

DESIGN OF EXPERIMENT ANALYSIS OF HIGH VELOCITY OXY-FUEL COATING OF HYDROXYAPATITE

by

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Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Master of Engineering is entirely my own work, that I have exercised reasonable care to ensure that the work is original, and does not to the best of my knowledge breach any law of copyright, and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

.....

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Dedications





(Engr. MD. SIDDIQUE ULLAH)



Mom

(SULTANA AKHTER)

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Abstract

"Design of Experiment Analysis of High Velocity Oxy-Fuel Coating of Hydroxyapatite"

By

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Due to the flexibility and cost effectiveness the high velocity oxy-fuel (HVOF) thermal spray process has been widely adopted by many industries. Though there are different types of flame spraying processes, the HVOF thermal spray process utilises only powder as the coating material rather than wire or rod. Carbon-hydrogen group of gases like propane, propylene, acetylene or even just pure hydrogen can be used as fuel gas in the HVOF process. In the Sulzer Metco Diamond Jet HVOF thermal spraying process powder material is melted by the use of combustion of oxygen and propylene gas and accelerated through a series of nozzles and deposited onto a workpiece. When the gun is in operation, air is used as the main cooling agent. The molten or semi molten particles are propelled out of the gun nozzle at supersonic velocities towards the substrate or forming die. By changing the propylene and oxygen ratio influences both the temperature and the velocity of the particles. HVOF has the potential to produce Hydroxyapatite HA (Bio-ceramic) coatings based on its experience with other sprayed materials, this technique should offer mechanical and biological results compared to other thermal spraying process such as plasma spray. Deposition of HA via HVOF is a new venture especially using the Diamond Jet, and the aim is for HVOF to provide superior coating results compared to Plasma spray, the process currently used in orthopaedic implants.

In this research Design of Experiment (DOE) models were developed to optimise the HVOF process for the deposition of HA through an optimised screening set of experiments. A preliminary process investigation was carried out before beginning the Design of Experiment study. In order to select suitable ranges for the production of HA coatings the parameters were first investigated. Currently five parameters (factors) were researched over two levels (maximum and minimum values for each factor) for Oxygen flow rate, Propylene flow rate, Air flow rate, Spray distance and Powder flow rate. Coating crystallinity and coating purity were measured as the responses to the factors used. The research showed that Propylene, Air Flow Rate, Spray Distance and Powder Feed Rate had the largest effect on the responses and current studies are now aiming to find the desired optimised settings to achieve high Crystallinity and Purity greater than 95%. This research found crystallinity and purity values of 93.81 % and 99.84 % respectively for a set of HVOF parameters which was even better than that achieved by the FDA approved plasma spray. Hence a new technique for HA deposition exist. The coating will allow bone within the femur to attach (graft) onto the implant using the HA material. HA is synthetic bone and turns to natural bone once in contact with living cells such as blood and human bone. HA does not cause any side effects in the human body.

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CHAPTER ONE

INTRODUCTION

CHAPTER: 1 Introduction

1.1 Introduction

Hydroxyapatite (HA) is a calcium phosphate bioactive material. Because of its excellent biocompatibility, bone bonding ability (allow bone cells to grow on its surface) and identical chemical composition which is similar to the mineral phase of hand tissue in human bones has made HA the splendid choice as implant material for many years. Another reason to use HA in dentistry and orthopaedics is their Ca/P ratio.

Of all the advanced coatings techniques, the High Velocity Oxy-Fuel (HVOF) is one of the most popular thermal spray technologies. Its flexibility and superior quality of coating has made it the excellent choice for many industries compared to other thermal spraying techniques though it is relatively new thermal spray process. In this process the powder particles melt at high temperature and impelled towards the substrate material to from a coating. The coating produces on the sample very quickly because of its high deposition rate. HVOF thermal spray process develops superior quality of coating compared to other thermal spray techniques, like plasma spray which is currently FDA approved to spray HA.

The main problems linked with HVOF thermal spray process are given below:

- Preparation methods of substrate surface
- Similar substrate and spraying materials
- Finding best optimised spraying parameters.

But these issues are apparent for all thermal spray process.

The flame temperature of HVOF thermal spray is between $2300 - 3000^{\circ}$ C which could cause decomposition of HA powder particles within the HVOF flame. Because of this new phases can arise, like α -tri-calcium phosphate (α - TCP) and β -tri-calcium phosphate (β -TCP). Amorphous calcium phosphate (ACP) phases are high when the particles on the substrate are quenching rapidly and this cause implant failure for long term use.

1.2 Objectives of the Research Project

The main objective of this research work is to investigate and optimise between the HVOF spray parameters for Hydroxyapatite applied onto stainless steel substrates (Often used in femoral implants) and the resultant coating properties. This was conducted using the Design of Experiment (DOE) technique to develop mathematical models. The developed models were useful in predicting responses like crystallinity and purity.

The next objective of this research is to achieve the crystallinity >45 % and purity >95 % and hopefully to achieve higher crystallinity and purity than that of the FDA approved plasma spray process. It is possible that for the first time Sulzer METCO Diamond Jet HVOF may achieve this requirement.

The following schematic diagram shows clearly the work programme of this project.



CHAPTER: 1 Introduction

1.3 Structure of Thesis

The thesis is divided into a number of sections as follows:

Chapter 2 gives a general introduction to surface engineering. A brief description of HVOF and Plasma thermal spray, the properties of HA, analysis of HA coating and the design of experiment (DOE) method are investigated

Chapter 3 contains the equipment, experimental method and support facilities. Detail description of the HVOF thermal spray equipment and its procedure is explained here. Coating characterisation equipment and then methods are discussed. Finally, process modelling and parameter level selected for screening are given.

Chapter 4 describes the results and discussions based on the findings. The results from characterisation (crystallinity and purity) of the materials used for optimising the HVOF process. Then the crystallinity model and purity DOE model was carried out. Overall findings of the optimisation experiment also included.

In chapter 5, the major conclusions from the results of the current research are outlined and also some recommendations for future research in this area are given.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

A comprehensive literature review relevant to the study is described in this chapter. Initially it describes surface engineering, then wear which effect engineering surfaces in service. A description of different coating techniques and thermal spray techniques are then explored. The HVOF (High Velocity Oxy-Fuel) thermal spray is explained and a summary of plasma spraying technique that has generally been used to produce HA coatings will also be described. Comparison between HVOF and plasma thermal spraying and advantages and disadvantages of HVOF system will be discussed next. An overview of bioceramics and a brief description of the properties of hydroxyapatite (HA) which include chemical structure, biological HA, temperature effect on HA, clinical performance of HA coated implants and HA powder are investigated. The properties required from HA coatings and analysis of HA coatings is detailed before finally addressing the Design of Experiment (DOE) method used in this work.

2.2 Surface Engineering

Surface engineering deals with the surface design and performance of solid materials. The life of a component depends on the surface characteristics of engineering materials. 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 [1]. On the basis of colour and texture, surface properties for certain engineering applications can be selected. An objective mind is essential so that engineering components can function when subjected to harsh environments. In order to design quality components with high service lives it is important is to understand the chemical and physical make up of the applied surfaces. Three of the most significant problems that need to be understood are: corrosion, fatigue and erosion-corrosion. Several surface properties that are applicable to the behaviour of engineering components are shown in *figure 2.1*.



Figure 2.1: Various surface properties, adapted from [2]

2.3 Wear

Wear is a process of removal of materials from one or both solid surfaces during solid state contact and occurs when contacting surfaces are in relative motion [3]. Wear is the main cause of material wastage. Load and relative motion can develop various kinds of wear modes, including rolling contact wear and impact wear, the modes of sliding wear or any combination of these types. The rate of removal can be continuous, steady and slow in general. The specific wear mechanisms which take place in each category and the five main categories (abrasion, erosion, adhesion, fatigue and corrosion) of wear are given in *figure 2.2*.



Figure 2.2: Various wear mechanisms

Abrasive wear occurs when a sharp and hard material slides against and cuts grooves through the surface of a softer material. Abrasive wear is also known as scoring, scratching or gouging. It has been shown that various thermally sprayed techniques such as the High Velocity Oxy-Fuel (HVOF) process enhances a materials resistance to abrasive wear [4-8]. Erosive Wear results from the effect of particles striking a surface. When there is loss of material from a solid surface due to relative motion in contact with a fluid that contains solid particles, erosive wear occurs. The angle of impingement and movement of the particle stream have significant effect on the rate of material removal [9]. Adhesive Wear is also known as seizing, scuffing, scoring or galling. According to Bhushan et. al. [3], adhesive wear occurs when two solid surfaces slide against each other under pressure. Surface Fatigue failure takes place when there is a repeating/cyclic stress during rolling or sliding contact. Fatigue life is influenced by lots of factors like surface finish, residual stresses, fretting and temperature [3]. Due to interaction between mating material surfaces and environment, corrosive wear occurs. Corrosive wear is formed when there is an external environmental chemical attack on a surface. In the prevention of corrosion, various material surfaces deposited by HVOF process have proved an effective tool in protecting these materials [10]. Coatings not only have to protect surfaces from a tribological point of view, they can also be used as a fixation device for Bioengineering. This is the subject of this research, however before Bioceramics and Hydroxyapatite (HA) is discussed the next section will describe coating techniques and benefits of using HVOF coatings.

2.4 Coating Techniques

When a material is deposited, onto a surface of an existing or another material (substrate) it is known as a coating. To improve surface properties of a bulk material is the aim of this coating. Coatings are formed using a mechanical bond between particle splats and the substrate or with previously applied lamella.

The selection of a particular deposition process depends on several factors, including [11, 12]:

- a) Limitation imposed by the substrate (for example maximum allowable deposition temperature)
- b) Process cost
- c) Process energy
- d) Chemical, process and mechanical compatibility of the coating material with the substrate

- e) The ability of the substrate to withstand the required processing
- f) Requirement and availability of the apparatus
- g) Ecological considerations
- h) Adhesion of the deposited material to the substrate
- i) Requirement of deposition rate
- j) Purity of the target material

Many coating deposition techniques are available nowadays. A synopsis is given in *figure 2.3*. The techniques are grouped under the heading of metallic and non-metallic. There are three categories in metallic coating deposition, hard facing being the most important in the context of this research. Further information on these techniques is detailed by Stokes [13]. Hard facing is divided into three techniques: welding, thermal spraying and cladding. Thermal spraying is of the most importance in this research; hence the following section concentrates on this technique.



Figure 2.3: Coating deposition technologies, adapted from [3, 13]

2.5 Thermal Spray Techniques

A young Swiss inventor named Dr. Max Schoop devised thermally spraying after observing his son playing with his toy cannon during the early part of the twentieth century [13]. Dr. Schoop observed that the hot lead shots when projected out of the cannon, stuck to almost any surface from which he discovered that if molten metal could be projected in the same way then a surface could be built with that material [13]. The rate of progress was slow until 1950s. With the innovation of low pressure plasma spraying, the Jet Kote HVOF technique and vacuum plasma spraying the antecedent growth occurred in the 1980s. In 1988 Metco Corporation introduced the Diamond Jet HVOF (High Velocity Oxy-Fuel) system, the process analysed in the current research. The demands of high technology industries like aerospace industry have lead to major advances in this field. Most metals, many ceramics, alloys, cements and even plastics can be thermally sprayed [3, 14]. Research in thermal spraying has progressed ever since which is shown in *figure 2.4*.



Figure 2.4: Timeline development of the thermal spray industry [15]

Thermal spraying is a coating process in which a coating material is heated quickly in a hot gaseous medium to become molten or semi-molten and at the same time projected at high velocity onto a substrate surface to develop a desired coating (*Figures 2.5 and 2.6*). *Figure 2.7* and *table 2.1* exemplifies a typical coating cross section of the laminar structure of oxides and inclusions. The coating material may be melted either by electric or flame heating.



Figure 2.5: Schematic of a Thermal Spray Process [16]



Figure 2.6: Schematic Diagram of a Thermal Spray Metal Coating [17]



Figure 2.7: Typical cross section of a thermal spray coating [18]

Table 2.1: Electrica	Heating and Flame	Heating Process
----------------------	-------------------	------------------------

Electric Heating	Flame Heating
Electric arc process	Flame spraying process
Low pressure plasma spraying	Spray and fuse process
Plasma arc process	HVOF thermal spray process

A detail description of all of these processes has been reported by Stokes [13], hence this is not described here. Plasma spraying is typically used to deposit bioceramics like Hydroxyapatite for femoral implant applications. So it will be discussed briefly here. However as HVOF was used as a new technique for depositing bioceramic hydroxyapatite, it will be discussed more thoroughly.

2.6 Plasma Spraying

Thermal spray processes that have been recently used for the production of bioceramic coatings include the Plasma Spray process and Detonation-Gun Spraying (D-gun) [19-21]. In the 1960's, the first industrial plasma spray guns appeared [22]. In the plasma spray process the thermal energy of an electric arc and its associated plasma is utilised for melting and projecting the coating material [3, 14, 23]. In plasma spraying the plasma gases are usually a mixture of Ar, He, N₂ and H₂. A schematic of the spray gun is shown in *figure 2.8*.



Figure 2.8: Schematic diagram of the plasma spray system [24]

The main advantage of the plasma spraying process is the high flame temperature that is generated. The temperature of the gas can be as high as 15,000-20,000°C, depending on the gas used, and the operating energy often reaches 720 MJ (682,800 BTU) [25]. Higher deposition is possible using the plasma spraying process compared with other thermal spraying techniques. The process may be used to apply thermal barrier materials, such as alumina and zirconia, and wear resistance coatings such as chromium oxide. The disadvantages of plasma spray process are the complexity of the process and relatively higher cost [15, 26].

Some of the significant characteristics related with the different thermal spraying process is given in *Table 2.2.* Powder injection may be axial, radial or central. According to Thrope et al. [33], injecting the powder beyond the flame provided the highest performance of the system. The combustion chamber is either at a right angle or a straight through orientation

with the barrel. Powder is injected beyond the flame at the beginning of the barrel in the case of some chamber combustion burners [27, 28].

Deposition Technique	Spray Gun Temp. (⁰ C)	Particle Velocity (m/s)	Coating Materials	Bond Strength (MPa)	Porosity (% Volume)	Hardness*
Plasma	16000	120-600	Metallic,	30-70	2-5	40R _h -
Spraying			ceramic,			50R _c
			compound			
HVOF	2800	1350	Metallic,	40-96	0.5-2	100R _h -
Sulzer			ceramic			50R _c
METCO						
DJ						
Gun ^{**}						

Table 2.2:	Comparison	of characteristics	for various thermal	spray processes	[3.1	61
1 abic 2.2.	Comparison	of characteristics	ior various therman	spray processes	[J, I	۰vj

* R_c = Rockwell hardness on C scale

* R_h = Rockwell hardness on H scale

** Thermal Spray Process used in this study

2.7 HVOF Thermal Spray Process

The HVOF (High Velocity Oxy-Fuel) thermal spray works on the principle of using thermal and kinetic energy for melting and accelerating powder particles to deposit desired coatings [2]. This process utilizes only powder as the coating material rather than wire and rod [3]. The fuel gases used in the HVOF process can be: propane, propylene, acetylene or even pure hydrogen. The gas temperature depends on two parameters, the ratio of oxygen and fuel gas flow rate and the choice of fuel gas. The HVOF thermal spray process can be divided into two categories:

- a. The continuous combustion HVOF system,
- b. The Detonation Gun HVOF system.

The fundamental principle of these two systems are the same except the use of different fuel gases, cooling systems and the fact that in the detonation gun system combustion is maintained by a timed spark, used to detonate the particle and gas mixtures [29]. This report concentrates on the continuous combustion HVOF system only as this is the process used here in this research and is a novel technique for depositing bioceramics.

Continuous Combustion HVOF System

There are different types of continuous combustion HVOF systems developed by different manufacturers. Jet-Kote was the first continuous combustion HVOF system. This system was developed by Gartner Thermal Spraying Company. The Diamond Jet (DJ HVOF gun) and the DJ Hybrid (water cooled) gun were developed by Sulzer METCO Coating Company. HV-2000 was developed by Praxair Surface Technologies, HP/HVOF (High Pressure HVOF) by TAFA and there are many more [30-32]. The working principle of these spraying systems are more or less the same [29]. In 1982 the Detonation Gun System was substitute by the continuous combustion Jet Kote HVOF thermal spray system [33-34]. The schematic diagrams of these HVOF thermal spraying processes are given in *Figure 2.9 and figure 2.10*.



Figure 2.9: Schematic of Jet-Kote HVOF thermal spray gun, perpendicular fed system [35]



Figure 2.10: Schematic of cross-section of the Sulzer Metco Diamond Jet spray gun axial system [13]

The HVOF thermal spraying gun consists of three sections: mixing zone, combustion zone and the nozzle. The body can be cooled by air or by water depending on the combustion temperatures used, however in this research air was used as the main cooling agent. To mix oxygen and fuel, co-axial jets are used. Combustion is initiated in the combustion zone by the use of a pilot flame or an external lighter. The powder flows by means of a carrier gas and is injected into the flame. The direction of surrounding expanded gas and the powder are all in the same direction.

Powder material is accelerated at a high velocity by the gas velocities travelling at 1350 m/s towards the substrate in the case of the Diamond Jet HVOF thermal spraying process [36]. Depending on the oxygen to fuel ratio or flow rate, the flame temperature for the HVOF process is between $2300 - 3000^{\circ}$ C [36]. Among all thermal-spraying processes, coatings produced by HVOF are less porous and have higher bond strength due to its high velocity and high impact of the sprayed powder [37]. The spray gun temperature for the HVOF system is less than 3000° C [13] compared to maximum temperature of the plasma spraying process

which is approximately $6000 \ ^{0}C$ [38] and because of this temperature difference the DJ HVOF system exhibits low thermal residual stress and consequently coatings of higher thickness may be deposited by this process [39].

The Diamond Jet (DJ) HVOF thermal spray process has been widely adopted in many industries due to its flexibility and cost-effectiveness [40]. Also this process is excellent for wear and corrosion resistance. Due to its use of high kinetic energy it expels the molten material at supersonic speed, this system is very effective in producing very low porosity and dense coatings with high bond strengths [41-44].

2.8 Combustion and Gas Dynamics of the HVOF System

The oxygen and fuel gas are mixed in the mixing zone of the gun under pressure and then directed towards the combustion zone. The ignition of the gases results in a chemical reaction and releases heat energy from combustion process. During the combustion process the pressure increases with the increase of temperature, which produces high gas velocities [45-46]. The simple chemical reaction at stochiometry (theoretically required for complete combustion) in terms of mass is as follows [47]:

$$C_{3}H_{6}+3.43O_{2}+XN_{2} \rightarrow 1.29H_{2}O+3.14CO_{2}+XN_{2}$$
 (eqn. 2.1)

After combustion the nitrogen is unaffected but propylene and oxygen form water and carbon dioxide gas. The water evaporates because of the high deposition temperature. The stoichiometric oxygen fuel ratio is 4.5 to 1. The energy released by the chemical reaction of the combustion gases is used to heat and accelerate both the spraying powder and the emerging gases. Temperature, pressure, density, gas composition and the area through which the gas travels are the main parameters on which the resulting gas velocity is dependent. However, the maximum obtainable gas velocity through the minimum cross sectional area is limited to the local sound velocity [47]. Significant research [33] and information [13] has been collected on the effects of gas dynamics on the HVOF gun and its influences on the final properties of the deposit.

Inside the combustion zone, the combustion gases are expanded in a converging diverging nozzle to achieve supersonic speed hence 'high velocity'. If propylene is the fuel gas the adiabatic flame temperature of the stoichiometric combustion gases is about 3000^{0} C [36]. The jet and flame temperatures are also dependent on the oxygen/fuel ratio as shown in *figure 2.11*. The flow chokes at the nozzle exit because of heat gain due to combustion and friction along the nozzle surface. As the combusted products pass the nozzle, the jet expands because the static pressure in the nozzle is greater than the ambient pressure and as a result expansion and compression waves occur in the free jet. The intersection of these compression and expansion waves from the bright region in the jet stream are usually known as shock diamonds [33, 45, 48].

Selection of the fuel gas is mainly determined by:

- a) Cost
- b) Coating material melting temperature
- c) Required coating properties of the substrate material

When high heat input is necessary, propylene or propane are mainly used as the fuel gas for the Diamond jet HVOF gun. Oxygen sensitive materials require hydrogen as the fuel gas. Acetylene is used as a fuel gas for high melting and oxide based ceramics. *Table 2.3* shows the summary of the spraying materials which are commonly used in the HVOF process. This research used propylene as a fuel gas. Generally propylene thermal properties and materials used would be similar to propane, hence one can extrapolate the values for propane in *table 2.3* to those for propylene.



Figure 2.11: Theoretical flame temperature against oxygen/fuel ratio [33]

Table 2.3: Summary of the spraying materials which can be used in the HVOF Process[49]

Type of Material	Spray Material	Fuel Gas	Hardness - HV _{0.3}
Metal	Cu	Propane	150 - 250
	Al	Propane	>120
	Mo	Propane, acetylene	600 -900
Metallic alloy	Steel	Propane, hydrogen	160 - 500
8	Nickel based alloy	Propane, hydrogen	400 - 750
	cobalt based alloy	Propane, hydrogen	400 - 750
Hard alloy	Nickel based alloy	Propane, hydrogen	250 - 800
	cobalt based alloy	Propane, hydrogen	400 - 700
Hard metal	WC-12 Co	Propane	1200 - 1700
	WC-10 Co-4 Cr	Propane	1000 - 1100
	WC-13Ni	Propane	about 1000
	Cr ₃ C ₂ -25 NiCr	Propane	about 900
Oxide ceramic	Cr ₂ O ₃	Acetylene	1200 - 1700
	Al ₂ O ₃	Acetylene	1200 - 1400
	Al ₂ O ₃ -40 TiO ₂	Acetylene	about 950

2.9 Comparison of HVOF and Plasma Thermal Spraying

The HVOF process is relatively simple and raises coating reproductibility. Though plasma spraying is currently the only FDA approved method for the production of HA coatings, the advanced features of the HVOF process give better results over plasma process like lower oxide content, improved wear resistance, crystallinity, lower porosity and higher bond

strength [13]. The difference in spraying parameters of HVOF and plasma spray process is given in *table 2.4*.

	HVOF	Plasma
Flame Temperature	3000 ⁰ C	11,000 ⁰ C
Gas Velocity	Mach 4	Subsonic to Mach 1
Torch of Substrate Distance	130-350 mm	75-150 mm
Angle of Deposition	$45^{\circ} - 90^{\circ}$	$60^{\circ} - 90^{\circ}$
Deposition Efficiency	75%	45%

 Table 2.4: Comparison of HVOF and Plasma Spraying Process Parameters [42]

2.10 Advantages and Disadvantages of the HVOF System

Particle velocity is an important factor in all thermal spraying processes, ensuring the higher the velocity, the higher the bond strength and the lower the porosity [33]. *Figure 2.12* shows how the quality of the coating improves with the velocity of the sprayed particles. There are many commercial thermal spray processes but HVOF gun can produce higher particle velocity than the other spray processes [33, 50-52].



Figure 2.12: Graphical illustration showing the improvement of quality of coating with velocity (FPS: Feet per second) [33]
Additional benefits of HVOF processes are as follows [13]:

- a) Lower flame temperature compared with plasma spraying
- b) More favourable environment due to less oxidizing atmosphere
- c) Strongly limited reaction and phase transformations
- d) High compressive residual stress possible
- e) Strong adhesion to substrates
- f) High cohesive strength
- g) High density
- h) Lower capital cost and ease of use compared to other processes
- i) More uniform and efficient particle heating due to high turbulence
- j) Reduced mixing with ambient air once jet and particle leave the gun
- k) Thicker coatings than with plasma and arc spraying can be produced
- 1) Lower ultimate particle temperatures compared to other processes
- m) Process can be automated
- n) Smooth as-sprayed surface finish
- o) Excellent machined surface finish

Table 2.5 shows summarises the reasons the HVOF process produces such high quality coatings.

Coating benefit	Main reasons for this benefit
Thicker coatings	Less residual stress
Lower oxide content	Less in flight exposure time to air
Improved corrosion barrier	Less porosity
Smoother as sprayed surface	Higher impact energies
Higher hardness ratings	Better bonding, less degradation,
	denser coatings
Greater chemistry and phase	Reduced time at higher temperature
retention	
Improved wear resistance	Harder, tougher coating
Fewer unmelted particle	Better particle heating
content	
Higher density (Lower	Higher impact energy
porosity)	
Higher bond and cohesive	Improved particle bonding
strength	

Table 2.5: Benefits of using HVOF coatings [13]

The main disadvantages of HVOF however are [13]:

- a) There is a possibility of overheating the substrate material because the amount of heat generated in the HVOF stream is very high. Cooling of the substrate to the required level is very significant. Cooling is carried out either using liquid CO₂ or air during spraying [53-55].
- b) To date mechanical masking is effective but masking of the part is still a great problem. However design an effective mask for a complex component with areas is very difficult and indeed time consuming [56].

2.11 Bioceramics

Ceramics used for the repair and reconstruction of diseased, damaged or worn out parts of the body are called bioceramics [57]. Ceramics are compounds between metallic and non-metallic elements; most frequently nitrides, carbides and oxides [58]. Most clinical applications of bioceramics relate to the dental and orthopaedic applications. Orthopaedic ceramics provide chemical materials with similarity between the composition of certain ceramic materials and that of tissues such as bone and teeth. Examples of the applications of various bioceramics are given in *table 2.6*. Ceramics use is small in range because of their inherent brittleness, micro cracks, low impact strength and low tensile strength.

Application	Ceramic
Coatings for chemical bonding	hydroxyapatite, surface-active glasses
Artificial tendons and ligaments	poly(lactic acid) (PLA)-carbon-fibre composites
Bone filler	alumina
Joint replacements	alumina, zirconia
Dental Implants	alumina, hydroxyapatite, surface-active glasses

 Table 2.6: Some bioceramics and their applications [59]

There are three main classes of bioceramics according to the response that they initiate within the body. These are [60]:

- a) Virtually inert ceramics
- b) Bioactive ceramics
- c) Resorbable bioceramics.

Bioceramics can be classified according to their compositions. These are [60]:

- a) Oxide ceramics
- b) Carbons
- c) Glasses and
- d) Calcium phosphate ceramics

Further information has been reported by Levingstone [60] on these classifications, hence this research will concentrate on the specific bioceramic of interest hydroxyapatite. There are variety of forms and phases to produce bioceramics and serve many different functions in repair of the body which are summarized in *figure 2.13*.



Figure 2.13: Clinical use of bioceramics [57]

2.12 Hydroxyapatite

2.12.1 Introduction

Hydroxyapatite (HA) is a hydrated calcium phosphate mineral. In 1788 Proust and Klaprota first recognised the similarity between calcium phosphate bioceramics and the mineral component of bone [61]. The development of many commercial and non-commercial calcium phosphate materials, including ceramic HA, non-ceramic HA, β -TCP, coralline HA, and biphasic calcium phosphates was based on this similarity. Albee [62] in 1920 first successfully repaired a bony defect with a calcium phosphate reagent, depicted as triple calcium phosphate compound.

Levitt and Monroe [63] developed methods for the production of ceramic materials for use in dental and medical applications in the late sixties and early seventies. The research continued and in the mid-seventies by authors in the USA, Europe and Japan where they worked simultaneously but independently for the development and commercialization of Hydroxyapatite [63].

Calcium phosphate ceramics have been used for dental implants, periodontal treatment, alveolar ridge augmentation, orthopaedics, maxillofacial surgery, and otolaryngology for about thirty years [64]. They are used as a coating material applied onto a tougher substrate because of their inherent brittleness in the case of loading bearing applications. For example HA coatings and HA composite coatings are used commercially for hip and knee replacements [60]. There are various different calcium phosphate compounds. Their chemical composition and Ca/P ratio are summarised in *table 2.7*.

Symbol	Phase's Name	Chemical Formula	Chemical Definition	Ca/P
МСР		$Ca(H_2PO_4)_2$	Monocalcium phosphate hydrate	0.50
DCPA	Monetite	CaHPO ₄	Dicalcium Phosphate Anhydrous	1.00
DCPD	Brushite	CaHPO.2H ₂ O	Dicalcium Phosphate Dihydrate	1.00
ОСР		$Ca_8H_2(PO_4)_{6.}5H_2O$	Octocalcium Phosphate	1.33
α-ΤСΡ		α -Ca ₃ (PO ₄) ₂	α-Tricalcium Phosphate	1.50
β-ΤСΡ	Whitlockite	β-Ca ₃ (PO ₄) ₂	β-Tricalcium Phosphate	1.50
ТТСР		Ca ₄ (PO ₄) ₂ O	Tetrecalcium phosphate	2.00
OHA		$Ca_{10}(PO_4)_6(OH)_{2-2x}O_x$	Oxyhydroxyapatite	1.67
OA		$\overline{\mathrm{Ca}_{10}(\mathrm{PO}_4)_6\mathrm{O}}$	Oxyapatite	1.67
HA		$Ca_{10}(PO_4)_6(OH)_2$	Hydroxyapatite	1.67

 Table 2.7: Some Calcium Phosphate Compounds [65-66]

2.12.2 Chemical Structure

Hydroxyapatite belong to the 'apatite' family which have a hexagonal structure. Compounds in this family have different composition but similar hexagonal structure. Werner [61] first named apatite as a mineral in 1786. The name was derived from the Greek word "to deceive" [61]. The chemical formula of HA is $Ca_{10}(PO_4)_6(OH)_2$ and it has Ca/P ratio of 1.67 [60]. Beevers and McIntyre first reported the structure of calcium HA and later refined by Kay et al. [63]. Most researchers advise that hydroxyapatite has a hexagonal crystal structure with a space group, P6₃/m [63, 67]. The atomic arrangement of calcium hydroxyapatite is given in *figure 2.14*. The *c*-axis perpendicular to three equivalent *a*-axis at angle 120⁰ to each other represent the arrangement of HA [70]. Ten calcium (Ca) atoms in the unit cell can be assorted into two types. Those are Ca₁ and Ca₂. In a hexagonal array, Ca₁ positions are occupied by four calcium atoms which are placed in polyhedrons site and six calcium atoms last Ca₂ position, situated at the corners of the hexagonal columns and also surround the OH⁻ ions [70]. PO₄ give structural stability for HA. The acceptance of a hexagonal P6₃ structure is limited because this structure gives a poor least squares fit to XRD diffraction. To get better

fit to diffraction patterns, two monoclinic models have also been suggested, P21/b [68] and P21 [69] and also more energetically favourable models of the structure of HA [69]



Figure 2.14: The atomic arrangement of calcium HA, Ca₁₀(PO₄)₆(OH)₂ [70]

2.12.3 Biological HA

Biological HA contains many impurities because of its apatite structure which allows the substitutions of many other ions. The impurities are typically calcium deficient and carbonate substituted. The Ca/P ratio of biological apatite is as low as 1.50. Sodium (Na⁺), magnesium (Mg²⁺), acid phosphate (HPO₄), potassium (K⁺), carbonate (CO₃²⁻), fluoride (F⁻), and chloride (Cl⁻) are the minor elements associated with biological apatites. Strontium (Sr²⁺), barium (Ba²⁺), and lead (Pb²⁺) are included as trace elements. Some of these minor and trace may be surface rather than lattice-bound. Synthetic HA and the main constituents of bone are compared in *table 2.8*.

Constituents (wt%)	НА	Bone
Са	39.6	24.5
Р	18.5	11.5
Ca/P ratio	1.67	1.65
Na	Trace	0.7
К	Trace	0.03
Mg	Trace	0.55
CO ₃ ²⁻	-	5.8

 Table 2.8: Comparison of bone and hydroxyapatite ceramics [71]

2.12.4 Process Involved in the Thermal Decomposition of HA

There are some processes involved in the thermal decomposition of HA. The heating of HA leads to three processes. These are [60]:

- a) Dehydroxylation
- b) Decomposition and
- c) Evaporation of water

The dehydroxylation reaction has been reported by many authors [72-73], is as follows:

Where V is vacancy and x < 1

Sridhar et al. [73] and Lazic et al. [74] reported the reaction involved in decomposition is as follows:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 2Ca_3(PO_4)_2(\beta) + Ca_4P_2O_9 + H_2O$$
 (eqn. 2.4)

Absorbed water and lattice water is present in the structure of hydroxyapatite. When HA is heated first the absorbed water begins to evaporate and later the lattice water starts to evaporate as reported by Sridhar et al. [73]. Further information on those techniques has been reported by Levingstone [60].

2.12.5 Temperature Effects on HA

In order to determine the effects of temperature on HA, researchers have used several techniques, such as Differential Thermal Analysis (DTA) [75-76], Thermo-Gravimetric Analysis (TGA) [74, 77], Fourier Transform Infrared Spectroscopy (FTIR) [78] and X-ray Diffraction (XRD) [78]. It is difficult to predict the exact temperature at which dehydroxylation and decomposition reactions occur.

The evaporation of water from hydroxyapatite occur between about 25°C and 600°C [73-75, 77]. The decarbonation occurs between 600°C and 700°C was reported by Park et al. [76] and Tampieri et al. [77] noted this decarbonation process at 800°C. This decarbonation process involves the decomposition of carbon which may not present in the crystals but due to handling carbon may be introduced. Tampieri et al. [77] found that decomposition began to occur from 1200°C and Sridhar et al. [73] reported that the decomposition of HA occur from 1050°C. The HA powder samples in this study were found not to show any phase transformation up to a temperature of 1450°C. Fazan [79] reported the melting temperature for HA to be 1550°C, 1630°C for TeCP and 1730°C for TCP. *Table 2.9* shows the temperatures ranges in which reactions occur for HA.

Temperature	Reactions
25-600°C	Evaporation of water
600-800°C	Decarbonation
800-900°C	Dehydroxylation of HA forming partially dehydroxylated (OHA) or completely dehydroxylated oxyhydroxyapatite (OA)
1050-1400°C	HA decomposes to form β -TCP and TTCP
<1120°C	β-TCP is stable
1120-1470°C	β -TCP is converted to α -TCP
1550°C	Melting temperature of HA
1630°C	Melting temperature of TTCP, leaving behind CaO
1730°C	Melting of TCP

Table 2.9: Thermal effects on Hydroxyapatite [60]

When HA powder is heated it has been found that the partial pressure of water in the surroundings atmosphere and the stoichiometry of the HA powder have the greatest effect on the phase formed. Fang et al. [80] reported the effect of stoichiometry on the thermal stability of HA from experiments where HA powder samples with Ca/P ratios being 1.52 to 1.68 were heated to 1100° C. *Figure 2.15* and *figure 2.16* shows the phase diagrams which depict the thermal behaviour of CaO-P₂O₅ system at high temperatures in environment with the presence of water vapour or without the presence of water vapour. *Figure 2.17* shows the system when no water vapour is present. In order to avoid the dehydroxylation and decomposition of HA during High Velocity Oxy-Fuel (HVOF) thermal spraying one should use a highly stable, crystalline, stoichiometric HA powder.



Figure 2.15: Phase diagram of the system CaO-P₂O₅ at high temperature. No water present [60, 81]



Figure 2.16: Phase diagram of the system CaO-P₂O₅ at high temperature; at a partial water pressure of 500mmHg [60, 81]



Figure 2.17: Influence of ambient water vapour pressure on phase composition [60, 81]

2.12.6 Mechanical Properties

There are different methods used in the manufacture of calcium phosphate and the mechanical properties of calcium phosphate vary depending on their manufacture route [82]. HA powder is different in grain size and in composition because of the difference in preparation methods of the HA scaffold materials. Small grain size gives greater fracture toughness. *Table 2.10* shows the comparison of the mechanical properties of typical orthopaedic HA and bone.

 Table 2.10: Mechanical Properties of HA and Bone [83]

Properties	Cortical Bone	Cancellous Bone	HA Scaffolds
Compressive Strength (MPa)	8-164	23	350-450
Tensile Strength (MPa)	82-114	10-20	38-48
Young's Modulus (GPa)	3.8-11.7	0.2-0.5	7-13

The resistance of a material to fatigue failure can be described in terms of the Weibull factor, n. Values of 50 to 100 are usually associated with good resistance [84]. The Weibull factor for pure HA was found to be 50 in a dry environment and 12 in a wet physiological environment [79]. Though HA is excellent biocompatibility and osteoconductivity but for use in load bearing applications HA is unsuitable. This is why HA is applied as a coating material on a substrate so that higher strength and fatigue resistance can be achieved.

2.12.7 Clinical Performance of HA Coated Implants

The Swedish Total Hip Replacement Register was the first National Joint Registry [85]. It was established in 1979 and renders useful data relating to the types of implants and the performance of implants [86]. Different countries use different cementless fixation techniques. According to the 1st Annual Report published by the National Joint Registry for England and Wales [87] in September 2004 presents that cementless cups and stems were used extensively in Australia and Canada than in Sweden or England and Wales. The researchers worked to improve the performance of uncemented implants. Infection (11%), dislocation (31%) and aseptic loosening (19%) were the main reasons for failure of uncemented implants [87]. In recent years, the performance of uncemented implant designs have much improved and they now have similar life expectancies to cemented implants [87]. *Table 2.11* shows different implant fixation techniques which was published by National joint registry in 2004 [87].

National joint registry	Cemented cups	Cementless cups	Cemented stems	Cementless stems
Australia	18.50%	81.50%	58.40%	41.60%
Canada	7%	90%	44%	55%
England & Wales	69.30%	30.70%	80.70%	19.30%

 Table 2.11: Implant fixation techniques [87]

* data only collected between April and December 2003

2.12.8 Hydroxyapatite Powder

The quality of coatings depends on the shape and microstructure of HA powders. In the case of flow properties, spherical particles are better than angular particles. More consistent coating is possible if the particle size range of the powder is narrow. The most important characteristics of HA powder is the composition and crystallinity. The ceramic HA for surgical implants should have a minimum HA content of 95% according to the ASTM Standard Specification (ASTM Designation: F1185-88, [88]). This HA content was determined by a quantitative X-ray diffraction analysis. A sample XRD pattern for hydroxyapatite powder is shown in *figure 2.19*. The maximum allowable total limit of all heavy metals is 50 ppm and the Ca/P ratio for HA used for surgical implants must be between 1.65 and 1.82 [88]. *Table 2.12* shows the maximum allowable limit for the concentration of trace elements.



Figure 2.18: XRD pattern for HA Plasma Biotal Powder [60]

Elements	ppm. max
Arsenic (As)	3
Cadium (Cd)	5
Mercury (Hg)	5
Lead (Pb)	30

 Table 2.12: Limits of the Concentrations of Trace Elements [89]

2.13 Properties and Analysis of Hydroxyapatite Coatings

2.13.1 Coating Purity

The most important methods for determining the atomic arrangements in matter is X-ray Diffraction (XRD). It is used to provide information on the physical state of the sample and also to identify the phases present in samples. To calculate the purity of HA coatings, one needs to sum the areas of all of the HA crystalline peaks and the sum of the area of the impurity peaks. The areas of all non-HA peaks that are found in the diffraction pattern. HA purity of a coating can also be determined by calculating the area in the region where the tallest peaks of impurity phases are present. Coating purity can be calculated using *equation* 2.5 [96].

$$Purity(\%) = \frac{\sum A_c - \sum A_i}{\sum A_c} x100$$
 (eqn. 2.5)

Where $\sum A_c =$ The sum of the areas of all HA crystalline peaks $\sum A_i =$ The sum of the area of the impurity peaks.

According to the ISO standard specification (ISO 13779-2:2000) [90] the maximum allowable level of other non-HA phases in plasma spray HA coating is 5%. The phase purity of HA coatings is important because of the differences in dissolution properties between the different calcium phosphate phases.

2.13.2 Coating Crystallinity

High crystallinity in the coating is derived mainly from the unmelted core of powder particles. The Crystallinity of a HA coating depends on the degree of melting of the powder particles. If particles are highly molten, on impact they either recrystallise or are converted to amorphous HA, depending on the rate of cooling [91-92]. The cooling rate depends on the degree of particle spreading and the temperature of the substrate. Coating thickness should be 20µm for recrystallisation of amorphous material to occur [92].

The crystalline content should be greater than 45% for a HA coating to have sufficient mechanical properties in vivo according to the ISO standard specification (ISO 13779-2:2000) [90]. For medical application the required crystallinity is more than 95% [90]. In general, the Crystallinity of HA plasma spray coatings is about 65-70% for biomedical use [93]. Dalton and Cook [94] found crystallinity to vary between 57 and 61 % by comparing four different commercially available plasma spray coatings.

There are three methods by which determination of the crystallinity of HA coatings can be achieved using X-ray Diffraction [96]:

- a) The Relative Intensity Method
- b) The Rietveld Method
- c) The Rutland Method

The most commonly used accurate method for determining crystallinity is the Rutland Method [91, 93, 95]. Further information on the other methods has been reported by Levingstone [96], hence this is not described here. According to the Rutland Method, crystallinity of HA coating can be determined by comparing the total area under the diffraction pattern with the area of the amorphous region of the pattern. Crystallinity of HA coating *equation 2.6* [96].

$$Crystallinity(\%) = \frac{\sum A_c}{\sum A_c + \sum A_a} x100$$

(eqn. 2.6)

Where $\sum A_c =$ The sum of the areas of all HA crystalline peaks and $\sum A_a =$ Tthe sum of the area under the amorphous peak.

2.13.3 Porosity

Porosity is an important parameter, though porosity required for HA coatings is unspecified by the Food and Drug Association (FDA). Sun et al. [91] states that porosity of commercially available HA plasma spray coatings can be as high as 50%. Porosity permits a greater degree of dissolution of the coating which, can have a positive influence on bone growth. The mechanical properties of a coating affects negatively if porosity increased. In the case of bonding degradation denser coatings are reported to be at lower risk.

The porosity of HA coatings is most commonly calculated from microscope images of the cross-section of the coated sample. The porosity of ceramics coatings is outlined in DD ENV 1071-5:1995 [97] according to the BSI standard testing method. Porosity of HA coating can be calculated using *equation 2.7* [96].

$$A = \frac{(x+x^1)}{y} \tag{eqn. 2.7}$$

Where A = The area fraction, X = The number of intersections of the grid that fall within a pore, $x^{1} =$ The number of intersections of the grid that fall on a pore boundary, y = The total number of grid intersections in the field of view.

2.13.4 Coating Thickness

Coating thickness is dependent on the following parameters:

- a) The number of passes of the HVOF gun
- b) The amount of powder fed into the HVOF flame
- c) The deposition efficiency

The coating thickness can be increased by increasing the number of passes of the HVOF gun. Thicker coating is dependent on higher powder feed rate. If the spray distance is increased then the deposition efficiency will decrease because unmelted portions of the particles may be deagglomerated and blown away before they impact on the substrate [91].

Plasma spray HA coatings have been produced in the range between 50 μ m and 200 μ m in thickness [98]. Thick coating provide better protection for the bone from metal-ion released from the substrate and remain in the body for longer times. Because of residual stresses, thicker coatings leads to cracking. Though thin coatings perform better mechanically; but, they provide less protection from metal-ion release from the substrate (Ti Alloy).

2.13.5 Coating Roughness

The roughness of the coating is affected by the size of the powder particles used. Thicker coatings have a greater surface roughness. Gross and Babovic [99] state that partially melted particles were not able to flatten on the coating surface giving rise to large undulations and thus higher coating roughness. Bone growth depends on coating roughness. Osteoblast cell attachment is affected by the surface roughness of the HA coating and thus bone growth on the coating once it is implanted into the body. Osteoblasts attach and proliferate better on rough surfaces, on the other hand fibroblasts and epithelial cells prefer smoother surfaces [100-101]. HA powder particles with an average size of 20 to 30 μ m were found to give a plasma spray coating roughness of 4 to 6 μ m [96].

The roughness of the surface of HA coating can be calculated using equation 2.8 [43]

$$R_a = \frac{\int_0^l |y| dx}{l} \qquad (eqn. 2.8)$$

Where $R_a = Absolute roughness$

The R_a parameter is the average distance between the surface of the coating and the mean line, as shown in the *figure 2.19*.



Figure 2.19: The R_a Parameter [Error! Bookmark not defined.]

2.14 Optimisation of Hydroxyapatite Coatings

2.14.1 DOE Experiments

A maximum of information with a minimum number of experiments can be found by varying the factors simultaneously with the help of statistical experiments [102]. Design of Experiments (DOE) usually deals with these statistical experiments. "Factors" or "Variables" represent the parameters chosen while using the DOE technique. The levels chosen as the different possibilities for each factor. Levels can be divided in two categories. One is qualitative and the other one is quantitative. The DOE technique gives the experimental output based on response found. The effect of each factor on a response using ANOVA techniques. *Equation 2.9* is a form which represents the responses as a polynomial equation [96].

$$Y = b_0 + \sum b_j X_j + \sum b_{ij} X_i X_j + \sum b_{ijk} X_i X_j X_k$$
 (eqn. 2.9)

Where *i*, *j* and *k* vary from 1 to the number of variables (b_0 , b_i , X_i , b_{ij} , b_{ijk}) $b_0 = The mean of the responses of all the experiment$ $b_i = Coefficient$ which represents the effect of the variable X_i , b_{ij} , $b_{ijk} = Which$ represent the effects of interactions of the variable X_iX_j and $X_iX_jX_k$ respectively

Sir R. A. Fisher [103] first introduce the Design of Experiment method in the early 1920's. Fisher formulated the method for agricultural experiments. Dr. Genechi Taguchi [103] brought out the DOE technique with further improvements in the 1940's. The implementation of DOE becomes easier after introducing a number of special orthogonal arrays.

2.14.2 Two-Level Factorial Experiment

Two-level full factorial experiments uses all possible factor levels. A two level experiment with k number of factors is known as 2^k experiment. The Design Expert by Stat-Ease offers 2 to 21 factors for up to experimental 512 runs. 2 levels minimises number of experiment tests but the DOE still gives optimal results using the models it applies. For this research a 2^5 experiment was used to study five factors which consisted of 32 experiments. The coded design for 2^5 experiment is shown in *table 2.13*. The factors are set as low level which is coded as -1 and high level which is coded as +1. In this DOE experiment, Replicate represents repeated samples and Block represent repeated experiment (for example 0 means no repeats and 1 means one experiment repeated). Responses (experimental measurements) are applied experiment. 1 to 999 responses can be measured with Design Expert. For this research two responses were selected. During this experiment few factors may exist which may have little or no effect on the results though those factors are not the primary concern. These factors should be taken out from the overall results. Centre points used in factorial design allow process stability. Usually in an experiment design, between 3 and 6 centre points are used [96].

Table 2.13: 5-factor, 2-level Factorial Experiment

Run	X1	X2	X3	X4	X5
1	-1	-1	-1	-1	-1
2	1	-1	-1	-1	-1
3	-1	1	-1	-1	-1
4	1	1	-1	-1	-1
5	-1	-1	1	-1	-1
6	1	-1	1	-1	-1
7	-1	1	1	-1	-1
8	1	1	1	-1	-1
9	-1	-1	-1	1	-1
10	1	-1	-1	1	-1
11	-1	1	-1	1	-1
12	1	1	-1	1	-1
13	-1	-1	1	1	-1
14	1	-1	1	1	-1
15	-1	1	1	1	-1
16	1	1	1	1	-1
17	-1	-1	-1	-1	1
18	1	-1	-1	-1	1
19	-1	1	-1	-1	1
20	1	1	-1	-1	1
21	-1	-1	1	-1	1
22	1	-1	1	-1	1
23	-1	1	1	-1	1
24	1	1	1	-1	1
25	-1	-1	-1	1	1
26	1	-1	-1	1	1
27	-1	1	-1	1	1
28	1	1	-1	1	1
29	-1	-1	1	1	1
30	1	-1	1	1	1
31	-1	1	1	1	1
32	1	1	1	1	1

2.14.3 Analysis of Variance (ANOVA)

DOE models can be assessed by using analysis of variance (ANOVA). The statistical significance of the models originated can be found out on the basis of a number of sufficiency measures. Adequate Precision, R^2 , Adjusted R^2 and Predicted R^2 are the most important. The range in predicted response relative to its related error (the signal to noise ratio) is evaluated by adequate precision. The value of adequate precision should be greater than 4. The response variables to the combined linear predictor variables are represented by the R^2 value. The value of R^2 is between 0 and +1. The fraction of the overall variation in the data calculated by the model is represented by the adjusted R^2 . The amount of variation in new data explained by the model is evaluated by the predicted R^2 . Difference between adjusted R^2 and predicted R^2 should be within 0.2 of each other.

A summary of the DOE studies investigated in this research is given in table 2.14.

Experiment Type	Description	Factors	Responses
2 ⁵ Factorial Design	5 factors; 2 levels; 2 responses; 32 experiments	Oxygen flow meter reading; Propylene flow meter reading; Air flow meter reading; Spray distance; Powder feed rate	Crystallinity; Purity

Table 2.14: Summary of DOE studies of HVOF sprayed HA coatings

2.14 Chapter Summary

This literature survey discussed the background knowledge about high velocity oxy fuel and plasma sprayed hydroxyapatite coatings and the properties of hydroxyapatite. By using plasma spray Levingstone [96] produced the highest average crystallinity of 87.6% and a highest average purity of 99.4%. The aim of this research is to establish if HVOF can be used to achieve similar crystallinity and purity results and perhaps propose the HVOF as a new method for depositing HA for orthopaedic implant applications.

CHAPTER THREE

EXPERIMENTAL PROCEDURES AND EQUIPMENT

3.1 Introduction

The High Velocity Oxy Fuel (HVOF) facility used in this current research is manually controlled continuous combustion Sulzer Metco Diamond jet thermal spray system. HVOF thermal spraying system includes three main units that is the control system, the spraying system and the support systems. The spraying system was supplied by Sulzer Metco and the controlling and support systems were purchased from different companies. A vaporizer unit was purchased during this research to achieve high flow rate of fuel gas. A schematic diagram of a complete thermal system is shown in *figure 3.1*. Suitable preparation for operator safety must be introduced because thermal spraying can be a hazardous operation.

3.2 Spraying System

The objective of Diamond Jet thermal spraying equipment is to transfer both thermal and kinetic energy to the powder particle with a high degree of efficiency and balance. Internal combustion of propylene and oxygen produce high particle velocities within an air cooled chamber. The HVOF thermal spraying consists of the followings [13]:

- 1. Diamond Jet (DJ) gun
- 2. Gas supply unit
- 3. Flow meter unit
- 4. Powder feed unit
- 5. Air control unit

The working principles and descriptions of these units are described in the following subsections.



Figure 3.1: Schematic of the HVOF thermal spray system [13]

3.2.1 Diamond Jet (DJ) Gun

Diamond Jet is a commercial name given by the manufacturer. *Figure 3.2* shows a schematic and photo of the Diamond Jet (DJ) gun used in this current research. The gun consists of five main assemblies. These are given below:

- 1. Control handle
- 2. Front end
- 3. Valve core
- 4. The main body and
- 5. Hose connection block

The approximate length of the gun is 228.6 mm, height including handle is 241.3 mm and 127 mm wide. The weight of the gun is 2.27 kg. The control handle contains a push button on-off switch. The flow of the powder from the powder feed unit to the gun is controlled by this onoff switch, however it does not turn off the flame. The front end assembly consists of six concentric assemblies as shown in *figure 3.3*. These are powder injector, siphon plug, nozzle assembly, nozzle nut, air cap and air cap body. The cross section view of the front end assembly is shown in *figure 3.4*. There are different regions in the front end assemblies. The fuel gas and oxygen are mixed together and burned at various stages at these regions. Propylene (C₃H₆) was used as a fuel gas in this current research. Siphon plug is the central part of this assembly. Gases are transferred from the hoses to the siphon plug through the valve core. Propylene gas enters the siphon plug in region three and oxygen in region two. In region three both of the gases are mixed and pass through the hole of the tip of the shell. Both the tip of the shell and the combustion process occurs at region four. When combustion takes place, compressed air circulates within the air cap body to cool the assembly at region five. The incoming gases from the back end of the gun with high pressure forces the combustion gas product out at supersonic speeds of 1350 m/s [37]. The valve core is a cylindrical part consists of O-rings, grooves and a series of passages are also shown in figure 3.4, housed within the gun body [37]. A lever type handle which is attached at the end of the valve core help to control the flow of gases through the gun. It is possible by selecting different positions of the valve core. The valve handle must be rotated to the full up position to turn off the flame. Air, fuel and oxygen hose connections are attached with the hose connection block. Allowing the gases to be transferred into the valve core and making the connection leak proof,

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gas tight plungers are also attached to the hose connection block. *Table 3.1* shows the concentric assemblies sizes used for HA deposition. Further information about this HVOF DJ gun has been reported by Stokes [104].



Figure 3.2: The Sulzer METCO Air-Cooled HVOF type Diamond Jet (DJ) gun [104]

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Figure 3.3: The HVOF DJ gun front-end hardware [104]



Figure 3.4: Schematic of the cross-section of the assembled Diamond Jet gun [104]

Concentric Assemblies	Siphon Plug	Shell	Gun Insert	Injector	Air Cap
Sizes Available	1 - 3	A - B	Jet 1 - 3	1 - 3	1 - 3
Sizes used for	2	А	Jet 3	3	2
HA deposition					

 Table 3.1: The concentric assembly used in the Diamond Jet HVOF process [37]

3.2.2 Gas Supply Unit

The pressure and flow of compressed air, nitrogen, oxygen and propylene gasses are controlled by the gas supply unit. High flow rate of oxygen is required because it is used as an oxidant during combustion. Four 70 kg cylinders of oxygen were used to achieve the high flow rates and pressures, shown in *figure 3.5*. Propylene was used as the combustion gas in the current HVOF thermal spraying system is shown in *figure 3.6*. In order to achieve the necessary flow rates and pressures, two 45 kg propylene cylinders and a vaporiser system pressurised by nitrogen were used. Compressed air is regulated by an air control unit, to filter and control the air pressure to the gun. The compressor is shown in *figure 3.7*. The compressed air operates at pressure at pressures in the range 6.8 to 10.2 bar and flow rates from 300 to 500 standard litres per minute [104]. Compressed air was used by the system for the following reasons:

- 1. The combustion chamber of the gun was cooled by a small proportion of the compressed air and majority of the air is fed through the nozzle assembly to accelerate the particles onto the substrate.
- 2. Some air is used to accelerate the Air Vibrator in the hopper unit.

Two cylinders of nitrogen gases were located outside of the HVOF lab. One nitrogen gas used as the powder carrier gas in the system and another nitrogen gas was used to pressurise the propylene cylinder / vaporiser.

Depending on the powder material used for deposition, suggested pressure / flow rate optimum values may be found in the Sulzer METCO data charts [37]. *Table3.2* shows a data sheet for stainless steel. However as hydroxyapatite has never been sprayed using the HVOF technique therefore no Sulzer Metco charts exist. Hence the optimised pressure / flow rates were the focus of this research. All of the gases were is located outside the thermal spraying housing area for safety reasons. Risk of fire can be minimize by checking the gas leaks regularly.

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Figure 3.5: Four oxygen cylinders used in the HVOF process



Figure 3.6: Two propylene cylinders used in the HVOF process



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Figure 3.7: Compressor used in the HVOF process to produce clean dry compressed air

Spray Parameters	Stainless Steel
Oxygen pressure	10.3 Bar
Oxygen flow	265.4 SLPM*
Propylene pressure	6.9 Bar
Propylene flow	71.4 SLPM [*]
Air pressure	5.2 Bar
Air flow	317 SLPM*
Nitrogen pressure	12.1 Bar
Nitrogen flow	317 SLPM*
Spray distance	200 mm
Powder feed rate	45 gm/min

|--|

* SLPM = Standard litre per minute

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3.2.3 Flow Meter Unit

The gas flow meter controls and monitors the supply gases, oxygen, propylene and compressed air required by the gun. A type DJF gas flow meter unit is shown in *figure 3.8*. The unit consists of flow measuring glass tubes, accurate flow adjustment valves and pressure gauges. Each flow measuring tapered glass tube consists of a float located within it, which moves up and down. The flow rate is different for different coating material and spraying condition of the gun. The flow rate of each individual gas increases or decreases by twisting the adjustment valve.

Oxygen and propylene flow lines are installed with flashback arrestors and check valves to avoid backfire which may occur in the combustion chamber of the gun [105]. Flashback arrestors guard against sudden increase of pressure and make the system safer. To prevent back flow of gases, check valves are installed at the inlet of the gun body. The pressure and flow rates may be adjusted within \pm 0.1 Bar and \pm 1 Flow Meter Reading (FMR); within a range from 0 to 11 Bar and 0 to 100 FMR respectively [106].

Equation 3.1 can be used to convert one flow meter (FMR) reading into Standard Litres per Minutes (SLPM). The gases are set at their dynamic flow rate level for stainless steel according to *table 3.2*. The gas pressure P_g used to produce the flow rate [104].

Standard Litres per Minute (SLPM) = FMR × $1.89 \times \sqrt{P_g}$ (eqn. 3.1)

Where $P_g = Gas \ pressure$

FMR= *Flow meter rate*

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Figure 3.8: Type DJF Diamond Jet gas flow meter unit used in the HVOF process [104]

3.2.4 Powder Feed Unit

The DJP powder feed unit used in this current research was manufactured by Sulzer Metco is shown in *figure 3.9*. The function of the powder feed unit is to deliver powder to the gun at an exact flow rate (g/min) and the unit is completely self contained [37]. The powder feed unit consists of:

- a) A hopper assembly
- b) load cell
- c) feed rate meter
- d) air vibrator
- e) control cabinet

When combustion occurs in the gun, the desired powder is fed from the powder fed unit through nitrogen gas which was used as a carrier gas to carry the powder particles in this case. The hopper is filled with the powder material. Powder drops into the powder port shaft due to vibration of air vibrator, gravitational force and nitrogen gas pressure within the chamber, as shown in *figure 3.10*. The carrier gas nitrogen transports the powder through the port shaft on its way to the combustion zone through the powder injector of the gun. Flow of the carrier gas nitrogen is regulated by using control knobs and this is set according to the data outlined in the application charts [37]. The powder is allowed to flow from the hopper to the combustion chamber by means of an on-off switch attached in the handle of the gun. The feed rate meter display the amount of powder flowing through the gun which is measure by the load cell provided. The weight of the hopper continuously recorded by the load cell attached to the hopper assembly. The flow rate can be displayed in gmin⁻¹ or lbs (hour)⁻¹. The feed rate meter has an accuracy of \pm 0.1 gmin⁻¹ and a range of 0 to 100 gmin⁻¹ [104]. There is a powder feed and pressure ON/OFF indicators located on the control panel of the feed unit system. A detail description is reported by Stokes [13], therefore it will not be expanded upon here.




Figure 3.9: The DJP powder feed unit used in the HVOF process [13]



Figure 3.10: A schematic cross section of the hopper assembly on the DJP powder feed unit [13]

3.2.5 Air Control Unit

The air control unit contains a pressure regulator and two filters as shown in *figure 3.11*. Adjusting the air pressure to the gun is provided by the regulator. A constant pressure in the system regardless of changes in the line pressure can be maintained by the regulator. One filter is placed in front of the regulator to remove oil, water and pipe scale. The other filter is located down stream to trap any additional oil or water, which remove the pressure drop through the regulator [105].



Figure 3.11: Picture of the Air control unit

3.3 Supporting Systems

Some support facilities are required to make the thermal spraying process safe and workable. The most important part is the safety of the operator and also proper functioning facilities must be in place before the operator commences to spray. The powder materials used during thermal spraying are very often hazardous. Therefore personal safety equipment is most important and must be worn before spraying. Some of the other supporting facilities and additional equipments discussed will be:

- a) Gun traverse unit
- b) Grit blasting unit
- c) The vaporiser unit
- d) Spray booth and exhaust system
- e) Facility isolation and
- f) Safety equipment

3.3.1 Gun Traverse Unit

Residual stress increases in the deposited material when thermal spraying process is carried out by manual operation [13]. To reduce the residual stress and control the spraying distance, a semi-automated process for traversing the spray gun was developed in the DCU Materials Processing Research Centre [13]. A LX-L20 Series Linear Stepper Motor (LX stands for Linear X-direction) operates using electro-magnetic principles was used to traverse the spray gun back and forth across the face of the substrate and was developed by the Parker-Hannifin Compumotor Division as shown in *figure 3.12*. The traverse unit has two main components. Those are:

- a) The stationary element is called the planet
- b) The gun is mounted on the moving element is known as forcer

A specially written computational program where the commands are given in LX language and developed by the Compumotor Division was used to control speed and acceleration during spraying. The following procedure was used to run the traverse unit [13]:

- MPI Set unit to incremental position mode*
- MFI Define Move-Form 1
- A0.3 Sets Acceleration to $0.3g (2.943 \text{ms}^{-2})$
- V10 Sets velocity to $10ips (0.254ms^{-2})^{**}$

Pre heat treatment loop (L5 - N)

L5	Loops following code five times for pre-spray treatment
D12000	Sets distance to 12,000 steps***
G	Execute the move (Go)
Н	Reverse the direction
G	Execute the move (Go)
Ν	Ends loop
Т3	Waits 3 seconds before carrying out next operation****
Spray loop (]	L20 - N)
L20	Loops twenty times

- D12000 Set distance to 12,000 steps
- G Execute the move (Go)

- H Reverse the direction
- G Execute the move (Go)
- N Ends loop
- C Initiates command execution to resume

* The moves that follow will be carried out in incremental moves

- ** ips = inches per second
- *** 1000 steps = 1 inch (0.0254 m)

**** Allows three second of a delay before running the next procedure (During these three seconds the powder feed is turned on)



Figure 3.12: Various planes and directions relevant to the linear traverse unit [13]

3.3.2 Grit Blasting Unit

There are several methods of preparing substrate surface for achieving good quality coating, grit blasting is one of them. A clean substrate surface is most important for adhesion of coating on the substrate surface. Increase of effective substrate surface by roughening is a well known method of cleaning a surface [37]. Because of roughness bond strength increases between a coating and its adjoining substrate. To prepare the substrate surfaces for this current research, a grit-blasting unit supplied by Sulzer METCO was installed as shown in figure 3.13. This unit is also known as Ventublast Mammouth. The internal area of the grit blasting cabinet is 0.87 m². The system also includes a grit collector facility and a hand held blasting gun. A compressor was used for grit blasting which supply clean dry air. The supply pressure used by the blasting equipment from the compressor is controlled by a pressure controller. The blasting gun is made of ceramic material. The grit is collected by a vacuum into a compressed air stream and forced from the gun to the substrate surface. Rebounding grit bounces of the substrate and is then collected under a grid chamber for recycled use. The substrate surface roughness varies in the range of 6 to 15µm which depends on air pressure and the blasting distance [13]. The entire process can be observed by the user through the visor of the blasting unit.



Figure 3.13: Picture of the grit blasting unit used to prepare samples for deposition

3.3.3 The Vaporiser Unit

The principal of the vaporiser unit is to evaporate liquid propylene and pressurise it. This vaporiser unit was installed new because previously propylene gas cylinders were placed inside the room which were heated up by increasing the room temperature and was not safe for the operator and the system. This vaporiser unit was installed by BOC gases U.K. and incorporated with the DCU HVOF thermal spray system.

The schematic diagram of this vaporiser which was used in this current research is shown in *figure 3.14*. This vaporiser is heated up by electrical power supply (heating element) and necessitates D-Ionised water plus 33% Glycol Mixture (Ordinary Anti-Freeze). It is necessary to ensure water level in vaporiser is near the top level of the vaporiser as shown in *figure 3.14(a)*. Before the power supply is turned on the Flame Proof Lid in figure 3.14(a) should be open and the vaporiser operating temperature as shown in figure 3.14(b) should be set to 70 ° C and the Cut-Off to 80 ° C. This means that if the temperature goes above 80 ° C, the green trip goes to an off position rather than the element burning out as shown in *figure 3.14(c)*. The green trip should switch in ON position to turn the vaporiser on again as shown in figure 3.14(c).



Figure 3.14: A schematic diagram of vaporiser and its initial set up [107]

Figure 3.15 shows a schematic diagram of the connection of vaporiser system. After turning on the power supply the operator has to wait for 30 minutes so that the vaporiser can heat up to the 70 ° C as shown in *figure 3.15(a)*. The waiting time may vary depending on the atmospheric temperature. The operator must open the nitrogen line and set the pressure regulator to 7 to 8 bar so that the propylene can flow to the HVOF process. After this the propylene lines are opened. Blue tap was opened first and then the red tap as shown in *figure 3.15(b)*. If the vaporiser is 50 ° C or higher then propylene will flow into the vaporiser. According to the BOC gas company manual the regulators, valves and lines should be replaced in every five years. A picture is shown in *figure 3.16* of the BOC propylene vaporiser unit used in this current research.



Figure 3.15: A schematic diagram of the connection of vaporiser unit [107]



Figure 3.16: Picture of the vaporiser unit used to pressurise propylene

3.3.4 Spray Booth and Exhaust System

While conducting spraying it is very important to remove the dust, fumes and over spray as early as possible for health and safety reasons. This is possible if a spray enclosure is used. To guide and contain all airborne dust, fume and overspray within its enclosure, a spray booth was used as shown in *figure 3.17* and which extracted the products through a 4CW wet collector extractor as shown in *figure 3.18*. The wet collector first sucks the air by a centrifugal fan from the operation area and picking up all the dust and fumes through a water reservoir where the waste products sink below [104]. It is most important to check the water level is topped up before the operator starts the spraying.

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Figure 3.17: The HVOF spray booth used to contain the air-born particles and fumes from the DJ gun



Figure 3.18: Picture and cross-section of the Sulzer METCO wet collector [104]

3.3.5 Facility Isolation

During the thermal spraying operation, HVOF DJ gun generates high noise level in the region of 126dB which is similar to that generated by a jet airplane [104]. When the extraction system is on then it generates 85db on its own and when the gun and extraction both are on then the noise level rise up to 130 dB [104]. Hence it is important not only keep the spraying equipment into a confined room, but also the room should be insulated with a sound proof material. A cavity wall of peg-board sheets was built in 1991 in the HVOF lab facility and the central portion was filled with fibreglass. The outside of the room is covered with aluminium sheeting to protect the surrounding room in case of fire which was shown in *figure 3.19*. Also an air compressor which is on during the thermal spraying operation, generates a noise level of 89dB [104]. When air compressor, the gun and extraction all are on at the same time, the noise level was measured 92dB in the isolation room and in the closest room outside the facility the noise level was measured as 64dB [104].



Figure 3.19: Schematic of the cross-section of the sound proof wall used in the HVOF thermal spray room (A) and the measure of the noise levels (B) [13,104]

3.3.6 Safety Equipment

The operational and installation manuals supplied by Sulzer METCO should be always followed by the operator for safety reasons. Because of that all personnel whoever will use the thermal spraying system must be properly trained in the safe use of the equipment and also must be familiar with the safety practices of the process. The basic precautions for thermal spraying are given below [104]:

- a) Good housekeeping which include check all tops, over head pipes regularly and allowable accretion of dust maximum 3mm.
- b) Appropriate maintenance and use of equipment.
- c) Proper gas or material storage and handling practices.
- d) Proper exhausting of gases and fumes.
- e) Safety protection which include clothing, ear, eyes and breathing protection.

Personal safety is always up to the operator during thermal spraying operation. The gas cylinders should be stored away from heat and water. All gas cylinders are always chained so that they can not fall. When the cylinders are not connected for use, valve caps should be inserted into the cylinders. It is very important to shut the valve, discharge and remove the regulator and put on the valve cap before moving any cylinder. In the case of Diamond jet equipment, all of the equipment should be maintained according to the maintenance procedure. If there is a need to replace any parts then the replaced part should be approved by Sulzer METCO. During powder pouring or powder changing and also thermal spraying, twofilter type respiratory mask must be worn, one for fine particles and the other for gases. The operator must wear a eye protective glass or shields of shade 5 (welding glasses) or higher which will give protection against any flying particles caused by the jet flow and against ultra-violet radiation from the spraying flame. If lenses and cover plates are scratched, damaged or pitted, then those should be replaced by new ones and thusly eve protectors must be inspected frequently. Heat resistant gloves and fire resistant clothing is necessary during thermal spraying operation. There are excessive noises when the extractor, compressor and the gun is on, because of that hearing protectors must be used all the times. To avoid ingestion or irritation of the powder material, hands must be washed by soap and water after the whole HVOF operation is finished.

3.4 Hydroxyapatite Powder

Captal 60-1 Thermal Spraying Hydroxyapatite powder was used for the biocoating supplied by Plasma Biotal Ltd. UK, as shown in *figure 3.20*. The average particle size of this powder was 45 µm and it was produced specially for thermal plasma spray applications.



Figure 3.20: Captal 60-1 Hydroxyapatite Powder

3.5 HVOF Spraying Procedure

The production of HA coatings using the HVOF thermal spraying process are described in the following sections:

- 1. Surface Preparation
- 2. Pre-heat treatment
- 3. Spraying process
- 4. Safety equipment

3.5.1 Surface Preparation

The condition of substrate surface plays a vital role in the case of deposition by most coating processes. Grit blasting is a well-known process for cleaning the surface and roughening the surface allows for good deposition. Therefore prior to spraying samples were grit blasted for HVOF spraying. This process was carried out using pure white alumina oxide (Al₂O₃), 500 μ m (mesh 36) in size applied to the stainless steel substrate. The blasting pressure was 5 Bar. To ensure the full surface roughness, the samples were grit blasted for 2 minutes. The HVOF thermal spraying operation was carried out as soon as possible after grit blasting, to ensure a freshly prepared surface was available for deposition.

3.5.2 Pre-Heat Treatment

To get rid of moisture on the substrate surface and to reduce residual stresses during spraying [13], pre-heat treating was conducted, as this is very important where the surface of the sample is exposed to a high temperature. The sample was heated up after igniting the gun up to the desired pre-heat temperature (200° C). In this current research 5 loops (10 passes) were applied for the pre-heating cycle.

3.5.3 Spraying Process

At first the vaporiser unit was turned on. After this the extractor hood was switched on and HA powder was poured into the hopper of the powder feed assembly. The compressor was turned on before igniting the gun, as helps to keep the gun cool. Lighting pressures and flow rates are given below in *table 3.3* were then set for igniting the gun.

Type of gases	Pressure Bar (psi)	Flow meter reading (FMR)
Oxygen	10.3 (150)	40-44
Propylene	6.9 (100)	35 - 40
Gun air	5.2 (76)	60 - 65
Nitrogen (Carrier Gas)	8.6 (125)	55

 Table 3.3: Lighting pressures and flow rates suggested by Sulzer METCO

The oxygen bottles were opened and its pressure and gas flow rate for lighting was set according to table 3.3. Finally the propylene bottles were opened and its parameters were set for lighting as well. Then the gun was ignited by a flint lighter and ready for spraying. Depending on the parameters chosen for optimised spraying, oxygen, propylene and air flow rates were varied and will be explained later (section 3.8). Nitrogen was used as a powder carrier gas which transports the powder from powder feed unit to the powder injector of the gun and was regulated by using control knobs on the powder feed unit. The flow of the HA powder from the powder feed unit to the gun was controlled by switching on the feed button on the gun. The flow rate of the gases and powder were then adjusted. There were 32 samples, each having different parameters according to screening experiment (section 3.8). For example, the oxygen flow meter reading was set to 45 FMR, Propylene flow meter rate was set to 40 FMR, air flow meter rate was set to 50 FMR and spray rate was set to 45 gm/min for Sample 24. Again 5 loops (10 passes) were applied after switching on the feed button on the gun for deposition. A spray distance of 150 mm was chosen for 16 samples and 300 mm for the other samples. A coated sample is shown in *figure 3.21*. After deposition the samples were ready for x-ray diffraction for measuring the crystallinity and purity.



Figure 3.21: HA coated sample

3.5.4 Safety Equipment

The HVOF thermal spray process is a risky process. In *table 3.4*, the items of personal protection used while spraying are given. Extraction was used at all times.

Hazard	Protective Equipment
High dB noise (~92 dB)	Ear plugs and Hearing protectors
Irritation from HA powder	Powder handling gloves and shades
UV light from jet flow	Eye protection (Shade 11)
High temperature of sprayed components	Flame resistance converalls and gloves
Fumes, Gases and Powders	Face mask with filters

Table 3.4: Presonal protection equipment used for HVOF spraying

3.6 Coating Characterisation Equipment

All of the samples deposited by any type of coating technique must be scientifically characterized either macro or microscopically to gain coating microstructural characteristics such as chemical composition, grain morphology, or the detection of large defects like cracks, adhesion failure and so on. A large indefinite number of optical techniques are available; such examples available in the Materials Processing Research Centre (MPRC) as Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) and Optical Microscope (OM) may be used. However the OM technique was not used in this research but further information on the operation of this technique may be found in the report by Stokes [13].

3.6.1 X-Ray Diffraction

X-ray diffraction (XRD) is a non-destructive measurement technique that evaluates out detailed information about the crystalline phases present in materials, chemical composition of these phases and structural properties which include grain size, strain state, phase composition and orientation. Complex structures can also be analyzed by X-ray diffraction such as DNA and proteins. The thickness of thin films and multilayers, and atomic arrangements in amorphous materials can also be determined by XRD [108]. The principle of the X-ray process is to measure relative shift of X-ray diffraction lines created on an irradiated surface by the use of a diffractometer [2]. According to Bragg's law, diffraction occurs at an angle of 2θ which is given by *equation 3.2* [2]:

 $n\lambda = 2d \sin\theta$

(eqn. 3.2)

where, *n*= *Integer*

 λ = Wavelength of X-ray beam d= Lattice spacing of crystal planes θ = The angle of diffraction

When a X-ray beam is applied onto a crystalline material at an angle θ with wavelength λ , diffraction occurs only if the distance between the rays received back or reflected from sequential planes differs by a complete number n of wavelengths. The Bragg's Law conditions are satisfied by different d-spacings if any change is made at the angle θ .

The diffractometer used in this experimental work is a Bruker D8 Advance as shown in *figure* 3.22. It is a four circle XRD system. Scanning goniometer allows scanning from negative 20 angle which is -110^{0} to positive angle up to 168^{0} , with CuK α radiation ($\lambda = 0.15406^{0}$ A) produced at 40 kV and 40 mA. A specimen platform is located at the centre of the goniometer which is adjustable in three directions.



Figure 3.22: Bruker D8 Advance diffractometer

3.6.2 Scanning Electron Microscope

The scanning Electron Microscope (SEM) offers superior quality of resolution and depth of focus. SEM is a type of electron microscope which scans the sample surface with a high energy beam of electrons. SEM is the preferred instrument used in material studies because of its wide range of application, given below [108]:

- Evaluation of chemical composition gradients on the surface of bulk samples over distances approaching 1 μm
- 2. Examination of fracture surfaces and deeply etched surfaces requiring depth of field well beyond that possible by the optical microscope
- 3. Examinations of metallographically prepared samples at magnifications well above the useful magnification of the optical microscope
- 4. Evaluation of crystallographic orientation of features on a metallographically prepared surface.

When scanning electron microscopes are fitted with a back scattering detector, it permits [104]:

- 1. Evaluation of the crystallographic orientations of grains with diameters as low as 2µm
- 2. Imaging of a second phase on unetched surfaces when the second phase has a different average atomic number
- 3. Observation of grain boundaries on unetched samples.

A source of electrons emitted from an electron gun is centred in a vacuum which is created by a diffusion or turbomolecular pump, into a close examination that is passed over the surface of a specimen in the scanning electron microscope [104]. A series of lenses detect the spot of electrons on the surface of the specimen. The emission of electrons and photons from the surface occur because the electrons emitted from the electron gun penetrate the surface. The detectors collect the output emitted electrons and this is used to modulate the brightness of a Cathode Ray Tube (CRT) [104]. An image of the sample is displayed onto a monitor when the electron beam collides on the sample and each of this strike established directly onto a corresponding point on the screen. The image can also be transmitted to a photographic plate for observation.

The scanning electron microscope used in this experimental work was the 'EVO LS 15' developed by Carl Zeiss, as shown in *figure 3.23*. It can be operated at magnifications from about 5X to 1,000,000X. Its X-ray analysis is 8.5mm analytical working distance and 35^{0} take-off angle. The chamber is 365mm (ϕ) x 275mm (h) and a maximum specimen height of 145mm can be used.



Figure 3.23: EVO LS 15 Scanning Electron Microscope [109]

3.7 Characterisation

3.7.1 Powder Morphology

Scanning Electron Microscope (SEM) was used to examine the morphology of the HA powder, by gaining higher magnification images of the powder. Parameters used for SEM analysis of HA powder are given below in *table 3.5*.

Table 3.5: Parameters used for SEM Analysis of HA powder

Parameter	Value
Accelerating Voltage (KeV)	15
Probe Current (pA)	150
Magnification (x)	50-2000

3.7.2 Phase Identification

All the phases in the HA powders and the coated samples were determined by X-ray Diffraction (XRD). To identify the phases, the Bruker D8-Advance Diffractometer was used. Parameters used for XRD scan of HA powder and all other samples coated by HA are given in *table 3.6*.

Table 3.6: Parameters used for XRD Scan of HA Powder and the coated samples

Parameter	Value
Scan Type	Locked couple
Range ($^{0}2\theta$)	20-60
Increment(⁰)	0.02
Scan Speed (sec/step)	5

Double sided tape was used to attach the samples to the XRD plate. To examine HA powder, it was mounted on a glass slide and double sided tape again used to attach the slide to the XRD plate. The Bruker Diffract Plus EVA software was used to determine the phases present

in the powder and the samples from the resultant diffraction pattern. In this software it is possible to match the XRD pattern to standard diffraction patterns to a library of J.C.P.D.S. files. This software was mainly used to calculate the impurity and crystalline areas.

3.7.3 Crystallinity Determination

The percentage of crystallinity was determined by the Bruker Diffract Plus EVA software. Initially the background noise was removed. Then the sum of the areas of all HA crystalline were calculated by area calculation tool in the EVA software. Next the sum of the area under the amorphous peak were calculated by same way. Finally the percentage of crystallinity was calculated using *equation 2.6*.

3.7.4 Purity Determination

The percentage of purity was also determined by the Bruker Diffract Plus EVA software. Background noise was removed and then the sum of the areas of all HA crystalline peaks were calculated by this software. Then the XRD pattern was matched to standard diffraction patterns in a library of J.C.P.D.S files which is given in *table 3.7*. After matching these, then the sum of the area of the impurity peaks were calculated. At last percentage of purity was calculated by using *equation 2.5*.

Elements	Symbol	Formulae	Peak 2θ(°)	J.C.P.D.S
Hydroxyapatite	HA	Ca ₁₀ (PO ₄) ₆ (OH)	31.8	9-432
α -tricalcium phosphate	α-ΤСΡ	α -Ca ₃ (PO ₄) ₂	30.8	9-348
β-tricalcium phosphate	β-ΤСΡ	β -Ca ₃ (PO ₄) ₂	31.1	9-169
Tetracalcium phosphate	TTCP	$Ca_4(PO_4)_2O$	29.8	25-1137
Calcium oxide	CaO	CaO	37.3	37-1497
Oxyapatite		$Ca_{10}(PO_4)_6O$	31.7	89-6495
Octacalcium phosphate	OCP	Ca ₈ H ₂ (PO4) 6.5H ₂ 0	31.6	26-1056
Dicalcium phosphate anhydrous	DCPA	CaHPO ₄	30.2	9-80
Dicalcium phosphate dihydrate	DCPD	CaHPO ₄ .2H ₂ 0	20.9	9-77

Table 3.7: J.C.P.D.S Standards for Calcium Phosphate Materials

3.8 Process Modelling

To complete the optimisation trials it is very important to develop suitable spraying procedure. Design of Experiment technique was used to determination the effects of various spray parameters on the HA coating produced (in terms of crystallinity and purity as these are two of the most important properties for femoral implants according to FDA regulations). This experimental work was carried out using a two-level factorial design. The design screen many factors to discover the most influential parameters / factors and how they interact with each other. The following sections will describe the details of the experimental work.

3.8.1 Software Selection

There are many Design of Experiment software packages available. In this research Design Expert 7 supplied by State-Ease Inc was used. This software package was selected because its user interface and statistical information made developed models easier to analyse.

3.8.2 Screening Design

Parameter Selection

A large number of parameters affect the HVOF thermal spray process. Parameters that are found to influence the coating properties should be selected for investigation when running a screening experiment. One should select as many process parameters as possible and only those which do not influence the coating properties can be omitted from the investigation.

Oxygen flow rate, propylene flow rate, air flow rate, spray distance, spray rate, powder, traverse velocity, deposition time, substrate roughness, gun nozzle and substrate pre-heat have been found to be important for HVOF thermal spray coating. Captal 60-1 thermal spray HA powder was used for all experimental work hence this was fixed, also this is approved for plasma spraying by the FDA, so it was a natural choice. Some authors reported that traverse velocity affect the coating although it was not added as a factor in the screening experiment. The speed chosen was that optimised by Stokes [13], so 200 mm/s was used. Deposition time for samples was not considered for further investigation because it only effects the thickness, therefore the aim was to produce between 200 to 300 µm thickness using 10 passes of the gun, which lies within FDA thickness requirement [96]. The substrate roughness role is an

important part in HVOF thermal spray coating but this was fixed to the same roughness optimised by Levingstone [96], $3.12 \mu m$. The gun nozzle used in the gun was kept constant for all samples. It was DJ3-9, recommended by Sulzer Metco. There were 5 loops to pre-heat the samples and it was constant for all the samples.

So those parameters selected for further screening which affects the properties of HVOF HA sprayed coatings include: oxygen flow rate, propylene flow rate, air flow rate, spray distance and powder feed rate. These all were easily controllable and adjustable. *Table 3.8* shows all those parameters that were not investigated during the experiments.

Parameter	Setting
HA Powder	Plasma Biotal Captal 60-1
Gun nozzle	DJ3-9
Substrate pre-heat	5 loops $\sim 200^{\circ}$ C
Traverse Velocity (mm/s)	200 mm/s
Deposition time (s)	Was not considered, but 200-300 µm
	thickness range
Substrate roughness (µm)	3.12 μm

 Table 3.8: Values of Parameters not varied in the study

Parameter Level Selection

As a two level factorial design was chosen the maximum and minimum possible settings for each parameter are given in *table 3.9*. Feasible coatings are produced by changing each of the parameters. Whether a feasible coating has been produced or not was inspected visually. It was done by checking the substrate coated surface because substrate material should not be visible through the coating.

Parameter	Minimum	Maximum
Oxygen flow meter reading (F.M.R)	30	45
(SLPM)	181.9	182
Propylene flow meter reading (F.M.R)	20	40
(SLPM)	99.3	198.6
Air flow meter reading (F.M.R)	35	50
(SLPM)	150.8	215.5
Spray Distance (mm)	150	300
Powder feed Rate (g/min)	15	45

Table 3.9: Equipment Limits for the Selected Spray Parameters

Experimental Design

A two level general factorial design was selected for the screening design for this research. Hence a 2^5 general factorial design was used. The whole screening experiment was done by Design Expert software. The full screening design is shown in *table 3.10*. In the screening study two responses were examined. These were coating crystallinity and purity calculated from the XRD Patterns. The crystallinity and purity are the most important properties because these responses will be compared later with the results of the plasma sprayed HA coating. The aim is to identify if crystallinity / purity results similar to plasma spraying can be achieved and if so then HVOF could be used also to deposit HA FDA approved coatings.

Sample	Exp	Oxygen	Propylene	Air	Spray	Powder feed
	Run	(F.M.R)	(F.M.R)	(F.M.R) (F.M.R) Dist		rate
					(mm)	(g/min)
1	29	30	20	35	150	15
2	26	45	20	35	150	15
3	11	30	40	35	150	15
4	8	45	40	35	150	15
5	30	30	20	50	150	15
6	16	45	20	50	150	15
7	22	30	40	50	150	15
8	3	45	40	50	150	15
9	4	30	20	35	300	15
10	20	45	20	35	300	15
11	13	30	40	35	300	15
12	12	45	40	35	300	15
13	6	30	20	50	300	15
14	1	45	20	50	300	15
15	17	30	40	50	300	15
16	2	45	40	50	300	15
17	31	30	20	35	150	45
18	24	45	20	35	150	45
19	7	30	40	35	150	45
20	10	45	40	35	150	45
21	21	30	20	50	150	45
22	27	45	20	50	150	45
23	28	30	40	50	150	45
24	9	45	40	50	150	45
25	15	30	20	35	300	45
26	23	45	20	35	300	45
27	14	30	40	35	300	45
28	25	45	40	35	300	45
29	19	30	20	50	300	45
30	18	45	20	50	300	45
31	32	30	40	50	300	45
32	5	45	40	50	300	45

Table 3.10: 2⁵ general factorial design

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

The results of the experimental work carried out are presented and discussed in this chapter. First of all, powder morphology and powder composition results from SEM and XRD are presented. Following this coating crystallinity and purity results are shown. Then five out of 32 samples were selected on the basis of higher, lower and medium parameters are discussed. Finally the models developed by the DOE for the optimising of the experiments, are described.

4.2 Hydroxyapatite powder

4.2.1 Powder Morphology

Figure 4.1 shows the micrograph of Plasma Biotal Captal 60-1 HA powder particles which were used for HA coating by the HVOF thermal spraying system. It is clear from the scanning electron micrograph that the particles consist of a mixed collection of smaller and agglomerate particles, due to the Plasma Biotal powder production process. Most of the particles contained spherical morphology and few particles with a slightly irregular morphology due to agglomeration. The irregular shape particles can contribute to poor particle flow ability within the hopper, powder feed hose and also into the flame while the spray process is in progress however this would be minimal due to the low amount of this powder shape. The average particle size is 45 μ m which was reported by the supplier. The morphological properties of this powder are similar to those of other commercial HA thermal spray powders [110].



Figure 4.1: Plasma Biotal Captal 60-1 HA Powder Micrograph

4.2.2 Powder Composition

The XRD pattern for the Plasma Biotal Captal 60-1 HA powder is shown in *figure 4.2*. This diffraction pattern was used to measure the purity and crystallinity of the HA powder by using *equation 2.5* and *equation 2.6* (in Section 2.13.1 and 2.13.2). By using the EVA software and the equations, the purity was found to be 99% which is greater than 95% requirement for HA powder (ASTM standard F1185-88 [111]). The crystallinity for HA powder was 99.94% which is greater than 95% (ISO 13779-1:2000 [112]). *Figure 4.2* shows the main phases were HA (JCPDS 9-0432) and there was a minor trace of tetracalcium phosphate (JCPDS 25-1137) found. Therefore the starting powder showed high level of purity/crystallinity for thermal spray applications.



Figure 4.2: Plasma Biotal CAptal 60-1 HA Powder XRD Pattern

4.3 Coating Crystallinity and Purity

Coating crystallinity and purity of the Plasma Biotal HA coated rectangular samples were found using the X-ray diffraction (XRD) technique. The XRD pattern for all samples contained crystalline peaks with evidence of an small amorphous phase. The standard diffraction pattern for HA (JCPDS 9-432) was compared with the peaks present in the diffraction patterns to the coating which prove that the analysed coating was HA. Coating crystallinity was found to vary for all samples (from 93.81% in sample 24 to 74.94% in sample 29), determined from the XRD patterns using *equation 2.6* and the procedure is adumbrated in Section 3.7.3. *Table 4.1* shows crystallinity results of the samples investigated. According to ISO 13779-2:2000 [112], the minimum crystallinity required for Bio-HA coatings is 45% but ideally one would like to achieve results similar to plasma spraying which is FDA approved for clinical use, thus >90% crystallinity. Five samples were selected (highlighted in the *table 4.1*) for discussion with regards to their coating morphology in next section as follows: sample 24 (Highest crystallinity), 29 (Lowest crystallinity), 11 (Medium

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crystallinity), 32 (All parameters were set high) and 8 (All parameters similar to sample 24 except for powder feed rate set to low).

The highest purity was found 99.89 %, and the lowest purity was found 97.56 % which meets the > 95 % purity required as outlined in the ASTM standard ISO 13779-1:2000 [112]. The crystallinity and purity results for all samples are presented graphically in *figure 4.3 and figure 4.4*. As purity was acceptable for all then the samples chosen as >95 %, then crystallinity variation is more important. Levingstone [96] optimised the plasma spraying process for HA deposition and found a set of parameters which produce a coating of 87.6 % crystallinity and 99.4 % purity. Hence already the HVOF system has proven as a novel method for HA deposition with maximum crystallinity and purity of 93.81 % and 99.84% respectively. However this research will find out why.

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Sample	Exp	Oxygen	Propylene	Air	Spray	Powder	Crystallinity	Purity
	Run	(F.M.R)	(F.M.R)	(F.M.R)	Distance	feed rate	(%)	(%)
					(mm)	(g/min)		
1	29	30	20	35	150	15	90.28	99.80
2	26	45	20	35	150	15	86.66	99.61
3	11	30	40	35	150	15	88.6	99.67
4	8	45	40	35	150	15	87.96	99.32
5	30	30	20	50	150	15	84.28	99.37
6	16	45	20	50	150	15	88.14	99.15
7	22	30	40	50	150	15	88.39	99.53
8	3	45	40	50	150	15	88.22	99.11
9	4	30	20	35	300	15	78.67	98.70
10	20	45	20	35	300	15	85.49	99.75
11	13	30	40	35	300	15	87.82	99.76
12	12	45	40	35	300	15	87.31	99.80
13	6	30	20	50	300	15	80.41	98.89
14	1	45	20	50	300	15	84.04	99.29
15	17	30	40	50	300	15	91.16	99.43
16	2	45	40	50	300	15	84.91	99.18
17	31	30	20	35	150	45	91.82	99.11
18	24	45	20	35	150	45	89.05	99.76
19	7	30	40	35	150	45	88.69	99.71
20	10	45	40	35	150	45	91.67	99.65
21	21	30	20	50	150	45	89.61	99.84
22	27	45	20	50	150	45	86.52	97.56
23	28	30	40	50	150	45	86.65	99.26
24	9	45	40	50	150	45	93.81	99.09
25	15	30	20	35	300	45	85.63	98.60
26	23	45	20	35	300	45	84.29	99.00
27	14	30	40	35	300	45	90.17	99.49
28	25	45	40	35	300	45	83	98.58
29	19	30	20	50	300	45	74.94	99.11
30	18	45	20	50	300	45	84.19	99.52
31	32	30	40	50	300	45	84.36	99.58
32	5	45	40	50	300	45	83.44	99.71

Table 4.1: Crystallinity and Purity Results



Crystallinity

Figure 4.3: Graphical Representation of Coating Crystallinity Results





4.4 Spray Temperature Effects and Coating Morphology

Recrystallization mainly depends on time and temperature and it is a process where a new set of undeformed grains take the place of deformed grains. The new grains form and become larger until they completely replace the parent material. To improve the grain structure crystallization of cold-worked metals and some heat treatments may be used. For recrystallization of a particle to occur the spray temperature should keep high. To keep the temperature high, all of the influencing parameters on temperature should be considered. If air flow rate is high it will keep the gun and thus the particle cool. Also particle velocity will increase and dwell time is short. So there will be less heat into the particle. Propylene flow rates should be kept high to get high heat and temperature into the particle. The oxygen flow rate should be high as it has a stoichiometric relationship with propylene, therefore high oxygen and propylene will increase the flame temperature thus helps the particle to recrystallize by the flame. Also the flame becomes larger therefore if more heat is in contact with the substrate then this recrystallizes the particles which have impacted the substrate. If the powder flow rate is low, then too much heat will be given to the particles allowing impurities like α -tricalcium phosphate and othe phases / oxides to form. If the powder flow rate is high then the heat input per particle is lower and less amount of impurity / phase changes occur. If the spray distance is short then the substrate is heated more, thus recrystallization formation will occur with each pass and if the distance is too long then the substrate cools freezing the particles in the state they formed in the flame. The following section looks at each parametric set up for maximum, medium and lowest crystallinity and thus associated purity levels, in terms of the above. Later the most influencing factors will be analysed gained from the DOE results.

Sample	Exp Run	Oxygen (F.M.R)	Propylene (F.M.R)	Air (F.M.R)	Spray Distance (mm)	Powder feed rate (g/min)	Crystallinity (%)	Purity (%)
24	9	45	40	50	150	45	93.81	99.09

Sample 24 (Maximum Crystallinity)

Firstly to break down each parameter in relation to spray temperature, the following can be stated:

- Oxygen flow rate 45 FMR which was set at maximum. So temperature will be high.
- Propylene flow rate 40 FMR which was set at maximum. So temperature will be high.
- Both oxygen and propylene are high so larger flame formed.
- Air flow rate 50 FMR which was set at maximum. So flame temperature will be cooled and this helps to keep gun and particles cool.
- Spray distance 150 mm which was set at minimum. So substrate will be heated more by larger flame. The hot spot from the flame incontact with the substrate will be higher in temperature.
- Powder feed rate 45 g/min which was set at maximum. So temperature in the particle is lower so less likely that phases like α-tricalcium phosphate can form.

A schematic diagram of sample 24 is given in *figure 4.5*, which shows the flame size when compressed air, oxygen, propylene and powder feed rate are high. T_L represents low temperature when compressed air is high and T_H represent temperature high when both oxygen and propylene flow rate are high. Here the hypothesis is that little crystallinity- and phase- loss occurs due to short dwell time of powder and as the powder feed rate was high. The flame is hotter and larger over the substrate. Thus recrystallizing the coating. Therefore high crystallinity and purity would be expected at these settings as they prove to be optimal in terms of maintaining crystallinity and purity levels compared to original powder.


Figure 4.5: Schematic diagram of sample 24

The XRD pattern for sample 24 is shown in *figure 4.6*. The peaks in the pattern show that the main phases are HA (JCPDS 9-0432) and there is also a minor trace of tetracalcium phosphate (JCPDS 25-1137) present. The crystallinity and purity for sample 24 is 93.81 % and 99.09 % respectively.



Figure 4.6: Sample 24 XRD Pattern

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Therefore due to high oxygen, propylene and air flow rate, a larger flame occurs and thus recrystallization of the surface occurs, which agrees with Levingstone [96]. Recrystallization reforms the deformed coating to higher crystallinity (93.81%) towards that of the initial powder.

The surface morphology of sample 24 which was coated by HA powder by the HVOF is shown in *figure 4.7*. This flame effect can be seen thus supporting the latter statement where a flattened surface can be observed. This flattened surface was formed by fully molten particles and the flame in contact with the sample surface melting the applied particles.



Figure 4.7: SEM micrograph of sample 24 with maximum crystallinity

Sample 29 (Minimum Crystallinity)

Sample	Exp Run	Oxygen (F.M.R)	Propylene (F.M.R)	Air (F.M.R)	Spray Distance	Powder feed	Crystallinity (%)	Purity (%)
					(mm)	rate (g/min)		
29	19	30	20	50	300	45	74.94	99.11

Again a summary of the parameter effect:

- Oxygen flow rate 30 FMR which was set at its minimum. So the temperature will be low.
- Propylene flow rate 20 FMR which was set at minimum. So temperature will be low.
- Both oxygen and propylene flow rate are low. So smaller and colder flame than that of sample 24.
- Air flow rate 50 FMR which was set at maximum. So more cooling thus lower particle temperature and higher particle velocity. So dwell time is low. So particles less molten.
- Spray distance 300 mm which was set at maximum. So substrate will be heated less.
- Powder feed rate 45 g/min which was set at maximum. So temperature in particle is even lower.

Due to low oxygen, propylene and high air flow rate, a small flame occurs and therefore the particles would be more semi molten to unmelted providing poor adhesion and poor quality coating. A schematic diagram of sample 29 is given in *figure 4.8*. T_L represent temperature low when compressed air, oxygen and propylene flow rate are high.



Figure 4.8: Schematic diagram of sample 29

The XRD pattern for sample 29 is shown in *figure 4.9*. The peaks in the pattern show that all phase present is HA (JCPDS 9-0432). A large amount of amorphous phase can be seen thus yielding only 74.94 % crystallinity. The purity was high as the flame temperature did not contribute to any phase formation.



Figure 4.9: Sample 29 XRD Pattern

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The surface morphology of sample 29 which was coated by HA powder by HVOF is shown in *figure 4.10*. The SEM micrograph shows no flattening of particles rather a more powder particle impingement. The most of the surface is partially melted particles/splats. Thus recrystallization did not occur producing a coating made of deformed particles with hence lower crystallinity which backs up the result formed (74.94%) and agrees with Levingstone [96].



Figure 4.10: SEM micrograph of sample 29 with minimum crystallinity

Sample 11 (Medium Crystallinity)

Sample	Exp Run	Oxygen (F.M.R)	Propylene (F.M.R)	Air (F.M.R)	Spray Distance	Powder feed	Crystallinity (%)	Purity (%)
					(mm)	rate (g/min)		
11	13	30	40	35	300	15	87.82	99.76

The parameters express the following opinion:

- Oxygen flow rate 30 FMR which was set at minimum. So temperature will be low.
- Propylene flow rate 40 FMR which was set at maximum. So temperature will be high.
- Stoichastically unbalanced so poor to medium flame (size and gas composition)
- Air flow rate 35 FMR which was set at minimum. So temperature will be medium to high in the particles.
- Spray distance 300 mm which was set at maximum. So substrate will be heated less, hence no or medium recrystallization.
- Powder feed rate 15 g/min which was set at minimum. So temperature in particle is higher than sample 29

Due to low oxygen, air flow rate and high propylene, middle size flame may occur and slight recrystallization will form is shown in *figure 4.11*, hence agrees with a medium crystallinity here of 87.82%. T_L represent temperature low and T_H represent temperature high.



Figure 4.11: Schematic diagram of sample 11

The XRD pattern for sample 11 is shown in *figure 4.12*. The peaks in the pattern show that the main phase present is HA (JCPDS 9-0432). The crystallinity and purity for this sample were found 87.82 % and 99.76 % respectively. A slight amount of amorphous phase can be seen. The purity was high again because of no contribution of phase formation of the flame temperature.



Figure 4.12: Sample 11 XRD Pattern

The surface morphology of sample 11 which was coated by HA powder by HVOF is shown in *figure 4.13*. The flattened surface is infact a mixture of the findings in samples 24 and 29 as seen from the SEM micrograph.



Figure 4.13: SEM micrograph of sample 11 with medium crystallinity

Sample 32 (All parameters were set to high)

Sample	Exp	Oxygen	Propylene	Air	Spray	Powder	Crystallinity	Purity
	Run	(F.M.R)	(F.M.R)	(F.M.R)	Distance	feed	(%)	(%)
					(mm)	rate		
						(g/min)		
32	5	45	40	50	300	45	83.44	99.71

For this sample:

- Oxygen flow rate of 45 FMR which was set at maximum. So the temperature will be high.
- Propylene flow rate 40 FMR which was set at maximum. So temperature will be high.

- Oxygen and propylene flow rate were high so flame size is large.
- Air flow rate 50 FMR which was set at maximum. So temperature will be lower as air cools gun but dwell time is lower so fast transfer of particle to substrate.
- Spray distance 300 mm which was set at maximum. So less substrate heating and therefore less recrystallization effects.
- Powder feed rate 45 g/min which was set at maximum. So the temperature in each particle is lower.

Because of high oxygen, propylene, air flow rate, spray distance and spray rate, a large size flame occurs, however the distance is also too high so possibility of less crystallinity occurring which matches the results found (83.44%). A schematic diagram of sample 32 is given in *figure 4.14*. T_L represent temperature low and T_H represent temperature high. Though all the parameters are high the crystallinity was found 83.44 % and large amount of morphous phase can be seen because of long dwell time of powder which effected to gain higher crystallinity. Purity was found higher again of 99.71 %.



Figure 4.14: Schematic diagram of sample 32

The XRD pattern for sample 32 is shown in *figure 4.15*. The peaks in the pattern show that the main phase present is HA (JCPDS 9-0432). The crystallinity and purity for sample 32 was 83.44 % and 99.71 % respectively.



Figure 4.15: Sample 32 XRD Pattern

Sample 8 (All parameters are like sample 24 except the powder feed rate is low)

Sample	Exp Run	Oxygen (F.M.R)	Propylene (F.M.R)	Air (F.M.R)	Spray Distance (mm)	Powder feed rate (g/min)	Crystallinity (%)	Purity (%)
8	3	45	40	50	150	15	88.22	99.11

Due to high oxygen, propylene, air flow rate, spray distance, large size flame occurs. Particle flow rate is low is shown in *figure 4.16*. So too much heating would occur in this setup. T_L represent temperature low and T_H represent temperature high



Figure 4.16: Schematic diagram of sample 8

Powder feed rate 15 g/min which was set at minimum. So temperature in particle is high and chance of phases like α -tricalcium phosphate to form because of too much heat. The XRD pattern for sample 8 is shown in *figure 4.17*. The peaks in the pattern show that the main phase present is HA (JCPDS 9-0432) and there is also a minor trace of tetracalcium phosphate (JCPDS 25-1137) present. Crystallinity and purity for sample 8 was found 88.22 % and 99.11 % respectively. A small amount of amorphous phase can be seen. Because of short dwell time and low powder feed rate, little crystallinity and phase loss occurs. Recrystallization occurs when flame is hotter and larger.



Figure 4.17: Sample 8 XRD Pattern

4.5 Influencing Factors

4.5.1 Introduction

The coatings were sprayed according to Table 3.10 in Section 3.8.2 for optimisation. All the results found were discussed in this section. First of all the experimental data found was analysed and then the models were discussed using the Design Expert Software. Two responses were measured, crystallinity and purity. All 32 coated samples were visually examined anterior to response measurement.

4.5.2 Crystallinity Model

Transform

Response ranges for crystallinity were selected from 74.94 to 93.81 %. The ratio of the minimum and maximum crystallinity was found 1.2518 which falls below the ratio of 3. That means power transforms have little effect in this case. Therefore, no ('None') transformation was selected for this model. *Figure 4.18* shows the transformation of the model screen in the Design Expert Software. This means that the responses were directly proportional to the factors imputed.

ransformation	Equation
ione iquare root latural log lase 10 log overse sqrt loverse lower ogit arcSin sqrt	None (lambda = 1.0) y' = y
	Use with a typical response.

Figure 4.18: Transformation selected none for crystallinity model

Effects

The main effects on the coating crystallinity were selected manually. In the effect list all factors were selected with greater than 5% contribution as shown in *figure 4.19* by 'M' which means model. The highest percentage contribution was found for spray distance (D) which was 32.33%. Propylene flow meter reading (B) percentage contribution was found 11.54%. Oxygen (A), Propylene flow (B) and Spray Distance (D) together has percentage contribution of 15.08% (ABD). Oxygen, air, spray distance and powder feed rate (E) percentage contribution was found to be 5.08% (ACDE).

y^{λ} Transform	Effects		Diagnostics	Model Graph:
Selection: Ma	nual 💌		Order: Mo	odified 👻
	Term	Stdized Effects	Sum of Squares 1%	Contribution
	tercept	DIGIEGO ENTODIO	dam of oquaroo 1/	Contribution
A-Oxygen fl	ow meter reading	0.45	1.63	0.34
MB-Propylene	flow meter reading	2.63	55.49	11.54
C-Air flow	meter reading	-1.50	18.06	3.76
M D-Spra	ay Distance	-4.41	155.41	32.33
E-Powd	er Feed Rate	0.34	0.95	0.20
ē	AB	-1.14	10.42	2.17
ē	AC	1.23	12.15	2.53
ē	AD	-0.012	1.250E-003	2.600E-004
ē	AE	0.061	0.030	6.243E-003
ē	BC	0.97	7.49	1.56
ē	BD	1.68	22.58	4.70
ē	BE	-0.67	3.55	0.74
ē	CD	-0.36	1.06	0.22
ē	CE	-1.10	9.64	2.00
ē	DE	-1.57	19.66	4.09
ē	ABC	-0.59	2.76	0.57
M	ABD	-3.01	72.48	15.08
e	ABE	1.14	10.42	2.17
e	ACD	-0.24	0.48	0.099
e	ACE	1.35	14.69	3.06
ē	ADE	-0.55	2.38	0.49
e	BCD	-0.21	0.35	0.073
e	BCE	0.31	0.79	0.17
e	BDE	-0.67	3.56	0.74
e	CDE	-1.08	9.27	1.93
e	ABCD	-0.27	0.60	0.12
e	ABCE	0.61	2.95	0.61
e	ABDE	-0.99	7.84	1.63
M	ACDE	1.87	27.86	5.80
e	BCDE	0.28	0.63	0.13
e 4	BCDE	-0.83	5.53	1.15
Lei	nth's ME	2.49		
Len	th's SME	4.74		

Figure 4.19: Effect list selected for crystallinity model

A half-normal probability plot is shown below in *figure 4.20* which shows all the selected big effects.



Figure 4.20: Half-normal probability plot after selecting all the big effects

The t-value scale provides more accurate and acceptable measure of relative effects as shown in *figure 4.21* which is known as Pareto Chart. It shows that all of the effects selected were not below the t-value limit 2.05183 which means a statistically acceptable model.



Rank

Figure 4.21: Pareto chart of effects

ANOVA

The ANOVA table and model statistics for crystallinity model are given in *table 4.2*. The ANOVA table shows that the model F value is 12.40 that implies the model is significant at a confidence level of 99%. The adjusted R^2 was found 0.5953 and predicted R^2 was found 0.5048 and the difference between this two was 0.0905 which is less than 0.2 and indicate that the model adequately fits the experimental data and that the model is again statistically acceptable.

Source	Sum of Squares	Mean	F-Value	p-value	Significance
		Square		Prob>F	
Model Significance	311.25	77.81	12.40	< 0.0001	significant
B-Propylene Flow rate	55.49	55.49	8.84	0.0061	
D-Spray Distance	155.41	155.41	24.76	< 0.0001	
ABD	72.48	72.48	11.55	0.0021	
ACDE	27.86	27.86	4.44	0.0445	
Residual	169.45	6.28			
Cor Total	480.70				
R ²	0.6475				
Adj R ²	0.5953				
Pred R ²	0.5048				
Adeq Precision	12.035				

Table 4.2: ANOVA table for the Crystallinity Model

It is clear from the table that spray distance has the greatest effect on coating crystallinity. Adequate precision was found 12.035 which is grater than 4, indicates an adequate signal. The final mathematical model for crystallinity is given in *equation 4.1* in terms of coded factors and in *equation 4.2* in terms of actual factor.

Crystallinity	= +86.57	(eqn 4.1)
	+1.32 * B (Propylene flow meter reading)	
	-2.20 * D (Spray distance)	
	-1.51 * A * B * D (Oxygen flow meter reading *	Propylene flow meter
	rea	ding * Spray distance)
	+0.93 * A * C * D * E (Oxygen flow meter rea	ding * Air flow meter
	reading * Spray distance	ce * Powder feed rate)

Crystallinity	=+90.77198 (eqn. 4.2)
	+0.080246 * Propylene flow meter reading
	-0.033372 * Spray Distance
	+6.09672E-006 * Oxygen flow meter reading * Propylene flow meter
	reading * Spray Distance
	-6.00379E-008 * Oxygen flow meter reading * Air flow meter reading
	* Spray Distance * Powder Feed Rate

As spray distance had the greatest effect (coded equation gave it a level of 2.20) but a negative effect. So it suggest that spray distance should be kept low to yield high crystallinity. This makes sense with the previous discussion as this allows the flame to have a larger effect on recrystallizing the coating.

The model shows Oxygen and Propylene flow rate and spray distance as the next most influencing negative interactive factors (A * B * D). Again this agrees with the previous statement that Oxygen and Propylene must be stiochomatically balanced. So their effects must be aligned. However it suggests keeping them all low (negative effect -1.51) to get high crystallinity. However, the third biggest effect is propylene flow rate (+1.32). So it should be kept high here. The reason for the contradiction is the large effect spray distance (+2.2 versus -1.51) has on the ABD result. So preference must be made to spray distance (*figure 4.22*). Hence the model is an interesting finding.



Figure 4.22: Effect of spray distance on crystallinity

Diagnostics

Figure 4.23 represents the Predicted vs Actual plot of both model and experimental data. It is a good fit because the data points lie close to the diagonal model line.



Figure 4.23: Predicted vs. Actual Plot for Crystallinity

CHAPTER: 4 Results and Discussion

The Diagnostics case studies given below in *table 4.3*, shows no red text which means that all points in the experiment were statistically close to the model, hence no outliers were found.

					Internall	y Externally	Influence	e on	
Standar	rd Actual	Predicte	ed		Studentize	ed Studentized	Fitted Va	lue Cook's	Run
Order	Value	Value	Residual	Leverage	Residual	Residual	DFFITS	Distance	Order
1	90.28	89.89	0.39	0.156	0.168	0.165	0.071	0.001	29
2	86.66	85.02	1.64	0.156	0.714	0.707	0.304	0.019	26
3	88.60	89.52	-0.92	0.156	-0.398	-0.392	-0.169	0.006	11
4	87.96	90.66	-2.70	0.156	-1.174	-1.182	-0.509	0.051	8
5	84.28	88.03	-3.75	0.156	-1.628	-1.683	-0.724	0.098	30
6	88.14	86.88	1.26	0.156	0.546	0.539	0.232	0.011	16
7	88.39	87.65	0.74	0.156	0.321	0.316	0.136	0.004	22
8	88.22	92.53	-4.31	0.156	-1.872	-1.969	-0.847	0.130	3
9	78.67	80.61	-1.94	0.156	-0.843	-0.838	-0.361	0.026	4
10	85.49	85.49	4.375E-003	0.156	0.002	0.002	0.001	0.000	20
11	87.82	86.25	1.57	0.156	0.681	0.674	0.290	0.017	13
12	87.31	85.11	2.20	0.156	0.956	0.955	0.411	0.034	12
13	80.41	82.48	-2.07	0.156	-0.898	-0.894	-0.385	0.030	6
14	84.04	83.62	0.42	0.156	0.183	0.179	0.077	0.001	1
15	91.16	88.12	3.04	0.156	1.321	1.341	0.577	0.065	17
16	84.91	83.24	1.67	0.156	0.724	0.718	0.309	0.019	2
17	91.82	88.03	3.79	0.156	1.648	1.706	0.734	0.101	31
18	89.05	86.88	2.17	0.156	0.942	0.940	0.404	0.033	24
19	88.69	87.65	1.04	0.156	0.452	0.445	0.191	0.008	7
20	91.67	92.53	-0.86	0.156	-0.372	-0.366	-0.158	0.005	10
21	89.61	89.89	-0.28	0.156	-0.123	-0.121	-0.052	0.001	21
22	86.52	85.02	1.50	0.156	0.653	0.646	0.278	0.016	27
23	86.65	89.52	-2.87	0.156	-1.246	-1.259	-0.542	0.057	28
24	93.81	90.66	3.15	0.156	1.369	1.392	0.599	0.069	9
25	85.63	82.48	3.15	0.156	1.371	1.395	0.600	0.070	15
26	84.29	83.62	0.67	0.156	0.291	0.286	0.123	0.003	23
27	90.17	88.12	2.05	0.156	0.891	0.888	0.382	0.029	14
28	83.00	83.24	-0.24	0.156	-0.106	-0.104	-0.045	0.000	25
29	74.94	80.61	-5.67	0.156	-2.464	-2.746	-1.182	0.225	19
30	84.19	85.49	-1.30	0.156	-0.563	-0.556	-0.239	0.012	18
31	84.36	86.25	-1.89	0.156	-0.823	-0.818	-0.352	0.025	32
32	83.44	85.11	-1.67	0.156	-0.725	-0.719	-0.309	0.019	5

Table 4.3: Diagnostics Case Statistics of Crystallinity

Current Transform: None Box-Cox Power Transformation

Constant	95% CI	95% CI	Best	Rec.
k	Low	High	Lambda	Transform
0.000			3.00	None

4.5.3 Purity Model

Transform

Response ranges for purity were selected from 97.56 to 99.84 %, although all parameter set ups are acceptable > 95 %. The ratio of minimum and maximum purity was found 1.02337 which falls below the ratio of 3. No transformation was selected.

Effects

The main effects on the coating purity were selected manually. In the effect list all those were selected which are greater than 5% contribution which is shown in *figure 4.24*. The highest percentage contribution was found for ACDE 10.57%, where A is oxygen flow meter reading, C is air flow meter reading, D is spray distance and E is powder feed rate.

y ^λ Tre	ansform		Diagnostics	Model Gra
Select	tion: Manual 🔻		Order: Mo	odified 👻
1	Term	Stdized Effects	Sum of Squares 1%	Contribution
	Intercept	ordized Enteets	oun or oquaros 70	Contribution
	xvgen flow meter reading	-0.11	0.098	1.36
MB-P	conviene flow meter reading	0.24	0.45	6.31
	C-Air flow meter reading	-0.17	0.23	3.15
ĕ	D-Spray Distance	-0.072	0.041	0.57
ĕ	E-Powder Feed Rate	-0.17	0.24	3.38
ĕ	AB	-0.14	0.15	2.12
ĕ	AC	-0.19	0.29	3.99
M	AD	0.27	0.58	8.08
-	AE	-0.12	0.11	1.55
ĕ	BC	0.032	8.128E-003	0.11
ĕ	BD	0.096	0.073	1.02
ĕ	BE	0.083	0.055	0.77
M	CD	0.30	0.71	9.81
6	CE	0.14	0.16	2.16
ĕ	DE	0.023	4.278E-003	0.060
M	ABC	0.26	0.54	7.56
141	ABD	-0.27	0.58	8.00
e	ABE	0.11	0.10	1.46
ĕ	ACD	0.20	0.33	4.59
ĕ	ACE	-0.059	0.028	0.39
ē	ADE	-0.033	8.778E-003	0.12
ē	BCD	-0.093	0.069	0.97
ē	BCE	0.049	0.020	0.27
ē	BDE	-0.13	0.14	2.01
M	CDE	0.29	0.69	9.64
e	ABCD	-0.087	0.060	0.84
e	ABCE	0.22	0.39	5.42
e	ABDE	-0.11	0.089	1.24
M	ACDE	0.31	0.76	10.57
e	BCDE	0.059	0.028	0.39
ē	ABCDE	-0.14	0.15	2.08
	Lenth's ME	0.45		20050000
	Lenth's SME	0.85		

Figure 4.24: Effect list selected for purity model

A half-normal probability plot is shown below in *figure 4.25* which shows all the selected big effects. The t-value scale provides more accurate and acceptable measure of relative effects is shown in *figure 4.26 which* is known as pareto chart.



Figure 4.25: Half-normal probability plot after selecting all the big effects



Figure 4.26: Pareto chart of effects

ANOVA

The ANOVA table and model statistics for purity model are given in *table 4.4*. The ANOVA table shows that the model F value is 5.13 that implies the model is significant. The adjusted R^2 was found 0.4828 and predicted R^2 was found 0.2882 and the difference between this two is 0.1946 which is less than 0.2 and indicate that the model adequately fits the experimental data. The R^2 results are low however, but as the range of purity results from maximum to minimum are very close the model would be very sensitive.

Source	Sum of	Mean Square	F-Value	p-value	Significance
	Squares			Prob>F	
Model	4.31	0.62	5.13	0.0011	significant
B-Propylene Flow rate	0.45	0.45	3.78	0.0636	
AD	0.58	0.58	4.84	0.0377	
CD	0.71	0.71	5.88	0.0232	
ABC	0.54	0.54	4.53	0.0437	
ABD	0.58	0.58	4.80	0.0385	
CDE	0.69	0.69	5.78	0.0243	
ACDE	0.76	0.76	6.33	0.0189	
Residual	2.88	0.12			
Cor Total	7.19				
R^2	0.5996				
Adj R ²	0.4828				
Pred R ²	0.2882				
Adeq Precision	9.630				

 Table 4.4: ANOVA table for the Purity Model

It is clear from the table that oxygen (A), air (C), spray distance (D) and powder feed rate (E) have the greatest effect on coating purity. Adequate precision was found 9.630 which is greater than 4, indicates an adequate signal. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case AD, CD, ABC, ABD, CDE, ACDE are significant

model terms. The final mathematical model for purity is given in *equation 4.3* in terms of coded factors and in *equation 4.4* in terms of actual factors.

1 (eqn 4.3)	Purity $= +99.31$
* B (Oxygen flow meter reading)	+0.12 *
* A * D (Oxygen flow meter reading * Spray distance)	+0.13 *
* C * D (Air flow meter eading * Spray distance)	+0.15 *
* A * B * C (Oxygen flow meter eading * Propylene flow meter reading * Air	+0.13 *
flow meter reading)	
* A * B * D (Oxygen flow meter eading * Propylene flow meter reading *	-0.13 *
Spray distance)	
5 * C * D * E (Air flow meter eading * Spray distance * Powder feed rate)	+0.15 *
5 * A * C * D * E (Oxygen flow meter reading * Air flow meter eading * Spray	+0.15 *
distance * Powder feed rate	

Purity=	+98.96085	(eqn 4.4)
	+0.027365	* Propylene flow meter reading
	+4.14034E-006	* Oxygen flow meter reading * Spray Distance
	+6.92639E-006	* Air flow meter reading * Spray Distance
	-9.35804E-006	* Oxygen flow meter reading * Propylene flow meter
		reading * Air flow meter reading
	-6.45140E-008	* Oxygen flow meter reading * Propylene flow meter
		reading * Spray Distance
	-8.25075E-007	* Air flow meter reading * Spray Distance * Powder
		Feed Rate
	+1.18802E-008	* Oxygen flow meter reading * Air flow meter
		reading * Spray Distance * Powder Feed Rate

One can see that each factor on interaction was almost equally rated (0.15-0.12) although sometimes positive or negative effect. However all parameters had an effect agreeing with previous discussions. Thus comparing to the coded equation for crystallinity where

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multipliers of 2.20 etc were involve. It shows that the factors had more influence on crystallinity than here (0.15) on purity.

Diagnostics

Figure 4.27 represent the Predicted vs Actual plot. It is a good fit because the data points lies close to the diagonal line.



Figure 4.27: Predicted vs. Actual Plot for Purity

Diagnostics case studies are given in *table 4.5* below. There was no red text which means that although figure 4.31 shows some experiments points lying well off the model line they were not statistically deviated away far enough to present a problem.

CHAPTER: 4 Results and Discussion

Table 4.5: Diagnostics Case Statistics of Purity

Standar	d A atreal	Duadiat	ad.		Internally	Externally	Influence on	Cookia	Dun
Standar	Valua	Voluo	Posidual	Lovorogo	Studentized Dosidual	Bosidual	FILLED VALUE	COOK S	Kun Ordor
				Deverage	1 050	1 053	0.608		20
1	99.60 00.61	99.40	0.31	0.250	2 367	2.647	1.528	0.040	29
2	99.01 00.67	98.90	0.71	0.250	2.307	2.047	0.086	0.234	20
5	99.07	99.72	-0.040	0.230	-0.132	-0.149	-0.080	0.001	0 0
4	99.32	99.13	0.17	0.230	0.381	0.373	0.551	0.014	0 20
5	99.57	99.44	-0.003	0.230	-0.217	-0.212	-0.125	0.002	50 16
0	99.13	98.93	0.20	0.230	0.084	0.070	0.390	0.019	10
/	99.33	99.14	0.39	0.250	1.280	1.304	0.735	0.009	22
8	99.11	99./1	-0.60	0.250	-2.007	-2.134	-1.243	0.108	3
9	98.70	98.04	0.003	0.250	0.210	0.206	0.119	0.002	4
10	99.75	99.74	6.8/5E-003	0.250	0.023	0.022	0.013	0.000	20
11	99.76	99.40	0.36	0.250	1.188	1.199	0.692	0.059	13
12	99.80	99.45	0.35	0.250	1.159	1.16/	0.6/4	0.056	12
13	98.89	99.21	-0.32	0.250	-1.061	-1.064	-0.614	0.04/	6
14	99.29	99.18	0.11	0.250	0.377	0.370	0.214	0.006	1
15	99.43	99.45	-0.024	0.250	-0.079	-0.078	-0.045	0.000	17
16	99.18	99.41	-0.23	0.250	-0.759	-0.752	-0.434	0.024	2
17	99.11	99.47	-0.36	0.250	-1.205	-1.217	-0.702	0.060	31
18	99.76	99.50	0.26	0.250	0.859	0.854	0.493	0.031	24
19	99.71	99.70	8.125E-003	0.250	0.027	0.027	0.015	0.000	7
20	99.65	99.75	-0.098	0.250	-0.327	-0.321	-0.185	0.004	10
21	99.84	99.45	0.39	0.250	1.305	1.325	0.765	0.071	21
22	97.56	98.34	-0.78	0.250	-2.609	-3.018	-1.742	0.284	27
23	99.26	99.16	0.10	0.250	0.340	0.333	0.192	0.005	28
24	99.09	99.11	-0.019	0.250	-0.065	-0.063	-0.037	0.000	9
25	98.60	98.65	-0.051	0.250	-0.169	-0.165	-0.095	0.001	15
26	99.00	99.14	-0.14	0.250	-0.469	-0.461	-0.266	0.009	23
27	99.49	99.42	0.072	0.250	0.242	0.237	0.137	0.002	14
28	98.58	98.85	-0.27	0.250	-0.900	-0.897	-0.518	0.034	25
29	99.11	99.19	-0.084	0.250	-0.281	-0.276	-0.159	0.003	19
30	99.52	99.78	-0.26	0.250	-0.865	-0.860	-0.497	0.031	18
31	99.58	99.44	0.14	0.250	0.467	0.459	0.265	0.009	32
32	99.71	100.01	-0.30	0.250	-1.000	-1.000	-0.578	0.042	5

Current Transform: None Box-Cox Power Transformation

Constant	95% CI	95% CI	Best	Rec.
k	Low	High	Lambda	Transform
0.000		3.00	None	

4.5.4 Overall Findings of the Screening Experiment

Here the Design of Expert numerical optimization is described. The previous analysis looked at crystallinity and purity as individual responses and provided equations/models for each. Now to optimise the factors for both responses (crystallinity and purity) together, the optimisation technique is used, which involves setting desired targets for each response. Therefore the crystallinity lower limit was selected as 92 % (lowest achieved in experiments) and the higher limit was selected 100% (desired to be as high as possible) which is shown in *figure 4.28* and for purity lower limit was selected 95 % and higher limit was selected 100% is shown in figure 4.29.

Lower Limits: 92 Weights: 1	Upper 100	_
Importance		
92.00		100.00
9	3. <mark>81</mark>	3
	92.00 9 Crystallinity	92.00 93.81 Crystallinity

Figure 4.28: Numerical optimization of crystallinity

Dxygen flow meter re Propylene flow meter Air flow meter reading Spray Distance Powder Feed Rate	Purity	•		
Crystallinity		Lower	Upper	
uny	Limits:	95	100	
	Weights:	1	1	-
Ontions		Importance:	+++ •	
95.00				100.00
	9	7.56	99.	84

Figure 4.29: Numerical optimization of purity

The best combined solution for maximum crystallinity and purity was found by Design of Expert was solution 1 is shown in *figure 4.30* where oxygen flow meter reading was selected as 45 FMR, propylene flow meter reading was selected 40 FMR, Air flow meter reading was selected 35 FMR, spray distance was selected 150 mm and powder feed rate was selected 45 g/min. All these parameters are almost same like sample 24 except air flow meter reading. In sample 24 air flow meter reading was selected 50 FMR and experimentally it was seen that the parameters selected for sample 24 also gave the highest crystallinity which is pretty much same of numerical optimization solution. However the model predicts for solution 1, a crystallinity of 92.53 % and purity of 99.88 %. Sample 24 produced a higher crystallinity result of 93.81 % and slightly lower purity of 99.09%. Therefore the models optimised solution is not as good as sample 24 in terms of crystallinity. So it is proved by the DOE optimization solution that parameters selected for sample 24 were the best parameters chosen

for highest crystallinity, yet still having high purity. So sample 24 will be deemed as the optimised research parameters for HVOF spraying of HA.

]		
Constraints		Lower	Upper	Lower	Upper				
Name	Goal	Limit	Limit	Weight	Weight	Importance			
Oxygen flow met	is in range	30	45	1	1	3			
Propylene flow r	is in range	20	40	1	1	3			
Air flow meter re	is in range	35	50	1	1	3			
Spray Distance	is in range	150	300	1	1	3			
Powder Feed Rate	is in range	15	45	1	1	3			
Crystallinity	is in range	92	100	1	1	5			
Purity	is in range	95	100	1	1	3			
Solutions									
Number O	xygen flow mPro	pylene flow Air	flow meter Spr	ay Distance Pov	vder Feed Rs	Crystallinity	Purity	Desirability	
1	45.00	40.00	35.00	150.00	45.00	92.53	<u>99.88</u>	1.000	Selec
2	44.81	39.87	36.92	150.15	41.38	92.02	99.70	1.000	
3	44.04	39.88	49.66	150.06	15.74	92.10	99.54	1.000	
4	44.81	39.87	48.08	150.15	18.62	92.02	99.48	1.000	
5	45.00	40.00	50.00	150.00	15.00	92.53	99.58	1.000	
6	44.04	39.88	35.34	150.06	44.26	92.10	99.82	1.000	
	43.50	39.92	50.00	150.04	15.21	92.01	99.55	1.000	
7									

Figure 4.30: Numerical optimization solution of highest Crystallinity and Purity

A 3D graph of response desirability by DOE is shown in *figure 4.31* which shows the highest crystallinity and purity is when oxygen flow meter reading is 45 FMR, propylene flow meter reading is 40 FMR (proving stoichiometry balance), Air flow meter reading is 35 FMR, spray distance is 150 mm and powder feed rate is 45 g/min. Accepting sample 24 results (where the air flow is 50 FMR not 35 FMR as in solution 1) then Crystallinity and purity of sample 24 is shown in *figure 4.32* and *figure 4.33*, for stoichiometry oxygen and propylene flow.



Figure 4.31: Desirability graph of highest Crystallinity and Purity



Figure 4.32: Crystallinity for sample 24



Figure 4.33: Purity for sample 24

4.6 Summary

All the parameters chosen for sample 24 are the best parameters which gives the highest crystallinity (93.81 %) > 90 % for FDA approved and 99.09 % purity which is > 95% for FDA. Levingstone [96] found crystallinity and purity of 87.6 % and 99.4 % by the already approved FDA plasma spray process. So HVOF is better than the plasma sprayed findings. Finally the HVOF is a new method for HA coating which gives higher crystallinity and purity than plasma spray.

CHAPTER FIVE

CONCLUSIONS

AND

RECOMMENDATIONS

5.1 Conclusions

In this current research, the experimental investigation to optimise the parameters for High Velocity Oxy Fuel thermal sprayed hydroxyapatite coatings were carried out for higher crystallinity and purity. The main conclusions from the current study are summarised as follows:

- The Design of Experiment (DOE) technique was capable to model for each of the HA coating responses (Crystallinity and Purity).
- From the ANOVA test it was found that spray distance had the greatest effect on crystallinity. Spray distance should be kept low for achieving higher crystallinity.
- Oxygen and Propylene must be stoichiometically balanced to get high crystallinity because they have negative effect.
- Oxygen, Air, Spray distance and Powder feed rate had the greatest effect on coating purity.
- Coating crystallinity was found maximum (sample 24) when oxygen flow meter reading was selected 45 FMR, propylene flow meter reading was selected 40 FMR, Air flow meter reading was selected 50 FMR, spray distance was selected 150 mm and powder feed rate was selected 45 g/min which is almost same like the DOE optimization solution. So the experimental result does not contradict the optimization result.
- Coating purity was also found higher for same parameters used in sample 24. Though according to DOE optimization solution if air flow meter reading is low then higher purity can be achieved but the crystallinity will be lower in that case. Hence already according to FDA sample 24this research already achieved > 95% purity.
- Compare to plasma spray the HVOF system has proven as a novel method for HA deposition with maximum crystallinity and purity of 93.81 % and 99.84% respectively

CHAPTER: 5 Conclusions and Recommendations

as only 87.6 % and 99.4 % crystallinity and purity was found using plasma sprayed FDA approved technique. Hence the aim of the research was achieved.

5.2 Recommendations for future work

The results documented in this present research have great contribution regarding HVOF sprayed hydroxyapatite coatings. For future research, the models developed by DOE will prove valuable. However recommendations for future investigation are as follows.

- Post spray heat treatment to increase the crystallinity from the as-sprayed coating.
- To understand the thermal behaviour of HA powder and it's melting temperature, Differential analysis (DTA) and Thermograviometric analysis (TGA) can be carried out.
- The porosity of HA coating can be calculated because it has a positive influence on bone growth.
- Find out the optimal value for coating roughness because osteoblast cell attachment is affected by the surface roughness of the HA coating.
- Coating thickness can be measured because thick coating provide better protection for the bone from metal-ion released from the Ti-alloy implant.
- For the production of stable base layer and surface active layer of the bi-layer coating, optimal spray parameters should be found.
- Cell culture study can be carried out to evaluate the in vivo response to the HA coating produced.

PUBLICATIONS

International Conference Papers

 M. K. Al Mamun, S. Hasan, M. Hasan, S. Hashmi and J. Stokes, "Designing and integrating a semi automated powder feed device to produce functionally graded materials (FGM) using the HVOF thermal spray process", Proceedings of the International Thermal Spray Conference & Exposition (ITSC), pp. 663-668, Maastrichat, Netherland, June 2-4, 2008

Poster Presentation

- S. Hasan and J. Stokes "Comparison of HVOF and plasma spray techniques used to produce bio ceramics HA coatings" Materials Processing Research Centre and National Centre for Plasma, Science & Technology, Dublin City University, Dublin 9, Ireland,24th May 2007
- S. Hasan and J. Stokes "Can HVOF thermal spray be used to produce bio ceramics HA coatings?" Materials Processing Research Centre and National Centre for Plasma, Science & Technology, Dublin City University, Dublin 9, Ireland,7th September 2007
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APPENDICES

APPENDIX A

Appendix A



Figure A1: Schematic drawing of the sample holder





Appendix A



Figure A3: Schematic drawing of the sample holder washer



Figure A4: Schematic drawing of the sample

APPENDIX B

Table A1: Crystallinity result for sample 1



Figure A5: Sample 1 XRD Pattern

Table A2: Crystallinity result for sample 2

Sample Name	Left Angle	Right Angle	Left In	t. Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 2	20	60		0	0 31.733	2.81755	216	216	0.789	31.985	2.405	39.354	2.2877	518.8	518.8
Sample Name	Left Angle	Right Angle	Left In	t. Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 2	20	60		0	0 31.733	2.81755	214	214	0.788	31.985	2.101	38.736	2.32275	449.6	449.6
Crystallinity (%)	86.66										-				



Figure A6: Sample 2 XRD Pattern

Table A3: Crystallinity result for sample 3

Sample Name	Left Angle	Right Angle	Left Int	Right In	nt Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 3	20	60	()	0 31.76	2.81517	231	231	0.944	32.097	1.892	38.045	2.3633	437.9	437.9
Sample Name	l eft Angle	Right Angle	l eft Int	Right In	t Obs Max	d (Obs. Max)	Max Int	Net Height	EWHM	Chord Mid	I Breadth	Gravity C	d (Gravity C.)	Raw Area	Net Area
Campio Hamo	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 3	20	60	(0 31.76	2.81517	229	229	0.943	32.097	1.692	37.721	2.38285	388	388
Crystallinity (%)	88.6														



Figure A7: Sample 3 XRD Pattern

Table A4: Crystallinity result for sample 4

Sample Name	Left Angle	Right Angle	Left In	t. Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 4	20	60)	0	0 31.704	2.81999	221	221	0.776	31.952	2.047	38.506	2.33606	452.8	452.8
Sample Name	Left Angle	Right Angle	Left In	t. Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 4	20	60)	0	0 31.704	2.81999	219	219	0.774	31.953	1.816	38.007	2.36561	398.3	398.3
Crystallinity (%)	87.96														



Figure A8: Sample 4 XRD Pattern

								•		-					
Sample Name	Left Angle	Right Angle	Left Ir	nt. Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 5	20	60	0	0	0 31.769	2.81437	205	205	0.956	32.09	2.25	38.674	2.32631	460.8	460.8
Sample Name	Left Angle	Right Angle	e Left Ir	nt. Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 5	20	60	0	0	0 31.769	2.81438	202	202	0.953	32.09	1.922	37.99	2.36662	388.4	388.4
Crystallinity (%)	84.28														

Table A5: Crystallinity result for sample 5



Figure A9: Sample 5 XRD Pattern

Design of Experiment Analysis of High Velocity Oxy-Fuel Coating of Hydroxyapatite

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Sample Name	Left Angle	Right Angle	Left In	t. Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 6	20	60)	0	0 31.744	2.81654	205	205	0.784	31.988	2.379	39.096	2.30219	488.5	488.5
Sample Name	Left Angle	Right Angle	Left In	t. Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 6	20	60)	0	0 31.744	2.81654	204	204	0.784	31.989	2.116	38.887	2.31408	430.6	430.6
Crystallinity (%)	88.14														

Table A6: Crystallinity result for sample 6



Figure A10: Sample 6 XRD Pattern

Table A7: Crystallinity result for sample 7

Sample Name	Left Angle	Right Angle	Left Int	Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 7	20	60	C		0 31.751	2.81597	228	228	0.787	32.004	2.08	38.591	2.33115	473.8	473.8
Sample Name	Left Angle	Right Angle	Left Int	Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 7	20	60	C		0 31.751	2.81597	226	226	0.947	32.085	1.854	38.233	2.35213	418.8	418.8
Crystallinity (%)	88.39														



Figure A11: Sample 7 XRD Pattern

Table A8: Crystallinity result for sample 9

Sample Name	Left Angle	Right Angle	Left Int	Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 9	20	60	()	0 31.738	2.81711	164	164	0.77	31.981	3.538	40.379	2.23195	580.5	580.5
Sample Name	Left Angle	Right Angle	l eft Int	Right	Int Obs Max	d (Obs. Max)	Max Int	Net Height	FWHM	Chord Mid	I Breadth	Gravity C	d (Gravity C.)	Raw Area	Net Area
campio namo	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 9	20	60	. 0)	0 31.738	2.81711	. 161	161	0.769	31.982	2.831	40.005	2.25195	456.7	456.7
Crystallinity (%)	78.67														



Figure A12: Sample 9 XRD Pattern

Sample Name	Left Angle	Right Angle	Left Int	Right	t Int Obs. Ma	x d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 10	20	60)	0 31.75	9 2.8153	3 167	167	0.798	32.014	3.61	40.165	2.24334	603.3	603.3
Sample Name	Left Angle	Right Angle	Left In	Right	t Int Obs. Ma	x d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
· · · ·	2-Theta °	2-Theta °	Cps	Cps	2-Theta	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 10	20	60)	0 31.75	9 2.8153	3 164	164	0.797	32.014	3.137	40.179	2.2426	515.8	515.8
Crystallinity (%)	85.49														



Figure A13: Sample 10 XRD Pattern

Table A10: Crystallinity result for sample 12

Sample Name	Left Angle	Right Angle	Left Int	Right In	t Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 12	20	60	C) (31.754	2.81574	209	209	0.785	32.007	2.257	39.141	2.29963	472.7	472.7
Sample Name	Left Angle	Right Angle	Left Int	Right In	t Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 12	20	60	C) (31.753	2.81575	208	208	0.785	32.009	1.988	38.756	2.3216	412.7	412.7
Crystallinity (%)	87.31														



Figure A14: Sample 12 XRD Pattern

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Sample Name	Left Angle	Right Angle	Left In	t. Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 13	20	60		0	0 31.753	2.81581	161	161	0.892	32.058	3.592	40.133	2.24504	577.9	577.9
Sample Name	Left Angle	Right Angle	Left In	t. Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 13	20	60		0	0 31.753	2.81581	158	158	0.889	32.059	2.949	39.953	2.25473	464.7	464.7
Crystallinity (%)	80.41														



Figure A15: Sample 13 XRD Pattern

Table A12: Crystallinity result for sample 14

Sample Name	Left Angle	Right Angle	Left In	t. Right	t Int Obs. I	Max d (Obs. Max) Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Thet	a [°] Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 14	20	60		0	0 31	751 2.8159	2 15	3 158	3 0.72	2 31.971	3.58	40.304	2.2359	567.2	567.2
Sample Name	Left Angle	Right Angle	Left In	t. Right	t Int Obs.	Max d (Obs. Max) Max Int.	Net Height	FWHM	Chord Mid	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Thet	a ° Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 14	20	60		0	0 31	751 2.8159	2 15	6 150	6 0.794	4 32.01	3.057	40.065	2.24873	476.7	476.7
Crystallinity (%)	84.04														



Figure A16: Sample 14 XRD Pattern

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Table A13: Crystallinity result for sample 15

Sample Name	Left Angle	Right Angle	Left Int	Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 15	20	60	C)	0 31.755	2.81561	192	192	0.783	32.013	2.609	39.614	2.27324	501.2	501.2
Sample Name	Left Angle	Right Angle	Left Int	. Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 15	20	60	0)	0 31.755	2.81561	191	191	0.783	32.013	2.393	39.33	2.28902	456.9	456.9
Crystallinity (%)	91.16														



Figure A17: Sample 15 XRD Pattern

Table A14: Crystallinity result for sample 16

Sample Name	Left Angle	Right Angle	Left In	t. Right I	nt Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 16	20	60		0	0 31.75	2.81608	200	200	0.77	31.999	2.526	39.453	2.28215	504.5	504.5
Sample Name	Loft Angle	Dight Angle	l off lo	t Diaht I	nt Obs. Max	d (Obs. Max)	Max Int	Not Hoight		Chard Mid	I Broadth	Crowity C	d (Cravity C.)	Daw Araa	Not Area
Sample Name	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 16	20	60		0	0 31.75	2.81608	198	198	0.769	31.999	2.163	38.981	2.30871	428.4	428.4
Crystallinity (%)	84.91														



Figure A18: Sample 16 XRD Pattern

Table A15: Crystallinity result for sample 17

Sample Name	Left Angle	Right Angle	Left Int	Right In	t Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
1960	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 17	20	60	0	(31.752	2.81585	221	221	0.781	32.005	2.164	38.712	2.32411	477.8	477.8
Sample Name	Left Angle	Right Angle	Left Int	. Right In	t Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 17	20	60	0	0	31.752	2.81585	220	220	0.78	32.005	1.996	38.254	2.3509	438.7	438.7
Crystallinity (%)	91.82														



Figure A19: Sample 17 XRD Pattern

Table A16: Crystallinity result for sample 18

Sample Name	Left Angle	Right Angle	Left Int	Right In	nt Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 18	20	60	0		0 31.746	2.81639	222	222	0.953	32.079	2.092	38.505	2.33615	463.9	463.9
Sample Name	Left Angle	Right Angle	Left Int	. Right Ir	nt Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 18	20	60	0		0 31.746	2.81639	220	220	0.951	32.079	1.877	38.078	2.36133	413.1	413.1
Crystallinity (%)	89.05														



Figure A20: Sample 18 XRD Pattern

Table A17: Crystallinity result for sample 19

Sample Name	Left Angle	Right Angle	Left In	t. Right	t Int O	bs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-	-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 19	20	60)	0	0	31.759	2.81523	256	256	0.707	31.975	1.753	38.079	2.36132	448.4	448.4
Sample Name	Left Angle	Right Angle	Left In	t. Right	t Int O	bs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-	-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 19	20	60		0	0	31.759	2.81523	254	254	0.943	32.095	1.568	37.513	2.39562	397.7	397.7
Crystallinity (%)	88.69															



Figure A21: Sample 19 XRD Pattern
Table A18: Crystallinity result for sample 20

Sample Name	Left Angle	Right Angle	Left In	t. Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 20	20	60	-	0	0 31.75	2.81605	236	236	0.94	32.086	1.941	38.729	2.32315	457.7	457.7
										20					
Sample Name	Left Angle	Right Angle	Left In	t. Right	Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 20	20	60		0	0 31.75	2.81606	235	235	0.94	32.086	1.785	38.231	2.35223	419.6	419.6
Crystallinity (%)	91.67														



Figure A22: Sample 20 XRD Pattern

Table A19: Crystallinity result for sample 21

Sample Name	Left Angle	Right Angle	Left Int	Right In	nt Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 21	20	60	C)	0 31.738	2.81712	280	280	0.725	31.95	2.272	38.697	2.32498	636.3	636.3
Sample Name	Left Angle	Right Angle	Left Int	. Right In	nt Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 21	20	60	C)	0 31.738	2.81712	278	278	0.81	31.993	2.05	38.349	2.34529	570.2	570.2
Crystallinity (%)	89.61														



Figure A23: Sample 21 XRD Pattern

Table A20: Crystallinity result for sample 22

Sample Name	Left Angle	Right Angle	Left Int	Right I	nt Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 22	20	60) ()	0 31.92	2.80144	48.2	48.2	0.752	32.126	3.324	40.608	2.21988	160.3	160.3
Sample Name	Left Angle	Right Angle	Left Int	. Right I	nt Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 22	20	60) ()	0 31.92	2.80144	47.6	47.6	0.748	32.126	2.912	40.345	2.23374	138.7	138.7
Crystallinity (%)	86.52														



Figure A24: Sample 22 XRD Pattern

Table A21: Crystallinity result for sample 23

Sample Name	Left Angle	Right Angle	Left Int	Right In	t Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 23	20	60	0	(31.755	2.81557	305	305	0.79	31.999	2.017	38.331	2.34636	616	616
Sample Name	Left Angle	Right Angle	Left Int	. Right In	t Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 23	20	60	0	(31.755	2.81557	302	302	0.79	32	1.767	37.71	2.3835	533.8	533.8
Crystallinity (%)	86.65														
					250 - 250 - - 100 - 100 - - 100 - - - 0 - 20	ml		4 2 TI	o heta	J.J.J.	Mum	eo			

Figure A25: Sample 23 XRD Pattern

Table A22: Crystallinity result for sample 25

Sample Name	Left Angle	Right Angle	Left Int	. Right	t Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 25	20	60	0		0 31.75	5 2.81559	195	195	0.773	32.014	2.848	40.332	2.23443	555.2	555.2
Sample Name	Left Angle	Right Angle	Left Int	. Right	t Int Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 25	20	60	0		0 31.75	5 2.81559	193	193	0.772	32.014	2.464	40.096	2.24702	475.4	475.4
Q	05.02														
Crystallinity (%)	05.03	1		-								2			



Figure A26: Sample 25 XRD Pattern

Table A23: Crystallinity result for sample 26

Sample Name	Left Angle	Right Angle	Left Int	. Right In	nt Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 26	20	60	()	0 31.764	2.81481	170	170	0.718	31.972	? <u>3.381</u>	40.221	2.24032	574.9	574.9
Sample Name	Left Angle	Right Angle	Left Int	. Right Ir	nt Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 26	20	60	()	0 31.764	2.81481	167	167	0.945	32.087	2.895	40.088	2.24747	484.6	484.6
Crystallinity (%)	84.29														



Figure A27: Sample 26 XRD Pattern

Table A24: Crystallinity result for sample 27

Sample Name	Left Angle	Right Angle	Left Int	Right In	t Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 27	20	60	C	(31.73	2.81776	234	234	0.941	32.06	1.963	38.319	2.34703	459.8	459.8
Sample Name	Left Angle	Right Angle	Left Int	Right In	t Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 27	20	60	C	(31.73	2.81776	233	233	0.941	32.06	1.779	37.809	2.37753	414.6	414.6
Crystallinity (%)	90.17														



Figure A28: Sample 27 XRD Pattern

Table A25: Crystallinity result for sample 30

Sample Name	Left Angle	Right Angle	Left In	t. Right I	nt Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 30	20	60		0	0 31.755	2.8156	187	187	0.932	32.092	3.05	39.647	2.27145	569.3	569.3
Sample Name	Left Angle	Right Angle	Left In	t. Right I	nt Obs. Max	d (Obs. Max)	Max Int.	Net Height	FWHM	Chord Mid.	I. Breadth	Gravity C.	d (Gravity C.)	Raw Area	Net Area
	2-Theta °	2-Theta °	Cps	Cps	2-Theta °	Angstrom	Cps	Cps	2-Theta °	2-Theta °	2-Theta °	2-Theta °	Angstrom	Cps x 2-Theta °	Cps x 2-Theta °
Sample 30	20	60		0	0 31.755	2.8156	184	184	0.93	32.093	2.606	39.47	2.28121	479.3	479.3
Crystallinity (%)	84.19														



Figure A29: Sample 30 XRD Pattern