

DESIGN AND FORMULATION OF BIOACTIVE COATINGS USING THERMAL SPRAY PROCESS

A Thesis Report

**Submitted in partial fulfilment of the requirement for the award of
Degree of**

**MASTER OF ENGINEERING
IN
PRODUCTION AND INDUSTRIAL ENGINEERING**

**Submitted By
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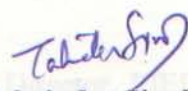
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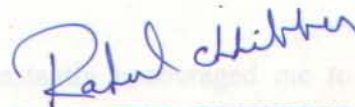
This is to certify that the work which is being presented in this thesis entitled "**Design and formulation of bioactive coatings using thermal spray process**", in partial fulfilment of requirement for the award of the Master Degree in Production & Industrial Engineering, submitted in the Mechanical Engineering Department, Thapar University, Patiala, is an authentic record of the research work carried out by me under the guidance of **Dr. Rahul Chhibber, Lecturer, Mechanical Engineering Department, TU, Patiala.**

The matter embodied in this thesis has not been submitted in part or full to any other university or institute for the award of any other degree.

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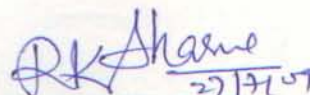

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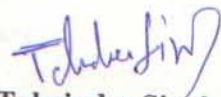
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I would also like to offer my sincere thanks to Dr. T.P.Singh, Director, RIEIT, Ropar and Sh. N.Karunanidhi, DGM ,R&D (Thermal spray division), Jodhpur without the help of them it might not be possible for me to come up to this level.

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Last but not least, I thank my parents, my sister and my son for always being there when I needed them most, and for supporting me through all these months. Also very special thanks to my wife Anudeep Kaur for her patience, while preparing HA powder.


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ABSTRACT

Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, commonly referred to as HA, has attracted wide spread interest from both the orthopaedic and dental fields due to its excellent biocompatibility and tissue bioactivity properties. Hydroxyapatite is chemically similar to the mineral component of bones and hard tissues in mammals. It is one of the few materials that are considered bioactive, meaning that it will support bone growth when used in orthopaedic and dental applications. Despite excellent properties as a biomaterial, the ceramic nature and the inherent mechanical properties of HA specifically brittleness, poor tensile strength and poor impact resistance have restricted its application in many load-bearing applications. HA coated implants combines the good strength with the excellent biocompatibility and bioactivity of the HA.

In the present investigation, an attempt is made to develop HA powder from fishbone and Chicken egg shell, a natural apatite rich substance through heat treatment method. Fishbone, a cheaper source of HA is generated as waste material during fish processing. Fourier transform-infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) techniques are employed to investigate the proof of formation of HA phase. The OH group is found at 3404.25cm^{-1} for fish bone and 3414.31cm^{-1} for egg shell powder and the same peak is also traced in HA powder. Similarly, The P-O group is also found at 1024.19cm^{-1} for fish bone and 875.73cm^{-1} for egg shell powder and the same peak is also traced in HA powder. SEM / EDX of powder is also done to show the microstructure of powders and the traces of the various elements like Ca, Mg etc. Further the blood clotting test shows that both the powders are efficient and compatible with human blood.

The coating of this HA powder is developed on SS 304L metal substrate by using High velocity oxy-fuel (HVOF) spray technique. Coated samples are obtained at various HVOF parameters. Samples are tested for Micro structural analysis, Hardness, Micro hardness, corrosion resistance etc., to find the optimum HVOF parameters.

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An implant is a medical device made to replace and act as a missing biological structure. The surface of implants that contact the body might be made of a biomedical material such as titanium, silicone or apatite. In orthopaedic surgery, implants may refer to devices that are placed over or within bones to hold a fracture reduction while prosthesis would be the more appropriate term for devices that replace a part or whole of a dysfunction joint. In this context, implants may be placed within the body (internal) or placed outside the body (external). Dental implants are one of the few medical devices which permanently cross the boundary between the inside and the outside of the body.

1.1 Bio materials for implants

Biomedical materials must not damage the body, must sustain minimal damage from the body, and must provide the required strength, especially high fatigue strength and toughness, for joints and other applications. The essence of a biomaterial is an economic (cheap) implant with the mechanical, physical, and chemical properties that provide structural capability without deleterious effects on the body. Biomaterial science can be defined as that branch of biomedical engineering dealing with the material aspects of medical devices and implants. The materials used for developing body implants or interfaces are commonly called biomaterials. According to Clemson Advisory Board for Biomaterials “A biomaterial is a systemically, pharmacologically inert substance designed for implantation within or incorporation with a living system”, a definition adopted at the sixth Annual International Biomaterials Symposium, April 20-24, 1974. Williams has defined biomaterials as “Any nonliving materials used in medical devices intended to interact with biological systems”. Only few biomedical composites are currently in medical use. This is mainly due to high development costs and concerns about their biocompatibility. Biocompatibility is the ability of a material to perform with an appropriate host response in a specific application. What this means is that for the intended function, in the location where an implant is located, the material should be compatible with its surroundings, and should be integrated with the surrounding tissue without deleterious effects. The biocompatibility of an artificial material in the body is extremely complicated and involves processes on several length

scales. When the material is placed in tissue, a race for the surface starts immediately. Within a few milliseconds, a layer consisting of water and bio molecules from the physiological liquid is formed on the implant surface. The chemical and topographical properties of the implant surface strongly influence the properties of the bio-layer, and this influence needs to be understood and controlled in order to optimize biocompatibility. Certainly, the proper functioning of the implant depends on whether it possesses the strength necessary to withstand loading within the expected range. A suitable modulus of elasticity is of major importance in some situations, when optimum load transmission from the implant into the surrounding bone is key to the successful functioning of the device. Materials which are to be implanted in the human body are subjected to an environment which is both hostile and at the same time extremely sensitive. In addition there is the crucial fact that the body's tissues are extremely sensitive to foreign materials and are very easily simulated into showing signs of poisoning and rejection. On top of this, mechanical parameters such as tensile strength, fracture toughness and elastic modulus of the implant, must be considered. Thus, to select materials for use in this environment attention must be paid to both the physical function and the biocompatibility of the candidate substrate. The use of medical implants allows improving patient's life and quite often it can bring patients to normal activity in personal and professional life. One of the most difficult problems, which are necessary to solve, is a proper selection of materials predicted for implant construction and implant coating. Biomaterials are used in vast range of biomedical applications such as surgical implants including joints, limbs, total hips, knees, artificial arteries, skins, dentures, heart valves, intra uterine devices (IUDs), pacemaker leads and cardiovascular nets. Fig.1.1 shows the clinical uses of inorganic biomaterials.

Ceramics are inorganic compounds that can be classified into five categories of biomaterials by their macroscopic surface characteristics or by their chemical stability in the body environment. They are carbon, alumina, zirconia, bioactive glass (glass ceramics) and calcium phosphate. The limitations of ceramic materials are their low tensile strength and fracture toughness. Their use in bulk form is therefore limited to functions in which only compressive loads are applied. The class of ceramics used for repair and replacement of diseased and damaged parts of musculoskeletal systems are termed bio ceramics. Bio ceramics became an accepted group of materials for medical applications, mainly for implants in orthopaedics, maxillofacial surgery and for dental implants. Table 1.1 shows the biomedical applications of bio ceramics.

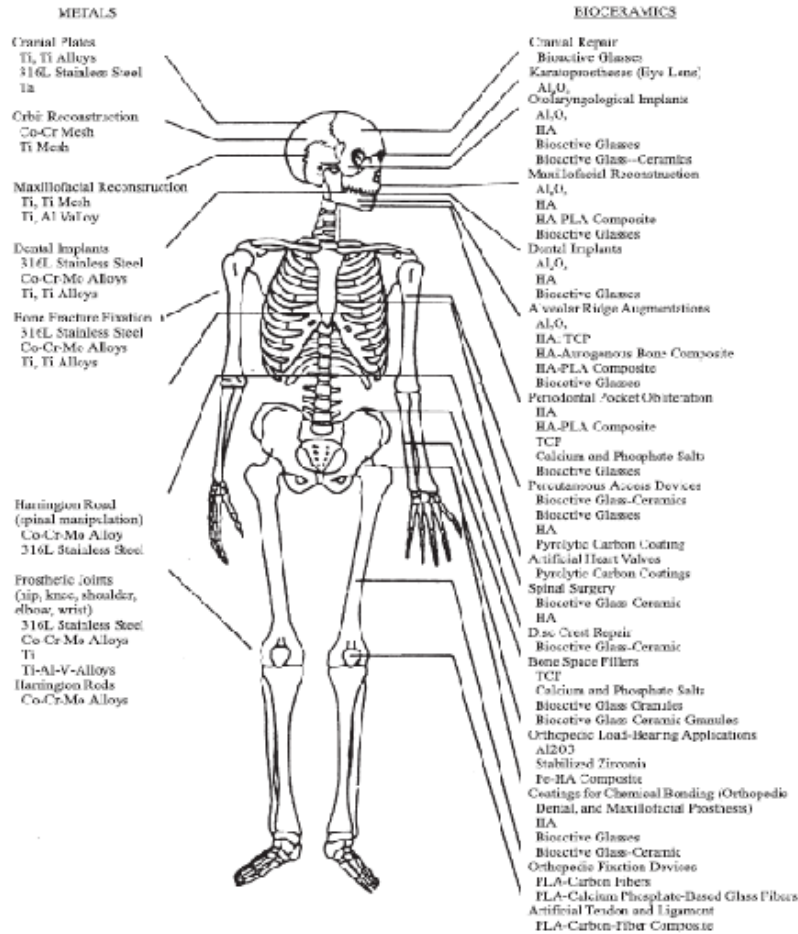


Fig.1.1 Clinical uses of inorganic biomaterials (Hench, 1985)

Devices	Function	Biomaterial
Artificial total hip, knee, shoulder, elbow, wrist	Reconstruct arthritic or fractured joints	High-density alumina, metal bioglass coatings
Bone plates, screws, wires	Repair fractures	Bioglass-metal fiber composite, Polysulfone-carbon fiber composite
Intramedullary nails	Align fractures	Bioglass-metal fiber composite, Polysulfone-carbon fiber composite
Harrington rods	Correct chronic spinal curvature	Bioglass-metal fiber composite, Polysulfone-carbon fiber composite
Permanently implanted artificial limbs	Replace missing extremities	Bioglass-metal fiber composite, Polysulfone-carbon fiber composite
Vertebrae Spacers and extenders	Correct congenital deformity	Al_2O_3
Spinal fusion	Immobilize vertebrae to protect spinal cord	Bioglass
Alveolar bone replacements, mandibular reconstruction	Restore the alveolar ridge to improve denture fit	Polytetra fluoro ethylene (PTFE) - carbon composite, Porous Al_2O_3 , Bioglass, dense-apatite
End osseous tooth replacement implants	Replace diseased, damaged or loosened teeth	Al_2O_3 , Bioglass, dense hydroxyapatite, vitreous carbon
Orthodontic anchors	Provide posts for stress application required to change deformities	Bioglass-coated Al_2O_3 , Bioglass coated tantalum

Table1.1 Biomedical Applications of Bio ceramics [7].

Metals and alloys: Fig.1.2 shows the history of metals, plastics, and ceramics for biomedical applications. There are three major classes of metals used in Bio-implants today: stainless steel, cobalt-chromium alloys and titanium (as alloys and commercially pure). In addition, dental casting alloys are based on precious metals (gold, platinum, palladium or silver), nickel and copper and may contain smaller amounts of many other elements, added to improve the alloys properties. Orthopaedic applications of metal alloys include arthroplasty, osteo synthesis and in spinal and maxillofacial devices. Metallic alloys are also used for components of prosthetic heart valve replacements, pacemaker casings and leads. Small metallic parts may be used in a wide range of other implants, including skin, wound staples, and vascular end prostheses. Dental applications of metals and alloys include fillings, prosthetic devices (crowns, bridges, and removable prostheses), dental implants and orthodontic appliances.

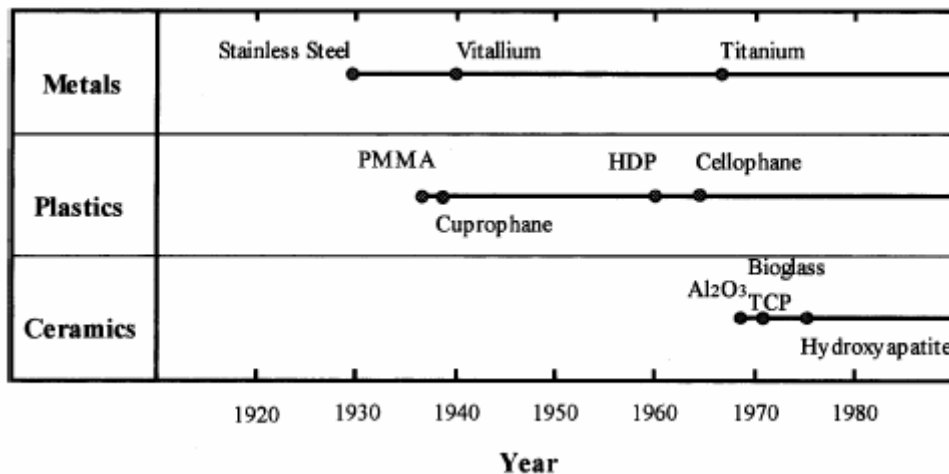


Fig.1.2 History of metals, plastics, and ceramics for biomedical applications [7].

Virtually all modern metal orthopaedic implants are fabricated from one of three alloy systems, the composition and the mechanical and physical properties of which conform to the specifications of the American Society for Testing and Materials. The Composition of SS, Co-Cr alloys, and Tin and its alloys as per ASTM is given in Table 1.2.

TABLE SPECIFICATIONS OF THE AMERICAN SOCIETY FOR TESTING AND MATERIALS									
Alloy System	Specification	Fe	C	Cr	Ni	Co	Ti	Al	V
Stainless-steel									
316L	F-138 (grade 2)	Balance	0.03 max.	17-19	13-15.5				
22-13-5	F-1314	Balance	0.03 max.	20.5-23.5	11.5-13.5				0.10-0.30
Cobalt									
Cast	F-75	0.75 max.	0.35 max.	27-30	1.0 max.	Balance			
Forged†	F-799	0.75 max.	0.35 max.	26-30	1.0 max.	Balance			
Wrought	F-90	3.0 max.	0.05-0.15	19-21	9-11	Balance			
Titanium									
Commercially pure	F-67 (grade 4)	0.5 max.	0.1 max.				Balance		
Extra-low interstitial	F-136	0.25 max.	0.08 max.				Balance	5.5-6.5	3.5-4.5
Ti-6Al-4V									

*Composition is given as the weight per cent.

†The same composition specifications are applicable to the wrought form of this alloy given by specification F-1537.

II

FOR THE COMPOSITION OF ALLOYS USED IN ORTHOPAEDIC IMPLANTS^{68*}

Mo	Mn	P	S	Si	N	Cu	Nb	W	O	H
2-3	2.00 max.	0.025 max.	0.01 max.	0.75 max.	0.10 max.	0.50 max.				
2-3	4.0-6.0	0.025 max.	0.010 max.	0.75 max.	0.20-0.40	0.50 max.	0.10-0.30			
5-7	1.0 max.			1.0 max.						
5-7	1.0 max.			1.0 max.	0.25 max.					
	1.0-2.0	0.04 max.	0.03 max.	0.40 max.				14-16		
					0.5 max.				0.4 max.	0.0125 max.
					0.05 max.				0.13 max.	0.012 max.

Table 1.2 : Composition of Alloys [8].

1.2 Failure of implants

Active research is currently conducted on developing new orthopaedic materials as shown in Table 1.3, current implant materials such as Co-Cr alloys and alumina are much stiffer than human cortical bone. The modulus mismatch between an implant material and the host tissue can cause bone to resorb at the implant bone interface, leading to implant instability and hence its eventual failure. Failure is one of the most important aspects of implant materials behaviour and directly influences the choice of materials and production methods in manufacturing. Because of the many variables involved, implant failure analysis is a complex area of study. Despite the care taken in their design, installation, operation, and machining, components fail.

Material	E (GPa)	σ (MPa)	ϵ (%)	K_{IC} (MN m ^{-3/2})
Co-Cr alloy	230	900-1540	10-30	~100
316L stainless steel	200	540-950	6-70	~100
Ti-6Al-4V alloy	106	900	12.5	~80
Alumina	400	450	~0.5	~3
Zirconia (Mg-PSZ)	200	450-700		7-15
Hydroxyapatite	45-116	60-190		~1
Polyethylene (high density)	1	30		>300
Cortical bone	7-30	50-150	1-3	2-12

E : Young's modulus σ : tensile strength ϵ : elongation at fracture K_{IC} : fracture toughness

Table 1.3: Mechanical Properties of current implant materials [8].

Causes of failure:

Wear: Wear is the main cause of failure of implants directly or indirectly, especially in the case of knee and hip joint prosthesis. To make the joint more efficient, minimization of wear is the most important aspect to be taken care of.

Corrosion: The metallic alloys used for fabrication of artificial joints undergo corrosion and release metallic ions into the patient's body. The metallic ions of these metals (Cobalt, Chromium, Nickel, but also the relatively inert Titanium) may combine with patient's proteins and trigger **allergic immune response**. One such allergy reaction is skin rash observed (very seldom) in patients with orthopaedic metal devices implanted in their bodies. Corrosion can cause an accelerated release of ions and surface deterioration of either the implant or associated prosthesis, and in some cases a loss of strength, leading to fracture.

Various types of corrosion in orthopaedic implants

I) Fretting Corrosion

This describes corrosion occurring at contact areas between materials under load subjected to vibration and slip.

II) Crevice Corrosion

This is a form of local corrosion due to differences in oxygen tension or concentration of electrolytes or changes in pH in a confined space, such as in the crevices between a screw and a plate. The narrower and deeper the crack is, the more likely crevice corrosion is to start.

III) Pitting Corrosion

It is a form of localized, symmetric corrosion in which pits form on the metal surface.

IV) Stress - Corrosion Cracking

It is a phenomenon in which a metal in a certain environment, especially those rich in chlorides, is subjected to stress and fails at a much lower level than usual as a result of corrosion.

1.3 Hydroxyapatite Coatings issues for Biomedical Implants

Calcium phosphate-based bioceramics have been in use in medicine and dentistry for more than 20 years now. The interest in one group member, hydroxyapatite, arises from its similarity to bone apatite, the major component of the inorganic phase of bone, which plays a key role in the calcification and resorption processes of bone. Different phases of calcium phosphate ceramics can be used in medicine, depending on whether a bioactive or a resorbable material is desired. However, the low strength of calcium phosphate bioceramics such as hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) have limited their scope of clinical applications and hence more research needs to be conducted to improve their mechanical properties. Hydroxyapatite is increasingly used, as implant material for medical applications owing to its chemical composition very similar to that of a major component of human bone (1). The most interesting property of HA is its excellent biocompatibility i.e. it helps to form a direct bond with the neighbouring bone (2). Hydroxyapatite has attracted wide spread interest from both the orthopaedic (3) and dental fields due to its excellent biocompatibility and tissue bioactivity properties. Hydroxyapatite is particularly attractive as a biomedical surface modifier used to increase the rate and longevity of implant fixation. Calcium phosphate ceramics and Hydroxyapatite in particular could be used to manufacture ideal biomaterials due to their biocompatibility and Osseo integration, as well as being the materials most similar to the mineral component of the bone

Despite excellent properties as a biomaterial, the ceramic nature and the inherent mechanical properties of HA specifically brittleness, poor tensile strength and poor impact resistance have restricted its application in many load bearing applications. Therefore, the concept of applying HA on to metallic implants as a surface was developed and the HA coated implant combine the good strength and ductility of the metal with the excellent biocompatibility and bioactivity of the HA. Hydroxylapatite coatings on metal substrates such as Ti-6Al-4V and 316L SS are used often in orthopaedics.

1.4 Thermal Spray Coating techniques

1.4.1 Arc Spray Process

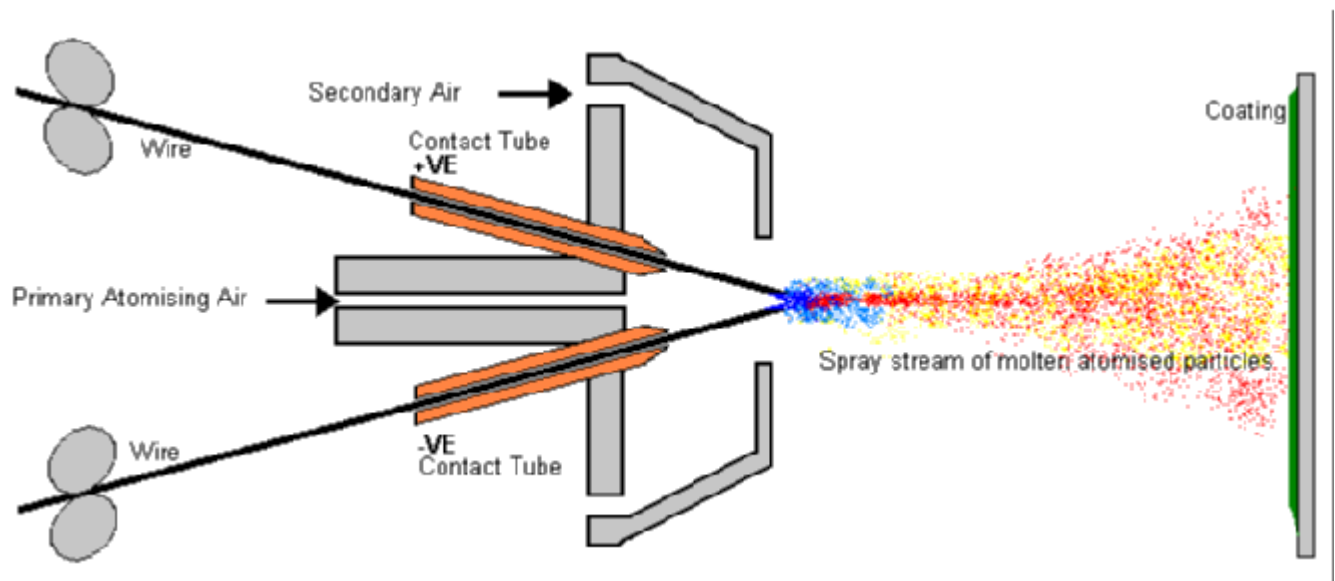


Fig.1.3 Schematic Diagram of the Electric Arc Wire Thermal Spray Process

(Ref: www.gordonengland.co.uk)

In the Arc Spray Process a pair of electrically conductive wires is melted by means of an electric arc as shown in Fig.1.3. The molten material is atomized by compressed air and propelled towards the substrate surface. The impacting molten particles on the substrate rapidly solidify to form a coating. This arc spray process carried out correctly is called a "cold process" (relative to

the substrate material being coated) as the substrate temperature can be kept low during processing avoiding damage, metallurgical changes and distortion to the substrate material. Electric arc spray coatings are normally denser and stronger than their equivalent combustion spray coatings. Low running costs, high spray rates and efficiency make it a good tool for spraying large areas and high production rates.

Disadvantages of the electric arc spray process are that only electrically conductive wires can be sprayed and if substrate preheating is required, a separate heating source is needed.

The main applications of the arc spray process are anti-corrosion coatings of zinc and aluminium and machine element work on large components.

1.4.2 Cold spray coating

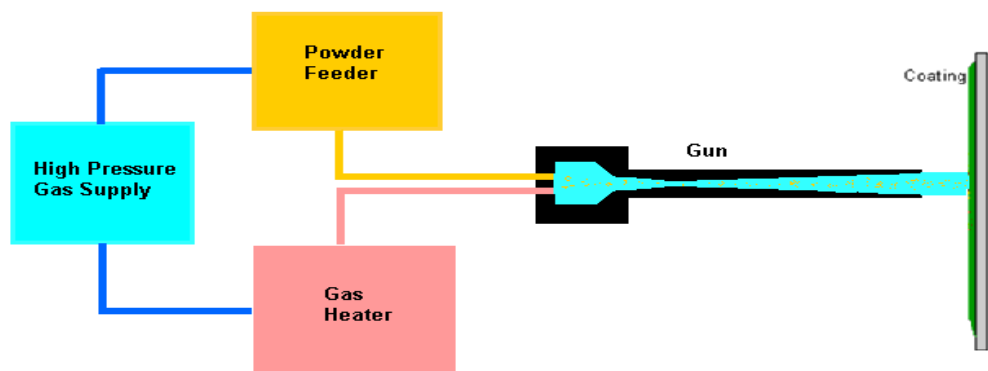


Fig.1.4 Cold Spray Process (Ref: www.gordonengland.co.uk)

Dr Antolli Papyrin and colleagues at the Russian Academy of Sciences were the first to demonstrate the cold spray process in the mid-1980s. The Cold Spray or cold gas-dynamic spraying process is the next progressive step in the development of high kinetic energy coating processes. Similar in principle to the other thermal spray methods, it follows the trend of increasing particle spray velocity and reducing particle temperature as with the HVOF processes, but to a more extreme level that it could be asked whether the process fits under the description of thermal spray.

The Cold Spray process as shown in Fig.1.4 uses the energy stored in high-pressure compressed gas to propel fine powder particles at very high velocities (500 - 1500 m/s). Compressed gas (usually helium) is fed via a heating unit to the gun where the gas exits through a specially

designed nozzle (De laval type convergent-divergent nozzle mostly) at very high velocity. Compressed gas is also fed via a high pressure powder feeder to introduce powder material into the high velocity gas jet. The powder particles are accelerated and moderately heated to a certain velocity and temperature where on impact with a substrate they deform and bond to form a coating. As with the other processes a fine balance between particle size, density, temperature and velocity are important criteria to achieve the desired coating. The particles remain in the solid state and are relatively cold, so the bulk reaction on impact is solid state only. The process imparts little to no oxidation to the spray material, so surfaces stay clean which aids bonding. No melting and relatively low temperatures result in very low shrinkage on cooling, plus with the high strain induced on impact, the coatings tend to be stressed in compression and not in tension like liquid/solid state reactions of most of the other thermal spray processes. Low temperatures also aid in retaining the original powder chemistry and phases in the coating, with only changes due deformation and cold working. Bonding relies on sufficient energy to cause significant plastic deformation of the particle and substrate. Under the high impact stresses and strains, interaction of the particle and substrate surfaces probably cause disruption of oxide films promoting contact of chemically clean surfaces and high friction generating very high localized heating promoting bonding similar to friction or explosive welding.

Coatings at present are limited to ductile materials like aluminum, stainless steel, copper, titanium and alloys. Hard and brittle materials like ceramics cannot be sprayed in the pure form, but may be applied as composites with a ductile matrix phase. Substrate materials are also limited to those that can withstand the aggressive action of the spray particles. Soft or friable substrates will erode rather than be coated. The cold spray process is still primarily in the research and development stage and only now becoming commercially available.

1.4.3 High Velocity Oxygen Fuel Thermal Spray Process (HVOF)

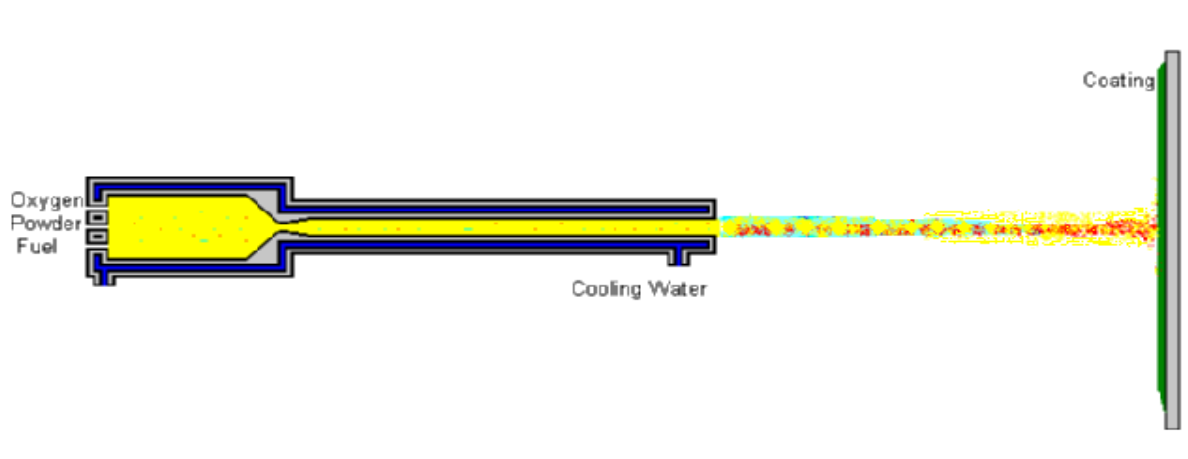


Fig.1.5 Schematic Diagram of the HVOF Process

(Ref: www.gordonengland.co.uk)

The HVOF (High Velocity Oxygen Fuel) Thermal Spray Process is the same as the combustion powder spray process (LVOF) except that this process has been developed to produce extremely high spray velocity. There are a number of HVOF guns which use different methods to achieve high velocity spraying. One method is basically a high pressure water cooled HVOF combustion chamber and long nozzle. Fuel (kerosene, acetylene, propylene and hydrogen) and oxygen are fed into the chamber; combustion produces a hot high pressure flame which is forced down a nozzle increasing its velocity. Powder may be fed axially as in Fig.1.5 into the HVOF combustion chamber under high pressure or fed through the side of De laval type nozzle where the pressure is lower. Another method uses a simpler system of a high pressure combustion nozzle and air cap. Fuel gas (propane, propylene or hydrogen) and oxygen are supplied at high pressure, combustion occurs outside the nozzle but within an air cap supplied with compressed air. The compressed air pinches and accelerates the flame and acts as a coolant for the HVOF gun. Powder is fed at high pressure axially from the centre of the nozzle. The coatings produced by HVOF are similar to those produce by the detonation process. HVOF coatings are very dense, strong and show low residual tensile stress or in some cases compressive stress, which enable very much thicker coatings to be applied than previously possible with the

other processes. The very high kinetic energy of particles striking the substrate surface does not require the particles to be fully molten to form high quality HVOF coatings. This is certainly an advantage for the carbide cermet type coatings and is where this process really excels.

HVOF coatings are used in applications requiring the highest density and strength not found in most other thermal spray processes. New applications, previously not suitable for thermal spray coatings are becoming viable.

Thermal spraying techniques are coating processes in which melted (or heated) materials are sprayed onto a surface. The "feedstock" (coating precursor) is heated by electrical (plasma or arc) or chemical means (combustion flame).

Thermal spraying can provide thick coatings (approx. thickness range is 20 microns to several mm, depending on the process and feedstock), over a large area at high deposition rate as compared to other coating processes such as electroplating, physical and chemical vapor deposition. Coating materials available for thermal spraying include metals, alloys, ceramics, plastics and composites. They are fed in powder or wire form, heated to a molten or semi molten state and accelerated towards substrates in the form of micron-size particles. Combustion or electrical arc discharge is usually used as the source of energy for thermal spraying. Resulting coatings are made by the accumulation of numerous sprayed particles. The surface may not heat up significantly, allowing the coating of flammable substances.

Coating quality is usually assessed by measuring its porosity, oxide content, macro and micro hardness, bond strength and surface roughness. Generally, the coating quality increases with increasing particle velocities.

In December 1994, *H.D. Steffens* said that the electric arc spraying has been successfully used for many industrial applications for more than 30 years. High-velocity oxygen fuel (HVOF) spraying is another well-established technology. Coatings produced by the HVOF process, especially carbide-containing coatings, exhibit excellent quality in terms of density and hardness. In February 1997, *Y. Wang* developed coated implants for biomedical engineering applications. The coating used on the implants is Hydroxyapatite (HA), a calcium-phosphate compound with attractive bioactive and biocompatible properties that can enhance the fixation process of biomedical implants. Thermal spraying provides an excellent means for depositing the HA coatings on implants. Among the popular thermal-spray techniques are combustion-flame spray, plasma spray, and high-velocity oxy-fuel spray.

As per *William R. Lacefield* (June 1999) Calcium phosphate ceramic coatings are commonly used to convert metallic surfaces into a more bioactive state and typically cause faster bone growth.

In the research work of *S. Pal* in January 2005, an attempt was carried out to develop the Bioactive coating on composite implants facilitates biological fixation between the prosthesis and the hard tissue, and increase the long-term stability and integrity of the implants.

In June 2006, *K. Prabakaran* developed Hydroxyapatite powder from fishbone through heat treatment method. Fourier transform-infrared spectroscopy (FT-IR) and x-ray diffraction (XRD) techniques were employed to investigate the proof of formation of HA phase.

G. Bolelli made a comparative study between High Velocity Oxygen-Fuel (HVOF) flame-sprayed and Atmospheric Plasma-Sprayed (APS) ceramics in the year November 2007. He claimed that HVOF coatings are superior to APS.

Following are the persons who are involved in the research work of development of Hydroxyapatite powder and bioactive coatings:

K. Prabakaran [1] *et al.*, developed hydroxyapatite powder from fishbone through heat treatment method. Fourier transform-infrared spectroscopy (FT-IR) and x-ray diffraction (XRD) techniques were employed to investigate the proof of formation of HA phase. Presence of characteristic peaks for hydroxyl and phosphate groups was identified by FT-IR studies. XRD analysis reveals the formation phase pure HA at 900°C. Electrochemical study involving cyclic polarization experiment was carried out to assess the corrosion resistance behaviour of HA coated 316L SS in Ringer's solution. The results have indicated the efficiency of fishbone-originated HA coatings on 316L SS surface.

Deepak K. Pattanayak [2] *et al.*, Hydroxyapatite (HA) powder was prepared by chemical solution technique. The dried powders were calcined at temperatures from 200 °C - 1000 °C and the phases present were identified by X-ray diffraction. The functional groups present were identified by FTIR spectrometry. Powders calcined at 400 °C were ball milled and palletized under uniaxial pressure at different loads. These pellets were sintered at different temperatures

varying from 900 °C - 1200 °C. The biaxial flexural strength was determined and the fractured surfaces were observed under scanning electron microscope.

S. Pal [3] *et al.*, The work was carried out to develop the Bioactive coating on composite implants facilitates biological fixation between the prosthesis and the hard tissue, and increase the long-term stability and integrity of the implants. It produces an intermediate region between bone and implant, and enhances the transition of stress between them. Hydroxyapatite coating was carried out on alumina ceramic particulate reinforced ultra high molecular weight polyethylene (UHMWPE) composite by simple spray-coating method followed by thermo-mechanical process. Applying several thin layers of bioactive materials over the substrate controlled the coating thickness. The coated implant materials were characterized by X-ray diffraction, scanning electron microscopy, scratch and three point cyclic bending test.

Amit Biswas [4] *et al.*, Studied the biocompatibility of Ti-6Al-4V by laser surface nitriding. Laser surface nitriding has been carried out by melting of sand blasted Ti-6Al-4V substrate using a high power continuous wave DIODE laser with nitrogen as shrouding environment (at a pressure of 5 l/min). Following laser treatment, a detailed characterization of the surface has been conducted. Micro hardness and biocompatibility have been evaluated. Laser surface nitriding led to formation of dendrites of TiN on the surface. The micro hardness is improved to 900- 950 VHN (in laser surface nitriding) as compared to 260 VHN of as-received substrate. Biocompatibility behaviour showed a better cell viability in laser surface nitrided Ti-6Al-4V sample as compared to as-received one.

K. Prabakaran [5] *et al.*, Hydroxyapatite (HA) ceramics are used extensively in different medical applications, as biomaterial for repair or replacement of bone tissues since it resembles mineral component of bone and teeth. However, synthetic HA exhibits low fracture toughness due to its lack of strength and brittleness, thereby providing an obstacle to its application in implants that must withstand high loads. Improvement of the mechanical properties can be achieved by the incorporation into resistant oxide phase, e.g. Zirconia partially stabilized by calcia. The preparation of homogeneously distributed zirconia- hydroxyapatite composites can be accomplished using a co-precipitation process of precursor reagent solutions. The present study describes the preparation and characterization of two fine composite powders of zirconia

and hydroxyapatite intended for biomedical implants. The composites were evaluated using XRD.

T. V. Thamaraiselvi and S. Rajeswari [6] Work carried out for surface modification of biomaterials to improve biocompatibility and corrosion resistance without changing their bulk properties is desired for many clinical applications and has become an emerging technology in biomaterial research and industry. The present study focuses on alkali treatment of 316 LVM using sodium hydroxide and evaluation through cyclic polarisation studies in Ringer's solution. The alloy was treated with various concentrations of sodium hydroxide and coated electrophoretically with hydroxyapatite (HA). The efficiency of hydroxyapatite coating on 316 LVM was tested in vitro through polarisation studies. The synthesized hydroxyapatites were characterized by Fourier transform infra-red spectroscopy (FT- IR) and X-ray diffraction studies (XRD). The results demonstrated that alkali treatment reduced its corrosion susceptibility and HA coating on the specimen further reduced its corrosion susceptibility.

T. V. Thamaraiselvi and S. Rajeswari [7] The uses of bioceramics have been revolutionizing the biomedical field in deployment as implants for humans. Many implant materials made of ceramics have been used for the past three decades. In the search to improve the biocompatibility and mechanical strength of implant materials, attention has been directed towards the potential use of ceramic/ceramic composites. The ceramic-based biomaterials have been accepted after biological evaluation through several in vivo and in vitro tests. In this review an attempt has been made to elicit some of the in vivo and in vitro studies performed on bioceramics, ceramic/ceramic composites and their applications as implants.

William R. Lacefield [8] In this paper, the biocompatibility of dental implant materials is discussed in the context of both the mechanical characteristics of the materials and the type of surface presented to the surrounding tissues. The proper functioning of the implant depends on whether it possesses the strength necessary to withstand loading within the expected range, with other properties such as elongation being of importance in some instances. A suitable modulus of elasticity may be of major importance in situations when optimum load transmission from the implant into the surrounding bone is key to the successful functioning of the device. Dental implants present a wide range of surfaces to the surrounding tissues based on surface composition, texture, charge energy, and cleanliness (sterility). Metallic implants are

characterized by protective oxide layers, but ion release is still common with these materials, and is a function of passivation state, composition, and corrosion potential. An effective surface treatment for titanium appears to be passivation or anodization in a suitable solution prior to implantation. Inert ceramic surfaces exhibit minimal ion release, but are similar to metals in that they do not form a high energy bond to the surrounding bone. Some of the newly developed dental implant alloys such as titanium alloys, which contain zirconium and niobium, and high-strength ceramics such as zirconia may offer some advantages (such as lower modulus of elasticity) over the conventional materials. Calcium phosphate ceramic coatings are commonly used to convert metallic surfaces into a more bioactive state and typically cause faster bone apposition. There is a wide range of ceramic coatings containing calcium and phosphorus, with the primary difference in many of these materials being in the rate of ion release. Although their long-term success rate is unknown, the calcium phosphate surfaces seem to have a higher potential for attachment of osteoinductive agents than do uncoated titanium and other more inert implant materials.

N. Ramesh Babu [9] *et al.*, Studied the Bioactive coatings on metallic implants facilitate joining between the prosthesis and the osseous tissue, and increase the long-term stability and integrity of the implant. Literature suggests that current coating techniques provide inadequate adherence of the coating to the implants. A Processing schedule was developed that minimizes reactions and produces thin coatings with the substrate. Hydroxyapatite and biphasic calcium phosphate coatings were carried out on 316 L SS implant by dip-coating method. The coated implant materials have been characterized by X-ray diffraction scanning electron microscopy and adhesion test. The results shows that the dip coated hydroxyapatite and biphasic coatings of thickness of about 5-7 micron strongly attach to the 316 L SS substrates.

S. Kannan [10] *et al.*, Developed a simple method for coating calcium phosphate on type 316 L SS through electrochemical deposition. An aqueous solution comprising chloride dehydrate and ammonium dihydrogen phosphate adjusted to Ca/P molar ratio of 1.67, was taken as electrolyte for deposition at constant current and temperature at different time duration. The resultant coatings were estimated for its Ca/P ratio, FT-IR spectra to identify the functional groups and further the in-vitro behavior of coatings were studied through cyclic polarization experiments in simulated body fluid conditions. The results from the studies showed that coating weight varied

with time duration and applied current. FT-IR spectra indicated the presence of CO₃ containing apatite and the coatings showed improved resistance to corrosion towards pristine 316 L SS.

T.K. Pal, S. Pal [11] A Single-stage long-term clinical trial was given for indigenously prepared hydroxyapatite coated titanium screw-type dental implant in six young adults using suitable designed and produced implant kit. Under local anaesthesia, bone was drilled at a very low speed (30 rpm) and implants were screwed in place. Clinical mobility was tested and radiographs were taken at a periodical interval up to 30 months. The implants were found to be clinically successful and radio graphically acceptable.

K.Hayashi [12] *et al.*, The in vivo biocompatibility of metals coated with several different types of ceramics (Titanium oxide, titanium nitride, and hydroxyapatite) was investigated. These composites had been devised for the purpose of incorporation into the stem of a total hip prosthesis. The materials were inserted into the mid-diaphyseal region of the femurs of adult dogs, and follow-up quantitative histological comparisons were performed for a period of up to 96 weeks. HA coated composites showed the best biocompatibility.

M.V.Capilla [13] *et al.*, in this paper, Clinical follow-up was conducted on 127 cylindrical implants placed in 21 patients after 5 years of function: 75 implants were coated with titanium plasma spray (TPS) and 52 implants were coated with hydroxyapatite (HA). The main aim of the study was to assess possible differences in clinical function and success rates for each implant type. Clinical and radiographic evaluations were conducted, and the periodontal indices of gingival bleeding, plaque, and calculus were measured. No significant differences were found between the 2-implant systems according th the periodontal parameters studied: however, 5-year success rate were 86.7 % fot TPS-coated implants and 94.3 % for HA-coated implants. Long-term success rates were outstanding for HA-coated implants and acceptable for TPS-coated implants after 5 years of function.

V.Simon [14] *et al.*, A new system of functionally graded materials was considered in this study. The samples were obtained by sintering titanium with hydroxyapatite powders. Hydroxyapatite types grains were prepared by sol-gel method. The sintering conditions lead to convenient values of samples density as compared with bone density. The bioactivity was tested in simulated body fluid. The size of hydroxyapatite type phases developed at the sample surface

after soaking for a week in SBF is about hundreds of micrometers and tends to form a continuous network of the new developed bioactive layer.

Matthew T. Walenciak [15] *et al.*, The purpose of this study was to compare mechanical shear strength and bone response with and without plasma sprayed hydroxyapatite (HA) coating. Results shows that HA coated implants enhanced the amount of linear bone contact when compared to uncoated implants. Finally, the HA coating was very stable, in the in vivo environment because it experienced no thickness reduction at any of the time periods.

Joo L. Ong [16] *et al.*, At present, no standard manufacturing guideline exists for depositing hydroxyapatite (HA) on implant surfaces. Although animal and in vitro studies have reported on the benefits of using HA-coated implants as well as the risks of dissolution, these short-term studies did not demonstrate that the dissolution of the HA coatings leads to a loss of implants. In the clinics, the recommendation is that HA- coated screw implants be used for the anterior maxilla and posterior mandible. Finally, besides the surgical skills, it is also important that the clinical investigators be well versed with the materials characterization needed for HA-coated implants.

Mora Melican [17] *et al.*, Enhanced bone attachment to orthopaedic implants is obtained with the use of bioactive hydroxyapatite (HA) coatings. The influence of HA crystallinity on coating dissolution and reprecipitation behavior in cell culture was also investigated. X-ray diffraction was used to determine the extent of the crystallographic changes taking place in the coatings.

Mingheng Li [18] *et al.*, In this paper, the work focused on the modelling and feedback control of an experimental high velocity oxygen-fuel (HVOF) thermal spray process. This paper tells about how the various parameters like the gas jet conditions (temperature, velocity (max. 500 m/s), and pressure (5 – 15 bar)), particle size, and material affects the quality of coating.

O. C. Brandt [19] High-velocity oxygen fuel (HVOF) thermal-sprayed carbide coatings are distinguished by high hardness, low porosity, and good wear resistance compared to other thermal spray technologies. However, for many engineering applications the ductility and fatigue resistance are the most important material properties. In the use of HVOF systems, these properties are influenced by many boundary conditions. This paper presents the effects of different spraying parameters on the fatigue resistance of samples coated by the HVOF process.

Yourong Liu [20] *et al.*, In this paper, the microstructure, mechanical properties and abrasion wear resistance of alumina/titania ceramic coatings deposited with nano- and micro-structured powders by high-velocity oxygen fuel (HVOF) and plasma spray (PS) processes is evaluated. The deposition guns have a strong influence on the mechanical properties and abrasive wear resistance of the coatings, but the powders do not. The coatings deposited by HVOF are significantly harder and tougher, and their abrasion resistance is two–three-fold higher. Plastic microcutting plays the predominant role in abrasion wear of the coating deposited by HVOF. A combination of brittleness and porosity results in fracture that dominates the abrasion wear of plasma-sprayed coatings. The abrasion resistance measured follows an Evans–Marshall equation modified to account for the effects of porosity.

L. Lusvarghi [21] *et al.*, Few papers deal with High Velocity Oxygen-Fuel (HVOF) sprayed ceramics. This two-part study thoroughly compares HVOF sprayed Al_2O_3 , nanostructured Al_2O_3 , Cr_2O_3 to Atmospheric Plasma Sprayed (APS) ones. The first part discusses microstructure and micromechanics. HVOF-sprayed ceramics achieve superior cohesion (lower porosity and lower average pore area). Size effects in Vickers micro indentation tests are different for HVOF and APS ceramics. At 1 N load, hardness is higher for HVOF coatings (no cracking). Under 5 N and 10 N loads, hardness decreases gradually for HVOF coatings; APS coatings are largely cracked at 5 N. HVOF-sprayed ceramics are tougher than APS ones and have higher elastic modulus.

G. Bolelli [22] *et al.*, This is the second part of comparative study between High Velocity Oxygen-Fuel (HVOF) flame-sprayed and Atmospheric Plasma-Sprayed (APS) ceramics. Dry particles abrasion test and dry sliding wear test at room temperature, 400°C and 700°C are performed. In dry sliding against SiC, at room temperature stable tribofilms are formed and mild wear occurs for all coatings. When temperature and normal load increase, making brittle cracking a significant wear mechanism, HVOF coatings become superior to APS ones, thanks to higher toughness. In dry particles abrasion, brittle fracture prevails; therefore, the tougher HVOF coatings outperform APS ones.

R.G.Mason [23] This paper deals with the evaluation of biomedical materials for compatibility with blood is a science in its infancy. Until recently, steel, glass, silicone-coated glass, and paraffin were the materials most frequently used in drawing, processing, and storing blood. Then with the advent of vascular prostheses and artificial heart valves came the need for materials

more compatible with blood than those available at the time. Some materials, such as stainless steel, Teflon, and Dacron were used in vascular or valvular prostheses even though they had a rather low degree of compatibility with blood. Materials poorly compatible with blood, such as these, can be used successfully in high flow systems when the total surface area of the foreign material is small. Problems with thrombosis frequently arise when large surface areas of poorly compatible foreign material are exposed to blood or when flow rates of blood past these materials are low. Recent interest in the artificial kidney and artificial heart has served to focus attention upon the great need for development of new materials highly compatible with blood.

H. S. Sidhu [24] *et al.*, In this paper, Cr₃C₂-NiCr, NiCr, WC-Co and Stellite-6 alloy coatings were sprayed on ASTM SA213-T11 steel using the HVOF process. Liquid petroleum gas was used as the fuel gas. Hot corrosion studies were conducted on the uncoated as well as HVOF sprayed specimens after exposure to molten salt at 900 °C under cyclic conditions. The thermogravimetric technique was used to establish the kinetics of corrosion. XRD, SEM/EDAX and EPMA techniques were used to analyze the corrosion products. All these overlay coatings showed a better resistance to hot corrosion as compared to that of uncoated steel. NiCr Coating was found to be most protective followed by the Cr₃C₂-NiCr coating. WC-Co coating was least effective to protect the substrate steel. It is concluded that the formation of Cr₂O₃, NiO and NiCr₂O₄ in the coatings may contribute to the development of a better hot-corrosion resistance. The uncoated steel suffered corrosion in the form of intense spalling and peeling of the scale, which may be due to the formation of unprotective Fe₂O₃ oxide scale.

H. D. Steffens [25] *et al.*, Electric arc spraying has been successfully used for many industrial applications for more than 30 years. High-velocity oxygen fuel (HVOF) spraying is another well-established technology. Coatings produced by the HVOF process, especially carbide-containing coatings, exhibit excellent quality in terms of density and hardness. One approach to obtaining both high deposition rates and dense coatings is to combine electric arc spraying and HVOF spraying in a technique known as the “Sonarc” process. This process allows many feed combinations through the simultaneous use of wire and powder. This paper presents the development of a prototype. Examples of composite materials and structures, their properties, and potential applications are given.

T. C. Hanson [26] *et al.*, Independent control of high velocity oxygen fuel (HVOF) spray particle velocity and temperature has not been possible in the past, confusing the effect of either parameter on coating properties. This study describes a method by which velocity and temperature may be varied independently. Commercial HVOF equipment that was fitted with a special conical supersonic nozzle having four distinct particle injection locations was used. The present results, which were predicted in simulations and demonstrated in experiments, revealed several pertinent facts. First, particle velocity is principally related to combustion chamber pressure and is relatively unaffected by other design or operating conditions. Second, particle temperature is related to particle residence time within the nozzle, which can be controlled by the choice of particle injection location. In these experiments, the impact velocity and temperature of stainless steel particles were controlled within the ranges 340 to 660 m/s and 1630 to 2160 K, respectively. This range of parameters produced significant variations in splat morphology, coating microstructure, and coating oxide content. Such particle control allows the effects of velocity and temperature on coating properties to be assessed and controlled independently. These results also have commercial application, potentially enabling the user to tailor particle impact velocity and temperature to achieve specific coating properties.

J. Fernandez [27] *et al.*, In this study, highly crystalline Hydroxyapatite (HA) powder was thermally sprayed on to Ti-6Al-4V substrates using the High-Velocity Oxy-Fuel (HVOF) process. Coatings were heat treated for 60 min at 700 °C to study the influence of the crystallization on chemical and mechanical properties. Characterization of the HA coatings was carried out by Fourier Transform Infrared Spectroscopy (FTIR) and x-ray diffraction (XRD). The results showed that the coatings were highly crystalline (82%) and no other phases of calcium phosphate were present. Coatings were 100% crystalline after the heat treatment. Bioactivity of the coatings was investigated by immersion in simulated body fluid. The dissolution/precipitation behaviour was studied and the degradation of HA coatings caused by the immersion test was studied by measuring the adhesion strength of the coatings. After immersion in SBF bond strength decreased for the sprayed coatings, without any thermal treatment, but it was constant for the heat-treated coatings. This phenomenon was related to the dissolution of the amorphous phase in the interface substrate-coating in the sprayed coatings.

K. A. Khor [28] *et al.*, The poor mechanical properties of Hydroxyapatite (HA) can be enhanced by forming a composite with a bio inert and mechanically strong metal alloy such as Ti-6Al-4V. Biomedical composites composed of titanium alloys and HA can offer concomitant bioactive properties as well as good mechanical strength and toughness. This paper describes an attempt to improve coating mechanical properties by forming a composite composed of HA and Ti-6Al-4V. Several compositions (20, 33, and 80 wt % HA) were prepared. Subsequent examination of the plasma-sprayed coatings revealed alternating HA-rich and titanium-rich lamella microstructures. The HA-rich regions appeared porous as a result of poor interparticle adhesion, with the 80 wt% HA coatings having the highest porosity. Mechanical property analysis showed the 20 wt% HA coating to have the highest storage modulus (60 GPa). This coating also had the highest bond strength (≥ 20 MPa max). The coatings tended to exhibit increased bond strength at thicknesses less than or equal to 60 μm . The excellent bond strength of the Ti-6Al-4V/HA composite is caused by the superior interfacial bond between the Ti-6Al-4V-rich splats and the substrate. The encouraging development of this composite raises the possibility of its use as a bond coat for plasma-sprayed HA on titanium-alloy implants.

Y. Wang [29] *et al.*, In recent years, coated implants have been actively researched and put to use in many biomedical engineering applications. The coating used on the implants is Hydroxyapatite (HA), a calcium-phosphate compound with attractive bioactive and biocompatible properties that can enhance the fixation process of biomedical implants. Thermal spraying provides a potent means for depositing the HA coatings on implants. Among the popular thermal-spray techniques are combustion-flame spray, plasma spray, and high-velocity oxy-fuel spray. This article investigates the versatility of thermal-spray techniques to perform spheroidization of HA powders, the preparation of HA-based bio composite powders and coatings, and the deposition of HA coatings.

J. D. Haman [30] *et al.*, In this paper, Plasma spraying is used to produce most commercially available bioceramic coatings for dental implants; however, these coatings still contain some inadequacies. Two types of coatings produced by the high- velocity oxyfuel (HVOF) combustion spray process using commercially available hydroxyapatite(HA) and fluorapatite (FA) powders sprayed onto titanium were characterized to determine whether this relatively new coating process can be applied to bioceramic coatings. Diffuse reflectance Fourier transform infrared

(FTIR) spectroscopy, x- ray diffraction (XRD), and scanning electron microscopy (SEM) were used to characterize the composition, microstructure, and morphology of the coatings. The XRD and FTIR techniques revealed an apatitic structure for both HA and FA coatings. However, XRD patterns indicated some loss in crystallinity of the coatings due to the spraying process. Results from FTIR showed a loss in the intensity of the OH groups due to HVOF spraying; the phosphate groups, however, were still present. Analysis by SEM showed a coating morphology similar to that obtained with plasma spraying, with complete coverage of the titanium substrate. These results indicate that with further optimization the HVOF thermal spray process may offer another method for producing bioceramic coatings.

K. Korpiola [31] *et al.*, A simple device was constructed for determining a value for the average combustion gas velocity at the exit plane of a high-velocity oxy fuel gun. This device was used to measure the velocities of a standard factory-made barrel nozzle and a specially designed de Laval nozzle as a function of the fuel/oxygen ratio and the total mass flow rate. The Mach number of the de Laval nozzle was 1.42. The maximum combustion gas exit velocities determined for the standard and the de Laval nozzles were 1100 and 1550 m/s, respectively. The maximum velocity depends on the fuel/oxygen ratio but is independent of the total flow rate. The effect of increased combustion gas velocity on coating quality is demonstrated.

A. Dolatabadi [32] *et al.*, During the decade, the high-velocity oxy fuel (HVOF) process proved to be a technological alternative to the many conventional thermal spray processes. It would be very advantageous to design a nozzle that provides improved performance in the areas of deposition efficiency, particle in-flight oxidation, and flexibility to allow deposition of ceramic coatings. Based on a numerical analysis, a new attachment to a standard HVOF torch was modelled, designed, tested, and used to produce thermal spray coatings according to the industrial needs mentioned above. Performance of the attachment was investigated by spraying several coating materials including metal and ceramic powders. Particle conditions and spatial distribution, as well as gas phase composition, corresponding to the new attachment and the standard HVOF gun, were compared. The attachment provides better particle spatial distribution, combined with higher particle velocity and temperature.

K. Tani [33] *et al.*, This article summarizes the present status and prospects for future progress of the thermal spraying business and technology in Japan. Organizations that have supported

thermal spraying business and technology consist of coating contract shops, producers and suppliers of spray equipment and consumables, and large companies that have been using thermal spray technology in their production lines. Moreover, out-side, non-commercial organizations such as universities, government, or local industrial institutes and academic societies for thermal spraying are reviewed. In terms of thermal spraying equipment, in particular, the installation of atmosphere-controlled plasma spray and high-velocity oxygen/fuel spray (HVOF) are investigated. Typical examples include industrial applications that are performed mainly by coating contract shops and large companies. In emerging spraying process technologies, synthesis of new materials using atmospheric plasma spray and atmosphere-controlled plasma spray, laser-assisted spraying, and new plasma torches are presented.

V. V. Sobolev [34] *et al.*, A mathematical model is developed to predict particle velocity and temperature during high-velocity oxy fuel (HVOF) spraying. This model accounts for internal heat conduction in powder particles, particle heating, fusion, cooling, solidification and the composite structure of the particles. Analytical results are obtained that describe particle velocity and temperature variations. The dependence of fluid velocity on particle density and volume fraction is shown. The results agree with empirically established HVOF spraying practice.

It was observed from the review of available literature that Hydroxyapatite is used extensively as a biomaterial for biomedical implant applications. Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, commonly referred to as HA, has attracted wide spread interest from both the orthopaedic and dental fields due to its excellent biocompatibility and tissue bioactivity properties. Hydroxyapatite is chemically similar to the mineral component of bones and hard tissues in mammals. It is one of the few materials that are considered bioactive, meaning that it will support bone in growth when used in orthopaedic and dental applications.

Despite excellent properties as a biomaterial, the ceramic nature and the inherent mechanical properties of HA specifically brittleness, poor tensile strength and poor impact resistance have restricted its application in many load-bearing applications. HA coated implants combines the good strength with the excellent biocompatibility and bioactivity of the HA.

Therefore, the concept of applying HA on to metallic implants is explored under this research work, as not much work has been done on development of coatings till now. Fig.3.1 shows the flow chart of the complete work which is done to develop the bio- active coatings.

3.1 Flow Chart of Experimental plan

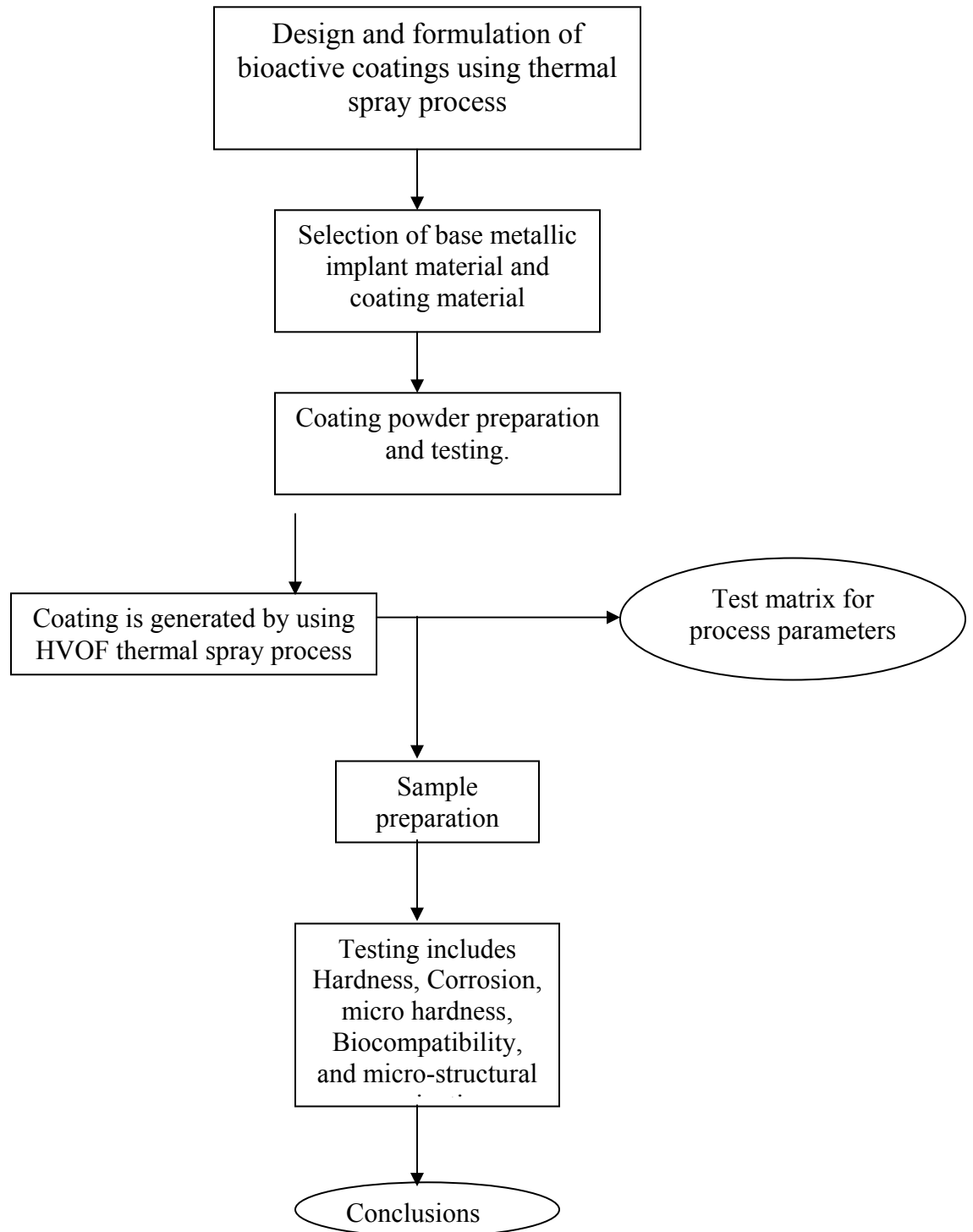


Fig.3.1 Flow Chart

4.1 Powder Preparation

In the present investigation, an attempt is made to develop Hydroxyapatite (HA) powder from fishbone and egg shell, a natural apatite rich substance through heat treatment method. Fishbone, a cheaper source of HA is generated as waste material during fish processing. Fourier transform-infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) techniques are employed to investigate the proof of formation of HA phase.

Commercially HA powder is very costly, so an attempt is made to prepare the powder from fish bone and egg shell as these sources consider as waste material. These are easily available and they are free of cost.

4.1.1 Steps for preparation of HA powder from fish bone

- 1) Fish bones are obtained from fish [Commercial name: *Soel fish*]. The fish named *soel* is available in large quantity at fish market, factory area, Patiala during November to April months. The fish bones are boiled in distilled water for 1 h and washed using a strong water jet to eliminate the fish meat.
- 2) The washed fish bones are then dried and heated in a oven at 500°C for 30 min. The appearance of fish bones after this heat treatment is shown in Fig.4.1



Fig.4.1 Fish bones

- 3) It is then crushed either in home mixer grinder or in crusher. The powder sample after crushing is shown in Fig.4.2



Fig.4.2 Fish bone powder

The powder size obtained after crushing is 30 microns. This is further reduced through Ball milling process as in Fig.4.3

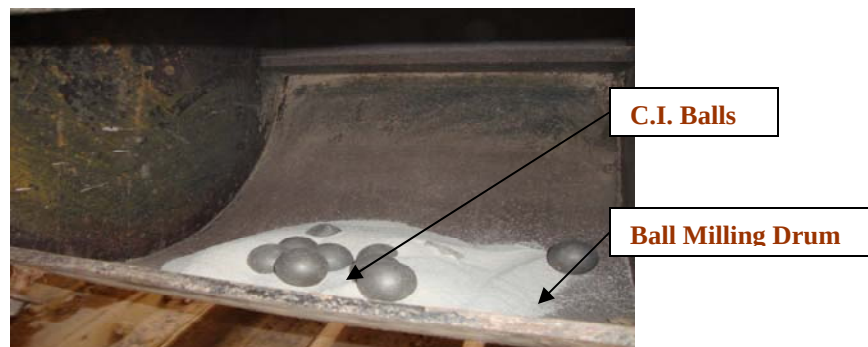


Fig.4.3 Ball milling of fish bone powder

The ball mill, a type of grinder, is a cylindrical device used in grinding (or mixing) materials like ores, chemicals, ceramic raw materials and paints. Ball mills rotate around a horizontal axis, partially filled with the material to be ground plus the grinding medium. Different materials are used as media, including ceramic balls, flint pebbles and stainless steel balls. An internal cascading effect reduces the material to a fine powder. Industrial ball mills can operate continuously fed at one end and discharged at the other end. Large to medium-sized ball mills are mechanically rotated on their axis, but small ones normally consist of a cylindrical capped

container that sits on two drive shafts (pulleys and belts are used to transmit rotary motion). The ball milling is carried out by C.I. sphere balls of 4.8 mm diameter and of 390 gm weight. The drum is rotated at 30 to 33 r.p.m.

4.1.2 Steps for preparation of HA powder from Chicken Egg Shell

- 1) Egg shells are collected from the boiled egg sellers in the *Tripuri Town market*, Patiala. The egg shells are boiled in distilled water for 1 h.
- 2) The egg shells are then dried and heated in a oven at 500°C for 30 min. The appearance of egg shells after this heat treatment is shown in Fig.4.4



Fig.4.4 Chicken egg shell

- 3) It is then crushed either in home mixer grinder or in crusher. The powder sample after crushing is shown in Fig.4.5

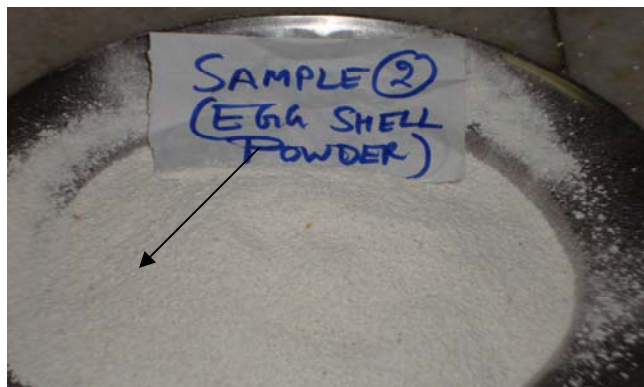


Fig.4.5 Egg shell powder

The powder size obtained after crushing is 50 microns. This is further reduced through Ball milling process.

4.2 Testing of Powder

Before coating of the powder on the metal substrate, the following tests are done on both the powders to show the presence of HA phase and to know the compatibility with human blood.

- 1) X-ray Powder Diffraction (XRD)
- 2) FT IR
- 3) Micro structural analysis
- 4) Blood Clotting test

4.2.1 X-ray Powder Diffraction (XRD)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined. Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays.

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ . The instrument used to maintain the angle and rotate the sample is termed a *goniometer*. For typical powder patterns, data is collected at 2θ from $\sim 5^\circ$ to 70° , angles that are preset in the X-ray scan.

4.2.1.1 Applications

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

Other applications include:

- Characterization of crystalline materials.
- Identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically.
- Determination of unit cell dimensions.
- Measurement of sample purity.

With specialized techniques, XRD can be used to:

- Determine crystal structures.
- Determine of modal amounts of minerals (quantitative analysis).

- Characterize thin films samples by:
 - o Determining lattice mismatch between film and substrate and to inferring stress and strain.
 - o Determining dislocation density and quality of the film by rocking curve measurements.
 - o Measuring super lattices in multilayered epitaxial structures.
 - o Determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements.
- Make textural measurements, such as the orientation of grains, in a polycrystalline sample.

The XRD results of fish bone powder and Hydroxyapatite powder are shown in Fig.4.6 and Fig.4.7 respectively.

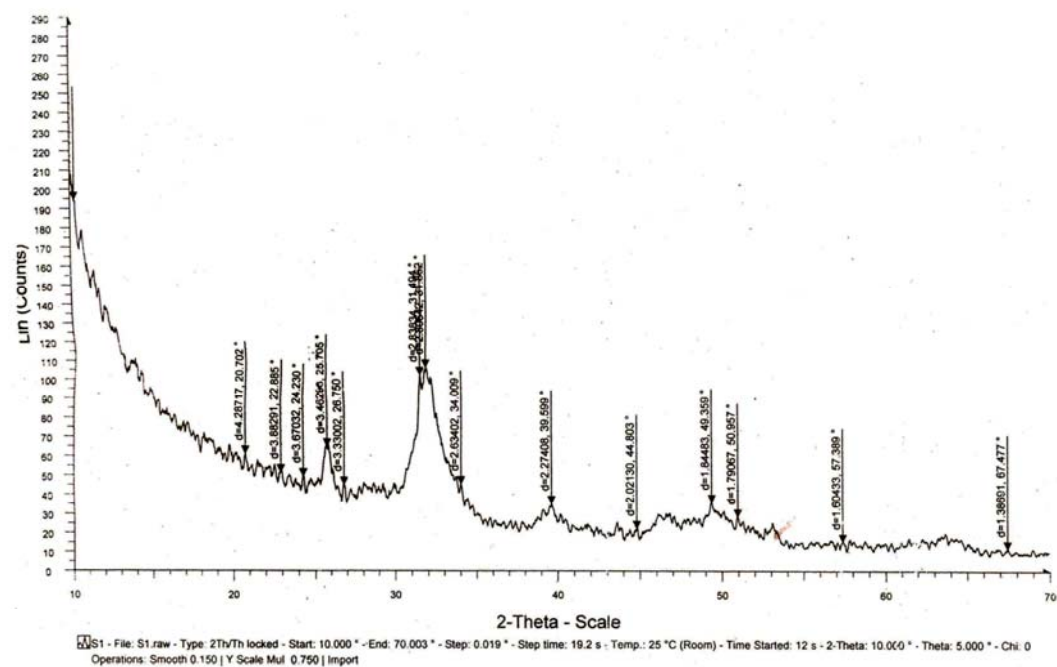


Fig.4.6 The XRD graph of Fish Bone

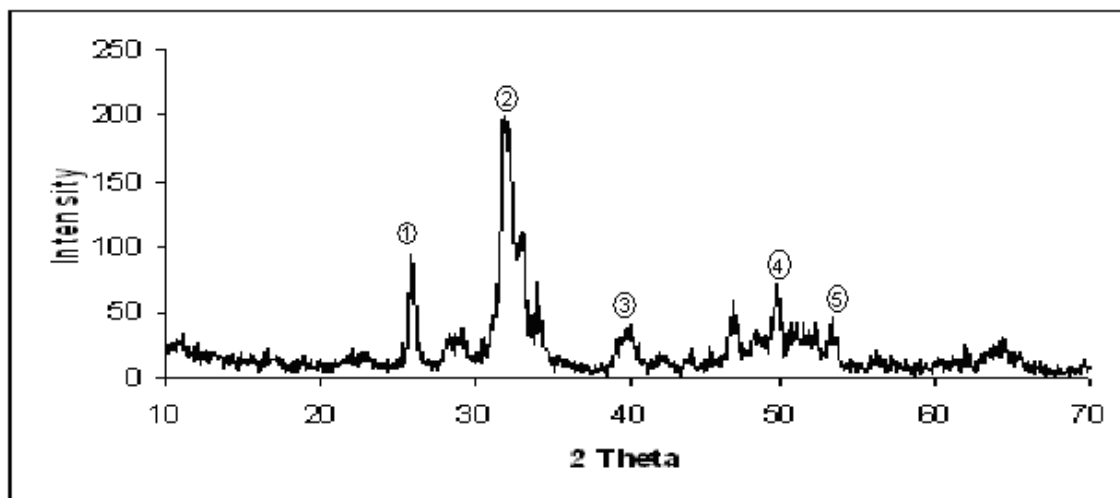


Fig.4.7 The XRD of Hydroxyapatite (Ref: www.scielo.br)

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Now compare the XRD peaks of Hydroxyapatite and the XRD peaks of fish bone. The following five peaks are observed and compared as follows:

Peak No.1: 25.705 °

Peak No.2: 31.862 °

Peak No.3: 39.599 °

Peak No.4: 49.359 °

Peak No.5: 53.000 °

The above comparison shows the traces of the HA in fish bone.

4.2.2 FTIR (Fourier Transform Infrared Spectrometry)

FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

So, what information can FT-IR provide?

- It can identify unknown materials
- It can determine the quality or consistency of a sample
- It can determine the amount of components in a mixture

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

The original infrared instruments were of the dispersive type. These instruments separated the individual frequencies of energy emitted from the infrared source. This was accomplished by the use of a prism or grating. An infrared prism works exactly the same as a visible prism which separates visible light into its colors (frequencies). A grating is a more modern dispersive element which better separates the frequencies of infrared energy. The detector measures the amount of energy at each frequency which has passed through the sample. This results in a spectrum which is a plot of intensity vs. frequency.

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. Most interferometers employ a beamsplitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beamsplitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beamsplitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. This means that as the interferogram is measured, all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make an identification, the measured interferogram signal can not be interpreted directly. A means of “decoding” the individual

frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.

The process (Fig.4.8) is as follows:

- 1. The Source:** Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).
- 2. The Interferometer:** The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.
- 3. The Sample:** The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.
- 4. The Detector:** The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.
- 5. The Computer:** The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation. The process layout is shown in figure as below:

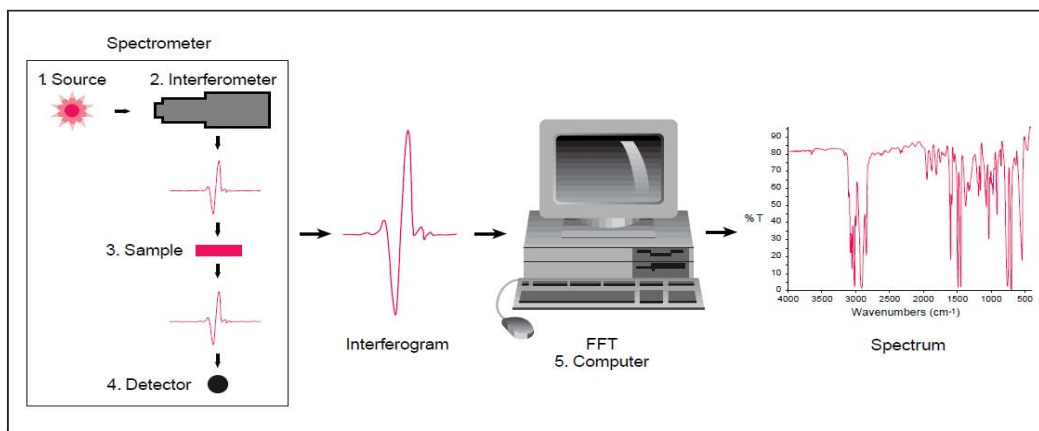


Fig.4.8 FTIR process (Ref: www.mmrc.caltech.edu/FTIR/FTIRintro.pdf)

4.2.2.1 FTIR comparison of fish bone powder, egg shell powder and Hydroxyapatite

The FTIR reports of fish bone powder, egg shell powder and Hydroxyapatite are shown in Fig.4.9, Fig.4.10 and Fig.4.11 respectively.

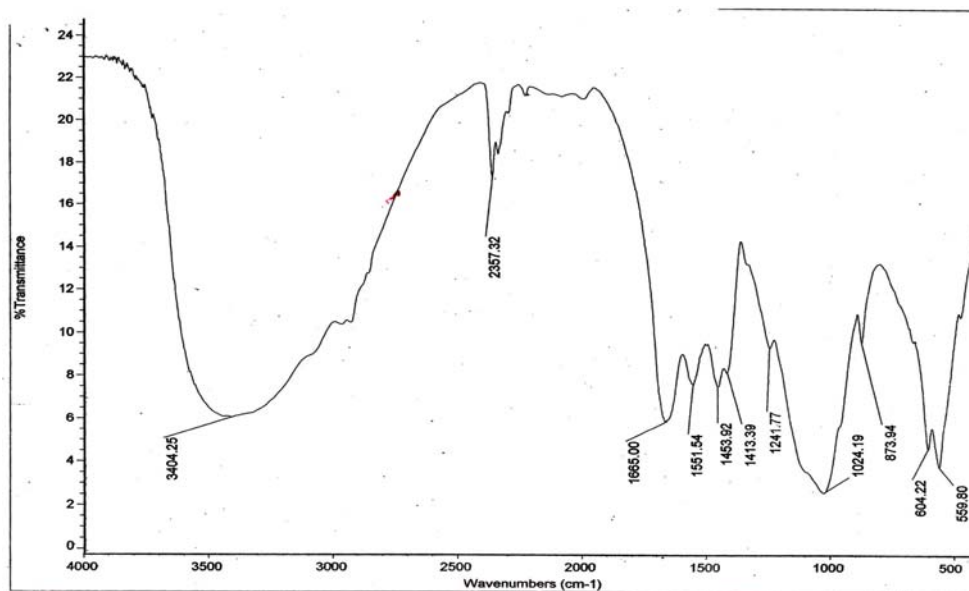


Fig.4.9 FTIR of fish bone powder

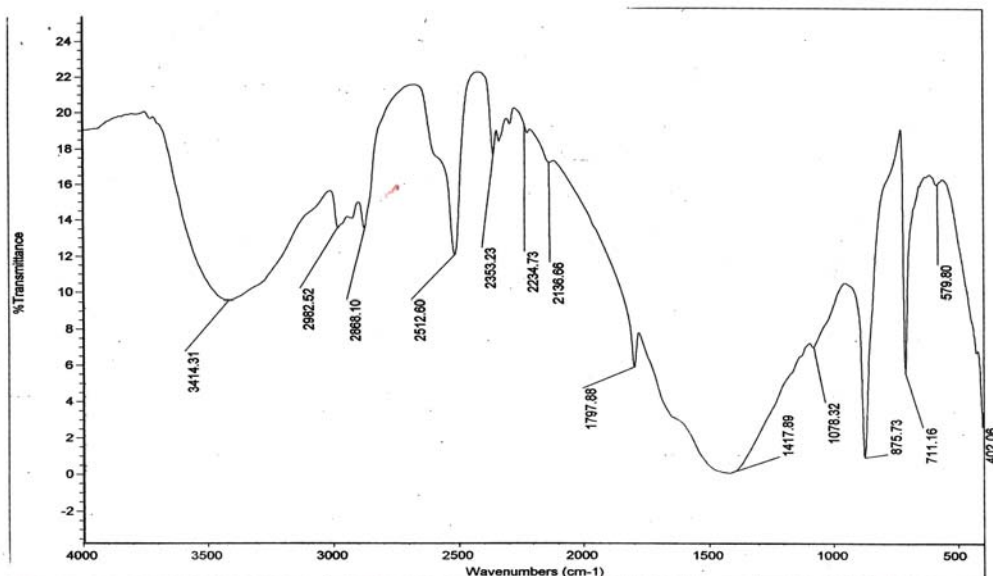


Fig.4.10 FTIR of egg shell powder

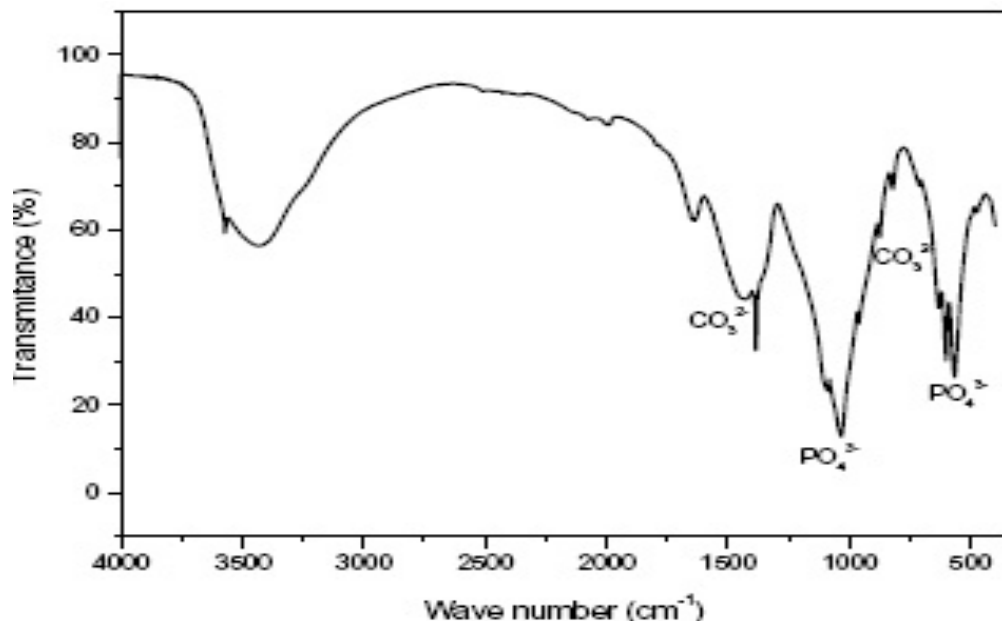


Fig.4.11 FTIR of HA powder (Ref: www.scielo.br)

The OH group is found at 3404.25cm^{-1} for fish bone and 3414.31cm^{-1} for egg shell powder and the same peak is also traced in HA powder. Similarly, The P-O group is also found at 1024.19cm^{-1} for fish bone and 875.73cm^{-1} for egg shell powder and the same peak is also traced in HA powder. So, it is clear from the above comparison that both the powders shows the traces of HA phase.

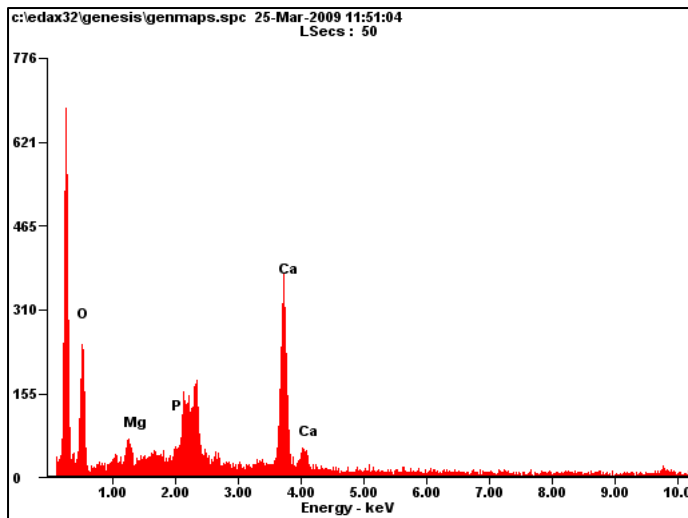
4.2.3 Micro structural analysis

This is done to show the microstructure of powders and the traces of the various elements like Ca, Mg, P etc.

Energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of XRF. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing x-rays that are characteristic of an element's atomic structure to be identified uniquely from each other.

To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or protons (see PIXE), or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured. The SEM/EDX of fish bone powder is shown from Fig.4.12 to Fig.4.15 and SEM/EDX of egg shell powder is shown from Fig.4.16 to 4.18.

4.2.3.1 Micro structural analysis of Fish bone powder



Element	Wt%
OK	60.62
MgK	03.78
PK	01.61
CaK	33.99

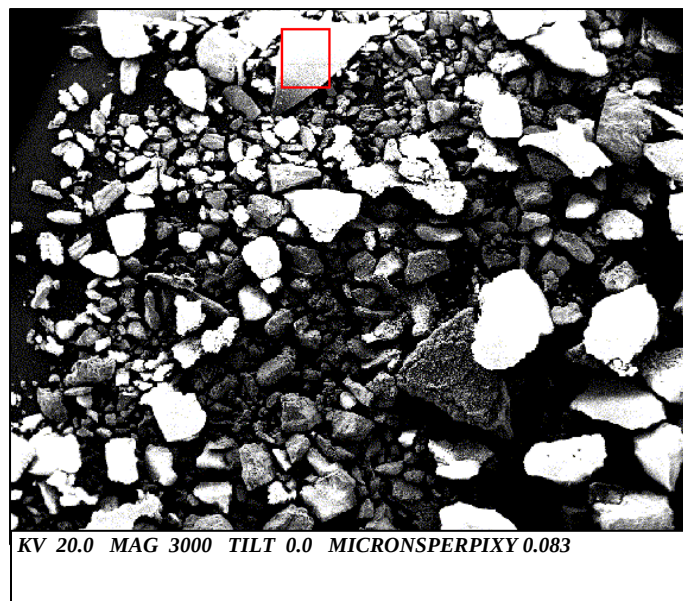
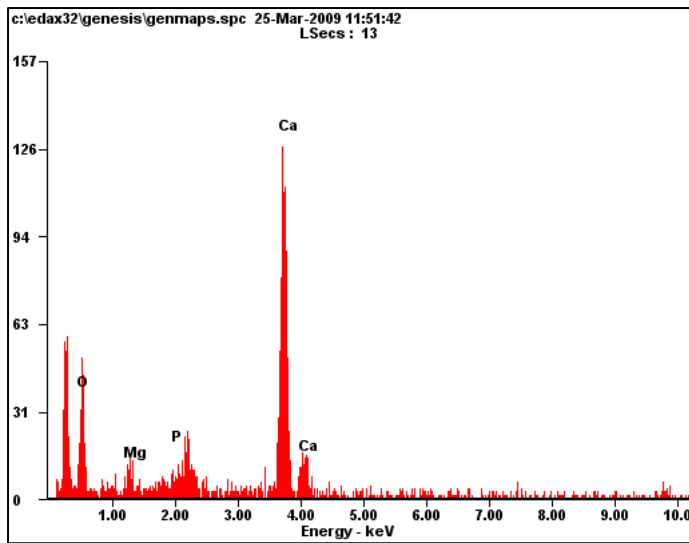


Fig. 4.12 Micro structural analysis of fish bone powder



<i>Element</i>	<i>Wt%</i>
<i>OK</i>	49.33
<i>MgK</i>	03.24
<i>PK</i>	02.40
<i>CaK</i>	45.03

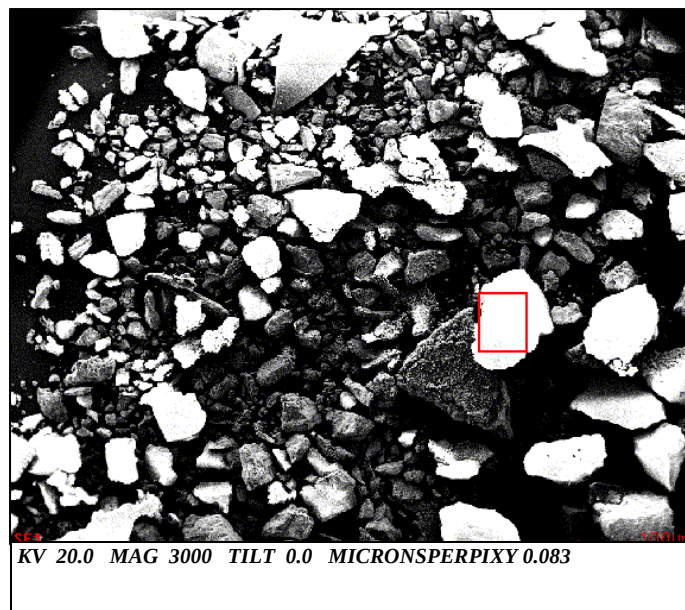
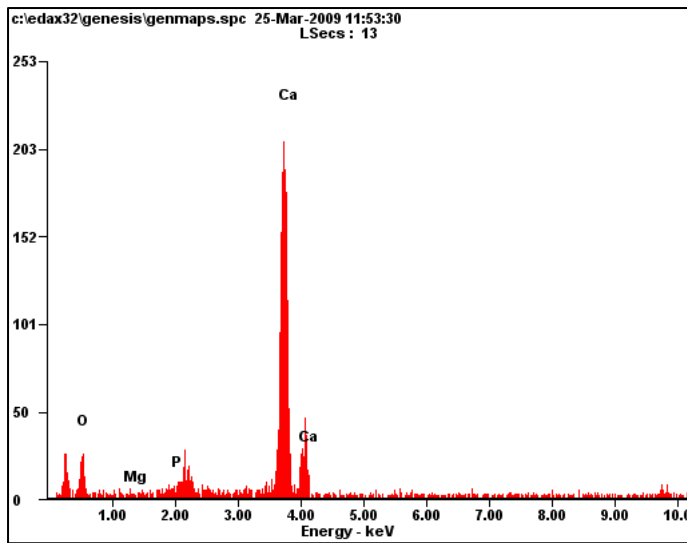
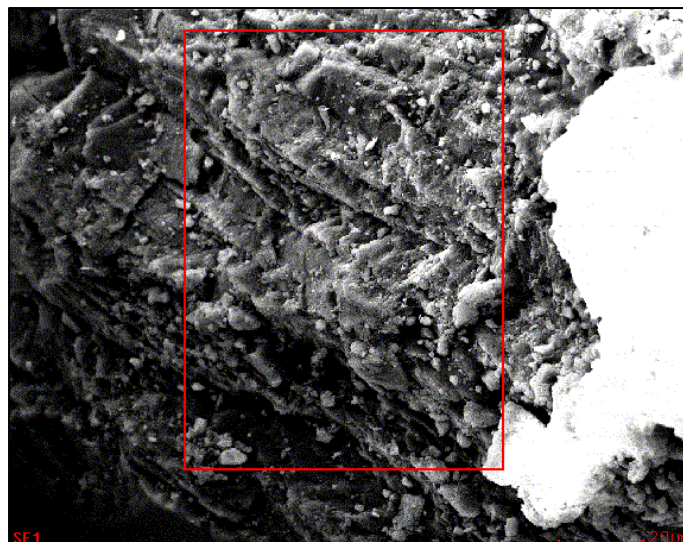


Fig. 4.13 Micro structural analysis of fish bone powder

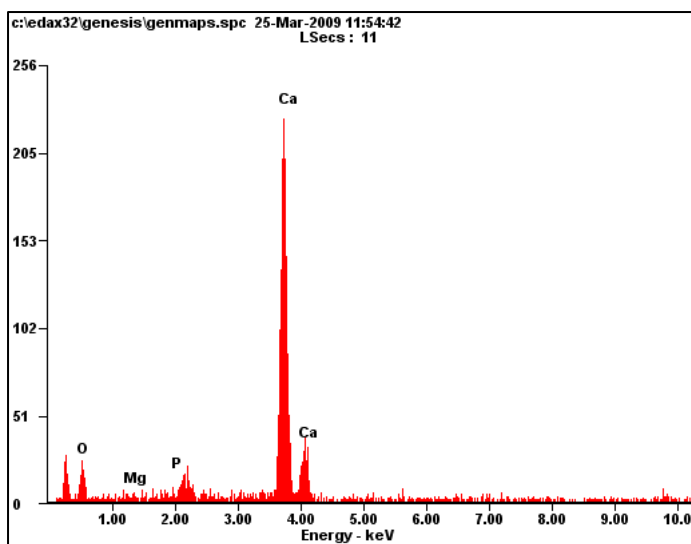


<i>Element</i>	<i>Wt%</i>
<i>OK</i>	33.92
<i>MgK</i>	00.52
<i>PK</i>	01.37
<i>CaK</i>	64.19

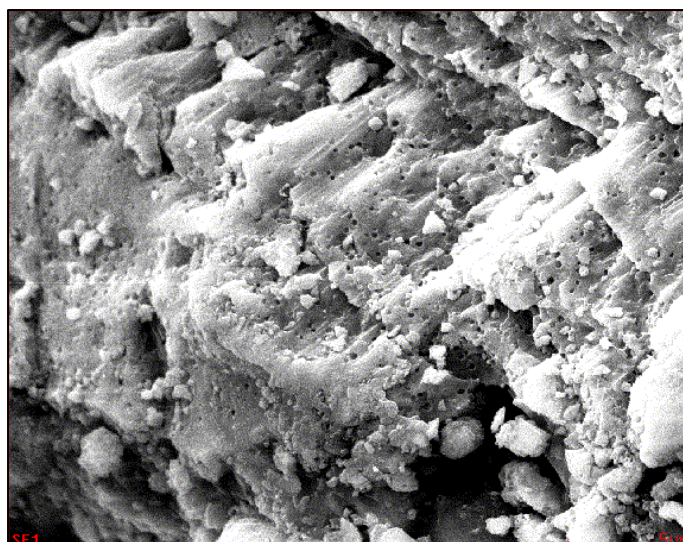


KV 20.0 MAG 3000 TILT 0.0 MICRONSPERPIXY 0.083

Fig. 4.14 Micro structural analysis of fish bone powder



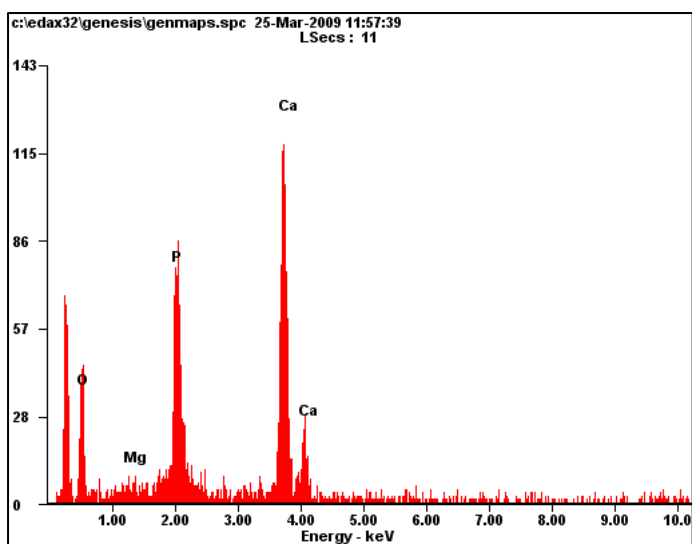
<i>Element</i>	<i>Wt%</i>
<i>OK</i>	30.39
<i>MgK</i>	00.75
<i>PK</i>	00.93
<i>CaK</i>	67.93



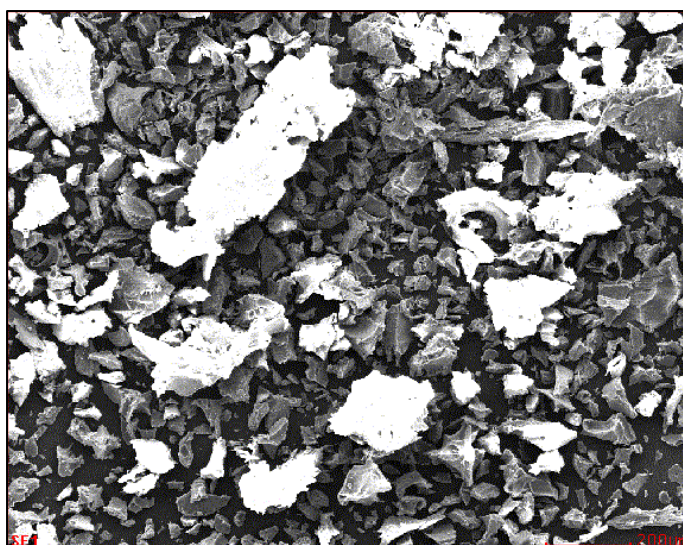
KV 20.0 MAG 3000 TILT 0.0 MICRONS PER PIX 0.083

Fig. 4.15 Micro structural analysis of fish bone powder

4.2.3.2 Micro structural analysis of Egg Shell powder

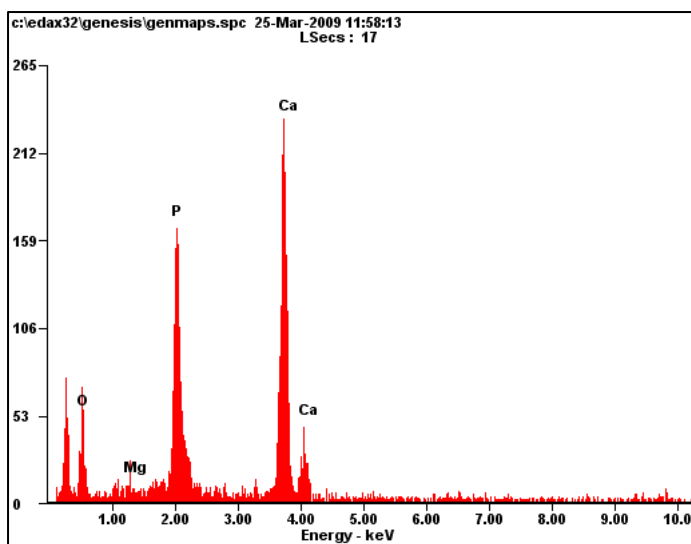


<i>Element</i>	<i>Wt%</i>
<i>OK</i>	42.38
<i>MgK</i>	00.69
<i>PK</i>	17.86
<i>CaK</i>	39.06

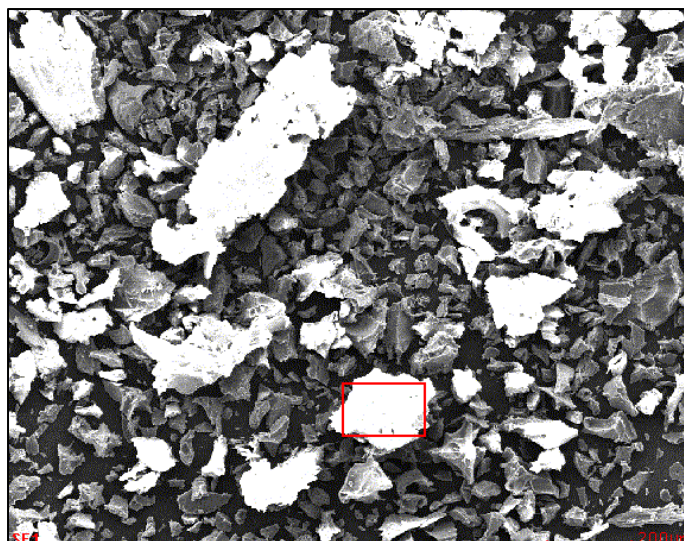


KV 20.0 MAG 3000 TILT 0.0 MICRONS PER PIXY 0.083

Fig. 4.16 Micro structural analysis of Egg shell powder

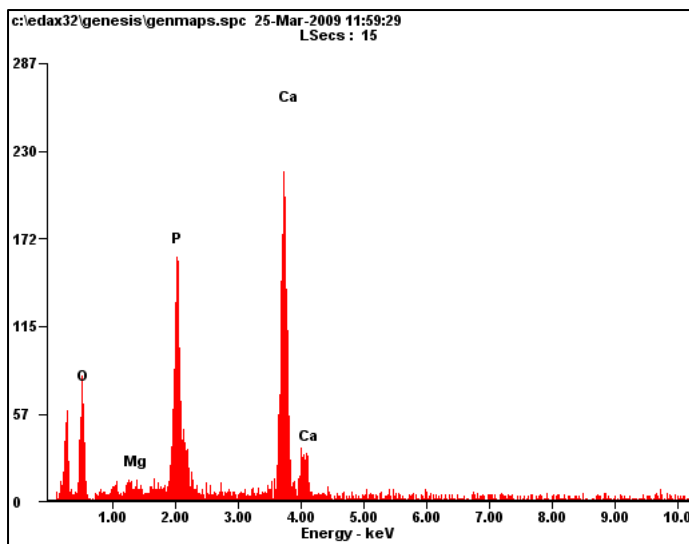


<i>Element</i>	<i>Wt%</i>
<i>OK</i>	34.98
<i>MgK</i>	01.26
<i>PK</i>	19.27
<i>CaK</i>	44.48



KV 20.0 MAG 3000 TILT 0.0 MICRONSPERPIXY 0.083

Fig. 4.17 Micro structural analysis of Egg shell powder



<i>Element</i>	<i>Wt%</i>
<i>OK</i>	40.38
<i>MgK</i>	00.73
<i>PK</i>	17.65
<i>CaK</i>	41.24

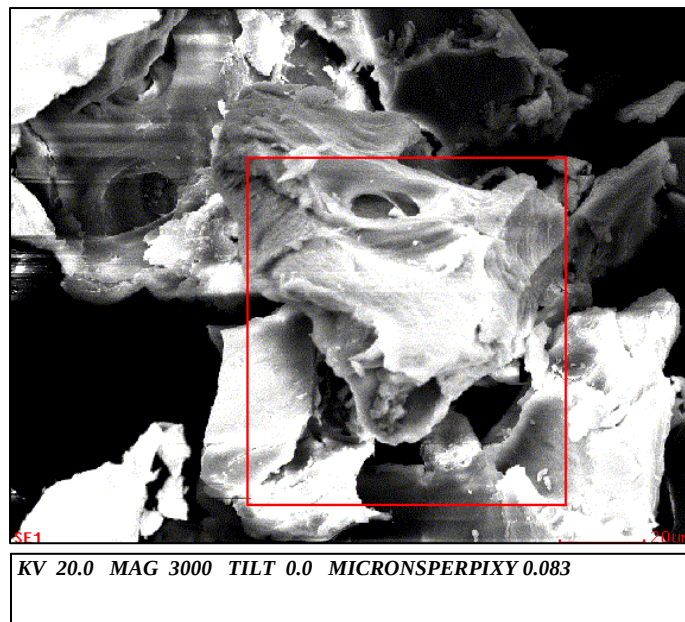


Fig. 4.18 Micro structural analysis of Egg shell powder

From the EDX/SEM report, it is cleared that the fish bone powder contains large amount of calcium as compared to egg shell powder. The amount of Ca in fish bone powder is 67.9%

by weight where as in egg shell it is 44.48%. But the fish bone powder contains less amount of phosphorous as compared to egg shell powder. The amount of P in fish bone powder is 2.4% only by weight where as in egg shell it is 19.27%. The maximum amount of Mg in fish bone powder is 3.78% and in egg shell powder it is 1.26%.

4.2.4 Blood clotting test

Before preceding the coating, one of the most important tests is to know the compatibility of the powders with human blood.

When blood vessels are cut or damaged, the loss of blood from the system must be stopped before shock and possible death occur. This is accomplished by solidification of the blood, a process called coagulation or clotting. A blood clot consists of a plug of platelets

Clotting also requires calcium ions (Ca^{2+}) (which is why blood banks use a chelating agent to bind the calcium in donated blood so the blood will not clot in the bag). Blood clotting is a natural process in which blood cells and fibrin strands rapidly form a clump to stop bleeding after a blood vessel has been injured. Eventually the clot will form a protective scab over a wounded blood vessel, allowing it to heal. If the body did not have the ability to form blood clot people would bleed to death after even a minor cut.

The blood clotting test is performed as follow:

1) First of all the blood sample is collected in capillary tube and place on test slide (Fig.4.19) and then note down the clotting time with the help of stop watch. The clotting time is 1 min. and 14 sec.



Fig.4.19 Blood sample collection

2) The test slide is seen under the microscope by using 10X (Fig.4.20) and 40X (Fig.4.21) magnifications.

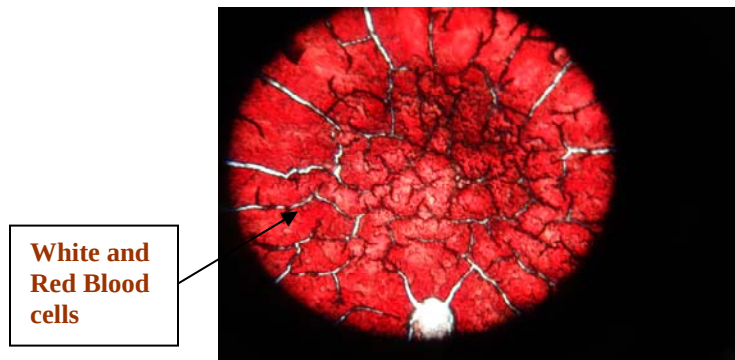


Fig.4.20 Normal Blood at 10 X magnification

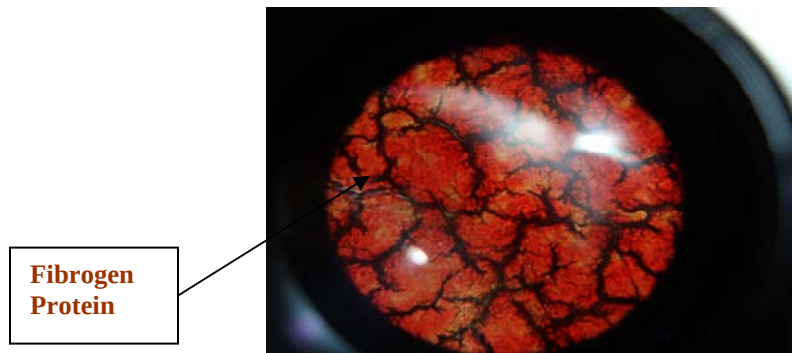


Fig.4.21 Normal Blood at 40 X magnification

3) Then again take the normal blood and mix with fish bone powder immediately and note down the clotting time. In this case the clotting time is reduced to 16.42 seconds. Now see this under microscope by using 10X (Fig.4.22) and 40X (Fig.4.23).

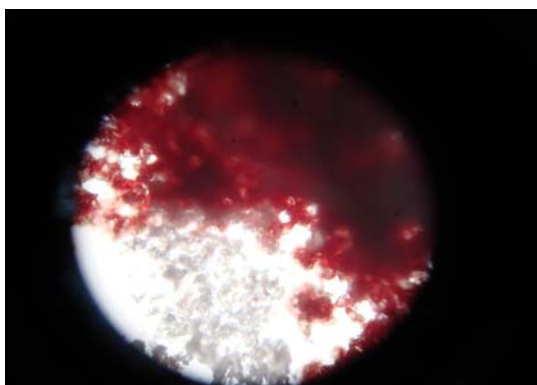


Fig.4.22 Normal Blood with fish bone powder at 10 X magnification

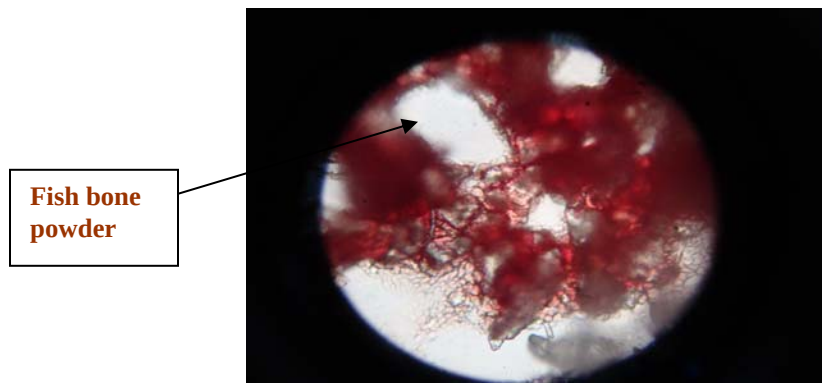


Fig.4.23 Normal Blood with fish bone powder at 40 X magnification

- 4) Now again take the normal blood and mix with egg shell powder immediately and note down the clotting time. In this case the clotting time is 36.46 seconds. Now see this under microscope by using 10X (Fig.4.24) and 40X (Fig.4.25).

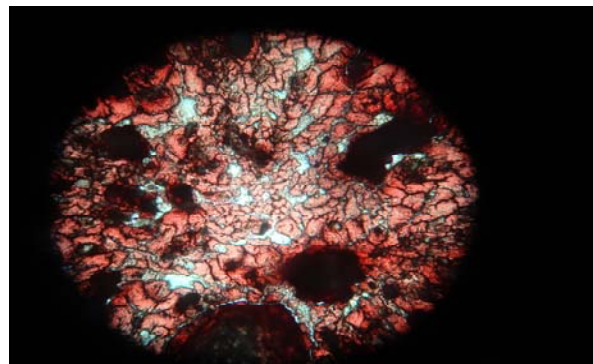


Fig.4.24 Normal Blood with egg shell powder at 10 X magnification

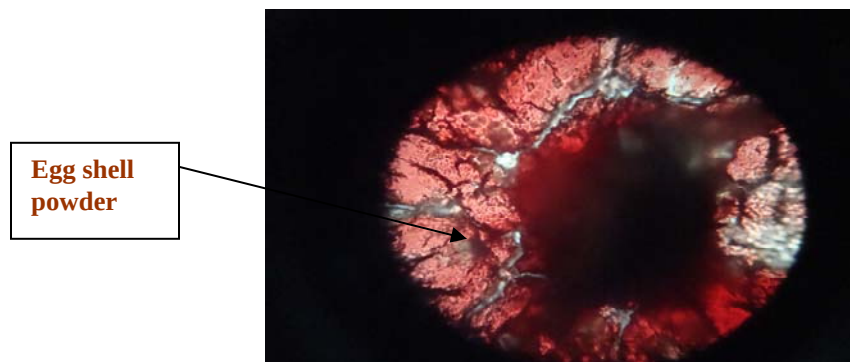


Fig.4.25 Normal Blood with egg shell powder at 40 X magnification

- 5) Now mix the normal blood with anticoagulant (Sodium citrate solution 3.8 % W/V) .The anticoagulants solution is that which prevents the blood clotting.



Fig.4.26 Normal Blood with anticoagulant at 40 X magnification

- 6) Mix the fish bone powder in the normal blood with anticoagulant ,the fish bone powder still produces blood clotting in 16.44 sec. and similarly the egg shell powder makes blood clotting in 38.42 seconds. Now see this under microscope by using 10X (Fig.4.27 and Fig.4.28). So, both the powders are efficient and compatible with human blood.

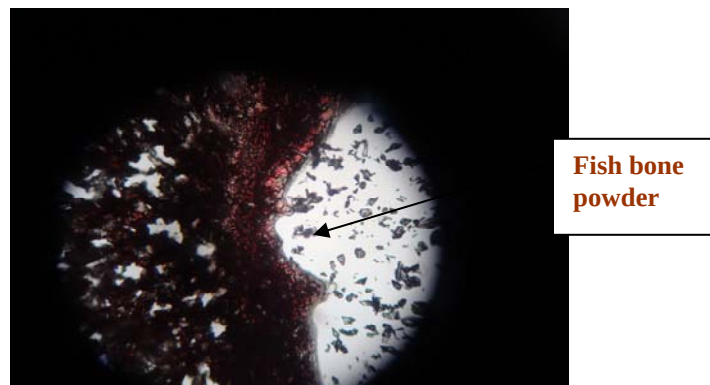


Fig.4.27 Normal Blood with anticoagulant and fish bone powder at 10 X magnification

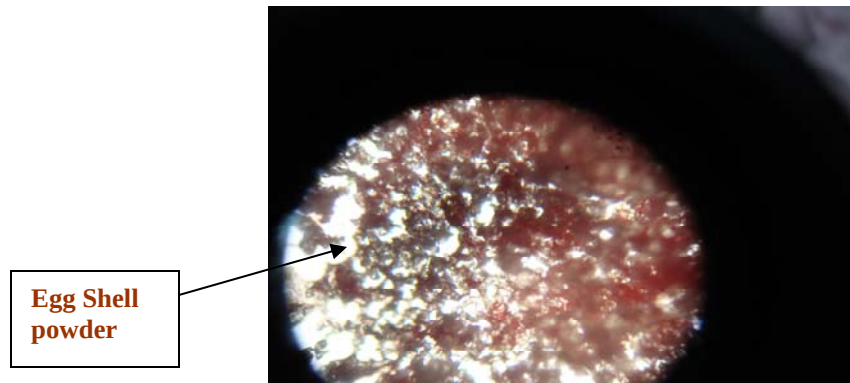


Fig.4.28 Normal Blood with anticoagulant and egg shell powder at 10 X magnification

4.3 Powder Coating

Hydroxyapatite is increasingly used, as implant material for medical applications owing to its chemical composition very similar to that of a major component of human bone. The most interesting property of HA is its excellent biocompatibility i.e. it helps to form a direct bond with the neighbouring bone.

However, the low strength of calcium phosphate bio ceramics such as Hydroxyapatite (HA) have limited their scope of clinical applications and hence more research needs to be conducted to improve their mechanical properties.

Despite excellent properties as a biomaterial, the ceramic nature and the inherent mechanical properties of HA specifically brittleness, poor tensile strength and poor impact resistance have restricted its application in many load bearing applications.

Therefore, the concept of applying HA on to metallic implants as a surface is developed and the HA coated implant combine the good strength and ductility of the metal with the excellent biocompatibility of the HA. Hydroxyapatite coatings on metal substrates such as Ti-6Al-4V and SS 304L are used often in orthopaedics. In this research work SS 304L is used as base metal substrate. The Composition and Mechanical properties of SS 304 L are shown in Table 4.1

Element	Weight %
C	0.08
Mn	2.00
Si	1.00
Cr	18.0-20.0
Ni	8.0-10.5
P	0.045
S	0.03
Properties	
Density ($\times 1000 \text{ kg/m}^3$)	8
Poisson's Ratio	0.27-0.30
Elastic Modulus (GPa)	193
Tensile Strength (Mpa)	515
Yield Strength (Mpa)	205
Elongation (%)	40
Reduction in Area (%)	50
Hardness (HRB)	88

Table 4.1 The Composition and mechanical properties of SS 304L

(Ref: www.efunda.com)

4.3.1 Preparation of metal substrate

The SS 304L is easily available at J.K.Tools and Industries, Factory area, Patiala. The material is available in the form of long strips of 1.5 mm thick (fig.4.29) which is cut into small rectangular pieces of 20mm x 30mm by tradle cutting machine as shown in Fig.4.29



Fig.4.29 Preparation of metal substrate

4.3.2 High Velocity oxy-fuel (HVOF) thermal spray process

After making the required sample size of metal substrate SS 304L , the next step is to developed coating of egg shell powder on it by using HVOF thermal spray process. Coating is carried out at Metallizing Equipment Co. Pvt. Ltd, E-101, M.I.A., Phase-II, Basni, Jodhpur.

The following are the main steps:

- 1) First of all the egg shell powder is placed in the powder feed mechanism (Fig.4.30).



Fig.4.30 Powder feeding

The powder feed mechanism supplies the flow of powder with the help of compressed air (4 kg/cm^2) at required spray rate to the nozzle.

- 2) Adjust the flow rate of acetylene (1.1 kg/cm^2) and oxygen (3 kg/cm^2) supply through control panel (Fig.4.31).

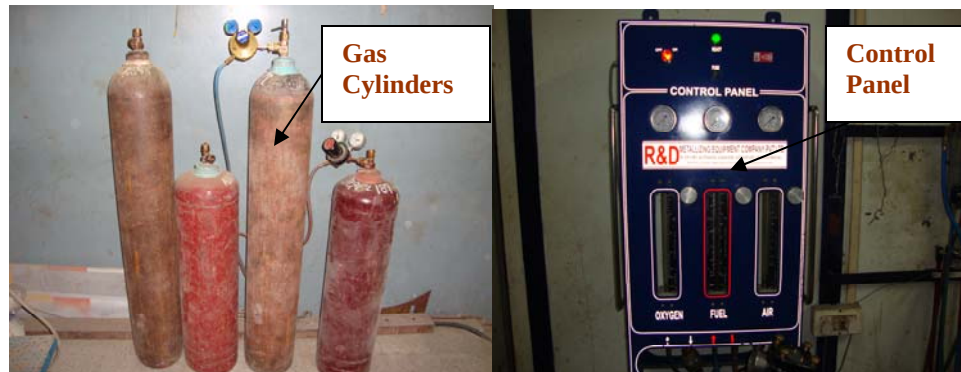


Fig.4.31 Control panel

- 3) Place the samples at the working table (as shown in Fig.4.32) and adjust the stand off distance. The stand off distance is the distance between work piece and nozzle.



Fig.4.32 HVOF nozzle

- 4) Ignite the nozzle and on the supply of powder to start the coating process.



Fig.4.33 Performing coating operation

the coating of egg shell is deposited on metal substrate as shown in Fig.4.33

- 5) Obtain the large number of samples by varying the parameters like Stand of distance, Powder flow rate, Oxygen flow rate and Acetylene flow rate.



Fig.4.34 Powder coated samples

5.1 Coating Results

Coating is carried out by varying the following parameters:

1) Stand off distance

It is varied from 4 inch to 12 inch in the step of 2.

2) Powder spray rate

It is varied from 15 gm/min. to 75 gm/min. in the step of 15.

3) Oxygen flow rate

It is varied from 40 m³/min. to 60 m³ /min. in the step of 5.

4) Acetylene flow rate

It is varied from 50 m³/min. to 70 m³ /min. in the step of 5.

1st Set of readings

Sample No.	Stand off distance (inch.)	Powder spray rate (gm/min.)	Oxygen flow rate(m ³ /min)	Acetylene flow rate(m ³ /min)
1	4	15	40	50
2	6	15	40	50
3	8	15	40	50
4	10	15	40	50
5	12	15	40	50

2nd Set of readings

Sample No.	Stand off distance (inch.)	Powder spray rate (gm/min.)	Oxygen flow rate(m ³ /min)	Acetylene flow rate(m ³ /min)
6	4	15	40	50
7	4	30	40	50
8	4	45	40	50
9	4	60	40	50
10	4	75	40	50

3rd Set of readings

Sample No.	Stand off distance (inch.)	Powder spray rate (gm/min.)	Oxygen flow rate(m ³ /min)	Acetylene flow rate(m ³ /min)
11	4	15	40	50
12	4	15	45	50
13	4	15	50	50
14	4	15	55	50
15	4	15	60	50

4th Set of readings

Sample No.	Stand off distance (inch.)	Powder spray rate (gm/min.)	Oxygen flow rate(m ³ /min)	Acetylene flow rate(m ³ /min)
16	4	15	40	50
17	4	15	40	55
18	4	15	40	60
19	4	15	40	65
20	4	15	40	70

5th Set of readings

Sample No.	Stand off distance (inch.)	Powder spray rate (gm/min.)	Oxygen flow rate(m ³ /min)	Acetylene flow rate(m ³ /min)
21	4	45	50	60
22	6	45	50	60
23	8	45	50	60
24	10	45	50	60
25	12	45	50	60

6th Set of readings

Sample No.	Stand off distance (inch.)	Powder spray rate (gm/min.)	Oxygen flow rate(m ³ /min)	Acetylene flow rate(m ³ /min)
26	8	15	50	60
27	8	30	50	60
28	8	45	50	60
29	8	60	50	60
30	8	75	50	60

7th Set of readings

Sample No.	Stand off distance (inch.)	Powder spray rate (gm/min.)	Oxygen flow rate(m ³ /min)	Acetylene flow rate(m ³ /min)
31	8	45	40	60
32	8	45	45	60
33	8	45	50	60
34	8	45	55	60
35	8	45	60	60

8th Set of readings

Sample No.	Stand off distance (inch.)	Powder spray rate (gm/min.)	Oxygen flow rate(m ³ /min)	Acetylene flow rate(m ³ /min)
36	8	45	50	50
37	8	45	50	55
38	8	45	50	60
39	8	45	50	65
40	8	45	50	70

9th Set of readings

Sample No.	Stand off distance (inch.)	Powder spray rate (gm/min.)	Oxygen flow rate(m ³ /min)	Acetylene flow rate(m ³ /min)
41	4	75	60	70
42	6	75	60	70
43	8	75	60	70
44	10	75	60	70
45	12	75	60	70

10th Set of readings

Sample No.	Stand off distance (inch.)	Powder spray rate (gm/min.)	Oxygen flow rate(m ³ /min)	Acetylene flow rate(m ³ /min)
46	12	15	60	70
47	12	30	60	70
48	12	45	60	70
49	12	60	60	70
50	12	75	60	70

11th Set of readings

Sample No.	Stand off distance (inch.)	Powder spray rate (gm/min.)	Oxygen flow rate(m ³ /min)	Acetylene flow rate(m ³ /min)
51	12	75	40	70
52	12	75	45	70
53	12	75	50	70
54	12	75	55	70
55	12	75	60	70

12th Set of readings

Sample No.	Stand off distance (inch.)	Powder spray rate (gm/min.)	Oxygen flow rate(m ³ /min)	Acetylene flow rate(m ³ /min)
56	12	75	60	50
57	12	75	60	55
58	12	75	60	60
59	12	75	60	65
60	12	75	60	70

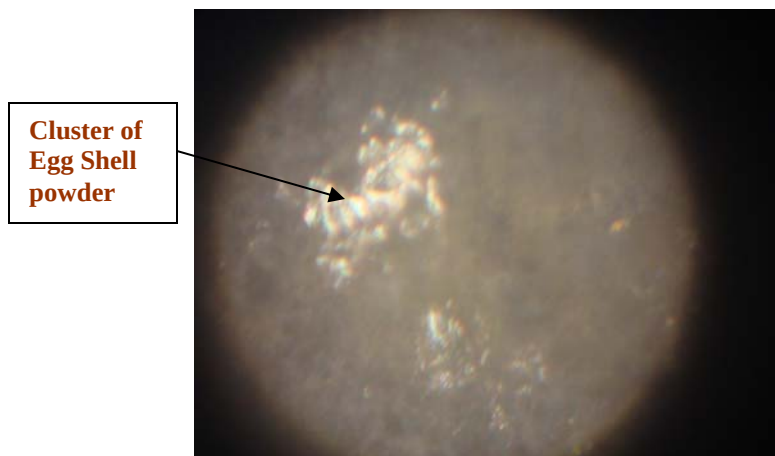
Table 5.1 Readings at different HVOF parameters

5.2 Microstructure Examination of coated samples

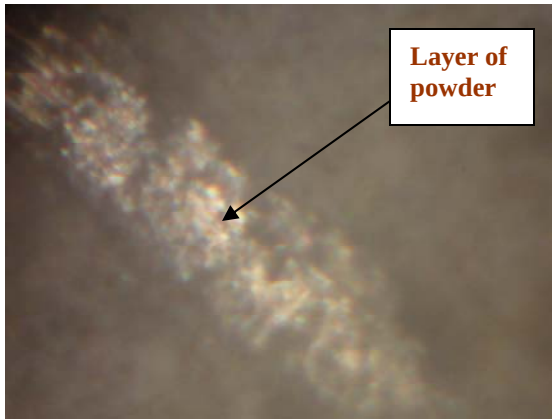
The microstructure examination of the coated samples is done with the help of metallurgical microscope by using magnification of 15X to show the presence of egg shell powder and its distribution on the metal surface. The microstructure of all the samples is shown below:



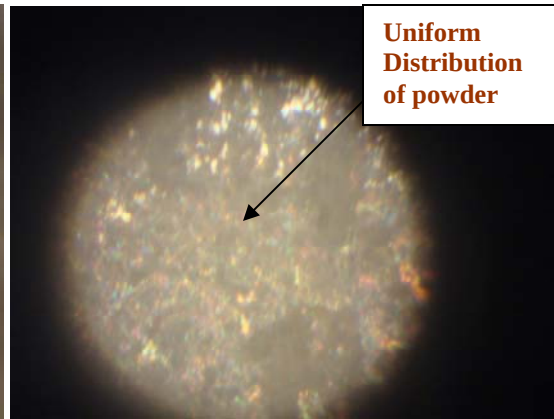
Sample No.1 (Traces of powder at 15X magnification, Stand off distance 4 inch., Powder spray rate 15 gm/min., Oxygen flow rate 40m³/min., Acetylene flow rate 50 m³/min.)



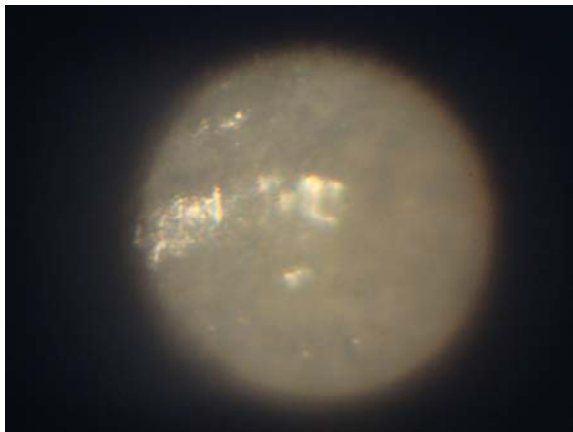
Sample No.2 (Stand off distance 6 inch., Powder spray rate 15 gm/min., Oxygen flow rate 40m³/min., Acetylene flow rate 50 m³/min.)



3 (Stand off distance 8 inch.)



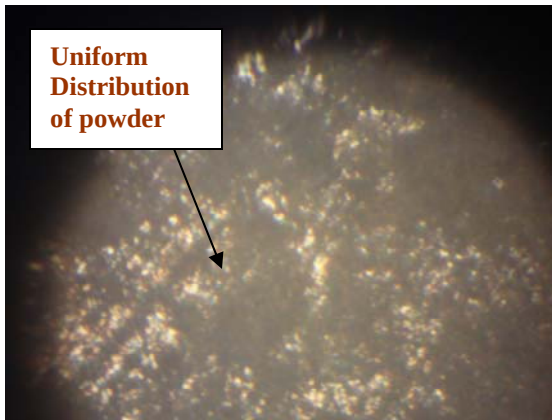
4 (Stand off distance 10 inch.)



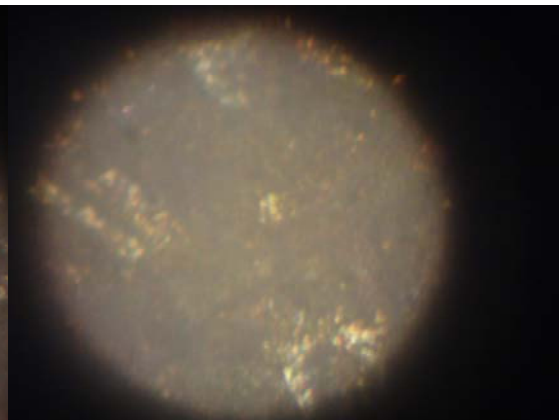
5 (Stand off distance 12 inch.)



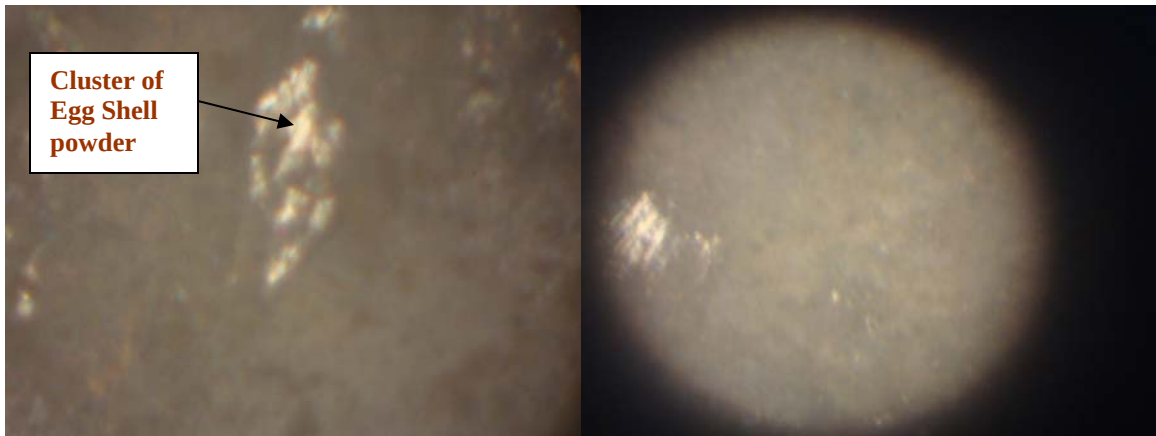
7 (Powder spray rate 30 gm/min.)



8 (Powder spray rate 45 gm/min.)

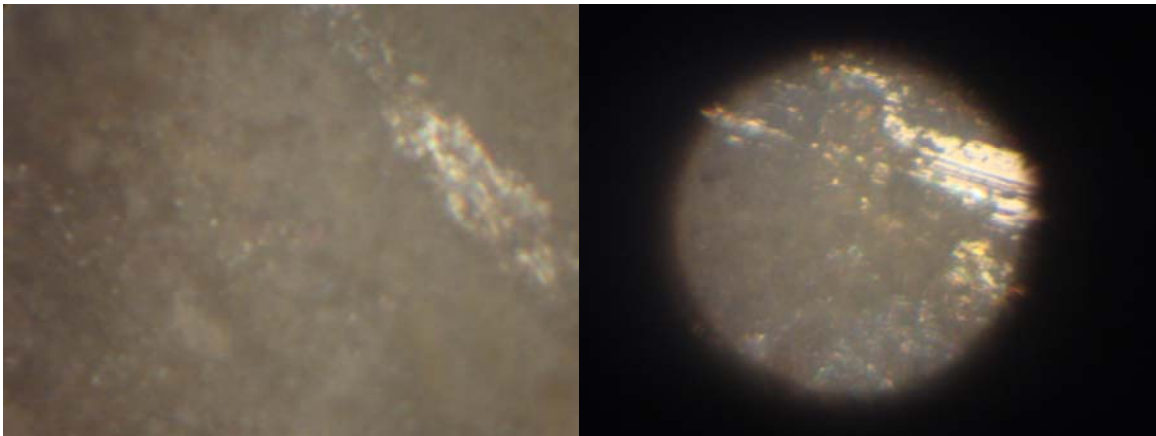


9 (Powder spray rate 60 gm/min.)



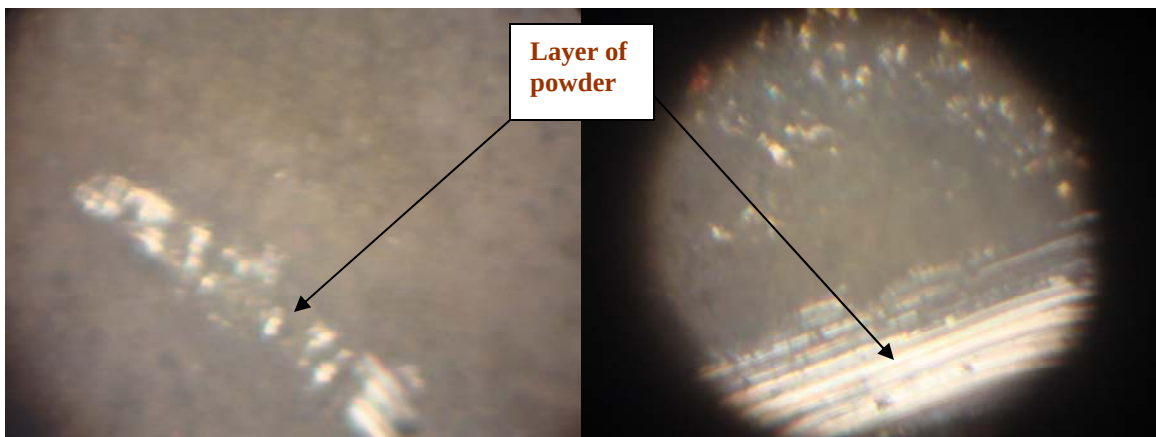
10 (Powder spray rate 75 gm/min.)

12 (Oxygen flow rate 45 m³/min.)



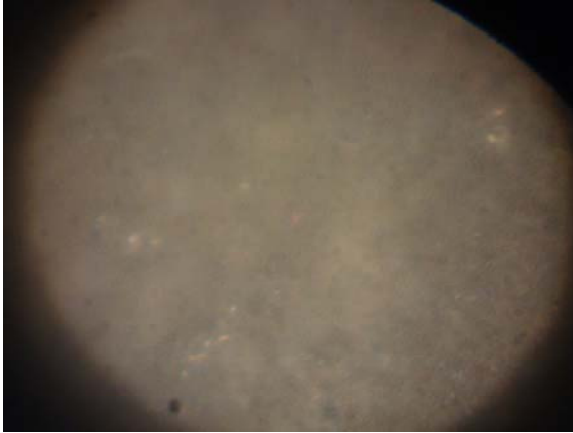
13 (Oxygen flow rate 50 m³/min.)

14 (Oxygen flow rate 55 m³/min.)



15 (Oxygen flow rate 55 m³/min.)

17 (Acetylene flow rate 55 m³/min.)



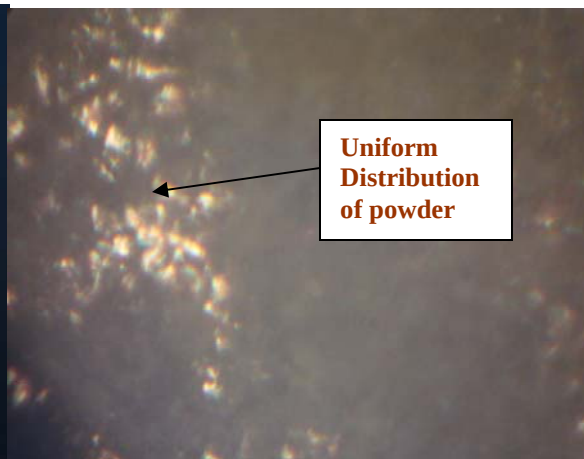
18 (Acetylene flow rate 60 m³/min.)



19 (Acetylene flow rate 65 m³/min.)



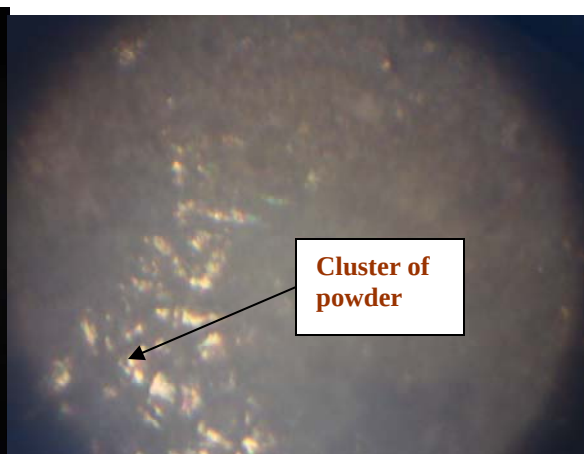
20 (Acetylene flow rate 70 m³/min.)



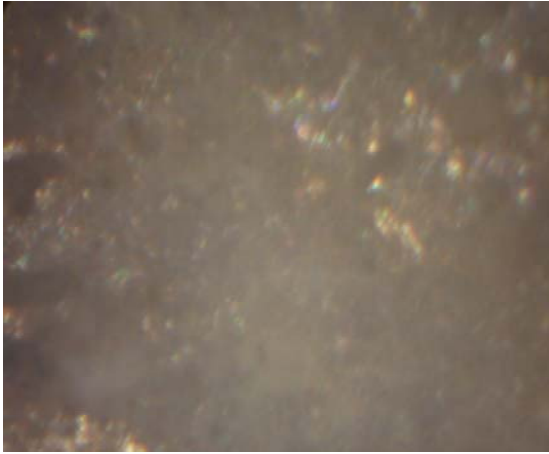
21 (Stand off distance 4 inch.)



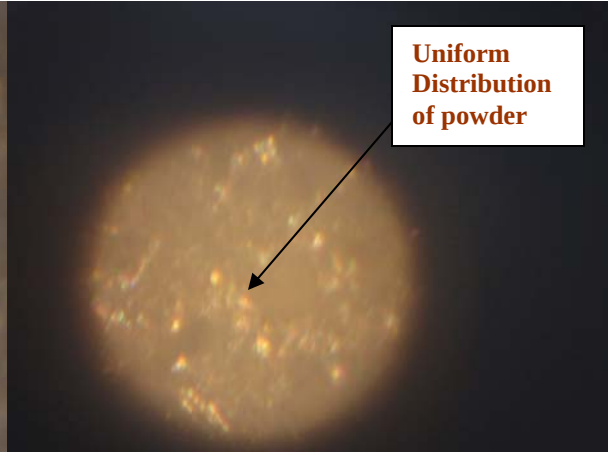
22 (Stand off distance 6 inch.)



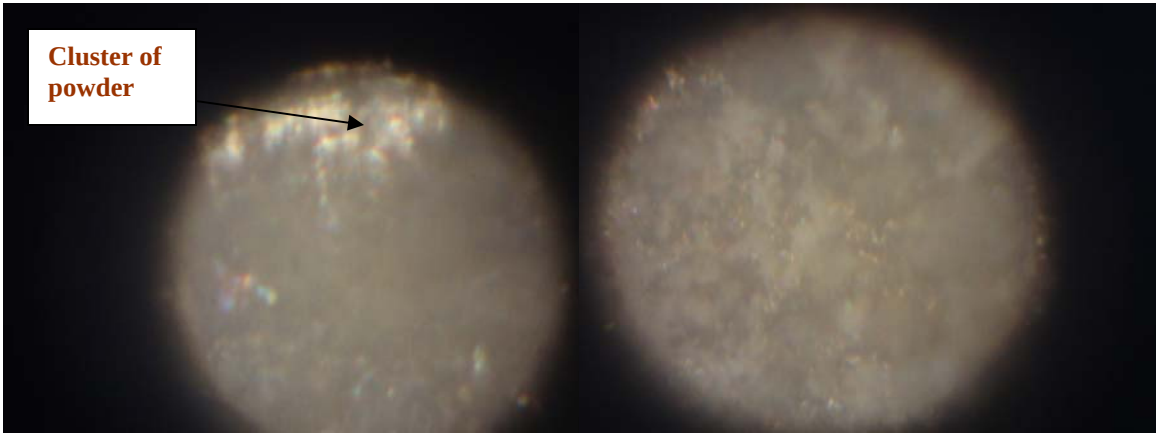
23 (Stand off distance 8 inch.)



24 (Stand off distance 10 inch.)

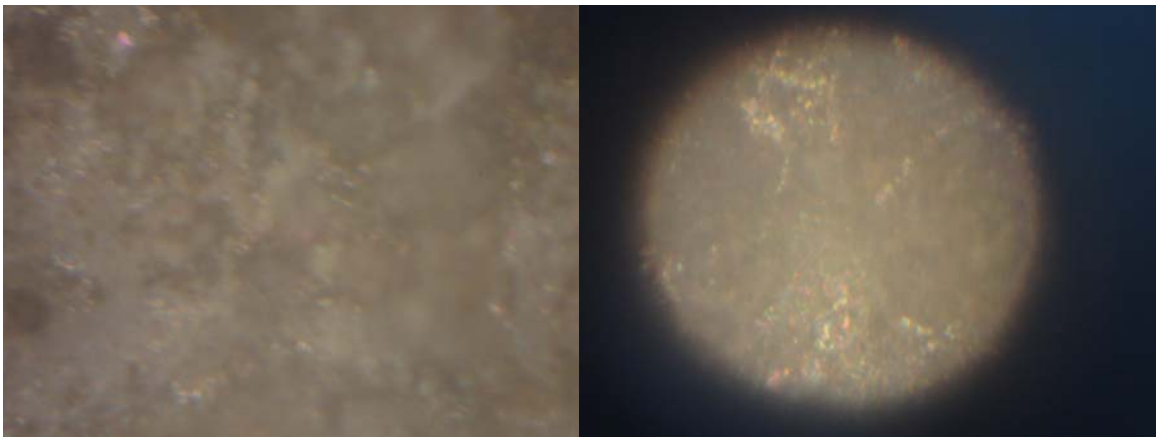


25 (Stand off distance 12 inch.)



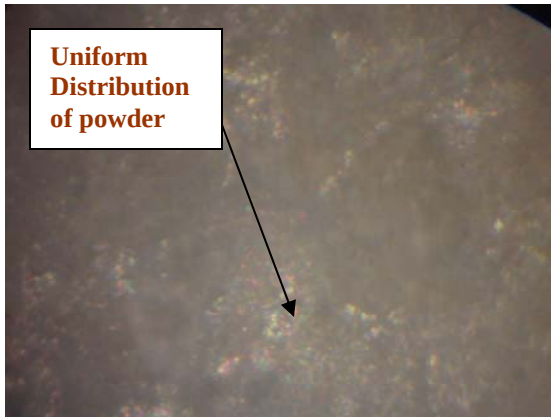
26 (Powder spray rate 15 gm/min.)

27 (Powder spray rate 30 gm/min.)

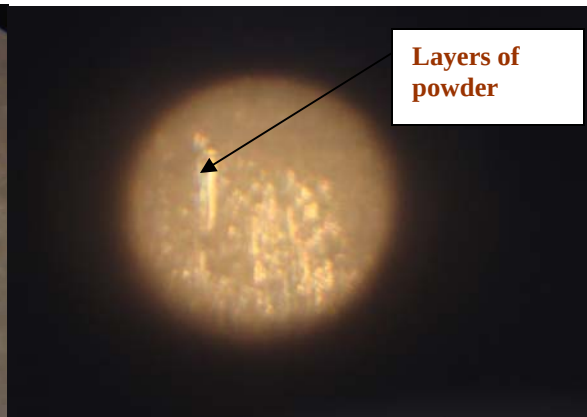


29 (Powder spray rate 60 gm/min.)

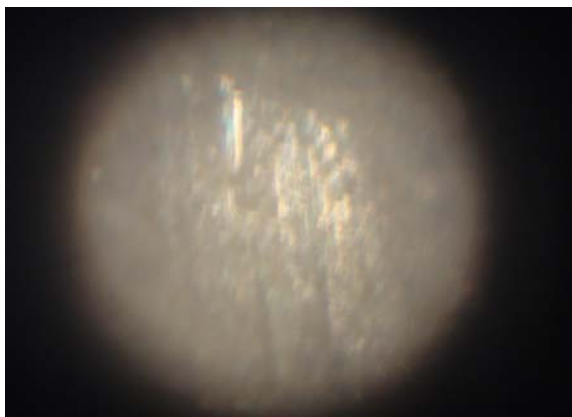
30 (Powder spray rate 75 gm/min.)



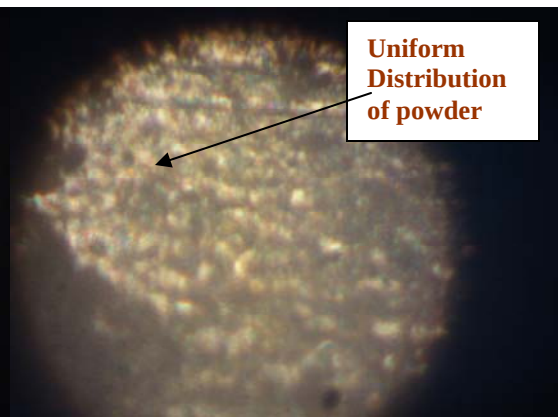
31 (Oxygen flow rate 40 m³/min.)



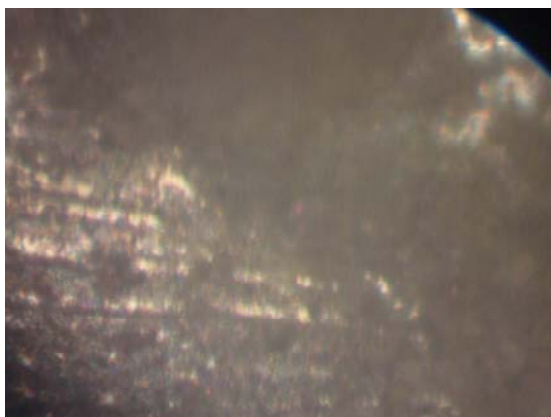
32 (Oxygen flow rate 45 m³/min.)



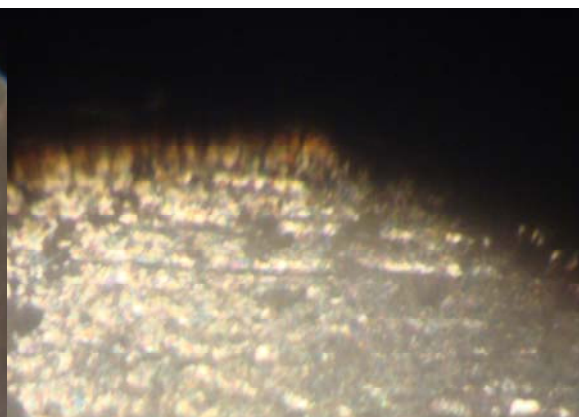
34 (Oxygen flow rate 55 m³/min.)



35 (Oxygen flow rate 60 m³/min.)



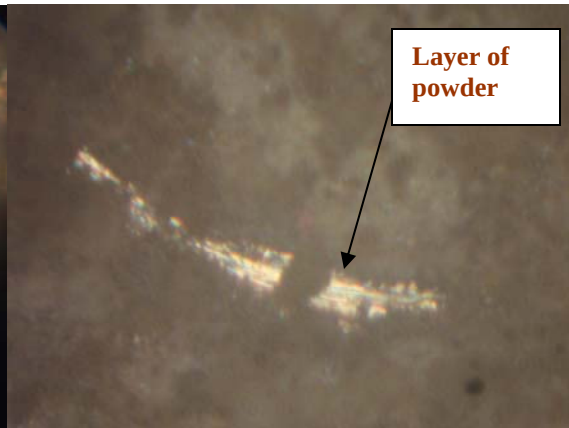
36 (Acetylene flow rate 50 m³/min.)



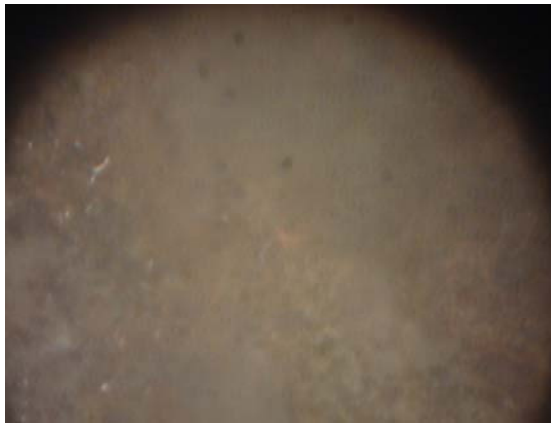
37 (Acetylene flow rate 55 m³/min.)



39 (Acetylene flow rate 65 m³/min.)



40 (Acetylene flow rate 70 m³/min.)



41 (Stand off distance 4 inch.)



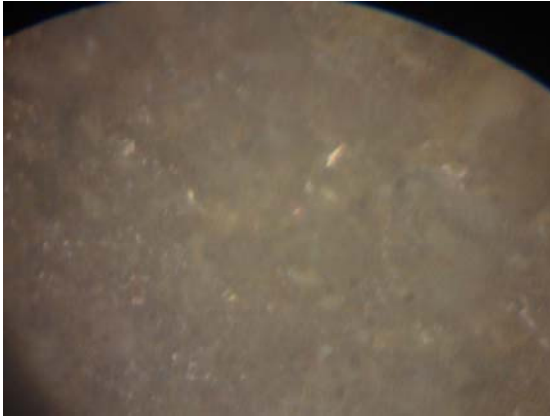
42 (Stand off distance 6 inch.)



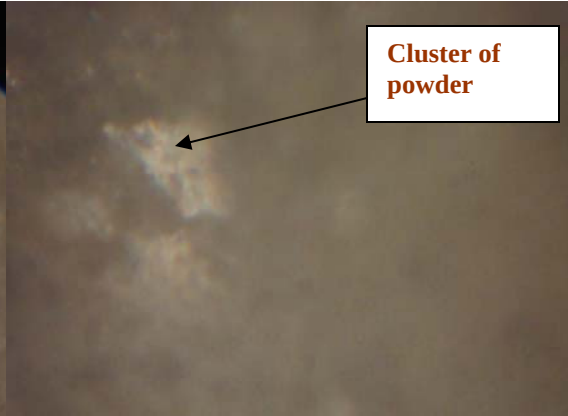
43 (Stand off distance 8 inch.)



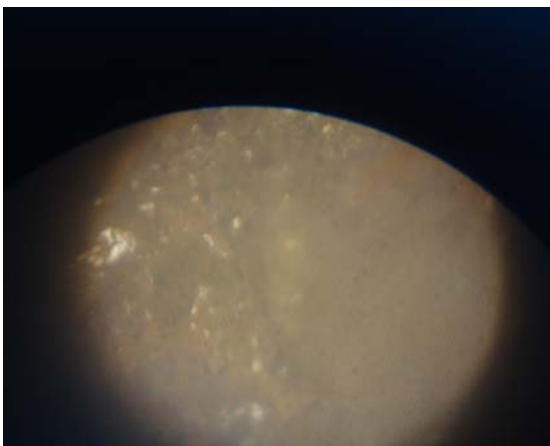
44 (Stand off distance 10 inch.)



45 (Stand off distance 12 inch.)



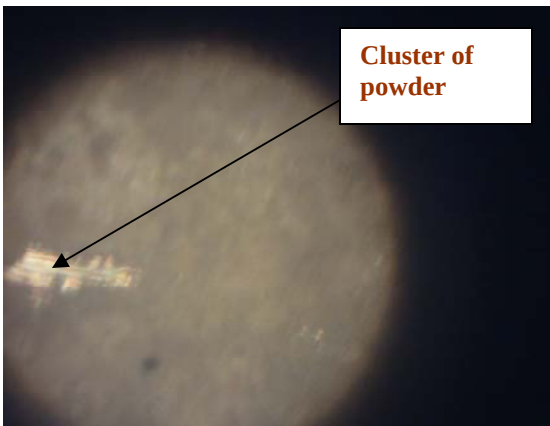
46 (Powder spray rate 15 gm/min.)



47 (Powder spray rate 30 gm/min.)



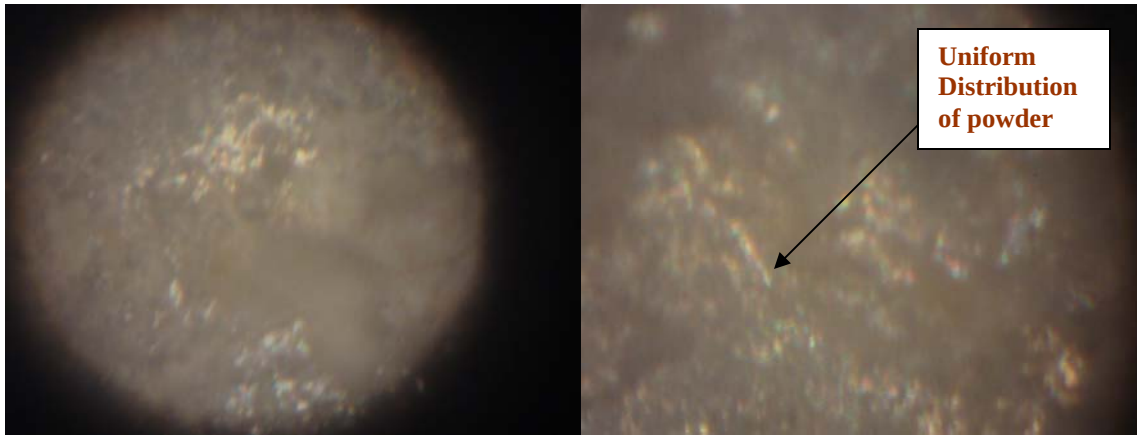
48 (Powder spray rate 45 gm/min.)



49 (Powder spray rate 60 gm/min.)

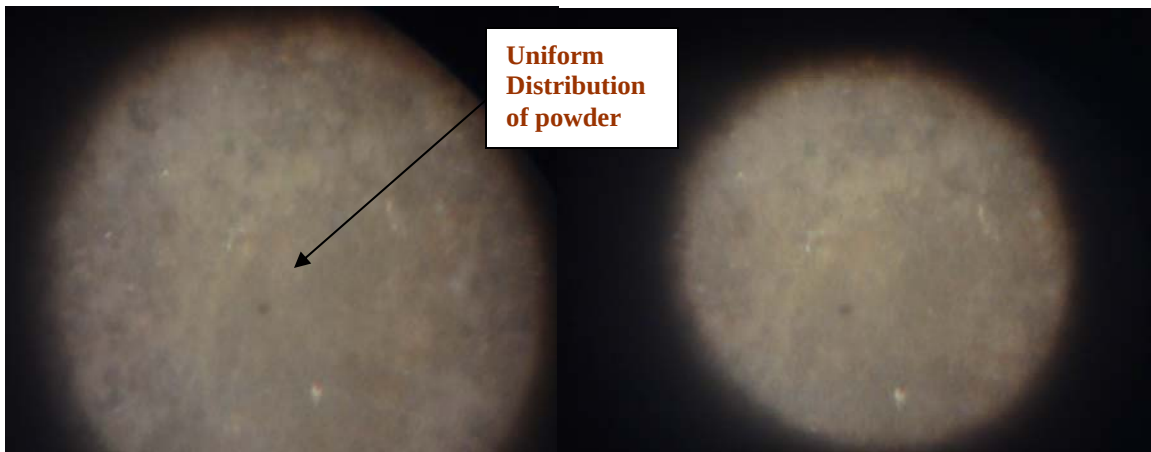


51 (Oxygen flow rate 40 m³/min.)



52 (Oxygen flow rate 45 m³/min.)

53 (Oxygen flow rate 50 m³/min.)



54 (Oxygen flow rate 55 m³/min.)

56 (Acetylene flow rate (AFR) 50 m³/min.)



57 (AFR 55 m³/min.)

58 (AFR 60 m³/min.)

59 (AFR 65 m³/min.)

Fig.5.1 Microstructure Examination of coated samples

5.3 Hardness and Micro hardness Measurement

The hardness is measured of all the coated samples by using Rockwell hardness tester. Five readings are taken at different points on 'C' scale by applying 150 Kg load for 10 sec for each sample.

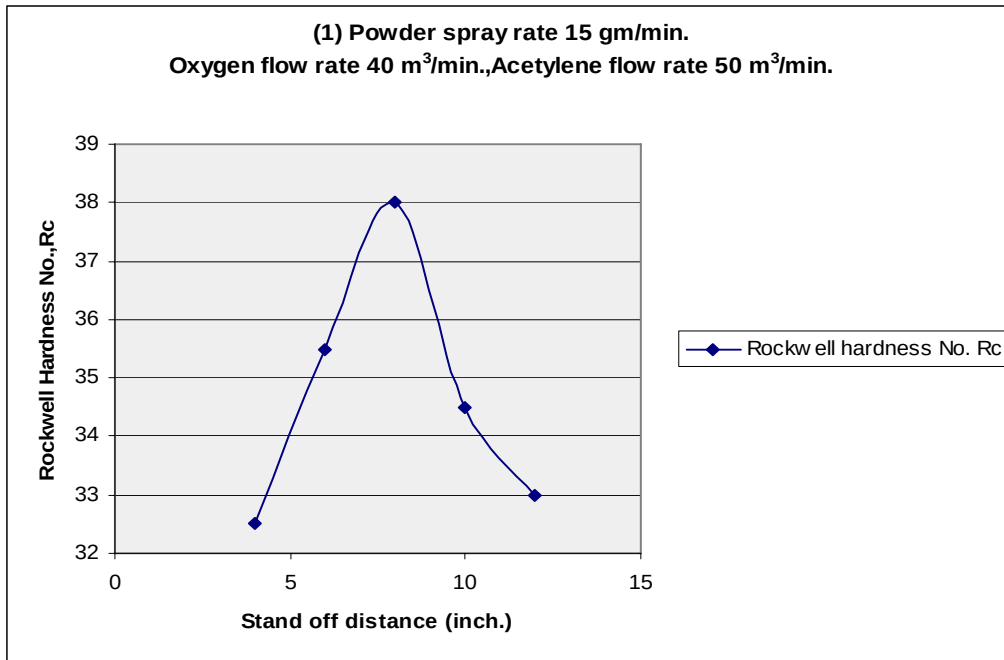
Similarly micro hardness is calculated by using MVH-II digital micro hardness tester. Five readings are taken at different points by applying 200 grams load for 20 sec for each sample.

Sample No.	Mean Rockwell hardness No. R _c	Mean Micro hardness VHN No.
1	32.5	218
2	35.5	245
3	38	272
4	34.5	227
5	33	236
7	35	245
8	38.5	272
9	40	270
10	40.5	302
12	44.5	334
13	43	323
14	46.5	350
15	48	335
17	38.5	272
18	36.5	263
19	35	245
20	35	245
21	48	335
22	55	390
23	56	370
24	58.8	540
25	60	597
26	40	292
27	45.5	358
29	46	340
30	50	413
31	38.5	282
32	44	334
34	46.5	358
35	58	413
36	55	495
37	48.5	384

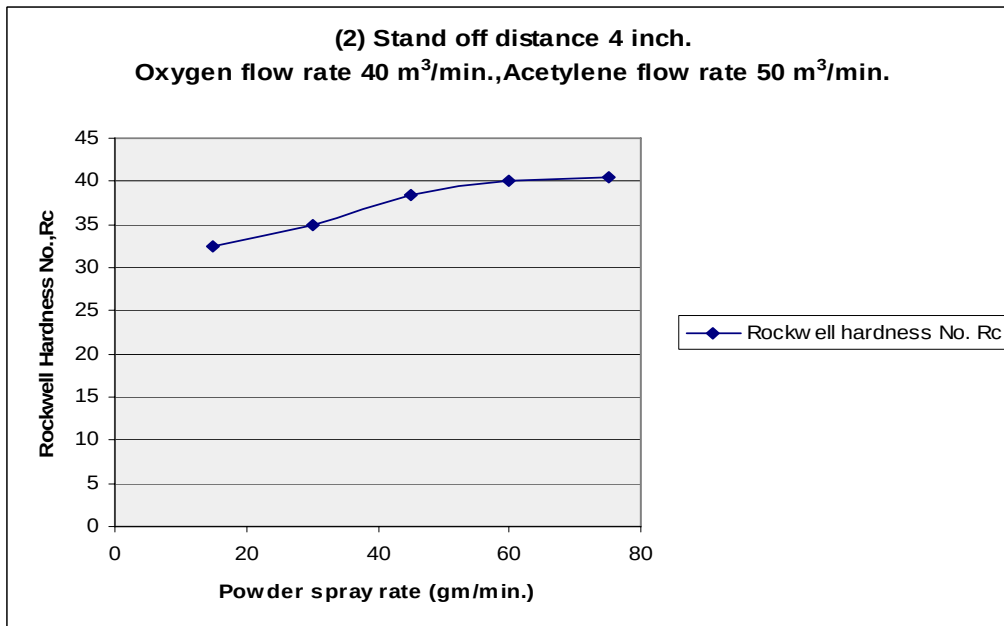
39	60	358
40	42	312
41	55	515
42	58	458
43	60	597
44	55.5	513
45	53	460
46	60	597
47	62.5	690
48	64	646
49	63.5	678
51	54.5	460
52	55	495
53	56	565
54	56.5	533
56	60	520
57	58.5	553
58	52	370
59	46.5	400

Table 5.2 Hardness and Micro hardness measurement

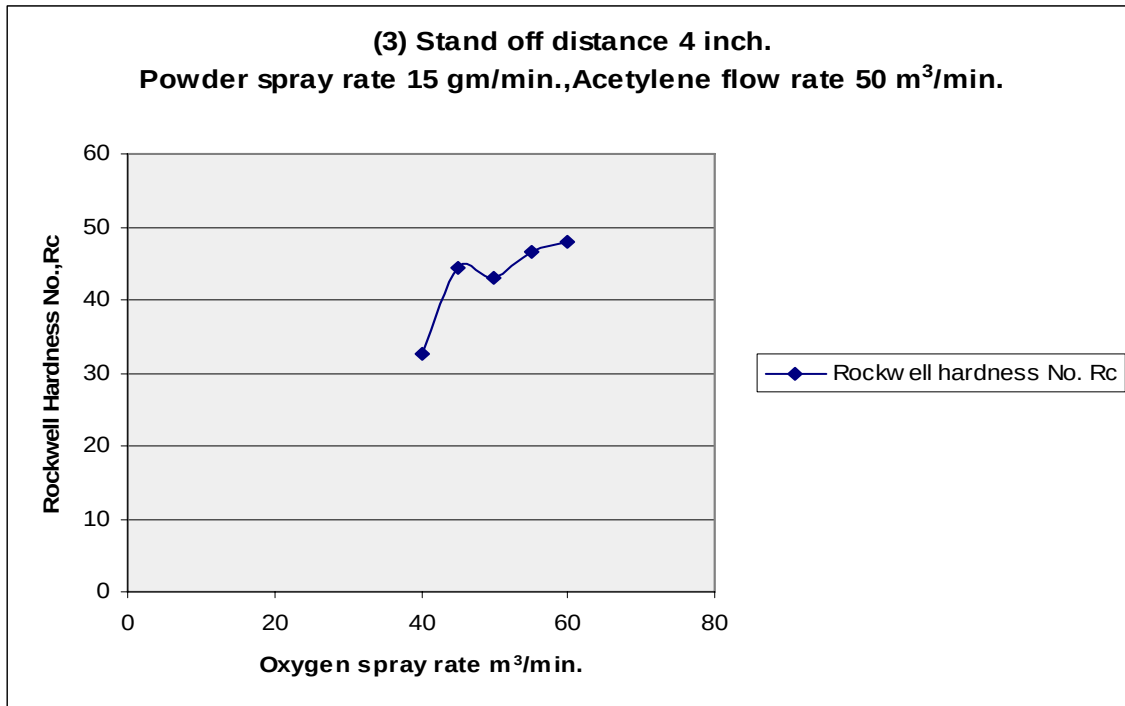
5.3.1 Graphs showing the trend of Rockwell hardness number, R_c at various HVOF parameters.



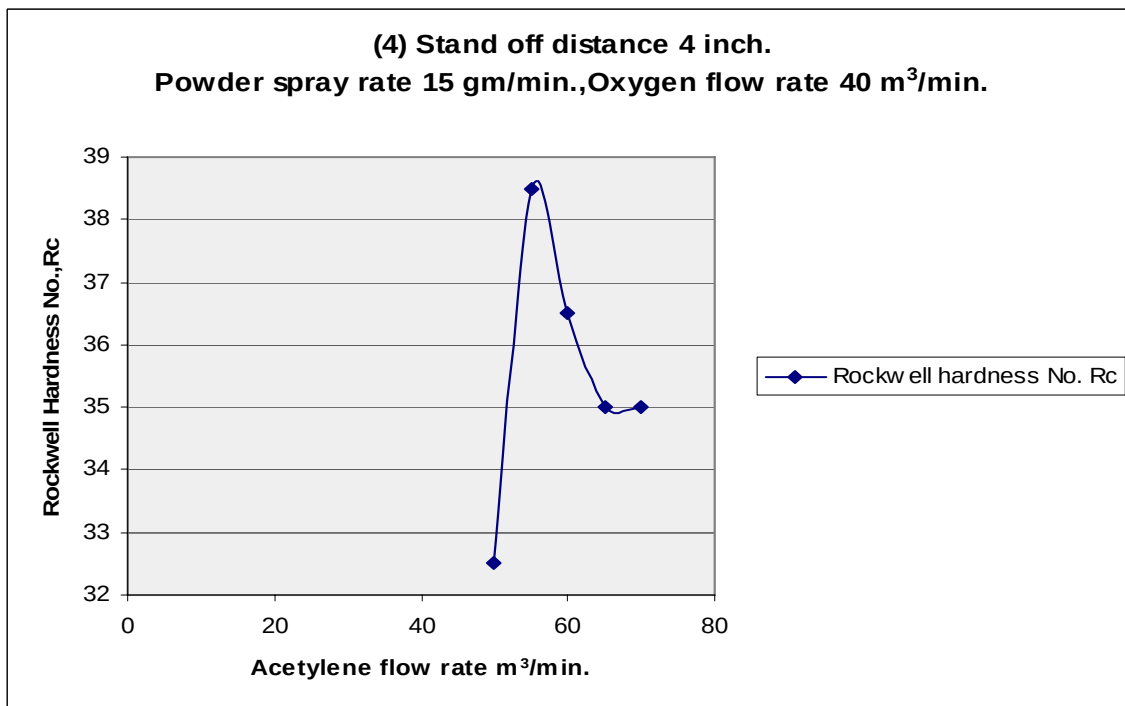
(1) Stand off distance Vs R_c at Powder spray rate 15 gm/min., Oxygen flow rate 40m³/min., Acetylene flow rate 50 m³/min.



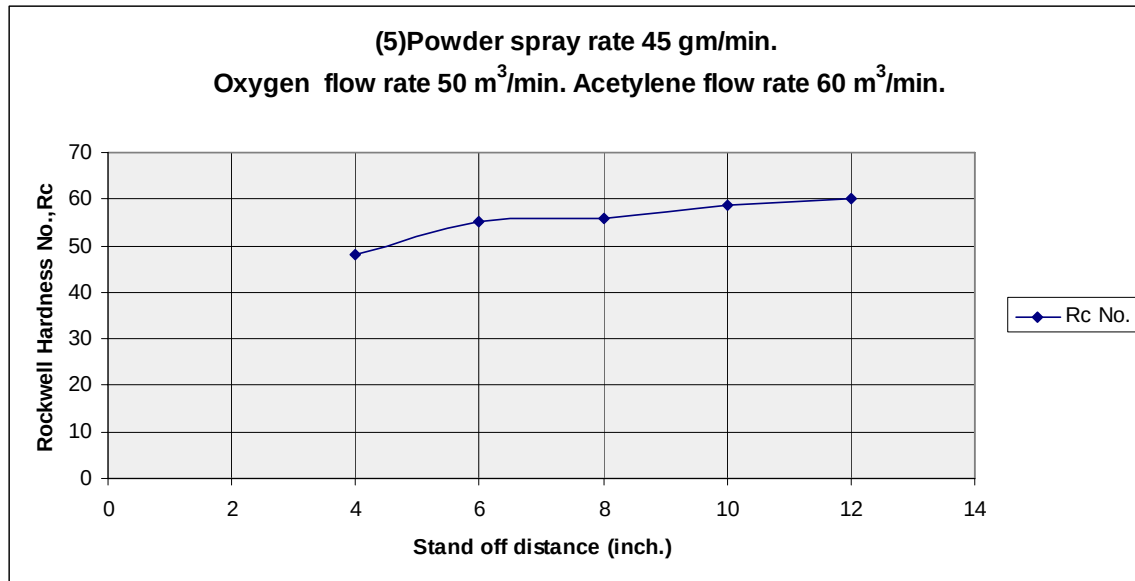
(2) Powder spray rate Vs R_c at Stand off distance 4 inch., Oxygen flow rate 40m³/min., Acetylene flow rate 50 m³/min.



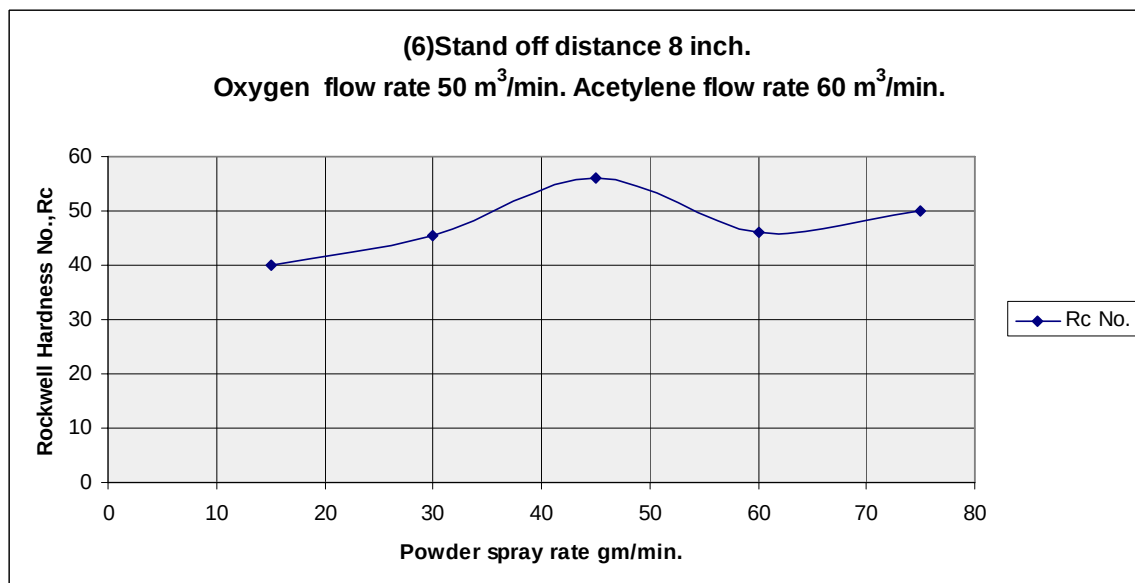
(3) Oxygen flow rate Vs Rc at Stand off distance 4 inch., Powder spray rate 15 gm/min., Acetylene flow rate 50 m³/min.



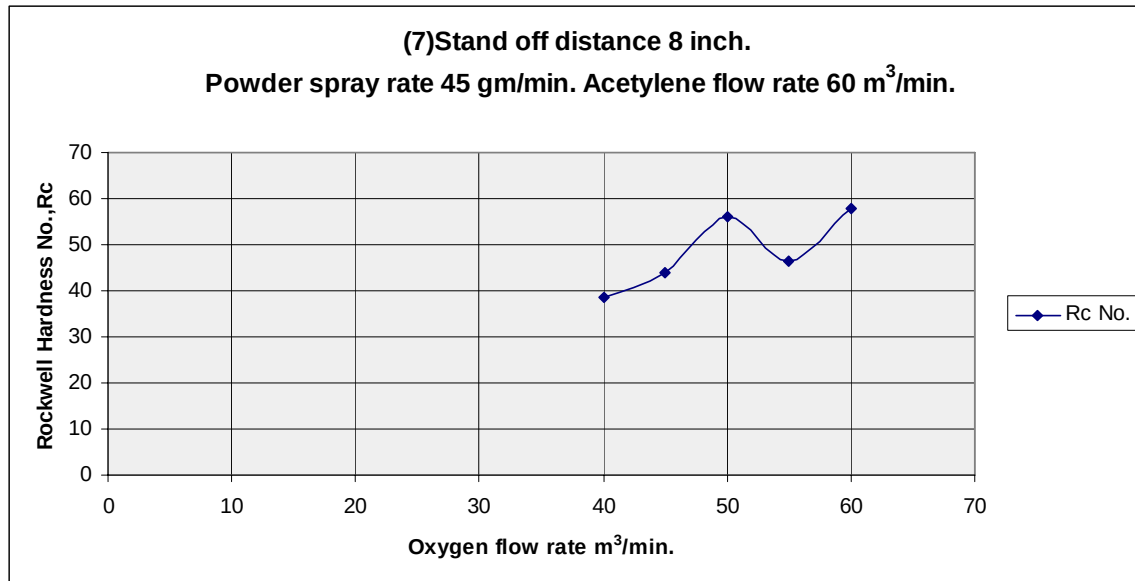
(4) Acetylene flow rate Vs Rc at Stand off distance 4 inch., Powder spray rate 15 gm/min., Oxygen flow rate 40 m³/min.



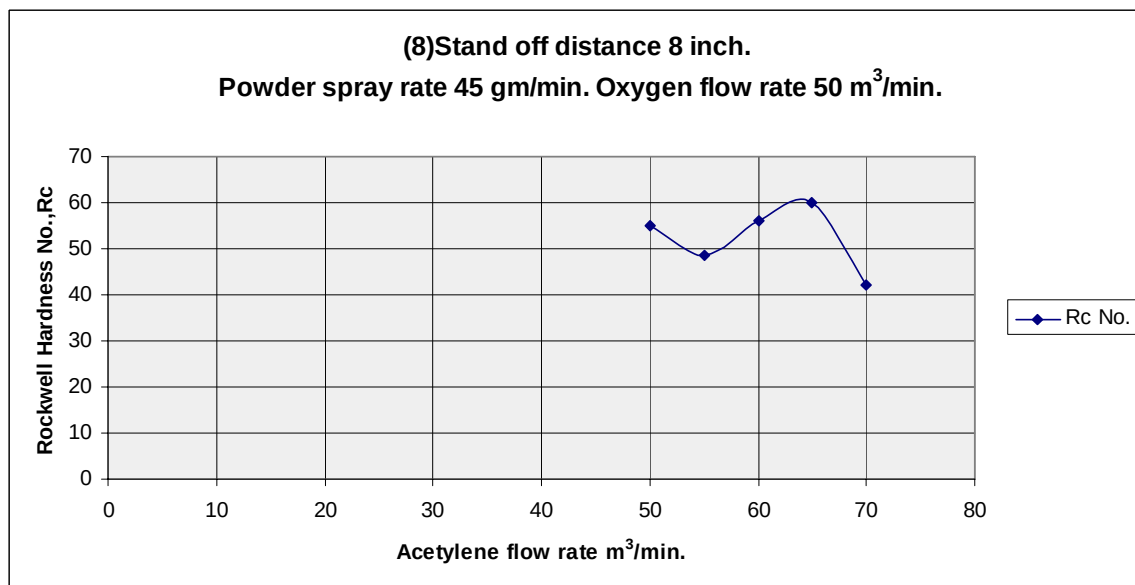
(5) Stand off distance Vs Rc at Powder spray rate 45 gm/min., Oxygen flow rate 50m³/min., Acetylene flow rate 60 m³/min.



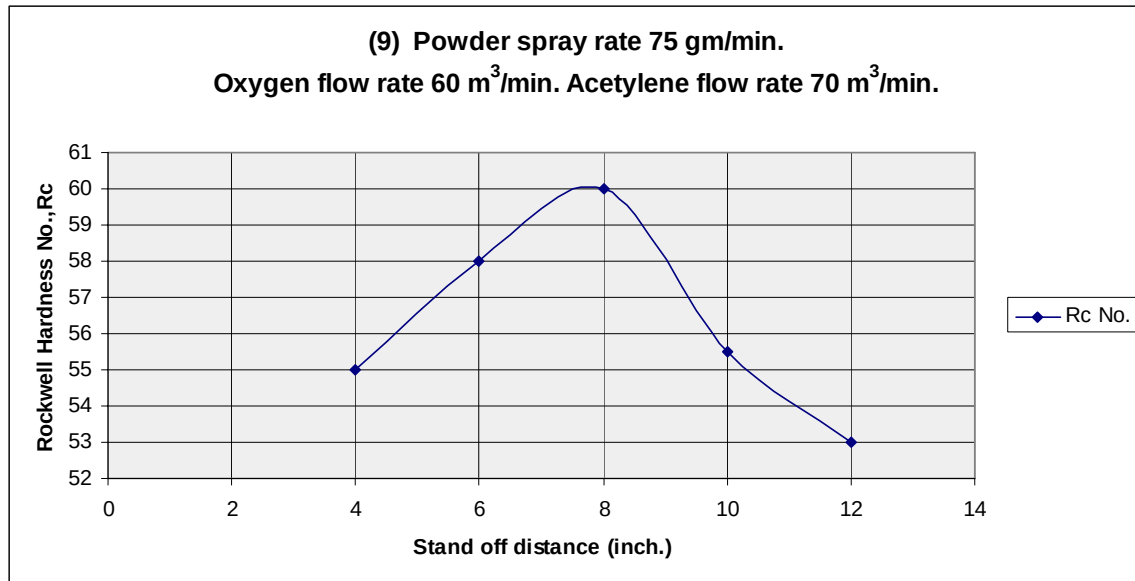
(6) Powder spray rate Vs Rc at Stand off distance 8 inch., Oxygen flow rate 50m³/min., Acetylene flow rate 60 m³/min.



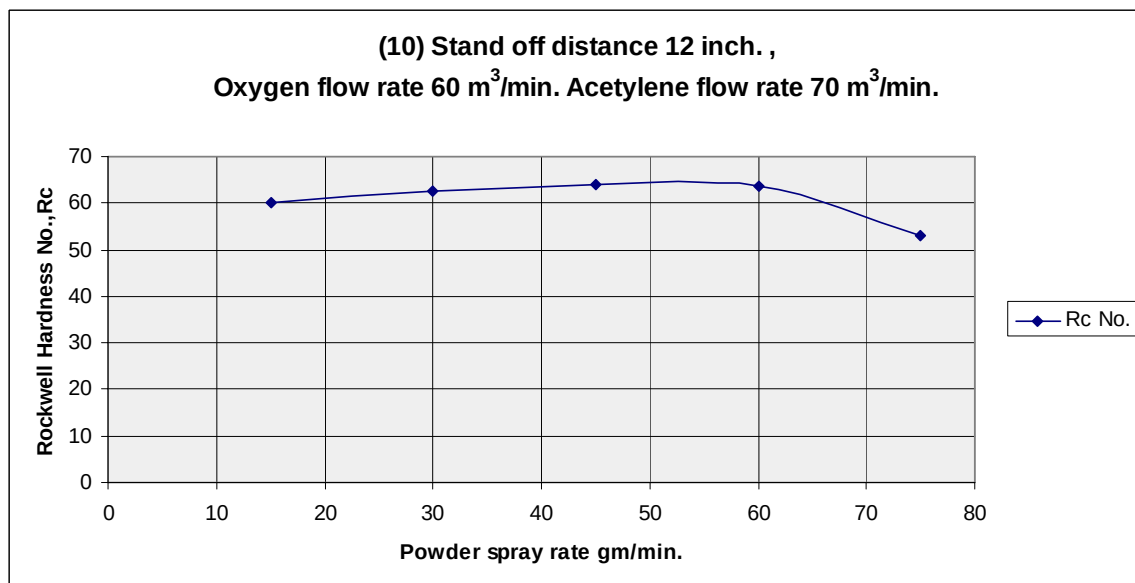
(7) Oxygen flow rate Vs Rc at Stand off distance 8 inch., Powder spray rate 45 gm/min., Acetylene flow rate 60 m³/min.



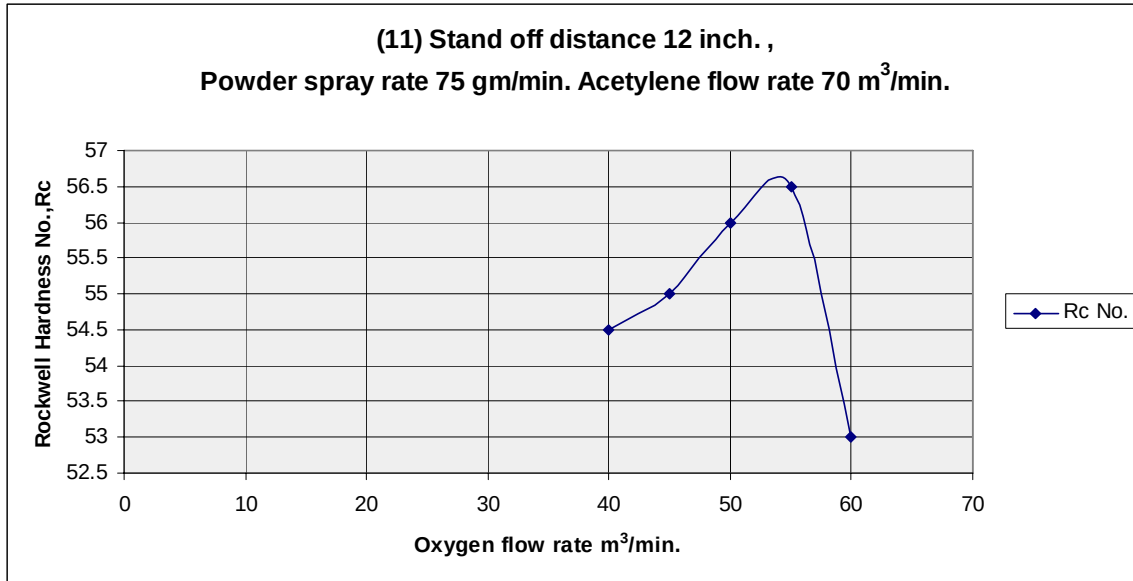
(8) Acetylene flow rate Vs Rc at Stand off distance 8 inch., Powder spray rate 45 gm/min., Oxygen flow rate 50 m³/min.



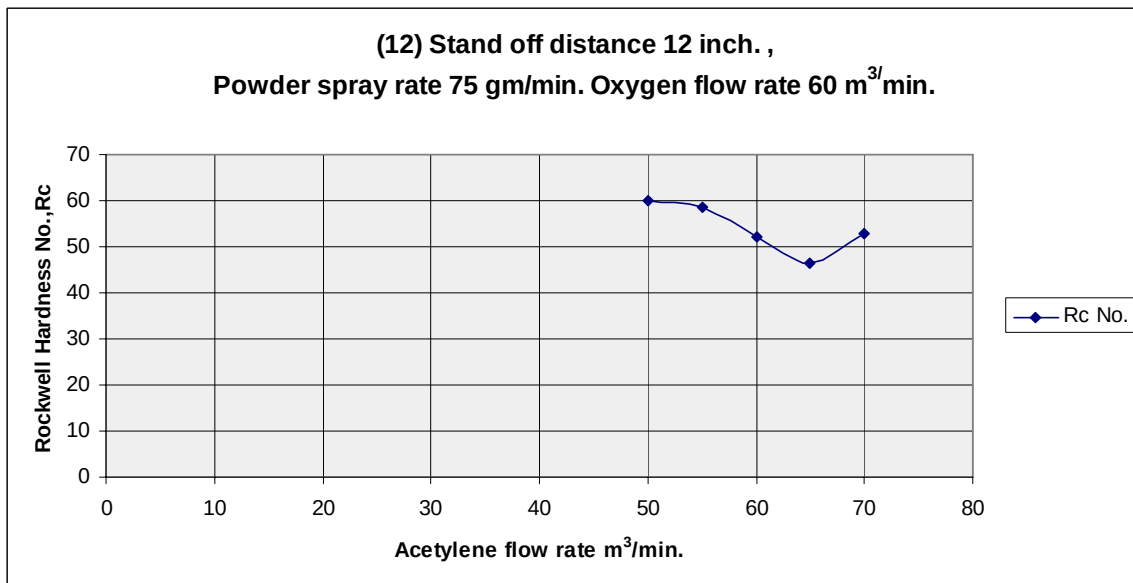
(9) Stand off distance Vs Rc at Powder spray rate 75 gm/min., Oxygen flow rate 60m³/min., Acetylene flow rate 70 m³/min.



(10) Powder spray rate Vs Rc at Stand off distance 12 inch., Oxygen flow rate 60m³/min., Acetylene flow rate 70 m³/min



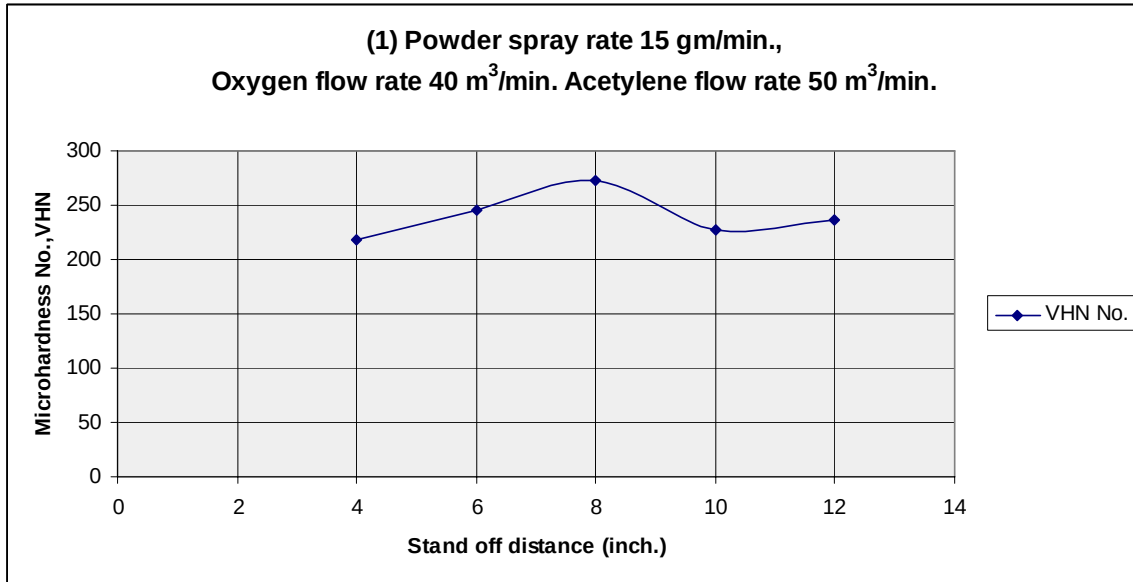
(11) Oxygen flow rate Vs Rc at Stand off distance 12 inch., Powder spray rate 75 gm/min., Acetylene flow rate 70 m³/min.



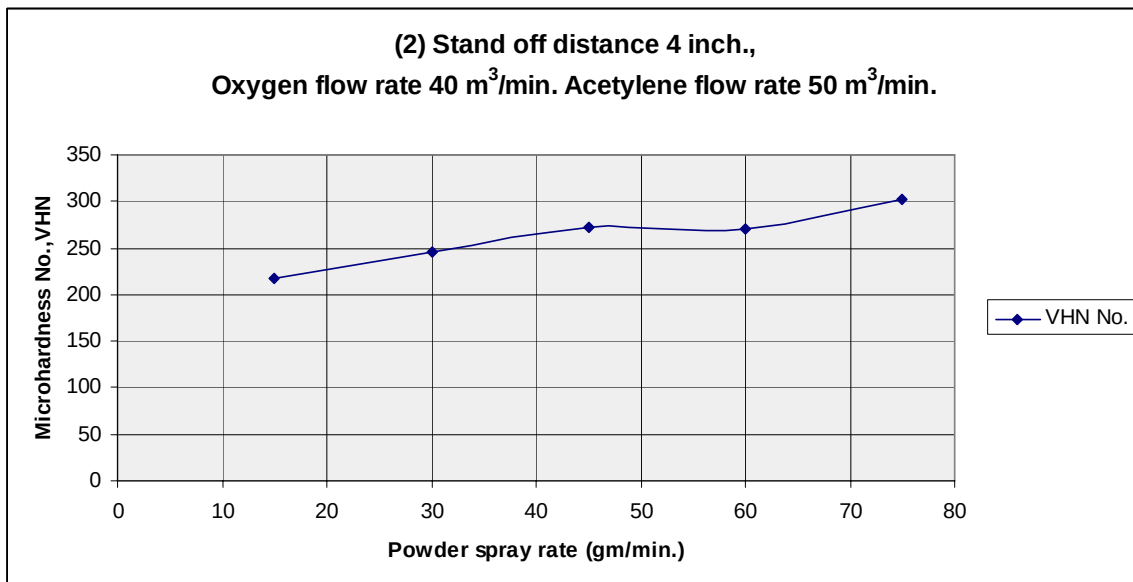
(12) Acetylene flow rate Vs Rc at Stand off distance 12 inch., Powder spray rate 75 gm/min., Oxygen flow rate 60 m³/min.

Fig.5.2 Graphs showing the trend of Rockwell hardness number, R_c at various HVOF parameters.

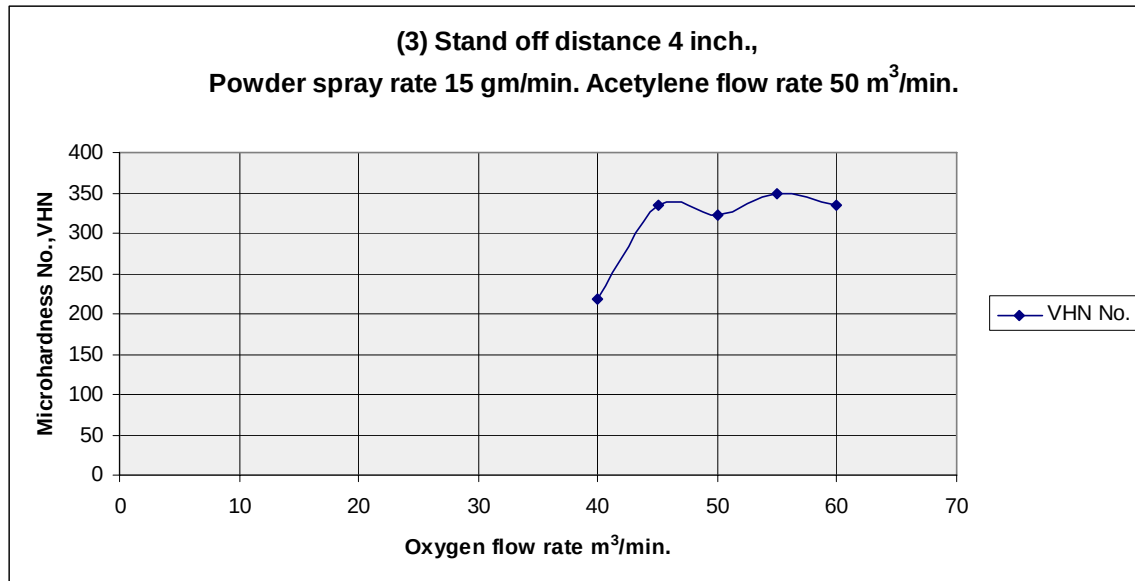
5.3.2 Graphs showing the trend of Micro hardness number, VHN at various HVOF parameters.



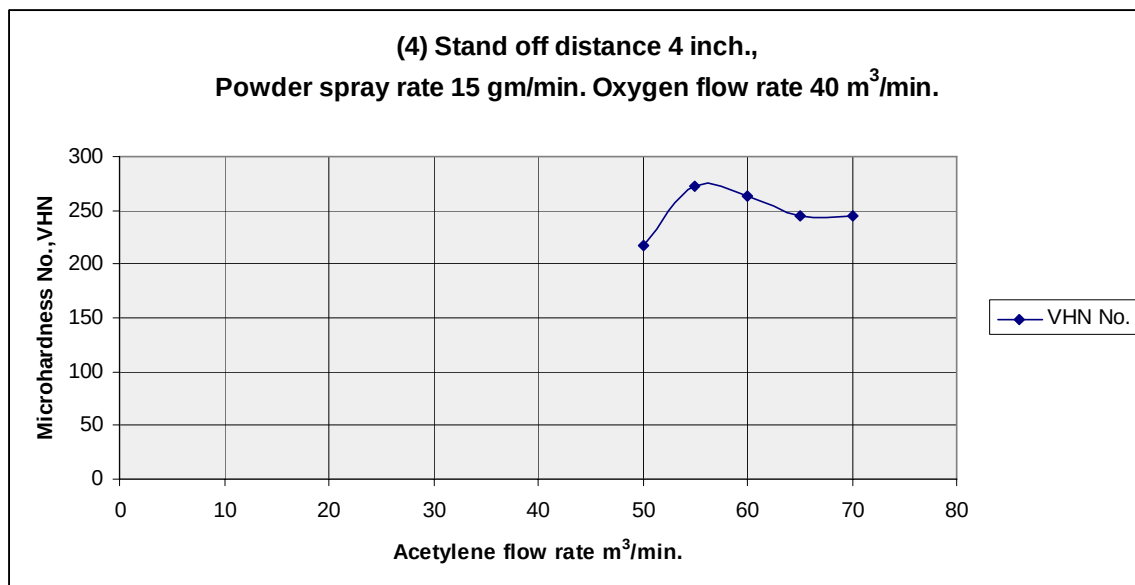
(1) Stand off distance Vs VHN at Powder spray rate 15 gm/min., Oxygen flow rate 40m³/min., Acetylene flow rate 50 m³/min.



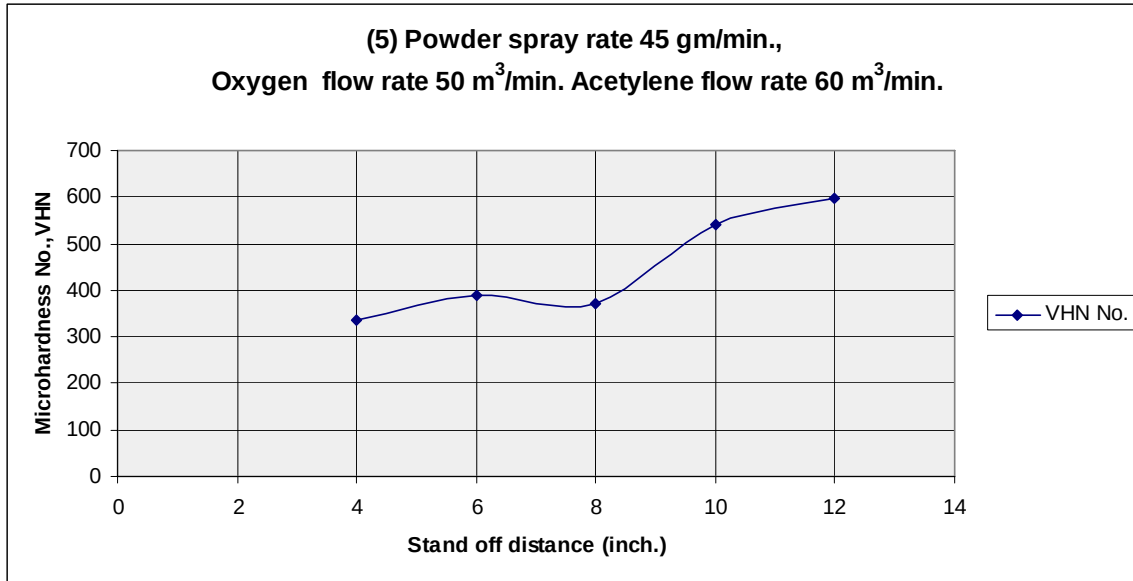
(2) Powder spray rate Vs VHN at Stand off distance 4 inch., Oxygen flow rate 40m³/min., Acetylene flow rate 50 m³/min.



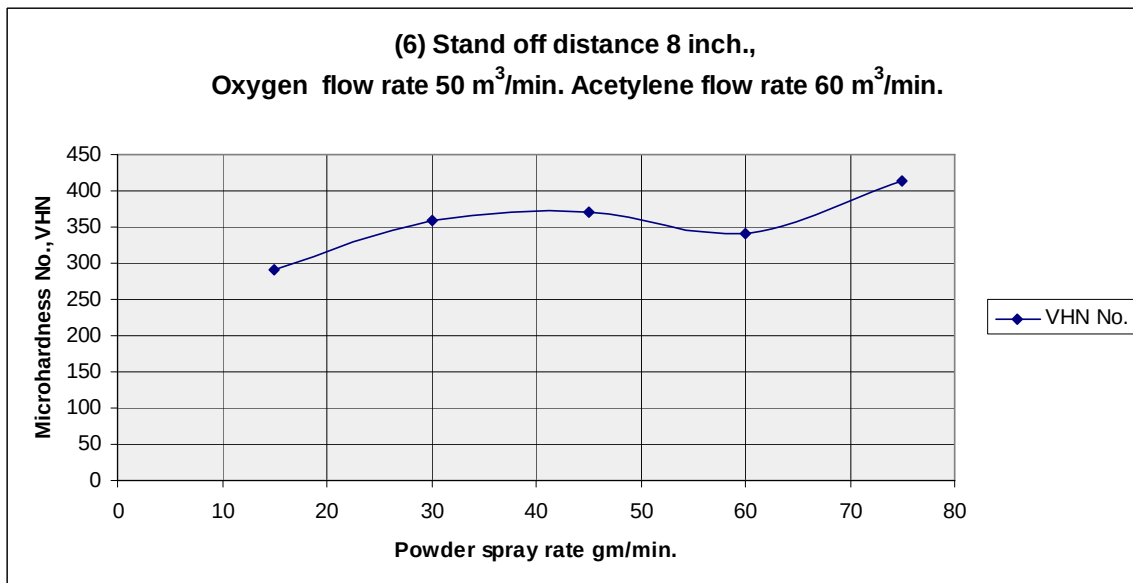
(3) Oxygen flow rate Vs VHN at Stand off distance 4 inch., Powder spray rate 15 gm/min., Acetylene flow rate 50 m³/min.



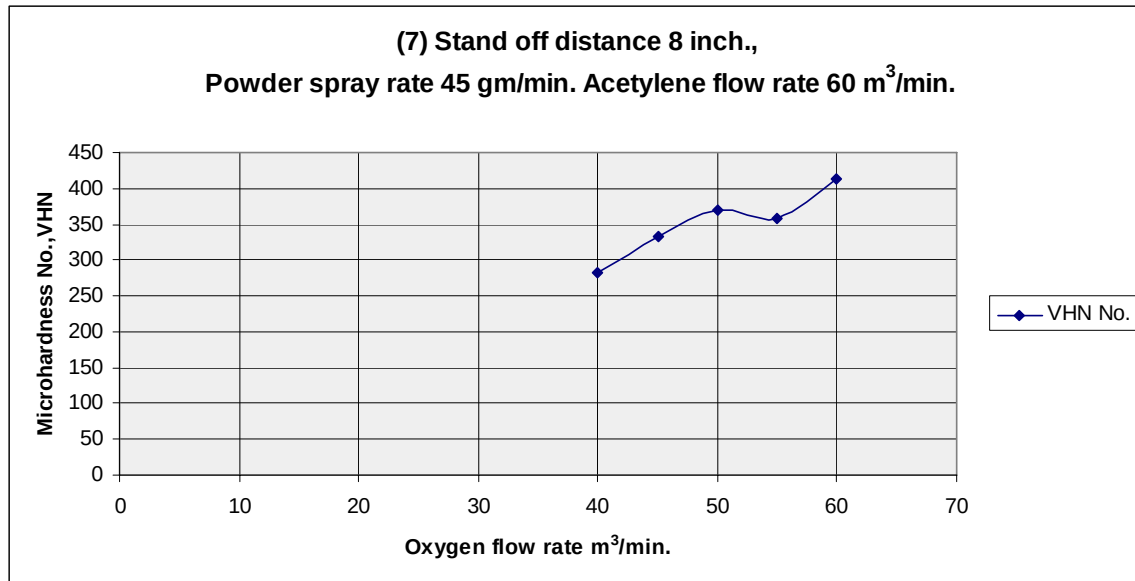
(4) Acetylene flow rate Vs VHN at Stand off distance 4 inch., Powder spray rate 15 gm/min., Oxygen flow rate 40 m³/min.



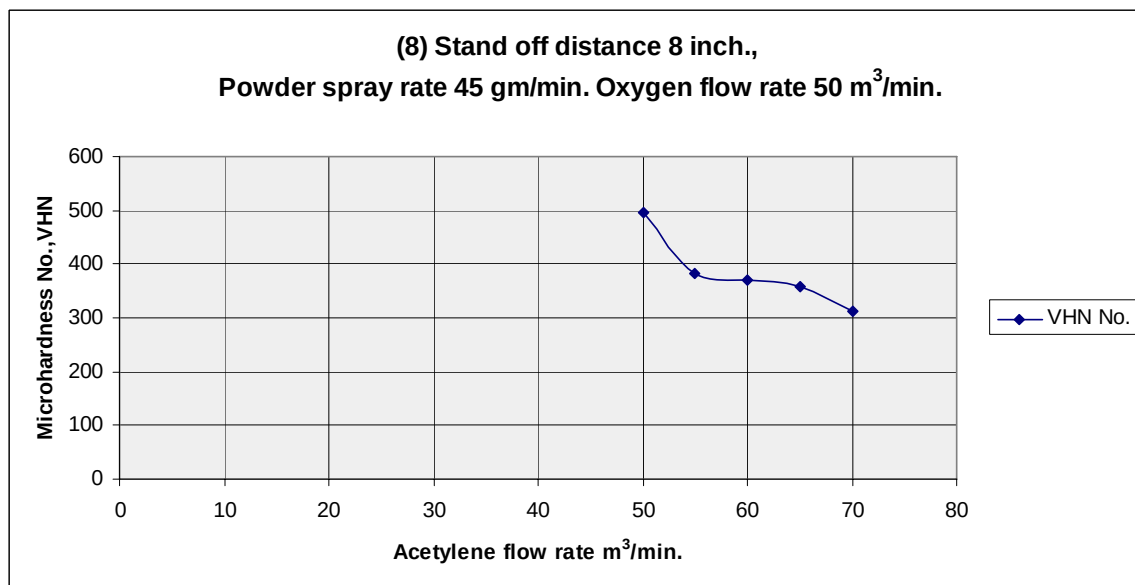
(5) Stand off distance Vs VHN at Powder spray rate 45 gm/min., Oxygen flow rate 50m³/min., Acetylene flow rate 60 m³/min.



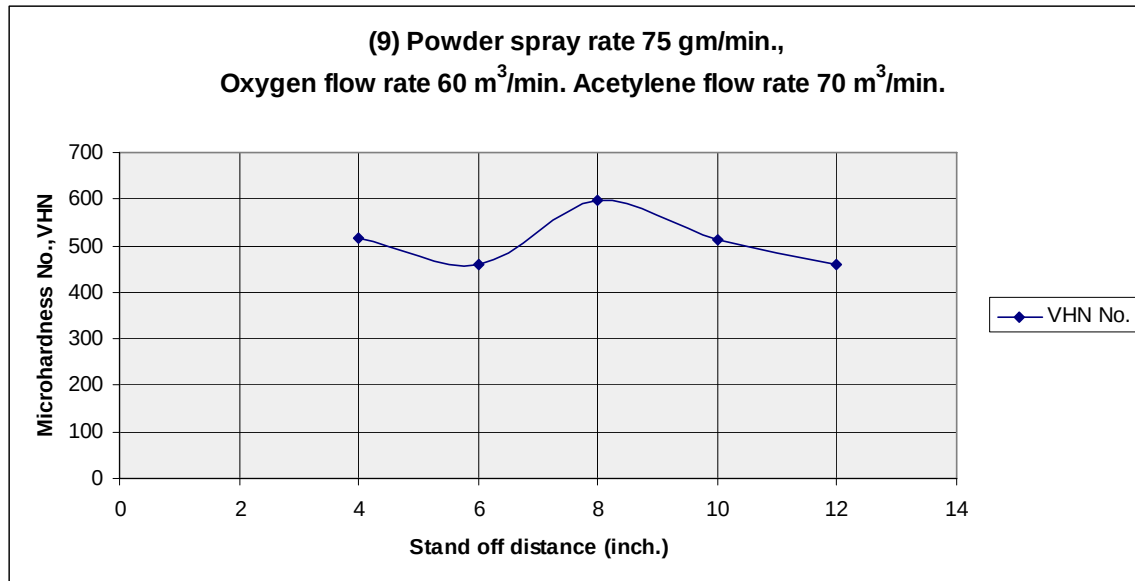
(6) Powder spray rate Vs VHN at Stand off distance 8 inch., Oxygen flow rate 50m³/min., Acetylene flow rate 60 m³/min.



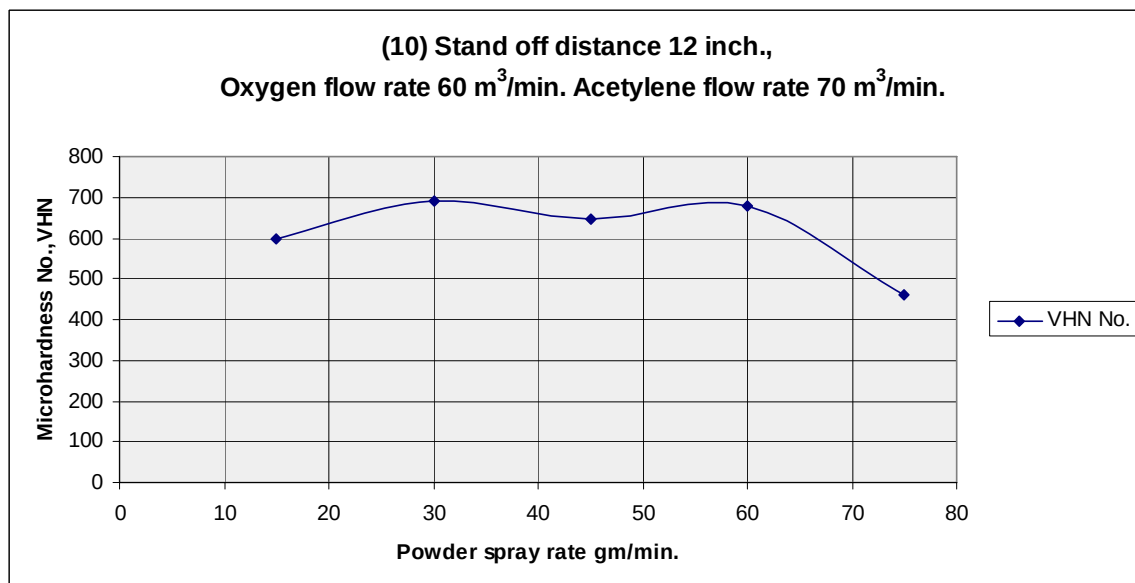
(7) Oxygen flow rate Vs VHN at Stand off distance 8 inch., Powder spray rate 45 gm/min., Acetylene flow rate 60 m³/min.



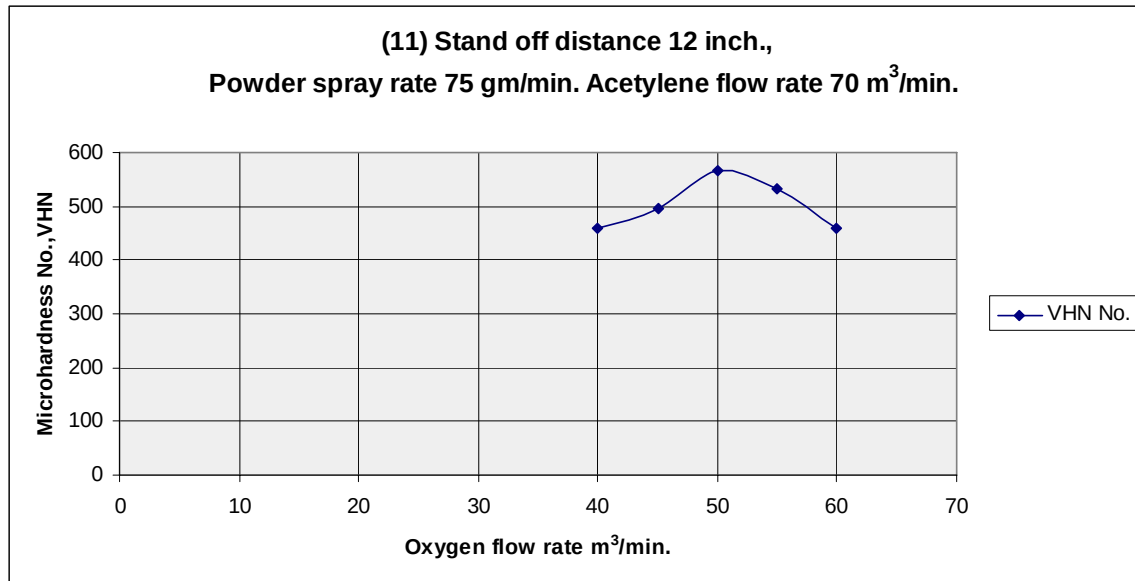
(8) Acetylene flow rate Vs VHN at Stand off distance 8 inch., Powder spray rate 45 gm/min., Oxygen flow rate 50 m³/min.



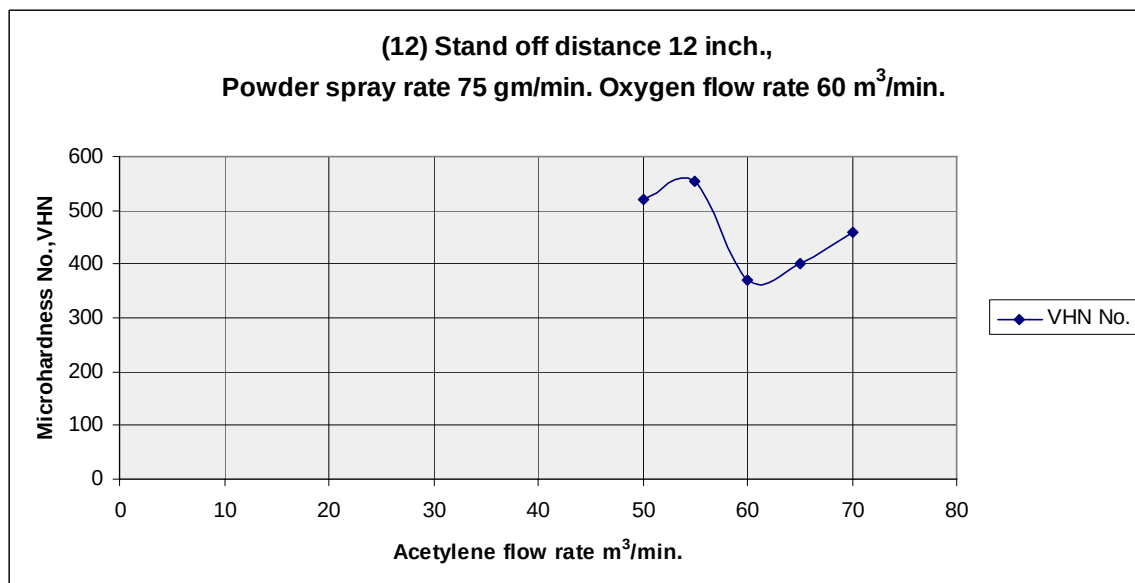
(9) Stand off distance Vs VHN at Powder spray rate 75 gm/min., Oxygen flow rate 60m³/min., Acetylene flow rate 70 m³/min.



(10) Powder spray rate Vs VHN at Stand off distance 12 inch., Oxygen flow rate 60m³/min., Acetylene flow rate 70 m³/min



(11) Oxygen flow rate Vs VHN at Stand off distance 12 inch., Powder spray rate 75 gm/min., Acetylene flow rate 70 m³/min.



(12) Acetylene flow rate Vs VHN at Stand off distance 12 inch., Powder spray rate 75 gm/min., Oxygen flow rate 60 m³/min.

Fig.5.3 Graphs showing the trend of Micro hardness number, VHN at various HVOF parameters.

5.4 Static Corrosion test

For Static Corrosion test coated samples at various HVOF parameters are taken and place in beakers with the help of wooden stick as shown in Fig.5.4 for 40 days. After 40 days the samples are weighted and compared with their initial weight to find out the percentage gain or loss in weight. Most of the samples are corroded along the edges as shown in figure.



Fig.5.4 Static Corrosion test

5.4.1 Corrosion Rate

The rate of corrosion may be reported by the weight gain in gram per square decimeter of surface area per day (gdd). It is given by following equation [36]:

$$\text{gdd} = \frac{(W_2 - W_1)}{2(lb + bw + lw)t}$$

Where,

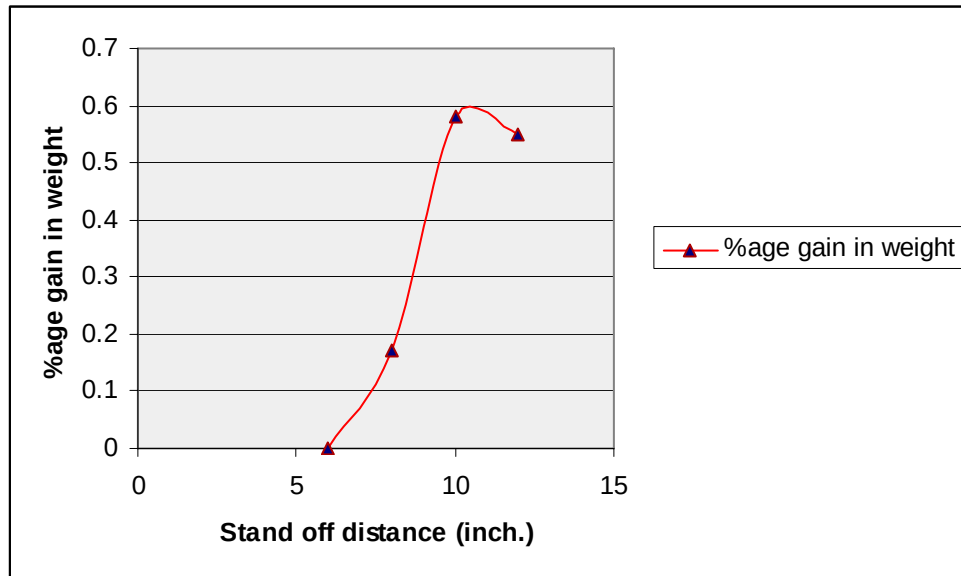
- | | | |
|-----------|---|---|
| W_1 | = | Initial weight of the samples in gms, |
| W_2 | = | Final weight of the samples in gms, |
| l, b, w | = | Length, width, thickness of the samples in decimeter, and |
| t | = | Time of exposure in days. |

The readings of Static Corrosion test and Rate of corrosion are shown in Table 5.3

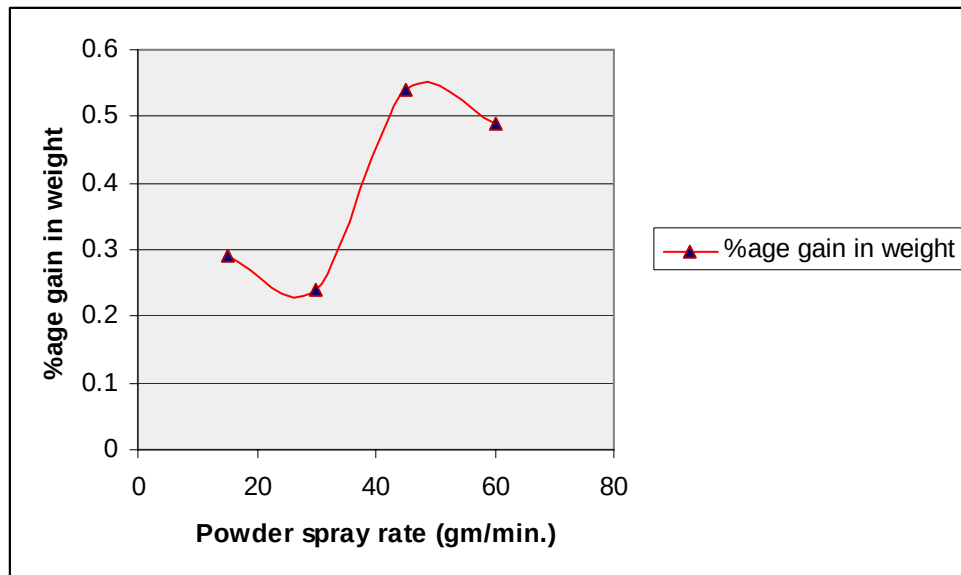
Sample No.	Initial Weight W1 (gm)	Final Weight W2 (gm)	Percentage gain in Weight $= (W2 - W1) / W1$	Rate of Corrosion $= (W2 - W1) / 2 (lb + bw + lw) t$ (gms/dm ² /day)
2	10.3	10.3	0	0.000
3	11.40	11.42	0.17	0.004
4	8.45	8.50	0.58	0.009
5	9.0	9.05	0.55	0.009
26	10.12	10.15	0.29	0.006
27	8.18	8.20	0.24	0.004
28	9.05	9.10	0.54	0.009
29	8.10	8.14	0.49	0.007
51	10.16	10.20	0.39	0.007
52	9.10	9.12	0.21	0.004
53	9.15	9.15	0	0.000
54	8.50	8.52	0.23	0.004
56	9.10	9.11	0.11	0.002
57	9.15	9.18	0.32	0.005
58	10.20	10.25	0.48	0.009
59	9.50	9.58	0.83	0.015

Table 5.3 Measurement of corrosion rate

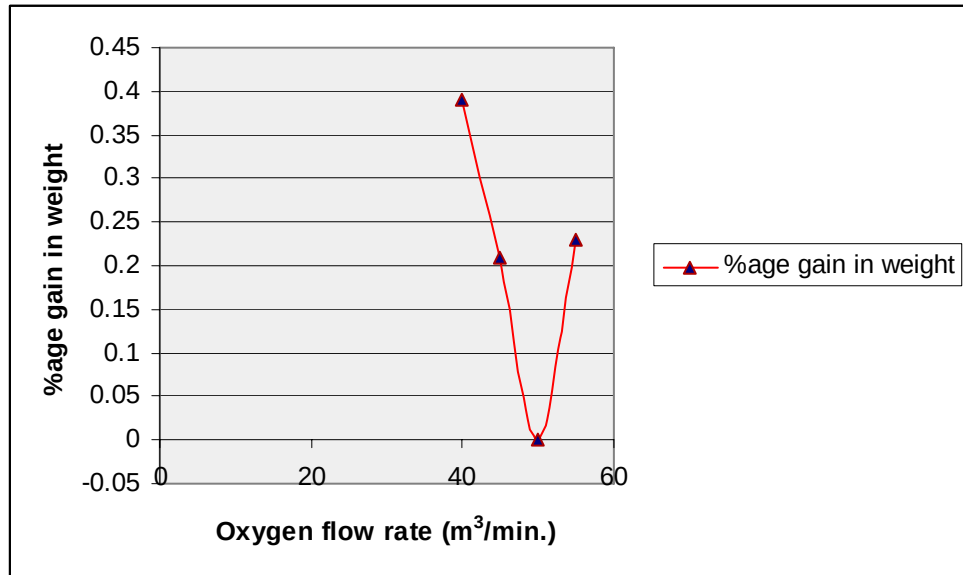
5.4.2 Graphs showing the trend of percentage gain in weight at various HVOF parameters.



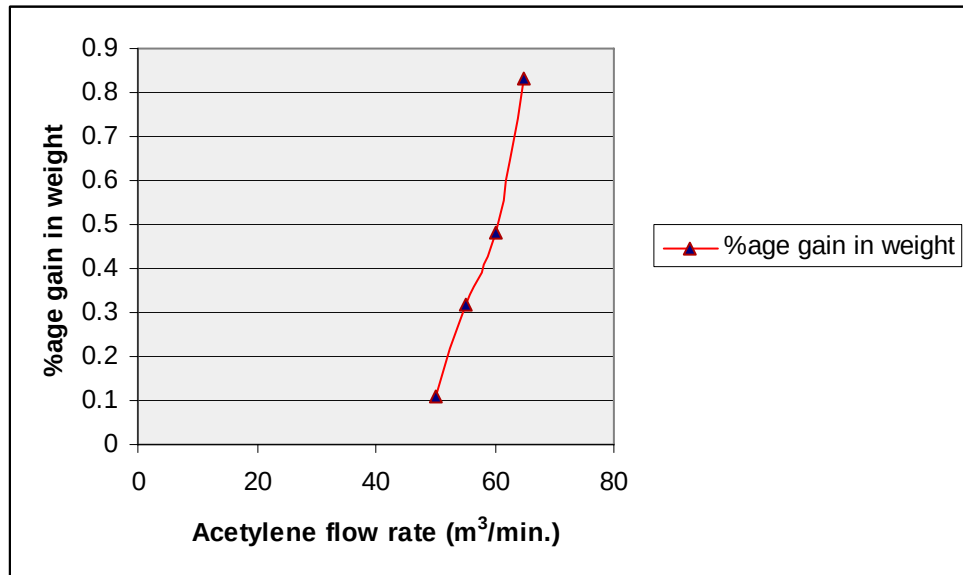
- (1) Stand off distance Vs %age gain in weight at Powder spray rate 15 gm/min., Oxygen flow rate 40 m³/min., Acetylene flow rate 50 m³/min.



- (2) Powder spray rate Vs %age gain in weight at Stand off distance 8 inch., Oxygen flow rate 50 m³/min., Acetylene flow rate 60 m³/min.



(3) Oxygen flow rate Vs %age gain in weight at Powder spray rate 75 gm/min., Stand off distance 12 inch., Acetylene flow rate 70 m³/min.



(4) Acetylene flow rate Vs %age gain in weight at Powder spray rate 75 gm/min., Oxygen flow rate 60 m³/min., Stand off distance 12 inch.

Fig.5.5 Graphs showing the trend of %age gain in weight at various HVOF parameters.

6.1 Conclusions

Following are the main conclusions drawn from the present research work:

- The XRD peaks of fish bone powder are strongly matched with XRD peaks of Hydroxyapatite (HA) as per following:

Peak No.1: 25.705 °

Peak No.2: 31.862 °

Peak No.3: 39.599 °

Peak No.4: 49.359 °

Peak No.5: 53.000 °

- In the FTIR, the OH group is found at 3404.25cm⁻¹ for fish bone and 3414.31cm⁻¹ for egg shell powder. Similarly, The P-O group is also found at 1024.19cm⁻¹ for fish bone and 875.73cm⁻¹ for egg shell powder and the same peaks are also traced in HA powder. These comparisons of FTIR conclude that both the powders shows the traces of HA phase.
- From the EDX/SEM report, it is clear that the fish bone powder contains large amount of calcium as compared to egg shell powder. The amount of Ca in fish bone powder is 67.9% by weight where as in egg shell it is 44.48%. But the fish bone powder contains less amount of phosphorous as compared to egg shell powder. The amount of P in fish bone powder is 2.4% only by weight where as in egg shell it is 19.27%. The maximum amount of Mg in fish bone powder is 3.78% and in egg shell powder it is 1.26%.
- During the biocompatibility test, the fish bone powder produces blood clotting in 16.44 seconds and the egg shell powder makes blood clotting in 38.42 seconds which shows that both the powders are efficient and compatible with human blood.

- The microstructure examination of the coated samples shows the uniform distribution of egg shell powder on SS 304L metal substrate. It is due to good flowability of egg shell powder as compared to fish bone powder.
- The fish bone powder chokes the nozzle of the spraying gun due to its poor flowability. So, it is very difficult to perform coating of fish bone powder with HVOF spraying technique.
- The maximum amount of Rockwell Hardness Number, Rc i.e.64 is obtained at Powder spray rate 45 gm/min., Stand off distance 12 inch., Oxygen flow rate 60m³/min., and Acetylene flow rate 70 m³/min.
- The maximum amount of Micro Hardness Number, VHN i.e.690 is obtained at Powder spray rate 30 gm/min., Stand off distance 12 inch., Oxygen flow rate 60m³/min., and Acetylene flow rate 70 m³/min.
- The coated samples show very good resistance to corrosion. The percentage gain in weight varies from 0 to 0.83% only. The acetylene flow rate has large effect on corrosion as percentage gain in weight continuously increasing with the increase in acetylene flow rate.

6.2 Scope for future work

- Coating characteristics of HVOF spraying technique may be compared with other thermal spray techniques like Plasma spraying, Wire spray method etc.
- Base metal may be varied like SS 316L, cobalt-chromium alloys and titanium to enhanced mechanical properties.
- Instead of fish bone powder and egg shell powder, some other biocompatible material like TiO₂ may be included in future.
- Coated samples may be implanted in SBF (stimulated body fluid) to see the blood and saliva compatibility.

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