Rare Earth Oxide Coating with Controlled Chemistry Using Thermal Spray

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RARE EARTH OXIDE COATING WITH CONTROLLED CHEMISTRY USING THERMAL SPRAY

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
in the Department of Mechanical, Materials and Aerospace Engineering
in the College of Engineering and Computer Science
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ABSTRACT

Cerium oxide (Ceria) at nano scale has gained significant attention due to its numerous technological applications. Ceria in both doped and undoped forms are being explored as oxygen sensor, catalysis, protective coating against UV and corrosion, solid oxide fuel cell (SOFC) electrolyte and newly discovered antioxidant for biomedical applications. Therefore, there is an imminent need of a technology which can provide a cost effective, large scale manufacturing of nanoceria and its subsequent consolidation, specially using thermal spray.

This dissertation aims to develop a scientific understanding towards the development of pure and doped ceria-based coating for a variety of technological applications, from SOFC applications to corrosion resistant coating. Atmospheric plasma spray (APS) and solution precursor plasma spray (SPPS) techniques for the fabrication of nano ceria coating were investigated. For feedstock powder preparation, a spray drying technique was used for the agglomeration of cerium oxide nano particles to achieve high density coating. Deposition efficiencies and coating porosity as a function of processing parameters were analyzed and optimized using a statistical design of experiment model. The coating deposition efficiency was dependent on the plasma temperature and vaporization pressure of the ceria nanoparticles. However, low standoff distance and high carrier gas flow rate were responsible for the improved density upto 86 ±3%. An alternative novel SPPS technique was studied for a thin film of cerium oxide deposition from various cerium salt precursors in doped and undoped conditions. The SPPS process allows controlling the chemistry of coating at a molecular level. The deposition mechanism by single scan experiments and the effect of various factors on coating
microstructure evolution were studied in terms of splats formation. It was found that the precursor salt (nitrate of cerium) with lower thermal decomposition temperatures was suitable for a high density coating. The high concentration and low spray distance significantly improve the splat morphology and reduced porosity (upto 20%). The feasibility of the trivalent cations (Sm$^{3+}$ and Gd$^{3+}$) doping into cerium oxide lattice in high temperature plasma was discussed and experimentally studied. XRD analysis revealed the nano crystalline characteristic of the coating and lattice expansion due to doping. The extensive transmission electron microscopy, Scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and thermo gravimetric were conducted to evaluate the precursors, and coating microstructure.

Due to facial switching between Ce$^{4+}$ and Ce$^{3+}$ oxidation state, the cerium oxide surface becomes catalytically active. Thus, the APS ceria coatings were investigated for their applicability under extreme environmental conditions (high pressure and temperature). The air plasma sprayed coated 17-4PH steel was subjected to high pressure (10 Kpsi) and temperature (300 °F) corrosive environment. The coated steel showed continuous improvement in the corrosion resistance at 3.5 wt% NaCl at ambient temperature for three months study whereas, high pressure did not reveal a significant role in the corrosion process, and however, one needs to do further research. The ceria coated steel also revealed the improvement in corrosion protection (by 4 times) compared to the bare steel at low pH, 300 °F and 4000 Psi environment. This study projects the importance of cerium oxide coatings, their fabrication, optimization and applications.
ACKNOWLEDGEMENTS

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# TABLE OF CONTENTS

LIST OF FIGURES .......................................................................................................................... xii

LIST OF TABLES .............................................................................................................................. xix

LIST OF ABBREVIATIONS ............................................................................................................... xx

CHAPTER 1: INTRODUCTION ......................................................................................................... 1

1.1 Overview on Plasma Spray Coating ......................................................................................... 3

1.2 Atmospheric Plasma Spray Coating of Nano Structure Ceramic Powder ......................... 7

1.3 Solution Precursor Plasma Spray (SPPS) .............................................................................. 10

1.3.1 Mechanism of Deposition ................................................................................................. 11

1.3.2 Microstructure Development in SPPS Process ................................................................. 14

1.3.3 Cerium Oxide .................................................................................................................... 17

1.3.4 Organization of Dissertation ............................................................................................ 18

CHAPTER 2: ATMOSPHERIC PLASMA SPRAY OF NANO STRUCTURED CERIUM OXIDE COATING .................................................................................................................. 21

2.1 Introduction ............................................................................................................................. 21

2.2 Design of Experiments in Thermal Spray Process .............................................................. 22

2.2.1 Factorial Design of Experiment ...................................................................................... 25

2.2.2 Response Surface Method (RSM) ................................................................................... 26

2.2.3 Application of Response Surface Method in Thermal Spray ......................................... 27
2.3 Materials and Methods

2.3.1 Powder Feed Stock Characteristics

2.3.2 Spray Drying

2.3.3 Spray Drying of Cerium Oxide Powder

2.3.4 Atmospheric Plasma Spraying

2.3.5 Optimization of Coating

2.4 Results and Discussion

2.4.1 Process of Spray Drying

2.4.2 Microstructural Features: APS of Cerium Oxide

2.4.3 Quadratic Model for Density

2.4.4 Quadratic Model for Deposition Efficiency

2.4.5 Model Diagnostic

2.4.6 Process Optimization and Correlation of Results with DOE

2.5 Conclusions

CHAPTER 3: SOLUTION PRECURSOR PLASMA SPRAY (SPPS) DEPOSITION OF NANO CRYSTALLINE CERIUM OXIDE

3.1 Introduction

3.2 Materials and Methods

3.2.1 Precursor and Coating Processing
3.2.2 Precursor and Coating Characterization ......................................................... 58
3.2.3 Numerical Modeling ......................................................................................... 60
3.3 Results and Discussion ....................................................................................... 60
  3.3.1 Phase Evaluation of SPPS Cerium Oxide Coating ........................................ 60
  3.3.2 Microstructural Characterization of as Sprayed SPPS Coatings .................... 62
  3.3.3 Grain Size Measurement of Coatings ............................................................. 66
  3.3.4 Thermal Decomposition of Precursors (TG-DTA Study) ............................... 68
  3.3.5 Numerical Modeling of Precursor Injection for Microstructure Evolution .... 74
  3.3.6 Thermodynamic Feasibility of Cerium Oxide Formation from Solution ......... 79
  3.3.7 Determination of Oxidation State of Cerium in SPPS Coated CNPs ............... 81
3.4 Conclusions ........................................................................................................ 84

CHAPTER 4: STUDY THE EFFECT OF PROCESSING PARAMETERS ON SPPS COATING
AND DOPED CERIUM OXIDE COATING DEVELOPMENT ..................................... 85
  4.1 Introduction ......................................................................................................... 85
  4.2 Materials and Methods ..................................................................................... 87
    4.2.1 Precursor Solution and Coating Processing ................................................ 87
    4.2.2 Solution Plasma Spray: Design of Experiment ........................................... 88
    4.2.3 Precursor and Coating Characterization .................................................... 90
  4.3 Results and Discussion ...................................................................................... 92
CHAPTER 6: CONCLUSIONS ........................................................................................................... 153
APPENDIX A: LIST OF PUBLICATIONS ..................................................................................... 156
APPENDIX B: LETTERS OF PERMISSION .................................................................................... 159
REFERENCES .................................................................................................................................. 171
LIST OF FIGURES

Figure 1 Schematic of thermal spray deposition

Figure 2 Enthalpy values of typical plasma spray gases as a function of temperature [24]

Figure 3 Processing parameters in plasma spraying

Figure 4 Deposition mechanism of agglomerated nano particles (a) partial melting and retention of nano particles (b) complete melting

Figure 5 Schematic of SPPS process illustrates formation of different morphology of the coating surface depending on the precursor injection in different zone of plasma flame (a) droplet evaporation, shell formation and volume precipitation (b) pyrolysis and sintering (c) melting (d) crystallization [40, 45]

Figure 6 Vaporization and precipitation routes for a solute droplet [42]

Figure 7 Microstructure of SPPS coating (a) YSZ low magnification SEM depicting through thickness vertical cracks [45] (b) Magnified image showing the micro and nano porosities [45](c) conventional YSZ APS coating for comparison (d) Surface of the SPPS coating (single scan)

Figure 8 Titanium oxide coating cross section microstructure prepared by different solution precursor concentration using SPPS (a) 0.775M [48] (b) 1.5M [37]

Figure 9 (a) Central composite design (b) Box-Behnken

Figure 10 Schematic of spray drying showing the injection of the suspension from top of the spray drying cylinder and collection of the dried agglomerated particles

Figure 11 Morphology of the cerium oxide particles. (a) TEM of nano ceria (b) SEM of spray dried agglomerated ceria particles (c) Cerium oxide coating
Figure 12 External injection at (1) 90° of the plasma jet (2) Outward injection direction (3) inward injection direction tilted by ± 30° from black center line .................................................. 33

Figure 13 TG-DTA of the spray dried powder showing the exothermic removal of PEG. Upward arrow indicates the exothermic direction. Inset shows the thermal decomposition of pure PEG. 38

Figure 14 SEM microstructure of the spray dried agglomerated ceria nano particles of different solid loading (a) 30wt% (b) 40wt% (c) 50wt% and right side is the particles size distribution... 40

Figure 15 (a) Normal plot of residuals (b) predicted versus actual plots for the model of density ......................................................................................................................................................... 47

Figure 16 (a) Normal plot of residuals (b) predicted versus actual plots for the model of deposition efficiency..................................................................................................................................................... 48

Figure 17 Microstructure of cerium oxide coating (a) Run number 28 (density 66%) (b) Run number 17 (density 81%)......................................................................................................................................................... 49

Figure 18 Predicted spray parameters for high density coatings ................................................. 52

Figure 19 A setup of the solution precursor plasma spray. The solution injector position is 13 mm away from nozzle exit and 8 mm from plasma jet axis. ............................................................... 57

Figure 20 X-Ray diffraction patterns of the SPPS cerium oxide coating prepared by different precursors viz (a) Cerium acetate (b) Cerium nitrate hexahydrate (c) Cerium sulfate tetrahydrate. XRD patterns indicate typical fluorite crystal structure of cerium oxide. (*) indicates the presence of oxysulfate phases in coating prepared by cerium acetate sesquihydrate precursor... 61

Figure 21 Surface morphology of SPPS cerium oxide coating prepared by (a) Cerium acetate (b) Cerium nitrate hexahydrate (c) Cerium sulfate precursors. Insets reveal the magnified images of
smaller sections of the corresponding coating (d) Magnified image indicates splat formation (1-2µm) along with fine unmelted particles. ................................................................. 63

Figure 22 HRTEM images of SPPS coating prepared by (a) Cerium acetate (b) Cerium nitrate hexahydrate (c) Cerium sulfate precursors indicating that coating consists of nano particles of cerium oxide. Insets show the low magnification TEM images, fast Fourier transform of lattice and SAED patterns........................................................................................................................................... 64

Figure 23 Histogram of grain sizes of nanocrystalline cerium oxide coating for each salt, measured in High resolution TEM micrographs using image analysis software. A total of 80 data points were counted from different HRTEM images. For irregular particles longer dimension was selected. ........................................................................................................................................... 67

Figure 24 TG-DTA curve of dried cerium acetate sesquihydrate at heating rate of 10 °C min⁻¹ in flowing zero grade air ........................................................................................................................................... 69

Figure 25 TG-DTA curve of dried Cerium nitrate hexahydrate at heating rate of 10 °C min⁻¹ in flowing zero grade air ........................................................................................................................................... 71

Figure 26 TG-DTA curve of dried Cerium sulfate tetrahydrate precursor and coating at heating rate of 10 °C min⁻¹ in flowing zero grade air ........................................................................................................................................... 73

Figure 27 Temperature profiles for 30µm droplets of different precursors with time, indicate water evaporation up to critical point followed by heating of the solid particles up to the melting point of ceria ........................................................................................................................................... 76

Figure 28 Trajectory of different size droplets of cerium nitrate precursor. This indicates that only larger size (>20µm) droplets penetrate plasma plume. Smaller droplets remain in the shear
layer of the plasma. For a clear representation, the plasma nozzle is shown away from the center line...

Figure 29 Temperature profiles for different size droplets of cerium nitrate precursor, show size dependent behavior of injected droplets. Larger size droplets (~50µm) pass through the hot zone of the plasma and attain low temperature (~500°C). Smaller droplets (~10µm) remain in the low temperature shear layer and reach the substrate in un-melted condition. 

Figure 30 XPS spectrum of Ce (3d) for cerium oxide coating prepared by (a) Cerium (III) acetate (b) Cerium (III) nitrate hexahydrate (c) cerium (IV) sulfate precursors. Peaks were deconvoluted to get the distinct spin-orbit doublet of 3d_{3/2} and 3d_{5/2}. (d) S 2p spectra indicating the presence of SO_4

Figure 31 Microstructure of the coating deposited by different plasma power. (Case 1) 21 KW. (Case 2) 32 KW plasma power. Macro-graphs show deposit peel off for the low power and adherent deposit for high power plasma. 

Figure 32 Position of plasma jet for plasma sprays parameters (case 4) (as shown in table 4). (a) The schematic view of the standoff distance used in experimentation (b,c,d) Actual photographs of plasma jet at different standoff distance. 

Figure 33 Particles dispersion with standoff distance and jet deflection after solution injection. 

Figure 34 Microstructure of single scan deposits on polished SS316 substrate at different standoff distances. (a) 60 mm (b) 50 mm (c) 40 mm. Substrates were pre-heated to 350 °C using plasma gun just before the spray. (d) Deposition on non-heated substrate from 40mm standoff 

Figure 35 Substrate heating profile for single scan experiment for cerium oxide deposition. ...
Figure 36 Mass loss and heat flow profile for Ce(NO$_3$)$_3$.H$_2$O.......................................................... 102
Figure 37 Microstructure of polished SS 316 substrate, heated to 700 °C. The fine grain on the surface is due to the surface oxidation while heating using plasma torch................................. 103
Figure 38 Microstructures of the deposits collected by single scan experiment on heated samples for 0.11M precursor. (a) Low magnification (b) high magnification (c) heating profile of substrate ........................................................................................................................................... 104
Figure 39 Microstructure of the deposits collected by single scan experiment on heated sample for 0.2M precursor. (a) low magnification (b) high magnification.............................................. 106
Figure 40 Microstructure of the deposit collected by single scan experiment on heated sample for 0.5M precursor. (a) low magnification (b) high magnification (c) Single splat consists of fine nano particles .............................................................................................................................................. 109
Figure 41 X-ray diffraction patterns of SPPS coatings prepared by different concentrations of precursor. The increase in the FWHM of the coating prepared by 0.11M indicates the coating consist of fine crystallites........................................................................................................................................ 110
Figure 42 Polished cross-section microstructure of the coatings from solution (a,b) 0.11M (c,d) 0.2M................................................................................................................................................................. 112
Figure 43 Polished cross-section microstructure of the coating from 0.5M solution precursor (a) low magnification (b) high magnification ....................................................................................... 113
Figure 44 Surface microstructure of the SPPS ceria coating at low and high magnification (a,b) 0.2M and (c,d) 0.5M solution precursor ......................................................................................... 114
Figure 45 TG-DTA curves at heating rate of 10 °C min$^{-1}$ from room temperature to 900 °C. (a) Ce(NO$_3$)$_3$.6H$_2$O (b) Sm(NO$_3$)$_3$.6H$_2$O (c) Gd(NO$_3$)$_3$.6H$_2$O .................................................................................................................................................. 117
Figure 46 TG-DTA of dried solution mixture (a) 90Ce(NO$_3$)$_3$.6H$_2$O-10Sm(NO$_3$)$_3$.6H$_2$O (b)  
80Ce(NO$_3$)$_3$.6H$_2$O -20 Sm(NO$_3$)$_3$.6H$_2$O ........................................................................................................... 120

Figure 47 TG-DTA of dried solution mixture (a) 90Ce(NO$_3$)$_3$.6H$_2$O-10 Gd(NO$_3$)$_3$.6H$_2$O (b)  
80Ce(NO$_3$)$_3$.6H$_2$O-20 Gd(NO$_3$)$_3$.6H$_2$O ........................................................................................................... 122

Figure 48 X-ray diffraction patterns of precursor mixtures dried at 110 °C ......................... 124

Figure 49 X-ray diffraction patterns of samarium doped cerium oxide SPPS coating. (a) 10 mol% 
(b) 20 mol% . CeO$_2$ standard (red line), Sm$_2$O$_3$ standard (green line) and (c) SS substrate ...... 126

Figure 50 Change in lattice parameter of CeO$_2$ coating with increase in dopant concentration 127

Figure 51 X-ray diffraction patterns of Gadolinium doped cerium oxide SPPS coating. (a) 
10mol% (b) 20 mol% . CeO$_2$ Standard (red line), Gd$_2$O$_3$ standard (green line) and (c) SS 
substrate .................................................................................................................................................. 127

Figure 52 Temperature profile of the substrate. First segment is the preheating of substrate, 
second segment is during coating, showing an increase and then stabilization in maximum 
temperature with increasing the number of scan ................................................................................. 129

Figure 53 Test coupons for the corrosion test. (a) Cerium oxide coated coupons (2.5X 2.5 X 
3mm) for the room temperature test (b) Cross section microstructure of the coating on 17-4PH 
steel (c) coupons (Φ~12.7mm, t~ 8mm) for the high pressure and temperature corrosion test. 135

Figure 54 Electrochemical corrosion test cell used for room temperature corrosion study 
consisting of the working electrode (test coupon), reference electrode Ag (Ag/AgCl) and counter 
electrode (Pt) .......................................................................................................................................... 135

Figure 55 High pressure and temperature corrosion test setup. (a) Front view of the set up (b) 
Inside view and (c) High pressure cell with electrodes ........................................................................ 136
Figure 56 A typical Nyquist plot and corresponding equivalent circuit model. .................. 138

Figure 57 Single time constant Bode plots (a) Impedance versus frequency (b) phase angle
versus frequency .................................................................................................................................. 139

Figure 58 Nyquist plot for the one time constant and corresponding Randels cell .............. 140

Figure 59 Electrified interface structure for a corroding coating metal............................... 141

Figure 60 Nyquist plot and equivalent circuit model for the entire spectrum and modified
Randels circuit for individual section ............................................................................................... 142

Figure 61 Open circuit potential for 17-4 PH SS, (a) polished, (b) grit blasted, and (c) ceria
coated, verses time in naturally aerated 3.5% NaCl at room temperature ................................. 145

Figure 62 Variation of corrosion resistance with time (a) polished 17-4 PH steel (b) Cerium
oxide coated grit blasted 17-4 PH steel.......................................................................................... 146

Figure 63 Microstructure of steel surface after corrosion test (a) Grit blasted surface (b) cross-
section of the grit blasted sample (The oxide layer has several breaks) (c) Cross-section of the
coated steel (d) polished surface. All samples were characterized after 72 days of exposure. .. 147

Figure 64 Effect of pressure on corrosion resistance of cerium oxide coated 17-4PH at 3.5wt%
NaCl and different ppm of dissolved H$_2$S .................................................................................... 149

Figure 65 Effect of temperature on percent change in Rcorr of polished and ceria coated steel in
3.5 wt% NaCl at 4000Psi .................................................................................................................. 150

Figure 66 Retention of the initial Rcorr of 17-4 PH steel in different surface conditions........... 151
LIST OF TABLES

Table 1 Characteristic of various thermal spray processes...
Table 2 Physical properties of the cerium oxide...
Table 3 Central composite design matrix for the APS cerium oxide coating...
Table 4 Summary of effect of spray drying parameters on properties of dried agglomerates...
Table 5 Surface area and pore volume of the spray dried agglomerated powders...
Table 6 ANOVA table for Density...
Table 7 ANOVA table for deposition efficiency...
Table 8 Solution precursor plasma spray parameters for cerium oxide coating...
Table 9 Concentration of Ce$^{3+}$ in coatings calculated from deconvoluted XPS peaks and average crystallite size from X-ray diffraction...
Table 10 Net enthalpy of CeO$_2$ formation and dehydration calculated from DTA plot...
Table 11 Desing of experiment for SPPS...
Table 12 Noumenclature for mixed solution precursors and respective coating...
Table 13 Properties of the most encountered solvents...
Table 14 Effect of plasma gun parameters on depososition efficiency...
Table 15 Average crystallite size of coating prepared by different concentrations of precursor...
Table 16 Density of the coating from different concentration solution precursor...
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>SPPS</td>
<td>Solution precursor plasma spray</td>
</tr>
<tr>
<td>SPS</td>
<td>Suspension plasma spray</td>
</tr>
<tr>
<td>CNP</td>
<td>Ceria nano particles</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid oxide fuel cell</td>
</tr>
<tr>
<td>YSZ</td>
<td>Yttria established zirconia</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>TBC</td>
<td>Thermal barrier coating</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>HR-TEM</td>
<td>High resolution transmission electron microscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>SLM</td>
<td>Standard liters per minute</td>
</tr>
<tr>
<td>SCFH</td>
<td>Standard cubic feet per hour</td>
</tr>
<tr>
<td>APS</td>
<td>Air plasma spray</td>
</tr>
<tr>
<td>HVOF</td>
<td>High velocity oxy fuel</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly ethylene glycol</td>
</tr>
<tr>
<td>DOE</td>
<td>Design of experiment</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo gravimetric analysis</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential thermal analysis</td>
</tr>
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CHAPTER 1: INTRODUCTION

Surface modification of the engineering materials has extended the operational life of many structures in term of resistance to wear and abrasion, corrosion, oxidation, fatigue and other forms of surface degradation. Among the various surface modification techniques, coatings form an important class. Numerous techniques have been developed for the deposition of thick and thin coatings such as chemical vapor deposition (CVD) [1], physical vapor deposition (PVD)[2], electro deposition [3], sol-gel [4], sputtering [5], molecular beam epitaxial (MBE) and thermal spray [6]. Thermal spray offers several advantages over other coating techniques such as high throughput, large area coating, deposition of compositionally graded material, and deposition capability of high to low melting point metals, thermal barrier coating [7], composites [8-10], polymers [11] and ceramics [12, 13]. Thermal spray processes are mainly used for overlay coating where materials are deposited in molten or semi solid state in layers of substantial thickness. A schematic overview of the thermal process is shown in Fig.1. Powder feed stock is injected into a hot plasma jet, which melts powder particles and accelerates resulting molten particles towards the substrate for deposition in layers. The various thermal processes, their characteristics and respective applications are shown in the Table 1.

Traditionally, thermal spray coating has been used for surface protection of engineering materials from wear, corrosion and oxidation. Recently researchers have shown their interest in, the conceptual basis for this technology for producing new functional surfaces and materials for a variety of technological applications such as fuel-cells [14], sensors for various operating conditions [15], electronic devices [16], photo catalysis [17] and nano structured coatings [18].
These new class of applications have diverted engineers and scientists towards nano structured materials/consolidation and their manufacturing techniques. Among different thermal spray processes the direct current (DC) plasma spray has revealed great interest for nano structured coating. Thus, various studies have been devoted to the improvement and implementation of cost-effective plasma-spray of finely structured or nanostructured layers on large surfaces, with these coatings exhibiting superior resistance to wear [19-21], erosion, cracking and spallation [22]. Two different routes of plasma spray can be used for the thick deposition of nano structured material, namely (1) Plasma spray of agglomerated nano powders and (2) solution plasma spray.

Figure 1 Schematic of thermal spray deposition
### Table 1 Characteristic of various thermal spray processes

<table>
<thead>
<tr>
<th>Spray Type</th>
<th>Feed type</th>
<th>Flame Temperature (°C)</th>
<th>Particles Velocity (m/s)</th>
<th>Material</th>
<th>Microstructural Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>HVOF</td>
<td>Powder</td>
<td>~4000</td>
<td>~400-800</td>
<td>Metal/cermets, Low melt ceramic</td>
<td>High density, Excellent adhesion, compressive stress</td>
</tr>
<tr>
<td>Plasma</td>
<td>Powder</td>
<td>~20,000</td>
<td>~80-300</td>
<td>Ceramic/metal</td>
<td>Porosity in ceramic coating</td>
</tr>
<tr>
<td>Wire</td>
<td>wire</td>
<td>~6000</td>
<td>~50-150</td>
<td>Metal</td>
<td>Dense, thick</td>
</tr>
<tr>
<td>Cold Spray</td>
<td>powder</td>
<td>~25</td>
<td>~400-800</td>
<td>Metal</td>
<td>Dense, compressive stress</td>
</tr>
<tr>
<td>Solution plasma</td>
<td>Salts precursor or suspension in liquid</td>
<td>~20,000</td>
<td>Ceramic</td>
<td>Porous/dense Thin/thick</td>
<td></td>
</tr>
</tbody>
</table>

### 1.1 Overview on Plasma Spray Coating

Plasma is the fourth state of matter consisting of neutral atoms, positive ions and free electrons. This is produced by transferring energy to gases until the energy level is sufficient to ionize the gases, so that electrons and ions can act independently of one another [23]. The plasma state can be achieved when, under an electric field, current can be sustained as the free electrons move through the ionized gas. A primary gas (Argon) is generally used to create a plasma plume, produced by a direct current (DC) or radio frequency (RF) high voltage discharge between the two electrodes. The resistance heating from the arc causes the primary gas to reach extreme
temperatures, dissociate and ionize to form plasma. In the DC plasma condition, gas heating is sufficient to generate core plasma temperature more than 20,000 °C, depending on the gas’ properties and its electrical breakdown characteristics. The enthalpy of the plasma depends on the gas mixture used.

![Figure 2 Enthalpy values of typical plasma spray gases as a function of temperature [24].](image)

Monatomic gases such as Argon and helium are easy to ionize into their respective ionic species, Ar⁰ and He⁰, and free electrons. On the contrary, di atomic gases such as H₂ and N₂ are hard to ionize, which is related to the high energy required for the dissociation of their molecular structure, and subsequent ionization. A DC plasma spray torch consists of an axially aligned cathode (thoriated tungsten) and copper anode (OFHC copper). Plasma gases (Ar, He, H₂ and N₂) flow around the water cooled cathode and nozzle constricts. Tungsten is used as a cathode,
due to its high melting point and good thermionic emitter, readily releasing electrons to maintain the arc discharge. DC plasma hardware is intensely water cooled to prevent melting and to minimize cathode and nozzle erosion. The plasma gas exits the nozzle as a free or neutral plasma flame, meaning it does not carry any current. The plasma gases are heated as they pass around and through the arc. The heated gases expand radially and axially, accelerating as they expand and exit through the nozzle. Once the plasma is stabilized the material to be coated is fed in to the plasma jet, mostly externally, in front of the torch. The rapid energy transfer to the powder is utilized to melt and accelerate them towards the intended area that is to be coated. Upon impact to the substrate, the molten particles form splats that solidify in microseconds. Subsequent molten particles deposit on the earlier solidified layer thus the coating consists of a lamellar structure with properties different from those of the bulk material. Generally plasma spray coatings are much stronger, denser and cleaner than other thermal spray processes. HVOF and detonation process can provide coatings close to the theoretical density but are limited to metallic materials.

The plasma spray process seems straightforward to understand and operate, and has been used in industries for many years. However, the various process parameters related to the plasma jet, powder physical characteristics and powder delivery make the process irreproducible and inconsistent. This results in poor quality and non repetitive production of coatings. There are various parameters which control the properties of the quality coatings as summarized in Fig. 3. Firstly, the plasma gas composition and flow rate dictate the temperature and velocity of the plasma jet, secondly the powder’s physical characteristics, such as melting point, size, morphology, size distribution and flow rate, influence the particle velocity and temperature of
the particles, which finally influences the coating microstructure and mechanical properties. The substrate conditions, such as roughness and preheating influence the splat morphology and adhesion of the coating.

Figure 3 Processing parameters in plasma spraying
1.2 Atmospheric Plasma Spray Coating of Nano Structure Ceramic Powder

Due to superior properties observed in nano structured bulk materials the study has been extended to the consolidation of nano materials with retained nano structure using thermal spray technique. Recently, thermal spray techniques have been demonstrated for nano structured coatings and bulk free standing parts [25-27]. These coatings have shown superior wear resistance (Al₂O₃-13%TiO₂) [20, 28] and durable thermal barrier (TBC) (YSZ) [22, 29] properties compared to conventional thermal spray coating. Conventional thermal spray coatings are made from micron sized powder (10-100 μm) feed stock. Despite their theoretical advantages, submicroscopic and nano powders (<100nm) have practical difficulties of feeding and transporting, if they are injected using conventional powder feeder. The uncontrolled agglomeration due to electrostatic attraction between nanoparticles and poor flowability are the main problems faced. Another problem is the injection/penetration of the fine light weight oxide particles into the plasma flame as compared to their coarse counterpart. This can cause the particles to travel along the outer and colder zones of lower heat transfer. Using a high carrier gas flow rate might provide a solution when dealing with fine particles. Often this may lead to intense cooling of the plasma flame. To overcome the aforementioned issues, nano particles are agglomerated to micron size particles (30-80 μm) using a spray drier. The mechanisms of agglomerated particle deposition and heat transfer are shown in Fig. 4.
Figure 4 Deposition mechanism of agglomerated nano particles (a) partial melting and retention of nano particles (b) complete melting

There are two types of interactions possible with a plasma flame, depending on the agglomerate size and spray parameter. First, is the melting of the outer layer of the agglomerate due to the heat transfer from plasma flame and retention of the nano particles in the core of agglomerate which, upon deposition, gives a bimodal distribution of the re-solidified molten and semi–molten portion. The second involves the complete melting of the agglomerates and deposition (Fig.4b). Therefore, controlling the plasma spray parameters is an important step to produce nanostructured coating which decide the microstructure and mechanical properties. Another tactic is to use agglomerates of different melting point materials [13]. During exposure
to plasma heat low melting point material melt first and keep high melting point constituent in coating matrix.

Various recent studies show the mechanical properties enhancement by retaining the nano grain microstructure. The abrasion wear study of TiO$_2$ coating prepared by conventional (fused and crushed powder) and nano structured TiO$_2$ powders using APS and HVOF showed a great improvement [28]. A reduction in abrasion wear levels of ~ 60% was reported for TiO$_2$ nano structured coating when process was switched from APS to HVOF [28]. The bond strength for HVOF nano TiO$_2$ coating of was 1.6 times higher than that of the APS conventional coating. Fatigue life of the HVOF nano TiO$_2$ was 1.7 times higher than that of the APS conventional TiO$_2$ [30]. The study on abrasion wear behavior of conventional and nanostructured Al$_2$O$_3$-13wt.% TiO$_2$ also revealed an enhancement of the wear abrasion resistance by 33% for the nano structure coating prepared by APS [31]. This improvement was further enhanced by change in spray method from APS to HVOF by 90% for the nano structured Al$_2$O$_3$-13wt.% TiO$_2$ coating. The high velocity process retain 52% of semi-molten nano structured Al$_2$O$_3$ -13wt% TiO$_2$ particles in the coating microstructure. The nano structure coatings for thermal barrier application have also showed improvement. Specially, Yttria stabilized zirconia (YSZ) is extensively used for protection of gas turbine component from high temperature degradation (>900°C) due to the oxidation and high temperature corrosion. The stringent requirement of high temperature application leave limited choice of materials and their specific properties. Plasma sprayed YSZ coating on hot section of turbine (made of super alloys) is a well established choice which need to have low thermal conductivity, low elastic modulus, high thermal shock resistance and high strain tolerance. The inherent porosity and cracks generation in plasma sprayed coating
fulfill the requirement at some extent. Recently, nano structured YSZ coatings have also received attention due to bimodal distribution of the grains. Chen et al. measured the thermal diffusivity of such coating and compared with them conventional YSZ coating up to 1200 C [32]. The lower diffusivity in nano structured coating compared to conventional counterpart was observed due to the presence of nano porosity network within the nano zone. The porous ceramic nanozones spread all over the coating microstructure in addition to the regular globular and intersplat porosities of the coating [33]. Liang and Ding described the high thermal shock resistance of nano structured TBC at high temperature upto 1300 C which may be caused by the enhancement of the fracture toughness of YSZ TBC [34]. The high toughness of the coating can be attributed to the presence of porous nano zone which acts as a crack arrester. Other plasma sprayed nano structured ceramic coatings including, nano alumina, nano titania and hydroxyapatite have exhibited their enhanced biocompatibility with osteoblast cells [35, 36]. This enhancement is translated to the enhancement of cell proliferation and better adhesion on the coating surface due to nano porosity and nano roughness.

**1.3 Solution Precursor Plasma Spray (SPPS)**

SPPS technique was initially started at in 90s for improving life of the YSZ based thermal barrier coating. This technique has been explored extensively in last one decade for various applications such as, nano structured coating for photo catalysis [37], porous electrode for SOFC [38, 39] superior YSZ thermal barrier coating [40] and yttrium aluminum garnet (YAG) [41].
In this process the liquid solution is generally atomized into the core of the plasma jet, keeping atomizing nozzle few millimeter away from the gun nozzle exit to synthesize the desired coating. These droplets in the range of 2-100 μm attain velocities up to 60 m/s. Depending on the droplets’s initial size and injection method (axial or transverse), these droplets further fragment into daughter droplets. The studies have suggested that the transverse injection affect the trajectory of the plasma jets; higher atomization pressure causes the droplets bypass the plasma flame and lower pressure does not allow penetration to the plasma jet [42]. The axial injection results in the fast heating of the droplets and melting, as compared to the transverse injection [43]. The mechanism of the droplet interaction and coating deposition on the substrate in SPPS method is discussed in the following section.

1.3.1 Mechanism of Deposition

Unlike the plasma spray coating of the powders, microstructure of the solution precursor plasma sprayed coatings differs in splat size and degree of melting. After injection of the solution droplets into plasma, the thermo-chemical interaction with the plasma jet can be summarized in following steps [40, 42, 44];

(a) Aerodynamic breakup

(b) Heating, vaporizing and internal precipitation

(c) Internal pressurization and droplet breakup

(d) Decomposition

(e) Solid particle heating and melting

(f) Evaporation from the melt

(g) Impact on the substrate
Figure 5 Schematic of SPPS process illustrates formation of different morphology of the coating surface depending on the precursor injection in different zone of plasma flame (a) droplet evaporation, shell formation and volume precipitation (b) pyrolysis and sintering (c) melting (d) crystallization [40, 45]

Figure 5 shows a basic configuration of the solution precursor plasma spray process. As the initial droplets enter into the plasma after primary atomization, secondary atomization occurs due to aerodynamic breakdown of the solution droplets. The time scale for the secondary break up corresponds to microseconds. Then droplets undergo rapid vaporization of the solvent. The diffusion of solutes from the center to the outer layer is slower than the vaporization, increasing the solute concentration at the surface until the level of super saturation is reached. Then the precipitation of solid shell starts (Fig. 5A). The shell porosities depend on the chemistry of the solution. For the smaller droplets less than 5µm volume precipitation occurs whereas the larger
droplets experience shell precipitation and fragmentation into smaller droplets depending on the mechanical properties of the shell and internal pressure. Furthermore, spatial distribution of the droplets in the plasma flame leads to having different deposition characteristics. The droplets which are just interacting with the outer lower temperature periphery of plasma evaporate and fragment into smaller droplets (Fig. 5, case A). Droplets travelling in the high temperature zone of the plasma experience pyrolysis (decomposition) and sintering, and final melting (case B and C). Finally recrystallization occurs after solidification if particles travel without deposition on the substrate (case D). The precursor concentration has also shown the effect on density of the deposits [46]. The higher concentration leads to the volume precipitation which results in the denser coating however, this would need increased the plasma energy for the complete pyrolysis and melting. The precursor with low concentration experiences the surface precipitation and shell formation resulting in semi-pyrolyzed deposition alongwith the coating. The modeling results show that the similar size solution droplets interaction to the plasma flame results in the following possibilities (Fig. 6) [42].

- Volume precipitation lead to the solid particle formation (route A)
- Super saturation near the droplet surface leads to the inelastic/elastic shell formation, the shell break up and formation of different structure depending on the permeability of the shell (B). B (I) (low permeability), B(II) (high permeability), B(III) (impermeable) inelastic shell. Whereas C corresponds to elastic shell formation due to the supersaturation.
Figure 6 Vaporization and precipitation routes for a solute droplet [42]

1.3.2 Microstructure Development in SPPS Process

Coatings prepared by SPPS technique are micro-structurally different from the conventional plasma spray coating in terms of the splat size, splat boundary, density and porosities. Various factors such as precursor concentration, solvent characteristic, method of injection and plasma spray parameter affect the microstructure of the coating. Figure 7 shows the cross section microstructure of the YSZ coating prepared by aqueous precursor (Fig. 7a, b) and for comparison YSZ APS coating from powder (Fig. 7c). SPPS coatings are typically made of the micron size splats (<5µm) (Fig 7d) which have grain sizes in nano range (10-100 nm), consist of nano and micron scale porosities. A unique feature in SPPS YSZ coating is the through-thickness cracks which arise from the stress relieving (Fig. 7b). These through thickness
cracks are due to the accommodation of stress arising from the pyrolysis shrinkage. During SPPS coating manufacturing unpyrolyzed particles also get deposited within the layers. These buried unpyrolyzed droplets decompose when coating temperature exceeds the decomposition temperature during the successive deposition of upper layers or post treatment of the coating. The in situ thermal decomposition generates tensile stresses within the coating which leads to the through thickness cracks within the coating. The fraction of unpyrolyzed particles can be controlled by the method of the atomization in plasma jet and the spray techniques. A few researches has revealed the dense coating possibility by controlling the content of unpyrolyzed solution deposits through the drops atomization and spray pattern [47]. Chen et al. have demonstrated the solution concentration effect on density of TiO₂ and YSZ SPPS coating [37, 46, 48]. The porous microstructure was observed in low solution precursor concentration coating whereas density enhances with concentration close to equilibrium saturation concentration (Fig. 8).
Figure 7 Microstructure of SPPS coating (a) YSZ low magnification SEM depicting through thickness vertical cracks [45] (b) Magnified image showing the micro and nano porosities [45](c) conventional YSZ APS coating for comparison (d) Surface of the SPPS coating (single scan)
1.3.3 Cerium Oxide

Cerium oxide is a rare earth oxide from lanthanide series. It is the most abundant rare earth material. It has fluorite crystal structure. Most of the other rare earth elements have stable trivalent valence state whereas, cerium exhibits dual valence state Ce$^{3+}$ and Ce$^{4+}$. A facile transition of oxidation state in cerium oxide from Ce$^{3+}$ to Ce$^{4+}$ and vice versa makes this oxide attractive for many scientific fundamental studies and technological important applications[49, 50]. In cerium oxide, changes in oxidation state from 4+ to 3+ introduce oxygen vacancies in fluorite lattice as a result this can be used as a conducting material for oxygen ions. It is proved that the change in valence state is dynamic and affected by the physical parameters such as, environment (reducing/oxidizing), temperature and presence of other ions [51, 52]. Due to its facile change in oxidation state it found many applications in diverse fields, such as an electrolyte in solid oxide fuel cell [53, 54], three way catalyst in auto motive to eliminate toxic
gases [55-57], water gas shift, high temperature corrosion protection of steel layer [58], and antioxidant for free radical scavenging in biological system[59, 60].

1.3.4 Organization of Dissertation

This dissertation focuses the development of rare earth cerium oxide nano structured coating using thermal spray technique such as atmospheric plasma spray and solution precursor plasma spray. Further coating was characterized by various analytical techniques and investigated for their applicability under extreme environmental conditions. The work also includes the design and development of the high pressure and temperature corrosion autoclave for investigating corrosion protection of the steel.

The different chapters in this dissertation are partial reproduction of various research papers published or communicated by author during the course of his doctoral studies at Surface Engineering and Nanotechnology Facility and Plasma Nano-Manufacturing Facility in the Advanced Materials Processing and Analysis Center at University of Central Florida, Orlando Florida USA.

The first chapter, which is the current one, gives overall background information of the overall process, technique, and motivation behind the research.

The second chapter presents the spray drying technique for agglomeration of cerium oxide nano particles to make them sprayable in the atmospheric plasma spray process. The suspension was prepared with different percentage of nano particles loading for spray drying. The statistical design of experiment (DOE) is used to optimize the cerium oxide coating parameters. The deposition efficiency and the density of the coating were optimized. The effect
of various plasma spray parameters on cerium oxide coatings is discussed along with the issues related to coating development.

In the third chapter author will investigate a novel solution precursor plasma spray (SPPS) technique for the direct deposition of cerium oxide coating from different cerium salts solutions as precursors. The study involves the injection of the water soluble precursor’s solution into the hot zone of the plasma plume using an atomizer to deposit nano ceria coatings. The decomposition of each precursor to cerium oxide is analyzed by thermo gravimetric-differential thermal analysis and validated by thermodynamic calculations. A numerical study of the droplet injection model has been employed for microstructure development during SPPS. X-ray photoelectron spectroscopy studies indicated the presence of a high concentration of Ce\(^{3+}\) (up to 0.32) in the coating prepared by SPPS. The processing and microstructure evolution of cerium oxide coatings with high non-stoichiometry are reported.

In the fourth chapter, effects of various factors on coating deposition behavior are studied. Among them the critical ones are concentration of the precursor, standoff distance and plasma power, which were varied and correlated to the microstructure development. The study was further extended for the synthesis of in situ doped samarium and gadolinium in cerium oxide lattice using, the premixed nitrate precursors of the samarium/gadolinium nitrate with cerium nitrate. TG-DTA study was performed on the mixed salt precursors in order to understand the mixed precursor’s decomposition behavior in the case of doped system. X-ray diffraction studies were performed to confirm the doping and the presence of the contamination from the unpyrolyzed precursor in the coatings.
In the fifth chapter, application of nanoceria coating is presented to protect 17-4PH precipitation hardenable steel under high pressure (up to 10k Psi) and temperature (up to 300 F), 3.5 wt% NaCl, acidic pH and hydrogen sulfide condition. This part of the dissertation demonstrates the design and development of the high pressure system coupled with the in situ electro-chemical impedance spectroscopy measurement. The high pressure cell was designed to mimic the down hole conditions in oil-well condition. First various coupons of stainless steel grade 17-4 PH were coated with cerium oxide by air plasma spray and electrochemically evaluated in naturally aerated 3.5% NaCl solution at room temperature. Electrochemical corrosion analysis as well as microstructure characterization techniques were employed to evaluate the effectiveness of plasma spray coated nanoceria coating as a corrosion inhibitor. Further, the corrosion resistance behavior of bare and cerium oxide coated 17-4 PH steel was measured under different pressure, temperature and H$_2$S concentration. The equivalent circuit model was used to analyze the electrochemical impedance data and mechanism of the corrosion mechanism.

In the sixth chapter, conclusion of this dissertation is presented.
CHAPTER 2: ATMOSPHERIC PLASMA SPRAY OF NANO STRUCTURED CERIUM OXIDE COATING

2.1 Introduction

Recently, bulk nano structured materials have received a lot of attention due to their superior wear resistance and mechanical properties. Various manufacturing techniques, such as, spark plasma sintering, rapid heating, severe plastic deformation, microwave sintering, electro deposition and thermal spray have been used to retain nano grains in bulk components. Among them thermal spray is one of the techniques that can provide direct bulk consolidation of nano particles without any post treatment. However, nano sized particles pose several difficulties while plasma spraying, unlike their micron sized counterparts. The physical characteristics, such as high surface area, low mass, and irregular shape of individual particles hamper the flowability of the nano powder to the plasma gun which results in lower deposition efficiency, poor density, and loss of powder due to vaporization. To surmount the aforementioned problems nano powders have been agglomerated by spray drying techniques into spherical shapes for uninterrupted flowability [61]. Plasma spraying of the agglomerated powder provides bimodal grain size distribution. The fully molten particles deposit as splats on the substrate whereas partially melted particle (outer surface melted and inner core unmelted) deposits as nano grains sandwiched between the solidified molten splats. However, depending upon the plasma spray condition, it is possible to achieve a fully molten state of particles which leads to a high density coating deposit. Recently, high density alumina, alumina-13% titanium oxide, and titanium oxide coatings have been prepared using plasma spray with agglomerated nano particles.
Various metal oxides have been reported for electrolytes in SOFC. Doped cerium oxide is one of the important electrolyte materials for intermediate temperature SOFC due to its high oxygen ionic conductivity at lower temperatures. To achieve high ionic conductivity the electrolyte materials need to have a high density. The traditional method of making ceria based electrolytes by powder pressing and sintering provides high density (~99%) materials, but the high sintering temperature along with the long sintering time (typically ~1600-1700 °C for 4-8h) makes the process costly. On the other hand, synthesis of thin, high density electrolytes by thermal spray can be a cost effective route. In fact, recently it was proposed that thermal spray can be an integrated approach for manufacturing of an entire SOFC component by deposition of layers of anode-electrolyte-cathode in single operation. However, the high vapor pressure of cerium oxide results in vaporization under the high temperature plasma jet, which affects the density and deposition efficiency of the coating. Thus, in the present work, efforts are made to develop high density cerium oxide electrolytes as plasma sprayed coating from agglomerated nano powder. The nano particles are spray dried to obtain spherical agglomerate for plasma spray. Since, the high vapor pressure and nano characteristic of the cerium oxide affect coating quality, a design of experiments technique was used to optimize coating deposition efficiency and density.

2.2 Design of Experiments in Thermal Spray Process

The large number of process variables in any manufacturing process makes process cumbersome for product optimization. Design of experiment (DOE) is a statistical tool by which
one makes purposeful changes to input variables of the process in order to observe the desired effects on the output and has found use in many industries e.g. chemical, pharmaceutical, electronics, automotive, goods manufacturing, etc. The traditional way of running experiments involves running one factor-at-a-time. This method is inefficient and often yields misleading outcomes. On the other hand, factorial designs (a basic type of DOE), requires a minimal number of experiments, and allows the identification of interactions in the processes. The information leads to important breakthroughs in the process understanding, improved quality, and reduced costs. As stated before the thermal spray process of coating deposition involves various process variables, some of which are inter-related while some independently control the quality of the coating. Varying individual parameters to improve the desired property of the coating wastes both time and material. Therefore, DOE becomes important in identifying the important parameters which are going to affect the required properties and their interaction. In thermal spray, properties of the coating are end application dependent. Some of the important properties of the coating are discussed in following section.

Thermal spray is the process of consolidation of metal/ceramic on the substrate in the form of coating, therefore the microstructure of the coatings results from solidification and sintering [6]. The coatings have a lamellar microstructure which determines the coatings properties. Various process variables and outcomes can broadly be categorized in following sub group [62].

**First group of variables are related to the feed stock property (input):**

(a) Powder particle size (finer, medium and coarse)
(b) Size distribution of the powder
(c) Powder morphology (spherical, angular, porous, etc.)
(d) Powder feed rate

Second group of variables are related to the plasma spray (input):

(a) Primary gas flow rate
(b) Plasma Current
(c) Secondary gas flow rate
(d) Standoff distance
(e) Electric power input
(f) Carrier gas flow rate

The measurable important properties while spraying (output)

(a) Velocity of the particles
(b) Temperature of the particles at impact

Properties of the coating dependent on the feed stock and plasma process (output)

(a) Density/porosity of the coating
(b) Deposition efficiency
(c) Microstructure (fine course)
(d) Tensile bond strength
(e) Erosion, wear rate and sliding wear rate
(f) Hardness
The relation between the process parameter (variables) and properties of the coating (responses) can be represented by following polynomial equation (regression equation) [62].

\[
Y = b_0 + \sum b_iX_i + \sum b_{ij}X_iX_j + \sum b_{ijk}X_iX_jX_k + \text{higher order terms}
\]

(2.1)

Where i,j,k vary from 1 to the number of variables; coefficient \(b_0\) is the mean of responses of all the experiments, coefficient \(b_i\) represents the effect of the variable \(X_i\), and \(b_{ij}\), \(b_{ijk}\) are the coefficient of regression which represent the effects of the intersection of variables \(X_iX_j\) and \(X_iX_jX_k\). A complete central composite design (CCD) experiment design allows estimation of a full quadratic model for each response. The coefficient of the regression equation can be determined by the following design of experiments approaches.

**2.2.1 Factorial Design of Experiment**

The simplest factorial design involves two factors (variables) each at two levels as shown by the square layout (2k, 2 level and k factors (k≈2)). The advantage of the factorial design becomes more pronounced with increasing numbers of factors. A factorial design with three factors at two levels requires only 8 runs (in the form of a cube). The factorial design of experiment covers a broader area from which inferences of the process can be drawn and it reveals interactions of factors.

Two level factorial DOE is used when interaction between the factors \(X_i\) and \(X_j\) are evaluated in equation 2.1. It is important to determine whether the factors are statistically
significant or not. The highest absolute value of the coefficient $b_i$ corresponds to the most significant factor $X_i$ or their interaction $X_iX_j$.

The full factorial approach covers all combinations of factors and provides important information on factors interactions. However, the number of experiments $n = 2^k$ increases rapidly with the increase in the number of factors (e.g. $k=6$, $n=64$ experiments). The “fractional factorial design ($2^{k-m}$)” is another approach where one can study many factors and still keep the experiments to a reasonable size [63]. These particular designs are especially good for screening many factors in search of the critical few which enables the obtainment of the main effects and also some first order interactions.

2.2.2 Response Surface Method (RSM)

Response surface methodology (RSM) is a statistical technique that is helpful for modeling and analyzing problems in which responses of interest are influenced by several factors, and the aim is to optimize this response. RSM is applied when the relationship between the response and factors are not linear and factors at multiple levels have to be used to determine quadratic $b_{ii}X_i^2$ or $b_{iii}X_i^3$ terms. RSM provides the interactive effects among the variables and determine the optimum conditions. The goal of RSM is to generate a map of response, either in the form of contours or as a 3-D, rendering and find the region of optimum response.

The important response surface methods can be further categorized as follows;

(i) Central Composite Design (CCD): A CCD has three groups of design points (a) Fractional factorial design points (b) axial and star points and (c) center points as
shown in Fig. 9. Each factor in CCD can have five levels. In Fig. 9 if \( n \sim 1 \), then three levels for each factor can be used to get the face centered cubic array.

(ii) Box- Behnken: This design includes all the middle points of the edges of the \( k \) factors cube. The center points are replicated for orthogonality to estimate the global standard deviation. Box-Behnken design was proposed by G.E.P. Box in 1978 [64]. This design allows a designer to adequately quantify a response with a reasonable number of tests. In general, Box-Behnken designs require three levels for each factor, thus allowing evaluation of second order models (Fig. 9b)

![Figure 9](image-url)  

(a) Central composite design (b) Box-Behnken

### 2.2.3 Application of Response Surface Method in Thermal Spray

As stated earlier, thermal spray techniques have various variables. Thus identification of optimized spray parameters not only saves time, but also money in many engineering industries.
Many different types of designs have been proposed in literature to optimize different properties of the coatings such as, density, porosity, microstructure, thermal conductivity, hardness, wear resistance, and elastic modulus. Various coatings material have been studied including, Al₂O₃-TiO₂ [65], ZrO₂ [66], YSZ [67], Tungsten[68], Hydroxyapatite [69], ZrO₂-Al₂O₃, etc., and SPPS coatings such as TiO₂ and Ni-YSZ [70]. A recent study by Anirudha et al.[71] provides an example for developing a process map, and optimizing YSZ coating properties using a central composite design.

2.3 Materials and Methods

2.3.1 Powder Feed Stock Characteristics

The nanocrystalline cerium oxide (50-80nm) was procured from Inframat Inc, Connecticut. The physical properties of the powder are listed in table 2. The morphological features of the particles were confirmed by TEM and it was seen that the initial nano particles were near hexagonal in morphology. Poly ethylene glycol (MW=3400) was used as a binder due to its low decomposition temperature and exothermic nature.

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting point</th>
<th>Surface Area (m²/g)</th>
<th>Density</th>
<th>Structure</th>
<th>Boiling point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerium oxide (CeO₂)</td>
<td>2600 °C</td>
<td>11-17</td>
<td>7.65</td>
<td>Fluorite</td>
<td>-</td>
</tr>
</tbody>
</table>
2.3.2 Spray Drying

Spray drying is the process of manufacturing dry solid agglomerated particulates by feeding solution/suspension of nano/micron particles. A schematic of the process is shown in the Fig. 10.

In brief, spray drying is extensively used in food and pharmaceutical industries for drying milk and medicine slurry in dry agglomerates. Similar concepts have been adopted by ceramic powder manufacturing industries [72]. This technique involves the atomization of the liquid feed stock into spray of fine droplets which come in contact with hot air in the drying chamber. The heat transfer from the surrounding hot air to the droplets, evaporates the solvent, and dries them into agglomerated powder particles. Dry powder is continuously collected away from the drying chamber. Various operating conditions such as drying temperature, air flow rate, injection flow rate, and power of ultrasonic atomization nozzle are adjusted according to the suspension characteristics (e.g. per cent solid loading, solvent, viscosity, etc.) [73, 74], and required physical properties of the spray dried powder (e.g. size, porosity, tape density, etc.). Spray dried agglomerated nano powders offer an advantage in thermal spray to tailor the coating from porous to high density. Additionally, spray dried powders are often spherical in shape, promoting free flowability to the plasma jet. Using this technique high density coatings were achieved for Al₂O₃-13 TiO₂, while, porous and durable thermal barrier coating was reported for YSZ [33, 75]. Recently, this technique has been used for the composite powder manufacturing such as Al₂O₃-CNT [76], Al₂O₃-TiO₂[28], YSZ-Al₂O₃[61]. Both the particle size and particles density are crucial for the coatings due to heat transfer from the plasma flame. Ideal powder should be dense enough and have narrow size distribution. If the spray dried powder is finer and has low density,
then it cannot be fed into the hot zone of the plasma jet, and will float on the periphery of the plasma plume or evaporate by super heating, resulting in poor bonding strength of the coating, and low deposition efficiency.

Figure 10 Schematic of spray drying showing the injection of the suspension from top of the spray drying cylinder and collection of the dried agglomerated particles
### 2.3.3 Spray Drying of Cerium Oxide Powder

The agglomeration of nano ceria powder was carried out in a laboratory tabletop Buchi B 290 (Buchi Corp. Newcastel, DE) spray drier. The suspension of ceria nano particles was prepared by first dissolving PEG (MW 3400) in DI water (10 wt% of the nano powder) followed by dispersing the nano particles with vigorous stirring and ultra-sonication. Three concentrations 30%, 40% and 50% Wt% of ceria suspension were prepared for spray drying. The initial particle size of the nano ceria and final spray dried particles are shown in figure 11 (a and b). The different weight percents of ceria particle suspensions were prepared in order to increase spray dried particles size while keeping other parameters constant. The suspension was kept at 80 °C in order to lower the enthalpy required for spray drying. The final average particle size was measured by image analysis software (IQ materials 2).
Figure 11 Morphology of the cerium oxide particles. (a) TEM of nano ceria (b) SEM of spray dried agglomerated ceria particles (c) Cerium oxide coating
2.3.4 Atmospheric Plasma Spraying

APS was used for the coating development from agglomerated nano particles. Praxair SG 100 DC plasma (SG100 Model Praxair TAFA, Concord, NH) torch (with the 8mm nozzle diameter and thoriated tungsten tipped cathode) mounted on a 6 axis robot (ABB Inc) was used for spraying at a 350mm/min traverse speed. Argon and hydrogen gases were used as primary and secondary gases, respectively. The plasma power (20-35kW), distance between substrate and torch, carrier gas flow rate, and secondary gas flow rate were varied to optimize deposition efficiency and density of the coating. The effects of internal and external injection at angle were also analyzed (Fig. 12).

Figure 12 External injection at (1) 90° of the plasma jet (2) Outward injection direction (3) inward injection direction tilted by ± 30° from black center line
Identical sized mild steel substrates were grit blasted, weighed, and pre heated to 200 °C before the coating. Various coated samples were prepared according to the design of experiments. Polished cross sections (1µm finish) of each sample were analyzed under SEM, and the density was determined by measuring the fraction of molten area in the image using image analysis software (at 500X with at least 3 images for each sample). The deposition efficiency (%) was calculated by measuring the coating weight, and dividing by the total powder released from the powder injector during deposition cycle. For each experiment the robot traverse speed and number of torch scans were kept constant.

2.3.5 Optimization of Coating

Central composite design (CCD) is a response surface method (RSM) which was used to optimize coating properties. The four critical factors; (1) plasma power (A) which depends on the hydrogen flow rate and torch current, (2) standoff distance (SOD), (3) powder flow rate (PFR) and (4) carrier gas flow rate (CFR), were included in the CCD. Each factor was varied at three levels, thus the CCD was a face centered cube. The design of experiments consisted of 30 experiments with six repeated center points as shown in Table 3. In table these experiments are randomly distributed however, to better understand those were arranged based on the position in a cube. The experiments were conducted randomly with respect to the number order of column 2 of table 3 to reduce the effect of systematic errors. The other parameters were kept constant such as primary gas flow rate, traverse speed of torch and number of scans. The two responses were optimized, deposition efficiency (DE) and density of the coating (or Density) calculated from cross-section of the coatings estimated by image analysis. The experimental results were analyzed using Design expert® 8 software.
Table 3 Central composite design matrix for the APS cerium oxide coating

<table>
<thead>
<tr>
<th>Run</th>
<th>Type</th>
<th>Plasma Power</th>
<th>Spray Distance (mm)</th>
<th>Powder Flow Rate (rpm)</th>
<th>Carrier gas (SCFH)</th>
<th>Efficiency (%)</th>
<th>Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>1</td>
<td>Center</td>
<td>30</td>
<td>70</td>
<td>3</td>
<td>7</td>
<td>29.8</td>
</tr>
<tr>
<td>28</td>
<td>7</td>
<td>Center</td>
<td>30</td>
<td>70</td>
<td>3</td>
<td>7</td>
<td>31.68</td>
</tr>
<tr>
<td>27</td>
<td>12</td>
<td>Center</td>
<td>30</td>
<td>70</td>
<td>3</td>
<td>7</td>
<td>25.89</td>
</tr>
<tr>
<td>29</td>
<td>15</td>
<td>Center</td>
<td>30</td>
<td>70</td>
<td>3</td>
<td>7</td>
<td>27.16</td>
</tr>
<tr>
<td>30</td>
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<td>Center</td>
<td>30</td>
<td>70</td>
<td>3</td>
<td>7</td>
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<td>Center</td>
<td>30</td>
<td>70</td>
<td>3</td>
<td>7</td>
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</tr>
<tr>
<td>23</td>
<td>3</td>
<td>Axial</td>
<td>30</td>
<td>70</td>
<td>3</td>
<td>6</td>
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<td>Axial</td>
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<td>70</td>
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<td>7</td>
<td>34.53</td>
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<td>70</td>
<td>3</td>
<td>7</td>
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<td>37.97</td>
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<td>80</td>
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<td>7</td>
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<td>29</td>
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<tr>
<td>17</td>
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<td>25</td>
<td>70</td>
<td>3</td>
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<td>Axial</td>
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<td>8</td>
<td>33.5</td>
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<td>80</td>
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<td>80</td>
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<td>80</td>
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<td>6</td>
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<td>60</td>
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<td>11</td>
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<td>80</td>
<td>3.5</td>
<td>6</td>
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<td>80</td>
<td>2.5</td>
<td>8</td>
<td>47.89</td>
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<td>Fact</td>
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<td>80</td>
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<td>Fact</td>
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<td>60</td>
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<td>6</td>
<td>34.8</td>
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<tr>
<td>10</td>
<td>19</td>
<td>Fact</td>
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<td>60</td>
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<td>8</td>
<td>81.7</td>
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<tr>
<td>3</td>
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<td>Fact</td>
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<td>80</td>
<td>2.5</td>
<td>6</td>
<td>28</td>
</tr>
<tr>
<td>12</td>
<td>25</td>
<td>Fact</td>
<td>35</td>
<td>80</td>
<td>2.5</td>
<td>8</td>
<td>34</td>
</tr>
</tbody>
</table>
### Results and Discussion

#### Process of Spray Drying

The first important step is the nano particles suspension preparation which influences the spray dried powder characteristics. Agglomerates of the ceria nano particles were prepared using three different weight percent loadings of ceria nano particles (30, 40 and 50 wt%) in solution. The dispersed ceria particles suspensions have pH 3.8 due to the positive surface charge, and this low pH helps in dispersing the nano particles. The increase in pH by adding NH$_4$OH leads to suspension flocculation and makes the suspension unsuitable for spray drying. Although the low pH (≤ 3.8) keeps the ceria nano particles in dispersion but it makes the suspension more acidic, which corrodes the spray drying accessories. Thus, in the present study, without any additional pH modifier, these particles were kept in a DI water suspension using vigorous ultra-sonication. Various spray drying parameters, such as ultrasonic nozzle power, flow rate of suspension, solid loading and temperature of the air flow were varied to optimize agglomerate size and shape. Their effects are summarized in table 4.

Increases in the ultrasonic nozzle power increase the frequency of vibration which leads to increased fragmentation of the solution droplets into smaller droplets resulting in a finer
agglomerate size. The appropriate liquid feed rate of the suspension depends on the solid loading and temperature of the spray drying chamber. Higher feed rates lead to larger suspension droplets, and increase the volume concentration of the droplets in the spray drying path. If the temperature of the chamber is lower, complete moisture removal does not occur, which results in sticking of the moist agglomerates to the cyclone wall and a consequent decrease in the yield.

Table 4 Summary of effect of spray drying parameters on properties of dried agglomerates

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Increase</th>
<th>Bulk Density</th>
<th>Agglomerate Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Feed Rate</td>
<td>↑</td>
<td>↓</td>
<td>—</td>
</tr>
<tr>
<td>Nozzle Frequency</td>
<td>↑</td>
<td>—</td>
<td>↓</td>
</tr>
<tr>
<td>Volume fraction of Solid in the Feed</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Binder Composition</td>
<td>Too much of binder leads to a loosely bound structure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spray Drying Temperature</td>
<td>↑</td>
<td>—</td>
<td>↓</td>
</tr>
</tbody>
</table>

Powder loading in the suspension has a strong influence on the density and size of the dried agglomerates. Increases in the powder loading increase the suspension viscosity leading to increased density. It was observed that the 30 wt percent solid content has lower spray dried particle size and larger BET surface area (8.2 m²/g). Increased in solid content increase the particle size and reduce the BET surface area (4 m²/g for 50 wt%). From SEM images, it can be
deduced that 50wt% solid loading particles are denser than the low solid content particles. This is further confirmed by the pore volume analysis (Table 5).

Now, considering the role of PEG as a binder, it is used to cover each nano particle surface to combine them strongly; PEG also acted as a dispersant to keep the nano ceria in suspension. The low decomposition temperature allow PEG to completely burn (<350 °C) in plasma jet as confirmed in a TG-DTA study (Fig. 13). Furthermore, the solvent water has higher surface tension (72.8 X 10^{-3} N/M, 25 °C) than other solvent such as ethanol. This leads to the larger particles size compare to the organic solvent keeping other parameters constant. The optimized parameters for the spray drying were drying temperature 145 °C, Feed rate 20 ml/min, ultrasonic nozzle power 2.5W and resulting BET surface area and pore volume are shown in table 5.

Figure 13 TG-DTA of the spray dried powder showing the exothermic removal of PEG. Upward arrow indicates the exothermic direction. Inset shows the thermal decomposition of pure PEG.
Figure 14 shows SEM micrographs of spray dried powders. A large fraction of the particles were in the 20-30 µm size range for the 30wt% suspension. As seen for the 50wt% loading, the size of the particles increases with solid loading and the surface also becomes smooth, although there is incidence of some particles in donut morphology. It is important to note that a fraction of the small particles were reduced, and a controlled size distribution was achieved for 50wt% solid loading.
2.4.2 Microstructural Features: APS of Cerium Oxide

Two types of injection techniques were employed for ceria coating using SG100 plasma torch; internal and external (Fig. 12) As explained in earlier sections the optimized spray dried agglomerated powder was the one that was prepared by 50 wt% solid loading due to the large size, low surface area, and low pore volume of the particles. This ensures good flowability of the
agglomerates. In the present study, DC arc plasma was generated using an Ar-H gas mix. The plasma flame has very high temperature in the core (>10000K) and decreases progressively in downstream. Cerium oxide’s melting temperature is 2800 °C. It was supposed that internal injection, where the plasma jet has highest temperature, would be appropriate, as is the case of other high MP ceramic materials such as Al₂O₃, TiO₂, and YSZ. However, the internal injection of ceria did not show any deposition on the substrate. This is attributed to the complete vaporization of the ceria particles in internal injection which is the core of the plasma jet; or to the possible reduction of CeO₂ to Ce₂O₃ due to the high temperature [77]. The melting and vaporization temperature of reduced form is lower than the CeO₂. Moreover, cerium oxide has high vapor pressure, which increases with the temperature and reduced particle size as per the following relationship [78].

\[
\mu_{c,r} - \mu_{r,\infty} = RT\ln\frac{p_r^{\infty}}{P_\infty^{\infty}}
\]

\[
\ln\frac{P_r^{\infty}}{P_\infty^{\infty}} = \frac{V_m}{RT} \frac{2\gamma}{r}
\]

Where, \(\mu\) ~ Free energy, \(\gamma\) ~ Surface energy, \(V_m\) ~ Molar volume and \(P_r\) ~ Vapor pressure of the particles.

On the other hand, external injection of the powder depicted some extent of deposition. Thus, three types of external injections which inject powder in different temperature zone of the plasma (shown in figure 12) were experimented. Injection scheme 1 and 2 yielded higher amounts of unmelted deposits compared to scheme 3. Therefore, scheme 3 was found to be appropriate for
ceria deposition. Position 3 is much close to the plasma jet exit and thus at a higher temperature than the other 2 positions. The spectroscopic data on temperature measurement of plasma flame suggests that the axial temperature decays by 2000K for each 8mm from the exit [79]. This causes a significant difference in the particle’s heat and thermodynamic state, resulting in melting and vaporization. In the present study inward injection by 30° toward the plasma exit provides enough temperature for melting. However, the change in plasma power may change the axial distribution of plasma temperature along the center line [79]. The plasma temperature also depends on the plasma gas mixture (in the present case Ar-H) composition and total volumetric flow rate through the nozzle. Therefore, to determine the optimized parameters for cerium oxide coating, a design of experiments was developed consisting of plasma power as a critical parameter, as explained in next section.

### 2.4.3 Quadratic Model for Density

A four variable quadratic equation model with all terms was fit to the 30 values of the density as shown in Table 3. The tests on individual regressing coefficient were done (α=0.1) with in the “t” test statistic. The terms that are not significant at the 90 % level are eliminated from the model equation by the backward elimination method [70, 80]. Backward elimination involves starting with all variables and testing them one by one for statistical significance, deleting those are insignificant. Analysis of variance (ANOVA) for density was done for the designed experiment to identify important factors, and regression was used to build a quantitative model relating the important factors to the density of the coating (Table 6).
### Table 6 ANOVA table for Density

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square (Square)</th>
<th>F Value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>1091.513</td>
<td>10</td>
<td>109.1513</td>
<td>8.142929</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>A-power</td>
<td>51.51125</td>
<td>1</td>
<td>51.51125</td>
<td>3.842584</td>
<td>0.0648</td>
</tr>
<tr>
<td>B-Standoff distance</td>
<td>82.13347</td>
<td>1</td>
<td>82.13347</td>
<td>6.12734</td>
<td>0.0229</td>
</tr>
<tr>
<td>C-Powder flow rate</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>0.149204</td>
<td>0.7036</td>
</tr>
<tr>
<td>D-Carrier gas flow rate</td>
<td>112.55</td>
<td>1</td>
<td>112.55</td>
<td>8.396482</td>
<td>0.0092</td>
</tr>
<tr>
<td>AB</td>
<td>69.09766</td>
<td>1</td>
<td>69.09766</td>
<td>5.154839</td>
<td>0.0350</td>
</tr>
<tr>
<td>AD</td>
<td>157.8164</td>
<td>1</td>
<td>157.8164</td>
<td>11.77346</td>
<td>0.0028</td>
</tr>
<tr>
<td>BD</td>
<td>56.06266</td>
<td>1</td>
<td>56.06266</td>
<td>4.182399</td>
<td>0.0549</td>
</tr>
<tr>
<td>A^2</td>
<td>97.61252</td>
<td>1</td>
<td>97.61252</td>
<td>7.282112</td>
<td>0.0142</td>
</tr>
<tr>
<td>B^2</td>
<td>202.021</td>
<td>1</td>
<td>202.021</td>
<td>15.07122</td>
<td>0.0010</td>
</tr>
<tr>
<td>C^2</td>
<td>71.28099</td>
<td>1</td>
<td>71.28099</td>
<td>5.317721</td>
<td>0.0325</td>
</tr>
<tr>
<td>Residual</td>
<td>254.6841</td>
<td>19</td>
<td>13.40442</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of Fit</td>
<td>106.812</td>
<td>14</td>
<td>7.629427</td>
<td>0.257974</td>
<td>0.9795</td>
</tr>
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<td>Pure Error</td>
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<td>29.57442</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>1346.197</td>
<td>29</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Ten terms were detected to make significant contribution to the density (Table 6). A model consisting of all 10 terms estimates the density, is shown in coded and actual processing parameter can be expressed by the following equation.

\[
\text{Density (\%)} = +73.55 + 1.69 \times A - 2.14 \times B + 0.33 \times C + 2.50 \times D - 2.08 \times A \times B - 3.14 \times A \times D - 1.87 \times B \times D - 5.86 \times A^2 + 8.44 \times B^2 + 5.01 \times C^2
\] (2.4)

\[
\text{Density (\%)} = +130.59542 + 21.71813 \times \text{power} - 9.46686 \times \text{SOD} - 119.59788 \times \text{PFR} + 34.44743 \times \text{CFR} - 0.041562 \times \text{power} \times \text{SOD} - 0.62813 \times \text{power} \times \text{CFR} - 0.18719 \times \text{SOD} \times \text{CFR} - 0.23456 \times \text{power}^2 + 0.084360 \times \text{SOD}^2 + 20.04409 \times \text{PFR}^2
\] (2.5)

Where, SOD: standoff distance; PFR: powder flow rate; CFR: carrier gas flow rate;

It can be noticed from the model equation (2.4) that all the factors are included in linear terms and only the factor PFR (D) does not appear among the 2 factor interactions terms. The plasma power, standoff distance, powder flow rate are the significant second order terms. The model equation suggests that the standoff distance is the most important factor (largest coefficient). The "F value" in ANOVA table 6 for density indicates that the terms which are the most important in the model equation. The terms that have larger F values are the carrier gas flow rate, interaction between power carrier gas flow rate, and the square of standoff distance. These are the terms that have the most important effect on density in the selected experimental space.

\textbf{2.4.4 Quadratic Model for Deposition Efficiency}

The equations for predicting deposition efficiency in coded and actual process variables can be expressed by the following expressions respectively.
Deposition efficiency = $+30.52 -1.86 \times B + 2.62 \times C + 5.58 \times D - 4.02 \times B \times D - 4.38 \times C \times D + 12.12 \times B^2$

(2.6)

Deposition efficiency = $+201.71736 - 14.33937 \times \text{Standoff distance} + 66.56333 \times \text{PFR} + 59.99069 \times \text{CFR} - 0.40188 \times \text{SOD} \times \text{CFR} - 8.76000 \times \text{PFR} \times \text{CFR} + 0.12119 \times \text{SOD}^2$

(2.7)

There are only 6 terms that were found to be statistically significant in having an effect on the deposition efficiency. Except “power” other 3 processing parameters appear in linear and 2 factor interaction terms. Only the factor standoff distance appears in the second order term, indicating a significant effect. The model equation indicates that only the standoff distance is an important parameter (highest coefficient). ANOVA table 7 indicates that the carrier gas flow rate and powder flow rate have important effects on the deposition efficiency (from F values). It is also important to note that the F value for “Lack of Fit” is highest, making it significant.
<table>
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<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
<th>Prob &gt; F</th>
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</thead>
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<td>Model</td>
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<td>394.8974</td>
<td>4.643876</td>
<td>0.0031</td>
<td>significant</td>
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<tr>
<td>B-Standoff distance</td>
<td>62.57076</td>
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<td>0.735814</td>
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<td>C-Powder Flow rate</td>
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<td>D-Carrier Gas F R</td>
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<td>3.038774</td>
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<tr>
<td>CD</td>
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</tr>
<tr>
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<td>1057.397</td>
<td>12.43468</td>
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<tr>
<td>Lack of Fit</td>
<td>1920.724</td>
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<td>15.19697</td>
<td>0.0035</td>
<td>significant</td>
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<td>Pure Error</td>
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<td>7.02159</td>
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<tr>
<td>Cor Total</td>
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<td>29</td>
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<td></td>
</tr>
</tbody>
</table>

### 2.4.5 Model Diagnostic

The model adequacy was checked by analyzing the residuals, predicted versus actual plots, testing lack of fit, and $R^2$ calculations. Residuals are the difference between the measured experimental response and the response predicted by the model equation. For the model adequacy the residuals should be normally distributed. The normal plot of residuals and predicted versus actual plots of the density are shown in figure 15. Analysis indicates that the residuals are on the lines, and the concentrated near the lines indicates that the residual normality
is good. The predicted versus actual plot shows that the data points are distributed evenly near the 45° line. Ideally, all of the measured points should be on the line. However, that is not possible for most cases. The smaller value of the “lack of fit” (F value 0.25) for the density model from the table 7 also indicates that the model adequately fits the data.

Figure 15 (a) Normal plot of residuals (b) predicted versus actual plots for the model of density

Now consider the normal plot, and the “predicted versus actual” plot for the deposition efficiency as shown in figure 16. The residuals for the deposition efficiency fall approximately on a straight line, confirming the normal distribution. The predicted versus actual plot shows that the measured points are equally concentrated, but not on the 45° line. This indicates the differences in predicted and measured values. The lack of fit (F value) value for the deposition efficiency model of 15.19 is very high (table 7), but this could be due to noise. The R squared value the part of the variation about the mean that is explained by the fitted model. The R
squared values for the density (0.8) is satisfactory but for the deposition efficiency (0.55), may not be good. However, the model for deposition efficiency can be used to navigate the design space.

Figure 16 (a) Normal plot of residuals  (b) predicted versus actual plots for the model of deposition efficiency
Figure 17 Microstructure of cerium oxide coating (a) Run number 28 (density 66%) (b) Run number 17 (density 81%)
2.4.6 Process Optimization and Correlation of Results with DOE

The process is optimized by design expert® software within the experimental limits. The present study targets the highest coating density with high deposition efficiency within the operational limit of the instruments. The optimization analysis shows that within the parameter limits, the maximum density of 93% can be achieved along with a deposition efficiency of 55.8%. The optimized parameters that can be used to obtain higher densities of coating are: Power= 30.35 KW; standoff distance = 60 mm; Powder FR= 2.5 and carrier gas flow rate = 8 SCFH.

Understanding the relationship between the parameters and responses shown in the model equation 2.2 and 2.6, can be used for optimization. Each response is a function of the processing parameters. Few parameters are linearly related to the response, and the effect from the higher order interactions may be confounded with the terms included in the model, since only a fractional factorial DOE was used for optimization. Thus, the possible physical explanation of the effect observed will be explained by only the linear terms in each model based on the theoretical consideration and experimental observation. The model equations were used for the explanation since the equation with the coded factors is independent of the numerical values of the factors.

For the density model equation, all four factors are included in linear term. From this portion of the equation it can be seen that the density of the coating is dependent on the power of the plasma jet, powder flow rate, carrier gas flow rate and standoff distance. However, plasma power (A) and powder flow rate (C) are not significant based on the (prob>F)>0.5 value of the linear term. However, the power term included in the 2 factor interaction and the quadratic term
has some effect on the density. Theoretically, the higher plasma power input gives more energy to melt the powder particles. Thus, particles will reach the substrate in a molten state during deposition leading to a denser coating. The density contours predicted from software indicates that the density can be increased up to 93% within the experimental limits by decrease of the standoff distance and increase of the carrier gas flow rate (Fig.18). The decrease in the standoff distance increases the density of the coating as per the model linear terms. With the longer standoff distance particles cool down and the plasma jet temperature becomes low, indicating that shorter standoff distances will increase the density. The other reason could be that sintering of the coating during deposition at such a short standoff distance, promotes higher density. The carrier gas flow rate (D) is imparted to the particles at sufficient momentum to penetrate into the plasma jet, so that they completely enter to the core of plasma and melt. In the present study, due to presence of porosity in agglomerated particles, they require high carrier gas flow rate to cross the radial plasma jet barrier. Therefore, higher carrier gas may improve density. In the case of the deposition efficiency model, only 2 terms were significant. The lower standoff distance term (B²) will increase the particles adhesion in molten state to the substrate resulting in improved deposition efficiency. The model also suggests that the plasma power is not critical for deposition efficiency. This can be true only in the present experiments limit.
Figure 18 Predicted spray parameters for high density coatings
2.5 Conclusions

Agglomerates of cerium oxide nano particles were optimized in terms of their size, surface area, and pore volume by increasing the solid loading and by tuning the spray drying parameters. The agglomerates prepared by higher loading of particles are high in density, low in pore volume and surface area. Further, the cerium oxide coatings were optimized by using design of experiment for optimized spray dried agglomerates. CCD was used to generate an experimental space, and quadratic models for predicting the density and deposition efficiency were obtained. The models were statistically significant, and the relationship between the parameters and responses were discussed based on the experimental observation and theoretical considerations. The highest density of 93 % is predicted with deposition efficiency of 55% within the experimental space limited by the instrument constrains and material properties.
CHAPTER 3: SOLUTION PRECURSOR PLASMA SPRAY (SPPS) DEPOSITION OF NANO CRYSTALLINE CERIUM OXIDE

3.1 Introduction

The cerium oxide has shown its importance in various applications such as electrolyte in solid oxide fuel cell [53, 54], three way catalysts in auto motive to eliminate toxic gases [55-57], water gas shift, high temperature corrosion protection of steel which are already protected by chromia and alumina oxide layer [58], etc.

Numerous techniques have been reported for the synthesis of doped cerium oxide such as sol-gel, co-precipitation, combustion synthesis, etc. Subsequently, various manufacturing techniques have been adopted to use this material in applications for example powder compaction and sintering, tape casting, sputtering. In order to prepare coating of doped cerium oxide CVD, PVD, MBE and sputtering have been reported. Recently, a cost effective method, thermal spray has been used for dense coating synthesis. The solution precursor plasma spray (SPPS) is a one of the modified thermal spray techniques, which uses premixed solution as a feed stock, have shown promise for synthesis of thin nano structured coating.

SPPS offers unique advantages on account of its ability to achieve considerably higher deposition rates than CVD and PVD methods and yet retain the nanostructures in the coatings. In the SPPS process, coatings are being fabricated in a single step by injecting a molecularly mixed precursor solution of desired coating constituents into a plasma jet. The precursor chemistry can be changed to obtain desired chemical changes in the thin films while obtaining a dense adherent...
coating. The capabilities of this process have been demonstrated successfully to produce YSZ based thermal barrier coatings for turbines [40, 45, 81], electrolytes for SOFC and materials for photo catalytic applications [37]. So far most of the work has been devoted to YSZ based TBC development using SPPS technique at University of Connecticut. This technique has derived a unique microstructure homogeneous porosities distribution with no inter-splat boundary and vertical cracks in TBC. These microstructural features are desirable for strain tolerance and low thermal conductivity when TBC are exposed to turbine operating temperature (1100 °C) for several hours. The YSZ coatings by this technique have shown thermal conductivity 1.0-1.2 W/m.K as compared to 0.8W/m.K for APS and 1.5-2.0 W/m.K for EB-PVD [82]. Furthermore, numerous theoretical studies have been performed to understand the in flight thermo physical phenomena.

It was shown that the injected droplets of the solution undergo various thermo physical treatments such as evaporation, precipitation, thermal decomposition, melting, and acceleration to the substrate followed by deposition on the substrate in the form of splats. The microstructure of SPPS coatings can be changed by controlling the size of the injected droplets.

To prepare the coating the selection of the precursor is very important. The characteristics of the coating, prepared by SPPS, are greatly influenced by the precursor chemistry. Therefore, prior knowledge of chemical decomposition of precursor salts is essential for obtaining high-quality coatings. It is imperative to select the precursor which completely decomposes with less energy. This chapter demonstrates the preliminary understanding of different precursor solution interaction with plasma jet and identification of the best precursor salt for cerium oxide coating development. The extensive TG-DTA study was performed to
analyze the decomposition behavior of precursors and intermediate phase formation, based on the weight loss and enthalpy data. Precursor dependent microstructure evolution of the coating, phase formation, and non-stoichiometry in cerium oxide were studied to get a better understanding the process. A numerical model was also developed for each precursor to simulate the droplet injection process for microstructure evolution.

3.2 Materials and Methods

3.2.1 Precursor and Coating Processing

Among the various cerium salts, three different salts namely cerium nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O~99%), cerium sulfate tetrahydrate (Ce(SO$_4$)$_2$·4H$_2$O~99%) and cerium acetate sesquihydrate (Ce(CH$_3$CO$_2$)$_3$·1.5H$_2$O~ 99.9%) were selected for the present study. The feed stock precursor solutions were prepared by dissolving individual salts in 1.5 L of DI water at a molar concentration of 0.11M. In order to study the change in precursor chemistry on SPPS coatings concentration and solvent (water) kept fixed.

Direct current air plasma spraying (APS) process was used for deposition of the oxides. Each precursor solution was injected in the radial direction through an air blast atomizer nozzle located in front of the plasma spray gun, (Model SG 100 Praxair TAFA, Concord, NH, USA). The distance between the injection of the solution and the face of the gun was 13.0 mm, and the injection height from the core of the plasma was 8.0 mm (Fig 19). These parameters were kept constant for each coating. Argon was used as a primary gas, and hydrogen was used as a secondary gas to increase the enthalpy of the plasma plume. Unlike the powder spray, in SPPS
the liquid solution is injected in the form of micron size (1-100µm) droplets into the plasma plume.

Figure 19 A setup of the solution precursor plasma spray. The solution injector position is 13 mm away from nozzle exit and 8 mm from plasma jet axis.

The solution drop experiences various thermodynamic, chemical and mechanical changes. The grit blasted 316-stainless steel substrate was prepared using alumina grit. Substrates were cleaned ultrasonically in acetone to remove fine grit particles and any grease present on the substrate’s surface. The solution flow rate and atomization pressure were optimized before actual coating deposition, in order to achieve adherent deposit of CeO₂. All the samples were preheated to 250 ºC using a plasma spray gun just before the spray for better adhesion of the coating. The
coating substrate was kept at a distance of 55mm from the gun. The plasma spray parameters, atomizer pressure and flow rates used in this study are listed in Table 8.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution injection rate (mL/min)</td>
<td>20</td>
</tr>
<tr>
<td>Primary gas (Ar) flow rate (s.l.m.)</td>
<td>48</td>
</tr>
<tr>
<td>Secondary gas (H₂) flow rate (s.l.m.)</td>
<td>8</td>
</tr>
<tr>
<td>Arc voltage (V)</td>
<td>50</td>
</tr>
<tr>
<td>Arc current (A)</td>
<td>800</td>
</tr>
<tr>
<td>Stand of distance (mm)</td>
<td>55</td>
</tr>
<tr>
<td>Nozzle internal diameter (mm)</td>
<td>7.5</td>
</tr>
<tr>
<td>Injection type</td>
<td>radial</td>
</tr>
<tr>
<td>Injection position (mm)</td>
<td></td>
</tr>
<tr>
<td>From the torch axis</td>
<td>13</td>
</tr>
<tr>
<td>From the nozzle exit</td>
<td>8</td>
</tr>
<tr>
<td>Atomization pressure (psi)</td>
<td>15</td>
</tr>
</tbody>
</table>

**3.2.2 Precursor and Coating Characterization**

The decomposition behavior of the each precursor, intermediate phase formation and enthalpy required for each decomposition stage were studied prior to the coating deposition. For that 100 ml of each precursor solution was dried at 105 °C for 10 h. Simultaneous differential thermal analysis (DTA) and thermo gravimetric analysis (TG) were carried out on dried
precursor solutions using TG–DTA analyzer (SDT Q600) in the flowing air (Dry air; Airgas, USA) (100 ml/min) at a heating rate of 10 °C/min. The simultaneous measurement of the weight change and the heat flow was recorded up to 800 °C for nitrate and acetate precursors and up to 1000 °C for sulfate precursors. The onset decomposition temperature was determined by Tangent (ascending peak slop line intersection with the base line) method using inbuilt instrument software. The weight loss calculation in the corresponding temperature range was carried out to determine decomposition reaction. The area of the exothermic/endothermic peak is the change in enthalpy calculated by performing peak integration. Linear base line was selected for numerical integration.

The microstructure of the coating was characterized using scanning electron microscopy (SEM; Carl Zeiss ultra 55). To evaluate the nanocrystalline characteristics of the coating, the TEM samples were prepared by stripping off portions of the coating from the substrate and grinding it using a mortar and pestle. The grounded powders were ultrasonically dispersed in ethanol, and TEM samples were obtained by taking a few drops of the suspension on the holey carbon coated copper grids and dried in a vacuum chamber for high resolution TEM analysis (Philips Tecnai F 30). Phase identification was performed using X-ray diffraction (XRD; Rigaku D-Max B diffractometer). XRD patterns were recorded for each coated surface using Cu-Kα radiation (λ~1.54 Å) in the range of 20-90° with a scanning speed of 0.5° min⁻¹ at 40 kV and 30mA. The crystallite size of the ceria coatings was determined using Scherrer formula using full width half maxima (FWHM) of the XRD peaks.
3.2.3 Numerical Modeling

To validate the effect of different precursor on the microstructure development during plasma spraying, a numerical study of droplet injection model has been employed. This model uses a 2D plasma field as a continuous phase and calculates heat and mass transfer between a single stream of droplets and the plasma field. The commercially available software “Fluent 6.3” was used in this study. The interaction between the droplet and the plasma field has been simulated by using a “Discrete Phase Model (DPM)”. DPM is a method of solving interaction (energy, momentum and mass) between droplets/particles with a surrounding gas phase. DPM incorporates the effect of turbulence on the droplet trajectory using either a stochastic tracking model or particle cloud model [83]. The properties for plasma and different precursors were adopted from the available literature [84, 85].

3.3 Results and Discussion

3.3.1 Phase Evaluation of SPPS Cerium Oxide Coating

The X–ray diffraction pattern of each coating prepared by SPPS is presented in Fig. 20. The coating prepared by cerium nitrate hexahydrate and cerium acetate sesquihydrate precursor exhibit the FCC fluorite structure, confirming the complete decomposition of the precursor solution to cerium oxide. The XRD pattern of the coating prepared by cerium sulfate tetra hydrate also reveals the presence of cerium oxide along with the presence of intermediate decomposed sulfate phases. The TG-DTA analysis of the precursors indicates that complete decomposition of the sulfate precursor occurs at 830 °C as compared to the acetate (~330 °C) and nitrate (~330 °C) precursors. As mentioned earlier, during the plasma spray process of solution,
droplets undergo various thermo chemical stages before deposition on the substrate along with unpyrolyzed solution droplets.

Figure 20 X-Ray diffraction patterns of the SPPS cerium oxide coating prepared by different precursors viz (a) Cerium acetate (b) Cerium nitrate hexahydrate (c) Cerium sulfate tetrahydrate. XRD patterns indicate typical fluorite crystal structure of cerium oxide. (*) indicates the presence of oxysulfate phases in coating prepared by cerium acetate sesquihydrate precursor.

The unpyrolyzed solution undergoes in situ decomposition on the substrate due to the heat from the plasma plume. It is important to mention that in the SPPS process, the spray distance used was 55mm and the substrate temperature reached upto~ 450-550 °C while spraying. During the spray process this temperature is sufficient to decompose the entrapped
unpyrolyzed nitrate and acetate precursors in the coating but it is insufficient to pyrolyze the entrapped sulfate precursor. The nitrate and acetate precursors decompose completely in to cerium oxide at 330 °C as no further weight loss was observed, confirmed by TG analysis. As the decomposition temperature of the cerium sulfate precursor is significantly higher than the substrate temperature which is achieved during the coating, the complete decomposition of unpyrolyzed cerium sulfate salt that reaches the substrate does not take place resulting in retaining of the intermediate sulfur compounds indicated by the TG-DTA

3.3.2 Microstructural Characterization of as Sprayed SPPS Coatings

Unlike the plasma spray coating of the powders, the microstructure of the SPPS coatings differs in splat size and degree of melting. Smaller splats (1-2µm) and various melting products are the characteristic features of the SPPS coatings. In the SPPS process, coatings may consist of various products resulting from the thermo-physical interaction of solution droplets and plasma flame besides splats such as unmelted spherical particles, broken shells and unpyrolyzed solution etc. The surface morphologies of each coating sprayed by various precursors are shown in Fig. 21(a-c).

Each micrograph reveals porosity, agglomeration of sintered particles, and a high degree of roughness in the coating. This type of microstructure can be attributed to the combined deposition of “solution and plasma flame interaction” products and in situ decomposition/sintering of unpyrolyzed solution at substrate.
Figure 21 Surface morphology of SPPS cerium oxide coating prepared by (a) Cerium acetate (b) Cerium nitrate hexahydrate (c) Cerium sulfate precursors. Insets reveal the magnified images of smaller sections of the corresponding coating (d) Magnified image indicates splat formation (1-2µm) along with fine unmelted particles.

The SEM micrographs do not show any remarkable changes in microstructure and surface morphology of the coating with change in solution chemistry. These aspects of microstructure development have been further studied using numerical modeling of droplet injection in section 3.3.2. Furthermore, HRTEM images depict the nanometer characteristics of the coating. Grain size less than 14nm were retained in all the coating (Fig. 22). The SAED confirm the nano crystalline nature of the coatings (Fig.22a-c, inset).
Figure 22 HRTEM images of SPPS coating prepared by (a) Cerium acetate (b) Cerium nitrate hexahydrate (c) Cerium sulfate precursors indicating that coating consists of nano particles of cerium oxide. Insets show the low magnification TEM images, fast Fourier transform of lattice and SAED patterns.
Spherical nano grain geometry has been observed in the coating prepared by using Ce(SO$_4$)$_2$·4H$_2$O as precursor whereas, irregular nano grains were observed in the coatings prepared by the other two precursors. Similar nano characteristics of the coating have been observed by various researchers for titanium oxide coating (grain size <20nm) [48] and yttria stabilized zirconia SPPS coating (grain size <100nm) [86]. In the SPPS process, the atomized solution droplets undergo an aerodynamic break up into tiny droplets during the interaction with the plasma jet [42, 87]. These droplets further breakup until volume precipitation takes place. Saha et al defined a critical drop size, below which all the droplets undergo volumetric precipitation followed by melting and deposition [84]. Droplets larger than the critical size can fragment into daughter droplets. The volume precipitation occurs for the small droplets whereas shell formation may be one of the possibilities depending on the heating rate of the droplets and nature of the precipitation during heating and evaporating phases that gives different morphologies including solid particles, hollow shell and fragmented shell [42]. However, not all precipitated particles deposit in the form of a pan cake (splat). Before impingement on the substrate, molten particles must have enough momentum to deposit in the form of a splat. Low momentum particles deposit as spherical particles, rather than splat and get entrapped within the splats (Fig. 21d). The present SPPS coating development can be defined in the following stages:

Shear deformation of droplets at atomizer exit $\rightarrow$ vaporization of water from droplets $\rightarrow$ decomposition of cerium salts solid particles $\rightarrow$ disintegration of droplet into finer droplets due to thermal decomposition (endothermic/exothermic) $\rightarrow$ sintering/shrinkage of fine solids $\rightarrow$ melting $\rightarrow$ splat formation/deposition upon impact.
3.3.3 Grain Size Measurement of Coatings

The average crystallite size for each coating was calculated using the Scherrer equation

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  \hspace{1cm} (3.1)

where \( \lambda \) is the wavelength of the X-rays, \( 2\theta \) is the diffraction angle, \( \beta \) is the corrected full width at half-maximum (FWHM) obtained using the (111) line of the high-purity LaB\(_2\) as the standard. In the present work, the following expression was used to calculate \( \beta \) due to the Lorentzian (Cauchy) profile of the X-ray peaks.

\[ \beta = \beta_0 - \beta_i \]  \hspace{1cm} (3.2)

where \( \beta_0 \) is FWHM observed and \( \beta_i \) is FWHM due to the instrument.

Table 9 shows the average crystallite size, measured for the (111) X-ray diffraction peak, which are in agreement with the grain size measured from TEM micrographs. HRTEM images analyzed using image analysis software (IQmaterials 2.0 Software) confirms the grain size distribution (Fig.23). The size distribution was based on randomly selected (80) data points in each image.

<table>
<thead>
<tr>
<th>Coating precursor</th>
<th>Concentration of Ce(^{3+})</th>
<th>Average crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(NO(_3))(_3) 6H(_2)O</td>
<td>0.26</td>
<td>13.3</td>
</tr>
<tr>
<td>Ce(CH(_3)CO(_2)) 1.5H(_2)O</td>
<td>0.32</td>
<td>9.7</td>
</tr>
<tr>
<td>Ce(SO(_4))(_2)-4H(_2)O</td>
<td>0.23</td>
<td>14.3</td>
</tr>
</tbody>
</table>
Nano crystalline features of the SPPS coating can be ascribed to, (1) very high cooling rate \((10^6 \, ^\circ C/\text{min})\) during deposition of molten particles on the substrate and (2) time spent by the plasma gun for the coating development was very short (in milliseconds for one pass). The consequence of these factors restricts the grain growth even though the heat imparted by the plasma jet to the coating is high. Coatings prepared by cerium acetate precursors showed a higher fraction of smaller (4-8nm) grains as compared to other coatings (Histogram, Fig.23).

![Histogram of grain sizes of nanocrystalline cerium oxide coating for each salt, measured in High resolution TEM micrographs using image analysis software. A total of 80 data points were counted from different HRTEM images. For irregular particles longer dimension was selected.](image)

The exothermic decomposition of acetate precursors between 200-350 °C to cerium oxide could generate a localized increase in the enthalpy as shown in Fig. 24. The localized increase in
enthalpy may cause a high rate of decomposition of injected droplets into cerium oxide and evolution of gaseous products leading to smaller particle deposit [88]. The process can be assumed similar to the combustion synthesis of fine metal oxide particles.

3.3.4 Thermal Decomposition of Precursors (TG-DTA Study)

To attain a complete oxide coating from a solution, it is required to choose the correct metal salt such that, during interaction with the plasma flame it should decompose into the desired metal oxide. The thermal decomposition of the precursor salt in plasma decides the final composition of the coating in the SPPS deposition process. Therefore, TG-DTA study was conducted for each precursor in air and is shown in Fig. 24-26. The decomposition of each precursor is discussed in the following sections.

3.3.4.1 Thermal Decomposition of Cerium Acetate Sesquihydrate Precursor

The TG-DTA for the acetate precursor is shown in Fig. 24. The decomposition of acetate precursors in air can be expressed in two stages. The first endotherm at 152 °C in the TG-DTA plot indicates dehydration of Ce (CH₃CO₂)₃ 1.5H₂O according to equation 3. A second sharp peak between 200-300 °C corresponds to an exothermic reaction and validates the decomposition of anhydrous cerium acetate to cerium oxide, water vapor and CO₂. The final weight loss (~ 44.96%) from the TG plot agrees well with the weight loss (~ 45.76%) calculated from the reaction 4.

\[
\text{Ce (CH₃CO₂)₃ 1.5H₂O} \rightarrow \text{Ce (CH₃CO₂)₃} + 1.5\text{H₂O} \quad (3.3)
\]

\[
2 \text{Ce (CH₃CO₂)₃} + 12.5 \text{O₂} \rightarrow 2\text{CeO₂} + 9\text{H₂O} + 12\text{CO₂} \quad (\Delta H \sim +546 \text{ kJmol}^{-1}) \quad (3.4)
\]
Figure 24 TG-DTA curve of dried cerium acetate sesquihydrate at heating rate of 10 °C min\(^{-1}\) in flowing zero grade air.

The complete decomposition of the cerium acetate precursor in air occurs at a temperature of ~330 °C. The characteristic sharp exothermic decomposition of cerium acetate can be correlated to the combustion process used for the synthesis of CNPs [89]. In such processes the energy liberated from the heat of reaction is high enough to directly render the cerium oxide phase from the precursor solution. The plasma spraying of such precursors has different chemical and physical nature. Besides the evaporation of water and the decomposition of the acetate precursor, the plasma heat triggers an exothermic explosion of the droplets into nanometer
CNPs. The process is very quick and does not allow the growth of nucleated CNPs and any changes in the stoichiometry of the cerium oxide nanoparticles.

### 3.3.4.2 Thermal Decomposition of Cerium Nitrate Hexahydrate Precursor

Figure 25 represents the experimental TG-DTA curve of Ce(NO$_3$)$_3$.6H$_2$O decomposition in air. Two major mass loss peaks were observed. The first mass loss peak up to 240 °C, is due to the removal of water of crystallization given in equation 5. The second mass loss is observed between 240-330 °C, and is due to the decomposition of anhydrous Ce(NO$_3$)$_3$ to CeO$_2$ and oxides of nitrogen. The observed 46.4% mass loss was in agreement with the theoretical mass loss of 47.2% as per equation 6. The difference in the mass loss is due to the initial absorption of moisture by cerium nitrate.

\[
\text{Ce(NO}_3\text{)}_3\cdot 6\text{H}_2\text{O} \rightarrow \text{Ce(NO}_3\text{)}_3 + 6 \text{H}_2\text{O} \tag{3.5}\n\]

\[
\text{Ce(NO}_3\text{)}_3 + \text{O}_2 \rightarrow \text{CeO}_2 + \text{Oxides of nitrogen} \quad (\Delta H \sim -121 \text{ kJmol}^{-1}) \tag{3.6}\n\]
Figure 25 TG-DTA curve of dried Cerium nitrate hexahydrate at heating rate of 10 °C min⁻¹ in flowing zero grade air

### 3.3.4.3 Thermal Decomposition of Cerium Sulfate Tetrahydrate

Multi stage decomposition was observed for the sulfate precursor. This can be divided into four stages. The decomposition products have different stability temperatures as depicted in the TG-DTA plot shown in Fig. 26. The first two endotherms correspond to the dehydration of the precursor to Ce(SO₄)₂ in the temperature range between 60 to 350 °C. The third endotherm reveals that the decomposition of the anhydrous sulfate salt to Ce₂(SO₄)₃ occurred between 445 to 522 °C. The final decomposition took place at 850 °C as indicated by the steep slope on the decomposition curves. The enthalpy change of reduction of Ce⁴⁺ to Ce³⁺ sulfate is lower than
the enthalpy change due to the loss of water and the final decomposition from Ce₂(SO₄)₃ to CeO₂. Ce₂(SO₄)₃ compound was found to be stable between 522 to 655 °C. The decomposition of the sulfate precursor can be shown by the following sequence and intermediate products.

\[
\begin{align*}
\text{Ce (SO₄)₂·4H₂O} & \rightarrow \text{Ce (SO₄)₂·2H₂O + x H₂O} \\
\text{Ce (SO₄)₂·2H₂O} & \rightarrow \text{Ce (SO₄)₂ + x H₂O} \\
2\text{Ce (SO₄)₂} & \rightarrow \text{Ce₂ (SO₄)₃ + SO₃ + ½ O₂} \quad (ΔH \sim -40 \text{ kJmol}^{-1}) \\
\text{Ce₂ (SO₄)₃} & \rightarrow 2\text{CeO₂ + 2SO₃ + SO₂} \quad (ΔH \sim -296 \text{ kJmol}^{-1})
\end{align*}
\]
Several oxysulfate compound formations have been reported at intermediate temperature ranges while different temperatures for dehydration, reduction and decomposition of sulfate precursor have also been reported (eq.3.7-3.9) [89-92]. The disagreement in the reported results can be ascribed to the different decomposition environments and heating rates. The calculated weight loss (39.43%) according to the equation 3.10 is in good agreement with the observed weight loss (39.29%) in the corresponding TG plot. This corroborates the formation of the intermediate Ce (III) compound according to equation 3.9. TG-DTA analysis supports the observation of several intermediate sulfate peaks in the XRD pattern along with cerium oxide
using cerium sulfate as the precursor for SPPS. As explained earlier, depending upon the droplet size, unpyrolyzed precursor droplets or partially decomposed precursor can reach the substrate. After deposition, the unpyrolyzed precursor decomposes when the coating temperature becomes higher than the precursors decomposition temperature. The decomposition temperature (to CeO$_2$) for cerium nitrate and cerium acetate precursors is well below the substrate temperature. This facilitates the formation of single phase CeO$_2$ coating, despite the deposition of unpyrolyzed solution during spray, whereas the decomposition temperature for cerium sulfate precursor is higher than the coating temperature, which results in incomplete decomposition. For confirmation, the coating prepared by sulfate precursor was scratched and investigated under TG-DTA (Fig. 26). DTA plot of the coating shows a single endothermic peak between 700-850 °C which corroborates the presence of oxysulfate in the coating along with CeO$_2$.

### 3.3.5 Numerical Modeling of Precursor Injection for Microstructure Evolution

We studied the heat and mass transfer to the precursor droplets based on their different chemistries in order to understand the in-flight thermo-physical phenomena that ultimately determine the final microstructure [93]. A numerical study was used to simulate the droplet injection process. Ozturk and Cetegen have performed an experimental study using Phase Doppler Anemometry at the exit of an air-blast nozzle to determine the statistical distribution of droplet sizes [93] which indicates the size and velocity distribution of the droplets injected from the nozzle. It clearly shows that the diameter distribution of the droplets generated by the nozzle follows a bell shaped curve with a mean around 35μm and mean velocity around 12 m/sec. As the present study uses a similar kind of nozzle, we have assumed the mean size of the injected droplets close to 30μm with an injection velocity of 12 m/sec for numerical simulation. It is
important to mention here that current model does not consider intermediate surface precipitation and shell breaking phenomena as reported in our previous work [84]. This being a conservative modeling considers continuous vaporization of solvent until the droplet reaches critical temperature or the solvent vaporizes completely. However, this model is capable of predicting the global temperature rise and final temperature of the particle very closely to the detailed modeling.

Figure 27 shows the temperature rise of the droplets of all three precursors with time. It shows two distinct zones. The first zone, termed as ‘vaporizing phase’ has a slower rise in the temperature. The temperature in this zone increases up to 374 °C, which is the critical point of water. At this temperature, water from the droplet completely vaporizes which in conjunction with pyrolysis leads to a solid particle formation. After this point the second phase, namely ‘solid particle heating’ starts. This phase is marked by very sharp rise in the temperature reaching the melting point of ceria. It is important to notice that the temperature of the droplet follows a similar trend for all of the precursors considered. A detailed analysis of the thermodynamic and thermo gravimetric properties of these precursors shows that the primary difference between the precursors is the heat of pyrolysis. However, a comparison of heat transfer from the plasma field to the droplet and required heat of pyrolysis shows that the latter is almost few orders of smaller in magnitude. An order of magnitude calculation for the amount of heat transfer from the plasma environment to the droplet is more than 500 times of required heat of pyrolysis of solutes. Thus, the effect of heat of pyrolysis does not have much effect on the temperature rise which results in almost the same temperature profiles as shown in Fig. 27. This plot suggests that for all three precursors, 30 μm droplets will reach the substrate, pyrolyze and melt during the flight. A
parametric study on cerium nitrate droplet diameter has also been performed to understand what happens to droplets which are either too small or too large. 10 and 50 micron droplets of cerium nitrate precursor were selected for a parametric study.

Figure 27 Temperature profiles for 30µm droplets of different precursors with time, indicate water evaporation up to critical point followed by heating of the solid particles up to the melting point of ceria.
Figure 28 Trajectory of different size droplets of cerium nitrate precursor. This indicates that only larger size (>20µm) droplets penetrate plasma plume. Smaller droplets remain in the shear layer of the plasma. For a clear representation, the plasma nozzle is shown away from the center line.

Figure 28 corresponds to the trajectories of these droplets. It reveals that larger droplets with higher inertia have a larger potential to penetrate the outer shear layer of the plasma and reach the core, where the temperature and velocity is the highest. The temperature rises for these three droplets are shown in Fig. 29. It can be noted from the figures that 30 micron droplets attain the melting temperature of CeO$_2$ before reaching the substrate. However, for both 10 and 50µm droplets, the temperature remains in the lower range. Droplets of 10µm do not have enough inertia to penetrate the shear layer of the plasma, thus these remain at the lower
temperature zone and do not reach a very high temperature. On the other hand, 50 micron droplets succeed in reaching the high temperature plasma core.

Figure 29 Temperature profiles for different size droplets of cerium nitrate precursor, show size dependent behavior of injected droplets. Larger size droplets (~50µm) pass through the hot zone of the plasma and attain low temperature (~500°C). Smaller droplets (~10µm) remain in the low temperature shear layer and reach the substrate in un-melted condition.

However, the droplets being larger in size contain a significant amount of solvent, which takes a longer time to vaporize. As a result, by the time the droplet turns into a solid particle, it reaches far down stream of the plasma where the temperature is comparatively lower. Thus, after comparing these results for different sized droplets, it can be commented that droplets around 20-45 µm diameter have a higher probability of reaching the substrate in a pyrolyzed and molten state.
A comparison of numerical simulation with the SEM images (Fig. 24) shows good agreement with very little change in the microstructure as functions of the precursor chemistry. Similarly, surface morphology of the coatings (Fig. 24) is in agreement with the simulation results shown in Fig. 6 which shows that the temperature rise is almost identical for all the precursors. SEM images however indicate traces of unmelted deposit which can be attributed to the deposition of unpyrolyzed smaller droplets (around 10 microns) or droplets with diameters greater than 45 microns. The presence of too large or too small droplets is unavoidable due to the constraints in the spray nozzle design that invariably lead to unpyrolyzed deposits. The difference in the grain size distribution among three precursors in Fig. 23 can only be attributed to different heats of pyrolyzation. The smaller grain size for acetate precursors is due to the positive heat of pyrolysis that can lead to a secondary pyrolyzation for this precursor, compared to the other two precursors which have negative heats of pyrolysis.

### 3.3.6 Thermodynamic Feasibility of Cerium Oxide Formation from Solution

The enthalpy of the plasma jet, evaporates the water content of the injected droplets, decomposes anhydrous droplets and intermediate products and finally heats the products to their melting temperatures for deposition on the substrate. Enthalpy of the plasma varies depending on the proportion of the primary and secondary gases. The specific mass enthalpy of the plasma flame can be expressed by the following expression for the mixture of argon and hydrogen plasma gases [94].

\[ \Delta h = \frac{\sum_{i=1}^{k} x_i \Delta H_i}{\sum_{i=1}^{k} x_i \Delta M_i} \]  \hspace{1cm} (3.11)
where, $x_i$ is the molar fraction of the $k$ chemical species present in the mixture, $\Delta H_i$ is the corresponding molar enthalpy and $M_i$ is the atomic mass. The enthalpy of H/Ar $\sim 1/6$ mixture is 25 MJ/kg calculated according to the equation 3.11 which is more than sufficient for the conversion of different cerium salts precursor to cerium oxide. Net enthalpy required for the formation of cerium oxide from different precursors is calculated from the TG-DTA plot and listed in Table 10.

Table 10 Net enthalpy of CeO$_2$ formation and dehydration calculated from DTA plot.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Net enthalpy of formation (CeO$_2$) (kJ/mol)</th>
<th>Enthalpy of dehydration (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(NO$_3$)$_3$·6H$_2$O</td>
<td>$\sim -268$</td>
<td>$\sim -99$</td>
</tr>
<tr>
<td>Ce(CH$_3$ CO$_2$) 1.5H$_2$O</td>
<td>$\sim +503$</td>
<td>$\sim -43$</td>
</tr>
<tr>
<td>Ce(SO$_4$)$_2$·4H$_2$O</td>
<td>$\sim -377$</td>
<td>$\sim -60$</td>
</tr>
</tbody>
</table>

Qualitatively it can be observed from the TG-DTA plot that the enthalpy change of dehydration is highest for the cerium nitrate hexahydrate due to its hygroscopic nature and six molecules of water of hydration compared to the other cerium salts. In plasma spray most of the heat is consumed for the evaporation of the water content of the droplets. After that, heat is utilized for decomposition of the anhydrous salts and melting of the cerium oxide. The enthalpy required for melting of cerium oxide particles can be calculated from the following expression.

$$\Delta H = \int_{298}^{T} C_p \, dt$$  \hspace{1cm} (3.12)$$

where $C_{p,m} (\text{JK}^{-1} \text{mol}^{-1}) = 71.152 + 0.01335 \, T - 1145425 \, T^{-2}$ \cite{95}
Assuming no phase transformation occurs in cerium oxide up to its melting point (2773 K), its enthalpy of fusion will be $\Delta H \approx 237.2$ kJ/mol. It is confirmed from the enthalpy data presented in Table 10 that plasma energy is sufficient for enthalpy of formation of cerium oxide from precursors and melting of the cerium oxide. However partially molten (spherical particles) and unpyrolyzed solution observed in the coatings, are typical characteristic of the SPPS process. These features are dependent on the various factors such as size and distribution of the precursor droplets, and its correct injection to the core of the plasma assuming correct plasma energy.

**3.3.7 Determination of Oxidation State of Cerium in SPPS Coated CNPs**

As mentioned earlier, oxygen non stoichiometry can be introduced by stabilizing cerium in the trivalent oxidation state in CNPs. We hypothesized that by changing the precursor chemistry, we can alter the oxidation state of cerium in CNPs and thereby introduce oxygen non-stoichiometry in the coatings. Figure 30 (a-c) shows the XPS spectra, the fitted curve and the deconvolution of peaks.
Figure 30 XPS spectrum of Ce (3d) for cerium oxide coating prepared by (a) Cerium (III) acetate (b) Cerium (III) nitrate hexahydrate (c) cerium (IV) sulfate precursors. Peaks were deconvoluted to get the distinct spin-orbit doublet of 3d_{3/2} and 3d_{5/2}. (d) S 2p spectra indicating the presence of SO₄.

Charging of samples was corrected by setting the binding energy of adventitious carbon (C 1s) at 284.6 eV. The complicated cerium XPS spectra were deconvoluted by peak fit (4.1) software for clear identification of Ce^{3+} and Ce^{4+} peaks. The characteristic peaks of Ce^{3+} are denoted by v₀, v' u₀ and u', whereas v, v'' v''', u, u'' and u''' correspond to the Ce^{4+}. The XPS
spectra for each coating indicates the mixed oxidation state of Ce$^{3+}$ 3d$_{3/2}$ & 3d$_{5/2}$ binding energy, main peaks at (901.4eV&881.5 eV ) and Ce$^{4+}$ 3d$_{3/2}$ & 3d$_{5/2}$ at (916.7eV&898.2eV). The Ce$^{3+}$ concentration is calculated by taking the ratio of the integrated peak areas corresponding to Ce$^{3+}$, to the total area under the XPS spectrum [96]. The concentration of Ce$^{3+}$ in each coating is shown in Table II. The highest Ce$^{3+}$ concentration (32%) has been found in the coating prepared by cerium acetate. No trace of nitrogen was observed in case of CeO$_2$ coatings prepared by a nitrate precursor, whereas XPS analyses indicated the presence of sulfur in the CeO$_2$ coatings prepared by sulfate precursors. The binding energy of S 2p$_{3/2}$ & 2p$_{1/2}$ (168.23eV & 169.38eV) corresponds to the presence of SO$_4$ type species (Fig. 30d) [97]. The presence of sulfur in the coatings is due to the deposition of unpyrolyzed sulfate precursors with cerium oxide particles.

In the present study, it is important to take cognizance of the retention of high concentrations of Ce$^{3+}$ in CeO$_2$ coatings developed by SPPS process. The non-stoichiometry in the fluorite structure may exist due to very high cooling rates. Similarly un-melted and partially melted particles may also have high non-stoichiometry due to high temperature exposure during travel in the plasma jet. It has been reported by various authors that the non-stoichiometry in CeO$_2$ increases with increase in the temperature[98, 99]. Furthermore, it is also established that the Ce$^{3+}$ concentration increases as the particle size is reduced [100, 101]. Therefore the ability to retain nanosized particles by SPPS could be one of the reasons for higher concentration of Ce$^{3+}$ ceria coatings.
3.4 Conclusions

The SPPS process has been established to synthesize high quality nano structured cerium oxide coatings with desired chemistry. The role of precursor chemistry and decomposition behavior has been demonstrated for microstructure development and different oxidation states of the coatings. Use of cerium acetate precursor for coating has shown the highest concentration of Ce$^{3+}$ (0.32) and the smallest crystallite size (9.7nm). Cerium acetate and cerium nitrate precursors have shown single phase nano crystalline cerium oxide coating whereas cerium sulfate precursors introduce traces of sulfur in the coating. It has been shown that substrate/coating temperature during plasma spray plays an important role in obtaining single phase cerium oxide coating. The difference in the concentration of Ce$^{3+}$ oxidation state in the coating is due to the differences in the decomposition behavior in the plasma plume. Numerical simulation results suggest that the smaller droplets (<10µ m) do not penetrate the shear layer and travel within the low momentum and low temperature zone of the plasma. Larger droplets (>40 µm) penetrate the plasma zone. However, they remain unmelted due to a short residence time in the hot zone of the plasma. Droplets of sizes 20-40 µm have been calculated for complete melting and deposition in the form of splat. The microstructure of the SPPS coating consisted of a variety of structures which were confirmed by the numerical modeling due to the wide distribution of injected droplets constrained by the nozzle design.
CHAPTER 4: STUDY THE EFFECT OF PROCESSING PARAMETERS ON SPPS COATING AND DOPED CERIUM OXIDE COATING DEVELOPMENT

4.1 Introduction

Surface modification by thermal spray is a relatively simple and economic process that has been widely used for various engineering applications, e.g. wear and corrosion resistance and thermal barrier coating. The conventional atmospheric plasma spray (APS) for the thermal barrier coating (TBC) provides unique porous microstructure with through-thickness micro-cracks [102-105]. These microstructural features provide low thermal conductivity and high strain tolerance in coating for high temperature protection of gas turbine components. The recent studies show solution precursor plasma spray provides different microstructure from APS process [38, 45, 86, 106, 107]. For example, (1) Smaller inter-splat boundaries reduce weak failure points (2) through thickness vertical cracks good for strain tolerance and (3) uniformly distributed porosities which are desired for low thermal conductivity and low elastic modulus [108].

Traditional way of coating deposition requires injection of micron sized (>30 µm) powders into a plasma jet. The micro-structure evolves by deposition of the micron sized molten particles which flatten upon deposition to the substrate and provide a base for subsequent incoming molten particles. The micro-structure not only consists of the layered structure but also semi molten, unmelted particles, trapped porosities, large inter-splat boundaries and cooling
cracks in splats. Besides, microstructure and deposition efficiency of the coating is also affected by particle distribution in plasma space, velocity and temperature of the particles. The interaction of the depositing material with plasma gas leads to the thermal and kinetics energy transfer to the material enabling melting and providing acceleration for deposit. In the SPPS process the deposition is the result of interaction of the liquid solution droplets to the plasma jet. The droplets undergo a series of thermo-physical and chemical transformation, such as solvent vaporization, solute precipitation on surface, shell rupture, volumetric precipitation, heating and melting of solid particles [84, 109]. Like APS, SPPS coatings evolve by the stacking of splats in each pass of the plasma torch. However, in SPPS splat sizes are smaller than APS and dependent on the initial droplets size as well as solute concentration. The coating development depends on the precursor droplet interaction within the plasma jet and the in situ decomposition of the unpyrolyzed precursor during the plasma spray which can be tuned to give low high density coatings. Due to smaller size of the particles after pyrolysis the kinetics of deposition changes affecting coating microstructure.

The motivation of the present study is to understand the coating deposition mechanism in SPPS technique for cerium oxide using a cerium nitrate liquid precursor alone and in doped condition. The study includes affect of various processing parameters, such as plasma power, standoff distance and solution concentration on coating micro-structure. Single scan experiments were performed to better understand single splat formation and unpyrolyzed precursor deposition.
Cerium oxide in the doped condition has been found as a promising solid electrolyte due to high oxygen ionic conductivity at intermediate temperatures (<700°C). As compared to the zirconia based electrolytes, ceria does not undergo any phase transformation at the SOFC operating temperature range. Cerium oxide itself has poor oxygen ionic conductivity. The doping of trivalent ions such as Gd$^{3+}$, Y$^{3+}$, Sm$^{3+}$, Nd$^{3+}$, and Pr$^{3+}$ increase the oxygen ion vacancies in the ceria host lattice which further increases the ionic conductivity and power density of the doped ceria based electrolytes [53, 110-112].

Due to technological importance of the doped cerium oxide, SPPS process was used to understand the feasibility of trivalent (Gd$^{3+}$ and Sm$^{3+}$) cations doping in cerium oxide. Study was conducted starting from decomposition behavior of the individual salt precursors and mixed salt precursor in 10 and 20 mol% Gd and Sm doped condition followed by coating evaluation. XRD analysis was conducted to identify the formation of doped single phase cerium oxide formation. The change in lattice parameter due to doping was determined. The microstructure of the single scan deposits, followed by coating surface and cross-section were characterized and analyzed.

### 4.2 Materials and Methods

#### 4.2.1 Precursor Solution and Coating Processing

As discussed earlier in chapter 3 the cerium nitrate hexahydrate found the best precursor for SPPS cerium oxide coating. Thus, different concentrations (0.11M, 0.2M and 0.5M) of feed stock precursor solutions were prepared by dissolving the stoichiometric amount of cerium nitrate hexahydrate (Ce(NO$_3$)$_3$.6H$_2$O Sigma Aldrich 99%) in DI water. In order to check the feasibility of doping of Gd$^{3+}$ and Sm$^{3+}$ in cerium oxide fluorite lattice in plasma spray,
gadolinium nitrate hexahydrate (Gd(NO$_3$)$_3$·6H$_2$O Sigma Aldrich 99%) and samarium nitrate hexahydrate (Sm(NO$_3$)$_3$·6H$_2$O Sigma Aldrich 99%) salts were used for the doping. To prepared 10 and 20 mol % samarium (or gadolinium) doped cerium oxide coating, stoichiometric amount of each dopant salts were dissolved with cerium nitrate in DI water to have the 0.11M liquid concentration precursors.

A small design of experiment was developed to evaluate the influence of plasma power, variation of distance between the substrate and spray gun, and effect of substrate temperature on coating adhesion and microstructure. Single scan experiments were performed using 0.2M cerium nitrate precursor concentration on pre-heated polished SS 316 substrate at different spray distance to evaluate splat morphology. Further optimized parameter for plasma power, substrate temperature and standoff distance were used to evaluate precursor concentration effect on surface microstructure prepared by single scan experiment and correlated to the coating microstructure. The substrate temperature was measured by k-type thermocouple attached to the back surface of the substrate. The temperature was recorded each second using an Omega (HH806AU) temperature reader. The hardware used to prepare coating, and the processes are the same as defined in chapter 3.

### 4.2.2 Solution Plasma Spray: Design of Experiment

Plasma spray coating technique has many process variables. The addition of solution precursor technique further increases these numbers. In order to get the desired properties in a coating, it is important to optimize these parameters. The classical approach of dealing each processing parameter requires a large number of experiments. However, based on prior studies
literature data, and material system, it has been shown that it is possible to discard some the experimental variables which are not significant [87, 113, 114]. In this study a small experimental design was developed to achieve low and high power plasma power, while keeping plasma spray hardware fixed as shown in Table 11. The current and hydrogen flow rate values were selected in such a way that minimizes the nozzle and cathode wear of the SG 100 spray gun used, and avoids coating contamination due to hard hardware erosion. The DC atmospheric plasma spraying (APS) process was used for deposition of the cerium oxide. The precursor solutions were injected in the radial direction through an air blast atomizer nozzle located in front of the plasma spray gun, (Model SG 100 Praxair TAFA, Concord, NH, USA). The 8mm diameter nozzle (PT 730) and theoriated tungsten tip cathode was used for plasma arc generation. The distances of the solution atomizer from the plasma torch (10 mm) and from the center line of the plasma plume (8 mm) were kept constant. The SG 100 spray torch was mounted on a 6 axes robot. The grit blasted and polished stainless steel 316 substrates were used for deposition.
<table>
<thead>
<tr>
<th>Case #</th>
<th>Current (Amp)</th>
<th>Argon (SCFH)</th>
<th>Hydrogen (SCFH)</th>
<th>Power (KW)</th>
<th>Atomizing gas pressure (psi)</th>
<th>Precursor flow rate (ml/min)</th>
<th>Travers speed (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>90</td>
<td>6</td>
<td>21</td>
<td>15</td>
<td>40</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>750</td>
<td>90</td>
<td>6</td>
<td>30</td>
<td>15</td>
<td>40</td>
<td>300</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>90</td>
<td>9</td>
<td>24</td>
<td>15</td>
<td>40</td>
<td>300</td>
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<td>4</td>
<td>750</td>
<td>90</td>
<td>9</td>
<td>32</td>
<td>15</td>
<td>40</td>
<td>300</td>
</tr>
</tbody>
</table>

4.2.3 Precursor and Coating Characterization

The stochiometric amount of Ce(NO$_3$)$_3$.6H$_2$O is dissolved with samarium nitrate, and gadolinium nitrate for 0.11M concentration in water to prepared precursor solution. The different precursor mixture’s nomenclatures are shown in table 12. The 50 ml of each precursor mixture were dried at 110 °C for 12 hr and crushed into dry powder using pestle mortar. Simultaneous differential thermal analysis (DTA) and thermo gravimetric analysis (TG) were carried out on as dried precursor powders using TG–DTA analyzer (SDT Q600) in flowing air (Dry air; Airgas, USA) (100 ml/min) at a heating rate of 10 °C/min. For each test 10-20 mg of powder was placed
in an alumina crucible. The simultaneous measurement of weight change and heat flow was recorded up to 900 °C. The inbuilt software with the instrument was used to calculate the enthalpy and weight loss. The area of the exothermic/endothermic peak is the change in enthalpy was calculated by performing peak integration. Linear base line was selected for numerical integration. Further, phase identification was performed using X-ray diffraction (XRD; Rigaku D-Max B diffractometer). XRD patterns were recorded for each mixed precursor powders and corresponding coating using Cu-Kα radiation (λ~1.54Å) in the range of 20-90° with step scan at speed of 0.02° min⁻¹ at 40kV and 30mA.

X-ray analysis was performed on Sm and Gd doped cerium oxide coating samples to identify the doping feasibility in SPPS process. The changes in the lattice parameter of the doped cerium oxide were calculated using high angle reflections peak by following Bragg’s law expression:

\[ 2d \sin \theta = n\lambda \]  \hspace{1cm} (4.1)
\[ d = \frac{a}{h^2+k^2+l^2} \]  \hspace{1cm} (4.2)

Where, d ~ inter planer spacing, θ ~ diffraction angle, a~ lattice parameter, and (h,k,l)~ diffraction plan indices. The average crystallite size was estimated based on the XRD peak broadening using the Scherrer formula as explained in chapter 3. Microstructures of the coating were characterized using scanning electron microscopy (SEM; Carl Zeiss ultra 55) and analyzed by IQmaterial and DM3 software.
4.3 Results and Discussion

In this chapter the effect of numerous process parameters on the cerium oxide coating microstructure and adhesion properties were studied and discussed separately in following subsections.

4.3.1 Solution Plasma Spray: Plasma Jet Parameters Optimization

Table 11 shows the list of plasma jet variables which decides the power, temperature and velocity of the plasma jet. Unlike the atmospheric plasma spray (APS), in the present study water based cerium nitrate precursor was injected in the form of droplets. In APS most of the energy is consumed in heating and melting the powder feed stock, and accelerating them to the substrate. In the case of the SPPS few additional steps such as evaporation of the solvent and decomposition of the precursor into their stable oxide consumes most of the plasma energy. This renders the plasma jet cooler in SPPS than in APS [115]. Table 13 shows the properties of the different solvents, which suggests that the water require more energy than ethanol to get fragmented and to get vaporized [115].

Table 13 Properties of the most encountered solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Surface tension $\sigma_s$ [J m^{-2}]</th>
<th>Viscosity $\mu_s$ [Pa s]</th>
<th>Specific heat $c_p$ [J K^{-1} kg^{-1}]</th>
<th>Latent heat of vaporization $L_v$ [J kg^{-1}]</th>
<th>Vaporization temp. $T_v$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>$72 \times 10^{-3}$</td>
<td>$10^{-3}$</td>
<td>$4.18 \times 10^{3}$</td>
<td>$2.26 \times 10^6$</td>
<td>373</td>
</tr>
<tr>
<td>Ethanol</td>
<td>$22 \times 10^{-3}$</td>
<td>$1.06 \times 10^{-3}$</td>
<td>$2.44 \times 10^{3}$</td>
<td>$0.84 \times 10^6$</td>
<td>351</td>
</tr>
</tbody>
</table>
Figure 31 Microstructure of the coating deposited by different plasma power. (Case 1) 21 KW. (Case 2) 32 KW plasma power. Macro-graphs show deposit peel off for the low power and adherent deposit for high power plasma
Therefore, it is important to select those parameters which can generate the high power plasma jet required. In the present study four different set of plasma parameters were adopted to determine the appropriate power for cerium oxide based coating for 0.11M molar concentration. Figure 31 shows the effect of plasma power on coating microstructure. Low hydrogen flow rate and current (Case 1) results in decreased plasma power which reduces the plasma velocity and temperature. This low power is sufficient for solvent evaporation of the injected droplets and decomposition but does not provide enough energy for melting after pyrolization nor momentum for adherent deposition. Moreover, the low velocity of the plasma allows easy solution droplet penetration with minimal fragmentation to smaller drops during interaction. Thus, large unmelted particles deposit with poorly treated unpyrolyzed solvent which eventually strip off due to thermal expansion (Photograph Fig.31 upper left). High power plasma has high velocity and temperature (table 14). During, plasma jet–droplets interaction, these droplets fragments into daughter droplets (smaller size) and experience volume precipitation, and complete melting and adherent deposition however, this decreases deposition efficiency [44]. The microstructure exhibits the smaller size adherent deposit Fig. 31 (case 4)
4.3.2 Standoff Distance Effect

The standoff distance is the distance between the substrate and plasma spray torch. Since, in the SPPS process, the solution is atomized into micron sized droplets (10-100um) and injected into the plasma jet, the interaction causes further fragmentation of the larger drops into finer droplets. After evaporation, decomposition and pyrolysis of the droplets the mass of the particles become small, resulting in the reduced momentum. The reduction in velocity does not allow molten particles to deposit on the substrate in molten condition if sprayed from the longer standoff distance as in the case of the APS of powders. Therefore, it is important to find out the correct standoff distance such that a high fraction of the molten mass deposits on the substrate. In the present study solution (0.2M cerium nitrate solution in water) was sprayed from three different standoff distances as shown in figure 32a. The plasma jet pictures were captured using digital camera at higher shutter speed to measure the jet length for constant plasma jet parameters (Table 4.2, case 4). From the figure 32 b it is clear that for the fixed plasma parameter the plasma jet length was near 50 mm. Thus, a +/- 10 mm standoff distance 50mm was used to evaluate the effect of spray distance on deposit microstructure.

<table>
<thead>
<tr>
<th>Hydrogen Flow rate</th>
<th>Current</th>
<th>Gun Voltage</th>
<th>Plasma Velocity</th>
<th>Plasma temperature</th>
<th>Deposition efficiency</th>
<th>Droplet size</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Low</td>
<td>Low</td>
<td>decreased</td>
<td>decreased</td>
<td>increased</td>
<td>increased</td>
</tr>
<tr>
<td>4</td>
<td>High</td>
<td>High</td>
<td>Increased</td>
<td>Increased</td>
<td>decreased</td>
<td>decreased</td>
</tr>
</tbody>
</table>

Table 14 Effect of plasma gun parameters on deposition efficiency
Figure 32 Position of plasma jet for plasma sprays parameters (case 4) (as shown in table 4). (a) The schematic view of the standoff distance used in experimentation (b,c,d) Actual photographs of plasma jet at different standoff distance.
Typically in SPPS processes standoff distance becomes important, due to a low momentum of molten particles which, drastically affect the micro structure and deposition efficiency. At longer distance of deposition, molten particles re-solidify due to the lower temperature of jet at farther distance and do not adhere to the substrate [116] whereas, larger particles reach to the substrate due to higher momentum and smaller particles resolidify. Figure 33 shows that the plasma jet gets deflected due to solution droplets pressure. The injection pressure should be enough such that the droplets reach the core of the plasma. The droplets injected at low pressure are poorly treated from the low temperature periphery of the flame and deposit as liquid.

4.3.2.1 Effect of Standoff Distance: Single Scan Experiment

Single scan experiments were carried out to determine the best standoff distance so that more fractions of molten particles deposit on the substrate. The deposits were collected on polished stainless coupons at different standoff distances (40 to 60 mm) based on the earlier
plasma jet length measurement. In order to get deposit, plasma torch scanned the substrate in raster pattern for single pass at the same velocity used for coating. The SEM images of the each single scan deposit collected on polished substrate are shown in Fig. 34. The deposit at 60 mm standoff distance was found to be gel in nature alongwith the high fraction of spherical particles. The mud cracks were observed in the deposit without any splats (Fig. 34a). These cracks might have generates as a result of solution drying due to substrate heating. At longer standoff distances the particles which were molten solidify before hitting the substrate and deposit as spherical particles engulfed in unpyrolyzed solution deposits which get pyrolyzed due to the substrate preheat (350 °C). The single scan deposit at 50 mm standoff distance reveals a fewer splats of size less than 2 micron shown by the red arrows and finer spherical unmelted particles (<1μm). The semi molten agglomerate of particles (< 3 μm) was also observed in deposit (Fig. 34b). Moreover, no mud cracks structure was observed. These observations indicate that at 50 mm distance some of the particles reach in molten state whereas large aggregate remain in semi molten condition. The microstructure of the single scan deposits at 40 mm shows a higher fraction of splats along with a small fraction of finer unmelted spherical particles. The splat size varies from sub micron to 5 μm. No mud cracks were observed. As discussed earlier, in SPPS process the particles have low inertia due to their smaller size and they decelerate very quickly and are therefore not able to travel the longer distance in plasma flame. Therefore, shorter standoff distance allows more particles deposition in molten condition on substrate as well as in situ sintering of coating by plasma jet. All the substrates were heated above the Ce(NO₃)₃.H₂O decomposition temperature using multiple plasma scans of the plasma gun just before coating. The temperature of the substrate was kept above 350 °C by varying the number of heating cycles.
for different standoff distance. Plasma spray parameters were kept constant for single scan experiments therefore number of heating cycle had to increase with standoff distance in order to keep substrate preheat temperature above 350 °C. The effect of the substrate temperature on the deposit microstructure is shown in Fig. 34d. The deposits on an unheated substrate at 40 mm standoff distance depict unpyrolyzed solution and cracks, owing to drying of the solution during scan. The substrate heating profile is shown in figure 35. It indicates that the substrate is heated upto 700 °C using multiple plasma scan which become cooler by the time SPPS become ready to spray. However, temperature was kept above 350 °C which is more than the precursor decomposition temperature.
Figure 34 Microstructure of single scan deposits on polished SS316 substrate at different standoff distances. (a) 60 mm (b) 50 mm (c) 40 mm. Substrates were pre-heated to 350 °C using plasma gun just before the spray. (d) Deposition on non-heated substrate from 40mm standoff.
Figure 35 Substrate heating profile for single scan experiment for cerium oxide deposition.

4.3.3 Solution Concentration Effect

In this study the effect of solution concentration on cerium oxide coating microstructure is evaluated. The increased solution concentrations increase the viscosity and decrease the surface tension [46]. Higher concentrations are also expected to increase in the yield of the coating due to the higher solute content. Therefore, this study is important for determining the conditions needed for high yield deposition, and dense splat morphology. The numerical studies on SPPS demonstrate the concept of volume precipitation and surface of the droplet precipitation [42]. The high concentration droplets undergo volume precipitation within the solvent, which leads to solid particle formation, melting and splat formation upon impact [84, 117].
The TG-DTA study of Ce(NO₃)₃·H₂O suggests that the precursor completely decomposes near 330 °C as shown in representative heat flow and mass loss data (Fig. 36). Only the lower concentration precursor was subjected to TG-DTA and it was assumed that the thermal profile will not be affected by the concentration variation. However, the energy required to pyrolyze the same size of the droplet in plasma process may vary with concentration.

![Graph](image)

Figure 36 Mass loss and heat flow profile for Ce(NO₃)₃·H₂O.

The three different concentration of the cerium nitrate precursor were deposited on polished and grit blasted (alumina grit size 30) SS316 substrate at standoff distance of 40 mm and rest of the parameters including solution flow rate, plasma power, primary and secondary gas flow rate, and atomization pressure were kept constant.
4.3.3.1 Effect of Precursor Concentration on Splat Formation: Single Scan Experiments

To better understand the effect of precursor concentration on splat formation, single scan experiments were again carried out. The SS 316 substrates were polished to 3 micron (diamond suspension) for the single scan experiments. These substrates were preheated to 750 °C using the plasma torch then cooled to 420-450 °C before spray. Figure 37 shows the micro structure of the substrate which was subjected to a similar preheating cycle as was used for the coating. The rough surface exhibited in the micrographs could be due to the surface oxidation while heating. For the single scan experiments the plasma torch was scanned at a traverse speed of 300 mm/s to collect deposit at a 40 mm distance. Figure 38 shows the microstructure of the collected deposits and substrate temperature profile for the 0.11M precursor.

![Microstructure of polished SS 316 substrate, heated to 700 °C. The fine grain on the surface is due to the surface oxidation while heating using plasma torch](image)

Figure 37
Figure 38 Microstructures of the deposits collected by single scan experiment on heated samples for 0.11M precursor. (a) Low magnification (b) high magnification (c) heating profile of substrate
The low magnification microstructure (Fig. 38a) shows a few splats along with the ruptured droplet shell and unmelted spherical particles. At a few locations porous agglomerates and porous mesh are also observed. The high magnification image (Fig 38b) shows the presence of variable size porous splats. It is supposed that these splats are formed from the impact of the partially melted particles [118]. Unlike the high concentration droplets, the droplets with low solute content do not experience volume precipitation. The droplet precursors with low concentration generally go through surface precipitation resulting in a coating consisting of semi-pyrolyzed material stack that exhibit soft porous structure [48]. It is clear from the images that for low concentration precursor, not all the injected droplets were completely vaporized.

Figure 39 shows the microstructure of the single scan deposits of the 0.2 M concentration precursor. These images confirm improved degree of melting and higher splat formation. A very small fraction of unmelted spherical particles were observed. It is important to note that the substrate is not covered by deposits whereas, for the dilute precursor substrate is covered by the unpyrolyzed solution which decomposes in situ from the high substrate temperature. Porous deposits and droplets shells were not observed, and splat sizes were larger for the precursor of 0.2M concentration.
Figure 39 Microstructure of the deposits collected by single scan experiment on heated sample for 0.2M precursor. (a) low magnification (b) high magnification
When the concentration of precursor was increased by 0.5M, the fraction of splats is increased (Fig. 40). The splot size was increased to 3.5 µm and are densely deposited in a manner similar to APS of powder feed stock. The high magnification image reveals that these splats are made of fine nano particles (Fig. 40c). It is obvious that the dense splats will increase the density of the coating compared to the porous splot which is confirmed by cross section microstructure of the thick coating in the following text.

All the experiments were conducted at constant parameters (standoff distance, injection pressure, solution flow rate, plasma power and primary gas flow rate) however the microstructure is different for each concentration. The equilibrium solution concentration (ESC) of Ce(NO$_3$)$_3$.6H$_2$O precursor at room temperature is 2.25 M [84]. When the concentration of solution (0.11M) was just the 4.4% of the ESC the microstructure is porous and containing broken shells, as opposed to the 22% ESC precursor (0.5M). Other factors of droplets formation such as, liquid viscosity and surface tension impact the size of the droplets and their fragmentation, which ultimately affect the microstructures. D Chen et al has shown in his droplet size measurement study using phase Doppler particle analyzer (PDPA) that changes in concentration do not affect the droplet size considerably [46, 119]. They used 0.6M and 2.4M solution concentrations of YSZ salts and observed negligible change in droplet size. The present study had similar change, as the concentration was increased by 5 times (from 0.1 to 0.5M) with the highest concentration used being 22% of the ESC. Thus it is reasonable to assume there will be negligible change in droplet size due to concentration variation.
The mechanism of droplets interaction with the plasma jet was studied by Basu et al. where they predicted a mathematical model for plasma-droplet interaction [42, 44]. According to their model, microstructure depends on the physio-chemical treatment of droplets in plasma. The heating rate and precipitation during the heating/vaporization, different particles morphologies obtained including the hollow and fragmented shells, solid particles. This finally tailors the microstructure. Plasma spray is high heating rate process; the large droplet size and slow diffusivity of the solute cause the surface precipitation which leads to the formation of crust that encapsulates the liquid. Small droplets with high diffusivity of the solute tend to precipitate volumetrically to form solid particles. In the case of a low concentration solution (0.11M) the surface precipitation front moves slower, by that time the larger droplets fracture into smaller daughter droplets until volume precipitation occurs due to internal pressure of the boiling liquid. If the formed shell is non-porous such particles directly deposit on to the substrate and collapse subsequently. Because of the high temperature of the substrate (>400 °C), the inner core liquid of such particles evaporate and pyrolyze in situ, and leaving a porous structure on the substrate (Fig.38a).
Figure 40 Microstructure of the deposit collected by single scan experiment on heated sample for 0.5M precursor. (a) low magnification (b) high magnification (c) Single splat consists of fine nano particles

For the higher concentration precursors the tendency toward volume precipitation will increase due to a higher specific mass and diffusive transport. Furthermore, it is easy to get an equilibrium solution concentration with increased solute loading. The spray pyrolysis studies on manufacturing the ceramic metal oxide have also demonstrated that volume precipitation can be achieved with solution near equilibrium concentration [120, 121]. More volume precipitation renders easier solid particles formation and melting, giving more molten splats on the substrate
as seen for 0.2M and 0.5M precursors (Fig. 39-40). It is important to note that the higher concentration solution gives larger splat sizes due to reduced tendency of crust formation and rupture. The substrate temperature more than the decomposition temperature of the precursor only helps to pyrolyze liquid precursor, which is deposited directly during spray. As the concentration is increased, volume precipitation of the droplets occurs in an earlier stage, allowing larger droplets to volume precipitate before further aerodynamic breakup, which leads to larger splats. The high magnification image of the single splat shows the individual splat consisted of the fine grain (<100 nm) (Fig. 40c). Further the average crystallite size was calculated using Scherrer equation for the coatings prepared by each precursor concentration from XRD data (Fig. 41) shown in table 15.

![Figure 41 X-ray diffraction patterns of SPPS coatings prepared by different concentrations of precursor. The increase in the FWHM of the coating prepared by 0.11M indicates the coating consist of fine crystallites.](image-url)
The crystalline size was smallest for the low concentration precursor (0.11M) whereas not much difference was observed between the 0.2M and 0.5M solution concentrations (table 15). These results also confirm the earlier observation of higher unpyrolyzed solution deposit in the case of low concentration precursor which is in situ pyrolyzed. This leads to embedded loose powdery deposit in between the splats, which could be the reason of lower average grain size.

**4.3.3.2 Microstructure of Coating**

In order to confirm single scan results, thick coatings were deposited from all three different concentrations solution precursors. The microstructure of the coating from the 0.11M solution precursor shows high porosities (average density~ 56). Porosity decreases and dense regions increase with increased solution concentration which can be noticed in SEM images (Fig. 42 and 43) and table 16. The uniform porosity distribution in the 0.2M solution precursor coating and thick dense area in the 0.5M coating corroborates the single scan experiments results.

**Table 15 Average crystallite size of coating prepared by different concentrations of precursor**

<table>
<thead>
<tr>
<th>SPPS coating</th>
<th>0.11M</th>
<th>0.2M</th>
<th>0.5M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average crystallite size</td>
<td>14nm</td>
<td>26nm</td>
<td>22nm</td>
</tr>
</tbody>
</table>

**Table 16 Density of the coating from different concentration solution precursor**

<table>
<thead>
<tr>
<th>Solution Concentration</th>
<th>0.11M</th>
<th>0.2M</th>
<th>0.5M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>56±4</td>
<td>68±3</td>
<td>76±4</td>
</tr>
</tbody>
</table>
Figure 42 Polished cross-section microstructure of the coatings from solution (a,b) 0.11M (c,d) 0.2M
Figure 43 Polished cross-section microstructure of the coating from 0.5M solution precursor (a) low magnification (b) high magnification

SEM microstructures of the coating top surface for different solution concentrations are shown in Fig. 44. The low magnification images are the typical SPPS surface which clearly illustrates the difference due to concentration variation. The high magnification microstructures
confirmed the surface is built by multiple stacking of the finer splats. However, the splats sizes are larger for coating from high concentration precursor.

Figure 44 Surface microstructure of the SPPS ceria coating at low and high magnification (a,b) 0.2M and (c,d) 0.5M solution precursor
4.4 Study Doped Cerium Oxide SPPS Coating

This section of the chapter demonstrates the deposition of samarium and gadolinium doped cerium oxide coating using SPPS. To understand the doping phenomena in such a dynamic plasma jet environment, the physical mixture of the cerium nitrate precursor with the compatible dopant (nitrate salts) in different mole per cent were subjected to TG-DTA study. The physical mixtures of precursors were consisted of Ce(NO$_3$)$_3$.6H$_2$O and Sm(NO$_3$)$_3$.6H$_2$O or Gd(NO$_3$)$_3$.6H$_2$O dissolved in DI water at an atomic ratio of Ce:Sm/Gd ~ 9:1 and 8:2 and total ionic concentration kept 0.1 M. The dissolved mixture was dried in an oven at 110 °C for about 12 h. The simultaneous TA-TG experiments were performed using a TIA instrument. All the experiments were carried out in air at flow rate of 100 ml/min against alumina pen as a reference at a heating rate of 10 C/min. The XRD patterns of each dried precursor were recorded using Brucker X-ray diffractrometer between 2θ ~ 25°-50°.

4.4.1 Results and Discussion

4.4.1.1 Understanding Thermal Decomposition of Precursors

The decomposition of the starting salts, Ce(NO$_3$)$_3$.6H$_2$O, Sm(NO$_3$)$_3$.6H$_2$O and Gd(NO$_3$)$_3$.6H$_2$O, with temperature were carried out separately in the air atmosphere are shown in Fig. 45. The TG-DTA of the dried precursor mixtures are shown in Fig. 46 and 47. The TG-DTA curves from RT to 900 °C shows different thermal decomposition steps. Cerium nitrate decomposes into cerium oxide in two steps, whereas, nitrate of gadolinium and samarium convert into their stable oxide in multiple steps. Ce(NO$_3$)$_3$.6H$_2$O converts into CeO$_2$ at around 330 °C. In contrast, Sm(NO$_3$)$_3$.6H$_2$O and Gd(NO$_3$)$_3$.6H$_2$O convert to their oxide at much higher
temperature at around 700 °C (Fig. 45b,c). For these three salts, the first step starts by removal of the adsorbed moisture from RT to 120 °C which is indicated by the broad endothermic peaks below 120 °C. Cerium nitrate decomposition steps are described in detail in chapter 3 includes removal of water of crystallization (180-237°C) and pyrolization into CeO₂ (between 237-330°C) as indicated by the two endothermic peaks.

Sm(NO₃)₃.₆H₂O turn into Sm₂O₃ through various intermediate steps (Fig 4.5b). These intermediate steps are associated with the release of initial moisture followed by the removal of crystallization water below 300 °C. The multiple peaks in mass derivative curve at low temperature (<300 °C) corresponds to the removal of water molecules. The mass loss of 27% corresponds to the 6 moles of water removal with moisture at 350 °C. The theoretical mass loss after removal of 6 mol of water is 24.3% which gives unstable Sm(NO₃)₃ at about 350 °C. The split in the endothermic peak between 350 to 445 °C is the indication of formation of anhydrous thermally unstable phase. This is in agreement with the previous studies by Wendland and Bear [122]. A major mass loss ~ 23.5% in TG (350-445 °C) correspond to the conversion of Sm(NO₃)₃ to the intermediate SmONO₃ oxy-nitrate compound (theoretical~ 24.3). The formation of intermediate oxy-nitrate compounds has also been reported earlier during decomposition of rare earth nitrate compounds [123-125]. These compounds are non-stochiometric and unstable. Upon further heating SmONO₃ decomposes to stable Sm₂O₃ at about 750 °C with mass loss of 11.6%, which is close to the theoretical value 12.1%. Further heating from 750 to 900 °C does not show any mass change which assures decomposition completed at around 750 °C. TG-DTA profile for Gd(NO₃)₃.₆H₂O follow similar trend as of samarium nitrate i.e. multi steps decomposition complete at around 700 °C (Fig. 45C). The first endotherm in the heat curve
corresponds to the moisture removal. The crystallization water removal endotherms were observed between 128 to 350 °C. These various endothermic peaks are corresponding to the heat required for separation of water molecule.

Figure 45 TG-DTA curves at heating rate of 10 °C min\(^{-1}\) from room temperature to 900 °C. (a) Ce(NO\(_3\))\(_3\).6H\(_2\)O (b) Sm(NO\(_3\))\(_3\).6H\(_2\)O (c) Gd(NO\(_3\))\(_3\).6H\(_2\)O

Total mass loss at the end of this endotherm (23.4%) is close to the release of 6 molecules of water and formation of anhydrous Gd(NO\(_3\)) at 350°C. The theoretical weight loss of six water molecule is 24 %. The weight derivative curve reveals three peaks at 387, 480 and 660 °C that coincide with the three endotherms as shown in Fig. 45c. The decomposition of the Gd (NO\(_3\))\(_3\) starts at 350 °C and completes in two stages. First plateau achieved at 429 °C and second plateau
starts at about 560 °C. The total weight loss corresponds to the first plateau is about 47.8% which corresponds to the decomposition of Gd (NO$_3$)$_3$ into GdONO$_3$ is close to the theoretical weight loss of 47.9%. The second plateau corresponds to removal of nitrate due to decomposition of GdONO$_3$. The weight loss from 560 to 750 °C is 3%. The decomposition completes at about 750 C and negligible weight loss was observed from 750-900 °C which confirms the formation of Gd$_2$O$_3$. It is clear from the aforementioned analysis that cerium nitrate decomposes at lower temperature than nitrate of samarium and gadolinium besides the mechanism of decomposition is different by formation of intermediate phase formation. It is important to note that in the case of mixture of both salts with cerium salt in solution can further complicate the situation by separate phase formation instead of doped single phase coating. Therefore, TG-DTA experiments were also performed on the mixed precursors. The TG-DTA profiles for the precursor mixtures reveal interesting facts. Only two broad endothermic peaks were observed in all four thermal profiles. The first endotherm can be assign to the removal of moisture and crystallization water, and the second endotherm can be simultaneous decomposition of dehydrate mixture into doped oxide. It is interesting to note that the TG-DTA profile of mixtures is similar to Ce(NO$_3$)$_3$.6H$_2$O. However, there is small variation in the decomposition temperature and mass loss.

First consider the mixture of Ce(NO$_3$)$_3$.6H$_2$O and Sm(NO$_3$)$_3$.6H$_2$O (9:1 and 8:2). For the 10mol%Sm doped mixture, the weight derivative reveals four peaks (Fig. 46a). The two peaks are between 102-147 °C correspond to the first endotherm at 140 °C due to the release of the water content and second endotherm at 271°C. The second broad peak in weight derivatives consist of one main peak (262 °C) with two shoulders at about 234 and 299 °C. It is interesting to note that the corresponding endotherm is similar in shape as of Ce(NO$_3$)$_3$.6H$_2$O (Fig.45a). There
is no separate peak for the crystallization water and overlap peaks pose difficulty in separation each mechanism. However, it is clear that onset of decomposition occur at 230 °C with major mass loss of 39 % by 325 °C. From 325 to 450 °C, an additional gradual weight loss of 3% occurs. The earlier TG-DTA data of Ce(NO$_3$)$_3$.6H$_2$O showed the decomposition was completed at about 330 °C and weight loss between 325 to 450 was 2%. In contrast the difference arises due to the addition of samarium nitrate. Moreover, the mass change from 450 to 700 °C was observed to be only 1% and negligible change was found above 700 °C. Nevertheless above results provide an indication that the mixture of solution completely decomposes to their mixed oxide at higher temperature. Thus, the coating substrate temperature should be higher than the decomposition temperature of the precursor for complete pyrolization of solution deposit in process.
Figure 46 TG-DTA of dried solution mixture (a) 90Ce(NO$_3$)$_3$·6H$_2$O-10Sm(NO$_3$)$_3$·6H$_2$O (b) 80Ce(NO$_3$)$_3$·6H$_2$O -20 Sm(NO$_3$)$_3$·6H$_2$O

In the case of increased samarium nitrate proportion in mixture (Ce: Sm = 8:2, mole/mole) the thermal profile seems to be similar to Ce:Sm=9:1 (Fig. 46b). However, the endotherm peaks
shifted to higher temperature due to increased Sm(NO₃)₃.6H₂O content which is having much higher decomposition temperature. The second peak of temperature derivative occurs in 225 to 355 ºC consists of one main peak with two shoulders (282 ºC and 330 ºC). The corresponding mass loss is 38.9% which is very close to the Ce: Sm= 9:1 mixture however the end temperature is increased. Further, mass loss analysis reveals the decomposition peaks shifted to higher temperature and doped oxide formation completes at 700 ºC. Beyond that not mass loss was observed.

Now consider the decomposition for the mixture of the Ce(NO₃)₃.6H₂O and Gd(NO₃)₃.6H₂O (9:1 and 8:2). Figures 47 (a, b) shows the TG-DTA profile for gadolinium nitrate salt mixture with cerium nitrate. For Ce:Gd=9:1 (mole/mole) solution mixture the main weight derivative peak have low temperature shoulder at 270 ºC, it could be due to the decomposition of the cerium nitrate whereas the higher temperature peak (296 ºC) correspond to the simultaneous decomposition of Gd(NO₃)₃. The mass loss from 335 to 450 was 2.76% indicates gradual decomposition of gadolinium oxynitrate. Only 0.9% mass loss was observed in 450 to 700 C temperature range in contrast to the 10% change in mass loss in the case of the pure Gd(NO₃)₃.6H₂O. The TG-DTA profile of Ce:Gd=8:2 (mole/mole) solution mixture is similar to the previous one with increased endotherm temperatures. The measure mass loss completed by 353 ºC followed by slow change in mass thereafter.
Figure 47 TG-DTA of dried solution mixture (a) 90Ce(NO$_3$)$_3$.6H$_2$O-10 Gd(NO$_3$)$_3$.6H$_2$O (b) 80Ce(NO$_3$)$_3$.6H$_2$O-20 Gd(NO$_3$)$_3$.6H$_2$O
4.4.1.2 X-Ray Diffraction Study of Precursors and Coating

The phase analysis was conducted on initial precursor mixture and coatings, in order to identify the doping of Sm and Gd in ceria lattice while SPPS deposition. The initial mixed dried precursors and coating are characterized by XRD. The similar TG-DTA profiles for the mixed precursors which were dried at 110 °C suggested that the possibility of formation single phase doped cerium nitrate hexahydrate such as Ce(Sm/Gd)(NO$_3$)$_3$.xH$_2$O.

The X-Ray diffraction patterns of the each mixed precursors are recorded and illustrated in figure 48. The diffraction data were collected from 2θ ~25 to 50° due to hygroscopic nature of the mixture even after drying at 110 °C. For comparison, the XRD pattern for the cerium nitrate was also recorded. The patterns seem to be the same for the each mixture, however there could be slight variation resulting of the moisture absorption during the data collection. To avoid such situation the precursor powder was mixed with nitrocellulose which makes a thin layer on powder crystals to keep minimum interferences from environmental moisture.
Figure 48 X-ray diffraction patterns of precursor mixtures dried at 110 °C.

Diffraction pattern for Ce:Sm (9:1 and 8:2, mole/mole) shows strong cerium nitrate peaks. The presence of additional peaks becomes intense with increased samarium nitrate content, which is noticed at 2θ~ 28.4°, 30.9°, and 45.15°. This corroborates that upon drying the dissolved salt solution mixture, part of the solution rectystallize into individual constituent. A slight shift in the peak position of Ce(NO₃)₃. xH₂O could be due to doping of Sm atoms in the lattice of Ce(NO₃)₃. xH₂O. This observation is very important for the coating deposition in SPPS.
technique. Upon injection of the mixed solution droplet, after water evaporation the solid precursor droplet quickly exposed to the intense heat of plasma. This heat is more than sufficient (as calculated in chapter 3) to decomposes the mixture as described in TG-DTA study followed by the pyrolysis, melting and re-solidification on substrate surface [119]. The SPPS method has been used to deposit coating using the single constituent liquid such as alumina [126] and zirconia [126]. Padture et al. also demonstrated this method for the YSZ coating deposit using aqueous solution of zirconium and yttrium salts [108] and not observed separate oxide phase formation.

Further in the present work, samarium and gadolinium oxide doped cerium oxide coatings were prepared. These coating were investigated using X-ray diffraction to determine the doping. The change in the lattice parameter of the cerium oxide coating due to Sm and Gd doping was calculated. Figure 49 shows the diffraction pattern of 10 and 20 mole % Sm doped CeO₂ deposited coating. The patterns were also compared with standard CeO₂ and Sm₂O₃ in the case of separate phase formation. The XRD patterns of the coating exhibits broad peaks that are indexed to the single phase fluorite structure of Ce₁₋ₓSmₓO₂₋ₚ type solid solution, (where x is the dopant in mol ~ 0.1 and 0.2 and y is due to oxygen vacancies creation). The change in lattice constant with dopant concentration calculated from high angle diffraction peak to minimize the error. In the present study (331) peak was used for lattice constant calculation. The difference in the lattice constant for Sm³⁺ and Gd³⁺ doping can be related to the difference in ionic radii of the cations. The peak position of XRD pattern of the doped coating was found to be shifted left (Fig. 49 and 51). This indicates the lattice expansion of the CeO₂. The ionic radius of the Sm³⁺ and Gd³⁺ are 0.1079 nm and 0.1053 nm respectively. In contrast the ionic radius of Ce⁴⁺ is 0.097 nm.
The larger radii of the trivalent cations dopant than Ce$^{4+}$ supposed to expand the lattice dimension of CeO$_2$. The present study also confirms the increase in the lattice parameter due to trivalent substitution which further increases with the concentration of the cations (Fig. 50).

Figure 49 X-ray diffraction patterns of samarium doped cerium oxide SPPS coating. (a) 10 mol% (b) 20 mol%. CeO$_2$ standard (red line), Sm$_2$O$_3$ standard (green line) and (c) SS substrate
Figure 50 Change in lattice parameter of CeO$_2$ coating with increase in dopant concentration

Figure 51 X-ray diffraction patterns of Gadolinium doped cerium oxide SPPS coating. (a) 10mol% (b) 20 mol% . CeO$_2$ Standard (red line), Gd$_2$O$_3$ standard (green line) and (c) SS substrate
The XRD patterns of the Gd doped coating are shown in Fig. 51, which indicates single fluorite structure of Ce$_{1-x}$Gd$_x$O$_{2-y}$ type oxide. Gd$^{3+}$ (0.1053 nm) doped cerium oxide coating also shows the similar trend of increase in lattice constant of Ce$_{1-x}$Gd$_x$O$_{2-y}$ type solid solution. The change in lattice constant due to Gd doping was observed smaller than that of Sm doping which is attributed to the smaller ionic radii of Gd$^{3+}$ than Sm$^{3+}$ion. These results support the possibility of doping in solution precursor plasma spray technique. The change in the lattice parameter is in good agreement with the reported literature values [128].

It is important to note here the coating synthesis by mixed solution precursor offer more challenges. Since difference in the decomposition temperature of the precursor constituent can lead to pyrolyze in their respective oxides. Moreover, during the SPPS deposition, precursor droplets interaction with the plasma jet leads to several products due to fragmentation of the larger droplets (30 µm) into fines until they volume precipitates, evaporate, decompose and pyrolyze. Importantly, during the deposition, solution droplets also travel along with the outer low temperature (~ 2000 °C) [79] region (jet periphery) of the plasma jet. The droplets those travel only along the hotter center line of the plasma jet melt and deposit as splats. The poorly treated drops deposit in unpyrolyzed form. Some time these precursor droplet’s deposits in the form of gel on the substrate surface which leave aggregated type morphology after plasma jet heat [129].
Figure 52 Temperature profile of the substrate. First segment is the preheating of substrate, second segment is during coating, showing an increase and then stabilization in maximum temperature with increasing the number of scan.

This situation was not observed in the present study supported by the XRD results. Since, in the present study the substrate was heated to 550 °C before deposition and coating temperature reaches to 650 °C due to multiples plasma torch scans (Fig. 52) which is not sufficient according to TG-DTA study for the mixed solution precursor (complete decomposition at 700 °C). However, XRD results do not indicate any intermediate phases of the samarium and gadolinium salts or their oxides. This could be attributed to the higher coating surface temperature. The actual surface temperature of the deposit could be higher since temperature was measured using back thermocouple attached to the substrate. The higher temperature in situ pyrolyzes the
solution deposit on substrate, which is poorly treated in plasma. Moreover the maximum weight loss due to decomposition of the mixed precursor occurs below 400 °C (Fig. 46 and 47), which is lower than the substrate initial temperature. The consequence of the trivalent cations doping in CeO₂ lattice increases the oxygen vacancy to maintain the stoichiometry according to the following reaction.

\[ 2\text{Ce}_\text{Ce}^x + 2\text{Re} + \text{O}_\text{O}^x \rightarrow 2\text{Re}_{\text{Ce}} + \text{V}_{\text{O}} + 1/2 \text{O}_2 \]  

(4.3)

where \([\text{Ce}_\text{Ce}^x] = \text{Ce}^{4+}, [\text{Re}] = \text{Re}^{3+}, [\text{V}_{\text{O}}] = \text{oxygen vacancy}, [\text{Re}_{\text{Ce}}] = \text{Re}^{3+} \text{ at Ce}^{4+} \text{ site}, \text{and } [\text{O}_\text{O}^x] \] is \(\text{O}^{2-}\) ion on a regular O lattice site.

Cerium oxide alone has very few oxygen vacancies. Few study reports the vacancy enhancement due to change in particle size which induces the non stoichiometry in lattice (Ce⁴⁺ → Ce³⁺) [101]. The presence of higher number of oxygen vacancy makes this material oxygen ion conductive which is one of the important desired properties for electrolyte in solid oxide fuel cell application. These oxygen ion vacancies are mobile at low temperature (450-700 °C) which allow its application for low temperature SOFC [130]. However, the change in oxygen state from Ce⁴⁺ to Ce³⁺ make this material rich in electrons and induces electronic conductivity concomitantly. Thus, in the past many investigations have been carried out to induce oxygen vacancies using lower valence cations doping and confirmed a promising approach to increase the oxygen ionic conductivity [53, 54]. Moreover, the lower valence cations such as Sm, Gd, Nd and Y are stable [131]. Various studies have been reported on consolidation of doped cerium oxide electrolytes such as tape casting, compaction and sintering and extrusion. Recently, cerium oxide based coatings have been prepared by induction plasma spraying of suspension of doped
cerium oxide nano powder and solution [132, 133] and showed the high density coating with improved ionic conductivity.

4.4 Conclusions

The process parameters for cerium oxide coating using SPPS process were optimized. The effect of plasma power, standoff distance and solution concentration on splat formation and coating microstructure were studied. The low standoff distance improves the density of the splat resulting improved quality of coating. The longer standoff distance leads to the unpyrolyzed solution deposit and unmelted spherical particles on substrate. Low solution precursor concentration has unpyrolyzed solution and broken shell deposit with smaller content of the splats results in porous splat and coating. High concentration solution precursor improves the splat and the coating density with reduced unpyrolyzed and semi molten deposit. The high concentration precursor experiences volume precipitation which leads to high density deposits. Substrate temperature should be higher than the 330 °C for cerium oxide coating whereas more than 600 °C is need for doped cerium oxide coating. Cerium nitrate is suitable precursor for the ceria and doped ceria coating. Decomposition study exhibits low pyrolyization temperature (330 °C) of cerium nitrate. The mixed precursors decompose near 500 °C into their oxides. Samarium and gadolinium doping in cerium oxide lattice is possible which is confirm by the XRD peak shift and lattice parameter expansion.
CHAPTER 5: STUDY THE CORROSION BEHAVIOR OF CERIUM OXIDE COATED 17-4 PH STEEL

5.1 Introduction

Coupled with its strength, the corrosion resistance of 17-4 PH stainless steel allows for its use in situations where austenitic type steel such as 304 and 316 will not function. One specific application is in underwater oil wells. Here the reducing sulfide and chloride environments dictate the corrosion resistance requirements. When used as a well pipe, the strength needs to be as high as possible as there is considerable strain due to the mechanical stresses and internal pressures. With proper heat treatment, 17-4 PH has the necessary strength [134]. However, when exposed to chlorides at elevated temperatures, 17-4PH steel experiences pitting as well as general corrosion. It is in this situation that rapid corrosion can occur with subsequent failures. Surface modification with cerium containing solutions has been shown to impart enhanced corrosion resistance of austenitic stainless steels, (SS), in chloride containing environments [135-137]. These modifications are generally from aqueous solutions and involve immersion of the substrate into a boiling solution for a period of time. It is reported that the treatment results in dissolution of MnS inclusions where initiation of pitting would otherwise be possible [138]. The boiling action in a nitrate solution at a low pH is itself a form of passivation procedure as this action removes free iron and facilitates oxide growth [139]. Further and a more important mode of protective action is considered, enrichment of chromium in the steels oxide layer as well as the modification of the oxide layer by the incorporation of cerium. The modified
oxide layer is considered to have a stronger chemical resistance than the native oxide [135]. Incorporation of cerium into the oxide layer can be achieved by other methods besides aqueous means. Ion implantation of cerium has proven to be an effective means of improving corrosion resistance of austenitic stainless steel. This has been shown to reduce the cathodic and anodic corrosion reactions by covering active sites [140]. It has been found that cerium oxide catalyzes chromium oxide in stainless steel during high temperature exposure to air due to its fluctuation in oxidation state from +3 to +4 [141, 142]. Thus, it is reasonable to assume that a plasma sprayed layer of cerium oxide may offer some corrosion protection to a martensitic stainless steel, such as 17-4 PH, in under water oil well conditions which are very corrosive to the alloy due to their chloride and hydrogen sulfide concentrations as well as low pH, reducing potential and high pressures. Moreover, plasma spray is a cost effective coating technology and applicable to industry [143]. In this work 17-4 PH SS was coated with nanoceria using plasma spray in an effort to enhance the steel corrosion resistance in 3.5 wt% NaCl with different pH, temperature and pressure conditions.

5.2 Materials and Methods

5.2.1 Spray Drying and Coating Development

Thermal spray grade powder was prepared by agglomerating nano ceria powder (50-80 nm, 10-17m²/g) using a Buchi B-290 (Buchi Corp., Newcastle, DE) research model spray dryer. These agglomerated particle ranging 30-50 µm were then used for plasma spraying. The optimization of spray drying parameters was carried out to achieve appropriate agglomerate’s particle size discussed in chapter 2. After spray drying the apparent density and flow rate of the
agglomerated powder was determined using a Hall flow meter according to the ASTM B 213 for flow rate and ASTM B 212 for apparent density.

DC atmospheric plasma spray (APS) was used for nano ceria coating using agglomerated powder. The powder was injected in front of the plasma spray gun (Model SG 100 Praxair TAFA, Concord, NH, USA) using an external injection port tilted towards the gun by 30°. Argon was used as a primary gas. Hydrogen was used as a secondary gas to increase the power of plasma jet. To increase the adhesion of the coating the grit blasted 17-4PH substrate was preheated to 300 °C using same spray gun. The substrate was kept at a distance of 80 mm from the gun. The plasma spray parameters were also optimized by varying powder flow rate, gun power and carrier gas flow rate which are listed in Table 3.

5.2.2 Coupons Preparation for Corrosion Testing

Rectangular (2.5X 2.5 X 3mm), and cylindrical (Φ 12.7mm & t = 8mm), Stainless steel, (17-4 PH) coupons, were prepared with and without coatings for subsequent electrochemical corrosion experiments (Fig. 53). In order to avoid heat effect samples were cut from sheet using a water jet. Bare coupons were prepared with polished and grit blasted surfaces. Polished surfaces were prepared by polishing mill finished bare coupons with silicon carbide paper followed by 1 µm diamond polishing. Prior to the ceria coating, the mill finished samples were grit blasted in order to form an effective surface for mechanical interlocking with the substrate.
Figure 53 Test coupons for the corrosion test. (a) Cerium oxide coated coupons (2.5X 2.5 X 3mm) for the room temperature test (b) Cross section microstructure of the coating on 17-4PH steel (c) coupons (Φ~12.7mm, t~ 8mm) for the high pressure and temperature corrosion test.

Figure 54 Electrochemical corrosion test cell used for room temperature corrosion study consisting of the working electrode (test coupon), reference electrode Ag (Ag/AgCl) and counter electrode (Pt)
5.2.3 High Pressure and Temperature Corrosion Cell

To evaluate the performance of the 17-4PH steel in coated and uncoated condition in a high pressure and temperature environment, an in house high pressure cell was developed using high pressure fitting rated 20Kpsi to simulate real down hole corrosion conditions. The pressure cell has three electrodes similar to any conventional corrosion cell including counter, reference and working electrodes (Fig.54).

Figure 55 High pressure and temperature corrosion test setup. (a) Front view of the set up (b) Inside view and (c) High pressure cell with electrodes
The cell volume is 350 ml. The high pressure was generated in the cell after filling the cell with electrolyte to its full capacity. The pressure was generated by an automatic reciprocating high pressure pump (with 100 Psi base pressure) that works on a differential area principle. Figure 55 shows the front and inside view of the high pressure corrosion test set up and the pressure cell itself. The high pressure fittings with high temperature epoxy were used for designing electrodes in order to avoid leak. The pseudo reference electrode made of Pt and Pt counter electrodes of the same surface area were used.

5.2.4 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) uses a range of low magnitude polarization voltages (5-20 mV). EIS is usually measured by applying an AC potential to the electrochemical cell and then measuring the current through the cell [144], where the impedance $Z(\omega)$ is composed of a real and an imaginary part. A plot of the real component (X axis) versus the imaginary (Y axis) component of impedance is known as a Nyquist plot (Fig. 56). Nyquist plots can be obtained by varying the frequency from MHz to mHz of AC voltage near the open circuit potential (OCP). Figure 56 shows single time constant, complex plane plot alongwith the analogous electrical circuit. The lowest polarization frequency is at the right side of the semicircle, and the highest polarization frequency is noted on the left side.
The semicircle shape in this type of plot is caused by a presence of the capacitor or capacitive reactance. The complex plane plot looks more like a straight line than a semicircle when a parallel resistor (e.g. corrosion resistance) is large. The solution (electrolyte) resistance corresponds to Rs (Fig. 56), and corrosion resistance corresponds to Rp. The relationship between the capacitance, corrosion resistance and the frequency at the semicircle apex can be expressed by the following equation.

\[
C = \frac{1}{R_p \omega}
\]  

(5.1)

Where, \( \omega \approx 2\pi f \), \( f = \) frequency, \( C \) is capacitance, and \( \omega_{\text{max}} = 2\pi f \) at the complex plane plot semicircle apex. The corresponding Bode magnitude plot for the single time constant is shown in Fig. 57.
Figure 57 Single time constant Bode plots (a) Impedance versus frequency (b) phase angle versus frequency

The X axis of the Bode plot magnitude plot contains values for frequency and the y-axis contains values of total impedance for each frequency. The slope is zero when polarization is through resistance and less than zero (negative) when capacitive reactance becomes part of the circuit response to a polarization.
5.2.4.1 Equivalent Circuit Model for EIS Spectra Analysis

EIS data can be analyzed by fitting it to an equivalent electrical circuit model. The most common circuit elements are resistors, capacitors and inductors. These models should be used after understanding the physical significance of the electro chemical process. Two basic models will be discussed in following text.

Figure 58 Nyquist plot for the one time constant and corresponding Randles cell

The simplified Randles cell is one of the most common cell models. It consists of a solution resistance \( R_1 \), a double layer capacitor and a charge transfer (or polarization resistance, \( R_2 \)). The electrical double layer (EDL) capacitance is in parallel with the charge transfer resistance. The Nyquist plot and corresponding equivalent circuit for the Randle cell is shown in
Fig 58. The Nyquist plot for Randles cell is always a semicircle. The solution resistance (from electrolyte) can be measured from the real axis value at the high frequency intercept and the polarization resistance is the diameter of the semicircle in ohm.

Figure 59 Electrified interface structure for a corroding coating metal

Fig. 59 shows a schematic of the corroding metal surface, consisting of two time constants. The negative and positive ions from the electrolyte are shown in coating layer. The metal corrosion circuit is nested with the coating circuit, indicates that the pores in the coating can cause metallic corrosion by providing areas where the electrolyte has direct access to the metal surface. For the coated metal surface the typical Nyquist plot and corresponding equivalent
model is shown in Fig. 60. The impedance behavior of the perfect coating is purely capacitive with very low capacitance in nF or pF range, which is represented by a normal to the real part impedance axis. Other coatings have some extent of porosity, and after a certain period of time, electrolyte penetrates into it and forms a new liquid/metal interface under the coating. The corrosion can occur at this new interface.

![Diagram of Nyquist plot and equivalent circuit model](image)

**Figure 60 Nyquist plot and equivalent circuit model for the entire spectrum and modified Randles circuit for individual section**

### 5.2.5 Equivalent Circuit Model for EIS Spectra Analysis

Measurements were performed utilizing a Princeton Applied Research potentiostat (model VSP). A frequency range of 100 kHz to 1mHz was scanned with a voltage amplitude of
10mV. The first set of coupons were exposed to 3.5% (wt./wt.) NaCl solution at room temperature for extended periods of time and the coupons were periodically removed and placed in a cell of the same chemical composition, where electrochemical impedance spectroscopy was employed to determine resistance to polarization (Rp), which is essentially equivalent to corrosion resistance [145]. The samples were then returned to the test solution for subsequent testing. Initially for comparison purposes, EIS measurements were performed on uncoated grit blasted samples. However, the grit blasted samples resulted in mostly scattered data. It became obvious that no useful information could be extracted from the data and thus, polished samples were solely employed for electrochemical comparison while microstructural comparison was made with the grit blasted samples. The second sets of samples were evaluated at high pressure and temperature. Both coated and uncoated samples were exposed to similar test conditions. The pressure effect was observed from 2000Psi to 10000 psi at 25 °C while temperatures varied from 25 °C to 150 °C in the 3.5wt.% NaCl solution.

5.3 Results and Discussion

5.3.1 Electrochemical Corrosion

5.3.1.1 Open Circuit Potential

Open circuit potentials (OCP) of samples were allowed to stabilize as can be seen in Fig. 61. Measurements were made against a Ag/AgCl reference electrode. It took approximately 5 hours before the OCP on polished and coated samples were stabilized. OCP for the polished sample settled around -170mV Ag/AgCl while the ceria coated sample settled around -200mV Ag/AgCl. In contrast the grit blasted sample never really stabilized. It started to settle around -
200mV \( \text{Ag/AgCl} \) and then began to rise. This instability is attributed to the more active surface exposure to the electrolyte owing to the grit blasting. This instability prevented EIS measurements, and attempts merely resulted in noise with little discernible data. The polished and coated samples open circuit potentials were stabilized in 10 h.

### 5.3.1.2 Electrochemical Impedance Spectroscopy

Variation in corrosion resistance measured from the Nyquist plot equivalent circuit model) plotted with exposure time (in days) is shown in Fig 62. As can be seen in Fig.62a, the bare 17-4 PH steel coupons resistance to polarization, \( (R_p) \) decreased in an exponential fashion with exposure time. Contrary to this the \( R_p \) of the coated samples increased with time as can be seen in Fig.62b. It is important to note here that the initial corrosion resistance values were higher for the bare polished steel due to the formation of the thin protective chromium oxide layer. This layer eventually is damaged in the electrolyte affecting the corrosion protection. The initial values of \( R_p \) (or \( R_{\text{Corr}} \)) for the coated steel is lower as the steel was having higher surface roughness due to the grit blasting. Though, the coated steel should have high resistance values but that would be the case with the intact coatings.
Figure 61 Open circuit potential for 17-4 PH SS, (a) polished, (b) grit blasted, and (c) ceria coated, verses time in naturally aerated 3.5% NaCl at room temperature
Figure 62 Variation of corrosion resistance with time (a) polished 17-4 PH steel (b) Cerium oxide coated grit blasted 17-4 PH steel.

The native oxide layer on the 17-4 PH failed with continued exposure to the NaCl solution allowing for eventual dissolution of the base metal while the coated material gained the corrosion resistance. The gain in corrosion resistance can be explained by the coating pores filling with corrosion products [146]. In the present study, the cerium oxide coatings were had
porosities up to 9 percent. These porosities are closed, and thus do not have much effect. The inter-splat boundaries could be connected by vertical cracks which were generated due to the rapid cooling of splats in plasma spray. This could be one of the reasons for the lower initial value of the Rp, which eventually increases with time. However, percentage improvement of Rp for coated steel within 12 days was more than the percent reduction of the Rp for the bare steel.

Figure 63 Microstructure of steel surface after corrosion test (a) Grit blasted surface (b) cross-section of the grit blasted sample (The oxide layer has several breaks) (c) Cross-section of the coated steel (d) polished surface. All samples were characterized after 72 days of exposure.
Cross sections of uncoated and coated samples are shown in Fig. 63. Several pits were visible on the rough surfaces of the sample (Fig. 63a). A broken oxide layer from the same sample’s cross-sections micro-structure reveals that this could provide a path for the electrolyte to attack the underlying surface. With the coated sample there were no visible indicators of pitting such as spots on the surface of the coating and in cross-section. The polished surface shows the general corrosion with oxide layer buildup.

### 5.3.2 High Pressure and Temperature Corrosion Study

The coated and uncoated samples were subjected to harsh corrosive condition in order to mimic the oil well environment. In the first study ceria coated samples were exposed to varying pressure at 3.5wt% NaCl solution with different concentrations of the dissolved H₂S. Figure 64 shows the pressure’s effect on the corrosion resistance of the coated steel at 10 and 30 ppm dissolved H₂S concentrations. It is interesting to note that there is a marginal change in Rcorr. At each pressure the system was stabilized to achieve constant OCP, at which time the EIS data was collected. At 30ppm H₂S concentration, the Rcorr trend was found to be decreasing with increasing pressure. However, this deviation in the Rcorr could be attributed to the exposure time. Further, the effect of temperature was measured on both coated and uncoated steel from room temperature to 300 °F at 4000 Psi in 3.5 wt % NaCl (Fig. 65). Drastic changes in Rcorr occurred with changes in temperature on coated and uncoated samples. This is to be expected as the corrosion rate is known to increase with temperature. The relative changes in Rcorr of the coated and uncoated samples are similar. This can be explained by the presence of pores in the coating, provides path for electrolyte penetration to the coating and substrate interface.
Figure 64 Effect of pressure on corrosion resistance of cerium oxide coated 17-4PH at 3.5wt% NaCl and different ppm of dissolved H₂S
Figure 65 Effect of temperature on percent change in $R_{corr}$ of polished and ceria coated steel in 3.5 wt% NaCl at 4000Psi
Furthermore, a comparative study was performed to evaluate the corrosion resistance of the 17-4 PH steel in different surface condition as shown in Fig. 66. Upon exposure to identical conditions samples with more substantial surface coatings retained a larger percentage of their initial corrosion resistance. It is also evident that smoother surfaces are more corrosion resistant when the bare polished and the grit blasted samples are compared. The rough surface promotes the pitting corrosion due to damaged protective chromia layer.
5.4 Conclusions

Even with the pre-coating surface preparation of grit blasting, 17-4 PH SS coated with nano ceria has proven to be more stable to corrosion resistance in 3.5% NaCl than the corresponding uncoated sample. Uncoated samples have demonstrated spontaneous oxide layer breakdown with subsequent surface corrosion. Pits are readily observed with SEM on the corroded uncoated samples. No observable degradation of the coated samples was witnessed.

Given that the nanoceria layer is porous it would be expected that there would be some corrosion of the underlying metal especially since it was grit blasted and not sealed as is customary for porous ceramic coatings [147]. However, there were no observable indications of corrosion of the underlying metal. This suggests that the ceria coating must stabilize the areas exposed by the pores. Stabilization of the 17-4 PH SS oxide is possibly the mode of protection as it is the oxide that provides a corrosion barrier to fluid contact. The pressure has marginal effect on corrosion resistance whereas temperature has drastically deteriorated the both coated and uncoated steel. The grit blasting treatment creates a lot of intentional pits and presence of pores in ceria coating decreases Rcorr.
CHAPTER 6: CONCLUSIONS

This dissertation research was focused on the development of cerium oxide based catalytic coatings with controlled chemistry using atmospheric plasma spray (APS) and solution precursor plasma spray techniques (SPPS). Both the techniques have been demonstrated for bulk nano structure consolidation of nano powders. Cerium oxide consolidation is always challenging due to high sintering temperature, unstable oxidation state and high vapor pressure. A significant contribution of this dissertation is the development of a cost effecting technique for cerium oxide coating which can be an unconventional route for SOFC electrolyte fabrication and corrosion protection of steel in harsh environment. A spray drying technique was demonstrated for nano particles agglomeration for manufacturing nano structure coating using thermal spray. A statistical design of experiment and response surface methodology was used to predict the relationship between the process variables and responses in the APS process. Quadratic models and response surface contours for predicting the density and deposition efficiency were developed. The highest density of 93 % is predicted with deposition efficiency of 55% within the experimental space which is limited by the instrument constrains and material properties. The most significant factors affecting the plasma spray coating of cerium oxide are standoff distance and carrier gas flow rate. This study demonstrated that the internal injection vaporizes cerium oxide particles, and high plasma power adversely affects the density and the deposition efficiency of the coatings. This research also demonstrates a solution based technique for the thin film cerium oxide coating. It has been shown that the injection of solution precursor of cerium salts or mixed salts provides ceria and doped ceria coating. Using water as a solvent for synthesis
of ceria coating alleviates overheating effect and provides oxidizing environment. This leads to good quality functional coating with controlled chemistry and considered to be significant contribution of this dissertation. Factors which considerably affect splats depositions, density and morphologies in SPPS are closely examined and optimized for high density coatings. It was demonstrated that the precursor salt (nitrate of cerium) with lower thermal decomposition temperatures (330 °C) was suitable for coating with high density. The high concentration (0.5M), low spray distance (40 mm) and high power plasma jet significantly improve the splat morphology and adhesion, with reduced porosity (upto 20%). The feasibility of the trivalent cations (Sm $^{3+}$ and Gd $^{3+}$) doping into cerium oxide lattice in high temperature DC plasma jet is experimentally proved, another key contribution of this research. XRD analysis revealed the nano crystalline characteristic of the coating and lattice expansion due to doping.

The APS ceria coatings were investigated for their applicability under extreme environmental conditions (high pressure and temperature). The air plasma sprayed coated 17-4PH steels coupons were subjected to high pressure (10 Kpsi) and temperature (300 °F) corrosive environment in autoclave to investigate the corrosion protection of the steel. A high pressure and temperature autoclave was designed and developed in house with EIS capability to achieve extreme conditions. This is a significant achievement in this Ph.D. study. The ceria coated steel showed continuous improvement in corrosion resistance at 3.5 wt% NaCl at ambient temperature for 3 months study whereas; high pressure may not have a significant effect. The ceria coated steel shows an improvement in corrosion protection (by 4 times) compared to bare steel at low pH, 300 °F and 4000 Psi environment. In summary, this dissertation presents a significant
understanding in developing large scale Nanoceria based coating with controlled chemistry using thermal spray techniques for functional applications.
APPENDIX A: LIST OF PUBLICATIONS


• D.Lahiri, V. Singh, et.al., Boron nitride nanotube reinforced hydroxyapatite composite: Mechanical and tribological performance and in-vitro biocompatibility to osteoblasts *J. Mechanical Behaviour of Biomedical Materials* 4(2011) 44.


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