Tailored microstructure of Gadolinium Zirconate based thermal barrier coatings subjected to thermal cyclic fatigue

Cliff Hamatuli
Yttria Stabilized Zirconia (YSZ) is the standard ceramic top coat material used for TBC application. Above 1200°C, issues such as CMAS (Calcium Magnesium Alumino Silicates) infiltration susceptibility, phase instability and high sintering rates limits its long durability. Therefore, new materials which can overcome these challenges without compromising the other requirements for TBCs are highly desirable. Gadolinium zirconate is one such material which has shown promising results for CMAS infiltration resistance. In this work, a relatively new TBC processing route, suspension plasma spray (SPS) has been employed to deposit gadolinium zirconate based TBCs. The primary aim of this study was to deposit two different coating systems (layered and composite) of gadolinium zirconate and YSZ composition using SPS technique and evaluate their thermal cyclic fatigue life performance. The layered system was a triple layered TBC with YSZ as the base layer, relatively porous GZ as the intermediate layer and dense GZ as the top layer. The blended TBC system comprised of a thin YSZ layer, an intermediate GZ+YSZ thick layer and dense GZ top layer. In the thermal cyclic fatigue test at 1100°C and 1200°C, it was observed that blended TBC had a lower thermal cyclic life than the layered TBC. It was shown that SPS is a promising technique to deposit columnar microstructure TBCs.
This thesis work has been conducted at Production Technology Centre, University West, Trollhattan, Sweden. Many thanks go to my university supervisor Mr. Satyapal Mahade and industry supervisor Mr. Anders Thibblin from Scania AB, Stockholm for their unprecedented guidance and help. I further extend my thanks and gratitude to my fellow students Sourabh Bhoje and Mohammed Jasim for their exceptional valuable input. I also would like to thank those who directly and indirectly contributed to this study. But above all thanks to the Swedish Institute (SI) for the scholarship they offered to me. None of this would have taken place without their financial support. Last but not the least; special thanks go to my parents for their support.
Affirmation

This master degree report, "Tailored microstructure of Gadolinium Zirconate based thermal barrier coatings subjected to thermal cyclic fatigue", was written as part of the master degree work needed to obtain a Master of Science with specialization in manufacturing degree at University West. All material in this report, that is not my own, is clearly identified and used in an appropriate and correct way. The main part of the work included in this degree project has not previously been published or used for obtaining another degree.

[Signature by the author]

06-08-2017

Date
Preface

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<td>APS</td>
<td>Atmospheric Plasma Spray</td>
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<tr>
<td>BC</td>
<td>Bond coat</td>
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<tr>
<td>CMAS</td>
<td>Calcium-Magnesium-Alumino-silicate</td>
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<tr>
<td>EB-PVD</td>
<td>Electron beam physical vapour deposition</td>
</tr>
<tr>
<td>GZ</td>
<td>Gadolinium Zirconate</td>
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<tr>
<td>HVAF</td>
<td>High Velocity Air Fuel</td>
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<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<td>SPS</td>
<td>Suspension Plasma Spraying</td>
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<td>TBC</td>
<td>Thermal barrier coating</td>
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<td>TC</td>
<td>Top coat</td>
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1. INTRODUCTION

Thermal barrier coatings play an important role of insulating metallic components that are exposed to high temperatures during operations. They are commonly used in aerospace industry to protect specific engine components such as turbine blades and vanes from failure as a result of exposure to high temperatures. Further, TBCs find their application in automobile industry where they protect specific parts or components of the engines such as exhaust manifolds and turbo chargers from high temperatures that are generated during combustion of gases in the combustion chamber. Most cited benefit of applying TBCs in gas turbine industry is that they make it possible to achieve higher engine efficiency by increasing the gas inlet temperature [1].

![Aero gas turbines diagram](image1)

Figure 1. Aero gas turbines are an example of some engine parts that need TBCs [13]
1.1 Objectives
The primary objective of this study is to investigate the possibility of producing a columnar micro-structured gadolinium zirconate and YSZ based TBC using SPS process which could provide a long TBC durability at elevated temperatures in gas turbines engines. In other words, this work aims to evaluate thermal cyclic fatigue life of the proposed TBC systems at two different test temperature, 1100°C and 1200°C respectively and investigate their failure modes.

1.2 Research questions
To achieve the above mentioned objective, the following research questions need to be answered:
1) What is the thermal cyclic life of the two proposed coating systems?
2) What is the failure mode and mechanism in the two TBC systems subjected to thermal cyclic fatigue test?

1.3 Scope and Limitations
The work is based on experiments and the following are some of the constraints that will be applicable for this study. During porosity characterization by image analysis method, it was difficult to measure fine scale porosity at low magnification and column gap porosity at high magnifications. Therefore, an additional method such as water intrusion or mercury intrusion porosimetry should be used and compared with image analysis results. TC was sprayed by SPS process which resulted in a columnar structure. This process is sensitive to several parameters such as the suspension properties, spray process parameters etc. A different set of parameters could yield a different microstructure and hence can result in varied functional performance. Additionally, the bond coat was deposited by HVAF process which is relatively new technique. The thermal cyclic lifetime of a TBC is dependent on the bond coat composition, processing route and top coat microstructure. Therefore, the results obtained in this study should not be generalized and must be treated exclusively.
2. BACKGROUND

2.1 Thermal Barrier Coatings

The basic applications of TBCs have been discussed in the introduction. This section aims to discuss the important features of the thermal spraying process. As can be seen in figure 2, a TBC has multiple layers and each of them play a distinct role. The substrate is nothing but the material to be protected from high temperatures. The choice of which material to use as a substrate is a function of requirement. Super alloys are commonly employed as substrates especially Nickel based ones for aerospace applications. For instance the substrate used in this study is a hastelloy-X though others such as Inconel are more often used. The layer immediately next to the substrate is called bond coat. As the name suggest, this layer serves the purpose of increasing bonding/adherence between the substrate and the top coat. At commercial level, bond coat materials are categorized as diffusion and overlay. An overlay is of type MCrAlY. Where M, Cr, Al, Y represents Nickel/Cobalt, chromium, Aluminium, active elements (e.g Ta, Y, Hf) respectively [15]. Further, the BC limits corrosion of the substrate which is usually caused by oxidation mechanism. During in situ service, (though not shown in the figure) another layer known as TGO forms on top of the metallic bond coat [16]. The primary function of this layer is to increase the TBC life by reducing the corrosion rate of the BC by forming an oxide layer (passivation). An alumina oxide serves this purpose better as compared to other oxides which cause failure as a result of mismatch in coefficient of thermal expansion [13, 17].

The final layer is called top coat (TC) and the material type used is a ceramic. The function of this layer is to offer insulation to all other layers discussed above. Therefore ceramic materials used as TC must have properties that can enable them to survive in high temperature conditions during in service. The state of art YSZ is one good example of a ceramic that is used as TC.
2.1.1 Yttria Stabilized Zirconia and Gadolinium Zirconate

This section extends the discussion of the TC materials and their properties requirements. The material type discussion will be limited to GZ and YSZ reason being that they are the ones that have been selected for this study. YSZ meets most of the thermal requirement properties of a TBC therefore it is the standard coating material in the industry. Specifically, some of these properties include low thermal conductivity, high fracture toughness, and high thermal cyclic life. Further, YSZ is good at resisting sintering and phase changes at most service temperatures (<1200°C). Unfortunately, its capability is only valid up to 1200°C. Above this temperature, YSZ undergoes phase transformation coupled with high sintering rates which thus reduces the durability of the TBC [18].

GZ is the alternative ceramic material with potential to counter some of the challenges faced by YSZ above 1200°C. It possess all important thermal properties requirement for a TBC together with the ability not to change phases, resists sintering and CMAS attacks (better than YSZ) above 1200°C[19-20]. Despite having all these good properties, GZ does not chemically compact well with TGO thus leading to inferior thermal cyclic life [21-22]. In order to improve the properties and curb some of the drawbacks of the two ceramics type (GZ and YSZ), multilayered TBCs are created which offer combined properties. In this study samples are multilayered.

2.2 Deposition methods

During thermal spraying, melting the particles demands usage of processes that generates high energy. EB-PVD and plasma spraying are the common example of such processes and will thus be discussed below.

2.2.1 Electron beam physical vapour deposition

When low pressure and vacuum states are achieved in the chamber, an electron beam is directed at the material to be melted (ceramic) which ultimately leads to vaporisation of the material. Vaporisation takes place below the substrate such that the vaporised material is directed onto it and solidifies thereon. This process is diagrammatically presented in figure 3.
Figure 3. EV-PVD Process [2]

Figure 4 shows the microstructure which is usually generated by EB-PVD process. As can be seen, columns that are normal to the substrate are created. Visible pores are seen between the column boundaries and they play an important role of reducing strain sensitivity. This is one of the benefits of EB-PVD as compared to plasma spraying processes that generate laminar structures [6]. Further, other researchers reported that this structure is good at resisting erosion as opposed to plasma sprayed coatings [7]. The drawback of this process compared to plasma spraying processes is that it has low rates of deposition while using high energy thus more expensive. Further, other studies has highlighted that due to the nature of the structure generated by this process, the thermal conductivity is higher than that of those generated by plasma spraying processes[6]. Other researchers has pointed out that the distance between columns demands that apart from acting as an adherer, the BC must also assume the role of a combiner of columns to reduce failure chances by spallation [8].
2.2.2 Plasma Spraying

As the name suggest, this process uses the energy of the plasma to melt feedstock. Deposition is primarily accomplished by directing energies from the plasma (thermal and kinetic energies) at the feedstock. This act melts the particles and deposits them onto the substrate. The plasma’s temperature capability is between 6000°C and 15000°C alongside with flame velocity range of 300 to 1000 m/s. Classification of plasma spraying is based on the phase of the feed materials. If the phase is a solid suspended in a liquid, the process is called SPS and if solid only, it is called APS.

2.2.2.1 Atmospheric Plasma Spray

In Atmospheric Plasma Spraying (APS) a high current arc is used to generate a thermal plasma jet. The arc is started by high voltage ignition and maintained by direct current electrical supply. Inert gases passing the gap between the electrodes are heated up by the arc thereby forming plasma and due to the free set energy; the temperature of the plasma jet can go up to 15000°C at the gun exit. Depending on feeding method used, the feedstock of usually 10 µm to 100 µm in size is fed into the plasma jet inside the nozzle and then ejected at 200-300 m/s speed. Near the torch end, shielding gases are fed to prevent oxidation during the spraying. On exiting, the ejected particles may be partially, fully or unmelted and are directed at the substrate on which upon impact form splats successively thus coat formation. Figure 5 schematically shows the summary of this process.
As opposed to EB-PVD, a microstructure generated by APS is lamellar and these lamellas are parallel to the substrate. This structure is characterised by cracks and voids which are mainly caused by stresses that form during the rapid cooling of the spats.

Further this structure is also characterised by high porosity [10]. This high porosity reduces the thermal conductivity [10] of the coating despite low strain tolerance by this structure as compared to that generated by EB-PVD [8]. Figure 6 shows a typical microstructure generated by APS.
With regard to advantages, as mentioned earlier, for the same thickness and material content thermal conductivity of an APS generated microstructure is lower as compared to that generated by EB-PVD [11]. The lower conductivity of APS is explained by difficulty of heat to cross a parallel lamellar (heat flow is normal to the lamellar) coating where as in EB-PVD the heat flows parallel to the columns thus higher conductivity [12]. Another advantage of APS over EB-PVD is that its deposition rate is higher thus less expensive. With comparison to EB-PVD, the drawbacks of APS are incapability of depositing of small particles sizes, low TCF life and it is not easy to deposit coatings on complex geometries [13].

2.2.2.2 Suspension Plasma Spraying

SPS is the conventional plasma spray that use nanosized particles. The process involves the same steps as the conventional APS outlined above; the difference is in the feedstock of the powder. Instead of feeding powder into the plasma in its dry state, a carrier liquid is used. The carrier liquid usually contains alcohol and a dispersion medium that generate a uniform and homogeneous coating using nanosized particles. SPS results in a columnar microstructure which is similar to that of EB-PVD using the plasma route.

Formation of columnar microstructure is a function of spray history thus it is important to discuss how such a structure is achieved. The process is initiated by injecting a suspension radially (normal to the plasma flame) or axially where injection is done inside the gun and is parallel to the plasma direction. Once injected, the suspension atomizes thereby forming fine droplets (100 nm to few more µm) from which the liquid evaporates so fast such that the particles melts and finally hit the substrate to create a coating [23]. Particles solidifies on top of splats successively and thus a columnar microstructure is formed (see figure 7) [13].
With comparison to APS, SPS allows formation of porous and columnar structure. This is possible due to the use of nanosized particles. Some researchers found that such small sizes give excellent TBCs properties [24-25]. Comparing SPS with EB-PVD, it is faster thus less costly [26] but the opposite is true when compared with APS. With regard to drawbacks, it is not easy to deposit coatings on complex geometries (similar to APS).

2.3 Failure modes in TBCs
In TBCs, if adhesion between the BC and TC is poor, the TC delaminates off the BC thereby rendering the substrate vulnerable to high temperatures and thus fails. Delamination occurs as a result of coefficient of thermal expansion differences between the BC and TC mainly caused by thermal stresses. Oxidation is another mode of failure where oxides (TGO) forms at the BC and TC/substrate interface. Ideally a thin oxide protective layer is formed to offer protection on the bond coat and substrate but when elements that form this protective layer are used up, then bond coat oxidation will continue and eventually form thicker oxides that delaminate and with time, the topcoat fails as a result of this form of oxidation [3]. The TGO layer has worse mechanical properties and lower CTE than the TC and BC which ultimately leads to higher stress concentration at the TGO/BC boundary on thermal cycling such that this stress is relieved as cracks (see figure 8 (d)) in the TGO layer[13]. Other researchers elsewhere [32] observed failure modes of single and double
layer coatings sprayed by SPS. They [32] found that at 1200°C, oxidation occurred faster and lead to spallation of the TBC. Further, they also at 1100°C (for a double layer) observed failure occurring close to the interface of GZ and YSZ but within GZ layer (see figure 8 (c)). Furthermore, for a single layer TBC at 1100°C, they observed failure occurring within the TGO layer which led to debonding of the TBC (spallation) and also large vertical cracks were observed (see figure 8 (a)). Another group of researchers investigated failure modes of APS sprayed TBCs that were subjected to 1121°C temperature in the controlled furnace and they observed the thickened TGO and cracking occurring at the BC/TGO and TGO/TC interfaces [34].

Figure 8. Failure modes of TBCs [32, 34]
3. EXPERIMENTAL METHODS

3.1 Sample and suspension preparations

Hastelloy-X (25.4 mm x 6.35 mm discs, 50 mm x 30 mm x 6 mm TCF plates) substrates were cleaned and had their surface roughened (approximately 3 μm Ra) by grit blasting them with alumina particles. Then bond coat (200 μm) comprising of NiCoCrAlY, AMDRY-386-0 was sprayed by the M3 gun using HVAF process. In order to get rid of unmelted particles and oxides that were formed during the spraying process (HVAF), the bond coat substrates were also grit blasted until a 5 μm (Ra scale) surface roughness was achieved. Further, before depositing the top coats, a plasma torch was used to preheat the samples; this was done to activate the bond coat surface.

Regarding suspension preparations, three ethanol based and one water based suspensions were manufactured by Treibacher Industrie AG, Austria. The first suspension consisted of 8YSZ having 500 nm as particles size plus a solid load of 25 wt%. The second suspension had GZ of median particle size was 500 nm with same solid content of 25 wt%. Third suspension was a 50:50 blend of GZ and YSZ of 500 nm median particle sizes with solid load content of the suspension kept at 25 wt%. The fourth suspension was water based for the dense GZ layer which had 1 μm median particle size and 40 wt% solid load in the suspension.

3.2 Coating deposition

As depicted in figure 9, the samples were mounted on a fixture (rotating) after which the coating was deposited by employing an Axial III plasma gun from Mettech (Northwest Mettech, Canada). Suspensions were fed using Nanofeed 350 suspension unit from Mettech (Vancouver; Canada). In order to create the two different types of microstructures that is columnar and dense, two set of parameters as shown in table 1 were used. More details regarding the spraying parameters used in this study are reported elsewhere [31]. The two coating systems deposited for this study are shown in figure 10. As shown in the figure, the rationale for selection of these architectures was to achieve the labelled properties exhibited by each layer and ultimately work at elevated temperatures.
Table 1. Parameters that were used for spraying the samples used in this study

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Columnar Layer</th>
<th>Dense Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median particle size of solute (nm)</td>
<td>500</td>
<td>1000</td>
</tr>
<tr>
<td>Solvent</td>
<td>Ethanol</td>
<td>Water</td>
</tr>
<tr>
<td>Enthalpy (kJ)</td>
<td>11.2</td>
<td>12.5</td>
</tr>
<tr>
<td>Power (kW)</td>
<td>122</td>
<td>89</td>
</tr>
<tr>
<td>Standoff distance (mm)</td>
<td>100</td>
<td>70</td>
</tr>
<tr>
<td>Solid load content (wt%)</td>
<td>25</td>
<td>40</td>
</tr>
</tbody>
</table>

Figure 9. Showing a rotating fixture and a gun [32]

Figure 10. Various coating layers deposited by SPS
3.3 Coating characterization

3.3.1 Metallographic preparation of pre and post tested samples

It is common practice that after the top coat, the samples must be cleaned and well-polished in order to get the best microstructure results during the microscopic analysis. This was accomplished with the following procedure for pre-tested and post tested samples. The samples were cut using a Struers machine at the speed of 2000 rpm, feed of 0.095mm and the length of 40mm. After cutting, a releasing agent was applied to the plastic molds followed by cold mounting of samples with a 5:1 ratio in weight of epoxy resin and hardener respectively. The solution was then vacuumed in order to remove the entrapped air from epoxy mounting material and a maximum of 20 hours was allowed as a mount setting time. After 20 hours of settling, the dried samples were grinded in order to prevent damaging of the polishing cloth during the polishing process. For identification purpose, the samples were labeled according to the materials or powders that were used as the top coat. This was followed by the polishing process using a Buehler PowerPro 5000 (Buehler, USA) machine with a U10 Program (TBC program). The detailed steps are given below:

Step 1: The samples were loaded in the sample holder in a balanced manner and a 125 µm disc made of silicon carbide was used. Water was supplied during the process to flush away the particles, reduce friction and for cooling. This step took 5 minutes.

Step 2: The above step was repeated using a 45 µm disc for 3 minutes.

Step 3: Following step 2 was step 3 where a 9 µm disc that had a polishing cloth and liquid (pink) diamond-9 micron were used in the process which lasted for 4 minutes 30 seconds.

Step 4: Step 3, setup was used except that a 3 µm disc was used with a 3 micron metadi liquid

Step 5: The last step which took 5 minutes was accomplished using a 0.05 µm disc using silicon dioxide as a liquid. Water was used in the last 10 seconds just for cleaning purpose.

3.3.2 Microstructures observation

After polishing, both as sprayed and tested samples were subjected to microstructure analysis using TM 3000 HITACHI at PTC, University West. In order to make the surface conductive, gold was sputtered after which the back scattered electron mode (BSE) in the SEM at various magnifications was used. Further, EDS analysis was performed simultaneously using Bruker equipment and quantax software.
3.3.3 Porosity measurement

In this study, porosity was measured for both as sprayed and failed samples that were considered. It was done using Image analysis method where a total of 120 SEM micrographs of 300x and 3000x were analysed and their average and standard deviations were determined. Contribution by column gaps was taken care by lower magnification (300x) and small porosity contribution was estimated by higher magnifications (3000x). Further, the higher magnification SEM micrographs were also used to investigate the sintering effect.

3.3.4 Micro hardness and crack length measurements

Vickers hardness test for the samples in this study were measured using HMV-2 series micro-hardness tester (SHIMADZU Corp., Japan) at University West. A diamond indenter with the load of 300g was employed as the main parameter during the testing. For each sample variation, 10 indents were taken on the intermediate layer (on the center in a straight line across the layer) and their mean values were measured. Further, the crack lengths from the indents were measured and the mean length values were determined.

3.3.5 Phase analysis

For XRD measurements, a SEIFERT TT 3003 X-ray diffractometer was employed as measuring equipment where the as sprayed discs of 25.4 mm diameter had their top surface exposed to Cu Kα at a 1.54 Å wavelength. Scanning was done with step size of 0.01 with 10 s times per step in two theta ranges of 15°-75°.

3.4 Thermal cyclic fatigue test

The TBCs (as sprayed) were subjected to TCF test where three TCF plates of layered (dense GZ/GZ/YSZ) and three TCF plates of blend (dense GZ/GZ+YSZ/YSZ) samples were tested at 1100°C. At 1200°C, two TCF plates of layered (dense GZ/GZ/YSZ) and two TCF plates of blended (dense GZ/GZ+YSZ/YSZ) were subjected to 1200°C for 1 hour and 10 minutes cooling (to 100°C) in a furnace-ENTECH AB which was controlled by a computer. Before cooling, a camera with good resolution was used to monitor and observe the behaviour of samples immediately after the heating process. The test was continued until visible spallation of 20% of the TBCs was observed. The mean and standard deviations values of the TCF life for the TBCs at the above mentioned temperatures were calculated and reported.
4. RESULTS AND DISCUSSION

4.1 Microstructure Analysis

This section discusses the microstructures of the as sprayed TBCs analyzed by SEM. The first TBC variation is the blend architecture which comprises of GZ (30µm), GZ+YSZ (210µm) and YSZ (60µm) with a total thickness of approximately 300 µm. As depicted in figure 12(a), the ceramic layer has a columnar microstructure where each column is separated by a small gap called columnar gap. The spray parameters chosen for this study were based on previous findings [32] which were engineered in such a way that a columnar microstructure could be achieved. Columnar microstructure is desired for TBCs application due to improved strain tolerance (which eventually improves the TBC durability). Additionally, high porosity in the TBC offers good insulation by reducing the thermal conductivity of the TBC. Furthermore, figure 12 (b) shows the dense GZ/ GZ+YSZ interface at higher magnification. Additionally, from figure 12, a cross sectional SEM micrograph with the elemental map of Gadolinium (Gd) and zirconium (Zr) is shown. The purpose of the blended layer was to enhance fracture toughness properties of the TBC system (reference for improved fracture toughness). Fracture toughness is mainly used as a design parameter which dictates selection of materials and also for assessing durability of materials. We need improved fracture toughness in TBCs to enhance their durability.

The second variation was a triple layered TBC system (GZ dense/GZ/YSZ) where the top to bottom layers were dense GZ (30µm), GZ (210µm) and YSZ (60µm) respectively. Total TBC thickness of approximately 300 µm was achieved. This TBC system’s microstructure and its elemental mapping comprising of Zr and Gd is presented in figure 13(a). The three layers showed a columnar microstructure. The dense GZ top layer was meant to provide erosion and CMAS resistance whereas the GZ (not dense) was meant to offer low thermal conductivity whereas YSZ offer high fracture toughness and thermo chemical reaction barrier to the TBC system. Figure 13(b) is the cross sectional SEM micrograph showing porosity.
Figure 12. SEM micrographs of the triple layer Dense GZ/GZ+YSZ/YSZ (a) Cross sectional SEM & EDS map of GD & Zr (we see both GD & Zr present in the GZ+YSZ layer). (b) GZ dense/GZ+YSZ interface at higher magnification.

Figure 13. SEM micrographs of the triple layer Dense GZ/GZ/YSZ (a) Cross sectional SEM & EDS map of GD & Zr (b) Shows porosity.
4.2 Porosity analysis

Image analysis was used to measure porosity for all pre and post tested samples that were considered in this study. With this method, it was possible to estimate both closed and open pores. As shown in figure 14 and in table 2, the porosity of the as sprayed TBC (at 300x and 3000x) of layered GZ dense/GZ/YSZ had a lower value of 14.62% as compared to blended GZ dense/GZ+YSZ/YSZ which had a higher value of 23.07%. The possible explanation could be that there were more pores in the blended layer of the blended GZ dense/GZ+YSZ/YSZ TBC system. We observe from figure 14 a reduction in porosity of the blended sample where the failed sample had low average porosity. The decrease is explained by the sintering process which might have occurred at the testing temperatures (1100°C). Further, since the blended layer accounted for 70% of the TBC, more YSZ might have been started to sinter since at 1100°C it was operating at its maximum. We observe almost unchanged porosity values of the layered GZ dense/GZ/YSZ TBC; reason could be that the testing temperature was too low to effect noticeable sintering because 80% of the TBC had GZ which has high resistance to sintering. Another observation is that the blended TBC had higher porosity before being tested. An explanation may have to do with the blending of the two ceramics and it need to be investigated thoroughly in future given the fact that they had the same parameters.

![Figure 14. Showing porosity contents of triple layer TBCs systems](image-url)
Table 2. Image analysis porosity results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Triple layer (GZ/YSZ)</th>
<th>Triple layer (GZ Dense, GZ+YSZ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tested (%)</td>
<td>14.84</td>
<td>18.9</td>
</tr>
<tr>
<td>As sprayed (%)</td>
<td>14.62</td>
<td>23.07</td>
</tr>
</tbody>
</table>

Figure 15 shows SEM micrographs at given magnifications which from microstructure point of view support the measured porosity conclusions where for as sprayed layered GZ dense/GZ/YSZ TBC the porosity experienced negligible change in comparison with the failed samples. Figure 16 shows the same comparison as just mentioned above except that the sample is blended GZ dense/GZ+YSZ/YSZ TBC. By visualizing, the microstructures indicate that the as sprayed samples had a higher porosity than the failed samples.

Figure 15. Showing porosity contents comparison of as sprayed and failed Dense GZ/GZ/YSZ
The major purpose for carrying out the XRD analysis was to confirm the phases formed after spraying. JCPDS standard was used to identify the peaks obtained from XRD analysis. Spare TBC specimens were taken after deposition of each layer during the spraying in order to analyze the phase content from each layer. As shown in figure 17, a metastable tetragonal prime phase of Yttria was observed in a zirconia phase (ZrO₂) for a single layered YSZ. It is worth mentioning at this point that a tetragonal prime phase is preferred as it does not undergo phase change within the temperature range of 20°C to 1200°C which happens to be the operating temperature range in most of the TBCs applications. For GZ layer, a cubic defect fluorite Gd2Zr2O7 was detected. This phase at elevated temperatures (>1400°C) tends to transform to cubic pyrochlore where oxygen vacancies occupy specific locations. As for a blended layer, we observe from the figure that both cubic defect
fluorite Gd₂Zr₂O₇ and tetragonal prime phase in ZrO₂ were present. This phase has combined benefits of both GZ and YSZ compositions. It is clear from the figure that monoclinic phase is absent in all three groups. Therefore, the general conclusion from this analysis could be that the feedstock materials' chemistry was maintained after the spraying process by avoiding any reaction between the two materials.

Figure 17. XRD analysis of the top surface of as sprayed TBCs.

4.4 Crack length analysis

In an attempt to estimate the fracture toughness of the triple coating TBC systems (blended GZ dense/YSZ+GZ and layered GZ Dense/GZ/YSZ), the cracks (see figure 18) that were generated by the indents were measured and their mean values are represented in figure 19 (also shown in table 3) where both blended GZ Dense/YSZ+GZ and layered GZ Dense/GZ/YSZ have similar lengths (taking into account the standard deviation). Further investigation is needed because given the fact that YSZ has higher fracture toughness as compared to GZ, the GZ Dense/GZ/YSZ sample could have generated higher crack lengths. Further, the unknown modulus of elasticity for the TBCs rendered it difficult to calculate the fracture toughness thus only crack length values are reported in this report.
Figure 18. Shows the micro cracks of the blended layer (GZ+YSZ)

Table 3

<table>
<thead>
<tr>
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<th>GZ Dense/GZ/YSZ</th>
<th>GZ Dense/YSZ+GZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crack length (mm)</td>
<td>17.75±14.1</td>
<td>20.73±12.4</td>
</tr>
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Figure 19. Crack lengths of the TBCs
4.5 Thermal Cyclic fatigue analysis

The layered and blended TBCs that have been sprayed in this study were subjected to a TCF test. The TBCs samples were exposed until the failure criteria of 20% spallation was attained.

As depicted in figure 20, at 1100°C the dense GZ (layered) had a higher life (698±4) than the dense GZ blended (which had 644±10). The possible explanation for this difference is difficult to determine as the life difference between the two coating systems is small also. This need a BRT test to investigate and determine the cause and this test is absent in this study.

As shown in the same figure (20), similar to the TCF test at 1100°C which had higher life with layered dense GZ (74±3), the TCF life at 1200°C showed the same where blended dense had low life (72±2). It is noticed that the life of TBCs at 1200°C is lower than that of 1100°C. The possible explanation for this could be that the temperature of 1200°C is too high such that oxidation rate is accelerated which ultimately lead to failure (spallation). Further at this temperature, high sintering rates could have ultimately limited the strain tolerance of the TBCs and thus leading to early failure. It can be seen that the life difference between the two sample types at 1200°C is very small. The reason for this as reported elsewhere [13] could be that the test at 1200°C limits the performance of the top coat as the metallic bond coats are not designed to counter such elevated temperatures.
Figures 20. TCF life of as sprayed TBCs exposed to 1 h of heating and 10 min of cooling at 1100 °C and 1200 °C.

Details of the failure at 1100°C for both dense GZ/GZ/YSZ and dense GZ/GZ+YSZ/YSZ samples are discussed below.

For the layered dense GZ/GZ/YSZ, as depicted in figure 21(d), failure commenced at the TGO/BC interface. It was reviewed in the background section that failure of TBCs that are subjected to a TCF test occurs mainly as a result of oxidation of the bond coat which clearly means that the bond coat chemistry, feedstock size and spraying parameters and process influences the life length of the TBCs. Further, spallation was also discussed earlier as the failure mode which we can clearly see in figures 21(b) to be the case. This failure type occurred due to the growth of the TGO (led to debonding) evidenced by the fact that failure initiated in this region (TGO). Further, figure 21(a) and (c) shows failure occurring in the GZ layer but near GZ/YSZ boundary. This is explained by the fact that the bond coat/TGO and ceramic expanded at different rates due to their mismatch in thermal coefficient of expansion which ultimately lead to high stress accumulation within the ceramic. These compressive stresses during cooling are further the reason why cracks propagated horizontally across GZ layer. Since GZ has lower fracture toughness than YSZ, cracks propagate easily in
GZ layer compared to the YSZ layer. This result was also reported elsewhere [32]. The TGO thickness was measured to be approximately $6.74 \pm 0.2 \, \mu m$ at failure and it comprised of chromium, nickel and aluminum oxides, according to the EDS analysis of the TGO layer shown in figure 21(e). In comparison with dense GZ/GZ+YSZ/YSZ critical TGO thickness, the unblended dense GZ/GZ/YSZ had a higher value ($6.74 > 5.65 \, \mu m$) which indicates that the dense GZ/GZ/YSZ topcoat was able to sustain higher oxide growth stresses than the dense GZ/GZ+YSZ/YSZ topcoat.

Figure 21. TCF failed triple layer dense GZ/GZ/YSZ at 1100°C (a) Cross sectional SEM micrograph (b) Photograph (c) SEM micrograph adjacent to crack opening (d) EDS analysis of the TGO.

Figure 22 shows the blended dense GZ/GZ+YSZ/YSZ SEM micrographs and its adjacent photograph. We observe spallation from the photograph by buckling and delamination occurring at the TGO/BC interface. The possible explanation is that there was a very high release of strain energy...
(produced during cooling) within the TC and the underlying TGO layer. Further, we observe extensive damages at this interface which is one of the characteristics of this event. Reasons of failure of layered dense GZ/GZ/YSZ are applicable here also because they share the common failure features except large vertical cracks (could have been formed as a result of column shrinkage due to higher sintering in the coating as a consequence of higher initial porosity) associated with blended dense GZ/GZ+YSZ/YSZ (see figure 22(a)). Figure 22(d) shows the same composition of the TGO as that of layered dense GZ/GZ/YSZ and the critical TGO thickness at failure was measured to be 5.65 ±1 µm.

![Figure 22](image-url)

Figure 22. TCF failed triple layer dense GZ/GZ+YSZ/YSZ at 1100°C (a) Cross sectional SEM micrograph (b) Photograph (c) SEM micrograph TGO/BC delamination (d) EDS analysis of the TGO.
5. CONCLUSION
In this study, two TBC variations, layered and blend architecture of gadolinium based TBCs were sprayed by SPS process and the thermal cyclic life comparison of the TBC sample group was done at 1100°C and 1200°C and their failure modes was analysed. The conclusions are outlined below. It was shown that:

1) Columnar microstructure in the YSZ and GZ blend could be achieved.
2) XRD results of the blend layer showed the presence of two distinct cubic and tetragonal phases.
3) A higher TCF life at 1100°C can be attained with dense GZ/GZ/YSZ triple layer than the blended TBC.
4) Tested samples at 1200°C showed a small life variance due to the operational limit of bond coat.
5) GZ+YSZ layer on the dense GZ/GZ+YSZ/YSZ and GZ layer on the dense GZ/GZ/YSZ TBC systems had similar crack length value.
6) Failure from within the TGO was observed in both layered and blended TBCs.
6. FUTURE WORK

1) In future, it would be good to determine the modulus of elasticity of the ceramics used in this study and determine the fracture toughness improvement resulting from blending the two ceramics.

2) Burner Rig test must be used in future to actually see the behaviour of these TBCs systems at such elevated temperatures.

3) In future, there is need to further examine and understand why dense GZ/GZ/YSZ TBC had a higher life than dense GZ/GZ+YSZ/YSZ by depositing TBCs of similar porosity contents.
7. REFERENCES


