Non-destructive Microstructural Evaluation Of Yttria Stabilized Zirconia, Nickel Aluminides And Thermal Barrier Coatings Using Electrochemical Impedance Spectroscopy

2004

Srinivas Vishweswaraiah
University of Central Florida

Find similar works at: https://stars.library.ucf.edu/etd

University of Central Florida Libraries http://library.ucf.edu

Part of the Engineering Commons

STARS Citation

https://stars.library.ucf.edu/etd/15

This Masters Thesis (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of STARS. For more information, please contact lee.dotson@ucf.edu.
NON-DESTRUCTIVE MICROSTRUCTURAL EVALUATION OF YTTRIA STABILIZED ZIRCONIA, NICKEL ALUMINIDES AND THERMAL BARRIER COATINGS USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

by

Mr. SRINIVAS VISHWESWARAIAH
B.E. Bangalore University, 2000

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Mechanical, Materials, and Aerospace Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Spring Term
2004

Major Professor: Dr. Yong-ho Sohn
Co-Advisor: Dr. Vimal Desai
© 2004 Srinivas Vishweswaraiah
ABSTRACT

There has been an urge for increasing the efficiency in advanced gas turbine engines. To fulfill these needs the inlet gas temperatures should be increased in the gas turbine engines, thermal barrier coatings (TBCs) have gained significant applications in increasing the gas inlet temperatures. Insulating characteristics of ceramic TBCs allow the operation at up to 150–250 °C higher gas temperatures. Because of the severe turbine engine operating conditions that include high temperature, steep temperature gradient, thermal cycling, oxidation and hot-corrosion, TBCs can fail by spallation at the interface between the metal and ceramic. The lack of understanding in failure mechanisms and their prediction warrant a development of non-destructive evaluation technique that can monitor the quality and degradation of TBCs. In addition, the development of NDE technique must be based on a robust correlation to the characteristics of TBC failure.

The objective of this study is to develop electrochemical impedance spectroscopy (EIS) as a Non-destructive evaluation (NDE) technology for application to TBCs. To have a better understanding of the multilayer TBCs using EIS they were divided into individual layers and EIS were performed on them. The individual layers included polycrystalline ZrO₂-7~8 wt.%Y₂O₃ (YSZ) (topcoat) of two different densities were subjected to sintering by varying the sintering temperature and holding time for three different thickness and hot extruded NiAl alloy buttons which were subjected to isothermal oxidation with varying temperature and time. NiAl is as similar to the available commercial bondcoats used in TBCs. Then degradation monitoring with electrolyte penetration was carried out on electron beam physical vapor deposited (EB-
PVD) TBCs as a function of isothermal exposure. Quality control for air plasma sprayed TBCs were carried out as a function of density, thickness and microstructure. Dense vertically cracked TBCs were tested as a function of vertical crack density and thickness.

Electrochemical impedance response was acquired from all specimens at room temperature and analyzed with an AC equivalent circuit based on the impedance response as well as multi-layered structure and micro-constituents of specimens. Physical and microstructural features of these specimens were also examined by optical and electron microscopy. The EIS measurement was carried out in a three-electrode system using a standard Flat Cell (K0235) from Princeton Applied Research™ and IM6e BAS ZAHNER™ frequency response analyzer. The electrolyte employed in this investigation was 0.01M (molar) potassium Ferri/Ferro Cyanide \(\{(K_3Fe(CN)_6/K_4Fe(CN)_6\cdot3H_2O)\}\).

The thickness and density were directly related to the resistance and capacitance of the polycrystalline YSZ with varying thickness and open pores. As the effective thickness of the YSZ increased with sintering time and temperature, the resistance of the YSZ \(R_{YSZ}\) increased proportionally. The variation in capacitance of YSZ \(C_{YSZ}\) with respect to the change in porosity/density and thickness was clearly detected by EIS. The samples with high porosity (less dense) exhibited large capacitance, \(C_{YSZ}\), compared to those with less porosity (high density), given similar thickness. Cracking in the YSZ monoliths resulted in decrease of resistance and increase in capacitance and this was related to the electrolyte penetration.

Growth and spallation of TGO scale on NiAl alloys during isothermal oxidation at various temperatures and holding time was also correlated with resistance and capacitance of the TGO scale. With an increase in the TGO thickness, the resistance of
the TGO (\(R_{\text{TGO}}\)) increased and capacitance of the TGO (\(C_{\text{TGO}}\)) decreased. This trend in the resistance and capacitance of the TGO changed after prolonged heat treatment. This is because of the spallation of the TGO scale from the metal surface. The parabolic growth of TGO during high temperature oxidation was inversely proportional to the capacitance of TGO, excluding the abrupt changes associated with the failure.

As a function of isothermal exposure for EB-PVD TBCs, initial increase in the resistance of YSZ with thermal exposure was observed perhaps due to the high temperature sintering of YSZ. The parabolic growth of TGO during high temperature oxidation was inversely proportional to the capacitance of TGO. An explanation based on electrolyte penetration into sub-critical damage is proposed for the gradual decrease in the resistances of YSZ and TGO with prolonged thermal exposure. Observation of exposed metallic bond coat surface on the fracture surface, which readily provides conduction, was related to the abrupt and large increase in the capacitance of YSZ and TGO.

A direct relation between the resistance of the YSZ (\(R_{\text{YSZ}}\)) and density of the YSZ was observed for APS TBCs with varying topcoat density. APS TBCs with varying topcoat chemistry and thickness were tested and directly related to resistance of topcoat. With the increase in the topcoat thickness, the capacitance decreased and the resistance increased. The higher values of \(C_{\text{CAT}}\) and \(R_{\text{CAT}}\) compared to that of \(C_{\text{YSZ}}\) and \(R_{\text{YSZ}}\) were related to the higher dielectric constant and resistivity of CaTiO\(_3\).

Dense vertically cracked TBCs were tested with varying crack density were tested and the variation in the resistance was related indirectly to the cracks and directly to the difference in the thickness of the topcoat.
EB-PVD TBCs with varying density (dense and columnar) were tested and the variation in resistance was attributed to the dense structure and columnar structure of the topcoat with columnar structure having lower resistance because of more electrolyte penetration through the columnar structure.

From this study, EIS showed a potential as a NDE technique for quality assurance and lifetime remain assessment of TBCs. Future work should continue on developing a mathematical model to study the impedance curves and come up with a model for individual layers of TBC and then sum them up to get the multilayered TBC response. The flexible instrument probe of EIS needs to be designed and tested for field evaluation of TBCs.
ACKNOWLEDGEMENTS

I am indebted to my advisor, Dr. Yong-ho Sohn for his support, guidance, thoughtful discussions and patience. I sincerely thank my associate advisor Dr. Vimal Desai for his continuous support, suggestions, encouragement and help.

I would like to thank the following people who supported this research with specimens and technical support.

I would like to give a special thanks to US-Department of Energy for funding this project.

I would also like to thank my colleagues Balaji Jayaraj, Barbara Franke, Sankar Laxman, Abby Lee Elliot, Jing Liu and Emmanuel Perez. Also I would like to thank Ms. Karen Glidewell and Ms. Kari Stiles, because of their patience in working with me for all the LOP’s (LPO). Finally, sincere thanks go to my parents for their support, patience, and understanding.
# TABLE OF CONTENTS

LIST OF TABLES .............................................................................................................. x
LIST OF FIGURES .......................................................................................................... xii

1 INTRODUCTION ...................................................................................................... 1
  1.1 Objective of present study ................................................................................... 6

2 LITERATURE REVIEW ........................................................................................... 8
  2.1 Thermal Barrier Coatings (TBCs) ....................................................................... 8
    2.1.1 Microstructure of Zirconia ........................................................................... 10
    2.1.2 Effect of Stabilizers ...................................................................................... 14
    2.1.3 Sintering ....................................................................................................... 16
  2.2 Processing of TBCs ............................................................................................ 17
    2.2.1 Air Plasma Sprayed Thermal Barrier Coatings ............................................... 17
    2.2.2 Properties of Plasma Sprayed Zirconia Layer ............................................... 19
    2.2.3 Electron Beam Physical vapor Deposited (EB-PVD) Thermal Barrier Coatings ................................................................................................................ 21
    2.2.4 Properties of EB-PVD Zirconia Layer ........................................................ 23
    2.2.5 Dense Vertically Cracked TBCs .................................................................. 24
    2.2.6 Metallic Bond Coat – Properties and Processing Techniques ....................... 25
  2.3 Failure of TBCs and its Mechanisms ................................................................... 27
    2.3.1 Air Plasma Sprayed TBCs ........................................................................... 28
    2.3.2 Electron-Beam Physical Vapor Deposited TBCs ........................................... 30
    2.3.3 Final Failure Modes ..................................................................................... 32
  2.4 Non-Destructive Evaluation Techniques ............................................................... 34
    2.4.1 Thermal Wave Imaging .................................................................................. 35
    2.4.2 Scanning Acoustic Microscopy (SAM) ....................................................... 36
    2.4.3 Photo Stimulated Luminescence Spectroscopy (PSLS) .............................. 38
    2.4.4 Electrochemical Impedance Spectroscopy .................................................. 39
  2.5 Electrochemical Impedance Spectroscopy ........................................................ 41
    2.5.1 Theory .......................................................................................................... 41
    2.5.2 Electrical Circuitry ........................................................................................ 43
    2.5.3 Data Representation ..................................................................................... 46
    2.5.4 Analysis of EIS Data .................................................................................... 47
    2.5.5 Constant Phase Element ............................................................................. 57

3 EXPERIMENTAL DETAILS .................................................................................. 59
  3.1 Sintering of YSZ .................................................................................................. 59
  3.2 Isothermal Exposure of NiAl ............................................................................... 60
  3.3 Isothermal Oxidation of EB-PVD TBCs ........................................................... 61
3.4 Air Plasma Sprayed TBCs ................................................................. 62
3.5 Dense Vertically Cracked TBCs .................................................... 63
3.6 EB-PVD TBCs with varying density ............................................... 63
3.7 Electrochemical Impedance Spectroscopy ...................................... 64
3.8 EIS Models for EB-PVD TBCs ....................................................... 66
3.9 EIS Models for YSZ ................................................................. 67
3.10 EIS Models for Nickel Aluminide .............................................. 68
3.11 EIS Model for as-coated APS (YSZ and CAT) and DVC TBCs ....... 69

4 RESULTS ............................................................................................ 71
4.1 Sintering of Yttria Stabilized Zirconia .......................................... 71
4.2 Isothermal Exposure of Nickel Aluminide ..................................... 86
4.3 Isothermal Exposure of EB-PVD TBCs ......................................... 91
4.4 Air Plasma Sprayed TBCs with varying density ............................ 95
4.5 Air Plasma Sprayed TBCs with thickness and chemistry ............... 97
4.6 Dense Vertically Cracked TBCs with varying crack density .......... 100
4.7 EB-PVD TBCs with varying density .............................................. 104

5 DISCUSSION ....................................................................................... 107
5.1 Sintering of Yttria Stabilized Zirconia, Isothermal Exposure of NiAl and Isothermal Exposure of EB-PVD TBCs ................................. 107
5.1.1 Sintering of Yttria Stabilized Zirconia ....................................... 107
5.1.2 Isothermal Oxidation of NiAl .................................................... 109
5.1.3 Isothermal Oxidation of EB-PVD TBCs .................................. 111
5.2 Air Plasma Sprayed TBCs with varying density ............................ 115
5.3 Air Plasma Sprayed TBCs with varying thickness and chemistry .... 116
5.4 Dense Vertically Cracked TBCs with varying crack density .......... 117
5.5 EB-PVD TBCs with varying density .............................................. 118

6 SUMMARY .......................................................................................... 119

LIST OF REFERENCES ........................................................................... 121
LIST OF TABLES

Table 1 Electrical elements and their impedance response. .................................................. 44
Table 2 Variables for the sintering experiment................................................................... 59
Table 3 The variables used in the isothermal oxidation of NiAl buttons of 2mm thickness. ........................................................................................................................................... 60
Table 4 Specimen description of TBCs investigated using EIS as a function of isothermal exposure ........................................................................................................................................... 61
Table 5 Specimen description of APS TBCs investigated using EIS as a density, thickness, and chemistry ........................................................................................................................................... 62
Table 6 Specimen description of DVC TBCs investigated using EIS as a function of crack density and crack orientation ........................................................................................................................................... 63
Table 7 Specimen description of EB-PVD TBCs investigated using EIS as a function of density ........................................................................................................................................... 64
Table 8 Description of abbreviations used in the ac electrical circuit for the models............. 67
Table 9 EIS results for YSZ; Density 3.85g/cm$^3$; Thickness 2mm, Room Cooled............ 73
Table 10 EIS results for YSZ; Density 3.85g/cm$^3$; Thickness 3mm, Room Cooled............ 74
Table 11 EIS results for YSZ; Density 3.85g/cm$^3$; Thickness 4mm, Room Cooled............ 75
Table 12 EIS results for YSZ; Density 4.07g/cm$^3$; Thickness 2mm, Room Cooled............ 76
Table 13 EIS results for YSZ; Density 4.07g/cm$^3$; Thickness 3mm, Room Cooled............ 77
Table 14 EIS results for YSZ; Density 4.07g/cm$^3$; Thickness 4mm, Room Cooled............ 78
Table 15 EIS results for YSZ; Density 4.07g/cm$^3$; Thickness 4mm, Temperature 1300ºC; Furnace Cooled ........................................................................................................................................... 78
Table 16 EIS results for NiAl isothermally exposed to various temperatures and holding times ........................................................................................................................................... 88
Table 17 TGO Thickness Measurement for varying temperatures and holding time........... 90
Table 18 EIS Results for Isothermally exposed EB-PVD TBCs ........................................... 93
Table 19 Measured thickness of the thermally grown oxide in EB-PVD TBCs isothermally oxidized at 1121ºC ........................................................................................................................................... 94
Table 20 EIS results for APS TBCs with varying densities .................................................... 96
Table 21 EIS Results for APS TBCs with varying thickness and chemistry......................... 98
Table 22 Thickness of the topcoat for APS YSZ and APS CAT TBCs. ............................. 98
Table 23 EIS results for DVC YSZ TBCs with varying crack density. ............................... 102
Table 24 EIS results for EB-PVD TBCs with varying density.......................................... 105
LIST OF FIGURES

Figure 1 A Schematic of a TBC superimposed with a temperature gradient across. ........ 2
Figure 2. Scanning electron micrographs of the TBCs (a) Air Plasma Sprayed TBC with
YSZ topcoat, (b) Air Plasma Sprayed TBC with CaTiO$_3$ topcoat and (c) Electron Beam
Physical Vapor Deposited TBC with YSZ topcoat............................................................. 3
Figure 3 Phase diagram of the ZrO$_2$-YO$_{1.5}$ system indicating the regions of the
metastable tetragonal t and tetragonal t’ zirconia polymorphs. [41] ............................... 12
Figure 4 Crystal structure of the (a) tetragonal (b) monoclinic and (c) cubic ZrO$_2$ ................................. 14
Figure 5. Effect of yttria content on the thermal cycle life of Y$_2$O$_3$-ZrO$_2$ thermal barrier
coatings as determined by Stecura. [51] ............................................................................. 15
Figure 6. (a) Schematic of the plasma spray gun (b) Arrangement for the APS coating
system. [57] .......................................................................................................................... 18
Figure 7. A schematic illustration of APS TBC structure. .............................................. 20
Figure 8. Back Scatter electron micrograph of as-coated APS TBC. ......................... 20
Figure 9. Effect of density of the ZrO$_2$ layer on the thermal cycle life of ZrO$_2$-Y$_2$O$_3$
Thermal Barrier Coatings. [51] ........................................................................................... 21
Figure 10. A schematic illustration of the EB-PVD process. [58] ........................................ 22
Figure 11. Backscatter electron micrograph of the as-coated EB-PVD TBC............. 23
Figure 12. Schematic showing different failure mechanisms in APS TBCs ............... 29
Figure 13. Schematic diagram showing the two types of failure in EB-PVD TBCs. [1] ... 31
Figure 14. Schematic illustrating failure by buckling in TBCs. ............................... 33
Figure 15. Schematic of failure by edge delamination in TBCs......................... 34
Figure 16. Schematic diagram of SAM principles. [79] ................................................. 37
Figure 17. Schematic illustration of basic photostimulated luminescence. [80] .............. 38
Figure 18. Convention EIS cell for laboratory measurements. [76] ................................. 40
Figure 19. Relationship between current and voltage in impedance measurements. ...... 42
Figure 20. Electrical Circuit (Randles Circuit) for A metal. [76] ................................. 44
Figure 21. (a) A serial combination of resistor and a capacitor. (b) Nyquist plot for the
electrical circuit shown. ...................................................................................................... 49
Figure 40. Variation in (a) Resistance and (b) Capacitance of YSZ: Density 4.07g/cm$^3$; Thickness 3mm. ................................................................................................................ 83
Figure 41. Variation in (a) Resistance and (b) Capacitance of YSZ: Density 4.07g/cm$^3$; Thickness 4mm; Quenched at atmosphere. ........................................................................ 84
Figure 42. Variation in (a) Resistance and (b) Capacitance of YSZ: Density 4.07g/cm$^3$; Thickness 4mm. (Air quenched and Furnace Cooled)...................................................... 85
Figure 43. SEM Micrographs showing the densification (sintering) of YSZ at various temperatures and sintering time ................................................................. 86
Figure 44. Typical (a) Nyquist plot and (b) Impedance plot for NiAl sample isothermally exposed at 1200ºC for 5 hours. ................................................................. 87
Figure 45. Variation in (a) Resistance and (b) Capacitance of TGO with isothermal exposure. ........................................................................................................ 88
Figure 46. Top surface secondary (SE) and backscatter (BSE) scanning electron micrographs for NiAl exposed at 1100ºC. ................................................................. 89
Figure 47. Top surface secondary (SE) and backscatter (BSE) scanning electron micrographs for NiAl exposed at 1200ºC ................................................................. 89
Figure 48. Top surface secondary (SE) and backscatter (BSE) scanning electron micrographs for NiAl exposed at 1300ºC. Clear indication of metal surface exposed. ... 90
Figure 49. Scanning backscatter electron micrographs of NiAl subjected to isothermal exposure showing the growth of TGO ......................................................... 91
Figure 50. Macrographs showing the top surface of isothermally exposed EB-PVD TBCs with spallation of the top surface at 600 Hours. .............................................. 92
Figure 51. Typical (a) Nyquist plot and (b) Bode plot for EB-PVD TBCs isothermally exposed at 1121ºC for 250 Hours ................................................................. 93
Figure 52. Variation in (a) Resistance of YSZ (b) Capacitance of YSZ (c) Resistance of TGO and (d) Capacitance of TGO as a function of Isothermal Hours at 1121ºC for EB-PVD TBCs ................................................................. 94
Figure 53. Cross sectional scanning electron micrographs showing the TGO thickness as a function of isothermal exposure at 1121ºC for EB-PVD TBCs ......................... 95
Figure 54. Variation of (a) topcoat capacitance and (b) topcoat resistance as a function of topcoat density. ..................................................................................... 96
Figure 55. Scanning electron micrographs showing the variation in the density of topcoat of the APS TBCs......................................................................................................................... 96
Figure 56. (a) Impedance and (b) Nyquist plots for APS TBCs with varying density..... 97
Figure 57. Variation in (a) Topcoat capacitance and (b) topcoat resistance of APS and TBCs as a function of thickness and chemistry................................................................. 98
Figure 58. (a) Impedance and (b) Nyquist plot for APS YSZ and APS CAT TBCs....... 99
Figure 59. Scanning electron micrograph of cross-sections of (a) YSZ552, (b) YSZ325, (c) CAT667 and CAT339. ......................................................................................................... 100
Figure 60. Nyquist plots of DVC YSZ TBCs as a function of vertical crack density.... 101
Figure 61. Impedance plots of DVC YSZ as a function of vertical crack density. ....... 102
Figure 62. Cross sectional back scatter electron micrographs of (a) 1 Crack per unit length, (b) 20 Cracks per unit length and (c) 70 cracks per unit length................................. 103
Figure 63. Variation in (a) capacitance and (b) resistance of YSZ as a function of density. ......................................................................................................................................... 104
Figure 64. (a) Impedance and (b) Nyquist plot of EB-PVD TBCs with varying density. ......................................................................................................................................... 105
Figure 65. Variation in (a) YSZ resistance and (b) YSZ capacitance as a function of topcoat density. ......................................................................................................................... 106
Figure 66. Changes in TGO capacitance as a function of oxidation time at (a) 1100ºC and (b) 1200ºC before spallation. ........................................................................................................ 110
Figure 67. Impedance plots for EB-PVD TBCs with varying isothermal exposure time. ......................................................................................................................................... 112
Figure 68. Changes in TGO capacitance as a function of time during isothermal oxidation of EB-PVD TBCs. ........................................................................................................ 114
1 INTRODUCTION

During the past decade, research efforts have been made to develop ceramic thermal barrier coatings (TBCs) for turbine parts because the traditional turbine materials have reached the limits of their temperature capabilities.

In today’s engine, the hot gas temperature exceeds the melting point of Ni-base superalloys by more than 250°C. The only way turbine parts for hot section can survive in such an environment is by excessive internal and external cooling, which, however reduces the overall thermal efficiency of the engine. In addition, the working parts of the turbine engines are subjected to severe mechanical and chemical stresses other failures. The concern is mainly to increase the efficiency of the engines by increasing fuel economy, increasing the operating temperatures and increasing the lifetime of superalloy. This is achieved by depositing TBCs on transition pieces, combustion lines, blades and vanes of the turbine engines. With TBCs it is possible to lower the metal temperature by 100-300°C depending on the coating thickness and thermal properties.

A TBC system usually consists of four layers: (1) a metal substrate (superalloy which is commonly Ni-based) providing structural strength; (2) a bond coat providing oxidation resistance (MCrAlY/(Ni, Pt) Al); (3) a ceramic topcoat (ZrO$_2$-7~8 wt% Y$_2$O$_3$; YSZ or CaTiO$_3$ (CAT)); and (4) a thermally grown oxide (TGO) formed between the ceramic topcoat and the bond coat due to high temperature oxidation of the bond coat as shown in Figure 1. YSZ coatings are deposited commonly by two methods either Air Plasma Spray (APS) or Electron Beam Physical Vapor Deposition (EB-PVD) whereas
bond coats are deposited by Low Pressure Plasma Spray (LPPS) and/or Vacuum Plasma Spray (VPS) for MCrAlY bond coat and a combination of electro-plating and chemical vapor deposition (CVD) for (Ni, Pt) Al bond coat. Typical microstructures of the different types of TBCs are shown in Figure 2.

In plasma sprayed thermal barrier coatings oxidation resistant MCrAlY bond coat is ~125µm thick, thin thermally grown oxide scale, primarily $\alpha$-$\text{Al}_2\text{O}_3$ is around 1-10 µm thick, and topcoat is around 200-500 µm for gas turbine engines and about 2mm for diesel engines.

![Figure 1 A Schematic of a TBC superimposed with a temperature gradient across.](image)

The selection of the TBC materials is restricted by some basic requirements: (1) high melting point, (2) phase stability between room temperature and operation temperature, (3) low thermal conductivity, (4) chemical inertness, (5) thermal expansion match with the metallic substrate, (6) good adherence to the metallic substrate and (7) low sintering rate of the porous microstructure. Hence, there are very few materials,
which can be used in the application. Zirconia in its stabilized form can satisfy most of the requirements stated above as a material for topcoat. Stabilized zirconia has the outstanding properties in terms of having low thermal conductivity. Also partially stabilized zirconia has excellent thermal shock resistance because of microcracking and transformation toughening. Considering the advantage zirconia has in terms of transformation, toughening and thermal shock the choice of the material is zirconia partially stabilized with yttria.

Figure 2. Scanning electron micrographs of the TBCs (a) Air Plasma Sprayed TBC with YSZ topcoat, (b) Air Plasma Sprayed TBC with CaTiO$_3$ topcoat and (c) Electron Beam Physical Vapor Deposited TBC with YSZ topcoat.
The main issue related to the TBCs is the lifetime. TBCs are prone to failure during the prolonged exposure to high temperatures and corrosive environment. Despite considerable efforts, the highly desirable prediction of their lifetime is a demanding task. It is very important to understand and improve the TBC lifetime in order to prevent catastrophic failure of the TBCs. Generally at high temperatures zirconia TBCs are permeable to oxygen. Therefore to protect the superalloy substrate from oxidation, an oxidation resistant bond coat is applied in between the topcoat and the substrate. This bond coat is 75 - 300 µm in thickness, and essentially dictates the failure of TBCs. At peak operating conditions the temperature at the bond coat surface exceeds 700°C, which results in bond coat oxidation and the formation of the TGO (1-10 µm). Although the formation of TGO is inevitable, an ideal bond coat is engineered to ensure that TGO forms as α- Al₂O₃ and its growth is slow, uniform and defect free. The growth of TGO during engine operation is the most important phenomena responsible for the spallation failure of TBCs.

Numerous literatures have reported the failure mechanisms of the TBCs. An extensive review of the failure mechanisms is given by Evans and Hutchinson. A detailed overview of the failure mechanism is presented in the next section. A short summary of the possible failure mechanism is as follows:

- Sintering increases the thermal conductivity and modulus of elasticity resulting in high metal surface temperature and enhancement of bond coat oxidation and creep. This results in stress-induced spallation at the interface between topcoat and TGO. Such cases are reported in APS processed TBCs.
- Thermal expansions mismatch stress between the TBC/TGO/bond coat layers.
• Growth of the TGO at the interface of the bond coat and TBC because of the bond coat oxidation, which results in stresses at the interface of the TGO/bond coat. [19, 20, 21]

• Cyclic creep of the bond coat. [19]

• Depletion of aluminum from the bond coat leading to the formation of the brittle oxides other than $\alpha$-$\text{Al}_2\text{O}_3$, such as spinels (NiAl$_2$O$_4$).

• Degradation of the metal ceramic interface toughness.

• Delamination and cracking. [22]

• Crack coalescence. [23]

Since there are various ways in which a TBC can fail it is essential to develop a non-destructive evaluation technique for assessing the lifetime and hence improve the quality. There are numerous NDE techniques: photoluminescence for determination of TGO residual stresses and phase compositions [24,25,26], infrared thermography [27] for determination of the delamination at the TGO/bond coat interface and acoustic emission [28,29] for crack identification. Impedance spectroscopy has been widely used as a NDE technique for the assessment of the TBCs particularly for the ceramic topcoat and the TGO. [30,31,32] Electrochemical impedance spectroscopy (EIS) is one of the techniques, which is being developed as a NDE tool for the evaluation of the TBCs. [33,34,35] EIS has been used before for corrosion testing and in applications involving use of paints and coatings. EIS has been proven very effective as a NDE because of the following advantages.

• EIS is known to have a well-established theoretical and practical background. [36]
• EIS is found to be suitable for various types of TBCs regardless of the chemistry (YSZ and CAT), deposition technique (APS/EBPVD), thickness of the topcoat as long as the ceramic topcoat is porous.\textsuperscript{[37]}

• EIS data is accurate and repeatable, in addition to rapid acquisition.

• Probe area is flexible.

• Sub-critical damages can be detected based on electrolyte penetration and related to the failure mechanisms.

1.1 Objective of present study

EIS is essentially an electrochemical technique, which involves electrolyte penetration through the different layers of the TBC, and hence electrical conduction is a very important factor. Electrolyte can penetrate through the porous topcoat or the damage within the topcoat, TGO or the bond coat. The principle objective of this thesis is to further develop EIS as a NDE technique for TBCs. This is done by examining the variation of the electrochemical impedance spectra as a function of critical variables related to TBC microstructure and failure by testing the individual layers of TBCs using EIS and to support the previous findings. The performed works in this thesis are as follows:

• Sintering of the open pores monolith YSZ of two different densities were examined by EIS as a function of sintering time, temperature and thickness.

• Isothermal exposure of NiAl i.e. growth and spallation of the TGO, was examined by EIS as a function of isothermal oxidation time and temperature.
• Degradation of the EB-PVD TBCs was examined with isothermal oxidative heat treatment at 1121°C for EB-PVD TBCs with (Ni, Pt) Al bond coat.

• Effect of variation in the density of the APS and EBPVD TBCs on EIS.

• Effect of variation in the thickness and topcoat chemistry of TBCs (APS YSZ and APS CaTiO$_3$ (CAT)) on EIS.

• Effect of variation in the crack density and thickness of the dense vertically cracked (DVC) TBCs on EIS.
2 LITERATURE REVIEW

2.1 Thermal Barrier Coatings (TBCs)

TBC is a multilayer system consisting of a ZrO$_2$ ceramic coating, generally stabilized with 7~8 wt.%Y$_2$O$_3$, on a MCrAlY or a (Ni, Pt) Al bond coat and a superalloy substrate. A schematic of the TBC with the temperature gradient across it is shown in Figure 1. The temperature gradient is essentially influenced by the thermal conductivity of the ceramic coating, thickness and the cooling air flow rate.\textsuperscript{[1,5,28]} Every layer in the TBC contributes towards the durability of the TBCs. TBCs often need to retain their integrity when subject to thermal cycling through large temperature ranges, despite significant thermal expansion misfit with the substrate.

Though TBCs are advantageous, failure in TBCs are inevitable. Failure mechanisms in TBCs have been described in the earlier section. Failure in TBCs occurs either between the TGO/Bond coat interfaces, TGO/TBC interface or within the TBC.

The following are the ways of improving the durability:

- Knowledge of the type of environment where the TBC is applied is very important because based on that fact TBCs have to be designed for durability.
- Thorough understanding of failure mechanisms is important in order to improve the durability of the TBC.
- Type of technique used to coat the ceramic layer plays an important role in durability of the TBCs. TBCs processed by EB-PVD have columnar structure which reduces
stress buildup within the body of coating. Strain within the coating is accommodated by free expansion of the columns into the gaps (inter-columnar porosity) which results in negligible stress buildup.\textsuperscript{[38]} TBCs processed by APS have low thermal conductivity but they have low erosion resistance whereas EBPVD TBCs have high erosion resistance but they have higher thermal conductivity than the APS TBCs, so selection of the type of topcoat should be based on the application.\textsuperscript{[38]}

- Oxygen is permeable through ceramic topcoat at high temperatures so in order to prevent the oxidation of the superalloy substrate intermediate layer in the form of bond coat is necessary. So durability of TBC depends on the selection of the bond coat. It is necessary to choose a bond coat which can form a stable oxide layer at a slower rate.\textsuperscript{[39]}

- Strengthened bondcoats with greater creep resistance leads to improved thermal cycle life.\textsuperscript{[40]}

Through experimentation, partially stabilized ZrO\textsubscript{2} with 6-8 wt.% Y\textsubscript{2}O\textsubscript{3} stabilizing oxides has been generally accepted as the optimum composition.\textsuperscript{[41]} The Y\textsubscript{2}O\textsubscript{3} partially stabilized ZrO\textsubscript{2} (PSZ) is usually applied to metallic substrate (bond coat), either by air plasma spray or electron beam physical vapor deposition technique. Plasma sprayed partially stabilized zirconia coatings have a rough surface and a lamellar structure with relatively large porosities between the splat-quenched grains. The presence of the porosities increases the thermal shock resistance of the coatings.\textsuperscript{[1,28,42]} Also the interface between the topcoat and the bond coat is rough which is responsible for the enhanced mechanical and structural integrity of the coating. Physical vapor deposited (PVD) PSZ exhibits strain tolerant and textured columnar grain structures with uniform and smooth
coating surface and a smooth interface between the topcoat and the bond coat. PVD coatings are proven to have very good strain tolerance and hence have demonstrated superior durability at high temperature cyclic oxidation and flight service environment. [28,43]

Another important layer of the TBC is the bond coat. For the performance and durability of the TBC bond coat plays an extremely important role. For proper functioning of the TBC system, it is important that the properties of the topcoat and bond coat be similar. One of them is the high thermal expansion coefficient of the bond coat. Additional properties desired include resistance of the bond coat to hot-corrosive environment, oxidative environment and creep. Bond coat can be of two types: MCrAlY or (Ni, Pt) Al, where M is Ni/Co or (NiCo). [11,44,45]

2.1.1 Microstructure of Zirconia

Insulating ceramics have been widely studied and preferred material for the topcoat material in a TBC system. Property of ceramic that are most important for application is the thermal expansion coefficient and thermal conductivity.

Zirconia based ceramics is the most widely studied and used TBC material because it provides the best performance in high-temperature applications such as diesel engines and gas turbines. [41] These ceramics have found be superior in terms of mechanical, chemical and physical properties when they form solid solutions with CaO, MgO, Y₂O₃, Sc₂O₃ and other rare earth oxides. [46] After various experimentation, choice of material has been ZrO₂ partially stabilized with Y₂O₃ (7~8 wt.%) (7-8 YSZ) for many
high temperature applications. The advantages of 7-8 YSZ are: high thermal expansion coefficient; low thermal conductivity and high thermal shock resistance. The issue has been that it has one drawback in that it can transform into one of the three different crystal structures based on the temperature. Figure 3 represents the phase diagram\(^{41}\) of the ZrO\(_2\)-Y\(_2\)O\(_3\), where we see that ZrO\(_2\) transforms from monoclinic to tetragonal phase at 1170°C and from tetragonal to cubic at about 2680°C. There occurs about 4% volume contraction during the monoclinic to tetragonal phase transformation, which causes pure zirconia to lose its structural integrity, and hence they crack and crumble when thermally cycled. Stabilizing the high temperature tetragonal phase zirconia down to ambient temperature for many high temperature applications is hence very essential.

There are various types of stabilization mechanisms. Many factors govern the stabilization mechanism such as the annealing temperature, holding time, quenching rates and grain size. There are few rules that assist in the stabilizing of the oxides, which are: the radius of the cation should be close to that of Zr\(^{4+}\) for minimum lattice distortion; the oxidation state of the oxide cation should be 2+ or 3+ and the crystal structure of the stabilizing oxide itself should be cubic or tetragonal.\(^{1}\) As mentioned earlier there are many oxides which can be used for stabilizing zirconia but the choice of the material is yttria in many high temperature applications because Y\(_2\)O\(_3\) is the most effective stabilizer. Sasaki et.al.,\(^{47}\) has seen that stabilizing efficiency of Y\(^{3+}\) is greater than Sc\(^{3+}\) and La\(^{3+}\).
Phase transformation of zirconia depends on the amount of the stabilizing oxide added. Different composition of $\mathrm{Y_2O_3}$ gives rise to different phases. A mixture of 2-3% of $\mathrm{Y_2O_3}$ with $\mathrm{ZrO_2}$ when sintered at 1400-1600°C and cooled at appropriate rates does not yield a mixture of equilibrium monoclinic and a cubic phase as predicted. Rather a metastable tetragonal (t) phase will be retained. This in turn may contain cubic phases, which depends on the preparation conditions. This phase is also known as Tetragonal Zirconia Polycrystalline (TZP) phase. For proper distinction from other phases it is also termed as Yttria-Tetragonal Zirconia Polycrystalline (Y-TZP) phase. While a mixture of 4-5 mol.\% $\mathrm{Y_2O_3}$ with $\mathrm{ZrO_2}$ when heated around 2200-2400°C or above the cubic phase temperature region and quenched rapidly, a metastable tetragonal (t') phase is formed.
The formation of t'-phase is very significant and is sometimes described as Y-PSZ or PSZ, to differentiate from fully stabilized zirconia (Y-FSZ or FSZ). The t and t’ are the low and high yttria phases respectively. The t-phase is considered as strongest ceramics because of its high strength and fracture toughness greater than 15 MPa√m. The fracture toughness of the TZP is a result of transformation toughening mechanism where there occurs a transformation from monoclinic phase under high stress (e.g. crack tip). When energy is dissipated at the crack tip and results in volume expansion further crack propagation will be arrested whereas the t'-phase does not transform under the mechanical stress and hence is called a non-transformable tetragonal phase.

After lot of experimentation the ceramists have come up with the following (1) the transformation of the cubic to the tetragonal t-phase is diffusion controlled; (2) the rapidly quenched tetragonal t'-phase is formed by a diffusionless transformation and (3) the tetragonal-to-monoclinic transformation toughening process is martensitic with the grain size and Y₂O₃ content being primary factors determining the martensitic start (Mₛ) temperature of the martensitic transformation. [49] Figure 4 shows the crystallographic structure of the three phases (cubic, monoclinic and tetragonal) of zirconia.

Concluding the most common and widely adopted TBC is the ZrO₂:7-8 wt.% Y₂O₃ (4-5 mol.% Y₂O₃) that can be either applied by APS or the EBPVD technique. These are the preferred techniques and they provide high cooling rates necessary to form the t'-phase. Even though the t'-phase does not undergo martensitic tetragonal to monoclinic phase transformation it is regarded to have excellent strength and toughness. [41]
2.1.2 Effect of Stabilizers

Different materials have been proposed for stabilizing Zirconia for the design of the TBC. Calcia (CaO) and Magnesia (MgO) –stabilized zirconia (ZrO$_2$) are no longer used as stabilizing agents for TBCs due to the phase instability, thermal cracking, lack of corrosion resistance and high temperature volatility (in case of MgO). Yttria (Y$_2$O$_3$) is shown to be the best stabilizer for zirconia TBCs till now. The thermal cycle life of yttria-stabilized zirconia TBCs for gas turbines is highly dependent upon the yttria concentration. Yttria (Y$_2$O$_3$) is the most widely studied and used stabilizer as it provides the best performance of TBC in high-temperature applications. The issue here is the high
dependence of yttria concentration on the thermal cycle life of TBC. [51] Figure 5 shows the variation of the thermal cycle life of the TBC with varying yttria concentration. From the figure it is a clear indication that 6-8 wt% yttria is the best choice as a stabilizer as it helps formation of t'-phase which is very stable at high temperatures. [51]

Figure 5. Effect of yttria content on the thermal cycle life of \( \text{Y}_2\text{O}_3\)-\( \text{ZrO}_2 \) thermal barrier coatings as determined by Stecura. [51]

Some of the other stabilizing oxides like ytterbium, scandia and india are also being tested. [52] Scandia and India have also shown better hot corrosion resistance but its thermo-mechanical properties and phase stability is not yet determined. [53,54] Since most
of the properties of these materials are still in testing process as of now 6-8YSZ is the best choice as a topcoat material for the TBC.

2.1.3 Sintering

Sintering is a thermal treatment for bonding particles into a coherent, predominantly solid structure by mass transport events that often occur on an atomic scale. This bonding leads to improved strength and lower system energy.

Zirconium oxide is useful in the toughened form because there is improved hardness, strength, fracture toughness, wear resistance and chemical inertness. Various stabilizers are added to control the microstructure and transformation toughening behavior, a typical additive is yttria. Since the melting temperature is very high and diffusion rates are low, small particle sizes are employed to promote rapid sintering densification. When properly synthesized and deagglomerated, zirconia powder can be sintered to near full density at temperatures of 1100°C in 1 hour. Because densification requires an active bulk diffusion process, it is necessary to heat zirconia powders rapidly to avoid low-temperature coarsening without densification. Fast firing and microwave heating techniques are employed to overcome this problem.\textsuperscript{[55]}

Many variants of these sintering cycles exist, and this variety provides a broad spectrum of dimensional changes, microstructures and properties. Since several factors are involved in achieving proper sintering, trial and error approach is often used in developing industrial cycles. In spite of all this sintering is incapable of curing defects introduced in the powder compacts prior to sintering.
2.2 Processing of TBCs

2.2.1 Air Plasma Sprayed Thermal Barrier Coatings

Initially bond coat is applied by low-pressure plasma spray (LPPS) technique and the topcoat is applied by the air plasma spray technique (APS). This technique is widely used in the industry. It is advantageous in that it is inexpensive, quick, and easy and is applicable to coatings of varying compositions and materials.\[56\]

Figures 6a-6b\[57\] shows schematic representation of the air plasma spray technique. Figure 6a shows the plasma spray gun while Figure 6b shows the entire arrangement. The plasma gun consists of tungsten cathode and tungsten anode surrounded by a cooling jacket (water cooled) and air passages for the carrier gas. Plasma is generated by striking a DC potential between the cathode and anode in the carrier gas (mixture of argon and hydrogen or hydrogen and nitrogen). The temperature of the plasma fume at the nozzle tip is around 6000-12000ºC and travels with a velocity in the order of 200-600 m/s. The standoff distance is around 10-50 cm to form the desired coating.
The plasma spraying technique may seem simpler but there are many complex factors to be considered and extensive work is being done to improve its reliability. Many factors must be controlled for optimization of the process, such as:

1. Torch design: nozzle diameter, powder injection location and injection angle.

2. Spraying operation: arc power, gas composition, plasma temperature, standoff distance, and surface preparation of the work piece.

3. Plasma powder material: size, shape, chemical homogeneity, and crystal phase distribution. \[45\]
2.2.2 Properties of Plasma Sprayed Zirconia Layer

Figure 7 shows the schematic cross-section of the air plasma sprayed TBC and Figure 8 shows a backscatter scanning electron micrograph of the APS TBC. Porosity is inherent to the plasma sprayed coatings. It is introduced as the molten droplets splat down. Porosity has an important role to play in the reliability of the TBCs, since it determines the heat insulation, thermal shock, thermal cycle tolerance and erosion resistance of the TBC. More the porosity means better heat insulation and spalling resistance while less porosity gives improved erosion resistance. In addition, thermal cycle life is sensitive to zirconia density. Low densities of zirconia are as detrimental as the high densities as shown in Figure 9.\[51\]

Traditional problem with plasma sprayed TBCs has been the lack of reproducibility. Experiments have been performed by varying processes and testing the thermal cycle life of the TBCs and the result obtained has a lot of scatter. The reason for this being, inhomogeneity in the powders, difference in the particle size, and non-uniformity.\[45\] The life of TBC is essentially determined by the percentage of the monoclinic and the tetragonal ($t'$) phase present in the topcoat. The more the monoclinic phase present lesser is the life of the TBC and more the $t'$-phase present longer is the life of the TBC. Figure 9 shows the variation in the thermal cycle life with varying density.
Figure 7. A schematic illustration of APS TBC structure.

Figure 8. Back Scatter electron micrograph of as-coated APS TBC.
2.2.3 Electron Beam Physical vapor Deposited (EB-PVD) Thermal Barrier Coatings

EB-PVD is widely used in the gas turbine industry for applying coatings to turbine blades and vanes for protection against oxidation and hot corrosion. A schematic of the EB-PVD production facility is shown in Figure 10. In order to coat zirconia it is essential to provide certain oxygen partial pressure within the chamber to maintain oxygen stoichiometry in the deposited ZrO₂. The process involves:

Figure 9. Effect of density of the ZrO₂ layer on the thermal cycle life of ZrO₂-Y₂O₃ Thermal Barrier Coatings.⁵¹
High power electron beam focused onto YSZ ingot target, which melts locally and produces the YSZ powders. The vapor deposits as a coating on parts, which are held in rotatable and retractable fixture above the vapor source. [58]

For best adhesion, the bond coat surface has to be smooth or preferable polished. Adhesion in EB-PVD TBCs involves a chemical bonding between zirconia and bond coat surface. [59]

Figure 10. A schematic illustration of the EB-PVD process. [58]
2.2.4 Properties of EB-PVD Zirconia Layer

Figure 11 shows backscatter electron micrograph of the as-coated EB-PVD TBC. The columnar microstructure of topcoat is clearly visible. This is the major advantage since this structure reduces stress buildup within the body of the coating. The advantage lies in the fact that strain within the coating is accommodated by free expansion or contraction of the columns into gaps which results in negligible stress buildup.\[38\] However, there is an increase in the heat conductivity of the coatings by a factor of 2 as compared to the plasma sprayed coatings, which is a disadvantage.\[60\] There is a thin layer of dense ZrO$_2$ between the bond coat and the upper columnar zirconia structure. This grows because of deficiency of oxygen initially in the chamber just before zirconia deposition. Its thickness is dependent on the time with which oxygen can bleed off after zirconia coating is started.\[38\]
EB-PVD coatings have excellent spalling resistance and have superior properties as compared to plasma sprayed ones in (1) longer thermal cycles (2) smoother surface finishes (3) better surface finish retention and (4) superior erosion resistance. The major disadvantages compared to the APS coatings are that the process is very expensive and loss in the thermal conductivity by a factor of almost 2.

2.2.5 Dense Vertically Cracked TBCs

Dense Vertically Cracked ("DVC") Thermal Barrier Coating ("TBC") is a ceramic coating, and by definition, is dense, hard and difficult to abrade. The dense vertically cracked thermal barrier coating is applied to such combustor components so as to produce a segmented ceramic structure having macrocracks formed therein which are oriented substantially perpendicular to an interface of the combustor component and the segmented ceramic structure.[61]

DVC TBCs have greater resistance to particle erosion and thermal strain than those previously employed in gas turbine engine combustors, which is particularly advantageous in the wet (or water injection) environment. This stems from the dense vertically cracked thermal barrier coating having a porosity of less than approximately 8% and a tensile strength in the range of approximately 4-7 ksi.

DVC TBCs are processed in the following way:

- Spraying a plurality of layers of a ceramic thermal barrier coating on the turbine component, utilizing a plasma-spray torch at a first distance from the component.
• Plasma-spraying a sacrificial layer of the ceramic thermal barrier coating on the turbine component, with the plasma-spray torch at a second, greater distance from the turbine component to thereby make the sacrificial layer less dense than the plurality of layers; and
• Abrading the sacrificial layer so as to remove some or the entire sacrificial layer to achieve a desired final coating thickness and surface roughness.

2.2.6 Metallic Bond Coat – Properties and Processing Techniques

Oxygen permeates through the zirconia topcoat at high temperatures. It is very important to protect the superalloy substrate from high temperature oxidation and hence the topcoat has to be backed with an oxidation resistant bond coat. Success of the TBC lies in the choice of the bond coat material. Bond coat in TBC system is the most crucial components
• Provides excellent adhesion of the ceramic topcoat to the superalloy substrate.
• It has very high oxidation resistance and hence protects the base metal from oxidation. (Al in the bond coat forms α-Al₂O₃ which has low oxygen diffusion)
• It is a barrier to hot corrosion (Cr in MCrAlY prevents hot corrosion)
• Bond coat functions as a Al reservoir for the growth of α-Al₂O₃
• Yttrium in the bond coat suppresses sulphur embrittlemnet and provides excellent adhesion.
In addition, bond coat requires: (1) strength with greater creep resistance, (2) good resistance to interdiffusion with substrate alloy and (3) should not form brittle phases. [11, 62]

Bond coats are sprayed on the metallic surface by plasma spray techniques in order to minimize formation of metal oxide phases. Low pressure plasma spray (LPPS) or vacuum plasma spray (VPS) are typically adopted techniques. The two commonly used bond coat materials are MCrAlY (M can be Ni, Co or NiCo) or Platinum modified diffusion Aluminide (Ni, Pt) Al. MCrAlY is deposited by LPPS or VPS. This technique gives high bond strength to the bond coat. In addition, bond coat surface must be rough to give proper adhesion to the zirconia topcoat. MCrAlY are generally used in the aviation engines. During the high temperature oxidation, an oxide film predominantly alumina forms at the interface between the bond coat and the zirconia topcoat. This is the basis for attachment for the ZrO\textsubscript{2} layer. The other category is the platinum modified diffusion aluminide (Ni, Pt) Al which is fabricated by electroplating a thin layer of Pt on the superalloy substrate and then aluminizing either by pack cementation or chemical vapor deposition technique.

The TGO layer, which grows during the high temperature oxidation of the bond coat, is very critical element. Sulphur in the environment can segregate and hence can cause embrittlement. Yttria present in the bond coat helps suppression of sulphur embrittlement. Chromium and aluminum content in the bond coat can increase the spallation life of TBC by more than 10 times. [39, 63] In case of the platinum modified diffusion aluminide bond coats, Pt alleviates the detrimental effect of the S.
Research is being carried out and different materials are being tested for the bond coat. Yttria from MCrAlY bond coat has been replaced by Yb (MCrAlYb) and has found to increase the spall life \[^{64}\] Other proposals are being made in modifying the TBC-bond coat interface to include the co-plasma spraying of SiC whiskers to improve cracking toughness of zirconia-bond coat interface.

2.3 Failure of TBCs and its Mechanisms.

Durability of the TBCs has been a major issue with respect to the benefits that can be received from TBCs. Durability is governed by a sequence of crack nucleation, propagation, and coalescence events. There are three salient elements analogous to those for low cycle fatigue failure of structural alloys. (1) Small cracks and separations nucleate at defects in (or near) TGO. (2) The tensile stresses that arise around these defects and the associated energy release rates govern the details. Once nucleated, the small cracks extend and coalesce, but the TBC remains attached at remnant ligaments and (3) Failure happens when remnant ligaments are detached, causing a separation large enough to create either a large-scale buckle or an edge delamination that results in spalls. \[^{65}\]

Development of a systems approach to TBC design and performance requires two bifurcations be recognized and characterized:

- TBCs made by plasma spray (PS) and electron beam physical vapor deposition (EB-PVD) are so disparate in their microstructure, morphology, and thermophysical properties that different failure mechanisms apply. Plasma sprayed coatings are used with roughened bond coat. Failure occurs by crack evolution in the TBC itself,
occurring in planes parallel to the substrate. In contrast, EB-PVD coatings are deposited on smooth bond coat and fail typically by loss of adherence of the TGO and bond coat.

- The dominant failure mechanisms are different for the two areas of application namely propulsion and power generation since they have completely different thermal histories. Systems used for propulsion and power peaking purposes experience multiple thermal cycles resulting in failure when the TGO thickness ranges from 1-5µm. Other power systems operate in isothermal mode with few cycles and these fail when TGO thickness is in the range 5-15µm. Hence thermal cycling diminishes the durability of the TBCs. [65]

- Failure mechanisms for the APS and EB-PVD TBCs are discussed in detail in the following section.

2.3.1 Air Plasma Sprayed TBCs

The mechanisms by which the APS TBCs fail are as follows. [66,67]

- Mechanism I : At the TGO/Bond Coat (BC) Interface

Two types of out-of-plane stresses act at the TGO/BC interface, one is the tensile stress at the crest and the other is the compressive stress at the troughs. During the thermal exposure there is a continuous growth of the oxide, hence the out-of-plane tensile stress increases resulting in the cracking at the TGO/BC interface at crest as shown in Figure 12.
Figure 12. Schematic showing different failure mechanisms in APS TBCs

- Mechanism II and III: At the TGO/Topcoat Interface and within the TBC

Differences in the thermal expansion coefficient mismatch of the topcoat and the bond coat results in compressive stresses during cooling. Another reason attributing to the stress is the sintering of the topcoat. The stresses are lower in magnitude than the TGO residual stresses, since the porous and cracked ceramic layer is more submissive than TGO, and it has a relatively lower thermal expansion coefficient mismatch with the bond coat. The interface between the ceramic and the bond coat layer is highly undulating, therefore out-of-plane stress results at the vicinity of the TGO/topcoat interface where there is tension at the crests and compression at the troughs. This results in the fracture if the TBCs at TGO/Topcoat interface at crests. The cracking occurs within highly brittle topcoat in the vicinity of the crest (III) as shown in Figure 12. \[67,68\]
Mechanism IV: At the TGO/Bond Coat (BC) Interface

With the TGO thickening at the expense of oxidation of the bond coat, thermal stresses which are locally dominated by thermal expansion mismatch between the bond coat and TGO combined is rather high than just the bond coat and topcoat. There is a certain critical thickness beyond which the coefficient of thermal expansion of the BC and TGO becomes lower than that of both bond coat and topcoat. This is reversal in the nature of the stresses in the troughs associated with the topcoat undulation from compressive to tension. The reversal from compression to tensile in the troughs causes cracking within the YSZ between crests shown in the Figure 12. [23]

2.3.2 Electron-Beam Physical Vapor Deposited TBCs

EB-PVD has a columnar structure and hence is more strain tolerant than the APS TBCs. Inelastic deformation of Zirconia layer occurs in the plasma sprayed TBCs during thermal cycling, but in case of EB-PVD it remains elastic, with the life-limiting factor appearing to be from the strain which develops in the thermally grown oxides. [1] Failure in the EB-PVD TBCs occurs at the bond coat/TGO or the TGO/topcoat interfaces. Figure 13 is a schematic representation of failure mechanisms in EB-PVD TBCs.
Figure 13. Schematic diagram showing the two types of failure in EB-PVD TBCs. \[69,70\]

- **Mechanism I: At bond coat/TGO interface**

  This is similar to that of the APS TBCs. The crests in case of EB-PVD TBCs are surface irregularities or undulations. Formation of voids and Ni/Co rich TGO is the reason for the degradation of the TGO/Bond coat interface. Development of voids and internal oxidation is observed to begin after the depletion of Al rich $\beta$-phase (NiAl). \[70\]

- **Mechanism II: At TGO/Topcoat interface**

  Here there is separation of the TGO from the topcoat with penetration of TGO into bond coat, which may be due to different mechanisms.

- TGO roughens because of the bond coat creep during cooling. \[70,71\]

- Phase transformation of the YSZ coatings and TGO

- Sintering of the YSZ

- Cavity formation in the bond coat is inherent of the CVD aluminizing process. There is a ridge corresponding to each grain boundary in a large polygonal grain structure of platinum aluminized bond coat. The ridge is transformed to a cavity partially filled
with oxide as a result of cycle and time dependent process during the thermal cycling.\textsuperscript{[72]}

- Bond coat undergoes heat treatment before the EB-PVD deposition, because of which there is presence of embedded oxides. These oxides growth is accelerated due to the cracking in the TGO.\textsuperscript{[72,73]}

- The other possible mechanism is the formation of the Ni/Co rich oxides (spinels) at the TGO/bond coat or between the TGO and TBC. These spinels are extremely brittle in nature. The occurrence of this structure is the cause for delamination in the TBC.\textsuperscript{[6]}

2.3.3 Final Failure Modes

The failure of TBC systems is typically associated with buckling and spalling of the ceramic topcoat from the thermally grown oxide. In addition the final failure occurs due to link-up of damage at the TGO/bond coat interface with pre-existing damage at the YSZ/TGO interface.

- Buckling

Buckling is separation of the TGO from the bond coat. Usually buckling occurs over a large area. A contiguous debonded region is necessary for the buckling to occur. The size of the debonded region depends on the growth of the TGO and increases with increase in TGO thickness. Once critical thickness is exceeded buckling occurs. In addition, buckle propagation is impelled by strain energy density in the TGO and resisted by the fracture toughness of the TGO/BC interface. The extent of propagation before
failure is dependent on the relative toughness of the TGO and the interface.\cite{74} Figure 14 represents the schematic of buckling failure in TBCs.\cite{74}

![Schematic of buckling failure in TBCs](image)

Figure 14. Schematic illustrating failure by buckling in TBCs.

- Delamination

Delamination by definition means peeling from specimen edge. It is one of the reasons for the failure of the TBCs. It occurs between the TGO and the Bond coat. There is separation of the interface as a result of thickening of TGO with increase in thermo mechanical stresses. When these separations become large edge delamination occurs.\cite{75} Figure 15 shows schematic representation of failure of TBCs by edge delamination.
2.4 Non-Destructive Evaluation Techniques

Non-destructive testing is a probabilistic method of evaluation or examination of the components or materials without affecting its usefulness. Non-Destructive evaluation techniques are essential for developing reliable thermal barrier coatings for industrial applications. In recent years, there has been a steady growth in the NDT. New methods are being developed to advance the knowledge of ceramic coatings for components in the hot gas-path of advanced, low emission gas-fired turbine engines. NDE primarily suffice the following:

- It is very flexible. (Flexible probes)
- Improved safety and cost effective
- Easier to identify the failure prone regions and damage mechanisms
- Prevent or reduce the damage because of failure.
Advances in TBCs, both EB-PVD and APS, are allowing higher temperatures in the hot-gas path of turbines as explained earlier. The life of thermal barrier coatings is important to ensure safety of the turbine engine components. In addition, there are very high costs incurred in the event of a failure. However, as their conditions become “prime reliant” their condition at expected or unexpected outages must be known. Data provided from the NDE techniques are very valuable: a) provides information on the reliability of the new coatings, b) defects in the components can be identified and catastrophic failures can be avoided, c) defect growth rates can be monitored and precautions can be taken and d) decisions can be made on replacement, repair or reuse of the components. The only way in which the lifetime assessment can be made without affecting its usefulness is by Non-destructive evaluation. In addition, the cost involved in NDE is very low in comparison to the costs incurred in the event of failure. Some of the NDE techniques are explained in the following section.\textsuperscript{[76,77,78]}

2.4.1 Thermal Wave Imaging.

Thermal wave imaging is an emerging technology for the non-destructive evaluation of subsurface features of opaque solids. In this technique, thermal waves are generated by localized, intensity-modulated energy source, such as a laser or electron beam. Thermal waves scattered from subsurface features can be detected by means of a number of techniques. One of them was Scanning Photoacoustic Microscope (SPAM) in which the detector, which is essentially a microphone, is placed in a closed gas cell. Another scheme detects the scattered thermal waves by means of so-called mirage effect.
or optical beam deflection method (ODB) in which a laser beam is deflected by density
gradient of the heated gas near the sample surface. One of the useful applications of
thermal wave imaging is to the detection of fatigue cracks in metals or fractures in brittle
solids. This technique is very simple in the sense that it is based on images and uses a
scalar (temperature) quantity to describe the wave. \[79\] It is also being used to determine
aircraft skin corrosion thinning. In addition to imaging the pattern of the subsurface
corrosion, it can make quantitative measurements of material loss less than 1% for
various regions in the image.

2.4.2 Scanning Acoustic Microscopy (SAM)

SAM is a relatively new technique and is now being used in applications. SAM
uses sound to create visual images of variations in mechanical properties of samples.
Since acoustic waves have, the ability to penetrate optically through opaque materials,
SAM provides surface and subsurface structural images non-destructively. SAM has
found wide applications in biology, integrated circuits, and metrology and in
semiconductor industries. However, the main advantage of SAM has been the ability of
distinguishing defects and discontinuities in the materials. It has also been used to
observe defects in the coatings.

This technique consists of a reflection type scanning acoustic microscope. There
is a piezoelectric transducer attached to the flat end of the buffer rod and excites a plane
wave ultrasonic beam into the buffer rod. The other end of the rod has a spherical lens,
which focuses the sound beam on the sample. The core of the microscope is the quartz
lens. A portion of the acoustic energy is transmitted into the sample and a portion is reflected back. The reflected energy is converted into electrical signal by the transducer. The return signal amplitude is collected and used to modulate the intensity of the display on the monitor at a location corresponding to the focal spot over the specimen. By bringing the lens closer to the specimen, it is possible to focus the acoustic waves inside the specimen, thereby viewing the interior of the specimen. Figure 16 is a schematic representation of the SAM. [79]

Figure 16. Schematic diagram of SAM principles. [79]
2.4.3 Photo Stimulated Luminescence Spectroscopy (PSLS)

Photo Stimulated Luminescence Spectroscopy has demonstrated the ability to assess, non-destructively, the residual stress and polymorphic transformation of $\text{Al}_2\text{O}_3$, which make up the thermally grown oxide.

The principle of PSLS is described by the “RAMAN EFFECT” which is scattering of light from a gas. PSLS is an optical method which works on the principle of laser that is when a photon emission of chromium ($\text{Cr}^{3+}$) impurity in $\alpha$-$\text{Al}_2\text{O}_3$ is excited, two distinct fluorescence transitions are allowed by the crystallographic symmetry of $\text{Cr}^{3+}$ site in $\alpha$-$\text{Al}_2\text{O}_3$ crystals corresponding to the R1 and R2 fluorescence peaks. Stresses in the TGO can be measured by calibrating the shift in the peaks. The shift in the fluorescence peaks is a result of strain in $\alpha$-$\text{Al}_2\text{O}_3$ crystals. Figure 17 shows schematic illustration of PSLS for TBCs. [80]

![Figure 17. Schematic illustration of basic photostimulated luminescence. [80]](image.png)
2.4.4 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy has gained extreme importance in the recent years. EIS provides a very detailed data on the effectiveness of a coating over a relatively small area. It provides very detailed data on a localized basis that can be used to predict the effectiveness of a coating over time and to quantify the actual effectiveness at various times. This technique is used for batteries, fuel cells, coatings, ceramics, semiconductors, sensors, and corrosion studies.

In an EIS experiment, the impedance is measured for a number of frequencies that span a range from a few milli-Hertz to 100 kilo-hertz, and the result is a complex number – the impedance – for each of the hundred to thousands of frequencies that are used. A complex number is a mathematical representation of two associated quantities, the real and the reactive components of electrical impedance in this case. Since complex numbers are used, a vector analysis method is needed. Also, in case of insulators, the impedance varies as the function of the applied voltage. The variation in the impedance is mainly due to the physical characteristics of material and the chemical nature of the interfaces developed between the electrode and electrolyte interface. Hence if a measurement is made over a suitable frequency range and impedance is analyzed the results obtained can give physical nature of the material and chemical nature of the interface. Conventional cell of EIS cell for lab measurements is shown in Figure 18. [76]
The advantages of EIS over the other techniques are the possibility of using very small amplitude signals without significantly disturbing the properties being measured. The advantages include:

- Rapid acquisition of data.
- Accuracy and precision of measurements
- Non-Destructive.
- Highly versatile.
2.5 Electrochemical Impedance Spectroscopy

2.5.1 Theory

The best way to understand EIS is to compare it with linear polarization. A system that is corroding contains both an oxidation and a reduction reaction. Each reaction produces a current ($i_c$) for the cathodic (or reduction) reaction and a current ($i_a$) for the anodic (or oxidation) reaction. The anodic current is proportional to the rate of corrosion, so the corrosion rate could be determined if $i_a$ could be measured. EIS has been used extensively in the corrosion studies and has proven to be a powerful and accurate method for measuring corrosion rates.\cite{76,36}

Ohm's law for DC signal is given by

$$ R = \frac{V}{I} $$  \hspace{1cm} (1)

where $R$ is the resistance which impedes the flow of current $I$ when a voltage $V$ is applied. When a known DC potential is applied to a circuit and the resulting current is measured by ammeter in series then the resistance $R$ can be computed.

For AC signal,

$$ Z = \frac{V}{I} $$  \hspace{1cm} (2)

where $Z$ is defined as the impedance. Figure 19 shows the relationship between current and voltage in impedance measurements.
In an EIS measurement, a small excitation signal is applied and electrochemical impedance response is measured. In a linear system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase.

In order to characterize the ac waveform, vector analysis is used. It can be described in terms of its amplitude and phase characteristics, or in terms of the real part and imaginary part of a complex number. Equation 2 can be represented in the vector form as:

$$\bar{Z} = \frac{\bar{V}}{\bar{I}}$$  \hspace{1cm} (3)

where the ac voltage ($\bar{V}$) can be represented as a complex number:

$$\bar{V} = \bar{V}^* + j\bar{V}^{**}$$  \hspace{1cm} (4)
The superscripts * and ** correspond to real and imaginary component of the vector. The resulting current ($\tilde{I}$) can also be represented as a complex number:

$$\tilde{I} = \tilde{I}^* + j\tilde{I}^{**}$$  \hspace{1cm} (5)$$

and the resulting expression for the ac impedance ($\tilde{Z}$) is defined in terms of the same coordinate axes as the current and voltage vectors as follows:

$$\tilde{Z} = \tilde{Z}^* + j\tilde{Z}^{**}$$  \hspace{1cm} (6)$$

The magnitude of the expression is given by

$$|Z| = \sqrt{(Z^*)^2 + (Z^{**})^2}$$  \hspace{1cm} (7)$$

and the phase angle ($\phi$) is defined as:

$$\phi = \arctan\left(\frac{Z^{**}}{Z^*}\right)$$  \hspace{1cm} (8)$$

2.5.2 Electrical Circuitry

In EIS, impedance is measured for a number of frequencies that span a range from few milli hertz to 100 kilohertz, and the result is a complex number. To make use of the complex numbers that are obtained from EIS measurement, the system under test is modeled as a collection of electronic components such as resistors and capacitors. As shown in Figure 20.
Figure 20. Electrical Circuit (Randles Circuit) for A metal.\textsuperscript{[76]}

The nature of these models involves a number of these components and the ways in which they are connected. The commonly used circuit elements are resistor, capacitors, and inductors. The circuit elements and their impedance response are tabulated in Table 1. The impedance of the resistor is independent of the frequency and has only real component. Since there is no imaginary impedance, the current through the resistor is always in phase with the voltage.

<table>
<thead>
<tr>
<th>Component</th>
<th>Current vs. Voltage</th>
<th>Impedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor</td>
<td>$V = IR$</td>
<td>$Z = R$</td>
</tr>
<tr>
<td>Inductor</td>
<td>$E = L \frac{di}{dt}$</td>
<td>$Z = j\omega L$</td>
</tr>
<tr>
<td>Capacitor</td>
<td>$I = C \frac{dE}{dt}$</td>
<td>$Z = \frac{i}{j\omega C}$</td>
</tr>
</tbody>
</table>
From the table C and L are defined as capacitance and inductance. The impedance of the capacitor does not have a real component and its imaginary component is a function of frequency, where \( \omega = 2\pi f \) (\( \omega = \) angular frequency and \( f \), is the frequency). In a capacitor impedance decreases with the increase in the frequency. The current through a capacitor is phase shifted –90 degrees with respect to the voltage, with current leading the voltage. Since the impedance of the capacitor varies inversely with the frequency, \( Z = (j\omega C)^{-1} \), at high frequencies a capacitor acts as a short circuit: its impedance approaches zero. At low frequencies, a capacitor acts as an open circuit, and the impedance approaches infinity.

The impedance versus frequency behavior for an inductor is opposite to that of a capacitor. Inductors have only imaginary impedance component and the current through the inductor is always 90 degrees out of phase with respect to the voltage. As the frequency increases, the impedance of an inductor increases. It acts as a short circuit (i.e., zero impedance) at infinitely low frequencies and has infinite impedance at very high frequencies.

The complex electrical circuits that are used to model the given system will usually comprise of serial and parallel combinations of simple elements like the resistors, capacitors and inductors; the impedance values of the individual components can be combined according to some simple rules governing the system impedance for circuit elements both in parallel and series combinations. For linear impedance elements in series, we can calculate the equivalent impedance from:

\[
Z_{\text{eq}} = Z_1 + Z_2 + Z_3
\]  

(9)
where $Z_1$, $Z_2$, $Z_3$ are the impedance of the elements (resistor or capacitor or inductor). For linear impedance elements in parallel, we can calculate the equivalent impedance from:

$$\frac{1}{Z_{eq}} = \frac{1}{Z_1} + \frac{1}{Z_2} + \frac{1}{Z_3}$$

(10)

### 2.5.3 Data Representation

Equations (2) and (3) can be expressed in complex number as:

$$V(t) = V_0 \cos(\omega t)$$
$$I(t) = I_0 \cos(\omega t - \phi)$$

(11)

$V(t)$ is the potential at time $t$, $V_0$ is the amplitude of the signal, and $\omega$ is the angular frequency. Similarly $I(t)$ is the current at time $t$, $I_0$ is the amplitude of the current and $\phi$ the difference between the current and voltage vector. The relationship between the angular frequency and frequency $f$ (Hz) is $\omega = 2\pi f$.

Therefore, the Eq. (3) can be represented as:

$$Z = \frac{V(t)}{I(t)} = \frac{V_0 \cos(\omega t)}{I_0 \cos(\omega t - \phi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \phi)}$$

(12)

Using Euler’s Expression

$$\exp(j\phi) = \cos \phi + j \sin \phi$$

(13)

it is possible to express the impedance as a complex function. The potential is then described as

$$V(t) = V_0 \exp(j\omega t)$$

(14)

and the current as,
\[ I(t) = I_0 \exp(j\omega t - j\phi) \]  

(15)

The impedance is thus represented as a complex number,

\[ Z(\omega) = \frac{V}{I} = Z_0 \exp(j\phi) = Z_0 (\cos{\phi} + j\sin{\phi}) \]  

(16)

The total impedance \( Z(\omega) \) of a circuit can be plotted as imaginary part of the impedance \( (Z^*) \) on the \( y \)-axis and the real part of the impedance \( (Z^\ast) \) on the \( x \)-axis called the Nyquist plot. The shortcoming of a Nyquist plot is that from a data point on the plot we cannot obtain the frequency that was used to record that point. Impedance of the same circuit can also be plotted as the absolute magnitude of the impedance \(| Z |\) and the phase angle \( \phi \) on the \( y \)-axis using the log frequency on the \( x \)-axis called the Bode plot.

2.5.4 Analysis of EIS Data

The modeling of any electrochemical is complicated and coatings are even more complicated. Depending on the impedance spectrum, a circuit model is constructed with the electrical elements as discussed above, which would exhibit the same impedance response as the measured one. Numerical values are assigned to the elements and values are modified to simulate the systems response more accurately. In an electrochemical cell, slow electrode kinetics, slow preceding chemical reactions and diffusion can impede the flow of electron or ion and can be considered as analogous to resistors, capacitors and inductors that impede the flow of electrons in an ac circuit. Hence an AC equivalent circuit can be developed with the resistors, capacitors and inductors in order to simulate a given system response. The EIS of a system can be separated into impedances
contributed by each of the elements. Each of the elements has a physical significance (microstructure, properties, degradation, oxide growth).

In a Nyquist plot, a pure resistance, $R$, is a single point on the $Z^\ast$ (Real) axis and in a Bode plot, it is a straight line parallel to the log $f$ axis at a height of the $R$-value. The straight line indicates that the impedance is independent of frequency and has no reactive component. The phase angle, $\theta$, is zero at all frequencies. Similarly for a Nyquist plot, shape of a pure capacitance, $C$, is a vertical line at $Z^\ast = 0$, indicating that the resistive component, $Z^\ast$, is zero, and that the reactive component, $Z^{\ast\ast}$, is inversely related to the frequency, $f$. In the Bode plot, shape for this capacitor is a straight line with a slope of $-1$ on a log $|Z|$ axis, indicating that $|Z|$ is inversely related to the frequency $f$ and the value of $\theta$ is $-90^\circ$ at all frequencies.

Resistors and capacitors give a characteristic shape in both Nyquist and Bode plots when combined to form simple systems. The equivalent circuit elements not only allow calculation of their individual values but also how they change with exposure/degradation indicating how they interact with each other clarifying the evolution of defects. For example, the resistor and capacitor in series combination shown in Figure 21a, gives a different plot shape as shown in Figure 21b when compared with the parallel resistor/capacitor combination shown in Figure 25.
A metal with a new coating generally has very high impedance and can be represented as a resistor and capacitor in series. The equivalent circuit model includes a resistor, \( R_S \) (solution resistance through the electrolyte) and a capacitor representing the coating. The nyquist plot for this circuit is shown in Figure 21b. The value of the capacitance cannot be determined from the nyquist plot. The capacitance value can only be determined by curve fitting or by examination of the data points. The solution resistance can be obtained from the intercept of the curve with the real axis. The maximum limit in the impedance for most of the EIS measurement is close to \( 10^{10} \, \Omega \). The Bode plot for the same circuit is shown in Figure 22. From this plot, we also get the
solution resistance but it does not appear because the impedance of the coating is higher than the solution resistance.

The Randles circuit shown in Figure 20 models the electrochemical impedance of an interface and fits many simple electrochemical systems. At the interface between an electrode and electrolyte, a double layer is established as shown in Figure 20 in which negatively charged ions (anions) line up at the electrode surface. Positively charged ions (cations) then line up in response to maintain electro-neutrality but are separated from the anions due to their sheath of hydration. This double layer acts, as a capacitor $C_d$ in parallel with the polarization resistance ($R_p$) due to the charge transfer reaction. Double layered capacitance is clearly shown in Figure 23. The ionically conducting electrolyte

Figure 22. Impedance and phase angle plot for the circuit shown in Figure 22a.
impedes the transfer of charge (ions) and, acts as a resistor, $R_S$ in series with the $C_d$ and $R_P$. This simple Randles circuit is a starting point for other more complex models.

A characteristic impedance and nyquist plot for the Randles circuit is shown in Figure 24. Nyquist plot for the Randles circuit is always a semi circle. The high frequency response in the Nyquist lies on the left followed by the low frequency response on the right. The real axis value at the high frequency intercept gives the solution.
resistance ($R_S$). This is closer to the origin, where as the other intercept at the lower frequency region gives the sum of polarization and solution resistance ($R_P + R_S$). Therefore, the diameter of the semicircle gives the polarization resistance. From the bode plot as shown in Figure 24, the solution resistance and sum of solution and polarization resistance can be found looking at the y-axis (Impedance $|Z|$).

![Nyquist Plot and Bode Plot](image)

Figure 24. Nyquist and Bode plots for the Randles circuit.

Since Randles circuit is not purely capacitive, the phase angle does not reach 90° and may approach if the values of $R_S$ and $R_P$ were more widely separated. \[81\]

EIS has been a very effective technique for the application in the coated metals. Typical equivalent circuit for the coated metals is shown in Figure 25.
Figure 25. Typical equivalent circuit model for coated metal/solution interface. $R_S$ is the solution resistance; $R_T$ is charge transfer resistance, $C_T$ is Faradaic capacitance of metal; $R_P$ is the pore resistance and $C_C$ is the capacitance of the intact film.

The circuit model, as shown in Figure 25, was used to describe the electrochemical process. The resistance, $R_P$, was interpreted as the pore resistance due to the electrolyte penetrating through pores within the coated paint film. The film capacitance, $C_C$, was interpreted as the capacitance of the electrical capacitor consisting of the metal and electrolyte, or simply as the capacitance of the intact film. Therefore, two semicircles, which present the relaxation processes of the film capacitor and double layer, appear in the Nyquist plot (Figure 26b).

Figure 26. (a) Typical bode plot for the painted metal/solution interface in the absence of diffusion. (b) Typical Nyquist plot showing two semi circles.
The corresponding Bode plot is shown in Figure 26a. From this plot, we can see two-phase angle maxima, one at the higher frequency domain usually containing paint film information, and one at lower frequency domain, containing the substrate information. The Bode phase plot shows phase angle reaching towards zero at corresponding low and high frequencies. Representing the resistive behavior of $R_S$ and $R_S+R_T$. This phase angle rise towards maximum value, at the intermediate frequencies, corresponds to the capacitive behavior(C).

In many cases, the Randles circuit shown in Figure 20 will not be adequate as a model for the painted metal/solution interface. Modification is done in order to account for diffusion processes within pores in the paint film and is modeled by the inclusion of Warburg or pseudo-impedance, $Z_{\omega_0}$, placed in series with $R_P$, where $Z_{\omega_0}$ is defined according to Eq. (17).

$$Z_{\omega_0} = \sigma \omega^{-\frac{1}{2}} (1 - j)$$

(17)

The substrate double layer capacitance, $C_{dl}$, may appear or may not appear in parallel with $R_P + Z_{\omega_0}$. Equivalent electrical circuit is shown in Figure 27 and corresponding nyquist and bode plots are shown in Figure 28. In this model, $R_S$ is the resistance of the electrolyte, $R_C$ and $C_C$ are the resistance and capacitance of the coating, $R_P$ is the polarization resistance, which is inversely proportional to the corrosion rate, $C_{dl}$ is the double layer capacitance at the electrode-electrolyte interface, and $Z_{\omega_0}$ is an impedance due to the diffusion of reactants to the surface of the electrode.

During the life of the coating, the equivalent circuit model no longer remains the same and changes. This change is dependent on processes such as moisture penetration, onset of corrosion and break up of coating. When a coating is new and effective, $R_P$, $R_C$,
$C_{dl}$ and $Z_{\omega}$ are not present and the model is similar to that shown in Figure 21a. As the moisture penetrates the coating, $R_C$ comes into play. When the corrosion starts, $R_P$ and $C_{dl}$ become operable. When the corrosion rate becomes high, $Z_{\omega}$ is present. If the pores in the coating clog over time, the corrosion rate decreases and $Z_{\omega}$ becomes needed to be considered, but if the coating breaks up $R_C$, $C_C$ and $Z_{\omega}$ become inoperable and the system acts like a bare metal.

Figure 27. Coated metal/solution interface equivalent circuit model in presence of diffusion
Figure 28. Typical (a) Nyquist (b) Bode plot for painted metal/solution interface in the presence of diffusion.
2.5.5 Constant Phase Element

A perfectly smooth homogenous electrode can be represented by an equivalent circuit made up of an electrolyte resistance ($R_S$) in series with the double layer capacitor $C_{dl}$ and the polarization resistance ($R_P$) in parallel to $C_{dl}$ as shown in Figure 20.

The constant phase element (CPE) is a non-intuitive circuit element that was discovered (or invented) while looking at the response of real-world systems. In some systems where the Nyquist plot (also called the Cole-Cole plot or complex impedance plane plot) was expected to be a semicircle with the center on the x-axis, the observed plot was indeed the arc of a circle, but with the center some distance below the x-axis.

These depressed semicircles have been explained by a number of phenomena, depending on the nature of the system being investigated. However, the common trend among these explanations is that some property of the system is not homogeneous or that there is some distribution (dispersion) of the value of some physical property of the system. Therefore, in the case of YSZ monoliths and APS TBCs (exposed and as received), a CPE is used rather than an ideal capacitor in the ac equivalent circuits (shown in Figures 32-34) where the depression of the semicircle is seen. The mathematics behind the CPE is far beyond the scope of this study. [83,84,85,86,87,88]

Generally, CPE is used if the material under investigation cannot be regarded as homogenous. Common examples of homogenous materials are: the surface of a bare solid metal, [85,86] coated metals, [86,87] solid electrolytes, [83] dielectrics, [88] and semiconductors. [89] The use of CPE is more suitable to describe the behavior of a non-ideal capacitor, which contains various phases as dielectric materials. In this study, YSZ
monolith and APS TBCs are considered, which are usually inhomogeneous in a physical sense because of the geometric defects such as surface roughness. These geometric defects give rise to frequency dispersion due to non-uniform distribution in the current density.\(^{90,91}\) Over a wide range of frequencies, such effects may be described with the empirical concept of a Constant Phase Element. The impedance of the CPE is given by:

\[
Z_{\text{CPE}}(j\omega) = A^{-1}(j\omega)^{-n}
\] (18)

where \(A\) is a constant that is independent of frequency, \(\omega\) is angular frequency, \(j = \sqrt{-1}\), and \(n\) is an exponential index, which represents a dispersion of relaxation frequency. When \(n=1\), the CPE represents an ideal capacitor, when \(n = 0\), CPE acts as a pure resistor. For highly contorted surface the value of \(n\) is around 0.5. For real metal or solid electrodes the value of \(n\) may vary from 0.9-1. Also the value of \(n\) varies if the bulk conductivity of the coating changes with the distance through the coating. In their text, MacDonald, et. al.\(^{74}\) point out that even though a particular theory may not give exactly CPE behavior, very often CPE behavior will fit experimental data so well that the deviations are totally masked by experimental noise and uncertainties. This is increasingly true as the complexity of a circuit model grows. In short, a CPE can act as a useful modeling element, even if the true nature of the system is unknown.
3 EXPERIMENTAL DETAILS

3.1 Sintering of YSZ

Specimens of YSZ having two different density (3.85 and 4.07 g/cm$^3$) received from Trans-Tech, Adamstown, PA, was cut into three different thickness (2mm, 3mm and 4mm). Buhler precision diamond cutting saw at low speed was used to avoid any damage to the surface. The variables for the sintering experiment (time, temperature and thickness) have been shown in Table 2.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1100</th>
<th>1200</th>
<th>1300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holding Time (Hours)</td>
<td>2, 5, 10</td>
<td>2, 5, 10</td>
<td>2, 5, 10</td>
</tr>
<tr>
<td>Thickness (mm) (Density 3.85 and 4.07 g/cm$^3$)</td>
<td>2, 3, 4</td>
<td>2, 3, 4</td>
<td>2, 3, 4</td>
</tr>
</tbody>
</table>

Sintering was done using the ThermoLyne 46100 high-temperature furnace. All the specimens after the holding time were air quenched to room temperature. Since few of the YSZ specimen cracked when quenched at room temperature, the sintering was repeated and then they were furnace cooled. All the specimens were coated with carbon paint on one end for conduction. EIS measurements were carried out for all the specimens to monitor the change in the impedance response for different variables as shown in Table 2. One sample from each density for different holding time and sintering temperature was chosen to mount and were put to microstructural examination. The YSZ
specimens were mounted using Buhler EPOTHIN low viscosity epoxy and polished with diamond pastes down to 0.25 µm finish for microstructural analysis using JEOL 6400 field emission scanning electron microscopy.

3.2 Isothermal Exposure of NiAl

Hot extruded NiAl disk specimens with equiaxed grain (~30 µm), received from National Aeronautics and Space Administration – Glenn Research Center (NASA-GRC), were isothermally oxidized at varying temperature and times. Isothermal oxidation was carried out using ThermoLyne 46100 high-temperature furnace. EIS measurements were done for all the specimens to record the variation in the impedance with varying temperatures and holding time. Scanning electron microscopy was incorporated to measure the thickness of TGO. The objective of this study is to monitor the change in the electrochemical impedance with respect to the oxidation of nickel aluminide. Nickel aluminide is an Al$_2$O$_3$ former like many commercial bond coats. Table 3 shows the different variables chosen for oxidation of NiAl and subsequent EIS measurements.

Table 3 The variables used in the isothermal oxidation of NiAl buttons of 2mm thickness.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1100</th>
<th>1200</th>
<th>1300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (Hours)</td>
<td>2, 5, 10</td>
<td>2, 5, 10</td>
<td>2, 5, 10</td>
</tr>
</tbody>
</table>
3.3 Isothermal Oxidation of EB-PVD TBCs

All EB-PVD TBC specimens, listed in Table 4 have been investigated in this study. All specimens were in the form of disks with an approximate diameter of 25.4 mm and thickness of 3.2 mm. Five specimens of type A EB-PVD TBCs were isothermally oxidized for 50, 100, 250, 400 and 600 h at 1121°C using ThermoLyne 46100 high-temperature furnace and EIS was carried out for each exposure time. The oxidation process includes heating up the specimen to 1121°C and held for certain duration and then air quenching to room temperature. All type A specimens were air quenched after the isothermal oxidation.

<table>
<thead>
<tr>
<th>Type</th>
<th>YSZ Deposition Method &amp; Thickness (µm)</th>
<th>Bond Coat Type &amp; thickness (µm)</th>
<th>Superalloy Substrate</th>
<th>Thermal Exposure Testing</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>EB-PVD; 125</td>
<td>(Ni, Pt) Al; 150</td>
<td>CMSX-4</td>
<td>Isothermal</td>
</tr>
</tbody>
</table>

EIS was carried out (a) to detect the change in the impedance response as a function of isothermal exposure time, (b) to detect the change in response of the impedance with the growth of oxide, (c) to find out if sub critical damage in TBCs would alter the impedance response and (d) to find out the effect of EIS on the lifetime of TBCs. After EIS measurement, cross-sectional samples were prepared using a Buehler Isomet precision diamond-cutting saw at low speed to retain the microstructural integrity of TBCs. These samples were vacuum impregnated in Stycast, and polished with diamond
pastes down to 0.25-µm finishes for microstructural analysis by JEOL 6400 field emission scanning electron microscope. Before the analysis by SEM, the samples were coated with carbon using the Carbon coater to make the surface conductive to the electrons in the SEM chamber.

3.4 Air Plasma Sprayed TBCs

A series of APS TBCs were different types listed in Table 5 were investigated in this study. The investigation was divided into 2 groups based on density, thickness, and chemistry. EIS was performed on two samples of APS 7YSZ with varying density (Group I). This was done to find out the EIS response for varying density. The second set of experiment included EIS on APS 7YSZ and APS CAT (Group II) to find out the impedance response as a function of varying thickness and chemistry. After EIS measurements, cross-sectional samples were carefully prepared for SEM analysis using the procedure described earlier.

Table 5: Specimen description of APS TBCs investigated using EIS as a density, thickness, and chemistry.

<table>
<thead>
<tr>
<th>Group</th>
<th>Chemistry Variable</th>
<th>TBC Processing</th>
<th>Microstructure Variable</th>
<th>Specification</th>
<th>Thermal Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>7YSZ</td>
<td>APS</td>
<td>Density&lt;sup&gt;+&lt;/sup&gt;</td>
<td>65 %</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>73.6 %</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>7YSZ</td>
<td>APS</td>
<td>Thickness%</td>
<td>552 µm</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>CaTiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
<td></td>
<td>325 µm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>667 µm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>339 µm</td>
<td></td>
</tr>
</tbody>
</table>

Note: <sup>+</sup> Measured by water and oil immersion technique (ASTM B328-73) by coating manufacturer. % Measured by optical and scanning electron microscopy.
3.5 Dense Vertically Cracked TBCs

Table 6 shows the specimen description of the DVC TBCs. EIS response was gathered for DVC TBCs with varying crack density (Group III). Variations of impedance response as a function crack density was tested using EIS and cross sectional samples were prepared for microstructural studies under SEM as described earlier.

Table 6 Specimen description of DVC TBCs investigated using EIS as a function of crack density and crack orientation.

<table>
<thead>
<tr>
<th>Group</th>
<th>Chemistry Variable</th>
<th>TBC Processing</th>
<th>Microstructure Variable</th>
<th>Specification</th>
<th>Thermal Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>7YSZ</td>
<td>DVC</td>
<td>Relative Crack Density*</td>
<td>1 CPL</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20 CPL</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>70 CPL</td>
<td></td>
</tr>
</tbody>
</table>

Note: * Relative cracks per (specific) length (CPL) measured by standard quantitative microscopy.

3.6 EB-PVD TBCs with varying density

The next set of samples investigated in this study was two EB-PVD samples with different density. One, which had dense microstructure and the other, having columnar microstructure. EIS was performed to check the variation in the impedance response of the Group V set of samples (Table 7) one having dense microstructure and the other columnar microstructure.
Table 7 Specimen description of EB-PVD TBCs investigated using EIS as a function of density.

<table>
<thead>
<tr>
<th>Group</th>
<th>Chemistry Variable</th>
<th>TBC Processing</th>
<th>Microstructure Variable</th>
<th>Specification</th>
<th>Thermal Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td>7YSZ</td>
<td>EB-PVD</td>
<td>Columnar Microstructure+</td>
<td>Dense</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Columnar</td>
<td></td>
</tr>
</tbody>
</table>

Note: * Qualitative observation made by optical and scanning electron microscopy.

3.7 Electrochemical Impedance Spectroscopy

EIS measurements were conducted using three-electrodes flat cell and IM6e BAS ZAHNER™ frequency response analyzer. The flat cell consists of platinum mesh auxiliary electrode, calomel reference electrode and the working or the test electrode to which the sample is connected (Figure 29). Circular area of diameter 1cm of TBC is exposed to the electrolyte. The electrolyte used was 0.01M (molar) Potassium Ferri/Ferro Cyanide \( \{K_3Fe(CN)_6/K_4Fe(CN)_6\cdot3H_2O\} \) solution. This is the chosen solution as electrolyte because it has highly reversible (redox) electrochemical exchange current density and does not interfere with the system. A typical experimental setup is as shown in Figure 30. Frequency range of 10 mHz to 1 MHz was used at a voltage of 10 mV.

Once the sample is loaded in the cell, a hold-time of a few minutes was followed in order for the DC potential to stabilize, i.e. the electrolyte has to penetrate through the pores of the TBCs. All impedance measurements were made three times per specimen for statistically confident analysis.
Figure 29. A 3-Dimensional Illustration of the standard flat cell.

Figure 30. A schematic illustration of instrumentation setup for electrochemical impedance spectroscopy. [92]
3.8 EIS Models for EB-PVD TBCs

The as-coated TBCs consist of a ceramic topcoat with porosity, bond coat, and substrate. In addition, the as-coated EB-PVD TBCs have very thin and uniformly developed TGO. As a result, the electrical impedance in EIS measurement will be attributed to the electrolyte resistance (conductivity of the electrolyte), ceramic topcoat (thickness), porosity in the topcoat, TGO and the interface between the TGO and bond coat.\[93] A model employed in this study is shown in Figure 31. The parameters used in the circuit are explained in Table 8. In this circuit for EB-PVD TBCs, an ideal capacitor is used rather than a constant phase element (CPE). This is because of the relatively smooth surface of the YSZ as well as the interface between the TGO and bond coat.

![Figure 31. A schematic microstructure of as-coated EB-PVD TBCs and the corresponding AC equivalent circuit employed for electrochemical impedance spectroscopy.](image-url)
Table 8 Description of abbreviations used in the ac electrical circuit for the models.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_S$</td>
<td>Solution resistance between the reference electrode and the topcoat surface</td>
</tr>
<tr>
<td>$R_{YSZ}$</td>
<td>The resistance of the ceramic topcoat</td>
</tr>
<tr>
<td>$C_{YSZ}$</td>
<td>The capacitance of the ceramic topcoat</td>
</tr>
<tr>
<td>$R_{PORE}$</td>
<td>The resistance of the pore (summation of the defects in the ceramic topcoat)</td>
</tr>
<tr>
<td>$C_{PORE}$</td>
<td>The capacitance of the pore (summation of the defects in the ceramic topcoat)</td>
</tr>
<tr>
<td>$R_T$</td>
<td>The transmission resistance of the double layer at the interface between the ceramic topcoat and the metallic bond coat</td>
</tr>
<tr>
<td>$C_T$</td>
<td>The capacitance of the double layer at the interface between the ceramic topcoat and the metallic bond coat</td>
</tr>
<tr>
<td>$R_{TGO}$</td>
<td>The resistance of the thermally grown oxide</td>
</tr>
<tr>
<td>$C_{TGO}$</td>
<td>The capacitance of the thermally grown oxide</td>
</tr>
</tbody>
</table>

3.9 EIS Models for YSZ

The electrochemical impedance of the YSZ monoliths in the EIS measurement system can be attributed to the electrolyte, YSZ thickness, porosity/density in the YSZ and interface between the YSZ/carbon paint (electrode) contacts. Therefore, the EIS ac equivalent circuit for the YSZ monoliths was modeled as shown in Figure 32. The circuit for YSZ monoliths consists of constant phase elements in the place of an ideal capacitor, because of the YSZ surface defects such as the pores that give rise to frequency dispersion and non-uniform distribution in the current density. The parameters used in the circuit are reported in Table 8.
Figure 32. EIS AC Equivalent circuit for ZrO$_2$- 7~8 wt.% Y$_2$O$_3$ with open pores.

3.10 EIS Models for Nickel Aluminide

The EIS ac equivalent circuit model for the nickel aluminide is shown in Figure 33. The electrochemical impedance response of this system depends on the electrolyte, thermally grown oxide (primarily alumina), the interface between the oxide and NiAl. NiAl is highly conductive and the electrical impedance is assumed negligible because it has very low resistivity.$^{[95]}$ The parameters used in the circuit are explained in Table 8.
3.11 EIS Model for as-coated APS (YSZ and CAT) and DVC TBCs

The as-coated samples consist of ceramic topcoat with porosity, bond coat, and substrate. As a result, the electrical impedance in EIS measurement will be attributed to the electrolyte resistance (conductivity of the electrolyte), ceramic topcoat (thickness), porosity in the topcoat and the interface between topcoat/ bond coat. A model is suggested in Figure 34. In the as-coated condition for APS and DVC TBCs, there is no significant presence of TGO. Hence, the TGO is not represented in terms of the electrical parameters. The circuit for APS and DVC TBC consists of constant phase elements in the place of an ideal capacitor, because of the YSZ (and CAT) surface roughness and the
YSZ (and CAT)-bond coat interfacial roughness that give rise to frequency dispersion due to the non-uniform distribution in the current density. [90,96] The parameters used in the circuit are explained in Table 8.

Figure 34. A typical microstructure of YSZ and CAT TBCs and the corresponding AC Equivalent circuit employed for the EIS.
4 RESULTS

4.1 Sintering of Yttria Stabilized Zirconia

TBCs investigated were a multi layer system consisting of ceramic topcoat, bond coat, and the superalloy. In order to prove the results obtained earlier for TBCs individual layers were investigated using EIS and scanning electron microscopy. Prior to EIS and SEM, YSZ monoliths were sintered as explained in the experimental section. Resistance and capacitance determined were based on the equivalent circuit shown in Figure 32. The accepted fitting error for this circuit was less than 5%. Typical Nyquist and impedance plots are shown in Figure 35a and 35b respectively. The resistance and the capacitance values for all the specimens investigated are presented in Table 9-15. Table 9-14 presents EIS results for YSZ specimens sintered and cooled at room temperature. Table 15 presents EIS result for YSZ of density 4.07g/cm³ and thickness 4mm sintered at 1300°C for five and ten hours and furnace cooled.

Consistently there was increase in resistance of YSZ and corresponding decrease in the capacitance with the increase in YSZ thickness, sintering temperature, and time as shown in Figures 36 to 40. In addition, the resistance values increase after 2 hours and 5 hours but have remained fairly constant after 10 hours of sintering. The key observation here was decrease in resistance and corresponding increase in capacitance for YSZ specimen of density 4.07g/cm³ of thickness 4mm when exposed to sintering temperature of 1300°C for five and 10 hours with room cooling as seen in Figure 41. Figure 41 also shows macrograph of the YSZ samples having macrocracks.
Since the YSZ samples of density 4.07g/cm$^3$ of thickness 4mm cracked when quenched after exposure to 1300°C for 5 and 10 hours, similar samples were prepared and sintered at same temperature and time and were furnace cooled to prevent cracking. EIS were performed on them and the results are shown in Figure 42. There is increase in resistance and corresponding decrease in capacitance of the YSZ.

After EIS, the samples were prepared for the microstructure as explained in the earlier section for YSZ of different densities, sintering temperature and time. The SEM micrographs clearly indicate the densification of YSZ with increase in the sintering temperature and holding time as shown in Figure 43. The values of the n for the sintered YSZ (Table 9-15) vary from 0.5-0.6. This is an indication of the roughness of the YSZ surface which is clearly shown in Figure 43.

![Figure 35. Typical (a) Nyquist and (b) Impedance plot for YSZ sintered at different times.](image)

72
<table>
<thead>
<tr>
<th>Time</th>
<th>$R_S$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>n</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_P$ (µF)</th>
<th>n</th>
<th>$R_P$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>54.19±3.2</td>
<td>3.69±0.54</td>
<td>0.53</td>
<td>137.7±3.55</td>
<td>1.24±0.14</td>
<td>0.134</td>
<td>707.4±42.4</td>
</tr>
<tr>
<td>5 Hours</td>
<td>54.11±0.3</td>
<td>2.89±0.2</td>
<td>0.55</td>
<td>146.66±0.56</td>
<td>1.68±0.12</td>
<td>0.14</td>
<td>885.93±90</td>
</tr>
<tr>
<td>10 Hours</td>
<td>29.11±1.7</td>
<td>1.252±0.1</td>
<td>0.57</td>
<td>150.5±6</td>
<td>5.53±0.12</td>
<td>0.136</td>
<td>734.33±6.5</td>
</tr>
</tbody>
</table>

Temperature 1100°C

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_S$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>n</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_P$ (µF)</th>
<th>n</th>
<th>$R_P$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>20.27±0.4</td>
<td>3.21±0.18</td>
<td>0.54</td>
<td>190.3±2.52</td>
<td>2.061±0.32</td>
<td>0.14</td>
<td>163±3</td>
</tr>
<tr>
<td>5 Hours</td>
<td>21.63±0.8</td>
<td>2.21±0.18</td>
<td>0.59</td>
<td>208.43±5.52</td>
<td>6.02±0.16</td>
<td>0.16</td>
<td>126.9±0.81</td>
</tr>
<tr>
<td>10 Hours</td>
<td>11.3±1.05</td>
<td>1.24±0.04</td>
<td>0.62</td>
<td>209.77±15</td>
<td>2.16±0.14</td>
<td>0.156</td>
<td>169.8±23.6</td>
</tr>
</tbody>
</table>

Temperature 1200°C

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_S$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>n</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_P$ (µF)</th>
<th>n</th>
<th>$R_P$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>20.77±0.3</td>
<td>3.17±0.03</td>
<td>0.59</td>
<td>241.57±3.6</td>
<td>8.31±0.24</td>
<td>0.19</td>
<td>219.57±2.1</td>
</tr>
<tr>
<td>5 Hours</td>
<td>32.96±0.9</td>
<td>1.726±0.28</td>
<td>0.6</td>
<td>258.4±7.3</td>
<td>2.083±0.66</td>
<td>0.192</td>
<td>232.9±71.4</td>
</tr>
<tr>
<td>10 Hours</td>
<td>28.37±1.2</td>
<td>1.25±0.05</td>
<td>0.65</td>
<td>271.4±7.15</td>
<td>0.81±0.04</td>
<td>0.21</td>
<td>327.63±7.26</td>
</tr>
</tbody>
</table>

Note: * AR = As Received
Table 10 EIS results for YSZ; Density 3.85g/cm<sup>3</sup>; Thickness 3mm, Room Cooled

<table>
<thead>
<tr>
<th></th>
<th>( R_S ) (Ω)</th>
<th>( C_{YSZ} ) (nF)</th>
<th>n</th>
<th>( R_{YSZ} ) (Ω)</th>
<th>( C_P ) (µF)</th>
<th>n</th>
<th>( R_P ) (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR*</td>
<td>39.87±2</td>
<td>3.69±0.1</td>
<td>0.51</td>
<td>241.3±3.3</td>
<td>5.208±0.21</td>
<td>0.13</td>
<td>131.7±3.3</td>
</tr>
</tbody>
</table>

**Temperature 1100°C**

<table>
<thead>
<tr>
<th>Time</th>
<th>( R_S ) (Ω)</th>
<th>( C_{YSZ} ) (nF)</th>
<th>n</th>
<th>( R_{YSZ} ) (Ω)</th>
<th>( C_P ) (µF)</th>
<th>n</th>
<th>( R_P ) (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>24.87±0.5</td>
<td>2.95±0.1</td>
<td>0.52</td>
<td>255.43±4.5</td>
<td>5.59±0.22</td>
<td>0.14</td>
<td>203.43±0.32</td>
</tr>
<tr>
<td>5 Hours</td>
<td>26.03±1</td>
<td>2.72±0.15</td>
<td>0.545</td>
<td>265.3±4.9</td>
<td>5.46±0.5</td>
<td>0.14</td>
<td>205.1±4.6</td>
</tr>
<tr>
<td>10 Hours</td>
<td>22.34±2.9</td>
<td>2.42±0.18</td>
<td>0.57</td>
<td>266.83±4.7</td>
<td>2.56±0.26</td>
<td>0.16</td>
<td>188.63±16</td>
</tr>
</tbody>
</table>

**Temperature 1200°C**

<table>
<thead>
<tr>
<th>Time</th>
<th>( R_S ) (Ω)</th>
<th>( C_{YSZ} ) (nF)</th>
<th>n</th>
<th>( R_{YSZ} ) (Ω)</th>
<th>( C_P ) (µF)</th>
<th>n</th>
<th>( R_P ) (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>24.97±0.5</td>
<td>1.22±0.02</td>
<td>0.55</td>
<td>266.17±5.8</td>
<td>3.66±0.54</td>
<td>0.134</td>
<td>118.5±18.1</td>
</tr>
<tr>
<td>5 Hours</td>
<td>23.98±2.05</td>
<td>1.14±0.01</td>
<td>0.59</td>
<td>269±7</td>
<td>3.54±0.6</td>
<td>0.15</td>
<td>99.09±12.8</td>
</tr>
<tr>
<td>10 Hours</td>
<td>21.67±0.22</td>
<td>0.82±0</td>
<td>0.61</td>
<td>275.8±1.44</td>
<td>3.43±0.1</td>
<td>0.16</td>
<td>96.05±10.1</td>
</tr>
</tbody>
</table>

**Temperature 1300°C**

<table>
<thead>
<tr>
<th>Time</th>
<th>( R_S ) (Ω)</th>
<th>( C_{YSZ} ) (nF)</th>
<th>n</th>
<th>( R_{YSZ} ) (Ω)</th>
<th>( C_P ) (µF)</th>
<th>n</th>
<th>( R_P ) (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>18.12±1.5</td>
<td>1.18±0</td>
<td>0.58</td>
<td>272.75±2.6</td>
<td>7.861±0.18</td>
<td>0.18</td>
<td>253.5±3.5</td>
</tr>
<tr>
<td>5 Hours</td>
<td>16.32±0.9</td>
<td>1.076±0.01</td>
<td>0.6</td>
<td>278.25±3.6</td>
<td>6.817±0.33</td>
<td>0.21</td>
<td>257.05±0.8</td>
</tr>
<tr>
<td>10 Hours</td>
<td>10.16±1</td>
<td>0.77±0.01</td>
<td>0.62</td>
<td>280.2±1.18</td>
<td>11.79±15</td>
<td>0.23</td>
<td>263.1±33.8</td>
</tr>
</tbody>
</table>

Note: * AR = As Received
Table 11 EIS results for YSZ; Density 3.85 g/cm³; Thickness 4mm, Room Cooled

<table>
<thead>
<tr>
<th></th>
<th>$R_s$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>n</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_p$ (µF)</th>
<th>n</th>
<th>$R_p$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR*</td>
<td>38.1±3.2</td>
<td>3.01±0.05</td>
<td>0.51</td>
<td>258.95±4</td>
<td>2.598±0.29</td>
<td>0.13</td>
<td>228.75±34</td>
</tr>
</tbody>
</table>

Temperature 1100°C

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_s$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>n</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_p$ (µF)</th>
<th>n</th>
<th>$R_p$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>21.64±1.12</td>
<td>2.989±0</td>
<td>0.51</td>
<td>279.1±0.3</td>
<td>2.342±0.06</td>
<td>0.135</td>
<td>220.5±15</td>
</tr>
<tr>
<td>5 Hours</td>
<td>27.475±0.27</td>
<td>2.926±0.1</td>
<td>0.538</td>
<td>290±1.13</td>
<td>4.926±0.14</td>
<td>0.14</td>
<td>215.65±0.1</td>
</tr>
<tr>
<td>10 Hours</td>
<td>17.73±2.5</td>
<td>2.5065±0.2</td>
<td>0.56</td>
<td>294.1±0.3</td>
<td>2.9655±0.5</td>
<td>0.14</td>
<td>202.7±0.3</td>
</tr>
</tbody>
</table>

Temperature 1200°C

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_s$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>n</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_p$ (µF)</th>
<th>n</th>
<th>$R_p$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>24.51±1.21</td>
<td>1.197±0</td>
<td>0.58</td>
<td>281.9±1.27</td>
<td>2.465±0.5</td>
<td>0.15</td>
<td>77.85±1.1</td>
</tr>
<tr>
<td>5 Hours</td>
<td>23.14±0.84</td>
<td>1.1455±0</td>
<td>0.613</td>
<td>294.6±1.97</td>
<td>2.275±0.15</td>
<td>0.154</td>
<td>81.06±1.4</td>
</tr>
<tr>
<td>10 Hours</td>
<td>14.84±1.55</td>
<td>0.821±0.02</td>
<td>0.63</td>
<td>298.13±1.9</td>
<td>1.41±0.67</td>
<td>0.158</td>
<td>69.89±3.1</td>
</tr>
</tbody>
</table>

Temperature 1300°C

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_s$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>n</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_p$ (µF)</th>
<th>n</th>
<th>$R_p$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>26.95±0.3</td>
<td>1.1595±0</td>
<td>0.61</td>
<td>296.8±4.1</td>
<td>5.829±0.5</td>
<td>0.17</td>
<td>130.35±1.3</td>
</tr>
<tr>
<td>5 Hours</td>
<td>18.83±0.1</td>
<td>1.13±0</td>
<td>0.628</td>
<td>299.5±6</td>
<td>8.33±0.35</td>
<td>0.22</td>
<td>146±2.5</td>
</tr>
<tr>
<td>10 Hours</td>
<td>13.165±1.27</td>
<td>0.769±0</td>
<td>0.66</td>
<td>307.6±7.9</td>
<td>1.63±0.12</td>
<td>0.24</td>
<td>454.7±43.2</td>
</tr>
</tbody>
</table>

Note: * AR = As Received
Table 12 EIS results for YSZ; Density 4.07 g/cm³; Thickness 2mm, Room Cooled

<table>
<thead>
<tr>
<th></th>
<th>$R_S$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>n</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_P$ (µF)</th>
<th>n</th>
<th>$R_P$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR*</td>
<td>60.71±0.66</td>
<td>2.58±0.12</td>
<td>0.53</td>
<td>212.13±3.18</td>
<td>0.941±0.19</td>
<td>0.14</td>
<td>257.83±22</td>
</tr>
<tr>
<td><strong>Temperature 1100°C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>$R_S$ (Ω)</td>
<td>$C_{YSZ}$ (nF)</td>
<td>n</td>
<td>$R_{YSZ}$ (Ω)</td>
<td>$C_P$ (µF)</td>
<td>n</td>
<td>$R_P$ (Ω)</td>
</tr>
<tr>
<td>2 Hours</td>
<td>25.8±0.9</td>
<td>2.28±0.12</td>
<td>0.5</td>
<td>256.5±8.4</td>
<td>2.51±0.2</td>
<td>0.12</td>
<td>109.7±4.8</td>
</tr>
<tr>
<td>5 Hours</td>
<td>29.54±1.14</td>
<td>1.969±0</td>
<td>0.53</td>
<td>278.55±0.5</td>
<td>3.075±0.8</td>
<td>0.15</td>
<td>132.6±21.5</td>
</tr>
<tr>
<td>10 Hours</td>
<td>30.14±2.7</td>
<td>1.65±0.1</td>
<td>0.56</td>
<td>284.67±4.2</td>
<td>2.79±0.15</td>
<td>0.15</td>
<td>102.65±4.6</td>
</tr>
<tr>
<td><strong>Temperature 1200°C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>$R_S$ (Ω)</td>
<td>$C_{YSZ}$ (nF)</td>
<td>n</td>
<td>$R_{YSZ}$ (Ω)</td>
<td>$C_P$ (µF)</td>
<td>n</td>
<td>$R_P$ (Ω)</td>
</tr>
<tr>
<td>2 Hours</td>
<td>26.35±0.4</td>
<td>2.12±0.03</td>
<td>0.58</td>
<td>272.8±7.17</td>
<td>9.44±9.7</td>
<td>0.14</td>
<td>131.7±9.8</td>
</tr>
<tr>
<td>5 Hours</td>
<td>19.76±5.6</td>
<td>1.84±0.1</td>
<td>0.59</td>
<td>284.65±1</td>
<td>3.74±1.33</td>
<td>0.163</td>
<td>333.55±16</td>
</tr>
<tr>
<td>10 Hours</td>
<td>18.79±2.41</td>
<td>1.476±0.05</td>
<td>0.62</td>
<td>297.2±3.3</td>
<td>3.092±0.52</td>
<td>0.165</td>
<td>171.1±31</td>
</tr>
<tr>
<td><strong>Temperature 1300°C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>$R_S$ (Ω)</td>
<td>$C_{YSZ}$ (nF)</td>
<td>n</td>
<td>$R_{YSZ}$ (Ω)</td>
<td>$C_P$ (µF)</td>
<td>n</td>
<td>$R_P$ (Ω)</td>
</tr>
<tr>
<td>2 Hours</td>
<td>24.55±0.56</td>
<td>1.81±0.04</td>
<td>0.59</td>
<td>300.85±5.86</td>
<td>2.95±0.07</td>
<td>0.14</td>
<td>255.3±0.56</td>
</tr>
<tr>
<td>5 Hours</td>
<td>17.39±4.07</td>
<td>1.583±0.03</td>
<td>0.61</td>
<td>306.57±3.67</td>
<td>2.35±0.7</td>
<td>0.15</td>
<td>222.77±12.9</td>
</tr>
<tr>
<td>10 Hours</td>
<td>12.33±2.28</td>
<td>1.36±0.05</td>
<td>0.6</td>
<td>313.27±13.9</td>
<td>1.01±0.75</td>
<td>0.18</td>
<td>166.17±12.2</td>
</tr>
</tbody>
</table>

Note: * AR = As Received
Table 13 EIS results for YSZ; Density 4.07 g/cm$^3$; Thickness 3mm, Room Cooled

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_S$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>n</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_{P}$ (μF)</th>
<th>n</th>
<th>$R_P$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR*</td>
<td>65.59±1.4</td>
<td>2.4±0.09</td>
<td>0.53</td>
<td>241.13±5.6</td>
<td>0.75±0.12</td>
<td>0.14</td>
<td>221.33±11.9</td>
</tr>
</tbody>
</table>

Temperature 1100°C

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_S$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>n</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_{P}$ (μF)</th>
<th>n</th>
<th>$R_P$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>30.49±0.8</td>
<td>2.1±0.11</td>
<td>0.52</td>
<td>312.35±5.8</td>
<td>2.05±0.4</td>
<td>0.14</td>
<td>125.3±7.7</td>
</tr>
<tr>
<td>5 Hours</td>
<td>31.83±0.8</td>
<td>1.79±0.02</td>
<td>0.54</td>
<td>326.8±8</td>
<td>2.5±0.4</td>
<td>0.15</td>
<td>125.6±11.9</td>
</tr>
<tr>
<td>10 Hours</td>
<td>29.81±1.6</td>
<td>1.51±0.05</td>
<td>0.58</td>
<td>332.8±3</td>
<td>1.98±0.26</td>
<td>0.15</td>
<td>128.5±5.8</td>
</tr>
</tbody>
</table>

Temperature 1200°C

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_S$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>n</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_{P}$ (μF)</th>
<th>n</th>
<th>$R_P$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>31±0.5</td>
<td>1.96±0.02</td>
<td>0.55</td>
<td>340±6.4</td>
<td>5.836±5</td>
<td>0.15</td>
<td>153.608±5.3</td>
</tr>
<tr>
<td>5 Hours</td>
<td>25.275±3.1</td>
<td>1.69±0.05</td>
<td>0.59</td>
<td>348.7±2.6</td>
<td>3.61±0.7</td>
<td>0.17</td>
<td>274.7±8.2</td>
</tr>
<tr>
<td>10 Hours</td>
<td>19.62±4.6</td>
<td>1.4±0.1</td>
<td>0.61</td>
<td>354.5±2.8</td>
<td>2.7±0.4</td>
<td>0.165</td>
<td>137.1±28.3</td>
</tr>
</tbody>
</table>

Temperature 1300°C

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_S$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>n</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_{P}$ (μF)</th>
<th>n</th>
<th>$R_P$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>26.295±1</td>
<td>1.75±0.1</td>
<td>0.55</td>
<td>359.2±5.7</td>
<td>2.25±0.05</td>
<td>0.156</td>
<td>216.05±2</td>
</tr>
<tr>
<td>5 Hours</td>
<td>20.43±2.9</td>
<td>1.44±0.06</td>
<td>0.59</td>
<td>362.16±3.1</td>
<td>1.73±0.67</td>
<td>0.17</td>
<td>206.45±13</td>
</tr>
<tr>
<td>10 Hours</td>
<td>19.36±2.4</td>
<td>1.25±0.06</td>
<td>0.61</td>
<td>387.3±11</td>
<td>3.57±2.87</td>
<td>0.19</td>
<td>217.02±27</td>
</tr>
</tbody>
</table>

Note: * AR = As Received
### Table 14 EIS results for YSZ; Density 4.07/cm³; Thickness 4mm, Room Cooled

<table>
<thead>
<tr>
<th></th>
<th>$R_S$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>$n$</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_P$ (µF)</th>
<th>$n$</th>
<th>$R_P$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR*</td>
<td>70.48±2.1</td>
<td>2.23±0.05</td>
<td>0.53</td>
<td>270.13±8</td>
<td>0.56±0.07</td>
<td>0.14</td>
<td>184.83±1.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Temperature 1100°C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>$R_S$ (Ω)</td>
<td>$C_{YSZ}$ (nF)</td>
<td>$n$</td>
<td>$R_{YSZ}$ (Ω)</td>
<td>$C_P$ (µF)</td>
<td>$n$</td>
<td>$R_P$ (Ω)</td>
</tr>
<tr>
<td>2 Hours</td>
<td>35.11±0.78</td>
<td>1.92±0.11</td>
<td>0.516</td>
<td>368.2±3.3</td>
<td>1.49±0.65</td>
<td>0.13</td>
<td>141.03±10</td>
</tr>
<tr>
<td>5 Hours</td>
<td>34.12±0.5</td>
<td>1.626±0.03</td>
<td>0.53</td>
<td>375.2±15.5</td>
<td>2.067±0.08</td>
<td>0.145</td>
<td>118.7±2.4</td>
</tr>
<tr>
<td>10 Hours</td>
<td>29.465±0.4</td>
<td>1.3715±0.04</td>
<td>0.56</td>
<td>380.95±1.9</td>
<td>1.175±0.37</td>
<td>0.16</td>
<td>154.4±7.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Temperature 1200°C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>$R_S$ (Ω)</td>
<td>$C_{YSZ}$ (nF)</td>
<td>$n$</td>
<td>$R_{YSZ}$ (Ω)</td>
<td>$C_P$ (µF)</td>
<td>$n$</td>
<td>$R_P$ (Ω)</td>
</tr>
<tr>
<td>2 Hours</td>
<td>35.74±0.5</td>
<td>1.808±0.02</td>
<td>0.54</td>
<td>407.2±5.6</td>
<td>2.227±0.11</td>
<td>0.15</td>
<td>175.45±0.9</td>
</tr>
<tr>
<td>5 Hours</td>
<td>30.79±0.7</td>
<td>1.555±0.04</td>
<td>0.53</td>
<td>412.75±4.31</td>
<td>3.495±0.09</td>
<td>0.145</td>
<td>215.85±0.07</td>
</tr>
<tr>
<td>10 Hours</td>
<td>18.73±6.9</td>
<td>1.33±0.1</td>
<td>0.59</td>
<td>415.63±2.2</td>
<td>1.969±0.24</td>
<td>0.17</td>
<td>136.4±25.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Temperature 1300°C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>$R_S$ (Ω)</td>
<td>$C_{YSZ}$ (nF)</td>
<td>$n$</td>
<td>$R_{YSZ}$ (Ω)</td>
<td>$C_P$ (µF)</td>
<td>$n$</td>
<td>$R_P$ (Ω)</td>
</tr>
<tr>
<td>2 Hours</td>
<td>28.04±1.5</td>
<td>1.674±0.1</td>
<td>0.55</td>
<td>417.7±5.6</td>
<td>1.557±0.04</td>
<td>0.137</td>
<td>176.8±3.45</td>
</tr>
<tr>
<td>5 Hours</td>
<td>26.51±1.79</td>
<td>1.704±0.1</td>
<td>0.57</td>
<td>402.27±15</td>
<td>1.67±0.1</td>
<td>0.16</td>
<td>207.2±3.04</td>
</tr>
<tr>
<td>10 Hours</td>
<td>24.085±1.42</td>
<td>2.365±0.52</td>
<td>0.54</td>
<td>365.95±16.89</td>
<td>2.2995±0.3</td>
<td>0.19</td>
<td>260.1±2.4</td>
</tr>
</tbody>
</table>

Note: * AR = As Received

### Table 15 EIS results for YSZ; Density 4.07/cm³; Thickness 4mm, Temperature 1300°C; Furnace Cooled

<table>
<thead>
<tr>
<th></th>
<th>$R_S$ (Ω)</th>
<th>$C_{YSZ}$ (nF)</th>
<th>$n$</th>
<th>$R_{YSZ}$ (Ω)</th>
<th>$C_P$ (µF)</th>
<th>$n$</th>
<th>$R_P$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 Hours</td>
<td>23.47±1.8</td>
<td>1.29±0.1</td>
<td>0.62</td>
<td>417.76±2.4</td>
<td>1.12±0.58</td>
<td>0.18</td>
<td>190.1±14</td>
</tr>
<tr>
<td>10 Hours</td>
<td>26.4±2.5</td>
<td>1.15±0.1</td>
<td>0.69</td>
<td>461.4±8.7</td>
<td>6.131±5</td>
<td>0.21</td>
<td>267.8±41</td>
</tr>
</tbody>
</table>
Figure 36. Variation in (a) Resistance and (b) Capacitance of YSZ: Density 3.85g/cm³; Thickness 2mm
Figure 37. Variation in (a) Resistance and (b) Capacitance of YSZ: Density 3.85g/cm$^3$; Thickness 3mm
Figure 38. Variation in (a) Resistance and (b) Capacitance of YSZ: Density 3.85g/cm$^3$; Thickness 4mm
Figure 39. Variation in (a) Resistance and (b) Capacitance of YSZ: Density 4.07g/cm$^3$; Thickness 2mm.
Figure 40. Variation in (a) Resistance and (b) Capacitance of YSZ: Density 4.07g/cm³; Thickness 3mm.
Figure 41. Variation in (a) Resistance and (b) Capacitance of YSZ: Density 4.07g/cm³; Thickness 4mm; Quenched at atmosphere.
Figure 42. Variation in (a) Resistance and (b) Capacitance of YSZ: Density 4.07g/cm³; Thickness 4mm. (Air quenched and Furnace Cooled)
4.2 Isothermal Exposure of Nickel Aluminide

The bond coat was investigated to get a clear understanding of the individual layers of TBC. With the oxidation of the bond coat there is a growth of thin layer of thermally grown oxide as described in the earlier section. Hence, NiAl has been chosen as a bond coat material for investigations. EIS and scanning electron microscopy was carried out on the NiAl discs. Resistance and capacitance determined were based on the equivalent circuit shown in Figure 33. The accepted fitting error for this equivalent circuit was less than 8%. Typical Nyquist and impedance plots are shown in Figure 44 a and b. The resistance and the capacitance values for all the specimens investigated are presented in Table 16. Secondary electron and back-scattered electron micrographs of the top surface of NiAl are shown in Figures 46-48 at varying isothermal temperatures namely 1100°C, 1200°C, and 1300°C. The results obtained from EIS shows that there is an increase in the resistance of the TGO and corresponding decrease in capacitance of TGO.
with the increase in temperature and holding time for 1100°C and 1200°C. However, for 1300°C after 5 hours and 10 hours of holding time there is a decrease in the TGO resistance and a corresponding increase in the capacitance as shown in Figure 45a and b respectively. SEM was carried out on the top surface of the NiAl. After 1300°C exposure for 5 and 10 hours, spallation of alumina was observed and shown in Figure 48 with the exposure of metal (NiAl) surface. With the metal surface exposed a decrease in resistance $R_{\text{TGO}}$ was observed. From these micrographs it is evident that with the increase in time and temperature of isothermal oxidation the density of the alumina scale increases. Cross sectional samples were prepared as explained earlier to measure the thickness of the TGO (primarily alumina). After the thermal exposure, there is increase in the thickness of the TGO with temperature and time as presented in Table 17 and shown in Figure 49. The value of $n$ for the constant phase element for $C_{\text{TGO}}$ is more than 0.9 (Table 17). This is an indication that there is a uniform growth of the TGO with minimum or no contortion in the surface.

![Figure 44](image)

**Figure 44.** Typical (a) Nyquist plot and (b) Impedance plot for NiAl sample isothermally exposed at 1200°C for 5 hours.
Table 16 EIS results for NiAl isothermally exposed to various temperatures and holding times

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_S$ (Ω)</th>
<th>$C_{TGO}$ (nF)</th>
<th>$n$</th>
<th>$R_{TGO}$ (MΩ)</th>
<th>$C_T$ (nF)</th>
<th>$n$</th>
<th>$R_T$ (MΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>197.3±1.9</td>
<td>1690.5±3.5</td>
<td>0.95</td>
<td>0.021±0</td>
<td>5.04±0.1</td>
<td>0.92</td>
<td>23.87±33</td>
</tr>
<tr>
<td>5 Hours</td>
<td>192.1±4.9</td>
<td>1252±91.9</td>
<td>0.93</td>
<td>0.023±0</td>
<td>4.14±0.1</td>
<td>0.93</td>
<td>0.034±0</td>
</tr>
<tr>
<td>10 Hours</td>
<td>167.66±0.2</td>
<td>8.72±0.6</td>
<td>0.94</td>
<td>13.41±1.7</td>
<td>202.28±122</td>
<td>0.92</td>
<td>10.8±3.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_S$ (Ω)</th>
<th>$C_{TGO}$ (nF)</th>
<th>$n$</th>
<th>$R_{TGO}$ (MΩ)</th>
<th>$C_T$ (nF)</th>
<th>$n$</th>
<th>$R_T$ (MΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>177.4±1.8</td>
<td>373.25±8.69</td>
<td>0.95</td>
<td>0.044±0</td>
<td>10.72±0.12</td>
<td>0.92</td>
<td>0.012±0</td>
</tr>
<tr>
<td>5 Hours</td>
<td>168.25±1</td>
<td>252.95±33.5</td>
<td>0.95</td>
<td>0.049±0</td>
<td>8.42±0.1</td>
<td>0.93</td>
<td>0.0084±0</td>
</tr>
<tr>
<td>10 Hours</td>
<td>174.43±0.9</td>
<td>5.69±0.02</td>
<td>0.97</td>
<td>18.73±0.1</td>
<td>91.59±3.2</td>
<td>0.91</td>
<td>9.57±1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>$R_S$ (Ω)</th>
<th>$C_{TGO}$ (nF)</th>
<th>$n$</th>
<th>$R_{TGO}$ (MΩ)</th>
<th>$C_T$ (nF)</th>
<th>$n$</th>
<th>$R_T$ (MΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Hours</td>
<td>312.6±0.29</td>
<td>52.81±1.6</td>
<td>0.95</td>
<td>0.581±0.02</td>
<td>7.018±0.1</td>
<td>0.91</td>
<td>0.049±0</td>
</tr>
<tr>
<td>5 Hours</td>
<td>155.55±1.9</td>
<td>651.8±90</td>
<td>0.96</td>
<td>0.034±0</td>
<td>4.77±0</td>
<td>0.93</td>
<td>0.0053±0</td>
</tr>
<tr>
<td>10 Hours</td>
<td>176.2±4.8</td>
<td>25920±1494</td>
<td>0.98</td>
<td>0.0097±0</td>
<td>30.52±1.6</td>
<td>0.94</td>
<td>11.77±16</td>
</tr>
</tbody>
</table>

![Figure 45. Variation in (a) Resistance and (b) Capacitance of TGO with isothermal exposure.](image)
Figure 46. Top surface secondary (SE) and backscatter (BSE) scanning electron micrographs for NiAl exposed at 1100°C.

Figure 47. Top surface secondary (SE) and backscatter (BSE) scanning electron micrographs for NiAl exposed at 1200°C.
Figure 48. Top surface secondary (SE) and backscatter (BSE) scanning electron micrographs for NiAl exposed at 1300°C. Clear indication of metal surface exposed.

Table 17 TGO Thickness Measurement for varying temperatures and holding time.

<table>
<thead>
<tr>
<th>Temperature 1100°C</th>
<th>Temperature 1200°C</th>
<th>Temperature 1300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposure Time</td>
<td>Thickness (µm)</td>
<td>Exposure Time</td>
</tr>
<tr>
<td>2hrs</td>
<td>0.9 ± 0.13</td>
<td>2hrs</td>
</tr>
<tr>
<td>5hrs</td>
<td>1.3 ± 0.26</td>
<td>5hrs</td>
</tr>
<tr>
<td>10hrs</td>
<td>1.8 ± 0.13</td>
<td>10hrs</td>
</tr>
</tbody>
</table>

Note: TGO thickness measurements made at magnification 2000X and 5000X
Figure 49. Scanning backscatter electron micrographs of NiAl subjected to isothermal exposure showing the growth of TGO.

4.3 Isothermal Exposure of EB-PVD TBCs

Five disks of EB-PVD TBCs were isothermally oxidized at 1121°C for 50, 100, 250, 400 and 600 h. Upon cooling to room temperature, the TBC with 600 h of isothermal oxidation failed by spallation of approximately 50% of the sample area. The remaining TBC (50% by area) was sufficient to carry out EIS measurement with consistent measurement area. A macrograph of top surface of the samples isothermally exposed is shown in Figure 50. The isothermally oxidized TBCs were non-destructively
examined by EIS. Typical Nyquist and Bode plots for an isothermally oxidized EB-PVD TBC specimen is shown in Figure 51. This electrochemical impedance is simulated with the equivalent circuit shown in Figure 31 by non-linear square-fit with least-square error less than 10%, and the resistance and capacitance of each TBC constituent were determined. Variations in the resistance and capacitance of the YSZ and TGO, namely, $R_{YSZ}$, $C_{YSZ}$, $R_{TGO}$, and $C_{TGO}$, as a function of isothermal oxidation time are shown in Figure 37 and the values are presented in Table 18. With an increase in time of the isothermal oxidation, there is an initial increase in $R_{YSZ}$. With the prolonged oxidation at high temperature, a decrease in $R_{YSZ}$ was observed after 250 h of oxidation. While this decrease in the $R_{YSZ}$ was gradual until 600 hours, at which failure was observed, the corresponding increase in the capacitance was abrupt only after 600 hours of oxidation as shown in Figure 52b. The TGO resistance and capacitance also exhibited an initial increase and the corresponding decrease, respectively, with time. Similar to $R_{YSZ}$, $R_{TGO}$ decreased gradually after 100 h of isothermal oxidation until failure at 600 h; however, an increase in $C_{TGO}$ at 600 h was abrupt as shown in Figure 52d. The growth of TGO during the isothermal oxidation at 1121°C is shown by secondary electron micrographs in Figure 53 as a function of thermal cycles. The variation of thickness is shown in Table 19.

![Macrographs showing the top surface of isothermally exposed EB-PVD TBCs with spallation of the top surface at 600 Hours.](image)

Figure 50.
Figure 51. Typical (a) Nyquist plot and (b) Bode plot for EB-PVD TBCs isothermally exposed at 1121°C for 250 Hours.

Table 18 EIS Results for Isothermally exposed EB-PVD TBCs

<table>
<thead>
<tr>
<th>Specimen ID</th>
<th>Isothermal Hours</th>
<th>Cc (nF)</th>
<th>Rc (KΩ)</th>
<th>(C_{\text{TGO}}) (nF)</th>
<th>(R_{\text{TGO}}) (KΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD61</td>
<td>50</td>
<td>7.1 ± 0</td>
<td>27.7 ± 0.15</td>
<td>23.4 ± 0.26</td>
<td>122.7 ± 0.99</td>
</tr>
<tr>
<td>LD55</td>
<td>100</td>
<td>7.5 ± 0.05</td>
<td>33.8 ± 0.53</td>
<td>17.8 ± 0.21</td>
<td>123 ± 0.57</td>
</tr>
<tr>
<td>LD38</td>
<td>250</td>
<td>8.2 ± 0.26</td>
<td>49.2 ± 1.11</td>
<td>11.8 ± 0.85</td>
<td>72.4 ± 4.2</td>
</tr>
<tr>
<td>LD58</td>
<td>400</td>
<td>9.1 ± 0.65</td>
<td>18.3 ± 0.86</td>
<td>9.11 ± 0.15</td>
<td>53.9 ± 2.62</td>
</tr>
<tr>
<td>LE21</td>
<td>600</td>
<td>96500 ± 28991</td>
<td>3.6 ± 0.93</td>
<td>6017 ± 580</td>
<td>9.564 ± 1.11</td>
</tr>
</tbody>
</table>
Figure 52. Variation in (a) Resistance of YSZ (b) Capacitance of YSZ (c) Resistance of TGO and (d) Capacitance of TGO as a function of Isothermal Hours at 1121ºC for EB-PVD TBCs

Table 19 Measured thickness of the thermally grown oxide in EB-PVD TBCs isothermally oxidized at 1121ºC.

<table>
<thead>
<tr>
<th>Isothermal Hours</th>
<th>TGO Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.9 ± 0</td>
</tr>
<tr>
<td>100</td>
<td>2.9 ± 0.4</td>
</tr>
<tr>
<td>250</td>
<td>4 ± 0.3</td>
</tr>
<tr>
<td>400</td>
<td>5 ± 0.4</td>
</tr>
<tr>
<td>600</td>
<td>-NA-*</td>
</tr>
</tbody>
</table>

* After 600 Hours of isothermal exposure, TBC failed by spallation hence no thickness data available
4.4 Air Plasma Sprayed TBCs with varying density

Two specimens of the APS TBCs with varying density (65% and 73.6% theoretical density) were examined by EIS and scanning electron microscopy. Resistance and capacitance determined based on equivalent circuit as shown in Figure 34 without TGO are presented in Table 20. The accepted fitting error for this equivalent circuit was less than 8%. While many values of resistance and capacitance are similar, there is a difference in the capacitance of ceramic topcoat $C_C$ and resistance of ceramic topcoat as a function of density as shown in Figure 54a and b. The topcoat capacitance decreased with the increase in the density (i.e., decrease in porosity) and correspondingly the resistance of the topcoat increased. The variation in microstructure of these two TBCs is shown in Figure 55. The impedance and the nyquist plots are shown in Figure 56.
Table 20 EIS results for APS TBCs with varying densities.

<table>
<thead>
<tr>
<th>Density</th>
<th>(C_C) (pF)</th>
<th>(R_C) (Ω)</th>
<th>(C_P) (µF)</th>
<th>(R_P) (KΩ)</th>
<th>(C_T) (nF)</th>
<th>(R_T) (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65%</td>
<td>547 ± 24</td>
<td>412 ± 0.4</td>
<td>193 ± 7.5</td>
<td>5 ± 0.3</td>
<td>5 ± 0.1</td>
<td>197 ± 2</td>
</tr>
<tr>
<td>73.6%</td>
<td>458 ± 37</td>
<td>422 ± 3.0</td>
<td>213 ± 2.5</td>
<td>4 ± 0.4</td>
<td>9 ± 1.8</td>
<td>196 ± 24</td>
</tr>
</tbody>
</table>

Figure 54. Variation of (a) topcoat capacitance and (b) topcoat resistance as a function of topcoat density.

Figure 55. Scanning electron micrographs showing the variation in the density of topcoat of the APS TBCs.
Figure 56. (a) Impedance and (b) Nyquist plots for APS TBCs with varying density.

4.5 Air Plasma Sprayed TBCs with thickness and chemistry

YSZ and CaTiO$_3$ TBCs with varying thickness were examined by EIS and microscopy. Resistance and capacitance determined based on equivalent circuit shown in Figure 34 without TGO are presented in Table 21. The accepted fitting error for this equivalent circuit was less than 5%. There is a significant increase in the resistance of ceramic topcoat with increasing thickness, and for CaTiO$_3$ TBCs as shown in Figure 57b. Increase in resistance also corresponds to decrease in capacitance as shown in Figure 57a. Nyquist plots and impedance spectra obtained from this series of specimens are shown in Figure 58. Variation in thickness was measured on these specimens using scanning electron microscopy as shown by secondary electron micrographs in Figure 59 and presented in Table 22.
Table 21 EIS Results for APS TBCs with varying thickness and chemistry.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$C_C$ (nF)</th>
<th>$R_C$ (Ω)</th>
<th>$C_P$ (mF)</th>
<th>$R_P$ (KΩ)</th>
<th>$C_T$ (nf)</th>
<th>$R_T$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ552</td>
<td>1.6 ± 0.01</td>
<td>308 ± 9.4</td>
<td>14.9 ± 0.08</td>
<td>1.9 ± 0.01</td>
<td>3600 ± 282</td>
<td>283 ± 10</td>
</tr>
<tr>
<td>YSZ325</td>
<td>2.0 ± 0.08</td>
<td>218 ± 4.3</td>
<td>15.0 ± 0.10</td>
<td>2.6 ± 0.10</td>
<td>3212 ± 47</td>
<td>335 ± 33</td>
</tr>
<tr>
<td>CTO667</td>
<td>13.3 ± 0.19</td>
<td>522 ± 6.1</td>
<td>5.6 ± 0.03</td>
<td>3.2 ± 0.32</td>
<td>300 ± 8</td>
<td>550 ± 14</td>
</tr>
<tr>
<td>CTO339</td>
<td>27.0 ± 0.26</td>
<td>295 ± 18</td>
<td>5.0 ± 0.08</td>
<td>4.6 ± 0.35</td>
<td>540 ± 55</td>
<td>555 ± 27</td>
</tr>
</tbody>
</table>

Figure 57. Variation in (a) Topcoat capacitance and (b) topcoat resistance of APS and TBCs as a function of thickness and chemistry.

Table 22 Thickness of the topcoat for APS YSZ and APS CAT TBCs.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Topcoat Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ552</td>
<td>552 ± 30</td>
</tr>
<tr>
<td>YSZ325</td>
<td>325 ± 17</td>
</tr>
<tr>
<td>CTO667</td>
<td>667 ± 25</td>
</tr>
<tr>
<td>CTO339</td>
<td>339 ± 30</td>
</tr>
</tbody>
</table>

Note: Thickness measurements made at 100X magnification
Figure 58. (a) Impedance and (b) Nyquist plot for APS YSZ and APS CAT TBCs.
Figure 59. Scanning electron micrograph of cross-sections of (a) YSZ552, (b) YSZ325, (c) CAT667 and CAT339.

4.6 Dense Vertically Cracked TBCs with varying crack density

YSZ DVC TBCs with varying crack density were examined by EIS and scanning electron microscopy. Crack density is defined relatively in terms of number cracks that
intersect with specified length using magnified images. Nyquist and impedance plots obtained from this series of specimens are shown in Figure 60 and Figure 61. Resistance and capacitance determined based on equivalent circuit (Figure 34) without the TGO are presented in Table 23. The accepted fitting error for this equivalent circuit was less than 5%. Table 23 also shows YSZ thickness for different samples. The thickness of YSZ is greatest for 70CPL and smallest for 1CPL. The cross sectional scanning electron micrograph showing the crack density is shown in Figure 62. There is an increase in the resistance and a corresponding decrease of ceramic topcoat with increasing crack density as shown in Figures 63a and b.

![Nyquist plots of DVC YSZ TBCs as a function of vertical crack density.](image)

Figure 60. Nyquist plots of DVC YSZ TBCs as a function of vertical crack density.
Figure 61. Impedance plots of DVC YSZ as a function of vertical crack density.

Table 23 EIS results for DVC YSZ TBCs with varying crack density.

<table>
<thead>
<tr>
<th>Cracks (CPL)</th>
<th>YSZ Thickness (µm)</th>
<th>$C_C$ (nF)</th>
<th>$R_C$ (KΩ)</th>
<th>$C_P$ (µF)</th>
<th>$R_P$ (KΩ)</th>
<th>$C_T$ (µF)</th>
<th>$R_T$ (KΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>240 ± 5</td>
<td>1.3 ± 0.3</td>
<td>1.0 ± 0.03</td>
<td>379 ± 4.3</td>
<td>28 ± 0.01</td>
<td>107 ± 2.33</td>
<td>1.3 ± 0.3</td>
</tr>
<tr>
<td>20</td>
<td>260 ± 5</td>
<td>0.9 ± 0.2</td>
<td>1.3 ± 0.03</td>
<td>310 ± 3.2</td>
<td>8 ± 0.01</td>
<td>67 ± 3.62</td>
<td>1.6 ± 0.4</td>
</tr>
<tr>
<td>70</td>
<td>300 ± 5</td>
<td>0.6 ± 0.2</td>
<td>1.5 ± 0.02</td>
<td>288 ± 2.9</td>
<td>6 ± 0.10</td>
<td>9 ± 4.01</td>
<td>0.7 ± 1.2</td>
</tr>
</tbody>
</table>
Figure 62. Cross sectional back scatter electron micrographs of (a) 1 Crack per unit length, (b) 20 Cracks per unit length and (c) 70 cracks per unit length.
Figure 63. Variation in (a) capacitance and (b) resistance of YSZ as a function of density.

4.7 EB-PVD TBCs with varying density

EIS was performed on two EB-PVD samples with varying density defined by inter-columnar spacing and column width; one defined as dense and one as columnar. For EB-PVD TBCs, equivalent circuit contains TGO even in as-coated conditions. The equivalent electrical circuit is as shown in Figure 31. The accepted fitting error for this equivalent circuit was less than 10%. Figure 64 shows Impedance and Nyquist spectra of these EB-PVD samples with varying columnar density, respectively. EIS results for these
TBCs are presented in Table 24. TBC with dense structure has lower capacitance and higher resistance as indicated in Figure 65 a and b.

Table 24 EIS results for EB-PVD TBCs with varying density.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$C_C$ (nF)</th>
<th>$R_C$ (Ω)</th>
<th>$R_P$ (KΩ)</th>
<th>$C_P$ (µF)</th>
<th>$C_O$ (µF)</th>
<th>$R_O$ (KΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dense</td>
<td>4.1 ± 0.1</td>
<td>75 ± 3.0</td>
<td>14 ± 1.5</td>
<td>1.3 ± 0.2</td>
<td>8.0 ± 1.2</td>
<td>15 ± 2.0</td>
</tr>
<tr>
<td>Columnar</td>
<td>6.8 ± 0.7</td>
<td>52 ± 1.3</td>
<td>7 ± 0.9</td>
<td>2.4 ± 0.6</td>
<td>14 ± 2</td>
<td>15 ± 1.0</td>
</tr>
<tr>
<td>Specimen</td>
<td>$C_T$ (µF)</td>
<td>$R_T$ (KΩ)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dense</td>
<td>10.2 ± 4.0</td>
<td>6.0 ± 0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Columnar</td>
<td>20.1 ± 4.0</td>
<td>3.0 ± 0.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 64. (a) Impedance and (b) Nyquist plot of EB-PVD TBCs with varying density.
Figure 65. Variation in (a) YSZ resistance and (b) YSZ capacitance as a function of topcoat density.
5 DISCUSSION

5.1 Sintering of Yttria Stabilized Zirconia, Isothermal Exposure of NiAl and Isothermal Exposure of EB-PVD TBCs

5.1.1 Sintering of Yttria Stabilized Zirconia

The electrochemical impedance response for the TBCs as a system or in particular (Topcoat, TGO) depends on the microstructural features such as pores and defects through which conductive electrolyte can penetrate. The linear relation between $R_{\text{YSZ}}$ and thickness can be expressed in ohms law as:

$$ R = \frac{D \cdot t}{A} $$ (19)

The variables $\rho$, $A$ and $t$ refer to electrical resistivity, area and thickness of the material exposed to the electrolyte. In these sintering experiments all the specimens were YSZ and $\rho$ is a constant for a particular material ($10^{10}$ $\Omega$-cm), $A$ is also a constant since the area of exposure to the electrolyte is an experimental constant. Therefore, finally the resistance is dependent on the thickness of the YSZ monoliths. As the thickness increases the resistance of the YSZ increases (Table 9-15 and Figures 36 to 40). In addition, YSZ sinters at higher temperatures i.e. the density increase (porosity decreases), which retards the penetration of electrolyte. In addition, with the increase in the density the effective resistivity increases. Hence, we see there is increase in resistance with increase in thickness, sintering time and sintering temperature. Figure 43 shows sintering of YSZ for
two different densities where the pores have reduced at higher temperatures. Since the electrochemical response is obtained only from the YSZ monoliths and since density is increasing with sintering time and temperature, the increase in resistance is attributed to densification of YSZ and its thickness. Decrease in \( R_{YSZ} \) for 4.07 g/cm\(^3\) density after being sintered at 1300ºC for 5 hours and 10 hours and cooled at room temperature was because of cracking as shown in Figure 41. The figure clearly shows cracks which proves that there was easier penetration of the electrolyte through the YSZ and hence we see decrease in the \( R_{YSZ} \). Further when the experiment was repeated with incorporation of furnace cooling to avoid cracking of YSZ we found that the \( R_{YSZ} \) increased for the same as shown in Figure 46.

The capacitance is a function of thickness and dielectric constant as:

\[
C = \varepsilon_v \cdot \varepsilon \cdot \frac{A}{t}
\]  

(20)

Here \( \varepsilon_v \) is permittivity of vacuum, which is a constant, \( \varepsilon \) is dielectric constant, which is a constant for a material and \( t \), is the thickness. Therefore, the relative value of \( C_{YSZ} \) decreases with increase in thickness. In addition, with the increase in density of YSZ the effective thickness increases with decrease in porosity. Therefore, with the increase in sintering time and temperature of the sintering capacitance of YSZ decreases as presented in Table 9-15 and shown in Figures 36 to 40. As porosity decreases the effective electrolyte penetration decreases and the dielectric layer increases there by decreasing the capacitance. In addition, there is no significant variation in the capacitance after 10 hours. With the cracking of YSZ as specified earlier the capacitance increased, this is because with cracking there is electrolyte penetration and effective thickness of YSZ decreases.
From Figures 36 to 40 and Table 9-16 we see that the values of capacitances are very low, i.e. there is a small variation in the capacitance with the increase in sintering time and temperature while there is distinctive change in the values of the resistances. From Eq.(19) and (20), the value of capacitance depends of the dielectric constant of YSZ, which is around 40-60 and the value of resistance depends on the resistivity of YSZ which is around $10^{10} \Omega$-cm. Resistivity value is more than 10 orders of magnitude higher than the dielectric constant, so with a small change in the thickness, the resistance values get more magnified as compared to capacitance value. The value of the impedance for the sintered YSZ is around 1KΩ.

5.1.2 Isothermal Oxidation of NiAl

Oxidation of NiAl leads to the formation of thermally grown oxide. Since NiAl is a metal, there is negligible resistance and hence the response of EIS is obtained only from the oxide layer, which is an insulator. The electrochemical response is dependent on TGO thickness and the defects in the TGO, which assists the conductive electrolyte to penetrate through. The resistance of TGO, $R_{TGO}$ follows Eq.(19). For NiAl isothermally exposed at 1100ºC and 1200ºC for 2, 5 and 10 hours shows an increase in the $R_{TGO}$ as shown in Figure 45a. The increase in resistance is attributed only to the growth of TGO.

The capacitance follows Eq.(20). The dielectric constant of TGO (primarily alumina) is a constant (~9 for alumina). Hence, $C_{TGO}$ is dependent mainly on the thickness of TGO. With the increase in the thickness of TGO, the impedance increases. Since capacitance is inversely proportional to the thickness and from Eq. (20) with the
increase in TGO thickness $C_{\text{TGO}}$ should decrease. For NiAl isothermally exposed at 1100°C and 1200°C for 2, 5 and 10 hours show decrease in the capacitance of TGO as shown in Figure 45b. Figure 66 clearly indicates the parabolic growth TGO and the growth inversely proportional to the capacitance of TGO ($C_{\text{TGO}}$) before spallation. Figure 49 clearly shows the growth of TGO with respect to isothermal oxidation time and temperature.

When NiAl specimens were oxidized at 1300°C and quenched to room temperature after 5 and 10 hours $R_{\text{TGO}}$ decreased and correspondingly the $C_{\text{TGO}}$ increased. The spallation of TGO was observed using SEM and is shown in Figure 48. With the spallation of the oxide scale, the metal surface is exposed to the conducting electrolyte and from Eq. (19) and (20) ‘t’ is almost zero and therefore the resistance, $R_{\text{TGO}}$ decreases and capacitance, $C_{\text{TGO}}$ increases substantially. Also with the spallation metal surface is exposed and since impedance of metal is very low compared to TGO, $R_{\text{TGO}}$ decreased and $C_{\text{TGO}}$ increased.

Figure 66. Changes in TGO capacitance as a function of oxidation time at (a) 1100°C and (b) 1200°C before spallation.
The impedance response obtained from the oxidized NiAl is only from the TGO since metal has zero resistivity. The impedance for the TGO is around 100 KΩ. In comparison to the impedance of the YSZ, TGO has higher impedance. The reason for this is that the TGO which grows on the NiAl is very dense compared to that of the YSZ which is highly porous. Also the resistivity of the $\alpha$-Al$_2$O$_3$ is higher than that of YSZ.

5.1.3 Isothermal Oxidation of EB-PVD TBCs

EIS results obtained from sintering of YSZ and isothermal oxidation of NiAl provided necessary insight to the EIS response obtained from EB-PVD TBCs. TBCs are composed of YSZ as topcoat, bond coat {(Ni, Pt) Al or MCrAlY}, TGO (alumina) and superalloy. Hence, the results obtained for EB-PVD should have results in correlation with the individual layers investigated.

The electrochemical impedance response of TBCs depends on the penetration of aqueous conductive electrolyte into YSZ coatings (open pores) and TGO. The relative value of $R_{\text{YSZ}}$ according to Eq. (19) depends on resistivity $\rho$ of YSZ coating.

The initial increase in the resistance of YSZ ($R_{\text{YSZ}}$) is due to high temperature sintering as shown in Figure 52a. Impedance plot of all the TBCs are shown in Figure 67. It is similar to the results obtained from sintering of YSZ. With sintering of YSZ due to several hours of heat treatment the open pores are reduced. This in turn hinders the penetration of electrolyte thereby increasing the impedance. Hence $R_{\text{YSZ}}$ increases with thermal exposure.
After prolonged thermal exposure, there is a decrease in the $R_{YSZ}$. This is due to the micro-cracks, which develop over time within the YSZ and allow easier penetration of electrolyte. Since the effective dielectric decreases with electrolyte penetration $R_{YSZ}$ decreases. For TBC exposed to 600 hours $R_{YSZ}$ decreased substantially. With the spallation of topcoat as shown in Figure 50 there is a total exposure of electrolyte to the bond coat (conductive) and therefore we see very low impedance for TBC exposed for 600 hours.

Though the capacitance ($C_{YSZ}$) is decreasing as presented in Table 18 during the initial hours of thermal exposure, there is no significant change as shown in Figure 52b. Capacitance is follows Eq. (20) as explained earlier. As seen in case of YSZ sintering the capacitance values are very close towards the end and a similar result is obtained in case
of TBC which is attributed to the dielectric constant of the YSZ being very small compared to that of the resistivity. In addition, since the YSZ thickness remains constant during the thermal exposure $C_{YSZ}$ does not vary significantly.

There is a sudden increase (in several orders of magnitude) in $C_{YSZ}$ when there is a spallation of YSZ topcoat, again since capacitance follows Eq.(20), YSZ thickness and hence effective dielectric is zero. This can be because of large-scale cracks so that the conduction occurs through electrolyte in contact with the exposed bond coat. Exposed metallic bond coat is observed frequently in failed EB-PVD TBCs. \cite{7, 63} Thereby we see $C_{YSZ}$ increases significantly as shown in Figure 52b.

In order to explain the variation of TGO resistance ($R_{TGO}$), isothermal oxidation of NiAl provided some insight. From Figure 52c, there is initial increase in the $R_{TGO}$, which can be attributed to the growth of TGO (as seen earlier for NiAl oxidation). Then after some prolonged thermal exposure, there is decrease in the $R_{TGO}$. This is attributed to the cracking of TGO and thereby the effective resistivity of TGO decreases lowering the impedance and hence the $R_{TGO}$. With failure $R_{TGO}$ decreased by a several order of magnitude. This is because of the exposure of bond coat to the electrolyte. \cite{93}

TGO capacitance ($C_{TGO}$) initially decreases as shown in Figure 52d. From the NiAl oxidation the reason for the decrease in capacitance is mainly due to the TGO growth, since capacitance is inversely proportional to thickness with $\varepsilon$ being constant for TGO (alumina). The thickness of the TGO is shown in Figure 53 was examined as a function of $C_{TGO}$ by excluding abrupt changes associated with TBC failure. Figure 68 clearly demonstrates that the parabolic growth of TGO is inversely proportional $C_{TGO}$. 

113
Figure 68. Changes in TGO capacitance as a function of time during isothermal oxidation of EB-PVD TBCs.

With failure of EB-PVD TBCs, an abrupt increase of several orders of magnitude is seen in $C_{\text{TGO}}$ as shown in Figure 52d. This can be because of large-scale cracks so that the conduction occurs through electrolyte in contact with the exposed bond coat. Exposed metallic bond coat is observed frequently in failed EB-PVD TBCs.\textsuperscript{[697]} The effective number of cations from electrolyte and anions from the metal surface increases for free conduction. The variation in the value of $C_{\text{TGO}}$ is not significant compared to the resistance $R_{\text{TGO}}$, the explanation for this is given by referring to Eq. (19) and (20). The dielectric constant of Al$_2$O$_3$ is around 9–11 while resistivity is in the order of $10^{14}$ $\Omega$-cm.
So with minor increase in thickness there is no major change in the $C_{TGO}$ as compared to the $R_{TGO}$.

The values of $R_{YSZ}$ are very less in comparison to $R_{TGO}$. As we earlier saw for sintered YSZ and oxidized NiAl, the values of $R_{TGO}$ for oxidized NiAl is higher than $R_{YSZ}$ for sintered YSZ. This implies that the maximum contribution to the total impedance of the system is from the oxide layer, since the $\alpha$-alumina that grows during high temperature oxidation is highly dense compared to that of YSZ in addition the resistivity of alumina is higher than that of YSZ.

5.2 Air Plasma Sprayed TBCs with varying density

The resistance follows Eq.(19). The resistance of YSZ ($R_{YSZ}$) has fairly remained constant with the increase in the density (Table 20). From Figure 55a and 55b, APS TBC having low density has greater thickness while the APS TBC with higher density has smaller thickness. Though the resistance is a function of thickness, it depends on the density of the material. With thicker topcoat and smaller density as shown in Figure 55a, there are lot more pores in the topcoat compared to thinner topcoat and greater density as shown in Figure 55b. With increase in porosity there is an easy penetration of electrolyte which eventually decreases electrochemical impedance response of the system and hence there is a decrease in $R_{YSZ}$ as shown in Figure 54b.

Ceramic topcoat capacitance is decreased with increase in density as shown in Figure 54a. Capacitance is a function of dielectric constant, thickness, and area (Eq.20). Essentially the value of $C_{YSZ}$ depends on the effective dielectric layer thickness. With the
increase in porosity there is greater amount of electrolyte penetrating through the topcoat and decreasing the dielectric gap hence the $C_{YSZ}$ increases. The samples with high porosity have higher $C_{YSZ}$ and samples with lower porosity have higher $R_{YSZ}$.

5.3 Air Plasma Sprayed TBCs with varying thickness and chemistry

Results of variation in $R_{YSZ}$ and $R_{CAT}$ are shown in Figure 57b. The resistance of the topcoat follows linear relation according to Eq. (20). There is increase in $R_{YSZ}$ with the increase in thickness of the topcoat (YSZ and CAT). The resistance is also a function of resistivity. The values of $R_{CAT}$ are higher than $R_{YSZ}$ values. This suggests that the resistivity of CaTiO$_3$ and YSZ is different. The value of resistivity for CaTiO$_3$ is in the order of $\sim 10^{14}$ $\Omega$-cm while that of YSZ is in the order of $\sim 10^9$ $\Omega$-cm. \[98\] Since the resistivity of CAT is higher than YSZ resistance increases for CAT topcoat. Impedance plot shows highest impedance for CAT for highest thickness and lowest impedance for YSZ with lowest thickness as shown in Figure 58a.

Capacitance is directly proportional to the dielectric constant and inversely proportional to the thickness. From the Figure 57a, the capacitance increases with increase in topcoat thickness (YSZ and CAT). Dielectric constant of CaTiO$_3$ is around 160 while that for YSZ is around 40-60 \[98\] and since capacitance is directly proportional to the dielectric constant for Eq. (20) capacitance values for CAT is higher than that of YSZ (Figure 57a).
5.4 Dense Vertically Cracked TBCs with varying crack density

The electrochemical impedance response for this system depends on the cracks. Vertical cracks may be considered open pores and they allow easier penetration of the electrolyte. It is important to note that if the cracks are interconnected then there is a flow of electrolyte through the topcoat if they are discontinuous then there is an obstruction to the flow of electrolyte. Resistance for interconnected cracks is lower than that of discontinuous cracks. Correspondingly, capacitance increases for interconnected cracks as the dielectric gap decreases with penetration of the electrolyte.

The resistance of YSZ increased with the increase in the crack density as shown in Figure 63b and as presented in Table 23. Resistance is directly proportional to the thickness of the YSZ from Eq.20. Though the cracks vary, there is a definite difference in the thickness of the topcoat. Hence, there is increase in the resistance of topcoat with the increase in the crack density. Not only the CPL increased from 1-70 the thickness of the topcoat also increased. This increase in thickness related to increase in impedance which resulted in increasing $R_{YSZ}$ with increasing CPL. These trends observed by EIS cannot be directly correlated with the crack density but it is very well proved in terms of the thickness of the YSZ.

Capacitance has inverse relation with the thickness (dielectric gap), there is a decrease in the $C_{YSZ}$ with the increase in the thickness of the topcoat. Since the trend observed here cannot be directly correlated with the crack density, it is defined in terms of the thickness. The plausible reasons for these inverse trends may be the cracks did not reach the bond coat surface. Variation of the crack density has been shown if Figure 62.
5.5 EB-PVD TBCs with varying density

The electrochemical impedance response for this system depends on dense and columnar structure of the TBCs. Columnar structure has a wide intercolumnar spacing compared to the dense structure. Electrolyte penetration through the columnar structure is much more easier compared to the dense EB-PVD structure. Impedance obtained is high for dense EB-PVD structure as shown Figure 64a. Hence, the $R_{YSZ}$ is high for the dense structure as shown in Figure 65a.

Capacitance ($C_{YSZ}$) depends on the dielectric gap, for columnar structure with the penetration of the electrolyte; the dielectric gap reduces there by increasing the capacitance. A higher CYSZ value for the columnar structure in comparison to lower value for dense structure is shown in Figure 65b.
6 SUMMARY

Electrochemical impedance spectroscopy was employed to non-destructively examine (1) Sintered YSZ monoliths with varying thickness and density, (2) Isothermally oxidized NiAl, (3) EB-PVD TBCs as a function of isothermal exposure, (4) APS and EB-PVD TBCs as a function of density, (5) APS TBCs as a function of varying topcoat thickness and chemistry, and (6) DVC TBCs as a function of thickness and crack density.

With the increase in thickness, sintering temperature and sintering time $R_{YSZ}$ increases and $C_{YSZ}$ decreased with density being constant. In addition the $R_{YSZ}$ increased with increase in density and $C_{YSZ}$ decreased. With the cracking in YSZ the $R_{YSZ}$ decreased and correspondingly $C_{YSZ}$ increased.

NiAl oxidation results in growth of TGO, with longer exposure to temperature the density and the thickness of TGO increases. With the increase in the TGO thickness $R_{TGO}$ increases and $C_{TGO}$ decreases. Prolonged heat treatment results in reverse trend in $R_{TGO}$ and $C_{TGO}$. This observation was attributed to the spallation of TGO scale from the NiAl thereby exposing the metal surface to the electrolyte. The parabolic growth of TGO during high temperature oxidation was inversely related to the capacitance of TGO with the abrupt changes associated with the failure being omitted.

For EB-PVD TBCs that were isothermally heat treated, $R_{YSZ}$ increased initially and $C_{YSZ}$ decreased. This observation was related to YSZ sintering which occurs during the thermal exposure. The increase and decrease in $R_{TGO}$ and $C_{TGO}$ was related to the TGO growth. Excluding the abrupt changes associated with failure, the parabolic growth of TGO during the isothermal exposure was inversely related to the capacitance of TGO.
Gradual decreases in $R_{YSZ}$ and $R_{TGO}$ was explained in terms of damage initiation and electrolyte penetration. With the spallation of YSZ/TGO there was an abrupt increase in the capacitance and decrease in the resistance since the electrolyte is in direct contact with the exposed metallic bond coat surface.

For TBCs with varying topcoat thickness and chemistry the $R_{YSZ}$ and $C_{YSZ}$ were variation in the resistance and capacitance was attributed to the material constant namely resistivity for the RYSZ or RCAT and dielectric constant for $C_{YSZ}$ and $C_{CAT}$.

For DVC TBCs with varying crack density the increase in thickness was related to increase in impedance which resulted in increasing $R_{YSZ}$ with increasing cracks per unit length.
LIST OF REFERENCES

50 J.D. Crawley, “Overview of Zirconia with respect to Gas Turbine applications.” *NASA TP-2286* (NASA Lewis Research Center, 1984)
55 Randall M. German, “*Sintering Theory and Practice*”, John Wiley and Sons Inc. 1996.
60 S.M. Meier, D.M. Nissley, K.D. Sheffler, *NASA Contractor Report 189111*, NASA Lewis Research Center, Cleveland, OH.


