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Plasma spray coatings for polymer composites

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PLASMA SPRAY COATINGS FOR POLYMER COMPOSITES

A Thesis by

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Bachelor of Engineering, Pune University, 2002

Submitted to the Department of Mechanical Engineering
and the faculty of the Graduate School of
Wichita State University
in partial fulfillment of
the requirements for the degree of
Master of Science

December 2006

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THERMAL SPRAY COATINGS FOR POLYMER COMPOSITES

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

Ikram Ahmed, Committee Chair

We have read this thesis and recommend its acceptance:

George Talia, Committee Member

Krishna Krishnan, Committee Member

ACKNOWLEDGEMENTS

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ABSTRACT

Thermal spray coating was studied as one of the techniques used for coating graphite reinforced polymer composites, which are extensively used in the aviation industry. These coatings were studied for improvement of surface properties such as erosion resistance, UV protection, hardness and electromagnetic shielding. NiAl (65%Ni,35%Al) intermetallic, NiAl (95%Ni,5%Al), Aluminum and Zinc coating were thermal-spray deposited using different procedures (plasma, flame, electric wire arc) onto polymer composite substrate. Two categories of coating were evaluated: Coatings with bond coat and coatings without bond coat. Different levels of pre-surface preparation for thermal spray coatings were also studied. The microstructures, micro-hardness and electrical conductivity of these coatings were determined. Effect of different parameters on coating properties like micro-hardness and electrical conductivity were studied.

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LIST OF SYMBOLS/ ABBREVIATIONS

TSC	Thermal spray coating
APS	Air plasma spray
VPS	Vacuum plasma spray
HVOF	High velocity oxyfuel
NiAl	Nickel Aluminum
Zn	Zinc
Al	Aluminum
FGM	Functionally graded materials
TBC	Thermal barrier coatings
DC	Direct current
PMC	Polymer matrix composite
MPa	Mega Pascal
mm	Millimeter
kW	Kilo Watt
$^{\circ}\text{C}$	Degree centigrade
$^{\circ}\text{F}$	Degree Fahrenheit
m/s	Meter per second
atm	Atmosphere
μm	micro meter
psi	Pound per square inch
SLPM	Standard liter per minute

LIST OF SYMBOLS/ ABBREVIATIONS (continued)

gm/sec	Gram per second
N6	NiAl (65:35)
N9	NiAl (95:5)
N6A	NiAl (65:35) with aluminum as bond coat
N6Z	NiAl (65:35) with zinc as bond coat
N9A	NiAl (95:5) with aluminum as bond coat
N9Z	NiAl (95:5) with zinc as bond coat
HV	Hardness by Vickers
R	Resistance
A	Area
ρ	Resistivity
l	Length
C	Conductivity

CHAPTER 1

INTRODUCTION

1.1 SURFACE ENGINEERING

In the age of rapid technological advancement and competition efficiency and cost saving are the key words. The demands on materials are many, like stability to withstand high speeds, cyclic stresses, extreme pressures etc. In engineering components, one would aim at material which has high strength and wear resistance, easy to fabricate and economical. It is important to understand the physical and chemical make up of the applied surfaces, in order to design quality components which yield high service lives.

Coating and surface modification technologies allow the engineer to improve the performance, extend the life and enhance the appearance for components. Additionally, it can enhance the performance of components by selectively applying coating without compromising the benefits of substrate material [1]. Furthermore, coatings are not restricted to the traditional application associated with wear and corrosion; they are also used for decorative effect, implant prostheses, and electrical insulation/conduction.

1.2 COATING AND THERMAL SPRAY TECHNOLOGY

1.2.1 COATING TECHNIQUES

When a material is added to the surface it is called as coating deposition process, whereas, if chemistry is altered, then the process is called as surface treatment. There are various coating deposition and surface treatments available for surface modification; the effectiveness depends on the particular surface and modification technique.

The selection of suitable coating technique depends on various factors such as functional requirement, size and shape, availability of coating material, level of adhesion desired, and availability of coating equipment cost. Also the coating deposition must be compatible with the substrate [2]. Fig.1-1 shows commonly used coating deposition techniques.

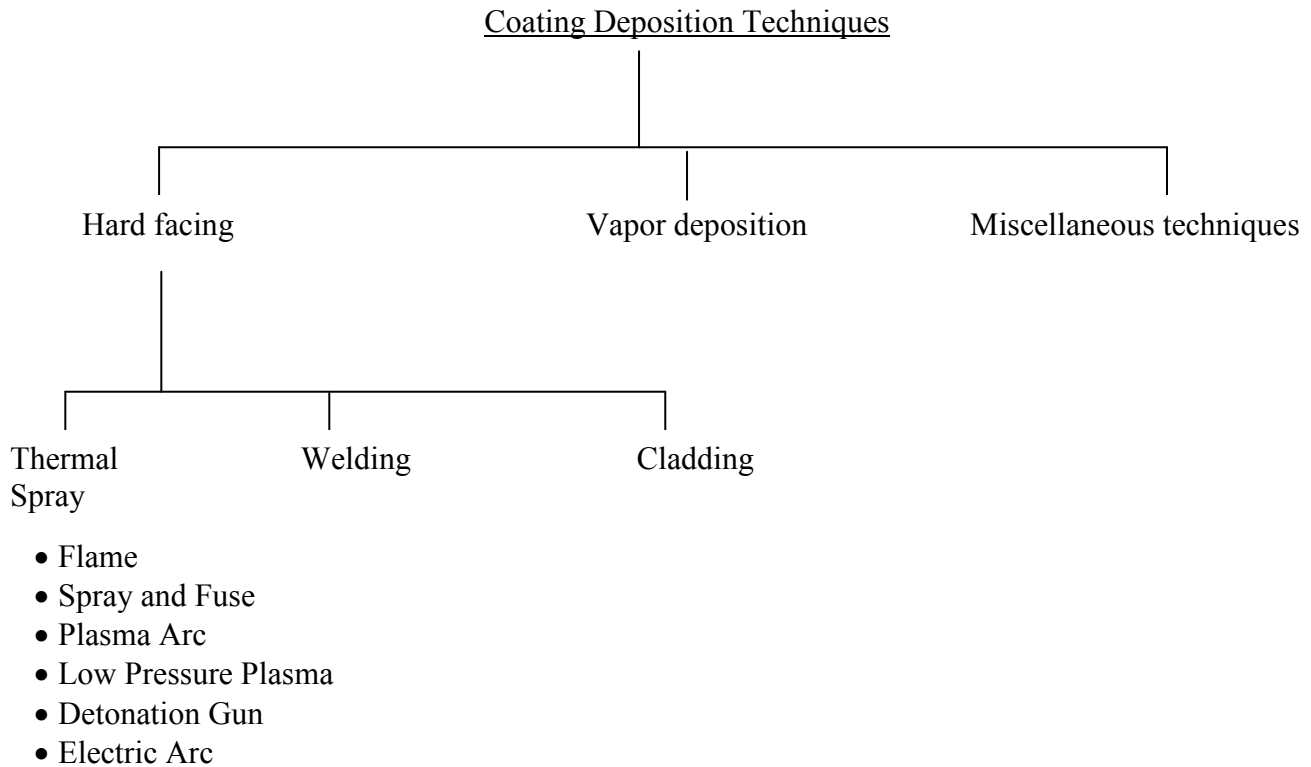


Figure 1-1: Classification of various coating deposition techniques (adapted from Bhushan, Gupta, 1991)

Hard facing technique is used to deposit a wear resistant material on to a worn out or new component subjected to wear. Thermal spray, welding and cladding fall under hard facing techniques. In cladding, a metallic foil or sheet is metallurgically bonded to a metallic substrate to produce a composite. Metals and alloys are re clad by diffusion bonding, braze, weld, and laser

cladding. In welding, a coating material is melted onto the substrate by gas flame, electric or plasma arc welding. Coating material may be in form of powder, rods, wire.

Surface coating technologies have the following advantages

- Technical advantage: Creation of new materials (composites) with property enhancement, or totally new functional properties
- Economic advantage: Expensive bulk materials can be replaced by relatively thin layers of different material

1.2.2 THERMAL SPRAY COATING (TSC)

A young Swiss inventor Dr Schoop invented thermal spraying in early nineteenth hundreds. Dr Schoop noticed that the hot lead shots that were projected out of cannon, stuck to almost any surface which led to the development of thermal spraying [3]. During next two decades Schoop and his associates developed different methods and produced variety of equipment designs. He designed a gun which uses oxygen and acetylene as heat source and compressed air to project the material on to the substrate.

Thermal spray describes a family of processes that uses the thermal energy generated by chemical (combustion) or electrical (plasma or arc) methods to melt and accelerate fine coating material onto the substrate. When the hot energetic particles impact the surface, they rapidly solidify. As subsequent particles impact the surface, a deposit thickness is built up forming lamellar structure as seen in Fig.1-2. Thin “splats” undergo rapid cooling typically in excess of 10^6 K/s. The most practical means of generating kinetic energy to propel molten particles is by gas stream through a nozzle. The speed is in the range of 50 to >1000 m/s. High temperature and speeds results in significant droplet deformation on impact on the surface.

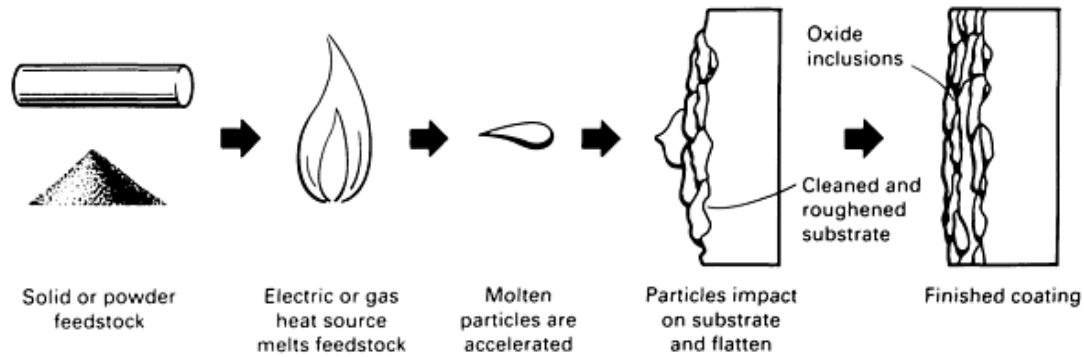
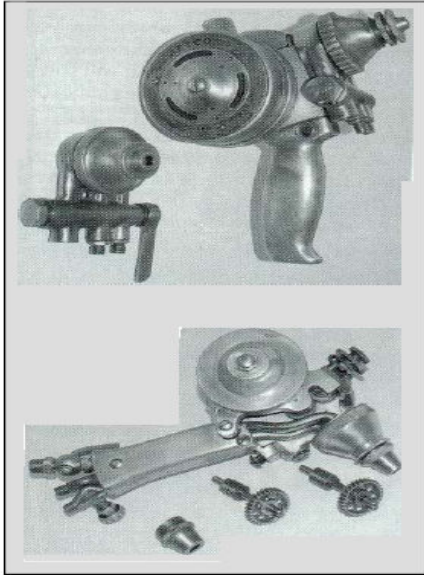


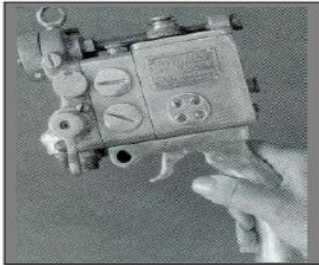
Figure 1-2: Schematic of thermal spray process [1]

Benefits of TSC are

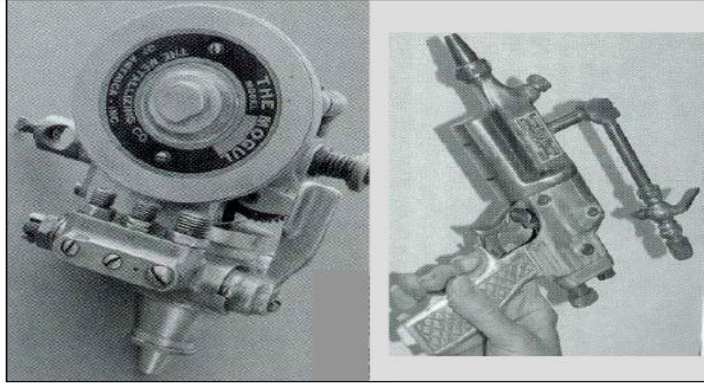
- Comprehensive choice of coating materials: metals, alloys, ceramics, cermets and carbides
- Thick coatings can be applied at high deposition rates
- Coatings are mechanically bonded to the substrate - can often spray coating materials which are metallurgically incompatible with the substrate, e.g. materials with a higher melting point than the substrate
- Components can be sprayed with little or no pre- or post-heat treatment, and component distortion is minimal
- Parts can be rebuilt quickly and at low cost, and usually at a fraction of the price of a replacement
- By using a premium material for the thermal spray coating, coated components can outlive new parts
- Thermal spray coatings may be applied both manually and automatically



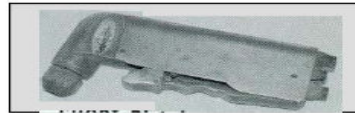
METCO 2E Metallizing Gun with two nozzles. See the 1950 USA penny welded onto the side to show year of manufacture



MULTIPLEX Metal Spray Gun by Britton company



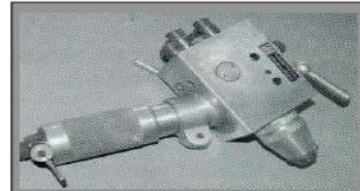
MOGUL 'DOT' Weld Pistol – used as preparation tool for bonding spray coatings. Its air operated piston caused a vibration, so the electrode (nickel, brass or aluminium) would make and break the arc, causing small nodules of deposit on the work piece, 1960



SHORI Pistol, Powder gun, 1948



Valentine Metal Gun company Wire Spray Gun



METALLGESELLSHAFT A.G. Wire Spray Gun

Figure 1-3: The evolution of thermal spray gun's from 1940's to 1960's, adapted from Dusa

(2001)

1.2.3 THERMAL SPAY PROCESS (TSP) CLASSIFICATION

Thermal spray process can be classified by the type of energy used to melt the coating material; these are grouped into three major categories: Plasma arc spray, Flame spray, and electric arc spray

1.2.3.1 PLASMA ARC SPRAY

Plasma arc spraying is one of the most sophisticated and versatile thermal spray methods. Plasma arc spray uses coating materials in the form of powders, which are heated with a plasma heat source and can be further classified as [4]

- a) Conventional plasma
- b) Vacuum plasma

a) Conventional Plasma

The conventional plasma is also commonly known as air or atmospheric plasma spray (APS). In APS, plasma is generated by superheating an inert gas- typically argon or argon-hydrogen mixture by a dc arc. Feedstock powder is introduced via inert gas carrier on to the substrate by plasma torch. Commercial guns operate at a power range of 20 to 200 KW. Temperature that can be obtained with commercial plasma equipment is greater than 11,000 °C (22,000 °F) and far above vaporization temperature of any know material.

b) Vacuum Plasma

Vacuum plasma spraying (VPS) is also commonly known as low pressure plasma spray (LPPS trademark of Sulzer Metco). VPS uses a modified plasma spray torch at a pressure range of 10 to 50 kPa (0.1 to 0.5 atm). Plasma torch becomes larger in diameter and length as a result of low pressure, and through the use of convergent/divergent nozzles higher gas speed can be obtained. Advantages of this low-pressure plasma technique include improved bonding and density of the deposit, improved control over coating thickness (even with an irregular work surface), and higher deposit efficiency.

1.2.3.2 FLAME SPRAY

Flame spraying is the oldest of the thermal spraying processes, a wide variety of materials can be deposited as coatings using this process and vast majority of components are sprayed manually. Flame spray uses the heat from combustion of fuel gas (usually acetylene or propane) to melt the coating material which can be in the form of powder, wire or rod. In flame spray process, fuel/oxygen ratio and total gas flow rates are adjusted to produce the desired thermal output. Jet speeds typically are below 100 m/s, generating particle speeds up to 80 m/s before impact. Externally combusted, or open flame, jet temperatures are generally above 2600°C (4700°F) [1]. Flame spray process typically yields 85% to 98% coating densities, depending upon coating material and technique. Flame spray includes low-velocity powder flame and wire flame processes and high velocity processes such as HVOF (high velocity oxy-fuel) and detonation gun (D-Gun)

a. Powder Flame Spray

Figure 1-4 shows a low velocity powder spray process. The powder is fed into the gun either by gravity flow or by pressurized feed, and carried to the gun nozzle, where it is melted and projected by the gas stream onto a prepared surface. Particle speed is relatively low (<100m/s), and bond strength of deposits is generally lower than high velocity processes. Spray rates are usually in the 0.5 to 9 kg/h range except for lower melting materials, which have higher spray rates. Oxyfuel powder guns are the lowest cost thermal spray equipment and easy to set up.

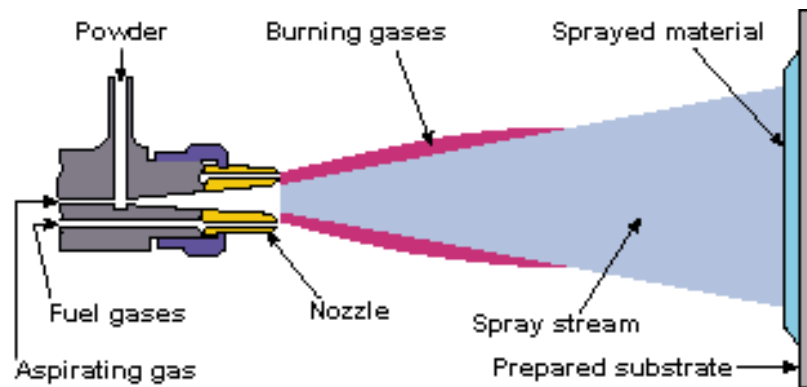


Figure 1-4: Powder spray (TWI-The Welding Institute)

b. Wire Flame Spray

Figure 1-5 shows a wire flame spray process. The coating material is in the form of wire, the wire is drawn into the flame by drive rolls that are powered by an adjustable air turbine or electric motor. The tip of the wire is melted as it enters the flame, atomized into particles by a surrounding jet of compressed air, and propelled onto a prepared surface. Common fuel gases are acetylene, propane, propylene, and natural gas, each combined with oxygen.

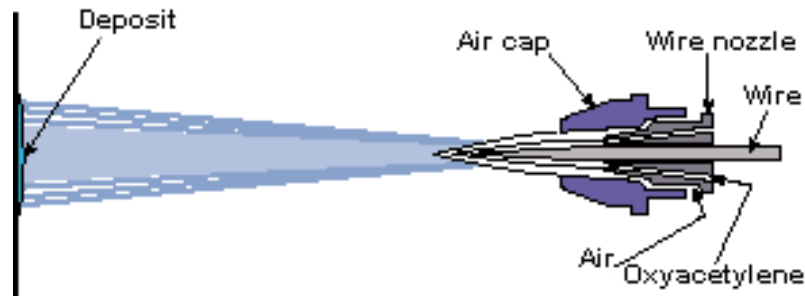


Figure 1-5: Wire flame spray (TWI-The Welding Institute)

c. High- Velocity Oxyfuel (HVOF)

HVOF spraying differs from conventional flame spraying in that the combustion process is internal, and the gas flow rates and delivery pressures are much higher than those in the flame spraying processes. In principle, high-volume combustible gases are fed into a combustion chamber, feeding into long confining nozzle and sprayed onto the substrate with high velocities as seen in Fig.1-6. Volume of gas flow along with the high temperature of combustion creates gas velocities in the range of 1525 m/s to 1825 m/s. HVOF uses hydrogen, propylene, propane, acetylene and kerosene as fuel gases.

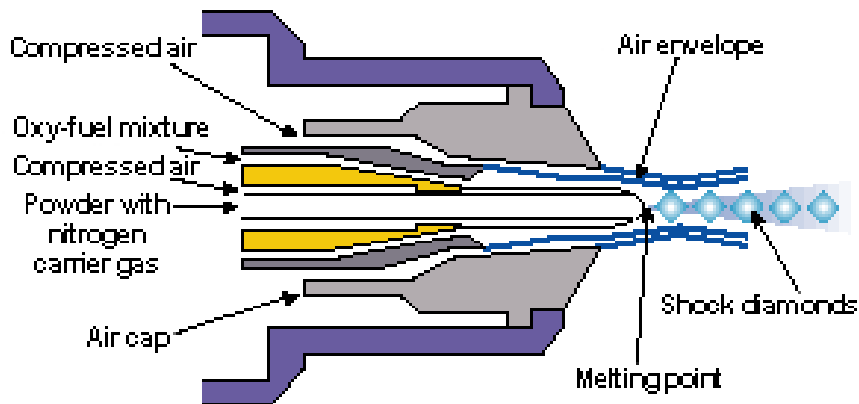


Figure 1-6: Internal combustion high velocity oxyfuel spray

Lower average particle temperature, compared to plasma spray; reduce the degree of particle melting and oxidation. Despite the lower average particle temperatures, high coating densities are still achieved through high particle impact velocities. HVOF sprayed coating density, adhesion, and oxide contents are comparable to high energy, plasma sprayed coatings [1].

1.2.3.3 ELECTRIC ARC SPRAYING

The electric arc spraying is used to spray metals in wire form; this spraying process along with the wire flame spray is also referred to as the metallizing process. Electric arc spraying differs from other thermal spraying processes, in that there is no external heat source, such as a gas flame or electricity induced in plasma [4]. In electric arc, heating occurs when two oppositely charged wires of sprayed material are fed together such that controlled arc occurs between them at the intersection. Figure shows an electric arc spray process. Thermal efficiency of electric arc is considerably higher than that of any other thermal spray process due to melting of wire in the arc. Air stream is used to atomize and accelerate the molten particles onto the substrate [1]. Electric arc transfers less heat to the substrate per unit of material sprayed than any other conventional TSP, owing to absence of a flame jet. Cooler deposit characteristic of electric arc spray minimizes the substrate heating compared to other TSP. Materials for electric arc are limited to conductive materials that can be formed in wires.

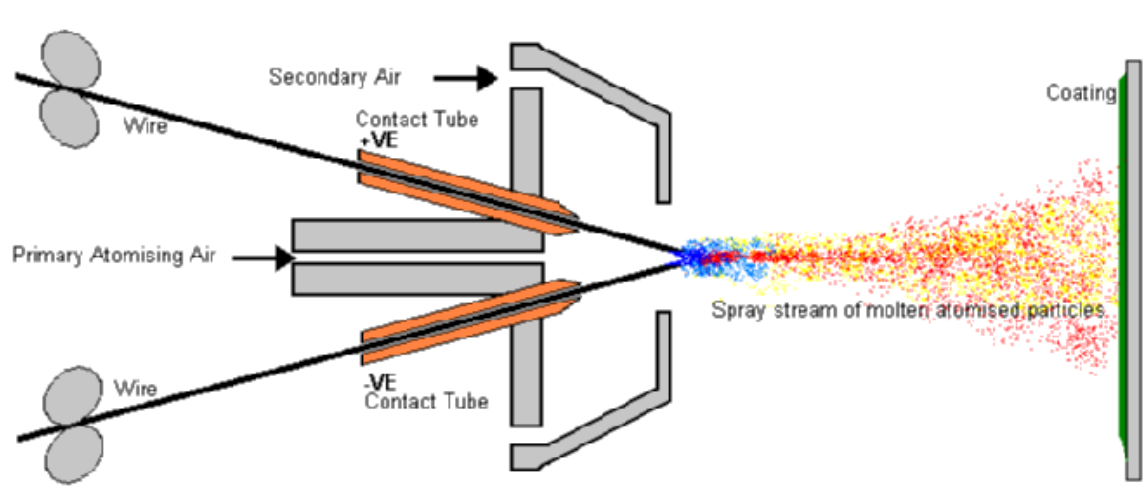


Figure 1-7: Electric Arc Spray Process [22]

Table 1-1, shows a comparison between different types of coating characteristics. HVOF shows highest adhesion with minimum porosity content followed by plasma spray technique.

	Particle Velocity m.s⁻¹	Adhesion MPa	Oxide content %	Porosity %	Deposition rate kg.hr⁻¹	Typical deposit thickness mm
Flame	40	<8	10-15	10-15	1-10	0.2-10
Arc	100	10-30	10-20	5-10	6-60	0.2-10
Plasma	200-300	20-70	1-3	5-10	1-5	0.2-2
HVOF	600-1000	>70	1-2	1-2	1-5	0.2-2

Table 1-1: Comparison of TSP and coating characteristics (adapted from TWI world centre for material joining technology)

1.3 MATERIALS FOR THERMAL SPRAY COATING

Selecting a material for an application involves study of the wear mode and satisfaction to requirements under operating conditions. Wide range of material is available today for tribological applications. Materials that can be plastically formed either in the solid or liquid state can be deposited by TSC. Where heating is involved, only those materials that remain stable upon heating can be sprayed. Instability may refer to oxidation or decomposition of the material [2].

Three basic types of deposits can be thermal sprayed:

- Single-phase materials
- Composite materials
- Layered or graded materials

Single-phase materials

Single phase materials such as metals, alloys, intermetallics, ceramics and polymers can thermally sprayed. Pure metals and metal alloys have been thermally sprayed, including tungsten, molybdenum, rhenium, superalloys, zinc, bronze, NiCr alloys, and cobalt/nickel base triballoys. Alloys have advantages due to their corrosion, wear, and/or oxidation resistance [1].

Applications include automotive cylinder coatings, piston rings, valves, turbine blades etc.

Ceramic materials are inorganic, nonmetallic materials. Most ceramics are compounds between metallic and nonmetallic elements. The term ceramic comes from the Greek word *keramikos*, which means burnt stuff, indicating that desirable properties of these materials are normally achieved through a high-temperature heat treatment process called firing. Ceramics like metallic oxides such as Al_2O_3 , stabilized ZrO_2 , TiO_2 , Cr_2O_3 and MgO ; carbides such as Cr_3C_2 , TiC , SiC ;

nitrides such as TiN and Si₃N₄. They provide wear resistance, thermal protection, and corrosion resistance. Ceramics being high temperature materials, they are mostly sprayed using plasma thermal spray process.

Intermetallics is the short summarizing designation for such intermetallic phases and compounds, i.e. chemical compounds between two or more metals with crystal structures which differ from those of the constituent metals. In a mechanical context, such compounds often offer a compromise between ceramic and metallic properties when hardness and/or resistance to high temperatures are important enough to sacrifice some toughness and ease of processing. Intermetallics such as TiAl, Ti₃Al, Ni₃Al, and NiAl have been thermally sprayed. Inert atmosphere is used during plasma spraying as most intermetallics react at high temperature and are very sensitive to oxidation.

Composite materials

Composite materials are engineered materials made from two or more constituent materials that remain separate and distinct on a macroscopic level while forming a single component. There are two categories of constituent materials: matrix and reinforcement. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart special physical (mechanical and electrical) properties to enhance the matrix properties. Different types of reinforcement such as particulates, fibers, and whiskers have all been produced and used in various applications. Particulate reinforced wear resistance cermet coatings such as WC/Co, NiCr and TiC are the most common applications. Reinforcement content varies from 10 to 90% by volume.

Functionally graded materials

Functionally graded materials (FGMs) are composite materials where the composition or the microstructure is locally varied as shown in Fig.1-8, so that a certain variation of the local material property is achieved. Modern FGMs are constructed for complex requirements, such as the heat shield of a rocket or implants for humans. The most immediate application of FGMs is thermal barrier coatings (TBCs), where large thermal stresses are minimized. FGMs are used in turbine components, rocket nozzles, chemical reactor tubes and critical furnace components.

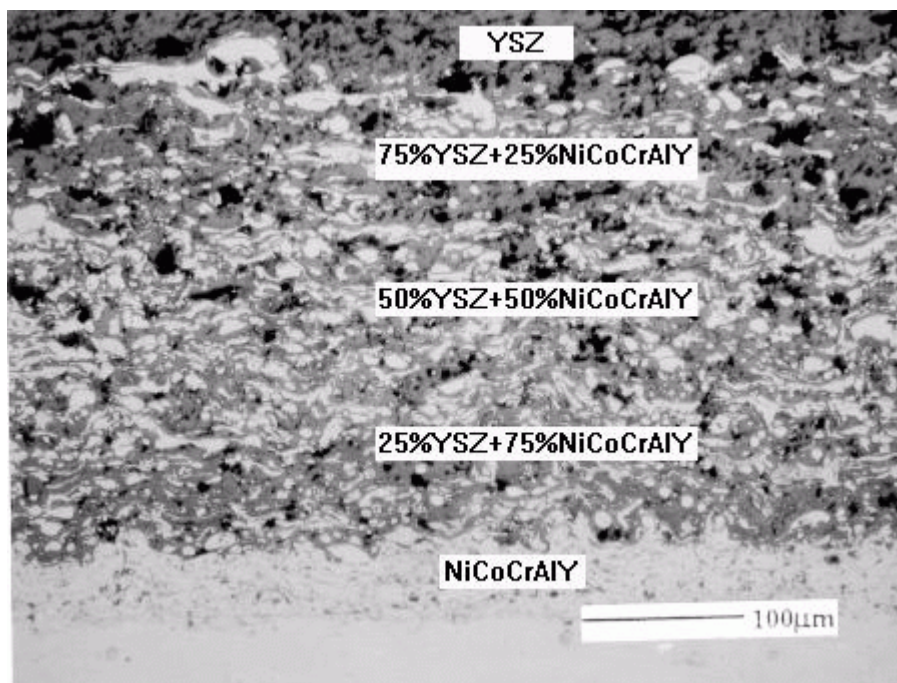


Figure 1-8: Microstructure of functionally grades coating [1]

1.4 THERMAL SPRAY ADVANTAGES AND APPLICATIONS

There is an ever increasing number of technical applications of metallic and ceramic coatings. Many of such applications are as a result of protection against wear, erosion, corrosion and thermal and chemical attack. Others result from the desire to impart new functional properties to conventional materials. Few industrial areas where TSC have been successfully used are as follows [4]:

- Wear and erosion control of machinery parts and turbine vanes
- Particle erosion control in boiler tubes and superheaters of coal fired power plants
- Chemical barrier coatings for ethane steam cracking furnace
- Wear control of friction properties in machinery parts
- Thermal and chemical barrier coatings of piston and valves in diesel engines
- Biomedical coatings for orthopedic and dental prostheses
- High temperature superconducting coatings for electromagnetic interference shielding

1.5 THERMAL PLASMA SPRAY

During the past three decades, the needs of the aircraft, aerospace and electronics industries have stimulated the development of processes to give coatings of generally higher quality and to extend the range of spraying. These requirements have led to the commercial introduction of plasma spraying.

1.5.1 PLASMA SPRAYING

Plasma spraying is a multipurpose thermal coating process. In this process plasma is produced and controlled by a specifically designed torch by excitation of an inert gas passing through an electric arc, generating a very hot ionized gas. A unique opportunity to mix and blend materials that are otherwise incompatible is provided by the plasma spraying process. Complex alloys, elemental materials, composites and ceramics can often be produced with this technique for use in target material fabrication. Material in the form of powder is injected into a very high temperature plasma flame where it becomes molten and accelerated onto the substrate to provide a coating [22]. Here, layer by layer, a buildup through intra-particle bonding and sintering reaction takes place [1, 3].

Fig.1-9 shows a Plasma spray gun which consists of an anode and cathode made of copper and tungsten respectively, both of which are water cooled. Plasma gas flows around the cathode and through the anode which is shaped as a constricting nozzle [22]. A high voltage discharge initiates plasma to cause localized ionization; this also generates a conductive path between cathode and anode to form a DC arc. Gas reaches extreme temperatures due to the resistance heating from the arc resulting in dissociation and ionization to form the plasma. The plasma exits the anode nozzle as a free or neutral plasma flame. After plasma is stabilized the electric arc extends down the nozzle, without shorting out to the nearest edge of the anode nozzle. Plasma arc is constricted by the cold gas around the anode nozzle resulting in higher temperature and velocity. External powder port (near the anode nozzle) is used to feed the powder into the plasma flame.

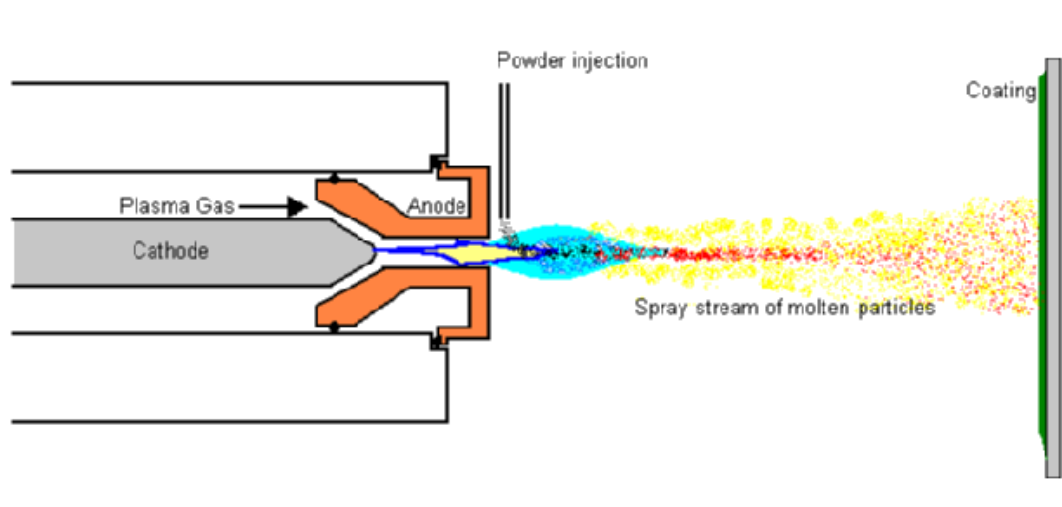


Figure 1-9: Plasma spray process [22]

PLASMA STATE

Plasmas are quasi-neutral multiparticle systems characterized by gaseous or fluid mixtures of free electrons and ions, as well as neutral particles with a high mean kinetic energy of electrons or all plasma components and a considerable interaction of the charge carriers with the properties of system [3]

PLASMA GENERATION

The different methods of plasma generation are applications of gas ionization, two basic mechanisms are:

- Application of heat, directly through the container wall, or indirectly through chemical processes or an electric current
- Transfer of energy without substantial temperature increase of the gas through particle or electromagnetic radiation

PLASMA GASES

Common plasma gases used are as follows

- Argon
- Helium
- Hydrogen
- Nitrogen

Typical plasma jets use argon together with another auxiliary gas. Argon- only creates relatively low-energy plasma. Nitrogen on the other hand, is one of the hottest plasma gases; it is reactive and has some material limitations. Helium increases the thermal conductivity of the plasma, increasing the heating capability of the plasma [1].

Typical plasma gas combinations

- Argon/helium
- Argon/hydrogen
- Nitrogen/hydrogen

SPRAY TORCHES:

1. RF torches

As shown in the Fig.1-10, the injector is positioned at the middle of the coil. The gas near the torch axis is heated by the coupling of coil and plasma within the ring which is located close to the wall. This heat is generated by convection-conduction process. As from the Fig.1-10, water cooled injector can be positioned axially with no coupling to the coil. Spray torches generally work at 3.6 MHz, with power levels up to 100kW [5]. As the gas velocity is roughly inversely proportional to the square of the torch inner diameter it means that plasma gas velocity is below 100ms^{-1} , corresponding to particle velocities below 60ms^{-1} and high residence times (in the

tens of milliseconds range). It allows the melting of metallic particles up to $200\mu\text{m}$ with argon in spite of its low thermal conductivity [5].

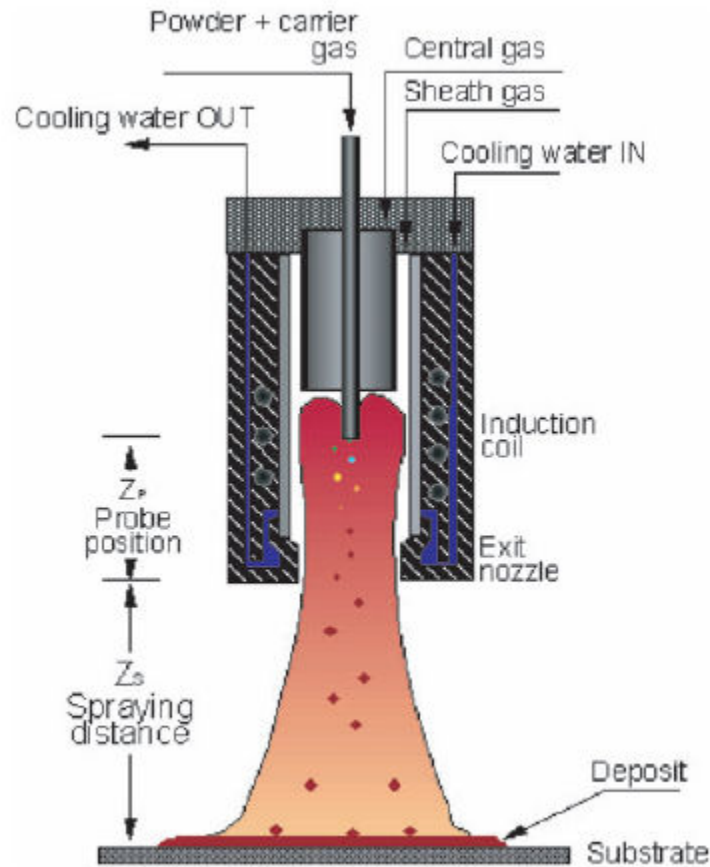


Figure 1-10: Details of RF torch, Conventional PF 50

2. DC arc plasma torch

DC arc plasma torch gas velocities are generally between 600 and 2300 m/s with radial injection [5]. A conventional plasma torch uses a stick type cathode which is made of thoriaated tungsten whereas an anode is made of copper (high purity oxygen free). This is often used with an insert of sintered tungsten.

CHAPTER 2

LITERATURE RIVIEW

Richard 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 [6].

James Sutter, George Leissler et al. [7] used a similar two layer technique to coat their material. The composite substrate in this case was made of polyimide resin. 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.

Again, Richard Knight et al. investigated the adhesive / cohesive properties of thermally sprayed functional graded coatings on polymer composites [8]. 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 [10].

James Sutter, M. Ivosevic et al. used a simple analytical process model to deposit polyimide using the high velocity oxy – fuel 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). These all coatings were used as bond coats. The top coats were WC – Co and D Gun sprayed CrC-Co [9].

Richard Knight et al. developed a simple analytical model for the deposition of thermosetting polyimide onto polymer composites by using HVOF thermal spray technology.

The model incorporated various heat transfer mechanisms which enabled surface temperature profiles of the coating simulated in the study. Thermal properties of the polyimide required for the simulations were determined by using the following analysis techniques

1. Differential Scanning Calorimeter
2. Thermo – Gravimetric.

Metallographic techniques were utilized to study the micro-structural characterization of the coatings and the morphology of polyimide splats sprayed with and without substrate preheating [10].

Seshadri K N et al studied the lightning effect of metallic coating on composite material. Resistive heating for temperature rise in metals was studied for different characteristics of metals. Also a major area of concern with CFC skins used on aircrafts for electromagnetic shielding was studied [11].

George Harris et al developed a new low density composite EMI shield using NASA developed bromine intercalated graphite to achieve electrically conductive epoxy matrix. They achieved a

potential weight savings of 88% compared to aluminum. Typical 2-ply composites have provided EMI shielding greater than 85dB [12].

Shacklette L W et al developed highly conductive polymer blends for EMI shielding by composing a matrix polymer such as PVC or nylon compound with an intrinsically conducting polymer. It demonstrated high level of shielding performance by use of metal or fibers mixed with polymer matrix [13].

Radford D W et al explored the possibility of creating a new family of ultra-lightweight conductive shield materials using metallized microballoons as conductive filler material. Shielding potential of ceramic microballoons coated with gold, silver, and aluminum in an epoxy resin were investigated. X-band microwave through transmission attenuation, electrical surface resistivity, and anechoic chamber relative shielding effectiveness tests were initially performed [14].

Wienhold, P.D et al performed EMI shielding effectiveness testing over the frequency range of 0.10-18 GHz using the dual chamber test method. Test panels consisted of conventional carbon fiber as well as several different panels with conductive surface materials. Surface conductivity and RF conductivity were measured over a similar frequency range using a test setup devised at APL [15].

Ramchandran, K et al prepared Al_2O_3 and TiO_2 powders by fused and crushed method. These powders were sprayed using air plasma process. Electrical conductivity, microhardness, adhesion, abrasive wear and microstructure were determined for these coatings. An increase in electrical conductivity was observed with an increase in Titania content [16].

Li, J et al Studied the effects of coating process, measurement directions and indenter loads on plasma sprayed $\text{Cr}_3\text{C}_2\text{-NiCr}$. Microhardness of coating was measured using Knoop indentation technique. The measured elastic modulus data exhibited much scatter than for the data of knoop hardness. It was concluded that knoop indentation test is not practicable to measure the elastic modulus of thermal sprayed coatings when the major diagonal of indenter is parallel to the interlamellar boundaries [17].

CHAPTER 3

PROJECT OBJECTIVES

3.1 PROBLEM DESCRIPTION

During 1940's, Polymer matrix composites (PMCs) were first developed for military and aerospace applications. PMC materials consist of strong fibers embedded in a resilient plastic that holds them in place. Their high strength to weight ratio's enabled their widespread use in the aircraft industry. Some other advantages include high modulus of elasticity, excellent fatigue properties and their resistance to corrosion. New commercial aircraft also contain more composites than their predecessors. A 555-passenger plane recently built by Airbus, for example, consists of 25 percent composite material, while Boeing is designing a new jumbo aircraft that is planned to be more than half polymer composites.

Adhesion of coating to a composite surface is a problem; solid, dense and well bonded coatings are required for the corrosion and erosion protection applications. Thermal stability of matrices in composite is low, thermal spray tends to burn off the fibers during the spraying process reducing the adhesion strength. The objective was to find an effective solution to improve hardness, electromagnetic shielding and adhesion of polymeric substrate. This also included the investigation of various materials and process parameters that would optimize these properties of the coatings.

3.2 PROJECT OBJECTIVES

The primary goal of the project was to identify coating needs and possible coating material. Second phase was to develop new coatings to enhance surface properties of the polymer matrix composites (PMC), such as property retention, erosion resistance, corrosion resistance and electro-magnetic interference. When compared to other coating processes, Thermal spray process was chosen for better surface enhancement as this process is economically viable and an efficient technology. Plasma spray process provides ability to spray a wide range of materials on polymer substrate which enables tailored property of the substrate. The study included exploration of several coatings used, two types of coatings were evaluated; coatings with bond coat and coatings without bond coat. Project also included study of effect of thermal spray parameters on the hardness strength and electrical conductivity of these coatings. Third phase was to carry out post coating activities; erosion test, adhesion test, hardness test, electrical conductivity measurements and microstructural characterization.

CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1 COATING SYSTEM

Coatings ranging in thickness from 90 to 200 microns were deposited onto composite substrate of size 8"x 2". Two type of coating techniques were evaluated; coating with bond coat and coating without bond coat. Coating without bond coating consists of a single coat of desired thickness onto the substrate. Coating with bond coat consists of an intermediate coat in between top coat and the substrate.

4.1.1 SELECTION OF MATERIALS

Several coating powders were coated and investigated for their performance with the substrate.

Initial runs were carried using

- NiAl – intermetallic (Nickel 65%, Aluminum 35%)
- NiAl (Nickel 95%, Aluminum 5%)
- CoNiCrAlY
- Aluminum
- Zinc

These materials were coated by themselves or in combination with each other. NiAl (65:35) is a nickel – aluminum based intermetallic compound with 65% nickel and 35% aluminum, these compounds have high strength and higher melting temperature. NiAl (65:35) compound was selected in order to produce a reactive sintering to form a dense and compact coating onto the substrate.

Figure 4-1 illustrates the reactive sintering process for forming the compound AB from a mixture of A and B powders. The initial compact is composed of mixed elemental powders, which diffusionally interact during heating. When the lowest liquidus temperature is reached, partial melting of the compact occurs. The liquid flows into pores between the solid particles resulting in densification. Also, the liquid is a rapid diffusion path between the elements, which facilitates compound formation. The final product is single phase and dense AB [18].

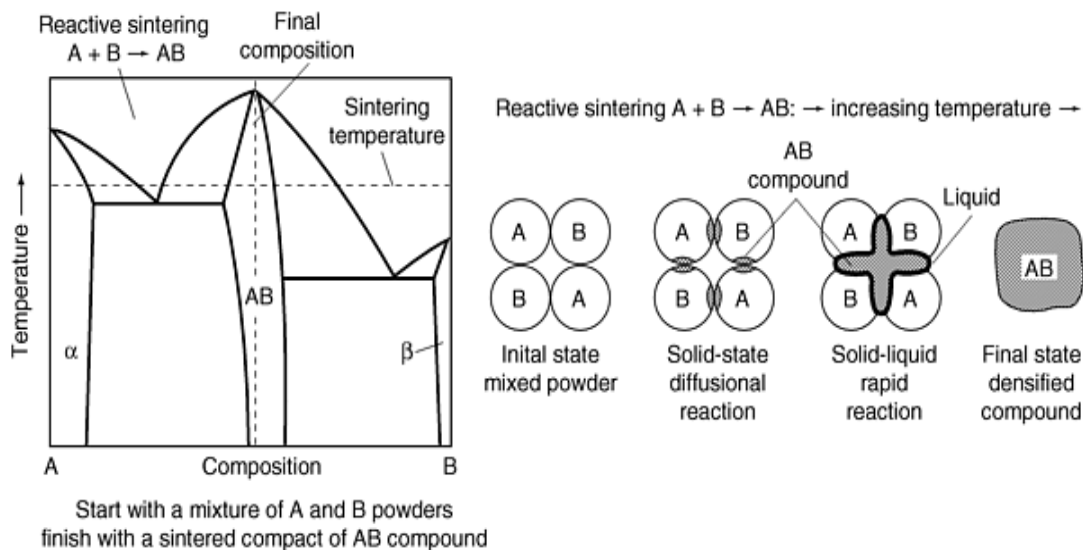


Figure 4-1: A binary phase diagram and the typical sequence of events expected in reactive sintering of compound AB from a mixture of A and B powders

NiAl (95:5) alloy consists of 95% nickel and 5% aluminum, primarily used as bond coat material for coating of metals. This alloy was chosen because it is easily available. Aluminum and zinc in its pure form are soft and conform well to the substrate, providing a better surface finish for top coat. Aluminum and zinc both were used as bond coat materials and sprayed using flame spray technology.

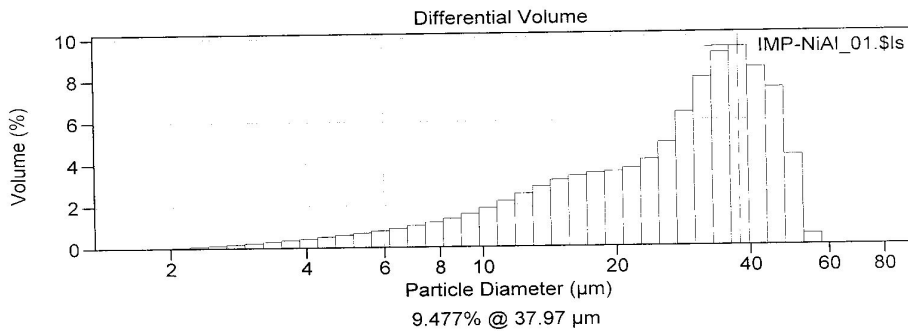
Particle size distribution analysis was carried out for NiAl (65:35) and NiAl (95:5) using Laser particle size analyzer, Beckman Coulter. Laser diffraction is one of the most commonly used techniques for particle size analysis. In this analysis, a representative cloud of particles passes through a broadened beam of laser light which scatters the incident light onto a Fourier lens. This lens focuses the scattered light onto a detector array and, using an inversion algorithm, a particle size distribution is inferred from the collected diffracted light data. Sizing particles using this technique depends upon accurate, reproducible, high resolution light scatter measurements to ensure full characterization of the sample [19]. Series of concentric rings of alternating maximum and minimum intensities formed due to the light scattered by particles is often called the Airy disk. The mean size of the distribution is determined by the first minimum or the closest to the centre of the Airy disk. Consequent maxima and minima contain information on the shape and width of the distribution, including any shoulders and tails. The true shape of the particle size distribution can be reported by accurately measuring the series of maxima and minima.

In the plasma spray process particles of the deposition material are injected into a plasma flame, which is produced by the ionization of an inert gas. The plasma heats the particles to a molten or semi-molten state. The particles then strike the substrate and quickly solidify. The impact of subsequent particles increases the thickness of the coating layer. The feedstock is prepared in a powdered form to facilitate control of the rapid melting and re-solidification of the coating material. [20]

Higher particle size results in non-uniform heating of particles and results in clogging of plasma torch nozzle. A finer particle size distribution results in uniform melting of particles and better deposition onto the substrate. Figs.4.2 and 4.3 gives the particle size distribution of NiAl (65:35) & NiAl (95:5) respectively. 9.477% particles of NiAl (65:35) fall near 37.97 μm , whereas 14.95% particles of NiAl (95:5) are near 80.07 μm .



File name: P:\glenn\Coulter-POWDER DATA\POWDER DATA\glenn\Data-2005\IMP-NiAl_01.\$is
 File ID: IMP-NiAl
 Sample ID: IMP-NiAl
 Operator: Glenn Bancke
 Run number: 1
 Comment 1: IMP-NiAl Surface Eng & Alloy Company
 Optical model: Fraunhofer.rfd
 Fluid R.I.: 1.333 Sample R.I.: 0 i0
 Residual: 0.78%
 LS 13 320 Dry Powder System Run length: 180 seconds
 Start time: 16:49 20 Jul 2005
 Obscuration: 3% Firmware: 2.02 0
 Software: 4.03

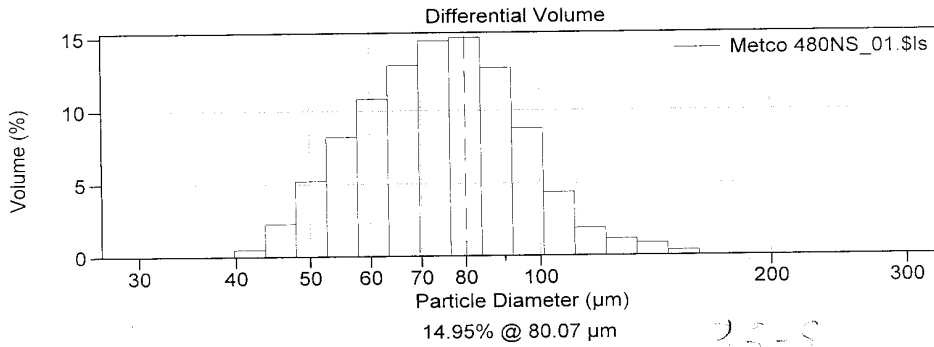


Volume Statistics (Arithmetic)		IMP-NiAl_01.\$is	
Calculations from 0.375 μm to 2000 μm			
Volume:	100%	S.D.:	12.99 μm
Mean:	27.81 μm	C.V.:	46.7%
Median:	29.01 μm	Skewness:	-0.084 Left skewed
D(3,2):	18.72 μm	Kurtosis:	-1.040 Platykurtic
Mode:	37.97 μm		
d ₁₀ :	9.659 μm		
d ₅₀ :	29.01 μm		
d ₉₀ :	44.99 μm		
% <	10	25	50
μm	9.659	16.61	29.01
			75
			38.21
			90
			44.99

Figure 4-2 Particle Size distribution of NiAl (65:35)

File name: P:\glenn\Coulter-POWDER DATA\POWDER DATA\glenn\Data-2005\Metco 480NS_01.\$ls
 File ID: Metco 480NS
 Sample ID: Metco 480NS
 Operator: Glenn Bancke
 Run number: 1
 Comment 1: Metco 480NS NiAl
 Comment 2: Lot W70574
 Optical model: Fraunhofer.rfd
 Fluid R.I.: 1.333
 Residual: 0.37%
 LS 13 320 Dry Powder System
 Start time: 15:35 24 Jun 2005
 Average Vacuum: 0.2" H2O
 Obscuration: 2%
 Software: 4.03

Sample R.I.: 0 i0
 Run length: 117 seconds
 Firmware: 2.02 0



Volume Statistics (Arithmetic) Metco 480NS_01.\$ls

Calculations from 0.375 µm to 2000 µm

Volume:	100%	S.D.:	18.66 µm		
Mean:	76.10 µm	C.V.:	24.5%		
Median:	74.20 µm	Skewness:	0.877 Right skewed		
D(3,2):	71.92 µm	Kurtosis:	1.330 Leptokurtic		
Mode:	80.07 µm				
d ₁₀ :	53.91 µm				
d ₅₀ :	74.20 µm				
d ₉₀ :	99.60 µm				
% <	10	25	50	75	90
µm	53.91	62.38	74.20	87.21	99.60

Figure 4-3 Particle Size distribution of NiAl (95:5)

4.1.2 SELECTION OF SUBSTRATE

Carbon epoxy composite finds various applications in several aircraft components like fuselage, aircraft skin and wings. Simple eight ply panels of carbon epoxy composite were laid up and cured due to the ready availability for this project. These samples were laid and cured at the National Institute for Aviation Research, at Wichita State University.

4.1.3 SELECTION OF SPRAYING METHOD

Wide range of materials like metals, alloys, ceramics, cermets and polymers can be coated using Thermal spray. Components can be sprayed with little or no pre- or post-heat treatment. Also thick coatings can be applied at high deposition rates. Parts can be rebuilt quickly at a low cost or at a fraction of the price of a replacement.

Plasma spray process was selected for top coating as it provides a wide range of temperature, it also offers high energy heat source with relative high velocity and produces continuous and dense coating. Plasma coatings have higher integrity and give better in-service performance than other coatings. The flame spray process was characteristically chosen as the process for producing the bond coating on the substrates; flame spray typically produces relatively high level of porosity and rough surface finish which aids in the adhesion of top coating.

4.1.4 SPRAY PARAMETERS

In the beginning, pilot runs were conducted with the following conditions of parameters as shown below and these parameters were selected as base parameters for further process development

Base Parameters:

- **Hydrogen flow rate:** *8.1 Standard liter per minute (SLPM)*
- **Argon flow rate:** *48 SLPM*
- **Surface preparation:** *Sand blasting at 50 psi*
- **Standoff distance:** 120 mm
- **Powder feed rate:** *40 gm/sec*
- **Plasma gun motion (XY direction):** *10 mm/sec*
- **Power:** *35 kW*

Based on the pilot runs using the above parameters, new process parameters were selected and each substrate was sprayed with two variables, power and standoff distance keeping all the other parameters constant throughout the matrix, reducing powder feed rate to 20 gm/sec. Each material was sprayed at four different combinations forming the spray matrix

4.1.5 SPRAY MATRIX

A spray matrix was designed on basis of base spraying parameters. NiAl (95:5) & NiAl (65:35) powders were sprayed at different combinations of power and standoff distance with and without bond coat as shown in Tables 4.1- 4.3. Single coat of NiAl was sprayed by plasma spray process whereas bond coat was sprayed using flame spray technique.

Single Coat

Sr. No	Coating Material	Power	Standoff distance
1	NiAl (63:35)	20	80
2	NiAl (63:35)	20	100
3	NiAl (63:35)	25	80
4	NiAl (63:35)	25	100
5	NiAl (95:5)	20	80
6	NiAl (95:5)	20	100
7	NiAl (95:5)	25	80
8	NiAl (95:5)	25	100

Table 4-1: Spray matrix for coating without bond coat

Bond Coat (Aluminum)

Sr. No	Coating Material	Power	Standoff distance
1	NiAl (63:35)	20	80
2	NiAl (63:35)	20	100
3	NiAl (63:35)	25	80
4	NiAl (63:35)	25	100
5	NiAl (95:5)	20	80
6	NiAl (95:5)	20	100
7	NiAl (95:5)	25	80
8	NiAl (95:5)	25	100

Table 4-2: Spray matrix for coating with aluminum as bond coat

Bond Coat (Zinc)

Sr. No	Coating Material	Power	Standoff distance
1	NiAl (63:35)	20	80
2	NiAl (63:35)	20	100
3	NiAl (63:35)	25	80
4	NiAl (63:35)	25	100
5	NiAl (95:5)	20	80
6	NiAl (95:5)	20	100
7	NiAl (95:5)	25	80
8	NiAl (95:5)	25	100

Table 4-3: Spray matrix for coating with zinc as bond coat

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

CHAPTER 5

EXPERIMENTAL SETUP

5.1 SUBSTRATE PREPARATION

The principle behind composite manufacture is the mixing of the reinforcement with the matrix and the solidifying of the matrix using heat and pressure into the net shape desired. With the variety of types of composites there are an associated variety of manufacturing methods including wet lay up, spraying, cold press molding, resin transfer and injection molding, Autoclave manufacture and hot press molding.

Autoclave manufacturing is favored method in aerospace industry; Hand or machine technique is used to apply Pre-impregnated fiber to the mould. Vacuum pump is used to remove the air after covering the fiber area with a rubber or plastic bag. Then the resin is cured by applying pressure and increased temperature by placing the mould in an oven or autoclave. The pre-preg layers are fused together to remove the excess resin by applying pressure which in turn allows the voids to collapse producing a laminate with a very low void content.

Autoclave cure cycle consists of a three-step process as shows in Fig.5.1.

1. Vacuum and pressure were applied while the temperature was raised to an intermediate level and held there for a definite period of time. This intermediate temperature was 132°C as shown in the Figure.
2. The holding time was 90 minutes
3. The cooling cycle consisted of 30 minutes until the ambient temperature (Approximately 20°C) was reached. The composite material was manufactured by Newport Adhesives

and Composites Inc., and procured from National Institute for Aviation Research at WSU Wichita, Kansas.

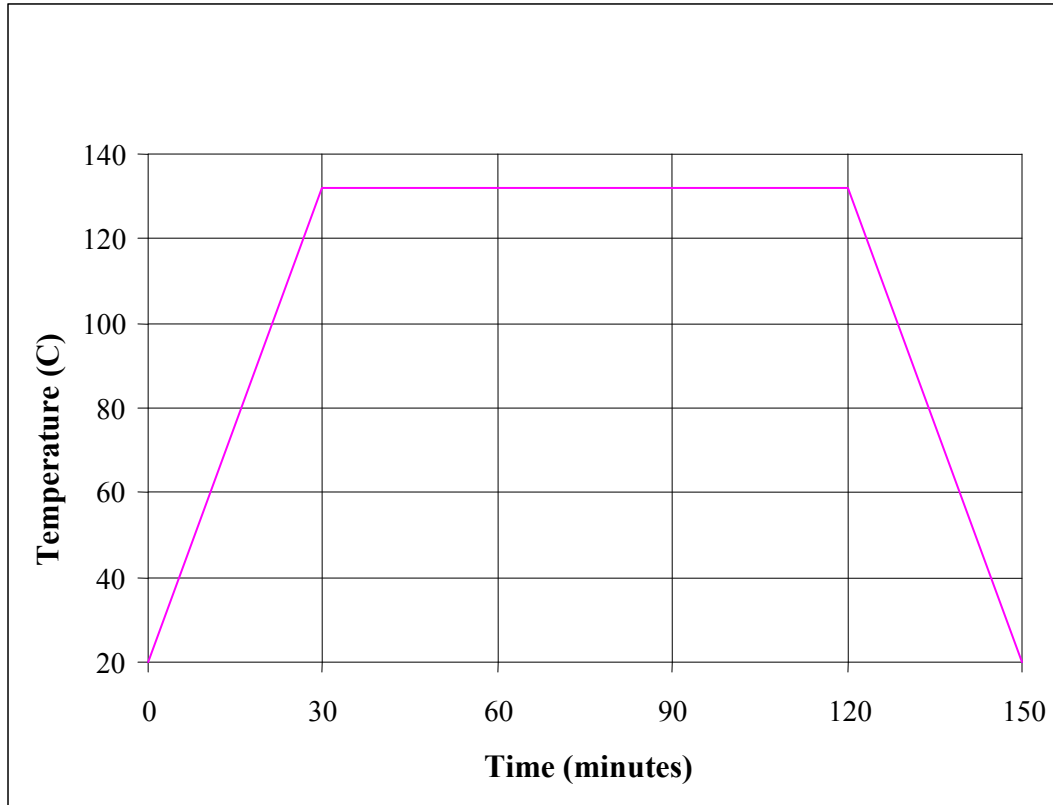


Figure 5-1: Curing Cycle for an eight ply composite substrate

5.2 PRE-COATING SUBSTRATE PREPARATION STUDY

Substrate surface finish and integrity is a crucial factor in influencing the coating properties. Adequate surface preparation has proved to provide sufficient bond strength between the deposit material and the receiving substrate. Grit blasting is used as one of the most common method for pre-treatment. Cured composite sample was cleaned with acetone and grit blasted at a pressure of 50 psi and at an angle of 90 degrees with alumina powder of mesh size 24. In order to remove the residual alumina particles the treated surface was exposed to compressed air.

A substrate surface experimental study was conducted at three levels of pre-spraying treatments; as-received composite; composite with moderate sand blasting; sand blasting satisfying “No Water Break Test”. The “No water break test” keeps a check on the amount of surface preparation required prior to spraying. Acetone was used to degrease the composite sample and the roughening was done with coarse polish paper. After every step of rough polishing distilled water was sprayed onto the surface, droplet formation concludes more surface preparation required for better adhesion of coating. On the other hand, if the droplets don’t break i.e. they completely wet the surface then it is said to have met the required amount of surface treatment.

Figures 5-2 – 5-4 show the cross-section of all three levels of surface treatments. Fibers are exposed and no resin is observed after “No water break test”. As a result of this the incoming spray material will form a poor bond with the substrate. Carbon fibers have a poor wettability with other materials resulting in poor bonding of coating. Also, it has been reported that commonly used surface treatment for metal substrate could cause damage to composite substrate. Therefore all the coatings were sprayed at moderate surface treatment.

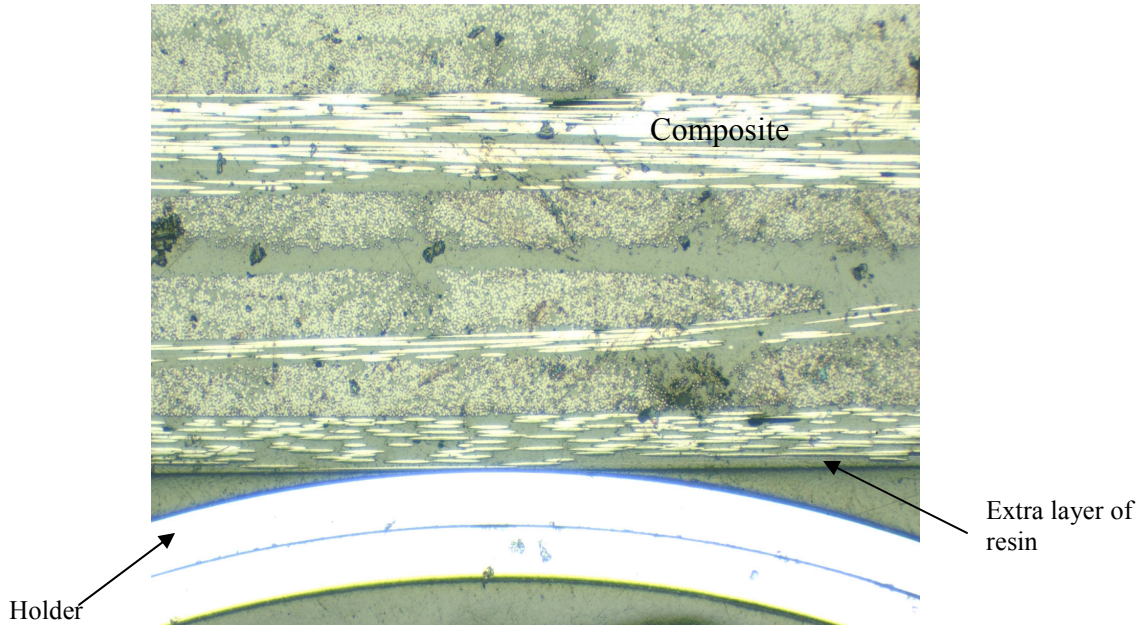


Figure 5-2: Cross-section of as received composite showing a layer of resin next to the holder

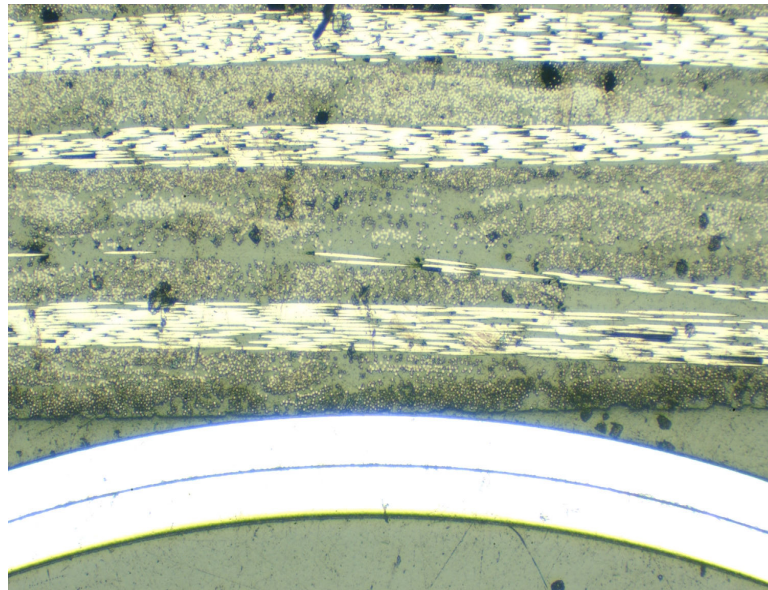


Figure 5-3: Cross-section of composite with moderate sand blasting

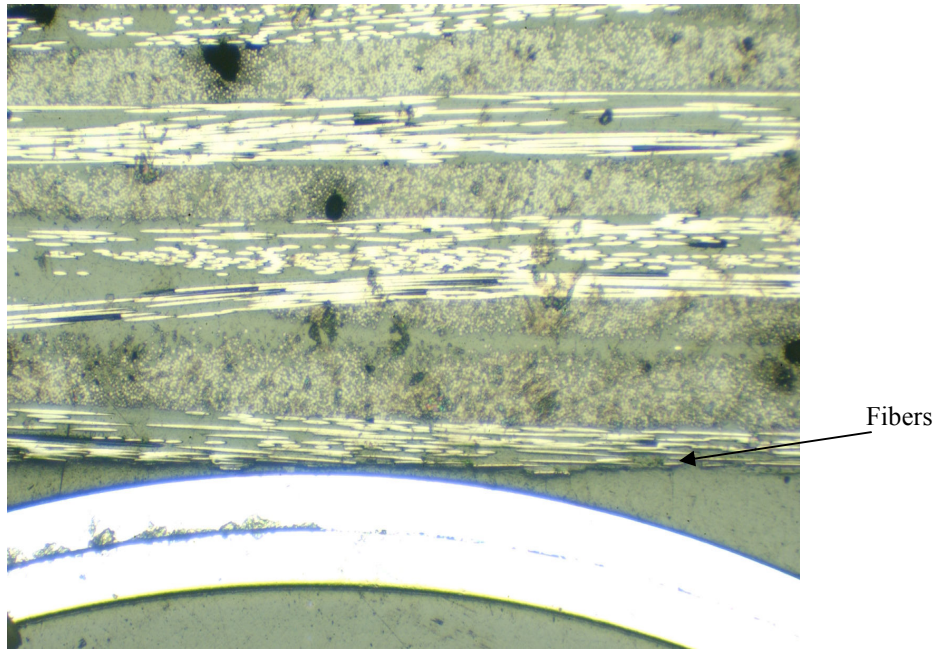


Figure 5-4: Cross-section of composite satisfying “No Water Break Test”

5.3 COATING PROCESS

Carbon epoxy composite samples were cut with diamond saw abrasive cutter in coupons of size 8" * 2". These coupons were surface treated and sprayed with feedstock material by air plasma process. Sulzer F4MB from Sulzer Metco with the Sulzer A2000 control system and a Sulzer Twin 10 powder feeder was used as the plasma torch during the deposition of the plasma sprayed coating.

Figure 5-4 shows the coating process setup, substrate was mounted on a rotating fixture; plasma torch motion was along the axis of rotation of fixture.

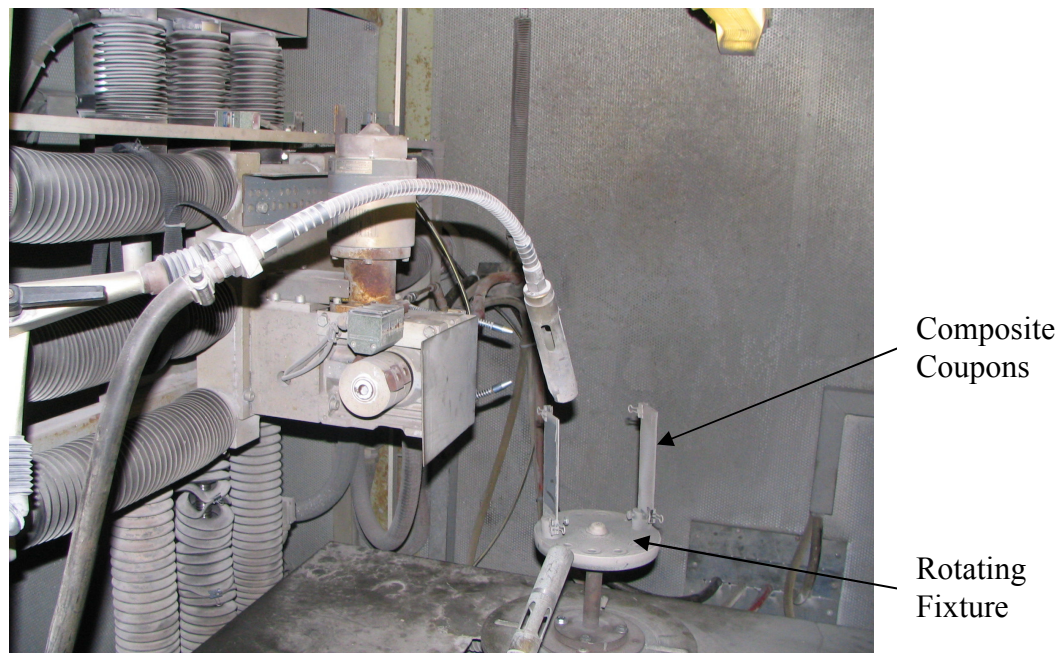


Figure 5-5: Coating process setup

CHAPTER 6

COATING CHARACTERIZATION

6.1 METALLOGRAPHICAL STUDY

Metallographic examination is a critical step in the assessment of thermal spray coating characteristics. Samples of plasma coatings are prepared similarly as the other metallographic samples. Analysis is usually carried out on coating cross-sections in order to evaluate imperfection structure and to achieve a detailed examination of the coating-substrate interface. Optical microscopy is used for basic studies of coating structure and its bonding to substrate. Coating thickness, pores, voids, cracks also can be observed with the help of optical microscopy. Electron scanning microscopy and X-ray microanalysis is employed for detailed study of a coating structure, its bonding with the substrate and phase distribution [21].

Following sections are recommended procedures for metallographic characterization:

- Specimen sectioning
- Cleaning
- Specimen mounting
- Rough grinding
- Polishing

SPECIMEN SECTIONING

Sectioning is critical for thermal spray coatings, if it is not performed properly, cracking, debonding, or excessive deformation of the coating and/or substrate may result in false or misleading microstructure. Specimens are usually cut using a diamond saw cutter.

CLEANING

Cleaning of specimens is carried out in order to remove the entrapped abrasive particles using water or other cleaning solvents. Drying of the specimen after sectioning is important to ensure adhesion between mounting media and the specimen.

SPECIMEN MOUNTING

A common practice of mounting sectioned thermal spray coating specimen is the use of a two part epoxy that cures at room temperature. Sectioned specimens are potted using resin and hardener solution in the ratio of 5:1 by weight is mixed and poured into the mould cavity. It normally takes 6-7 hours for the solution to harden.

GRINDING

Grinding is used to produce flat specimens, with all specimen surfaces in one plane prior to subsequent grinding. The initial grinding should use an abrasive that is coarse in order to remove all damage due to sectioning.

POLISHING

Polishing is conducted in two stages- rough polishing and fine polishing. Rough polishing consists of abrasive papers of different grit size, common sequence of papers is 200, 320, 400, and 600, with a preferred polishing time of 30 sec to maximum of 90 sec. Fine polishing consists of abrasive solutions of 5, 1, 0.3, 0.05 microns. Diamond dust or aluminum oxide (Al_2O_3) is normally used as abrasive solutions.

COATINGS WITHOUT BOND COATING

As stated in the prior section, NiAl (95:5) and NiAl (65:35) were sprayed without bond coating. Figures below show the microstructure at base parameters followed by microstructure of coating at combination of power and standoff distance at two levels.

Figure 6-1 – 6-3 shows the microstructure of NiAl (95:5) and NiAl (65:35) at base spraying parameters. Fig.6-1 shows a porous, non-uniform coating, and a bridging problem. With increase in number of coating layers bridging problem is eliminated as seen in Fig.6-2, coating is more uniform and shows some degree of porosity. NiAl (65:35) particles are not completely melted and show a porous and non-uniform coating as seen in Figure 6-3.

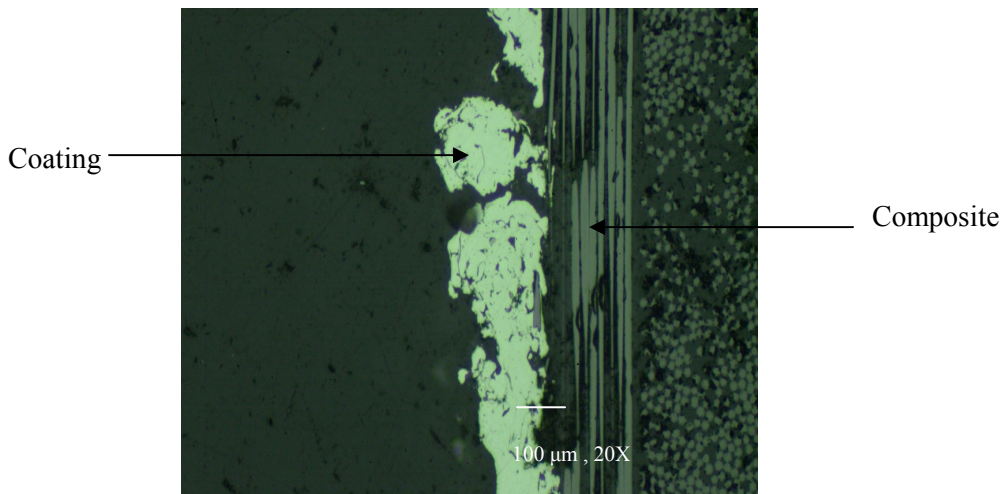


Figure 6-1: NiAl (95:5), Plasma spray, 4 cycles

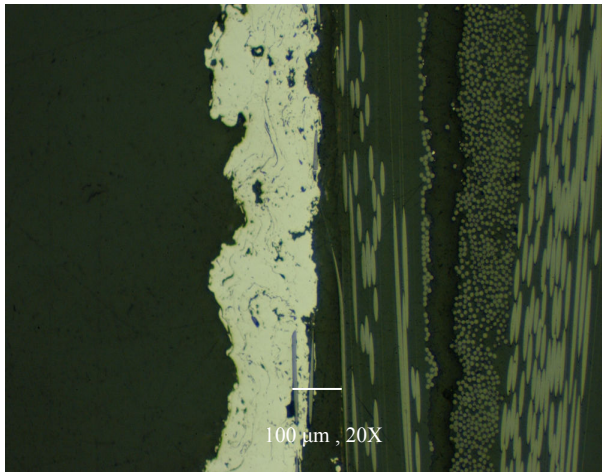


Figure 6-2: NiAl (95:5), Plasma spray, 8 cycles

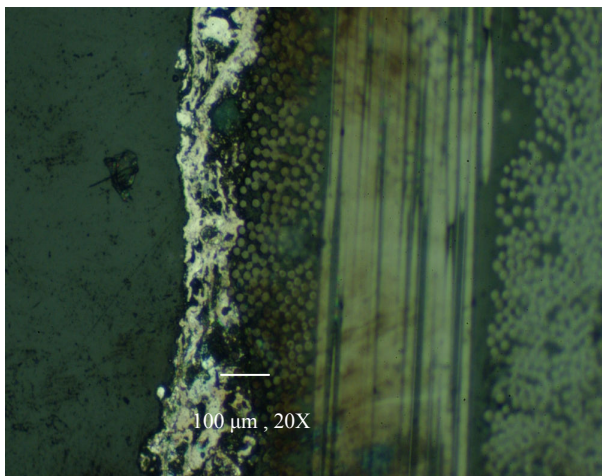


Figure 6-3: NiAl (65:35), Plasma spray

Figure 6-4 – 6-8 shows microstructure of NiAl (95:5) and NiAl (65:35) at two varying parameters; power and standoff distance keeping rest parameters constant. Fig.6.4 shows NiAl (65:35) at 20 kW power and a standoff distance of 80 mm, uniform coating with some degree of porosity is observed. Low power results in more uniform heating of particles, resulting in uniform coating.

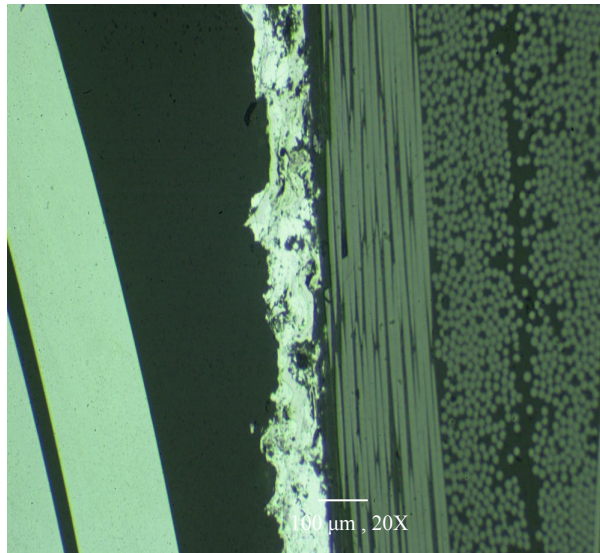


Figure 6-4: NiAl (65:35), 20 kW, and 80 mm (Power, and Standoff distance)

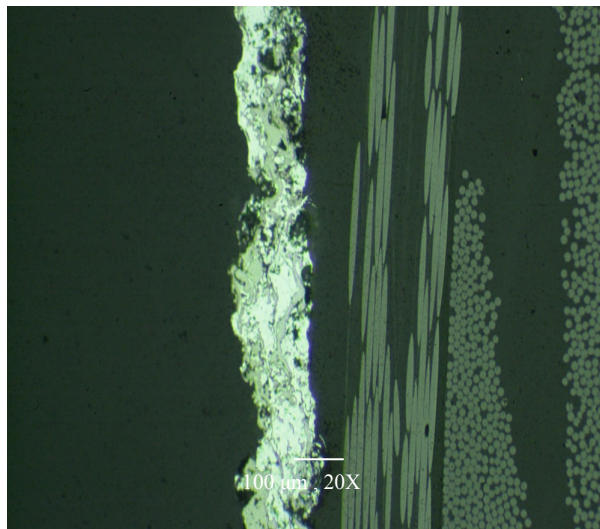


Figure 6-5: NiAl (65:35), 20 kW, and 100 mm

High standoff distance and low power results in a non-uniform and porous coating as seen in Fig.6-6, Fig.6-7 shows a uniform coating and some degree of porosity. Particle size distribution of NiAl (95:5) was same as NiAl (65:35) resulting in uniform heating of particles at 20 kW and 25 kW power.

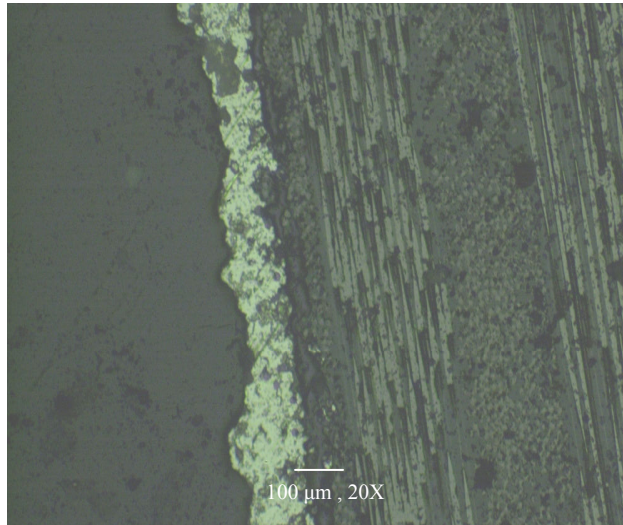


Figure 6-6: NiAl (95:5), 20 kW, 100 mm

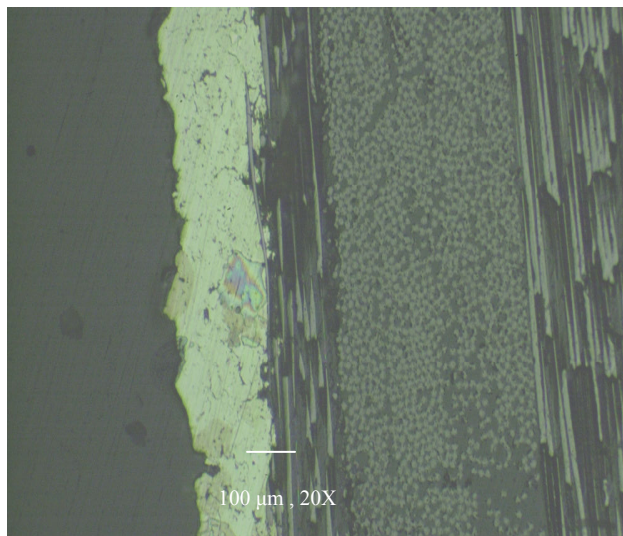


Figure 6-7: NiAl (95:5), 25 kW, 80 mm

COATINGS WITH BOND COATING

NiAl (95:5) and NiAl (65:35) were sprayed as top coating by plasma spray technique. Aluminum and zinc were sprayed as bond coating by electric arc technique. Figures below show the microstructure at base parameters followed by microstructure of coating at combination of power and standoff distance at two levels.

Figure 6-8 shows microstructure of NiAl (95:5) as top coat, with aluminum as bond coat at base spraying parameters. Coating is more uniform and shows some degree of porosity. Zinc and aluminum in wire form were sprayed using electric wire arc technique

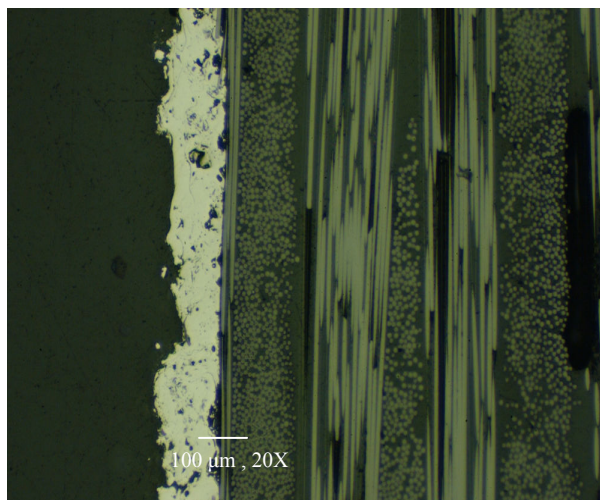


Figure 6-8: NiAl (95:5) top coat, aluminum bond coat: electric arc

Figure 6-9 shows that the NiAl top coating has penetrated in the zinc bond coating. A thin top coating was achieved as compared to bond coating thickness. Increase in number of coating layers tends to peel off the coating, possibly due to high residual stresses. It is difficult to differentiate between the top coating and bond coating resulting in inconclusive hardness measurements. For NiAl (95:5) as top coat, 25 kW and 20 kW power resulted in chequered pattern, a trial run at 16.5

kW power with standoff distance 80 mm was conducted which resulted in a thin and more uniform top coating.

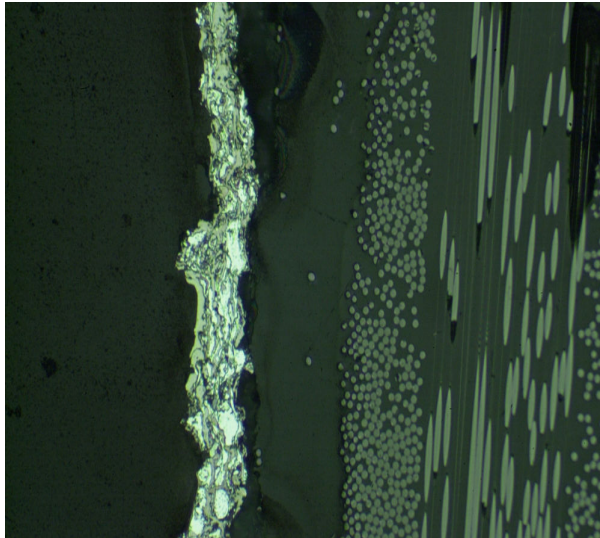


Figure 6-9: NiAl (65:35)-top, Zinc-bond coat, 20KW, and 80mm

6.2 HARDNESS TESTING

Hardness is the property of a material to resist plastic deformation; it may also refer to resistance to bending, scratching, abrasion or cutting. Hardness is not an intrinsic material property dictated by precise definitions in terms of fundamental units of mass, length and time. A hardness property value is the result of a defined measurement procedure [24]. Variety of testing methods can be classified as static indentation test, scratch test, plowing test, rebound test, damping test, cutting test and abrasion test. In static indentation test an indenter is forced against a surface perpendicular to it; the dimension of the deformation zone is used to obtain a parameter. Indentation test constitutes of vast majority of metallurgical tests for examples Vickers, Rockwell, Brinell, Knoop and Meyer tests., essentially divided into two classes, micro-hardness and macro-hardness tests. Micro-indentation hardness test utilizes a load lighter than 200gf, which produces minute impressions of about 50 μm . These tests are ideally suited to investigate changes in hardness at the microscopic scale. There are a number of considerations in microhardness testing, sample preparation is usually necessary in order to provide a specimen that can fit into the tester, make a sufficiently smooth surface to permit a regular indentation shape and good measurement, and be held perpendicular to the indenter.

Hardness measurement of thermal spray coatings is a straight forward process and not as difficult as metallographic preparation. Thermal spray coatings have somewhat rough surfaces compared to other materials, the roughness is minimized by abrasion during the metallographic preparation prior to hardness testing.

Vickers Hardness Test:

Vickers hardness test method consists of indenting the test material with a diamond indenter, in a form of pyramid with a square base and an angle of 136 degrees between opposite faces [23]. A load of 1 to 100 kgf is normally applied for 10-15 seconds. The two diagonals of the indentation left in the surface of material are measured after removal of the load as shown in Fig.6-10 [24].

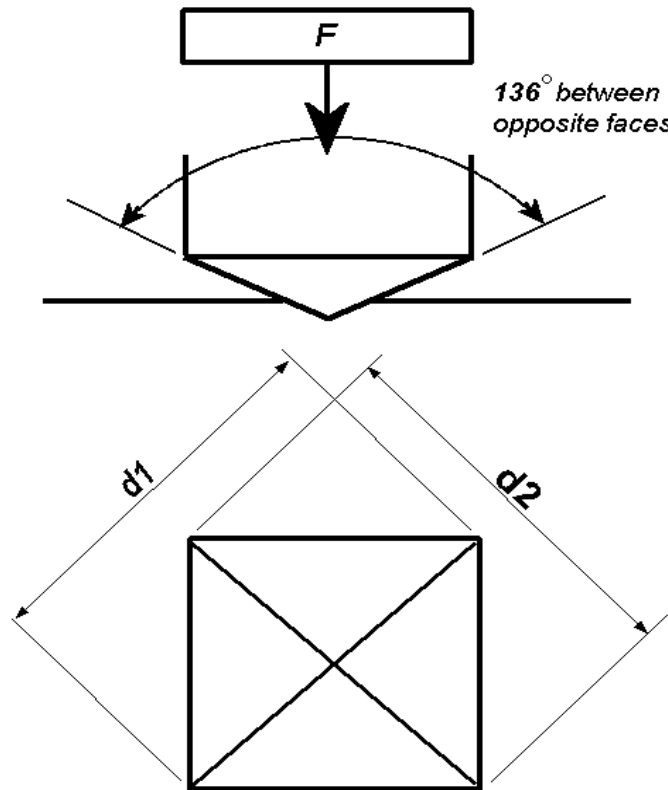


Figure 6-10: Indentation by Vickers test

Firstly, specimens are polished and prepared as in metallographic preparation. Machine is calibrated, and a specific indentation load is applied through the indenter. The diagonals of deformed indentation are measured. Hardness instrument calculates the mean diagonal value and gives the final hardness value in HV (Hardness using Vickers test). Hardness values for coatings with and without bond coating are reported in Table 6-1-6-3. Three indentations were taken per sample and an average value was computed along with standard deviation for all values.

Sr No	Coating	Power	Standoff distance	Average Hardness	Standard Deviation
1	N6	20	80	92.8	4.10
2	N6	20	100	57.7	3.08
3	N6	25	80	Too thin to determine	
4	N6	25	100	82.2	16.83
5	N9	20	80	Too thin to determine	
6	N9	20	100	188.2	2.15
7	N9	25	80	147.4	2.84
8	N9	25	100	Too thin to determine	

Table 6-1: Microhardness of coating without bond coat

Sr No	Bond Coat	Power	Standoff distance	Average Hardness	Standard Deviation
1	N6A	20	80	Too thin to determine	
2	N6A	20	100	50.5	1.97
3	N6A	25	80	45.3	3.34
4	N6A	25	100	39.5	0.72
5	N9A	20	80	Too thin to determine	
6	N9A	20	100	81.9	55.07
7	N9A	25	80	72.9	15.01
8	N9A	25	100	Too thin to determine	

Table 6-2: Microhardness of coating with aluminum bond coat

Sr No	Coating	Power	Standoff distance	Average Hardness	Standard Deviation
1	N6Z	20	80	89.5	8.18
2	N6Z	20	100	58.9	8.53
3	N6Z	25	80	Too thin to determine	
4	N6Z	25	100	45.0	1.53
5	N9Z	20	80	151.2	0.98
6	N9Z	20	100	147.0	11.34
7	N9Z	25	80	182.4	8.04
8	N9Z	25	100	144.9	22.10

Table 6-3: Microhardness of coating with aluminum bond coat

NiAl (95:5) is more metallic compound which yields higher micro-hardness values as seen in Fig.6-11; also optical microscopy and porosity analysis show more porosity for NiAl (65:35) which results in less micro-hardness values as compared to NiAl (95:5). Hardness values are indeterminable for thin coatings having coating thickness less than 100 microns; also it is difficult to differentiate between top coat and bond coat, which may result in inappropriate hardness values. Microhardness of composite was determined for comparison with coating hardness values. Microhardness of bare composite was found to be 55-60 HV, whereas microhardness of epoxy was 14-17 HV. Microhardness of coating is higher than that of epoxy and composite, which ensures that indentation was taken onto the coating surface.

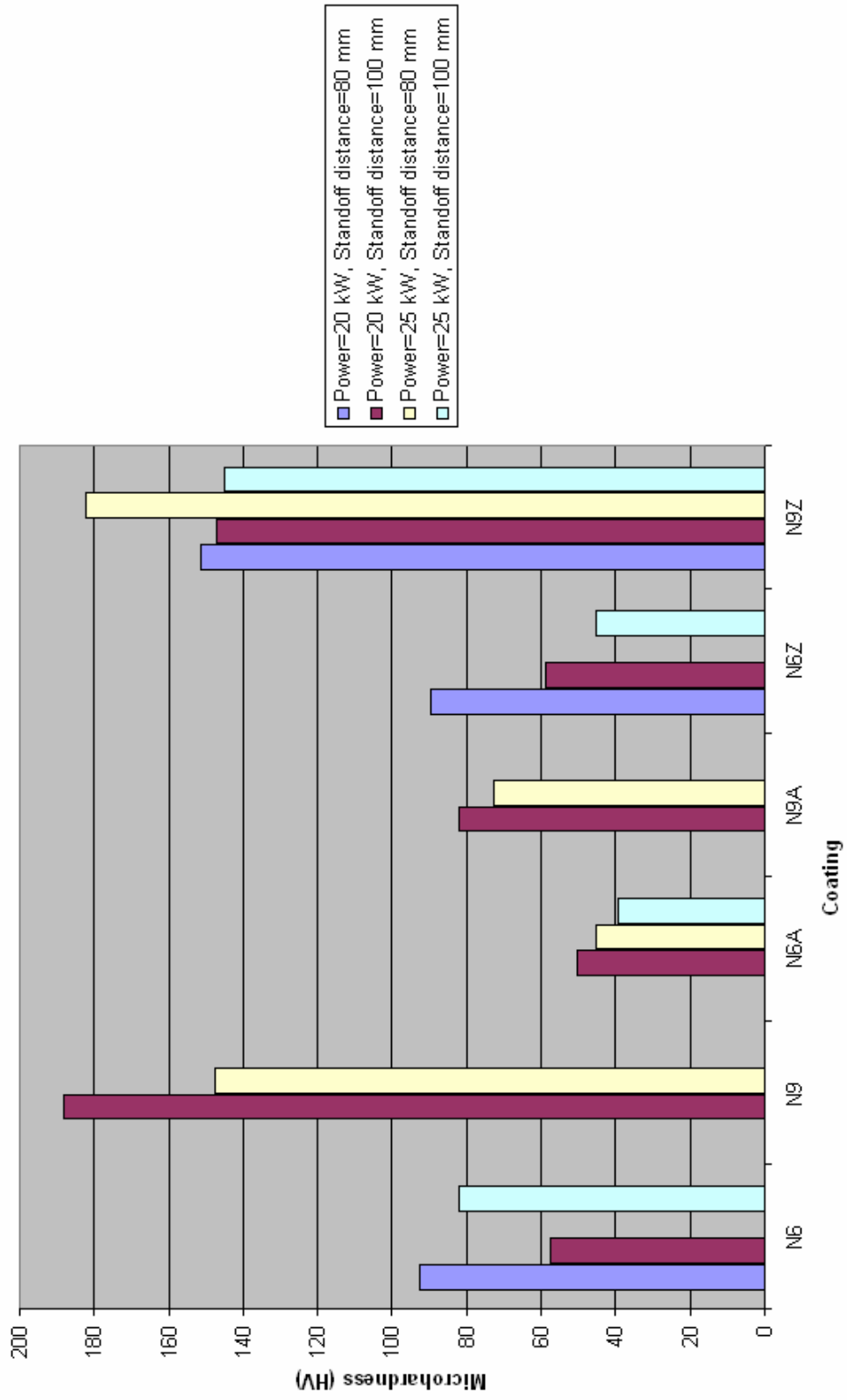


Figure 6-11: Microhardness of coatings with and without bond coat

6.3. ELECTRICAL CONDUCTIVITY

Electrical conductivity is a measure of a material's ability to conduct an electric current. An electrical potential difference across a conductor results in movable charges, giving rise to an electric current.

DEICING:

Deicing is a procedure by which frost, ice, slush or snow is removed from an aircraft to render it free of contaminations. Electrical heating is one of the techniques for deicing; it includes resistance heating and induction heating.

Resistance heating involves passing an electric current through a resistor, which is the heating element. The materials of heating element cannot be too low in electrical resistivity, as this would result in high current requirement resulting in high power consumption. The heating materials cannot have too high resistivity either, as this would result in the low current. The resistance heating of an electrical conductor is a function of its conductivity, cross sectional area, density, specific heat, temperature co-efficient and current density. The energy deposited in a conductor by given current increases with temperature as most materials have higher resistance at higher temperatures. The temperature rise is given by [11]

$$\Delta T = \frac{(I^2 S) \rho}{CdA^2}$$

Where,

ΔT - is the temperature rise in degrees centigrade

$I^2 S$ - is the action integral (I is the current in amperes and S is the time in seconds)

ρ – is the specific resistance of material in ohm-meter

C – is the specific heat of the material in Joules/Kg/degree centigrade

d – is the density in Kg/m³

A – is the cross section in m²

ELECTRO-MAGNETIC SHIELDING:

Electromagnetic interference is radiated or conducted energy that adversely affects circuit performance, and thus disrupts a device's electromagnetic compatibility.

A major area of concern with carbon fiber composites (CFC) skins used in aircraft is the poor electromagnetic shielding offered by such skins. A thin metal layer increases the electromagnetic protection, the protection offered is usually defined in terms of shielding effectiveness which is a function of material characteristics; electrical conductivity, permeability and thickness of material [23]

ELECTRICAL-CONDUCTIVITY MEASUREMENTS:

Electrical resistivity of thin coatings is measured using two-point resistivity probe technique. In this method, a specimen is kept on an insulated substrate and the resistance between the two ends is directly measured using ohmmeter. Once the resistance R is measured, the resistivity can be obtained by following formula,

$$\rho = (R \cdot A) / l$$

ρ = Resistivity

R = Resistance

A = Area

l = length of specimen

Conductivity is reciprocal of resistivity and hence given as,

$$C = 1/\rho$$

Conductivity can be calculated using above formula. The advantage of this method is its simplicity. Errors involved include all contact resistances between the probe and the specimen.

Procedure:

- Composite specimen were cut in size of 1* 1 square inch coupons
- Electrical conductivity of bare composite was determined
- Electrical conductivity of specimen with coating was determined
- The difference in the conductivity values of bare composite and coated sample gave the conductivity value of the coating

Figure 6-12 shows electrical conductivity values measured for all coatings with and without bond coating. Higher electrical conductivity is observed for NiAl (65:35) single coat and for NiAl (95:5) with zinc and aluminum as bond coat as compared to NiAl (95:5) single coat. NiAl (95:5) single coat showed non-uniform coating and also followed a chequered pattern resulting in low conductivity values. Conductivity obtained is far less than the bulk material values, which can yield higher resistance heating for de-icing effect.

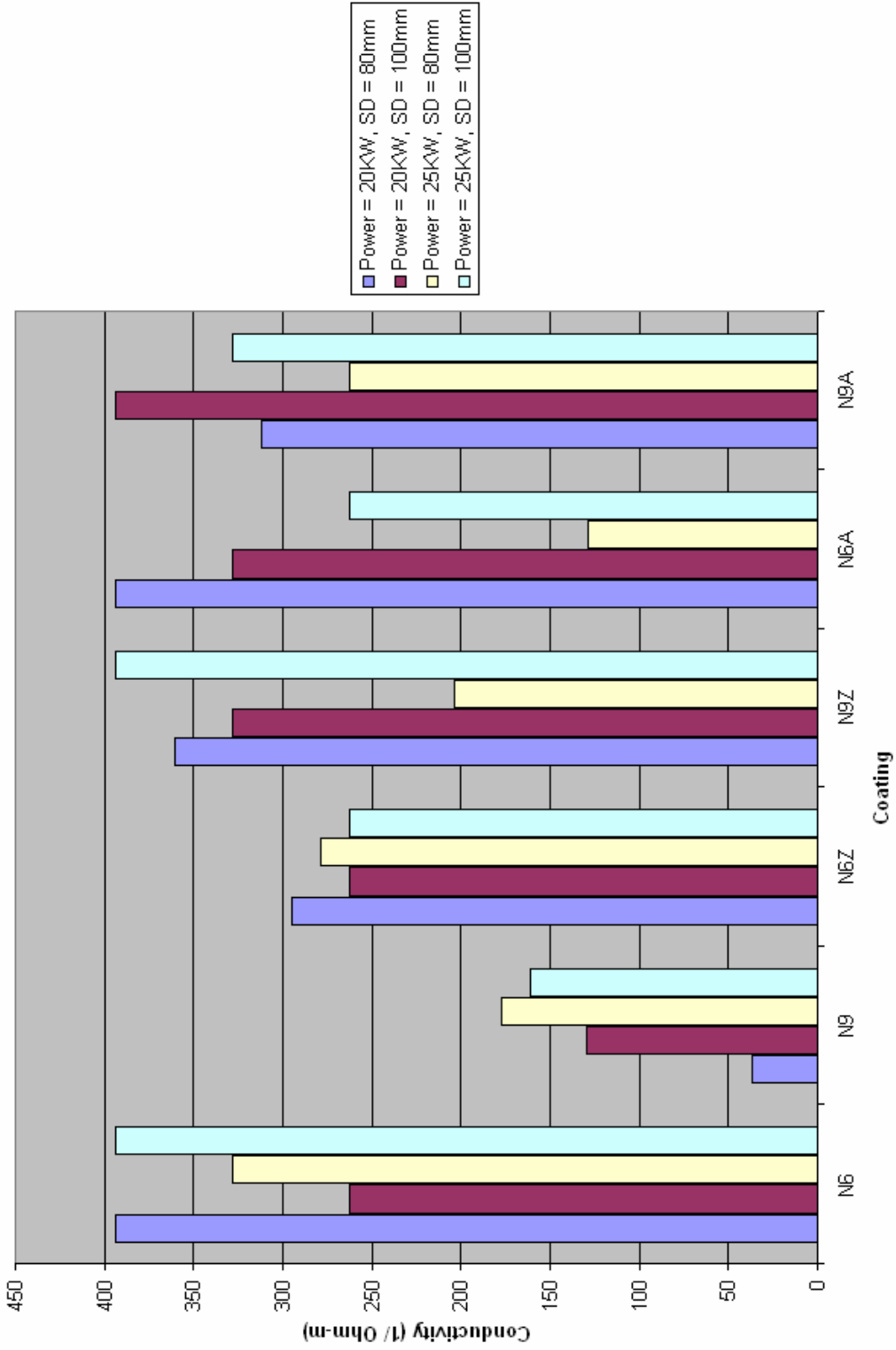


Figure 6-12: Electrical conductivity of coatings with and without bond coat

CHAPTER 7

COATING PERFORMANCE

7.1 EFFECT OF THERMAL SPRAY PARAMETERS

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 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 torch for a longer duration. This could project excessive heating of the particles and hence evaporation before they hit the substrate [1]. On the contrary, a lower standoff distance could cause excessive heating of the substrate resulting in fiber burn off. Also, if the particles do

not reside for a sufficient time in the jet, it results in unmelted particles. These unmelted particles are trapped within consecutive coating layers, decreasing the adhesion of coating to the substrate.

7.1.1 EFFECT OF PARAMETERS ON COATING HARDNESS

Figure 7-1 and 7-2 shows effect of standoff distance and power on microhardness of coatings respectively. Standoff distance of 80 mm at 20 and 25 kW power shows higher hardness for all coatings as compared to hardness at 100 mm, as in Fig.6-13. For 20 kW power and a standoff distance of 80 mm, higher hardness is observed as compared to 20 kW power and 100 mm standoff distance. With an increase in power, standoff distance should be increased for better hardness.

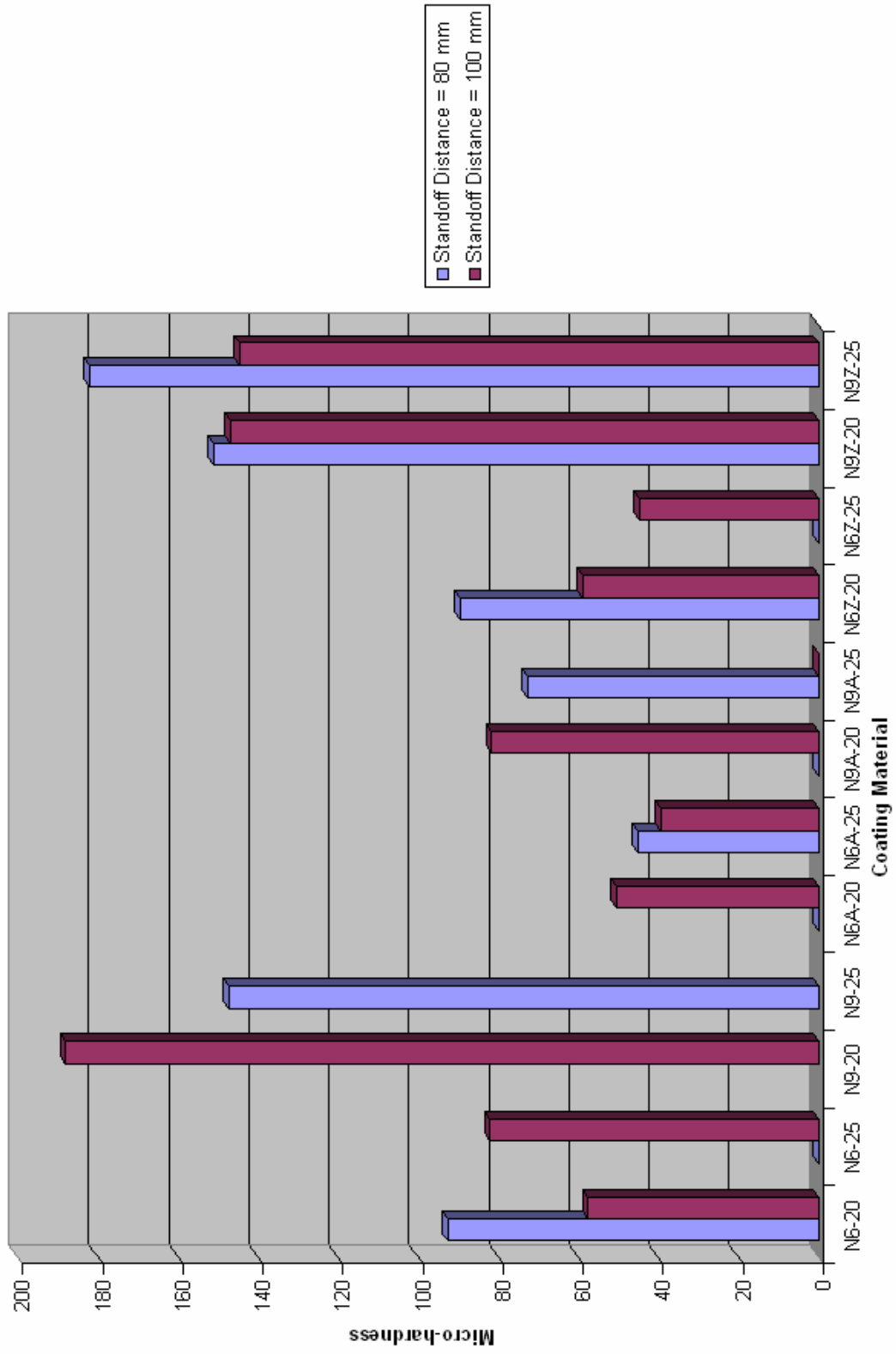


Figure 7-1: Effect of standoff distance on microhardness of coating

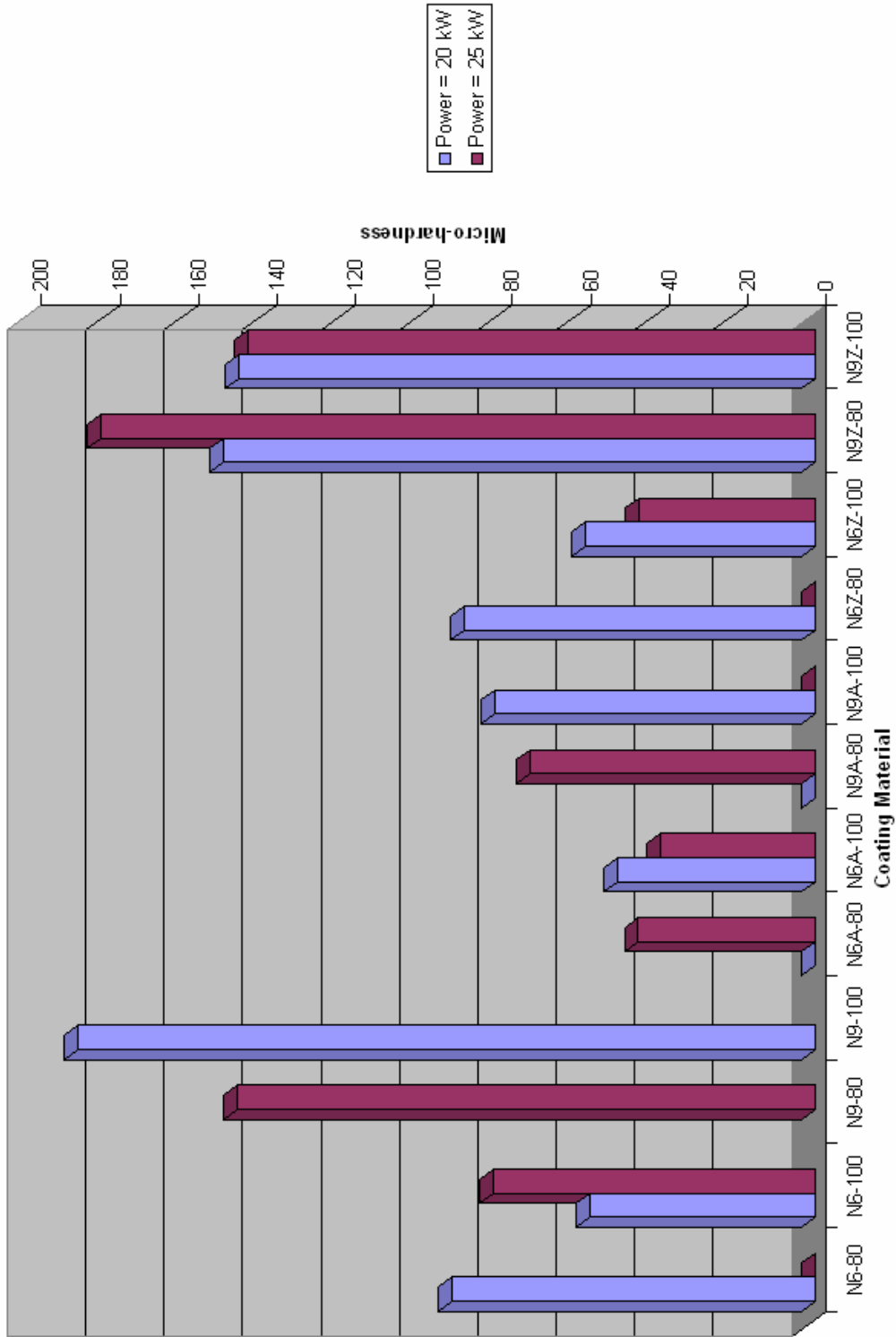


Figure 7-2: Effect of power on microhardness of coating

7.1.2 EFFECT OF PARAMETERS ON ELECTRICAL CONDUCTIVITY

Figure 7-3 and 7-4 shows effect of power and standoff distance on electrical conductivity of coatings respectively. Power does not affect the conductivity significantly. Though, in general, the conductivity is lower at 80 mm and 25 kW, 100 mm and 20 kW (standoff distance and power) respectively. Non uniform coating is achieved at high standoff distance and low power as a result of non-uniform melting of particles.

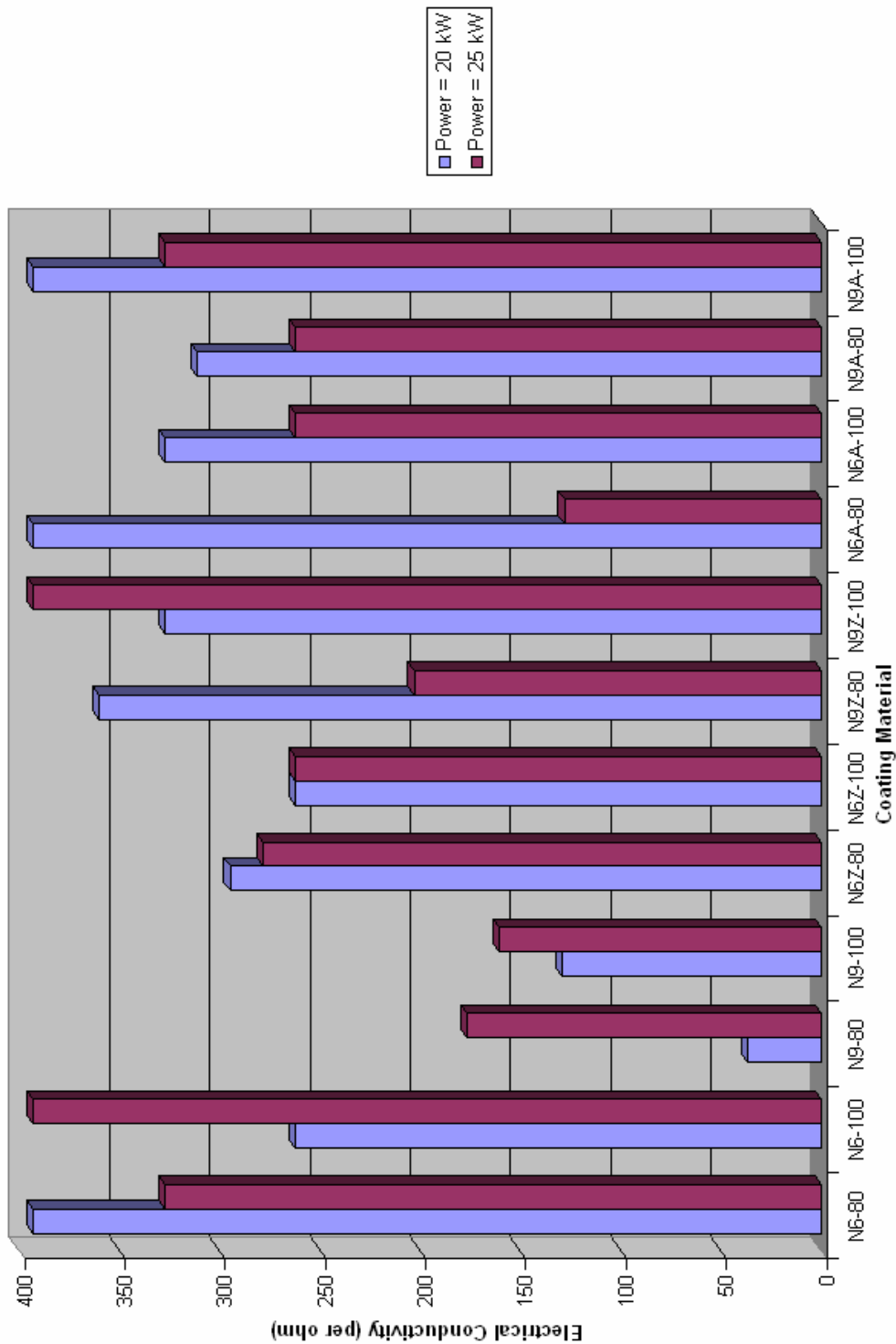


Figure 7-3: Effect of power on electrical conductivity of coating

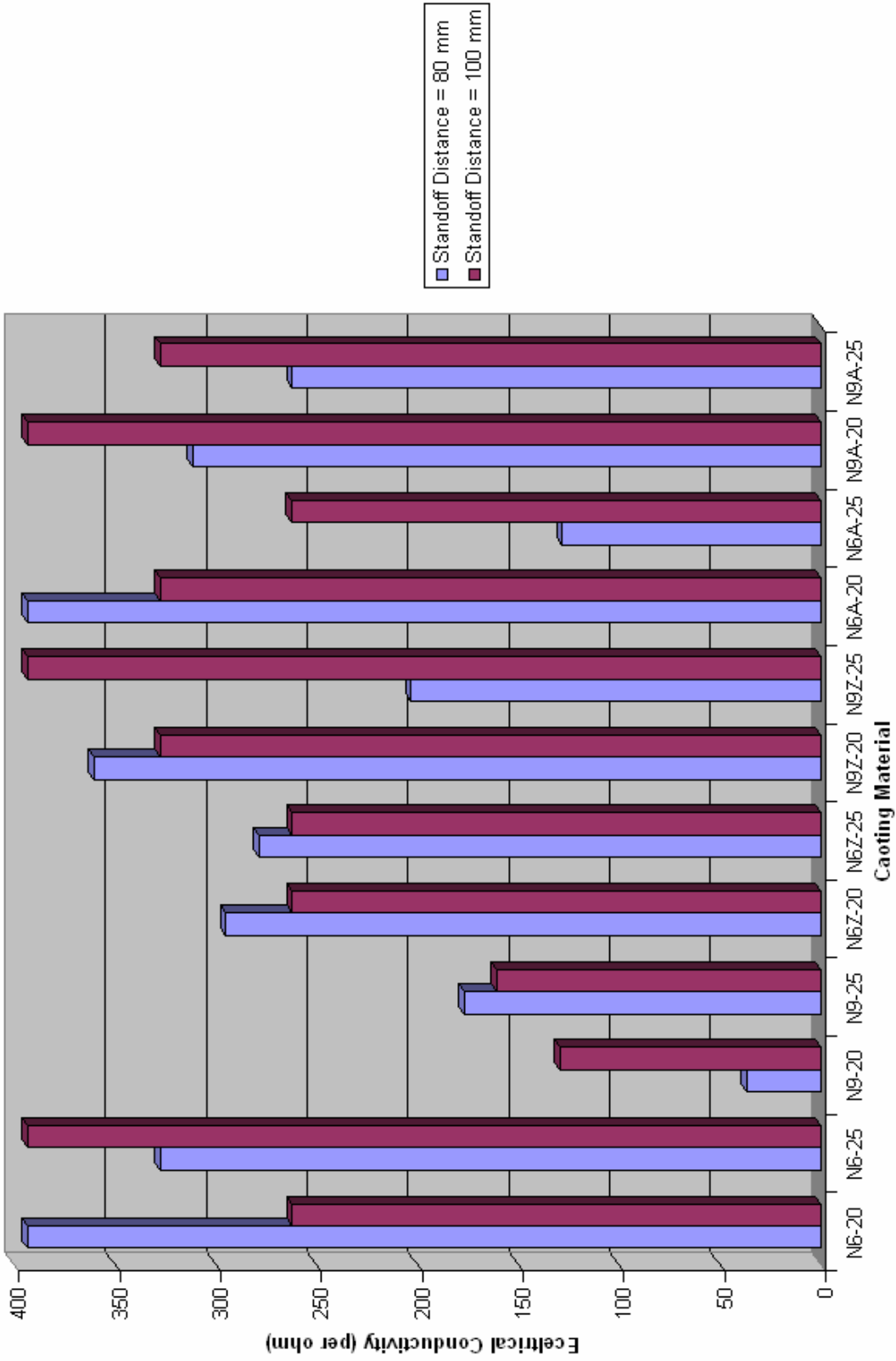


Figure 7-4: Effect of standoff distance on electrical conductivity of coating

CHAPTER 8

SUMMARY AND CONCLUSION

This study was an effort to develop a new coating for polymer matrix composite substrate in order to improve surface properties, hardness, electrical conductivity, porosity, and erosion resistance. NiAl (65:35) intermetallic alloy and NiAl (95:5) were selected as coating materials. Intermetallics were short-listed from binary phase diagrams; whereas NiAl (95:5) is usually used to coat metal substrate by plasma spray. A substrate surface characterization study was conducted to determine optimum pre-surface preparation. Substrate was coated with and without bond coat at base parameters and at two varying parameters; standoff distance and torch power.

Significant conclusions:

- PMC can be successfully coated with thermal spray coating
- Wide range of materials including intermetallics which yields better properties to provide high strength can be coated by plasma spray
- Surface characterization study at three levels suggests that moderate sand blasting should be carried out for pre-surface treatment prior to coating; this was evident from “No water break” test.
- Microhardness of coatings on an average has been increased three times microhardness of bare composite
- NiAl (95:5) shows higher hardness values as compared to NiAl (65:35) which correlates well with microstructure analysis and porosity data
- Coating has increased the electrical conductivity on an average by 400 times as compared to bare composite

- Intermetallic compound with and without bond coat shows higher electrical conductivity as compared to other nickel aluminum alloy
- Two coating parameters were varied from base parameters keeping rest constant; namely standoff distance and torch power
- Torch power and standoff distance individually, does not significantly affect microhardness and electrical conductivity values

CHAPTER 9

FUTURE RECOMMENDATION

Numerous other intermetallic and conductive powders could be sprayed as well as their process parameters could be optimized and examined with various tests. A better understanding of coating behavior can be obtained by coating response in different conditions. Testing like, thermal fatigue, mechanical fatigue and 3 point bend test could be conducted to evaluate coating response. Aluminum wire mesh is presently used in aircrafts for EMI shielding, which adds to 5 % of total weight, hence a more conductive material could be sprayed and tested for EMI protection. Testing techniques could be developed to measure electromagnetic effect and de-icing effect on coatings. A design of experiment could be conducted for spraying parameters to narrow the working range in order to optimize the coating parameters. Post heat treatment methods could be developed for coatings. A detail study of powder size distribution could be conducted to achieve more uniform and non-porous coatings. A residual stress analysis will help study the effect of increase in coating layers and top coating thickness without coating peel off.

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