PROCESS ENGINEERING OF CERAMIC COMPOSITES AND COATINGS

MODIFIED WITH CHEMICALLY BONDED COMPOSITE SOL-GEL

by

Yu Chen Yao

B.A.Sc., The University of British Columbia, 2006

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

The Faculty of Graduate Studies
(Materials Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

October 2009

©Yu Chen Yao, 2009
ABSTRACT

This work explores the possibilities of the application of chemical bonding to process ceramic-ceramic composites by employing ceramic sol-gel as the core processing technique. The principal rationale is that chemical bonding produces ceramic bond at substantially lower temperatures under 600°C, opening new processing possibilities. Versatility of the chemically bonded composite sol-gel alumina is demonstrated by the two final product forms: coatings and wear resistant composites. In Thermal Barrier Coating (TBC) application, an additional ceramic layer is sandwiched between two layers of Plasma Sprayed TBC, to improve overall thickness and thermal insulation. Such combination creates an unique Hybrid Thermal Barrier Coating (HTBC) with the chemically bonded ceramic layer ranging between 200-500μm between two ~100μm traditional air plasma sprayed barrier films. The HTBC has dual microstructure, adjustable porosity and varying composition, including alumina and yttria stabilized zirconia. The chemically bonded ceramic layer provides vertical microstructure beneficial in enhancing thermal strain tolerance. Thermal cyclic tests (30-1050 °C) showed good performance of the hybrid coating up to 1000 cycles. In the Carbon-Carbon Composites (CCC), pores are infiltrated with alumina particles, which are hardened to a wear resistant phase through chemical bonding. The infiltration process is facilitated by vacuum impregnation followed by heat treatment.
in air at 300-500°C, to create a Ceramic Carbon-Carbon Composite (C^4). Meanwhile, the infiltration also achieves densification at a rate faster than traditional Chemical Vapour Infiltration (CVI) process. The time saving of the ceramic vacuum impregnation process compared to the traditional CVI promises significant reduction of the processing costs, possibly up to a factor of 10 (from the current ~$1,000/kg, to the target ~$100/kg). The CCC as high performance light weight braking pads are almost exclusively used in aerospace and racing vehicles due to prohibitively high cost. The faster vacuum impregnation process could potentially migrate the C^4 to general automotive applications. The C^4 were tested for abrasive and sliding wear resistance. The results show a reduction in volume loss as compared to similar porosity CCC. The process of chemically bonding alumina-based ceramics is thus effective in introducing alumina-based ceramic composite phase to both a coating system and a porous monolith ceramic.
Table of Contents

Abstract ................................................................................................................................. ii

Table of Contents ................................................................................................................ iv

List of Tables ......................................................................................................................... vi

List of Figures ....................................................................................................................... vii

Nomenclature ....................................................................................................................... x

Acknowledgements ........................................................................................................... xi

1 Introduction ....................................................................................................................... 1

2 Technical and Theoretical Background ......................................................................... 5
  2.1 Fundamentals of Sol-Gel Processing ......................................................................... 5
  2.2 The Role of Alumina in Sol-Gel Processing ............................................................ 7
  2.3 Composite Sol-Gel .................................................................................................... 9
  2.4 Chemically Bonded Composite Sol-Gel .................................................................. 11
    2.4.1 Aluminum Orthophosphate ............................................................................. 12
    2.4.2 Aluminum Metaphosphate ............................................................................ 13
  2.5 Thermal Barrier Coatings ......................................................................................... 15
  2.6 Carbon-Carbon Composites .................................................................................... 19
    2.6.1 CCC Processing ............................................................................................. 21
    2.6.2 CCC Wear and Friction ................................................................................. 24

3 Scope and Objectives ....................................................................................................... 25
  3.1 Hybrid TBC Coatings with CB-CSG (HTBC) ...................................................... 25
  3.2 Deposition of HTBC on Hot Gas Turbine Impingement Plates ......................... 27
  3.3 Ceramic Carbon-Carbon Composites (C^{4}) ....................................................... 28

4 Experimental Setup and Methodology .......................................................................... 30
  4.1 CB-CSG Composite TBC (HTBC) ......................................................................... 30
    4.1.1 CB-CSG Slurry Preparation ......................................................................... 30
    4.1.2 Substrate Preparation .................................................................................. 33
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1.3</td>
<td>CB-CSG Deposition</td>
<td>35</td>
</tr>
<tr>
<td>4.1.4</td>
<td>Heat Treatment and Post Processing</td>
<td>39</td>
</tr>
<tr>
<td>4.1.5</td>
<td>Coating Analysis and Performance Evaluation</td>
<td>40</td>
</tr>
<tr>
<td>4.2</td>
<td>Processing of HTBC on Hot Gas Turbine Impingement Plates</td>
<td>46</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Slurry and Surface Preparation</td>
<td>47</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Bond Coat and YSZ Top Coat Deposition</td>
<td>48</td>
</tr>
<tr>
<td>4.2.3</td>
<td>CB-CSG Deposition</td>
<td>51</td>
</tr>
<tr>
<td>4.2.4</td>
<td>Mounting Coupons for Analysis</td>
<td>52</td>
</tr>
<tr>
<td>4.3</td>
<td>Ceramic Carbon-Carbon Composites (C⁴)</td>
<td>53</td>
</tr>
<tr>
<td>4.3.1</td>
<td>CCC Sample Preparation</td>
<td>54</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Slurry Preparation</td>
<td>55</td>
</tr>
<tr>
<td>4.3.3</td>
<td>Vacuum Impregnation</td>
<td>55</td>
</tr>
<tr>
<td>4.3.4</td>
<td>Analysis of C⁴</td>
<td>57</td>
</tr>
<tr>
<td>5</td>
<td>Results and Discussion</td>
<td>59</td>
</tr>
<tr>
<td>5.1</td>
<td>Process Engineering of HTBC</td>
<td>59</td>
</tr>
<tr>
<td>5.1.1</td>
<td>Substrate Selection</td>
<td>59</td>
</tr>
<tr>
<td>5.1.2</td>
<td>The Effect of PVA Content on Porosity</td>
<td>60</td>
</tr>
<tr>
<td>5.1.3</td>
<td>Addition of α-Alumina</td>
<td>63</td>
</tr>
<tr>
<td>5.1.4</td>
<td>Surface Treatment on NiCrAlY Bond Coat</td>
<td>66</td>
</tr>
<tr>
<td>5.1.5</td>
<td>Microstructure of HTBC</td>
<td>70</td>
</tr>
<tr>
<td>5.1.6</td>
<td>Phase Analysis of CB-CSG</td>
<td>75</td>
</tr>
<tr>
<td>5.1.7</td>
<td>CB-CSG Coating Adhesion</td>
<td>77</td>
</tr>
<tr>
<td>5.1.8</td>
<td>Thermal Cycling of HTBC</td>
<td>85</td>
</tr>
<tr>
<td>5.2</td>
<td>HTBC on Hot Gas Turbine Impingement Plate</td>
<td>93</td>
</tr>
<tr>
<td>5.3</td>
<td>Ceramic Carbon-Carbon Composites</td>
<td>99</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Densification of CCC by CB-CSG</td>
<td>99</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Wear Test of C⁴</td>
<td>106</td>
</tr>
<tr>
<td>6</td>
<td>Conclusions and Recommendations for Future Work</td>
<td>108</td>
</tr>
<tr>
<td>6.1</td>
<td>Summary and Conclusions</td>
<td>109</td>
</tr>
<tr>
<td>6.2</td>
<td>Recommendations for Future Work</td>
<td>112</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>114</td>
</tr>
</tbody>
</table>
List of Tables

Table 1. Properties of 99.9% alumina.................................................................7
Table 2. Slurry group I with boehmite and 10μm YSZ........................................31
Table 3. Slurry group II with boehmite, 10μm YSZ, and PVA..............................32
Table 4 Slurry group III with boehmite, 10μm YSZ, and PVA ............................32
Table 5. Slurry group IV with boehmite, 10μm YSZ, and PVA ...........................32
Table 6. Slurry group V with boehmite and 1.3μm YSZ ..................................32
Table 7. Slurry group VI with boehmite, A16, and 1.3μm YSZ ..........................33
Table 8. Coating type and target thickness of individual layers ..........................39
Table 9. Density and porosity of as-received CCC samples ..............................54
Table 10. Pull-out tests results with adhesion strength normalized to the detachment area...............................................................................................................................80
Table 11. Coating type 2 with thin CB-CSG layer and their percentage of coating remaining at different cycle counts .............................................................87
Table 12 Coating type 3 with thin CB-CSG layer and their percentage of coating remaining at different cycle counts .................................................................89
Table 13. Resulting thickness of different coating types deposited on impingement plate ..............................................................................................................................94
Table 14. Weight of HP group CCC samples throughout different impregnation cycles. .....................................................................................................................99
Table 15. Weight of LP group CCC samples throughout different impregnation cycles. .................................................................................................................100
Table 16. Weight of FD group CCC samples throughout different impregnation cycles. .................................................................................................................100
Table 17. Density and porosity of samples from HP group before and after the vacuum impregnation .....................................................................................103
Table 18. Density and porosity of samples from LP group before and after the vacuum impregnation .....................................................................................103
Table 19. Density and porosity of samples from FD group before and after the vacuum impregnation .....................................................................................104
Table 20. Results from abrasive wear (ASTM G65 test with rubber wheel and Ottawa Sand) ..........................................................106
Table 21 Results from sliding wear (modified ASTM G65 test with steel wheel). ...107
Table 22. Summary of the wear tests ................................................................107
List of Figures

Figure 1. Polycondensation of TEOS in water...............................................................6
Figure 2. A schematic of composite Sol-Gel processing incorporating inert filler particles into dispersed colloidal sol.24 ........................................................................11
Figure 3. Typical APS TBC deposited by Northwest Mettech (North Vancouver, BC, Canada). ........................................................................................................................17
Figure 4. SEM of CCC showing (a) woven carbon fiber, and (b) graphitized fiber bundle...........................................................................................................................22
Figure 5. Collection of spray content for measurement of spray rate.......................36
Figure 6. Various coating combinations.......................................................................38
Figure 7. Thermal cycling apparatus ............................................................................42
Figure 8. Heating profile for thermal cycling ..............................................................43
Figure 9. (a) Thermocouple embedded in ceramic cement with one side in contact with exposed CB-CSG fragment; (b) A fractured view confirming the contact of thermocouple and CB-CSG fragment. ........................................................................43
Figure 10. Converting image to black and white and calculate their respective area to obtain percentage of coating delamination. .................................................................43
Figure 11. Adhering the pull-out stud onto coating surface with epoxy while holding the contact tight with a metal clip. ........................................................................45
Figure 12. Stage for pull-out tests showing (a) the top platform with the central down-ward pulling grip, and (b) a sample placed face down on the platform with the pull-out stud secured to the grip................................................................................45
Figure 13. Schematic of the pull-out test. .....................................................................46
Figure 14. Hot gas turbine impingement plates ...........................................................46
Figure 15. Working location of the impingement plates is indicated by arrow. ............47
Figure 16. Movement of plate and APS torch during Bond coat deposition ...............48
Figure 17. Movement of APS torch during YSZ top coat deposition............................49
Figure 18. Coupon holder for impingement plate.........................................................52
Figure 19. Coupon holder and coupon installed onto an impingement plate. ...............53
Figure 20. 2-chamber vacuum desiccator for vacuum impregnation. .........................56
Figure 21. Schematic of apparatus in G65 abrasive test.............................................58
Figure 22. (a) Front and (b) back of CB-CSG coating with bond coat remaining on Fe-Ni substrates after 60 thermal cycles at 1050°C........................................59
Figure 23. SEM on gel casts of 30wt% YSZ in 2M boehmite with (a) 0.24M PVA and (b) 1.19M PVA......................................................................................................................61
Figure 24. SEM on gel casts of 25wt% YSZ in 1.5M boehmite with (a) no PVA and (b) 0.71M PVA .............................................................................................................................61
Figure 25. SEM on gel casts of 19wt% YSZ in 1.5M boehmite with (a) no PVA and (b) 0.71M PVA .............................................................61
Figure 26. SEM on gel casts of 11wt% YSZ in 1.5M boehmite with (a) no PVA and (b) 0.71M PVA .............................................................62
Figure 27. SEM of CB-CSG coating with (a) 0.48M PVA and, (b) 0.95M PVA. ......63
Figure 28. CB-CSG coating on bare Hastelloy-X after 100 hours at 1000°C. ............65
Figure 29. Spallation of thick CB-CSG coating off of the Hastelloy-X substrate after heat treatment at 500°C.................................................66
Figure 30. CB-CSG coating on bond coat with (left) and without (right) pre-oxidation treatment. .............................................................................................................67
Figure 31. Progression of thermal shocking of CB-CSG coating on bond coat with (left) and without (right) pre-oxidation. Thermal shocks included 1050°C for 15 minutes followed by immediate water quenching at room temperature.................68
Figure 32. (a) SEM and (b) EDS spot analysis (location indicated by the square) showing the intermediate layer between TGO and CB-CSG coating containing phosphate. .................................................................69
Figure 33. SEM showing no intermediate layer between TGO and CB-CSG coating without phosphoric acid..................................................70
Figure 34. Samples intercepted before complete coverage of CB-CSG coating. Triangles mark original “peaks” from the APS YSZ layer; circles mark the “valleys”. .................................................................................................................................72
Figure 35. CB-CSG (250–300µm) coating on APS YSZ top coat ..........................73
Figure 36. SEM images of the surface morphology at 35° incident angle of view, ....73
Figure 37. EDS mapping for CB-CSG columns showing distributions of Al, P, and Zr. .................................................................................................................................74
Figure 38. SEM images of (a) the cross section, and (b) EDS mapping of CB-CSG coated on bottom APS-YSZ layer. .................................................................75
Figure 39. XRD data (a) before and (b) after 10 thermal cycles between 1000 °C and 30°C. .................................................................................................................................76
Figure 40. Interface between CB-CSG and APS YSZ layers at (a) 5k and (b) 10k magnifications. .................................................................................................78
Figure 41. SEM Images of type II CB-CSG composite TBC.................................78
Figure 42. Coating detached by pull-out stud not conforming to contact area. .........79
Figure 43. Adhesion strength of CB-CSG from pull-out test. .................................81
Figure 44. SEM showing the pull-out sample (a) before the pull-out test and (b) after the pull-out test. .................................................................82
Figure 45. SEM showing thin necks at the root of each CB-CSG columns.............83
Figure 46. Schematic illustration of possible stud placements over the columnar
Figure 47. Detachment of coating type 4 in the CB-CSG layer.

Figure 48. Type 2 coating used for thermal cycling test.

Figure 49. Type 2 coatings with thin (200~300μm) CB-CSG layer. (a) T2thin-1 after 1000 cycles; (b) T2thin-2 after 1000 cycles; (c) T2thin-3 after 1000 cycles; (d) T2thin-4 after 2000 cycles; (e) T2thin-1 after 3000 cycles.

Figure 50. Type 2 coatings with thin (200~300μm) CB-CSG layer. (a) T3thin-4 and (b) T3thin-5 after 150 cycles.

Figure 51. CB-CSG on top of thin APS YSZ of ~100μm.

Figure 52. CB-CSG on top of thick APS YSZ of ~200μm.

Figure 53. APS YSZ filling in the valleys of CB-CSG columnar structure.

Figure 54. SEM of type 2 CB-CSG Composite TBC in turbine impingement plate.

Figure 55. SEM of type 4 CB-CSG Composite TBC in turbine impingement plate.

Figure 56. SEM of type 5 CB-CSG Composite TBC in turbine impingement plate.

Figure 57. Bonding interface of type 2 coating between CB-CSG layer and bottom APS YSZ layer.

Figure 58. Bonding interface of type 2 coating between CB-CSG layer and top APS YSZ layer.

Figure 59. Bonding interface of type 4 coating between CB-CSG layer and bond coat.

Figure 60. Bonding interface of type 4 coating between CB-CSG layer and top APS YSZ layer.

Figure 61. Bonding interface of type 5 coating between CB-CSG layer and bond coat.

Figure 62. Percentage of total weight gain at each A16 impregnation cycles for group HP.

Figure 63. Percentage of total weight gain at each A16 impregnation cycles for group LP.

Figure 64. Percentage of total weight gain at each A16 impregnation cycles for group FD.

Figure 65. CCC from LP group (a) before and (b) after the vacuum impregnation with calcined alumina.
**Nomenclature**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>316SS</td>
<td>316 Stainless Steel</td>
</tr>
<tr>
<td>A16</td>
<td>α-alumina by Almatis, Germany with 0.4 μm particle size</td>
</tr>
<tr>
<td>APS</td>
<td>Air Plasma Spray</td>
</tr>
<tr>
<td>C4</td>
<td>Ceramic Carbon-Carbon Composite</td>
</tr>
<tr>
<td>CB-CSG</td>
<td>Chemically Bonded Composite Sol-Gel</td>
</tr>
<tr>
<td>CCC</td>
<td>Carbon-Carbon Composite</td>
</tr>
<tr>
<td>CSG</td>
<td>Composite Sol-Gel</td>
</tr>
<tr>
<td>CVI</td>
<td>Chemical Vapour Infiltration</td>
</tr>
<tr>
<td>EB-PVD</td>
<td>Electron Beam Physical Vapour Deposition</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl Alcohol</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>TBC</td>
<td>Thermal Barrier Coating</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>YSZ</td>
<td>Yttrium Stabilized Zirconia</td>
</tr>
</tbody>
</table>
Acknowledgements

I offer my most sincere gratitude to Dr. Tom Troczynski for providing this valuable research opportunity. His guidance and insight is of tremendous value in this body of work. I also thank Dr. Hyungkeun Kim for his sharing of experience and knowledge in the sol-gel processing which inspired a great part of my methodologies. As well, I fully appreciate Mr. Alan Burgess, the CEO at Northwest Mettech Corp, for granting us the Thermal Barrier Coating project and financial assistance. The work of Dr. Igor Yaroslavski being the liaison between our lab and the company has also been greatly valuable.
1 Introduction

As an engineering material, ceramics possess many desirable properties such as low thermal expansion, high hardness, wear resistance, chemical stability, and low thermal conductivity. However, cost, processing difficulties, as well as its brittle nature have limited ceramic materials to very specific applications. Effectively, the industry does not recognize ceramic as a versatile material. Instead, metals and polymers are more frequently chosen over ceramics in material selections, while ceramics are often “last choice” solutions where all other materials fail. The unique characteristics of ceramics, such as hardness and refractory properties, are quite often irreplaceable by other materials. Therefore, ceramics are often used as a product “modifier” such as a coating or as a component of composite materials.

In the present research, a novel form of ceramic processing known as Chemically Bonded Composite Sol Gel (CB-CSG) is studied as a low cost, low temperature, microstructurally controllable, and simple method to modify existing products. Essentially, this investigative work aims to explore the possibility of enhancing these products with an additional composite ceramic phase introduced by CB-CSG. The flexibility of CB-CSG process allows the supplementary ceramic phase to be created in multiple forms, for
example as an extra layer to a coating system, or a wear resistant secondary phase in a porous body. The primary constituent of the CB-CSG in this work is alumina (aluminum oxide). Alumina is chosen for its well-known properties such as chemical and thermal stability, strength, hardness, availability at relatively low cost, and chemical bonding capability with phosphoric acid. In the coating form, CB-CSG is applied as an extra layer to the common Air Plasma Sprayed (APS) Thermal Barrier Coating (TBC). The TBC is a system of layers including the base bond coat, the upper protective top coat, and the in-service forming Thermally Grown Oxide (TGO). The main function of TBC is to protect alloy parts from high temperatures and harsh environments. The use of TBC has enabled the industry to push the operating temperatures of gas turbines into new heights exceeding 1300°C. The high operating temperature yields higher fuel efficiency as well as power output, but is also the underlying cause of TBC failures. In exposure to high temperature, the ceramic top coat of TBC experiences complex failure mechanisms involving thermal and TGO evolution stresses. Over time, stresses from thermal gradients, differential thermal expansions and contractions, and thermal cycling shocks work to propagate microcracks in the TBC + TGO layers. The stress increases with the overall thickness of the TBC. As a result, there is a critical TBC thickness beyond which the high stress will cause premature delamination. For this reason,
industry standard for typical TBC is in the range of 300 to 500 μm, although thicker coatings (up to 1mm) would be desirable to improve thermal and corrosion protection of the substrates. The role of CB-CSG in this research is to add an additional thermal insulation layer that is relatively porous and compliant, thus providing good thermal insulation and low thermal stresses at any given strain. As well, by adjusting deposition parameters, the CB-CSG layer can exhibit a vertically textured microstructure that has been shown in the past to further improve resistance of TBC to thermal cyclic stress. Such novel CB-CSG composite TBC is termed Hybrid TBC (HTBC), reflecting its dual microstructure and composition originating from the CB-CSG and APS layers. To seek compatibility of HTBC between the CB-CSG layer and the traditional APS ceramic layer, the experimental work here deposited CB-CSG onto the APS ceramic top coat by compressed-air pressure spraying (much like spray-painting), followed by heat treatment. Various formulae of CB-CSG mixtures were tried. The resulting coatings were examined by SEM, EDS, XRD. The performance of the HTBC was evaluated by pull-out test, thermal sintering and thermal cyclic shock tests.

With some minor variation in the processing sequence and content ratios, the CB-CSG used for the coatings was transformed into an infiltration agent onto porous
Carbon-Carbon Composites (CCC). CCC is composed of graphite deposited on woven carbon fiber matrix by means of Chemical Vapor Infiltration (CVI), or alternatively known as Chemical Vapor Deposition (CVD). The CCC is an excellent material due to its strength to weight ratio and consistent performance over a broad range of temperature. Such characteristic makes it ideal for aerospace applications. The present research worked with materials destined for airplane braking pads, but intercepted at an early CVI processing stage where the CCC is not yet fully densified. The higher porosity (up to ~40vol%) of the intercepted CCC allows CB-CSG to infiltrate the CCC body with fine ceramic particles, and subsequent chemical bonding at modest temperatures, resulting in higher density, hardness, and wear resistance of such composite. As an added bonus, phosphoric acid used in the CB-CSG process may act as oxidation inhibitor for the CCC, but this aspect is designated for “Future Work”. Experimental work performed here includes process engineering such as vacuum impregnation of calcined alumina, boehmite, and phosphoric acid into CCC with porosity in the range of 11% to 40%. The resulting composite is evaluated for microstructure, porosity and density. Mechanical performance is tested by ASTM wear test.
2 Technical and Theoretical Background

2.1 Fundamentals of Sol-Gel Processing

The development and history of Sol-Gel technique since the 1800s is well introduced by Hench and West in their publication “The Sol-Gel Process”\(^1\). Over the years, the term Sol-Gel has become quite broad. Generally, Sol-Gel is accepted as a system where colloids, which may or may not be networked, are suspended in a stable solution. To be more specific, the route to sol-gel begins with the formation of chemical species in a solution. Take for example the widely studied silicon based tetraethyl orthosilicate (TEOS) sol-gel. TEOS, $\text{Si}($OC\(_2\)H\(_5\))_4$ is a colorless liquid phase alkoxide. When dispersed in water, TEOS undergoes hydrolysis by disassociating its alkyl groups, such that one or more of the following reactions will occur\(^2\):

\[
\begin{align*}
\text{Si}($OC\(_2\)H\(_5\))_4 + H_2O &\rightarrow \text{Si}(OH)(OC\(_2\)H\(_5\))_3 + C_2H_5OH \\
\text{Si}($OC\(_2\)H\(_5\))_4 + H_2O &\rightarrow \text{Si}(OH)_2(OC\(_2\)H\(_5\))_2 + 2C_2H_5OH \\
\text{Si}($OC\(_2\)H\(_5\))_4 + H_2O &\rightarrow \text{Si}(OH)_3(OC\(_2\)H\(_5\)) + 3C_2H_5OH \\
\text{Si}($OC\(_2\)H\(_5\))_4 + H_2O &\rightarrow \text{Si}(OH)_4 + 4C_2H_5OH
\end{align*}
\]

Consider the last reaction where TEOS loses all of its alkyl group and results in silicic acid $\text{Si}(OH)_4$. In such solution, two silicic acid molecule can condense to form
Likewise, the pair can further associate with other silicic acid molecule to form chains as illustrated by the following figure.

\[
\begin{align*}
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} \\
\text{OH} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{OH} & + & \text{OH} & \quad \text{Si} & \quad \text{O} & \quad \text{OH} & \quad \rightarrow & \quad \text{OH} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{OH} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

Figure 1. Polycondensation of TEOS in water.

The polycondensation of silicic acid is quite sensitive to the solution’s conditions such as concentration, pH, temperature, and aging time. Changes to the solution’s condition can result in agglomeration of colloidal precipitates, condensation of colloids into separate particles, or continued gelation into fully polymerized state. The significance of these progressions is in the end texture of the sol-gel. Partlow and Yoldas classify the texture of polycondensed sol-gel system into a polymeric type and a colloidal type\(^3\). The classification has a qualitative importance towards the formation of monolithic end product. Therefore, many researches have focused on the effect of sol-gel conditions such as concentration\(^4\), pH, and temperature in terms of colloidal characteristics of sol-gel. It is also appropriate to note here that while classic studies of sol-gel are mostly on polycondensation of sols into colloids, this work evaluates sols by dispersed alumina and AlOOH fine powders. The role of alumina, being both the gel phase and filler
phase, is discussed in more detail in the next section.

The beauty of sol-gel is in its versatility. Once a stable sol-gel is achieved, a wide selection of processing route can be tailored to the final product. Common product types include film, fiber, powder, aerogel, xerogel, and monolith. Processing routes are often spinning, casting, and coating.

2.2 The Role of Alumina in Sol-Gel Processing

Alumina is a very popular ceramic due to its high hardness, strength, thermal and chemical stability, thermal resistivity, and abundant quantity. The combination of these properties makes it an excellent refractory and wear resistant material. Table 1 shows some highlights of alumina properties.

<table>
<thead>
<tr>
<th>Properties</th>
<th>99.90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>3.9</td>
</tr>
<tr>
<td>Dielectric Strength (kV/mm)</td>
<td>~35</td>
</tr>
<tr>
<td>Volume Resistivity (Ohm.cm)</td>
<td>&gt;10¹⁴</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m·K)</td>
<td>28-35</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient (20-1000°C x10⁻⁶/K)</td>
<td>8</td>
</tr>
<tr>
<td>Specific Heat (J/K·kg)</td>
<td></td>
</tr>
<tr>
<td>Compressive Strength (MPa)</td>
<td>2200 - 2600</td>
</tr>
<tr>
<td>Hardness (Vickers kgf/mm)</td>
<td>1500 - 1650</td>
</tr>
</tbody>
</table>
When properly dispersed and aged, certain species of alumina can form gel. Yoldas\textsuperscript{6,7} has established that aluminum alkoxides $\text{Al(OR)}_3$, such as $\text{Al(OCH}_7\text{)}_3$, and $\text{Al(OC}_4\text{H}_9\text{)}_3$, can hydrolyze and polycondense into alumina sol-gel. The gelation process is favored when acid is added at 0.03 moles per mole of alkoxide\textsuperscript{8}. The resulting sol-gel forms bayerite ($\text{Al(OH)}_3$), which can be densified into monolithic products, or precipitated out at about 100°C as a highly homogeneous and pure boehmite (AlOOH) powder. A less experimented route to forming alumina sol-gel is to take the commercially available boehmite powder and re-disperse it back into aqueous form. Thiruchitrambalam et al. have successfully produced alumina monolith from both alkoxide derived sol-gel as well as gelatinous boehmite from powder dispersion\textsuperscript{9}. In this work, it is also demonstrated that boehmite can gel by dispersion method such as ultrasonication or ball milling. However, excessive gelation is not desired here since the gel is employed only as a carrier of an additional inert ceramic filler phase. The delivering method, being pressure spray and vacuum infiltration, requires the gel to retain a degree of flowing capability. Therefore, the alumina gel is agitated with a ball mill to break up the network before each use.

Besides the boehmite used as a gel phase precursor, alumina in its calcined form,
α-alumina, is used as a second phase in CB-CSG (hence the “composite” sol-gel). α-Alumina acts as inert ceramic filler to lend its mechanical advantages, such as hardness and thermal insulation, to the final product. Essentially, the addition of α-alumina demonstrates the concept of making a composite product with sol-gel processing, as described below.

2.3 Composite Sol-Gel

One weakness in Sol-Gel processing is shrinkage that accompanies the drying stage. Up to 85% volume shrinkage can be seen for TEOS based sol-gel\textsuperscript{10,11,12}. As water is desorbed from the system, the 3D structure formed by the colloids would experience large capillary stress up to 100 to 200MPa\textsuperscript{13}. The shrinkage induced stress can cause processing complications such as cracking and defects\textsuperscript{14,15}. There is usually a critical thickness associated with any type of sol-gel\textsuperscript{16} so that thin films and fibers are less prone to shrinkage cracks. The shrinkage can be reduced by conditioning the precursor and polycondensation process. Brooks et al\textsuperscript{10,17} managed to reduce the shrinkage to as low as 50% by employing a sugar-based silsesquioxane precursors for silicic gel. However, such reduction requires aging of sol-gel as long as 2 month.
Another method to reduce sol-gel shrinkage is by adding in a second phase material into the Sol-Gel system. The second phase should be inert so that it shall not dissolve in the solution to become part of the gel. The inert phase is to act as filler materials so that during drying the 3D network will not collapse. Troczynski et al.\textsuperscript{18,19,20} has reported many uses of ceramic powders, such as silica and alumina, as filler particles for the use of abrasive and catalytic coatings. The inert particles allows greater final density, lower porosity, and lower sintering temperature. Research by Badkar\textsuperscript{21} et al. and Becher et al.\textsuperscript{22} indicates that sintering alkoxide derived boehmite gel at 1600°C achieves a density of 3.0g/cc (75% theoretical density) while doping the boehmite gel with MgO achieves 3.8g/cc (95% theoretical density) at the same temperature. This indicates that densification of sol-gel monolith is only comparable to traditional powder processing. Kumagai et al.\textsuperscript{23}, however, have shown that by adding some α-alumina at 2% in dry weight to boehmite gel, 3.92g/cc (98% theoretical density) can be achieved at 1600°C. This indicates that besides reducing shrinkage, a second phase in the sol-gel system can also promote higher degree of sintering. The sol-gel system with the addition of a second phase material is thus named Composite Sol-Gel (CSG). To summarize, CSG has the benefit of further modifying the Sol-Gel system to gain more performance of the final product. As well, CSG can decrease the temperature required to achieve a desired
density. A schematic of the composite Sol-Gel processing is illustrated in Figure 2. 

![Figure 2. A schematic of composite Sol-Gel processing incorporating inert filler particles into dispersed colloidal sol.](image)

**2.4 Chemically Bonded Composite Sol-Gel**

The Chemically Bonded Composite Sol-Gel (CB-CSG) is a ceramic processing technique uniquely developed by the Ceramics Group of UBC Materials Engineering (UBCeram). In order to further assist the processing of CSG, a reactive agent is introduced into the system to promote bonding and networking of the CSG at the drying and densification stages.
stage. The chemical bonding between the reactive agent and the colloids results in decreased firing temperature required to achieve the hardness and density that are normally obtained only through much higher temperature. For example, an alumina based Sol-Gel may utilize phosphoric acid as the chemical bonding agent to form aluminum orthophosphates at 500°C. The resulting product is comparable in density and hardness to a traditional alumina Sol-Gel fired at 1000°C\(^{24,25}\).

The chemical bonding between alumina and phosphoric acid may actually produce more than just aluminum orthophosphate (AlPO\(_4\)). Other phosphate phases may form as well, such as aluminum metaphosphates Al(PO\(_3\))\(_3\), monoaluminum phosphate Al(H\(_2\)PO\(_4\))\(_3\), and triphosphate hydrate AlH\(_2\)P\(_3\)O\(_{10}\)\(^{26}\). Of these, the aluminum orthophosphates AlPO\(_4\) and aluminum metaphosphates Al(PO\(_3\))\(_3\) are known as the primary phases. Further insight into aluminum phosphates are discussed in the following section.

2.4.1 Aluminum Orthophosphate

Aluminum orthophosphate can form at a relatively low temperature of around 140°C. Both anhydrous and hydrated types of alumina can be used as reactants\(^{27}\). However, the anhydrous type starting alumina favors the formation of cristobalite AlPO\(_4\) through the intermediate AlPO\(_4\)•H\(_2\)O phase, while hydrated starting alumina favors berlinitic AlPO\(_4\)\(^{27}\).
A simple example of aluminum orthophosphate formation can be seen through the reaction of boehmite $\text{AlOOH}$ and phosphoric acid $\text{H}_3\text{PO}_4$. At 133$^\circ$C, boehmite reacts with phosphoric acid to form:

- $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$
- $\text{AlPO}_4 \cdot 1.67\text{H}_2\text{O}$
- $\text{AlPO}_4 \cdot \text{H}_2\text{O}$

Further dehydration yields $\text{AlPO}_4$ in both berlinite and cristobalite forms\textsuperscript{28}.

Formation of $\text{AlPO}_4$ can also be promoted by several factors such as have a low phosphate to alumina ratio of around 1:1, and by using fine-particle alumina with high surface area. Such conditions were used by Gonzalez et. al. to carry out the reaction at a low temperature (150–500$^\circ$C) and long duration of 10 days\textsuperscript{29}.

### 2.4.2 Aluminum Metaphosphate

Aluminum metaphosphate $\text{Al(PO}_3)_3$ forms at a higher temperature compared to aluminum orthophosphate. For example, hydrated alumina can react with phosphoric acid at 255$^\circ$C to form amorphous $\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ as an intermediate phase, while further heating to 450$^\circ$C drives the amorphous $\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ to partial crystallization and initiates the formation of aluminum metaphosphate which completes at around 800$^\circ$C\textsuperscript{30}. 
Generally, Al(PO₃)₃ formation is preferred when phosphate is in high ratio to alumina (P:Al=3:1). Of the two types of Al(PO₃)₃, type-A (circular polymeric form) and type-B (linear polymeric form), Al(PO₃)₃-B forms at around 500°C followed by Al(PO₃)₃-A at around 800°C. Even higher phosphate to alumina ratio (6:1<P:Al<23:1) results in the exclusive formation of Al(PO₃)₃-A at 500-800°C firing range.

When taking place with the presence of YSZ, the influence of YSZ to alumina phosphating seems to be minimal. J. Fu et al. used thermo-gravimetric technique to describe alumina phosphating in YSZ. It was found that phosphoric acid reacts with boehmite and calcined alumina above 150°C according to the chemical reactions below:

\[
\text{AlOOH} + 3\text{H}_3\text{PO}_4 \rightarrow \text{Al(H}_2\text{PO}_4)_3 + 2\text{H}_2\text{O}
\]

\[
\text{Al}_2\text{O}_3 + 6\text{H}_3\text{PO}_4 \rightarrow 2\text{Al(H}_2\text{PO}_4)_3 + 3\text{H}_2\text{O}
\]

Dehydration of the monoaluminum phosphate induces transformation into aluminum triphosphate to form chemical bond:

\[
\text{Al(H}_2\text{PO}_4)_3 \rightarrow \text{AlH}_2\text{P}_3\text{O}_{10} + 2\text{H}_2\text{O}
\]

Increasing temperature to 500°C further dehydrates AlH₂P₃O₁₀ to form aluminum metaphosphate:

\[
\text{AlH}_2\text{P}_3\text{O}_{10} \rightarrow \text{Al(PO}_3)_3 + \text{H}_2\text{O}
\]
In summary, it is shown that alumina and phosphoric acid react at different temperatures to form stable and meta-stable phases. This is a major advantage when this present work has chosen alumina as both the primary sol-gel phases and secondary ceramic filler phase.

2.5 Thermal Barrier Coatings

Thermal Barrier Coating systems (TBC) are used in environments with high temperatures such as those in hot gas power generator, aviation turbines, and automotive motors. Thickness of TBC coating can vary depending on application, yet approximately 300 to 500 μm is a common range. Traditional TBC consists of multiple layers including the metal alloy substrate, the bond coat, the thermally grown oxide layer (TGO), and the Yttrium Stabilized Zirconia (YSZ) top coat. Paired with internal cooling, the multi-layer TBC system is designed to create a temperature gradient, up to ~200C, between the superalloy substrate and the high temperature environment such as flowing hot gas. Therefore, the operating temperature of the device with TBC can be increased, which translates to higher working efficiency as well as lower greenhouse gases emission.
Two primary methods of TBC deposition are the Electron Beam Physical-Vapor-Deposition (EB-PVD) and Air Plasma Spray (APS). The main difference between EB-PVD and APS TBCs is their microstructure. EB-PVD TBC is a high quality coating consisting of columnar structures which help to alleviate stresses\textsuperscript{34}. The gaps between the columns provide room for the coating to expand and contract, thus complying to the thermal strain experienced in service.

While APS TBCs also contain pores for strain compliance, its denser lamellar structure is inferior at doing so than EB-PVD TBCs. However, the disadvantage of EB-PVD is its high equipment cost as well as substrate’s geometry limitations. On the other hand, the advantages of APS are its ability to coat large and geometrically complex parts and its lower cost. However, the disadvantage of APS is its lamellar microstructure preventing a very thick coating over 300μm. An emerging coating technique using High Velocity Oxy-Fuel (HVOF) technology is also employed in some cases for the bond coat layer. Some report a more fully stabilized tetragonal phase of YSZ when HVOF is used for coating deposition\textsuperscript{35}. Figure 3 shows a typical TBC with distinguishable lamellar porous microstructure.
There is great interest in the industry to improve the quality of TBC as it can lead to higher energy efficiency and shorter downtime. Some intriguing research involves depositing the top ceramic coating in functionally graded layer in terms of ceramic top coat composition or porosity. Composition variation of the ceramic top coat is done by mixing in various ratios of bond coat material and YSZ when depositing top coat\textsuperscript{36}. Therefore it is possible to achieve better adhesion with bond coat with higher ratio of bond coat material at the bottom layers while maintaining a good erosion and thermal resistance with higher ratio of YSZ at the top layers. Porosity variation is done by adjusting APS deposition parameters such as power, current, gun to substrate distance,
and substrate temperature. By modifying porosity, higher strain compliance may be achieved. Surface modification of the top coat is also being investigated with known methods including laser glazing, liquid metal impregnation, atmosphere and temperature controlled spraying (ATCS) using cryogenic cooling, and hybrid spray processing using laser irradiation assisted APS. The main goal for surface modifications is to develop a high performance top layer in order to resist most of the corrosions and erosions.

Alternatively, surface treatment is also done to improve coating adhesion. The bond coat of TBC is commonly of M-CrAlY type. A number of publications suggest that some pre-oxidation of the bond coat can improve bonding of the ceramic top coat. The pre-oxidation is said to form a thin layer of stable alumina that will slow the progression of TGO. Tolpygo et al. heat treats 35μm bond coat at 1150°C for 5 hours, after which EB-PVD were used to coat a 130-150μm YSZ top coat. The coatings were thermal cycled between room temperature and 1150°C. Samples without pre-oxidation failed in 750 cycles while samples with pre-oxidation reached beyond 2000 cycles. Lih et al. also conducted surface pre-oxidation with temperature between 1000 to 1300 °C for 10 hours. Lih reports that the TBC without pre-oxidation survived up to 180 thermal
cycles between 1050°C and room temperature, while the TBC with pre-oxidation survive between 1100 to 1520 thermal cycles.

2.6 Carbon-Carbon Composites

The other candidate for applying CB-CSG in this work is Carbon-Carbon Composite (CCC), currently used mostly for airplane braking pads, but also smaller niche applications such as racing cars. Until recent years, the employment of CCC has been hindered by the high manufacturing cost and processing difficulties. However, beyond the obstacles, CCC has shown high potentials in many engineering applications. When used as breaking pads, the tribological properties are actually not the main advantages of CCC. In fact, the coefficient of friction (COF) of CCC on steel rotors varies between the range of 0.2 to 0.6\(^46\), which is not high compared to COF of steel on steel being around 0.75\(^47,48\). Likewise, CCC oxidize rapidly above \(\sim 1050^\circ C\), at which point wear loss is as low as 2% of the total weight loss (the rest 98% accounts for oxidation weight loss)\(^49\). Such severe oxidation is dangerous in some critical situations such as aborted takeoff. Significant effort continues to decrease oxidation sensitivity of CCC. The main advantages of CCC as a brake pad material are its strength to weight ratio, high thermal conductivity at \(\sim 150 W/m\cdot K\)^{52}, extremely low thermal expansion at \(\sim 1.3\times10^{-6}/^\circ C\)
to $6.1 \times 10^{-6}/°C$ between room temperature and $1650°C$ (2D fabric laminate with 30% fiber)$^{50}$, high heat capacity of $\sim 2J/g\cdot K$ at $1000°C$$^{51}$, stable mechanical performance over a wide range of temperature, and non-toxicity.

The density of CCC generally falls between the range of 1.3 to 2.5 g/cm$^3$ depending on porosity and ratio of carbon fiber and graphite$^{52}$. Over steel brakes with service life half as long (density around 7.6g/cm$^3$), CCC brake pads save about 40% weight compared to steel$^{52}$. In terms of thermal conductivity, CCC can range from less than 10W/m·K to over 200W/m·K$^{53}$. The wide range is contributed by the material and structural design of CCC, such that it has the carbon fiber, graphite matrix, and 3-dimensional fiber architecture$^{54}$. The thermal conductivity of carbon is high so that along the fiber and graphite of a CCC, the thermal conductivity would be high. However, depending on the way that the CCC’s fiber structure is woven, interlayer pores and boundaries may be present to decrease thermal conductivity. These factors also mean that thermal conductivity can be tailored to application. For braking pads, high thermal conductivity will allow CCC to direct heat away from the surface during service, thereby decreasing temperature experienced by the brake pads and the rotor. Despite the high thermal conductivity, there is still a large energy build up at the brakes contact surface.
Therefore, the low thermal expansion of CCC is ideal in keeping the brake pad un-warped. Baxter et al.\textsuperscript{55} conducted dilatometry on CCC (44% carbon fiber in volume) to determine the in-plane CTE to be $3.6 \times 10^{-6}$/K and through thickness CTE to be $4.3 \times 10^{-6}$/K. High heat capacity over a broad range of temperature will also assist in the stability of mechanical performance during the energy intensive braking operation. Cezairliyan et al.\textsuperscript{56} has measure CCC by pulse heating method over a temperature range of 1227°C to 2727°C and obtained specific heat capacity values over 2 J/g·k. As well, the carbon dioxide CO\textsubscript{2} and carbon monoxide CO vapor generated is non-toxic and would quickly dissipate in open air.

\subsection*{2.6.1 CCC Processing}

Details of the manufacturing and machining of CCC mostly remain proprietary information in the industry, to the extent that we even can not disclose the supplier of our CCC used in this work. However, harder and denser (i.e. porosity $\sim$12vol%) CCC brake pads are generally processed by Chemical Vapor Infiltration (CVI). During the CVI, hydrocarbon is vaporized at temperatures ranging from 700°C to 2000°C\textsuperscript{52}. The hydrocarbon gas infiltrates and deposits into woven carbon fiber performs, and decomposes into carbon and residues (e.g. hydrogen in the simplest case of CH\textsubscript{4} used).
Figure 4 shows the CCC used in the present research. The woven fiber are sheathed by graphite from CVI process as can be seen Figure 4b.
CCC formation by CVI can take a very long time. By the traditional isothermic-isobaric infiltration, the entire process can take weeks to achieve the target high density. This is especially true for thicker samples. The reaction kinetic is non-linear and decreases drastically over time\textsuperscript{57}. As a consequence, very long residence time is required for samples requiring very high density (i.e. density > 1.9g/cc)\textsuperscript{58}. The process would also require intermediate surface grinding to remove the surface "skin" in order to open up pore entries\textsuperscript{59}. The details and technical aspects to various CVI processes are thoroughly reviewed in a literature by Golecki\textsuperscript{60}, including several variants of CVI processes. Advanced CVI technologies using combinations of temperature gradient, pressure gradient, microwave-heating, and catalytic enhanced deposition can improve a great deal over the classic isothermic-isobaric CVI. The bests of these newer developments can speed up the densification process from weeks to days. However, a common downfall is the complexity of these advanced equipments, often resulting in limited sample quantity, geometry, and overall cost\textsuperscript{45}. The present experimental work seeks to demonstrate that it is possible to eliminate a large portion of CVI process time and cost by replacing the slow end-stage CVI with infiltration of alumina-based CB-CSG.
2.6.2 CCC Wear and Friction

Alumina-based CB-CSG is selected to assist in the CCC due to its high hardness (refer to Table 1), which has enabled alumina in high wear applications such as pipe linings and thread guides. The advantage in wear and abrasion resistance should be beneficial to the CCC brake pads.

CCC has fundamentally two wear mechanisms at modest temperatures (i.e. at negligible oxidation rate) divided into the dust wear regime and film wear regime. The dominance of the two regimes is influenced by a number of factors from material variables and environmental variables. Material variables include CCC strength, hardness, microstructure, and chemistry. Environmental variables include braking speed, braking force, water adsorption and desorption. The interactions between these variables are very difficult to characterize. It is generally understood that dust wear dominates under low energy braking, while the film wear dominates under high energy braking. It is not the goal of the present research to control the wear mechanism by infiltrating CCC with CB-CSG. However, it is expected that the alumina will positively affect the overall wear performance.
3 Scope and Objectives

The research explores the possibilities for modification of ceramic coatings and composites using CB-CSG technology, focusing on processing modified TBC and CCC. CB-CSG’s main advantage of being relatively low temperature processing and simple equipment is demonstrated. CB-CSG is tested as an intermediate layer in the APS-TBC coatings, as well as a wear resistant third phase in a porous CCC body. In the case of TBC coatings, CB-CSG is sprayed as a thermal insulating coating to modify and enhance the properties of the traditional APS TBC system. In the case of CCC, CB-CSG is used as an impregnating slurry for delivering phosphate bonded alumina into porous CCC brake pads.

3.1 Hybrid TBC Coatings with CB-CSG (HTBC)

One of their biggest challenges of TBCs is the need to withstand numerous thermal cycles between over 1000°C and ambient temperature. While TBCs processed by the more expensive EB-PVD possess columnar texture (regarded as the best solution in its strain tolerance), much research is done on APS TBC in order to reach a comparable strain tolerance as those in columnar EB-PVD coatings. The present research attempts to create a hybrid coating that adopts a vertical texture similar to the columnar EB-PVD,
into the APS TBC by using the CB-CSG process. We investigated a multi-layered HTBC system that consists of 1) bond coat on a substrate, 2) thin (50~100um) YSZ APS layer, 3) CB-CSG layer with variable thickness (100~300um), and 4) thick (100~200um) YSZ TBC top layer.

The specific objectives of this part of the work include:

1. Investigation of process parameters for deposition of the CB-CSG layer on the APS YSZ layers. Optimization of slurry chemistry to create a CB-CSG layer with enough integrity to withstand the high temperature and velocity associated with deposition of the thick APS top coat. Creation of vertical texture for enhanced strain compliance of the composite coating may be achieved by adjusting CB-CSG deposition parameters, such as spray pressure, rate, and distance.

2. Characterization of the HTBC system, including (i) Scanning Electron Microscopy (SEM) of the vertically textured microstructures; (ii) X-Ray Diffraction (XRD) and Energy Dispersive Spectroscopy (EDS) on the CB-CSG layers for composition and phase analysis; and (iii) Evaluation of the coatings durability by pull-out tests and thermal cycling between 1050°C and ambient temperature.
3.2 Deposition of HTBC on Hot Gas Turbine Impingement Plates

At a relatively early stage of this research project, the company Liburdi Turbine Services Ltd (Hamilton, ON) expressed interest in testing the HTBC on some impingement plates from a hot gas turbine. Liburdi indicated that long-term coating survival on these plates is not critical, but the extra-thermal protection would be advantageous for extending the plates lifetime. The plates would receive a constant temperature of around 800°C without any thermal cycling. This was an opportunity to determine if our lab-scale process for HTBC coatings could be transferred to an industrial environment. The goals of this part of the project were to:

1. Work with Northwest Mettech to integrate CB-CSG process into their APS procedure, to provide large-area coverage of the plates with HTBC.

2. Coat different combination of APS YSZ and CB-CSG layers on-site

3. Attach test coupons on the plates for simultaneous deposition and post analysis of HTBC, and characterize the coupons for the microstructure (SEM) and chemical composition (EDS)
3.3 Ceramic Carbon-Carbon Composites (C^4)

The CCC blocks originated from incomplete CVI cycles and thus retained porosity in the range of 11% to 40% by volume. The density of the porous CCC blocks ranged from 1.3g/cc to 1.7g/cc. It was desired for the final density to reach no less than 1.8g/cc after CB-CSG infiltration. The phosphate-bonded-alumina phase (CB-CSG) introduced into the pores by vacuum impregnation into CCC is constituted as separate continuous phase, with primary and secondary phases being carbon fibers and graphite matrix (in addition to remnant porosity remaining after impregnation). The role of the alumina-based CB-CSG was mainly to fill the pores and improve wear performance of the CCC (it is anticipated that oxidation resistance of such multi-phase composite also improves but this was not verified in the present project). The resulting product is a Ceramic Carbon-Carbon Composite, hereby termed C^4.

The specific objectives of this part of the project were following:

1. To investigate the process of infiltration of porous CCC blocks with CB-CSG alumina with vacuum impregnation technique; to optimize the number of infiltration cycles to achieve an end density of at least 1.8g/cc

2. To compare effects of initial porosity of CCC on final density of C^4.
3. To characterize as-received CCC and C\textsuperscript{4} after vacuum impregnation, including (i) microstructure evaluation by SEM; (ii) porosity and density measurements by Archimedes technique; (iii) determination of wear performance by ASTM G65 Dry Sand/Rubber Wheel test as well as Steel Wheel test without sand.
4 Experimental Setup and Methodology

4.1 CB-CSG Composite TBC (HTBC)

Typical research steps taken with CB-CSG composite-modified TBC (i.e. leading to HTBC) involves slurry and substrate preparation, deposition with compressed-air gun spraying, heat treatment, additional top-coat APS YSZ layer deposition, and post coating analysis. The detailed procedures to each step are detailed in the following sections.

4.1.1 CB-CSG Slurry Preparation

Different slurry compositions have been attempted to increase bonding capability, control porosity, and improve coating integrity. The solvent for all mixtures are commonly distilled water. AlOOH (Boehmite, purchased from Condea, Germany) with 1μm average (d$_{50}$) particle size of dry powder is used for sol preparation (according to manufacturer’s specifications, when properly dispersed into water, d$_{50}$ particle size of boehmite decreases to about 20nm). Calcined α-alumina (A16, Almatis, Germany) with 0.4μm d$_{50}$ average particle size is used for part of ceramic inert filler phase. Yttrium Stabilized Zirconia (YSZ) batches ranging from 3μm to 35μm in average particle size (d$_{50}$) were supplied by Northwest Mettech located in North Vancouver, BC. These YSZ powders were obtained for initial evaluation of the influence of their particle size towards the final microstructure. However, the experimental work eventually settled on using
YSZ with 1.3µm d₅₀ particle size from Inframat, USA, due to their advantageous behaviour in the slurry (i.e. limited settling), and also better reactivity towards phosphates during chemical bonding process. Polyvinyl Alcohol (PVA) was also used in some mixtures as pore former in an attempt to increase coating porosity. The different types of slurry are organized into six groups as is detailed in the following Table 2-7. With the exception in group III, all other slurry types contained 1.5M of boehmite as hydrated alumina sol. Note that for comparative clarity, the concentrations are expressed in terms of both grams relative to a given water quantity, or in molar concentration for dissolving components (i.e. AlOOH and PVA), or total weight percent (including water) for inert particulate content (i.e. YSZ and Al₂O₃).

Table 2.

<table>
<thead>
<tr>
<th>Slurry group with boehmite and 10µm YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GROUP I</strong></td>
</tr>
<tr>
<td>H₂O</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
<tr>
<td>c</td>
</tr>
</tbody>
</table>
Table 3. Slurry group II with boehmite, 10μm YSZ, and PVA

<table>
<thead>
<tr>
<th>GROUP II</th>
<th>H₂O</th>
<th>AlOOH</th>
<th>10μm YSZ</th>
<th>PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mL)</td>
<td>(g)</td>
<td>(M)</td>
<td>(g)</td>
<td>wt%</td>
</tr>
<tr>
<td>a</td>
<td>50</td>
<td>4.5</td>
<td>1.5</td>
<td>18</td>
</tr>
<tr>
<td>b</td>
<td>50</td>
<td>4.5</td>
<td>1.5</td>
<td>12.4</td>
</tr>
<tr>
<td>c</td>
<td>50</td>
<td>4.5</td>
<td>1.5</td>
<td>6.75</td>
</tr>
</tbody>
</table>

Table 4. Slurry group III with boehmite, 10μm YSZ, and PVA

<table>
<thead>
<tr>
<th>GROUP III</th>
<th>H₂O</th>
<th>AlOOH</th>
<th>10μm YSZ</th>
<th>PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mL)</td>
<td>(g)</td>
<td>(M)</td>
<td>(g)</td>
<td>wt%</td>
</tr>
<tr>
<td>a</td>
<td>50</td>
<td>6</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>b</td>
<td>50</td>
<td>6</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>c</td>
<td>50</td>
<td>6</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>d</td>
<td>50</td>
<td>6</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>e</td>
<td>50</td>
<td>6</td>
<td>2</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 5. Slurry group IV with boehmite, 10μm YSZ, and PVA

<table>
<thead>
<tr>
<th>GROUP IV</th>
<th>H₂O</th>
<th>AlOOH</th>
<th>10μm YSZ</th>
<th>PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mL)</td>
<td>(g)</td>
<td>(M)</td>
<td>(g)</td>
<td>wt%</td>
</tr>
<tr>
<td>a</td>
<td>50</td>
<td>4.5</td>
<td>1.5</td>
<td>18</td>
</tr>
<tr>
<td>b</td>
<td>50</td>
<td>4.5</td>
<td>1.5</td>
<td>12.4</td>
</tr>
<tr>
<td>c</td>
<td>50</td>
<td>4.5</td>
<td>1.5</td>
<td>6.75</td>
</tr>
</tbody>
</table>

Table 6. Slurry group V with boehmite and 1.3μm YSZ

<table>
<thead>
<tr>
<th>GROUP V</th>
<th>H₂O</th>
<th>AlOOH</th>
<th>1.3μm YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(g)</td>
<td>(M)</td>
<td>(g)</td>
<td>wt%</td>
</tr>
<tr>
<td>a</td>
<td>50</td>
<td>4.5</td>
<td>1.5</td>
</tr>
<tr>
<td>b</td>
<td>50</td>
<td>4.5</td>
<td>1.5</td>
</tr>
<tr>
<td>c</td>
<td>50</td>
<td>4.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>
CB-CSG slurries are prepared by dispersing boehmite in distilled water using ultrasound for 10 minutes followed by adding YSZ and A16 in quantities as indicated above. If PVA is required, it is first added to the distilled water before anything else and agitated with a magnetic stirrer for 2 hours or until the PVA crystals are fully dissolved. The mixtures containing all ingredients are subsequently ball milled for 24 hours, for full dispersion and homogenization. Before each use, the slurries are also ball milled again for at least 20 minutes to break up the gel network for easier flow.

### 4.1.2 Substrate Preparation

Initial depositions are done on a Fe-Ni type alloy substrates received from Northwest Mettech. Parts of coating analysis done at the early stage of this research project are based on samples with this Fe-Ni alloy. However, as the research reached the stage where thermal cycling is involved, it quickly became apparent that the Fe-Ni alloy has an
inadequate oxidation resistance at the temperatures of interest (>1000°C). Therefore, latter samples were done on Hastelloy-X (34.8 mm x 24.4 mm x 3.6 mm, received from Sulzer Innotec, Switzerland), which according to specifications is oxidation resistant up to 1100°C. The Hastelloy-X is a high quality superalloy with weight percent composition of 47 Ni, 22 Cr, 18 Fe, 9 Mo, 1.5 Co, 0.6 W, 0.1 C, <1 Mn, <1 Si, and <0.008 B. Since the Hastelloy-X samples were of limited quantity, 316 stainless steel (316SS) was occasionally used for coatings that were not expected to go through high temperature analysis. All substrates were sandblasted with 24 grit aluminum oxide at 60psi (sandblaster model 48X36/DP850 by Trinco USA) to obtain a rough surface for better mechanical interlocking by the coating. Samples are then coated with the bond coat film (Ni-Cr-Al-Y alloy), followed with “traditional” TBC (zirconia stabilized with 8wt% yttria in solid solution, termed YSZ) by Northwest Mettech with APS. Typical thickness of bond coat was around 50μm while thickness of YSZ was selected around 100μm or 200μm depending on research needs. As literature suggests pre-oxidation of bond coat can be beneficial to the adhesion of YSZ top coat\textsuperscript{44,45}, some of the substrates coated with the bond coat by APS were pre-oxidized in furnace at 1000°C for 30 minutes. The treated samples were then used for coatings type 5 described in the next section.
4.1.3 CB-CSG Deposition

During coatings deposition, different types of slurries listed in Section 4.1.1 were sprayed onto the substrates using pressured air gun (Delta XT, Graco USA) at 40 psi. The deposition started with a fine mist with a spray rate of about 0.3mg/min·mm². As the coating thickness builds up, the spray nozzle was gradually opened to a heavier spray rate of about 2mg/min·mm². The spray rates were determined by collecting the spray droplets in a beaker filled with absorbent paper towels over a period of time (Figure 5). Note that the spray rates do not reflect the actual deposition rate received by the substrate. The actually deposition rate was affected by environmental variables such as air suction from fume hood, particles bouncing off of the substrate’s surface, and distance between nozzle to substrate (about 50cm).
At regular intervals, 30wt% phosphoric acid (diluted from 86%, Fisher Scientific, Canada) is also sprayed onto the coating to promote chemical bonding during the subsequent heat treatment of the coatings. The intervals are indicated by weight gain. Samples are routinely weighed during spraying to monitor weight change. Typical practice is to switch to phosphoric acid ($\text{H}_3\text{PO}_4$) after each 10 to 20 mg weight gain. Approximately 5 to 10 mg of phosphoric acid is then applied to the substrate.

In order to better control texture, thickness and porosity during spray coating, the substrates were maintained at elevated temperature. A hot plate of 200°C is placed
beneath the substrates for flash evaporation of the slurries. Flash evaporation partially dehydrated CB-CSG particles in mid-air to prevent splatter or out-flow of CB-CSG droplets upon contacting the substrate. Several types of coatings were investigated as shown in Figure 6. Coating type 1 is the traditional TBC structure used as a standard for comparison. Coating type 2 is the main interest of the current study, in hopes that the YSZ phase in the APS ceramic layer will provide good bonding to the YSZ phase in the CB-CSG layer, as well as that the top APS ceramic layer will provide protection of the softer CB-CSG layer from the in-service environment. However, in the interest of expanding the understanding around the HTBC characteristics, other combination of APS layer and CB-CSG layer were investigated also. Coating types 3 and 4 were used to evaluate the possibility of saving cost and time by eliminating one of the two proposed APS ceramic layers. The critical point of coating type 4 was to see if the CB-CSG layer would adhere well enough to the bond coat; while the critical point of coating type 3 was the capability of the CB-CSG layer surviving the harsh in-service environment without any protection. Coating types 5 and 6 were also assessed for the feasibility of emergency repair of in-field TBC. Quite frequently in the industry, inspections would reveal a small area where the TBC is damage, prevent the machine to run safely. The idea of coating types 5 and 6 is to patch up areas where TBC has spalled off the substrate as a
temporary measure which would allow the machinery to operate until replacement part is available. The minimized downtime may translate to a large saving in cost. The target thickness of each layer in each type is listed in Table 8.

Figure 6. Various coating combinations
Table 8. Coating type and target thickness of individual layers

<table>
<thead>
<tr>
<th>Type</th>
<th>Bond Coat</th>
<th>Lower APS YSZ</th>
<th>CB-CSG</th>
<th>Upper APS YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>0</td>
<td>0</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>100</td>
<td>250</td>
<td>200</td>
</tr>
<tr>
<td>2a</td>
<td>50</td>
<td>100</td>
<td>500</td>
<td>200</td>
</tr>
<tr>
<td>3a</td>
<td>50</td>
<td>100</td>
<td>250</td>
<td>0</td>
</tr>
<tr>
<td>3b</td>
<td>50</td>
<td>200</td>
<td>250</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>0</td>
<td>250</td>
<td>200</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>0</td>
<td>250</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>250</td>
<td>0</td>
</tr>
</tbody>
</table>

4.1.4 Heat Treatment and Post Processing

After the desired thickness is achieved, as indicated by weight gain, the samples were placed into a furnace at 250°C. The temperature was then ramped to 500°C at a rate of ~15°C per minute. The samples were heat treated at 500°C for 30 minutes, after which the furnace was shut off to be cooled down overnight. The heat treatment was expected to complete the chemical bonding of phosphoric acid and alumina (e.g. aluminum hydroxide and calcined alumina), as evidenced by XRD studies. For coating types 2 and 4 in Figure 6, the samples were sent back to Northwest Mettech where a final layer of YSZ is coated by APS.
4.1.5 Coating Analysis and Performance Evaluation

Evaluation of the CB-CSG composite TBC was divided into three parts — characterization of the coating slurry, microstructure and phase analysis of the coating, and performance of the coatings under pull-out adhesion test and thermal cycling.

The characterization of the slurry was done for group III described in section 4.1.1, which consists of mixtures with varying quantities of PVA. Slurries type (a), (b), and (c) of the group IIII were gel casted, aged and dried at room temperature for 48 hours, followed by drying in an oven at 70°C for 24 hours, and finally heat treated at 500°C for 30 minutes (as described above). The resulting dry gel was fractured by hand. The fragments were brought under SEM for microstructure analysis. Slurry types (d) and (e) were used to produce coatings in comparison with coating with PVA.

Coating analysis focused on microstructure, phase, and chemical composition. For microstructure and chemical composition, the samples were cut in half. The cross section was mounted in epoxy and polished by 6μm diamond polisher. SEM and EDS analysis were completed by S-3000N (Hitachi, Japan). For phase analysis, type 3 coatings before and after 10 high temperature thermal cycles were examined with XRD (Multiflex X-Ray Diffractometer, Rigaku Co, Japan). The thermal cycles included 5
minutes hold at 1050°C followed by convection air cooling to under 50°C in 10 minutes.

For performance evaluation, samples went through thermal loading, thermal cycling, and pull-out test. Thermal loading was done by an electric furnace (Exciton, Iran) at 1050°C. Thermal cycling was done with a tube furnace where a mechanical feeder is located at the lower entrance (Figure 7). A timer was set to send the sample stage into the furnace for 6 minutes followed by pulling the stage out for 9 minutes. The travel time of the stage into and out of the furnace was less than 3 seconds, thus negligible. The Hastelloy-X samples (34.8 mm x 24.4 mm x 3.6 mm) used had good oxidation resistance up to 1100°C, at which exposure for 100 hours would yield approximately a 40um of oxidized layer. The furnace was set to 1080°C to ensure that the samples will reach 1050°C but does not exceed 1100°C. A 10cm fan forced atmospheric air over the stage when it is out of the furnace to provide fast cooling. Thermal profile of the temperature experienced by the samples was simulated by attaching a thermocouple to the back of a delaminated CB-CSG coating. The thermocouple contacted the coating on one side. The rest is embedded in ceramic cement to ensure that the fastest heating is through the coating (Figure 9). Such set up does not represent the exact thermal profile experienced by coated samples as a real sample would experience more complex modes of thermal
transfer. Instead, this set up is believed to be a close reflection. The thermocouple is connected to a chart recorder. The resulting chart is transcribed and plotted into excel.
Figure 8. Heating profile for thermal cycling

Figure 9. (a) Thermocouple embedded in ceramic cement with one side in contact with exposed CB-CSG fragment; (b) A fractured view confirming the contact of thermocouple and CB-CSG fragment.

The samples were also photographed at regular intervals to record the degree of spallation. Images of the coatings gone through thermal cyclic tests are analyzed by
Image J (Authored by Wayne Rasband, Research Services Branch, National Institute of Mental Health, Bethesda, Maryland, USA) to determine the percentage of coating delaminated from the substrate. Basic process involved converting the image of the sample to black and white (Figure 10). Through Image J, the black area and total area were measured to obtain a percentage of coating remaining and delaminated.

![Figure 10. Converting image to black and white and calculate their respective area to obtain percentage of coating delamination.](image)

Pull-out test was done with a pull-down testing module (Quad Group, USA) on a universal materials tester platform (Romulus IV, Quad Group, USA). Stainless steel pull-out studs (parts# 901106) with a contact diameter of 2.75mm were glued by epoxy to type II coating (Figure 11). After the glue was set, the stud was mounted onto a vertical pulling platform. The sample was secured against the rim of the pull well, while the stud was pulled down by a mechanical clamp (Figure 12). The pull-out force was applied at a rate of 1 N/s. The maximum force was set to 500N, although the test never
exceeded 100N before coating failed. A schematic of the pulling device is provided in Figure 13.

Figure 11. Adhering the pull-out stud onto coating surface with epoxy while holding the contact tight with a metal clip.

Figure 12. Stage for pull-out tests showing (a) the top platform with the central down-ward pulling grip, and (b) a sample placed face down on the platform with the pull-out stud secured to the grip.
4.2 Processing of HTBC on Hot Gas Turbine Impingement Plates

A total of six impingement plates from a hot gas turbine were received from Liburdi (through Northwest Mettech). The plates measured 16.3” in diameter with five 5.22” large holes and numerous 0.15” small holes, Figure 14. In service, the plates are located just upstream from the flame nozzles as shown in the schematic Figure 15.
Of the six plates, only three were coated with HTBC. The other three were coated with traditional TBC for reference. Coating types II, IV, and V (refer to Section 4.1.3) were applied to each of the three plates available.

4.2.1 **Slurry and Surface Preparation**

For the coating of impingement plates, slurry (a) and (b) from Group I listed in section 4.1.1 were used, with the mixing procedures identical to the test samples. The plates were sandblasted with 24 grit aluminum oxide at 60psi (sandblaster model 48X36/DP850 by Trinco USA).
4.2.2 Bond Coat and YSZ Top Coat Deposition

Bond coats and YSZ top coats were deposited by Northwest Mettech. Each plate was coated individually in the APS chamber. For bond coats, the plate was mounted on a turn table rotating at 200rpm. At the same time, the APS torch mounted on robotic arm moved back and forth over the samples surface. The movement is depicted in Figure 16.

![Figure 16. Movement of plate and APS torch during Bond coat deposition](image)

For YSZ top coat, the robotic arm was programmed to move across the plate in X and Y direction while the plate remains stationary. The movement of the torch is schematically shown in Figure 17.
Figure 17. Movement of APS torch during YSZ top coat deposition

For type II coatings, the torch repeated the XY scanning program twice in order to deposit a thicker YSZ coating. The equipments and parameters used are detailed as follows:

**BOND COAT**

**Materials**
- Material: Co-210-24/Co-241-3
- S/N: 032126-15
- Balance: Co; 32% Ni; 21% Cr; 8% Al; 0.5% Y
- Manufacturer: Praxair
- Particle Size: ~20um
- Powder Type: Co type
- Density: 8.0 g/cm³

**Equipment:**
- Powder feeder:
  - Model: THERMICO
  - S/N: MPF-ZSR-HP (Mettech Feeder #1)
  - Stirrer: Yes
  - Wheel Rotation: 4.75 rpm
  - Calibration 100 g/min
- Plasma torch:
Model: Mettech 600 Series
Nozzle: 7/16 in.
Total Gas Flow: 250 slpm (spray liter per minute)
Argon: 70% (175 slpm)
Nitrogen: 10% (25 slpm)
Hydrogen 20% (50 slpm)
Current Set Point: 230 x 3 Amp (3 power supplies to 3 electrodes)
Stand Off Distance: 200 mm (distance from torch to substrate)
Carrier Gas: argon
Carrier Flow: 12 slpm
Spray Rate: 100 g/min

YSZ TOP COAT
Materials
Material: #204 YSZ TSP (Thermal Spray Powders)
Lot No.: 06112007
Manufacturer: Saint-Gobain Coating Solutions
Particle Size: 10 – 75 um
Powder Type: YSZ
Density: 5.6 g/cm³

Equipment:
Powder feeder:
Model: THERMICO
S/N: MPF-ZSR-HP (Mettech Feeder #1)
Stirrer: Yes
Wheel Rotation: 6 rpm
Calibration: 54 g/min

Plasma torch
Model: Mettech 600 Series
S/N: Model 600A
Nozzle: 1/2 in.
Total Gas Flow: 150 slpm (spray litre per minute)
Nitrogen: 80% (120 slpm)
Hydrogen 20% (30 slpm)
Current Set Point: 230 x 3 Amp (3 power supplies to 3 electrodes)
Stand Off Distance: 170 mm
Carrier Flow: 6 slpm
Spray Rate: 54 g/min
Spray Pattern: X-Y Program
Travel Speed: 600 mm/s

4.2.3 CB-CSG Deposition

The normal in-lab procedure for deposition of CB-CSG on APS-YSZ included a hot plate beneath the sample for flash evaporation of the slurry droplets (as will be shown in the Results section, this helped control porosity and texture of the coatings). With the impingement plates, however, hot plate was unfeasible due to the plates’ size and geometry. Instead, the plate was heated by the plasma torch with hydrogen plasma. The plasma torch and plate were set up to move the same way it does when depositing the bond coat (refer to Figure 16). However, the rotational speed of the turn table was reduced to 70rpm. The surface temperature reached approximately 400°C after 30 repetition of the robotic arm movement. While the plate was still being spun at 70rpm, CB-CSG was sprayed at 40psi onto the plate’s surface. At the same time, two propane torches were held by another operator near the surface of the plate in an attempt to keep the surface hot enough (this was verified from time to time by hand-held optical pyrometer). When the surface temperature dropped below 150°C, the plate was reheated by the plasma torch. The plate’s size and environment prevented the proper
monitoring of weight gain by CB-CSG coating. Consequently, intervals between phosphoric applications were determined by the operator’s experience.

4.2.4 Mounting Coupons for Analysis

A circular coupon holder was made and installed onto the plate as shown in Figure 18 and Figure 19. The circular coupon mount was fastened to a large hole on the impingement plate at a depth where the coupon is flush with the plate’s surface. This method ensured that the coating on the coupon accurately reflects the coating on the plates. After completion of all coating layers, the coupons were analyzed by SEM and EDS (S-3000N, Hitachi, Japan).

Figure 18. Coupon holder for impingement plate.
4.3 Ceramic Carbon-Carbon Composites (C^4)

CCC samples with various densities and shapes were received from an undisclosed company. These samples were intercepted at different CVI densification stages. The porosities and densities therefore can be divided into three distinctive groups — highly porous (HP) with porosity between 30% and 40%, low porosity (LP) with porosity between 21% and 25%, and “fully” densified by CVI (FD) with porosity between 11% and 13% (all porosities by volume). Detailed density and porosity data specific to each as received sample are listed in Table 9.
Table 9. Density and porosity of as-received CCC samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk Density (g/cc)</th>
<th>vol% Open Porosity</th>
<th>Imperv Density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-1</td>
<td>1.23</td>
<td>38.81</td>
<td>2.01</td>
</tr>
<tr>
<td>HP-2</td>
<td>1.34</td>
<td>30.76</td>
<td>1.93</td>
</tr>
<tr>
<td>HP-3</td>
<td>1.39</td>
<td>31.18</td>
<td>2.02</td>
</tr>
<tr>
<td>HP-4</td>
<td>1.25</td>
<td>38.90</td>
<td>2.05</td>
</tr>
<tr>
<td>HP-5</td>
<td>1.29</td>
<td>34.50</td>
<td>1.96</td>
</tr>
<tr>
<td>HP-6</td>
<td>1.38</td>
<td>31.83</td>
<td>2.02</td>
</tr>
<tr>
<td>HP-7</td>
<td>1.20</td>
<td>40.21</td>
<td>2.00</td>
</tr>
<tr>
<td>HP-8</td>
<td>1.32</td>
<td>34.30</td>
<td>2.01</td>
</tr>
<tr>
<td>LP-1</td>
<td>1.56</td>
<td>24.32</td>
<td>2.07</td>
</tr>
<tr>
<td>LP-2</td>
<td>1.56</td>
<td>23.21</td>
<td>2.03</td>
</tr>
<tr>
<td>LP-3</td>
<td>1.57</td>
<td>22.99</td>
<td>2.04</td>
</tr>
<tr>
<td>LP-4</td>
<td>1.60</td>
<td>21.11</td>
<td>2.02</td>
</tr>
<tr>
<td>LP-5</td>
<td>1.61</td>
<td>21.52</td>
<td>2.05</td>
</tr>
<tr>
<td>LP-6</td>
<td>1.58</td>
<td>22.42</td>
<td>2.04</td>
</tr>
<tr>
<td>LP-7</td>
<td>1.57</td>
<td>22.24</td>
<td>2.02</td>
</tr>
<tr>
<td>LP-8</td>
<td>1.54</td>
<td>24.20</td>
<td>2.03</td>
</tr>
<tr>
<td>FD-1</td>
<td>1.80</td>
<td>11.44</td>
<td>2.03</td>
</tr>
<tr>
<td>FD-2</td>
<td>1.78</td>
<td>12.12</td>
<td>2.03</td>
</tr>
<tr>
<td>FD-3</td>
<td>1.78</td>
<td>12.46</td>
<td>2.03</td>
</tr>
<tr>
<td>FD-4</td>
<td>1.79</td>
<td>11.59</td>
<td>2.03</td>
</tr>
<tr>
<td>FD-5</td>
<td>1.79</td>
<td>12.19</td>
<td>2.04</td>
</tr>
<tr>
<td>FD-6</td>
<td>1.78</td>
<td>11.73</td>
<td>2.01</td>
</tr>
<tr>
<td>FD-7</td>
<td>1.77</td>
<td>11.97</td>
<td>2.01</td>
</tr>
</tbody>
</table>

4.3.1 CCC Sample Preparation

Before each vacuum impregnation process, CCC samples were fired at 300°C for 30min to remove any impurity. A pressure air gun was used to blow any residual carbon dust
4.3.2 Slurry Preparation

Calcined alumina powder (A16 SG, Almatis, Germany) with $d_{50}$ of 0.4$\mu$m was used as the main filler for CCC by vacuum impregnation. To promote dispersion, 0.2 dry wt% of citric acid dispersant ($C_6H_8O_7$, Fisher Scientific) was dissolved first in distilled water by magnetic stir bar. A16 was then dispersed into the solution at 72 total wt% (equivalent to 39vol%, assuming 3.98 g/cc density for alumina and 1.00 g/cc density for the liquid). The slurry was then ball milled for 24 hours. For alumina sol, AlOOH (boehmite, Condea, Germany), was dispersed in distilled water at 1.5M concentration. Dispersion involved first ultrasonic break up the boehmite agglomerates in water, then overnight mixing with magnetic stirring. Well-dispersed boehmite slurry is transparent to visible light, indicating particle size significantly smaller than the light wavelength (380 to 750 nm for visible light$^{63}$).

4.3.3 Vacuum Impregnation

A two-chamber vacuum desiccator was designed for vacuum impregnation (Figure 20).
The lower chamber held the sample while the upper chamber held the slurry. The two chambers were separated by a valve and were connected to a vacuum pump as depicted in Figure 20.

There were three stages to completing the impregnation of the CCC samples. Stage 1 impregnated the CCC with A16 slurry; stage 2 with alumina sol; and stage 3 with phosphoric acid. For stage 1, a sample was loaded into the lower chamber and partial vacuum to reach ~29 mmHg. The sample was held at vacuum for 10 minutes after which the valve separating the two chambers was opened to allow slurry to flow into the lower chamber. The sample remained submerged in the slurry for 30 minutes after which it was dried at 75°C for 10 minutes and then heat treated at 300°C for 20 minutes.
To ensure maximum infiltration of A16 into CCC, stage 1 was repeated 3 times for HP and LP samples and twice for FD samples. Between the cycles, the sample’s surface was cleaned by a razor blade and wire brush to remove the alumina cake formed during vacuum impregnation, and thus facilitated access of the slurry into the sample body. Stages 2 and 3 were almost identical in procedure as stage 1, except that the upper chamber was instead loaded with 1.5M alumina sol and phosphoric acid respectively. As well, after impregnation of phosphoric acid during the stage 3, the sample was heat treated at 350°C for 30 minutes and cooled down overnight.

### 4.3.4 Analysis of C⁴

After completion of all the vacuum impregnation stages, C⁴ sample were evaluated for their increase in density by Archimedes technique. Microstructure analysis before and after the impregnation were done by SEM (S-3000N, Hitachi, Japan). Wear test was performed at NRC Institute for Fuel Cell Innovation. ASTM G65 abrasive sand test was employed. A schematic of the test apparatus is shown in Figure 21.
The test included a rubber lined wheel with a diameter of 228.5mm and a thickness 12.7mm. A bale weighing 11.5lb was used to load the specimen against the rotating wheel. The wheel rotated at 200rpm while abrasive sand (Ottawa sand) flowed between the wheel and specimen at a rate of 300 to 400 g/min. Each sample was weighed before and after 100 revolutions on the wear test. As an alternative to abrasive wear, C4 was also tested with a steel wheel. Technically, the steel wheel test does not conform to the ASTM G65 guideline. However, the steel wheel test should simulate the sliding wear mechanism of the brake pad on rotor. As well, steel wheel test showed lower wear and thus requires 1000 revolutions to show a distinguishable wear scar.
5 Results and Discussion

5.1 Process Engineering of HTBC

5.1.1 Substrate Selection

During the early stage of the project, the concern was actually over failure of substrates, instead of HTBC, during the high-temperature thermal cycling of the coated samples. It was determined that the Fe-Ni alloy substrates cannot keep up with HTBC and would critically fail due to oxidation at just over 60 thermal cycles (Figure 22). The TBC coating involved showed little damage compared to the substrate.

![Figure 22](image)

Figure 22. (a) Front and (b) back of CB-CSG coating with bond coat remaining on Fe-Ni substrates after 60 thermal cycles at 1050°C.

Hastelloy-X was therefore acquired as substitute. However, Hastelloy-X still could not provide the originally targeted 1150°C thermal testing standard due to the lack of oxidation resistance beyond 1100°C. Such is the reason why 1050°C was chosen as testing parameter.
Sample stage used to hold specimen during thermal cycling was another evidence of how tough the TBC was. The sample stage was originally designed with 99.5% pure alumina crucibles. However, it was found that the alumina stage began to crack and eventually fell apart before the TBC did. This again demonstrated the severity of the thermal cycle test and TBC’s strength in withstanding such test.

5.1.2 The Effect of PVA Content on Porosity

The addition of PVA into the slurry would result in higher porosity in the coating due to PVA burn out during heat treatment. The porosity in turn may decrease thermal conductivity of the coating. To investigate into this matter, slurry types III (a) and (e) described in Table 4 section 4.1.1 were first gel casted and fractured to conduct SEM on the fracture surface. The difference in slurry III(a) and (e) were PVA concentrations of 0.24M, and 1.19M respectively. The SEM micrographs of the resulting materials are shown in Figure 23.
Figure 23. SEM on gel casts of 30wt% YSZ in 2M boehmite with (a) 0.24M PVA and (b) 1.19M PVA

It is seen in Figure 23 that the addition of PVA between 0.24M and 1.19M does not pose significant change in morphology of the gel cast composite. Therefore the next step compared different boehmite to YSZ ratios with and without PVA content at 0.71M (comparing slurry group I and IV).

Figure 24. SEM on gel casts of 25wt% YSZ in 1.5M boehmite with (a) no PVA and (b) 0.71M PVA

Figure 25. SEM on gel casts of 19wt% YSZ in 1.5M boehmite with (a) no PVA and (b) 0.71M PVA
Comparison of SEM micrographs in Figure 24, Figure 25, and Figure 26 reveals that even at different boehmite to YSZ ratios, PVA changed very little in terms of microstructure and porosity. It is also observed that even without PVA, the gel casts of different slurries were already quite porous. The porosity created many pathways for the burn out of PVA to escape from. Therefore, the effect of PVA was minimized in the gel cast composites. However, to process the composites as coatings, the slurries were pressure sprayed onto substrates, which would usually form microstructures denser than its gel cast counterpart, and thus will limit the amount of pathways for PVA to escape. It is in this case where PVA was speculated to have a greater effect on porosity. Slurries III(b) and (d) with 0.48M and 0.95M of PVA respectively were thus sprayed coated onto 316SS substrates for comparison (Figure 27).
Visually the microstructures of the CB-CSG coatings showed the slightest difference in porosity between 0.48M and 0.95M PVA. It was possible that further increase the amount of PVA would gain higher porosity. However, addition of 0.95M PVA had significantly increased the viscosity of the slurry to a point where the slurry could not be sprayed smoothly. Therefore, from a processing point of view, PVA is not a suitable candidate for controlling porosity. As well, judging from gel casts done at different boehmite to YSZ ratios, precursor composition of CB-CSG is seen to have a much greater effect on porosity.

### 5.1.3 Addition of α-Alumina

Initial evaluations of CB-CSG coatings were done on slurries with boehmite and 10μm average particle size YSZ. During the mid-stage of the project, α-alumina (A16) was added in as a third phase in the slurry due to the lack of coating integrity (e.g. very low
scratch resistance) with only boehmite and YSZ. Coatings without A16 (from slurry group V) also tend to crumple after 70 hours of 1000°C thermal loading. Literature shows that calcined alumina (A16) can be mixed in with other sol components to promote better chemical bonding\(^{65}\). It was expected that some chemical bonding through phosphoric acid would occur between the alumina from boehmite and the alumina from A16. As well, with higher portion of the ceramic filler phase (A16 and YSZ), there would be less unreacted boehmite. Therefore, A16 was introduced into the slurry making up slurry group VI. The literature also describes successful coating when the calcined solids component is between 80% and 90wt%. Therefore, for the new slurry types, boehmite gel component was fixed at 16 wt%, while the rest of 84% was made up with varying ratios of A16 and YSZ — 20:80 for slurry (a), 30:70 for slurry (b), and 40:60 for slurry (c). Slurries (a), (b), and (c) from group VI exhibited greater integrity and consistency. Coatings from this group could last through the initial thermal loading test at 1000°C for 100 hours without visible damage. It was then decided that slurry (b) from group VI would be the primary coating composition considering that it would yield about 60wt% in YSZ (for compatibility with APS YSZ top coat) and still had a significant amount of \(\alpha\)-alumina at 25wt% to minimize the CTE mismatch between YSZ and boehmite. The A16 acquired was 0.4\(\mu\)m in particle size (\(d_{50}\)). Therefore, YSZ
powder with particle size of 1.3 μm was selected so to optimize packing ratio and increase coating homogeneity.

The new types of slurry produced substantially stronger coating. Initial assessment of these coating around 50μm thick shows good integrity after 100 hours of thermal loading on bare Hastelloy-X substrates (Figure 28).

![Figure 28. CB-CSG coating on bare Hastelloy-X after 100 hours at 1000°C.](image)

However, a critical thickness of around 200μm was observed as coatings reaching beyond this thickness tend to spall off after heat treatment (Figure 29). It was believed that the higher thickness induced more stress at the bonding interface due to CTE mismatch between the coating and the substrate. Note that this result was from coating evaluation on bare substrates with only sandblasting for bonding improvement. The result improved when there is a bond coat or APS YSZ top coat underneath.
5.1.4 Surface Treatment on NiCrAlY Bond Coat

It was suggested by literatures\textsuperscript{44,45,66} that pre-oxidizing bond coat can have a positive effect on coating adhesion of APS and EB-PVD deposited YSZ. The pre-oxidation may form a stable aluminum oxide that will hinder further growth of Thermally Grown Oxide (TGO). The slower TGO development in turn translates to longer durations in thermal cyclic tests.

Samples with bond coat were tested by heat treating at 1050°C for 30 minutes. The samples were then coated with slurry VI(b). Following the coating, a thermal shock test was conducted by loading samples in furnace at 1050°C for 15 minutes and then immediately immersed in distilled water at room temperature. CB-CSG coatings with and without bond coat pre-oxidation were tested for this thermal shock at the same time.
The samples before the test can be seen in Figure 30.

Figure 30. CB-CSG coating on bond coat with (left) and without (right) pre-oxidation treatment.

Quenching the coating from 1050°C into cool water is considered quite a severe test.

Delamination commenced almost immediately. Figure 31 shows the progression of the delamination from the first thermal shock to the seventh.
Figure 31. Progression of thermal shocking of CB-CSG coating on bond coat with (left) and without (right) pre-oxidation. Thermal shocks included 1050°C for 15 minutes followed by immediate water quenching at room temperature.

From the thermal shocking, it was obvious that samples with pre-oxidation produce negative results, which is in contradiction of the literatures. A second repetition of the test showed very similar result. Upon examination of the coating under SEM, it was
found that there is an intermediate layer between TGO and CB-CSG layer (Figure 32).

EDS scanning revealed that this intermediate layer contains phosphate.

Figure 32. (a) SEM and (b) EDS spot analysis (location indicated by the square) showing the intermediate layer between TGO and CB-CSG coating containing phosphate.

It was highly possible that the phosphoric acid used for chemical bonding has reacted with the TGO to form a brittle scale. To confirm this hypothesis, CB-CSG was again
coated on bond coat with pre-oxidation, however without phosphoric acid application. The result showed that the intermediate layer is not present (Figure 33).

Figure 33. SEM showing no intermediate layer between TGO and CB-CSG coating without phosphoric acid.

This set of experiment concluded that while bond coat pre-oxidation may be beneficial to APS or EB-PVD deposited YSZ top coat, in the case of CB-CSG where phosphoric acid was used, the benefit was eliminated by the formation of phosphate scale on TGO. The result was actually worse in thermal cyclic performance.

5.1.5 Microstructure of HTBC

Under high magnification, the surface of APS YSZ is seen to be undulated. Such undulation can be amplified into vertical texture under favorable conditions. Figure 34 shows samples intercepted before a full session of CB-CSG coating. It is evident that
the vertical columns rose from peaks of the substrate’s surface undulation (indicated by triangles). Through repetitive testing of the process parameters it was determined that favorable conditions calls for a very slow rate of spray rate (~0.3mm/min·mm²) and a hotplate underneath the substrate at ~200°C. This condition flash evaporated the fine slurry mist, likely even before the droplets contact the substrate. The dehydrated droplets were limited from creating splats or flow out to form “pancake stacks”\textsuperscript{67}. Preferential growth was the second factor where the dehydrated droplets were dragged out by carrier gas and conglomerated on the peaks. This is confirmed by Figure 34 showing very rarely does a “growth” occur in a valley of the undulation.
Figure 34. Samples intercepted before complete coverage of CB-CSG coating. Triangles mark original “peaks” from the APS YSZ layer; circles mark the “valleys”.

Evolution of these initial CB-CSG asperities as spraying was continued can be seen in Figure 35, which shows the CB-CSG layer deposited on the APS YSZ layers. The deposition rate was gradually increased to about 2mg/min-mm² during coating to speed
up coating process. The texture of the 250–300 μm coating thickness had a very strong vertical orientation. Angled view of the surface also shows the 3D texture of the fully coated CB-CSG (Figure 36).

Figure 35. CB-CSG (250–300μm) coating on APS YSZ top coat

Figure 36. SEM images of the surface morphology at 35° incident angle of view,

Figure 35 is insightful regarding the evolution of the vertical columns due to clearly visible lines, much like tree rings in the cross section of the trunk. These light-colored
lines in the CB-CSG coating are actually phosphate-rich films formed due to excessive applications of phosphoric acid between passes of sol gel spraying. Under EDS mapping (Figure 37), the white lines show uniform Al, P, and Zr.

Figure 37. EDS mapping for CB-CSG columns showing distributions of Al, P, and Zr.

It was believed that both Al and Zr represent Al$_2$O$_3$ and YSZ in the films respectively. However, P could represent monoaluminum phosphate (Al(H$_2$PO$_4$)), aluminum metaphosphate (Al(PO$_3$)$_3$) and/or aluminum orthophosphate (AlPO$_4$)\textsuperscript{68} or zirconium phosphate (Zr(HPO$_4$)$_2$·2H$_2$O)\textsuperscript{69}. The exact phosphate phase is difficult to identify as their peaks are overlapping. However, in forgoing studies\textsuperscript{68,69,70}, it was determined that phosphate sealing is effective in improving corrosion resistance of thermal sprayed coatings, while thermal shock resistance suffered due to increase in coating stiffness. Therefore, to achieve the removal of this excess of surface-segregated phosphate,
application of each phosphoric acid was decreased in quantity, but increased in frequency in order to gain a more uniform distribution of P. Figure 38(a) shows SEM images of the cross section in (a), and EDS mapping in (b) of such better process controlled CB-CSG (e.g., uniformly distributed phosphate is confirmed by EDS mapping). It was observed that alumina, YSZ and phosphate are well distributed without significant localized area of excess in any element.

Figure 38. SEM images of (a) the cross section, and (b) EDS mapping of CB-CSG coated on bottom APS-YSZ layer.

5.1.6 Phase Analysis of CB-CSG

XRD results, Figure 39, compare phase composition of the as-deposited CB-CSG coating (Figure 39a) and after thermal cycling between 1000 °C and 30 °C (Figure 39b). In Figure 39a, typical peaks of YSZ and α-alumina are observed; mono aluminum phosphate (Al(H₂PO₄)₂) peak appears at 2θ=~27deg (the mono aluminum phosphate
transforms to the refractory AlPO₄ after thermal cycling at 1000 °C, refer to Figure 39b).

![Figure 39. XRD data (a) before and (b) after 10 thermal cycles between 1000 °C and 30°C.](image)

It is thus confirmed that chemical reaction between the boehmite sol precursor and phosphoric acid took place during heat treatment, to form the mono-aluminum phosphate, providing cohesion of the CB-CSG layers and adhesion to the YSZ-APS layers. Zirconium phosphates appeared after thermal cycling at 1050 °C, although exact chemical formula of these zirconium phosphates remains controversial since a few different types of zirconium phosphates show peaks at similar ranges of 2θ. The possible compounds include ZrP₂O₇, α-(ZrO)₂P₂O₇ and/or Zr(HPO₄)·2H₂O. According to the literature, the
peak at about $2\theta=15^\circ$ in Figure 39b matches well with $\alpha$-(ZrO)$_2$P$_2$O$_7$ while peaks of other zirconium phosphates may overlap. Zirconium phosphates are also well known for good thermal shock resistance $^{15,72,73,74}$. Due to the relatively low thermal expansion ($1.5\times10^{-6}/^\circ\text{C}$) of zirconyl phosphate (ZrO)$_2$·P$_2$O$_7$, from room temperature to 1000$^\circ\text{C}$, its high thermal shock resistance and stability have been reported$^{16,17}$. Therefore, it is believed that the zirconium phosphates formed may improve HTBC service life, while aluminum phosphates provide chemical bonding between alumina powders as well as bonding between alumina and YSZ.

5.1.7 CB-CSG Coating Adhesion

Under SEM, the CB-CSG layer appears well attached to the underlying (bottom) APS YSZ layer (Figure 40). A bigger challenge was for the coating to survive the APS deposition of the upper YSZ layer (Type 2 and 4 coatings as described in section 4.1.3). Molten particles leave the APS nozzle with over 2500$^\circ\text{C}$ temperature, traveling at 200 ~ 300 m/s$^{75}$. The combined energy of high temperature and velocity can be quite destructive. Yet, it had been demonstrated that the CB-CSG coatings can survive the process without destruction of the columnar microstructure (Figure 41).
Figure 40. Interface between CB-CSG and APS YSZ layers at (a) 5k and (b) 10k magnifications.

Figure 41. SEM Images of type II CB-CSG composite TBC.

Evaluation of coating adhesion was done by pull-out test. The pull-out stud had a contact area of 5.94mm² (2.75mm in diameter). However, the area of coating detached by the stud often did not exactly conform to the contact area (the head of the stud), but instead exhibited irregular geometries (Figure 42).
The detachment area was therefore measured with a caliper and the data normalized to the measured pull-out area. A total of 18 pull-out tests are done to 6 samples with coating type 2 (bond coat + APS YSZ + CB-CSG + APS YSZ). Table 10 lists the adhesion strength at the point of coating detachment as calculated by using stud size as well as normalized with detachment area. A plot of the normalized adhesion strength is shown in Figure 43.
Table 10. Pull-out tests results with adhesion strength normalized to the detachment area.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test #</th>
<th>Detachment Area (mm²)</th>
<th>Force (N)</th>
<th>Max Adh Str. (MPa)</th>
<th>Normalized Str. (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stud</td>
<td>5.94</td>
<td>12.25</td>
<td>13.65</td>
<td>2.40</td>
<td>1.11</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>16.25</td>
<td>39.27</td>
<td>6.90</td>
<td>2.42</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>23.08</td>
<td>20.44</td>
<td>3.59</td>
<td>0.89</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>31.82</td>
<td>26.63</td>
<td>4.68</td>
<td>0.84</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>22.480</td>
<td>75.49</td>
<td>13.26</td>
<td>3.36</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>8.09</td>
<td>8.06</td>
<td>1.42</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>16.84</td>
<td>62.66</td>
<td>11.01</td>
<td>3.72</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>18.06</td>
<td>36.11</td>
<td>2</td>
<td>0.63</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>10.29</td>
<td>5.85</td>
<td>1.03</td>
<td>0.57</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>30.58</td>
<td>42.22</td>
<td>7.42</td>
<td>1.38</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>53.47</td>
<td>19.58</td>
<td>3.44</td>
<td>0.37</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>19.63</td>
<td>52.34</td>
<td>9.19</td>
<td>2.67</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>66.14</td>
<td>37.06</td>
<td>6.51</td>
<td>0.56</td>
</tr>
<tr>
<td>5</td>
<td>13</td>
<td>21.648</td>
<td>52.33</td>
<td>9.19</td>
<td>2.42</td>
</tr>
<tr>
<td>5</td>
<td>14</td>
<td>45.26</td>
<td>16.79</td>
<td>2.95</td>
<td>0.37</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>14.20</td>
<td>24.93</td>
<td>4.38</td>
<td>1.76</td>
</tr>
<tr>
<td>6</td>
<td>16</td>
<td>53.3</td>
<td>18.09</td>
<td>3.18</td>
<td>0.34</td>
</tr>
<tr>
<td>6</td>
<td>17</td>
<td>41.90</td>
<td>49.91</td>
<td>8.77</td>
<td>1.19</td>
</tr>
</tbody>
</table>
Examining the detached coating showed the failures occur in the CB-CSG layer, which coincided with prediction — that CB-CSG is softer than APS YSZ. SEM confirmed this prediction by showing detachment points in the CB-CSG layer (Figure 44).
Figure 44. SEM showing the pull-out sample (a) before the pull-out test and (b) after the pull-out test.
Generally speaking, the adhesion strength was low. As a standard of comparison, concrete has tensile strength in the range of 2.5MPa to 4MPa\textsuperscript{76,77,78}. The low strength can be explained by the nature of columnar growth. As mentioned previously, the columns require very slow initial deposition. As a result, the attachments to the bottom APS YSZ layer often showed thin necks. It is believed that the thin roots of the columns are the points of failure as pointed out in Figure 45. It is also seen in Figure 44 that the fracture line is located at the bottom part of the CB-CSG layer.

![Figure 45. SEM showing thin necks at the root of each CB-CSG columns.](image)

The graph in Figure 43 also shows there is a large deviation in the tests. This can be explained by the columnar structure. Figure 36 shows that each column can be as large as 0.5mm in diameter, which is about 20% of the stud’s diameter. It is then easy for the
stud to “misplace” its edge and cause error in the test. An illustration is shown in Figure 46 to better express the idea of “misplacement”. Compounded with the necking characteristics of the columns as well as the bumpy surface, it is understandable how the stud may sometimes be placed over a weaker section while other times over a stronger section.

![Figure 46. Schematic illustration of possible stud placements over the columnar structure](image)

Essentially, the HTBC is a complex coating system with the CB-CSG layer containing non-homogeneous defects. While the pull-out test gives us an approximate insight into the adhesion of the CB-CSG coating to the APS YSZ layer, the performance of HTBC is not accurately reflected. Whereas the test provides a tensile load, the working conditions of TBC generally do not require high tensile strength. The primary goal of the additional CB-CSG porous textured film was to alleviate thermal strain and increase overall thickness. Therefore, a more relevant evaluation to the adhesion character
would be thermal cycling test described in the next section.

5.1.8 Thermal Cycling of HTBC

For coatings that went through the thermal cycling test between 1050°C and room temperature, type 4, 5, and 6 coatings (CB-CSG layer directly on bond coat or alloy) failed prematurely. Type 4 coatings would detach entirely (Figure 47) within the first 15 cycles, while type 5 and 6 coatings would crumple into small flakes. It seems that the difference in CTE between the metallic components (bond coat and alloy substrate) and the CB-CSG (with 40wt% alumina) may be too high. Hence the softer CB-CSG fell apart when the substrate underwent a large thermal expansion. Type 2 and 3 coatings lasted much longer, and thus were selected primary test subject in comparison with the reference TBC coatings (type 1 without CB-CSG).

![Figure 47. Detachment of coating type 4 in the CB-CSG layer.](image)
Samples with type 2 and 3 coatings faired better with an APS YSZ layer below to facilitate a similar CTE. However, due to edge effect (higher stress at sharp corners and edges), the samples at times experienced small amount of chipping at the corners and edges. These types of chipping are not considered to be coating failures. The most promising set comes from type 2 coatings with the CB-CSG layer at 250~300μm and ~100μm APS YSZ above and below (Figure 48).

Table 11 shows the percentages of coatings remaining at various cycle counts for this test group (approximated by Image J as described in section 4.1.5). Samples from this set lasted over 1000 thermal cycles with very minimum coating delamination. Two of the samples were evaluated at 2000 and 3000 cycles. Even at such high number of cycles, the degree of delamination (~10% at 2000 cycles and ~30% at 3000 cycles) is still considerably low.
Figure 48. Type 2 coating used for thermal cycling test.

Table 11. Coating type 2 with thin CB-CSG layer and their percentage of coating remaining at different cycle counts.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>500</th>
<th>1000</th>
<th>2000</th>
<th>3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2thin-1</td>
<td>100%</td>
<td>98%</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>T2thin-2</td>
<td>100%</td>
<td>100%</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>T2thin-3</td>
<td>100%</td>
<td>100%</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>T2thin-4</td>
<td>NA</td>
<td>94%</td>
<td>88%</td>
<td>NA</td>
</tr>
<tr>
<td>T2thin-5</td>
<td>92%</td>
<td>NA</td>
<td>90%</td>
<td>71%</td>
</tr>
</tbody>
</table>
Another test group with a lower degree of success is the type 3 coating with thin CB-CSG (100~150μm) layer. This group had a rather mixed result as shown in Table 12. The samples would either last up to 100 cycles or almost immediately fail within 20 cycles. The failed samples showed CB-CSG layer crumpling into small flakes much like the failure mode of type 5 and 6 coatings (CB-CSG directly on bond coat). Further analysis revealed that the CB-CSG that fail prematurely were built on top of a thinner layer of APS (~100μm, Figure 51), while the ones with more success were built on top of a thicker layer of APS (~200μm, Figure 52).
Table 12 Coating type 3 with thin CB-CSG layer and their percentage of coating remaining at different cycle counts.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Percentage of Coating Remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td>T3thin-1</td>
<td>0%</td>
</tr>
<tr>
<td>T3thin-2</td>
<td>0%</td>
</tr>
<tr>
<td>T3thin-3</td>
<td>0%</td>
</tr>
<tr>
<td>T3thin-4</td>
<td>NA</td>
</tr>
<tr>
<td>T3thin-5</td>
<td>97%</td>
</tr>
</tbody>
</table>

Figure 50 Type 2 coatings with thin (200~300μm) CB-CSG layer. (a) T3thin-4 and (b) T3thin-5 after 150 cycles
Figure 51. CB-CSG on top of thin APS YSZ of ~100μm.

Figure 52. CB-CSG on top of thick APS YSZ of ~200μm.
The two successful test groups suggest that the thermal shock resistance is still dependent on the APS YSZ. When there was a top APS YSZ layer over the CB-CSG, the coating functioned very well with thermal cycle counts well over 1000. Only at around 2000 cycles did the coating start to show signs of degradation. One reason for the high performance may be that the top APS YSZ layer was acting as a protecting barrier. As well, we can see in Figure 53 the top APS YSZ filled in the valleys between the CB-CSG columns and almost comes in contact with the bottom APS YSZ at certain points. This may have the effect of anchoring down and holding together the soft CB-CSG. Where there was not a top layer of APS YSZ, CB-CSG relied on a thick layer of APS YSZ above 200µm underneath it to minimize the effect of thermal expansion from the metallic bond coat and substrate.
Figure 53. APS YSZ filling in the valleys of CB-CSG columnar structure.
5.2 HTBC on Hot Gas Turbine Impingement Plate

The opportunity to test HTBC coating on the impingement plate was a great chance to transfer in-lab process to an industrial environment. The difficulties of the task included a very short time frame, the lack of tightly controlled environment, as well as only one chance to perform the coating. After the coatings process, the impingement plates were installed and operated continuously for one year. Liburdi maintenance service after one year checked the parts with an endoscope and reported that the impingement plates were intact and the coatings did seem to remain. However, the brief message from Liburdi carried very little information regarding detailed condition of the coatings. Therefore, the discussion here would focus on the processing experience on these impingement plates and the test coupons retrieved.

Coating types 2, 4 and 5 (as outlined in 4.1.2) were deposited on three separate plates. Procedures were as described in Section 4.2. The coupons were brought back for SEM and EDS analysis. The thickness of each layer in each coating type is shown in Table 13.
Table 13. Resulting thickness of different coating types deposited on impingement plate.

<table>
<thead>
<tr>
<th>Coating type</th>
<th>Bond Coat</th>
<th>APS YSZ</th>
<th>CB-CSG</th>
<th>APS YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>50 um</td>
<td>30 - 40 um</td>
<td>20 um</td>
<td>70 um</td>
</tr>
<tr>
<td>4</td>
<td>70 - 80 um</td>
<td>N/A</td>
<td>60 um</td>
<td>30 - 40 um</td>
</tr>
<tr>
<td>5</td>
<td>70 - 80 um</td>
<td>N/A</td>
<td>60 um</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Type 2 coating shows a very thin layer of the CB-CSG layer at just about 20μm. Indeed, the target thickness was not achieved due to operator’s inexperience with such working environment. The usual technique of monitoring deposition progress by checking weight gain was not applicable in such situation. Coating type 4 and 5 do show improved CB-CSG thickness to around 60μm. The overall coating microstructures with element distinctions are shown in Figure 54, Figure 55, and Figure 56.

Figure 54. SEM of type 2 CB-CSG Composite TBC in turbine impingement plate.
The first thing to notice is the lack of any vertical texture in the coatings. This was not
out of expectation since the condition favoring columnar growth was virtually non-existent. During the coating session, no continuous heat source was provided for flash evaporation. The plates experienced fast cooling by forced convection from both the 70rpm rotation as well as a suction duct right above the working area. Effort was made to keep the surface temperature to 150°C by pre-heated with hydrogen plasma before spraying as well as using two propane welding torches to provide some fast drying effect. However, dehydration of the spray droplets was still very limited. The short time frame also restricted the use of slow rate of spraying, which further encouraged the outflow of droplets as they contact the surface. As a result, the coatings seen are very porous but lack the columnar structure. Closer examination does show however good interfacial bonding between the CB-CSG and APS YSZ as well as between CB-CSG and bond coat.

Figure 57 Bonding interface of type 2 coating between CB-CSG layer and bottom APS YSZ layer.
Figure 58. Bonding interface of type 2 coating between CB-CSG layer and top APS YSZ layer.

Figure 59. Bonding interface of type 4 coating between CB-CSG layer and bond coat.

Figure 60. Bonding interface of type 4 coating between CB-CSG layer and top APS YSZ layer.
In summary, despite the low thickness, HTBC on turbine impingement plates is considered successful since the overall coating structure is achieved. Without analysis of the coating after service, it is hard to quantify the performance. HTBC under such environment can benefit from more experience and process optimization.
5.3 Ceramic Carbon-Carbon Composites

5.3.1 Densification of CCC by CB-CSG

Primary goal in the CCC processing was to densify the porous CCC samples to no less than 1.8g/cc (~11.5% porosity). The batches of CCC blocks were divided into HP, LP, and FD groups as outlined in 4.3.1. To achieve densification, samples were vacuum impregnated with $\alpha$-alumina (A16), AlOOH (boehmite), and phosphoric acid by process described in Section 4.3.3. The results from the vacuum impregnation are presentation in the following Table 14, 15, 16.

Table 14. Weight of HP group CCC samples throughout different impregnation cycles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Weight [g]</th>
<th>A16 Impreg #1 [g]</th>
<th>A16 Impreg #2 [g]</th>
<th>A16 Impreg #3 [g]</th>
<th>Boehmite Impreg #1 [g]</th>
<th>Boehmite Impreg #2 [g]</th>
<th>Phosphoric Acid Impreg #1 [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-1</td>
<td>36.530</td>
<td>54.272</td>
<td>57.559</td>
<td>57.729</td>
<td>57.889</td>
<td>58.007</td>
<td>59.365</td>
</tr>
<tr>
<td>HP-2</td>
<td>40.032</td>
<td>55.399</td>
<td>58.817</td>
<td>59.810</td>
<td>59.873</td>
<td>59.877</td>
<td>61.119</td>
</tr>
<tr>
<td>HP-3</td>
<td>41.259</td>
<td>55.556</td>
<td>58.481</td>
<td>59.893</td>
<td>59.934</td>
<td>59.952</td>
<td>61.111</td>
</tr>
<tr>
<td>HP-4</td>
<td>37.498</td>
<td>54.518</td>
<td>57.975</td>
<td>59.100</td>
<td>59.183</td>
<td>59.221</td>
<td>60.565</td>
</tr>
<tr>
<td>HP-5</td>
<td>38.438</td>
<td>54.939</td>
<td>58.031</td>
<td>58.640</td>
<td>58.720</td>
<td>58.777</td>
<td>60.081</td>
</tr>
<tr>
<td>HP-6</td>
<td>40.676</td>
<td>55.272</td>
<td>57.954</td>
<td>59.230</td>
<td>59.292</td>
<td>59.317</td>
<td>60.491</td>
</tr>
<tr>
<td>HP-7</td>
<td>179.920</td>
<td>274.900</td>
<td>300.840</td>
<td>300.820</td>
<td>300.720</td>
<td>300.750</td>
<td>306.480</td>
</tr>
</tbody>
</table>
Table 15. Weight of LP group CCC samples throughout different impregnation cycles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Weight [g]</th>
<th>A16 Impreg #1 [g]</th>
<th>A16 Impreg #2 [g]</th>
<th>A16 Impreg #3 [g]</th>
<th>Boehmite Impreg #1 [g]</th>
<th>Boehmite Impreg #2 [g]</th>
<th>Phosphoric Acid Impreg #1 [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP-1</td>
<td>53.002</td>
<td>65.881</td>
<td>70.383</td>
<td>71.220</td>
<td>71.322</td>
<td>31.268</td>
<td>72.081</td>
</tr>
<tr>
<td>LP-2</td>
<td>46.088</td>
<td>56.770</td>
<td>59.154</td>
<td>59.164</td>
<td>59.225</td>
<td>59.292</td>
<td>60.035</td>
</tr>
<tr>
<td>LP-3</td>
<td>46.240</td>
<td>56.860</td>
<td>59.405</td>
<td>59.386</td>
<td>59.441</td>
<td>59.482</td>
<td>60.197</td>
</tr>
<tr>
<td>LP-4</td>
<td>50.091</td>
<td>58.386</td>
<td>60.773</td>
<td>60.760</td>
<td>60.876</td>
<td>60.962</td>
<td>61.727</td>
</tr>
<tr>
<td>LP-5</td>
<td>47.212</td>
<td>56.729</td>
<td>58.948</td>
<td>58.895</td>
<td>58.949</td>
<td>58.984</td>
<td>59.678</td>
</tr>
<tr>
<td>LP-6</td>
<td>381.540</td>
<td>460.500</td>
<td>462.700</td>
<td>skipped</td>
<td>463.200</td>
<td>463.400</td>
<td>467.900</td>
</tr>
<tr>
<td>LP-7</td>
<td>386.250</td>
<td>462.600</td>
<td>463.500</td>
<td>skipped</td>
<td>465.200</td>
<td>465.700</td>
<td>470.600</td>
</tr>
</tbody>
</table>

Table 16. Weight of FD group CCC samples throughout different impregnation cycles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Weight [g]</th>
<th>A16 Impreg #1 [g]</th>
<th>A16 Impreg #2 [g]</th>
<th>Boehmite Impreg #1 [g]</th>
<th>Boehmite Impreg #2 [g]</th>
<th>Phosphoric Acid Impreg #1 [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FD-1</td>
<td>54.099</td>
<td>56.123</td>
<td>56.166</td>
<td>56.229</td>
<td>56.224</td>
<td>56.586</td>
</tr>
<tr>
<td>FD-2</td>
<td>53.720</td>
<td>58.185</td>
<td>58.471</td>
<td>58.508</td>
<td>skipped</td>
<td>58.978</td>
</tr>
<tr>
<td>FD-3</td>
<td>53.675</td>
<td>58.074</td>
<td>58.270</td>
<td>58.320</td>
<td>skipped</td>
<td>58.825</td>
</tr>
<tr>
<td>FD-4</td>
<td>53.638</td>
<td>58.208</td>
<td>58.580</td>
<td>58.609</td>
<td>skipped</td>
<td>59.088</td>
</tr>
<tr>
<td>FD-5</td>
<td>53.895</td>
<td>57.451</td>
<td>57.747</td>
<td>57.827</td>
<td>skipped</td>
<td>58.319</td>
</tr>
<tr>
<td>FD-6</td>
<td>218.130</td>
<td>228.160</td>
<td>228.090</td>
<td>228.940</td>
<td>229.200</td>
<td>230.690</td>
</tr>
<tr>
<td>FD-7</td>
<td>218.060</td>
<td>222.460</td>
<td>222.430</td>
<td>223.290</td>
<td>223.790</td>
<td>224.920</td>
</tr>
</tbody>
</table>
Figure 62. Percentage of total weight gain at each A16 impregnation cycles for group HP.

Figure 63. Percentage of total weight gain at each A16 impregnation cycles for group LP.
Figure 64. Percentage of total weight gain at each A16 impregnation cycles for group FD.

Table 14, 15, and 16 show the weight of each sample at different stages of the vacuum impregnation. Figure 62, 62, and 63 illustrate the weight gains at each cycle in terms of total weight gain. Note that the impregnations with boehmite and phosphoric acid were done to facilitate chemical bonding. The densification occurred during the A16 impregnation stages, mostly during the very first impregnation. Repetitions of A16 impregnation were done to ensure maximum infiltration of A16. After the complete impregnation process, the samples far exceed the original target of 1.8g/cc. Table 17, 18, and 19 show the porosity and density of the samples before and after the impregnation. A sample from the LP group is taken under SEM for microstructure verification before and after the impregnation (Figure 65).
Table 17. Density and porosity of samples from HP group before and after the vacuum impregnation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Bulk Density [g/cc]</th>
<th>Initial Porosity [%]</th>
<th>Final % porosity</th>
<th>Percent of Initial Porosity Filled [%]</th>
<th>Final Bulk Density [g/cc]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-1</td>
<td>1.23</td>
<td>38.81%</td>
<td>15.40%</td>
<td>60.31%</td>
<td>1.99</td>
</tr>
<tr>
<td>HP-2</td>
<td>1.34</td>
<td>30.76%</td>
<td>9.30%</td>
<td>69.78%</td>
<td>2.04</td>
</tr>
<tr>
<td>HP-3</td>
<td>1.39</td>
<td>31.18%</td>
<td>10.88%</td>
<td>65.11%</td>
<td>2.05</td>
</tr>
<tr>
<td>HP-4</td>
<td>1.25</td>
<td>38.90%</td>
<td>15.45%</td>
<td>60.28%</td>
<td>2.02</td>
</tr>
<tr>
<td>HP-5</td>
<td>1.29</td>
<td>34.50%</td>
<td>12.42%</td>
<td>64.02%</td>
<td>2.01</td>
</tr>
<tr>
<td>HP-6</td>
<td>1.38</td>
<td>31.83%</td>
<td>11.39%</td>
<td>64.22%</td>
<td>2.05</td>
</tr>
<tr>
<td>HP-7</td>
<td>1.20</td>
<td>40.21%</td>
<td>15.00%</td>
<td>62.71%</td>
<td>2.03</td>
</tr>
<tr>
<td>HP-8</td>
<td>1.32</td>
<td>34.30%</td>
<td>13.34%</td>
<td>61.12%</td>
<td>2.02</td>
</tr>
</tbody>
</table>

Table 18. Density and porosity of samples from LP group before and after the vacuum impregnation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Bulk Density [g/cc]</th>
<th>Initial Porosity [%]</th>
<th>Final % porosity</th>
<th>Percent of Initial Porosity Filled [%]</th>
<th>Final Bulk Density [g/cc]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP-1</td>
<td>1.56</td>
<td>24.32%</td>
<td>7.51%</td>
<td>69.11%</td>
<td>2.12</td>
</tr>
<tr>
<td>LP-2</td>
<td>1.56</td>
<td>23.21%</td>
<td>8.94%</td>
<td>61.49%</td>
<td>2.03</td>
</tr>
<tr>
<td>LP-3</td>
<td>1.57</td>
<td>22.99%</td>
<td>8.69%</td>
<td>62.18%</td>
<td>2.04</td>
</tr>
<tr>
<td>LP-4</td>
<td>1.60</td>
<td>21.11%</td>
<td>9.73%</td>
<td>53.93%</td>
<td>1.96</td>
</tr>
<tr>
<td>LP-5</td>
<td>1.61</td>
<td>21.52%</td>
<td>8.66%</td>
<td>59.78%</td>
<td>2.03</td>
</tr>
<tr>
<td>LP-6</td>
<td>1.58</td>
<td>22.42%</td>
<td>11.60%</td>
<td>48.23%</td>
<td>1.93</td>
</tr>
<tr>
<td>LP-7</td>
<td>1.57</td>
<td>22.24%</td>
<td>11.75%</td>
<td>47.15%</td>
<td>1.91</td>
</tr>
</tbody>
</table>
Table 19. Density and porosity of samples from FD group before and after the vacuum impregnation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Bulk Density [g/cc]</th>
<th>Initial Porosity [%]</th>
<th>Final % porosity</th>
<th>Percent of Initial Porosity Filled [%]</th>
<th>Final Bulk Density [g/cc]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FD-1</td>
<td>1.80</td>
<td>11.44%</td>
<td>8.70%</td>
<td>23.95%</td>
<td>1.88</td>
</tr>
<tr>
<td>FD-2</td>
<td>1.78</td>
<td>12.12%</td>
<td>6.65%</td>
<td>45.16%</td>
<td>1.95</td>
</tr>
<tr>
<td>FD-3</td>
<td>1.78</td>
<td>12.46%</td>
<td>7.05%</td>
<td>43.43%</td>
<td>1.95</td>
</tr>
<tr>
<td>FD-4</td>
<td>1.79</td>
<td>11.59%</td>
<td>5.87%</td>
<td>49.30%</td>
<td>1.97</td>
</tr>
<tr>
<td>FD-5</td>
<td>1.79</td>
<td>12.19%</td>
<td>7.47%</td>
<td>38.68%</td>
<td>1.93</td>
</tr>
<tr>
<td>FD-6</td>
<td>1.78</td>
<td>11.73%</td>
<td>8.39%</td>
<td>28.48%</td>
<td>1.87</td>
</tr>
<tr>
<td>FD-7</td>
<td>1.77</td>
<td>11.97%</td>
<td>10.05%</td>
<td>16.07%</td>
<td>1.82</td>
</tr>
</tbody>
</table>
Figure 65. CCC from LP group (a) before and (b) after the vacuum impregnation with calcined alumina.

Samples from the HP group had the highest final porosity mostly in the rage of 10~15%, although they all met the 1.8g/cc density target (1.8g/cc correlates to ~12% porosity in a normal CCC sample). The FD group had the lowest final porosity due to its low
porosity to begin with. This indicates that the LP group with the initial porosity of 21~25% may be the most beneficial for this vacuum impregnation process, and therefore was chosen as the candidate for wear resistance test by ASTM G65.

5.3.2 Wear Test of C^4

Procedure and set up of the wear test is described in section 4.3.4. The three candidates of the test were CCC with 24% porosity (LP), vacuum impregnated C^4 with ~10% porosity, and the reference samples of “fully” CVI densified CCC with 11% porosity (FD). Results from the rubber wheel with sand abrasion test are shown in Table 20, while results from the steel wheel sliding wear test are shown in Table 21.

Table 20. Results from abrasive wear (ASTM G65 test with rubber wheel and Ottawa Sand).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Density (g/cc)</th>
<th>Porosity (%)</th>
<th>Wt Loss (g)</th>
<th>Volume Loss (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C^4-1</td>
<td>2.01</td>
<td>9.89%</td>
<td>0.0168</td>
<td>0.00835803</td>
</tr>
<tr>
<td>C^4-2</td>
<td>2.04</td>
<td>8.72%</td>
<td>0.0129</td>
<td>0.00633774</td>
</tr>
<tr>
<td>FD-1</td>
<td>1.80</td>
<td>11.36%</td>
<td>0.0152</td>
<td>0.00842105</td>
</tr>
<tr>
<td>FD-2</td>
<td>1.80</td>
<td>11.36%</td>
<td>0.0136</td>
<td>0.00753463</td>
</tr>
<tr>
<td>LP-1</td>
<td>1.54</td>
<td>24.20%</td>
<td>0.0182</td>
<td>0.01181383</td>
</tr>
<tr>
<td>LP-2</td>
<td>1.54</td>
<td>24.20%</td>
<td>0.0230</td>
<td>0.01492957</td>
</tr>
</tbody>
</table>
Table 21 Results from sliding wear (modified ASTM G65 test with steel wheel).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Density (g/cc)</th>
<th>Porosity (%)</th>
<th>Wt Loss (g)</th>
<th>Volume Loss (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4-3</td>
<td>2.00</td>
<td>10.49%</td>
<td>0.5848</td>
<td>0.29220108</td>
</tr>
<tr>
<td>C4-4</td>
<td>2.05</td>
<td>8.72%</td>
<td>0.5248</td>
<td>0.25637282</td>
</tr>
<tr>
<td>FD-3</td>
<td>1.80</td>
<td>11.36%</td>
<td>0.5606</td>
<td>0.31058180</td>
</tr>
<tr>
<td>FD-4</td>
<td>1.80</td>
<td>11.36%</td>
<td>0.6225</td>
<td>0.34487543</td>
</tr>
<tr>
<td>LP-3</td>
<td>1.54</td>
<td>24.20%</td>
<td>0.6289</td>
<td>0.40822627</td>
</tr>
<tr>
<td>LP-4</td>
<td>1.54</td>
<td>24.20%</td>
<td>0.5545</td>
<td>0.35993237</td>
</tr>
</tbody>
</table>

Table 22. Summary of the wear tests.

<table>
<thead>
<tr>
<th>Group</th>
<th>Abrasive Volume Loss (cc)</th>
<th>Sliding Volume Loss (cc)</th>
<th>Abrasive Wear Loss (%)</th>
<th>Sliding Wear Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4</td>
<td>0.00734788</td>
<td>0.27428695</td>
<td>92%</td>
<td>84%</td>
</tr>
<tr>
<td>FD</td>
<td>0.00797784</td>
<td>0.32772861</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>LP</td>
<td>0.01337170</td>
<td>0.38407932</td>
<td>168%</td>
<td>117%</td>
</tr>
</tbody>
</table>

Table 22 summarizes the results from both abrasive and sliding wear tests. It can be seen that compared to the FD group, C4 improved the wear resistance by 8~16%. This is a very promising result showing that vacuum impregnation of alumina into CCC can not only avoid the end stages of expensive CVI, but can also improve the wear resistance. The process may therefore result in light-weight composites of relatively low-cost, allowing penetration of general automotive markets (from the current aerospace and racing cars markets). More evaluations are needed to determine viability of such
hypothesis.
6 Conclusions and Recommendations for Future Work

6.1 Summary and Conclusions

In this work, CB-CSG has been utilized to enhance the two types of composite ceramics: the laminar TBC and the 3D CCC, by introducing the chemically-bonded alumina phase as an added-on functional component of the system. Versatility of the relatively low-temperature CB-CSG technology was also demonstrated by the two unique processing methods. In the TBC, CB-CSG had successfully turned the top coat into a composite ceramic layer with YSZ and alumina. Optimization of this composite ceramic layer began with porosity control by PVA addition. SEM micrographs of gel casts and coating cross sections showed negligible effect of PVA when the coating alone already exhibits porous microstructure. However, the effect of increased porosity by PVA burn out may be more substantial when the coating is less porous. A16 calcined alumina was added into the CB-CSG along with boehmite and YSZ in order to i) minimize CTE mismatch between YSZ and boehmite, ii) facilitate some chemical bonding with phosphoric acid and boehmite to improve cohesive strength between the filler phase and gel phase, and iii) to provide another high temperature stable phase for thermal insulation. A good working ratio of the CB-CSG slurry has been found to be 9wt% A16 and 21wt% YSZ in 1.5M boehmite gel. Pre-oxidation of the bond coat was
attempted in order to achieve a stable alumina oxide layer (TGO) that may bond direct
with the CB-CSG layer. However, phosphoric acid used in the CB-CSG process reacted
with the TGO to form a brittle layer where delamination would occur.

CB-CSG process offers a unique control in the coating microstructure. In this work
with APS TBC, vertical texture in the CB-CSG layer had been achieved in the effort to
mimic the strain compliant microstructure seen in EB-PVD TBC. Columns in the
CB-CSG layer were built by combining factors of substrate surface roughness, flash
evaporation (~200°C), and slow rate of deposition 0.3mm/min-mm². The thickest
CB-CSG layer with columnar structure achieved is around 500μm. Phase analysis
showed phosphate phases of both aluminum phosphate and zirconium phosphate. This
confirms chemical bonding of the ceramic particles at the 500°C heat treatment
temperature.

Mechanical evaluation by pull-out test showed adhesion strength in the range of 0.3–3.7
MPa. The inconsistent data was most likely caused by measurement procedure, e.g.
misplacements of the pull-out studs over the rough columnar tops. The low strength
was contributed by thin “necks” at the roots of the columnar structures. Thermal cyclic
evaluation showed promising results despite of the relatively low adhesion strength. Samples with coating type 2 (bond coat + thin APS YSZ + CB-CSG + thick APS YSZ) showed minimum damage up to 1000 thermal cycles between 1050°C and room temperature. Even after 3000 cycles, there was still ~70% coating remaining on the substrate. Note that in aerospace applications, a single thermal cycle is equivalent to a takeoff and landing cycle. Samples with coating type 4 without a top APS YSZ for protection survived up to 150 cycles with ~70% coating remaining, provided that the APS YSZ layer between CB-CSG and bond coat is at least 200μm to minimize the CTE mismatch.

The same CB-CSG deposition technique was transferred to an industrial environment to coat hot gas turbine impingement plates. SEM analysis of coupons, attached to the plates during coating, show that the overall coating structures were achieved. However, thickness and columnar structure were missed due to time constraint and the lack of the proper heat source.

CB-CSG technology had been used to infiltrate the CCC body with calcined alumina particles. It was seen that a high degree of densification can be achieved. Three test
Abrasive wear and sliding wear tests were done to the LP samples before and after vacuum impregnation of CB-CSG, as well as the FD samples. Results showed an improved wear resistance of the C⁴ over both the FD and LP samples. Compared with the FD samples, C⁴ reduced volume loss by 8% in the abrasive wear and 16% in the sliding wear. Compared with the LP samples, C⁴ reduced volume loss by 45% in the abrasive wear and 29.5% in the sliding wear. The C⁴ samples are expected to be significantly less expensive to process than the classical CCC materials.

6.2 Recommendations for Future Work

The simplicity of equipment allowed the present research to quickly establish compatible processes between CB-CSG and APS TBC. However, because of the simplicity, the
resultant coating is very dependent on environmental variables and operators skills. Therefore, in the continuation of this research, a more controlled coating environment should be established. Parameters such as spraying rate, nozzle movement, and hot plate temperature should be programmable in order to eliminate human errors. A mechanical setup can also employ a dual spray gun design to deposit both CB-CSG and phosphoric acid at once to promote phosphate homogeneity. As well, substrate in disk or rod shape would be more ideal since they can minimize edge effect.

C⁴ showed a high degree of success in both the densification as well as the wear resistance aspects. Further research should focus on decreasing the resistance of particle penetration into the CCC body. For example, finer powder can be used so it may infiltrate into smaller pores. Viscosity may be controlled by dispersants such as citric acid. Pressurized (autoclave) chamber may be set up to force more complete infiltration. Oxidation resistance of C⁴ is another area of interest. With literatures suggesting oxidation inhibition by phosphates, the C⁴ should be compared to CCC samples. The result may prove further benefits of C⁴ over conventional CCC.
References


V. Tolpygo and D. Clarke, “The effect of oxidation pre-treatment on the cyclic life of


T. Troczynski and Q. Yang, “Process For Making Chemically Bonded Sol-Gel Ceramics”, University Of British Columbia, , U.S. Pat. 6,284,682 B1


X. Q. Cao, R. Vassen, and D. Stoever, “Ceramic materials for thermal barrier coatings”,

118


