were selected such that x1000 magnification should capture
features like columnar spacing, big vertical cracks, and micron-sized pores, whereas x10000 should capture features like submicron and nano-sized pores. While capturing the higher magnification micrographs, it was made sure that these micrographs should not contain any big features (which were already captured at lower resolution) in order to avoid repetition. This technique is explained in detail in Paper C. The image analysis technique adopted for this work is time-consuming but can provide an estimate of all types of pores (connected, non-connected, vertical cracks, branching cracks etc.) present in the coating. This is not possible using techniques like Archimedean porosimetry or MIP.

4.3 Evaluation of thermal conductivity

Thermal conductivity is a measure of the amount of heat flow through a material (in this case a TBC). The most common method to evaluate the thermal conductivity of a TBC is to derive it from its diffusivity. Thermal diffusivity is measured experimentally. Thermal conductivity is calculated using the following equation:

\[
\lambda = \alpha \rho C_p
\]  \hspace{1cm} (2)

where \( \alpha \) (\( m^2 s^{-1} \)) is the thermal diffusivity, \( C_p \) (\( J kg^{-1} K^{-1} \)) is the specific heat capacity, \( \rho \) (\( kg m^{-3} \)) is the coating density and \( \lambda \) (\( W m^{-1} K^{-1} \)) is the thermal conductivity.

The most widely used experimental technique for thermal diffusivity measurement of a TBC is the laser flash analysis (LFA) technique \([75]–[77]\). Several types of LFA equipments are available today so that thermal diffusivity can be measured either at room temperature or higher temperatures (up to 1500ºC) as well as in ambient atmosphere and controlled atmosphere (Argon). The schematic of a typical laser flash equipment during the LFA experiment is shown in Figure 16.

During the laser flash experiment a laser pulse is fired at the rear face of the sample (at the substrate). The heat pulse travels through the sample and the resulting temperature increase at the surface of the top ceramic coat is measured with an InSb infra-red detector at a high sampling rate. The thermal diffusivity is calculated by the equipment using the following equation \([78]\):

\[
\alpha = 0.1388L^2/t_{(0.5)}
\]  \hspace{1cm} (3)

Where \( \alpha \) (\( m^2 s^{-1} \)) is a thermal diffusivity, \( L \) (\( m \)) is the thickness of the sample and \( t_{(0.5)} \) (\( s \)) is the time taken for the rear face temperature of the TBC to reach half of its maximum rise. Detailed information about the origin and usage of equation
3 for diffusivity measurement in TBC can be found elsewhere [78]. It should be noted that it is only the thickness which is an input by the user to the LFA equipment, \( t_{(0.5)} \) and hence \( \alpha \) is calculated by the equipment. An average of five laser shots is made for each measurement when the sample is at a steady state condition.

As zirconia is transparent to the laser wavelength used for measurements, the samples need to be coated with a layer of graphite or gold to prevent the laser pulse from traveling through the ceramic layer and allow energy from laser light to absorb [79]. The wavelength used in this work was 1064 nm (LFA 427, Netzsch Gerätebau GmbH, Germany), which is transparent to zirconia, hence, the samples were coated prior the diffusivity measurements.

![Figure 16: Schematic of the laser flash analysis equipment, note that the sample is placed in a specimen holder with a substrate facing the laser beam](image)

The diffusivity measurement can be done on free standing single layer (only ceramic top coat/TBC) or a multi-layer (top coat + bond coat + substrate) TBC system. Since there is no need to remove the ceramic top coat, the latter one is preferred. The latter one can also provide more realistic value as multilayerd systems are used in-service conditions.
TBC CHARACTERIZATION TECHNIQUES

Thickness measurement in this work was performed by optical microscopy by taking around 200 measurements all across the coating cross-section. Thickness for each layer in a multilayered TBC system \( L \) in the equation 3) is an important factor on the accuracy of the results in a LFA experiment. It can be seen from the equation 3 that thickness has a square dependence on the thermal diffusivity. An error of 20 \% in the total thickness \( L \) of the TBC system can give almost 50\% change in thermal conductivity [78].

The specific heat capacity can be measured using differential scanning calorimetry (DSC). For this work the specific heat capacity measurement was not performed, instead the values from existing databases on the same material (4 mol. \% YSZ) for specific heat capacity were used [15], [24].

4.4 Evaluation of thermal-cyclic fatigue lifetime

Lifetime assessment of TBCs is rather difficult, since it is hard to provide the realistic conditions as it is in-service on real components. However, accelerated and simplified tests are used to estimate the lifetime for comparative purposes [2], [80]. TCF and thermal shock are two tests, which are typically used to estimate the lifetime of TBCs. The latter one is beyond the scope of this work.

In TCF testing, samples are heated in a furnace (in air and normal atmospheric conditions) up to 1100°C for a period of 1 hour followed by rapid cooling, using compressed air to approximately 100°C within 10 minutes. This heating and cooling is termed as one cycle. After each cycle, a visual record of the samples’ surface is made and samples are repeatedly cycled in this fashion until failure. This allows crack evolution to be observed and cycles to failure to be estimated. The criterion for failure in TCF testing is when the coatings show more than 20\% spallation of the whole coating surface. The more extensive description of this technique is provided in Paper A and Paper B.
Microstructure and its effect on the thermal conductivity of a TBC system

As stated in the previous chapters, the microstructure of a TBC is an important characteristic as it can contain various microstructural features which have a strong influence on its performance. These different microstructural features could be due to the various factors such as feedstock material and size, spraying technique, spraying temperature, in-flight particle velocity, etc. This chapter is focused on investigating various types of possible microstructures which can be produced using liquid feedstock thermal spraying. In addition, the effect of various microstructures on the TBCs thermal conductivity is also discussed.

Figure 17 shows various possible routes which can be utilized to produce a specific type of microstructure as presented in section 3.1.2. The routes shown in Figure 17 summarize the results from an extensive experimental study that was performed with various liquid feedstock thermal spray techniques and discussed in detail in Papers (A, B, C and D), which are appended at the end of this thesis.

Solution precursor plasma spraying (investigated in Paper A) and suspension flame spraying (investigated in Paper B) have produced TBCs with vertically cracked type microstructure. However, conventional solid powder feedstock plasma spraying can also produce vertically cracked structure under certain spraying conditions, which has been shown elsewhere [81].

Suspension plasma spraying on the contrary has shown to be able to produce all three types of typical SPS microstructures i.e. vertically cracked, highly porous and columnar. Investigations in Paper A and Paper B gave the first hint of a microstructure with features resembling like columns using suspension plasma spraying. This was further investigated in Paper C and Paper D where axial suspension plasma spraying was utilized and it was found that it is possible to obtain, not only columnar, but also other types of microstructures as discussed in section 3.1.2 and shown in Figure 17 below.
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Various features present in the microstructure were investigated, since they can influence the performance of the TBC. These features and their formation are mostly governed by the different deposition/spraying conditions (investigated in Paper C and Paper D). As explained in chapter 3, the important features observed in all the three types of microstructures are: inter-pass porosity bands, branching cracks, vertical cracks, columns, inter-columnar spacing and other fine scale pores (closed connected, non-connected pores, fine cracks etc.). The total porosity content of the coating, has a significant impact on thermal conductivity as explained in chapter 3 and also investigated in all Papers (A, B, C and D). Not only the total porosity content, but the distribution of these different features in the microstructure also showed a significant influence on thermal conductivity (investigated in Paper C and Paper D).

As shown in Figure 18, higher fine scale porosity and interpass porosity bands or branching cracks give lower thermal conductivity (investigated in Paper B and Paper C), whereas higher number of vertical cracks and inter-columnar spacings can increase the thermal conductivity (investigated in Paper C). Moreover, the effect of vertical cracks or inter-columnar spacing can be minimized if the total porosity content is increased by increasing the other fine scale porosity in the microstructure (investigated in Paper D).
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As explained in earlier sections 3.2 and 3.3, vertical cracks, inter-columnar spacing, if very large or wide, may allow the passage of hot gases to flow through them, which can increase the thermal conductivity of the coating. However, inter-pass porosity bands are almost perpendicular to the direction of heat flow, so they can help in decreasing the thermal conductivity. Other fine scale pores also help in reducing the thermal conductivity.

For a TBC application, lower thermal conductivity is needed which then can be achieved by controlling the above features by selecting a proper spray process and optimizing the process parameters. However, low thermal conductivity alone is not sufficient and better strain tolerance in a TBC is also needed which was out of the scope of this work.
Conclusions
This research work has explored the relationships between process parameters, coating microstructure, thermal diffusivity and thermal conductivity in liquid feedstock thermal sprayed TBCs. The following conclusions are drawn from this work correspondingly with the research questions stated earlier in chapter 1.

The liquid feedstock technology was shown to provide large opportunities in creating different types of microstructures by varying different spray techniques and process parameters. Predominantly three different types of microstructures were obtained using the various liquid feedstock sprayed techniques. The types were categorized as highly porous, vertically cracked and columnar. The three different types were shown to give significantly different thermal properties. Axial suspension plasma spraying was shown as a promising technique to produce various microstructures including all the three types, as well as low thermal diffusivity and low thermal conductivity coatings.

Examples of microstructural features that were observed in the coatings were fine pores (submicron and nano-sized), coarse pores (micron-sized), vertical cracks, inter-columnar spacing, interconnected porosity bands and branching cracks. It was found that all these features influence the total porosity content of the coating, which in turn was shown to have a significant influence on the thermal properties of the coatings. The porosity was categorized as open porosity, i.e. pores which are accessible to an external fluid, and closed porosity. Image analysis on SEM micrographs was shown capable of estimating both closed and open porosity and to provide a fair estimate of the total porosity if two different magnifications were used. Image analysis seems thus to provide the best estimate of the total porosity compared to the two other techniques investigated, water impregnation and MIP which only could estimate the open porosity.

It was found that liquid feedstock plasma spraying enables an increase of the total porosity content in the coating compared to solid feedstock plasma spraying. Higher total porosity content and presence of fine pores and grains seems as the most probable reason to the significantly reduced thermal diffusivity and conductivity.

Liquid feedstock spraying and specifically axial suspension plasma spraying seems thus as very promising technique to produce high thermal insulation coatings.
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This research work has explored the relationships between process parameters, coating microstructure, thermal diffusivity and thermal conductivity in liquid feedstock thermal sprayed TBCs. The following conclusions are drawn from this work correspondingly with the research questions stated earlier in chapter 1.

The liquid feedstock technology was shown to provide large opportunities in creating different types of microstructures by varying different spray techniques and process parameters. Predominantly three different types of microstructures were obtained using the various liquid feedstock sprayed techniques. The types were categorized as highly porous, vertically cracked and columnar. The three different types were shown to give significantly different thermal properties. Axial suspension plasma spraying was shown as a promising technique to produce various microstructures including all the three types, as well as low thermal diffusivity and low thermal conductivity coatings.

Examples of microstructural features that were observed in the coatings were fine pores (submicron and nano-sized), coarse pores (micron-sized), vertical cracks, inter-columnar spacing, interconnected porosity bands and branching cracks. It was found that all these features influence the total porosity content of the coating, which in turn was shown to have a significant influence on the thermal properties of the coatings. The porosity was categorized as open porosity, i.e. pores which are accessible to an external fluid, and closed porosity. Image analysis on SEM micrographs was shown capable of estimating both closed and open porosity and to provide a fair estimate of the total porosity if two different magnifications were used. Image analysis seems thus to provide the best estimate of the total porosity compared to the two other techniques investigated, water impregnation and MIP which only could estimate the open porosity.

It was found that liquid feedstock plasma spraying enables an increase of the total porosity content in the coating compared to solid feedstock plasma spraying. Higher total porosity content and presence of fine pores and grains seems as the most probable reason to the significantly reduced thermal diffusivity and conductivity.

Liquid feedstock spraying and specifically axial suspension plasma spraying seems thus as very promising technique to produce high thermal insulation coatings.
Future work

High temperature changes in the microstructures were noticed in this work but not investigated. Investigation of high temperature changes in the microstructures such as sintering and pore coarsening could be the first step in extending this work.

Effect of various suspension characteristics and individual process parameters in the axial suspension plasma spraying technique on columnar structured coatings’ microstructure is also of specific interest, which can also be investigated in future work.

Mechanical properties such as erosion resistance and lifetime such as thermal-cyclic fatigue and thermal shock are also important characteristics of a TBC, which could be a possible route for future research.

The work also showed that the axial suspension plasma spraying can obtain extremely porous as well as dense coatings, which can be utilized for solid oxide fuel cell applications; where a porous anode and dense electrolyte is needed. Hence, this can also be a possible path for this research work in future.
7 Future work

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References


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REFERENCES


Summary of appended publications

Paper A - Characterization of Thermal Barrier Coatings produced by various thermal spray techniques using solid powder, suspension and solution precursor feedstock material

The paper was a first attempt in the extensive screening study, which was performed in this thesis work; to achieve a microstructure for the TBC application with a lower thermal conductivity using liquid feedstock. Existing liquid feedstocks (Suspension and Solution) were chosen, which were sprayed using plasma spraying along with conventional solid powder feedstock. A comparative study was performed on SPS, SPPS and APS sprayed TBCs; which were sprayed using 4 mol. % yttria-partially stabilized zirconia suspension, solution and powder feedstocks respectively. It was found that a TBC with a microstructure resembling columnar type (inherently strain tolerant structure) can be produced using SPS, with a much reduced thermal conductivity, about half of that of the conventional APS TBC. Apart from this, it was also found that vertically cracked microstructures can be produced using SPPS. However, both SPS and SPPS coatings had a shorter lifetime than a conventional APS coating.

Paper B - Comparative study of suspension plasma sprayed and suspension high velocity oxy-fuel sprayed YSZ thermal barrier coatings

The second paper was a continuation of the first study where suspension was found to be the most feasible feedstock. Hence, this paper was focused on achieving different microstructures using suspension as a feedstock, and different spraying techniques. A comparative study was performed on a 4 mol. % YSZ suspension sprayed TBCs, with S-HVOF and SPS. Suspension was injected axially and radially in S-HVOF and SPS respectively. It was found that two different types of microstructures namely, vertically cracked and columnar type resembling structure can be predominantly achieved using S-HVOF and SPS techniques respectively. SPS resulted in highly porous coatings with extremely low thermal conductivity and relatively high thermal cyclic fatigue lifetime; whereas S-HVOF resulted in comparatively dense coatings with higher thermal conductivity and lower TCF lifetime. Apart from this, significant influence of initial powder size in the suspension (D50) was also noticed on coating porosity and its thermal properties. Reduction in D50 resulted in higher porosity and lower thermal conductivity in both SPS and S-HVOF coatings.
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Paper C- Characterization of microstructure and thermal properties of YSZ coatings obtained by axial suspension plasma spraying (ASPS)

Although both techniques i.e. S-HVOF and SPS, explored in study presented in Paper B showed several advantages, they also showed some limitations. S-HVOF had the limitation of achieving the desired high porosity due to the high particle velocity involved, and radial injection SPS showed overspray problems due to the radial injection. In an attempt to overcome these problems, it was decided to use ASPS. A screening study was performed in order to explore various possible microstructures which can be obtained by ASPS. It was found that ASPS can generate predominantly three different types of microstructures which are highly porous, vertically cracked and columnar type. These types were discussed in this paper in detail.

One further aim of this study was to investigate the relationship between the different microstructures and the thermal properties of the obtained coating. It was found that ASPS can be a potential technique to produce low thermal conductivity TBCs, lower than the conventional APS and EB-PVD TBCs. All three different types (highly porous, columnar (feathery columnar) and vertically cracked) discussed in this paper, showed varied scale porosity in a micron, submicron and nano-sized scale. Higher porosity, lower column density and higher inter-porosity bands present in the coating resulted in lower thermal diffusivity and conductivity. Image analysis was also shown as a promising technique to estimate the total porosity in the coatings.

Paper D- Influence of microstructure on thermal properties of axial suspension plasma sprayed YSZ thermal barrier coatings

This paper continued the study performed for Paper C where the ASPS technique was explored to achieve various microstructures. This paper was focused on discussing only columnar type microstructures and their influence on thermal properties. It was shown that the ASPS technique can produce a columnar structured TBC similar to EB-PVD coatings; but, with lower thermal conductivity due to the high amount of fine scaled microstructural features present in the coating. Higher total porosity content resulted in lower thermal diffusivity and thermal conductivity. No clear relationship between the column density and the thermal properties was found. Just the total porosity was shown to have a significant effect. Higher spray distance and surface speed along with other process parameters resulted in lower crystallite size, higher total porosity and higher column density which resulted in lower thermal diffusivity and thermal conductivity of the coating.
Microstructure and Thermal Conductivity of Liquid Feedstock Plasma Sprayed Thermal Barrier Coatings

Thermal barrier coatings (TBCs), are widely used to provide thermal insulation to components, in both power generation and aero engine gas-turbine. Improvement of the thermal insulation by reducing the thermal conductivity of the coating, allows for a higher combustion temperature which both reduces fuel consumption and certain emissions, that is why there is a constant need to find new coating solutions.

This work was focused on exploring a new type of feedstock technique i.e. a liquid feedstock in various thermal spraying processes. Suspension plasma, suspension flame and solution precursor plasma spraying are examples of techniques that were utilised. The liquid feeding solution, is an alternative to the conventional solid powder feedstock spraying, was shown superior to the solid feedstock spraying. By the use of liquid feedstock spraying a large variety of microstructures such as highly porous, vertically cracked and columnar structures could be produced. It was shown that there are strong relationships between the microstructures and the thermal properties of the coatings. Specifically axial suspension plasma spraying was shown as a very promising technique to produce various microstructures as well as low thermal diffusivity and low thermal conductivity coatings.