SPRAY FORMING OF THIN WALLED NET-SHAPED COMPONENTS OF HARD MATERIALS BY HIGH VELOCITY OXY-FUEL THERMAL SPRAYING PROCESS

BY

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DUBLIN CITY UNIVERSITY

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SEPTEMBER 1994

DEDICATED TO

MY PARENT, WIFE & SONS

DECLARATION

I hereby declare that this material, which I now submit for the assessment on the programme of study leading to the award of Ph.D. is entirely my own work. To the best of my knowledge, the results presented in this thesis originated from the presented study, except where references have been made. No part of this thesis has been submitted for a degree at any other institution.

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ABSTRACT

Spray forming is a near-net shape fabrication process in which a spray of finely divided molten particles of metallic material is deposited onto a suitably shaped substrate to form a coherent solid. This technology offers unique opportunity for simplifying material processing by elimination of a number of unit operations and can be an alternative to conventional metal working technology for the production of certain type of components. The components thus formed may have some properties viz. hardness and wear resistance, surpassing those of their cast and wrought counter parts.

Cemented carbide belongs to a class of hard wear resistant refractory materials which are very difficult to process. This material can be used to make thin-walled inserts which can be utilised to improve the surface property of the engineering components.

A high velocity oxy-fuel thermal spraying system has been installed. This coating process has been employed to spray form thin walled near net shaped components. Materials used to fabricate components were tungsten carbide/cobalt, nickel chromium alloy and stainless steel. Special attention was given to determine the processing parameters of tungsten carbide/cobalt components.

Forming cores of different sizes, shapes were made from different materials. Materials in the form of powder were deposited by spraying with the HVOF thermal spray gun on the forming core surface after applying a releasing layer on the forming core. The releasing layer was so chosen that it facilitated deposition without fracture and after deposition it can be debonded easily from the forming core such that the deposited layer can be separated without fracture. Heating and cooling of the forming core-deposit assembly at different stages of spray forming process have profound effect on the success in obtaining the component without fracturing. Optimum ranges of values of the processing variables for different types of material were determined.

The effects of the processing parameters on the properties of the components were also investigated. The density of the spray formed components vary between 96-99.5% of the theoretical values. The other properties of the components such as hardness, roughness and composition were also measured and compared with the standard values.

The components thus formed were found to be brittle. To improve the toughness of tungsten carbide/cobalt components, multi-layer components were fabricated. The toughness of the multi-layer component was found to be higher than the single layer tungsten carbide/cobalt component. Components of materials with gradual change in composition were also fabricated to improve the toughness of tungsten carbide/cobalt components.

Depending upon the processing variables, the spray formed components contain residual stress. For tungsten carbide/cobalt component the amount of residual stress was measured and the effect of processing variables on the level of residual stress was investigated. An optimum condition was established to obtain stress free tungsten carbide/cobalt component.

These spray formed components were found to be suitable as replaceable insert in a nozzle or cylinder for low stress application. These replaceable inserts can be fitted with adhesives or can be shrink fit with their counter parts. The cost analysis of fabricating tungsten carbide/cobalt component shows that spray forming might be a viable alternative route for the production of carbide components.

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Spray forming of near net shaped component is advancing very rapidly due to its versatility and superior qualities. This process may be used to produce components of any shape in a cost affective way. Commercially, the spray forming field has been dominated by the Osprey process [1,2]. Flame Thermal spraying has also been used for fabricating components. Plasma thermal spraying has been utilised for spray forming components of many kinds of materials including ceramics [3]. Production of free standing components using vacuum and controlled atmosphere plasma spraying process using metals, ceramics and composites had also been reported. These components have less porosity and essentially retained the composition of the pre-alloyed starting powder.

For some engineering applications removal of as little as 0.1 mm to 0.2 mm from the surface of a engineering component through wear or erosion may render it unserviceable or reduce efficiency. If this amount can be replaced, the part could be given a new lease of life. This can be done either by coating or by putting a replaceable insert. For internal surface of holes or cylinders the present state of the art of coating has limitation by depth to diameter ratio. Internal surface of small holes and cylinders can be best surface engineered by fitting replaceable thin walled insert, made from very hard materials like carbide. The applicability of these inserts will be more where local wear resistance is of paramount importance. Spray forming might be a process of forming these inserts.

Newly designed High Velocity Oxy-Fuel (HVOF) thermal spraying process has overcome the lack of integrity and high porosity of traditional flame spraying process and particularly well suited for spraying carbide materials [4]. New types of HVOF system are emerging into the market with the capability of spraying ceramics with high density.

Nowadays the deterioration of surface of components in service is reduced by

achieving desirable surface properties by either modifying the surface properties or by coating the surface. An approach of making components of different layers i.e hard material at the surface and soft material inside or vice versa can be a solution to wearing problem. A gradual change of hard material on the surface to a soft material inside might provide better hardness and strength to the components. Spray forming process may be applied in forming such components of different combinations of materials.

This thesis is primarily concerned with the methods of improving the surface qualities of the components. The desired properties of internal surfaces can be achieved by inserting thin wall replaceable inserts made from hard wearing materials. The feasibility of manufacturing thin wall near net-shaped components by HVOF thermal spraying process is investigated. These components will be used as a replaceable insert to improve the surface properties like wear resistance, low friction and low corrosion. Attempts are made to manufacture components with different materials with special attention to carbide composites. Components are also made from different combinations of materials at different layers so that surfacing can be done, if required, for proper fitting with the components. Property characterisation of components of varying sizes and shapes has been done. The effect of process variables on the production of the components and the properties has been investigated. Attention is also given to optimise the process so that it can be utilised in the industry for production purpose.

1.1.1 ORGANISATION OF THE THESIS

The remainder of this chapter gives a brief description of surface engineering, thermal spraying processes, spray forming processes, present methods of forming carbide components and the objectives of this study. Chapter two contains the description of experimental equipment and support facilities and chapter three describes the experimental procedures and test materials. In chapter four data, results and discussion are given. Chapter five contains the conclusions.

1.2 LITERATURE SURVEY ON SURFACE ENGINEERING

Surface engineering is one of the newest sciences though it is one of the oldest arts. It seems that man has long recognized the decorative and protective value of coatings. We are told (Genesis 6:14) that Noah waterproofed the ark by coating it " within and without with pitch". The early Egyptians used a variety of metallic coatings including gold for both decoration and protection. Involvement with thin films dates back to the metal ages of antiquity. Practitioners of that time were concerned with the purity, cost, uniformity, adhesion, colour and durability of the coating materials. These issues are still of vital concern today. The deterioration and failure of engineering components in service through surface related phenomena led, in the early 1980's, to the development of the interdisciplinary subject, surface engineering [5-7].

1.2.1 OBJECTIVES OF SURFACE ENGINEERING

Surface engineering can be defined as the branch of science that deals with methods for achieving the desired surface requirements and their behaviour in service for engineering components [8].

Surface for certain application can be selected on the basis of subjective judgement viz. colour or texture for decoration. However, a surface not only defines the outer limits of bodies, it also performs a variety of engineering functions completely different from those required by the bulk materials. Engineering components are required to operate against each other in an aggressive environment, so that an objective judgement is essential as well.

Engineering environments, particularly in high-tech industries, are normally complex. Combined chemical and physical degradation is quite normal in such environments. In more basic industries the phenomenon which causes the most significant damage to the economy of an industry is wear. It is appropriate to consider the mode of component degradation and failure in service and to combine the result of both analyses in order to design better surfaces. For example, in machining process as the loads, speeds and operative temperatures of the cutting tools continue to increase, attention has been increasingly focused on to materials such as ceramics. Such materials are difficult to shape into the complex geometries of many cutting tools but they can be readily deposited as coating onto traditional materials shaped by the established cutting and forming processes. Although ceramics are brittle in a solid form, when deposited as coating they loose their brittleness and conform to the toughness of the base materials. Improved surfaces of tools not only improve the life of the tools but also improve the finish of the machined parts.

Similarly in tribological application, effective lubrication reduces friction and wear between moving surfaces.Conventional liquid lubricants fail under extreme conditions such as low pressure, corrosive or oxidative environment, high load and high speed. Very often bulk materials are either incapable of satisfying design requirements or are too expensive. Surface coating can satisfy requirements, such as hard surface with a ductile core at minimal cost. Ceramics, cermets and self-lubricating solids may appear to be ideal wear resistant materials that suit many tribological applications provided that their strength and toughness are acceptable.

1.2.2 SURFACE PROPERTIES RELEVANT TO THE BEHAVIOUR OF ENGINEERING MATERIALS

The behaviour of materials is greatly dependent upon the surface of the material, the shape of the mating surfaces, environment, and operating conditions. Various surface properties that are relevant to the behaviour of engineering components are shown in Figure 1.1 [9].

The surface properties of materials change markedly in different environments. The top surface of bulk material is known to consist of several zones having different physio-chemical characteristics particular to the bulk material itself. The construction of a metal surface is shown schematically in Figure 1.2. At the base of surface layer there is a zone of work hardened materials on the top of which is a region of amorphous or microcrystalline so called Beilby layer, which results because of the melting and surface flow. On the top of the Beilby layer there is an oxide layer, the formation of which depends on the environment and surface oxidation mechanisms. On the top of the oxide layer the surface contains a layer of adsorbate, which is generally water vapour or hydrocarbons from the environment that may have condensed and become physically or chemically adsorbed to the surface. In addition, the whole texture of the surface layer has a series of irregularities with different amplitudes and frequencies of occurrence [9].

The surface topography depends upon the process of forming e.g casting, moulding, cutting and abrading. The geometrical texture of the surface is controlled by the characteristics of the finishing process. A polished metal surface may look macroscopically like a mirror, while the same surface viewed microscopically is not smooth and does contain surface irregularities called asperities (Figure 1.3). A surface profile results mainly because of three different components of surface profile viz. roughness, waviness and errors of form. Figure 1.4 shows three components of surface texture.

1.2.3 SURFACE INTERACTION WITH THE ENVIRONMENT

The mechanism of surface interaction with the environment, which leads to change of surface properties and influence deterioration of the surface directly or indirectly can be divided into reconstruction, segregation, physisorption, chemisorption, chemical reaction. Schematic of these mechanisms are shown in Figure 1.5.

Reconstruction takes place when the outermost layer of atoms of the solid surface undergoes a structural change. In a binary alloy material, solute atoms can diffuse from near surface regions to cover the surface of the solvent and segregate there. The solute segregation on the surface takes place because it reduces the surface energy of the atoms. Therefore the segregation of alloying elements towards the grain boundaries influences the surface energy of an interface which has a direct effect on the energy of adhesion. It also has considerable influence on wear. Surface reconstruction results in a remarkable change in the coefficient of friction.

One of the most common types of surface interaction that can take place with a clean surface is the physical adsorption (physisorption) of species on that solid surface. By this process molecules are attracted to the surface because of Van der Waals type electrostatic force. This adsorption process is relatively weak process and very small amount of energy is required to remove the physisorbed atoms. The result of physisorption is the reduction of the modulus and yield stress of metals as well as nonmetals in the presence of an adsorbed films [10]. As a result of this effect, lower stress is developed when asperities collide.

Chemisorption is a much stronger bonding than that associated with physisorption. Chemisorption occurs when the individual gaseous atoms interact with a solid surface and the atomic species become bonded to the solid surface. The higher the surface energy of the solid surface, the stronger the tendency to chemisorption. Bond strength is also a function of chemical activity of the solid surface, reactivity of the adsorbing species and its structure. Due to the chemisorption, the adhesion behaviour of the surface changes significantly. The quality of the adsorbed species on a solid surface and its concentration change the adhesion properties of the surface. The naturally occurring oxides present on metals prevent their destruction during rubbing.

With metals in contact with both metals and nonmetals, compound formation by chemical reaction has been observed to occur on the solid surface. The compound formation produces strong interfacial bonds at the contacting surfaces and influences adhesion behaviour.

1.2.4 FRICTION AND WEAR

Friction and wear are two mechanisms by which surface in service is deteriorated. Friction is the resistance to relative motion of the contacting bodies which results in a serious cause of energy dissipation. Friction experienced during a sliding condition is known as sliding friction and that experienced during a rolling condition is known as

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rolling friction. The degree of friction is expressed as the coefficient of friction. Despite extensive research on the subject, no simple model could be developed so far to predict or calculate the coefficient of friction for a given pair of materials [9]. Friction originates from complicated molecular-mechanical interactions between contacting bodies and these interactions differ from one application to another.

The frictional forces have different components such as adhesion component, ploughing component and deformation component. The adhesion component of friction is due to the formation and rupture of interfacial bonds. These bonds are the results of interfacial interatomic forces that depend on the degree of penetration of asperities. In the case of rolling of metals, the adhesion component is not dominating factor for determining the order of coefficient of friction. When one of the contacting surface is harder than the other, the asperities of the harder surface may penetrate and plough into the softer surface (Figure 1.6). If there is any tangential motion, the ploughing resistance is added to the friction forces. Thus ploughing component of friction depends not only on the material properties but also on geometric properties of the asperities, penetrated wear particles and direction of motion. When the asperities of two sliding surfaces come into contact with each other they have to deform in such a way that the resulting displacement field is compatible with the sliding direction. Major part of the energy dissipation due to friction is associated with the plastic deformation of the contacting materials. Although energy is required to deform a metal elastically however most of the energy is recoverable. Friction force can also arise when the wear debris is a viscoelastic or plastic substance, that sticks to the sliding interface and undergoes repeated deformation resulting in consumption of energy. In short friction is a serious cause of energy dissipation.

Wear is a process of removal of materials from one or both solid surfaces in solid state contact. It occurs when contacting surfaces have relative motion. It is very steady and continuous process. Wear is classified into many categories, which are based on quite distinct and independent phenomena as follows.

Adhesive wear

Adhesive wear (some times called as "galling" or "scuffing") which occurs when two solid surfaces slide against each other under pressure [9]. Under this condition sometimes the yield stress is exceeded and the asperities deform plastically until the real area (Figure 1.7) of contact has increased sufficiently to support the applied load. In the absence of surface films the surface projections or asperities cold weld together. Continued sliding causes the junction to be sheared and new junction to be formed. These events cause fracture of the mating surfaces and lead to the generation of wear particles. This leaves projection on one surface and cavities on the other which may lead to further damage. This mechanism of generating wear particles as a result of adhesive wear process is shown in Figure 1.8. Very small amount of contaminant minimize or even prevent adhesion wear under purely normal loading [11]. Since both adhesion and fracture are influenced by surface contaminants and the environment, it is difficult to relate the adhesive wear process only with the bulk properties of solid surfaces.

Abrasive wear

Abrasive wear (some times called as scratching, scoring or gouging depending on the degree of severity), occurs when material is removed from one surface by another leaving hard particles of debris between the two sliding surfaces [9]. There are two general situations : (1) The harder of the mating surfaces rubout the other surface as grinding or cutting and (2) The harder surface is a third body, generally a small particle of grit or abrasive caught between the two mating surfaces, and abrades either one or both of them. In this process asperities of the harder surface press into the softer surface with plastic flow of the softer surface occurring around the asperities from the harder surface. With relative tangential motion, the harder surface removes the softer material by combined effects of microploughing, microcutting and microcracking.

Fatigue wear

A surface of a component, subjected to repeated load experiences continual application and release of stress. These repeating stresses in a rolling or sliding contact might cause fatigue failure. These effects are mainly based on the action of stresses in or below the surfaces without need of direct physical contact of the surfaces under consideration. The shear stress is maximum some distance below the surface in a pure rolling contact. Crack for failure of the component will initiate from the point where shear stress is maximum and the crack will move nearer to the surface (Figure 1.9). Therefore subsurface and surface fatigue wear are the dominant failure modes in rolling element bearing [9]. Any imperfection of the material also influences this failure.

Erosive wear

Erosive wear is a life limiting phenomenon for components working in an erosive environment. This is caused by the impingement of solid particles or small drops of liquid or gas. The impact of these particles on moving or static surfaces of components results in severe erosion. The basic mechanism of erosive wear is shown in Figure 1.10. Movement of the particle stream relative to the surface is a vital feature of erosion and the angle of impingement has significant effect on the rate of material removal. The response of engineering materials to the impingement of solid particles or liquid drops varies greatly depending on the type and state of materials to which these engineering materials are exposed.

Fretting wear

When components are subjected to very small relative vibratory movements at high frequency a type of interactive wear takes place, called "fretting". This mode of wear is initiated by adhesion and is amplified by corrosion. However the main effect is caused by abrasion. Fretting wear normally occurs between components which are not intended to move e.g. press fit components. It is observed that the environment plays a strong role in the wear of surface that undergo fretting.

Corrosive wear

Corrosive wear occurs due to dynamic interaction between environment and mating material surfaces. In the first step the contacting surfaces react with environment and reaction products are formed on the surface. In the next step attrition of the reaction products occurs as a result of crack formation and/or abrasion in the contact interactions of the materials. This process results in increased reactivity of the asperities because of increased temperature and changes in the mechanical properties of the asperities.

1.2.5 REDUCTION OF SURFACE DETERIORATION IN SERVICE

There are two alternative means of reducing the deterioration of surface in service: (1) a change of service condition to offer a less destructive environment and (2) a selection of more resistant materials for the surfaces of a component [8]. There are, of course, limits to what can be achieved with the first method as the engineering tendency is to make environment to become more, rather than less aggressive.

The achievement of desirable surface properties involves either modification of surface properties or modify the properties of the bulk materials to meet the surface demands. In the past it had been the practice to manufacture components from a single material and to impart specific properties to the surface, the component is treated and its microstructure and/or chemical composition is changed. These processes are called surface treatment techniques. The other methods of achieving desirable surface properties are surface coatings. Recent developments have not only produced improved modification methods but perhaps more significantly have created totally reliable surface coating.

1.2.6 COATING PROCESSES

The act of building a deposit on a substrate is called coating. The conventional way of applying coating is the wet processes in which coating is applied in the form of liquid or solution. The advanced way of applying coating is dominated by the dry process

which means the coating is deposited to a substrate in the vapour (gaseous) or moltensemi-molten state. The term deposition is related with two terms "diffusion" and "over lay" (Figure 1.11). Diffused coatings are applied by complete inter-diffusion of material applied to the substrate into the bulk of the substrate material. Examples of these are the diffusion of oxygen into metals to form various sub-oxide and oxide layers. An overlay coating is an add-on to the surface of the part. Depending upon the process parameters an inter-diffusion layer between the substrate and the overlay coating may or may not be present [12].

The physical dimension of thickness of thick and thin film is not quite distinct. A thickness of 1 micron is often accepted as the boundary between the thick and thin film [13]. A recent view point is that a film can be considered thick or thin depending on the application and discipline. According to this idea, a coating used for improving the surface properties is a thin film where as that used for bulk properties is a thick film.

(i) COATING-SUBSTRATE SYSTEM

The performance of the coating applied to engineer the surface of a component does not only depend on the type of the coating but also on the coating-substrate combination. The first consideration is that the substrate must be able to support the coating without causing strain to the coating to failure. As such, the coating-substrate complex systems act together to perform the desired performance. Figure 1.12 illustrates some of interrelated properties of the complex system which may be controlled within specified limits to ensure that the overall engineering requirements of the system are fulfilled.

There are a large number of process parameters such as gas flow rates, gas composition, pressure, environment, substrate temperature and geometry, which determine the quality of coating. The application area is another factor affecting the process variables. Therefore, understanding the relationship between these process variables is required, to select an optimum coating-substrate composite system towards a definite application. Figure 1.13 shows the relationship of coating process variables and their applications.

(ii) CLASSIFICATION OF COATING PROCESSES

A coating process can be divided into three steps: (1) Synthesis or creation of depositing species, (2) Transport of the species and (3) Accumulation or growth of coating on the substrate. These steps can be completely separate from each other or be super-imposed on each other depending upon the process under consideration [12]. The synthesis or creation and transport of the depositing species can be done in three distinct phases viz. Vapour (gaseous) phase, Liquid phase and molten or semi-molten phase. Figure 1.14 shows the various surface coating techniques. Some of the different coating processes are described below [9].

(ii)a Thermal spraying

In this process finely divided metallic or non-metallic coating materials are sprayed at molten or semi-molten state on a substrate without penetrating the substrate to form a spray deposit [14]. Thermal spraying is a cold working process and the substrate is seldom heated above 150 °C [15]. As a result a part can be fabricated fully heat treated prior to coating. Almost any material that can be melted without decomposition, vaporisation, sublimation or dissociation can be thermally sprayed. Theoretically, there is no limit to the coating thickness which may be applied. However, internal stress set up in coatings limits the maximum thickness for a adherent coating. Thermal sprayed coating can be applied to most materials including glass and plastics [9,14].

A detail description of this process will be presented in different sections of this chapter as it has been used as a method of production of components in the present work.

(ii)b Welding

In the welding technique, the coating is deposited by melting the coating material onto the substrate by gas flame, electric arc or plasma arc welding process. The coating materials are supplied in the form of powder, paste, rod, strip or wire. Any material that
can be melted and cast may be utilised in the form of welding. In contrast to the thermal spraying process which does not penetrate the substrate metal, welding process melts a portion of the surface. Mixing of a proportion of substrate metal can affect the composition and the microstructure and hence the wear resistance. Only very thick coating can be deposited by this process. The deposition rates of this process are very high and control of uniformity of coating thickness is difficult. However, the process is expensive and is used only for specialised applications.

(ii)c Cladding

In the cladding process, a metallic foil or sheet is metallurgically bonded to a metallic substrate to produce a composite structure. The metallic powders or other fillers can also be clad to the metallic substrate. Metals and alloys are clad by deformation cladding, diffusion bonding, braze cladding, and laser cladding. Clad surface produced by cladding with wrought material experiences no problems of porosity and nonstoichiometry. Cladding usually denotes the application of a relatively high thickness (typically 1 mm or more) of clad metal whereas a coating is usually thinner [9]. Limitations of this process are that cladding materials in many cladding processes must be available in sheet form, and it is difficult to clad parts having complex and large shapes.

(ii)d Vapour deposition

This is one of the oldest techniques used for depositing thin films. In this process a vapour is generated by boiling or subliming a source material then the vapour is transported from the source to the substrate where it condenses to a solid film. Vapour deposition process has the ability to produce thin coatings with high purity, high adhesion, and unusual microstructure at high deposition rates. Most nongassing substrate materials which can withstand the deposition temperature can be coated by this process. Coatings deposited by this method generally do not require post finishing. A major disadvantage of vapour deposition process is the high capital cost and processing cost associated with vacuum system.

There are three classes of vapour deposition techniques, physical vapour deposition (PVD), chemical vapour deposition (CVD), and physical chemical vapour deposition (P-CVD). Typical particle kinetic energy range for various vapour deposition processes are presented in Table 1.1 [9].

Physical Vapour Deposition (PVD)

Physical vapour deposition is used to apply coatings by condensation of vapours in vacuum (10^{-6} to 10 Pa) atomistically at the substrate surface. This technology is versatile, enabling one to deposit virtually every type of inorganic materials (metals, alloys, compounds and mixtures) as well as some organic materials. The deposition rates can be varied from 10 - 750,000 Å per minute. The thickness of the deposits can vary from a few angstroms to a few micro-metres [9,12,13,16,17]. There are three physical deposition processes namely evaporation, ion plating and sputtering.

Evaporation PVD Process

In the evaporation process, vapour is produced from a material located in a source which is heated by direct resistance, radiation, eddy current, electron beam, leaser beam or an arc discharge. The process is usually carried out in vacuum so that the evaporated atoms undergo an essentially collisionless line-of-sight transport prior to condensation on the substrate. The substrate is usually at ground potential i.e. not biased. A schematic of a vacuum evaporation system illustrating electron beam heating is shown in Figure 1.15. In this process the deposit thickness is the greatest directly above the centre-line of the source and decreases away from it. This problem is overcome by imparting a complex motion to the substrate or by introducing a gas at a low pressure into the chamber so that the vapour species undergo multiple collisions during transport from the source to substrate. The latter technique is called gas-scattering evaporation or pressure plating.

Most pure metals, many alloys and compounds that do not undergo dissociation can be directly evaporated in vacuum. In the more general sense, when a compound is evaporated or sputtered, the material is not transformed to the vapour state as a compound state but as fragments there of. The fragments have to recombine on the substrate to reconstitute the compound. Satisfactory methods of preparing alloys and compounds with proper stoichiometric coatings include reactive evaporation, multiple-source evaporation, and flash evaporation. A plasma is some times included in the reactive evaporation to enhance the reaction between the reactants and to cause the generation of ions and energetic neutrals. This process is known as activated reactive evaporation.

The source material is normally in the form of powder, wire, or rod. Typically coating thickness ranges from 0.1-100 μ m [13]. Most substrate materials can be coated by this process. The major advantages of evaporation are that it is simpler and cheaper compared to other vacuum deposition processes and it gives high deposition rates. The direct evaporation process is incapable of providing precise control of the stoichiometry of compound coatings. Many of the shortcomings of evaporation have been overcome by introducing the reactive gas deposition, ionizing the evaporant atoms, and biasing the substrate.

Ion Plating

Ion plating is a generic term applied to atomistic film deposition processes in which the substrate surface and/or the depositing film is subjected to a flux of high energy particles sufficient to cause changes in the interfacial region or film properties compared to the nonbombarded deposition. Ion plating processes can be classified into two broad categories: glow-discharge (plasma) ion plating performed in low vacuum (0.5-10 Pa) and ion beam ion plating performed in high vacuum (10^{-5} to 10^{-2} Pa) [12,13,18].

In the glow discharge ion plating processes, the material to be deposited is evaporated through ordinary evaporation, but it passes through a gaseous glow discharge on its way to the substrate, thus ionizing the evaporated atoms in the plasma. Condensation of the vapour takes place under the action of ions from either a carrier gas or the vapour itself. The glow discharge techniques can be classified based on the deposition system configuration, mode of production of vapour species, and method of enhancement of ionization of vapour species. Some important characteristics of various glow discharge ion plating process are presented in Table 1.2.

In ion beam ion plating processes, the ion bombardment source is an external ionization source (gun). These guns utilize various ion beams -single or cluster ion beams. Ion beams can be of inert gas ions or ionized species of coating material beams, and sputtering. By using a beam of desired ionized species, alloys or compounds can be formed. Ion beam plating is performed at high vacuum. A wide variety of metallic and nonmetallic coatings have been applied onto metallic and nonmetallic substrate by ion plating processes.

Sputtering

Sputtering is a process whereby the coating material is dislodged and ejected from the solid surface due to the momentum exchange associated with surface bombardment by energetic particles. The sputtered material is ejected primarily in atomic form from the source of the coating materials, called the target. The substrate is positioned in front of the target so as to intercept the flux of sputtered atoms. Thus, the atoms of coating material deposited on the substrate give rise to a coating. The ability to control coating composition makes sputtering useful in the electronic industries. Sputtered coatings are used for various metrological applications. The combination of hardness and corrosion resistance of various sputtered coatings make them suitable for many decorative and tribological applications. The sputtering process can be classified on the basis of the means of producing high energy ions: glow-discharge sputtering process and ion beams sputtering process.

A glow-discharge sputtering system is shown in Figure 1.16. The target is connected to a negative voltage and faces the substrate to be coated. A gas is introduced to provide a medium in which a glow discharge can be initiated and maintained. When the glow discharge is started, positive ions from the plasma strike the target with sufficient energy to dislodge the atoms by momentum transfer. The flux of sputtered atoms collides repeatedly with the working gas atoms before reaching the substrate, where it condenses to form a coating of the target material. By biasing the substrate to a negative potential as an electrode prior to coating, conductive contamination is removed by sputtering and coating nucleation sites are generated on the surface. There are different glow-discharge sputtering techniques. Some important characteristics of various glow discharge sputtering techniques are shown in Table 1.3 [9,13].

In ion beam sputtering processes, the ion bombardment source is an external ionization source used to sputter away the coating material from a target. Ion beams can be inert-gas ions or ionised species of coating materials. The coatings applied by ion beam sputtering at relatively low pressure in the range of 10^{-5} - 10^{-2} Pa are very pure and the resulting coatings are very hard with excellent adhesion [18].

Chemical Vapour Deposition (CVD)

Chemical vapour deposition (CVD) is the process in which a volatile component of coating material is thermally decomposed or chemically reacts with other gases or vapours to produce a nonvolatile solid that deposits atomistically on a suitably placed hot substrate surface. The CVD reactions generally take place in the temperature range of $150 \,^{\circ}$ C to $2200 \,^{\circ}$ C at a pressure varying from 60 Pa to atmospheric [9]. The coating quality depends on the substrate cleanliness, compatibility of coating and substrate materials, thermodynamics, and kinetics of the reaction involved. A schematic of conventional CVD process is shown in Figure 1.17.

CVD is a versatile and flexible technique to produce a wide range of metallic and nonmetallic coatings on any nongassing substrate. The coating deposition rates are very high, and processing cost is generally relatively low. CVD coatings generally exhibit near theoretical density, controlled grain size and excellent adhesion but the requirement of high substrate temperature limits their application. Sometimes CVD processes are carried out at reduced pressure to make the process more thermodynamically favourable. In conventional or low-pressure CVD processes sometimes it is required to limit the growth to a very small portion of the substrate. Then a laser beam is used to heat the limited area of the substrate.

Physical-Chemical Vapour Deposition

Physical-Chemical vapour deposition (P-CVD) processes are the hybrid processes which use glow discharge to activate CVD processes. These are broadly referred to as plasmaenhanced CVD (PECVD) or plasma-assisted CVD (PACVD) processes. This process involves the techniques of forming solid deposits by initiating chemical reactions in a gas with an electric discharge. Instead of requiring thermal energy as in CVD, the energetic electrons in the plasma can activate almost any chemical reaction. The reactions proceed at high rate in a system at low processing temperature. Practically any gas or vapour including polymers can be used as a precursor material. Because of the relatively low deposition temperature PECVD techniques are suitable for the coating deposition on a variety of substrate. Coatings produced by this process are pin hole free, hard and have excellent adhesion [9,12,13].

(ii)e Miscellaneous Techniques

Wetting process

The is a process in which the coating material is applied in the liquid form and then becomes solid by solvent evaporation, drying, or cooling. Atomized liquid spray, dipping, spin-on coating, and brushing are included in this process.

Atomized liquid spray process are widely used for paint application of organic and inorganic solid lubricants. Several types of liquid spray equipment are available. All the spray techniques atomize the fluid into tiny droplets and propel them to the substrate. After spraying the coating is air-cured or heat cured and burnished.

In dip coating the substrate is dipped into a liquid bath. After immersion the substrate is withdrawn and the excess coating materials are removed. The metal coatings applied by the dipping process include zinc, aluminium, tin and lead. The thickness,

uniformity, and adhesion of the coating depend on the viscosity of the bath, rate of immersion and withdrawal, temperature and the number of dips. The well-known galvanizing, babbitting are all hot dipping processes. These techniques are used for coatings applicable for low friction, corrosion resistant, decoration.

Brush, pad, and roller coating processes are the mechanical processes commonly used in many industries. Most coating suspensions which can be applied by spray coating process can also be applied by brush, pad, and roller coating processes.

Electrochemical deposition

In electrochemical deposition process metallic coatings are deposited on solid surfaces by the action of electric current. Electrodeposition of metal from aqueous solution is mainly limited by the decomposition potentials of the metals to be deposited. The system consists essentially of an electrolytic bath, a dc power source and two electrodes connected with anode and cathode. An electric potential is applied to the cell and metal is deposited on the cathode by electrochemical dissolution from the donor metal. This is the most convenient method of applying coatings with high melting points, such as chromium, nickel, copper, iron, silver, gold, and platinum.

Chemical Deposition

Metal coatings are produced by chemical reduction with the necessary electrons supplied by a reducing agent present in the solution. Almost any metallic or nonmetallic, nonconducting surfaces including polymers, ceramics, and glasses can be plated. Coating deposited by this process can be hard and more wear resistant than electroplated deposits.

(iii) PROPERTIES OF THE COATING

Physical properties of the coating vary widely depending on the coating processes and the process parameters. The large number of variables involved have limited the number of fundamental investigations of the process property relationship. The microstructure of coating dictates many of the physical properties of the coating. Some of the important properties of the coating and their probable variation are highlighted below.

(iii)a Bonding

Adhesion and adhesive strength are macroscopic properties that depend on the bonding within the deposited particles or atoms and bonding across the interfacial region and the local stresses generated during deposition. The bonding and local stresses are determined by the environment, the chemical and thermal properties of the coating and the substrate materials, coating morphology, mechanical property, defected morphology of the interfacial region and external stresses [19]. Bonding depends on the processes and their mode of growth of coating from source material.

In the case of atomistically deposited coating, the nature and condition of the substrate surface determine many of the factors which control nucleation, interface formation and film growth. These in turn control the interfacial properties. When atoms impinge on a surface, they lose energy to the surface and finally condense by forming stable nuclei. A strong surface atom interaction will give a high density of nuclei and a weak interaction will result in widely spaced nuclei and nucleate by collision with absorbed atoms or other atoms migrate on the surface. It has been proposed that the nuclei density and the nuclei growth mode determine the effective interfacial contact area and the development of voids in the interfacial region (Figure 1.18) [20]. Nuclei density and orientation formed during deposition can be affected by ion bombardment, electric fields, gaseous environment, contaminant layers, surface impurities, surface defects and deposition techniques. In addition to the effective contact area the mode of growth of the nuclei will determine the defect morphology in the interfacial region and the amount of diffusion and reaction between the depositing atoms and the substrate material [21].

Interface may be classified into different types viz mechanical, monolayer-tomonolayer (abrupt), compound, diffusion or pseudo-diffusion and combinations thereof. Formation of different types of interface depends on the substrate surface morphology, contamination, chemical interactions, the energy available during interface formation and the nucleation behaviour of the depositing atoms.

The mechanical interface is characterized by mechanical interlocking and the strength of this interface will depend on the mechanical properties of the materials and surface roughness. The monolayer to monolayer type interface is characterised by an abrupt change of coating material to substrate material. This type of interface may be formed because of no diffusion, lack of solubility between materials, little reaction energy available, or the presence of contaminant layers.

A compound interface may be formed either by an intermetallic compound or some other chemical compound such as an oxide. In this type of interface, there may be abrupt physical and chemical discontinuities associated with the abrupt phase boundaries. Often during compound formation there is segregation of impurities at the phase boundaries and stress could be generated due to lattice mismatching. Porosity may develop in the interfacial region [13].

In the diffusion type of interface there is gradual change in composition, intrinsic stress and lattice parameters across the interface region. Due to the diffusion rates "Kirkendell" porosity may be formed [13]. Diffusion process may be important in the defect structure of the interface region.

A combination of several types of interfacial regions is possible by controlling the environment or film composition during the initial phase of the film deposition as well as heating during and after film deposition.

As the nuclei join together the film begins to form. The properties of the coating are determined by the manner in which a film develops. In the vapour deposited process spit or small droplets of source material may be ejected with the vapour which land on the substrate and incorporated with the coating [13]. The composition of the droplet is different and therefore can be the initiator of corrosion. The spit may also fall leaving

the pinhole behind which can be stress raiser and sit for fatigue crack initiation. Spit and foreign particle can induce preferential growth of the deposit termed as flake which can lead to crack formation or nucleation of corrosive attack.

(iii)b Composition of the coating

The composition and the stoichiometry of the compound of the deposit in different coating processes is controlled by deposition parameter. For some alloys and composites some times the constituents segregate out in patches. The more volatile components of the film may affect the film stoichiometry. Impurities may arise from a number of sources. In vacuum process oxygen, nitrogen, hydrogen and carbon are common from residual gases, vacuum leaks and out gassing [19]. In sputter deposition, the implantation of several atom of the sputtering gas is not at all unusual, particularly when a substrate bias is used.

(iii)c Residual stresses

Deposited coatings almost always contain residual stress [13]. It appears at the interfacial region in a very complex manner due to geometric effects, variation in the physical properties of the material and the usually non homogeneous nature of the film and interfacial material. The presence of pores and voids in the interfacial region will give stress concentration and alter the value of the tensile and shear components of the interfacial stress. The total stresses are composed of a thermal stress due to the difference in the coefficient of thermal expansion of the coating and substrate materials and an intrinsic stress arises from the accumulation effect of crystallographic flaws which are incorporated into the film during deposition. The intrinsic stress is a function of the deposition process. It may be affected by a number of processing and growth parameters, film deposition rate, angle of incidence, presence of residual gas, deposition temperature and gas incorporation [22]. Residual stress in evaporated metal films is tensile and on the other hand residual stress in the sputtered metal films can be either tensile or compressive depending on the deposition parameters [23].

(iii)d Hardness of coating

The process parameters such as deposition rate, pressure, temperature and ion bombardment can cause considerable change in microstructure resulting in change of hardness. An increase in substrate temperature commonly increases the coating hardness for refractory compounds in contrast to the behaviour of the metal films. Other factors affecting the hardness value are interatomic forces, stress level, adhesion of the coating, impurity content and film texture [12,13].

(iv) Applications of coatings

The performance and life of a component that is subjected to friction, wear, high temperature and corrosion can be considerably improved by selection of suitable materials with a suitable coating. Such coating provides a greater flexibility in the design and selection of materials for a particular component. For giving protection and providing decoration, the majority of manufactured goods and architectural and industrial structures are coated. A few uses of coating are described below.

Coatings for tribological applications

In general, the standard requirements for multifunctional optimization of tribological surfaces are score resistance, conformability, embeddability, compressive strength, fatigue strength, thermal conductivity, wear resistance, corrosion resistance and cost.

Hard coatings of oxides, carbides, nitrides, borides and silicides deposited by thermal spraying, vacuum and other deposition processes are successfully used in various bearing applications. Various coatings have been developed for application in high vacuum and high temperature especially in application with no external lubrication.

Coatings for gears, cams tappets and piston rings

Gears, cams and tappets are extensively employed in machines to transform motion. Wear of these components can be reduced by applying a coating. The types of coating include chemically deposited oxide coatings on ferrous metal, electrochemically deposited Sn and Al, and TiN and TiC coatings applied by PVD and CVD. Several plasma-sprayed coatings of composites such as WC/Co, Cr_3C_2/Ni -Cr, Mo-Cr-Ni alloy etc. have been developed for achieving improved scuffing resistance under conditions of marginal lubrication for piston rings [24].

Coatings for cutting tools

Coatings of various ceramic materials, such as TiC, TiN, Al_2O_3 , ZrC, HfN on high speed steel and cemented-carbide substrate have been deposited by various deposition techniques. The low deposition temperatures of evaporation, ion plating, and sputtering are well suited for coating tools. Coating shows an improvement in tool life by a factor of 2 to 10 depending on the type of cutting tool and the coating. HSS tools and drills coated with TiN by magnetron sputtering to a thickness of 2 to 5 μ m are most commonly used commercially.

Coatings for architectural and industrial structures and products

For protection and decoration, majority of architectural and industrial structures are coated by paints. Paint coatings are very diversified. These coatings include varnishes, paints, and enamels for both interior and exterior use. Coatings are also used on a very wide range of materials including metal, wood, paper, textiles, leather, glass, and plastics. These coatings are essential to the efficient functioning of many industrial operations.

Other applications of coatings

Abradable coatings are used as rub-tolerant seals in the compressor and turbine section of aircraft gas turbine engines. Thermal-barrier coatings of zirconia, which has insulating properties and hot corrosion resistance are used in hot sections of turbine engines. These coatings are applied by plasma spraying. Hard coatings of TiC-N deposited by CVD, SiC deposited by sputtering have been found to enhance resistance to erosion of gas turbine blades. The performance of various forming dies, punches and moulds can be improved by putting hard coating on the surfaces. It has been reported [25,26] that an improvement in useful life upto a factor of 10 to 200 has been obtained.

1.2.7 SURFACE MODIFICATION TECHNIQUES

This thesis is mostly concerned with surface coating but for completeness a brief discussion is included about surface modification.

Surface modification processes are in daily use for improving hardness and wear resistance. These processes do not build a coating over a surface, rather modify the surface itself and impart hardness, corrosion and chemical resistance to a surface and sometimes lower friction. These processes may be classified into three categories, (i) microstructural, (ii) chemical diffusion and (iii) ion implantation [9,27].

(i) MICROSTRUCTURAL SURFACE MODIFICATION TECHNIQUES

By only heating and cooling the microstructure of the components can be changed and these processes are known as heat treatment. In these processes heating rate and cooling rate are controlled in such a way that the specific properties of the solid can be obtained. These processes can be divided into two groups. Firstly, there are some heat treatment processes by which the whole component changes its properties such as Normalizing, Annealing, Austenitizing, Quenching, Tempering. Secondly, there are some heat treatments by which only the surface properties of the component are changed such as induction hardening, laser hardening and electron beam hardening. These processes are known as surface hardening processes. Process parameters of some surface hardening processes and their applications are given in Table 1.4. The basic principles of heat treatment as stated above are almost the same for the old and the new methods but the improvements are only in the process control, time of processing and scale of production. The basic idea of new developments is to heat the specific area or surface of the component to a precisely controlled temperature and cool it at different rates as per requirements.

(ii) SURFACE MODIFICATION BY CHEMICAL DIFFUSION

Surface hardness and the wear resistance properties of engineering components can be improved without affecting the bulk properties by some chemical changes of the surface material involved. By this method some chemical species are allowed to diffuse into the surface of the bulk material. High hardness is obtained through the formation of compounds and quenching is not required. The core remains comparatively soft and tough. The basic process used is thermochemical, because some heat is required to enhance the diffusion of hardening species into the surface and subsurface region of a part. The typical elements diffused in the surface include nonmetal (e.g. carbon and nitrogen), metalloids (e.g. boron and silicon) and metals (e.g. chromium and aluminium) [27]. The depth of diffusion depends on the temperature, the chemical composition and the concentration gradient of a given hardening species. Hardening species used in the processes may be in the form of gas, liquid or ions. Process parameters of some commonly used diffusion treatments are given in Table 1.5.

(iii) SURFACE MODIFICATION BY ION IMPLANTATION

Ion implantation involves the production of ionized species from gas, vapour, or a sputtered surface and acceleration of the ions by an electric field towards the component surface to be treated. Energies required are usually between about 10 kev and 200 kev [27]. A limit is set to the lowest energy which can be used by the fact that the ions must penetrate the thin oxide films normally present on metallic surfaces. The process is carried out in a moderate vacuum, so that undue scattering or neutralization of the

charged particles should not occur. The depths ($0.01-1.0 \mu m$, typically $0.1 \mu m$) to which the composition is modified are still very small compared with those normally encountered in surface coating and surface treatments. Whereas in the case of carbon and nitrogen in steel, secondary effects may occur which carry the implanted material to a greater depth. This process is mainly used in semiconductor industries.

1.3 THERMAL SPRAYING PROCESS

1.3.1 INTRODUCTION

Thermal spraying was originally invented by Schoop in 1910 [15,28]. He developed a crude spraying gun using Oxygen and acetylene as the heat source and compressed air to project the molten materials. By this process almost any material that melts without decomposition, vaporisation, sublimation or dissociation can be deposited. Non metallic materials like hard ceramics, cermets, and some polymers can be sprayed by this technique. Theoretically there is no limit to the thickness of coating. However, internal stress set up in coatings limits the maximum thickness for an adherent coating [29-31]. Thermal spray coatings with compressive stress have been reported which claims that there is no thickness limit of depositing these coatings [32]. Thermal sprayed coating can be applied on most materials including glass and plastic [33].

1.3.2 SPRAY AND DEPOSITION OF COATING PARTICLES

Thermal spraying is the process by which finely divided metals or non-metallic materials are deposited in a molten or semi-molten state on a substrate to form a sprayed deposit. So, the aim of the spraying apparatus is to spray the particle in the direction of the substrate and to condition the particles so that when they strike the substrate they are prone to adhere. The spraying device must produce a hot zone containing so much enthalpy that the spraying particle melt or soften in the hot zone. Moreover in the hot zone a gas flow must exist exerting such a drag that the particles arrive at the substrate having the required momentum. The basic criterion of thermal spraying is that the particles should melt completely without excessive vaporization and remain soft until they impinge onto the substrate. Vaporisation produce a sponge like coating structure [14]. Smaller particle size will ensure more complete melting but the velocity gradient restricts the particle to enter into the hot zone. Therefore some of the particles do not melt sufficiently and are transported on the periphery and deposited. Further these particles cool more rapidly and therefore solidify before impact and give rise to defective coating. The formation of oxide in the film is also controlled by the rate of cooling, the size and shape of the powder particles, the velocity of the particles and their location within the heat zone.

In thermal spraying the proper deposition and the quality of the coating depend on the spray process, the associated fuel, raw material characteristics and kinetics. The raw materials characteristics are particularly influential when the process uses the powder materials. Particle shape, size, density, oxide content all contribute to the quality of the end product. For melting of solid particles in a heated gas the material related variables are heat transfer coefficient, conductivity, melting temperature and specific heat. The following equation relates the material variables with the gas flow dynamics and the particle's characteristics [14].

$$\frac{(K\Delta T)^2}{V\mu} \ge \frac{L^2 d^2}{16 P}$$
(1.1)

where,

S

- S = particle travel distance (spray distance)
- K = average boundary layer thermal conductivity
- ΔT = average boundary layer temperature gradient
- V = average effluent velocity
- μ = average viscosity of the heated gas
- L = particle heat content per unit volume at melting temperature
- d = average particle diameter

P = particle density

According to equation 1.1 there is a critical particle residence time and a critical particle size for which complete melting could be achieved. The residence time is determined mainly by gas velocity and spray distance.

1.3.3 GENERATION OF SPRAYED LAYER

The exiting stream of a thermal spray gun during spraying coating material reveals a conical shape. In the stream, the coating material particles remain concentrated in the central zone and are sparse in the outer portions (Figure 1.19) [34]. The particle in the outer periphery of the deposit are widely spaced and poorly adhered to the substrate. The spray deposit density ratio is largely dependent on the particles within the peripheral region. The final sprayed coating contains a mixture of material from each zone, because the gun and the substrate moves relative to each other during coating application.

During the spraying process, particles are heated and transported with different velocities and flatten on the substrate or on the previously deposited layers. The substrate surface or the previously deposited layer influences the formation of metastable phase in the fluid particle, resulting from rapid solidification of the molten particles. As the freezing time of a particle is about 0.1-1 μ second it does not influence the heat transfer of the next particle arriving at the same point [35,36]. Because of the high kinetic energy of the molten particles considerable liquid flow and radial sliding occur upon particle impact. This spreading depends on substrate surface topography and on the surface tension of the liquid particles. In the Figure 1.20 [14] a schematic of the planar morphology of a solidifying particle is shown. From the central zone where the particle first comes into contact with the substrate, heat is extracted through the substrate and the solid-liquid interface moves away from the substrate and a thin extended area with a peripheral rim is formed. This thin region may not be in full contact with the substrate.

The particle solidifies and cools at the same time. All the particles have the same mean direction when arriving at the substrate. Consequently a shadow effect occurs, causing porosity (Figure 1.21). The molten particles could cover up certain amount of irregularities of the surface. Narrow holes can not be filled up. The valleys in the surface of a substrate or the lamellae can include some air or gas which causes pores and adherence failure. With the increase of velocity and momentum of the impacting particles this problem could be reduced. During impact and flattening process the particle may burst. This phenomenon is governed by the mechanics of the impact, the energy of the particles and the movement of the fluid still present in the particle.

The proper splash or wetting of the particle depends on the proper stand off distance. When the standoff distance is too short the particle does not become completely molten and the solid centre core can rebound away from the surface resulting in a void. If the standoff distance is too long the molten particle may solidify before the impact and may rebound or stick to the surface resulting in less deposition efficiency or higher porosity. The extent of flattening depends on factors such as degree of melting, viscosity of the liquid and wetting of the surface. Coating may contain voids arising from outgassing, shrinkage or topographical effects (e.g. shadowing) and if it is a metal processed in air would probably include oxide.

1.3.4 PROPERTIES OF THERMAL SPRAYED COATINGS

(i) MICROSTRUCTURE OF THE THERMAL SPRAYED COATINGS

A thermal sprayed coating applied in an air environment is a heterogeneous mixture of sprayed material, oxide inclusion and porosity [3,9]. During the flight the particles interact in some way chemically and physically with the environment. A thermal spray coating consists of lenticular splats whose boundaries are parallel to the substrate surface (Fig 1.21). This structure is due to the impact of the molten or semi-molten powder particles. As a result of rapid cooling, some coatings may have no crystalline structure, and some have a thin amorphous layer next to the substrate followed by crystalline structure. Thick sprayed deposits reveal directionally oriented columnar grains near the interface where rapid cooling occurs through the substrate. The columnar orientation gradually decreases as the thickness of the coating increases. The change from columnar to random grain morphology is believed to be produced by the effective lowering of the

cooling rate, because of the generation of heat of fusion, which gives time to reform and change structure [13]. Radially elongated grains are rarely observed in thick coatings. This is due to the high thermal conductivity of metals. Thin regions under the impact of the subsequently arriving molten droplets probably recrystallize into randomly oriented grains [14]. Another feature of the rapid solidification in thermal spraying is the formation of structural defects such as vacancy, coagulation and dislocation. However the structure depends heavily on quench rate.

(ii) COMPOSITION OF THERMAL SPRAYED COATINGS

The composition of the coatings may vary from the composition of the sprayed material in thermal spraying due to the reaction of the molten particle with the gaseous environment. Particularly the extent of their oxidation is very important to the properties of the coating. In a study of the effect of oxidation on aluminium and bronze, it was found that even minor oxidation during deposition is detrimental to compressive strength both parallel and perpendicular to the surface. However discrete oxide particles on the other hand not only strengthen the coating but also add wear resistance [37].

The loss of carbon from tungsten carbide coating through oxidation has been reported [38-41]. Metallic or cermet coating may also react with air forming oxide scales on the particle and dissolving the gases in the molten droplet. The extent of these reactions varies with the process parameters. As a result of rapid quenching a nonequilibrium phase may be present. In alumina coating, slightly superheated particle on impact on high thermal conductive substrate gives delta and theta phase in addition to gamma with alpha suppressed. Due to super heating selective evaporation of one component in an alloy or decomposition to a gas or reaction with the atmosphere may happen. The loss of compounds will be more rapid in case of a fine powder than a coarse powder. In thermal spraying, residual stress develops as a result of cooling of individual powder particles on splat from above their melting point to the room temperature. The total stress is composed of a thermal stress and an intrinsic stress. The magnitude of the thermal stress is a function of spray gun parameters, deposition rate, the thermal properties of both the coating and substrate materials and the amount of auxiliary cooling used [42-44]. The intrinsic stress arises from the accumulation of splats of the molten particles and inclusion of impurities in the deposited coating. Use of finer powder also leads to higher residual stress [13]. In thick sprayed coating residual stress increases linearly with coating thickness after some critical thickness [14]. Residual stress causes the interface to experience shearing stress which can cause cracking and spalling (Figure 1.22).

Normally coatings suffer tension as a result of residual stress [22,45]. Methods which reduce tensile stress in the coating and hence reduce shear stress at the interface are a) expanding the substrate before spraying by preheating, b) selecting a coating material with low shrinkage properties and c) building up part way with a low shrinkage material [9,13,14].

(iv) BOND STRENGTH

Adhesion and cohesion are of paramount importance for spray coating. The mechanism of bonding of thermally sprayed coating in many respects is still not well defined [46]. The mechanical interlocking has been considered the most important mechanism by many investigators [47]. The main conditions for physical adherence are an intensive and permanent contact and a decrease in the Gibbs free energy of the system consisting of the substrate and the lamellae. To ensure an intensive contact the surface has to be clean and moreover approach each other to within the field of attraction of the atoms of the surface i.e within 5 Å. The approach of two very clean surface without any mechanical stress to within the field of attraction of the atoms decreases the Gibbs free energy and thereby enhances adhesion. In principle the total decrease of the Gibbs free

energy as contact occurs, is given by [36]

$$\Delta G = \Delta G_{surf} - T_{cont} \Delta S_s + \Delta H_s$$
(1.2)

where,

 Δ G _{suf} represents the decrease of the Gibbs free surface energy due to the reduction of the state of energy of the atoms of the surface by means of the total or partial recovery of the free bonds of the surfaces atoms.

The term ΔS_s represents the production of entropy in the contacts as a consequence of the diffusion of atoms in the surface zone.

The enthalpy of solution ΔH_s is the change of the minimum of the potential curve because of solution of a particular material's atom in a lattice of other atoms, when both of these materials are coming in contact.

In short, in a contact interface the tendency toward adhesion is raised as ΔG becomes more negative i.e

- 1) if ΔG_{surf} has a more negative value when both contacting surface are cleaner;
- 2) if the contact temperature has a higher value. In that case T $_{cont}$ ΔS_s has a more negative value;
- 3) if atoms of both materials making contact form a state of ordering or an intermetallic compound. In that case ΔH_s has a more negative value.

Other mechanisms have been suggested as contributing to the bond strength which include inter-diffusion or alloying, epitaxy, partial welding and chemical absorption. Chemical absorption occurs when there is great affinity of the sprayed metal to the base material. The mechanism is one of exchange of electron valency. Epitaxy means a controlled and similar growth on the basic structure of a foreign substance which is similar in structure. The super active state of the highly energized area of the surfaces aids the development of epitaxial layers. There are some microstructural evidences that when the refractory metal is sprayed on steel or nickel or chromium on aluminium, there is some inter-diffusion i.e a metallurgical bond is formed [47]. Partial welding between particles is always found in the transition zone as well as in the sprayed layers themselves. Oxide cementing was cited as important in bonding metals or cermets to metals [30]. In general oxides on the surface of the substrate or oxidation that occurs during spraying decrease bond strength.

(v) HARDNESS

Thermal sprayed coatings possess a heterogenous structure consisting of the coating material, oxide and voids. As a result the macrohardness values are less than those of equivalent material in either a cast or a wrought form. Hardness is usually less for a given material if the coating is applied in an inert atmosphere as compared to spraying in air [48,49]. Although oxidation may increase the hardness of the coating, it reduces internal strength of the coating and thus may be detrimental to the coating performance. Hardness in thermal sprayed coating is normally measured on a test specimen which may differ from those on actual parts due to difference in angle of deposition and stand off distance and in some cases due to difference in residual stress.

(vi) ANISOTROPY IN THERMAL SPRAY COATINGS

Succeeding particles in thermal spraying acquire the same lenticular shape over the material already deposited. As a result the coating develops an anisotropic lamellar structure parallel to the interface. The mechanical as well as other properties of thermal sprayed coating are anisotropic for its structure and directional solidification. This anisotropy is probably more pronounced for cermets and metallic coating [50].

(vii) OTHER EFFECTS

The mechanical properties of thermal sprayed coatings are sensitive to the deposition parameters used. As such any general tabulation of properties would be misleading [13,14]. The ductility of metallic thermal spray coating is slightly better than cast iron but less than most cast metals. The ductility of sprayed coating rarely exceeds 2 % [15]. Surface finish of a coated surface is extremely important. The smooth finish that can be obtained on a given coating is a function of its composition and the method of deposition. Normally most of the coatings deposited by thermal spray need surface finishing.

Corrosion resistance of a deposited coating is different than its cast or sintered composition. For example alpha alumina is very corrosive resistant, but when it is sprayed, alumina is a mixture of phases all of which are not corrosive resistance [45]. Most thermal sprayed coating have varying degrees of inter connected porosity that allow attack of the substrate in corrosive environments. Galvanic corrosion can occur in some environments when improper selection of coating composition is made.

1.3.5 TYPES OF THERMAL SPRAYING

Thermal spraying can be of different types depending on the type of heat source it uses. When thermal energy of oxygen-fuel is used by a thermal spraying process, the process is known as thermal flame spraying. When thermal energy generated from electricity is utilised then the process is called as arc spraying and in plasma thermal spraying process the thermal energy generated from electricity combined with a gas injection is used.

(i) PLASMA SPRAYING PROCESS

In plasma spraying the thermal energy of an electric arc and its associated plasma is utilised for melting and projecting the coating materials [9,12,13,14]. Figure 1.23 shows a plasma spray system which consists of a circular orifice anode and an inner cathode enclosed in a chamber and positioned in line with the nozzle. The gas flow in the region

of the arc column is heated, expanded and accelerated during the production of plasma. Coating materials in powder form are introduced into the plasma, melted and propelled onto the workpiece. The heat content, temperature and the velocity of the plasma jet are controlled by the nozzle type, the arc current, the mixture ratio of gases and the gas flow rate. The high temperature of the plasma flame which can be upto 20,000 °C is enough to melt any material whether metal, alloy or ceramics. Standard plasma guns are rated up to 40 kW with powder particle velocity of about 120 to 400 m/s. The latest high energy guns are rated upto 80 kW to produce high kinetic energy by the high enthalpies. The average powder particle velocities can be over 600 m/s for the high power gun [51]. The adhesion of the plasma sprayed coating materials depends on the preparation of the substrate, the spraying distance, fluidity, momentum of the composition of the particle, the inclusion of contaminant during the flight and the spraying process.

For proper adhesion, cohesion and no vaporisation of the coating materials, dwell time of the coating material in the hot zone should be decreased, spraying distance relative to the length of the hot zone should be increased or enthalpy of the hot gas should be decreased. To maintain the above conditions a new plasma spraying process was designed which is the low pressure controlled atmosphere plasma spraying process also referred to as vacuum plasma spraying process [52-55]. Figure 1.24 shows a low pressure and controlled atmosphere plasma spraying system. In this process the plasma gun and the work piece are enclosed in a vacuum tank. This increases the velocity and length of plasma jet and decreases the power density. All operations (pretreatment, spraying, post heat treatment if required) are carried out in an inert low pressure (typically 7 kp or 50 torr) atmosphere. This development permits the application of complex coating system with proper stoichiometry and structure, high coating adhesion and low porosity [56-58].

Plasma spraying is the most widely used thermal spraying process which can be used to spray all materials on almost all substrates and it is favourable for mass production. However, the deposition efficiency of plasma spraying process is lower than other thermal spraying process. The flexibility of this process in terms of spray distance and spray direction is less and the investment and the energy expense are high comparing with other thermal spraying processes [9].

(ii) ELECTRIC ARC THERMAL SPRAYING

In electric arc thermal spraying, an electric arc is struck between two converging wires close to their intersection point, as shown in Figure 1.25. The high temperature arc melts the wire electrodes which are formed into high-velocity molten particles by an atomizing gas flow. The wires are continuously fed to balance the loss. The molten particles are then deposited onto a substrate. By this process only relatively ductile and electrically conductive materials which can be drawn in the wire form can be deposited [9,14].

(iii) FLAME THERMAL SPRAYING

In the flame spraying process, fine powder or wire is carried in a gas stream and is passed through an intense combustion flame, where it melts. The gas stream, expanding rapidly because of the heating, sprays the molten powder onto the substrate, where it solidifies. A schematic diagram of a flame spraying gun is shown in the Figure 1.26. Flame spraying equipment is transportable for *in situ* work and is widely used by industries for the reclamation of worn or out-of-tolerance parts. However, coatings produced by the flame spraying process are relatively porous and have low adhesive bond strength [9]. The flame spraying processes are widely used for corrosion resistance and reclamation of worn or out of tolerance parts.

To improve the coating qualities of the flame spraying process a new spraying process was developed which is known as High Velocity Oxy- Fuel (HVOF) thermal spraying process. There are two types of HVOF processes, pulsed combustion HVOF process and continuous combustion HVOF process.

(iii)a Pulsed combustion HVOF (D-Gun) process

This process was developed by Union Carbide Corporation Limited during the middle of 1950's and is only available through their coating service department [59]. A schematic view of the detonation gun is shown in Figure 1.27. In this process oxygen and fuel gas with uniformly dispersed fine powder are repetitively injected into a shotgun-like barrel at a pressure of one atmosphere. A timed spark ignites the mixture and hence the pressure inside the barrel rises. Because of the geometry the flame front accelerates to a detonation wave which is supersonic. This detonation wave propagates and ignites the mixture so rapidly that the pressure in the barrel cannot be relieved because pressure is relieved at or below the speed of sound. Due to the detonation phenomenon a significant rise in pressure and temperature is observed. Figure 1.28 shows the variation of theoretical flame temperature and exhaust temperature with chamber pressure. The combustion gas instantly heats the particles to a molten state and hurls them at supersonic speed from the gun to the substrate surface. The velocity of the particle leaving the gun barrel varies as the pressure in the barrel decays. After the powder has exited the barrel, a pulse of Nitrogen gas purges the barrel. The cycle is repeated about 4 to 8 times per second. The quality of the coating sprayed by this process is superior to traditional flame spraying and plasma spraying processes. The better quality is mostly due to more kinetic energy of the powder particle [59-61].

(iii)b Continuous combustion HVOF process

A rapid development of HVOF system took place since the introduction of Jet-kote as the first continuous combustion HVOF system . This thermal spraying is the most significant development in the thermal spraying industries since the development of plasma spraying process. These systems evolved during the last nine years. The advanced HVOF systems are now challenging the coating qualities of most successful coatings produced by detonation gun spraying process [62-69]. There are different types of continuous combustion HVOF system developed by different manufacturers, namely Jet Kote, Diamond Jet, CDS Gun. The schematic diagrams of these HVOF thermal spraying processes are given in Figures 1.29-1.31 respectively. The working principles of these spraying systems are more or less the same [70]. The gun consists of three sections, mixing zone, combustion zone and the nozzle. During operation the body is cooled by air or by water. The fuel and oxygen are mixed by means of co-axial jets and guided to the combustion zone where a pilot flame or external igniter initiates the combustion. During the combustion the gas is allowed to expand in the nozzle where it is accelerated. The powder is accelerated by the carrier gas and injected into the flame. The powder has the same direction of flow as the direction of surrounding expanded gas. As the combustion continues, the gas achieves supersonic velocity. On the way from the combustion zone through the nozzle the powder particles are heated and are further accelerated. Due to the high velocity and high impact the coating is less porous, highly dense and has higher bond strength [71-78].

Combustion and gas dynamics of HVOF systems

Oxygen and fuel gas at high pressure are mixed in the mixing zone of the gun and then directed towards the combustion zone. After ignition a chemical reaction takes place and releases heat energy from combustion process. As combustion continues the pressure inside the combustion chamber increases and the hot gas flows with high velocity. Propylene, propane or acetylene and oxygen are used for combustion. The simple chemical reaction of the gases at stoichiometry in terms of mass is as follows [79].

$$C_{3}H_{6} + 3.43 O_{2} + X N_{2} = 1.29 H_{2}O + 3.14 CO_{2} + X N_{2}$$

The stoichiometric oxygen fuel ratio is 4.5 to 1. The energy released by the chemical reaction of the combustible gases is used to heat and accelerate both the emerging gases and the entrained powder. The gas velocity is a function of variables such as gas composition, pressure, temperature, density and the area through which the gas travels. However, the maximum obtainable gas velocity through the minimum cross sectional area is limited to the local sound velocity [79].

The local velocity of sound in a perfect gas is defined by:

$$C = \sqrt{K R T} \tag{1.3}$$

where,

C = the sound velocity.

K = ratio of specific heats

R = gas constant

T = local temperature

The condition in which the gas velocity is equal to the sonic velocity is called the critical state. At critical state a nozzle can discharge the maximum mass flow rate say m. The critical mass flow rate can be defined as:

$$m = \rho V A \tag{1.4}$$

where,

 ρ = critical density V = critical gas velocity A = critical area

This equation can be rewritten in terms of total pressure and total temperature as:

$$m = \left[\frac{K}{R} \left(\frac{2}{(K+1)}\right)^{\frac{(K+1)}{(K-1)}}\right]^{\frac{1}{2}} \frac{P_0 A}{T_0^{\frac{1}{2}}}$$
(1.5)

where,

 $P_0 = total pressure at critical state$

 T_0 = total temperature at critical state

When the critical flow condition is reached, the flow is said to be choked. From these equations it can be seen that by increasing the pressure the mass flow rate increases and by increasing the temperature the mass flow decreases. Figure 1.32 shows the variation of gas velocity with the chamber pressure. The chamber is maintained at a certain pressure which differs for different design of the HVOF system.

The combustion gases are expanded in a converging diverging nozzle to achieve supersonic speed. The adiabatic flame temperature of the stoichiometric combustion gases is about 2900 °C (assuming propylene as fuel gas). Flame and jet temperature also vary with oxygen/fuel ratio as shown in Figure 1.33. Within the HVOF device, both heat addition due to combustion and friction along the nozzle surface tend to choke the flow at the nozzle exit. As the combustion products exit the nozzle, the jet expands because the static pressure in the nozzle is greater than the ambient pressure and expansion and compression waves occur in the free jet (Figure 1.34). The intersections of these waves form the bright regions in the effluent stream are commonly known as shock diamonds [59,80-82].

Figure 1.35 shows the temperature, pressure and velocity variation in the flow with oblique shocks. The cyclic change of the flow will extend to infinity in the absence of friction and air entrainment. In fact the oblique shock pattern reduces in the diameter and continues only until enough out side air is entering into the jet to substantially reduce the temperature and velocity.

Effect on particles

During combustion, powder particles are injected in to the centre of the combustion chamber with a carrier gas. Other designs of HVOF are also available in which powder particles are injected radially into the gas stream at the converging diverging throat area of the nozzle. This powder is turbulently mixed and accelerated to high speed and heated within the hot gases. The gas-powder mixture leaves the barrel as a high velocity jet and is pointed towards the surface to be coated. Since the particles are injected into the supersonic flow, each particle will pass through the shock waves. From the measurement of velocity of powder particles of different size and different materials (Figure 1.36) it is evident that the particle velocities are highest on the central axis and decrease radially outward. This is caused by the viscous shear forces acting between the jet and the ambient air. The particles decelerate due to the viscous shear effects and exhibit slower velocities near the outer boundary of the flame than near centre of the flame. The centreline mean velocity measurements of 5 µm alumina and 11-45 µm WC/Co are shown in Figure 1.37 and 1.38 respectively. As the alumina particles exit the nozzle, they rapidly accelerate until approaching the average gas velocity which occurs approximately 5 cm away from the nozzle exit and then the particles decelerate as the average gas velocity decreases. The WC/Co particles of larger size do not attain gas velocities at the nozzle exit. As the particles exit the nozzle they accelerate until they achieve the local average gas velocity which occurs near 15 cm away from the nozzle exit.

As no exact heat transfer correlation to calculate the temperature of the particles exposed to supersonic flow was available, the temperature of the particle leaving the barrel were calculated (Figure 1.39) assuming some of the parameters as it varies with so many factors [59].

Design to increase the velocity of the flame

The basic requirement of an HVOF system is to burn fuel and oxidant in an enclosed volume or chamber and build up a pressure so that the gases expand through an orifice as they exhaust and accelerate to the atmosphere. A number of burner designs can be used to accomplish this. These designs can be classified in to two groups, viz. throat combustion burners and chamber burners [59].

In throat combustion burner (Figure 1.40) the fuel and oxidant are mixed and injected at a pressure into a combustion region. A higher pressure is maintained at the back of the burner. Powder is injected axially and the flow stream and the particles accelerate in normal HVOF fashion. Compressed air is used for cooling internally and externally. A guided flow of air between the chamber walls and the flame contains and constricts the flow and reduces wall heating. This design increases air dilution of the combustion stream and reduces the flame temperature and therefore is not suitable with long barrel spray gun. Advantages of the design are its simplicity, less weight and the possibility of manual operation.

Different types of chamber burners are evolved. These are right angle/central injection, straight through/axial injection and straight through/radial injection (Figure 1.40). These systems are water cooled and machine mounted. The incorporation of a longer barrel makes it possible to have a longer high temperature zone.

Advantages and disadvantages of HVOF systems

Particle velocity is a critical factor in all thermal spraying processes. Quality of the coating improves with the velocity of the sprayed particle as shown in Figure 1.41. HVOF guns can produce particle velocities that are considerably higher than the other currently available commercial thermal spray processes. Additional benefits of HVOF processes are as follows.

- (a) More favourable environment due to less oxidizing atmosphere.
- (b) More uniform and efficient particle heating due to high turbulence.
- (c) Much shorter exposure time in flight due to high particle velocity.
- (d) Reduced mixing with ambient air once jet and particle leave the gun.
- (f) lower ultimate particle temperatures compared to plasma or arc guns.

For the above mentioned advantages, the coating benefits are higher density, improved corrosion resistance, higher hardness, better wear resistance, higher bond and cohesive strengths, lower oxide content, fewer unmelted particle content, better chemistry and phase retention, thicker coating and smoother as-sprayed surfaces.

The main disadvantages are:

(1) The heat content in the HVOF stream is very high. Therefore over heating of the substrates are quite likely. Therefore extra cooling of the substrate is necessary.

(2) Masking of the part is still a great problem as only mechanical masking is effective [83].

1.4 SPRAY FORMING

1.4.1 INTRODUCTION

The earliest concept of spray forming process was described by Brennan in 1958 [82] for the production of strip but was never used in practice. Since 1960 spray forming has been used for fabricating components. The principal developer of the spray forming process is Singer [85,86]. He developed a variant forming process applied to strip. Spray forming is a logical development of the atomization process for the generation of powder having a consistent and well defined size [1,2,87]. Following this early development the preform process has been applied to the preparation of a variety of near-net shapes. A schematic of this process is shown in Figure 1.42. Materials to be spray formed are heated to their melting temperature and atomized by spray nozzle. These atomized particles impinge on the flat bed substrate and solidify as individual particle in intimate contact with the neighbours. The atomized droplets are partially cooled in flight, depositing on the substrate surface and freezing progressively to form sheet, strip or thicker section deposits. Different treatment such as hot rolling, hipping or any other methods may be used to improve the bonding of the particle [86,90,91].

The main objectives of spray forming were to reduce the steps for production of engineering products at lower cost and eliminate or reduce substantially the contamination and to improve the quality of the products. Another benefit of spray forming is the significant reduction in the as-cast grain size. This grain refinement is desirable for improvement of both the strength and the fracture toughness. The combination of under cooling and high solidification rate provides a basis for obtaining unique properties in conventional or specific composition. These are distinct advantages for a number of aerospace structural applications.

Since the spray forming produces a near net shape, very little machining is necessary. The mandrel can be reused for many times so the cost of mandrel is insignificant in the overall cost. The major expenditure is involved in installing and operating the equipment. For these reasons spray forming is rapidly gaining much attention world wide.

1.4.2 TYPES OF SPRAY FORMING

Spray forming is one of the several forming processes applied for the production of engineering components. There may be two different ways of spray forming.

Firstly, the common type of spray deposition involves the feeding of material in the form of wire or powder into a gun where it is heated to its melting or softening temperature and breaks up into a stream of spray droplets and allowed to deposit on to the preforms. This process is known as thermal spraying. Heat needed for melting the material can be generated from electrical resistance, radiative heat from plasma or from combustion of fuel and oxygen. By this method a small quantity of the material can be heated uniformly, thus the deposition rate is low [84].

Secondly, the entire amount of materials to be spray formed is heated above the melting temperature before the atomization process is performed. This process allows high deposition rate and the ability to achieve a dynamic heat balance. This process is commercially known as Osprey forming [84,85].

(i) THERMAL SPRAY FORMING

Thermal spraying is one of the numerous well known coating processes. If a coating can be removed without unacceptable damage or distortion from the substrate, the discrete free-standing body remains which reproduces the shape of the surface of the substrate. To be of practical value the coating process should be rapid, giving a coating of acceptable thickness and strength, be applicable to a variety of coating and substrate materials and yield components that need little post fabrication treatment.

Traditionally, the flame spraying process lacked sufficient thermal and kinetic energy to yield highly densed coating for various materials particularly for refractory and ceramic materials. Plasma spraying, however, does not suffer from such limitations. So this process has been used for a long time for the production of free standing objects [92]. But the porosity level of these components produced by air plasma spraying is high (5-16 %) and often it is contaminated by the oxide. So vacuum plasma and controlled atmosphere plasma spraying have earned much more attention among the researchers [92-99]. Equally components can be built up with different materials at different layer or as composite. New developments in thermal spraying technology offer exciting possibility for extending the potential of spray forming.

(ii) OSPREY FORMING

In the osprey process as shown in Figure 1.43 a material is melted and subjected to gas atomization under inert conditions. Nitrogen and argon gases are commonly used for production of inert atmosphere. The atomized droplets are collected in a mould or group of moulds in which final solidification occurs. A key part of this process is the achievement of partial solidification before impingement. The liquid droplet size, the droplet velocity, metal flow rate, gas-to-metal flow rate ratio and flight distance are carefully controlled to achieve certain degree of under cooling of the liquid. Upon impingement on the deposition surface, the viscous semisolid droplets spread laterally by a rather high velocity shearing process. This shearing process breaks up any dendrites formed in the droplets before impact and thereby supplying many new nucleation spots in the under cooled liquid. Ideally the material then solidifies at a high velocity by heterogeneous nucleation followed by formation of equiaxed grains. This spray forming can achieve quite high deposition rates of 15 and 100 kg/min for aluminium and steel respectively [100,101].

Osprey forming of thick section of stainless steel followed by hipping and heat treatment results in an excellent combination of properties. These properties are isotropic due to preservation of hipping of the equiaxed as-cast grain structure. The tensile strength, ductility and toughness of the spray formed and hipped material appear to be as good or better than those of high strength aluminium alloy cast strip. Alloys that have been processed by the osprey process include stainless steels, high speed steels, nickel based superalloys.

Experiments to co-spray aluminium atomized droplets with SiC particles to form an in situ metal matrix composite were reported [84]. A schematic of the co-spray nozzle configuration is shown in Figure 1.44.

1.5 BACKGROUND OF THIS WORK

1.5.1 PRESENT METHODS OF FABRICATING CARBIDE COMPONENTS

Cemented carbides belong to a class of hard, wear-resistant refractory materials in which the hard carbide particles are bonded together or cemented by a soft and ductile metal binder. Although the term cemented carbide is widely used in the United States, these materials are better known as hard materials internationally. Among these hard materials WC is the most popular.

WC was first synthesized by the French chemist Henri Moissan in the 1890's. The first cemented carbide produced was tungsten carbide with a cobalt binder. The use of powder metallurgy techniques by Schrocter in 1923 provided the way for obtaining a fully consolidated product [102].

Nowadays cemented carbides are manufactured by a powder metallurgy process consisting of a sequence of steps. Finely divided WC particles are mixed with metallic binder by intensive milling so that every carbide particle is coated with binder materials. Then this powder is used to make the component by compacting, sintering and post sintering operations.

Unlike most metal powders, cemented carbide powders do not deform during the compacting process. Generally they can not be compressed to much above 65 % of the theoretical upper limit of density. Despite this low green density, carbide manufacturers have developed the technology to achieving good dimensional tolerances in the sintered products. These compacted components are sintered in vacuum in hydrogen atmosphere. During the final sintering operation, cobalt melts and draws the carbide particle together. Shrinkage of the compact ranges from 17-25 % on a linear scale. Hot isostatic pressing (HIP) technology provides a new technique to sinter carbide component without residual internal porosity, pits and flaws.

A large number of cemented carbide products are shaped after sintering, because of surface finishing, tolerance and geometry requirements. The forming operation is both time consuming and expensive. Sintered material is formed with metal bonded diamond or silicon carbide wheels, turned with a single point diamond tool or lapped with slurries containing diamond powder.

1.5.2 FACTORS EFFECTING THE PROPERTIES OF CEMENTED CARBIDE

Three possible variables affect the mechanical properties of WC-Co composites. These are carbon content, cobalt content and the grain size. Less amount of carbon helps the formation of brittle lower carbides. Impact strength or shock resistance is a function of cobalt binder content and tungsten carbide grain size. Higher cobalt levels and larger tungsten carbide grain size increase impact strength. In corrosion attacks of cemented carbides, the WC component is not usually affected. However, the binder metal corrodes and to increase corrosion resistance lesser binder metal and finer tungsten carbide grain size are needed. Nickel binder grades exhibit higher corrosion resistance.
1.5.3 AREAS OF APPLICATIONS

Apart from cutting tools, there are many applications for cemented carbides. These may be generally categorized as wear parts. Properties which are paramount for wear part application include abrasion resistance, impact strength and corrosion resistance. Some typical examples of application of carbide components are given in Table 1.6.

1.5.4 OBJECTIVES OF THIS STUDY

It is quite clear that spray forming may be an alternative forming process for the production of engineering components. The scope of thermal spraying as a tool of production has not been considered until very recently. Some researchers are using vacuum plasma spraying for spray forming. Recently developed HVOF thermal spraying process has the potentiality to be used for the production of engineering components, particularly with those materials which are difficult to process such as carbide and ceramics.

The production cost of carbide components, particularly for low stress application, is the main item that limits its application. For the lack of machining facility thicker carbide component has to be made and used where a thin component might serve the purpose due to its high hardness and wear resistance properties. Thin carbide components can be used as inserts to improve the wear properties of internal surface of holes and cylinders which can not be coated by this traditional coating process.

In the present research HVOF thermal spraying process for developing freestanding engineering components has been studied with a view to:

- 1) Verifying the feasibility of using the HVOF thermal spraying process as a production process of engineering components especially thin-walled ones.
- 2) Spray forming components of different shapes and sizes, and of different materials which includes Nickel base alloy, Stainless steel and Tungsten carbide-cobalt.

- Standardizing the spray forming process for the production of carbide components and determination the process variables which have an effect on the production of these components.
- 4) Characterising the properties of the components made by this process.
- 5) Making components by multi-layers of different material to increase the toughness of carbide components and to facilitate the fixation of carbide components with other components.
- Measuring the stresses in the component formed by this process and finding a way of producing stress-free components.



Figure 1.1 Various surface properties relevant to engineering components (9).



Figure 1.2 Schematic representation of a metal surface (9).



Figure 1.3 Surface asperities of a nominal smooth surface (9).



Figure 1.4 The three components of surface profile (9).



Figure 1.5 Schematic diagrams of various surface interactions (9).

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ploughing of softer surface by an asperity of harder surface



ploughing by foreign particle entrapped between moving surface

Figure 1.6 Schematic diagrams of ploughing of softer surface (9).







Figure 1.8 Schematic of adhesive wear mechanism (9).







Figure 1.10 Typical events in erosive wear.



Figure 1.11 Schematic illustration of the diffused coating and overlay coating.



Figure 1.12 Interrelated properties of coating substrate system.



Figure 1.13 The inter-relationship of coating, substrate, process and application.



Figure 1.14 Classification of various coating techniques.



Figure 1.15 Schematic of vacuum evaporation process (13).



Figure 1.16 Schematic of a glow discharge sputtering coating system (9).



Figure 1.17 Schematic of conventional CVD system (9).







Figure 1.19 Schematic of spray pattern of thermal spray system.



Figure 1.20 Schematic of the deposition of particle and the planar morphology of a solidified particle.

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Figure 1.21 Lamellar structure of a thermal sprayed coating showing the voids and pores (14).



Figure 1.22 Schematic of cracking and spalling of thermal spray coating due to residual stress.



Figure 1.23 Schematic of plasma spray gun (9)



Figure 1.24 Schematic of a low pressure and controlled atmosphere plasma spraying system (14).



Figure 1.25 Schematic of electric arc spray gun (14).



Figure 1.26 Schematic of flame spray gun (14).



Figure 1.27 Schematic of detonation-gun spray process (14).

STOICHIOMETRIC RATIO - HEPTANE/OXYGEN



Figure 1.28 Variation of theoretical flame temperature and exhaust temperature with chamber pressure [59].







Figure 1.30 Schematic of diamond jet HVOF thermal spraying gun (68).

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Figure 1.31 Schematic of CDS HVOF thermal spraying gun (78).



Figure 1.32 Gas velocity in HVOF system vs gun chamber pressure [59].



Figure 1.33 Variation of theoretical flame temperature with oxygen/fuel ratio [59].



Figure 1.34 Shock formation of an under expanded jet [59].



Figure 1.35 Variation of Mach number, temperature and pressure in a typical HVOF gas stream [59].



Figure 1.36 Laser Velocimeter 2-D particle velocity distribution [79].







Figure 1.38 Centreline WC/12%Co particle distribution measured by Laser Velocimeter [79].



Figure 1.39 Projected gas and particle temperature for 6 inch barrel [59].



WATER COOLED



THROAT COMBUSTION BURNER



CHAMBER COMBUSTION BURNER

Figure 1.40 Different design of combustion chamber of HVOF systems [59].



Figure 1.41 Graphical illustration showing the improvement of quality of coating with velocity [59].



Figure 1.42 Schematic diagram of a spray forming process [84].



Figure 1.43 Schematic of an Osprey forming system [102].



Figure 1.44 Schematic of a spray forming system with co-spray nozzle [84].

Deposition technique	Types of coating materials	Types of substrate	Kinetic energy (eV)	Deposition temperature ^o C	Coating thickness (um)	Relative adhesion
Direct evaporation	Any pure metal, many alloy and compound	Any nongassing materials	0.1-1	200-1600	0.1-1000	Fair at high temperature
Activated reactive evaporation	Almost any	Any nongassing materials	5-20	200-1600	0.1-1000	Fair to good at high temperature
Glow discharge ion plating	Almost any	Substrate must withstand bombardment heating	10-100	100-300	0.02-10	Generally good
Ion beam plating	Almost any	Substrate must withstand bombardment heating	100-10,000	100-500	0.02-10	Excellent
Glow discharge sputtering	Essentially any	Any nongassing materials	10-100	100-300	0.02-10	Generally good
Ion beam sputtering	Almost any	Any nongassing materials	100-110,000	100-500	0.02-0.5	Good to excellent
Chemical vapour deposition (CVD)	Essentially any	Any that can withstand deposition temperature and chemical attack	0.1-1	150-2200	0.5-1000	Excellent
Plasma enhanced chemical vapour deposition (PECVD)	Essentially any, Diamond, Polymers	Any nongassing materials that can withstand deposition temperature	10-500	100-500	0.1-2	Good to excellent

Table 1.1 Process parameters of various vapour deposition techniques.

Deposition technique	Deposition pressure (Pa)	Typical vapour source(s)	Comments
DC/RF diode	5 X 10 ⁻¹ -10	Resistive,rf induction, electron beam heating.	Simple, thickness uniformity over a large area, but relatively high deposition pressure.
Triode	10 ⁻³ -10 ⁻¹	Resistive,rf induction, electron beam heating.	Low deposition pressure, relatively high deposition rates system more complex, does not produce produce uniform coating over large surface areas.
Alternating	5X10 ⁻¹ -10	Resistive,rf induction, electron beam heating.	Vapour source and ionization arrangement can be optimized separately, but relative motion of substrate needed.
Hollow cathode discharge	10-2-10-1	HCD electron- beam heating.	Relatively low deposition pressure and high deposition rates, but system more complex.
Cathodic arc	10 ⁻³ -10 ⁻¹	Cathodic arc heating.	Low deposition pressure, very high plasma density can be achieved, very high deposition rates but system more complex.

Table 1.2 Some important characteristics of various Glow-discharge ion plating processes.

Deposition technique	Deposition pressure Pa	Deposition temperature ° C	Comments	
DC/RF diode	5 X 10 ⁻¹ -10	100-300	Simple, relatively ease in fabrication and thickness uniformity over large area but relatively high deposition pressure and relatively high substrate temperature.	
Triode	10 ⁻³ -10 ⁻¹	100-150	Low deposition pressure, relatively high deposition rates and low substrate temperature. However, more complex, does not produce produce uniform coating over large surface areas, difficulty of scaling, emitter to reactive gases.	
Magnetron	10 ⁻³ -10 ⁻¹	100-150	Low deposition pressure, very high deposition rates, low substrate temperature, can be scaled up and commonly used for industrial production. However, more complex than planar diode systems.	

Table 1.3 Some important characteristics of various Glow discharge sputtering processes.

Treatments	Treatment temp. ^o C	Case dept. micron	Advantages/ disadvantages	Applications
Induction	850-1100	250-5000	Fast, large case depth,high capital cost and cannot treat certain shapes.	Carns, rotating shafts, machine ways, swivel pins, steering joints, gears, valves and bearing surfaces.
Flame	750-1000	250-5000	Simple, cheap,flexible However, lack of process control.	Large sections, e.g., rolls, machine beds,dices, track rails.
Laser	1000-1300	1-100	Local heating allows shallow case depth for less component distortion can treat complex shapes.	Cylinder liners, gear, crankshafts.
Electron beam	1200-1300	1000-3000	Fast, large case depth, However, expensive.	Automobile transmission clutch cams.
Work hardening Metal working	20⁰C or low		A supplemental hardening process, Expensive and time consuming.	Wear plates earthmoving equipment, chute liners, piston bars.
Shot peening	100°C or lower	100-500	A supplemental hardening process, Time consuming.	Large ring gear,shaft, structural component of aircraft.

Table 1.4 Process parameters, properties and applications of heat treatment processes.

Treatments	Diffusion element	Treatment temperature (⁰C)	Case depth (µm)	Advantage/Disadvantage	Application
Carburizing	С	800-950	50-6000	Cheap, higher case depth possible treatment causes component distortion	Cams and camshaft, rockers, rocker shaft, bushes and transmission gear
Carbonitriding	C,N	800-870	25-500	Less distortion than carburizing, wear resistance and corrosion resistance better than carburizing, slower rate of case formation	Bearing cages, gears, air compressor, cylinders, camshafts.
Nitriding	Ν	500-590	5-250	High hardness, distortion reduced due to low process temperature and lack of quenching, however, long processing time required.	Crank and camshafts, transmission parts, bushes, rotating parts, high speed cutters
Nitro-carburizin	g N,C	570	5-250	Lower hardness but better wear resistance	Extrusion and die casting dies, gear, pumps, cylinder liners, crankshafts.
Boriding	В	900-1100	5-250	Highest hardness of any surface treatment process	For extreme abrasive wear and for tribo-oxidation. For tools, draw punch taps, forming dies, wear plates.
Chromizing	Cr	950-1300	100-200	Not brittle, good oxidation resistance, steel can be later heat treated.	Steam power equipments, water and steam fixtures, valves, connectors pipes.
Aluminizing	Al	750-1000	200-500	Resistance to corrosion and oxidation at high temperature.	Aircraft gas turbine blades, pyrometer protection tubes, flue stacks, boiler tubing.
Siliconizing	Si	950-1200	500-1250	Improves wear resistance, but main purpose is corrosion and oxidation resistance. Steel can be heat treated afterward.	Pump shafts, pipeline, fitting nuts, bolts, rollers for bottle washing machine.
Sherardizing	Zn	350-450	•	Low temperature process impart resistance to wear and corrosion.	Threaded parts, e.g. bolts, washers, nuts, scaffolds clips.

Table 1.5 Process parameters, properties and applications of chemical diffusion surface modification processes.

Table 1.6 Typical applications of carbide components.

Type of applications	Areas of applications
Light impact, High abrasion resistance applications.	Blast nozzle, Guide rings, Bearing, Spray nozzle, Powder compacting dies, Valve stems, Plastic extrusion dies, Wear pads, Valve sets.
Medium impact, medium abrasion resistance application.	Aluminium extrusion dies.
Corrosion resistance application.	Seal rings, Nozzle, Ball valve, Metering chokes.
CHAPTER 2

EXPERIMENTAL EQUIPMENT

2.1 INTRODUCTION

To achieve the objectives of this investigation, a HVOF thermal spraying system was utilised. It consists of two systems viz. 1) the spraying system and 2) the support system. The spraying system alone can not be able to deposit coating until it is geared with some support facilities. Since this spray system is hazardous, for the safety of the equipment and the operators, a support system is essential.

Main items of the set-up were procured from commercial sources. However, some items were designed and manufactured at site conforming to the requirements of the procured items. The whole system was then installed and commissioned to facilitate carrying out of the investigation.

2.2 SPRAYING SYSTEM

This system mainly consists of the spraying equipment and its associated measurement and controlled units. Descriptions of these equipment and their working principles are presented in the following sub-sections.

2.2.1 SPRAYING EQUIPMENT

A HVOF thermal spraying equipment was installed. This is a manual control, continuous combustion, Diamond Jet thermal spraying equipment, manufactured by Metco Ltd. The objective of this equipment is to transfer both kinetic and thermal energy to the powder particle with a high degree of efficiency and balance. High velocity is generated by internal combustion of oxygen and propylene within a air cooled chamber. The equipment includes:

- (a) Diamond Jet Gun
- (b) Powder feed unit

- (c) Gas flow meter unit
- (d) Gas regulator and manifolds
- (e) Air control unit

(i) DIAMOND JET GUN

The picture of the Diamond jet gun is shown in Figure 2.1. Diamond jet is a commercial name. The gun is approximately 9 inches long, 9.5 inches high (including handle) and 5 inches wide. Its weight is approximately 5 pounds. The gun can be used in either hand held or machine mount configuration. It has fixtures for machine mount operation which permits mounting the gun on handling equipment or any other machine tools. The gun comprises of five main assemblies. These are front end, control handle, hose connection block, valve core and the main body (Figure 2.2).

The front end (Figure 2.3) consists of the air cap body, air cap, nozzle nut, nozzle assembly, siphon plug and powder injector. The control handle contains a push button on-off switch which controls the powder flow from the powder feed unit to the gun. However it can not turn off the gun. The hose connection block consists of the air, fuel and oxygen hose connections and gas tight plungers for making the connection leak proof and allowing the gases to be transferred into the valve core. The valve core shown in Figure 2.4 is a cylindrical part consisting of a series of passages and grooves and O-rings. This is housed within the gun body. A lever type handle is attached to the end of the valve core. Rotational movement of the valve core permits the flow of gases through the gun. For oxygen and propylene there are different sizes of hole in the valve core. To turn off the flame of the gun the valve handle must be rotated to the full up position. All these parts are attached with the gun body to work together to generate and control spray of molten or semi-molten metal powder with high kinetic and thermal energy.

The main function i.e generation of the spray with high kinetic and thermal energy, is performed by the gun front end assembly. The kinetic energy and thermal energy generated by the gun depend on the design parameters of these parts of the assembly and the flow rate and pressure of fuel gas, oxygen and air. Different material powder needs different kinetic and thermal energy and these variation are controlled by the different combination sets of these parameters. All these parts are replaceable and need to be changed for different type of material powder. For safe operation and maintenance the working principle of these parts are to be known. Therefore a detail description of this assembly is given below.

(i)a Front end assembly

This is the area where the fuel gas and oxygen are mixed and burned. The combustion product is also accelerated from here due to nozzle action. Powder particles are injected in the combustion zone during combustion. For the convenience of explaining the working method of this assembly, sectional views of the gun are shown in Figure 2.4 and 2.5.

The central part of this assembly is the siphon plug. In the Figure 2.4 different zone area of the siphon plug are shown. There are holes passing through the gun body to transfer gases to the siphon plug from the hoses. Holes for propylene and air run parallel to the gun body and holes for oxygen and nitrogen are obliquely placed through the gun body. Propylene gas comes to zone 3 of the siphon plug and oxygen comes to zone 2. Both the gases are mixed at zone 3 and the mixture passes through the hole of the insert to the tip of shell. At the tip of the shell and insert the combustion takes place (zone 5). The pressure at the combustion zone is about 35 psi [59]. Due to the high back pressure of all incoming gases the flame front moves outward and due to the nozzle action, the velocity of the combustion product increases upto 4500 feet/second [68]. The nozzle action is given by the internal surface profile of the air cap. With the change of the profile of the air cap the kinetic energy is changed. Nozzle nut is used to fix the shell and insert with the siphon plug. The proper tightening of the nozzle nut is important for proper working of the gun. Air cap, siphon plug, insert, shell and nozzle nut are fitted to the air cap body which is in turn fitted with the gun body.

Compressed air comes to zone 4 and from this zone it goes to the combustion

zone through the hole on the nozzle nut. Air is guided by the outer surface of the shell and the inner surface of the air cap such that it creates a layer of air over the inner surface of the air cap. Due to this air layer the air cap is thermally insulated from hot combustion product of the combustion zone. Powder injector, connected with the powder feed unit is fitted at the back of the siphon plug. The front end of the powder injector is extended up to the tip of the insert which helps to inject the powder at the very centre of the combustion stream.

For proper functioning and to avoid the danger of accident, the front end assembly must be installed correctly and tightened accurately. The different zones as mentioned earlier contain different type of gases at different pressure during the spraying operation. The pressure of the gases at different zones (Figure 2.4) are different. The pressure sealing is maintained only by the use of O-rings. So any leaking through the O-rings makes the system unbalanced and affects proper functioning of the gun and may cause serious damage to the system. During installation care should be taken so that the air cap, nozzle shell, nozzle insert, siphon plug and powder injector are of the correct type. The design of these parts vary with the type of fuel gas the system is using. According to the type of powder materials used the design of all these parts except the siphon plug varies. All these parts are to be fitted sequentially without using any tool and should be hand tightened. Only the nozzle nut is to be slightly tightened by using tools to avoid loosening during operation due to the rise of temperature. All O-rings should be lubricated by lubricating powder (graphite powder) and must be occasionally checked to ensure that they are in good condition.

(ii) POWDER FEED UNIT

The powder feed unit is a completely self contained unit, designed to deliver powder to the gun at a precise flow rate (Figure 2.6). This system is equipped with an integral powder feed rate meter, which continuously displays the spray rate.

The unit is a single hopper system comprised of a hopper assembly, control cabinet and control panel. Carrier gas flows to the gun via the hopper assembly and gas

flow meter. There is a pressure gauge in the line. With the help of the control knobs the pressure and flow of the carrier gas can be controlled. The hopper assembly comprises of a hopper, powder port shaft (pickup shaft), air vibrator and control valves (Figure 2.7). The powder port shaft is located in the throat of the hopper and at the mid span of this shaft there is a radial hole. The air vibrator is mounted in the base of the hopper. A load cell is used to weigh the hopper assembly. Control valves are used to control the carrier gas.

(ii)a Working principle of the powder feed unit

Powder kept in the hopper, drops into the powder port shaft due to gravity. By controlling the valves, carrier gas is allowed to pass through the powder port shaft. While passing through the shaft, carrier gas picks up the powder and inject it at the very centre of the combustion zone by powder injector. The amount of the powder flowing with the carrier is controlled by the amount of carrier flow, the hole size of the powder port shaft, the amplitude of the vibration of the air vibrator and the differential pressure between the hopper and the carrier flow line. The amplitude of the vibration can be controlled by increasing the flow of air into the air vibrator. With the increase of hopper pressure the flow of powder with the carrier gas will increase and this increased pressure is indicated on a dial of the powder feed unit. The fluidity of the powder is maintained by passing pressurised carrier gas through a filter placed at the entrance of the shaft hole. The vibration of the hopper and the gas pressure ensure a constant supply of powder at the vicinity of the hole opening.

The quantity of powder delivered from the hopper is determined by the rate at which the hopper loses weight. The load cell fixed with the hopper assembly continuously weight the hopper and this result is calculated against a certain period of time and displays the flow rate of powder in pounds per hour or grams per minute. Therefore, any change of flow rate of powder can not be detected instantly.

(iii) GAS FLOW METER UNIT

The gas flow meter unit shown in Figure 2.8 controls and monitors fuel gas, oxygen and air required by the gun. It consists of flow measuring glass tubes, close coupled pressure gauges and accurate flow adjustment valves. There is a float located within each flow measuring tapered glass tube, free to travel up and down. As the float rises flow area increases and as it descends flow area decreases. Gas flowing through the flowmeter causes the float to rise to a point of dynamic balance, which is a true indication of the flow. The use of the close coupled pressure gauges and the flow adjustment valves permits to maintain the accuracy of the gas flow as required.

To guard against any danger of backfire, flashback arrestor and check valves are installed in both oxygen and propylene line. Flash back arrestors are fixed at the outlet of the flow meter unit and designed to stop the flow of gas from the flowmeter to the gun in the event of sudden pressure rise in the hose line due to increase of temperature or hose fire. Check valves are also provided at the inlet of the gun body to prevent a back flow of gases.

(iv) GAS REGULATORS AND MANIFOLDS

The compressed gas cylinder used with Diamond jet system is equipped with pressure regulators with gauges to adjust the supply gas pressure of the gas cylinder to correct working pressures. These gas regulators consist of high pressure regulator and metallic tube manifolds which enable several gas cylinders to be connected together. Some of the manifolds are supplied with non-return valves.

(v) AIR CONTROL UNIT

This unit consists of a pressure regulator and two filters (Figure 2.9) The regulator provides a means for adjusting air pressure to the gun. It holds the required pressure constant regardless of fluctuation in the line pressure. One filter, ahead of the regulator is used to remove water, oil and pipe scale. The second filter is placed down stream to

trap additional oil and water which condense out as a result of pressure drop through the regulator. The filter bowls have sight glasses to show the level of trapped liquid and also have manual drain to permit removal of the liquid without shutting down the system.

Unregulated air line is provided at another outlet after filtering in the first filter. This air is controlled by a shut-off valve. From here air is supplied to the air vibrator of the powder feed unit through a "Y" connector. A regulator is provided to control the air pressure as required by the vibrator. Another line from the "Y" connector is kept free for any other use, if needed.

2.3 SUPPORT SYSTEM

The thermal spraying system needs some support facilities to make the process safe and workable. Clean substrate surface is of prime importance for good quality coating. For uniform coverage of coating on the substrate mechanical handling equipment for the substrate movement and for gun movement is necessary. All spray powders have some calorific value and some of them are hazardous. Safety for the operator is very important for this type of system. Therefore, for proper functioning and safety some support facilities were built up. These are electric supply and gases supply units, isolated room and spray booth, grit blasting equipments, mechanical handling units, exhaust system and furnace.

During the investigation of fabricating components it was observed that some parameters have very influential effect on the obtaining of the components. These parameters are temperature at different stages of the process and the coating thickness. Therefore for measuring these parameters some measuring instruments were also installed. These measuring equipment are also included with this support system.

2.3.1 ELECTRIC SUPPLY AND GASES SUPPLY UNITS

Powder feed unit, air compressor, dust collector of the grit blasting equipment and wet collector unit need electric power supply at different voltage at different amount. Table 2.1 lists the type and amount of power needed by different units of the spraying system.

The HVOF system needs different types of gases to operate the system. The type of gases and their quantities and pressure are listed in Table 2.2. Nitrogen is required for powder feeding as a carrier gas. To maintain the required consumption one nitrogen gas cylinder with commercial grade purity is enough for the proper operation of this system.

Oxygen is used as oxidant for combustion. To maintain the huge flow rate of this gas, at least four cylinder of oxygen with commercial grade purity should be connected together.

Propylene is used as a fuel for combustion. It is recommended that at least three 45 kg cylinders are to be connected together. The purity of the propylene should be 99 % as suggested by the manufacturer. However during this investigation 96 % pure propylene were used and this reduced purity of the gas was within the acceptable range as per manufacturer recommendation, though it might reduce the life of the nozzle.

A supply of clean, dry compressed air is required for the use of the gun. A compressor is installed to compress air with the range of pressure 6.8 bar to 10.2 bar at a flow rate of 1500 standard litre per minute (SLPM). An air reservoir of capacity 300 litre was installed to store air to ensure a constant supply of air to the gun.

2.3.2 ISOLATED ROOM AND SPRAY BOOTH

The potential hazards associated with thermal spraying are toxic materials that may generate in the thermal spraying process, airborne metal dust and fumes, and the noise level. The probable adverse environmental conditions of thermal spraying operation require a well protected area where the spraying operation can be done. Dust , fumes and overspray must be removed from the work area as rapidly as possible. The most effective way of achieving these objectives is through the use of spray enclosures. A spray booth (Figure 2.10) was installed to guide and contain all airborne dust, fume and over spray so that they can be properly extracted by the wet collector. The spray booth helps to minimize danger from dust explosions and adequate ventilation. The operator is supplied with equipment for protection against noise, dust, fumes and rays. For the protection of personnel working in the vicinity of the spray room, the room was isolated. It is always preferable to keep the oxygen and propylene cylinder outside the spray room. From this consideration, in the present installation a room is divided into two part: the front room and the spray room. The compressor and the gas cylinders are put into the front room and the spray room is isolated by a sound proof wall. The design considerations of the sound proof room are given below.

(i) CONSTRUCTION OF SOUND PROOF SPRAY ROOM

A plan of the spray room is shown in Figure 2.11. Three sides of the room were built up with double layered sound absorbent walls, in addition to the brick walls. The roof of the room was also protected with double layer sound absorbent ceiling (Figure 2.12). Each layer of the sound proof wall is made up of different layers of sound absorbing materials. For the side walls, frame structures (Figure 2.13) of 1.22 X 2.64 metres rectangular shape were made from 44 X 44 X 3 mm box sectioned steel bar. Both the sides of the frame were covered by peg boards and the space within was filled up with tightly packed glass wool. These frames were placed side by side to cover the total side wall. Frame structures made for roof were made of 1.22 X 3.91 metres size and these frames were also covered by peg board and glass wool as the side wall frames. These frames were placed on the side wall frames in two layers. Between the layers wooden blocks were positioned for strong support. At the entrance of the room two doors (one opening inside and another opening out side) were made in a similar pattern as the side wall frame. An extra outer layer of aluminium sheet of 3 mm thickness was given to the doors. The outside area of the sound absorbent side walls, facing the brick walls, was also covered with aluminium sheet. During suction of the exhaust fan, the door which opens out side closes tightly and prevents sound to go outside. For ventilation air ducts were made passing through a side wall. The air ducts were fitted with silencers to absorb sound such that the sound can not propagate through the duct.

The noise level at any location depends on factors such as equipment operating parameters, back ground noise, room size and wall, floor and ceiling material. Therefore to determine the exact noise level of any room, it is necessary to measure the sound level. To check the effectiveness of the sound proof walls the noise level of the spray room was measured by a db meter putting it at the location where normally an operator will stand during spraying. It was found that the noise level was 126 db. The noise level at the front room (outside the spray room) was 96 db when the gun was on and the compressor was on. When only the compressor was on the noise level of the front room was 89 db. Therefore it is quite obvious that with the addition of the sound proof wall the noise level of the spray room is reasonably protected.

2.3.3 GRIT BLASTING APPARATUS

The adhesion of the coating is directly related with the cleanliness of the substrate surface and the total surface area of the substrate. Increase of effective substrate surface by roughening is a well known method. The function of abrasive blasting equipment is cleaning and roughening the substrate surface. Therefore a grit blasting equipment supplied by Metco Ltd was installed. The commercial name of this unit is Ventublast Mammoth. It has a large capacity grit blasting cabinet with 42 by 32 inches internal dimension of the work area. An eye level visor gives visibility over the entire work area. The system also includes a hand-held blasting gun and dust collector. The abrasive medium is dispensed from a hopper at the cabinet base. The blasting gun is of the suction type with a straight nozzle made of ceramic material. When air is flowing through the nozzle at some section of the nozzle a vacuum is generated due to the increase of velocity of air. Due to the vacuum grit is drawn from the base of the cabinet to that section of the nozzle and propelled by the air to the substrate. The grit drops through a grate, returns to the hopper and is recycled. Clean dry air from the compressor is used for grit blasting. A pressure controller is used to change the supply pressure of

the compressed air used by the blasting equipment. The roughness of the substrate is controlled by controlling the air pressure, grit size and spray distance. The best way of doing this is by changing the grit size. For thermal spraying normally three grade size grit are used viz. coarse, fine and very fine. Broken down abrasives and dust are exhausted into a series of filter bags in a separate collector.

2.3.4 EXHAUST SYSTEM

To minimize the danger of dust explosion and prevention of fumes and dust accumulation resulting from spraying, adequate ventilation must be provided for spray booths and other confined spaces. The velocity of air in the gun area sweeping fumes into the exhaust system should be at least 300 linear feet per minute. To clean the dust from the air it is better to be wetted down and keep in water. Therefore a metro type 4CW wet collector was installed for the HVOF spray system.

Figure 2.14 shows a cut away cross section drawing of the wet collector showing how the scrubbing activity is produced. The dust laden air is drawn through the inlet and passes under the scroll, picks up and mixes with water. The turbulence of this mixture of water, dust and air is intensified by directional change of the air flow. Finally the air flows through the moisture eliminator where water and dust drops out and air escapes upward. The cleaned air is extracted through a centrifugal fan housed in the upper section of the wet collector and exhausted to the atmosphere. A door is provided to scrape out the wet dust in the form of sludge. The water level of the wet collector is designed to work automatically but due to faulty design it does not work automatically. So occasionally water is to be fed to maintain the designed level. The unit is rated to exhaust water wash and scrub 2000 to 2500 cfm of air when ideal condition of water level is maintained.

2.3.5 MECHANICAL HANDLING UNITS

For better coating quality and uniform coverage of the coating on the substrate a continuous movement of the substrate and the gun is essential. For a cylindrical

substrate a rotary motion can be given by a variable speed motor through a chuck of a lathe. The traversing unit of the lathe carriage can be used for to and fro motion of the gun. Therefore a semi automatic lathe was installed having rotational speed 40 to 2500 rpm and traversing speed 0.05 mm per rotation to 3.5 mm per rotation. The size of the chuck was 200 mm and the height of the centre of the chuck from the bed is 200 mm and the length of the bed was about 1 metre.

2.3.6 FURNACE

A furnace made by Lenton thermal designs of the type EF 10/8 was used to heat the sample during experiments (Figure 2.15). The furnace is equipped with the analogue temperature controller which can control the temperature within ± 3 °C. The range of temperature between which the furnace can be used is 0 to 1000 °C. A cylindrical box was made inside the furnace. This box was connected with a nitrogen gas cylinder through a flexible tube. A flow meter was also provided to control the flow rate of nitrogen in to the box. This box was used to heat the object in a nitrogen atmosphere.

2.3.7 TEMPERATURE MEASURING INSTRUMENT

To measure the temperature of the static body thermocouples of type K were used. When the body is rotating at high speed it was not possible to measure the temperature by any device which needs physical contact. Therefore for non-contact temperature measurement a pyrometer was installed. This is an optical fibre thermometer made by Accufiber of the type Model 10 (modified low temperature), which can measure the temperature between the range of 200-1000 $^{\circ}$ C. A picture of the used optical pyrometer is shown in Figure 2.16.

The pyrometer works on the principle that all substances at temperature above absolute zero emit radiant energy as the result of the atomic and molecular agitation that is associated with the temperature of the substances. The rate of emission of the radiation per unit area increases with increase in temperature. Accordingly, the temperature of a substance can be measured by means of a suitable device responsive to such radiation energy. An optical pyrometer can collect the radiant energy from the work piece at a distance of a few inches to many feet (upto 16 feet). This type of sensor is used when direct contact or close proximity sensors are impractical.

2.3.8 COATING THICKNESS MEASURING INSTRUMENT

A coating thickness measuring instrument known as Fisherscope Multi of the type 760 C (Figure 2.17) was installed to measure the thickness of the coating. This instrument uses the eddy-current method and the magnetic induction method.

A schematic of the eddy-current thickness gauge is shown in Figure 2.18. When high frequency current is passed through the exciter/sensing coil and the coil is brought near an electrically conductive material, then eddy current is induced in the material. This current, in turn, reacts with the sensing coil, causing back emf energy loss and a change in coil impedance. It is the impedance change that the instrument measures and converts into a thickness proportional signal. By calibrating the gauge with standard coating of known thickness, the meter can be directly used to measure the unknown thickness of the coating provided that the substrate coating on a magnetic substrate forms the nonmagnetic gap in the circuit and the inductance of the coil is diminished as the air gap is increased. If a magnetic coating on a nonmagnetic substrate is measured, the inductance increases with coating thickness. Figure 2.19 shows schematically the essential elements of this type of thickness measuring instrument. These methods can measure the coating thickness with a uncertainty of less then 10 % or 0.5 µm which ever is the greater [101], provided that they are properly calibrated.



Figure 2.1 Picture of a Diamond Jet Gun.



Figure 2.2 Schematic showing the different assemblies of the gun.





INJECTOR

AIR CAP



SIPHON PLUG



INSERT



Figure 2.3 Schematic of the front end parts and cross section of the front end assembly.

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Figure 2.4 Schematic top cross sectional view of the gun.



Figure 2.5 Schematic of side cross sectional view of the gun.



Figure 2.6 Picture of the powder feed unit.



Figure 2.7 Schematic diagram of the powder feed unit

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Figure 2.8 Picture of the gas flow meter.



Figure 2.9 Picture of the Air control unit.







Figure 2.11 Schematic diagram of the spray room showing the arrangement of the equipment.

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Figure 2.12 Front sectional view of the sound proof walls of sound proof room.







Figure 2.14 A cut out cross section of the wet collector.



Figure 2.15 Photograph of the furnace with the cylindrical box connected with nitrogen cylinder.



Figure 2.16 Photograph of the optical pyrometer control system.



Figure 2.17 Picture of the coating thickness measuring instruments.





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Figure 2.19 Operating principle of thickness measurement by magnetic induction.

Name of the unit	Voltage	Hz	Phase	Power (kW)
Air Compressor	380/415	50	3	19
Wet- collector	380	50	3	5.5
Powder feed unit	120	50/60	2	0.2
Dust collector for grit blasting unit	400/440	50	3	0.4
Furnace	110/230	50/60	2	3

Table 2.1 List of electric power and voltage needed by different units of used experimental system.

Table 2.2Flow rate and pressure of different gases needed by different
units of used HVOF thermal spraying system.

Type of gas	Name of the unit	Working pressure (Bar)	Maximum flow rate needed (SLPM)
Oxygen	Spray gun	10.3	284
Propylene	Spray gun	6.9	81
Nitrogen	Spray gun (Carrier gas)	8.6	20
Air	Spray gun	5.2	415
Air	Vibrator	1.4	20
Air	Grit blasting	2-9	1500
Air	Extra cooling	as required	as required

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 PROCEDURE FOR COATING BY THERMAL SPRAY PROCESS

Coating by thermal spray process with acceptable qualities needs very careful attention to every step in the total process. Every coating-substrate combination has to be treated differently to achieve proper qualities. The entire thermal spray coating process can be divided mainly into three steps: surface preparation process, spraying process and post spray process.

3.1.1 SURFACE PREPARATION PROCESS

Any substrate to be coated must be clean from oxide scales, oils, machining lubricants and other foreign materials like dusts. The steps followed for surface preparation are: degreasing, removal of oxides or other foreign materials, masking for roughening, roughening, masking for spraying and putting bond coat.

Degreasing is required to removal oil and grease from the substrate surface as well as from the pores of the substrate surface. This is especially important if the component has been in service. For degreasing, the substrate is to be flooded with cold solvent. Trichloroethylene is used as a solvent for degreasing. A porous substrate which absorbs oil in service has to be preheated to remove absorbed oil. After degreasing it is important that the area to be sprayed is not touched by hand or any other means that may spoil the surface.

Oxide layer and other contaminant materials are generally removed by grit blasting. Grit blasting should not be relied upon to remove heavy scale, since it may simply embed scales inside the surface. These embedded scales create an area where the sprayed coating is weakly bonded. Prior to grit blasting the components should be degreased to prevent contamination of grit blasting media. Masking is required to protect areas not to be sprayed from grit during blasting. Commercially aluminium oxide, chilled iron, sand, crushed steel and silicon carbide are used as abrasive grit. Most commonly used abrasive grit is aluminium oxide. Three different sizes of grit are used to make different type of roughness. These types are designated as coarse, fine and very fine. Coarse grit is used to roughen the surface when the coating thickness will be more than 250 μ m [9]. Finer grit is used to roughen the surface when thin coating is to be deposited. Air pressure required for grit blasting varies from 200-600 kPa. Clean and dry air should be used to avoid contamination of the grit and substrate. Nozzle to substrate distance should be between 50-150 mm. Variation of distance within this range appears to have very little effect on the roughness. It is always preferable to control roughness by changing grit size rather than changing pressure or distance [102]. The angle of impact should be less than 90° to avoid embedding grit into the substrate surface.

Masking used for grit blasting might not be suitable for subsequent thermal spraying due to the temperature and kinetic energy of the sprayed particle. For HVOF process, only mechanical masking is effective. During masking care should be taken not to contaminate the spray area.

Certain materials can bond with clean surfaces that have not subsequently been prepared by roughening. These materials contain certain percentages of Nickel and Aluminium which metallurgically bond with the substrate. This types of coating is known as bond coat. By applying a initial coating of these materials the bond strength of the final coatings can be improved.

3.1.2 SPRAYING PROCESS

Depending on the type of application, the coating material to be deposited on the substrate is to be decided. Considering the coating material and the shape, size and material of the substrate, the rotational speed and the traverse speed of the spray gun are to be decided. The rotational speed of the substrate and traversing speed of the gun should be such that the deposition rate of the coating per spray is less than 75 µm for general metallic material and for carbide it should be about 15 µm. In general it is good practice to traverse the gun as fast as possible. However, any sign of spiral deposition on the substrate should be avoided.

Before commencing spraying, the substrate is to be preheated to remove moisture and condensation from the surface. Preheating also reduce thermal stress that may arise due to difference in the coefficient of thermal expansion between the substrate material and the coating material. Flame of the gun should not be used directly to preheat the substrate. However, its flame may be used indirectly to preheat the substrate. The preheating temperature of steel substrate should be 90-150 °C and should never cross 200 °C. For aluminium the preheating temperature should be 50 °C. Copper and magnesium substrate should not be preheated [15].

Before spraying, the process parameters are to be adjusted. The process parameter includes pressure and flow of gases, air pressure and flow, spray rate, spray distance and spray gun parameter. The process variables depend on the type of coating material to be deposited.

During spraying, cooling may be required to prevent the coating and the substrate from overheating and to allow continuous spraying, especially when applying a thicker coating. Large components are unlikely to need additional cooling, but for smaller components cooling is essential. Clean and dry air is suitable for cooling. If air cooling is not sufficient to control the temperature of the substrate, interruption of spray is essential.

3.1.3 POST TREATMENT PROCESS

Thermal spray coatings usually exhibit two common features in the as-deposited condition. Firstly, the surface finish of the coated surfaces is such that they look like a sand paper and secondly they are porous. Typical surface roughness of a sprayed coating ranges from 5-15 μ m [9], which is too rough for most tribological application. Grinding is the preferred method for finishing the coating. Wet grinding with a wheel of medium hardness is recommended. The wheel should be dressed frequently to avoid glazing which is a very common problem with sprayed coating. Over spray should be removed first by grinding outwards from the sprayed area. Certain coating materials can be finished by turning with carbide tools.

In some applications the porous nature of the coating is advantageous as its porosity helps to retain lubricants. However, there are some cases where it needs sealing up the pores in the sprayed coating, particularly when the coating is exposed to harsher environments. Sealing is the process by which the pores of a coating are filled to eliminate the possibility of infiltration of fluids or corrosive media that can contribute to premature failure. Epoxy and resin seals are effective in highly porous coating. All sealers should be applied after spraying and before any finishing. After finishing a light coat of seal material should be reapplied to ensure optimum sealing. Coating sprayed by HVOF thermal spraying process has low porosity and therefore normally HVOF thermal spray coating does not need sealing.

3.2 INSTALLATION OF THE SPRAY SYSTEM AND TEST RUN

The spray equipment and most of the support facilities used for this investigation were supplied by Metco Ltd. The sound proof room was built and the spray system with its support facilities were installed by technical staff of the workshop. Test runs were carried out by depositing coatings of nickel chromium alloy, WC/Co and stainless steel materials on substrates made from mild steel plate. These tests were undertaken to gain experience on how to use the equipment and how to control the spray parameters. For spraying with the spray gun the following steps are to be taken.

- After setting all the equipment in their proper location the gun is ready for lighting and spraying. If there is any part missing, particularly the gun front end assembly, bodily injury or equipment damage is quite likely to occur.
- (2) The gun is to be pointed to the spray booth and exhaust unit is to be switched on.
- (3) Gas bottles of all types are to be opened and set to the required pressure as shown in Table 3.1.
- (4) Powder feed unit is to be switched on and the pressure and flow of the carrier gas are to be set to the required values.

- (5) Air control and regulator unit are to be adjusted for requisite pressure and flow of air for the flow meter unit and the air vibrator unit.
- (6) The pressure and flow of air, oxygen and propylene are to be finally adjusted by the knob of gas flow meter unit.
- (7) To purge out any dust in the gun holes and to ensure proper adjustment of pressure and flow of gases the valve of the gun is to be turned full on for a few seconds and closed immediately. Any change of pressure and flow indicated by the flow meter unit is to be adjusted.
- (8) For lighting the gun, the valve of the gun is to be opened upto lighting position (marked by a dent on the valve handle) and lighter is to be struck very near to the tip of the gun. As soon as the gun lights, immediately the gun valve is to be opened gradually to full open position.
- (9) After lighting, a certain time has to be allowed to pressurise the powder feed unit which is indicated by zero reading of the feed rate meter.
- (10) For spraying different type of powder materials, the flow of gases is to be adjusted accordingly after lighting and spraying can be commenced. The value of flow rate for individual powders are available from the manufacturer with the application data for the powders.

If there is some interruption of spraying i.e if the gun is off for some time, there is no need to go back to the lighting pressure and flow setting. With the changed setting if it is not possible to light the gun then it is advisable to set the pressure and flow for lighting.
3.3 PROBLEM ENCOUNTERED WITH THE SPRAY GUN

During the initial test run of the spray gun it was found that the gun back fired quite frequently. By back fire it is meant that momentarily the flame of the gun goes inside the siphon plug of the gun with a "pop" and burns inside the gun. During back firing any delay to stop the flow of fuel gas to the gun will cause melting of the component of the gun and even more dangerous problem may happen. Frequent backfire or permitting the gases to burn in the siphon plug too long makes it necessary to clean the holes in the siphon plug. It may also cause the nozzle nut to loosen. According to the suppliers recommendation, the gun will not back fire unless something is definitely wrong. The cause of the backfire should be found and corrected before commencing coating operation.

3.3.1 CAUSES OF BACK FIRE AND REMEDY MEASURES

At the time of backfire the valve of the spray gun to control the flow of gases was closed immediately. After dis-assembling the front end components it was found that carbon soot was deposited on some area of the siphon plug. This soot was deposited as a result of burning of gases at the area where fuel and oxygen are mixed. The causes of backfire as explained in the manual of the spray gun are as follows:

- A leak at the nozzle assembly O-rings.
- Dirt or damaged nozzle shell O-rings.
- A leak at the siphon plug O-rings.
- Dirt in the siphon plug holes.
- Improper lighting pressure.

All the above causes of backfire were checked thoroughly. It is quite unusual to have such problems with a new system. It was observed that there was no such problem as explained in the manual to cause backfire. Therefore spraying with the gun was tried again and again, and found that there was backfire. Sometimes it was at the start of lighting the gun and sometimes it was after few seconds. Very occasionally spraying could be started but could not be continued due to backfire. In the manual the causes of backfire were not well explained and even during further correspondence and discussion with the manufacturer the exact causes of backfire was not properly explained. They orally suggested that the temperature of the spray room should be kept about 15 °C during spraying and that might help to avoid the backfire problem. Spraying with room temperature about 15 °C was tried and found that the gun still backfires. Therefore a detailed investigations were carried out to find the exact cause of backfire.

During the investigation spraying was tried with different sets of front end assembly. The flow rates and pressures of different gases were varied during spraying. The effect of room temperature was also investigated.

It was observed that some nozzle inserts and shells were causing backfire whereas some were not causing backfire though both were new and not damaged. Therefore it was concluded that some O-rings of the nozzle inserts and shells can seal the gases and some can not. This may be due to their improper dimension or hardness or both.

The variation of supply pressure of gases within 10 % of the standard pressure has no effect on backfire. Investigations were only carried out with 10 % variation of pressure.

The moisture content in the air has no effect on the cause of backfire. The moisture of air was varied by using the unfiltered air for spraying.

Moisture in the fuel gas may be the most deciding factor to cause backfire. The fuel gas used for the system is propylene and this gas is supplied in the liquid form in a cylinder which has to vaporise continuously to maintain the continuous flow. The supply pressure of the propylene is 100 psi. At this pressure a room temperature of upto 15 $^{\circ}$ C is not sufficient to maintain a continuous flow of propylene at dry condition at the specified rate even though the vapour pressure of propylene is about 100 psi at a temperature of 5.6 $^{\circ}$ C. It was found that one of the criteria to avoid the backfire is to keep the room temperature above 20 $^{\circ}$ C.

With proper O-rings on the front end assembly of the gun and 20 °C room temperature the problem of backfiring was almost solved. With these setting there was backfire at very few occasions. Some incidents might be due to the fluctuation of flow of gases or any other reasons. For this system the flow rate of gases are very high and for the safety of the system a lot of valves at different locations on the flow path are installed which caused the fluctuation of flow and it was not possible to avoid such fluctuation. This problem might be an inherent problem of the system itself. Therefore, careful attention while spraying is a must for this spraying process.

3.4 DEPOSITION AND CHARACTERISATION OF COATINGS DEPOSITED ON MILD STEEL SUBSTRATE

On test runs, coatings of different materials were deposited on a mild steel substrate. The materials used were Tungsten carbide/Cobalt, Nickel chromium alloy and Stainless steel commercially designated as Diamalloy 2003, 2001 and 1003 respectively. Three millimetre thick mild steel plates of circular shape were used as substrate. The substrates were degreased by trichloroethylene and roughened by grit blasting. Coarse size grit was used for blasting and the air pressure was maintained at 300 kPa. The substrate was clamped in a vice and the gun was positioned at some standard distance according to the type of coating material used (Table 3.2). As the HVOF thermal spraying process can deposit coating with high bond strength, the bond coat was not used for depositing coating. The spray parameters used are shown in Table 3.2. These standard values were supplied by the manufacturer of the spray system. Before spraying the substrate was preheated to a temperature of about 100 °C and this temperature was measured by fixing a thermocouple at the back of the sample. The traversing speed of the gun was maintained by hand such that the temperature of the substrate did not rise above 150 °C. During traversing care was taken to cover the whole surface area of the substrate with an equal thickness of coating. The coating characterisation was performed on the coated sample. Properties measured were hardness, thickness, roughness and porosity for all the deposited coating materials. The relative wear and bond strength were measured only for WC/Co coating deposited on different size and shape of samples. The results of characterisation of these coating are furnished in Table 3.3.

3.5 PROPERTY CHARACTERISATION EQUIPMENTS AND METHODS

The properties of the deposited coating measured includes thickness, hardness, roughness, porosity, wear and adhesive bond strength. The methods of measuring these properties and the instruments are described below.

3.5.1 THICKNESS MEASUREMENT

Thermal spraying process is normally used to deposit coating of thickness from 50 μ m to more than 1000 μ m. Eddy current and magnetic induction type coating thickness measurement methods are very effective to measure the coating thickness within this thickness range. By these methods the thickness of the coating can be measured without destroying the coating on substrates. A instrument known as Fisherscope Multi of the type 760 C was used for this investigation (2.3.8).

This instrument has to be calibrated with same coating-substrate combination before use. Therefore, samples of different coating thickness were deposited with the same coating and substrate material combination for calibration. For this purpose a mild steel rod of 17 mm diameter was used as substrate. Coatings of different material were deposited on this substrate by rotating it at 800 rpm and traversing the spray gun at a constant speed of 3 mm per rotation. The thickness of the coating was varied by varying the number of spray. After spraying small pieces of sample were cut from the coated substrate (Figure 3.1). The two ends of the cylindrical sample were grounded and polished to measure the coating thickness by optical microscope. Readings of coating thickness were taken at two end surfaces of the samples. Four readings at each surface were taken and averaged to have an average coating thickness of the samples. These samples were used as the standard sample of known coating thickness to calibrate the thickness measuring instrument. A few samples were also made of known coating thickness to check the accuracy of the thickness measurement. As this instrument is standardised with samples of known coating thicknesses, further calibration of this instrument is not needed. The thicknesses of these samples were measured by the instrument and found that the variation of the measured thicknesses were within 5 % of the known thicknesses. With the help of this calibrated instrument the coating thicknesses of the samples made during test run were measured and these are presented in Table 3.3.

3.5.2 HARDNESS MEASUREMENT

Hardness is usually measured in three different methods. These are static indentation, rebound or dynamic and scratch method. In the static indentation method a ball or a diamond cone or a pyramid is forced into the material being tested. The relationship of total load to the area or depth of indentation provides the measurement of hardness. This method has served quite well for hardness tests performed using loads of 200 gm and higher. However, hardness tests performed at lower loads called microhardness test, depend on applied load. Hardness tests with the load range less than 200 gm gives wide scattered value and the scattering increases as load deceases. The scatter is due to real error involved in making load, dimension measurement and used hardness definition [105].

Though microhardness measurement suffers from scatter value for low load, still it is widely used for measuring hardness of coating. In this study hardness was measured at a load of 300 gm to avoid scattering due to load. The instrument used was Leitz miniload 2 Vickers, Knoop and scratch hardness tester. The range of test loads that can be used by this instrument is 5 gm to 2000 gm. Hardness of thermally sprayed coating are normally measured along the cross-section of the coating. Therefore coated samples were sectioned and mounted for grinding and polishing. Polished samples were positioned on the platform of the hardness tester and indented with a load of 300 gm. By focusing the microscope the width of the indentation were measured at a magnification of 500 X. The values of hardness of the coatings are presented in Table 3.3.

3.5.3 ROUGHNESS MEASUREMENT

The roughness of any surface is most commonly measured along a single line profile and is characterised as arithmetic average of the heights of the peaks and troughs of the surface. This can be defined as the arithmetic height of the roughness component irregularities from the mean line measured within the sample length. The mean line can be defined as a line such that the area between the surface profile and the mean line, above the mean line is equal to that below the mean line. Various contact type and noncontact type instruments are available to measure roughness. A contact-type stylus instrument is most popular to measure roughness. The stylus instrument amplifies and records the vertical motion of a stylus while moving at a constant velocity relative to the surface to be measured.

The roughness of as sprayed coating of different materials was measured by a stylus type instrument known as Surftest-402/Mitutoyo. The average roughness of the deposited coatings are given in Table 3.3.

3.5.4 POROSITY MEASUREMENT

The common techniques used to measure porosity are, direct observation methods and indirect detection methods. Direct observation methods allow observation of both isolated voids (closed porosity) and through pores (open porosity). Indirect detection methods includes mercury porosimeter, optical dielectric constant test, pore corrosion test, radiography method and density measurement. Direct observation technique uses optical microscopy, scanning electron microscopy, transmission electron microscopy and x-ray scattering.

By using optical microscope porosity of coating can be measured by comparing micro-photograph of the sample taken by a microscope with another micro-photograph of sample of known porosity. Porosity can be measured by optical microscope by directly measuring the pore area on the view field of a microscope and comparing this area with the total viewing area. A microscope equipped with computerised analysis system is available to determine the area of the pore on any specified size of field within the focusing area of the microscope. This instrument works on the principle that the focusing area of the microscope is directed to a video camera, which converts the visible light image into an electronic signal. These electronic signals then represents the image. A computer then processes the signal by digitizing the electronic signals. On the computer screen the image focused by the microscope can be seen. The pores on the sample are seen as darker area while other area is bright. Computer program can calculate the darker area by assigning different colour to the different brightness area. This method of measuring pores or voids which are darker might suffer from some error if the colour of the matrix of the sample contains some black component like carbide.

For this type of measurement metallographic preparation of the coating is required. This is often difficult because a coating sample is the combination of hard and soft materials, which normally require different polishing technique. Pullout is a common problem that can substantially increase the apparent porosity in brittle coatings, such as carbide and ceramics. Conversely, for coating that contain soft and ductile phases smearing of these ductile materials can produce artificially low apparent porosity values [106]. Metallographic preparation consists of cutting the specimen, mounting them within epoxy, grinding and polishing. Cutting and mounting are normally done manually by high speed saw made of abrasive. Grinding and polishing can be done manually or by automatic equipment. For reproducibility it is better to use automatic system, particularly for hard material where pull out is a common problem.

In this investigation cutting and mounting of WC/Co coating samples were done manually. Grinding and polishing were done by two methods. During the characterisation of a coating deposited for initial test, grinding and polishing of WC/Co sample were done by manually operated 'Struer' polishing instrument. During characterisation of spray formed component of WC/Co material, grinding and polishing were done by an automatic system known as Motopol 12 polishing machine. All metallographic preparation of coatings deposited from nickel alloy and stainless steel material were done by using Struer polishing instruments. Porosity measurements were taken using Reichert MEF₃ optical microscope and a Quantimet 570 image analysis

system. The measured porosity values of these coatings are presented in Table 3.3.

3.5.5 WEAR RATE MEASUREMENT

The relative abrasion wear test of WC/Co coating was done by grinding the coating and stainless steel 316L sample together. Two samples of tungsten carbide/cobalt coating and one stainless steel sample of same size were mounted with same load on Struer polishing instrument system. Silicon carbide paper was used to grind them for a definite period. The weight loss per unit time was recorded and this gives the relative wear of the WC/Co coatings. The result of the wear test is presented in Table 3.3.

3.5.6 ADHESION BOND STRENGTH MEASUREMENT

Adhesion strength is the stress required to remove a coating from a substrate. Many techniques have been developed to measure coating adhesion. Most of them are qualitative. The quantitative measurement of adhesion can be done for thermal spray coating in a simple way by pull test as most of the thermal spray coating have adhesion strength below 100 kPa. In this method a force of increasing magnitude is applied in a direction normal to the interface until the interface is disrupted. Coatings on metal substrates are tested in this manner and this method is described by ASTM C633-79. In this test the coating is deposited on one face of the cylindrical substrate. This coating is bonded by suitable adhesive with the face of another cylindrical component. To ensure proper alignment, these two parts were positioned on a V-block. A small blob of the adhesive (Permabond ESP) was applied on the mating surfaces of the coated and uncoated parts and was spread over the surfaces as evenly as possible. A clamp was then used to press the two parts together to remove any entrapped air bubbles which might be present within the adhesive. The clamped sample with the V-block were put inside the oven to heat cure the adhesive at a temperature of 150 °C for an hour. The size and shape of the adhesive strength test sample is shown in Figure 3.2. After proper bonding the coating is to be grounded around the base so that extra load due to excess adhesive and shear stresses can be avoided during the tensile test. A loading fixture is to be used to pull the component of the test sample upto failure. Flexible pin joint (Figure 3.2) is recommended for the loading fixture to take care of the slight misalignment. This test is performed at room temperature. As per given standard the thermal spray coating thickness should be greater than 0.38 mm because the adhesive might penetrate through the pores of the coating. The speed of loading should be about 0.1 mm per minute.

The strength of the adhesive is the main limiting factor during testing adhesive bond strength of coating by this method. Adhesive Manufacturer generally does not supply the tensile bond strength of the adhesives. They often supply the shear strength. Therefore to select adhesive of proper tensile strength two types of commercially available adhesive were tested. These adhesives were Araldite 2005 made by Ciba-Geigy and Permabond ESP 109. Two end surfaces of two cylinder specimens, similar to tensile bond strength test sample without coating were bonded and pull tested. Different conditions were maintained during sample preparation and it was found that the tensile strength of the adhesives were quite different. Table 3.4 shows the test results of the adhesives. It was found that Permabond ESP 109 adhesive give maximum tensile strength which is 80 kPa when the bonded surfaces were roughened and heat cured at 150 °C for one hour. Therefore, for subsequent tests this adhesive with other conditions for best strength was used.

During the test run of the HVOF system the adhesive bond strength of deposited coating was measured only for WC/Co coating and this value is shown in Table 3.3.

3.6 TEST RUN WITH INDUSTRIAL COMPONENT

A printing roll which was in service, made of aluminium and coated with chrome plating was used to investigate whether this component can be recoated by HVOF thermal spray coating. During service this component worn out at different locations and the depth of wearing was less than 0.5 mm. The size and shape of the printing roll are shown in Figure 3.3. To coat this component, nickel chromium alloy material was selected considering the hardness required by the customer and the availability of the grinding facility.

First try was performed to coat only the wornout areas by masking the other areas of the roll. As only mechanical masking is effective for HVOF system, the roll was covered with metallic sheet exposing only the worn out area. After degreasing and grit blasting the coating was deposited maintaining standard spray parameters for this coating material. The preheating temperature was about 50 °C. During spraying it was found that deposited coating was spalling off from some edges of the grit blasted area. It was observed that those areas were not perfectly cleaned and at some minute locations previous chrome plating material were present. Therefore, the same areas of the printing roll were again grit blasted to clean the deposited coating and previous chrome coating. The roll was recoated with the same method and with the same material. This time the coating did not spall off. After grinding the excess deposited coating material it was found that at some locations the edges of the applied coating fractured and peeled off. This might be due to weaker bond strength at the edges due to improper cleaning or lack of matching with the previous chrome coating or improper method of grinding.

Second try to coat the worn out roll was performed after completely cleaning the chrome coating by grinding. After grinding the two ends of the roll were masked and the surface of the roll was degreased, grit blasted and coated with nickel chromium alloy up to thickness of 0.5 mm. During grinding the coating was locally peeled off. The cause of peeling off the coating was investigated and it was found that the methods followed during grinding was wrong. During grinding the coating, frequent redressing of the grinder is needed and this was not maintained at the time of grinding. Therefore, the same roll was recoated with the similar procedure after cleaning all the previous coating. This time after grinding the coating on the roll was found quite perfect. The photograph of the coated printing roll is given in Figure 3.4. Therefore, it was concluded that the proper grinding of coating is one of the essential process parameter, that has to be carefully controlled for proper application of coating.

3.7 TEST RUN TO MAKE FREE STANDING COMPONENT

Initial trials to make free standing thin wall component were carried out using nickel chromium alloy material because the coating of this material is tougher than WC/Co material. The procedure followed to make thermal spray free standing object was as

follows:

- 1) Forming cores are to be made from any suitable material.
- The shape of the forming core should be simple and size should be convenient to spray.
- 3) The material of free standing components are to be sprayed on the surface of the forming core to a suitable thickness such that it can be separated.
- Separation of the deposit from the core former by any suitable means without fracture.

The separation of the deposit from the core former can be done by two ways:

- 1) By destroying the core former after deposition of spray materials.
- 2) Without destroying the core former.

3.7.1 TRIAL TO MAKE FREE STANDING COMPONENT BY DESTROYING FORMING CORE

Separation of the deposit by destroying the core former can be done in many ways. This includes melting, machining and selective leaching or oxidation of the core material. Though separating by destroying the forming core is not a suitable method for mass production yet separation by melting was tried by making the forming core from Lead as it has low melting point. Conical core formers were made from this material. This forming core was positioned on the lathe through a mandrel which was held in the chuck. Nickel chromium alloy material was sprayed on the forming core while the forming core was rotating at 540 rpm. The traversing speed of the gun was maintained by hand. Standard spray parameters (Table 3.2) were used during spraying. The component thus formed was deformed and fractured.

3.7.2 TRIAL TO MAKE FREE STANDING COMPONENT WITHOUT DESTROYING FORMING CORE

To separate the deposit easily a conical shaped core with a taper angle 10 degree was made. Two forming cores were positioned side by side to have a double cone shape such that after deposition these cores can be pulled outward to separate the deposit from the substrate. A through hole along the axis of each conical forming core was made and threaded. These holes were used to fix two samples together by a mandrel. During pulling for separation these threaded holes can be utilised to fix some fixture needed for applying the load. On one side surface of each forming core, three holes of diameter 1.2 mm and depth of 5 mm were made at different distance from the centre of the forming core. These holes were used to position thermocouples to measure the temperature of the forming core. The shapes and sizes of the forming core are presented in Figure 3.5.

(i) SEPARATION OF THE DEPOSIT FROM THE FORMING CORE BY PREHEATING THE CORE

Two conical forming cores were fixed with the lathe chuck with the help of threaded rod and the gun was positioned in front of the forming core. The forming core was allowed to rotate at 800 rpm. Before spraying the powder material, the flame of the gun was used to heat up the substrate to different temperature. The traverse of the gun was controlled manually. During preheating, the gun was kept at a distance about 200-250 mm from the core to heat it uniformly. The temperature of the forming core was measured by putting a thermocouple into the hole drilled in the side surface of the forming core. During measuring the temperature, the gun was put off and the rotation of the forming core was stopped. After preheating, the powder material of nickel chromium alloy and WC/Co were sprayed on the core former. During spraying, standard spray parameters for these materials were used (Table 3.2). The average temperature. The control of core temperature during spraying was maintained manually by interruption of spraying. During spraying the material, occasionally temperature was measured by interruption of spray.

Similar trials were performed with different preheating temperatures, thicknesses of the deposit and cooling rates. The preheating temperature was varied from 150-450°C for aluminium forming cores and 300-600 °C for stainless steel forming cores (Table 3.5). The thickness was varied between 0.1-1 mm for both forming cores. The deposit with the core was cooled at different cooling rates in atmosphere without any flow of air and with a slow cooling rate in preheated furnace (Figures 3.6 and 3.7). However, it was not possible to obtain proper free standing objects.

(ii) SEPARATION OF THE DEPOSIT FROM THE FORMING CORE BY PUTTING EPOXY RELEASING LAYER

The next trial was done by putting a layer (releasing layer) of epoxy on the surface of the forming core which might help deposition and after deposition it can be leached or burnt out easily for the separation of the deposit from the forming core [93,94]. Therefore, a toughened single part epoxy adhesive (Permabond ESP 109) with higher bond strength was used to put an inter-layer on the forming core. This epoxy adhesive can withstand temperatures of about 300 °C with proper bond strength. After putting the epoxy adhesive as a releasing layer on the forming core of double conical shaped, it was heat cured at 200 °C in an oven for 15 minutes. After curing, the thickness of the releasing layer was measured by a micrometer. Then the forming core was fixed in the chuck of a lathe. The spray gun was positioned at a distance of about 200 mm and the spraying parameters were maintained as standard for nickel chromium alloy coating material. During spraying the core former was allowed to rotate at 800 rpm and the traverse speed of the gun was maintained by hand such that the temperature of the substrate did not rise above 150 °C. During this process, spraying was interrupted to measure the temperature of the substrate by putting the thermocouple into the hole of the forming core. Though, during spraying the substrate temperature did not rise above 150 °C, the consolidation of deposit as a continuous layer was not achieved.

The thickness of the releasing layer of epoxy material was varied between 0.1-0.4 mm (Table 3.6) by increasing the number of application and was measured by a micrometer. The coating material was sprayed exactly the same way but formation of

a component was not possible.

To absorb the impact of the sprayed particle and to reduce penetration of the hot particles into the epoxy layer, an aluminium foil was fixed on the forming core surface over the releasing layer. The epoxy adhesive acts as an adhesive to bond the aluminium foil with the releasing layer. After that, the coating material was sprayed similarly as before. The formation of the component by this process was also not possible.

A releasing layer of epoxy and metal powder mixture was applied on the forming core surface such that the adhesive will provide bonding strength and the metal powder will provide thermal conductivity and resist the spray particle from embedding into the epoxy-metal powder layer. Aluminium metal powder of 75 µm average particle size was mixed with the epoxy. The proportion of metallic material in the mixture was 10 % by weight. The metal powder and the epoxy were mixed and then applied on the forming core surface. After applying this layer the forming core with the applied layer was kept in a furnace at a temperature of 200 °C for 15 minutes for curing. Nickel chromium alloy material was sprayed as before and it was observed that the deposition of sprayed material was better than before. But with increased thickness the deposit spalled off.

Subsequently different thickness of the releasing layer made from aluminium powder and epoxy mixture were applied on the forming core. The thickness varied between 0.2 to 0.3 mm. The proportion of aluminium in the metal-epoxy mixture was varied from 10-60 % by weight. In place of aluminium, nickel chromium alloy material (Diamalloy 2001) was also used with similar proportion. The thickness of the releasing layer made by using nickel chromium alloy was also varied from 0.2 mm to 0.3 mm. Spraying to deposit nickel chromium alloy was performed with same method. However the result of forming free standing component was almost same i.e, no success.

(iii) SEPARATION OF THE DEPOSIT FROM THE FORMING CORE BY PUTTING METALLIC RELEASING LAYER

Low melting metal like tin and aluminium can be used as an releasing layer. Due to the availability of aluminium metal powder for conventional flame thermal spray coating, it was thought as a better choice to try with this powder. In addition to this the cost of aluminum powder is less then other low melting metal powders. Therefore, a commercially available aluminium powder designated as Metco 54 N-1 was used to spray as a releasing layer. The HVOF thermal spraying system was used to spray this layer on the core surface.

The spray of inter layer on the core substrate was done in the similar way as spraying nickel chromium alloy material. Two forming cores of conical shape were positioned on the lathe chuck through a mandrel as before. The aluminium releasing layer was sprayed on the forming core without preheating the forming core. During spraying the releasing layer, the gun parameters were selected arbitrarily and the spray parameters (Table 3.7) such as flow rates of gases were selected from the application data table of HVOF process. The lowest value of flow rate of the application data table was selected as the melting temperature of aluminium is the lowest, compared to all the material present in the application data table. At the time of spraying the releasing layer, the temperature of the forming core rises upto 70-80 °C. Some time was allowed to cool down the forming core. After that, the forming core with the releasing layer was preheated to different temperature ranging from 300-500 °C and then the nickel chromium alloy material was sprayed on the forming core. After cooling, the deposit and the forming core assembly was transferred to a furnace. In the furnace it was heated upto 700 °C to melt the aluminium releasing layer such that during melting the aluminium comes out and creates a gap between deposited layer and the forming core. Therefore after cooling, the deposited component might separate from the forming core after cooling. By this method, free-standing components made from nickel chromium alloy were obtained. A number of trials were performed in similar way to see the exact effect of the process variables on the ease of separation of the deposit.

3.8 PROCEDURE FOR FABRICATING FREE STANDING COMPONENT

For a given shape of product the forming core was held by the lathe chuck through a mandrel and was allowed to rotate at a certain speed. A pyrometer (Figure 3.8) was focused onto the side surface of the forming core such that it can measure its average temperature all the time during the spraying process. Aluminium material was applied as a releasing layer, by spraying with HVOF thermal spraying process upto certain thickness. The thickness was measured by a coating thickness measuring instrument. The forming core was preheated by the flame of the gun to a certain predetermined temperature and after that the material to be deposited was sprayed. While spraying, the temperature of the core was monitored continuously and the temperature was maintained within certain limits. The forming core temperature during spraying was controlled by supplying extra cooling air, by increasing the distance of the gun from the core, by putting more than one sample at a time and/or by interrupting the spray process. The thickness of the free-standing components was controlled by controlling the flow rate of the powder and/or the time of spraying. Immediately after spraying, the forming core with the deposit was transferred to the preheated furnace to heat the assembly to a certain temperature for a predetermined time. Then the core-deposit assembly was cooled at different conditions and at different cooling rates. After cooling the free standing component was separated easily.

3.8.1 MATERIALS USED FOR FABRICATING COMPONENTS

For fabricating the free standing component, three types of commercially available material powder were used. These were chosen so that they covers a wider range of hardness, thermal expansion and strength. These are Tungsten Carbide/Cobalt, Nickel Chromium alloy and Stainless Steel similar to AISI 306, commercially known as Diamalloy 2003, 2001 and 1003 respectively. The particle size distribution of these powders are shown in Figures 3.9-3.11. The composition of these powder materials are presented in Table 3.8. The main attention was given to fabricating Tungsten carbide/cobalt component.

The materials used for making the forming core were aluminium, copper, mild steel, stainless steel 316L, D2 steel. The size and shape were varied which includes cylindrical, conical (single cone and double cone), complex with convex and concave surface. Figure 3.12 shows the size and shape of the forming core. To obtain components with built-in holes conical shaped core formers were also made from stainless steel 316L with single or multiple holes. A collapsible core was made from stainless steel 316L to make component with convex and concave surface. This forming core was made such that it can collapse internally releasing the deposit from the forming core surface. After collapsing it can be removed easily without causing any damage to the free standing objects. The surface of the forming cores was fine machine finished.

The effects of process variables were measured only for conical shaped forming core. The shape and size of this core is shown in Figure 3.5.

3.8.3 MEASUREMENT AND CONTROL OF PROCESS VARIABLES

To observe the effect of the releasing layer thickness on the ease of separation of the deposit, it was required to deposit the releasing layer thickness to a predetermined thickness and to measure the thickness. The average particle size of the aluminium powder (Metco 54NS-1) used during the test run was 75 µm which was too large to deposit uniformly as a releasing layer of thickness less then 60 µm. Therefore, in some initial tests the releasing layer was deposited using this aluminium powder and after putting this layer, the thickness was reduced by rubbing uniformly with sand paper. With this releasing layer formation and separation of component was possible. However, the thickness of the releasing layer, thus formed was not sufficiently uniform and therefore another commercially available aluminium powder was used (Good fellow) having average particle size 50 µm. This powder was not a standard one for thermal spraying yet it was used for HVOF thermal spraying with some difficulty. The main problem with this powder was that it was not flowing properly with the carrier gas of this system and some times blocking of the powder feed unit line was observed. Therefore, after

every spray of this powder the cleaning of the powder feed unit and the total flow path of this powder was necessary. Therefore, to ease the process of applying releasing layer on the forming core, 10 to 15 forming cores were positioned through a long mandrel with the lathe chuck. Spraying of the releasing layer on the forming core was done simultaneously on these forming cores. After applying the releasing layer the thickness of this layer was measured by using coating thickness measuring instrument (section 2.3.8).

The roughness of the forming core was controlled by grinding with sand paper and by roughening with grit blasting. The roughness was measured by a stylus type roughness tester (3.5.3).

The forming core was preheated by the flame of the spray gun before commencing spraying material. During preheating, the temperature of the surface of the forming core may vary from the body temperature of the forming core and therefore a certain time was allowed before spraying such that the temperature of the whole forming core became uniform. The temperature of the forming core was monitored continuously by the pyrometer and during spraying the temperature of the forming core, by extra cooling air, by interruption of spray or by using more than one forming core to deposit material simultaneously.

Post heating of the deposit and the forming core assembly was done in a furnace (2.3.6). The heating rate was controlled by preheating the furnace at different temperatures. The cooling rate was controlled by putting the sample into the furnace at closed position and also at partial open position, and in atmosphere with no air flow and with forced air flow. The cooling rates used at different conditions are shown in Figure 3.6.

Throughout the whole fabricating process the temperature of the forming core at different stages of the process has been found to have a profound effect on the production of the free standing thin wall components. Therefore, a continuous temperature measuring equipment is necessary to monitor the temperature of the forming

core while preheating, spraying and subsequent releasing. Since the forming core is rotating at high rpm, a non-contact type of temperature measurement is necessary.

A pyrometer (2.3.7) was installed on the tail stock of the lathe focusing the side surface of the forming core which is held in the chuck of the lathe as shown in Figure 3.8. This equipment can measure the temperature of the forming core while spraying continues. The radiation coming from the hot forming core is sensed by the pyrometer sensor and the temperature is displayed. While spraying continues, the radiation from the molten hot particles and from the flame influence the measurement of temperature of the forming core. To avoid this influence, the pyrometer was housed in a metallic tube (Figure 3.13). The tube was fitted with two shields with a small hole at the centre of each shield. The distance of the pyrometer sensor and the two shields are so adjusted that the radiation from only the hot forming core can reach the sensor. In addition, the internal surface of the tube, the total surface of the shields and the total surrounding area were painted black to absorb the radiation from the sprayed materials and the flame. With this arrangement the pyrometer was calibrated by a thermocouple.

3.8.4 CALIBRATION PROCEDURE OF THE PYROMETER

A cone shaped forming core was placed on a mandrel and fixed with the chuck of the lathe. The pyrometer was focused to the side surface of the forming core. This calibrating core has three holes of 1.5 mm diameter and 5 mm depth on the focused surface. The positions of the holes were at a distance 3 mm, 6 mm and 9 mm from the outer edge of the focused surface of the forming core. The HVOF thermal spraying gun was used to heat the forming core while the core was rotating at 800 rpm. The traverse of the gun was controlled by hand such that the total surface could be heated uniformly. When the temperature of the forming core was above 200 °C the pyrometer was showing the average temperature of the forming core. Only when the flame of the gun was passing through the space between the forming core and the pyrometer sensor the readings shown by the pyrometer fluctuated. However, when the flame of the gun was shifted from the focusing area of the pyrometer the reading of the pyrometer quickly settled down and showed the average temperature of the forming core. To measure the

actual temperature of the forming core the flame of the gun was put off and the rotation of the forming core was stopped. Very quickly three thermocouple were positioned into the three holes of the forming core and the temperature shown by the thermocouples and the pyrometer were recorded. It was observed that all three thermocouple showed very little variation of temperature. For a stainless steel forming core the variation of temperature was less than 2 %. The time required for positioning the thermocouples into the holes of the forming core after heating by flame of the HVOF thermal spray gun, might be sufficient to minimize the variation of temperature at different distances from the outer surface. The inconsistency of variation might arise due to improper contact of the thermocouples with the surface of the hole. The temperature of the forming core, obtained by averaging the three temperatures shown by three thermocouples, was assumed to be the true temperature of the forming core. During measuring the temperature with the pyrometer the emissivity value of the surface whose temperature is to be measured, is to be given. Emissivity of any surface depends on its cleanliness, brightness and temperature. During this investigation it was observed that the cleanliness of the forming core surface could not be maintained and with the temperature increase, the colour of the stainless steel substrate surface changes. Therefore the difference between the true temperature and the pyrometer reading was found less at lower temperature of the forming core and higher at higher temperature of the forming core. This tendency of different deviation was reduced by heating the forming core to 500 $^{\circ}$ C temperature and then with this colour the emissivity value for this material and surface was adjusted by trial and error, such that the deviation was less within the used range of temperature. This is because the changed colour of the stainless steel surface at higher temperature did not change when it was cooled. Ultimately the variation of the true temperature and the temperature measured by pyrometer was reduced as shown in Figure 3.14. This curve was used as the calibration curve of pyrometer for stainless steel substrate for the rest of the experiment. The selected average emissivity value for stainless steel was 0.3. The change of colour with aluminium forming core was also present. As the temperature rises the brightness of the aluminium surface become dull. For this material, emissivity value was selected by trial and error method, and found that the same calibration curve (Figure 3.14) can be used to measure the temperature of aluminium forming core. For the forming core made from copper, the change of colour

and oxidation on the surface was such that the calibration was not possible and measurement of temperature of this forming core by using the pyrometer was not possible. Therefore, the temperature of this forming core was measured by thermocouples at some discrete points during preheating and spraying.

3.8.5 SELECTION OF ROTATING SPEED AND TRAVERSING SPEED

The rotation of the forming core and the traversing speed of the gun have a profound effect on the uniformity of thickness of deposition and on the uniformity of temperature of the forming core during preheating and spraying. To fixup these values the rise of temperature of the forming core at different traversing speeds at different distances between the forming core and the gun was measured. These are presented in Figures 3.15 - 3.17. For uniform thickness of the deposit, the distribution of the spray particle in the spray stream of the gun was measured and the pattern of distribution for different material is shown in Figures 3.18.and 3.19. During the initial tests traversing speed of the gun was maintained by positioning the gun on the traversing unit of the lathe. For further tests the similar traversing speed was imitated by traversing the gun with hand for ease of control.

3.8.6 FABRICATION OF COMPONENTS OF DIFFERENT SIZE AND SHAPE

Though the main attention was focused on the fabrication of conical shaped components, other different shapes were also fabricated during this study. Almost every shape has its own difficulty to fabricate and some extra care was needed during the fabrication of other shapes. The fabricating processes for these shapes are discussed under this headings.

(i) CONICAL SHAPED COMPONENTS WITH BUILT-IN HOLE/HOLES

Free standing component of tungsten carbide/cobalt material were also fabricated with built in holes. To make these type of components the forming core was made from stainless steel containing single and multiple holes (Figure 3.12). The depth of holes on

the forming core was about half the diameter of the forming core. This was done such that while spraying the material on the forming core the sprayed material on the hole area could not build up as a continuous layer with the rest of the deposited material on the forming core surface. Two methods were used to make built-in hole/holes of the formed component. In the first method, a cylindrical rod was positioned in the hole of the forming core such that one end of the cylinder remain protruding by about 1.5 mm above the curved surface of the forming core. Therefore, the material sprayed during fabrication of the component on the hole area was deposited on the end surface of the cylinder. After spraying and post heating the deposit and forming core, the cylinder was removed and thus a hole was created in the fabricated component. In the second method, the hole was kept uncovered such that the sprayed material on the hole area was deposited inside the hole, leaving a hole on the sprayed component. During separation of the deposit from the forming core it was found that some material also deposited on the inside edge of the hole as a continuous layer with the formed component. However, this extra material inside the hole area was weakly bonded with the formed component. Therefore, before separation of the component from the forming core, this material was easily removed by filing. To mask the end of the hole in the mandrel some asbestos cotton was put in the hole/holes. During spraying, sprayed deposit accumulated on the asbestos cotton. After spraying and separation of the free standing object, the deposited material inside the hole/holes of the forming core was cleaned very easily.

(ii) COMPLEX SHAPED COMPONENTS

A collapsible forming core shown in Figure 3.12 was made from six small pieces. These pieces are joined together with two end plates by screws. A mandrel was passed through the hole of the die to fix this forming core with the chuck of the lathe. This forming core is designed such that if the mandrel is removed and when the small parts are not screwed with the end plates, all the small parts will collapse inwards. While spraying on the collapsible forming core, sprayed material may also be deposited on the end plate as a continuous layer. In that case the component formed may not be the true shape as wanted. Therefore to keep a gap between the deposited material on end support and on the surface of the die, a gap was created by putting an extra collar between the end plate

and the main body of the collapsible forming core. The gap created was about 0.5 mm. After fixing all parts of the collapsible die, the releasing layer of aluminium was applied using the similar procedure as before. Method of fabricating a component by collapsible die is the same as the method of fabricating other components of conical shape. During separation of the forming core, care should be taken during unscrewing of the small parts of the die. Gripping load of the forming core might cause fracture of the deposited layer during unscrewing. Initially the deposited layer remain attached with the forming core and can withstand higher gripping load. When it is just unscrewed the formed layer loses it support as it become separated from the core. After unscrewing all small pieces can be removed one after another.

(iii) SMALLER DIAMETER COMPONENTS

During fabricating components of smaller size the traversing speed of the spray gun was controlled by hand because the traversing unit used during this study has the maximum value of 3.5 mm per rotation which is not sufficient for maintaining the uniformity of temperature of the forming core. In this case the traversing speed could not be measured. The temperature was controlled by counting the number of passes per minute which was maintained about 100 to 120 passes per minute. For making components of smaller diameter and longer length, higher traversing speed was used. This higher speed was managed by traversing the spray gun by hand at higher speed. In that case the number of passes per minute was about 200 or more.

(iv) MULTI-LAYER COMPONENTS

Spray formed components can be made by putting different types of material in different layers of the component. By putting different types of material at different layers, the toughness of the component can be improved. The combination of harder layer and softer layer in a multi-layer component can be arranged in two ways. The hard layer may be the inner most layer or it may be the outer most layer. When the inner layer is the hard layer, then the total component should be spray formed. When the outer layer is the hard layer then the inner layer may be made from any of low cost materials and then thick or thin layer can be applied as required and the combined layer will act as a component. In that case it should be assured that the bonding between the layers should be such that, both layers will act together to withstand the external load.

(iv)a Multi-layer component with harder inner layer

To manufacture the multi-layer component with a hard inner layer, different methods were used. In the first method, the WC/Co material was sprayed as the first layer onto the surface of the forming core to different thickness after preheating the forming core. The thickness of the first layer was varied between about 0.1-0.4 mm. Spraying of the first material was stopped when the temperature of the forming core was about 100 °C above the preheating temperature of the forming core. After spraying the first layer, the forming core was covered with asbestos cloth to reduce the rate of cooling of the forming. The WC/Co powder material of the powder feeder was changed with nickel chromium alloy material very quickly such that the temperature of the forming core. The second layer with nickel chromium alloy material was sprayed before post heating the forming core. The thickness of this second layer was varied between 0.1 mm to 1.0 mm. During the spraying and post heating the sprayed deposit did not fracture but during cooling the formed component fractured.

In the second method a thin-walled component was made from WC/Co material. The formed component was then reassembled on to the forming core and positioned on the chuck of the lathe through mandrel for respray. Then a second material was sprayed to obtain thicker coating on the formed WC/Co spray formed component after cleaning by sand paper and by grit blasting. The material used to put the extra layer was aluminium and nickel chromium alloy. The spray parameter used for aluminium material is shown in Table 3.7 and for nickel chromium alloy is shown in Table 3.2. During spraying the second layer, care was taken such that the temperature of the forming core did not rise above 100 °C. The thermal expansion of the forming core was higher as it was made from steel and thermal expansion of the component was lower as it was made from WC/Co. Therefore, at higher temperature the forming core over which the

component is positioned might cause fracture due to the higher thermal expansion. The rise in temperature was controlled by extra cooling and/or by interruption of spray.

Due to post heating, the surface of the WC/Co component contains oxide on its surface which reduces the adhesion of the resprayed material with the surface of the component. For improved adhesion of the second layer material with the surface of the previously formed component, a third method was used in which different steps were used to improve the adhesion. These steps are 1) post heating while making a component was performed in a nitrogen atmosphere 2) during spraying for fabrication of WC/Co component a layer of mixed material (nickel chromium alloy and WC/Co) was sprayed as the top layer of component. The combination of steps 1 and 2 was also performed.

To do the above tests after spraying WC/Co material the powder from the powder feeder was changed with a mixed powder made from mixing the WC/Co and nickel chromium alloy and sprayed using the spray parameters as of WC/Co material. After spraying this material as a top layer on the WC/Co layer, the component was separated from the forming core after post heating. The post heating and cooling was performed in the furnace with air environment and in nitrogen environment. The next layer was sprayed on this component after fixing it with the forming core on the lathe chuck. During spraying the last layer, conditions for spraying were maintained as those for the second method.

Mixed powder material was prepared from WC/Co and nickel chromium alloy. A certain amount of WC/Co material was mixed with a certain amount of nickel chromium alloy and both the powders were put in a can. The can with the powder was fixed with the chuck of the lathe by griping the can at its side through a G-clamp. The can was rotated at a rpm of 40 for 10 minutes. The proportion of the nickel chromium alloy material in the mixture was varied from 10-40 % by volume to achieve satisfactory adhesion between the two layers.

Multi-layer components were also made from graded material, the first layer was

sprayed with WC/Co composite and gradually this material was substituted with Nickel Chromium alloy. During making these components, WC/Co material was sprayed on the forming core to a thickness of about 0.2 mm (this thickness was assumed from the time of spray and flow rate of the powder material). After that a mixed powder material made from WC/Co and nickel chromium alloy material was used to spray on the previously sprayed material. After spraying this material to a certain thickness the mixed powder material was changed with another mixed powder material which contains higher proportion of nickel chromium alloy. In this way three to four layers of different proportion of mixed material were sprayed. The sprayed deposit with the forming core was post heated to separate the deposit from the forming core. The method used for post heating is similar to forming conical WC/Co component. The total thickness of the component was varied from 0.6-1.2 mm. The thickness of the individual layers made from mixed material could neither be measured nor assumed as during spraying the flow rates of mixed powder were not uniform.

(iv)b Multi-layer component with harder outer layer

As thermal spray can be used to almost any substrate therefore to make a component with outer surface of hard material, an inner core of conical shape was made from low cost material like aluminium. The thickness of this aluminium forming core was about 2 mm. After that the core was fixed with the chuck of the lathe with suitable fixture i.e by a mandrel. While the core was rotating the spray gun was used to preheat the core at different temperature and then the depositing material was sprayed continuously upto the required thickness. The preheating temperature was maintained from 200-400 °C. For the outer layer, two types of materials were used; these were tungsten carbide cobalt and nickel chromium alloy. During spraying, standard spray parameters were used except for the preheating temperature. To check the bonding of the spray deposit with the forming core substrate tensile bond strength and ductility tests were performed.

3.8.7 PROPERTY MEASUREMENT OF SPRAY FORMED COMPONENT

During the fabrication of spray formed component, the spray conditions used were different from those used for coating. Therefore, measurement of properties of the spray formed component was essential. The measurements taken can be classified into two types viz. 1) measurement taken for single layer components, 2) measurement taken for multi-layer components.

(i) MEASUREMENT OF PROPERTIES OF SINGLE LAYERED COMPONENT

The properties, measured for single layered component were hardness, porosity, ductility, residual stress and composition. The effects of spray parameters on the hardness and porosity of the sprayed WC/Co material were investigated. During these investigations the spray parameters varied were 1) flow rate of oxygen, 2) flow rate of propylene, 3) flow rate of air, 4) spray rate of powder material and 5) distance between the spray gun and the forming core. The values of these spray parameters and the resulting hardness and porosity of the deposits are presented in Table 3.9. The hardness and porosity of the components were measured using the method described in section 3.5.2 and 3.5.4. The method of measuring ductility, residual stress and composition are described below.

(i)a Method used for measuring ductility of sprayed material

To determine ductility of the sprayed material a standard bend test method was used [103]. For the bend tests, specimens were made from aluminium sheet as shown in Figure 3.20. The dimensions of the specimens were 70 x 10 x 1.9 mm. Since the samples were thin and not strong enough to withstand the flow force of the spray stream of the gun at higher temperatures, these were held against a mild steel plate and the thermocouple was placed between the sample and the supporting plate to measure the temperature of the sample while spraying. WC/Co and nickel chromium alloy materials were deposited on one surface of the sample upto a thickness ranging from 150 μ m to 350 μ m. The thickness was calculated from the measurement of thickness of the substrate before and after depositing the materials by using a micrometer. Before

spraying the materials, the substrates were preheated to a predetermined temperature with the help of the flame of the gun containing no powder material and then the material was sprayed. During spraying, care was taken such that the average spraying temperature remained within ± 20 °C of the preheating temperature. The temperature was controlled by extra air cooling and/or by interruption of spray. The spray parameters used are shown in Table 3.2. After spraying the side edges of each sample were ground and polished because the deposited materials on the side edge of the sample may affect the test results. A three point loading system as shown in Figure 3.20 was used to measure the ductility of the sample. A tensile testing machine (Instron) was used to load the sample with a loading speed of 0.5 mm per minute. To help identification of the point of fracture a magnifying glass was used. From the deflection at break the ductility of the deposited coating was calculated using the following equation according to reference [103].

$$D = \frac{4 \delta S}{L^2} \times 100 \tag{3.1}$$

where,

D = Ductility

 δ = Total thickness

S = Vertical displacement

L = Distance between two extreme supports

(i)b Method to measure the residual stress

For assessing the residual stress in the free standing component, these components were formed using a cylindrical core having a slit on the surface as shown in Figure 3.21. Components thus formed are shown in Figure 3.22. Depending on the fabricating conditions the size of the slit in the formed components increases or decreases after forming and releasing from the core. Measuring the change in the size of the slit, the residual stress was calculated using the mathematical relation used for the calculation of deflection of a curved beam. Figure 3.23 schematically shows the sample as a curved beam. The equation used for the analysis is as below (Appendix B).

$$STRESS = \frac{2 \delta E Y}{4.3 R^2}$$
(3.2)

where,

 δ = Deflection

E = Young's Modulus

Y = Any distance of surface from the neutral axis

R = Radius of curvature

It is assumed that the radius of curvature is large compared with the thickness of the cross-section ie. plane section remain plane after bending. The fabricating variable tried were: spray rate, flow rate of gases, spray distance, pre-heating temperature, spraying temperature, post heating time and temperature.

(i)c Method used to measure the composition of the WC/Co component

During the deposition of WC/Co material the change of colour of the deposited material at different stages of fabrication was observed and the composition is one of the major deciding property of the components. Therefore, the composition of this deposited material was investigated. During making the samples for these tests, standard spray parameters (Table 3.2) were used.

X-ray diffraction was performed on deposits on the core before and after post heating for Tungsten carbide-cobalt components and also on a coating of the same material sprayed on a substrate without preheating.

To compare the amount of oxygen and carbon present in the free standing

component and in the deposited coating, relative quantitative measurement were done. The carbon and oxygen contents of the cleaned free-standing object and coating deposited from WC/Co materials were analyzed by using wave length spectrometry. At the same time to ascertain the variation of the elements along the cross-section of the free standing component, relative quantitative measurements for different element present, were done. Three locations were chosen for each component such that it covers the total cross-sectional area. A Joel 8600 'Superprobe' SEM fitted with both the wave length and energy dispersive analysis facilities was used to measure these quantities.

Principle of SEM

The process used in SEM principally involves the generation of a primary beam of electrons from an emission source which are then accelerated by a voltage of between 1-30 keV and directed down the centre of an electron optical column consisting of two or three magnetic lenses. These lenses cause a fine electron beam to be focused onto the specimen surface. Scanning coils made to pass through the corresponding deflection coils of a cathode ray tube so as to produce a similar but larger raster on the viewing screen in a synchronous fashion.

Various phenomena occur at the surface of the sample including secondary electron emission which in this case is used to form the image. There is one-to-one correspondence between the number of secondary electrons collected from any particular point on the specimen surface and the brightness of the analogous point on the cathode ray tube screen. Consequently, an image of the surface is progressively built up on the screen. Some of the electrons are inelastically scattered by the K, L, or N electrons shell in the atom losing their energy in the form of x-rays and it is these which are detected in energy dispersive x-ray analysis (EDAX). The energy lost is characteristic of the scattering atom and intensity is used to establish the concentration of the element. EDAX utilises a solid state detector to measure the x-ray radiation which is more sensitive to elements of higher atomic mass. ED analyzers have been used to detect elements above fluorine (atomic number 9). Problems are encountered when elements whose x-ray energies are too close together coexist in a sample. Other factors limiting light element detection are window thickness and electronic noise.

Wavelength diffractometers (WD) are also available as an accessory on some SEMs. In the WD method, a crystal of known spacing d separates x-rays according to Bragg's law, $n\lambda = 2d\sin\theta$ so that at a diffraction angle of θ (collection angle of 2θ), x-rays of specific wavelengths are detected. To cover the whole range, the diffractometers are usually equipped with many crystals.

(ii) MEASUREMENT OF PROPERTIES OF MULTI-LAYERED COMPONENT

The properties, measured for multi-layered component were toughness, adhesion between the layers and penetration of the sprayed material into softer substrates. The method of measuring these properties are described below.

(ii)a Test for adhesion between different layers

The multi-layer components comprises the layers of 1) WC/Co and aluminium, 2) Nickel chromium alloy and aluminium and 3) WC/Co and nickel chromium alloy.

For adhesion bond strength, tests were carried out according to ASTM C633-79. The shape and dimensions of the sample are shown in Figure 3.2. Since the density of the coating deposited by HVOF thermal spraying process is high, lower thickness than the standard was used to determine the bond strength. The range of coating thickness used was 200 to 300 µm as measured by an optical microscope at different locations of a sample. To measure the bond strength of the sprayed material on aluminium substrate, samples with aluminium substrate were made for bond strength test. The test sample was composed of two parts, one was coated and another was uncoated. The coated sample was made after spraying on one end surface of the cylindrical surface. Materials used for coating were WC/Co and nickel chromium alloy. Standard spray parameters (Table 3.2) were used to deposit these material. To investigate the effect of roughness on bond strength, some of the sample surfaces were roughened and some others were polished before spraying material on sample surface. The uncoated part was roughened to ensure

proper bonding with adhesive. Two cylindrical parts of the sample were attached together by adhesive and the method used for this was described in section 3.5.6. After bonding and cooling the excess adhesive was polished off. A Instron tensile testing machine was used to pull the sample at a cross head speed 0.1 mm per minute.

To investigate the bond strength between different layers of multi-layer component, tensile testing specimens were also made by spraying WC/Co and nickel chromium alloy materials. The end surface of the cylindrical sample made from stainless steel was coated with different layers of the sprayed materials. During spraying these materials standard spray conditions (Table 3.2) were used. The initial layer on the sample substrate was sprayed by WC/Co material and the second layer was sprayed from nickel chromium alloy material. These test samples were fixed by adhesive with another cylindrical specimen as stated before and pull tests were done in similar way as before.

(ii)b Determination of depth of penetration of sprayed particle into aluminium substrate at different substrate temperature

Some of the polished samples were used to determine the depth of penetration of the sprayed particles. These samples are preheated at a set preheating temperature and then the powder material was sprayed. An optical microscope was used to measure the depth of penetration of the spray particle by observing the cross section of the sample.

(ii)c Measurement of toughness of the component

To compare the qualitative toughness of the component formed by WC/Co material and by multi-layer, these components were dropped from different heights on the floor of the laboratory. The component which did not fracture was dropped thrice.

To measure the toughness of the sprayed material of different powders, the toughness was measured on the sample made from these materials by tension test. It is known that the area under the stress strain curve for a material is the toughness of that material. Therefore specimens for tensile test were made from the sprayed material. The shape and size of the specimen are shown in Figure 3.24. This testing of specimen comprised of aluminium substrate of the same shape and size made from aluminium sheet of thickness 1.90 mm. These specimens were machined and positioned on a vice with a support of steel plate at the back. Thermocouples were positioned at the back of the aluminium substrate. Different material were sprayed on different aluminium substrate after preheating the substrate to 450 °C temperature. Material used to spray on the substrate were 1) WC/Co, 2) nickel chromium alloy and 3) a mixed material, made from WC/Co and 40 % by volume nickel chromium alloy. The thickness of the sprayed material on aluminium substrate was varied from 0.3-1.8 mm for nickel chromium alloy material and 0.3-0.5 mm for other two materials. During spraying the WC/Co and nickel chromium alloy material, standard spray parameters (Table 3.2) were used. The mixed materials were sprayed using the spray parameters as of WC/Co material. After spraying, the samples were cooled in atmosphere. Aluminium layer on the gauge length area of the specimen were ground by filing, leaving only with sprayed materials. The shape of the specimen thus formed is shown in Figure 3.24. To avoid a bending effect during tensile loading and to facilitate gripping during loading, a small piece of aluminium of 1.9 mm thick was fixed on the gripping area of the specimen such that the sprayed layer remains between the aluminium layers.

The tension test were preformed on a tensile testing machine (Instron) and with the help of a chart recorder the load-deflection curve was obtained. The cross-head speed maintained was 0.5 mm per minute and the load range was varied for different thickness of the sample, to obtain the accuracy of the measured load. From these measured load- deflection curves the stress-strain curves were plotted. The areas under the curves were calculated by counting the squares of the graph under the curves.











Figure 3.3 Schematic of the printing roll showing the dimension.



Figure 3.4 Photograph of the printing roll.



SIZES	AVERAGE DIAMETER (B+C)/2 mm	DIMENSION A mm	DIMENSION B mm	DIMENSION C mm
SMALLER	21.5	25	20	23
MEDIUM	33.5	30	30	37
BIGGER	48	20	46	50

Figure 3.5 Shape and size of the conical forming core.


Figure 3.6 Cooling rate of the forming core placed in ambient atmosphere.



Figure 3.7 Cooling rate of the forming core in furnace at different condition.





Figure 3.8 Photograph showing the arrangement of the sample and the pyrometer on the lathe.

High Size	Under X	High Size	Under 7	High Size	Under %	H1gh Size	Under %	High Size	Under 7	High S1ze	Under %	Span 1.63
564 524 488 454 422 392 365	100 100 100 100 100 100 100	254 236 219 204 190 176 164	100 100 100 100 100 100 100	114 106 98.6 91.7 85.3 79.3 73.8	100 100 100 99.9 99.9 99.7 99.5	51.3 47.7 44.4 41.2 38.4 35.7 33.2	96.5 95.5 94.4 93.1 91.7 90.2 88.3	23.1 21.4 19.9 18.5 17.2 16.0 14.9	70.6 65.9 61.1 56.3 51.7 47.2 42.6	10.4 9.64 8.97 8.34 7.76 7.21 6.71	20.4 16.9 13.8 11.1 8.9 7.0 5.4	D[4,3] 19.94µm D[3,2] 13.53µm D[v,0,9]
339 315	100 100	153 142	100 100	68.6 63.8	99.1 98.7	30.8	85.9 82.9	13.9	38.0 33.3	6.24 5.80	4.1 3.1	35. 39μm
293 273	100 100	132 123	100 100	59.3 55.2	98.1 97.3	26.7 24.8	79.2 75.1	12.0 11.2	28.7 24.3			D[v,0.1] 8.06μm
Source Focal Preser	e = length ntation	:Sar h = 3 h = p	nple 300 mm 11	Beam Lo Obscu Volur	length og. Dif gration ne dis	= 14 f. = = 0.1 tribut	1.3 mm 3.790 7069 tion	Mode Volun Sp.S.	I 1ndp ne Conc .A 0,	c. = (.4434).0387 % m [*] /cc.	D[∨,0.5] 16.78µm



Figure 3.9 Particle size distribution of tungsten carbide cobalt material powder.

High Size	Under X	High Size	Under %	High Size	Under %	High Size	Under 7	High Size	Under %	High S1ze	Under %	Span 0.76
564 524	100 100	254 236	100 100	114 106	100	51.3	93.6 87.8	23.1 21.4	11.7	10.4 9.64	0.0	D[4,3] 35,51µm
488 454 422	100 100 100	204 190	100 100	91.7 85.3	100	44.4	79.9	18.5	6.2 5.0	8.34	0.0	D[3,2] 31.88µm
392 365 339	100 100 100	176 164 153	100 100 100	79.3 73.8 68.6	100 100 99.9	35.7 33.2 30.8	41.6 33.2	14.9	3.7 2.6 1.6	6.71	0.0	D[v.0.9] 48.88µm
315 293 273	100 100 100	142 132 123	100 100 100	59.3 55.2	99.7 99.0 97.3	28.7 26.7 24.8	25.9 19.9 15.2	12.9	0.8	5.60	0.0	D[∨.0.1] 22.01µm
Source Focal Prese	e = lengt ntatio	:Sar h = : n = p	nple 300 mm il	Beam Lo Obscu Volur	length og. Dif uration me dis	= 14 f. = = 0.7 tribu	4.3 mm 3.678 1659 tion	Mode Volur Sp.S	1 indp me Conv .A 0	c. = 0 .1882	0.0135% m [*] /cc.	D[∨,0.5] 35.42µm



Figure 3.10 Particle size distribution of nickel chromium alloy powder.

High Size	Under X	High Size	Under Z	High Size	Under 7	High Size	Under X	High Size	Under 7	High Size	Under 7	Span 0.37
564 524	100 100	254 236 210	100 100	114 106	100 100	51.3	100 100	23.1 21.4	37.3	10.4	0.0	D[4,3] 24.49µm
400 454 422	100	204 190	100	91.7 85.3	100	41.2	99.8 99.8	18.5	2.4	8.34	0.0	D[3,2] 23.95م
365 339	100	164 153	100	73.8	100	33.2 30.8	99.4 96.8	14.9	0.0	6.71	0.0	D[v,0.9] 29.01 חוג
293 273	100 100 100	132 123	100 100	59.3 55.2	100 100	26.7 26.7 24.8	72.6 54.6	12.0	0.0	5.80	0.0	D[v,0.1] 19.96µm
Source Focal Preser	lengtl itatio	:San n = 3 n = p*	nple 300 mm	Beam Lo Obscu Volur	length og. Dif gration ne dis	= 14 f. = = 0.0 tribut	4.3 mm 4.376 0307 tion	Mode Volur Sp.S	l 1ndp me Conv A D	c. ≃ (.2505	0.0017 % m [*] /cc.	D[v,0.5] 24.34µm



Figure 3.11 Particle size distribution of stainless steel material powder.









CONICAL SHAPE WITH BUILT-IN HOLES

Figure 3.12 Forming cores of different size and shape.



Figure 3.13 Schematic of the cross section of the tube holding pyrometer sensor.



Figure 3.14 Calibration curve for pyrometer.



Figure 3.15 Curve showing the rise of temperature of the forming core per pass of spray at different temperature range for different traversing speed of the gun.



Figure 3.16 Curve showing the rise of temperature of the forming core per pass of spray at different distance of the substrate from the gun at different traversing speed of

the gun.



Figure 3.17 Curve showing the rise of temperature of the forming core per pass of spray for different size (average diameter) at different range of temperature.



Figure 3.18 Curve showing the distribution of the particle in the spray stream for tungsten carbide cobalt material.



Figure 3.19 Curve showing the distribution of the particle in the spray stream for nickel chromium alloy.



Three point bend test mechanism

Figure 3.20 Schematic of bend test sample and three point bend test mechanism.

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Figure 3.21 Schematic of cylindrical forming core with slit used for the residual stress measurement.



Figure 3.22 Picture showing the components made for the measurement residual stress.

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Figure 3.23 Schematically shows the orientation of stress measuring sample as curved beam.



Figure 3.24 Schematic of toughness test sample showing the size and shape.

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Types of gases	Pressure (Bar)	Flow meter reading	Flow rate (SLPM)
Oxygen	10.3	40-44	252-278
Propylene	6.9	35-40	67-77
Gun air	5.2	60-65	415-449
Carrier gas (Nitrogen)	8.6	55	14

Table 3.1 Lighting pressure and flow rate of gases.

Table 3.2 Spray parameters used by HVOF thermal spraying process for depositing differenttypes of materials.

	Types of material				
	Stainless steel	Nickel chromium alloy	WC/Co		
Gun parameters					
Siphon plug	2	2	2		
Shell	A	A	Α		
Gun Insert	3	3	Jetted 2		
Injector	3	3	2		
Air cap	2	2	3		
Spray parameters					
Oxygen pressure(Bar)	10.3	10.3	10.3		
Oxygen Flow (SLPM [*])	265.0	278.0	265.0		
Propylene pressure (Bar)	6.9	6.9	6.9		
Propylene Flow (SLPM)	71.0	74.0	73.0		
Air pressure (Bar)	5.2	5.2	5.2		
Air Flow (SLPM)	318.0	338.0	325.0		
Spray Distance (mm)	200.0	150.0	200.0		
Spray rate (gm/min)	45.0	38.0	38.0		

Table 3.3 Properties of the coating deposited during test run.

Properties	Type of material							
-	Stainle	ess steel	Nickel ch	romium	WC/Co			
0. 1 1	Test	Standard	Test	Stand	ard Tes	t		
Standard	result	value	result	value	result	value		
Thickness (µm)	200-540	-	200-550	-	200-400	-		
Hardness (Hv,0.3)	320-360	350-450	700-840	600-750	1089-1157	1015-1035		
Porosity (%)	0.5	negligible	1.0	negligible	3.0	0.5		
Average roughness Ra (µm)	10.0 *	9-11	8.5	5-10	3.8	2.5-4		
Relative wear	· _	-	-	_	20	-		
Bond strength (MPa)	1 -	-	-	-	70	83		

* Variation of roughnesses for different materials mainly depend on the particle sizes of the powder materials.

 Table 3.4
 Tensile strength of the adhesives at different surface conditions of the testing sample.

Type of adhesive	Surface condition of the test sample	Curing temperature and time	Tensile strength (MPa)
Permabond 109 ESP	Roughened by grit blasting	150°C for 1 hour	81
Permabond 109 ESP	Fine machine finished	150°C for 1 hour	42
Araldite 2005	Roughened by grit blasting	80°C for 15 minutes	40
Araldite 2005	Fine machine finished	80°C for 15 minutes	30

Forming core material	Depositing material	Surface condition of the forming core	Incident angle of the sprayed material	Preheating temp. of the forming core (°C)	Post spray operation	Remarks
Aluminium	Nickel Chromium alloy	Fine machine finished and degreased	80 to 90° with forming core surface	200	Air cooled	The thickness of the deposit was 0.4 to 1.2 mm and it was fractured or stuck with forming surface.
Aluminium	Nickel chromium alloy	Fine machine finished and degreased	80 to 90° with forming core surface	350	Air cooled	The thickness of the deposit was 0.4 to 1.2 mm and in all tests the deposit stuck with forming core surface.
Aluminium	Nickel chromium alloy	Fine machine finished and degreased	80 to 90° with forming core surface	450	Air cooled	The thickness of the deposit was 0.4 to 1.2 mm and in all tests the deposit stuck with forming core surface.
Stainless steel	Nickel chromium alloy	Fine machine finished and degreased	80 to 90° with forming core surface	400	Air cooled	The thickness of the deposit was 0.4 to 1.2 mm. In all test it fractured during cooling. surface
Stainless steel	Nickel chromium alloy	Fine machine finished and degreased	80 to 90° with forming core surface	600	Air cooled	The thickness of the deposit was 0.4 to 1.2 mm. In all tests the deposit fractured.

Table 3.5 Test results of separating sprayed deposit from the forming core without releasing layer.

(continue to next page)

cont. table 3.5

Forming core material	Depositing material	Surface condition of the forming core	Incident angle of the sprayed material
Aluminium	WC/Co	Fine machine finished and degreased	80 to 90° with forming core surface
Aluminium	WC/Co	Fine machine finished and degreased	80 to 90° with forming core surface
Aluminium	WC/Co	Fine machine finished and degreased	80 to 90° with forming core surface
Stainless steel	WC/Co	Fine machine finished and degreased	80 to 90° with forming core surface
Stainless steel	WC/Co	Fine machine finished and degreased	80 to 90° with forming core surface

Preheating temp. of the forming core (^o C)	Post spray operation	Remarks
200	Air cooled	The thickness of the deposit was 0.2 to 0.5 mm and it was fractured or stuck with forming surface.
350	Air cooled	The thickness of the deposit was 0.2 to 0.75 mm and in all tests the deposit stuck with forming core surface.
450	Air cooled	The thickness of the deposit was 0.2 to 0.75 mm and in all tests the deposit stuck with forming core surface.
400	Air cooled	The thickness of the deposit was 0.2 to 0.75 mm. In all tests the deposit fractured during cooling.
600	Air cooled	The thickness of the deposit was 0.2 to 0.75 mm. In all tests the deposit fractured during cooling.

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cont. table 3.5

1.0

Forming core material	Depositing material	Surface condition of the forming core	Incident angle of the sprayed material
Stainless steel	WC/Co	Polished with fine (1200) sand paper	80 to 90° with forming core surface
Stainless steel	WC/Co	Polished with fine sand paper	80 to 90° with forming core surface
Stainless steel	WC/Co	Polished with fine sand paper and grease was applied.	80 to 90° with forming core surface
Stainless steel	WC/Co	Polished with fine sand paper and grease was applied.	20 to 30° with forming core surface *
Stainless steel	WC/Co	Polished with fine sand paper and grease was applied.	30 to 40° with forming core surface *

Preheating temp. of the forming core (^o C)	Post spray operation	Remarks
400	Air cooled	The thickness of the deposit was 0.2 to 0.75 mm and in all tests the deposit was fractured during cooling.
400	Furnace cooled	The thickness of the deposit was 0.2 to 0.75 mm and in all tests the deposit was fractured during cooling.
400	Air cooled	The thickness of the deposit was 0.2 to 0.75 mm and in all tests the deposit was fractured during cooling.
400	Furnace cooled	The thickness of the deposit was 0.2 to 0.75 mm. In all tests the deposit was fractured during cooling.
400	Furnace cooled	The thickness of the deposit was 0.2 to 0.75 mm. In all tests the deposit was fractured during cooling. (continue to next page)

cont. table 3.5 Forming core material	Depositing material	Surface condition of the forming core	Incident angle of the sprayed material	Preheating temp. of the forming core (°C)	Post spray operation	Remarks
Stainless steel	WC/Co	Polished with fine (1200) sand paper	80 to 90° with forming core surface	600	Air cooled	The thickness of the deposit was 0.2 to 0.75 mm and in all tests the deposit was fractured during cooling.
Stainless steel	WC/Co	Polished with fine sand paper	80 to 90 [°] with forming core surface	600	Furnace cooled	The thickness of the deposit was 0.2 to 0.75 mm and in all tests the deposit was fractured during cooling.
Stainless steel	WC/Co	Polished with fine sand paper and grease was applied.	80 to 90° with forming core surface	600	Air cooled	The thickness of the deposit was 0.2 to 0.75 mm and in all tests the deposit was fractured during cooling.
Stainless steel	WC/Co	Polished with fine sand paper and grease was applied.	20 to 30° with forming core surface *	600	Furnace cooled	The thickness of the deposit was 0.2 to 0.75 mm. In all tests the deposit was fractured during cooling.
Stainless steel	WC/Co	Polished with fine sand paper and grease was applied.	30 to 40° with forming core surface *	600	Furnace cooled	The thickness of the deposit was 0.2 to 0.75 mm. In all tests the deposit was fractured during cooling.

* During spraying initial layer this angle was maintained and distance of gun from the forming core was increased upto 300 mm. After depositing initial layer the spray angle was changed to 80 to 90° .

Table 3.6 Test results to separate deposited layer from the forming core through epoxy releasing layer

Material used for releasing layer	Type of metallic material used to mix with epoxy material	Proportion of mixed metallic material (by weight)	Thickness of the releasing layer (mm)	Condition of the sprayed deposit
Epoxy (Permabond ESP 109)	none	-	0.1	Releasing layer eroded
Ероху	none	-	0.25	Releasing layer spalled off without deposition
Ероху	none	-	0.4	Releasing layer spalled off without deposition
Ероху	Aluminium	9	0.2	Deposited layer spalled off after slight deposition
Ероху	Aluminium	50	0.2	Deposited layer spalled off after slight deposition
Ероху	Aluminium	60	0.2	Deposited layer spalled off when it was 0.4-0.5 mm thick.
Ероху	Aluminium	60	0.3	Deposited layer spalled off when it was 0.4-0.5 mm thick.
Ероху	Nickel alloy	9	0.2	Deposited layer spalled off after slight deposition
Ероху	Nickel alloy	50	0.2	Deposited layer spalled off after slight deposition
Ероху	Nickel alloy	60	0.3	Deposited layer spalled off when it was 0.4-0.5 mm thick.
Ероху	Nickel alloy	60	0.3	Deposited layer spalled off when ir was 0.4-0.5 mm thick.

	Types of aluminium powder			
	Metco 54NS-1 (average size 75 µm)	Good fellow (average size 50µm)		
Gun parameters				
Siphon plug Shell Gun Insert Injector Air cap	2 A jetted 2 2 3	2 A Jetted 2 2 3		
Spray parameters				
Oxygen pressure(Bar) Oxygen Flow (SLPM) Propylene pressure (Bar) Propylene Flow (SLPM) Air pressure (Bar) Air Flow (SLPM) Spray Distance (mm) Spray rate (gm/min)	10.3 196.0 6.9 44.0 5.2 269.0 200-300 15-20	10.3 196.0 6.9 44.0 5.2 269.0 200-300 **		

Table 3.7 Spray parameters used by HVOF thermal spraying process for applying aluminium releasing layer.

** No definite spray rate of this powder could be maintained.

Type of material	Ingridients of the material				
Tungsten Carbide/Cobalt	Tungsten Carbide - 88.5 %				
(WC/Co)	Cobalt - 11.5 %				
Nickel chromium alloy	Nickel - 72.0 % Chromium - 17.0 % Silicon - 4.0 % Boron - 3.5 % Iron - 1.0 % Cobalt - 1.0 %				
Stainless steel *	Manganese, Silicon,				
(similar to type 316	Molybdenum, Iron,				
stainless steel)	Nickel, Chromium.				

Table 3.8 Composition of powder materials used for fabricating free standing components.

* The percentage of the ingredients are not known.

Sample Gases F		Flow (SLPM)		Spray	Spray	Hardness	Hardness	Porosity	Porosity
No	Oxygen	Propylene	Air	Distance (mm)	Rate (gm/min)	range Hv,0.3	average Hv,0.3	range %	average %
1	265	73	325	175	38	1140-1190	1160	1.5-2.2	1.7
2	284	73	325	175	38	1135-1170	1155	1.5-1.9	1.7
3	221	73	325	175	38	1160-1215	1185	1.6-2.0	1.75
4	265	84	325	175	38	1165-1220	1187	0.8-1.5	1.3
5	265	67	325	175	38	1100-1145	11156	1.8-2.3	2.1
6	265	73	380	175	38	1160-1200	1182	1.8-2.3	2.0
7	265	73	311	175	38	1140-1180	1157	1.2-1.6	1.5
8	265	73	325	225	38	1020-1075	1049	1.8-2.3	1.95
9	265	73	325	125	38	1270-1320	1294	1.3-1.8	1.49
10	265	73	325	175	23	1190-1220	1210	1.6-2.0	1.85
11	265	73	325	175	50	1115-1155	1130	2.5-3.0	2.6

Table 3.9 Spraying parameters for Tungsten Carbide-Cobalt components and the resultant properties of the components.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

This study is mainly concerned with the fabrication of components by spray forming using HVOF thermal spraying process. However, in the course of establishing the correct method to form these components, a large variety of other experiments were carried out to become familiar with the HVOF thermal spraying process and to know the processing variables that may affect the qualities of the deposited coating. These initial experiments include depositing coatings on mild steel substrates, coating an industrial component (printing roll) made from aluminium and the characterisation of coatings deposited by HVOF thermal spraying process. For these experiments different types of coating materials were used. In this section results of test runs of the spray facilities to deposit coating on different substrate surfaces and the results of tests to fabricate components by spray forming will be presented.

4.2 INITIAL TESTS TO DEPOSIT COATINGS AND THEIR PROPERTIES

Initial tests were performed with three types of coating materials mentioned in section 3.4. The spraying parameters used to deposit these coating were standard values as supplied by the manufacturer (Table 3.2) [68]. The property characterisation of these deposited coatings was performed and the results are presented in Table 3.3. From these results it can be observed that the values of Vicker hardness (300 gm load) were 320-360, 700-840 and 1089-1157 for coatings deposited using stainless steel, nickel chromium alloy and WC/Co materials respectively. The average roughness of coatings deposited by stainless steel, nickel chromium alloy and WC/Co materials were 10, 8.5 and 3.8 respectively. These values of hardness and roughness are in good agreement with the results supplied by the manufacturer [68]. The wear rate of the WC/Co coating was measured (section 3.5.5) and was found to be 20 time less than that of the stainless steel. This result of relative wear test could not be compared with any previously published result because the result of this type of wear test for these coating materials was not available in the literature. However, it can be observed that the wear rate of this coating material is very low as compared with stainless steel. The porosity

levels for all these coating materials were measured on the ground and polished cross sections (section 3.5.4). The porosities for stainless steel, nickel chromium alloy and WC/Co coating materials were about 0.5, 1.0 and 3 % respectively. The porosity levels of stainless steel and nickel alloy were in good agreement with the standard values [68], but the porosity level of WC/Co coating was higher than the given standard value. This might be due to the wrong method of metallographic preparation. Use of silicon carbide paper for grinding the WC/Co specimen might have caused some pull-outs resulting in the development of some artificial porosity of the polished surface [106].

The bond strength of the coatings deposited using WC/Co material has lower than the specified value [68]. The reasons for this lower bond strength value might be due to the difficulty of maintaining the standard conditions during sample preparation. While preparing the tensile test samples, the gun was traversed by hand and the sample remained static. The gun was traversed manually because it has to be traversed at high speed which the installed mechanical handling equipment (lathe) could not do. Yet the traversing speeds maintained by hand during spraying on the tensile test specimens were not sufficient to control the temperature of the substrate during preheating and spraying. For thermal spray process, it is recommended that preheating temperature of the substrate should be about 150 °C. The temperature of the substrate should not rise above 200 °C during spraying. In addition, the temperature of the substrate during spraying should not differ much from the substrate preheating temperature. Due to the small size of the tensile testing specimen (substrate), and the high temperature and heat content of the HVOF thermal spray stream, the temperature of the substrate rises more than 50 °C for every pass of the spray stream. Therefore it was quite impossible to keep the temperature uniform throughout the total spraying operation on the test sample. Moreover, proper positioning of the thermocouple, very near to the substrate surface of tensile testing specimen on which the spray material was deposited, was not possible.

Though the standard procedure was followed during cleaning the substrate, yet the cleanliness of the surface might not be perfect which also affected the tensile bond strength of the WC/Co coating. The cause of the lower tensile bond strength of WC/Co coating deposited on mild steel substrate was not investigated thoroughly, because that

was not an objective of this investigation.

4.3 INITIAL TESTS TO FABRICATE FREE STANDING COMPONENTS

Initial trial for fabricating free standing components was performed by making a forming core of a conical shape (section 3.7.1 and 3.7.2). The powder material of nickel chromium alloy was sprayed on the substrate by using HVOF thermal spraying process. The standard spraying parameters (Table 3.2) were used during spraying this material.

The fabrication process of a free standing component by HVOF thermal spraying can be divided into two steps: 1) deposition of the sprayed materials on any suitable forming core and 2) separation of the deposited layer from the forming core.

During the investigation it was observed that, as long as the temperature of the substrate during spraying remained within some range of the substrate preheating temperature, the deposition of sprayed material on any substrate can be done without causing any fracture of the deposits. For deposition of a thick layer which is required to fabricate components, it is always better that the preheating temperature of the substrate is higher. This is because, during spraying on a substrate by HVOF thermal spraying process, the temperature of the substrate rises upto a certain steady state temperature. This steady state temperature depends on the size and the material of the substrate and on the spray parameters. Therefore, if the substrate preheating temperature is closer to the steady state temperature, the control of temperature of the substrate during spraying is easier. If the substrate preheating temperature is low then interruption of spray during deposition of a thicker layer is essential. This investigation more attention was given to form the component by continuous spraying.

For making free-standing components the forming core must be separated from the deposited material after spraying. Separation of the deposits could be done in two ways: 1) by destroying the forming core after deposition by machining or by melting and 2) by putting a releasing layer which can be leached and/or debonded after deposition.

4.3.1 SEPARATION OF THE DEPOSITED LAYER BY DESTROYING FORMING CORE

Destroying the forming core by machining could cause fracture of the deposit due to the force needed during machining and therefore was not tried as a method of separation. Separation by melting the forming core was performed by making the forming core with lead (section 3.7.1). During spraying the powder material of nickel chromium alloy, the edge of the forming core was deformed due to its low melting temperature and high impact of the sprayed particles. At the same time the impacted particles also penetrated into the core surface and thus the shape of the forming core was deformed. As a result after melting the forming core, the free standing object formed by the deposits collapsed due to non-uniformity of the shape and thickness.

Since repeated use of the forming core should be a criterion for mass production process, separation of the deposits by melting the forming core was not tried with any other material having a low melting temperature like aluminium.

4.3.2 SEPARATION OF THE DEPOSITED LAYER WITHOUT DESTROYING FORMING CORE

Separation of the sprayed deposit from the forming core (without destroying forming core) can be done in two different ways. These are: 1) preheating the forming core and 2) putting a releasing layer between the forming core and the deposit.

(i) PREHEATING THE FORMING CORE

The utilisation of the difference between the coefficient of thermal expansion of the coating material and forming core material is reported [93] for spray forming of cylindrical components by using vacuum plasma thermal spraying. In this work the authors preheated the substrate before spraying the material and, after spraying, the substrate was cooled and then the free standing components were separated. A similar method for separating the deposit from the forming core was investigated in this work

to fabricate components. In this method forming cores of double conical shape, made from aluminium and stainless steel materials were preheated and after that powder materials of nickel chromium alloy and WC/Co were sprayed by using the HVOF thermal spraying process (section 3.7.2).

The preheating temperatures of the substrates were selected from the calculation of the difference in the coefficient of linear thermal expansion of the depositing materials and the core materials. During calculation the average diameter of the core was considered. The curve in Figure 4.1 shows the gap that might be created between the outer surface of the forming core and the inner surface of the deposit upon cooling the core-deposit assembly from different preheating temperatures. The minimum preheating temperature selected for the aluminium forming core during depositing nickel alloy material was 200 °C and, upon cooling, this preheating temperature should create a gap of about 70 µm that might be sufficient to separate the deposit from the core. For WC/Co depositing material and forming core made from aluminium, the minimum preheating temperature of the substrate was selected as 150 °C.

During the tests with the aluminium forming core, it was observed that after spraying and cooling, the deposited layer from the aluminium forming core did not separate and was rather stuck with the forming core. Due to the thermal mis-match the deposited layer for some of the samples were cracked but did not peel off. This may be due to the diffusion of the spray particles with the aluminium core substrate. The preheating temperature of the aluminium forming core was varied from 200-450 °C for nickel chromium alloy material and 150-450 °C for WC/Co material and even then it was found that the deposited layer were varied from 0.4-12 mm for nickel chromium alloy and 0.2-0.75 mm for WC/Co materials but the separation of the deposited layer from the forming core was not possible. The preheating temperatures, thicknesses of the deposit and their conditions for different forming core material are presented in Table 3.5.

A similar trial of depositing both materials on a preheated stainless steel forming

core was also performed. This time the minimum preheating temperatures of the forming core were selected from the Figure 4.1 as 400 °C and 300 °C for nickel alloy and WC/Co material respectively. After spraying the deposit-forming core assembly was cooled in ambient air. The rate of cooling is shown in Figure 3.6. After cooling it was observed that the deposited layer fractured during cooling. This might be due to the strong adherence of the deposited material with the core surface. During cooling the induced thermal stress causes fracture of the deposited layer. The thickness of the deposited layer was varied. When the thickness is less, the deposited layer was fractured into small pieces. With the increase of thickness the pattern of fracture was changed. Figure 4.2 shows a fractured nickel chromium deposited component. The thickness of this fractured component is about 1.1 mm and it was deposited at the preheating temperature of 400 °C on stainless steel forming core.

To reduce the bond strength of the sprayed material with the forming core, the angle of incidence during the spray to form the initial layer on the forming core, was varied. It was reported that the bond strength of the sprayed material reduces with the decrease of the incident angle [107]. After preheating the forming core, the material was sprayed on the forming core with different angles of incidence. The value of the incident angle was varied from 30-45°. In all these experiments the deposited material fractured during cooling. The localised adherence of the deposited material could not be avoided by decreasing the angle of incidence. In addition to the decrease of the angle of incidence of the sprayed material, the surface of the forming core was made non-adherent by putting oily material like grease. A silicone grease whose working temperature is about 300 °C, was applied to make the surface of the forming core non-adherent. However, even the use of both the grease and the variation of angle of incidence could not reduce the adhesion of the sprayed deposit to a value such that the sprayed deposit could be separated without fracture from the forming core with or without preheating.

The rate of cooling might also have an effect on the fracture of the deposit. To investigate the effect of rate of cooling on the separation of the sprayed deposit, the deposit with the forming core was cooled at different cooling rates as shown in Figures
3.6 and 3.7. It was observed that reduced cooling rate did not improve the ease of separation of the deposit from the forming core and it was found that in all these tests, the deposited layer fractured during cooling.

The cause of fracture might be due to the induced thermal stress which developed during cooling the deposit and the forming core. The stress developed during cooling was calculated and presented in Table 4.1. During calculation (shown in appendix A) the inner surface of the deposit was assumed in proper bonding with the outer surface of the core. From Table 4.1 it can be seen that the change of temperature of 100 °C from the equilibrium temperature is sufficient to cause fracture of the WC/Co deposit layer since at this change of temperature the induced stress is sufficient to cause fracture of the deposited layer. From the calculation it is seen that for nickel chromium alloy the change of temperature from equilibrium temperature should be about 300 °C to initiate cracking. However in actual test with nickel chromium alloy the deposited layer was fractured when the temperature difference is about 400 °C. For the above calculation the tensile strength and Young's modulus of the sprayed material were assumed to be one third of the standard value for these materials [50]. Due to the anisotropy of the deposited material the induced stress might differ from the calculated value.

4.3.2.2 SEPARATION OF THE DEPOSIT BY APPLYING RELEASING LAYER

HVOF thermal spraying process is designed for higher density and higher bond strength of the coating. This quality is achieved by increasing the kinetic energy of the spray particle. To achieve this high kinetic energy it needs a huge amount of heat energy which causes the rise of temperature of the substrate very quickly. Higher density of the coating is preferable but for spray forming the bond strength should only be sufficient to let the coating consolidate without cracking. A reduced level of bonding might result in poor thermal contact between the substrate and the coating and hence during the deposition and separation cracking of the deposit is quite likely to occur. From the above it was concluded that the method of separating the deposit from the substrate sprayed by HVOF thermal spraying process might be different from the method of separating the deposit from the substrate sprayed by plasma process [93,94]. Therefore, to separate the HVOF thermal sprayed deposit after spraying on any substrate, a releasing layer might be applied between the deposited layer and the substrate which has the following properties.

- 1) The releasing layer has to withstand the thermal energy of the impacted particle.
- 2) The releasing layer material should be compatible with the depositing material and forming core material.
- 3) The releasing layer must have good adherence with the forming core surface such that proper bonding of the deposit with the forming core is achieved during deposition.
- 4) The releasing layer should be easily leachable or can be de-bonded after deposition.
- 5) The application of the releasing layer on the forming core surface should be easy and the cost of the releasing layer material should be reasonably low.

(ii)a Separation by applying epoxy releasing layer

Considering the above points an epoxy was selected (section 3.7.2) to act as an releasing layer material. After putting a releasing layer of 0.1 mm thickness the material to be deposited was sprayed on the forming core. It was found that build up of deposit, as a continuous layer was not possible. At some locations on the forming core surface, the sprayed material was deposited but over most of the area the releasing layer was eroded. The same test was repeated several times and similar results were obtained. This erosion of the releasing layer by the impact of the sprayed particle might be due to the lower thickness of the releasing layer [92].

Therefore, similar tests were performed with different releasing layer thickness. The result of these tests are tabulated in Table 3.6. From this table it can be observed that at higher thickness of the releasing layer, the formation of the deposit as a continuous

layer was possible. However, after depositing upto certain thickness the formed layer peeled off due to the poor cohesive bonding among the sprayed deposit. Though the applied epoxy can withstand 300 °C temperature and the average temperature of the forming core during spraying was less than 150 °C yet the epoxy might burn out and remain attached with the deposited particle. The deposited material mixed with the burnt epoxy might cause the weaker cohesive strength within the particle of the deposited layer. During spraying, the molten particle with a temperature of about 1300 °C (melting point temperature of nickel) impacts on the epoxy releasing layer surface and penetrates into the epoxy layer. After penetration the particle dissipate heat to the surrounding. Due to the low thermal conductivity of the epoxy the dissipation rate of heat is less and hence the rise of local temperature was such that the epoxy close to the impacted particle burnt out and remained attached with the deposited particle. Therefore cohesive bonding within the sprayed nickel chromium alloy particle was not strong enough to form a component.

To reduce the erosion of the releasing layer and to reduce the penetration of the hot particle into the epoxy layer, an extra aluminium layer on the epoxy releasing layer was made by putting an aluminium foil on the releasing layer surface. It was thought that due to the high bonding strength of the epoxy the aluminium foil should remain bonded with the forming core surface and might reduce the penetration and erosion of the releasing layer. During spraying nickel chromium alloy material on the forming core, the aluminium foil helped to reduce the penetration of hot particle into the epoxy layer and initiated deposition of sprayed material as a continuous layer. However, the rise of temperature of the foil was so quick and so high that the epoxy lost its bonding with the aluminium foil. Due to the impact of the deposited particle and the high velocity force of the HVOF spray stream, the deposited layer fractured and spalled off along with the aluminium foil.

To improve the cohesion between the sprayed deposit and to increase the dissipation of heat of the sprayed particle, a mixture of metallic powder and epoxy was used to put a releasing layer. The methods of applying this mixed layer were described in section 3.7.2. After applying about 0.2 mm thick releasing layer, nickel chromium

alloy material was sprayed on the forming core and it was found that the deposition and growth of a continuous layer of the deposit was better than before. However, when the thickness of the deposited layer reached about 0.4-0.5 mm, the layer spalled off. Different thicknesses of the mixed releasing layer were applied on the forming core to see its effect on the separation of the deposited layer from the substrate. The results of these tests are tabulated in Table 3.6. The increased thickness of the mixed releasing layer did not provide sufficient cohesive bonding within the deposited material particles and therefore ultimately the deposited layer spalled off.

It was observed that the mixed releasing layer could only reduce the penetration of the sprayed particle but could not prevent the burning of the epoxy material surrounded by the sprayed molten particle. The heat transfer rate from the sprayed particle was not sufficient to prevent burning of the epoxy materials. Therefore increased amount of metallic material was mixed with the epoxy and applied as a releasing layer on the forming core surface. Similar tests were carried out. The proportion of the metallic material in the epoxy mixture was varied from 9-60 % (by weight) of the total. The nickel chromium alloy material was also used to mix with epoxy such that the sprayed nickel chromium alloy might get bonded easily with the same material present in the releasing layer. The increased amount of metallic material could only delay the fracture of the spray deposit during spraying but did not assist in forming a free standing object. The addition of nickel chromium alloy with the releasing layer epoxy did not improve the situation. This might be due to the formation of a thin boundary layer of the epoxy between the mixed releasing layer and the surface of the forming core during curing of the releasing layer. Due to this thin epoxy layer the conduction of heat from the deposited material to the forming core body was not sufficient as the releasing layer acts as an insulator to heat conduction. It was observed that powder of metallic material mixed with the epoxy was not in good contact with the forming core surface.

Therefore it was concluded that the releasing layer should also have the following properties in addition to the properties stated before.

- The releasing layer should dissipate heat from the sprayed particle very quickly such that the local rise of temperature can not cause burning or vaporising of the releasing layer material.
- 2) The layer should have proper bonding with the substrate throughout the whole spraying operation and at elevated temperature the bonding should be sufficient to absorb impact of the sprayed material.

(ii)b Separation by applying metallic releasing layer

Considering the above properties of the releasing layer it was concluded that a metal to metal contact between the releasing layer material and the forming core is required for proper conduction of heat from the sprayed particle to the forming core. Metal powder of lower melting temperature may act as a releasing layer if that can be applied on the forming core with proper adhesion. After spraying the material with which the component will be made, the releasing layer might be melted out or debonded by some means to separate the deposit from the forming core.

The probable low melting temperature metal powders are tin and aluminium. Considering the availability, ease of application and economy, aluminium was selected to be used as a releasing layer. Commercially available aluminium powder (section 3.7.2) for thermal spraying was procured and used for putting the releasing layer by spraying with HVOF thermal spraying process though it is not recommended by the vendor to spray by this thermal spraying process.

Aluminium powder was sprayed on double cone shaped forming core to a thickness of about 0.15 mm (section 3.7.2). Nickel chromium alloy material was then sprayed on the aluminium coated forming core after preheating it. The preheating temperature of the forming core was about 100 °C. During spraying it was observed that there was no problem of formation of the deposited layer. After spraying, the deposit-forming core assembly was cooled in air and then transferred to the furnace to heat the assembly for melting the aluminium releasing layer. During heating, when the temperature of the forming core was about 550-600 °C, the deposited layer cracked which was evident from some fine cracking line on the deposited layer surface. The cause of cracking might be due to the mismatch of thermal expansion of the depositing material and the forming core material. To reduce the mismatch during heating, further test was performed by preheating the forming core to a higher temperature. When the preheating temperature of the forming core was about 300 °C, the depositing material was sprayed such that the temperature of the forming core lies between 250-400 °C. After deposition and cooling, the forming core with the deposit was transferred to the furnace and heated upto 700 °C. At this temperature, it was observed that the aluminium releasing layer melted and the molten aluminium was coming out through the gap between the deposited layer and forming core surface (Figure 4.3). After cooling the deposit-forming core assembly, it was found that the deposit did not fracture but remained attached with the forming core with solidified aluminium. During cooling, the forming core with the deposit was in the furnace. The gap between the deposit layer and the forming core was not sufficient so that all the molten releasing layer could not come out and some of it remained stuck in between the deposited layer and the forming core surface. Therefore after cooling, the molten aluminium solidified and bonded the deposit with the forming core surface. Further tests were carried out keeping all the process parameters the same as before and attempt was made to separate the deposit when the releasing layer was in molten state. While separating the forming core from the deposited layer (when they were hot) it was observed that the deposited layer was not separating. This was due to the fact that the edge of the sprayed deposited layer was sightly overlapped the edge of the forming core. Without cleaning this overlapped material it was not possible to separate the forming core from the deposited layer when both were at high temperature.

Similar tests were carried out by varying the aluminium releasing layer thicknesses, the preheating temperature of the forming core, the post heating time and the temperature to meltout the releasing layer for the separation of the deposit. The results of these tests are presented in Table 4.2. Eventually it was found that when the releasing layer thickness was about 0.12 mm thick and the preheating temperate was 350 °C, a free standing component could be separated without causing any crack. Figure 4.4 (b) shows the photograph of the double cone shaped free standing component made from

nickel chromium alloy. The thickness of the formed component was 0.9 mm. The temperature to heat the deposit-forming core assembly, required for separation after spraying was 700 °C and the time of heating was about 20 minutes. After post heating, the sample was cooled in the furnace (closed condition Figure 3.7). It was found that during this post heating at this temperature the aluminium releasing layer was not melted out but became a powder-like material which did not have adhesion neither with the deposited layer nor with the forming core surface. During the post heating, the aluminium releasing layer may have reacted with the surrounding material and became a non-adherent powder. The spray forming process of the free standing component made from nickel chromium alloy is shown by a curve in Figure 4.5. This curve shows the variation with time of the temperature of the forming core during the fabrication of spray formed component. The fabrication process comprises of preheating, spraying, handling to transfer the forming core into the furnace, post heating required for separation and cooling.

Tests to fabricate components with different materials were performed by the same method as of fabricating the component of nickel chromium alloy. The materials used were stainless steel and WC/Co. With the similar procedure, as used for fabricating the nickel chromium alloy material component, fabrication of stainless steel component was also possible. Figure 4.4 (c) shows the doubled cone shaped spray formed stainless steel component. The thickness of this component is 1.2 mm. The preheating and post heating temperature required to fabricate this component was 350 °C and 700 °C respectively. The time required for post heating was about 20 minutes. The thickness of the releasing layer was about 0.1 mm. While depositing this material the spraying parameters used were as per standard (Table 3.2) except the flow rate of the powder material. To obtain a thicker layer of deposit quickly, higher flow rate (50 gm/minute) was used during depositing this material. However, with the similar process, the fabrication of WC/Co component was not possible. Tests to fabricate component with WC/Co material were performed by varying the aluminium releasing layer thickness, the preheating temperature of the forming core, the temperature of the forming core during spraying, the cooling before putting into the furnace for post heating needed for separation, and the temperature and time of post heating the deposit-forming core assembly. Spray parameters used were as per standard except the flow rate of the powder material. For this material a flow rate of 50 gm/minute was used during depositing this material on the forming core surface. From the calculation of induced stress in the sprayed WC/Co deposit during cooling (Table 4.1), it was ascertained that before complete separation of the deposited layer from the forming core surface, the deposit will fracture if the temperature of the deposit-forming core assembly goes 100 °C below the preheating temperature. Therefore, it was obvious that cooling after spraying and before separation of the deposit from the forming core surface must be avoided for this material. For different combinations of above said variables, the fabrication of WC/Co component was possible. Figure 4.4(a) shows the WC/Co double cone shaped component of 0.5 mm thick. The thickness of the releasing layer was about 0.1 mm and the preheating and post heating temperatures used for this component were 450 °C and 670 °C respectively. Post heating time was about 20 minutes and cooling was performed in the furnace. After spraying, the forming core with the deposited material was transferred as quickly as possible such that the temperature drop during handling was less than 50 °C from the preheating temperature. This temperature can be easily maintained by heating the deposit-forming core assembly to a higher temperature before finishing the spraying of the material. The curve in Figure 4.6 shows the temperature and time at different steps of fabrication process of WC/Co component. This curve is similar to the curve used for fabrication of nickel chromium alloy component except the handling time required to transfer the forming core into the furnace after spraying.

Using similar process, a number of components of double cone shaped were formed to measure the properties of the free standing components of different materials.

4.4 PROPERTY CHARACTERISATION OF FORMED COMPONENTS

The spray formed components are not entirely free from porosity. The level of porosity was measured on polished cross-sections using an image analyzer (section 3.5.4). Figures 4.7(a)-4.7(c) show the micrographs of the free standing components made from different types of materials. Several readings were taken to obtain an average value of the porosity. The hardness of the samples was measured with a Vickers hardness tester

under a load of 300 g on the polished cross-sectioned surfaces of the components (section 3.5.2). Roughness of the as sprayed free standing objects was measured (section 3.5.3) at both the outer and inner surfaces.

The average porosity level found for those components made from WC-Co composite was 4% (Table 4.3). The average porosity of Nickel Chromium alloy component was less than 1% while that of stainless steel component was less than 0.5%. The hardness value of the component (Table 4.3) made from WC-Co varies between 1106-1249 (HV 0,3) with an average value of 1189. The hardness of nickel base alloy and stainless steel components varies between 736-982 (HV 0,3) with an average value of 848 and between 394 to 448 (HV 0,3) with an average value of 412 respectively. The average roughness of the inner surface for WC-Co components varies between 1.9 to 8.35 μ m (Table 4.3) and for the outer surfaces of the components made by Nickel base alloy and stainless steel powder were 3.2 and 9.3 microns, and 3.0 and 7.8 microns respectively.

Comparing Table 3.3 and Table 4.3, it can be observed that the porosity level for the components made from WC-Co was 1 % higher than the porosity of the coating deposited on a substrate with the same material by the same process during the initial test. This may be due to the higher flow rate of the powder used for the fabrication of free-standing objects. But the porosity level of the components made from Nickel chromium alloy was less than 1 % and the porosity of stainless steel component was less than 0.5 %. From this observation it is quite clear that components with very low porosity can be made by using HVOF process. The hardness values of the components are higher than the normal value of the coatings deposited on a substrate from the same powder by using the same process. The increased hardness might be due to the higher from the same processing temperature which may cause some oxidation of the sprayed material during fabrication.

4.5 FABRICATION OF SPRAY FORMED COMPONENTS AND IDENTIFICATION OF PROCESSING VARIABLES

The HVOF thermal spraying process was used to fabricate components of different size and shape. Three types of material were used to fabricate these components. The process variables were as described earlier. The components thus formed are presented in Figures 4.8-4.10. In Figure 4.8 components made from nickel chromium alloy are presented. In this Figure three conical components of differing size and one cylindrical shape are shown. In Figure 4.9 three conical components of different size and of cylindrical shape component made from stainless steel are shown. In Figure 4.10 similarly shaped components made of WC/Co material are presented. The processing variables used in the manufacture of all these components are presented Table 4.4.

From these figures it is clear that thin walled near net-shaped free standing components of different sizes can be made by using HVOF thermal spraying process. The processing variables for different material are different. The processing variables which might affect ease of fabrication are as follows.

1) The material of the forming core.

- 2) The size of the forming core.
- 3) The roughness of the forming core surface.
- 4) The preheating temperature of the forming core.
- 5) The equilibrium of the temperature of the forming core during deposition.
- 6) The thickness of the inter-layer.
- 7) The post heating temperature, time and rate of the deposit-forming core assembly after deposition for the separation of the deposit.

- 8) The cooling rate of the deposit-forming core assembly after post heating.
- 9) The variation of the properties of the component made from WC/Co material with the spraying parameters.

4.6 EFFECT OF PROCESSING VARIABLES

To determined the effect of process variables on the manufacturability of the components a particular shape of the forming core was selected to measure all the processing variables. The conical forming core of average diameter 33.5 mm shown in Figure 3.5 was selected. This was chosen because of the ease of separation of the deposit from the forming core. Special attention was given to the processing variables for fabricating component from WC/Co material.

4.6.1 EFFECT OF THE FORMING CORE MATERIAL

Conical forming cores of average diameter 33.5 mm (Figure 3.5) were made from D2 steel, stainless steel 316L, copper, mild steel and aluminium. These forming cores were used to investigate the effect of the forming core material on the fabrication process. It was found that the forming cores made from aluminium were unsuitable due to the fact that for the pre-heating and post heating temperatures the aluminium based releasing agent gets bonded with the core and causes fracture of the deposited components. The copper made cores were found to be satisfactory for the production of components. However, a problem was encountered in measuring and hence controlling the temperature while spraying. With the rise of temperature, copper oxidised and changed its surface colour so rapidly that it was very difficult to measure the temperature using the pyrometer. Therefore, continuous measurement of temperature was not possible. From time to time during the fabrication of the components, the temperature of the forming core was measured with the help of a thermocouple by interrupting the spraying operation. Between these intervals the temperature of the forming core was assumed to remain within the measured values. Cores made from D2 steel, stainless steel and mild steel were also found to be satisfactory except that due to the oxidation, the life of mild steel core was found to be short. The property of the forming core material which most affects the fabrication of the spray formed objects is the coefficient of thermal expansion. The preheating temperature of the forming core depends on the coefficient of thermal expansion of the material of the forming core (Figure 4.11). The curve in Figure 4.11 shows that with the increase of the coefficient of linear thermal expansion the minimum preheating temperature increases. The range of preheating temperature for these forming core materials is shown in Figure 4.12. From the graph it is shown that for every forming core material of a definite size, there are three different zones of the preheating temperature. When the preheating temperature lies within the lower zone of the bar graph the deposit will fracture during the post heating needed for the separation of the deposit. When the preheating temperature lies within the middle zone of the bar graph there is some chance of fracturing of the deposited material during post heating. This may be due to the directional inhomogeneity resulting anisotropy within the deposited material. This inhomogeneity of the deposited material is a characteristic of the sprayed deposit and might be due to the inclusion of porosity, foreign impurities and oxides. When the preheating temperature of the forming core lies within the upper zone, it is quite likely that free standing components will be formed successfully unless other factors cause fracture of the deposited components.

4.6.2 EFFECT OF SIZE AND SHAPE OF THE FORMING CORE

Figure 4.13 shows the effect of the size of the forming core on the preheating temperature of the forming core. These results are for a forming core made from stainless steel 316L and for making of WC/Co component. From Figure 4.13 it is seen that the minimum preheating temperature for obtaining WC/Co component decreases linearly with the average diameter of the forming core. In this Figure, two zones are shown, one indicates the safe operation zone i.e zone 1. When the preheating temperature lies within the other zone (zone 2), it is uncertain whether a component will be formed successfully or not. When preheating temperature lies below the temperature indicated by zone 2, fracture of the deposited layer during post heating is likely to occur.

Figure 4.14 shows a photograph of different sizes and shapes of some components made from WC/Co material. The sizes, thickness and spray parameters for fabrication of these component are presented in Table 4.5.

4.6.3 EFFECT OF THE ROUGHNESS OF THE FORMING CORE SURFACE

The roughness of the forming cores was varied by grinding the surface using sand paper and by grit blasting. Table 4.6 shows the effect of surface roughness of the forming core on the roughness of the spray formed component. From Table 4.6 it is observed that though the average roughness of the forming core is 0.83 and 4.7 μ m due to grinding and grit blasting respectively, after applying a releasing layer the average roughness changes to 4.2 and 4.0 μ m for ground and grit blasted surface respectively. The average roughness of the inner surface of the formed components using these two forming cores was 2.92 and 3.16 μ m, and for outer surface was 3.98 and 3.72 μ m. During deposition, due to the preheat temperature of the forming core and the impact of the deposited material, the sprayed material penetrates into the interlayer and therefore the roughness of the inner surface does not depend on the roughness of the surface of the forming core. The roughness of the outer surface is mostly governed by the size of the sprayed powder particles, and is unlikely to depend on the roughness of the forming core surface.

However, the roughness of the forming core surface does have some effect on the fabrication process of the component. The releasing layer, which was deposited by thermal spraying using HVOF thermal spraying process should have proper adhesion with the forming core surface. Roughening and cleaning the forming core surface increases the bond strength of the sprayed releasing layer which helps the deposition of spray formed object during spraying. It was observed that a smooth surface and improper cleaning of the forming core resulted in the fracturing of the spray formed component during spraying. This might be due to the improper bonding of the releasing layer with the forming core. This test was performed using a cleaned and roughened forming core surface was about 4.7 µm. During fabrication of the first component, using this

forming core, the deposited layer was not fractured. During making a second component with the same forming core, the forming core was not cleaned. Keeping all the fabricating conditions constant it was not possible to obtain a component as during spraying the deposited layer was fractured. The same forming core was used for a third time. This time the forming core was cleaned by only sand paper which cleaned the surface but reduced the roughness. This time the roughness of the forming core surface was about 1.9 µm and the formation of a component without fracture was possible. When the same forming core surface was polished to a surface average roughness of less than 1.0 µm the deposited layer fractured during spraying. During the deposition all other parameters were identical. Similar results were obtained after repeating the same procedure thrice.

4.6.4 EFFECT OF PREHEATING TEMPERATURE OF THE FORMING CORE

The preheating temperature of the forming core is one of the critical factors which influences the ease with which the component may be released from the preform as illustrated in the Figure 4.15. When stainless steel material was sprayed on to a stainless steel core a preheating temperature of less than 200 °C (for a core with 33.5 mm average diameter) led to high releasing load to separate the components from the core and as a result fracture of the deposits occurred during separation. The separation load increases with the decrease of preheating temperature and the core size (average diameter). When the preheating temperature is more than 300 °C, the deposition and releasing of the component made from stainless steel with a stainless steel or mild steel core can be achieved with ease. The maximum preheating temperature attempted was 600 °C, beyond that, the releasing agent applied is dispersed from the surface of the core during spraying due to the high velocity of the flame. The safe range of the preheating temperature for a nickel chromium alloy component (for 33.5 mm diameter core size) is 350 °C to 600 °C. For the preheating temperature lower than 250 °C there is every chance of fracture of the component occurring during either the deposition or the post heating stages. The preheating temperature of between 350-250 °C is an overlapping zone where a component may or may not be formed. For Tungsten carbide components of similar size, the safe preheating temperature range is 425-550 °C. Above this temperature there is evidence of fracture which may be attributed to oxidation and formation of very brittle tungsten oxides during spraying and/or reduction of bond strength of the releasing agent with the core. With the increase of the preheating temperature for WC/Co deposits, the chance of oxidation increases and this could be observed by the colour change of the deposits on the core. At temperatures lower than 400 °C the deposits fracture during post heating. This may be due to the lower coefficient of thermal expansion of tungsten carbide composite in relation to the coefficient of thermal expansion of the core material. The preheating temperature range of 400-425°C for stainless steel cores sometimes leads to fracturing of the deposits.

4.6.5 EFFECT OF TEMPERATURE OF THE FORMING CORE DURING SPRAYING

The temperature of the forming core during spraying has a significant effect on the manufacture of the free-standing components made from WC/Co material. However, for the other two materials it has almost no effect as long as it is maintained at or above 300 $^{\circ}$ C of the preheating temperature before releasing from the core. For the carbide components large deviation of the spraying temperature from the mean spraying temperature during spraying causes fracture of the free-standing component. During spraying the WC/Co material, if the temperature of the forming core rises about 425 $^{\circ}$ C, a light brown colour appears on the surface of the deposit which shows the formation of lower carbides such as W₃C, which is very brittle and has higher hardness than WC. With increasing temperature of the forming core this light brown colour changes to deep brown and after that into pink. This change of colour shows the increasing amount of lower carbide in the sprayed deposit. With the increased amount of lower carbide the chance of fracturing the deposited layer increases. A careful control of the temperature of the forming core during spraying to around 425 $^{\circ}$ C reduces the amount of lower carbide formation.

Therefore, during spraying of carbide material, the distance of the gun and the traverse of the gun need to be adjusted such that the temperature rise (Figures 3.15-3.17) during spraying can be better controlled. Otherwise during deposition the deposited layer might fracture. If the size of the component is small the adjustment of the distance

of the gun from the core and the gun traverse is not sufficient to control the spray temperature. In that case the equilibrium of temperature is maintained by interruption of spray or by forming more than one component during a given spraying operation.

Depending on the size and material of the component there are some optimum ranges for gun traverse, gun distance from the core and the number of the components being formed at a time, provided that the spray condition such as the flow of different gases to the gun remains the same. It is preferable that the spraying temperature is kept within \pm 50 °C of the preheating temperature for carbide component. For other materials it can be widely varied. From Figures 3.15-3.17 it is seen that at a traverse speed of 3 mm per rotation the rise of temperature for one pass of spray is fairly uniform at higher temperature. The distance of the core from the gun should be maximum, however, higher distances might reduce spraying efficiency and hardness, and increase porosity for WC/Co material. As such a traverse speed of 3 mm per rotation was chosen for all the materials and the spray temperature was controlled by forming two samples for each of the smaller and medium size cores and one sample for the bigger size core for single spraying operation.

4.6.6 EFFECT OF AIR COOLING TO CONTROL THE TEMPERATURE OF THE FORMING CORE DURING SPRAYING

Extra air cooling can be used to cool the forming core in order to control the temperature to within reasonable limits during spraying. However, it was observed that due to the increased flow of cooling air the amount of formation of lower carbide on the deposited material increases and the increased amount is seen by the change of colour of the deposits. Increased amount of cooling air also causes the fracture of the deposited component. The cause of fracture may be due to the increased amount of brittle lower carbides or due to the thermal mismatch of the deposit and the forming core. The cooling air can cool the outer surface of the deposit rapidly but not the forming core. Therefore due to air cooling, the thermal mismatch between the deposit and the forming core is more which might cause fracture of the sprayed deposit.

The change of colour of the sprayed WC/Co deposit can be used as an indication of the temperature of the deposit-forming core assembly and thus supplies a means to control the temperature of the forming core during fabrication. Figure 4.16 shows the temperature of the sprayed deposit and the colour of the deposit. With the increase of temperature the colour of the deposit changes from grey to light brown, brown, pink, bluish grey and then light blue. This change of colour is very distinct and can easily be recognised during spraying.

4.6.8 EFFECT OF POST HEATING RATE, TEMPERATURE AND TIME

The post heating temperature and soaking time of the core together with the deposit are very critical on the ease of separation of the component from the core. The rate of heating of the deposit-forming core assembly was varied and this is shown in Figures 4.17 and 4.18. From Figure 4.17 it is shown that the time of heating of the depositforming core assembly from temperature 400 °C to 680 °C varies from 5-27 minutes. Figure 4.18 shows that the time required to heat the deposit-forming core assembly from temperature 500 °C to 680 °C varies from 3-24 minutes. It was found that the heating rate does not have significant effect on the ease of separation of the free-standing component from the core. Figure 4.19 shows the effect of forming core temperature on the ease of separation of the deposit. This Figure, drawn on the basis of about 100 tests on the carbide components, shows that for post heating temperatures below about 600 ^oC the deposit can not be separated without causing fracture. Also, if the temperature is higher than about 675 °C there is every possibility that the deposit will crack due to excessive oxidation and thermal expansion mismatch during post heating. It is also true that with increasing temperature the amount of oxidation for the carbide component increases but it is reasonably low at about 600 °C. For the other two materials the post heating temperature is between 625 °C to 750 °C.

The effect of post heating at different temperatures can be increased by increasing the heating time. Figure 4.20 shows the effect of time and temperature of the post heating on the separation of deposits with different releasing layer thickness. If the releasing layer has a higher thickness the separation of the deposit from the forming core can be performed by heating the deposit-forming core assembly at a given temperature for a longer time. If the thickness of the releasing layer is 60 µm and the post heating temperature is 670 °C the time required for separation of the deposit is about 3 minute. With the same releasing layer thickness if the post heating temperature is 600 °C the time required to separate the deposit is about 15 minute.

4.6.9 EFFECT OF COOLING RATE

The cooling rate of the deposit-forming core assembly also has significant effect on the process, particularly for the carbide components. Figures 3.6 and 3.7 show four different cooling rates used to fabricate components. Figure 3.6 shows the cooling rate of the forming core when it is placed in air with and without forced flow of air. Figure 3.7 shows the cooling rate of the forming core when it is placed in the furnace with the door closed and when partially opened. When the core deposit assembly was cooled by forced air, in all tests the deposited layer of WC/Co material fractured due to higher temperature difference between the deposited layer and the inner core. Components of the other two materials also could not be cooled with forced air but they are not as sensitive as the carbide components as some times these components were formed successfully after cooling with forced flow of air. Slower rates of cooling are preferable for the successful manufacture of the component but longer time in hot environment increases the chance of oxidation and formation of lower carbides for the carbide components. Therefore, it is better to cool in the air without any forced flow. To avoid oxidation or formation of lower carbide, a controlled atmosphere post heating and cooling is advisable for the carbide component.

A nitrogen atmosphere post heating was attempted to reduce the oxidation and formation of lower carbide of the carbide components. However, the nitrogen atmosphere could only reduce the amount of formation of lower oxide but could not stop the formation of lower carbides. The reduction in the amount of carbide formation was identified by the change of colour of the formed components.

4.6.10 EFFECT OF RELEASING LAYER THICKNESS

The thickness of the releasing agent has no significant effect on the deposition of the component materials on the surface of the core as long as it has proper bonding with the forming core surface. However, it influences the ease of separation of the component from the core. Figures 4.19 and 4.20 show the effect of the releasing agent thickness for WC/Co components. If the thickness of the releasing agent is too low the deposit will stick with the core at some places and when attempting to separate the component, the stuck area will cause fracture of the total component due to residual stress generated for thermal mismatch and for partial releasing of the component. If the releasing agent is not uniformly applied some local area may also get bonded causing localised fracture (Figure 4.21) or complete fracture of the component. This was prominent when the releasing agent thickness was less then about 55 micron. If the releasing agent is too thick the deposit will crack for all materials. This releasing agent works on the principle that at a certain temperature it oxidises and/or reacts with the surrounding materials and becomes non-sticking interlayer and thus allows the deposit to separate from the core. It was also found that the longer the post heating duration the surer is the safe separation of the deposit from the core. Thus, the critical range of the thickness of the releasing agent can be widened by adjusting the post heating temperature and the soaking time. But too thick a releasing agent can not be made fully non-sticking. In that case the releasing agent sticks with both the preform and the component surfaces causing fracture of the components.

4.6.11 EFFECT OF DIMENSION OF THE FABRICATED COMPONENT ON THE PROCESSING PARAMETERS

During the fabrication of the component the sprayed layer of the deposit is in close contact with the outer surface of the forming core, so that the inner diameter of the formed component should be equal to the outer diameter of the forming core during spraying at high temperature. After cooling the deposit-forming core assembly and due to the releasing layer, a gap is created between the inner surface of the formed component and the forming core. Therefore, the inner diameter of the cooled spray formed component is a little greater than the outer diameter of the forming core. While making a forming core for fabricating a component of certain specified inner diameter, an allowance for this dimensional change during fabrication is to be subtracted from the outer diameter of the forming core. This correction for diameter of the forming core depends on the material and the dimension of the forming core, and the releasing layer thickness. Figure 4.22 shows the diametral allowance that should to be subtracted from the diameter of the forming core during fabrication of the forming core for forming a component of specified inner diameter. The effect of the releasing layer thickness on the gap created upon cooling the deposit and forming core could not be measured due to the lack of proper control of the thickness of the releasing layer and the absence of exact coefficient of thermal expansion of the sprayed material.

4.6.12 EFFECT OF TRAVERSING VELOCITY ON FORMING COMPONENT

During the fabrication of components of longer length, the control of the uniformity of temperature during spraying is very important. This is because during spraying at one end of the forming core, the other end cools down due to the induced flow of the spray stream and hence fracturing of the sprayed deposit is quite likely. This problem of the difference in temperature along the length of the forming core can be reduced by traversing the gun very fast. Figure 4.14 (g) shows a component of cylindrical shape of 85 mm length and 0.92 mm thick. The number of passes per minute of spray used was about 200 or more.

The resulting thickness of the component made following this procedure was found to be non-uniform. The formed component has higher thickness at the two ends than that at the middle. This variation of thickness is about 0.1 mm for the component shown in Figure 4.14 (g). This arises due to the non-uniform velocity of traverse of the spray gun. For a lateral to and fro motion, the velocity of the traversing unit at the two extreme points of traversing length is zero and at the middle it has the maximum velocity. As the spray gun has a lateral to and fro motion during deposition, it deposits less material at the middle portion of the forming core and deposits more material at the two ends. This is more prominent when the motion of the spray gun was controlled by hand. When the motion of the spray gun was controlled by the traversing unit of the lathe, the variation of the thickness was less and this is due to the manner in which the direction of motion of the traversing unit of the lathe was changed. As the lathe is semi-automatic, the change of direction of motion is done manually. This non-uniformity of thickness can be controlled by traversing the spray gun even at greater length then the forming core such that when changing the direction of the traversing unit the spray is directed out beyond the forming core. Note that spraying beyond the forming core will reduce the efficiency of deposition of spraying materials.

4.6.13 OTHER EFFECTS

During fabricating components of different shape and size it was observed that every individual shape and size has some aspects which need careful attention while making these components. Some of these aspects are described below.

(i) FABRICATION OF COMPONENT WITH BUILT-IN HOLE/HOLES

Two methods were used to fabricate the components with built-in hole/holes (section 3.8.6). In the first method, where a cylindrical insert (plug) was used to create a hole, the extended portion of the rod creates a shadowing effect such that the sprayed material could not deposit on some areas very near to the edge of the hole. Therefore the shape of the hole was not uniform. This non-uniformity and sticking of the deposit to the surface of the cylindrical insert causes fracture of the formed component during separation. In the second method, when the sprayed material was allowed to pass into the hole and deposit inside the hole, the fabrication of the components with built-in hole/holes was possible. However, in this method the edges of the holes were overlapped by the sprayed deposit which created a problem in separating the deposit from the forming core. After post heating and cooling, the edges of the holes should be cleared before complete separation of the components from the forming core. Figure 4.23 shows two components made from WC/Co materials having single and multiple hole. All holes are 5 mm diameter.

(ii) FABRICATION OF COMPLEX SHAPED COMPONENTS

Figure 4.24 shows components having concave and convex curvature. In this Figure three components are shown. These are made from nickel chromium alloy, stainless steel and WC/Co material as designated in the Figure as (a), (b) and (c) respectively. These are made using the collapsible forming core (section 3.8.6). As the collapsible core is made from some small pieces, there is some discontinuity of the surface. If there is a gap between the mating pieces of the forming core, the deposited layer may crack along that line while spraying and ultimately cause fracture of the components. This is very critical for the carbide components. Gaps of about 100 micron width were made intentionally between the mating pieces and attempts were made to form the components. These attempts were unsuccessful as the components fractured. An aluminium metal putty was then used to fill the gap and from there on the use of the collapsible core caused no problem. An increased gap of 200 micron with filler metal putty was attempted in a similar manner but did not work because the relevant area could not withstand the temperature and failed to transfer heat adequately and hence the releasing agent on that area peeled off.

4.7 FABRICATION OF MULTI-LAYER COMPONENT

Components formed by spray forming of WC/Co material were found to be brittle in nature and require extreme care during handling. To increase the toughness of the carbide component, tests were performed to put an extra layer with a tougher material. This was done in two ways (section 3.8.6), (1) by putting a toughening layer on the WC/Co component and (2) by forming a component with the WC/Co material on a tougher material such that the deposited WC/Co material has proper adhesion with the forming core. Therefore, a spray formed component can be made with WC/Co or any material as inner hard layer with an outer tougher layer or can be made with an outer hard layer with a inner tougher layer.

During the fabrication of carbide components, after spraying WC/Co materials, nickel chromium alloy material was sprayed as an extra layer before post heating. During spraying and post heating there was no fracture of the deposit. After post heating, during cooling the total deposit fractured. The cause of fracture may be due to the mismatch of thermal expansion of the layers of different materials. The thickness of the inner carbide layer was varied from 0.2 mm to 0.5 mm and the thickness of the outer nickel alloy layer was also varied from 0.1 mm to 0.8 mm. When the outer layer was of lower thickness the component fractured into small pieces while for a thicker outer layer the pattern of fracturing was different (Figure 4.25).

Spraying extra layers was tried after complete separation of the component from the core former. Due to post heating, the outer surface of the separated component made from carbide material is oxidised. Therefore the surface of the component was cleaned with sand paper and then aluminium was sprayed. Superficially the component looked good (Figure 4.26) but the adhesion between the carbide material and the aluminium was found to be very poor. In micrograph (Figure 4.27) showing the two layers of material, it can be seen that these layers are separated by a demarkation line indicating no significant bonding between them. However, by a drop test it was seen that the extra layer improved the toughness of the component. A WC/Co component of 0.2 mm thickness without any extra layer fractured when it was dropped from a height of about 6 inches. While a WC/Co component of 0.2 mm thick with an extra layer formed by spraying aluminium of thickness about 1 mm did not fracture when it was dropped from a height of about 3 feet on to the lab floor a few times.

Similarly an extra layer of nickel chromium alloy was deposited onto a cleaned carbide component after complete separation from the forming core. The WC/Co component was cleaned by sand paper and by grit blasting using lower air pressure (200 kPa). After spraying it was found that the deposit did not stick to the substrate. Due to the oxidation of the carbide component during post heating, the adhesion of the sprayed nickel alloy material with the formed component surface is so low that the sprayed

nickel alloy material could not be deposited as a continuous layer and after deposition on some areas the deposited layer peeled off (Figure 4.28). Therefore, to keep the outer surface of the carbide component oxide free, carbide component was fabricated by post heating in nitrogen atmosphere. This modification of post heating improved the surface quality but could not completely stop the oxidation of the component. With this reduced oxide surface, spraying of nickel alloy was tried and it was found that initially the spray material was deposited but after certain thickness (about 0.2 mm) the layer peeled off (Figure 4.29).

Therefore when fabricating components with WC/Co material a top layer was given with a mixed powder (section 3.8.6). The mixture material was made from the combination of WC/Co and nickel chromium alloy in different proportions. When the mixed layer was made from 10 % (by volume) nickel chromium alloy material and 90 % (by volume) WC/Co material, during deposition of the extra layer from nickel alloy the formation of continuous layer was not possible because this amount of nickel chromium alloy material in the top layer of the formed component is not sufficient to provide proper bonding with the sprayed material. Figure 4.30 shows the component with mixed layer (10 % nickel chromium alloy) on the top surface and while respraying with nickel chromium alloy material for extra layer, the sprayed material adhered at some areas of the surface and in some areas the deposited layer spalled off. When the mixed layer was made from 40 % (by volume) nickel chromium alloy and 60 % (by volume) WC/Co material, this mixed layer has sufficient bonding to allow deposition of the nickel chromium alloy material as an extra layer. Figure 4.31 shows a component made from WC/Co material of thickness about 0.4 mm and then a mixed layer of 40 % nickel chromium alloy and 60 % WC/Co material was applied as a very thin layer such that the mixed layer barely covered the whole surface. Then the component was separated from the core by post heating in nitrogen atmosphere. After post heating, nickel chromium alloy was applied such that the total thickness of the component was about 1.0 mm. The adhesion of the extra layer to the mixed layer is sufficient because the nickel material within the mixed layer did not oxidise during post heating and it helped bonding the deposited nickel alloy material. The thickness of the extra layer made from nickel chromium alloy was varied and it was found that for upto about 0.6 mm thickness the component was formed satisfactorily without fracture. When the thickness was increased beyond that, the component fractured due to the increased stress in the extra layer, see Figure 4.32. In this figure a cylindrical component of 84 mm length and 17 mm inner diameter is shown. The inner layer is made from 0.9 mm WC/Co material and a mixed thin layer of 40 % nickel. After the separation of the component from the forming core an extra layer was applied in nickel chromium alloy of up to 0.6 mm thickness. At this thickness the component was fractured due to induced stress.

During spraying of mixed materials, spray parameters used were the same as for spraying WC/Co materials (Table 3.2). These spray conditions are not standard for this mixture of powder and the flow rate of this powder was not uniform during spraying. Therefore the porosity of the deposited material was high. The micrograph of the cross section of this component is given in Figure 4.33 which shows the porosity level of the mixed layer.

Toughening with nickel alloy can be done during the fabrication of carbide components with gradual substitution of carbide powder with nickel base alloy powder. After spraying about 0.2 mm thick carbide layer, a layer with 10 % (by volume) nickel alloy and the rest WC/Co was applied. The proportion of nickel alloy was increased gradually from 10 % to 20 %, 30 %, and 40 %. The component thus formed was found to be quite good (Figure 4.34). Spraying with higher proportions of nickel was tried but the component fractured. The cause of fracture may not be due to the higher proportion of nickel alloy but because during spraying the powder was not flowing properly through the powder feeder. The proportion of the mixture actually deposited on the surface may vary due to the problem of flowing of powder with the carrier gas. The uneven flow of powder may be due to improper mixing of the powder (section 3.8.6).

4.7.2 MULTI-LAYER COMPONENT WITH HARDER OUTER LAYER

To fabricate multi-layer components with a soft layer inside and a hard layer outside, forming cores of 2 mm thickness of conical shape were made from aluminium (section 3.8.6). Aluminium was chosen as the substrate as it is widely used for making engineering components. In addition to this, the cost of aluminium is low and it can be easily machined. The extra layer of hard material was sprayed onto the surface of the aluminium component. The hard material used was WC/Co and nickel chromium alloy. This material was sprayed, using the standard spray parameters (Table 3.2). The extra layer acts as a thick coating on an aluminium substrate. While coating the aluminium substrate, it is recommended [15] that the temperature of the substrate should not rise above 50 $^{\circ}$ C. With this limitation it is difficult to spray deposit on aluminium to make components because the small size of component used makes it quite impossible to keep the temperature below 50 $^{\circ}$ C.

For manufacturing components using spray forming, it is necessary to make a component by continuous spraying and the rise of temperature during fabrication of the component should be such that the process is not rendered too difficult. This investigation was carried out to determine an easier way of depositing hard material on aluminium substrates such that smaller as well as larger aluminium components can be coated with higher thickness and with high bond strength. The effect of roughening the substrate surface before coating to improve the bond strength was also investigated.

If the substrate is preheated before spraying to a certain level of higher temperature, then spraying can be continued without interruption and a higher thickness layer can be deposited without difficulties. This is because, during spray coating on a substrate by HVOF thermal spraying process, the temperature of the substrate rises to a certain steady state temperature. This steady state temperature depends on the size and the material of the substrate, and spray parameters. If the substrate is preheated to a temperature near to the steady state temperature then it is easier to control the temperature and spraying can be continued without interruption. Therefore, WC/Co and nickel chromium alloy materials were sprayed on a aluminium forming core (3.8.6) and components were fabricated with the outer layer in harder material. The thickness of WC/Co deposited layer on aluminium layer was varied from 0.2-0.5 mm and for nickel chromium layer on aluminium layer was varied between 0.5-1.5 mm. Figure 4.35 shows the photograph of a component made from aluminium inner layer and nickel chromium alloy outer layer of 0.5 mm thickness.

4.8 MEASUREMENT OF DIFFERENT PROPERTIES OF MULTI-LAYER COMPONENT

The effect of preheating the substrate on different properties of the sprayed deposit were investigated. The adhesion of WC/Co and nickel chromium alloy material with the aluminium substrate and the change of ductility of the sprayed material with the substrate preheating temperature were measured. To investigate the effect of roughness of the substrate surface, a number of samples were polished and some were roughened by grit blasting. The variation of hardness with the processing temperature was also measured. These tests were carried out as explained in section 3.8.7.

The result of the bond strength tests are presented in Figure 4.36. This Figure shows the adhesive bond strength of the coating to the substrate at different substrate preheating temperatures. The bond strength of the WC/Co sprayed material is greater than that of nickel chromium alloy material. The range of average adhesive bond strength for WC/Co is between 47 to 59 MPa and for Nickel base alloy it is between 28 to 43 MPa, at different substrate preheating temperature. To obtain an average value at each temperature five samples were tested and it was found that there is some variation of bond strength. These variations can be attributed to the different mode of failure of the coating during the pull tests (Figure 4.37). This figure shows only the mode of failure of two samples during pull test. Photograph (a) shows the two parts of a pull test sample, in which the coating was deposited on the part shown in the L.H.S. This coating was totally peeled off during the pull test and remained attached to the part shown in the R.H.S. of the picture. In photograph (b) the coating was deposited on the left side half and this coating partially peeled off during the pull test. The coating materials and substrate temperatures are different in these two cases. Though the

variation of bond strength was found to be different at any particular preheating temperature for each material, it is evident that the average bond strength of these materials to an aluminium substrate increases at higher substrate preheating temperatures. With the higher substrate temperature the thermal mismatch is greater, but better diffusion of the coating particles increases the bond strength so much that it nullifies the effect of increased thermal stress and increases the bond strength of the coating. Figure 4.38 shows the penetration of a sprayed particle into the aluminium substrate to a depth of 30-35 µm at preheating temperature 400 °C and 15-20 µm at substrate preheating temperature 50 °C. This penetration of the sprayed particle increased the diffusion and thus increase the bond strength of the deposited material. The curve in Figure 4.36 shows that the bond strength has less increasing trend at lower substrate preheating temperature and have higher increasing trend at higher temperature. This may be due to insufficient diffusion of the sprayed particles at that temperature. This trend is similar for both the materials used. The bond strength test results could not be compared with results obtained by other investigators because the bond strength of coatings on aluminium substrates is not available in the literature.

Adhesion between the layers of WC/Co and Nickel chromium alloy was measured by pull test (section 3.5.6). The tensile bond strength was found to be more than 70 MPa. At this strength always the adhesive failed. The bond strength between the WC/Co layer and the mixed material (WC/Co and 40 % nickel chromium alloy) was also tested and the tensile bond strength was also found to be more than 70 Mpa.

The results of the ductility test are presented in Figure 4.39. From the bend test the ductility of the spray coating was found to be very low, which is to be expected because the thermally sprayed coatings have low ductility [12]. Curves in Figure 4.39 show the variation of ductility of the coatings at different temperatures. The ductility of the coatings at higher temperatures increased slightly for Nickel base alloy. The ductility of tungsten carbide did not change due to the change in substrate temperatures. The curve in Figure 4.40 shows the variation of ductility of the nickel alloy coating with thickness at a certain substrate preheating temperature and it is evident that with increasing thickness there is only marginal increase in ductility of this material.

From this investigation it was evident that when the preheating temperature of the aluminium substrate was low (50 $^{\circ}$ C) and if the temperature of the substrate during spraying rises up to 200 $^{\circ}$ C then the coating simply peels off. When the substrate preheating temperature is higher, ie. the preheating temperature is closer to the steady state temperature of that substrate, the control of substrate temperature during spraying is easier and thicker coatings can be applied without any interruption of the spraying process. It was evident that with an aluminium substrate when the preheating temperature is between 300-400 $^{\circ}$ C the coating does not peel off even when there is some variation in the substrate temperature during spraying.

The effect of surface preheating to avoid surface roughening is summarised in Table 4.8 which shows that without roughening higher bond strength can be achieved by preheating the substrate at certain high temperature.

The curves in Figure 4.41 show the variation of hardness of two materials at different substrate temperatures. For tungsten carbide/cobalt material the variation is not significant. For nickel alloy the curve shows some increasing trend with the increase of substrate preheating temperatures of upto 300 $^{\circ}$ C and after that the curve has a decreasing trend of upto 400 $^{\circ}$ C. This may be due to the annealing effect on the nickel coating material.

4.9 MEASUREMENT OF TOUGHNESS

To measure the toughness of the component made from multi-layer and mixed material, test samples were made from the material which were used for making the multi-layer component (3.8.7). These are WC/Co, nickel chromium alloy and mixture of these two with a proportion of 40 % by volume of nickel chromium alloy.

Figure 4.42 shows the load-deflection curves generated by the chart plotter during testing WC/Co, nickel chromium alloy and mixed material specimen. While fixing the samples with the grip of the tensile testing machine, some samples were fractured during fixing due to higher fixing load. To avoid fracture, samples were fixed with the grip at

lower gripping load resulting some slip during tension tests (Figure 4.42). In addition, the load deflection curves shows some initial load which arise due to the self weight of the gripping fixture. Therefore, to locate the starting point of loading, the load deflection curves were extended upto zero load assuming that these curves are linear. These intersection points of zero load and extended lines were assumed as the starting points of loading and were taken as the reference points for calculating actual elongation. Using these load deflection curves and the dimension of the specimens, the stress-strain curves are drawn and presented in Figures 4.43-4.45 for WC/Co, nickel chromium alloy and mixed material specimen respectively. It is known that the area under the stressstrain curve gives the toughness of the tensile testing specimen. From the area under the curves shown in Figures 4.43-4.45, it was found that nickel chromium alloy sprayed material has 9.9 times more toughness than the WC/Co sprayed material and the mixed material has 1.7 times more toughness than the WC/Co material. It was also observed that the average tensile strength of nickel chromium alloy, WC/Co and mixed material are 235, 54 and 68 Mpa respectively. The tensile strength of nickel chromium alloy sprayed material are in good agreement with the result reported in reference [50]. The ductilities of these sprayed material as shown by the load deflection curve in Figure 4.42 are slightly higher than the ductility value obtained by bend test. This may be due to the slip in the grips which were made from aluminium sheet.

From the above test it is quite clear that with the addition of extra layer of nickel chromium alloy or mixed material on WC/Co component, the toughness of the formed component has increased.

4.10 MEASUREMENT AND CONTROL OF RESIDUAL STRESS IN WC/Co COMPONENT

A careful cracking along the length of the conically shaped free standing component made by HVOF thermal spraying, shows that the component either opens up or closes (Figure 4.46) depending on the fabricating condition. This change of shape is due to the residual stress which depends on the fabricating conditions.

Therefore cylindrical components with a slit were made under different spraying conditions. The variables are: spray rate, spray distance, flow of fuel gas and oxygen, preheating temperature of the core, spraying temperature and post heating temperature and soaking time. For each of the above variables there is some standard range of values to obtain a properly formed component. For measuring the residual stress, in each trial, a maximum or minimum value of one variable was selected, keeping other variables constant (Table 4.9). It was found that in all these tests the residual stress in the components were such that when the components were separated from the forming cores they bent inward. However, the level of the bending stress was different. Ultimately it was realised that by changing the post heating temperature and the soaking time the effect of residual stress could be varied from bending inward to bending outward. Therefore, keeping all other variables as standard and changing the post heating temperature and soaking time (one at a time), the level of residual stress in the component was measured. Figures 4.47 and 4.48 show the effect of post heating temperature and soaking time on residual stress respectively. From Figures 4.47 and 4.48 it is seen that during post heating the inward bending stress starts to relax and at a certain temperature and after a certain time this residual stress becomes fully relieved. After further heating type of residual stress changed and caused the sample to bend outward. This may be attributed to the differential grain growth at the outer layer and inner layer during the post heating which act as sintering. The grain in the inner surface has less space to accommodate the growth and therefore during grain growth a compressive stress is developed. While at the outer periphery the grain are free to grow in size. As a result after post heating at higher temperature or post heating for of longer time the component opens up when cracked.

Finally a component was made without residual stress by using the parameters for stress free condition as determined from Figure 4.47. The conditions used for fabricating the stress free component are presented in Table 4.10. It was found that the stress level of the component is negligible, that is, after cracking it did not open up or close up.

Therefore it can be concluded that HVOF thermally sprayed WC/Co component contains residual stress which causes inward or outward bending of the component when

cracked. However, the level of bending stress might be different with different spray parameters. This bending stress can be controlled by controlling post-heating the sprayed deposit at specified temperature and time.

4.11 EFFECT OF SPRAYING PARAMETERS ON THE PROPERTIES OF THE WC/Co COMPONENT

The WC/Co components were made under different spray conditions and the resulting properties in terms of the hardness and porosity are given in Table 3.9. The spray parameters varied were: 1) flow rate of oxygen, 2) flow rate of propylene, 3) flow rate of air, 4) spray distance and 5) spray rate of depositing material. The standard values of these variables for depositing coatings using this material were supplied by the equipment manufacturer. The standard values given by the manufacturer were concerned with the properties of the coating such as hardness, porosity and bond strength. The bond strength of the coating with the substrate is a very crucial property. For spray forming, bonding of the depositing material with the substrate is not required. Therefore the standard values of spray parameters set by the manufacturer are not valid for spray forming operation. Hardness and porosity are the main concern of this investigation. Therefore tests were carried out to evaluate the effect of the spray parameters on the hardness and porosity of the sprayed WC/Co materials. During this test, values of the spray parameters were selected around the standard values set by the manufacturer because too wide a variation of the spray parameters might have a detrimental effect on the hardware of the HVOF thermal spraying system.

The properties required for the component depends on the type of application. As this study is not restricted to any definite application, optimization of the spraying parameters towards a definite optimum property (hardness and porosity) of the deposited free standing component was not carried out. Therefore, the effect of the individual spraying parameter only is of interest here. During these tests one variable was varied while keeping all other variables constant and the effect of this variable on hardness and porosity are presented graphically in different figures. To measure these properties, samples were sectioned, mounted, ground and polished. A fully automatic Motopol 12 polishing machine was used to polish the sample to a surface finish of 0.5 micron. Porosity measurements were taken by using a Reichert MEF₃ optical microscope and a Quantiment 570 image analysis system. The results are average values based on measurements taken at randomly selected locations for each sample. Hardness was measured with a Vickers hardness tester under a load of 0.3 kg on the polished cross section. Micrographs showing the porosity in the deposited materials are presented in Figures 4.49-4.52. The level of porosity in the deposited materials is 0.8 %, 1.0 %, 2 % and 3 % as shown in Figures 4.49-4.52 respectively.

Curves in Figure 4.53 shows the variation of hardness and porosity of the deposited material for the variation in flow rate of oxygen between 284-221 standard litre per minute (SLPM). The average hardness and porosity values change from 1155-1185 Hv,0.3 and 1.7-1.75 % respectively. Figure 4.54 shows that the variation of the flow rate of propylene between 84-67 SLPM causes the variation of average hardness and porosity 1187-1115 Hv,0.3 and 1.3-2.1 %. Figure 4.55 shows that the variation of the flow rate of air between 380-311 SLPM causes the variation of average hardness and porosity 1182-1157 Hv,0.3 and 2.0-1.5 %. Figure 4.56 shows that the variation of the spray distance between 225-125 mm causes the variation of average hardness and porosity 1049-1294 Hv,0.3 and 1.95-1.49 %. Figure 4.57 shows that the variation of flow rate of powder material between 50-23 gm per minute causes the variation of average hardness and porosity 1130-1210 Hv,0.3 and 2.6-1.85 %.

Therefore, it can be observed that the spray distance is the dominant factor influencing the hardness of the depositing material. Both the higher spray and air flow rates produce higher porosity in the deposited material. Increased flow rate of propylene increases the hardness but has little effect on the porosity of the deposit. Flow rate of oxygen has little effect on both the hardness and porosity compared to other variables.

During making a sample using the shortest spray distance the rise in temperature was so quick that a change of colour of the depositing material was observed and that might produce some amount of lower carbide which is harder and hence high hardness results were obtained.

4.12 COMPOSITION OF THE DEPOSITED WC/Co MATERIAL

During the deposition of the WC/Co material, the change of colour of the deposited material at different stages of fabrication was observed. In addition, the composition of the sprayed material is one of the major deciding property of the components. Therefore the composition of this deposited material was investigated.

X-ray diffraction was performed on the deposits on the core before and after post heating for Tungsten carbide-cobalt components and also on a coating of the same material sprayed on a substrate without preheating. The typical XRD spectra are given in Figures 4.58-4.61. The XRD spectra of the coating shown in Figure 4.58, shows WC phase in the deposit with some proportion of decomposed W_2C and M_6C (Co₃W₃C-eta) phases. These phases are quite likely in the coatings deposited by HVOF process [105]. Figure 4.59 shows the XRD traces for the deposited material on the core before post heating. These two traces give almost identical peaks for different phases of WC-Co materials. Fig. 4.60 is the XRD spectra of the outer surface of the as obtained free standing component after post heating. This trace is quite different and shows the different phases of oxides of WC and the colour of the surface is bluish. After cleaning the outer surface by sand paper, XRD was performed and the spectra is shown in Figure 4.61. Analysis of all these traces shows that after cleaning, the compositional phases of the free standing object is similar with small proportion of oxide phases in the component. Therefore, it is clear that post heating makes the outer layer of the component oxidised and this oxidised layer can be removed by easy rubbing with sand paper.

The percentage of the amount of each composition in the formed component are calculated from the ratio of intensity of the peaks in the XRD trace for the composition and is presented in Table 4.11. This table also shows the percentage of composition for this powder material and the deposited coating reported in reference [105]. From Table 4.11 it can be seen that the percentage of WC in the deposited coating is about 57 %

which is 12 % less than the amount of WC, present in the starting powder. However the amount of WC in the deposited coating is 11 % higher than that of the reported value. The percentage of WC in the formed component is about 53 %. During the fabrication of the component some amount of WC might lose its carbon and formed lower carbide due to higher temperature of the fabricating process. During the fabrication the formation of lower carbide was observed by the change of colours. Due to the higher percentage of W_2C the hardness of the deposited material is higher and the brittleness of the formed component is also higher.

To compare the amount of oxygen and carbon present in the free standing component and in the deposited coating, relative quantitative measurements were performed. At the same time to ascertain the variation of the elements along the crosssection of the free standing component, relative quantitative measurements for different element present, were performed. A Joel 8600 'Superprobe' SEM fitted with both the wave length and energy dispersive analysis facilities were used to measure these quantities.

To compare the carbon and oxygen contents of the cleaned free-standing object and coating deposited from WC-Co materials were analyzed by using wave length spectrometry. The count rates obtained for carbon over 100 second in central region of both samples are given in Table 4.12. It was found that the variation of the count is less than 500, which is considered to be very small in terms of the wave length spectrometry. Extremely low oxygen count rates were measured indicating that no substantial amount of oxygen was present in either sample.

To compare the compositional variation along the cross-section of the free standing component and deposited coating, the energy dispersive analysis was done as shown in Figure 4.62-4.67. Three locations were chosen for each component such that it covers the total cross-sectional area. This analysis indicates that no significant compositional (W and Co) variation was present between the samples.

4.13 COST ANALYSIS OF THE FORMED COMPONENT

The cost of forming a component by using the HVOF thermal spraying process includes the following items. The initial cost of all equipment and cost of labour are not included.

- 1) Cost of the material of the forming core.
- 2) Machining of the forming core.
- 3) Cost of the material for releasing layer.
- 4) Cost of applying the releasing layer.
- 5) Cost of preheating the forming core.
- 6) Cost of material with which the component is to be made.
- 7) Cost of spraying the depositing material.
- 8) Cost of post heating.

If it is assumed that a component is to be made from WC/Co material. The length and inner diameter of the component are 80 mm and 17 mm respectively. The thickness of the component is 1 mm.

<u>Cost of items 1 and 2</u>: Since a forming core can be made from any stainless steel and can be used repeatedly, the cost of forming core is not a significant factor compared to the other cost.

<u>Cost of items 3 and 4</u>: The amount of material to be sprayed as a releasing layer is about 3 gm. Assuming a deposition efficiency of 25%, the material needed is 12 gm. The cost of 2 kg of material for the releasing layer is \pounds 90. Therefore for each component the material cost for the releasing layer is about \pounds 0.54. The time required to spray the releasing layer is about 20 seconds. From the reported data [79], the cost for one hour spray by the HVOF thermal spraying process is about \pounds 22. Therefore cost of applying the releasing layer is about \pounds 0.12.

<u>Cost of item 5</u>: For preheating, the HVOF spray gun was used and the time required to raise the temperature of the forming core to the preheating temperature is about 45
seconds. Therefore the cost required for preheating is about £0.28.

<u>Cost of items 6 and 7</u>: After fabrication, the weight of the component should be about 60 gm. Assuming the target efficiency is about 50 % (as during spraying all the time the spraying material may not be sprayed on the forming core) and the deposition efficiency is about 50% (during spraying the powder material, some powder is always carried with the flowing stream and does not deposit), the powder material required to form this component is 240 gm. The cost of 1 kg of WC/11.5%Co (Diamalloy 2003) material is about £60. Therefore the cost of material required is about £14.5. The time required for spraying to form this component is about 7 minutes. Therefore the cost of spraying is about \pounds 2.6.

<u>Cost of item 8</u>: Time required for post heating is about 15 minute. The cost required to operate a furnace of power 3 kW for 15 minute is about £0.07.

Total cost = Material cost + Fabrication cost.

 $= \pounds 14.5 + \pounds 3.61 = \pounds 18.11$

4.14 TYPICAL USE OF THIN-WALLED WC/Co COMPONENT

The component thus formed by spraying WC/Co powder material can be used with different engineering components as a replaceable insert to improve the wear property of the engineering components. In Figure 4.68 two nozzle like components made from aluminium are shown which are fitted with thin-walled WC/Co insert. In Figure 4.68 (a), a 0.2 mm thick WC/Co insert has been fixed with the nozzle with adhesive and in Figure 4.68 (b) a 0.25 mm thick WC/Co insert has been shrunk fit. During fitting the shrunk fit insert, the aluminium nozzle was heated to about 100 °C and the WC/Co insert was dropped in it. After cooling it was found that the thin-walled insert is properly fitted with the aluminium nozzle. The cylindrical component shown in Figure 4.14 (g) was chopped at its two ends to provide a proper finish of its ends and also to investigate whether the spray formed WC/Co component can be machined. It was found that diamond saw can be used to cut these WC/Co component if needed.



(Curves 1,2 and 3 are drawn for aluminium forming core and stainless steel, nickel chromium alloy and WC/Co depositing materials respectively. Curves 4 and 5 are drawn for stainless steel forming core and nickel chromium alloy and WC/Co depositing materials respectively.)

Figure 4.1 Curve showing the gap that will form between the sprayed deposit layer and the forming core surface upon cooling the forming core from preheating temperature.



Figure 4.2 Photograph showing the mode of fracture of the WC/Co component.



Figure 4.3 Schematic of deposit-forming core assembly showing the location through which molten releasing material came out.



Figure 4.4 Photograph of the double cone shaped component made from different materials. a) WC/Co, b) Nickel chromium alloy and c) Stainless steel.



Figure 4.5 Time-temperature curve showing the fabrication process of spray formed component from nickel chromium alloy material.

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Figure 4.7a Micrograph showing the porosity of the components made from WC/Co material (maginfication 380 X).



Figure 4.7b Micrograph showing the porosity of the components made from Nickel chromium alloy material (maginfication 380 X).



Figure 4.7c Micrograph showing the porosity of the components made from Stainless steel material. (maginfication 380 X).



Figure 4.8 Photograph of nickel chromium alloy components of different sizes and shapes. a) conical shape of larger diameter, b) cylindrical shape, c) conical shape of smaller diameter, d) complex shape and e) conical shape of medium diameter.



Figure 4.9 Photograph of stainless steel components of different sizes and shapes. a) • conical shape of larger diameter, b) cylindrical shape, c) conical shape of smaller diameter, d) complex shape and e) conical shape of medium diameter.



Figure 4.10 Photograph of WC/Co components of different sizes and shapes, (a) cylindrical shape, (b) conical shape of large diameter and (c) conical shape of medium diameter.



Figure 4.11 Curve showing the variation of preheating temperature with the coefficient of thermal expansion of the material by which the forming core were made.



Figure 4.12 Bar graph showing the safe range of preheating temperature for different type of material of the forming core.



Figure 4.13 Diagram showing the safe zone of preheating temperature for different size of conical shaped component of WC/Co material.









Figure 4.15 Diagram showing the safe zone of preheating temperature for making free standing component from different materials using 33.5 mm diameter (average) forming core.







Figure 4.17 Heating rate of the forming core during post heating from 400°C







Figure 4.19 Diagram showing the relation between releasing agent thickness and the post heating temperature for separation of the deposit from the forming core.



Figure 4.20 Curve showing the relation of post heating time and temperature at different releasing layer thickness for proper separation of the deposit from the forming core.



Figure 4.21 Photograph of WC/Co component having localised fracture.



Figure 4.22 Curve showing the allowance which is to be subtracted from the diameter of the stainless steel forming core to make a spray formed component of WC/Co material of specified inner diameter.



Figure 4.23 Photograph of WC/Co components with single and multiple built-in hole/holes.



Figure 4.24 Photograph of complex shaped components of different materials.



Figure 4.25 Photograph showing the mode of fracture of multi-layered component.







Figure 4.27 Micrograph showing the poor bonding between WC/Co and aluminium layer (magnification 160 X).



Figure 4.28 Photograph showing the peeling of nickel chromium alloy layer from WC/Co component due to weak bonding.



Figure 4.29 Photograph showing the peeling of nickel chromium alloy layer from WC/Co component which was post heated in nitrogen atmosphere, due to weak bonding.



Figure 4.30 Photograph of the component with partially deposited nickel chromium alloy layer on WC/Co component.



Figure 4.31 Photograph of the multi-layered component made from WC/Co and nickel chromium alloy material.



Figure 4.32 Photograph of fractured multi-layered component made from WC/Co and nickel chromium alloy material.



Figure 4.33 Micrograph of the component made from WC/Co and nickel chromium alloy mixed material (40 % nickel alloy and 60 % WC/Co) (magnification 160 X).



Figure 4.34 Photograph of WC/Co component with mixed material on the top layer.



Figure 4.35 Photograph of the multi-layer component with aluminium inner layer and nickel chromium alloy outer layer of 0.5 mm thick.



Figure 4.36 Adhesive bond strength of deposited material at different substrate preheating temperature.



(a) complete separation of the coating.



(b) partial separation of the coating.

Figure 4.37 Photograph showing the mode of failure of the coating during pull test.



substrate preheating temperature 50 °C



substrate preheating temperature 400 °C

Figure 4.38 Photograph showing the depth of penetration of the sprayed particle into the aluminium substrate. (magnification 500X).



Figure 4.39 Ductility of different deposited material sprayed at different substrate preheating temperature.



Figure 4.40 Variation of ductility of the deposited material with thickness of the deposited layer.



Figure 4.41 Hardness of deposited material sprayed at different substrate preheating temperature.



Figure 4.42 Load-elongation curves for (a) nickel chromium alloy, (b) mixed material (60% WC/Co and 40% nickel chromium alloy and (c) WC/Co materials.


Figure 4.43 Stress-strain curves for nickel chromium alloy deposited material.



Figure 4.44 Stress-strain curves for mixed (40% by volume nickel chromium alloy and 60% WC/Co) deposited material.



Figure 4.45 Stress-strain curves for WC/Co deposited material.





Figure 4.46 Photograph of the cracked components showing the effect of residual stress by open up and close up of the crack.



Figure 4.47 Curve showing the relation between residual stress and post heating time.



Figure 4.48 Curve showing the relation between residual stress and post heating temperature.



Figure 4.49 Micrograph showing 0.8 % porosity in WC/Co component (maginfication 380 X).







Figure 4.51 Micrograph showing 2.0 % porosity in WC/Co component (maginfication 380 X).







Figure 4.53 Curve showing the variation of hardness and porosity with the change of flow rate of oxygen during spraying WC/Co material.



Figure 4.54 Curve showing the variation of hardness and porosity with the change of flow rate of propylene during spraying WC/Co material.



Figure 4.55 Curve showing the variation of hardness and porosity with the change of flow rate of air during spraying WC/Co material.



Figure 4.56 Curve showing the variation of hardness and porosity with the change of distance of the spray gun from the forming core during spraying WC/Co material.



Figure 4.57 Curve showing the variation of hardness and porosity with the change of flow rate of powder material during spraying WC/Co material.



Figure 4.58 X-Ray diffraction pattern for WC/Co coating deposited without preheating condition.







Figure 4.60 X-Ray diffraction pattern for WC/Co free-standing component after post heating.



Figure 4.61 X-Ray diffraction pattern for WC/Co free-standing component after post heating and cleaning.



Figure 4.62 Energy dispersive analysis pattern of WC/Co coating (about 0.5 mm thick) at within 50 µm of the outer surface of the cross-section.



Figure 4.63 Energy dispersive analysis pattern of WC/Co coating (about 0.5 mm thick) at central region of the cross-section.



Figure 4.64 Energy dispersive analysis pattern of WC/Co coating (about 0.5 mm thick) at within 50 µm of the inner surface of the cross-section.



Figure 4.65 Energy dispersive analysis pattern of WC/Co free-standing cleaned component (about 0.7 mm thick) at within 50 µm of the outer surface of the cross-section.



Figure 4.66 Energy dispersive analysis pattern of WC/Co free-standing cleaned component (about 0.7 mm thick) at central region of the cross-section.



Figure 4.67 Energy dispersive analysis pattern of WC/Co free-standing cleaned component (about 0.7 mm thick) at within 50 µm of the inner surface of the cross-section.



Figure 4.68 Photograph showing the application of thin-walled WC/Co component. (a) WC/Co component is fixed with the aluminium nozzle with adhesive, (b) WC/Co component is shrunk fit with aluminium nozzle.

Table 4.1 Calculated induced stress in the deposited materials due to thermal mis-match between deposited material and the forming core material.

Depositing material	Young's modulus of depositing material (GPa)	Coefficient of thermal expansion of depositing material x 10 ⁻⁶ /K	Equilibrium temperature (°C) *	Change of temp. from equilibrium temp. (°C)	Induced hoop stress (MPa)	
WC/Co	193	7	500	100	200	
WC/Co	193	7	500	200	400	
Nickel chromium alloy	67	13	500	100	95	
Nickel chromium alloy	67	13	500 200		189	
Nickel chromium 67 alloy		13	500	300	284	
Nickel chromium 67 alloy		13	500	400	378	

(Stainless steel was used as forming core material. $E_{steel} = 193$ GPa, $\alpha_{steel} = 18 \times 10^{-6}/K$)

* The temperature at which sprayed material were deposited and it is assumed that at this temperature there is no stress within the deposited material.

Table 4.2Test results to separate deposited layer from the
forming core through aluminium releasing layer.

Depositing material	Releasing layer thickness (µm)	Remarks
Nickel chromium alloy	213	Molten releasing layer stuck with the deposit and separation of the deposit from the forming core was not possible
Nickel chromium alloy	196	Molten releasing layer stuck with the deposit and separation of the deposit from the forming core was not possible
Nickel chromium alloy	173	Molten releasing layer stuck with the deposit and separation of the deposit from the forming core was not possible
Nickel chromium alloy	154	Molten releasing layer stuck with the deposit and separation of the deposit from the forming core was not possible
Nickel chromium alloy	138	Molten releasing layer stuck with deposit, but fabrication was possible
Nickel chromium alloy	122	Fabrication of component was possible
Nickel chromium alloy	115	Fabrication of component was possible
Nickel chromium alloy	93	Fabrication of component was possible
Nickel chromium alloy	76	Fabrication of component was possible

Materials	Porosity	Hardr	ness	Roughness (Ra)		
	%	Range (HV 0.3)	Average (HV 0.3)	Inner surface (µm)	Outer Surface (µm)	
WC/Co	4	1106-1249	1189	1.9-8.33	4.82-8.1	
Nickel Chromium Alloy	1	736-982	848	3.2	9.3	
Stainless Steel	0.5	394-448	412	3.0	7.8	

Table 4.3 Different properties of the spray formed components.

Table 4.4 Typical values of processing variables for fabricating free-standing components of
different materials.

Type of material	Thickness of the releasing layer (µm)	Preheating temp. (°C)	Spraying temp. (°C)	Spraying time (min)	Post heating temp. (^o C)	Post heating time (min)	Cooling condition	Thickness of the component (µm)
WC/Co	60-110	425-550	425-600	3-10	600-680	3-30	Cooled in atmosphere or in furnace	100-1200
Nickel chromium alloy	60-110	350-550	350-650	3-10	650-700	10-30	Cooled in atmosphere	200-1500
Stainless steel	60-110	200-550	200-650	3-10	650-700	10-30	Cooled in atmosphere	200-1500

Sample identification	Shape of the component	Average diameter (mm)	Length (mm)	Thickness (mm)
(a)	Conical	33.5	30	0.96
(b)	Conical	33.5	30	1.2
(c)	Conical	48.0	20	0.26
(d)	Cylindrical	40.0	40	0.42
(e)	Conical	21.5	25	0.45
(f)	Complex	31.5	40	0.41
(g)	Cylindrical	17.0	85	0.98
(h)	Complex	46.0	50	0.38

Table 4.5 Sizes and thicknesses of different WC/Co components as shown in Figure 4.14.

Table 4.6 Results showing the effect of surface roughness of the forming core on the fabrication of WC/Co components.

	Forming core surface		Forming core	Forming core surface		nt surface	Component surface	
			after applying releasing layer		inner surface	outer surface	inner surface	outer surface
Roughness	Polished by sand paper	Roughened by grit (C grade) blasting	Polished forming core	Roughened forming core	Made from polished forming core	Made from roughened forming core	Made from polished forming core	Made from roughened forming core
Ra (µm)	0.83	4.7	4.2	4.0	2.92	3.16	3.98	3.72
Rmax (µm)	8.1	37.0	40.5	27.0	22.4	27.0	28.4	37.0

No. of sample	Average Roughness in micron	Cleanliness	Remarks
1	4.7	Cleaned by sand blasting	Fabrication of component was possible
2	4.7	Forming core reused without cleaning	Deposit fractured during spraying
3	1.9	Forming core reused after cleaning by sand paper	Fabrication of component was possible
4	1.9	Forming core reused without cleaning	Deposit fractured during spraying
5	<1.0	Forming core reused after cleaning and polishing	Deposit fractured during spraying

Table 4.7Effect of surface roughness and cleanliness of the forming core on the
fabrication of WC/Co components.

Table 4.8	Bond strength and	ductility o	f coating	at different	aluminium	substrate
	surface condition.					

	Roughen at 50°C st temperatu	substrate Surface ubstrate preheating are.	Smooth substrate Surface at 400°C substrate preheating temperature.		
	WC/Co	Nickel chromium alloy	WC/Co	Nickel chromium Alloy	
Bond strength (MPa)	47	28	63	46	
Ductility %	0.76	0.86	0.76	1.08	

Sample	Spray rate	Spray distance	Flow ra	te of gases		Preheating temp. (C)	Temp. during	Post heating temp. (°C)	Post heating time (min).	Type of bending stress.
	(Bill)	(mm)	Oxygen	Propylene	Air	top. (\$)				
1	45	200	265	73	325	450	450-500	650	30	bending inward
2	30	200	265	73	325	450	450-500	650	30	bending inward
3	38	200	265	73	325	450	450-500	650	30	bending inward
4	38	225	265	73	325	450	450-500	650	30	bending inward
5	38	150	265	73	325	450	450-500	650	30	bending inward
6	38	200	284	73	325	450	450-500	650	30	bending inward
7	38	200	221	73	325	450	450-500	650	30	bending inward
8	38	200	265	84	325	450	450-500	650	30	bending inward
9	38	200	265	67	325	450	450-500	650	30	bending inward
10	38	200	265	73	380	450	450-500	650	30	bending inward
11	38	200	265	73	311	450	450-500	650	30	bending inward
12	38	200	265	73	325	550	550-600	650	30	bending inward
13	38	200	265	73	325	425	425-475	650	30	bending inward
14	38	200	265	73	325	450	450-650	650	30	bending inward
15	38	200	265	73	325	450	450-475	650	30	bending inward
16	38	200	265	73	325	450	450-500	690	30	bending outward
17	38	200	265	73	325	450	450-500	620	30	bending inward
18	38	200	265	73	325	450	450-500	650	100	bending outward
19	38	200	265	73	325	450	450-500	650	15	bending inward

Table 4.9 Effect of fabrication parameters on the residual stress of the WC/Co component.

Table 4.10 Conditions to make stress free spray formed WC/Co component.

Spray parameters		Conditions of the forming core				
Flow of Oxygen (SLPM	I) - 265	Preheating temperature (°C)	-	450		
Flow of propylene (SLP	PM) - 73	Temperature (°C) during sprayin	ng -	450-500		
Flow of air (SLPM)	- 325	Post heating temperature (°C)	-	650		
Spray rate (gm/min)	- 38	Post heating time (min)	-	80		
Spray distance (mm)	- 200					

Table 4.11 Composition in the powder and sprayed WC/Co material obtained from the relative intensities of XRD traces.

Sample	Phase relative intensity					Percent of phase present				
	WC	W ₂ C	W	WCO	Co ₃ W ₃ C	wc	W ₂ C	W	WCO	Co ₃ W ₃ C
Starting powder [42]	62	23	5	-	-	69	25.5	5.5	÷	•
Coating deposited by HVOF [42]	44	35	17	-		46	36	18		
Coating (Fig. 4.58)	67	33	-		12	57	32		•	11
Component before post heating (Fig.4.59)	61	36		-	9	53	37			9
Component after fabrication (Fig.4.61)	121	69	-	10 .	13	53	37		5	6

Table 4.12	Counts to determine relative carbon quantity in WC/Co coating and in free
	standing components.

Sample identification	Counts	
	Location 1	Location 2
WC-Co Coating deposited without preheating.	14661	14334
WC-Co Cleaned free-standing component.	14259	14527

CHAPTER 5

CONCLUSIONS

1.5

5.1 CONCLUSIONS

Spray forming of near net shaped thin walled hollow components using HVOF thermal spraying process has been investigated. Components have been successfully formed in tungsten carbide/cobalt, nickel chromium alloy and stainless steel materials. Component formed are of cylindrical, conical with or without holes and complex shaped. This method should provide a cost effective way of making carbide components of a variety of sizes and shapes.

While fabricating spray formed components, material is to be sprayed on a forming core which is subsequently separated from the forming core. Proper separation of the sprayed layer from the forming core can not be achieved by preheating the forming core or by increasing the spray distance or by decreasing the angle of incidence of the sprayed particle or by applying high temperature grease. During the deposition of spray materials the adhesion of the sprayed material with the substrate should be sufficient such that the spray layer does not fracture during spraying. After spraying the adhesion of the sprayed layer with the forming core surface has to be poor such that the sprayed layer can be separated without fracture. These conditions of sprayed deposit can be maintained by putting a releasing inter layer.

An epoxy layer whose working temperature is about 300 °C, is not suitable to withstand the high temperature and high heat content of the spray stream and the high impact of the sprayed particle of the HVOF gun. A mixture of metallic material with the epoxy adhesive is not a solution to protect the epoxy releasing layer against the erosion and burning of epoxy material. The releasing layer which is to be applied on the forming core surface should have a proper thermal conductivity to allow transfer of the heat of the sprayed material to the forming core and to the environment very effectively.

Aluminium of 99 % purity and with certain range of particle sizes has been identified to act as a releasing layer which had sufficient bonding with the forming core

surface upto the temperature at which deposition takes place. This releasing layer can also be made non-adherent through some post treatment after spraying. The thickness of the releasing agent has profound effect on the ease with which the free standing components can be released form the forming core. During the forming operation the forming core surface remains unaffected allowing the same forming core to be used repeatedly. This reduces the production cost and makes the process very suitable for mass production.

The forming core can be made from different types of materials such as mild steel, stainless steel, D2 steel and copper. The coefficient of thermal expansion of the forming core material has some effect on a number of processing parameters, such as types of the depositing material, preheating temperature and size of the forming core. The difference between the dimensions of the inner diameter of the component and the outer diameter of the forming core also depends on the coefficient of thermal expansion of the forming core material and its dimension. The roughness and cleanliness of the forming core surface have some effect on the occurrence of fracture of the sprayed layer during spraying.

The process of heating and cooling of the forming core at different stages of the spray forming process has the influential effect in obtaining the component in proper condition. The preheating temperature of the forming core is one of the critical factors which influences the ease with which the component may be released. For every combination of the depositing and forming core materials there is some definite range of preheating temperature. The temperature of the forming core during spraying affects fracture of the WC/Co deposited layer during spraying. A large deviation from the preheating temperature during spraying might cause fracture of any of the depositing material used. Variation of temperature during spraying along the length of the forming core of higher length and smaller diameter. Variation of temperature of the forming core during spraying is more critical for WC/Co material than for other two materials used for fabricating components. Extra cooling air should not be used to control the temperature of the forming core during spraying. Spray distance or number of samples

or traversing speed of the gun should be adjusted to control the temperature of the forming core during spraying.

Before the separation of the sprayed deposit from the forming core, the forming core-deposit assembly should not be allowed to cool down to a much lower temperature. Therefore, after deposition of the material the forming core-deposit assembly should be transferred to a preheated furnace as quickly as possible to avoid much cooling of the forming core. This is more critical for a WC/Co component than for the other two materials. Post heating of the forming core is essential to separate the deposit from the forming core surface. The temperature and soaking time of post heating are crucial to make the releasing layer non-adherent with the forming core surface. The post heating temperature and soaking time are also depend on the releasing layer thickness. The heating rate during post heating has no significant effect on the ease of separation of the free standing component. The cooling might cause fracture of the free standing component. Very slow cooling might cause more oxidation of the free standing component, particularly for WC/Co component. Otherwise slower cooling is preferable for obtaining components without fracture.

Measurement and control of temperature during preheating and spraying operation are essential. This is more true for WC/Co components. During spraying a WC/Co component, the sprayed surface changes colour with temperature which is very distinctive. This can be utilised to control and monitor the temperature of the WC/Co deposit while spraying.

The hardnesses of the spray formed components are found to be higher than the cast and wrought materials. The porosity levels of WC/Co components are found to be 0.8-3.0 %. By choosing the processing variables the porosity and hardness of the WC/Co components can be adjusted upto certain limits. For nickel chromium alloy and for stainless steel the porosity levels are less than 1 % and 0.5 % respectively. The compositional analysis of WC/Co components shows that there is no significant compositional variation present within the samples.

The components formed by this process are found to be brittle. However the toughness of a WC/Co component can be increased by putting multi-layers with other materials such as aluminium and nickel chromium alloy. It is found that this extra layer increases the toughness and may provide a means of attaching these components with some other components. However, there is some limitation to the thickness of this extra layer beyond which the stress set up in the layer may induce cracking of the component. Toughening of the component can be achieved by fabricating the component initially with a hard material and finally with the mixed material. In the mixed material, the harder material is gradually substituted with a tougher material. The proportion of the mixture can be varied upto a certain limit. However, complete substitution of the harder material by a tougher material may cause fracture of the component. Multi-layer components can also be made with an aluminium inner layer and harder material outer layer. The adhesion of these harder sprayed materials deposited at higher preheating temperatures of aluminium substrate are found to be satisfactory to act as multi-layer components.

The spray formed components made from WC/Co contain residual stresses. The amount of residual stress depends on the values of processing parameters. Parameters can be selected to obtain a component with the desired type of residual stress.

Thin-walled spray formed WC/Co components can be fitted as replaceable inserts in a nozzle or in a cylinder with adhesive or can be shrunk fit. The edges of the formed component can be chopped by diamond cutter if needed to fix it properly.

5.2 RECOMMENDATIONS FOR FUTURE WORK

During this investigation it was found that with the decrease of coefficient of thermal expansion of the forming core material the preheating temperature decreases. Therefore further investigation can be carried out to make free standing components by WC/Co material using a forming core which is made of a material such that the thermal expansion of the forming core material is almost equal to the thermal expansion of the sprayed deposit. In that case preheating might be avoided and at the same time the

control of temperature during spraying might be easier.

The material of the releasing layer has been chosen from commercially available material which is not standard for use by a HVOF process, caused problem of flow during the tests. An alternative powder of the same composition can be selected which can flow with the carrier gas of the powder feeder or a method is to be developed to maintain the proper flow of the powder used.

During the investigation it was found that the residual stress within the spray formed WC/Co components is always compressive when the post heating temperature and time are less. Variation of other processing parameters resulted in compressive residual stress within the formed component. However, it was also found that the level of the compressive residual stress varied with the change of the values of processing parameters. The effect of the processing parameters on the residual stress can be investigated in detail to determine the overall effect of the processing variables on the residual stress of the component.

The application of multi-layer to improve the toughness can be investigated in more detail to determine the maximum thickness of the extra layer. The residual stress within the component might have some effect on the thickness of the extra layer.

Manufacturing of components with a harder initial layer and gradually substituting the harder material with tougher material by mixing the tougher and harder material at different proportions might be worthwhile to investigate to make tougher components with WC/Co material. In that case WC/Co materials with different proportion of cobalt can be used to make a tougher and thicker component.

During the tests of fabricating WC/Co components, it was found that at higher preheating temperatures, formation of lower carbide in WC/Co material produces higher hardness. This can be done intentionally to create a harder surface layer of WC/Co material which contains lower carbide and the rest of the layer of the component can be made of WC/Co of higher cobalt content. This component might have both higher

hardness layer and higher toughness layer. For other materials also the same procedure can be investigated by spraying an initial layer with a controlled amount of oxidation and the rest of the deposition could be done without oxidation. This process might help to obtain a component of any material with higher wear resisting surface property.

During the investigation it was not possible to maintain the uniformity of thickness of the component due to the lack of proper control of the traversing unit and the flow rate of the powder. A traversing unit which has higher traversing speed and better control can be designed to obtain component of uniform thickness. A fully automatic traversing unit would be preferable. To make a component with different combination of powders, a powder feeder with the facility of using more than one powder is needed.
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APPENDIX A

CALCULATION OF THERMAL STRESS IN THE DEPOSITED LAYER INDUCED DURING COOLING OF THE FORMING CORE-DEPOSITED LAYER ASSEMBLY

If an unstressed compound cylinder constructed from two tubes of different materials is heated or cooled uniformly, all parts of the compound cylinder will change its dimensions at different ratio and differential thermal stress will be set up. If the two tubes of the compound cylinder are bonded together, one will restrict the change of dimension of the other and a compromise situation will be reached (if either of the two does not fracture). The situation is illustrated in Figure A-1.

During spray forming, let us assume that the forming core and the deposited layer act as two tubes of different materials. The inner tube (forming core) is made of steel and the outer deposited layer is made of WC/Co or nickel. The sprayed deposit is properly bonded with the forming core surface when being deposited. The temperature of the deposit and the forming core during spraying is T_2 . It is assumed that at this temperature the thermal stresses within the forming core and the deposited layer are zero. As the inner cylinder of mild steel has a higher coefficient of thermal expansion than that of the outer cylinder of the deposited material, a radial tensile pressure (P) will develop at the common interface by virtue of the differential contraction of the tubes during cooling. As a result a tensile hoop stress will be generated in the inner core and a compressive hoop stress will be generated in the outer shell.



Figure A-1. Schematic of the forming core with the deposit during spraying and after cooling.

From the Figure A-1,

Total diametral gap between the free positions of the surfaces of the inner core and outer deposited layer = $2\delta_{core} + 2\delta_{deposit}$

The change in diameter, $2\delta_{core}$, of the forming core $= \varepsilon_{core}$. d The change in diameter, $2\delta_{deposit}$, of the deposited layer $= -\varepsilon_{deposit}$. d (negative since it is a decrease in diameter) where,

d	= Interface diameter after cooling
e core	= Diametral strain of the forming core
E deposit	= Diametral strain of the deposited layer

So that,

$$2(\delta_{core} + \delta_{deposit}) = (\varepsilon_{core} - \varepsilon_{deposit}) d = (\alpha_{core} - \alpha_{deposit}) (T_2 - T_1) d$$

Therefore,

$$\varepsilon_{\text{core}} - \varepsilon_{\text{denosit}} = (\alpha_{\text{core}} - \alpha_{\text{denosit}}) (T_2 - T_1)$$
(A.1)

where,

 α = Coefficient of thermal expansion T₂ = Temperature of the compound cylinder during spraying

 T_1 = Temperature of the compound cylinder after cooling

Since diametral strain = circumferential strain, it can written that

$$\varepsilon_{core} = \frac{1}{E_{core}} \left[\sigma_{t \ core} - \upsilon_{core} \ \sigma_{r \ core} - \upsilon_{core} \right]$$

and

$$\varepsilon_{deposit} = \frac{1}{E_{deposit}} \left[\sigma_{t \ deposit} \ -\upsilon_{deposit} \ \sigma_{r \ deposit} \ -\upsilon_{deposit} \ \sigma_{l \ deposit} \right]$$

where,

 σ_t is the hoop stress

 σ_r is the radial stress

 σ_i is the longitudinal stress and

v is the Poisson's ratio

For simplicity, it is assumed that longitudinal stress is zero.

Therefore,

The diametral strains can be written as follows,

$$\varepsilon_{core} = \frac{1}{E_{core}} [\sigma_{t \ core} \ -\upsilon_{core} \ \sigma_{r \ core}]$$
(A.2)

and

$$\varepsilon_{deposit} = \frac{1}{E_{deposit}} [\sigma_{t \ deposit} - v_{deposit} \ \sigma_{r \ deposit}]$$
(A.3)

As stated earlier, due to the differential thermal contraction the radial stress induced at the common interface will be, $\sigma_r = + P$ (tensile).

Combining equations A.1, A.2 and A.3 the following equation can be obtained,

$$\frac{1}{E_{core}} [\sigma_{t \ core} - v_{core} \ . \ P] - \frac{1}{E_{deposit}} [\sigma_{t \ deposit} - v_{deposit} \ . \ P]$$
$$= (\alpha_{core} - \alpha_{deposit}) (T_2 - T_1) \qquad (A.4)$$

Now, using Lamé equations for the common interface, the equation for the hoop stress can be obtained as follows;

$$\sigma_{t \text{ core}} = \frac{P}{\left(\frac{1}{R_{i \text{ core}}^{2}} - \frac{1}{R_{o \text{ core}}^{2}}\right)} \left[\frac{1}{R_{i \text{ core}}^{2}} + \frac{1}{R_{o \text{ core}}^{2}}\right]$$
(A.5)

and

$$\sigma_{t \ deposit} = \frac{P}{\left(\frac{1}{R_{o \ deposit}^{2}} - \frac{1}{R_{i \ deposit}^{2}}\right)} \left[\frac{1}{R_{o \ deposit}^{2}} + \frac{1}{R_{i \ deposit}^{2}}\right] \quad (A.6)$$

A4

Substituting for $\sigma_{t \text{ core}}$ and $\sigma_{t \text{ deposit}}$ in equation A.4 the expression for determining the interface pressure (radial stress) is obtained as follows,

$$\frac{P}{E_{core}} \left[\left(\frac{1}{\left(\frac{1}{R^{2}_{i \ core}} - \frac{1}{R^{2}_{o \ core}}\right)} \right) \left(\frac{1}{R^{2}_{i \ core}} + \frac{1}{R^{2}_{o \ core}} \right) - \upsilon_{core} \right]$$

$$- \frac{P}{E_{deposit}} \left[\left(\frac{1}{\left(\frac{1}{R^{2}_{o \ deposit}} - \frac{1}{R^{2}_{i \ deposit}}\right)} \right) \left(\frac{1}{R^{2}_{o \ deposit}} + \frac{1}{R^{2}_{i \ deposit}} \right) - \upsilon_{deposit} \right]$$

$$= \left(\alpha_{core} - \alpha_{deposit} \right) \left(T_{2} - T_{1} \right) \qquad (A.7)$$

where,

$$R_{i \text{ core}} = \text{Inner radius of the forming core (4 mm)}$$

$$R_{o \text{ core}} = \text{Outer radius of the forming core (17 mm)}$$

$$R_{i \text{ deposit}} = \text{Inner radius of the deposited layer (17 mm)}$$

$$R_{o \text{ deposit}} = \text{Outer radius of the deposited layer (18 mm)}$$

$$E_{\text{ core}} = \text{Young's modulus of steel (200 GPa)}$$

$$E_{\text{ deposit}} = \text{Young's modulus of WC/Co (193 Gpa)*, or nickel chromium}$$

$$alloy (67 \text{ Gpa)*}$$

Once the interface pressure is determined using equation A.7, the hoop stresses at the common interface can be calculated using equations A.5 and A.6.

* For deposited material Young's modulus is assumed to be one third of the standard value of the matrix material [50].

APPENDIX B

CALCULATION OF RESIDUAL STRESS

To calculate the residual stress the spray formed component was formed with a slit. The sample thus formed is shown below. The residual stress was calculated assuming the sample as a curved beam.



From the figure

Vertical deflection:
$$\delta = \int_{\theta_1}^{\theta_2} \frac{L}{E I} (R - R\cos\theta) (R - R\cos\theta) R d\theta$$
 (A.8)

where,

L = Load needed to cause the deflection E = Young's modulus I = Moment of inertia about centroidal axis R = Radius of curvature of the curved beam $\theta_1 = 7.64^0$ $\theta_2 = \pi$

After integration and rearranging,

$$L = \frac{\delta E I}{4.3 R^3} \tag{A.9}$$

1.10

When the radius of curvature is large compared with the dimension of the cross-section then it can be assumed that plane section remain plane after bending. The thickness of the sample formed during this investigation is about 1 mm which is small compared to the radius of curvature (17 mm).

The bending stress is given by,

$$Stress = \sigma = \frac{MY}{I}$$
(A.10)

where,

M = Moment at any pointY = Distance of any surface from the neutral axis

Using equations A.9 and A.10 the equation for the residual stress can be obtained as,

Residual stress =
$$\frac{2 \delta E Y}{4.3 R^2}$$
 (A.11)

where, E = Young's modulus of WC/Co material (193 GPa, as appendix A)

APPENDIX C

PUBLICATIONS ON THIS WORK

- 1. Helali.M.M. and Hashmi.M.S.J. "A comparative study of plasma spraying and high velocity oxy-fuel (HVOF) thermal spraying", Proc. of the 10th conf. of the Irish Manufacturing committee (IMC-10),pp. 377-387, Galway, 8-10th Sept. 1992.
- 2. Helali.M.M. and Hashmi.M.S.J. "Production of free standing objects by high velocity oxy-fuel (HVOF) thermal spraying process", Journal of Materials Processing Technology (in Press),1994.
- 3. Helali.M.M., Begum.S. and Hashmi.M.S.J. "Improving adhesion bond strength of high velocity oxy-fuel (HVOF) thermal spraying coatings on aluminium substrate", Accepted for proc. 11th conf. of the Irish Manufacturing committee (IMC-11), 31 Aug.-2 Sept., Belfast, 1994.
- 4. Helali.M.M. and Hashmi.M.S.J. "To coat or not to coat engineering components", Transaction of the IEI. Vol-18. (in Press), 1994.
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