

Deposition of Zirconium Carbide onto a substrate

B. van der Walt



orcid.org 0000-0001-8191-7221

Dissertation submitted in fulfilment of the requirements for the degree *Master of Engineering in Mechanical Engineering* at the North-West University

Supervisor:

Prof J. Markgraaff

Graduation May 2018

Student number: 21707200

PREFACE

I would like to express my deep gratitude to Professor J Markgraaff, my study leader and supervisor, for his patient guidance, enthusiastic encouragement and useful critiques of my research work. I have learned a great deal from you academically and personally. I would also like to thank Dr H. Bissett, for his advice and assistance in keeping my work on track as well as the support and jokes along the way.

My grateful thanks are also to Dr L. Tiedt and Mr R. van der Merwe for their advice and assistance with the SEM analysis, to Mr T. Ntsoane and Ms Z. Senthoo who conducted the XRD analysis for this research, Dr M. Britton and Mr J. Mokgawa for their guidance and help with the ICP-OES analysis and finally Dr S. Lötter for helping a mechanical engineer understand his chemistry a little better. To the technicians, Mr M. Makofane and Mr P. Smit, at Applied Chemistry situated on the Necsa campus for their continuous help and inputs during the experimental work.

I would also like to extend my thanks to the Department of Science and Technology (DST) and the Advance Materials Initiative (AMI) program who supplied the necessary funding to make this dissertation possible.

Finally I wish to thank my friends and family for their support and encouragement throughout my study. Especially my mother and father for their love, support and motivation.

ABSTRACT

The incident at Japan's Fukushima Daiichi nuclear power plant was aggravated by the lack of resistance of the zirconium alloy to steam oxidation. Zirconium alloys have been known to oxidise and produce hydrogen in a steam environment which can explode as in the case of Fukushima. To avoid oxidation at high temperatures by steam, the use of a corrosion resistant coating has been suggested. ZrC is a coating material under consideration because it has a high melting point, good mechanical strength, good thermal conductivity, and good corrosion resistance. ZrC also has properties beneficial to the nuclear industry such as a low neutron absorption cross-section and fission product resistance.

In order to deposit ZrC onto the Zr fuel rods coating techniques such as chemical vapor deposition, pulsed laser deposition, magnetron sputtering and plasma spraying have been identified as candidate techniques. The selected method should produce a dense uniform coating with excellent adhesion, be reproducible, and of reasonable cost. Therefore the plasma spraying method was chosen as it was thought to be the most flexible and easily adaptable for the purpose of depositing ZrC onto Zr-alloy fuel rods.

Plasma spraying coatings are dependent on many parameters that can influence the coating integrity. The particle temperature and velocity were identified as two crucial parameters, therefore experimental parameters were chosen to optimise these properties. The parameters are plasma power input (11.0, 16.5, and 22.0 kW), spray distance (60, 80 and 100 mm) and particle injection velocity (10, 15 and 20 m/s). Additionally the spraying atmosphere was also considered because of the risk of oxygen contamination during atmospheric spraying.

This research was done using a button type dc non transfer arc plasma torch to deposit ZrC coatings onto stainless 304 substrates. The feedstock powder was analysed to determine its size and composition to help determine the spray parameters. A simulation using the Jets&Poudres program was used to verify that the plasma sprayed ZrC particles temperature and velocity were high enough to deposit. A SEM was used to investigate the surface and cross-sections of the coatings, while EDS and XRD was used to confirm their composition.

It was found that an increase in plasma power produces better coatings, while the ideal spray distance was 100 mm and injection velocity was 15 m/s. XRD confirmed that all atmospheric plasma sprayed coatings had oxygen contamination while the inert spray runs were oxide free. In contrast the atmospheric coating deposited and formed coatings while the inert samples had many un-melted particles with an inconsistent structure. All coatings displayed weak adhesion and some form of porosity in the coating structure.

CONFERENCE PROCEEDINGS

The following articles were produced presented at conferences during the duration of this study:

SAIMM: The Nuclear Materials Development Network Conference (NMDN)

Van der Walt, B., Markgraaff, J. & Bissett, H. (2015). Manufacturing processes for zirconium carbide layer deposition. SAIMM AMI Nuclear Materials 2015 Conference: 59-64.

SAIMM: The Precious Metals Development Network Conference (PMDN)

Van der Walt, B. & Bissett, H. (2017). Deposition of zirconium carbide layers using a plasma spraying method. SAIMM AMI Precious Metals 2017 Conference: 33-45.

ACRONYMS AND ABBREVIATIONS

AC	Alternating current
BSE	Back-scatter electron
CVD	Chemical vapor deposition
DC	Direct current
Demin-water	Demineralised water
D-gun	Detonation gun
EDS	Energy dispersive spectroscopy
GENMIX	General Mixing
HVOF	High-velocity oxy-fuel flame
ICP-OES	Inductive coupled plasma emission spectroscopy
JCPDS	Joint committee on powder diffraction standards
LTE	Local thermal equilibrium
Necsa	South African nuclear energy company SOC Ltd.
NERVA	Nuclear engine for rocket vehicle applications
PLD	Pulsed laser deposition
PSD	Particle size distribution
PVD	Physical vapor deposition
PWR	Pressurised water reactor
PyC	Pyrocarbon
RF	Radio frequency
SDD	Silicon drift detector
SEM	Scanning electron microscopy
TRISO	Tristructural-isotropic
WNA	World nuclear association
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction
ZrC	Zirconium carbide

TABLE OF CONTENTS

PREFACE	I
ABSTRACT	III
CONFERENCE PROCEEDINGS	IV
ACRONYMS AND ABBREVIATIONS	V
CHAPTER 1 INTRODUCTION.....	1
1.1. Background	2
1.2. Problem Statement.....	3
1.3. Aim	3
Bibliography.....	4
CHAPTER 2 LITERATURE REVIEW: ZIRCONIUM CARBIDE	5
2.1. Introduction	6
2.2. Survey of ZrC General Properties	7
2.3. Crystal Structure	8
2.4. Chemical Properties	8
2.5. Phase Relationship.....	9
2.6. Thermal Properties.....	10
2.7. Conclusion.....	11
Bibliography.....	12
CHAPTER 3 LITERATURE REVIEW: DEPOSITION METHODS FOR ZRC	13
3.1. Surface Treatment and Coatings.....	14
3.2. Deposition Methods	14
3.2.1. Chemical Vapor Deposition	15

3.2.2.	Pulsed Laser Deposition	16
3.2.3.	Magnetron Sputtering	17
3.2.4.	Plasma Spraying.....	19
3.3.	Conclusion	21
3.4.	Scope	22
	Bibliography.....	23
 CHAPTER 4 LITERATURE REVIEW: NON-TRANSFER ARC DC PLASMA SPRAYING		24
4.1.	Introduction	25
4.1.1.	Plasma Torch	26
4.1.2.	Plasma Generation	28
4.1.3.	Particle Injection.....	29
4.1.4.	Particle and Plasma Plume Interaction	30
4.1.5.	Substrate Preparation	33
4.1.6.	Coating Structures	35
4.2.	Conclusion.....	37
	Bibliography.....	38
 CHAPTER 5 IMPLEMENTATION OF DC PLASMA SPRAYING		40
5.1.	Introduction	41
5.2.	Spraying Setup	41
5.2.1.	Substrate Holder.....	47
5.2.2.	Temperature Measurement.....	47
5.3.	Powder Composition, Particle Size and Morphology.....	47
5.5.	Plasma Temperature and Efficiency Calculation.....	50

5.6.	Particle Temperature and Velocity Simulations	51
5.4.	Substrate Preparation	55
5.7.	Coating Procedure.....	56
5.8.	Summary	58
	Bibliography.....	59
CHAPTER 6 DEPOSITED COATINGS MICROSTRUCTURE AND COMPOSITION.....		60
6.1.	Coating Characterisation	61
6.1.1.	Coating Microstructure	61
6.1.2.	Coating Composition	74
6.2.	Conclusion	84
	Bibliography.....	86
CHAPTER 7 SUMMURAY, CONCLUSION & RECOMMENDATIONS		87
7.2.	Conclusion.....	89
7.3.	Recommendations.....	90
	Bibliography.....	91
ANNEXURE A: PROPERTIES OF ZIRCONIUM CARBIDE.....		92

LIST OF TABLES

Table 3-1: List of parameters of coating process applicable to ZrC coatings	21
<i>Table 5-1: Simulation parameters used for the Jets&Podres program</i>	<i>52</i>
<i>Table 5-2: Modified ASTM A 380 - 06 standard</i>	<i>56</i>
<i>Table 5-3: Experimental parameters.....</i>	<i>57</i>

LIST OF FIGURES

<i>Figure 1-1: Fukushima Daiichi nuclear power plant after the hydrogen explosion (WNA, 2017).....</i>	<i>2</i>
<i>Figure 2-1: Nuclear fuel rod assembly showing the cladding that a coated has been suggested for, modified from WNA (2017)</i>	<i>7</i>
<i>Figure 2-2: ZrC powder</i>	<i>7</i>
<i>Figure 2-3: ZrC crystal structure</i>	<i>8</i>
<i>Figure 2-4: Zr-C phase diagram, modified from Katoh et al. (2013)</i>	<i>9</i>
<i>Figure 2-5: Mode of cracking due to the mismatch of thermal coefficient of a ceramic coating (α_c) and the thermal coefficient of a metal substrate (α_m): (1) Edge cracks in ceramic when $\alpha_c < \alpha_m$, and (2) core cracks in ceramic when $\alpha_c > \alpha_m$. Modified from (Uday et al., 2016)</i>	<i>10</i>
<i>Figure 3-1: Schematic illustration of conventional CVD process</i>	<i>15</i>
<i>Figure 3-2: Schematic illustration of PLD process</i>	<i>16</i>
<i>Figure 3-3: Illustration of schematic magnetron sputtering process</i>	<i>18</i>
<i>Figure 3-4: Gas temperatures and velocity of different thermal spray processes modified from Fauchais et al. (2014)</i>	<i>19</i>
<i>Figure 3-5: Schematic illustration of a typical plasma spray torch.....</i>	<i>20</i>
<i>Figure 4-1: Schematic of a typical plasma spray process and coating structure modified after Fauchais et al. (2014)</i>	<i>25</i>
<i>Figure 4-2: Schematic illustration of a plasma torch showing the components, modified from Fauchais et al. (2014)</i>	<i>26</i>
<i>Figure 4-3: Different types of cathodes used in plasma torches1) Rod type cathode, 2) Button type cathode</i>	<i>27</i>
<i>Figure 4-4: Schematic illustration of typical anode designs with radial gas injection: 1) Straight anode, 2) Step change anode and 3) cascading anode, modified from (Zhukov et al., 2007)</i>	<i>28</i>

<i>Figure 4-5: Powder injected into a plasma torch using a multi-injector configuration, modified from (Fauchais et al., 2014)</i>	<i>30</i>
<i>Figure 4-6: Trajectories of particles with different masses injected into a plasma, modified from Fauchais et al. (2014)</i>	<i>31</i>
<i>Figure 4-7: Schematic illustration of plasma spraying process and coating formation, modified from Bernecki (2004)</i>	<i>32</i>
<i>Figure 4-8: Schematic illustration of particle deposition (splats) relative to grit blasted surface peak sizes. 1) Splat size adapted to peak size. 2) Too small splat sizes relative to peak sizes. 3) Too large splat size relative to peak sizes, modified from Fauchais et.al. (2014)</i>	<i>34</i>
<i>Figure 4-9: Illustration of irregularity created through an abrasive particle hitting the substrate surface, modified from Fauchais et al. (2014)</i>	<i>34</i>
<i>Figure 4-10: Schematic illustration of a plasma sprayed coating, modified from Lovelock (2015)</i>	<i>35</i>
<i>Figure 5-1: Laboratory floor plan for atmospheric plasma spray setup: 1) Gas cylinders, 2) Gas flow meters, 3) Power supply, 4) Water inlet manifold flow meters , 5) Water outlet manifold flow meters, 6) Water cooling tower, 7) Plasma spray chamber, 8) Plasma torch, 9) Powder feeder, 10) Powder feeder controller</i>	<i>41</i>
<i>Figure 5-2: Inert plasma spray chamber: 1) Plasma torch, 2) pressure gauge, 3) powder feeder, 4) substrate temperature controller, 5) thermal couple read-out, 6) swing check valve, 7) front loading door</i>	<i>43</i>
<i>Figure 5-3: Cross-section view of necsa designed DC plasma torch: 1) Cathode, 2) Insulating material, 3) Anode nozzle, 4) Cathode cooling water inlet, 5) Cathode cooling water outlet, 6) Gas inlet and 7) Anode cooling water inlet</i>	<i>44</i>
<i>Figure 5-4: Necsa non-transfer DC plasma torch: 1) Negative pole, 2) Positive pole, 3) Anode water inlet, 4) Anode water outlet, 5) Cathode water outlet, 6) Cathode water inlet, 7) Gas inlet and 8) Anode nozzle gas outlet.....</i>	<i>44</i>
<i>Figure 5-5: Plasma torch anode, cathode and gas vortex injector</i>	<i>45</i>

<i>Figure 5-6: ERIEZ A series commercial powder feeder: 1) cylindrical track access latch, 2) carrier gas inlet, and 3) carrier gas and powder outlet.....</i>	<i>46</i>
<i>Figure 5-7: The powder feeder injection setup at the anode nozzle</i>	<i>46</i>
<i>Figure 5-8: Heated substrate holder 1) heating element, 2) plasma plume shield plate, 3) heating element stand, 4) heating element, and 5) heating control knob</i>	<i>47</i>
<i>Figure 5-9: XRD pattern of feedstock powder.....</i>	<i>48</i>
<i>Figure 5-10: Particle size distribution incremental volume and cumulative volume graph</i>	<i>49</i>
<i>Figure 5-11: SEM micrograph of feedstock powder showing the large and fine particles.....</i>	<i>50</i>
<i>Figure 5-12: Illustration of plasma temperature and velocity in a typical plasma spraying setup.....</i>	<i>52</i>
<i>Figure 5-13: Particle temperature at the centre for an 11.0 kW, 16.5 kW and 22.0 kW plasma</i>	<i>53</i>
<i>Figure 5-14: Particle velocity for an 11.0 kW, 16.5 kW and 22.0 kW plasma</i>	<i>54</i>
<i>Figure 5-15: Plasma and particle interaction during spraying process</i>	<i>55</i>
<i>Figure 5-16: Plasma torch generating a plasma using nitrogen gas</i>	<i>57</i>
<i>Figure 6-1: Sample cast in a resin and polished in order to observe the coating cross-section</i>	<i>61</i>
<i>Figure 6-2: SEM micrograph showing un-deformed particles on the surface of sample PS_0 1</i>	<i>62</i>
<i>Figure 6-3: SEM micrograph of sample PS_01 cross-section showing lack of deposited coating as well as crack along the coating surface deposited at 11.0 kW.....</i>	<i>62</i>
<i>Figure 6-4: SEM micrograph showing un-deformed particles on the surface of sample PS_02</i>	<i>63</i>
<i>Figure 6-5: SEM micrograph of sample PS_02 cross-section showing a few deposited particles on the substrate surface deposited at 16.5 kW</i>	<i>63</i>
<i>Figure 6-6: SEM micrograph showing high amount of deformed particles on the surface of sample PS_03.....</i>	<i>64</i>

<i>Figure 6-7: SEM micrograph of sample PS_03 cross-section showing a coating with weak adhesion to the substrate deposited at 22.0 kW.....</i>	<i>64</i>
<i>Figure 6-8: SEM micrograph showing deformed and un-deformed particles on the surface of sample PS_04.....</i>	<i>66</i>
<i>Figure 6-9: SEM micrograph of sample PS_04 cross-section showing the unsuccessful fusing of particles in coating as well as weak adhesion to the substrate.....</i>	<i>66</i>
<i>Figure 6-10: SEM micrograph showing un-deformed particles on the surface of sample PS_0 5.....</i>	<i>67</i>
<i>Figure 6-11: SEM micrograph of sample PS_05 cross-section showing heat damage to the substrate and deposited particles (BSE mode).....</i>	<i>67</i>
<i>Figure 6-12: SEM micrograph showing un-deformed particles on the surface of sample PS_0 6.....</i>	<i>69</i>
<i>Figure 6-13: SEM micrograph of sample PS_06 cross-section showing good mechanical interlocking of particles to substrate</i>	<i>69</i>
<i>Figure 6-14: SEM micrograph showing deformed particles on the surface of sample PS_07</i>	<i>70</i>
<i>Figure 6-15: SEM cross-sectional view of sample PS_07 deposited with a particle injection of 20 m/s</i>	<i>70</i>
<i>Figure 6-16: SEM micrograph of sample PS_08 with un-deposited particles on the surface....</i>	<i>72</i>
<i>Figure 6-17: SEM micrograph of sample PS_09 with un-deposited particles on the surface....</i>	<i>72</i>
<i>Figure 6-18: SEM cross-section of sample PS_04 showing un-melted core of ZrC particle with elemental mapping. The coloured dots denote the elemental distribution.</i>	<i>74</i>
<i>Figure 6-19: SEM cross-section of sample PS_02 with elemental mapping: (e) carbon (f) iron (g) oxygen (h) zirconium (BSE was unavailable). The coloured dots denote the elemental distribution.....</i>	<i>75</i>
<i>Figure 6-20: SEM back scatter cross-section of sample PS_03 with elemental mapping: (i) carbon (j) iron (k) oxygen (l) zirconium. The coloured dots denote the elemental distribution.</i>	<i>76</i>

Figure 6-21: SEM back scatter cross-section of sample PS_04 with elemental mapping: (m) carbon (n) iron (o) oxygen (p) zirconium. The coloured dots denote the elemental distribution.	77
Figure 6-22: SEM back scatter cross-section of sample PS_06 with elemental mapping: (q) carbon (r) iron (s) oxygen (t) zirconium. The coloured dots denote the elemental distribution.	78
Figure 6-23: Elemental mapping of sample PS_08 illustrating Zr and C as combined particles on the surface of the substrate.....	79
Figure 6-24: Elemental mapping of sample PS_09 illustrating Zr and C as combined particles on the surface of the substrate.....	80
Figure 6-25: Superimposed XRD analysis for samples PS_BL_01, PS_BL_02, PS_BL_06 and PS_BL_07.....	81
Figure 6-26: Superimposed XRD analysis for samples PS_BL_03 and PS_BL_04	82
Figure 6-27: Superimposed XRD analysis for sample PS_BL_05.....	83
Figure 6-28: Superimposed XRD analysis for samples PS_BL_08 and PS_BL_09	84

CHAPTER 1

INTRODUCTION

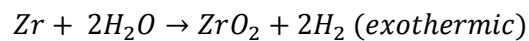
“Problems worthy of attack

Prove their worth by hitting back”

-Piet Hein (1905 – 1996)

1.1. Background

In March 2011, the Fukushima Daichi nuclear power plant in Japan was shut down after a magnitude 9.0 earthquake resulted in a tsunami hitting the shores of Fukushima. According to the World Nuclear Association (WNA) this led to the flooding of the emergency electric generators powering the cooling pumps, resulting in their failure. After the loss of coolant, the heat build-up inside of the reactor resulted in steam. The steam then reacted with the zirconium (Zr) fuel rod cladding producing hydrogen gas and zirconium oxide (Eq. 1-1). The greatest damage to the complex and release of radiation was caused by the subsequent explosions of hydrogen gas that built up inside of the reactors, most likely due to an electrical spark (Figure 1-1).



Eq. 1-1



Figure 1-1: Fukushima Daiichi nuclear power plant after the hydrogen explosion (WNA, 2017)

To avoid the production of hydrogen, during a loss of coolant accident (LOCA), a protective coating for the zirconium alloy fuel rods have been suggested by the nuclear engineering community. A coating material under consideration as a potential coating material is zirconium carbide (Katoh *et al.*, 2013). Zirconium carbide (ZrC) is considered as a suitable coating because of its high melting point (3 500°C), good mechanical properties, resistant to steam (below 700°C), and properties of value to nuclear fuel neutronics such as a low neutron absorption cross-section and good resistance to fission product attack (Murtaza *et al.*, 2011; Ogawa & Ikawa, 1986).

Although ZrC has successfully been deposited onto tristructural-isotropic (TRISO) fuel kernels (Wongsawaeng, 2010) research is required in order to successfully coat large nuclear fuel rods made of zirconium.

1.2. Problem Statement

Zr alloy fuel rods pose a hazard when loss of cooling is experienced when Zr under these conditions of emergency and accidental water supply, may react with steam, to form hydrogen that can explode. Coating of Zr fuel rods with a ZrC, which is a ceramic, has been suggested as a solution to prevent this reaction and the possible built-up of hydrogen.

The problem with the coating of metal (Zr) by a ceramic is that of wettability, which may influence the long-term integrity of the coating, inclusive of adhesion strength through differential expansion.

1.3. Aim

The aim of this study is the identification through review of literature of a suitable technique with the potential of producing a large scale ZrC coating on Zr alloy fuel rod. The chosen technique will then be used to deposit ZrC onto metal substrates to determine the feasibility of large scale coating on Zr fuel rods inclusive of the adhesion of the Zr coating with the view of investigating potential envisaged metallurgical modifications to yield long-term integrity.

Bibliography

- Andersson, M., Urbonaitė, S., Lewin, E. & Jansson, U. 2012. Magnetron sputtering of Zr–Si–C thin films. *Thin Solid Films*, 520(20):6375-6381.
- Craciun, D., Socol, G., Stefan, N., Bourne, G. & Craciun, V. 2009. Chemical composition of ZrC thin films grown by pulsed laser deposition. *Applied Surface Science*, 255(10):5260-5263.
- Katoh, Y., Vasudevamurthy, G., Nozawa, T. & Snead, L.L. 2013. Properties of zirconium carbide for nuclear fuel applications. *Journal of Nuclear Materials*, 441(1–3):718-742.
- Murtaza, G., Hussain, S.S., Rehman, N.U., Naseer, S., Shafiq, M. & Zakaullah, M. 2011. Carburizing of zirconium using a low energy Mather type plasma focus. *Surface and Coatings Technology*, 205(8–9):3012-3019.
- Ogawa, T. & Ikawa, K. 1986. Reactions of Pd with SiC and ZrC. *HIGH TEMP. SCI. High Temp. Sci.*, 22(3):179.
- Uday, M.B., Ahmad-Fauzi, M.N., Noor, A.M., Noor & Srihar, R. 2016. Current Issues and Problems in the Joining of Ceramic to Metal. (In Ishak, M., ed. Joining Technologies. Rijeka: InTech. p. Ch. 08).
- WNA. 2017. Fukushima Accident. <http://www.world-nuclear.org/information-library/safety-and-security/safety-of-plants/fukushima-accident.aspx> Date of access: 31 January 2017.
- Wongsawaeng, D. 2010. Performance modeling of Deep Burn TRISO fuel using ZrC as a load-bearing layer and an oxygen getter. *Journal of Nuclear Materials*, 396(2–3):149-158.
- Wu, H., Li, H.-j., Fu, Q.-g., Yao, D.-j., Wang, Y.-j., Ma, C., Wei, J.-f. & Han, Z.-h. 2011. Microstructures and Ablation Resistance of ZrC Coating for SiC-Coated Carbon/Carbon Composites Prepared by Supersonic Plasma Spraying. *Journal of Thermal Spray Technology*, 20(6):1286-1291.

CHAPTER 2

LITERATURE REVIEW: ZIRCONIUM CARBIDE

*“The success of a project greatly depends
on periodic visualization of the outcome.”*

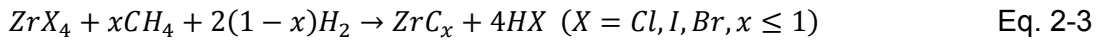
-Bhupesh B. Patil (1964 -)

2.1. Introduction

The development of ZrC can be traced back to the 1960's where it was proposed for use in the Rover Nuclear Engine for Rocket Vehicle Applications (NERVA) at Los Alamos Scientific Laboratory (Panda *et al.*, 2005). The current interest of ZrC is its use as a protective coating on nuclear fuel rods. The cladding material used for nuclear fuel rods (Figure 2-1) in pressured water reactors (PWR), such as the Daichi nuclear plant in Fukushima (Japan), is made of a zirconium alloy.

These nuclear fuel rods will start to oxidise on contact with the primary circuit water slowly forming a passivation layer. This effect is however accelerated in the case of increased temperatures forming a thicker oxidation layer. The corrosion of Zr alloys has a negative effect on the in-reactor time of the nuclear fuel rods, where the maximum allowance of the oxide thickness is only a few hundred microns (Féron, 2012).

ZrC can be produced using a variety of techniques such as the reduction of ZrO_2 which proceeds via Zr_2O_3 and ZrO at $950^\circ C - 1\ 200^\circ C$ to form ZrC (Eq. 2-1). ZrC has also been formed by sintering ZrH with an excess of graphite (Eq. 2-2). Alternatively, a vapour phase fabrication method can be used to form ZrC from a zirconium-halide in the presence of hydrogen and hydrocarbon vapour (Eq. 2-3).



In spite of past development efforts of ZrC limited data was available, but due to the current proposed nuclear applications much more information and research has come to light. In this chapter the properties of ZrC, with a special interest in its properties of value to the coating of nuclear fuel rods, will be reviewed.

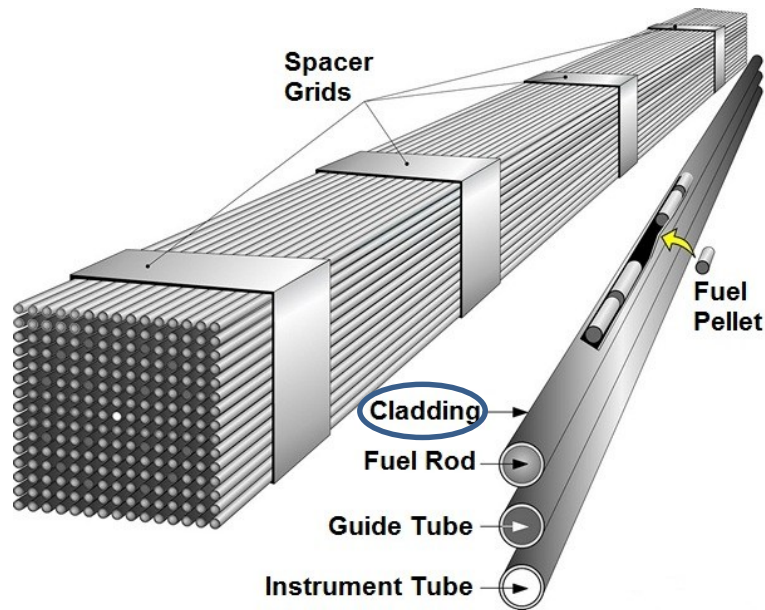


Figure 2-1: Nuclear fuel rod assembly showing the cladding that a coated has been suggested for, modified from WNA (2017)

2.2. Survey of ZrC General Properties

ZrC is usually in a grey metallic powder form (Figure 2-2) and associated with characteristics such as high hardness, high melting point, electrical conductivity and high strength (Annexure A). These properties make ZrC a useful ceramic for a variety of applications.



Figure 2-2: ZrC powder

An attractive property of ZrC, especially for the nuclear industry, is its low neutron absorption cross-section (Zr 0.185 barns and C 0.0034 barns) and good resistance to fission product attack making it a strong contending candidate for use as an in-reactor material (Liu *et al.*, 2012). ZrC has not yet been implemented in a commercial application mainly due to the lack of a fully developed commercially viable sintering process. On the other hand, ZrC has made an appearance in developing prototypes and as a coating material (Fahrenholtz, 2014).

2.3. Crystal Structure

The only stable structure of ZrC (at stoichiometry) is the mono-carbide with carbon atoms in the octahedral sites. The major crystal structure is cubic closed cubic packed with a Fm3m space group of the sodium chloride type (Figure 2-3). The metal to metal bonds is known to be significantly weaker than the metal to carbon bonds, which are a combination of ionic and covalent bonds (Storms, 1967).

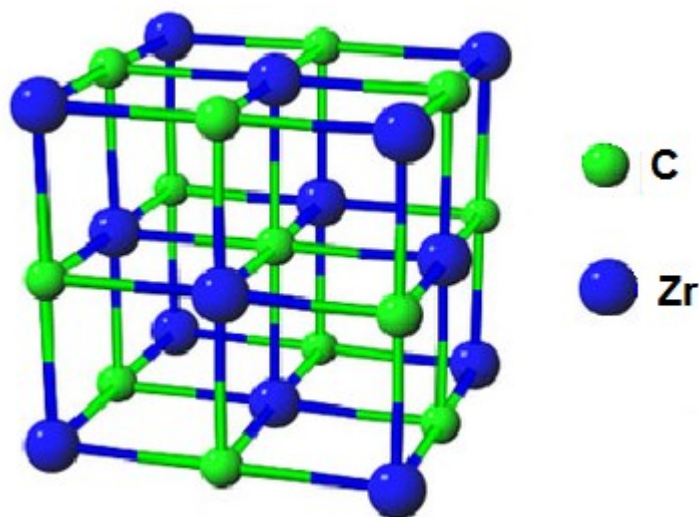


Figure 2-3: ZrC crystal structure

ZrC has been reported to hold structural stability in a wide range of sub-stoichiometry. The interstitial atomic sites are easy to form a high concentration of C vacancies, for example, the concentration of C vacancies accommodated in ZrC is as high as 50 %. Previous studies have found that carbon vacancies significantly affect the mechanical properties, thermos-physical properties and microstructural stability under irradiation (Zhang *et al.*, 2015).

2.4. Chemical Properties

ZrC is essentially inert to cold concentrated acids with the exception of HNO_3 , $\text{HNO}_3 + \text{HF}$, $\text{HCl} + \text{HNO}_3$ and $\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$. (Kato *et al.*, 2013). Toth (1971) states that oxidising acids will dissolve the carbide at an elevated temperature. Alkali solutions have no effect on ZrC, however, Br_2 , H_2O_2 and $\text{K}_3\text{Fe}(\text{CN})_4$ will cause a gradual attack at higher temperatures.

Ky *et al.* (1973) has studied the hydrolysis of ZrC in water vapor at various temperature ranges and found that above 700°C ZrC will react with steam and produce H_2 , CO and CO_2 . It was also found that carbon poor ZrC was more reactive to water at 315°C than carbon saturated ZrC.

2.5. Phase Relationship

Although the phase relationships for ZrC has been extensively investigated for many years, there exists a great deal of controversy about the proposed diagrams. These proposed data was mainly determined by thermodynamic calculations and previous data. Due to ZrC being prone to oxygen and nitrogen contamination experimental results have been difficult to obtain. Katoh *et al.* (2013) mentions that these diagrams are at best close approximations and suggest that a combination of the diagrams be used (Figure 2-4).

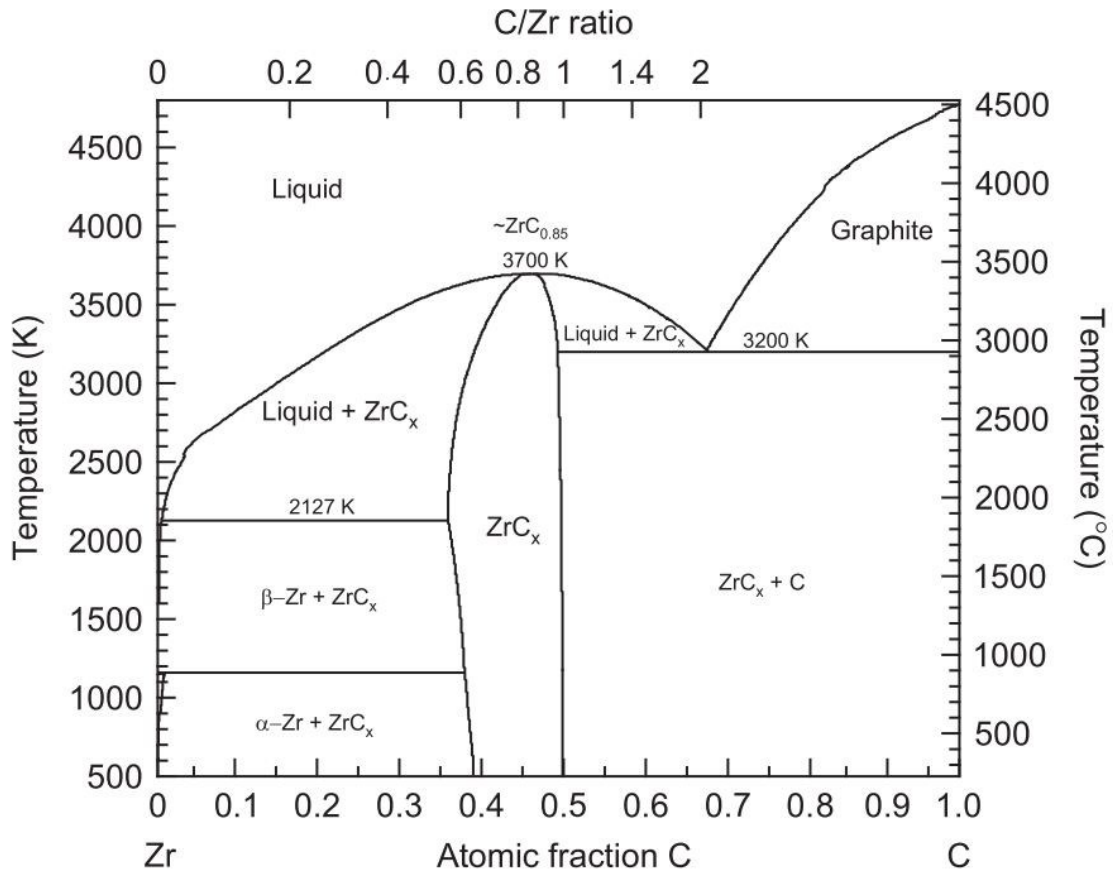


Figure 2-4: Zr-C phase diagram, modified from Katoh *et al.* (2013)

Within the Zr – C phase diagram a single intermediate compound exists (the mono-carbide), which exists between ZrC_{0.55} and ZrC_{0.98}. It has been mentioned by Katoh *et al.* (2013) that the mono-carbide has superior thermal and mechanical properties when compared to the carbon-rich ZrC + C. The highest melting point 3 700 K can be found within this range at the composition of approximately ZrC_{0.85} (46 at.% C).

2.6. Thermal Properties

One of the requirements for a candidate material to be used for fuel rod coatings is its ability to effectively conduct heat. The most common heat conduction in ceramics occurs via the lattice vibrations. Literature indicates that thermal conductivity of ZrC is quite different from that of most other ceramics and metals and increases with increasing temperature. This behaviour can be contributed to the conduction band to thermal conductivity, as well as fairly high phonon conductivity, which dominates in most ceramic materials (Uday *et al.*, 2016).

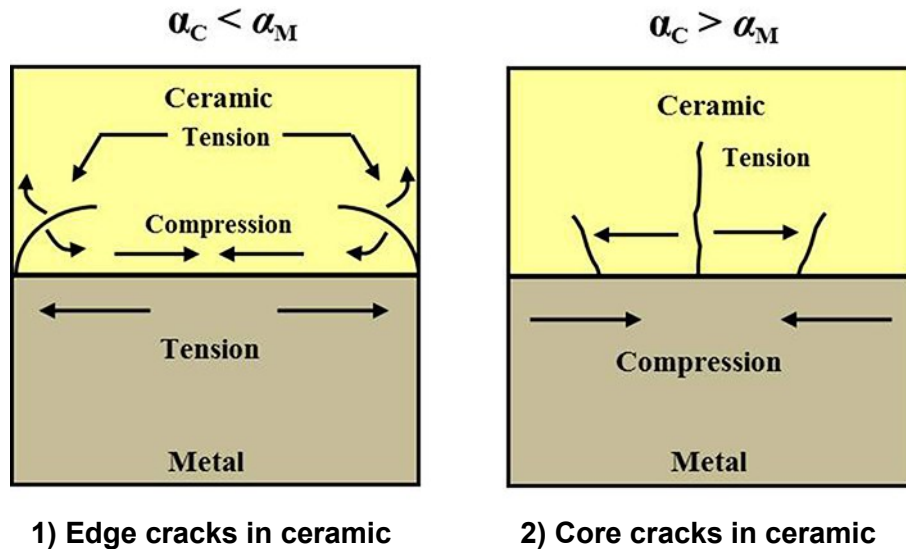


*Figure 2-5: Mode of cracking due to the mismatch of thermal coefficient of a ceramic coating (α_c) and the thermal coefficient of a metal substrate (α_m): (1) Edge cracks in ceramic when $\alpha_c < \alpha_m$, and (2) core cracks in ceramic when $\alpha_c > \alpha_m$. Modified from (Uday *et al.*, 2016)*

The thermal expansion is an important factor when considering materials to be used for coatings. Where a large mismatch in thermal expansion of the metal (α_m) and ceramic (α_c) could result in coating failure where cracks can occur on the edge of the coating when $\alpha_c < \alpha_m$ or in the core of the coating when $\alpha_c > \alpha_m$. A mismatch in thermal expansion coefficients is to be expected when coating a Zr based alloy (metal) with ZrC (ceramic) because Zr has a thermal expansion of $5.99 \times 10^{-6}/K$ and ZrC has a thermal expansion of $6.60 \times 10^{-6}/K$.

2.7. Conclusion

ZrC is a material of both scientific and technological interest thanks to its mechanical, thermal and chemical properties. The following properties of ZrC are believed to make it a good candidate material as a fuel rod coating:

- Low neutron absorption cross-section
- Resistance to fission product attack
- High melting point (above 3 000°C)
- Chemically inert
- Greater resistance to steam (up to 700°C) than Zr
- Small difference in thermal expansion coefficient of Zr ($6.60 \times 10^{-6} / ^\circ\text{K}$) and ZrC ($5.99 \times 10^{-6} / ^\circ\text{K}$).

Although ZrC is a promising material for a wide variety of industries a complete understanding of the heat transport, thermodynamic and mechanical properties of ZrC_x ($x < 1$) is limited due to lack of information with regards to non-stoichiometric ZrC. Therefore future investigation of ZrC is still required.

Bibliography

- FAHRENHOLTZ, W. G. 2014. A Historical Perspective on Research Related to Ultra-High Temperature Cermics. *In: FAHRENHOLTZ, W. G., WUCHINA, E. J., LEE, W. E. & ZHOU, Y. (eds.) Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications*. Hoboken, New Jersey: Wiley.
- FÉRON, D. 2012. 2 - Overview of nuclear materials and nuclear corrosion science and engineering. *Nuclear Corrosion Science and Engineering*. Woodhead Publishing.
- KATOH, Y., VASUDEVAMURTHY, G., NOZAWA, T. & SNEAD, L. L. 2013. Properties of zirconium carbide for nuclear fuel applications. *Journal of Nuclear Materials*, 441, 718-742.
- KY, B., UCHIDA, K. & IMOTO, S. S. 1973. Hydrolysis of Zirconium Nitrides and Carbides. *Journal of the Japan Institute of Metals*, 37, 411-416.
- LIU, B., LIU, C., SHAO, Y., ZHU, J., YANG, B. & TANG, C. 2012. Deposition of ZrC-coated particle for HTR with ZrCl₄ powder. *Nuclear Engineering and Design*, 251, 349-353.
- PANDA, B., HICKMAN, R. R. & SHAH, S. 2005. Solid Solution Carbides are the Key Fuels for Future Nuclear Thermal Propulsion. NASA Marshall Space Flight Center, Huntsville, AL, United States.
- STORMS, E. K. 1967. *The Refractory Carbides* New York and London, Academic Press.
- TOTH, L. E. 1971. *Transition Metal Carbides and Nitrides*, New York and London, Academic Press.
- UDAY, M. B., AHMAD-FAUZI, M. N., NOOR, A. M., NOOR & SRITHAR, R. 2016. Current Issues and Problems in the Joining of Ceramic to Metal. *In: ISHAK, M. (ed.) Joining Technologies*. Rijeka: InTech.
- WNA. 2017. *Fukushima Accident* [Online]. World Nuclear Association. Available: <http://www.world-nuclear.org/information-library/safety-and-security/safety-of-plants/fukushima-accident.aspx> [Accessed 31 January 2017].
- ZHANG, Y., LIU, B. & WANG, J. 2015. Self-assembly of Carbon Vacancies in Sub-stoichiometric ZrC_{1-x}. 5, 18098.

CHAPTER 3

LITERATURE REVIEW: DEPOSITION METHODS FOR ZrC

“There is more than one way to skin a cat”

-Unknown

3.1. Surface Treatment and Coatings

In the late 1950's the decorative coatings used for toys, textiles, etc. which provided the initial thrust for the development of surface engineering. Since then the surface engineering industry underwent a dramatic growth in sales of equipment and products associated with surface enhancement. People often don't realize how important surface engineering has become to our modern society. There already exists a wide variety of surface modification and coating deposition method (Lovelock, 2015).

According to Fauchais *et al.* (2014), surface engineering can be implemented in a wide range of industrial sectors, from hip implants for the medical sector to aircraft landing gear for the aeronautical sector. Coatings are desirable and even necessary, in certain instances, for the following reasons:

- Improve functional performance by e.g. allowing higher temperature exposure through the use of thermal barrier coatings.
- Improve component life by reducing wear due to abrasion, erosion and corrosion.
- Extending component life by rebuilding the worn part to its original dimensions avoiding the need for replacing the entire component e.g. a shaft or axle rebuild.
- Reduce component cost by improving the functionality of a low-cost material with an expensive coating.

The aim of this chapter is to investigate several coating methods that are able to deposit quality ZrC layers onto a substrate.

3.2. Deposition Methods

In a previous investigative survey of coating technologies (van der Walt *et al.*, 2015) the following potential methods, to deposit ZrC on a substrate, were identified:

- Chemical vapor deposition (CVD)
- Pulsed Laser Deposition (PLD)
- Magnetron Sputtering
- Plasma Spraying

The methods and their applicability were investigated and compared against each other to determine the best possible method in regards to the deposition of ZrC.

3.2.1. Chemical Vapor Deposition

The CVD method can be described as the deposition of a solid onto a heated substrate through the thermal decomposition and reaction of precursor gasses. CVD is classified as a vapor transfer process with strong adhesion as a result of diffusion bonding of the coating and substrate. A schematic diagram of the CVD process is shown in Figure 3-1.

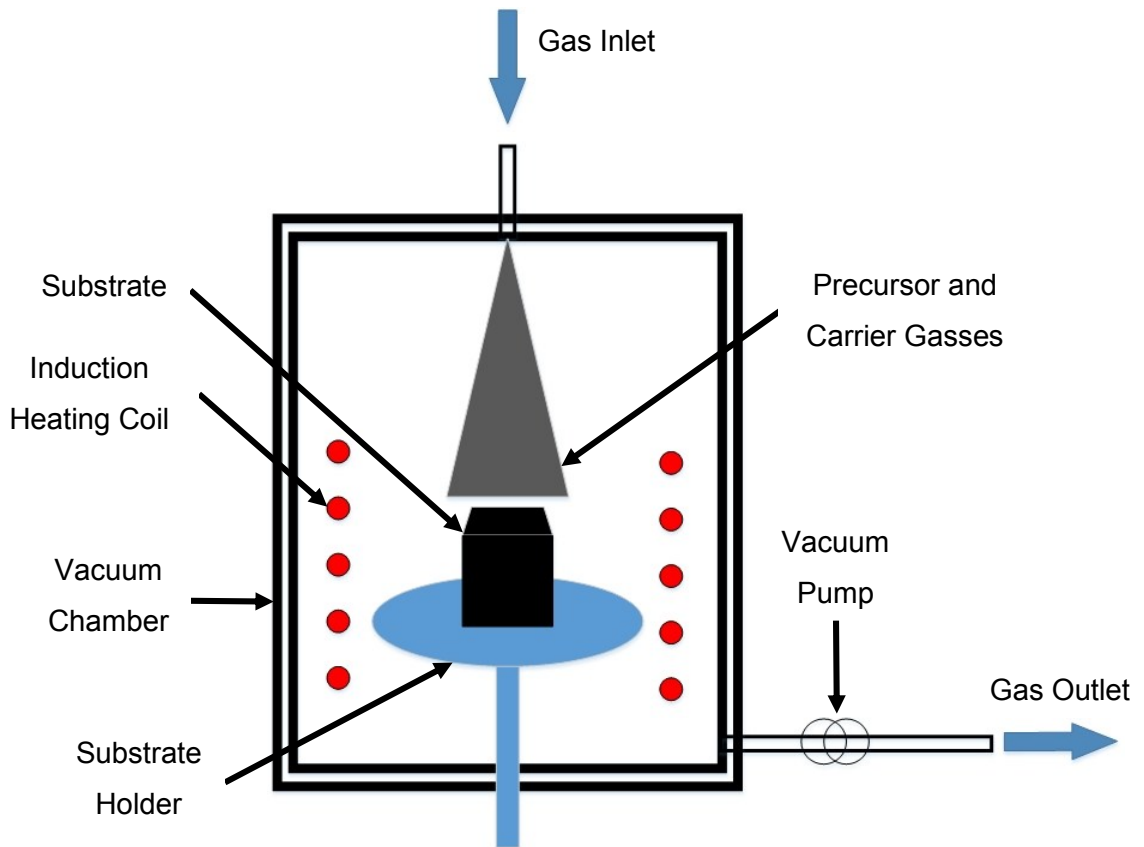


Figure 3-1: Schematic illustration of conventional CVD process

During the CVD process, the precursor gas or gasses thermally decomposes and reacts on and near the hot substrate surface forming a solid film. CVD is an omnidirectional coating technique being able to coat substrates with complex geometries, holes and deep recesses.

One pronounced disadvantage of CVD is that it is most versatile at high temperatures (above 600°C) where many substrates, including Zr-alloys, are not stable at such high temperatures. As in the case of Liu *et al.* (2009), who used a CVD fluidised bed setup to coat SiC kernels with ZrC using ZrCl_4 with C_3H_6 , H_2 and Ar as reacting and carrier gasses. They found that as the substrate temperature increased (up to 1600°C) the density and adhesion also increased. But this temperature would be too high for Zr-alloy and could influence its microstructure and composition.

The substrate temperature can be lowered using an organic-metal CVD process. For example, Won *et al.* (2007) used an organic-metal namely tetra-neopentyl zirconium ($\text{Zr}[\text{CH}_2\text{C}(\text{CH}_3)_3]_4$) as a precursor gas to grow a ZrC coating at a substrate temperature of 400°C. But the process resulted in a low growth rate (100 nm/h – 150 nm/h) with great difficulty in controlling the stoichiometry of the coating due to the complex precursor gas used.

The CVD process is notorious for its toxic and corrosive by-products as a result of the chemical reactions that occur during coatings (Bernecki, 2004). Consequently, these gasses need to be trapped and neutralised before being exhausted into the atmosphere. This will add to the cost of the overall system as well as raise certain environmental and operator health concerns.

3.2.2. Pulsed Laser Deposition

The PLD method is classified as a physical vapor deposition (PVD) technique. The PVD process is defined as the creation of vapors in a vacuum from a solid material source and their subsequent condensation onto a substrate. Unlike CVD, PVD is a line-of-sight process conducted at lower temperatures (180°C – 500°C) with a physical bond forming between the coating and the substrate rather than a chemical bond. Figure 3-2 shows a schematic illustration of the PLD process.

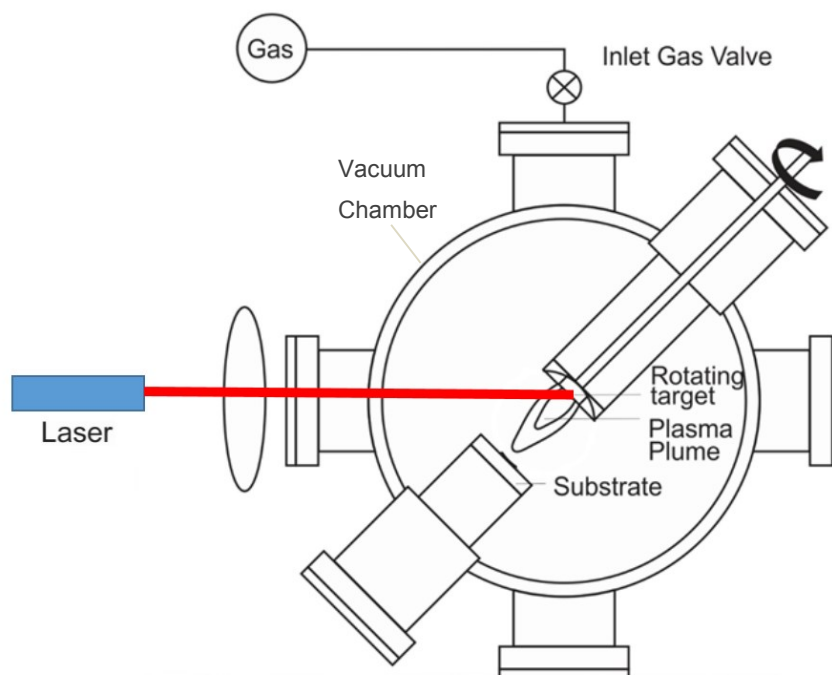


Figure 3-2: Schematic illustration of PLD process

PLD is known to deposit a wide variety of materials using a high energy laser (2 J/cm^2 - 5 J/cm^2). The laser is used to melt, evaporate and ionise the target material, this process is known as ablation. The ablation process produces a luminous plasma which expands away from the target towards the substrate where a coating is formed.

The use of a laser and an inert/vacuum atmosphere makes the process extremely clean, although cases of particulate inclusion have been reported. For example, Woo (2005) used a PLD technique to deposit ZrC and found the presence of particulate inclusion present in the coating.

Although the process is able to deposit a wide range of materials with good stoichiometry control, the mechanisms of material transfer is not yet fully understood. This makes reproducibility of coatings difficult. The process has also, to the knowledge of the author, only been done on small scale and it is thought that upscaling the process would significantly increase the cost of instruments and operating.

3.2.3. Magnetron Sputtering

The same as PLD, magnetron sputtering is classified as a PVD method, but instead of using ablation to deposit a coating it uses the sputtering effect. Sputtering is the process of bombarding energetic particles (up to $1\,000 \text{ eV}$) onto the surface of a target material in which the material is removed through momentum exchange. These energetic particles are normally ions of a heavy inert gas (such as argon) generated through a glow discharge at a pressure of 0.13 to 13 Pa . This sputtering technique can deposit a layer of virtually any material because the material is passed into the vapor phase through a mechanical process rather than a chemical or thermal method (Bernecki, 2004). A schematic illustration of the PLD process is shown in Figure 3-3.

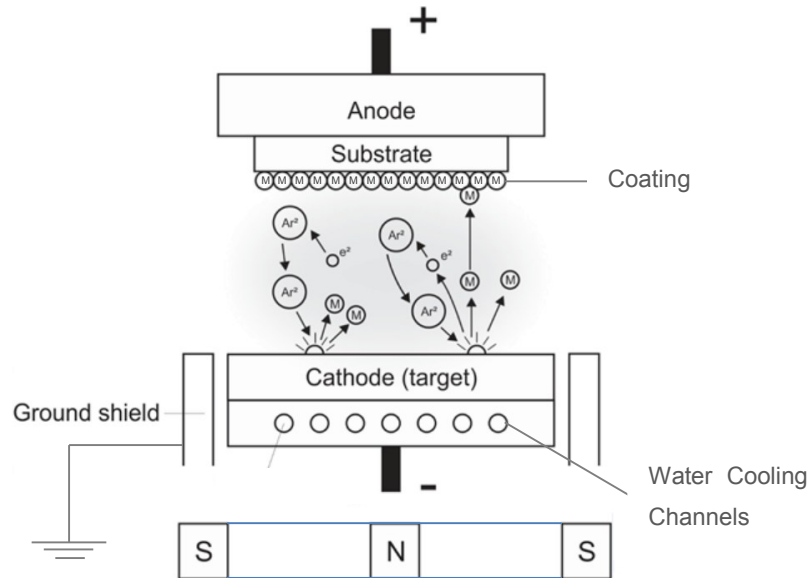


Figure 3-3: Illustration of schematic magnetron sputtering process

The layer density of a sputtered coating is dependent on factors such as the substrate temperature and deposition rate. Where magnetron sputtering deposition rates have been recorded to be rather low. The introduction of a magnetic field to the process can increase the sputtering effect by intensifying the ions bombarding the target surface, this process is known as magnetron

Andersson *et al.* (2012) deposited ZrC and ZrSiC films using a non-reactive DC magnetron sputtering technique. A vacuum chamber with a base pressure of 10^{-7} Pa was used under an Ar gas environment to generate an Ar gas plasma at 0.4 Pa. The sputtering targets used were Si, C and Zr (all with a purity of 99.9%) at a deposition temperature of 25°C – 290°C.

Magnetron sputtering is a strong contender as viable coating method because of the fact that during the process the compound is not decomposed into constituent elements. The stoichiometry of the compound can therefore be retained in the substrate layer, which is of very high importance if future research finds that ZrC_x with a specific stoichiometry (where $x < 1$ or $x > 1$) exhibits properties of value to the coating application (such as a matching thermal expansion coefficient or a higher tolerance to radiation).

It is thought that the present sputter coating technology is not yet suited to deposit coatings of ZrC on the scale of fuel rods because, to the knowledge of the authors, it has only been applied using relatively small chambers. Fauchais *et al.* (2001) states that depositing on a larger scale decreases the deposition rate which would possibly also compromise coating properties such as density and integrity. However, the magnetron sputter technique remains a potentially important method that needs further consideration.

3.2.4. Plasma Spraying

Thermal spraying is a generic term which can be used to refer to several coating methods. Thermal spray processes are classified in one of two categories: combustion and electrical. Combustion includes detonation gun (D-gun) spraying, low-velocity flame spraying and high-velocity oxy-fuel flame spraying (HVOF), while electrical processes have wire arc, plasma thermal spraying and cold spray.

The thermal spray coatings are formed by depositing, onto a prepared surface, a stream of particles (metallic or non-metallic). These particles flatten upon impact with the surface to form platelets called splats with several of these splats combining to form a coating. Thermal spray is a line of sight method thus limiting the coating of parts with advanced geometries.

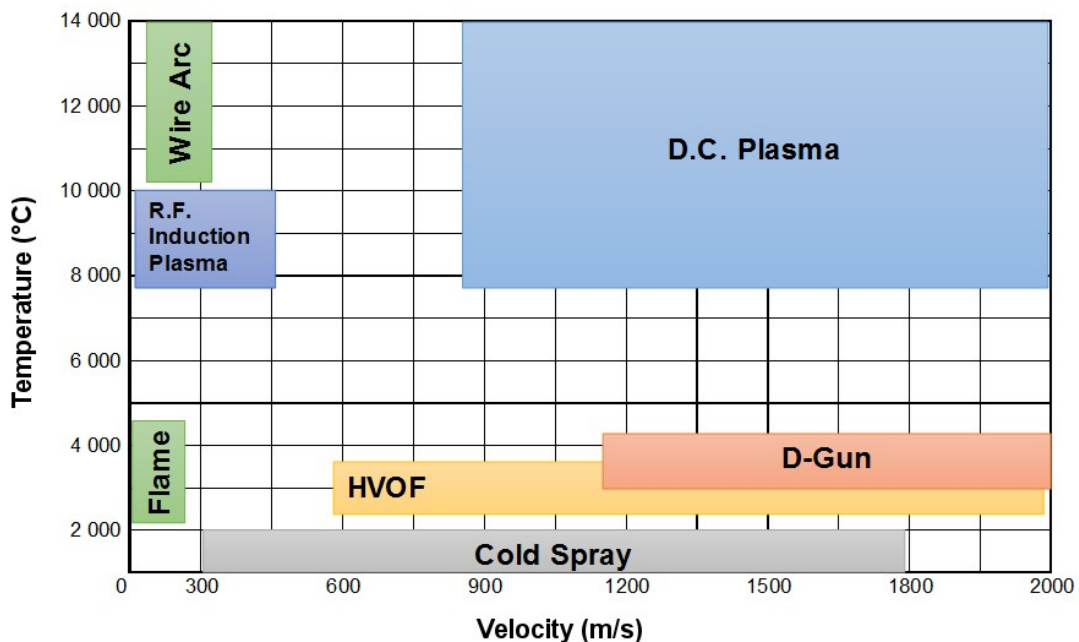


Figure 3-4: Gas temperatures and velocity of different thermal spray processes modified from Fauchais et al. (2014)

All thermal spray methods consist of generating an energetic gas flow of hot or cold gasses with the use of a specialised torch or gun. The torch or gun is a device used for feeding, accelerating, heating and directing the flow of the deposition material towards a substrate. Each thermal spray process has a gas temperature and gas velocity associated with it (Figure 3-4), making individual techniques more suitable for certain types of materials.

By investigating the graph in Figure 3-4 a suitable thermal spray method, to deposit ZrC can be found. Because of the high energy required to deposit ZrC, due to its low thermal conductivity and high melting point a process with a high gas velocity and temperature is required. The plasma spraying process will be able to melt and successfully deposit the ceramic material as it is the process with the highest temperature and gas velocity. According to Fauchais *et al.* (2014), ceramics are generally deposited with plasma spraying due to the high melting point of the ceramic itself and the high velocity from the process.

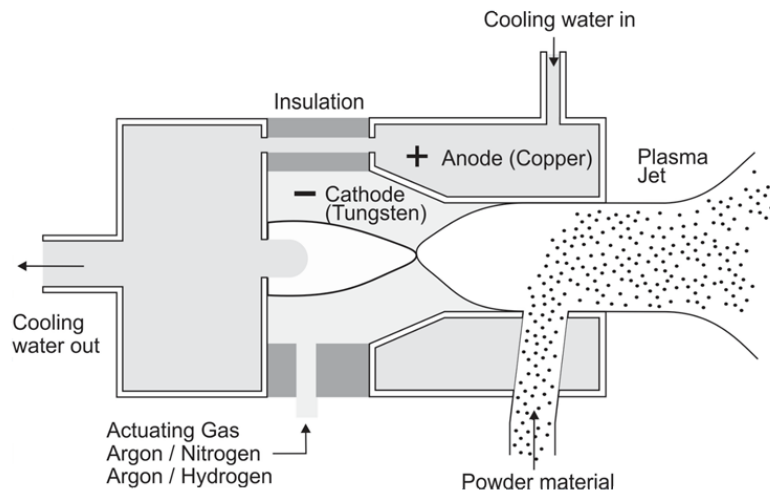


Figure 3-5: Schematic illustration of a typical plasma spray torch

A schematic of a plasma torch is illustrated in Figure 3-5. Which show the anode and cathode, between which an electric arc is struck to heat a gas and generating a plasma. Powder is injected into the plasma jet accelerating and melting the powder towards a substrate. If the particle's heat and momentum is high enough to deposit, a coating will be formed.

Kim *et al.* (2013) and Mauer *et al.* (2013) both used a plasma-arc powder spraying technique to successfully deposit ZrC onto a substrate. The latter produced a Zr + ZrC coating of 50 μm using a multi-coat system. They used a low working pressure of 100 Pa with a power input of 150 kW. The former sprayed a number of different ceramics, including ZrC, onto a niobium substrate. The ZrC coatings, deposited by Kim *et al.* (2013), had a fairly uniform thickness and good adhesion. It was also found that the substrate, when depositing a coating, can be at a low temperature as long as the thermal expansion of the substrate is close to the thermal expansion of the coating material (Matejka & Benko, 1989). Plasma spraying is a process that has produce moderately dense and uniform coatings, from 50 μm to several millimetres thick, at a high deposition rate (1–2.5 g/s) resulting in a strong droplet/substrate bond strength as high as 69 MPa (Bernecki, 2004).

Since plasma spraying is mostly used to produce coatings on structural materials, it is well suited for large-scale items to be coated. Fauchais *et.al.* (2014) describes the equipment used for thermal spraying as inexpensive when compared to PVD and CVD. Furthermore, the plasma spraying process can be modified from atmospheric to a controlled atmosphere or vacuum conditions. This would reduce the expected formation of zirconium oxide and zirconium oxycarbides. The plasma spray process appears to be flexible and has been used in the past to deposit quality ceramics coatings.

3.3. Conclusion

In order to determine the most worthwhile method able to deposit a ZrC coating, the following criteria need to be considered:

- Deposition rate
- Scale-up potential
- Deposition environmental requirements
- Adhesion strength of layer on substrate
- Equipment and operating cost
- Porosity density potential
- Final layer composition.

These parameters were taken into consideration, by the author to evaluation of coating techniques applicable to deposition of ZrC coating (Table 3-1).

Table 3-1: List of parameters of coating process applicable to ZrC coatings

Criteria	CVD	PLD	MS	PS
Deposition Rate	✗	✗	✗	✓
Scale-up Potential	✗	✗	✗	✓
Deposition enviroment	✗	✗	✗	✓
Adhesion Stregnth	✓	✗	✗	✗
Equipment and Operating Cost	✗	✗	✗	✓
Coating Density	✓	✗	✗	✗
Coating Composition	✗	✗	✓	✗

By looking at the coating criteria for this study (Table 3-1) it can be seen that the plasma spray method is best suited for the deposition of ZrC coatings onto nuclear fuel rods. The plasma spray process has also been proven to be flexible and easily adaptable to a wide variety of coating situations. The process has a fast deposition rate and low operating cost compared to the other techniques making this technique a promising candidate for depositing ZrC onto Zr-alloy.

3.4. Scope

Chapter 4 will be a more focused discussion on the chosen coating technique and its influencing properties with regards to coating quality. Chapter 5 will discuss the experimental setup, equipment and procedure as well as the analysis techniques used in this research. This is followed by Chapter 6 where the various analysis and experimental results will be interpreted and discussed. Finally, Chapter 7 will give a brief summary of the work done in this research followed by the conclusions and recommendations established during the preceding of this research.

Bibliography

- Andersson, M., Urbonaitė, S., Lewin, E. & Jansson, U. 2012. Magnetron sputtering of Zr–Si–C thin films. *Thin Solid Films*, 520(20):6375-6381.
- Bernecki, T. 2004. Surface Science. (In Davis, J.R., ed. Handbook of Thermal Spray Technology. ASM International. p. 14-35).
- Fauchais, P., Vardelle, A. & Dussoubs, B. 2001. Quo vadis thermal spraying? *Journal of Thermal Spray Technology*, 10(1):44-66.
- Fauchais, P.L., Heberlein, J.V.R. & Boulos, M.I. 2014. Thermal Spray Fundamentals. United States of America: Springer US.
- Kim, J.H., Kim, H.T., Woo, Y.M., Kim, K.H., Lee, C.B. & Fielding, R.S. 2013. Interaction studies of ceramic vacuum plasma spraying for the melting crucible materials. *Nuclear Engineering and Technology*, 45(5):683-688.
- Liu, Q., Zhang, L., Cheng, L. & Wang, Y. 2009. Morphologies and growth mechanisms of zirconium carbide films by chemical vapor deposition. *Journal of Coatings Technology and Research*, 6(2):269-273.
- Lovelock, H. 2015. Introduction to thermal spray coatings. *African Fusion*(Issue).
- Matejka, D. & Benko, B. 1989. Plasma Spraying of Metallic and Ceramic Materials: Wiley.
- Mauer, G., Hospach, A. & Vaßen, R. 2013. Process development and coating characteristics of plasma spray-PVD. *Surface and Coatings Technology*, 220:219-224.
- Van der Walt, B., Markgraaff, J. & Bissett, H. 2015. Manufacturing processes for zirconium carbide layer deposition. SAIMM AMI Nuclear Materials 2015 Conference: 59-64.
- Won, Y.S., Varanasi, V.G., Kryliouk, O., Anderson, T.J., McElwee-White, L. & Perez, R.J. 2007. Equilibrium analysis of zirconium carbide CVD growth. *Journal of Crystal Growth*, 307(2):302-308.
- Woo, J. 2005. Growth of Epitaxial Zirconium Carbide Layers Using Pulsed Laser Deposition. University of Florida.

CHAPTER 4

LITERATURE REVIEW: NON-TRANSFER ARC DC PLASMA SPRAYING

“Never worry about theory, as long as the
machinery does what it’s supposed to do.”

-Robert A. Heinlein (1907 – 1988)

4.1. Introduction

The plasma spray processes is a high-velocity heat treatment of a material, with the aim of accelerating and heating a material to a certain temperature and velocity, in order to deposit a coating. Fauchais *et al.* (2014) describes the plasma spraying process to have up to 70 different influencing factors, which can affect the quality of the deposited coating. A few of these influencing factors are shown in Figure 4-1.

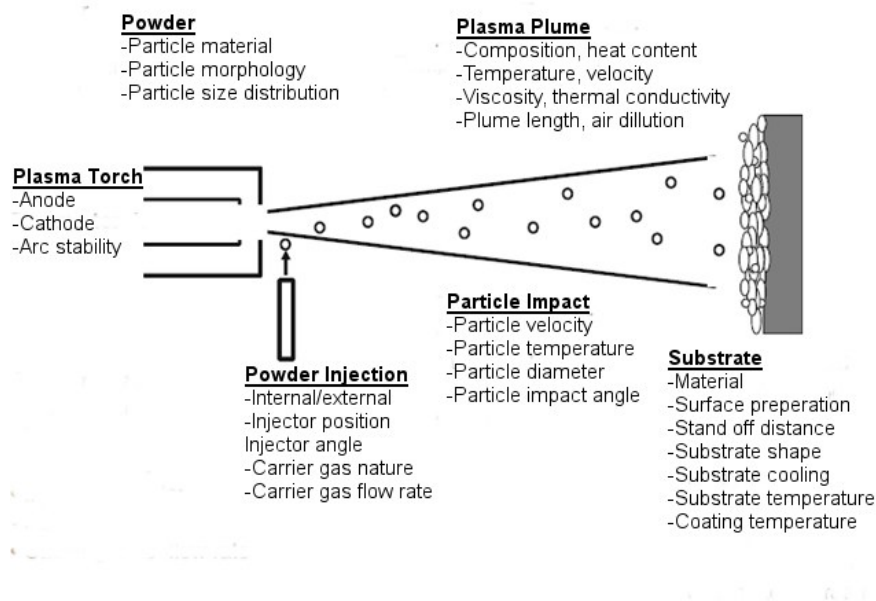


Figure 4-1: Schematic of a typical plasma spray process and coating structure modified after Fauchais et al. (2014)

In order to better understand the parameters that will affect the plasma sprayed coatings the following influencing factors will be discussed in this chapter:

- Plasma Torch
- Plasma generation
- Particle Injection
- Particle and plasma plume interaction
- Substrate preparation
- Coating formation

4.1.1. Plasma Torch

Plasmas can be generated using energy sources such as microwaves, gamma radiation, alternating currents (AC), DC or RF. DC plasma spraying is arguably the most flexible of the thermal spray processes with respect to the wide variety of spraying materials available (Bernecki, 2004; Fauchais *et al.*, 2014). The most common torch used in plasma spraying is the non-transfer DC plasma torch.

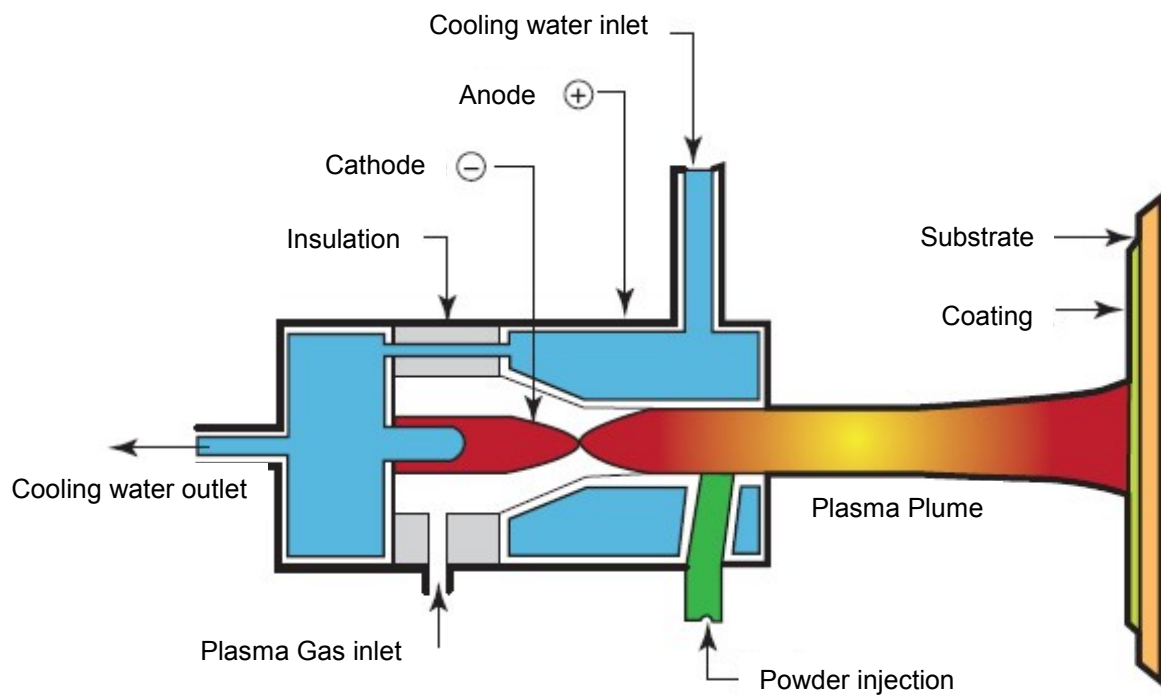


Figure 4-2: Schematic illustration of a plasma torch showing the components, modified from *Fauchais et al. (2014)*

The non-transfer DC plasma torch makes use of an arc as a source of heat to ionise a gas which in turn melts and propels the coating material towards a workpiece. The arc is struck between the anode nozzle and cathode, housed inside of the plasma torch, which acts as electrodes (Figure 4-2).

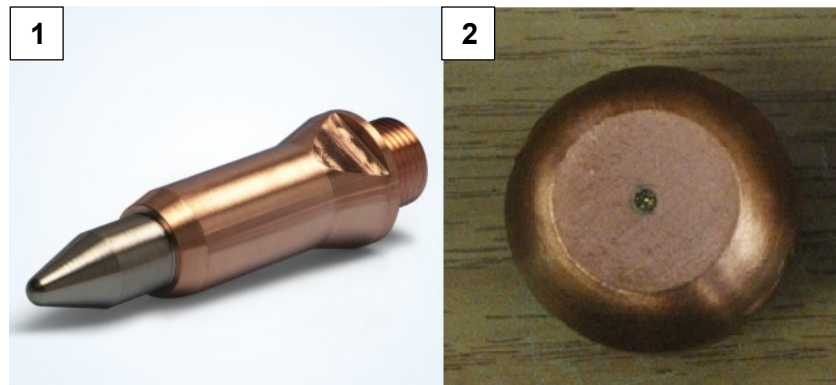


Figure 4-3: Different types of cathodes used in plasma torches 1) Rod type cathode, 2) Button type cathode

The cathode is the main source of electrons which is also the initiation point of the electric arc. There are primarily two types of cathodes used in plasma spraying (Figure 4-3): 1) the rod type and 2) the button type. The most commonly used cathode for non-transfer DC arc plasma torches is the rod type which is typically made of thoriated tungsten. The rod type cathode is associated with plasma temperatures of between 8 000°K and 14 000°K and plasma velocities of 500 to 2 600 m/s with conventional anodes (with diameters of 6 – 8 mm).

The button type cathode is a fixed water-cooled copper holder housing a thoriated tungsten button or in the case of working with oxidising gases a refractory metal such as Hf or Zr. The arc is centred on the button and elongated using a strong vortex formed using the plasma gases. The gas velocity of button type cathodes (5 – 7 g/s) is higher than that of rod type cathodes (0.7 – 2 g/s), this due to the high gas velocities required to stabilise the electric arc. The plasma temperatures associated with button type cathodes are between 8 000°K and 10 000 K with plasma velocities below 2000 m/s. According to Fauchias *et.al.* (2014), the button type cathode is usually used in high power and high deposition applications where the cathode attachment has a high current density.

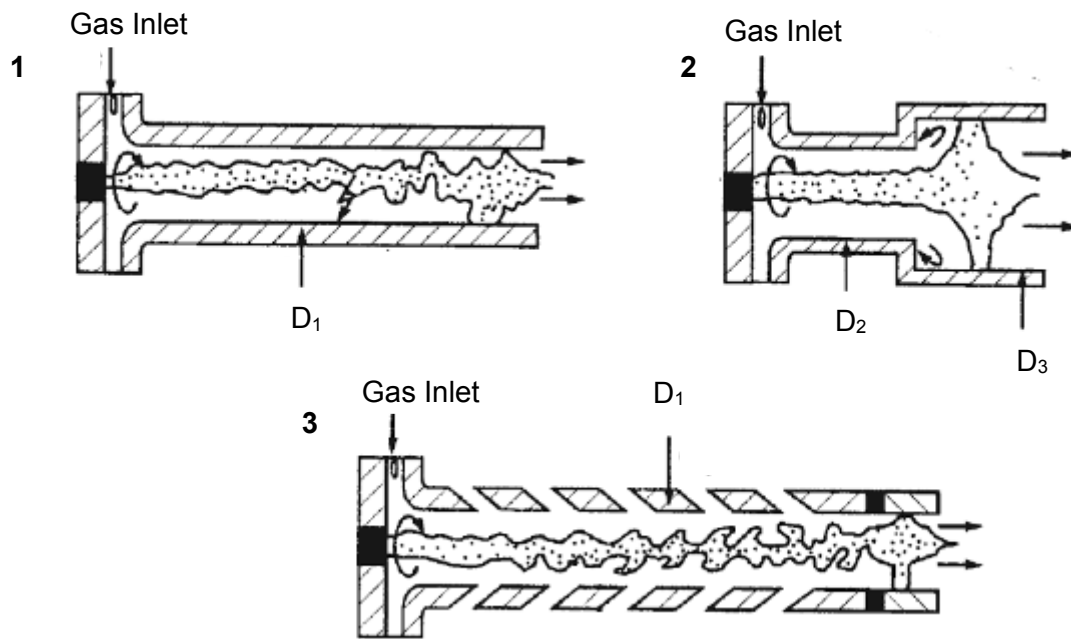


Figure 4-4: Schematic illustration of typical anode designs with radial gas injection: 1) Straight anode, 2) Step change anode and 3) cascading anode, modified from (Zhukov et al., 2007)

The anode design will influence the arc stability and plasma gas flow. A typical anode is made of copper with cylindrical channel acting as an electrode and secondly as a gas nozzle. The straight anode (Figure 4-4 no.1) is the most commonly used and relies on a self-setting arc principal. This means that the arc will self-adjust in the anode according to the ampere and voltage inputs.

But for a more consistent and stable arc, the use of a step change anode (Figure 4-4 no.2) or cascading anode (Figure 4-4 no.3) can be used. The drawback of these anodes is the enhanced anode erosion that follows, this can be limited by using a low arc current setting. The step change anode as the name implies has a step with a change in diameter in the anode. This anode requires a strong vortex to help elongate the arc and attach just after the step change. With the cascading anode, the anode consists out alternating segments of insulation and copper. The arc will attach close to the cathode, the gas flow from the generated plasma will then help transfer the arc to the next segment thus elongating the arc.

4.1.2. Plasma Generation

A plasma, also known as the fourth state of matter, consists out of neutral atoms, positive ions and free electrons. It has been estimated that 98 % of the known universe exists in a plasma state. Plasmas can be divided into two groups' namely cold plasmas and thermal plasmas, the latter is used for the plasma spraying process.

A plasma is formed when energy is transferred into a gas causing it to ionise allowing the electrons and ions to act independently of one another, once the energy source is removed the electrons and ions recombine releasing light and heat energy. A thermal plasma can be explained as the state where the electron and ion populations have similar energy levels causing more kinetic interactions in the plasma known as local thermal equilibrium (LTE) (Bernecki, 2004).

Non-transfer DC arc plasma torches generate a plasma jet by ionising a continuously flowing gas with an electric arc. The arc generates a high-temperature plasma through resistive energy dissipation that travels via the electrical arc through the gas. As the gas temperature will rise until the gas becomes ionised, increasing the gasses electrical conductivity (Fauchais *et al.*, 2014). The arc will be formed between the cathode and anode for which there are several different variations and combinations as discussed in section 4.1.1.

The most common gasses used in DC plasma spraying are Ar, Ar-H₂, Ar-He, Ar-He-H₂, N₂, or N₂-H₂ mixtures which can produce temperatures between 8 000 and 14 000°C and velocities of between 500 and 2 800 m/s depending on the plasma gasses (Fauchais *et al.*, 2014; Vardelle *et al.*, 2016; Vardelle *et al.*, 2015). The thermal conductivities of the plasma increase as one proceeds from pure argon to argon-helium mixtures, to argon-hydrogen mixtures and to argon-helium-hydrogen ternary mixtures or nitrogen-hydrogen mixtures, resulting in increased heating rates. However, the flow velocities will also increase with the addition of molecular gases resulting in reduced particle residence times in the plasma (Fauchais *et al.*, 2016).

4.1.3. Particle Injection

The particle injection is mainly dependent on the properties of the powder that is to be sprayed. For ideal particle injection, the right parameters must be chosen according to the sprayed material used keeping in mind the injection velocity, particle melting temperature, particle heat conductivity and the size distribution of the particle.

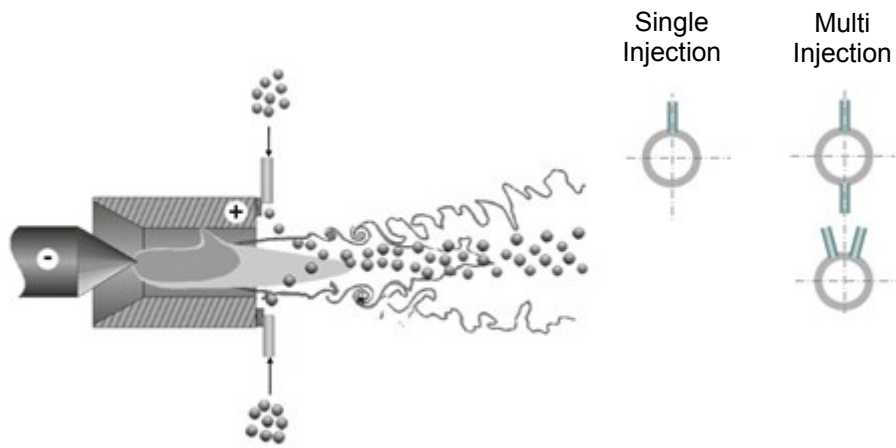


Figure 4-5: Powder injected into a plasma torch with single and multi-injection configurations, modified from (Fauchais et al., 2014)

In general plasma spraying makes use of a carrier gas to inject particles into the plasma plume. For plasma spraying the use of a single or multiple radial powder injection configuration (Figure 4-5) can be used. The radial injection can be done either by injection from the inside the anode nozzle (internal) or from the outside at the anode nozzle exit (external). External injection requires a lower particle speed than internal injection because when the plasma jet expands at the anode nozzle exit it has a lower velocity. A lower velocity will lead to a longer residence time in the plasma plume. As a result of this materials with high melting points such as carbides, nitrides and borides should be injected externally (Fauchais *et al.*, 2004).

Particles that are being injected will also collide and crash into each other and the injector's walls while being transported by the carrier gas. This will cause the particles to diverge at the injector's exit. The particle diverges at the exit will increase when the particles are smaller than $20\ \mu\text{m}$ with a specific mass of $6\ 000\ \text{kg/m}^3$ or smaller (Vardelle *et al.*, 2001).

4.1.4. Particle and Plasma Plume Interaction

During the plasma spraying process proper particle trajectory, heat and mass transfer control are crucial aspects for successfully depositing quality coatings. In fact, the process so strongly depends on this that even a slight deviation from the optimal range can easily lead to poor coating results. In this section, the joint and individual effects of the particle, plasma plume, surrounding atmosphere and spray distance will be discussed.

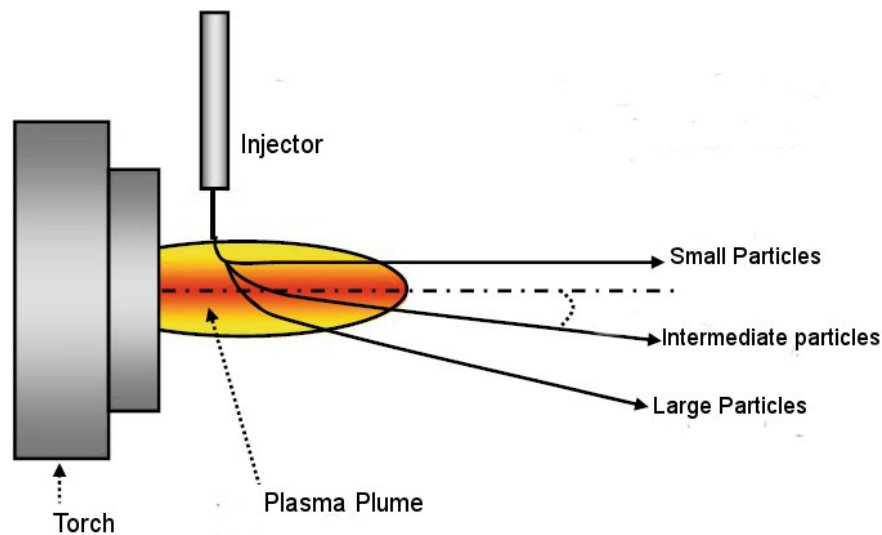


Figure 4-6: Trajectories of particles with different masses injected into a plasma, modified from Fauchais *et al.* (2014)

The particle mean velocities at the injector exit are almost the same whatever their sizes may be, because of how particles injection force is proportional to its mass (Vardelle *et al.*, 2001). In general, the smaller mass and greater mass particles will remain on the fringes of the plasma plume (Figure 4-6) where the smaller mass particles are likely to evaporate and the larger mass particles may not be fully melted at the point of impact. It is also possible for both the smaller and larger particle mass sizes to be ejected from the plasma before reaching the substrate. However the intermediate sized particles will travel the optimum route through the plasma plume, therefore for dense coatings, a small particle size distribution is required (Herman, 1991).

The heat transfer mechanisms found in the case of a single sphere surrounded by a hot gas is convection from the hot gas and radiation loss of the particles surface to its surrounding atmosphere. While the particle itself propagates heat to its centre at a rate depending on the materials thermal conductivity.

When the particle temperature starts approaching its boiling temperature the particle melting and evaporation rates increase rapidly. Taking note of this fact it will be almost impossible to spray a powder which melting and boiling points are not separated with at least 300°K (Vardelle *et al.*, 2015). The principal can be kept in mind were instead of vaporising the material decomposes, which explains why it is considered difficult to spray most borides, nitrides and carbides (Fauchais *et al.*, 2014).

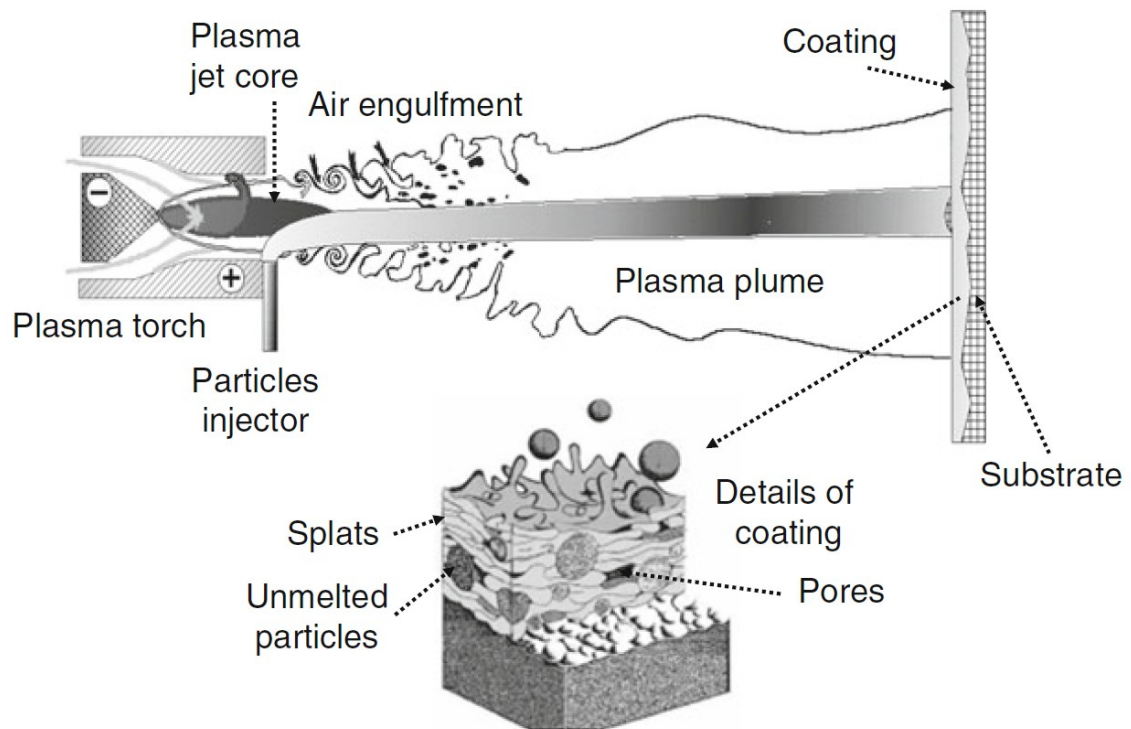


Figure 4-7: Schematic illustration of plasma spraying process and coating formation, modified from Bernecki (2004)

The plasma spraying process is notorious for atmospheric engulfment, meaning that the surrounding atmosphere will be entrapped into the plasma plume due to eddy currents forming at the fringes of the plasma plume (Figure 4-7). The concentration of the entrained gas will increase as the distance from the nozzle to the substrate increases. This is beneficial in cases such as reactive plasma spraying where for example titanium is sprayed in a N_2 plasma forming a titanium nitride coating. But in the case of atmospheric plasma spraying the entrapped oxygen from the air can have a devastating effect by reacting with the sprayed material and oxidising the powder (Hu et al., 2015).

To avoid oxidation an inert atmosphere can be used. This is done by spraying in a controlled atmosphere chamber filled with an inert gas or a soft vacuum (~ 10 kPa). But the drawback is that this process is very costly in both gas consumption and equipment cost. Cheaper alternatives such as shroud nozzles have also been implemented. The shroud nozzle is attached to the front of the plasma torch with the aim of blasting a blanket of inert gas around the plasma plume (Fauchais *et al.*, 2014).

The spray distance is known as the distance between the anode nozzle exit and the part to be coated. The optimal spray distance is where the average size particle reaches the maximum temperature and critical velocity because future downstream both these quantities decrease. However, at these distances, the plasma plume is still very hot. Fauchais *et al.* (2014) pointed out that the optimal distance for plasma spraying is between 50 to 60 mm but because of the high heat flux of the plasma plume (4 - 8 MW/m²), the substrate will be exposed to an extreme heat resulting in thermal damage. To prevent damage from the plasma plume's heat the spray distance is increased to between 90 and 120 mm to where the heat flux is below 2 MW/m².

4.1.5. Substrate Preparation

The proper preparation of a substrate's surface is essential to the coating process because of the critical influence it has on the bonding and adhesion of the coating. The substrate preparations consist out of three steps:

- Cleaning
- Roughening
- Adsorbates and condensates removal

The first step is the cleaning of the substrate, this is done to remove any contamination on the surface such as oil, grease, paint, rust, scale or moisture which would have negative effects on the adhesion of the coating to the substrate. This process will vary depending on the substrate but in most cases, a standard cleaning process for materials has been standardised (Vardelle *et al.*, 2016).

According to Fauchais *et al.* (2014), the adhesion of a thermal spray coating will significantly increase with the roughening of the intended substrate surface. But the degree of roughness has to be compatible with the mean size of the splat. The roughness should be adjusted to achieve the parameters that will result in the best coating adhesion, as shown in Figure 4-8.

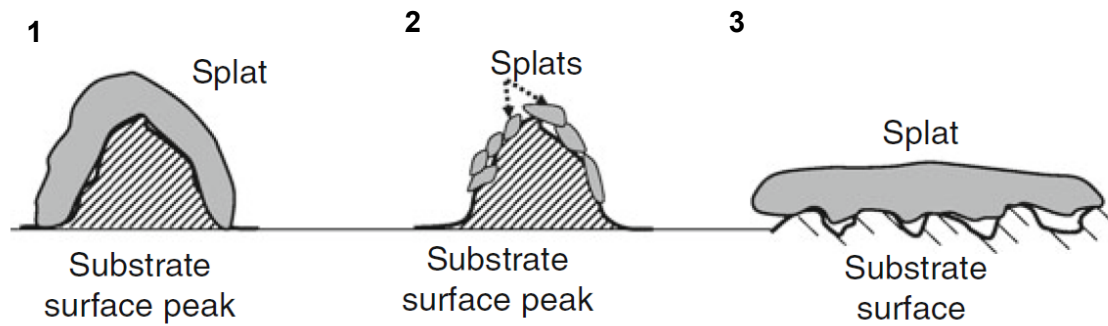


Figure 4-8: Schematic illustration of particle deposition (splats) relative to grit blasted surface peak sizes. 1) Splat size adapted to peak size. 2) Too small splat sizes relative to peak sizes. 3) Too large splat size relative to peak sizes, modified from Fauchais *et.al.* (2014)

The most common process for surface roughening is the grit blasting process. Dry abrasive particles are propelled towards the substrate at high speeds. The particles are usually sharp and angular acting as small chisels upon impact by cutting small irregularities into the surface (Figure 4-9). The grit particles can break down during the grit blasting process, thus in order to maintain control of the roughness and uniformity the grit that is used must continuously be sieved to remove small particles (Matejka & Benko, 1989).

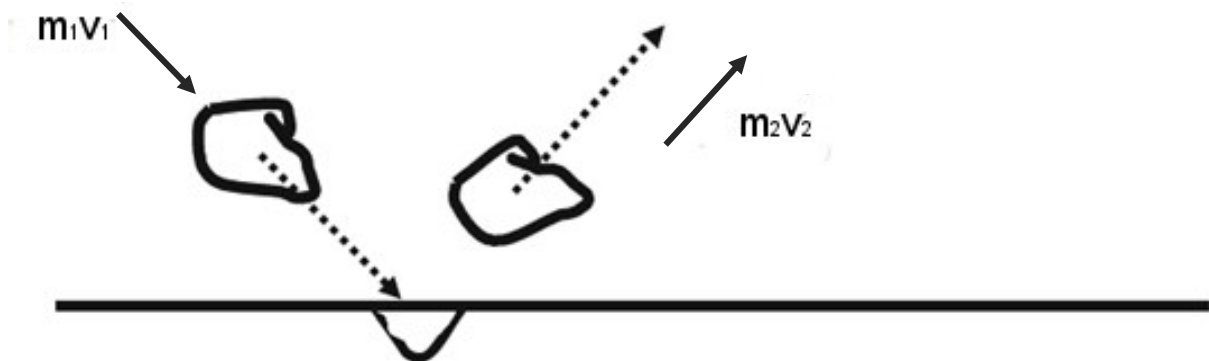


Figure 4-9: Illustration of irregularity created through an abrasive particle hitting the substrate surface, modified from Fauchais *et al.* (2014)

The degree of roughness and surface stress due to blasting will depend on the type of machine, blasting distance, grit material and grit size which must be carefully optimised for the desired effect. However, Fauchais *et al.* (2004) mentions that the main disadvantage of the grit blasting process is the grit residue, which in most cases is not easy to remove from the substrate and even harder to avoid. But this process remains the most cost effective method.

Any surface, especially in the presence of an oxide layer, is polluted by adsorbates and condensates. When a molten particle flattens on the substrate it traps the adsorbates and any vapors between the flattened droplet surface and the substrate (Fauchais *et al.*, 2016). During a few hundreds of nanoseconds, the local gas pressure can reach a few thousands of MPa which can lead to devastating coating failures (Li & Li, 2003).

For a high-quality coating with good adhesion, it is necessary to first remove the adsorbates and condensates. The adsorbates and condensates removal can be done by either preheating the substrate, blasting the substrate with dry ice or by using a laser upstream of the spray process (Fauchais *et al.*, 2014; Li & Li, 2003). The most common process is the substrate heating which can be done with the plasma torch or a dedicated substrate heating element. The Adsorbates and condensates are removed by heating the substrate to a temperature high enough to allow the adsorbates and condensates to evaporate (Yang *et al.*, 2013).

4.1.6. Coating Structures

The substrates and particles transitional temperature is the influencing factor that governs the flattening behaviour of the particle impacting on the substrate. The flattening behaviour can be described as the fundamental coating mechanism for plasma spraying. The particle flattening is closely related to the in-flight temperature, velocity, particle size, particle material and impacting angle.

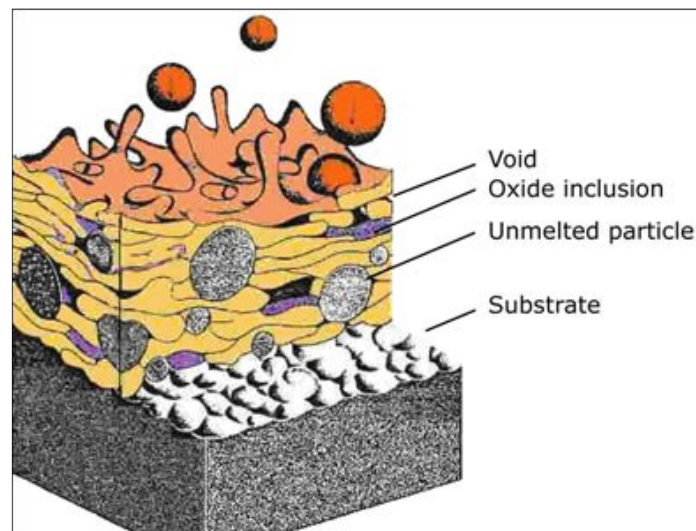


Figure 4-10: Schematic illustration of a plasma sprayed coating, modified from Lovelock (2015)

At the point of impact, the particle will form a splat on the substrate surface if the velocity and degree of melting for the particle is high enough for deposition. A coating is formed when multiple particles form overlaying splats (lamellae), with a few tens of μs between successive particle impacts, solidify and adhere to each other. As the lamellae that form are only a few μm thick with diameters from a few tens to a few hundreds of micrometres depending on the particle size. The forming of a plasma sprayed coating is illustrated in Figure 4-10.

The substrates and particles transitional temperature is the influencing factor that governs the flattening behaviour of the particle impacting on the substrate. The flattening behaviour can be described as the fundamental coating mechanism for plasma spraying. The bonding mechanism between the splats and substrate and later on splats and deposited layers is known as a mechanical bond. It must be noted that the wettability improves after splats start depositing on the initially deposited coating, this is due to the improve wettability of a liquid with a solid of the same material.

Another type of bonding mechanism that can occur is diffusion between the coating and substrate. Diffusion will only occur at high substrate temperatures (higher than 0.6 times the melting temperature, and if the oxide layer on the substrate surface has mostly been removed. The diffusion effect is mostly observed when spraying in a soft vacuum with a superalloy unto a superalloy substrate after the oxide layer has been destroyed.

The final bonding mechanism that can occur is a chemical bond. This will happen if the impacting droplet melts the surface of the substrate and both materials make a new material. This is the case when the particles effusivity is larger than the substrates. The effusivity can be described as the square root of the specific mass, thermal conductivity and specific heat of a material.

4.2. Conclusion

In this chapter, the plasma spraying parameters influencing the coating quality was discussed. It was decided from the aforementioned work that for ideal deposition the particle velocity and particle temperature are arguably the most important factors. Therefore for the experimental procedure parameters relating to these properties will be used. The experimental parameters will be the plasma power input, substrate distance, particle injection and spraying atmosphere.

The plasma power was chosen because it directly correlates with the plasma temperature and plasma velocity. The substrate distance was chosen because of the higher plasma velocity and plasma temperature closer to the plasma source. The particle injection if done properly will allow the particles to reach the centre of the plasma which has higher values for the plasma temperature and plasma velocity than the plasma fringes. In order to avoid oxygen contamination an alternative atmosphere should be implemented.

Bibliography

- Bernecki, T. 2004. Surface Science. (In Davis, J.R., ed. Handbook of Thermal Spray Technology. ASM International. p. 14-35).
- Fauchais, P., Vardelle, A., Vardelle, M. & Fukumoto, M. 2004. Knowledge concerning splat formation: An invited review. *Journal of Thermal Spray Technology*, 13(3):337-360.
- Fauchais, P., Vardelle, M. & Goutier, S. 2016. Latest Researches Advances of Plasma Spraying: From Splat to Coating Formation. *Journal of Thermal Spray Technology*, 25(8):1534-1553.
- Fauchais, P.L., Heberlein, J.V.R. & Boulos, M.I. 2014. Thermal Spray Fundamentals. United States of America: Springer US.
- Herman, H. 1991. Powders for Thermal Spray Technology. *KONA Powder and Particle Journal*, 9:13.
- Hu, C., Ge, X., Niu, Y., Li, H., Huang, L., Zheng, X. & Sun, J. 2015. Influence of Oxidation Behavior of Feedstock on Microstructure and Ablation Resistance of Plasma-Sprayed Zirconium Carbide Coating. *Journal of Thermal Spray Technology*, 24(7):1302-1311.
- Li, C.-J. & Li, J.-L. 2003. Evaporated-gas-induced splashing model for splat formation during plasma spraying. *Surface and Coatings Technology*, 184(1):10.
- Lovelock, H. 2015. Introduction to thermal spray coatings. African Fusion(Issue).
- Matejka, D. & Benko, B. 1989. Plasma Spraying of Metallic and Ceramic Materials: Wiley.
- Vardelle, A., Moreau, C., Akedo, J., Ashrafizadeh, H., Berndt, C.C., Berghaus, J.O., Boulos, M., Brogan, J., Bourtsalas, A.C., Dolatabadi, A., Dorfman, M., Eden, T.J., Fauchais, P., Fisher, G., Gaertner, F., Gindrat, M., Henne, R., Hyland, M., Irissou, E., Jordan, E.H., Khor, K.A., Killinger, A., Lau, Y.-C., Li, C.-J., Li, L., Longtin, J., Markocsan, N., Masset, P.J., Matejcek, J., Mauer, G., McDonald, A., Mostaghimi, J., Sampath, S., Schiller, G., Shinoda, K., Smith, M.F., Syed, A.A., Themelis, N.J., Toma, F.-L., Trelles, J.P., Vassen, R. & Vuoristo, P. 2016. The 2016 Thermal Spray Roadmap. *Journal of Thermal Spray Technology*, 25(8):1376-1440.
- Vardelle, A., Moreau, C., Themelis, N.J. & Chazelas, C. 2015. A Perspective on Plasma Spray Technologie. *Plasma Chemistry & Plasma Process*, 35(3):19.
- Vardelle, M., Vardelle, A., Fauchais, P., Li, K.I., Dussoubs, B. & Themelis, N.J. 2001. Controlling particle injection in plasma spraying. *Journal of Thermal Spray Technology*, 10(2):267-284.

Yang, K., Fukumoto, M., Yasui, T. & Yamada, M. 2013. Role of substrate temperature on microstructure formation in plasma-sprayed splats. *Surface and Coatings Technology*, 214:138 - 143.

Zhukov, M.F., Zasyppkin, I.M., Timoshervskii, A.N., Mikhailov, B.I. & Desyatkov, G.A. 2007. Thermal Plasma Torches Design, Characteristics, Applications. Cambridge: Cambridge International Science Publishing Ltd.

CHAPTER 5

IMPLEMENTATION OF DC PLASMA SPRAYING

“Never tell people how to do a thing.

Tell them what to do and they will surprise

you with their ingenuity.”

-General George S. Patton (1885 - 1945)

5.1. Introduction

The research done was carried out in the plasma laboratories at South Africa Nuclear Energy Company SOC Ltd. (Necsa). In this chapter the systems and the main individual parts used will be described, substrate preparation, powder characterisation, plasma spray simulation and plasma calculation used in this research.

5.2. Spraying Setup

A schematic representation of the plasma spraying laboratory floor plan with images of the individual parts is shown in Figure 5-1. The plasma spraying setup consisted out of a gas system, power supply, cooling water supply, plasma spray chamber, plasma torch, powder feeder and a heated substrate holder.

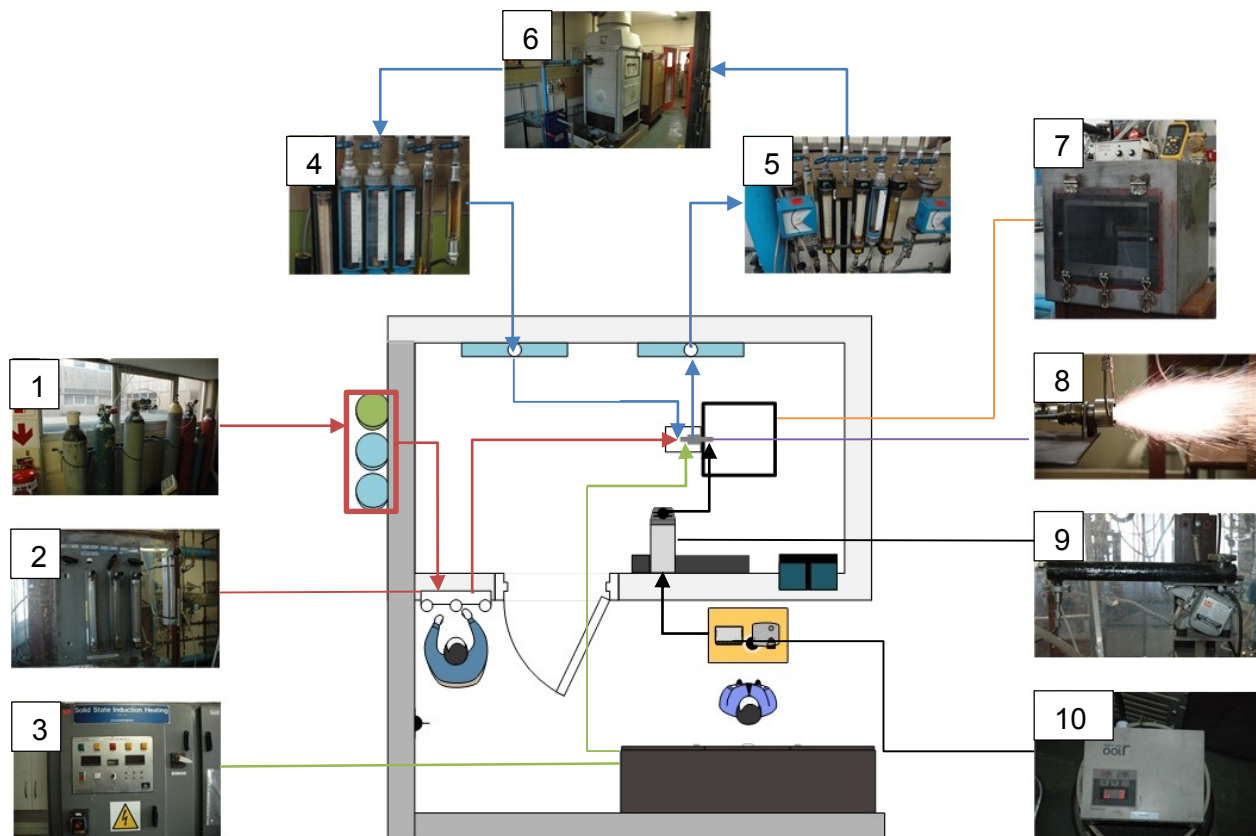


Figure 5-1: Laboratory floor plan for atmospheric plasma spray setup: 1) Gas cylinders, 2) Gas flow meters, 3) Power supply, 4) Water inlet manifold flow meters , 5) Water outlet manifold flow meters, 6) Water cooling tower, 7) Plasma spray chamber, 8) Plasma torch, 9) Powder feeder, 10) Powder feeder controller

The plasma spraying gas system used Ar as a powder carrier gas and inert atmosphere. A combination of Ar and N₂ gases were used to generate the plasma. Each gas cylinder was fitted with pressure gauges and flow regulators (1). A combination of 1/4" stainless steel and plastic tubing was used to connect the gas bottles to the plasma torch. Gas flow to the plasma torch was controlled with Fischer Porter gas flow meters (2). High purity gasses were used, typically 99.999% pure as to avoid contamination and deterioration of components.

The plasma spraying setup made use of a cooling water system for the plasma torch anode and cathode. The system consisted out of an inlet (4) and outlet manifold (5) fitted with flow meters and a cooling tower. The whole system used only demin-water.

The power supply (3) used for the plasma setup is a high-frequency current controlled rectifier used to deliver a smooth DC current. The power supply has a 30 kW capacity with a maximum of 200 ampere output. The current was set according to the experimental parameters whereas the volts was adjusted by increasing the plasma gas flow which in turn elongated the arc.

In order to establish an initial arc, a starting circuit was employed. The starting circuit consists out of a high voltage transformer and capacitor which allows the initial breakdown of the spark gap. This breakdown creates a voltage spike in the power supply circuit creating the initial arc between the anode and cathode.

The spraying chamber (7) had the capacity to spray under normal atmospheric conditions or under an inert gas atmosphere. The spray chamber with its corresponding peripherals, as shown in *Figure 5-2*, is a 500 mm x 500 mm x 500 mm stainless steel box designed to conduct this research.

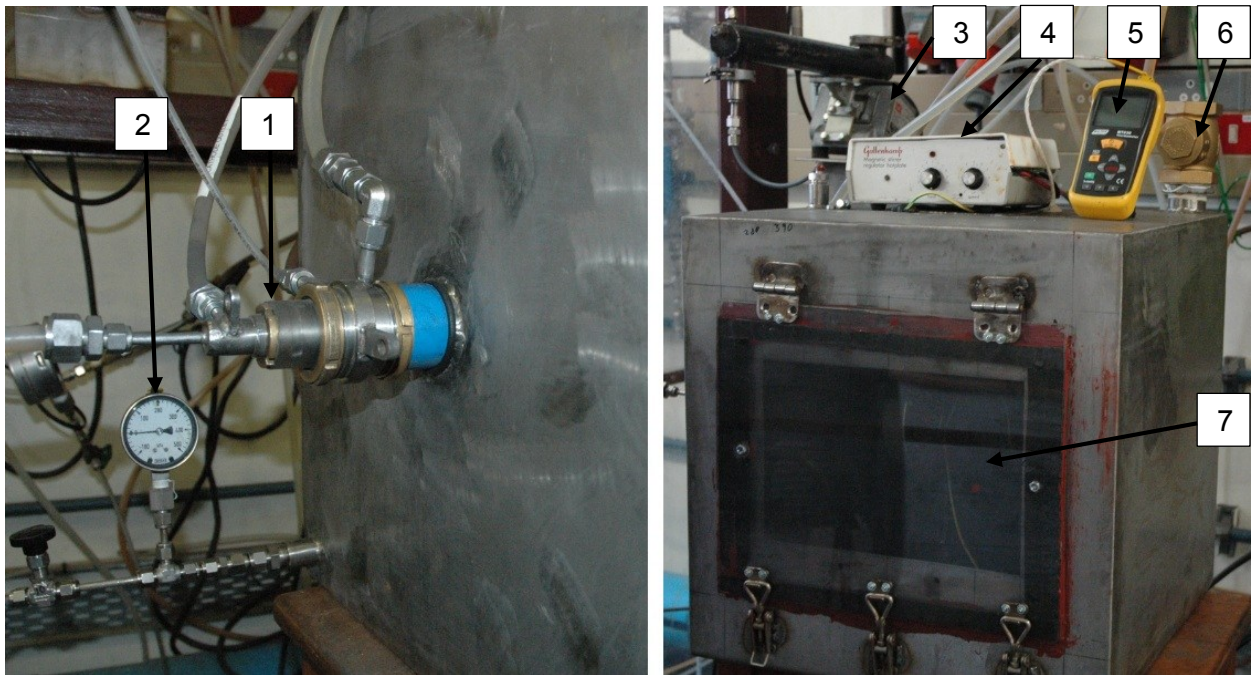


Figure 5-2: Inert plasma spray chamber: 1) Plasma torch, 2) pressure gauge, 3) powder feeder, 4) substrate temperature controller, 5) thermal couple read-out, 6) swing check valve, 7) front loading door

The spray chamber was designed to easily attach the plasma torch (1), powder feeder (3) and substrate heater (4). The chamber was fitted with a pressure gauge (2) to avoid unnecessary high pressures. The substrate temperature was displayed on the thermal couple read-out (5) which was attached to type k thermal couple positioned on the back of the substrate. The chamber was fitted with a check swing valve (6) to release high pressures created during plasma spraying and a front loading door (7) to easily insert and remove the substrate before and after spray runs.

The coatings were deposited using a DC non-transfer arc plasma torch developed at Necsa. The plasma torch was initially used for plasma gasification before being repurposed into a plasma spraying torch. A cross-section of the plasma torch is shown in *Figure 5-3* and the plasma torch is displayed in *Figure 5-4*.

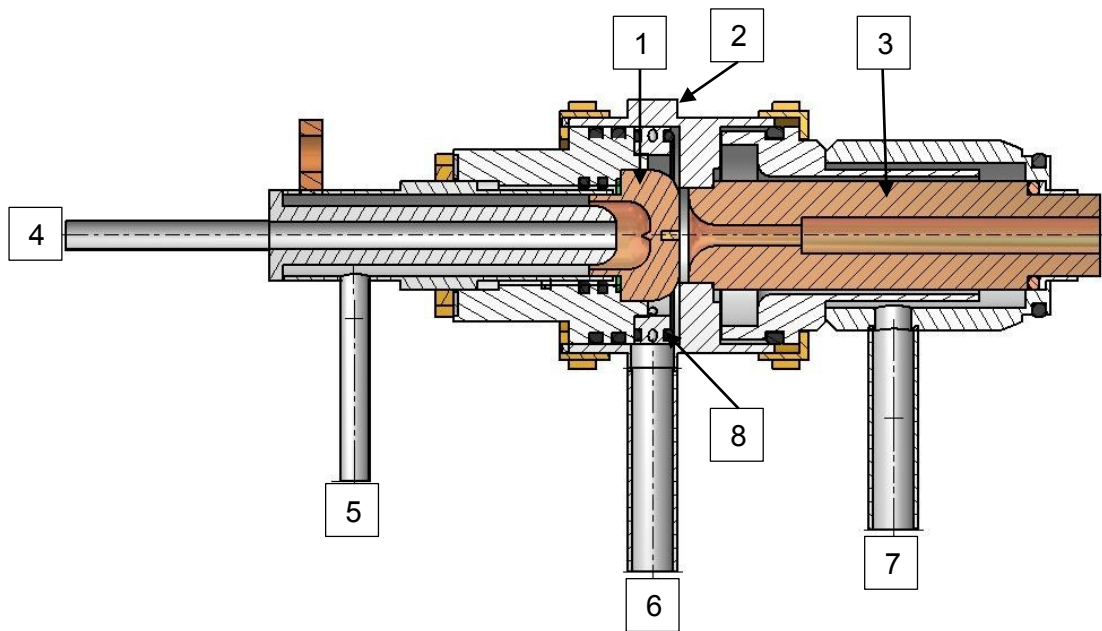


Figure 5-3: Cross-section view of necsa designed DC plasma torch: 1) Cathode, 2) Insulating material, 3) Anode nozzle, 4) Cathode cooling water inlet, 5) Cathode cooling water outlet, 6) Gas inlet, 7) Anode cooling water inlet and 8) gas vortex spinner

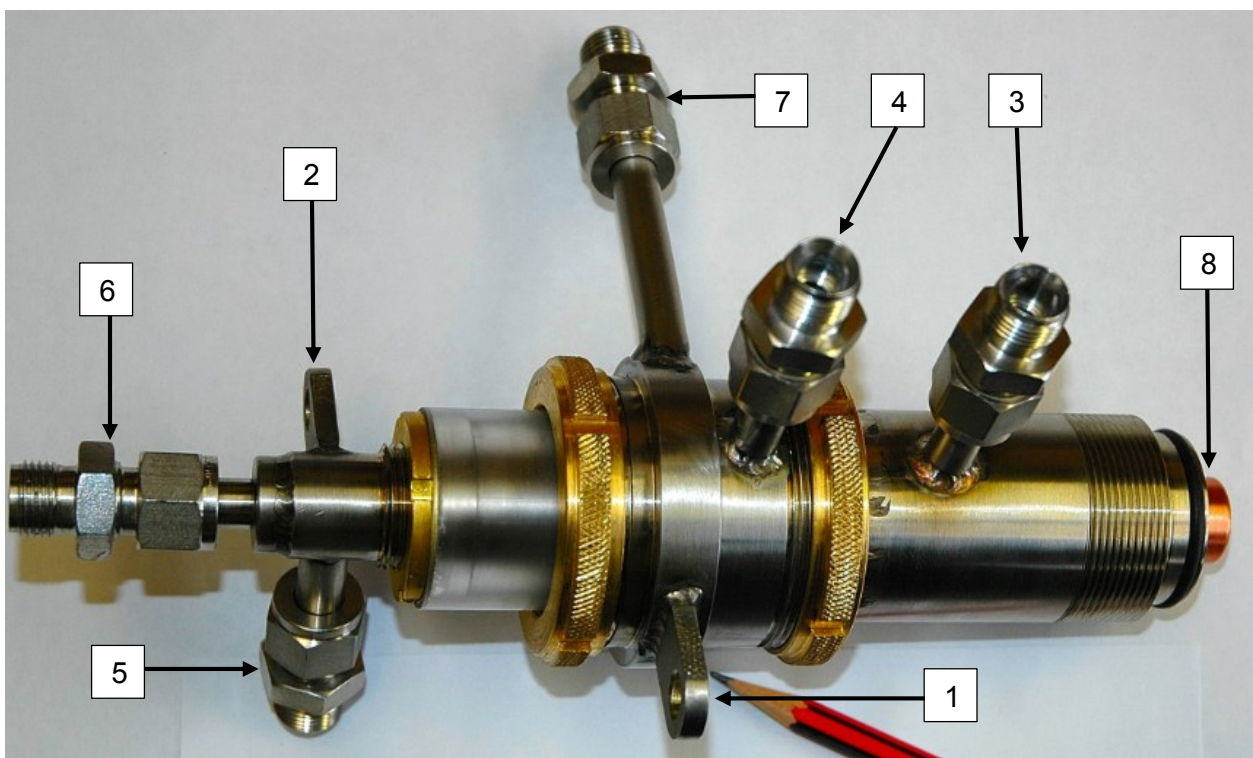


Figure 5-4: Necsa non-transfer DC plasma torch: 1) Negative pole, 2) Positive pole, 3) Anode water inlet, 4) Anode water outlet, 5) Cathode water outlet, 6) Cathode water inlet, 7) Gas inlet and 8) Anode nozzle gas outlet

The negative (1) and positive (2) connection points are shown in Figure 5-4, this is where the power supply and initial arc supply are connected. Both the anode and cathode are water cooled and in Figure 5-4 the anode water inlet (3) and outlet (4) as well as the cathode water inlet (5) and outlet (6) is shown. The torch is sealed with O-rings at both ends of the cathode and anode to help ensure there are no water leaks due to the high-pressure water flow.

The gas inlet (7) is connected tangent to the plasma torch and feeds gas directly into the spinner (Figure 5-3, 8) to form a strong vortex to help stabilise the arc. The gas is ejected out of the plasma torch through the anode nozzle (8) where it rapidly expands forward.

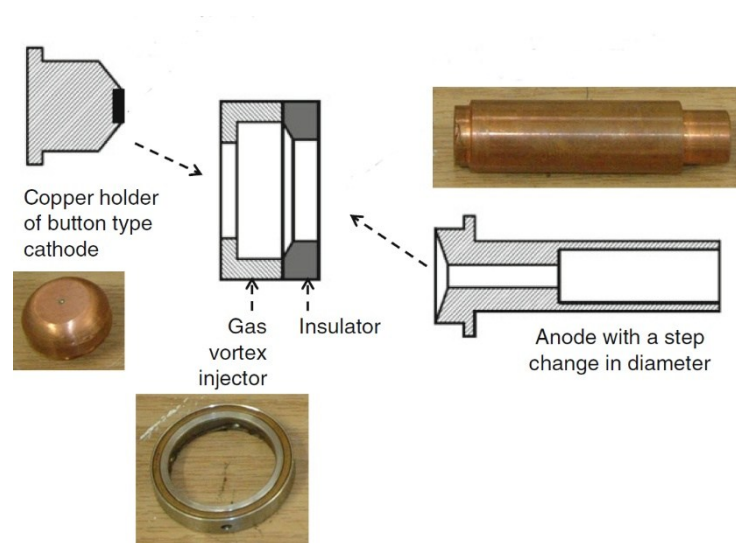


Figure 5-5: Plasma torch anode, cathode and gas vortex injector

The plasma torch consists out of a button type cathode with a tungsten insert and a cylindrical copper anode with a step, a vortex spinner and plasma torch housing (Figure 5-5). A non-conductive material is fitted between the anode and cathode to ensure an arc is struck between the formerly mentioned parts.

The powder feeder used was an ERIEZ A series vibrating powder feeder fitted with a cylinder powder track (Figure 5-6).



Figure 5-6: ERIEZ A series commercial powder feeder: 1) cylindrical track access latch, 2) carrier gas inlet, and 3) carrier gas and powder outlet

The powder is loaded into the cylindrical track (1) where it was fed forward using vibrations after which carrier gas, which was fed into the powder feeder (2), carried the powder out (3) toward the anode nozzle. The powder feeder was controlled by adjusting the vibration Hz via a control box. The powder feeder has a maximum load capacity of 1 kg and a maximum vibration of 50 Hz.



Figure 5-7: The powder feeder injection setup at the anode nozzle

The powder was injected into the plasma plume externally using a twin injection configuration (Figure 5-7). The powder injectors were ¼' copper tubes positioned at 90° and 270° at the anode nozzle exit.

5.2.1. Substrate Holder

The heated substrate holder was made to better control the substrate's temperature, remove adsorbates and condensate as well as enhance wettability of the coating and substrate.

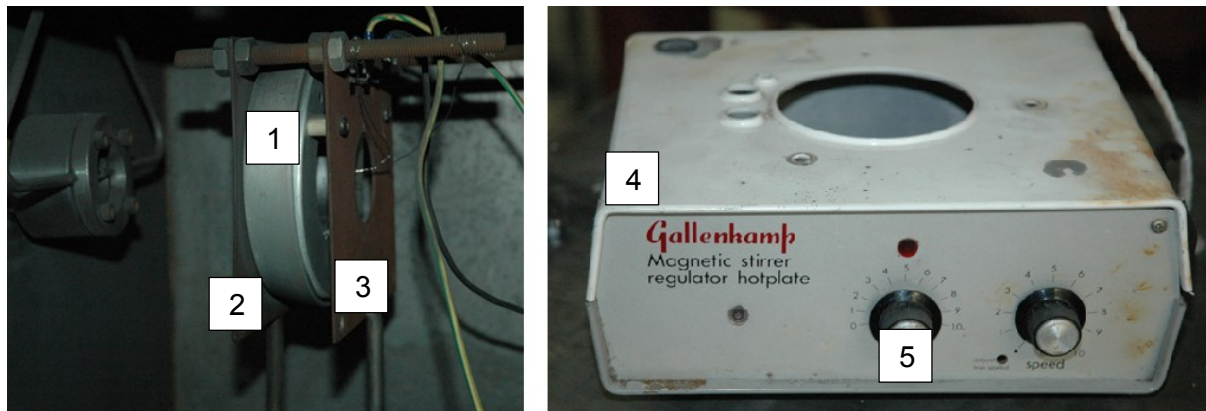


Figure 5-8: Heated substrate holder 1) heating element, 2) plasma plume shield plate, 3) heating element stand, 4) heating element, and 5) heating control knob

The substrate holder was made out of a Gallenkamp thermostat hotplate (Figure 5-8) by removing the hotplate's heating element (1) and installing it unto a stand (3) in front of the plasma torch with a shielding plate (1). The hotplates control box (4) was used to control the substrate temperature using the left side knob (5). The substrate was heated through the heating element of the hotplate which was mounted directly onto the element. The temperature was measured using a type K thermocouple which was connected unto the back of the substrate through the heating element.

5.2.2. Temperature Measurement

Temperature measurements were done on the cooling water inlet, outlet and heated substrate holder. The cooling water used type J thermocouples to capture the temperature at the inlet manifold, cathode water outlet and anode water outlet. The substrate temperature was measured using a type K thermocouple to measure the substrate temperature before the coating process.

5.3. Powder Composition, Particle Size and Morphology

For the ZrC coatings commercially available ZrC powder (99.5 wt.%, $\approx 5 \mu\text{m}$) was supplied by Changsha Langfeng Metallic Material Co., LTD (China) to be used as feedstock for the plasma spraying. The feedstock powder underwent a comprehensive characterisation before plasma spraying as the powder properties (morphology, composition and particle size distribution) was of great importance to the coating process.

An SPECTRO ARCOS Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and combustion analysis techniques (LECO® CS 774) were used to determine a quantitative analysis of the feedstock powder. The ICP-OES cannot analyse for carbon thus combustion analyser was utilised for the carbon analysis. According to stoichiometry, pure ZrC will have a composition of 88.36 % Zr and 11.64% C. The detected zirconium and carbon compositions were 83.80 % and 11.61 %, which correlates well with the aforementioned values. This is indicative of a 94.80 % pure ZrC composition. The remaining 5.20 % may be ascribed to impurities, i.e. Fe, Hf, Ti and V, present in the analysed samples.

Phase identification of the feedstock powder and coatings were carried out using a Bruker AXS X-ray diffraction (XRD) machine with a D8 advance diffractometer and a Cu tube as an X-ray source. The spectra obtained were compared to the JCPDS (Joint Committee on Powder Diffraction Standards, USA) database using devoted computer codes to identify the crystallised phases.

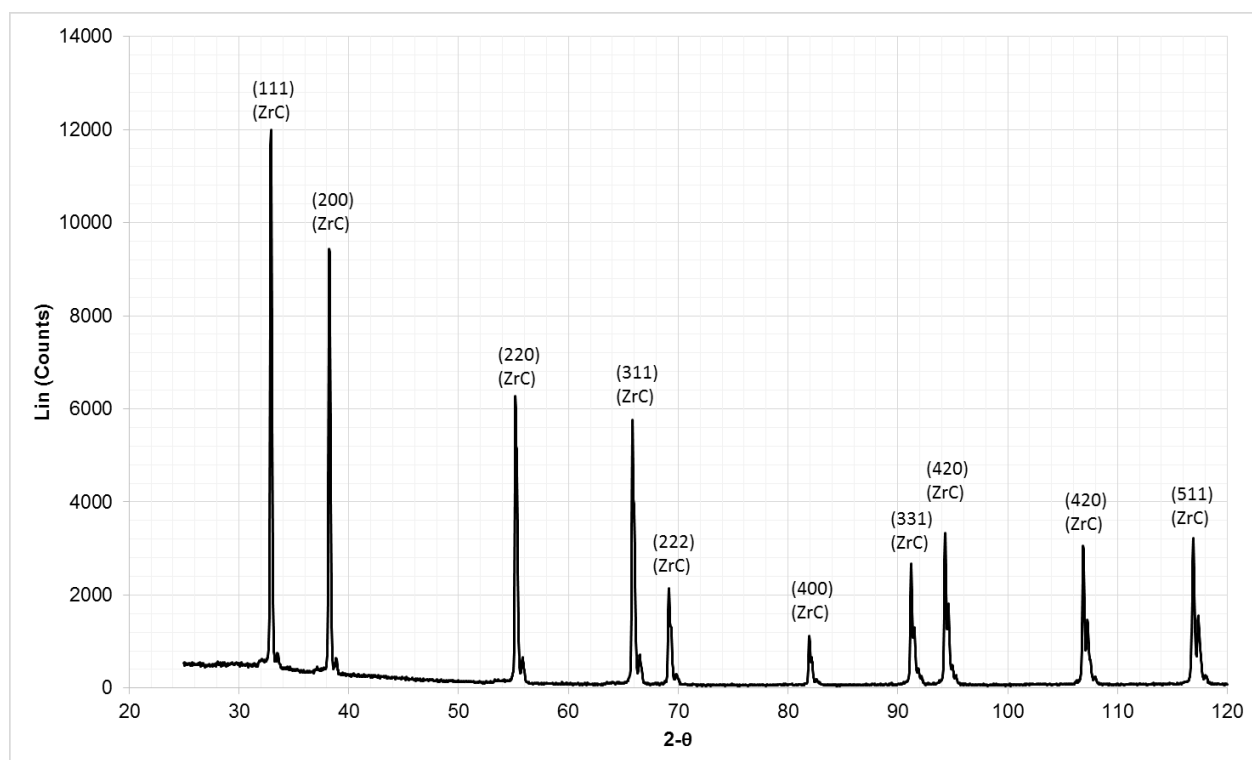


Figure 5-9: XRD pattern of feedstock powder

An XRD technique was used for a qualitative analysis of the powder where the detected peaks from the feedstock powder matched diffraction pattern of the JCPDS 03-065-4932 ZrC pattern (Figure 5-9).

A Saturn DigiSizer® high-definition particle size distribution (PSD) analyser was used to determine the particle median size (d₅₀) and the percentile by volume of the particle sizes were. In order to better disperse the powder before analysing a surfactant (Triton® x-100) was added

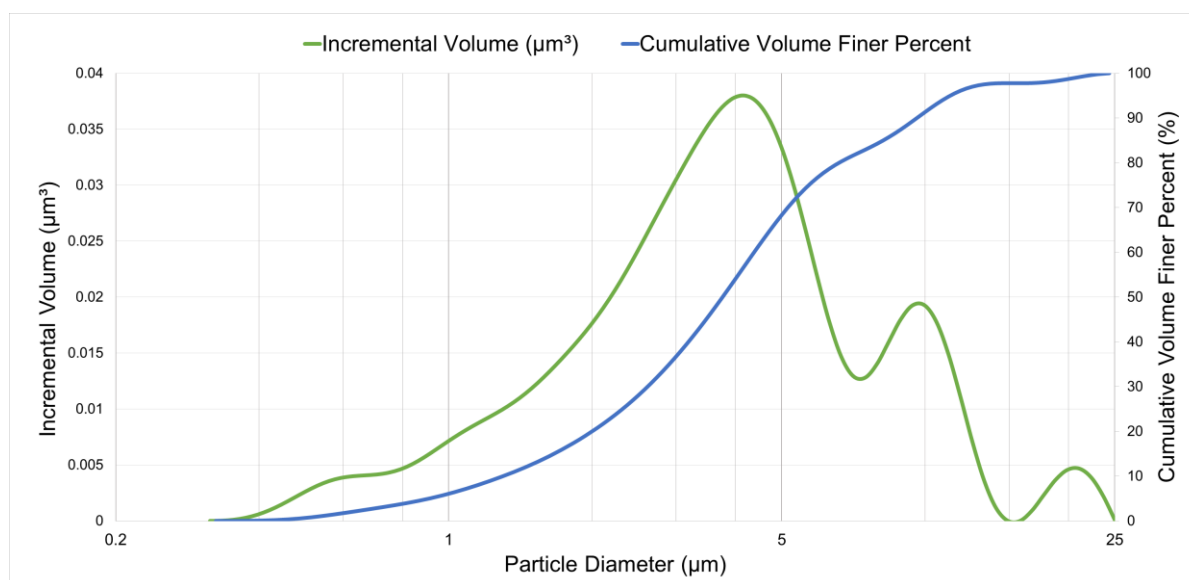


Figure 5-10: Particle size distribution incremental volume and cumulative volume graph

The particle size analysis revealed that the powder had a d₅₀ (median) of 3.76 µm and an average particle size distribution of 1.30 µm to 9.61 µm (Figure 5-10). The average particle size was smaller than the expected 5.00 µm as received from the supplier but a narrow particle size distribution was observed. If a dense coating is required a narrow size distribution and small average size particles are required (Herman, 1991). This correlates well with the measured particle sizes and research aim to deposit a dense coating.

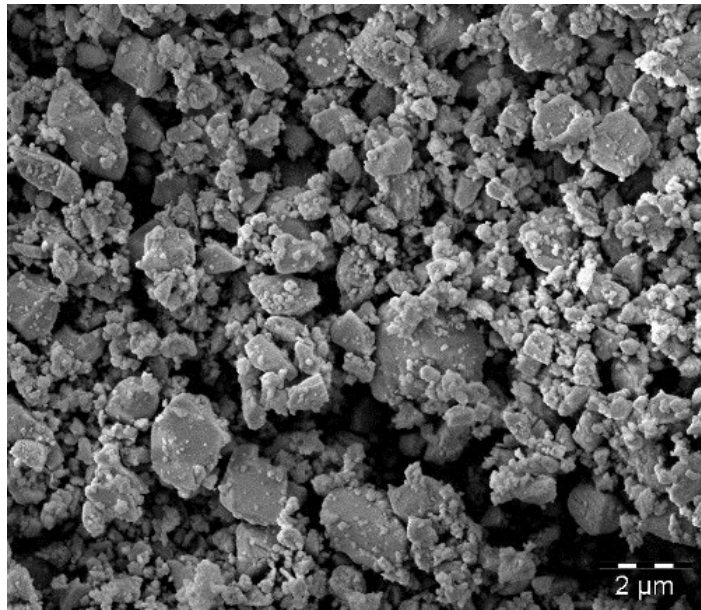


Figure 5-11: SEM micrograph of feedstock powder showing the large and fine particles

A SEM micrograph of the feedstock powder (*Figure 5-11*) was taken to determine the morphology of said powder. The micrograph revealed that the powder has sharp, angular and irregular shapes with a mixture of large particles and small fines. According to Fauchais *et.al.* (2014), the particle morphology will also influence the coating structure. Irregularly shaped particles will be more difficult to feed evenly into a plasma than spherical particles, however heat and momentum transfer increases for such particles in a plasma assuring a complete particle melting.

5.5. Plasma Temperature and Efficiency Calculation

The ASTM E341 – 96 (standard practice for Measuring Plasma Arc Gas Enthalpy by Energy Balance) was used to determine the plasma torch efficiency and temperature. The calculations done found that the efficiency of the 11.0 kW plasma it was 57.3 %, for the 16.5 kW plasma it was 59.7 % and for the 22 kW plasma it was 60.2 %. It was observed that as the power input increases so does the efficiency of the plasma torch.

The plasma temperature was calculated using the remaining enthalpy determined from the energy balance and finding the correlating temperature using the thermodynamic properties of nitrogen (Jacobsen & Stewart, 1973). The plasma temperatures were calculated to be 5 745°C (11.0 kW), 6 107°C (16.5 kW) and 6 279°C (22.0 kW).

5.6. Particle Temperature and Velocity Simulations

The plasma spraying simulation Jets&Poudres, created by Pateryron (2009), was used to investigate the experimental runs before spraying the samples. The Jets&Poudres program is specifically designed for computation of particles' thermal properties and trajectory for various materials injected into a plasma plume at different points and velocities. The Jets&Poudres program is built in Visual Basics and is based on the **general mixing** (GENMIX) computer code and thermodynamic gas properties obtained from the T&TWinner database (Patankar & Spalding, 1983).

The GENMIX code handles two-dimensional parabolic flows, free of recirculation that is characterized by high Reynolds and Peclet numbers. The GENMIX code creates a self-adaptive grid which will enlarge or contract to only cover the regions of interest thus directing computational power only to the parts of interest.

The following assumptions are used as a first approximation for the plasma flame:

- Steady-state plasma plume
- Plasma gas flows in one direction
- The recirculation or diffusion effects are in one direction

The following assumptions used in the simulation concerning the feedstock powder was:

- Powder particles have spherical shapes
- Powder didn't influence the characteristics of the plasma plume
- The drift forces have significant influence on the particles in the plasma plume
- The gravitational forces have significant influence on the particles in the plasma flame
- Powder material can be melted but not evaporated in the plasma flame

The code calculates initially the specific enthalpy from the ratio of efficient power to the mass flow rate, from which the plasma gas temperature is obtained. From this temperature the specific volume of the gas and its mean velocity are determined. A uniform radial profile of temperature and velocity (corrected by the kinetic energy) is assumed at the exit of the nozzle. The mixing and cooling of the plasma and atmospheric gas will be used to determine the final profiles of temperature and velocity (Figure 5-12). The code neglects the effect of the powder carrier gas flow but has been found to be in close range to actual plasma spray runs.

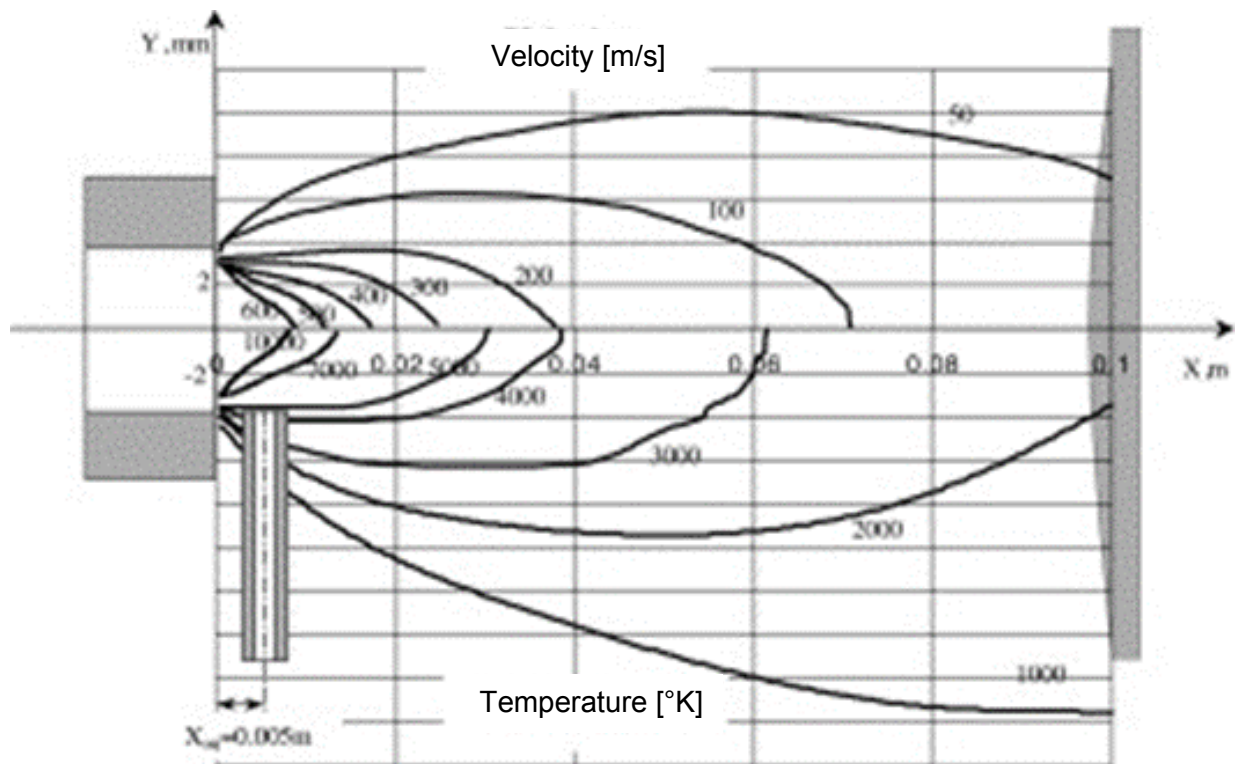


Figure 5-12: Illustration of plasma temperature and velocity in a typical plasma spraying setup

The Jets&Poudres plasma spray simulation program was used to confirm that the particle velocity and temperature were high enough to deposit a coating. Table 5-1 shows the parameters used in the simulations. The simulation parameters that were varied is the plasma power input, these values were 11, 16.5 and 22 kW, as this was the minimum to the maximum operating range for the plasma torch used. The particles were injected in the centre of the plasma plume to simulate the ideal conditions.

Table 5-1: Simulation parameters used for the Jets&Podres program

Simulation Parameter	Plasma Efficiency [%]	Spray Distance [mm]	Plasma Gas [-]	Exit Nozzle Size [mm]	Injector distance from Nozzle [mm]
Input Value	60	100	Nitrogen	8	4.5

The particle needs to be able to deform upon impact with the substrate surface thus the particle velocity and temperature are two key components in the deposition of good quality coatings. This is because the plasma spraying method's main coating mechanism is mechanical interlocking (Fauchais *et al.*, 2014).

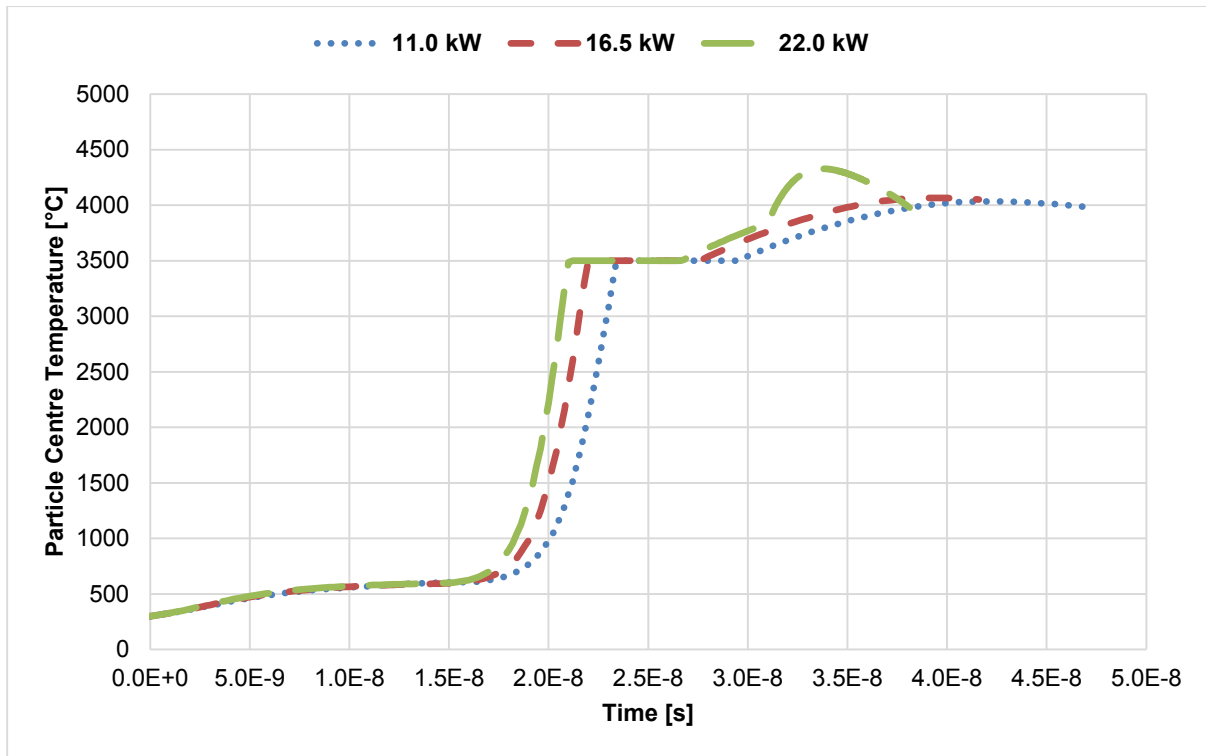


Figure 5-13: Particle temperature at the centre for an 11.0 kW, 16.5 kW and 22.0 kW plasma

The temperature at the centre of the particles for the 11.0, 16.5 and 22.0 kW are all above 3 500°C (ZrC melting point) therefore all particles can be assumed as completely molten before hitting the substrate (Figure 5-13). A sudden increase in particle temperature for the highest power input (22.0 kW) was observed at 3.0E-8 s. This could be ascribed to the evaporation of the particle as it is a common occurrence in plasma spraying (Chandra & Fauchais, 2009).

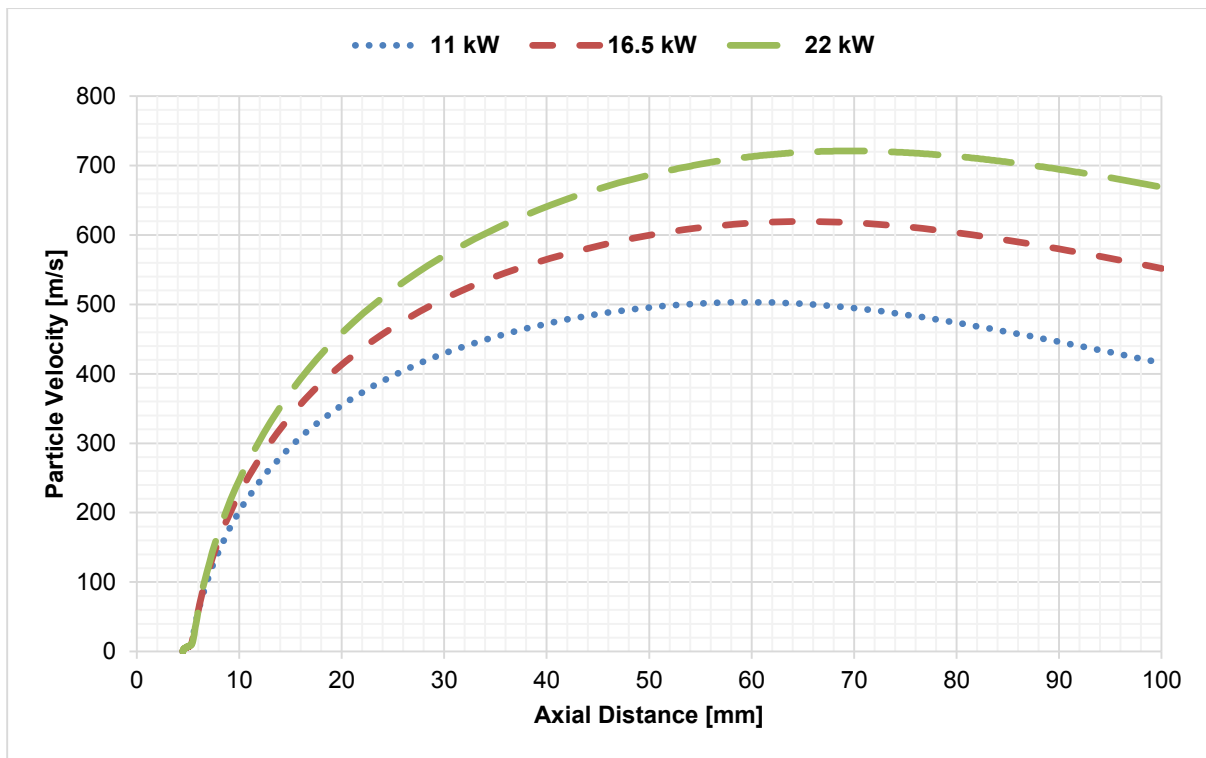


Figure 5-14: Particle velocity for an 11.0 kW, 16.5 kW and 22.0 kW plasma

The velocity of the particles at different power inputs was simulated (Figure 5-14) where it was observed that the particle velocity increases as the plasma power does. This is because the higher plasma power input requires a higher plasma gas flow as well as the rapid gas increase at the nozzle exit caused by the increased plasma temperature. The highest velocity for the particles can be observed at between 60 and 70 mm, although this appears to be the ideal substrate distance for deposition. Fauchais *et al.* (2014) stated that even though the particle velocity reaches a maximum closer to the torch, the plasma plume may be too hot and the substrate could suffer damage.

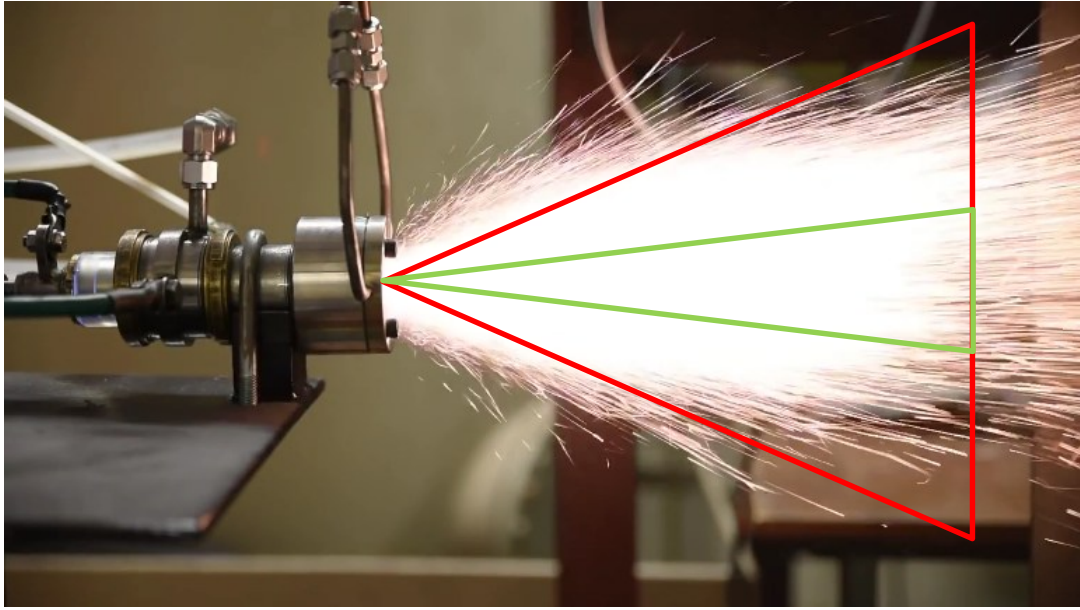


Figure 5-15: Plasma and particle interaction during spraying process

It is important to note that the particle velocity will decrease if instead of travelling through the centre of the plasma plume the particle remains on the plasma fringes. This generally occurs when particles don't penetrate the plasma and remains on the fringes or pass through the plasma, as shown in *Figure 5-15*, where the red triangle indicates the particles being ejected out of the plume before reaching the substrate and the green triangle indicates the ideal deposition path (Mundo *et al.*, 1995).

5.4. Substrate Preparation

The substrates used were cut from a stainless steel 304 plate into suitable sample sizes (30 mm x 30 mm x 3 mm) for coating preparations. The substrates of stainless steel 304 were used in place of a Zr-alloy for the initial evaluation of parameters.

Each sample was grit blasted with alumina and compressed air (6 bar) to roughen the substrate surface. The substrates were then chemically cleaned using the steps in Table 5-2 which were modified from the ASTM standard A 380 – 06: Standard practice for cleaning, descaling, and passivation of stainless steel parts, equipment and systems. These samples are then sealed in plastic to avoid any direct contamination before being plasma sprayed.

Table 5-2: Modified ASTM A 380 - 06 standard

Step No #	Description	Temperature [°C]	Time [min]	Operation Medium
1	Sonication	Ambient	30 ± 5	Demin Water
2	Degrease	75 ± 5	30 ± 5	10% Alkederust
3	Rinse	Room	10 ± 5	Demin Water
4	Acid Pickling	Room	30 (max)	2% HF 4% HNO ₃
5	Hot Rinse	70 ± 5	10 ± 5	Demin Water
6	Final Rinse	Room	10 ± 5	Demin Water
7	De-Water	Room	2 to 5	Propanol
8	Drying	Room	N/A	Nitrogen

5.7. Coating Procedure

The powder was loaded into the powder feeder and the substrate was placed into the substrate holder. The substrate holder itself would be positioned in front of the plasma torch in line with the anode nozzle at a distance depending on the experimental parameters. Using the heating element of the substrate holder the sample would be heated to 200°C before spraying to: 1) to enhance wettability, 2) decrease residual stresses between the substrate and coating, and 3) decrease the possibility of introducing thermal stresses.

The plasma would be started by first opening the Ar gas and using the arc initiator. After a stable Ar plasma was generated, N₂ gas was slowly added while simultaneously closing the Ar gas. This was done until a stable N₂ gas plasma was attained (Figure 5-16). The gas flow and power input was then set depending on the experimental parameters. After the plasma was stable the powder was fed into the plasma plume depositing for 10s. After the spray runs the sample was left to cool for at least 1 hour before being removed from the substrate holder. The purpose of this was to allow the coating and substrate too cool down and thus avoiding coating failures.

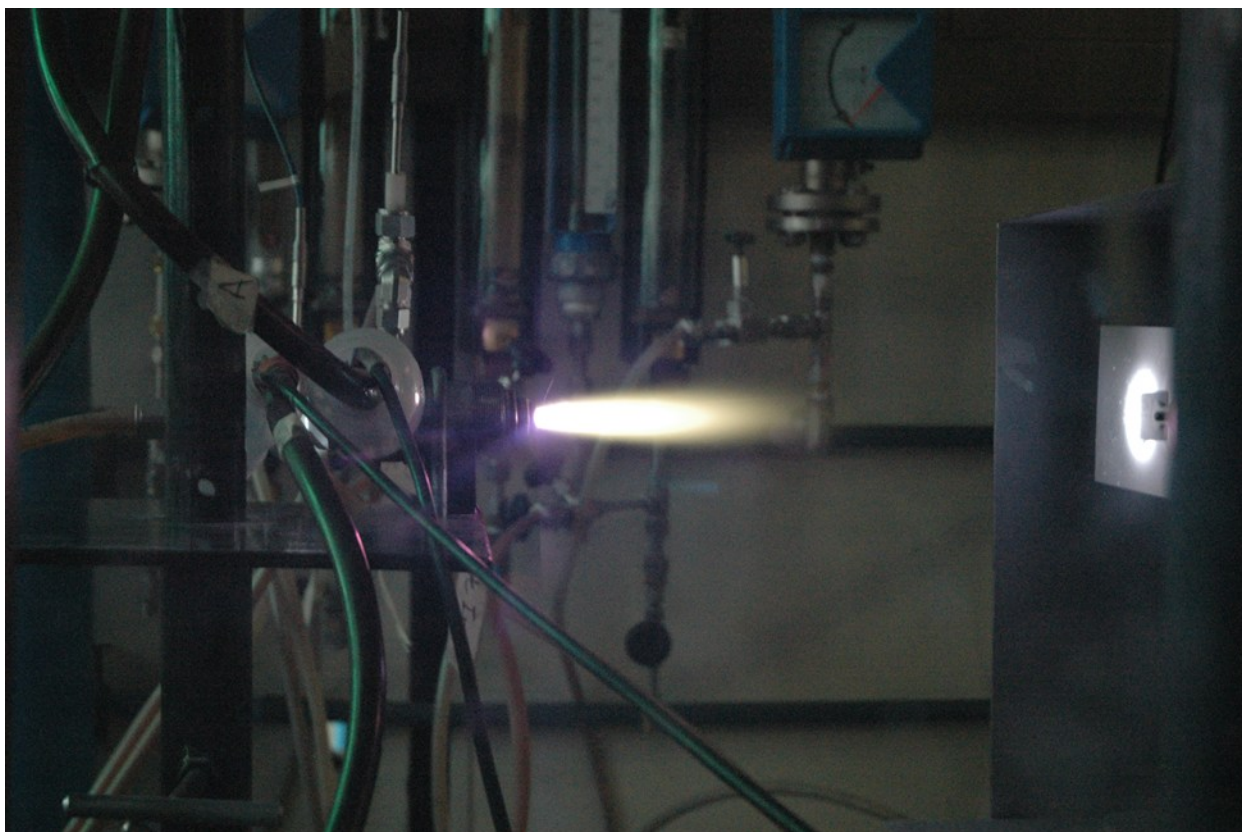


Figure 5-16: Plasma torch generating a plasma using nitrogen gas

The experimental parameters to be used in this experimental work (Table 5-3), cover the following parameters: 1) Spray Power (PS_01, PS_02 and PS_03), 2) Spray distance (PS_04 and PS_05), 3) Particle injection velocity (PS_06 and PS_07) and 4) Spray atmosphere (PS_08 and PS_09).

Table 5-3: Experimental parameters

Sample #	Amps (A)	Plasma Power (kW)	Plasma Gas (slpm)	Carrier Gas (m/s)	Spray distance (mm)	Spray Atmosphere (-)
PS_01	100	11.0	31.2	15	100	Air
PS_02	150	16.5	38.1	15	100	Air
PS_03	200	22.0	45.0	15	100	Air
PS_04	200	22.0	45.0	15	80	Air
PS_05	200	22.0	45.0	15	60	Air
PS_06	200	16.5	38.1	20	100	Air
PS_07	200	11.0	31.2	10	100	Air
PS_08	200	22.0	45.0	15	100	Argon
PS_09	200	22.0	45.0	15	80	Argon

For the inert plasma spray runs the chamber would be flushed with Ar gas for 40 min, before a spray run was conducted, to ensure an inert atmosphere

5.8. Summary

The experimental setup, equipment, powder analysis, plasma and procedure were described and supported through the use of schematic diagrams and photos of the equipment used. The powder characteristics techniques that will be used for the analysis were also described as well as a short description of the simulation program Jets&Poudres. The plasma torch calculations were done to determine the plasma temperature and efficiency while the plasma simulations determined the particle temperature and velocity.

The feedstock powder was confirmed to be ZrC with ICP-OES, combustion analysis and XRD while the particle size was determined with the PSD analyser to have a d50 of 3.755 μm . A SEM micrograph revealed the powder to have a sharp, angular and irregular morphology.

The plasma torch and spray calculations were done using ASTM standards and the plasma jets simulation program Jets&Poudres. The calculations determined that the higher the power input the more effective and hotter the plasma will be with a maximum efficiency of 60.24 % and plasma temperature of 6 279°C. The simulations showed that the particles temperature and velocity were high enough in order to deposit a coating if the particle travels the optimum route through the plasma.

Bibliography

Chandra, S. & Fauchais, P. 2009. Formation of Solid Splats During Thermal Spray Deposition. *Journal of Thermal Spray Technology*, 18(2):148-180.

Fauchais, P.L., Heberlein, J.V.R. & Boulos, M.I. 2014. Thermal Spray Fundamentals. United States of America: Springer US.

Mundo, C., Sommerfeld, M. & Tropea, C. 1995. Droplet-wall collisions: Experimental studies of the deformation and breakup process. *International Journal of Multiphase Flow*, 21(2):151-173.

Patankar, S.V. & Spalding, D.B. 1983. PAPER 5 - A CALCULATION PROCEDURE FOR HEAT, MASS AND MOMENTUM TRANSFER IN THREE-DIMENSIONAL PARABOLIC FLOWS. Numerical Prediction of Flow, Heat Transfer, Turbulence and Combustion. Pergamon. p. 54-73).

Pateyron, B. 2009. Jets&Poudres <http://jets.poudres.free.fr/en/home.html> Date of access: 2017/01/15 2017.

CHAPTER 6

DEPOSITED COATINGS MICROSTRUCTURE AND COMPOSITION

“Each type of knowledge has value,
However, from an engineering point of
View, practical knowledge seems to be
More valuable than theoretical knowledge.

-Eraldo Banovac (1948 – 1998)

6.1. Coating Characterisation

In this chapter, the SEM micrographs of the top and cross-section of the samples are shown and discussed, as well as the EDS mapping and XRD results presented in this study.

Using a Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) analyses were done on the surfaces and cross-sections of the coated substrates. The former was used for obtaining micrographs of the cross-section and surface of the coating, while the latter was used for elemental mapping of the samples. The EDS scans were done on a Quanta 200 3D SEM with an Apollo X Silicon Drift Detector (SDD) at Necsa. The EDS results were confirmed using XRD.

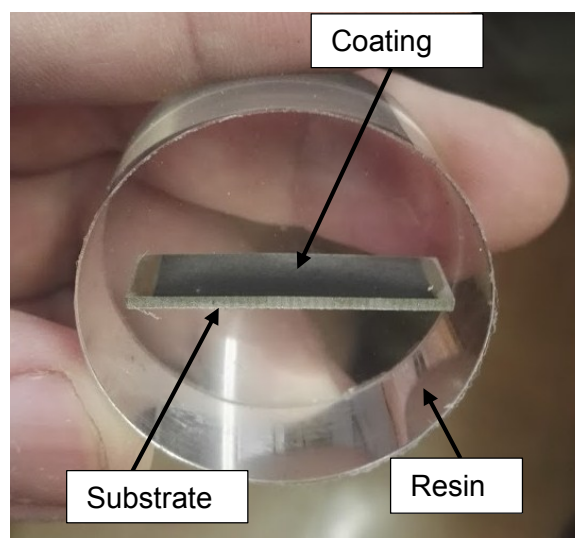


Figure 6-1: Sample cast in a resin and polished in order to observe the coating cross-section

The coated plates were cross-sectioned to observe the coating microstructure as well as the coating substrate bonding. The samples were sectioned using a diamond saw developed at the North West University (NWU). The samples were then cold cast into an epoxy resin and polished using a Struers® Tegramin-20 polisher using SiC grit paper (320 to 1 000), Struers® MD Largo and finally Struers® MD Dac.

6.1.1. Coating Microstructure

Figure 6-2 to Figure 6-7 shows the top and cross-section SEM micrographs for samples PS_01, PS_02 and PS_03. The samples were sprayed to determine the effect of the increase in plasma power, the power was varied between 11.0 and 22 kW (which was the maximum limit of the system). Furthermore the samples had a spray distance of 100 mm, a particle injection of 15 m/s and were all conducted using an atmospheric plasma setup.

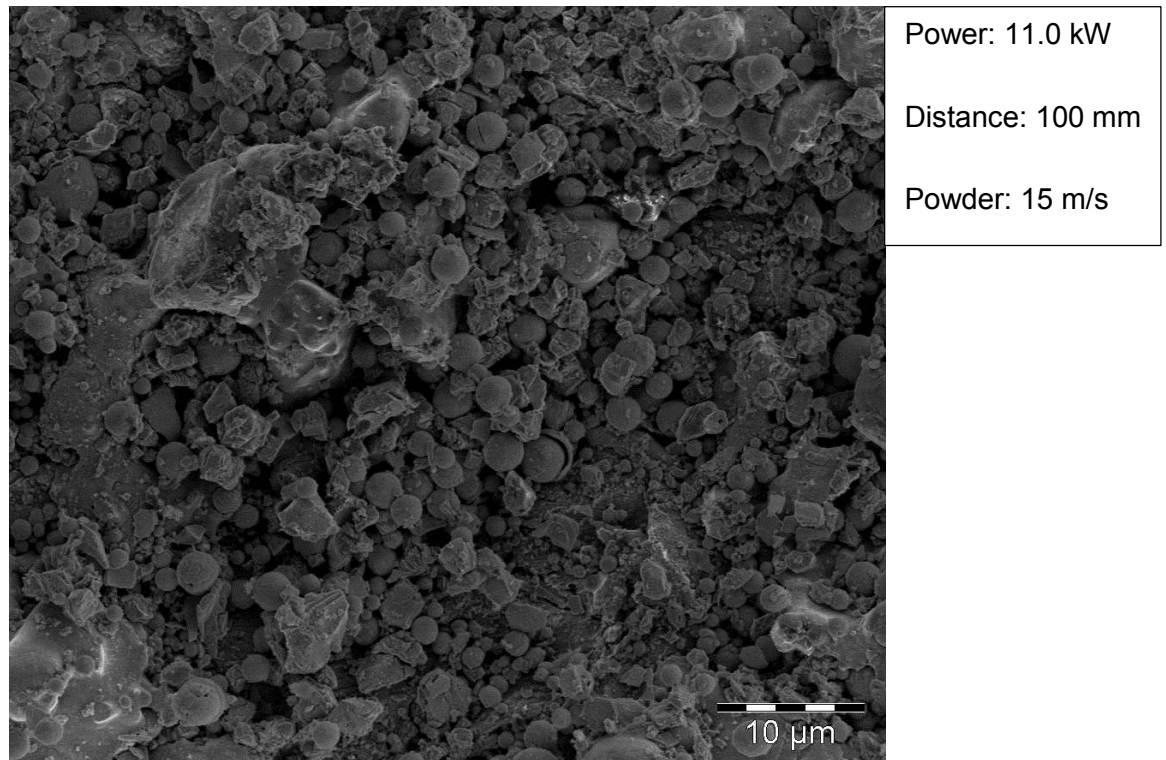


Figure 6-2: SEM micrograph showing un-deformed particles on the surface of sample PS_0 1

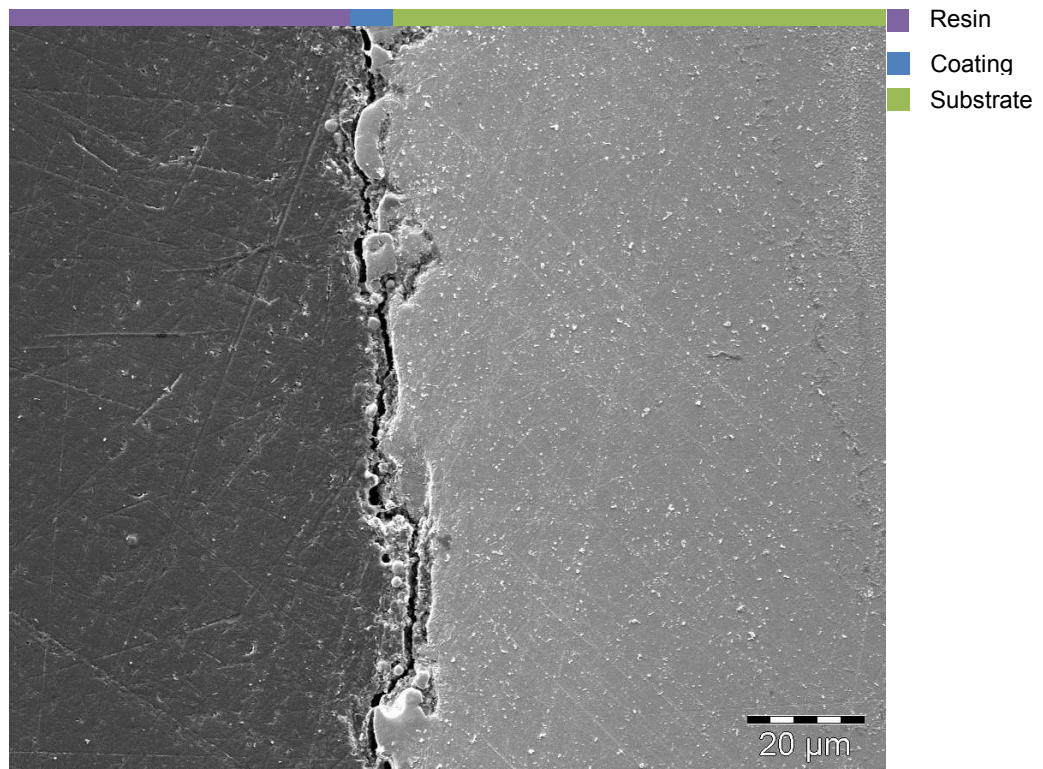


Figure 6-3: SEM micrograph of sample PS_01 cross-section showing lack of deposited coating as well as crack along the coating surface deposited at 11.0 kW

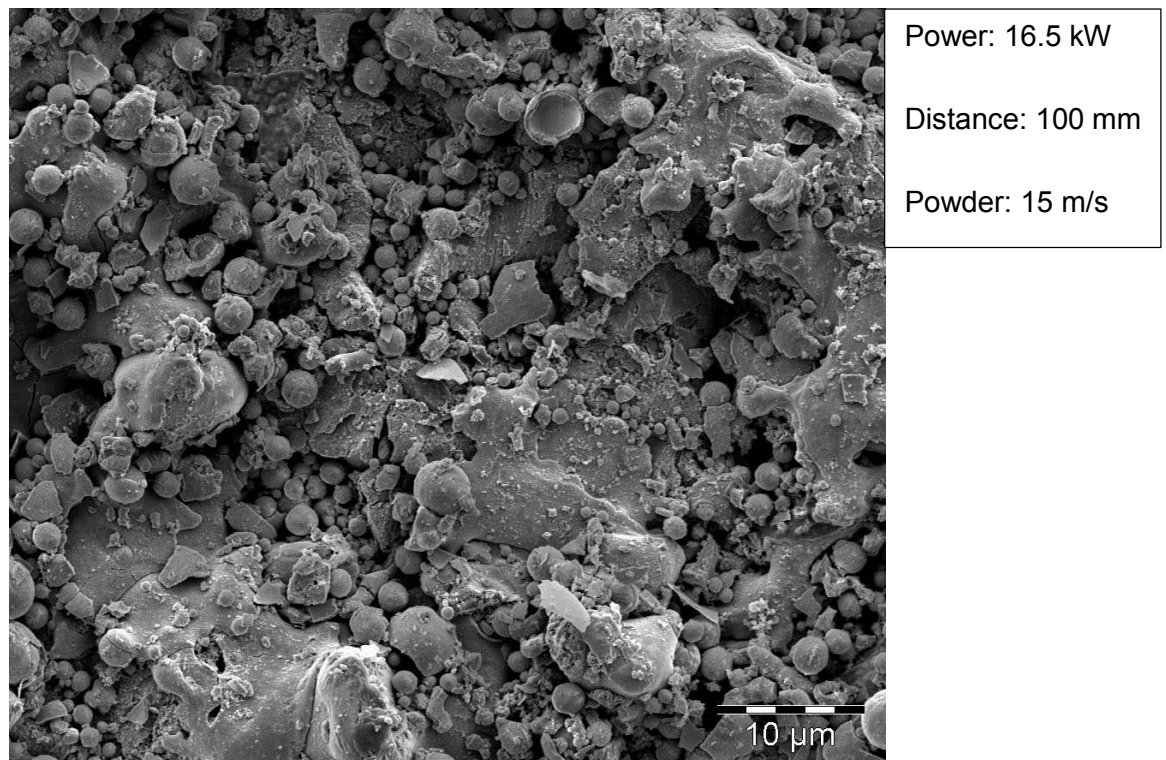


Figure 6-4: SEM micrograph showing un-deformed particles on the surface of sample PS_02

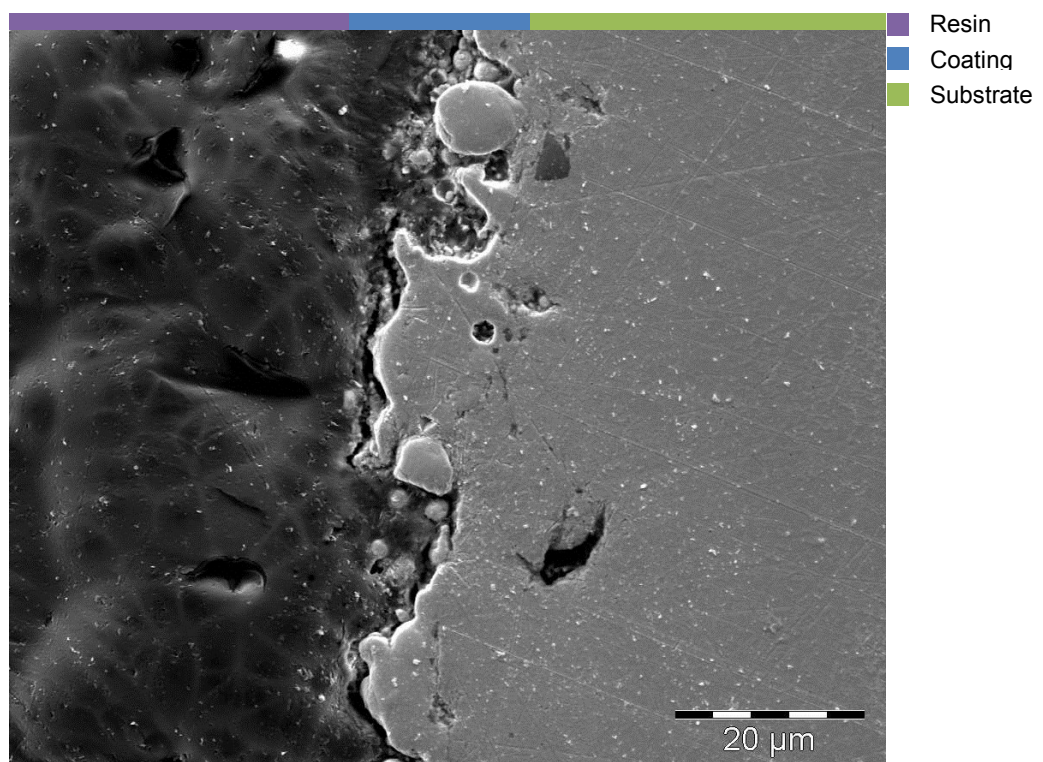


Figure 6-5: SEM micrograph of sample PS_02 cross-section showing a few deposited particles on the substrate surface deposited at 16.5 kW

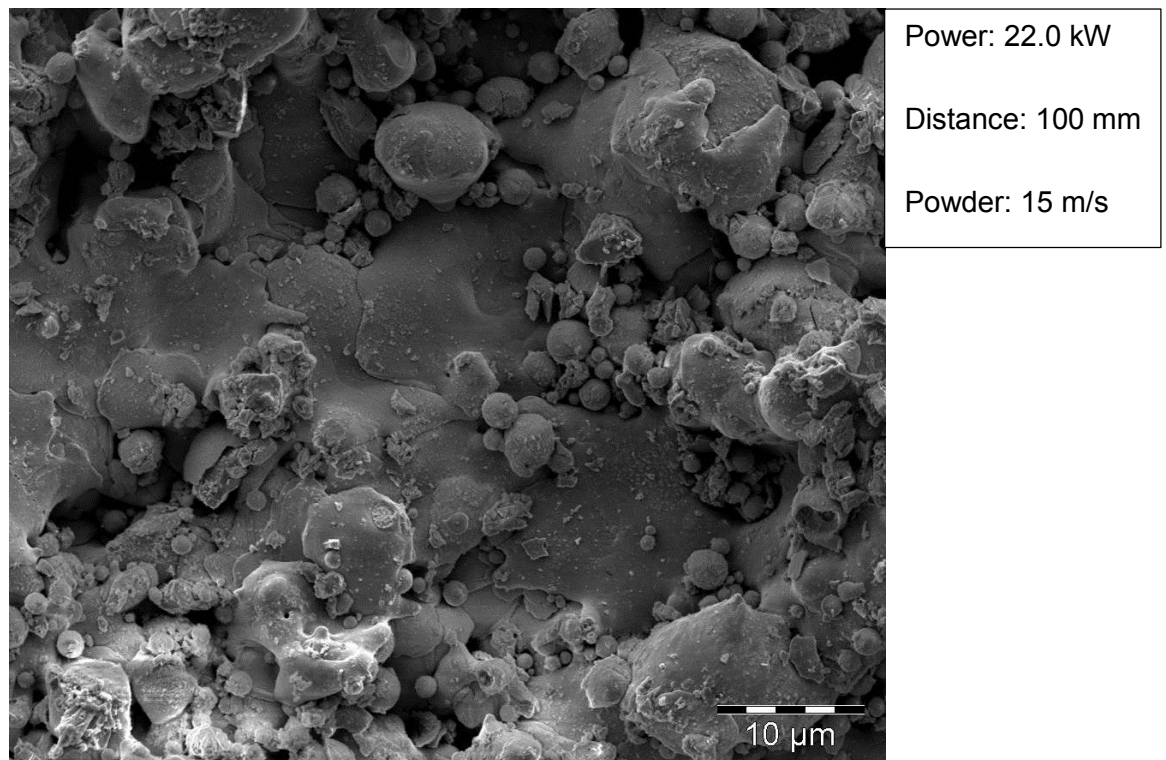


Figure 6-6: SEM micrograph showing high amount of deformed particles on the surface of sample PS_03

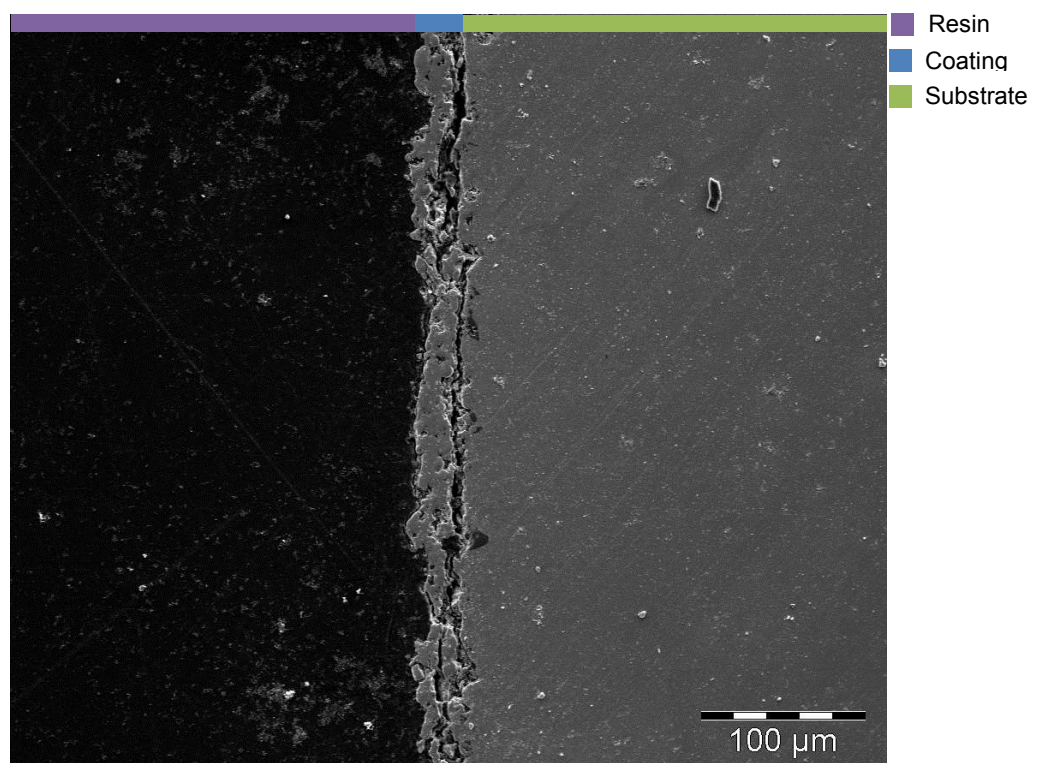


Figure 6-7: SEM micrograph of sample PS_03 cross-section showing a coating with weak adhesion to the substrate deposited at 22.0 kW

The SEM micrographs of the surface for samples PS_01 (Figure 6-2), PS_02 (Figure 6-4) and PS_03 (Figure 6-6) which was sprayed at 11.0 kW, 16.5 kW and 22.0 kW, show that as the power input increases the number of deposited particles increases. Samples PS_01 and PS_02 had non-uniformed surface structures whereas sample PS_03 started to show a more uniform structure with a few surface defects and un-deformed particles.

The cross-sections of samples PS_01 (Figure 6-3), PS_02 (Figure 6-5) and PS_03 (Figure 6-7) indicates that sample PS_03 had a denser, thicker and more uniform coating structure. This could be because of the higher power input resulting in increased velocity and particle melting which led to better powder deposition. But PS_03 cross-section also revealed weak substrate coating adhesion which can be an indication of weak wetting between the coating and substrate or residual stresses in the coating after post spraying operations or even both.

The lack of coatings at lower power inputs (11.0 and 16.5 kW) suggests that the coatings should be deposited at a higher power in order to increase deposition. Therefore the rest of the samples were coated using a high power input of 22.0 kW.

The following figures (*Figure 6-8 to Figure 6-11*) shows the top and cross-section SEM micrographs for samples PS_04 and PS_05. From the plasma simulations, it was observed that the closer the substrate was to the plasma torch the higher the particle velocity. Therefore aforementioned samples were coated at 60 and 80 mm using an atmospheric plasma setup, to observe the effect of spray distance on the coatings.

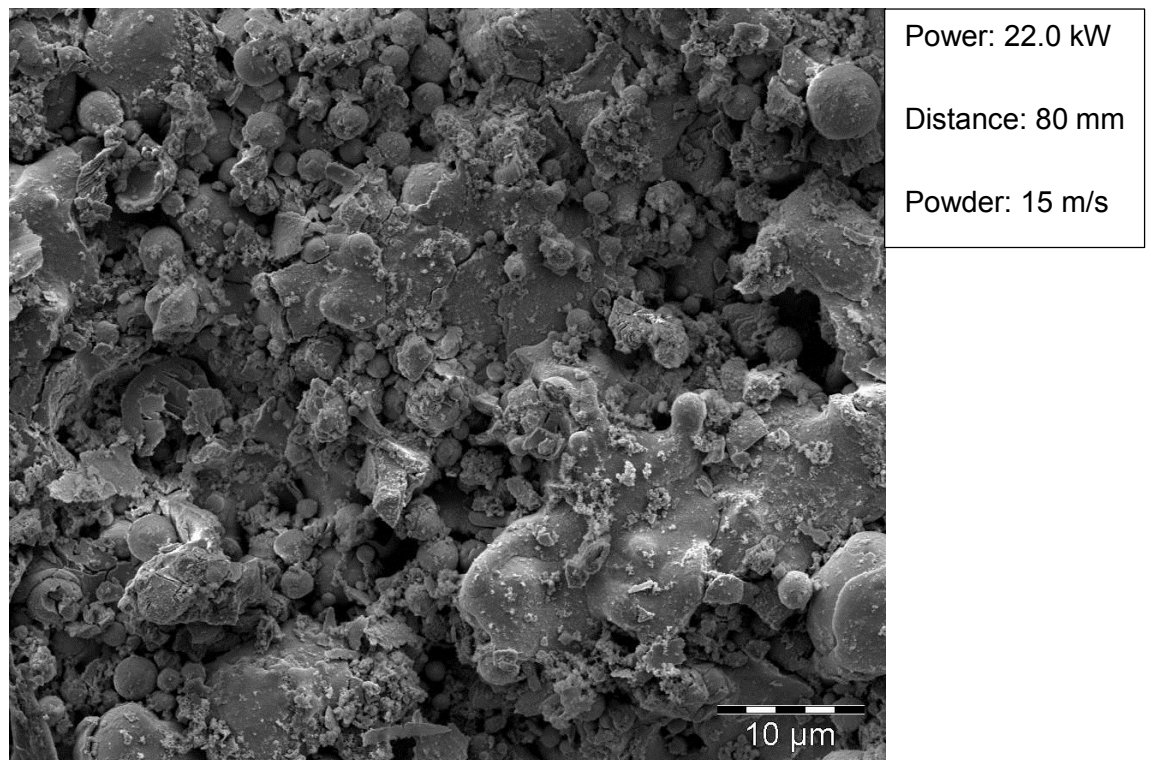


Figure 6-8: SEM micrograph showing deformed and un-deformed particles on the surface of sample PS_04

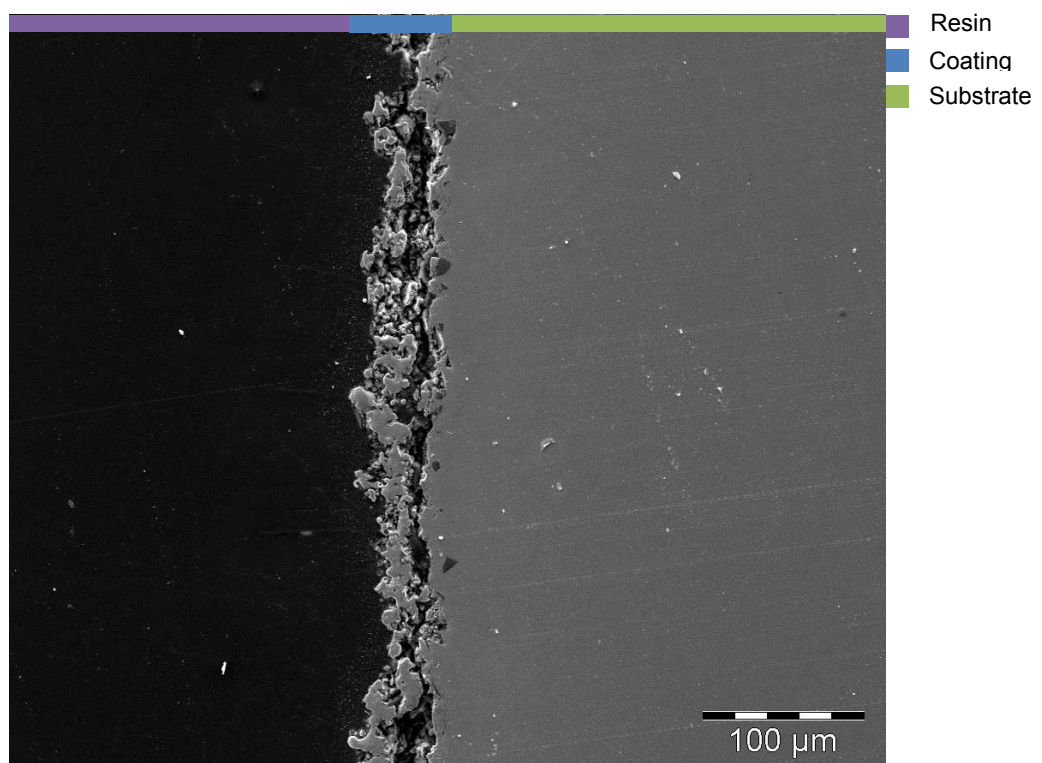


Figure 6-9: SEM micrograph of sample PS_04 cross-section showing the unsuccessful fusing of particles in coating as well as weak adhesion to the substrate

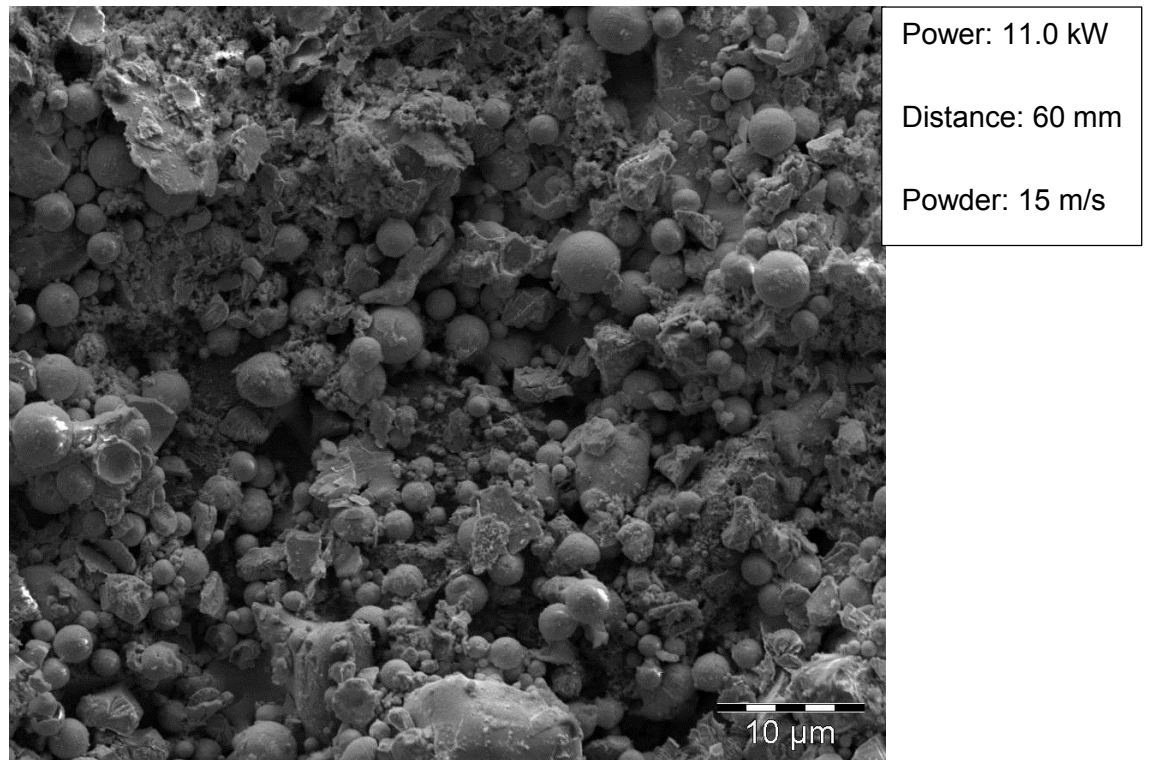


Figure 6-10: SEM micrograph showing un-deformed particles on the surface of sample PS_0 5

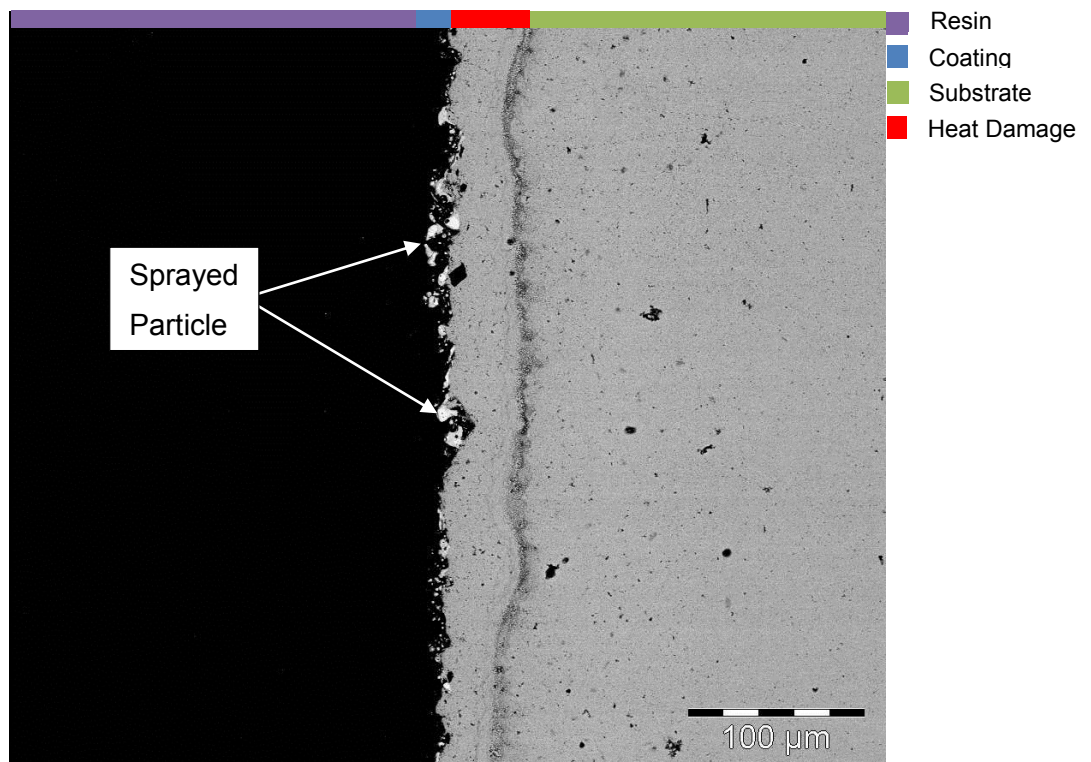


Figure 6-11: SEM micrograph of sample PS_05 cross-section showing heat damage to the substrate and deposited particles (BSE mode).

The surface of sample PS_04 (Figure 6-9), sprayed at 80 mm, had less un-deformed particles than the surface of sample PS_05 (Figure 6-11) which was sprayed at 60 mm. The surface structure of sample PS_04 had more un-deposited particle compared to that of sample PS_03.

The cross-section of sample PS_04 (Figure 6-9) indicated a coating with pores and weak adhesion. The pores can be ascribed to the splats not properly fusing together resulting in coating defects and voids. As with sample PS_03, sample PS_04 also had weak substrate coating adhesion. The cross-section of sample PS_05 (Figure 6-11) resulted in little to no deposited particles and the presence of a heat affected zone from the immense heat of the plasma at 60 mm. The low deposition could be an indication of the particles not being hot enough to deposit and instead just deflecting off the substrate surface.

The results from sample PS_04 and PS_05 showed that even though the particles had a higher velocity closer to the plasma torch, the particles did not have a sufficient temperature to allow deposition. It is thought that the particles injections should be optimised so that the particles will travel the optimum route through the centre of the plasma plume where the temperature and velocities are higher than the plasma fringes.

The following figures (*Figure 6-8 to Figure 6-11*) shows the top and cross-section SEM micrographs for samples PS_06 and PS_07. The samples were coated at 100 mm with a 22 kW plasma input using the atmospheric plasma spray setup. It was thought that the particle injection could still be optimised and thus sample PS_06 was deposited with a 10 m/s injection velocity and sample PS_07 with a 20 m/s injection velocity.

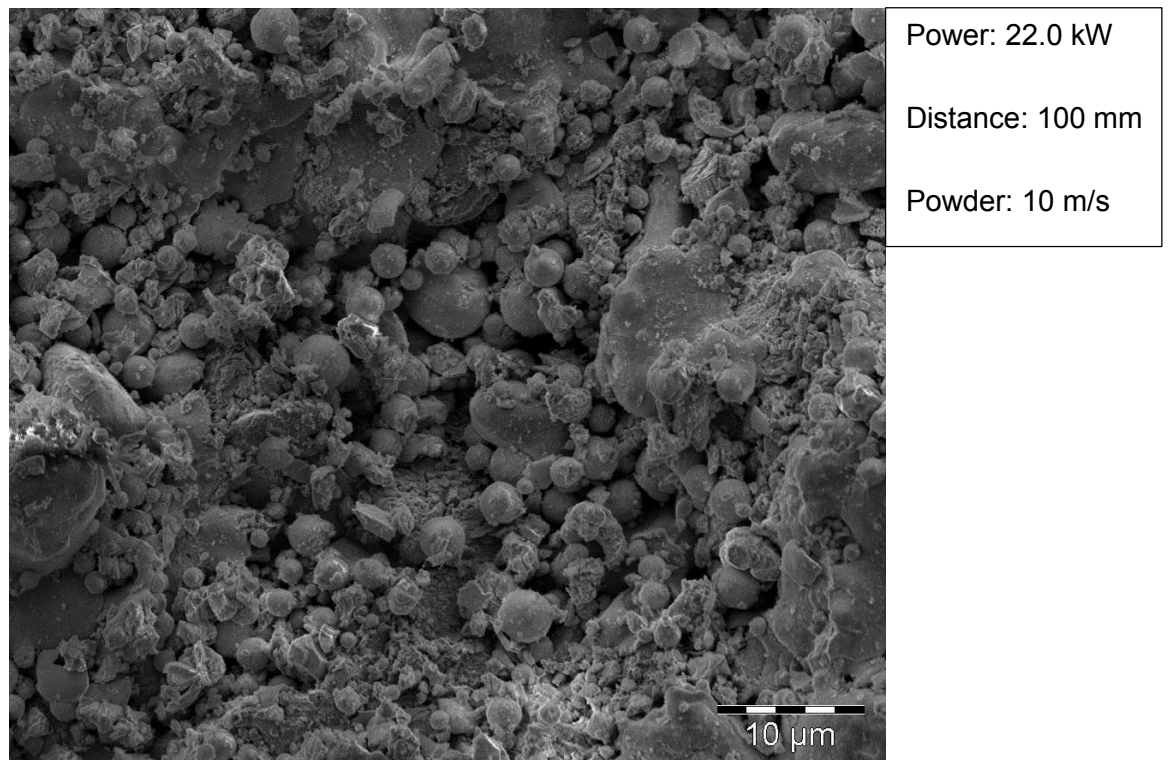


Figure 6-12: SEM micrograph showing un-deformed particles on the surface of sample PS_0 6

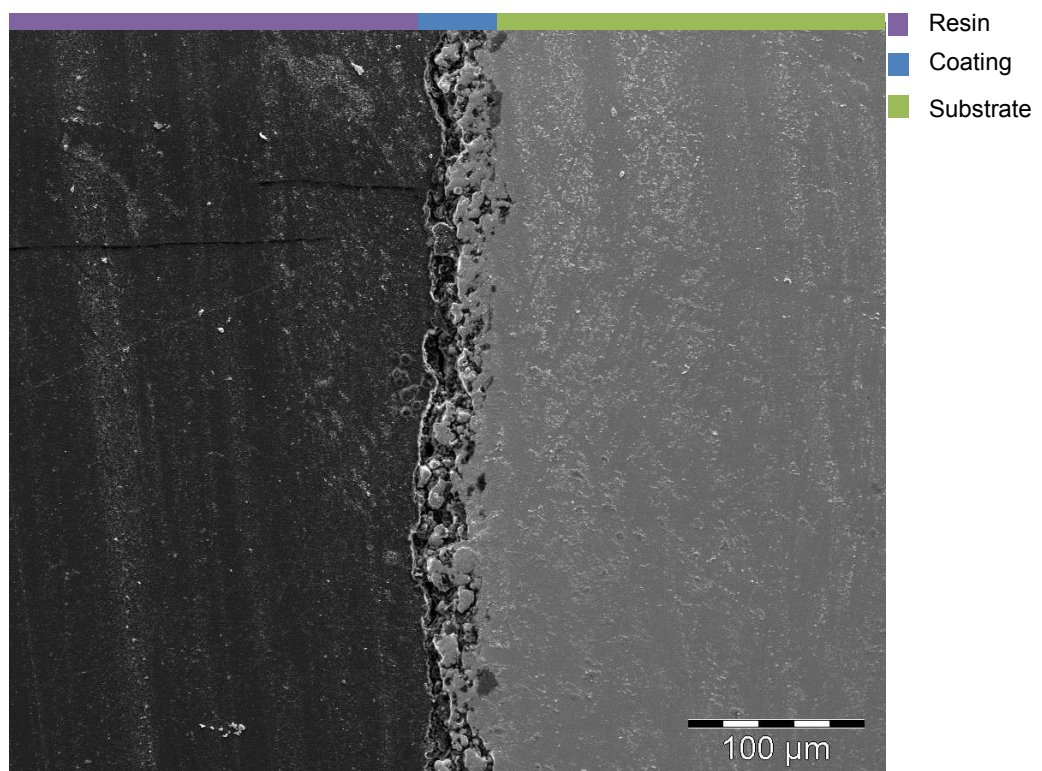


Figure 6-13: SEM micrograph of sample PS_06 cross-section showing good mechanical interlocking of particles to substrate

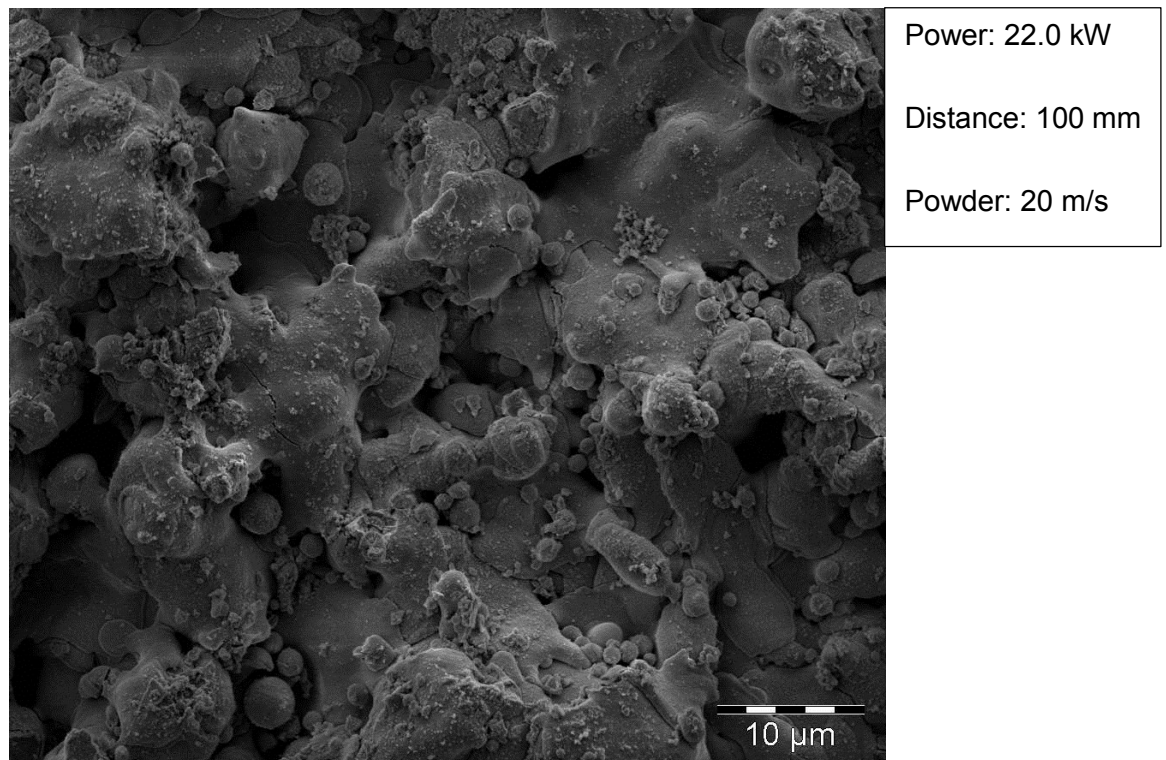


Figure 6-14: SEM micrograph showing deformed particles on the surface of sample PS_07

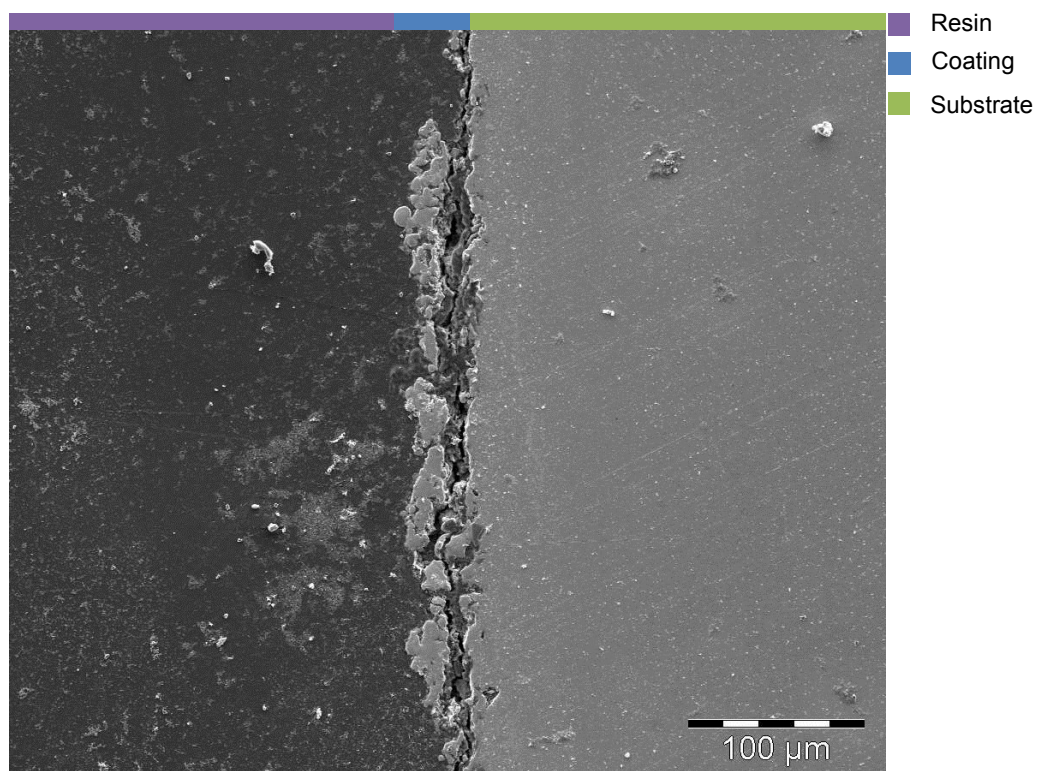


Figure 6-15: SEM cross-sectional view of sample PS_07 deposited with a particle injection of 20 m/s

The particle injection speed was varied from 15 m/s (PS_03) to 10 m/s for sample PS_06 and 20 m/s for sample PS_07. It was observed that the surface of sample PS_06 (Figure 6-12) had more un-melted particles than sample PS_07 (Figure 6-14). This was contrary to the cross-sections of the coatings which revealed that sample PS_07 (Figure 6-15) had almost no coating whereas sample PS_06 (Figure 6-13) had a coating with good mechanical interlocking but a large number of voids. A large number of voids is the result of the un-melted particles not properly fusing creating cavities and coating defects.

It is thought that for sample PS_07 the higher injection velocity cooled the plasma plume resulting in many particles not properly depositing upon impact with the substrate. Whereas with sample PS_06 only the largest particles, with greater mass and higher momentum, were injected into the plasma plume while the smaller particles were either ejected or remained on the fringes. The increased substrate and coating adhesion could be attributed to the larger particles (greater mass) hitting the substrate with a higher momentum resulting in improved mechanical interlocking or the lack of residual stresses as the coating was porous and non-uniform.

The possibility of oxygen contamination remains a strong factor with atmospheric plasma spraying because of air engulfment, as discussed in Chapter 4. Therefore samples PS_BL_08 (Figure 6-16) and PS_BL_09 (Figure 6-17) were both deposited under an Ar atmosphere inside of the spraying chamber using the same parameters as PS_03 (plasma power input: 22.5 kW, spray distance: 100 mm and particle injection velocity: 15 m/s).

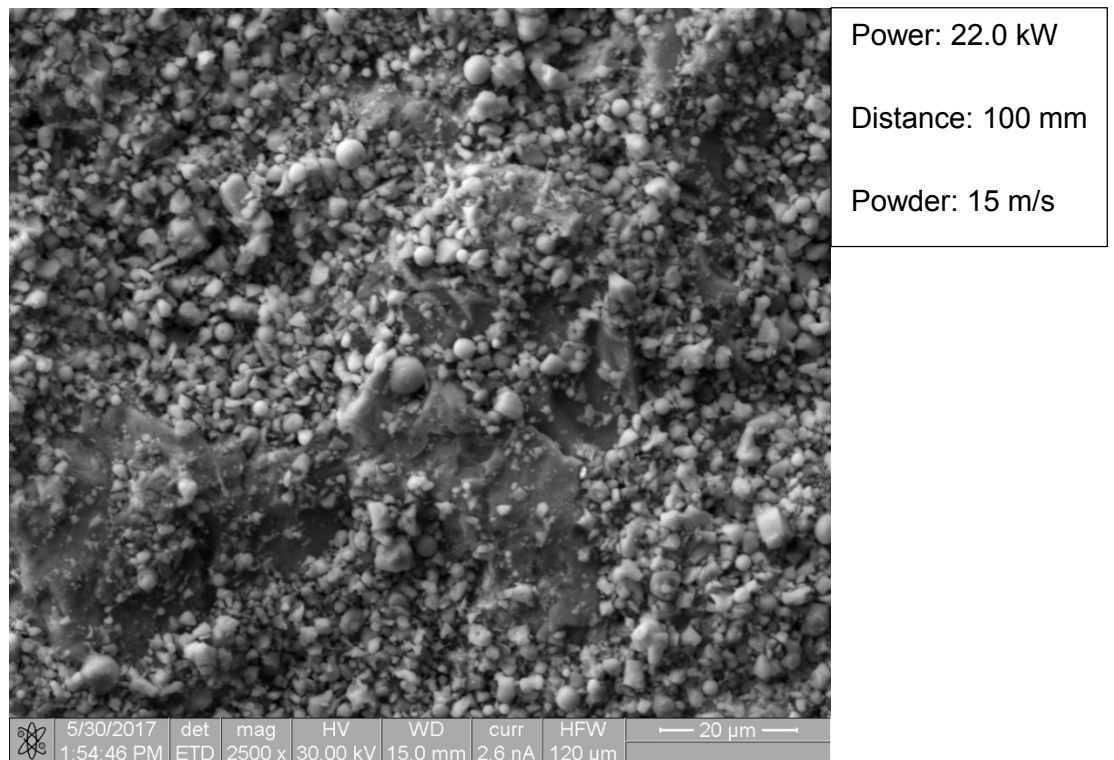


Figure 6-16: SEM micrograph of sample PS_08 with un-deposited particles on the surface

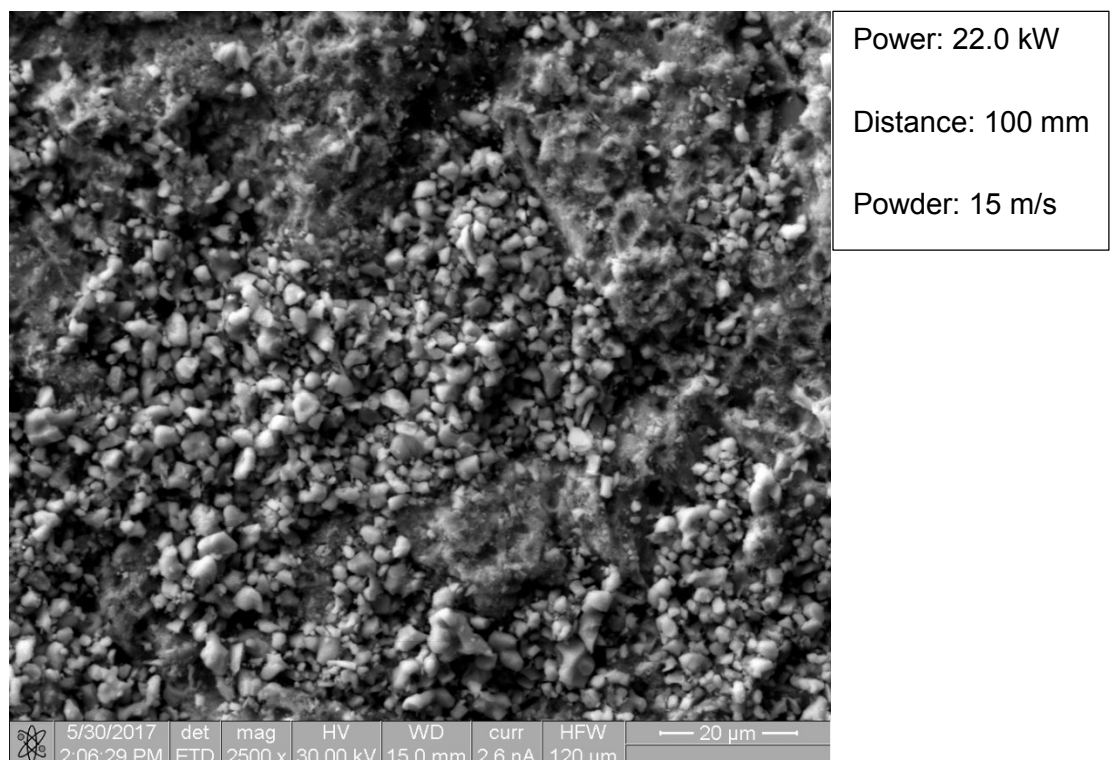


Figure 6-17: SEM micrograph of sample PS_09 with un-deposited particles on the surface

Because of the lack of deposited particles on the surface of the samples, it was thought unnecessary to cross-section samples PS_08 and PS_09. The surface micrographs of both the coatings showed that the majority of the sprayed powder remained un-melted with some spherical particles on the surface indicating some form of heat treatment in the particles. It is thought that the particles remained un-melted because of the higher melting of ZrC compared to oxygen/nitrogen contaminated ZrC (Toth, 1971). Both of the samples displayed inconsistent particle deposition with large open areas through which the substrate can be seen. This indicates that most of the sprayed particles rebounded off of the substrate because of inadequate particle temperature.

6.1.2. Coating Composition

EDS was used in the elemental mapping mode to observe the elements present in the coating structure. Using the SEM's back-scatter electron (BSE) function many bright spots surrounded by darker areas in the coating structures could be observed (Figure 6-18). Hu *et al.* (2015) describe these bright spots as the un-melted ZrC core whereas the darker grey areas are contaminated with oxygen forming ZrO_2 . It is thought that because ZrC has many stable sub-stoichiometry ratios that the grey areas may, in fact, be a stable zirconium oxycarbide.

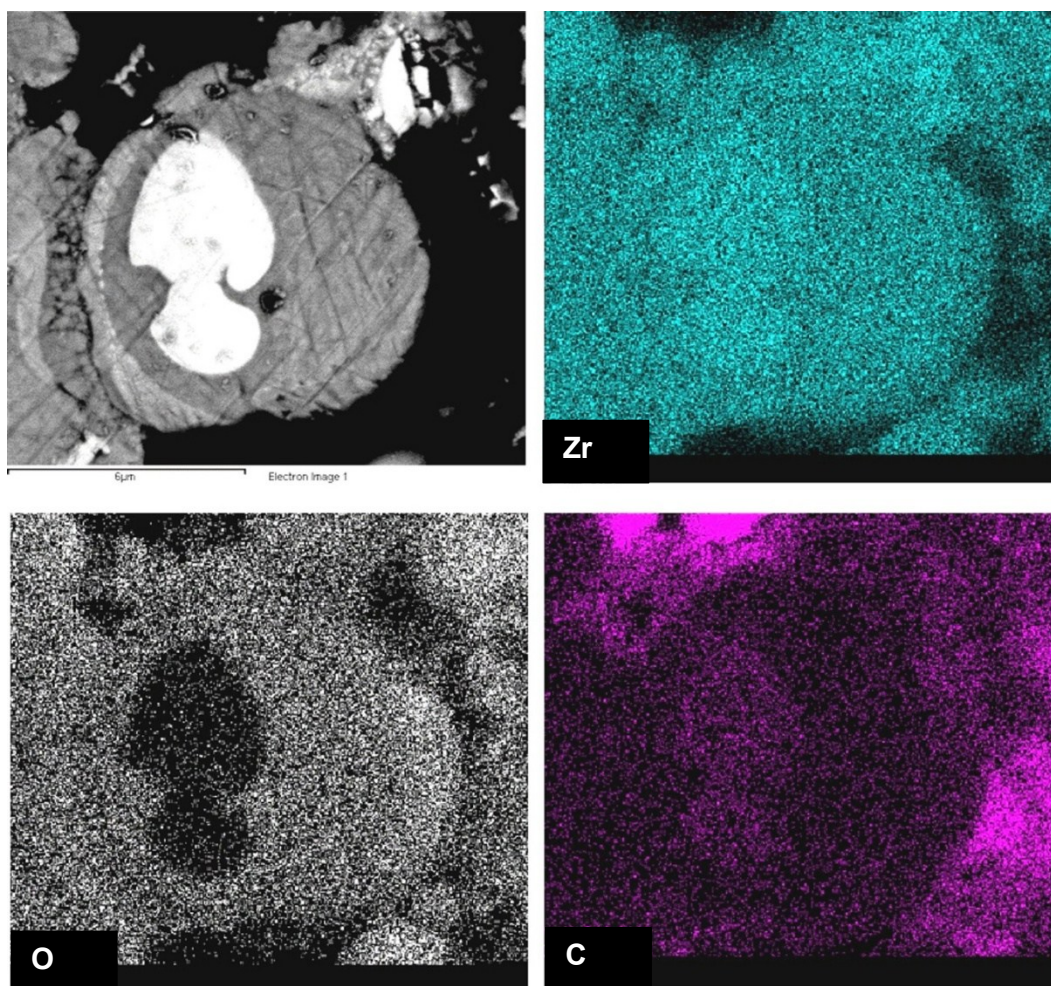


Figure 6-18: SEM cross-section of sample PS_04 showing un-melted core of ZrC particle with elemental mapping. The coloured dots denote the elemental distribution.

Cross-sectioned SEM micrographs in BSE mode of the samples are shown Figure 6-19 (PS_02), Figure 6-20 (PS_03), Figure 6-21 (PS_04) and Figure 6-22 (PS_06). Samples PS_01, PS_05 and PS_07 were not future investigated because of the lack of deposited particles on the substrates. But it was thought to investigate samples PS_08 and PS_09 to confirm the composition of the particles found on the samples surfaces, therefore elemental mapping analysis was done for these two samples (Figure 6-23 and Figure 6-24).

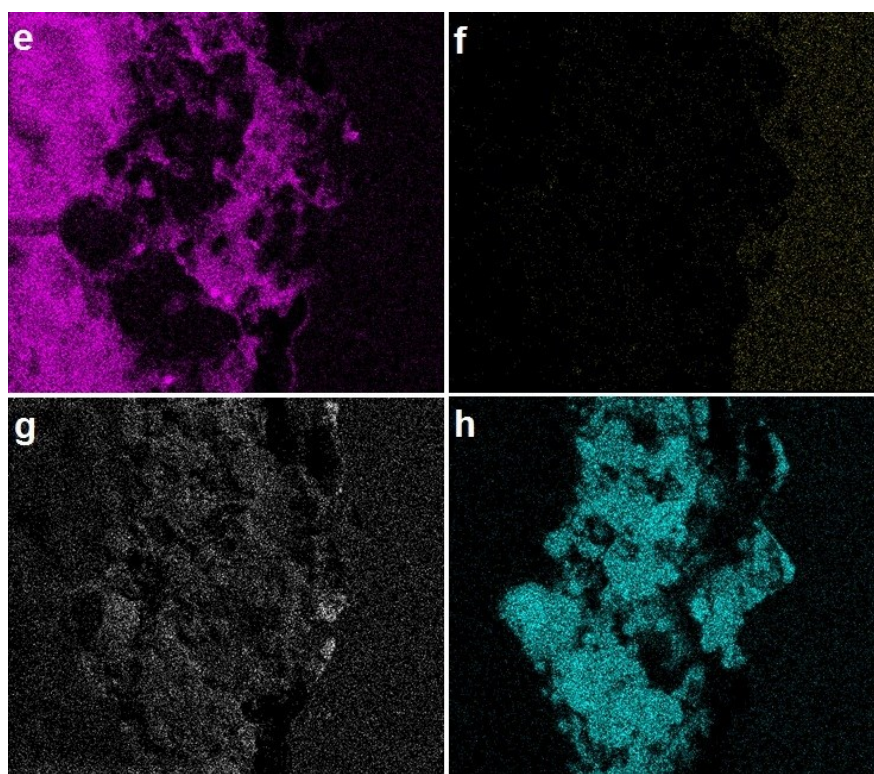
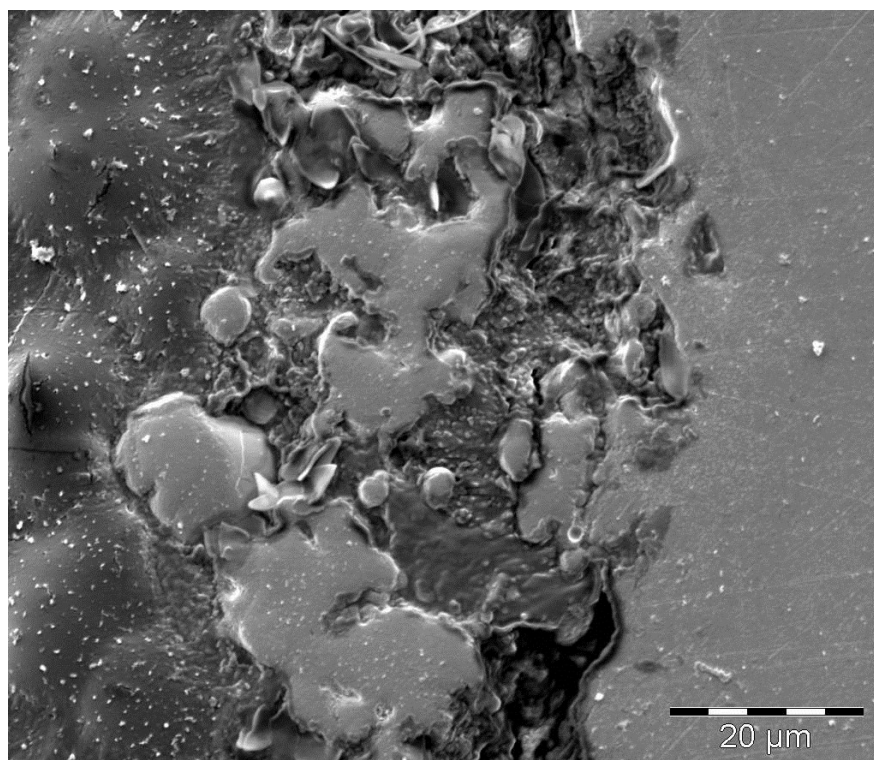


Figure 6-19: SEM cross-section of sample PS_02 with elemental mapping: (e) carbon (f) iron (g) oxygen (h) zirconium (BSE was unavailable). The coloured dots denote the elemental distribution.

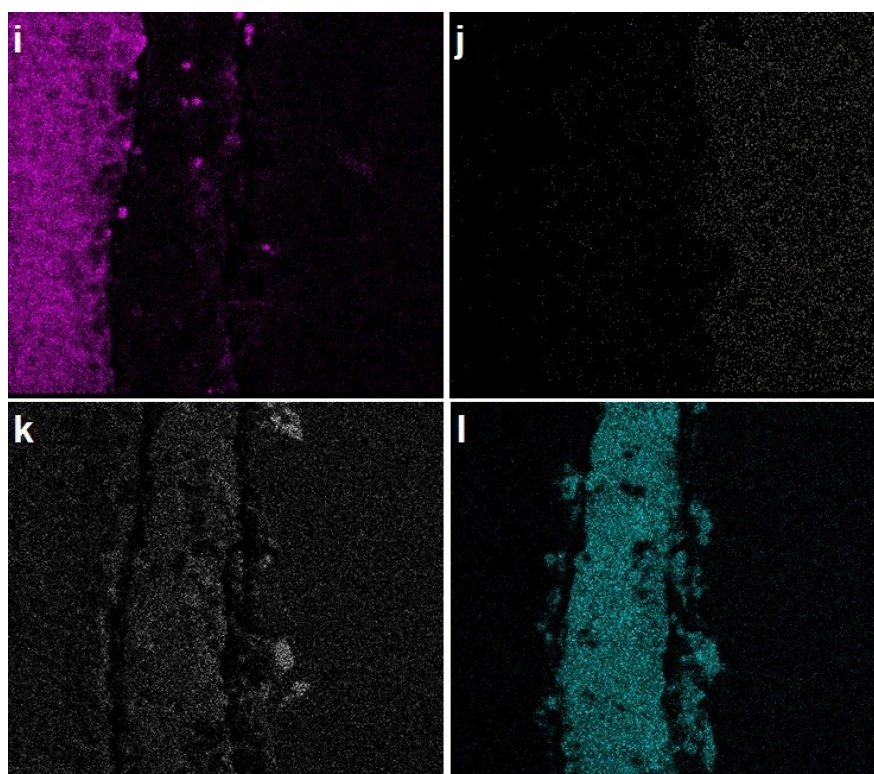
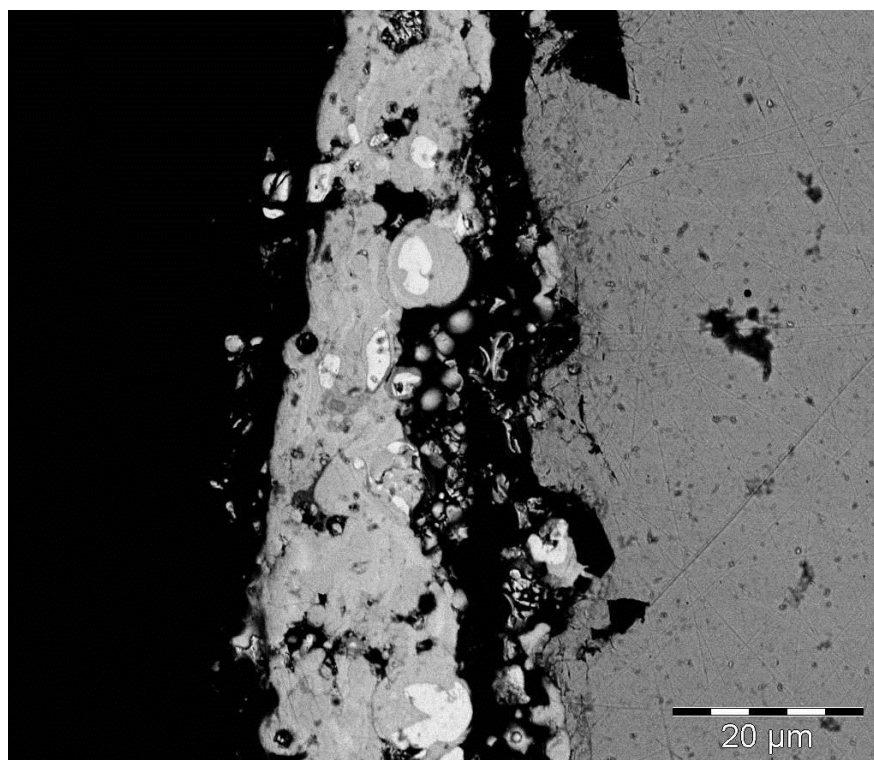


Figure 6-20: SEM back scatter cross-section of sample PS_03 with elemental mapping: (i) carbon (j) iron (k) oxygen (l) zirconium. The coloured dots denote the elemental distribution.

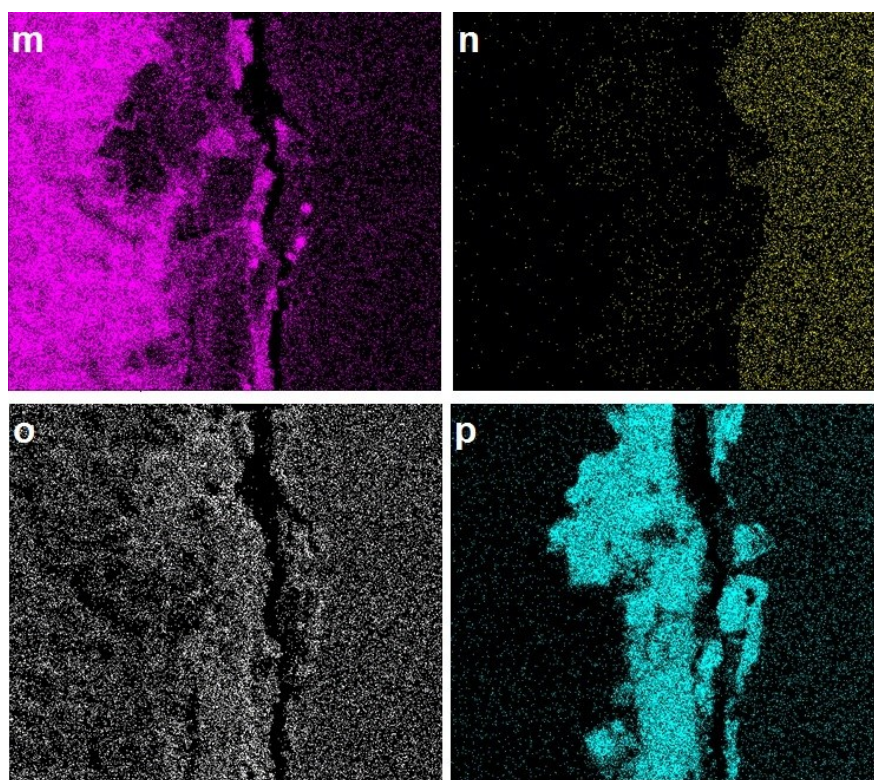
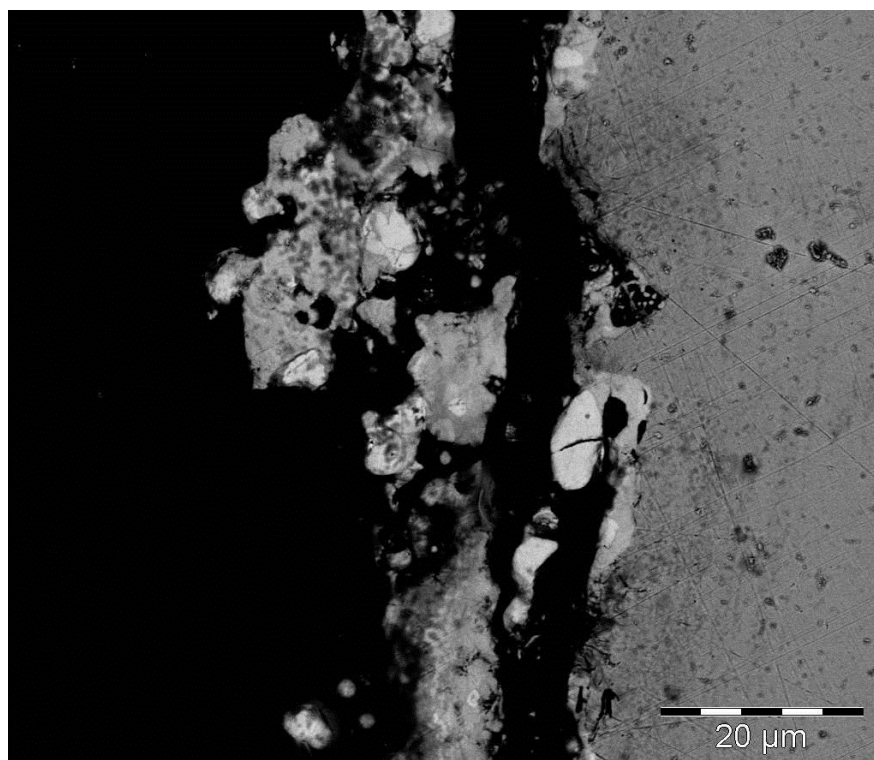


Figure 6-21: SEM back scatter cross-section of sample PS_04 with elemental mapping: (m) carbon (n) iron (o) oxygen (p) zirconium. The coloured dots denote the elemental distribution.

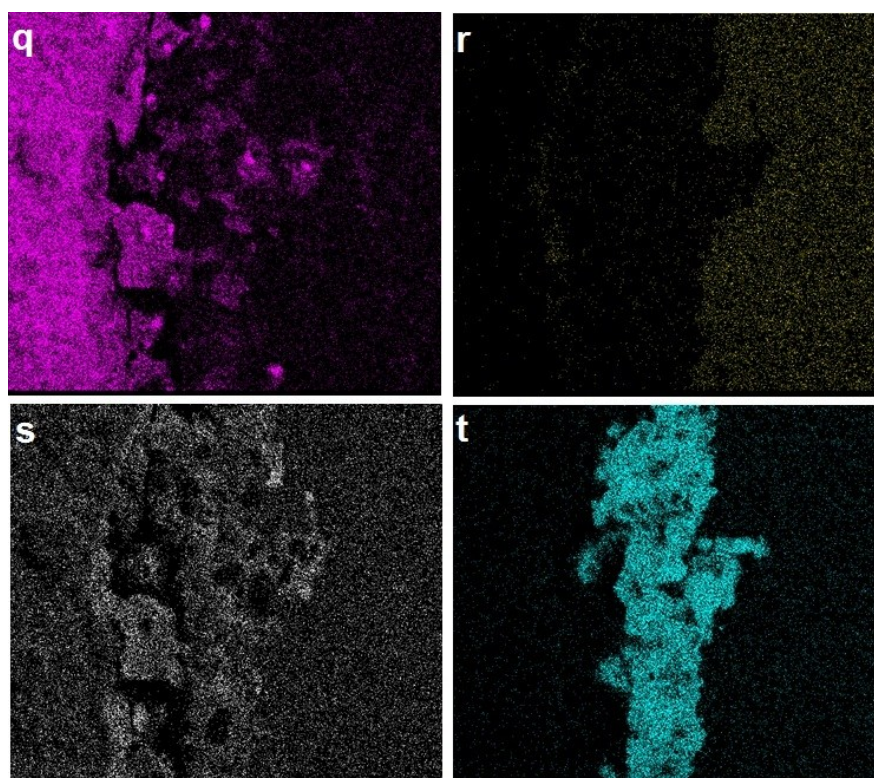
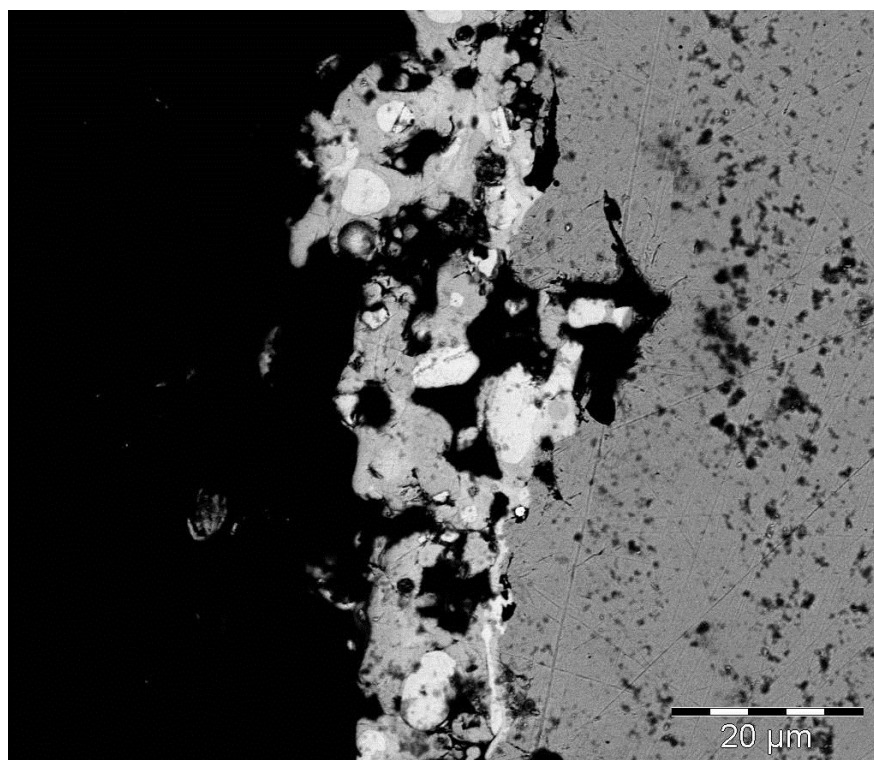


Figure 6-22: SEM back scatter cross-section of sample PS_06 with elemental mapping: (q) carbon (r) iron (s) oxygen (t) zirconium. The coloured dots denote the elemental distribution.

It was observed with elemental mapping that a high concentration of oxygen was present in all the cross-sectioned coating structures (Figure 6-19, Figure 6-20, Figure 6-21 and Figure 6-22). This indicates that the atmospheric spray runs were in fact contaminated with oxygen from air engulfment during spraying. The coatings also had low concentrations of carbon, with the exception of small carbon islands found in the coatings. These carbon islands correlating well with the bright spots thought to be ZrC. Although un-melted particles is a common occurrence in plasma spray coatings, it is an indicator of unsuccessful particle heating.

When comparing sample PS_03 (Figure 6-20) with sample PS_06 (Figure 6-22), the latter has more and larger bright spots than the former. This can be due to the difference in the particle injection velocity, where PS_03 was 15 m/s and PS_06 was 10 m/s. The lower injection velocity resulted in only the larger particles being injected into the centre of the plasma plume. These larger particles are more difficult to melt and can be ascribed to the large number of un-melted cores observed in sample PS_06.

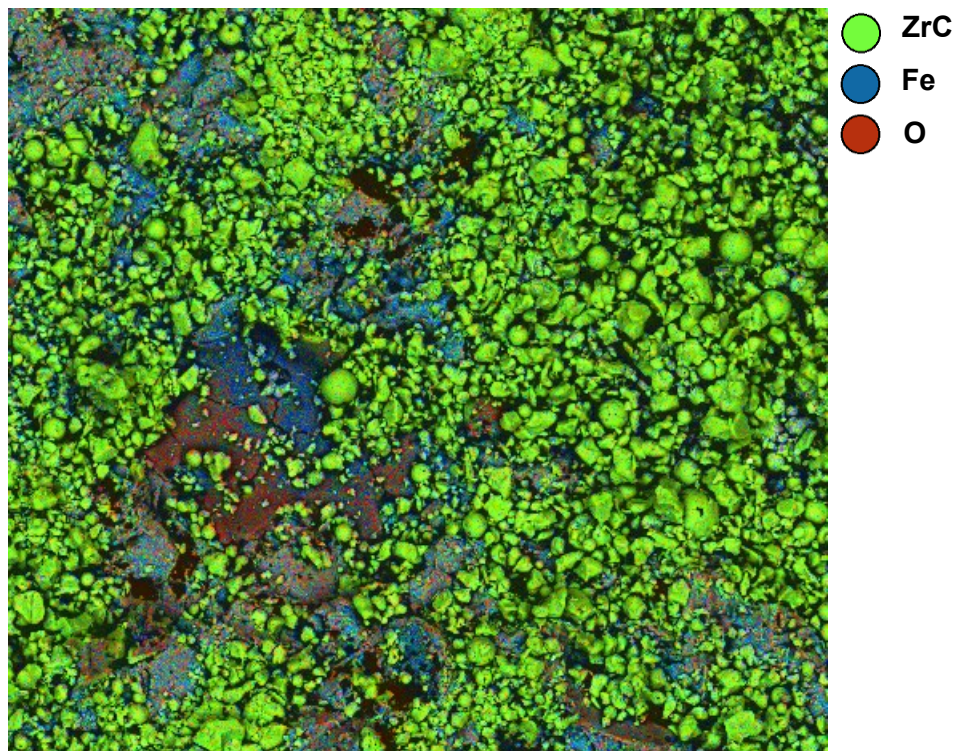


Figure 6-23: Elemental mapping of sample PS_08 illustrating Zr and C as combined particles on the surface of the substrate

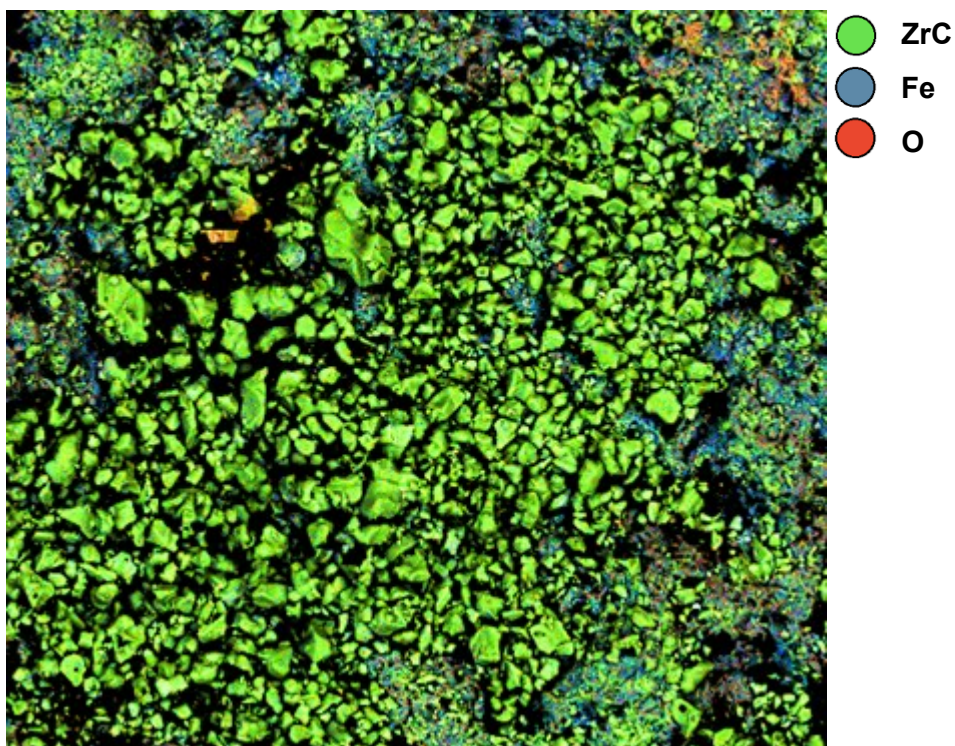


Figure 6-24: Elemental mapping of sample PS_09 illustrating Zr and C as combined particles on the surface of the substrate

The surface mapping of samples PS_08 (Figure 6-23) and PS_09 (Figure 6-24) was observed where it was seen that both samples had no oxygen matching the sprayed particles on the substrate, whereas the carbon and zirconium correlated well with each other and the sprayed particles. This suggests that the powder had no oxygen contamination and it is suspected that the particles on the substrate surface remained ZrC.

The composition of the coatings was confirmed using an XRD technique. The resulting XRD analyses are shown in Figure 6-25, Figure 6-26, Figure 6-27 and Figure 6-28, where the presence of ZrC, ZrO₂ and Cr diffraction peaks were identified. The Cr present in the XRD analysis is suspected to be from the substrate which was stainless steel 304.

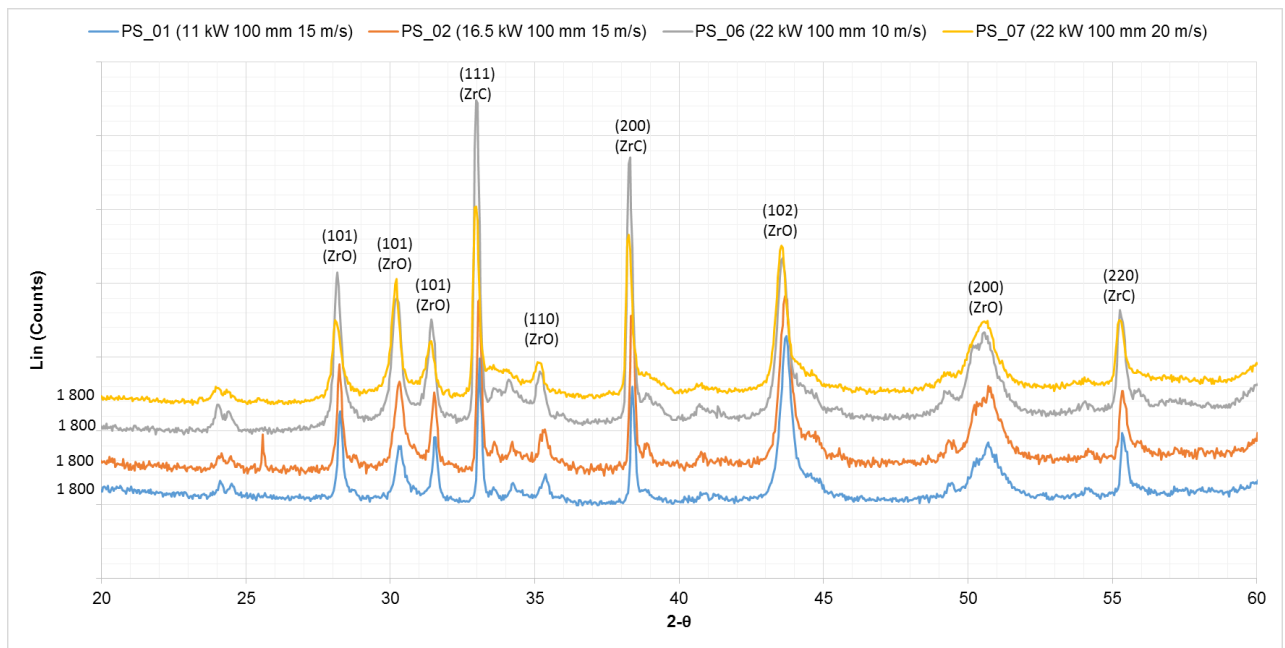


Figure 6-25: Superimposed XRD analysis for samples PS_BL_01, PS_BL_02, PS_BL_06 and PS_BL_07

The XRD patterns of samples PS_01, PS_02, PS_06 and PS_07 (Figure 6-25) correlated well with each other indicating that the samples had the same composition. The peaks observed correlated with that of the diffraction patterns for ZrC and ZrO₂. The presence of ZrO₂ is an indication of oxygen contamination, while samples PS_01 (11.0 kW) and PS_02 (16.5 kW) were done at lower power inputs compared to samples PS_06 and PS_07 (22.0 kW) which had different injection velocities to the aforementioned samples.

Therefore it is thought that the coatings from the before mentioned samples were deposited at lower temperatures, because of the lower plasma power input for PS_01 and PS_02 and the particle injection velocity for PS_06 and PS_07 where the majority of the particles did not successfully penetrate the plasma plume and was therefore not exposed to high temperatures. It is thus thought that a higher amount of un-melted particles are included in these coatings.

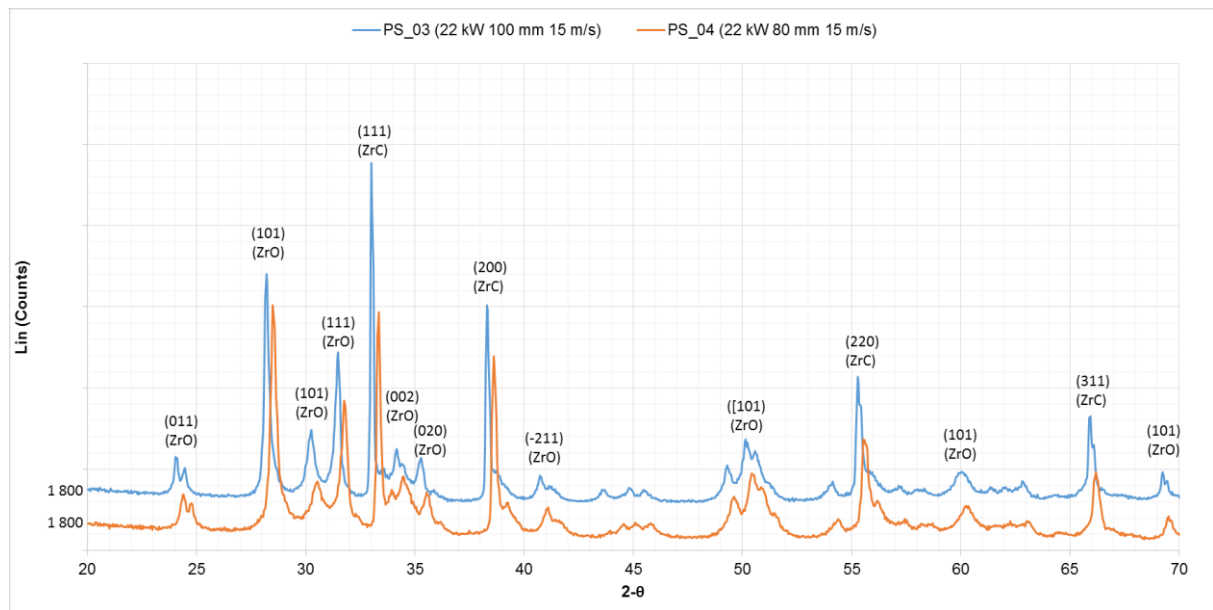


Figure 6-26: Superimposed XRD analysis for samples PS_BL_03 and PS_BL_04

It was found that samples PS_03 and PS_04 (Figure 6-26) also shared the same peaks which correlated with the diffraction pattern of ZrC and ZrO₂. The samples had the same parameters with the exception of the spray distance where PS_03 was 100 mm and PS_04 was 80 mm. Both of the samples were coated under nearly identical conditions explaining the matching diffraction patterns.

It should be noted that the displacement observed between the two patterns is due to a faulty analysis.

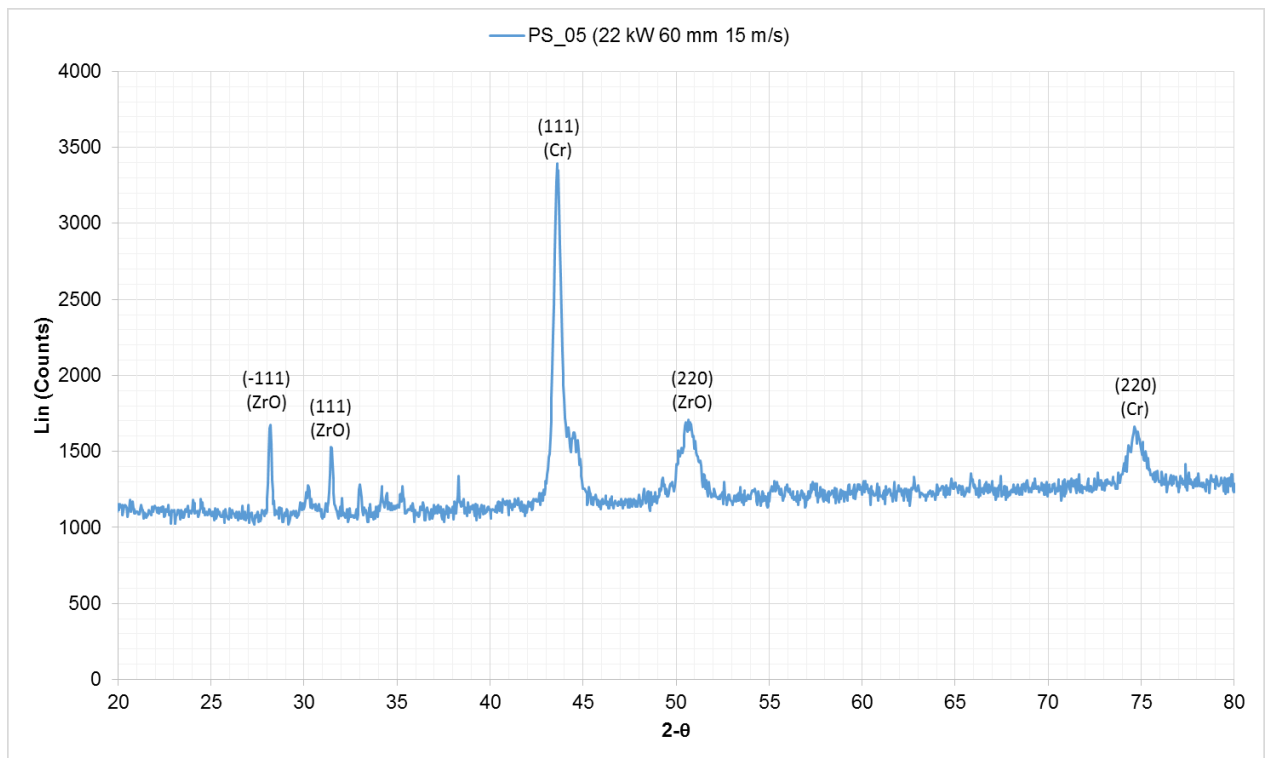


Figure 6-27: Superimposed XRD analysis for sample PS_BL_05

Sample PS_05 (Figure 6-27) had a diffraction pattern, unlike any other sample as it only contained ZrO and Cr with no traces of ZrC. The sample had the same parameters as PS_03 but a substrate distance of 60 mm. It was thought the distance was too short and all the ZrC particle rebounded off of the substrate surface with the only particles depositing being the ones oxidised resulting in the ZrO₂ peaks identified on the surface of the sample.

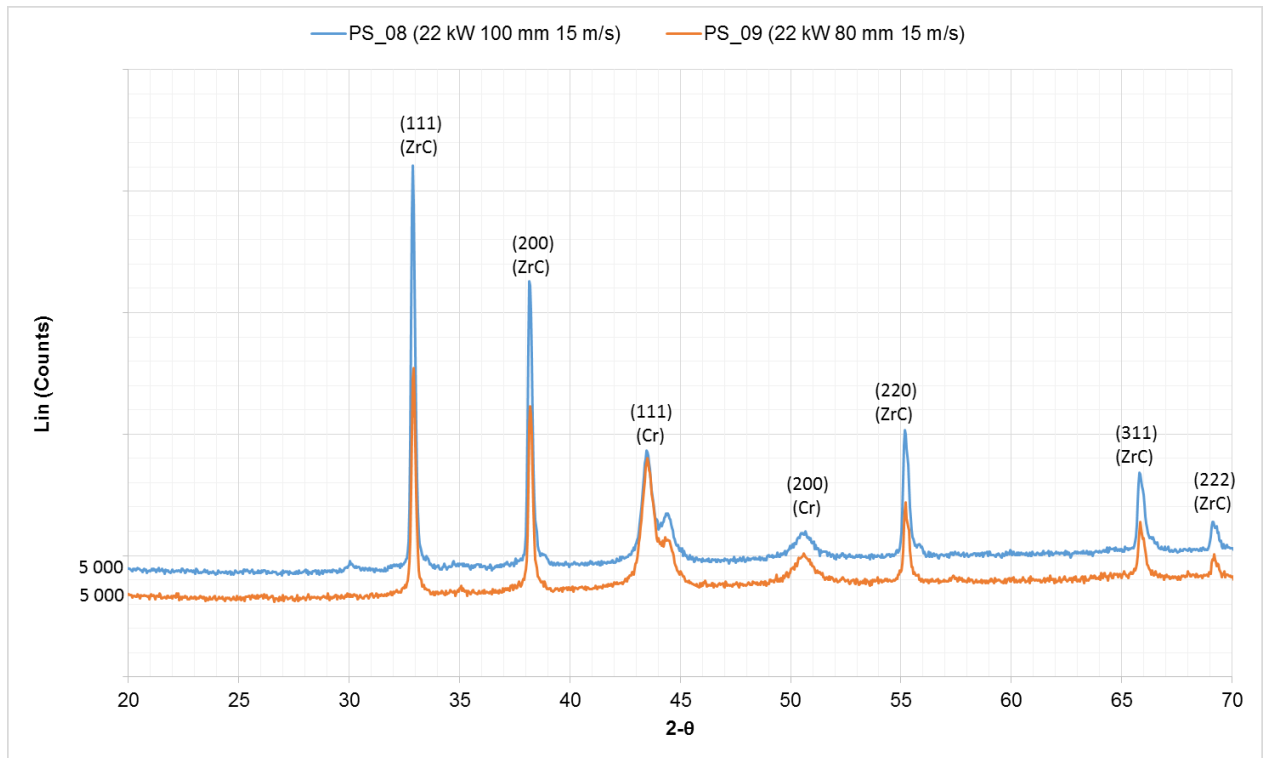


Figure 6-28: Superimposed XRD analysis for samples PS_BL_08 and PS_BL_09

Observing samples PS_08 and PS_09 (Figure 6-28) it was found that samples peaks correlated well with the diffraction pattern of ZrC. This is in agreement with the EDS mapping that also showed no oxygen contamination on the surface of samples PS_08 and PS_09.

6.2. Conclusion

In this chapter, the coating analysis results from the experimental study were reported and discussed.

This research investigated the influence of plasma power input, substrate distance, particle injection and spraying atmosphere on the deposited coatings was investigated. The results showed that as the plasma power increases so does the deposition of the powder were the higher power input samples had denser and more homogeneous coatings than those with lower power inputs. The substrate distance determined that even though according to the simulations the ideal spraying distance was 60 mm the plasma plume was still too hot resulting in heat damage to the substrate. It was observed that the highest particle deposition occurred at a spray distance of 100 mm. The powder injection revealed that the best injection velocity was 15 m/s. The lower injection velocity led to fewer particles being injected into the plasma and a higher velocity coating had a large number of voids due to the unsuccessful melting of the sprayed particles. Improved adhesion was also found at a lower injection velocity but the coating was non-uniform and porous.

The EDS mapping and XRD revealed that all the samples coated under atmospheric conditions had been contaminated with oxygen. Whereas the inert plasma spray runs, done under an Ar atmosphere, had no oxygen contamination but the powder did not deposit. It was confirmed by XRD that the inert samples were in fact ZrC. This is because of the lower melting point of zirconium oxycarbide and zirconium oxide which explains the deposition of the coatings during atmospheric spraying.

In view of the oxidation of the atmospheric spray runs valuable information could still be obtained through investigating the atmospheric spray samples.

Bibliography

Chandra, S. & Fauchais, P. 2009. Formation of Solid Splats During Thermal Spray Deposition. *Journal of Thermal Spray Technology*, 18(2):148-180.

Fauchais, P.L., Heberlein, J.V.R. & Boulos, M.I. 2014. Thermal Spray Fundamentals. United States of America: Springer US.

Herman, H. 1991. Powders for Thermal Spray Technology. *KONA Powder and Particle Journal*, 9:13.

Hu, C., Ge, X., Niu, Y., Li, H., Huang, L., Zheng, X. & Sun, J. 2015. Influence of Oxidation Behavior of Feedstock on Microstructure and Ablation Resistance of Plasma-Sprayed Zirconium Carbide Coating. *Journal of Thermal Spray Technology*, 24(7):1302-1311.

Jacobsen, R.T. & Stewart, R.B. 1973. Thermodynamic Properties of Nitrogen Including Liquid and Vapor Phases from 63K to 2000K with Pressures to 10,000 Bar. *Journal of Physical and Chemical Reference Data*, 2(4):757-922.

Vardelle, A., Moreau, C., Themelis, N.J. & Chazelas, C. 2015. A Perspective on Plasma Spray Technologie. *Plasma Chemistry & Plasma Process*, 35(3):19.

CHAPTER 7

SUMMURAY, CONCLUSION & RECOMMENDATIONS

“There is no real ending.

It’s just the place where you stop the story”

-Frank Herbert (1920 – 1986)

7.1. Summary

ZrC has become a promising material for a wide range of applications in different industries because of its high melting point, hardness and being chemically inert. Because of these properties and its low nuclear cross-section, ZrC has gained great interest in the nuclear energy field as a protective coating for Zr-alloy fuel rods.

Many different coating techniques already exist and several techniques have been identified in order to deposit ZrC coatings. These coating techniques are CVD, PLD, Magnetron Sputtering and plasma spraying. It was argued that plasma spraying process was the best suitable for depositing ZrC on Zr-alloy fuel rods because it is flexible and can easily be adapted for the intended purpose of coating fuel rods. The process also has a fast deposition rate and low operating cost.

In this research, ZrC coatings were deposited onto stainless steel 304 using a plasma spraying method. The plasma spray process has many different parameters which can influence the coating, in this research the following parameters were thought to be of interest to deposit dense oxide free coatings i.e. plasma power input, substrate spray distance, particle injection velocity and spray atmosphere.

A laboratory scale plasma spray setup was used to conduct the experiments for this research. The setup consisted out of a non-transfer DC plasma torch with a button type cathode, a powder feeder, gas supply, power supply and cooling water system. The plasma torch could be used in an atmospheric setup or fitted onto a spray chamber for inert gas spraying. In order to confirm if the plasma torch was able to deposit ZrC, a simulation model using the Jets&Poudres program was set up.

The powder was analysed before spraying to determine its properties that might influence the coating such as the chemical composition, particle size and distribution. ICP-OES, combustion analysis and XRD determined that the feedstock powder was ZrC, while PSD analysis determined that the powder had a d_{50} of 3.755 μm with a small distribution. The deposited coatings were analysed using SEM micrographs in conjunction with EDS and XRD to observe the coatings surfaces and cross-sections as well as the composition.

The atmospheric spray runs were all had signs of oxidation while the inert sprays remained ZrC but where not melted and did not form a proper coating. The atmospheric coatings are thought to have deposited due to the lower melting point of zirconium oxycarbide and zirconium oxide compared to ZrC.

Taking this into account other valuable conclusions could still be obtained from the atmospheric spray samples. The plasma power input showed that an increase in power produced better coatings in terms of density and thickness. The ideal substrate distance was found to 100 mm as anything closer resulted in decreased particle deposition, heat damage or porous coatings. The powder injection velocity was shown to be optimised for 15 m/s anything slower or faster resulted in unsatisfactory coatings.

7.2. Conclusion

The following conclusions can be drawn from the work done in this research and literature study:

- Generally in the plasma spraying community a rod type plasma torch is used, whereas in this research a button type plasma torch was utilised. It is thought that the button type setup could be successfully used for plasma spraying.
- It was found that by increasing the plasma power input higher quality coatings were produced. The work conducted by Hu *et al.* (2015), where ZrC was deposited using a 40 kW power supply is nearly double that which was used in this research (22 kW). It is thought that by implementing a power supply with an even larger capacity even better coatings can be successfully deposited.
- The substrate distance should not be too close to the plasma as this will result in heat damage. The ideal distance should be 100 mm which is in agreement with Fauchais *et al.* (2014) who suggests a spray distance of 100 – 120 mm.
- The particle injection velocity will differ when using a different powder (be it size or composition) as well as a higher plasma power. Therefore the particle injection should be optimised for deposition of different materials and parameters (Vardelle *et al.*, 2001).
- The work done by Hu *et al.* (2015) supports the claim that when ZrC is plasma sprayed under atmospheric conditions it will be contaminated with oxygen. Therefore it is crucial to deposit ZrC under an inert gas.
- Although plasma spraying is a promising coating method, it is still in its infancy when it comes coating ceramics onto metals. It is thought that future research is still required in this field in order to successfully deposit ZrC onto Zr-alloy.

7.3. Recommendations

The work done in this research has hopefully laid the foundation towards successfully depositing dense, oxide-free ZrC coatings onto Zr-alloy fuel tubes. The following recommendations are therefore given:

- The plasma power input should be increased. The power should be in excess of at least 40 kW or more.
- A substrate distance of at least a 100 mm should be used.
- Due to the lack of oxygen resistance (above 500°C) ZrC should be deposited in an inert or vacuum atmosphere.
- A larger particle size or agglomerated particles should be used for better penetration of the plasma or an alternative feeding mechanism such as suspension liquids should be used.
- To help overcome the wetting problem the transition temperature should be determined for ZrC and Zr-alloy. As a secondary measure, a suitable intermediate coating could be deposited such as SiC or the existing ZrO₂ layer could be increased by heating the fuel tube. This will increase the wettability between the new substrate surface and deposited coating.

The plasma spraying method clearly shows potential as a coating technique although many parameters will still need to be optimised in order to deposit a proper ZrC coating.

Bibliography

Fauchais, P.L., Heberlein, J.V.R. & Boulos, M.I. 2014. Thermal Spray Fundamentals. United States of America: Springer US.

Hu, C., Ge, X., Niu, Y., Li, H., Huang, L., Zheng, X. & Sun, J. 2015. Influence of Oxidation Behavior of Feedstock on Microstructure and Ablation Resistance of Plasma-Sprayed Zirconium Carbide Coating. *Journal of Thermal Spray Technology*, 24(7):1302-1311.

Vardelle, M., Vardelle, A., Fauchais, P., Li, K.I., Dussoubs, B. & Themelis, N.J. 2001. Controlling particle injection in plasma spraying. *Journal of Thermal Spray Technology*, 10(2):267-284.

ANNEXURE A: PROPERTIES OF ZIRCONIUM CARBIDE

Property	Minimum Value	Maximum Value	Unit
Atomic Volume	0.0076	0.0078	m ³ /kmol
Density	6.6	6.73	Mg/m ³
Energy Content	150	200	MJ/kg
Bulk Modulus	220	270	GPa
Compressive Strength	7908.8	8741.3	MPa
Ductility	0.00205	0.00226	-
Elastic Limit	790.9	874.1	MPa
Endurance Limit	673.48	785.73	MPa
Fracture Toughness	2	3	MPa.M ^{1/2}
Hardness	23750	26250	MPa
Loss Coefficient	1.00E-05	2.00E-05	-
Modulus of Rupture	949.4	1049.4	MPa
Poisson's Ratio	0.22	0.25	-
Shear Modulus	140	174	GPa
Tensile Strength	790.9	874.1	MPa
Young's Modulus	346	430	GPa
Latent Heat of Fusion	680	760	kJ/kg
Maximum Service Temperature	1100	1200	K
Melting Point	3303	3530	K
Minimum Service Temperature	0	0	K
Specific Heat	334	368	J/kg.K
Thermal Conductivity	21	25	W/m.K
Thermal Expansive	6.6	6.8	10 ⁻⁶ /K
Resistivity	78	82	10 ⁻⁸ ohm.m