PROTECTIVE THERMAL SPRAY COATINGS FOR POLYMER MATRIX COMPOSITES

A Thesis by

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I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science with a major in Mechanical Engineering.

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We have read this thesis and recommend its acceptance:

George E Talia

Krishna Krishnan
DEDICATION

To my parents Dr. Kalpana Vyawahare and Mr. Mohan Vyawahare and my fiancée Ms.

Bijal Shah
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ABSTRACT

Polymer matrix composites were coated with metals, alloys and intermetallic compounds using the thermal spray coating technology. Air plasma spraying and flame spraying were the two spraying techniques primarily used during this entire study. Coatings were sprayed with two configuration; coatings with bond coating and coating without bond coating. Pilot runs were conducted to develop thermal spray process parameters for a two factor study, namely torch power and torch-substrate standoff distance, with other process parameters kept constant. Eventually a process window was established to carry out the final coating runs. Scanning electron microscopy was carried out to determine coating porosity and evaluate the microstructures and mechanical testing was performed to determine the bond strength and the erosion resistance of the coatings due to sand blasting. It is seen that the nickel aluminum intermetallic compound has better erosion resistance and bond strength than the nickel aluminum alloy. It is also seen that the process parameters, torch power and torch-substrate standoff distance do not significantly affect the coating properties.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE NO.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td>1.1 Theory</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Technology and processes</td>
<td>2</td>
</tr>
<tr>
<td>1.2.1 Thermal spray processes using electric energy</td>
<td>3</td>
</tr>
<tr>
<td>1.2.2 Thermal spray processes using combustion</td>
<td>7</td>
</tr>
<tr>
<td>1.3 Thermal spray process characteristics</td>
<td>11</td>
</tr>
<tr>
<td>1.4 Materials for thermal spray processes</td>
<td>16</td>
</tr>
<tr>
<td>1.5 Thermal spray merits and applications</td>
<td>20</td>
</tr>
<tr>
<td>1.6 Thermal plasma spraying (TPS)</td>
<td>22</td>
</tr>
<tr>
<td>1.6.1 History</td>
<td>22</td>
</tr>
<tr>
<td>1.6.2 The plasma state</td>
<td>23</td>
</tr>
<tr>
<td>1.6.3 Formation of plasma coatings</td>
<td>24</td>
</tr>
<tr>
<td>1.6.4 Gases in TPS</td>
<td>25</td>
</tr>
<tr>
<td><strong>2. LITERATURE REVIEW</strong></td>
<td>30</td>
</tr>
<tr>
<td><strong>3. PROJECT OBJECTIVES</strong></td>
<td>34</td>
</tr>
<tr>
<td>3.1 Problem description</td>
<td>34</td>
</tr>
<tr>
<td>3.2 Project goals</td>
<td>35</td>
</tr>
<tr>
<td><strong>4. COATING SYSTEM SELECTION</strong></td>
<td>36</td>
</tr>
<tr>
<td>4.1 Selection of substrate</td>
<td>36</td>
</tr>
<tr>
<td>4.2 Selection of coating materials</td>
<td>37</td>
</tr>
</tbody>
</table>
4.3 Selection of spray technology

5. EXPERIMENTAL PROCEDURE
5.1 Substrate Preparation
5.2 Pre-coating substrate surface preparation
5.3 Coating application

6. COATING CHARACTERIZATION
6.1 Coating spray matrix
6.2 Scanning electron microscopy
6.3 Erosion test by sand blasting
6.4 Adhesion strength

7. COATING PERFORMANCE EVALUATION
7.1 Effect of thermal spray parameters
7.1.1 Effect of parameters on coating porosity
7.1.2 Effect of parameters on mass loss due to erosion

8. SUMMARY AND CONCLUSION

9. FUTURE WORK

10. REFERENCES

11. APPENDIX
11.1 Porosity values and confidence intervals
11.2 Erosion strength test by sand blasting values
11.3 Photograph showing pre-erosion samples
11.4 Photograph showing post-erosion samples
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.5  Adhesion strength test values</td>
<td>85</td>
</tr>
<tr>
<td>11.6  Particle size distribution for N6 coatings</td>
<td>86</td>
</tr>
<tr>
<td>11.7  Particle size distribution for N9 coatings</td>
<td>87</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE NO.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Schematic of a generic thermal spray coating process</td>
<td>2</td>
</tr>
<tr>
<td>2. Schematic of a generic electric arc spray process</td>
<td>4</td>
</tr>
<tr>
<td>3. Schematic of a generic plasma spray process</td>
<td>6</td>
</tr>
<tr>
<td>4. Schematic of a generic powder flame spray process</td>
<td>8</td>
</tr>
<tr>
<td>5. Schematic of a generic wire flame spray process</td>
<td>9</td>
</tr>
<tr>
<td>6. Schematic of a generic HVOF spray process</td>
<td>10</td>
</tr>
<tr>
<td>7. Schematic of a generic D-gun process</td>
<td>11</td>
</tr>
<tr>
<td>8. Photomicrograph showing the microstructure</td>
<td>14</td>
</tr>
<tr>
<td>of an HVOF sprayed 80Ni-20Cr alloy</td>
<td></td>
</tr>
<tr>
<td>9. Enthalpy of plasma with respect to temperature</td>
<td>27</td>
</tr>
<tr>
<td>10. Curing cycle for an eight ply composite substrate</td>
<td>40</td>
</tr>
<tr>
<td>11. Composite with no surface treatment (as cured)</td>
<td>42</td>
</tr>
<tr>
<td>12. Composite with medium surface treatment: “no-water break test”</td>
<td>42</td>
</tr>
<tr>
<td>not passed</td>
<td></td>
</tr>
<tr>
<td>13. Composite treated to “no water break test”</td>
<td>43</td>
</tr>
<tr>
<td>14. False color display of the grey values used to</td>
<td>49</td>
</tr>
<tr>
<td>determine coating porosity</td>
<td></td>
</tr>
<tr>
<td>15. Confidence intervals for percentage porosity in all coatings</td>
<td>50</td>
</tr>
<tr>
<td>16. Microstructure of N6 coating at torch power</td>
<td>53</td>
</tr>
</tbody>
</table>
25 kW, standoff distance 80 mm

17. Microstructure of N6 coating at torch power

20 kW, standoff distance 80 mm

18. Microstructure of N6A coating at torch power

20 kW, standoff distance 80 mm

19. Microstructure of N9A coating at torch power

20 kW, standoff distance 80 mm

20. Erosion test mass loss chart

21. Loss of mass with respect to time

22. Adhesion strength chart

23. Effect of standoff distance on coating porosity

24. ‘t’ distribution for $\alpha = 0.05, n_1,n_2 = 10$

25. Effect of power on coating porosity

26. Effect of power on mass loss

27. Effect of standoff distance on mass loss
INTRODUCTION

1.1 Theory

Surface engineering is defined as the design of a composite system of a surface and a substrate together to give a performance which cannot be achieved by either the surface or the substrate alone. The system can consist of a coating with or without an interface, a modification of the surface or subsurface, or a combination of the two on a substrate. Surfaces can be engineered to improve their appearance; to protect them from their environment; and to enhance their mechanical or physical performance. This is possible by the application of any of the four main types of processes: 1) molten (thermal spraying, welding); 2) gaseous (vapor deposition, ionized plasma); 3) solution (electroless or electrolytic plating, resin bonding) and 4) solid (friction welding, roll cladding) [1].

A coating is generally a layer applied on a surface either for protection or for an aesthetic purpose. As stated by the American Society of Materials’s Handbook of Thermal Spray Technology, “Thermal spray coating is a generic term for a group of coating processes used to apply metallic or nonmetallic coatings. Energy sources are used to heat the coating material (in powder, wire, or rod form) to a molten or semimolten state. The resultant heated particles are accelerated and propelled towards a prepared surface by either process gases or atomization jets. Upon impact, a bond forms with the surface, with subsequent particles causing thickness buildup and forming a lamellar structure, depending on several process conditions. The thin “splats” undergo very high cooling rates, typically in excess of $10^6$ K/s for metals” [2]. Figure 1 shows a schematic of a generic thermal spray process.
1.2 Technology and Processes

Members of the thermal spray family of processes are typically grouped into two major categories:

- Thermal spray processes using electric energy
- Thermal spray processes using combustion
Cold spray is a material deposition process in which coatings are applied by accelerating powdered feedstock of ductile metals to speeds of 300 to 1200 m/s (985 to 3940 ft/s) using gas-dynamic techniques. The process is commonly referred to as “cold gas-dynamic spraying” because of the relatively low temperatures (0 to 800 °C, or 32 to 1470 °F) of the expanded gas and particle stream that emanate from the nozzle. Powder feed rates of up to 14 kg/h (30 lb/h) are possible.

Selection of the appropriate thermal spray method is typically determined by:

• Desired coating material

• Coating performance requirements

• Economics

• Part size and portability

1.2.1 Thermal spray processes using electric energy

A] Electric Arc Spraying

In the electric arc spray process (also known as the wire arc process or twin wire electric arc process), two consumable wire electrodes connected to a high-current direct-current power source are fed into the gun where they establish an arc that melts the tips of the wires. The molten metal is then atomized and propelled toward the substrate by a stream of air. The process is energy efficient because all of the input energy is used to melt the metal.

Spray rates are driven governed by operating current and vary as a function of both melting point and conductivity. Substrate temperatures can be very low, because no hot jet of gas is directed toward the substrate. Electric arc spraying can be also carried out using inert gases
or in a controlled-atmosphere chamber [2]. Figure 2 shows a schematic of a generic electric arc spray process.

Figure 2: Schematic of a generic electric arc spray process [2].
B] **Plasma Spraying**

B.1] Conventional Plasma Spraying

The conventional plasma spray process is commonly referred to as air or atmospheric plasma spray (APS). Plasma temperatures in the powder heating region range from about 6000 to 15,000 °C (11,000 to 27,000 °F), significantly above the melting point of any known material. To generate the plasma, an inert gas, typically argon or an argon-hydrogen mixture is ionized and dissociated by a D.C. arc. Powder feedstock is introduced via an inert carrier gas and is accelerated toward the workpiece by the plasma jet. Provisions for cooling or regulating the spray rate may be required to maintain substrate temperatures in the 95 to 205 °C (200 to 400 °F) range. Commercial plasma spray guns operate in the range of 20 to 200 kW. Accordingly, spray rates greatly depend on gun design, plasma gases, powder injection schemes, and materials properties, particularly particle characteristics such as size, distribution, melting point, morphology, and apparent density [2].

B.2] Vacuum Plasma Spraying

Vacuum plasma spraying (VPS), also commonly referred to as low-pressure plasma spraying (LPPS, a registered trademark of Sulzer Metco), uses modified plasma spray torches in a chamber at pressures in the range of 10 to 50 kPa (0.1 to 0.5 atm). At low pressures the plasma becomes larger in diameter and length, and, through the use of convergent/divergent nozzles, has a higher gas speed. The absence of oxygen and the ability to operate with higher substrate temperatures produce denser, more adherent coatings with much lower oxide contents [2].

Figure 3 shows a schematic of a generic plasma spray process.
Figure 3: Schematic of a generic plasma spray process [2]
1.2.2 Thermal spray processes using combustion

Thermal spray processes using combustion include low-velocity powder flame, rod flame, and wire flame processes and high-velocity processes such as HVOF and the detonation gun (D-Gun) process (D-Gun is a registered trademark of Praxair Surface Technologies Inc.) [2].

A] Flame Spraying

In this process, a consumable (usually a powder or a wire) is heated and propelled onto a substrate to form a coating. Flame spraying is the oldest of the thermal spraying processes. A wide variety of materials, mostly metallic, can be deposited as coatings using this process and the vast majority of components are sprayed manually. Flame spraying has some distinct advantages, including ease of application and low cost, compared with the other spraying processes [2].

A.1] Powder flame Spraying

In the powder flame process, powdered feedstock is aspirated into the oxy fuel flame, melted, and carried by the flame and air jets to the workpiece. Particle speed is relatively low (<100 m/s), and bond strength of the deposits is generally lower than the higher velocity processes. Porosity can be high and cohesive strength is also generally lower. Spray rates are usually in the 0.5 to 9 kg/h (1 to 20 lb/h) range for all but the lower melting point materials, which spray at significantly higher rates. Substrate surface temperatures can run quite high (about 200 to 300 C) because of flame impingement [2]. Figure 4 shows a schematic of a generic powder flame spray process.
Figure 4: Schematic of a generic powder flame spray process [2]
A.2] Wire Flame Spraying

In wire flame spraying, the primary function of the flame is to melt the feedstock material. A stream of air then atomizes the molten material and propels it toward the workpiece. Spray rates for materials such as stainless steel are in the range of 0.5 to 9 kg/h (1 to 20 lb/h). Again, lower melting point materials such as zinc and tin alloys spray at much higher rates. Substrate temperatures often range from 95 to 205 °C (200 to 400 °F) because of the excess energy input required for flame melting. In most thermal spray processes, less than 10% of the input energy is actually used to melt the feedstock material. [2]. Figure 5 shows a schematic of a generic wire flame spray process.

Figure 5: Schematic of a generic wire flame spray process [2]
B] High-Velocity Oxy-fuel (HVOF)

In HVOF, a fuel gas (such as hydrogen, propane, or propylene) and oxygen are used to create a combustion jet at temperatures of 2500 to 3100 °C (4500 to 5600 °F). The combustion takes place internally at very high chamber pressures, exiting through a small-diameter (typically 8 to 9 mm, or 0.31 to 0.35 in.) barrel to generate a supersonic gas jet with very high particle speeds. The process results in extremely dense, well bonded coatings, making it attractive for many applications. Either powder or wire feedstock can be sprayed, at typical rates of 2.3 to 14 kg/h (5 to 30 lb/h). [2]. Figure 6 shows a schematic of a generic HVOF process.

Figure 6: Schematic of a generic HVOF process [2]
C] Detonation Gun (D-Gun)

In the detonation gun process, pre-encapsulated “shots” of feedstock powder are fed into a 1 m (3 ft) long barrel along with oxygen and a fuel gas, typically acetylene. A spark ignites the mixture and produces a controlled explosion that propagates down the length of the barrel. The high temperatures and pressures (1 MPa, or 150 psi) that are generated blast the particles out of the end of the barrel toward the substrate. Very high bond strengths and densities as well as low oxide contents can be achieved using this process. [2]. Figure 7 shows a schematic of a generic D-gun process.

![Schematic of a generic D-gun process](image)
1.3 Thermal Spray Process Characteristics

The term “thermal spray” describes a family of processes that use the thermal energy generated by chemical (combustion) or electrical (plasma or arc) methods to melt, and accelerate fine particles or droplets to speeds in the range of 50 to >1000 m/s (165 to >3300 ft/s). The high particle temperatures and / or speeds achieved result in significant droplet deformation on impact at a surface, producing thin layers or lamellae, often called “splats,” that conform and adhere to the substrate surface. Solidified droplets build up rapidly, particle by particle, as a continuous stream of droplets impact to form continuous rapidly solidified layers. Individual splats are generally thin (~1 to 20 µm), and each droplet cools at very high rates (>10⁶ K/s for metals) to form uniform, very fine-grained, polycrystalline coatings or deposits. Sprayed deposits usually contain some level of porosity, typically between 0 and 10%, some unmelted or partially melted particles, fully melted and deformed “splats,” metastable phases, and oxidation from entrained air. Thermal spray process jets or plumes are characterized by large gradients of both temperature and velocity. Feedstock is usually in powdered form with a distribution of particle sizes. When these powdered materials are fed into the plume, portions of the powder distribution take preferred paths according to their inertia. As a result, some particles may be completely unmelted and can create porosity or become trapped as “unmelts” in the coating. Use of wire and rod feedstock materials produces particle size distributions because of non-uniform heating and unpredictable drag forces, which shear molten material from the parent wire or rod. The level of these coating defects varies depending on the particular thermal spray process used, the operating conditions selected, and the material being sprayed, as described later. Figure 8 is a
photomicrograph of a thermal-sprayed 80Ni-20Cr alloy coating applied via the high velocity oxy-fuel (HVOF) process showing the characteristic lamellar splat structure. The microstructure shown in Fig. 8 includes partially melted particles and dark oxide inclusions that are characteristic of many metallic coatings sprayed in air. Such coatings exhibit characteristic lamellar microstructures, with the long axis of the impacted splats oriented parallel to the substrate surface, together with a distribution of similarly oriented oxides.

Coating oxide content varies with the process—wire arc, plasma, or HVOF. The progressive increases in particle speed of these processes leads to differing levels of oxide and differing degrees of oxide breakup on impact at the surface.
Figure 8: Photomicrograph showing the microstructure of an HVOF-sprayed 80Ni-20Cr alloy [3]

Oxides may increase coating hardness and wear resistance and may provide lubricity. Conversely, excessive and continuous oxide networks can lead to cohesive failure of a coating and contribute to excessive wear debris. Oxides can also reduce corrosion resistance. It is important to select materials, coating processes, and processing parameters that allow
control of oxide content and structure to acceptable levels for a given application. Thermal spray coatings may contain varying levels of porosity, depending on the spray process, particle speed and size distribution, and spray distance. Porosity may be beneficial in tribological applications through retention of lubricating oil films. Porosity may be also beneficial in coatings on biomedical implants. Lamellar oxide layers can also lead to lower wear and friction due to the lubricity of some oxides. The porosity of thermal spray coatings is typically less than 5% by volume. The retention of some unmelted and/or resolidified particles can lead to lower deposit cohesive strengths, especially in the case of “as-sprayed” materials with no post-deposition heat treatment or fusion. Other key features of thermal spray deposits are their generally very fine grain structures and columnar orientation.

Thermal-sprayed metals, for example, have reported grain sizes of less than 1 µm prior to post-deposition heat treatment. Grain structure across an individual splat normally ranges from 10 to 50 µm, with typical grain diameters of 0.25 to 0.5 µm, owing to the high cooling rates achieved (~10^6 K/s) [3].

The tensile strengths of as-sprayed deposits can range from 10% to 60% of that of cast or wrought materials, depending on the spray process used. Spray conditions leading to higher oxide levels and lower deposit densities result in the lowest strengths. Controlled-atmosphere spraying leads to ~ 60% strength, but requires post-deposition heat treatment to achieve near 100% values. Low as-sprayed strengths are related somewhat to limited intersplat diffusion and limited grain recrystallization during the rapid solidification characteristic of thermal spray processes. The primary factor limiting adhesion and cohesion
is residual stress resulting from rapid solidification of the splats. Accumulated residual stress also limits thickness buildup [3].

1.4 Materials for Thermal Spray Processes

Three basic types of deposits can be thermal sprayed:

- **Single-phase materials**, such as metals, alloys, intermetallics, ceramics, and polymers
- **Composite materials**, such as cermets (WC/Co, Cr₃C₂/NiCr, NiCrAlY/Al₂O₃, etc.), reinforced metals, and reinforced polymers
- **Layered or graded materials**, referred to as functionally gradient materials (FGMs)

Examples of these, along with their particular advantages and applications, are described below.

**• Single-Phase Materials**

Metals

Most pure metals and metal alloys have been thermal sprayed, including tungsten, molybdenum, rhenium, niobium, superalloys, zinc, aluminum, bronze, mild and stainless steels, NiCr alloys, cobalt-base Stellites, cobalt/nickel-base Triballoys, and NiCrBSi “self-fluxing” alloys. Sprayed alloys have advantages due to their similarity to many base metals requiring repair, their high strength, and their corrosion, wear, and/or oxidation resistance. Applications include automotive/diesel engine cylinder coatings; piston rings or valve stems; turbine engine blades, vanes, and combustors; protection of bridges and other corrosion prone infrastructure; petrochemical pumps and valves; and mining and agricultural equipment.
Ceramics

Most forms of ceramics can be thermal sprayed, including metallic oxides such as Al₂O₃, stabilized ZrO₂, TiO₂, Cr₂O₃, and MgO; carbides such as Cr₃C₂, TiC, Mo₂C, and SiC (generally in a more ductile supporting metal matrix such as cobalt or NiCr); nitrides such as TiN and Si₃N₄; and spinels or perovskites such as mullite and 1-2-3-type superconducting oxides.

Sprayed deposits of these materials are used to provide wear resistance (Al₂O₃, Cr₂O₃, TiO₂, Cr₂O₃, TiC, Mo₂C, and TiN), thermal protection (Al₂O₃, ZrO₂, and MgO), electrical insulation (Al₂O₃, TiO₂, and MgO), and corrosion resistance. Ceramics are particularly suited to thermal spraying, with plasma spraying being the most suitable process due to its high jet temperatures. One of the most popular cermet is tungsten carbide–cobalt. It is widely used in the industry because of its excellent wear and abrasion resistance. It is also very useful for achieving high sliding-wear resistance and friction properties.

Intermetallics

Intermetallics such as TiAl, Ti₃Al, Ni₃Al, NiAl, and MoSi₂ have all been thermal sprayed. Most intermetallics are very reactive at high temperatures and very sensitive to oxidation; hence, inert atmospheres must be used during plasma spraying. Research has also been conducted on thermal spray forming/consolidation of bulk intermetallic deposits.

Polymers

Polymers also can be thermal sprayed successfully, provided they are available in particulate form. Thermal spraying of polymers has been practiced commercially since the 1980s, and a growing number of thermoplastic and thermosetting polymers and copolymers have now been sprayed, including urethanes, ethylene vinyl alcohols (EVAs), nylon 11,
polytetrafluoroethylene (PTFE), ethylene tetrafluoroethylene (ETFE), polyetheretherketone (PEEK), polymethylmethacrylate (PMMA), polyimide, polycarbonate, and copolymers such as polyimide/polyamide, Surlyn (DuPont), and polyvinylidene fluoride (PVDF). Conventional flame spray and HVOF are the most widely used thermal spray methods for applying polymers.

• **Composites**

Particulate-, fiber-, and whisker-reinforced composites have all been produced and used in various applications. Particulate-reinforced wear-resistant cermet coatings such as WC/Co, Cr₃C₂ / NiCr, and TiC / NiCr are the most common applications and constitute one of the largest single thermal spray application areas.

Thermal spray composite materials can have reinforcing phase contents ranging from 10 to 90% by volume, where the ductile metal matrix acts as a binder, supporting the brittle reinforcing phase.

• **Layered or graded materials**

Developed in the early 1970s, FGMs are a growing application area with significant promise for the future production of (a) improved materials and devices for use in applications subject to large thermal gradients, (b) lower-cost clad materials for combinations of corrosion and strength or wear resistance, and (c) improved electronic material structures for batteries, fuel cells, and thermoelectric energy conversion devices. The most immediate application for FGMs is thermal barrier coatings (TBCs), where large thermal stresses are minimized. Component lifetimes are improved by tailoring the coefficients of thermal expansion, thermal conductivity, and oxidation resistance. These FGMs are finding use in turbine components, rocket nozzles, chemical reactor tubes, incinerator burner nozzles, and other critical furnace
components. Figure 4 illustrates an example of a thermal-sprayed FGM proposed for the protection of copper using a layered FGM ceramic structure. Successful fabrication of this structure would have application for improved burner nozzles, molds, and furnace walls. Other FGMs are being developed for:

- Thermal protection of lightweight polymeric insulating materials in aircraft components
- Production of graded metallic/oxide/intermetallic advanced batteries and solid oxide fuel cells
- Production of oxide/metal/air-type electrode/electrolyte systems
- Forming of composite gun barrels
- Biomedical implant devices for enhanced bone-tissue attachment
- Ceramic outer air seals in aircraft gas turbines and other “clearance-control” coatings in rotating machinery
- Thick, multilayer TBCs for heavy-duty diesel engine pistons
- High-performance dielectric coatings for electronic devices
- Wear-resistant coatings for diesel engine piston rings
- Oxidation-resistant coatings for high-temperature conditions. Future growth of FGM applications will ensure that thermal spray processes, particularly HVOF and plasma spray processes, will increase and develop, provided that material properties can be controlled and processing costs optimized.
1.5 Thermal Spray Merits and Applications

Merits and Demerits

A major advantage of thermal spray processes is the extremely wide variety of materials that can be used to produce coatings. Virtually any material that melts without decomposing can be used. A second major advantage is the ability of most thermal spray processes to apply coatings to substrates without significant heat input. Thus, materials with very high melting points, such as tungsten, can be applied to finely machined, fully heat-treated parts without changing the properties of the part and without excessive thermal distortion of the part. A third advantage is the ability, in most cases, to strip off and recoat worn or damaged coatings without changing part properties or dimensions. A disadvantage is the line-of-sight nature of these deposition processes. They can only coat what the torch or gun can “see.” Of course, there are also size limitations. It is impossible to coat small, deep cavities into which a torch or gun will not fit.

Applications

Typical applications of metallic and ceramic coatings are:

• wear and erosion control of machinery parts and turbine vanes, shrouds and blades in coal-fired power generating stations;

• particle erosion control in boiler tubes and superheaters of coal—fired power plants;

• chemical barrier coatings for ethane steam cracking furnace tubes for coking and erosion protection;
• wear control and improvement of friction properties in a variety of machine parts, including pump plungers, valves, bearings, and calendar and printing rolls;

• metal coatings for corrosion protection of engineering structures such as steel and concrete bridges in coastal regions:

• corrosion protection against liquid metals in extrusion dies, ladles and tundishes;

• corrosion protection of equipment for petrochemical and chemical plants, and high-temperature corrosion in internal combustion engines;

• thermal and chemical barrier coatings for pistons and valves in adiabatic diesel engines and related machinery, as well as aerospace gas turbine blades and combustor cans;

• resurfacing of worn equipment, for example in railway applications, ship building and maintenance, and mining tools and equipment;

• superalloys for aerospace gas turbine vanes and shrouds to prevent hot gas erosion and corrosion;

• ceramic membranes for osmotic filtering and ultrafiltration;

• biomedical coatings for orthopedic and dental prostheses with biocompatible properties based on hydroxyapatite and tricalcium phosphate;

• stabilized, zirconia electrolyte and electrocatalytic active compound coatings for SOFCs;

• high-temperature superconducting coatings for electromagnetic interference (EMI) shielding;

• abradable coatings and seals for clearance control in gas turbines;
• coatings to protect concrete floors from corrosive action of fruit juices and other agricultural products;

• sealing of concrete floors in dairy industrial operations;

• thick metal overlays for sputter targets;

• diamond-like coatings for wear applications and for heat sinks in high-power electronic chips [4].

1.6 Thermal Plasma Spraying (TPS)

1.6.1 History

Plasma spraying technology is an improved development of flame metallizing. The metallization process was invented and patented in Switzerland by Dr. Ing. Max Ulrich Schoop in 1910. Schoop also invented the arc spraying technique which was far from perfection because of the primitive electrical equipment, mainly the direct-current sources. For this reason the arc spraying process was considerably surpassed by the flame spraying process, which started to develop in the USA in the early thirties; its application was extended by the application of zinc and aluminum anticorrosion coatings and the renovation of machine parts by spraying steel and bronze. At that time, the method of spraying powder materials was employed, rather than the initial spraying of wire. In Europe, mainly in Germany, Schoop and his followers tried to employ powder metallization, however with limited success. Rapid improvement and development of this technology was observed in the fifties, connected with the fast development in the powder materials, thus opening new fields for the application of metallization. At that time, besides some hardfacing materials, alumina and zirconia also became interesting [3].
1.6.2 The plasma state

According to the definition of H. Langmuir, plasma is the highly ionized state of mass, consisting of molecules, atoms, ions electrons and light quantums. One cubic centimeter contains about $10^{10}$ to $10^{10}$ charged particles [2].

An alternative definition states that ‘plasmas are quasi–neutral multi particle systems characterized by gaseous or fluid mixtures of free electrons and ions, as well as neutral particles (atoms, molecules, radicals), with a high mean kinetic energy of electrons or all plasma components ($\langle \varepsilon \rangle \sim 1$eV to 2MeV per particle) and a considerable interaction of the charge carriers with the properties of the system.

Since the states of matter can be defined by the mean kinetic energy $\varepsilon$ of the constituent particles, there exists an energy threshold $\varepsilon_n$ at the phase boundaries that marks the transition among states and can be treated as typical binding energies. A criterion of existence of the $n$-th state of matter is $\varepsilon_n \leq \langle \varepsilon \rangle \leq \varepsilon_{n+1}$. With increasing $\langle \varepsilon \rangle$ i.e. increasing temperature, matter passes through the states $n = 1 \ldots 3$ (solid,liquid,gaseous), and finally through ionization of gas atoms, free electric charge carriers appear that characterize the systems as fourth state of matter. This is plasma.

Principally, the properties of a gas are primarily dependent upon the movement of its individual molecules. During this movement, the molecules mutually exchange the energy and the pulse due to collisions of their elementary particles. If a certain amount of energy is supplied to a gas, the velocity of molecules increases. The higher this velocity the more frequent are the mutual collisions of particles. A temperature increase of the affected gas is thus a natural consequence of this energy process. The velocity of the particles may attain
such a high level that, in case of a diatomic gas, the molecules disintegrate into atoms due to mutual collisions. This process taking place in the plasma arc is called as dissociation. When higher levels of energy are supplied, the velocity can achieve such a high level that not only molecules are dissociated but also electrons can be forced out from the electron envelope of atoms. This process is called as ionization.

The final consequence of the whole dissociation and ionization processes is plasma as a state of mass containing the electrically charged particles. However, it must be noted that the plasma is, as a whole, neutral, since within it, the same number of electrically positive and negative charges must be distributed [3].

1.6.3 Formation of plasma coatings

The process of plasma coating formation consists of several stages which affect the properties of the plasma layer. Mainly, the high thermal and kinetic energy of the plasma beam enables the melting and acceleration of the particles of the supplied powder. The method of powder transport to the plasma torch, together with the shape and granularity of the powder, then affect the formation of the paths of the particles at a certain velocity. Interaction for the molten material with the plasma beam and the surrounding atmosphere affects the way the particles in the plasma beam melt and transform physically and chemically. The mechanical, chemical and thermal conditions at the impingement of the molten particles on the substrate complete the overall character and properties of the sprayed layer. Macroscopic properties of plasma-spray coatings, such as hardness, porosity, and mechanical strength, are determined by their microstructure. Understanding what parameters affect microstructure of coatings and, for example, what causes formation of porosity could result in better design of the process [3].
1.6.4 Gases in TPS

At present the gases such as argon, helium, hydrogen, nitrogen and to a lesser extent air and water, are brought to the plasma state.

The plasma forming gases are divided into two basic groups; one–atom and two–atom gases. Argon and helium belong to the first group, while nitrogen and helium belong to the other. The basic physical and chemical characteristics of applied plasma forming gases are tabulated below.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unit</th>
<th>Argon</th>
<th>Helium</th>
<th>Nitrogen</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative molar weight</td>
<td></td>
<td>39.944</td>
<td>4.0002</td>
<td>28.016</td>
<td>2.0156</td>
</tr>
<tr>
<td>Specific weight at 0 °C and 101.32 Pa</td>
<td>(kg·m⁻³)</td>
<td>1.783</td>
<td>0.1785</td>
<td>1.2505</td>
<td>0.0898</td>
</tr>
<tr>
<td>Specific thermal capacity $c_p$ at 20 °C</td>
<td>(kJ·kg⁻¹·K⁻¹)</td>
<td>0.511</td>
<td>5.233</td>
<td>1.046</td>
<td>14.268</td>
</tr>
<tr>
<td>Thermal conductivity coefficient at 0 °C</td>
<td>(W·m⁻¹·K⁻¹)</td>
<td>0.01633</td>
<td>0.14363</td>
<td>0.02386</td>
<td>0.17543</td>
</tr>
<tr>
<td>Ionization potential</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>one-stage</td>
<td>(V)</td>
<td>15.7</td>
<td>24.05</td>
<td>14.5</td>
<td>13.5</td>
</tr>
<tr>
<td>two-stage</td>
<td>(V)</td>
<td>27.5</td>
<td>54.1</td>
<td>29.4</td>
<td>—</td>
</tr>
<tr>
<td>Temperature</td>
<td>(K)</td>
<td>14000</td>
<td>20000</td>
<td>7300</td>
<td>5100</td>
</tr>
<tr>
<td>Arc voltage</td>
<td>(V)</td>
<td>40</td>
<td>47</td>
<td>60</td>
<td>62</td>
</tr>
<tr>
<td>Arc input</td>
<td>(kW)</td>
<td>50</td>
<td>65</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td>Coefficient of energy utilization for gas heating</td>
<td>(%)</td>
<td>40</td>
<td>48</td>
<td>60</td>
<td>80</td>
</tr>
</tbody>
</table>

The task of the gaseous environment in the plasma torch consists first of all in plasma formation and also protection of the electrodes against oxidation and their cooling. The
plasma forming gas is selected on the basis of the desired temperature and velocity of the plasma beam and the degree of inert material in the sprayed material and the substrate.

The process of plasma formation of a two atom gas differs from that of a one atom one. The difference consists on the fact that the ionization of two atom gas atoms starts after dissociation of its molecules. Hydrogen dissociates by 90% at 5000 K temperature, while Nitrogen dissociates at a temperature of about 8500 K, a difference caused by different dissociation energies of these gases. Different enthalpies and plasma temperatures are other important discussions between the one atom and two atom gases. As evident from Fig. 9, N₂ at 8000 K has an enthalpy 5 times higher than argon, since the energy gained by the one atom gases in the plasma column is given by the specific heat and the ionization energy, while in two-atom gases in addition, the great volume of energy is obtained from dissociation of molecules into atoms [2].

Nitrogen

Nitrogen dissociation starts at 5000 K and is 95% complete at 9000 K. Ionization of N₂ atoms starts at 8000 K, is 50% complete at 15000 K, 95% at 20000 K and 98% at 22000 K. N₂ enthalpy is plotted in Fig. 9. The sections of the curves with steeper slopes correspond to dissociation and simpler ionization. Above 7000 K, the nitrogen plasma contains greater heat volume than the other gases at the same temperature. Due to higher enthalpy and longer plasma beam, hard to melt materials can be more easily deposited with such plasma than with the argon plasma in the case when sufficient output would be impractical. For the same distance, a greater standoff distance must be maintained with nitrogen plasma than with argon plasma. The N₂ used in plasma torches must be free of O₂; if it is not, poisonous nitrogen oxide is formed and unfavorable electrode oxidation may also occur [2].
Figure 9: Enthalpy of plasma with respect to temperature [3]
Hydrogen

Hydrogen dissociation starts at 2000 K and is completed at 6000 K. Atomic H\textsubscript{2} is fully ionized at 25000 K. Hydrogen dissociation requires lower energy than that required by nitrogen. It has the highest thermal conductivity of all other plasma gases. 

*Hydrogen plasma requires the highest arc voltage and the highest input to the arc.* The temperature of the hydrogen plasma is lower than any of the other plasmas. The plasma torch working with hydrogen must be perfectly tight since any oxygen present may form an explosive mixture with the hydrogen. Besides, the hydrogen impingement on the surface of the cold metals may cause formation of undesired water droplets.

Argon and helium

Argon plasma has been repeatedly studied while the dependence of ionization potential on the temperature was determined. Argon ionization starts at 9000 K and is completed at 22000 K. Enthalpy of these one atom gases is considerably lower than the diatomic gases. Moreover; they have been preferred because of the following reasons:

- They are easier to transfer to plasma state than other gases
- They provide a stable electric arc
- They require a lower working voltage
- Temperature of these plasmas is highest compared to the other plasmas

From the viewpoints of their effects on the sprayed material, argon and especially helium assure high inertness of environment. Because Argon and Helium do not dissociate, their beam is very bright, short and constricted. Such a beam allows local deposit of the spraying
layer, facilitating considerably higher spraying efficiency. Helium also has excellent thermal conductivity. It is a very expensive and precious gas [3].
LITERATURE REVIEW

The thermal spray technology has evolved into an advanced interdisciplinary science and is attracting increasing attention in several applications. This technology is a highly complex process with several variables, affecting the coating deposition process.

Limited work has been done in the surface protection of polymer composites using the thermal spray technology. Polymer matrix composites are attractive materials for aerospace applications because of the high strength to weight ratio relative to metals.

Knight et al. investigated the microstructure and properties of thermally sprayed functionally graded coatings for polymer composites. They designed a functionally graded coating structure based on a polyimide matrix filled with varying volume fractions of WC–Co. The graded coating architecture was produced using a combination of internal and external injection of feedstock using computer controlled feeders [8].

Leissler et al. [7] used a similar two layer technique to coat their material. The bond coat was mixed with 5% polyimide to improve compatibility with the substrate. A design of experiments approach was used to study the coating durability and weight loss and tensile adhesion tests were conducted. Mathematical modeling was attempted for performance and durability protection.

Knight et al. investigated the adhesive / cohesive properties of thermally sprayed functional graded coatings on polymer composites [9]. Adhesive/cohesive strengths of the FGM coatings were measured and compared with those of pure polyimide and polyimide / WC-Co composite coatings and also related to the tensile strength of the uncoated PMC substrate perpendicular to the thickness. The nature and locus of the failures were characterized.
according to the percent adhesive and/or cohesive failure, and the interfaces tested and layers involved were analyzed by scanning electron microscopy.

Sutter et al. used a simple analytical process model to deposit polyimide using the HVOF technology. The aim of the study was to investigate the effect of external surface preheating on the deposition behavior and curing reaction of the thermally sprayed polyimide. The model incorporates various heat transfer mechanisms and enables surface temperature profiles of the coating to be simulated, primarily as a function of the surface preheating temperature.

Ashari et al. investigated various techniques and coatings such as electroplating, electroless nickel and plasma coatings of nickel and polymeric materials such as Nylon 11, polyimides and polyether – etherketone (PEEK). All these coatings were used as bond coats. The top coats were WC – Co and D Gun sprayed CrC-Co [10].

Knight et al. developed a simple analytical model for the deposition of thermosetting polyimide onto polymer composites by HVOF thermal spray technology. The model incorporated various heat transfer mechanisms and enables surface temperature profiles of the coating which was simulated. Thermal properties of the polyimide needed for the simulations were determined by Differential Scanning Calorimetry and Thermo – Gravimetric Analysis. Microstructural characterization of the coatings and the morphology of polyimide splats sprayed both with and without substrate preheating were analyzed using standard metallographic techniques [11].

Sutter et al. investigated the adhesion and integrity of oxidation protective barrier coatings for high temperature polyimides by isothermal aging and thermal cycling. Three coating techniques (metal – organic chemical vapor deposition, magnetron sputtering, and plasma
enhanced chemical vapor deposition) were employed to deposit different coating materials such as alumina and silicon nitride on graphite reinforced polyimides. [12].

Naik et al. researched two erosion resistant coatings that are useful for both low and high temperature applications. The coatings have been optimized for adhesion, erosion and surface roughness. Results have been described for vigorous hot gas / particulate erosion rig and engine testing of uncoated and coated polymer composite fan bypass vanes from the AE 3007 regional jet gas turbine (Rolls Royce) [13].

Vasquez et al. studied the effect of surface modification on adhesion of a metal bond coat to polyimide composites. This study examined the effect that a silica layer has, on the adhesion of a proprietary metal bond coat to PMR-15 and PMR-II-50 composite surfaces. The surfaces of PMR-15 and PMR-II-50 samples were modified by the following methods: grit blasting; grit blasting, ultra-violet/ozone (UV/ozone) etch, UVCVD of silica; and grit blasting, RF oxygen plasma etch, PECVD of silica. Adhesion pull tests were conducted and the fracture surfaces were examined using both optical and electron microscopy [14].

Pizem et al. explored the formation, degree of crystallinity, and adherence of dense titania thin film coatings on a high-temperature polyimide resin (PMR-15). Solution pH and temperature was adjusted, to obtain either amorphous titania or oriented crystalline anatase films.

Miyoshi et al. conducted an investigation to examine the erosion behavior of uncoated and coated polymer matrix composite (PMC) specimens subjected to solid particle impingement using air jets. Tungsten carbide-cobalt (WC-Co) was the primary topcoat constituent. Prior to
top coating, bondcoats were applied to the PMC substrates to improve coating adhesion. All erosion tests were conducted with Arizona road-dust (ARD), impinging at angles of 20° and 90° on both uncoated and two-layer coated PMCs at an airflow velocity of 229 m/s and at a temperature of 366 K [16].

Yan-Liang et al studied the Feasibility of depositing Al₂O₃ coating on carbon fiber reinforced polymer matrix composite (PMC) with Ni-3% Al powder, aluminum or zinc as the bond layer. Shear strength and thermal cycling resistance of the coatings were tested [17].
3.1 Problem description

Polymer matrix composites (PMCs) were first developed during the 1940’s, for military and aerospace applications. Their widespread use particularly in the aircraft industry is mainly because of their high strength to weight ratios. Other considerable advantages they offer are their high stiffness (modulus of elasticity), exceptional fatigue properties and their resistance to corrosion.

Polymer composites have been reported to show concerns with erosion properties. Erosion resistant coatings are needed to protect the composites materials, at least through the first overhaul, and preferably for the full life of the component [13]. Sutter et al. conducted an investigation to compare bare and coated polymer composites. The results proved a ten – fold increase in the erosion resistance of the coated components as compared to bare composite materials. This and a number of similar studies conducted so far have proved that surface treatment of composites would certainly provide an appreciable protection to the soft surface of these composites [8] [9] [10] [17]. Such treatment may contribute to longer PMC component lives, reduced erosion-related breakdowns, decreased maintenance costs, and increased PMC reliability. Eventually, the coatings could lead to overall economic savings.

Hard, dense and well bonded coatings are needed for the erosion protection application. However, it has been reported that adhesion of these coatings to a composite surface may pose a challenge. The thermal stability of the matrices used in these composites is relatively
low. The molten droplets of thermal spray coatings have been reported to burn off the epoxy instead of adhering to the same [10]. Thus the problem is to find an effective solution to improve the erosion resistance of the polymeric substrates by investigating various materials and processing parameters which may optimize the properties of the coatings.

3.2 Project goals

The primary goal of this work was to develop strategies to improve the surface of PMC by depositing coatings by thermal spraying, and tailoring of these coatings to make them strong, dense and having good bonding strength with the substrate. This included the exploration of several coatings with or without an extra layer of bond coating to the substrate. Typically, strong coatings used for wear resistance applications may have adhesion strength between 800 and 2000 psi. A second goal was to throw light on the effect of thermal spray parameters on the adhesive strength and erosion strength of these coatings. The thermal spray process was chosen for surface enhancement mainly because thermal spraying is an economically viable and an efficient technology when compared to other coating processes such as electrospraying, fluidized bed spraying, vapor deposition or sputtering [18].

Also, because of the inherent features associated with the plasma spraying process, one can spray a wide range of materials on the polymeric substrate, and can thus tailor the properties of its surface.
COATING SYSTEM SELECTION

4.1 Selection of substrate

The carbon epoxy composite material was selected as the substrate due to the ready availability of this PMC component for testing purposes within the project time frame.

Carbon epoxy materials are commonly fabricated by hand lay-up of unidirectional fibers or woven fabrics and impregnation with the epoxy resin. The molding, called as bag molding, is done by placing the fiber tapes in a die and introducing high-pressure gases or a vacuum via a bag to force the individual plies together. Another method to form carbon epoxy composites with a constant cross section like round, pie, etc. is pultrusion in which the fibers are drawn from spools, passed through a polymer resin bath for impregnation, and gathered together to produce a particular shape before entering a heated die. A method for forming composite parts of intricate shapes is resin transfer molding (RTM) in which a carbon fiber perform (usually prepared by braiding held under compression in a mold) is impregnated with resin. The resin is admitted at one end of the mold and is forced by pressure through the mold and the preform. Subsequently, the resin is cured. The carbon epoxy composite is used in several components of a modern-day aircraft some of which include the skin, fuselage and wings.

The samples were prepared at the National Institute for Aviation Research, at Wichita State University. The samples can be prepared in several configurations, however, simple eight ply panels with 0-90-0 configurations were laid up and cured. A ply is basically a prepreg which
is a resin impregnated cloth or mat that can be stored for later use. The resin in the prepreg is partially cured to a tack-free stage and this state is called as B-staging. The plies can be arranged on top of each other in several configurations such as 0-90-0, 0-45-0 etc. where these numbers indicate the angle in degrees. The selection of the number of plies and the configuration depends on several factors such as strength, failure mode etc.

4.2 Selection of coating materials

The goal was to explore several coating powders and investigate their performance with respect to their interaction with the substrate. Initial pilot runs consisted of the following materials:

- NiAl 65-35 (Ni – 65%, Al – 35%)
- NiAl 95-5 (Ni – 95%, Al – 5%)
- Zn
- Al

These pilot runs consisted of these coatings by themselves or with a bond coating. For the latter, typically, Zn and Al were sprayed as a bond coating material, whereas NiAl 65-35 and NiAl 95-5 were chosen as the top coating material.

A bond coating can be defined as a preliminary (or prime coat) of material that improves adherence of the subsequent spray deposit [19]. Ni-Al 65-35 is an ordered intermetallic compound with about 65% nickel and about 35% aluminum. The ordered structure makes these compounds extremely strong and hard and makes them melt at very high temperatures. The objective was to produce a reactive coating onto the substrate in which the elemental metal powders of nickel and aluminum would react with each other as well as with the substrate at high temperatures and form a dense, strong and a compact layer onto the
substrate (or the bond coating). Ni-Al 95-5 is a nickel rich alloy primarily used as a bond coating material in thermal barrier coating applications. This alloy was chosen because of its ease of availability and to study the variation due to the stoichiometry.

Zinc and aluminum in the pure forms were used as the bond coating materials because they are soft materials which conform well to the substrate, and when flame sprayed, provide a rough surface which aids the anchoring of the top coating.

4.3 Selection of the spray technology

As discussed earlier, the thermal spray technology can deposit a wide array of materials namely, metals, alloys, ceramics, cermets and polymers. Thick coatings can be deposited at high deposition rates with little substrate preparation and post-spray distortion. Components can also be repaired at low cost, and usually at a fraction of the price for a total replacement. The flame spray and the plasma spray process were chosen for most of the coating runs. The flame spray process was typically chosen as the process for producing the bond coating on the substrates because the flame sprayed surface typically consists of a relatively high level of porosity and rough surface finish. The porosity and the characteristic rough surface finish create a surface which will aid in the anchoring of a dense top coating.

The plasma spray process was chosen for the top coating because it is a versatile process offering a wide temperature range and a high quality of coating. The idea was to choose a high energy heat source and the relatively high velocity process (but not so high as to damage the soft polymer composite surface) to produce a dense and a continuous coating.
EXPERIMENTAL PROCEDURE

5.1 Substrate preparation

Autoclave processing was used to cure the thermoset prepregs. This curing of thermoset composites involves mechanical, thermal and chemical processes. Thermoset composites are materials that are capable of being cured by heat into an infusible and insoluble material. Once cured, a thermoset cannot be returned to the uncured state. Mechanically, pressure is applied to remove trapped air and to consolidate the individual plies and fibers whereas volatiles are vaporized during curing. Chemically, a crosslinking reaction must be initiated and taken to completion to form a rigid matrix of the resin. Crosslinking is a process in which individual polymer chains are linked together by covalent bonds to form one giant molecule. Crosslinking is most commonly initiated through the application of heat, though it also may be initiated by exposure to ultraviolet light, microwaves, or high-energy electrons (e-beam curing). In the autoclave process, high pressure and heat was applied to the part through the autoclave atmosphere, with a vacuum bag used to apply additional pressure and protect the laminate from the autoclave gases. The cure cycle for a specific application is usually determined empirically and, as a result, several cure cycles may be developed for a single material system to account for differences in laminate thickness or to optimize particular properties in the cured part. The cure cycle carried out in this case is as shown in Fig. 10.
The typical autoclave cure cycle as implemented here, was a three-step process. First, vacuum and pressure were applied while the temperature was ramped up to an intermediate level and held there for a definite period of time. This intermediate temperature was 270 F as shown in Fig. 10. The heat reduces the resin viscosity, allowing it to flow and making it easier for trapped air and volatiles to escape. After this holding time of 90 minutes, the cooling cycle consisted of 30 minutes until the ambient temperature was reached (approximately 20 C). The composite material was manufactured by Newport Adhesives and Composites Inc., under the trade name NB 321. The material was procured from National Institute for Aviation Research, Wichita, Kansas.
5.2 Pre-coating substrate surface preparation

Surface preparation is an important factor in influencing coating properties. As discussed earlier, a thermal spray coating does not require an elaborate surface treatment, as compared to other coating technologies. The most commonly used pre-treatment method for thermal spray applications is grit blasting.

The cured composite substrate coupons were cleaned with acetone to remove moisture, dirt and oil and then grit blasted with alumina powder of grit size 24. The grit blasting angle was 90 degrees and the blasting pressure used was 50 psi. The treated surface of the substrate was blown with compressed air to remove any remaining alumina particles on the surface.

During the course of conducting the pilot runs, a surface treatment study was conducted for the composite samples. The coupons were treated at three different levels of grit blasting, low medium and high, and the cross section of the grit blasted surface was studied. The microstructures are shown in the following figures. The highest level of grit blasting is also called as the “no water - break test”. This test is very similar to the ASTM F-22 standard which is frequently used in the plating and anodizing operations. According to this standard, a cured composite sample is degreased with acetone and then its surface is roughened with a coarse sand paper. After every step of coarse roughening, distilled water is sprayed onto the composite sample and its behavior is assessed. If the water spray sheets off, then the surface is not sufficiently roughened. However, if the water spray tends to bead onto the surface, then the surface roughening is sufficient. It can be observed that the no water break test appears to damage the fibers which may result in poor adhesion with the coating.
Figure 11: (As-cured) composite with no surface treatment

Figure 12: Cured composite with medium surface treatment; not passed the “no water break test”
From the microstructure in Fig. 13, it can be observed that grit blasting to meet the “no water break test” severely damages the carbon fibers. It has also been reported in the literature that the most commonly used surface treatment of grit blasting for metallic substrates, can cause damage to PMC [8]. This could be because the surface of a PMC is much softer than any metallic substrate. As a result of this treatment state of the carbon fibers, the incoming sprayed material will form a poor bond with the substrate. It is known that carbon fibers have a poor wettability with other materials [18] and hence its exposure to the coating droplets will reduce the bond strength of the overall coating. Hence all the coatings were sprayed on a minimally treated surface.
5.3 Coating application

The as-cured composite substrate panels were sectioned with a diamond cutter and sized to coupons of two inch by eight inch. These coupons were grit blasted and then sprayed with the coating materials. The torch used during the deposition of the plasma sprayed coating was Sulzer F4MB from Sulzer Metco with the Sulzer A2000 control system and a Sulzer Twin 10 powder feeder. The nozzle was 1.8 mm in diameter. The substrate was mounted on a rotating fixture and the torch was traversing linearly (parallel to the axis of rotation) against the rotating substrate and thus depositing the desired coating. The flame spray device was the Sulzer Metco 10E single wire combustion torch.
COATING CHARACTERIZATION

6.1 Coating spray matrix

Initially, pilot runs were conducted with the following conditions of parameters as shown below. These parameters were used as base parameters for further process development.

- **Power**: 35 kW
- **Argon**: 48 SLPM
- **Hydrogen**: 8.1 SLPM
- **Powder feed rate**: 40 gm/sec
- **Plasma torch motion (XY direction)**: 10 mm/sec
- **Surface preparation**: Sand blasting
- **Sand blasting pressure**: 50 psi

Based on the pilot runs using the above parameters, new process parameters were chosen and substrates were sprayed with two variables, namely, power and standoff distance. All the other parameters were kept constant throughout the matrix. Thus each material (feedstock) was sprayed at four different combinations forming the spray matrix as follows:

<table>
<thead>
<tr>
<th>Combination</th>
<th>Power (kW)</th>
<th>Standoff Distance (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>100</td>
</tr>
</tbody>
</table>
The spray matrix consisted of the following materials used for spraying:

**Coatings without bond coat:**

- NiAl 95-5 (95% Ni, 5% Al)
- NiAl 65-35 (65% Ni, 35% Al, intermetallic compound)

**Coatings with bond coat:**

- Aluminum-bond coat, NiAl-95-5 top coat
- Zinc-bond coat, NiAl-95-5 top coat
- Aluminum-bond coat, NiAl-65-35 top coat
- Zinc-bond coat, NiAl-65-35 top coat

Designation for the material-parameter combination is as follows:

<table>
<thead>
<tr>
<th>Material</th>
<th>Parameter (Power (kW)/Standoff Combination (mm))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20/80</td>
</tr>
<tr>
<td>NiAl 65-35</td>
<td>N6 20/80</td>
</tr>
<tr>
<td>NiAl 95-5</td>
<td>N9 20/80</td>
</tr>
<tr>
<td>NiAl 65-35(t)+Al(b)</td>
<td>N6A 20/80</td>
</tr>
<tr>
<td>NiAl 6535(t)+Zn(b)</td>
<td>N6Z 20/80</td>
</tr>
<tr>
<td>NiAl 95-5(t)+Al(b)</td>
<td>N9A 20/80</td>
</tr>
<tr>
<td>NiAl 95-5(t)+Zn(b)</td>
<td>N9Z 20/80</td>
</tr>
</tbody>
</table>

Thus for example, N6Z 25/80 coating would indicate a coating with zinc as the bond coating and NiAl 65-35 as the top coating sprayed at a power of 25 kW and standoff distance of 100 mm.

\[ t = \text{top coating}, \quad b = \text{bond coating} \]
6.2 Scanning electron microscopy

Samples were characterized for microstructural features using a scanning electron microscope of JEOL make of model JSM 6460 LV.

Coating porosity was determined for all the coatings and the results are as shown in Fig. 15. Porosity was determined using microscopy software named AnalySIS. This automatic image analyzer is coupled with the SEM. It consists of setting the grey level on the microscope image to separate the microstructural features. A grey value is defined as a number between 0 and 255 that represents a particular shade of grey. A false color display is used as shown in Fig. 14 which is actually the visualization of gray values using colors that have nothing to do with actual image’s colors. Using a false color display, each gray value is assigned to a certain color. Once the false color coded image is defined manually, AnalySIS will automatically create a measurement sheet showing the absolute area and the proportional area of all the phases. Thus a quantitative evaluation of the area with regard to each separate grey value is obtained. Porosity values were determined by measuring the fraction of the darkest areas in the total area of the micrograph. A sample size of ten was chosen to calculate the mean, standard deviation and the confidence interval values. Confidence intervals were determined for all the porosity values using t distribution. A ‘t’ distribution was used because of a small sample size. Generally, a sample size less than thirty is considered to be a small sample size.

Confidence interval is basically an interval within which the value of the parameter or parameters in question is expected to lie.
For any unknown parameter ‘x’,

\[ P (L < x < U) = 1 - \alpha, \text{ where,} \]

L and U are the lower and upper control limits respectively and,

\[ (1 - \alpha) \text{ is the confidence coefficient.} \]

This means that for an \( \alpha \) value of 0.05, if one repeatedly calculates porosity area fractions with sample size ten and calculates confidence intervals every time, the confidence intervals one achieves, will include the sample mean 95% of the time. In that sense, there is a 95% chance that any specific confidence interval actually contains the population mean.

The following relation was used to calculate the confidence intervals:

\[ \text{Confidence Interval} = \bar{x} \pm \left( t_{\alpha/2} \times s / \sqrt{n} \right), \text{ where,} \]

\[ \bar{x} = \text{mean of ten readings for each coating}, \]

\[ s = \text{standard deviation}, \]

\[ n = \text{sample size}, \]

\[ t_{\alpha/2} = \text{t value obtained from a table; value with an area of } \alpha/2 \text{ to its right as seen in a t distribution.} \]
Figure 14: False color display of the grey values to determine coating porosity.
Figure 15: Confidence intervals for percentage porosity in all coatings.
Some of the coatings show a high void content. Fig. 15 shows the confidence intervals for all the readings. It can be seen that the mean coating porosity for coatings in the N9 group is relatively lower than that in the N6 group. This may be because of the fact that N9 coatings behave in a quasi-metallic manner because of the relatively higher percentage of nickel. In N6 coatings, the coating feedstock was manufactured by mechanical alloying (physical mixing), which implies that the homogeneity in the particle size and shape is much less than that in N9 (which was manufactured by gas atomization). Hence, one could speculate that owing to the relatively non-homogenous particle morphologies of N6 powders as compared to N9, the inclusion of unmelted and larger particles could be higher in N6 coatings.

From Fig. 15 it can be seen that the confidence interval is very high for N9A 25/80, N9Z 20/80, and N6A 20/80 indicating that the projected value of porosity could fall in a wider range. Almost all the coatings from the N9 group show relatively lower porosity values. However, the lowest porosity value was found to be that for N6A 20/100 which corresponds to a mean value of 0.693%, whereas the highest value was to found to correspond to N6 25/100 with a mean value of 9.594%.
DISCUSSION ON MICROSTRUCTURES

Coatings without bond coating

As mentioned in section 6.1, N6 and N9 were the coatings sprayed without any bond coating. Figure 16 and Fig. 17 show the microstructures of N6 material at a standoff distance of 80 mm with a torch power of 25 kW and 20 kW, respectively.

The grayish region shows pure aluminum whereas the white layer indicates pure nickel in both the above microstructures, as found out by energy dispersive X-ray spectroscopy. Energy dispersive spectroscopy is a microanalysis technique performed in conjunction with scanning electron microscopy. This technique utilizes x-rays that are emitted from the sample during bombardment by the electron beam to characterize the elemental composition of the analyzed volume. When the sample is bombarded by the electron beam of the SEM, electrons are ejected from the atoms comprising the sample’s surface. A resulting electron vacancy is filled by an electron from a higher shell, and an X-ray is emitted to balance the energy difference between the two electrons. The X-ray detector measures the number of emitted X-rays versus their energy. The energy of the X-ray is characteristic of the element from which the X-ray is emitted and this is how the presence of the element is determined.

The darkest regions correspond to the coating porosity. It can be seen that the area of porous regions in the 25 kW microstructure as shown in Fig. 16 is greater than that in the 20 kW microstructure as shown in Fig. 17. Reduction in power results in a reduced plume temperature as a result of which the particles may just be heated to the appropriate temperature to melt and fuse onto the polymer substrate.
Figure 16: Typical microstructure (cross section) of a N6 coating. Power is 25 kW and standoff distance is 80 mm.
Figure 17: Typical microstructure (cross section) of a N6 coating. Power is 20 kW and standoff distance is 80 mm.
Coatings with bond coating

N6A, N6Z, N9A and N9Z were the coatings with a bond coat. The microstructure in Fig. 18 shows that the top coating has penetrated in the bond coating. The NiAl top coat has become fused with the aluminum bond coating. Also the top coating achieved was thinner than the bond coating, because of the inability to get a top coating greater than 50 microns. Higher number of passes (greater thickness) resulted in the coating getting peeled, possibly due to higher residual stresses. In Fig. 19, an abrupt transition from the bond coating to the top coating can be seen. This may be the reason for the lower erosion resistance for N9 coatings as compared to the N6 coatings, because the later have their top coating (N6) in intimate contact with the bond coating (either aluminum or zinc); whereas, in case of N9, there does not seem to be any apparent penetration at the interface of the bond and top coatings.
Figure 18: microstructure (cross section) of a NiAl 65-35 top coat with an aluminum bond coat. Power is 20 kW and standoff distance is 80 mm.
Figure 19: microstructure (cross section) of a NiAl 95-5 top coat with an aluminum bond coat. Power is 20 kW and standoff distance is 80 mm.
6.3 Erosion test by sand blasting

Erosion testing by sand blasting was carried out on all the samples using a standard erosion tester. Testing was performed as per ASTM standard G76-02. However, testing was conducted at an extremely severe pressure of the sand blasting media to see the effects of accelerated erosion. After the sand blasting process, samples were thoroughly washed with distilled water, and then blown with compressed air. All samples were allowed to dry in ambient atmosphere for several days before making weight loss measurements. The grit blasting media used was alumina with grit size 80 microns. All test samples were held at 90 degrees to the sand blasting guns. The erosion test result table is shown in the appendix. Figure 20 shows the mass loss of different coatings at different parameters. This erosion test was conducted at different periods and the mass loss after each period (20 seconds) was measured. The mass loss shown in the graph is the steady state mass loss after 4 erosion cycles (80 seconds). Appendix 11.2 shows values mass loss after each cycle. It can be seen from Fig. 20 that for almost all of the coatings from the N6Z group, the mass loss was negligible. Also, the N6 coatings showed negligible mass loss for the powers 20 and 25 kW, each with standoff distance 100 mm. Most of the coatings with aluminum as the bond coating, showed relatively weaker erosion strength as compared to the coatings with zinc as the bond coating.

Similar testing for bare (as-cured) composite samples revealed a mass loss of 0.178 gm/square inch which is about 2.5 times that of the weakest coating which is N9Z 25/80.
Figure 20: Mass loss of coatings in grams after 4 cycles of erosion, arrows showing coatings with relatively lower mass loss.
Figure 21: Mass loss of coatings with respect to time at 20 kW and 80 mm standoff distance.
6.4 Adhesion strength

The adhesion strength or bond strength of the coatings was measured using a coating adhesion tester according to ASTM D4541–02—“Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers”. According to this method, the greatest perpendicular force borne by the entire substrate coating system is determined. Failure will occur along the weakest plane within the system comprised of the test fixture, adhesive, coating system and substrate. Figure 22 shows the bond strength of all the coatings. It can be seen that coatings with NiAl 65-35 as the top coat show a higher bond strength that the ones with NiAl 95-5 as the top coat. This could be because of the partial ionic nature of the bond formed between the elemental nickel and aluminum powders. All the coatings failed at the interface between the composite and the coating. The adhesive used to test all the samples was the Scotch Weld Epoxy Adhesive 2216 from 3M, which had bond strength of 3000 psi. The adhesion test was performed by M.E Taylor Engineering Inc. with the Patti 2A make of adhesion tester.
Figure 22: Adhesion strength results for all coatings.
One important aspect of this study was the development of plasma spray parameters for depositing coatings on polymer matrix composites. This development work was the result of the initial difficulty in obtaining a satisfactory coating builds up. During the first phase of the project, a discontinuous coating pattern was observed for the N6 coatings. In the second phase however, a uniform and dense coating was observed for the same number of passes. This was because of variation in the parameters like torch power (current) and standoff distance.

The power was reduced to 20 kW and 25 kW from 35 kW. With reduced power, one has just the appropriate temperature to melt the particles uniformly and then bond them on the substrate. A higher torch power of 35 kW (which actually translates into a higher plume temperature) may have resulted in damaging the surface preparation of the substrate, as a result of which most of the coatings with the 35 kW power showed poor adhesion.

Delamination was observed for coatings with thickness greater than of 150 microns. Also, the number of passes was linear with respect to weight but not linear with respect to the thickness. For e.g. one pass would yield a 25 micron thick coating but 2 passes will not necessarily result in 50 microns of thickness. It would actually be about 35-40 microns. This is because the coating becomes denser and denser as the passes go on increasing i.e. it fills the porosity of the previous passes. Hence the total thickness is not proportional to the number of passes.
COATING PERFORMANCE EVALUATION

7.1 Effect of thermal spray parameters

According to some researchers, there are hundreds of parameters that can potentially influence the properties of the coatings. However, for economic (time limitations) and theoretical reasons (interdependence of parameters), it is not possible to control all possible parameter variations. In fact, only eight to twelve parameters are routinely controlled at preset levels.

The most commonly used control parameters are:

- Power input,
- Standoff distance,
- Arc gas pressure,
- Auxiliary gas pressure,
- Powder gas pressure,
- Powder feed rate,
- Grain size/shape,
- Injection angle, (orthogonal, downstream, upstream)
- Surface roughness,
- Substrate heating,
- Spray distance,
- Spray divergence, and
- Spray atmosphere
Among the most important primary parameters that influence the coating properties and the overall deposition efficiency are the torch power, arc gas flow rate and the standoff distance.

Theoretically, a higher standoff distance would mean that the feedstock would dwell in the plasma plume for a longer duration. This could project into excessive heating of the particles and hence evaporation of the particles before they hit the substrate. On the contrary, a lower standoff distance could cause excessive heating of the substrate as the substrate will be closer to the tip of the nozzle. Also, if the particles do not dwell for a sufficient time in the jet, the resulting coating microstructure will consist of unmelted particles.

7.1.1 Effect of parameters on coating porosity

The variation in standoff distance has no significant effect on the porosity, as can be seen from Fig. 23. However, the variation in power does apparently seem to have, a significant effect on the coating porosity; because other than N6 with standoff distance 100 mm and N6A with standoff distance 80, all other coatings with power rating of 25 kW have lower coating porosity than the ones with 20 kW. The lowest mean percentage coating porosity achieved amongst all the coatings also corresponds to power rating of 25 kW.

However to gain confidence in drawing conclusions about the effect of power on the mean percentage porosity, hypothesis testing can be used. A statistical hypothesis is basically a statement either about the parameters of a probability distribution or the
parameters of a model. The hypothesis reflects some conjecture about the problem situation.

We may think that the mean porosities at the two power levels are equal. This may be stated formally as:

\[ H_0: \mu_1 = \mu_2 \]

\[ H_1: \mu_1 \neq \mu_2, \]

where \( \mu_1 \) and \( \mu_2 \) are the two coating porosities at 20 and 25 kW respectively and the statement \( H_0: \mu_1 = \mu_2 \) is called the null hypothesis and \( H_1: \mu_1 \neq \mu_2 \), is called a two-sided alternate hypothesis because it would be true if \( \mu_1 < \mu_2 \) or \( \mu_1 > \mu_2 \).

Since we have two samples here, we could use a two-sample t test, and assume that the variances of the mean percentage porosities were identical for both the power ratings.

The appropriate test statistic to compare these two mean porosities is:

\[
t_0 = \frac{\bar{y}_1 - \bar{y}_2}{S_p \left( \frac{1}{n_1} + \frac{1}{n_2} \right)^{0.5}}
\]

where, \( \bar{y}_1 \) and \( \bar{y}_2 \) are the mean coating porosities at the two power ratings 20 and 25 kW, respectively,

\( n_1 \) and \( n_2 \) are the two samples sizes,

\( S_p^2 \) is an estimate of the common variance given by,

\[
S_p^2 = \frac{(n_1 - 1) S_1^2 + (n_2 - 1) S_2^2}{n_1 + n_2 - 2}
\]
S\(_1\) and S\(_2\) are two individual sample variances.

Our null hypothesis is that the mean coating porosities are the same. In other words, if this hypothesis is proved false, then there is a significant difference between the two mean coating porosities. Else, the contrary is true.

Thus, H\(_0\): \(p_1 = p_2\) is the null hypothesis. Calculating with the following values:

\[
\bar{y}_1 = 4.0674, \\
\bar{y}_2 = 3.7618, \\
S_1 = 1.226602711, \\
S_2 = 6.323944622, \\
S_p^2 = 20.74 \\
n_1 = 10 \\
n_2 = 10
\]

We have \(t_0 = 0.15\).

Comparing \(t_0\) with \(t_{\alpha/2, n_1 + n_2 - 2}\), which can be obtained from the table for percentage points for the t distribution, we have,

\[t_0 < t_{\alpha/2, n_1 + n_2 - 2}, \text{ where,}
\]

\[t_{\alpha/2, n_1 + n_2 - 2}\] is the upper \(\alpha/2\) percentage point of the t distribution with \(n_1 + n_2 - 2\) degrees of freedom.

This means that our hypothesis is true and that the mean percentage porosities of the coatings at the two different power ratings are not significantly different.

The above procedure could be explained as follows. If one is sampling from independent normal distributions, then the distribution of \(\bar{y}_1 - \bar{y}_2\), is N \([p_1 - p_2, \sigma^2 (1/n_1 + 1/n_2)]\).
Thus if $\sigma^2$ were known, and if $H_0: p_1 = p_2$ were true, the distribution of

$$Z_0 = \frac{\bar{y}_1 - \bar{y}_2}{\sigma \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

would be $N(0,1)$. However in replacing $\sigma$ by $S_p$, the distribution of $Z_0$ changed from standard normal to $t$ with $n_1 + n_2 - 2$ degrees of freedom. Now, if $H_0$ is true, $t_0$ in Equation 1 would be distributed as $t_{n_1 + n_2 - 2}$ and consequently we would expect $100 (1- \alpha)$ percent of the values of $t_0$ to fall between $-t_{\alpha/2, n_1 + n_2 - 2}$ and $t_{\alpha/2, n_1 + n_2 - 2}$. A sample producing a value of $t_0$ outside these limits would be unusual if the hypothesis were true and is the evidence that $H_0$ should be rejected. However, in this case, the value of $t_0 (0.15)$ is inside the limits mentioned above as shown in Fig. 25. Hence the null hypothesis cannot be rejected.

Thus the $t$ distribution with $n_1 + n_2 - 2$ degrees of freedom is the appropriate reference distribution for the test statistic $t_0$. That is, it describes the behavior of $t_0$ when the null hypothesis is true.
Figure 23: Effect of standoff distances 80 and 100mm on the coating mean % porosity
Figure 24: Effect of Power ratings 20 and 25 kW on the mean percentage coating porosity
Figure 25: $t$ distribution showing critical region for $\alpha = 0.05$, $n_1 = 10$, $n_2 = 10$
7.1.2 Effect of parameters on mass loss due to erosion

The above two figures show that the thermal spray parameters, namely power and standoff distance do not affect the mass loss due to erosion significantly. However, in general, the porosity is lower at a standoff distance of 100 mm, which can be derived from the fact that mass loss is low for both levels of power 20 and 25 kW for the materials N6 and N6Z. Also mass loss is especially higher for the coatings with top coat as N9 with standoff distance as 80 mm.
Figure 26: Effect of power on the mass loss of coatings
Figure 27: Effect of standoff distance on the mass loss of the coatings
SUMMARY AND CONCLUSION

This study was an attempt to demonstrate the ability to develop strategies to improve the surface of the PMC substrate. Initially, intermetallic alloys were selected from binary diagrams. From those materials, pilot runs were performed on as received composite surfaces. Based on those results, surface treatment study was conducted to determine the optimal substrate conditions for good bonding. The second phase of the spray runs comprised of new substrate preparation characteristics along with new process parameters.

Significant conclusions are as follows:

a. Polymer matrix composites can be successfully deposited with thermal spray coatings. Successful deposition of a wide array of materials shows that thermal spray coating is a viable technology for the polymer composite surface protection. A heavy importance was placed on nickel based intermetallics because of their inherently better properties to provide high mechanical strength and erosion resistance as compared to pure metals.

b. Surface preparation parameters used for application of paints do not apply for thermal spray coating application. This was evident from the “No water break test”, which proved that excessive surface preparation by sand blasting leads to damage to the composite surface resulting in the exposure to fibers.

c. To understand the spray-substrate interactions, a range of parameters need to be developed to study their effect on the performance of the coating. Typically, the spraying was carried out within a wide range, for the two spray parameters namely, torch power and standoff distance.
d. The results shown by erosion testing by sand blasting indicate, in general, a higher mass loss resistance for nickel aluminum intermetallic compound as compared to the nickel alloy. The coating with bond coat as zinc especially showed a higher erosion resistance as compared to one with aluminum. The lowest mass loss value is about 0.01 gm per square inch of composite surface, which translates to about 1 gm per 100 square inch of composite surface. The mass loss values for bare composite are much higher than the coated composite surface (2.5 times higher than the weakest coating). This indicates that the coating definitely provides surface protection in terms of the erosion properties.

e. Porosity values were higher for intermetallic compounds as compared to alloys. This could be because of the presence of a more heterogeneous intermetallic feedstock as compared to the nickel alloy feedstock. The heterogeneity was also because of a wider particle size distribution for N6 feedstock as compared to the N9 one. This indicates that the particle size distribution may create a significant impact in developing the coating properties. Porosity values fell well within the standard range of 0 – 10% as described in literature.

f. Bond strength values correlated well with the erosion strength values, for e.g., N6Z showed higher bond strength as compared to N6A. The bond strength of all the coatings could further be improved by using thermally sprayed polymer bond coats.

g. N6 stand-alone coatings were successfully sprayed (without bond coating). This could completely eliminate the bond coating process and would in turn result in cost savings. Also, the absence of a bond coat such as zinc would result in
elimination of a galvanic cell (and hence corrosion), which otherwise would have been created in the presence of zinc.
FUTURE WORK

Consideration of response to several conditions, will give a better understanding of the coating behavior. Further testing of the coatings may be conducted for bending, thermal fatigue and mechanical fatigue of the sprayed coatings. Several other intermetallic powders could be sprayed and their process parameters developed and their performance investigated with the various tests performed in this study. In addition, elaborate statistical analysis could be used for determination of acceptable widths of confidence interval based on appropriate sample size selection. Correlation coefficients could be calculated using correlation equations to determine statistically the effect of several parameters such as standoff distance, power, powder feed rate on coating properties such as porosity, erosion resistance etc.

In addition post spray heat treatments could be developed to further consolidate the coatings.
LIST OF REFERENCES


11. APPENDIX

11.1 Porosity values and confidence intervals

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Appendix 1: Mean, standard deviation and confidence intervals (max,min) for coating porosities. R1…R10 = readings, SD = standard deviation, n = sample size.
### 11.2 Erosion strength test by sand blasting

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Appendix 2: Erosion strength test readings after each cycle. Loss indicates steady state loss after 4 cycles each of 20 seconds. Highlighted values indicate lowest mass loss.
11.3 Erosion strength test by sand blasting: pre-erosion samples
11.4 Erosion strength test by sand blasting: post-erosion samples
11.5 Adhesion strength readings

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11.6 Particle size distribution for N6 powder
11.7 Particle size distribution for N9 powder

![Particle size distribution diagram for N9 powder]

- Differential Volume
- Volume (%)
- Particle Diameter (µm)
- 14.95% @ 80.07 µm