1.1 Preamble

This thesis deals with plasma spraying, a well known thermal spraying technique which comes under surface modification technologies. In this chapter different surface modification technologies have been introduced first and then the individual thermal spraying processes have been discussed briefly. This has been followed by a more elaborate discussion on plasma spraying. Finally, a brief chapter wise overview of the thesis has been presented. The objective of this chapter is to familiarize the reader with the manufacturing process under study.

1.2 On Surface Modification

Surface engineering is one of the most important fields of study in interdisciplinary engineering sciences. The basic idea of surface engineering is to improve the performance of the engineering components by imparting some property on the surface of the component which the base material does not have. Modern high performance machinery is subjected to extremes of temperature and mechanical stress. Hence, these machines and its components need surface protection against high temperature, corrosive media or mechanical wear and tear. Surface engineering techniques are used widely to repair and resurface metallic parts and also to build up tribological, anticorrosive and thermal barrier coatings. High temperature erosion protection of boiler tubes, fire chambers of coal-fired power plants and bio-ceramic coatings for orthopedic and dental prosthetic implants are some examples of application of such techniques or more specifically, surface coatings.
Surface engineering involves:

(i) chemical/thermochemical treatment of the surface to bring about some microstructural changes.

(ii) application of a coating/clad layer having suitable properties.

The choice of the appropriate surface technological tool depends on the application.

1.3 On Techniques of Surface Modification

Common techniques of surface modification technology are listed in Figure 1.1 (Budinski, 1988). This thesis deals with plasma spraying, a well known thermal spraying technique. A brief overview of thermal spraying is given below.

1.3.1 Thermal Spraying

Thermal spraying is the generic term used to define a group of processes utilized for the deposition of finely divided metallic or nonmetallic materials onto a prepared substrate to form a coating. The coating material may be in powder, rod or wire form (www.keytometals.com, date accessed 17-11-2011).

The thermal spray gun uses a plasma arc, a combustible gas mixture or an electric arc to generate the heat necessary to melt the coating material. The material changes to a plastic or molten state when heated and is accelerated by the process gas. These particles strike the substrate, flatten upon impact, and form thin pancake shaped splats which bond to the substrate and to each other. The splats build up a coating with a lamellar structure (www.keytometals.com, date accessed 17-11-2011).

Coatings can be deposited using different combinations of equipment and consumables. Basic thermal spray systems typically consist of a spray gun that houses a heat source, a powder supply, a gas supply and a wire or powder feeder. The scheme of generic thermal spray coating process is shown in Figure 1.2 (www.keytometals.com, date accessed 17-11-2011).

Any material can be sprayed as long as it is melted by the heat source employed and does not undergo degradation or vaporization during heating (Little, 1979; Longo, 1985). One interesting feature of thermal spraying is that metallurgical compatibility between the coating and the substrate, in general, can be ignored (Budinski, 1988). In addition, the substrate temperature rarely exceeds a few hundred degree Celsius which enables hard metal or ceramic coating to be deposited on thermosetting plastic also.

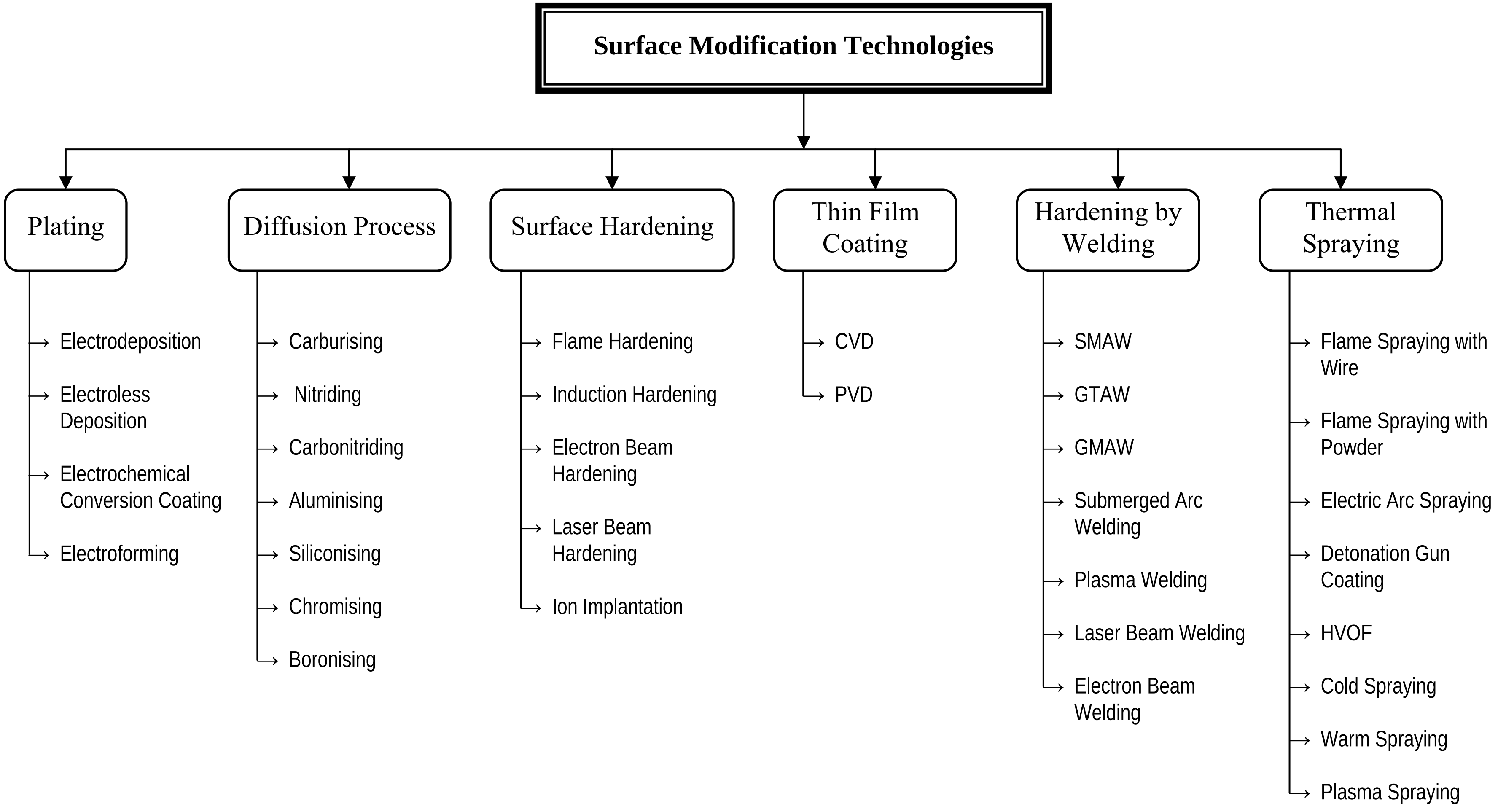

Figure 1.1: Various forms of Surface Modification Technologies (Budinski, 1988).

The common thermal spray processes are shown in Figure 1.3 (Lugscheider and Weber, 1990). The processes mentioned above are discussed briefly in the following articles. Plasma spraying has been discussed in some details.

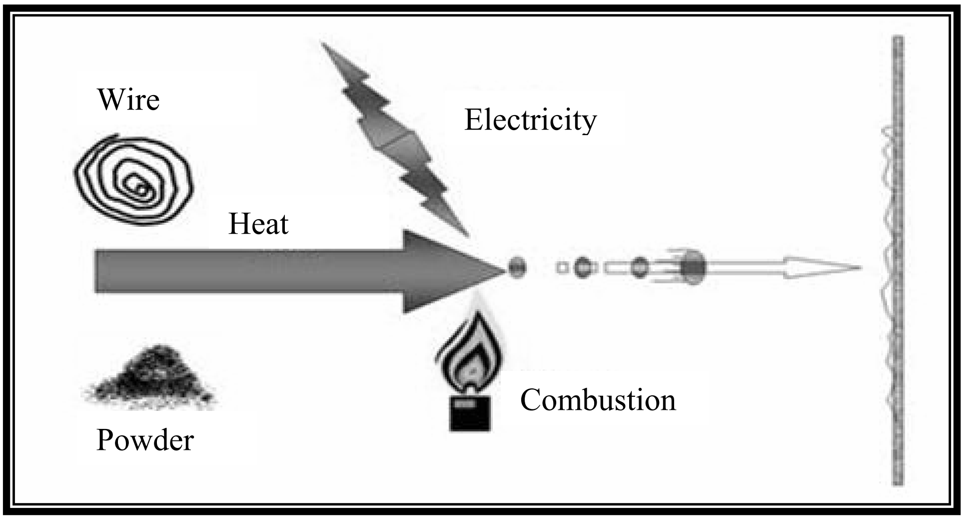

Figure1.2: Scheme of Thermal Spray Coating Processes.
(www.keytometals.com, date accessed 17-11-2011)

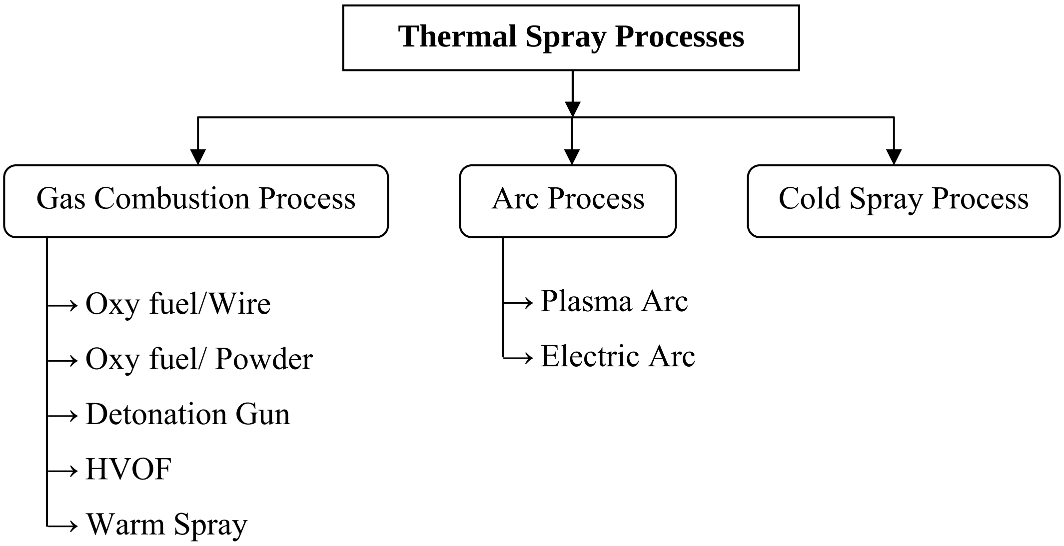

Figure 1.3: Thermal Spraying Processes.

Flame Spraying with Wire: The arrangement is shown in Figure 1.4. The spraying system consists of the following:

(i) spraying gun,
(ii) wire feed arrangement,
(iii) oxygen and acetylene gas supply system, and
(iv) air compressor.

A mixture of oxygen and acetylene is allowed to enter the combustion chamber of the spraying gun. After combustion, a high temperature flame comes out of the nozzle of the gun. The feedstock in the form of a wire is continuously fed to the flame which melts the tip of the wire to form a liquid droplet. A compressed air jet is used to remove the droplet from the tip and carry it with a high velocity towards the target surface placed in front of the gun. The continuous wire feeding is accomplished by a set of rollers rotating at a preset speed (Morris, 1951; Little, 1979; Longo, 1985).

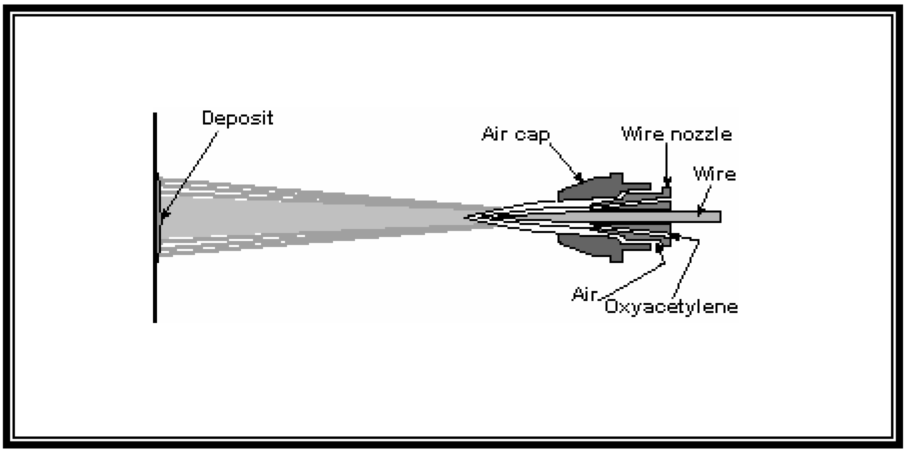

Figure 1.4: Schematic of Wire Flame Spraying.
(www.twi.co.uk, date accessed 24-12-2011)

Advantages: (Budinski, 1988)

- Set up cost is comparatively low.
- Thick metallic layer can be built up easily and hence it is quite useful for rebuilding purpose.

Limitations:

- Coating-substrate bond strength and yield per hour is limited.

Flame Spraying with Powder: The arrangement is shown in Figure 1.5. In this case also an oxy-acetylene flame is used to melt the powder feedstock. The powder is fed directly into the flame by a stream of compressed air or inert gas (argon or nitrogen). The carrier gas feeds the powder into the combustion flame where it is heated to a molten or semi molten condition (Meringolo, 1983; Longo, 1985).

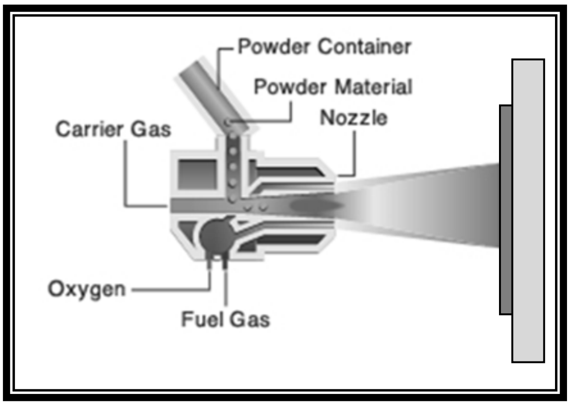

Figure 1.5: Schematic of Flame Spraying with Powder Feedstock.
(www.tocalo.co.jp/english/technical/powderflame.html, date accessed 23-05-2012)

Advantages: (Budinski, 1988)

- Set up cost is low.
- A large number of alloys (even cermets) are available in powder form.

Limitations:

- Deposition rate is slow and bond strength is also limited.

Electric Arc Spraying: Electric arc spraying is a thermal spraying process with a very high yield. In this process an electric arc is struck between two continuous consumable wire electrodes which serve as the feedstock material. The electric arc melts the tip of the electrodes and a jet of compressed gas (usually air) is used to atomize the molten tip into fine droplets and propels them towards the substrate. The process is simple to operate and can be used either manually or in an automated manner. Electric arc spraying can be done using conductive materials only, e.g., Al. It is possible to spray a wide range of metals, alloys and metal matrix composites in wire form. A combination of high arc temperature and particle velocities greater than 100 m/s gives the arc sprayed coatings a better bond strength and lower porosity levels as compared to flame sprayed coatings. The process is capable of spraying at a high deposition rate (Xu *et al.*, 1995). However, use of compressed air for droplet atomization and propulsion results in a coating with high oxide content. Figure 1.6 shows the arrangement of electric arc spraying.

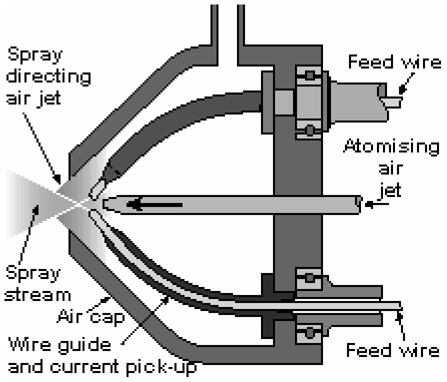

Figure 1.6: Schematic of Electric Arc Spraying.
(www.twi.co.uk, date accessed 24-12-2011)

Advantages:

- High deposition rate.
- Equipment cost is relatively low.

Limitations:

- Only conductive materials can be sprayed.

Detonation Gun (D-gun) Coating: Figure 1.7 shows the operation of a detonation gun in schematic representation. Detonation spraying makes use of a gun equipped with a specially designed chamber where metered amounts of oxygen and acetylene are supplied along with the powder particles of coating material suspended in nitrogen. The mixture is then ignited with the help of a spark plug and a detonation occurs followed by formation of shock waves. The high velocity shock wave front travels down the length of the barrel at a velocity much higher than that of sound. This wave front accelerates the powder particles already heated to a plastic state by the energy of detonation and finally forces them out of the barrel and projects them to the base metal. The high kinetic energy of each particle is converted to additional heat upon impact with the base metal surface, thereby producing a strong bond.

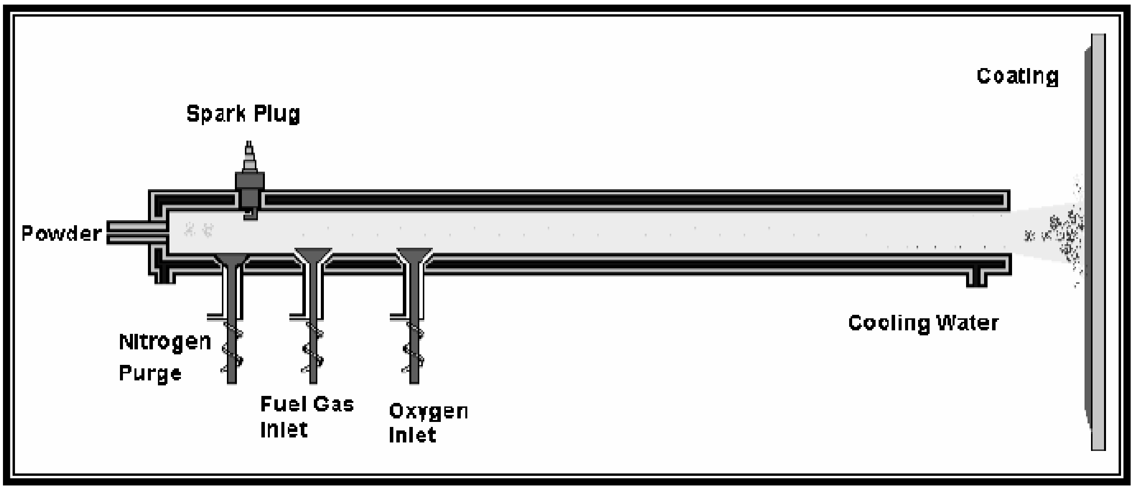

Figure 1.7: Schematic of Detonation Gun Coating.
(www.welding-technology-machines.info, date accessed 24-02-2012)

Because of the high level of noise generated during firing, the gun is usually located within concrete sound absorbing walls. The process is completely automated and is aimed and fired by remote control. This process also requires other systems like fuel and purge gas control, powder feeding, gun cooling and sparkplug operation (Meringolo, 1983; Longo, 1985).

Advantages:

- Can deposit metals, alloys and ceramics.
- Excellent bond strength.
- Very dense coating with porosity less than 1%.

Limitations:

- The process requires very elaborate arrangement.
- The process makes very loud noise.

High Velocity Oxy-Fuel Spraying (HVOF): Figure 1.8 shows the schematic diagram of HVOF spraying system. During operation of the process fuel (kerosene, acetylene, propylene and hydrogen) and oxygen are fed into the combustion chamber. Combustion produces hot gaseous products at a high pressure. This hot gas is made to exit through a nozzle at a high velocity. Powder is fed to the flame by a carrier gas. The higher particle velocity helps in improving coating adhesion. The powder to be sprayed often does not melt completely but attains a semi molten state in contact with the high temperature and high velocity gas stream. When these particles strike the prepared substrate with a very high velocity, they solidify to form a very dense coating (Sobolev *et al.*, 1997; McCartney, 1998).

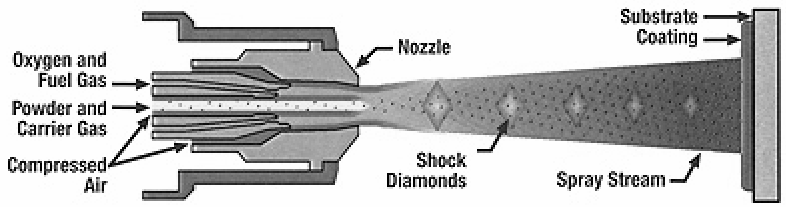

Figure 1.8: Schematic of HVOF Spraying.
(www.twi.co.uk, date accessed 24-12-2011)

Advantages:

- Coatings are dense with very low porosity.
- Excellent bond strength.
- Low oxide metallic coatings.
- Very popular for cermets like WC-Co.

Limitations:

- High gas consumption.
- Usage of combustible gas at high pressure is possible only with adequate safety measures.
- Not a very suitable coating process for ceramics like alumina.

Cold Gas Dynamic Spraying: The Cold Spray or cold gas-dynamic spraying process is the next progressive step in the development of high kinetic energy coating processes. The process uses the energy stored in high pressure compressed gas to propel fine powder particles at very high velocities (500 - 1500 m/s). Compressed gas (nitrogen, helium) is fed via a heating unit to the gun where the gas exits through a specially designed nozzle (laval type mostly) at a very high velocity. Compressed gas is also fed via a high pressure powder feeder to introduce the feedstock into the high velocity gas jet. The powder particles are accelerated and moderately heated to a certain velocity and temperature where on impact with a substrate they deform and bond to form a coating. The schematic of the process is shown in Figure 1.9. As with the other processes a fine balance between particle size, density, temperature and velocity are important criteria to achieve the desired coating. The particles remain in the solid state and are much colder compared to the other thermal spray process. Hence, the process is known as cold spraying. The process imparts little to no oxidation to the spray material, so surfaces stay clean which aids bonding. No melting and relatively low temperatures result in very low shrinkage on cooling, plus with the high strain induced on impact, the coatings tend to be stressed in compression and not in tension. Low temperatures also aid in retaining the original powder chemistry and phases in the coating. At present the process is most suitable for coating ductile materials like aluminium, stainless steel, copper, titanium and its alloys.

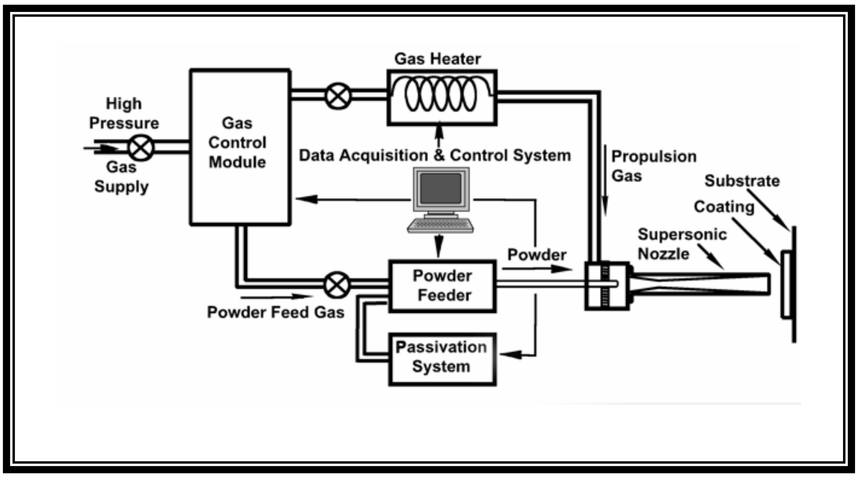

Figure 1.9: Schematic of Cold Spraying.
(www.ktech.com, date accessed 17-08-2012)

Advantages:

- No or very little oxidation.
- High hardness due to cold working.
- No phase transformation due to no or small rise in temperature.

Limitations:

- High gas consumption.

Warm Spraying: Figure 1.10 shows the schematic of the warm spraying process, which is a modified form of HVOF spraying system. A mixture of kerosene and oxygen is burnt continuously to generate a hot gas, into which nitrogen gas is injected between the combustion area and the converging–diverging nozzle of the mixing chamber. By adjusting the flow rate of the nitrogen gas, the flame temperature and concentrations of the gas can be controlled. It is a novel modification of high velocity oxy-fuel spraying, in which the temperature of combustion gas is lowered by mixing nitrogen with the combustion gas, thus bringing the process closer to the cold spraying. The resulting gas contains unreacted hydrocarbons and oxygen, and thus is not as clean as cold spraying. However, the process involves higher temperature and hence ensures higher deposition efficiency. Again, in this case the processing temperature is lower compared to HVOF and hence the degree of melting and chances of possible chemical degradation of the feedstock is less. These advantages make this technique suitable for spraying materials like titanium, metallic glasses or plastics which either oxidize or otherwise degrade quickly at high temperature environment (Kuroda *et al*., 2008).

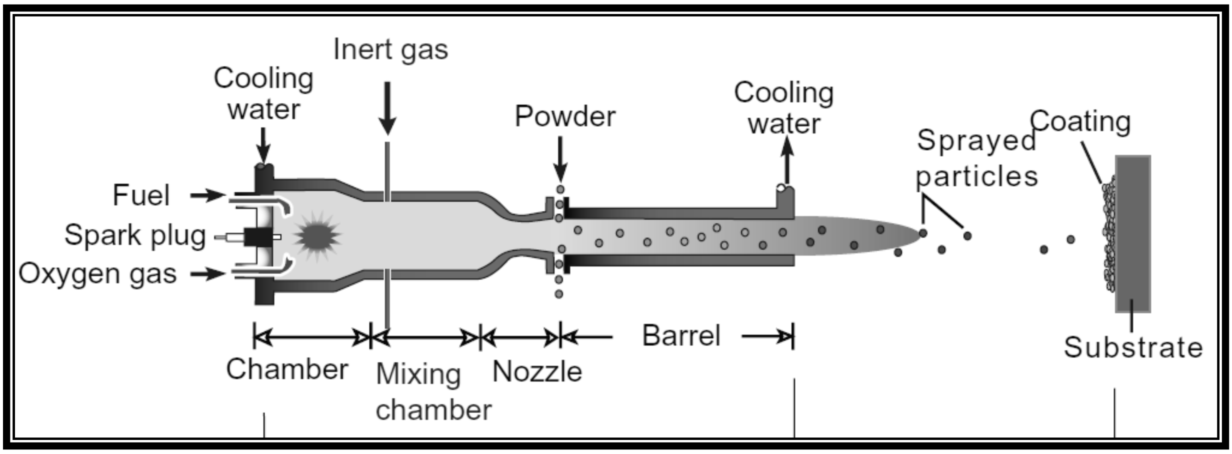

Figure 1.10: Schematic of Warm Spray Process (Kuroda *et al*., 2008).

Advantages: (Kuroda *et al*., 2008)

- The undesirable processes like oxidation or decarburization can be controlled effectively.
- High coating density.
- Suitable for oxidation prone metals like titanium or its alloys.

Limitations: (Kuroda *et al*., 2008)

- The process as not as clean as cold spraying.

1.3.2 Plasma Spraying

In this case material in the form of powder is injected into a very high temperature plasma flame, where it is rapidly heated and accelerated to a high velocity. The hot molten or semi molten particles impact on the substrate surface and form splats. The consecutive layers of splats build up the coating with a lamellar structure (Little, 1979; Powloski, 1995; Heimann, 1996; Budinski, 1988). This plasma spray process is known as a "cold process" since the substrate temperature is kept low during processing, thus, avoid damage, metallurgical changes and distortion of the substrate material. The schematic of plasma spray coating is shown in Figure 1.11.

The plasma spray gun comprises of an annular copper anode and a tungsten tipped copper cathode, both of which are water cooled. Plasma gas (argon, nitrogen, hydrogen, helium) is forced through the gap between the electrodes. The plasma is initiated by an electric discharge which causes localized ionization and a conductive path for a DC arc to form between cathode and anode. The high temperature arc heats the gas to a temperature as high as 10,000 °C, effecting ionization of the gas to form a stable plasma. The plasma exits the anode nozzle as a flame. Powder is fed into the plasma flame most commonly via an external powder port mounted near the anode nozzle exit. The powder, in contact with the very hot and rapidly expanding plasma gas, is rapidly heated and accelerated towards a substrate kept in front of the nozzle (Heimann, 1996).

The plasma spray process is most commonly used in normal atmospheric conditions and known as atmospheric plasma spraying (APS) process. It is also possible to conduct plasma spraying in protective environments using vacuum chambers normally back filled with a protective gas at low pressure. This process is known as vacuum plasma spraying (VPS) or low pressure plasma spraying (LPPS) (Heimann, 1996).

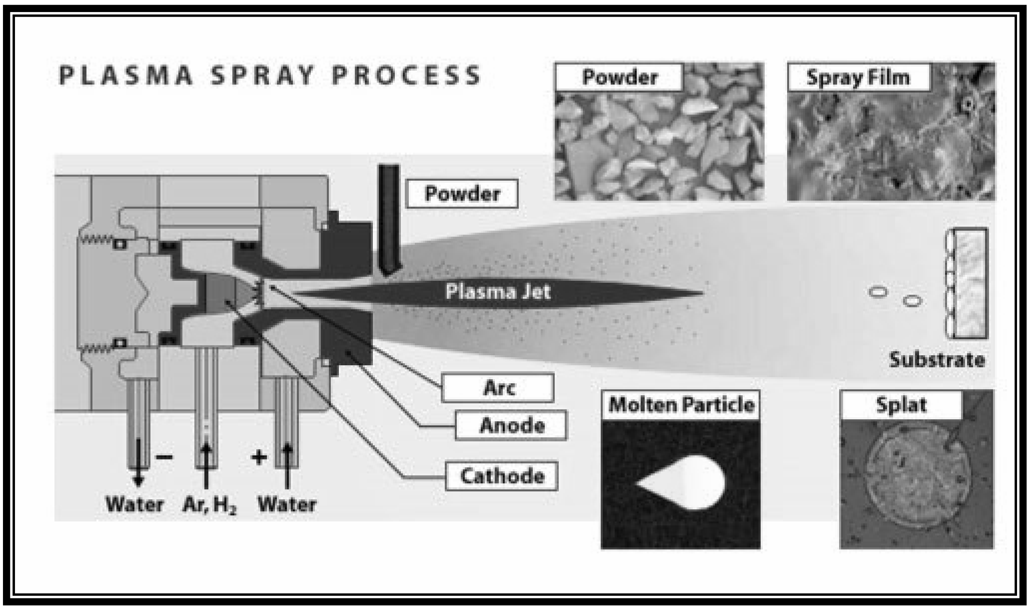

Figure 1.11: Schematic of Plasma Spray Coating (Budinski, 1988).

Plasma spraying is capable of depositing very high melting point materials like tungsten or zirconia. It probably accounts for the widest range of thermal spray coatings and applications. Limitations of the plasma spray process are relative high cost of the set up and complexity of the process.

The equipment consists of the following modules as shown in Figure 1.12.

- ***The plasmatron***: It is also known as the gun. It contains the electrodes for creating the arc. The plasmatron is connected with water cooled power supply cable to cool the electrodes, power supply and gas supply hoses (Sulzer Metco Manual, 1993).

- ***The power supply unit***: The DC plasma arc normally utilizes electricity at low voltage (40 – 70 V) and high current (300 – 1000 A). The power supply unit transforms and rectifies the available power (3 phase, AC, 440 V) to requirement (Sulzer Metco Manual, 1993).

- ***The powder feeder unit***: The powder to be sprayed is kept inside a hopper. The powder is fluidized by a separate pressurized gas line and fed to the plasma arc. The powder mass flow rate (kg/h) can be precisely controlled by the powder feeder (Sulzer Metco Manual, 1993).

- ***The chilled water supply unit***: To cool and increase the service life of the electrodes and other components in the power supply line, chilled water is circulated into the plasmatron, the power supply unit and the power cables. For this purpose a chiller equipped with a pump is integrated to the equipment (Sulzer Metco Manual, 1993).

- ***The control unit***: It is the brain of the plasma spraying system. Its functions are to control current, gas flow rate etc. The control unit contains electronic circuits, solenoid valves and other interlocking arrangements which are essential for safe running of the system. For example, the arc can start only if the coolant supply is on and the water pressure and flow rate are adequate (Sulzer Metco Manual, 1993).

- ***The compressor***: Compressed air is required to switch on the control unit through a pneumatic switch and to vibrate the hopper containing powder for easy flow. This is accomplished by a pneumatic vibrator installed in the base of the hopper (Sulzer Metco Manual, 1993).

- ***The gas supply unit***: The plasma forming gas is usually a two component gas mixture, where the major constituent is known as the primary gas and the other as secondary gas. Typical examples of such mixtures are Ar – 10 vol% He/H_2 or N_2 – 10 vol% H_2. However it is also possible to create plasma from a single gas like nitrogen or argon (Sulzer Metco Manual, 1993).

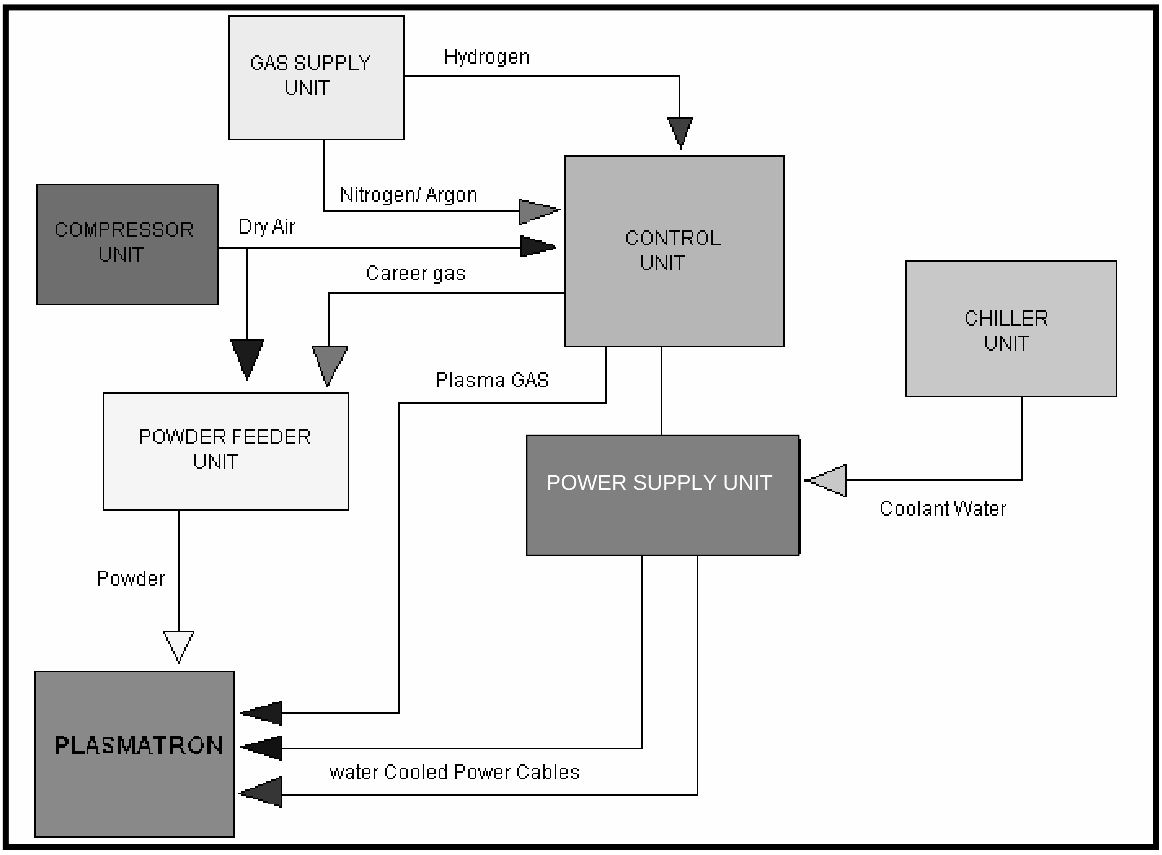

Figure 1.12: Schematic of Modules of Plasma Spraying System.

1.3.3 The Requirements for Thermal Spraying

Roughness of the substrate surface: The clean substrate surface is made rough in order to remove the layer of oxides, to increase the effective surface area and finally to improve the contact between the first layer of splats with the substrate. The surface is made rough usually by process called grit blasting.

An arrangement for grit blasting is shown in Figure 1.13. Two rubber hoses are connected to a blasting gun. One hose is connected to the compressed-air supply and the other is connected to the bottom of the abrasive supply tank or “pot.” The gun consists of an air nozzle that discharges into a larger nozzle. The high velocity air jet while expanding into the larger nozzle creates a partial vacuum in the chamber. This vacuum draws the abrasive into the outer nozzle and expels it through the discharge opening. Examples of common grit materials are aluminium oxide, silicon carbide, chilled iron grits, etc. The roughness of the grit blasted surface depends upon air pressure, stand-off distance and blasting angle (Chander *et al.*, 2009).

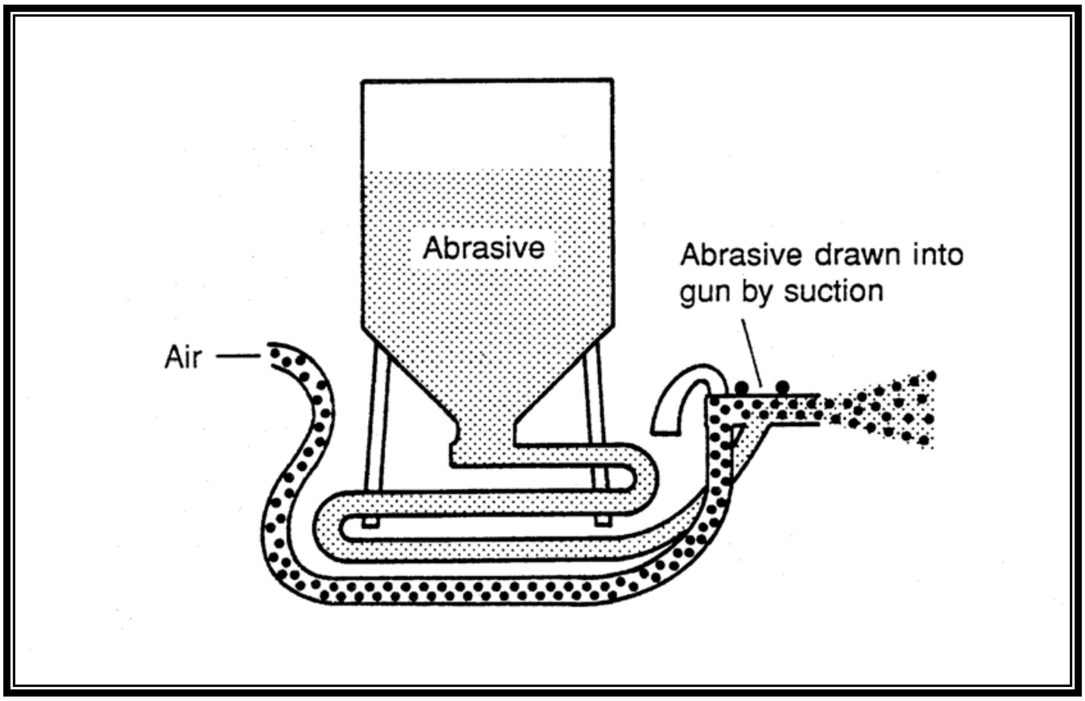

Figure 1.13: Schematic of a Grit Blasting Equipment.
(www.epa.gov/ttnchie1/ap42/ch13/bgdocs/b13s02-6.pdf, date accessed 19-01-2013)

Cleanliness of the substrate: The component surface should be free from oil, grease or dirt so as to improve the contact between the first layer of splats and substrate. A common laboratory practice to clean the substrate surface is ultrasonic cleaning using a solvent like trichloroethylene. For larger components air jet is commonly used. However, in more complicated cases, cleaning of the surface can be carried out by hot vapor degreasing, vapor blasting, pickling or a combination of processes. Spraying should be done immediately after blasting and cleanings. Otherwise an oxide layer tends to grow and water vapor from the surrounding atmosphere condenses on the nascent surface. These are detrimental to coating adhesion (Funk and Goebe, 1985).

Bond coat: Ceramics have a relatively lower coefficient of thermal expansion (α) as compared to the metallic substrates and hence during cooling undergo a differential thermal contraction with respect to the substrate. In addition, the molten splats undergo shrinkage during solidification. These effects introduce a residual stress in the coating. If this stress exceeds a limit then the coating may peel off. To control this problem a suitable coating material which has an intermediate α value is applied on to the substrate first, followed by the top coat. This intermediate layer is known as bond coat. The as-sprayed bond coat also provides a naturally rough surface suitable for top coat application. The choice of bond coat is dependent on the top coat chemistry. For example, in the case of alumina top coat, a Ni-Al or Ni-Cr alloy bond coat is used whereas for zirconia thermal barrier coatings, a NiCrAlY is well accepted (Lee *et al*., 1996).

Cooling water: The water used for the purpose of cooling should be distilled to prevent corrosion of electrode and nozzle (Sulzer Metco Manual, 1993).

Process parameters in plasma spraying: Plasma spraying involves a number of process parameters which determine the degree of powder melting, adhesion strength, deposition efficiency and the final coating characteristics (Novak, 1988). The ratio of powder deposited to the amount of powder fed is known as deposition efficiency. The process parameters and their effects have been discussed in several reports (Fisher, 1972; Gruner, 1984; Eaton and Novak, 1986). Some important process parameters and their effects on the process are briefly discussed below:

- *Arc power*: The arc is produced by consuming electrical power. The plasma gas is ionized by this power. This hot ionized gas heats and melts the powder. Part of power is dissipated by radiation and gun cooling system. The mass flow rate and effective melting of the powder is determined by the arc power. With an increase in arc power, the deposition efficiency increases owing to adequate melting of powder. However, increasing the arc power indefinitely does not result in a monotonic increase in deposition efficiency. In fact, it can result in decrease in deposition efficiency owing to vaporization of a fraction of the powder (Funk and Goebe, 1985; Ramchandran and Selvarajan, 1998).

- *Plasma gas*: The neutral gas molecules injected in the arc are subjected to the electron bombardment and undergo ionization. Both temperature and enthalpy of the gas increases as it absorbs energy. The enthalpy-temperature characteristics of several gases are given in Figure 1.14. Nitrogen and hydrogen are diatomic gases. They first undergo dissociation followed by ionization. Thus they need higher energy input to enter the plasma state. This extra energy increases the enthalpy of the plasma. In addition, presence of hydrogen increases the thermal conductivity of the plasma, thereby improving particle heating (Heiman, 1996; Escure *et al.*, 2003; Tekmen *et al.*, 2009). Also, an increase in hydrogen concentration in the plasma results in a higher particle speed (Guessasma *et al.*, 2005: Kanta *et al.*, 2009). On the other hand, the mono-atomic plasma gases, i.e., argon or helium, approach a much higher temperature in a lower enthalpy range (Ingham and Fabel, 1975). The gas creates the plasma and provides momentum to the particles. Hence, particle momentum increases with an increase in plasma gas flow rate (Qunbo *et al.*, 2008; Kanta *et al.*, 2009). However, too large a flow rate tends to cool the plasma.

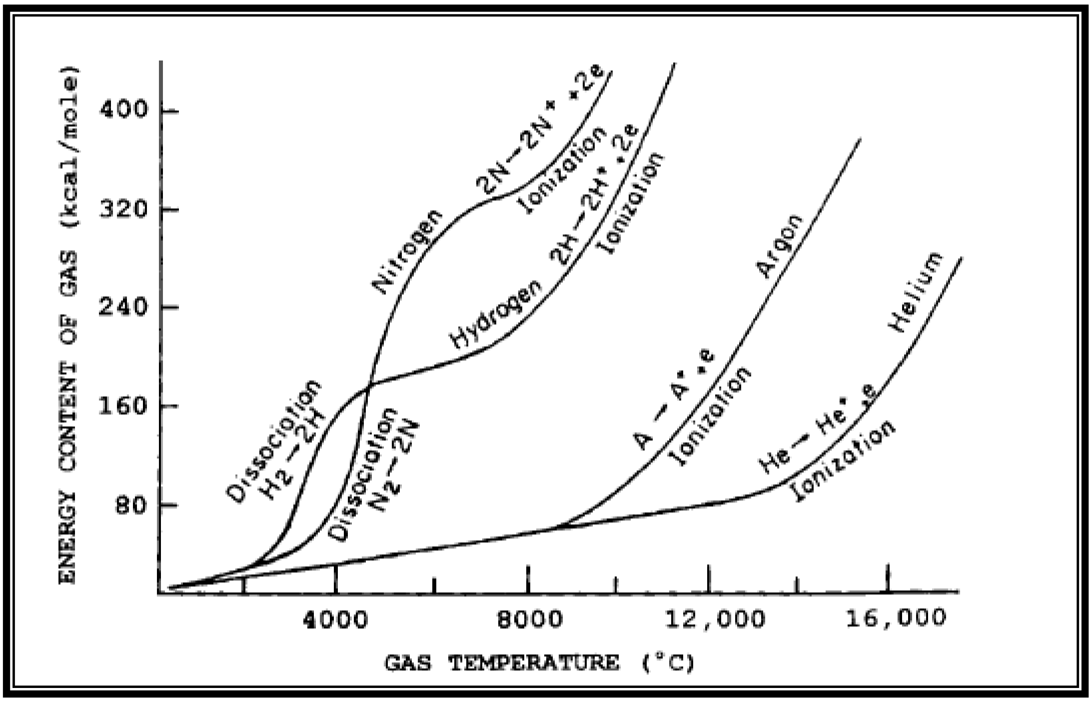

Figure 1.14: Energy Content of Typical Plasma Gases as a Function of Temperature (Ingham and Fabel, 1975).

- *Carrier gas*: The carrier gas is used to move the powder in the plasma plume from the hopper. Normally the primary gas itself is used as a carrier gas. A very low flow rate cannot convey the powder effectively to the plasma jet. On the other hand a very high flow rate pushes the powders away from the hottest region of the plasma jet leaving a large fraction of particles in unmelted state. Thus, there is an optimum flow rate for each powder at which the fraction of unmelted powder is a minimum, and hence the deposition efficiency is maximum (Fisher, 1972).

- *Mass flow rate of powder*: The mass flow rate determines the coating thickness and other mechanical properties. The ideal mass flow rate largely depends on the powder chemistry, size and other powder parameters. Spraying with a low mass flow rate keeping all other conditions constant results in under utilization of the process and slow coating buildup. On the other hand, a very high mass flow rate may lead to incomplete melting, resulting in high coating porosity. The unmelted powders also may ricochet off the substrate surface keeping the deposition efficiency low (Novak, 1988).

- *Stand-off distance*: The distance between the tip of the gun and the substrate surface is called stand-off distance. A shorter stand-off distance may not offer sufficient time in flight for heating the powder particles resulting in less melting and hence, more unmelted particles in the coating. Too large a stand-off distance may result in freezing of molten particles before reaching the target (Funk and Goebe, 1985; Oki *et al.*, 1998). It is found in the case of alumina that the porosity increases and the thickness of the coating (hence deposition efficiency) decreases with an increase in stand-off distance beyond an optimum value. (Oki *et al.*, 1998).

- *Substrate cooling*: During a long spraying session, the substrate might get heated up and may develop thermal-stress related distortion followed sometimes by a coating peel-off. Such situation arises where thick deposits are to be applied. To decrease the substrate temperature, it is cooled by an auxiliary air supply system. This system consists of an air jet which normally runs parallel to the plasma plume. Sometimes inclined air jet or multiple air jets are also used. The other important function of this cooling air jet is to remove the unmelted particles from the coated surface and thus reducing the porosity (Funk and Goebe, 1985).

- *Powder related variables*: The important powder related variables are powder shape, size and size distribution, processing history, phase composition, etc. These variables have a very significant effect in determining coating quality. For example, too fine a powder might get vaporized during heating resulting in a decrease in deposition efficiency. On the other hand, very large particles may not melt fully and therefore is unsuitable for coating purpose. Another important feature is the shape of the powder. A spherical powder does not have the same flow characteristics as the angular ones, and hence, ideally should not be sprayed using the same set of parameters (Elvers *et al.*, 1990; Powloski, 1995).

- *Preheating of the surface*: As mentioned earlier, the grit blasted nascent surface of the substrate absorbs water and other absorbates and condensates from the environment. Before spraying, the substrate should be preheated to remove these contaminants from the surface (Funk and Goebe, 1985; Fauchais *et al.*, 2004).

- *Angle and location of powder injection port*: There are two important parameters which control the trajectory of the particle to be sprayed. These are angle and location of powder entry port. The various options are shown in Figure 1.15. These parameters are set depending upon the properties of the materials to be sprayed. For high melting point materials, a longer dwell time in the arc is required to ensure proper powder melting, e.g., alumina. On the other hand a low melting point material like aluminium is compatible to a smaller dwell time. Nozzle angles can be acute, 90° or obtuse (Figure 1.15). In the case of powder delivery at an obtuse angle, the momentum of powder particles changes its direction to follow the arc stream and hence dwell time in the arc increases, thus enabling melting of high melting point materials like ceramics. For metal powder spraying, the nozzle is kept vertical i.e. nozzle angle 90°. The nozzle angle can be further reduced and set almost parallel to the arc stream axis, i.e. co-axial with the arc stream for very low melting point materials like plastics or epoxy.

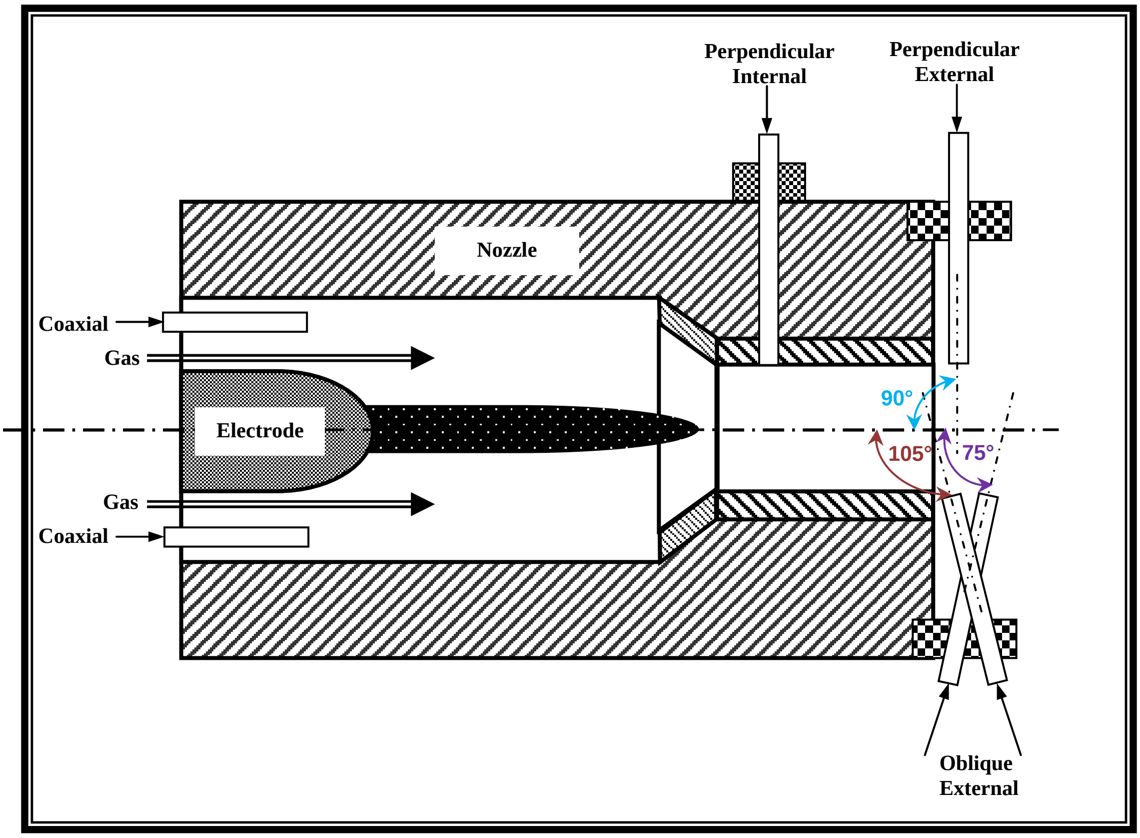

Figure 1.15: Various Angles and Location of Powder Injection for Plasma Spraying (Heimann, 1996).

Like nozzle angle, the location of the powder-entry port along the arc axis is also an important variable for plasma spraying. This port can be located either inside or outside the nozzle. For a high melting point material the internal powder feed port is located as far back along the nozzle as possible so as to ensure a long dwell time. Again, the powder does not penetrate the arc near the inlet orifice of the nozzle because, at this point, the arc is highly ‘pinched’ and the arc gas velocities exert a repulsive action on the injected particles (Fisher, 1972). It is therefore normal practice to locate such powder entry port fairly near the nozzle exit. For the purpose of spraying low melting point materials such as epoxy resins or plastics, it is possible to reduce the dwell time by introducing the powder into the arc at various points outside the nozzle (Heimann, 1996).

1.4 An Overview of Mullite

Mullite rarely occurs as a mineral in nature. In fact, the word Mullite has been derived from “Isle of Mull’; a place off the west coast of Scotland where the only naturally occurring deposits of Mullite have ever been found (www.kyanite.com, date accessed 20-07-2010). Mullite is commonly denoted as $3Al_2O_3{\cdot}2SiO_2$ (i.e. 60 mol% Al_2O_3). However it is actually a solid solution with the equilibrium composition limits of 60-63 mol% Al_2O_3 below 1600 ºC. In spite of its rare occurrence in natural rocks, mullite is perhaps one of the technologically most important phases in both traditional and advanced ceramics. The importance of mullite and its ceramics is well documented in a large number of publications which appeared in recent years (Li and Khor, 2002a; Schneider *et al.*, 2008; An *et al.,* 2011; Salmijazi *et al*., 2012).

The following is a summary of important features of mullite (Schneider *et al.*, 2008):

- High thermal stability, low thermal expansion coefficient and thermal conductivity, high creep resistance and corrosion stability together with suitable strength and fracture toughness.

- Mullite can be synthesized from alumina, silica, alumino-silicates and kyanite, refractory grade bauxite, Al_2O_3 rich sheet silicates and clay. These are available in large quantities on earth.

Mullite displays a large variety of appearances, ranging from Czochralski-grown single crystal to polycrystalline and poly phase ceramics. Mullite can also be processed to from very large products or very tiny engineering components of high purity & homogeneity. Figure 1.16 shows some applications of mullite (Schneider *et al.*, 2008).

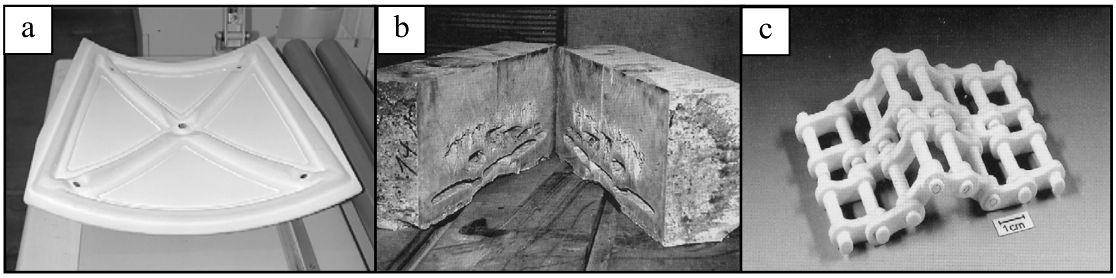

Figure 1.16: Applications of Mullite (a) Panel for Re-entry Space Vehicle, (b) Fused Mullite Refractory Bricks, (c) Sintered Mullite Based Conveyor Belt (Schneider *et al.*, 2008).

Most of the applications of mullite has made use of monolithic ceramics, e.g., porcelain, construction and engineering ceramics, refractories, kiln furniture, creep resistance materials, substrate for catalytic converters, electronic devices and other advanced ceramics, e.g., optically translucent ceramics for high temperature furnace windows. However, it is possible to use mullite as coating and as mullite matrix composites (Schneider *et al.*, 2008).

New mullite materials and coatings that have more controlled mechanical and physical properties are expected to provide opportunities for a wider use of the material. The good mechanical properties of high purity mullite at high temperatures can make it a potential candidate for high temperature applications.

Thus it is expected that demand for mullite coated products will increase in the coming years. Hence, it is essential to develop a technology for producing good quality mullite coatings.

1.5 Overview of the Thesis

This work involves plasma spraying of a zircon-alumina powder, mixed in a known weight ratio, to finally produce a mullite coating on a Ni-5 wt% Al bond coated low carbon steel substrate. Mullite ($3Al_2O_3{\cdot}2SiO_2$), a hard wear resistant phase, is formed as a reaction product of the two powder ingredients. Chapter 1 presents an overview of the various thermal spray processes with special emphasis to plasma spraying. A thorough literature survey is given in Chapter 2 and on the basis of this literature survey a set of pointed objectives for this work has been framed. The details of the experimental procedures followed in the study have been discussed in Chapter 3. The Chapter 4 deals with the microstructure and related aspects like hardness and porosity of the coatings produced using different parametric sets. The typical splat shapes obtained during coating deposition have also been presented. The quantitative phase analysis of the coatings, i.e., mullite yield under various parametric conditions has been discussed in Chapter 5. In Chapter 6 wear performance of the coating, as compared to standard tribological coatings like plasma sprayed alumina, has been reported and the wear mechanism has been discussed in detail. The conclusions and contributions of this work have been summarized in Chapter 7.

1.6 Summary

This chapter is an overview of the coating technique used in this study, namely, plasma spraying. In addition, the basic idea of surface engineering has been introduced and some other thermal spraying techniques have been discussed briefly. An overview of mullite has been presented. This is followed by a brief chapter wise overview of the thesis. The next chapter will deal with the literature survey on the topics of interest followed by framing of the objective of this thesis.