B. TECH. PROJECT REPORT

On

Development and Characterization of Co-Cr-Ti Functionally Graded Material for Biomedical Applications

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Development and Characterization of Co-Cr-Ti Functionally Graded Material for Biomedical Applications

A PROJECT REPORT

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CANDIDATE'S DECLARATION

We hereby declare that the project entitled **"Development and characterization of Co-Cr-Ti Functionally Graded Material for Biomedical Applications"** submitted in partial fulfillment for the award of the degree of Bachelor of Technology in 'Mechanical Engineering' completed under the supervision of **Prof. Neelesh Kumar Jain, Mechanical Engineering** IIT Indore is an authentic work.

Further, we declare that we have not submitted this work for the award of any other degree elsewhere.

Signature and name of the student(s) with date

CERTIFICATE by BTP Guide(s)

It is certified that the above statement made by the students is correct to the best of my/our knowledge.

Signature of BTP Guide(s) with dates and their designation

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Abstract

Additive manufacturing (AM) is a bottom-up manufacturing philosophy in which a product is manufactured directly from its computer-aided design (CAD) model by depositing the material in thin successive layers. This unique feature allows paperless, material-efficient, and faster manufacturing of any complex or customized component without use of any expensive tooling. Biomaterials are widely used to replace in form of implants (total joint replacement) and restore the function of medical devices (pacemakers, artificial hearts, etc.). The main precondition for the selection of biomaterials is its compatibility with the human body. An essential consideration in the selection of biomaterials for a long period of time without rejection such as biocompatibility, high corrosion resistance, wear resistance, suitable mechanical properties, and osteointegration. Indian society of hip and knee surgeon (ISHKS) joint registry estimated over 1,20,000 knee replacement and 70,000 hip replacements takes place annually in India. Average cost of knee replacement surgery in India is 6,600 (USD) i.e. around Rs. 6 lakhs to 8 lakhs which is not affordable by many Indian people. This includes revision surgeries (primarily due to stress shielding effect and lower biocompatibility) which costs more than original joint replacement surgeries and require patient to stay in hospital for longer durations. Main challenges include reduction in cost of implants and number of cases of revision surgery. To overcome these challenges, there is a need to develop a biocompatible material whose density should be less to conventional material like stainless steel SS 316L, Co-Cr-Mo alloy, and Ti-6Al-4V, and Young modulus should be closer to that of human bone so that stress shielding effect is minimized. The main objective of this project is the development of Co-Cr-Ti biocompatible material and manufacturing of artificial knee implant using Co-Cr-Ti powder by micro -plasma transferred arc deposition (MPTAPD) based additive manufacturing process, which is economical, material and energy-efficient, and provides good quality of deposition.

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Chapter 1

Introduction

The main objective of this chapter is to provide brief idea about the processes of additive manufacturing(AM). In this chapter we will discuss the concept behind the additive manufacturing processes, different types of additive manufacturing processes, advantages of using additive manufacturing processes over other conventional manufacturing processes and some applications of AM. Then there will be a brief introduction of Micro plasma transferred arc powder deposition processes(μ-PTAPD) which we will be using for our experimental analysis and we will see various biomedical implants used now-a-days. At the end we will discuss about knee implant and the components present in it.

1.1 Concept of additive manufacturing

In this process a product or part is manufactured by successive layer by layer deposition directly from the CAD model being inputted. By this process we can avoid using expensive tooling for the manufacturing of complex products. AM processes are material-efficient because they incur a small loss of the product material than subtractive, primary accretion, and deformative type manufacturing processes. Being material-efficient makes them energy saving and consequently environment friendly as well AM can be used to fabricate parts made of metals, alloys, polymers, ceramics, composites and functionally graded materials.

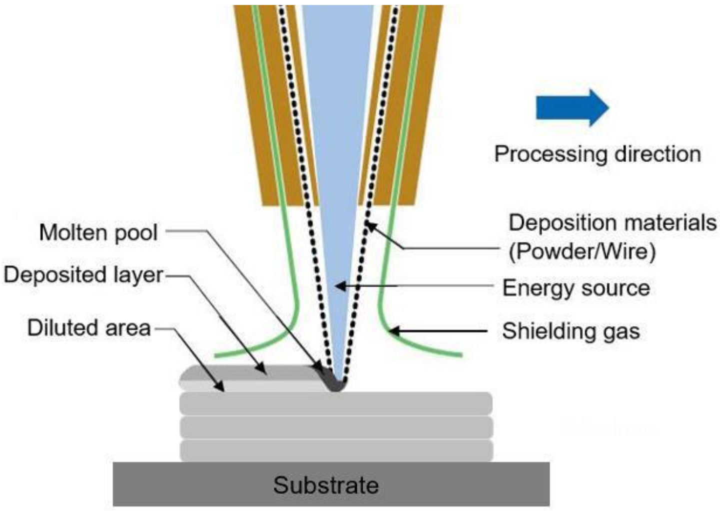

Fig 1.1: schematic diagram of additive manufacturing

1.2 Advantages of additive manufacturing

Some of the advantages of this process are we can manufacture most of the complex parts by successive layers of deposition which are made up of different materials such composites, polymers etc., we can also repair damaged components or parts which are complex at low costs, we can also do texturing or coating to change the surface of a component. Main advantage of this processes is the manufacturing cost of component will be less when compared to conventional machining processes because there is very less wastage of material.

1.3 Applications of additive manufacturing

Initially, concept of AM was used for manufacturing model and prototype of the parts. Recently, development of AM has been focused on manufacturing of free-form surfaces/geometry of the metallic components. Various applications of AM include rapid prototyping, rapid manufacturing, rapid tooling, repairing and surface modification.

1.3.1 Rapid Prototyping

Rapid Prototyping is the application of AM in which a part or product is manufactured layer-by-layer to form a prototype of the product or part from the CAD model for the purpose of visualization, realization or evaluation. Rapid Prototyping models are also used for replication of the product behavior under actual service conditions and functional testing.

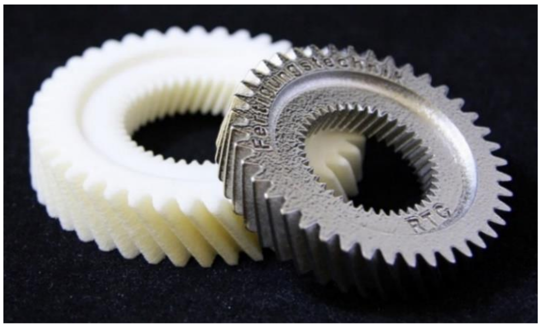

Fig 1.2: Rapid prototyping

1.3.2 Rapid Manufacturing

Rapid Manufacturing is used to manufacture real life products or components from the CAD model which is advanced than the rapid prototyping. It can be used for manufacturing of fully functional, long-term end-use products, add delicate features to an existing component and enables the creation of complex products with internal features to increase functionality. Rapid manufacturing includes major applications in direct parts manufacturing of components required in automotive, aerospace, household appliances and biomedical applications

1.3.3 Rapid Tooling

Rapid tooling is the fast fabrication of the different tools or dies or moulds for different manufacturing processes such as casting, sheet metal forming , injection moulding, electric discharge machining (EDM), electro chemical machining (ECM) process, etc. using a CAD-based automated additive manufacturing. Production of parts using rapid tooling ensures shorter production time as compared to that of a conventional tool manufacturing

1.3.4 Repairing

Engineering components such as dies, moulds, and gears are frequently subjected to local impacts, thermal stresses, corrosion, erosion, fatigue and other severe work environment during their service life. It results in the development of various defects before completion of their expected service life and adversely affect their service performance. AM is a cost-effective, material-efficient, wastage and inventory reducing, and replacement lead time saving option by economically repairing the damaged parts.

1.4 Micro plasma transferred arc powder deposition(μ-PTAPD)

Additive manufacturing processes are basically divided into types based on the energy source used.

(i) Energy beam-based processes.

(ii) Arc-based processes.

One of the processes in Arc based is the Micro plasma transferred arc powder deposition processes. In this process a pilot arc is generated between the negatively charged tungsten electrode and the positively charged constricted nozzle which is made up of copper. Plasma gas is supplied to the nozzle which will be ionized by the pilot arc generated thus forming the high-power plasma between the nozzle and substrate. Alongside plasma gas shielding gas is supplied for protecting the deposition process from reacting with atmospheric gases. Powder gas is used to force the powder to flow through the plasma thus gets melted and deposited on the substrate. The main advantages of using this process is this will consume less power and there will be very low material distortion. Due to very less heat affected zone as compared to other deposition processes it is called MICRO plasma transferred arc additive deposition processes.

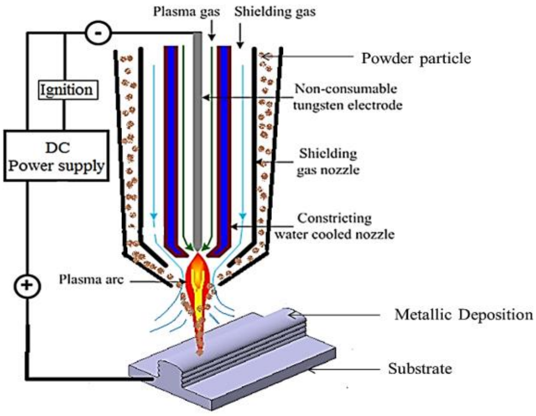

Fig 1.3: Schematic diagram for μ-PTAPD

1.5 Introduction to knee implants

A total knee replacement is a surgical procedure whereby the diseased knee joint is replaced with artificial material. The knee is a hinge joint that provides motion at the point where the thigh meets the lower leg. The thighbone (or Femur) abuts the large bone of the lower leg (Tibia) at the knee joint. During a total knee replacement, the end of the femur bone is removed and replaced with a metal shell. The end of the lower leg bone (Tibia) is also removed and replaced with a channeled plastic piece with a metal stem. Depending on the condition of the kneecap portion of the knee joint, a plastic "button" may also be added under the kneecap surface. The artificial components of a total knee replacement are referred to as the prosthesis.

1.5.1 Types of Knee replacements

1.5.1.1 Total Knee Replacements

There are two types of total knee replacements currently used on the market. The first is the posterior-stabilized type, which involves the removal of the posterior cruciate ligament. This is needed when the posterior cruciate ligament can no longer support loading. The second type of total knee replacement is the cruciate-retaining model, which preserves the posterior cruciate ligament.

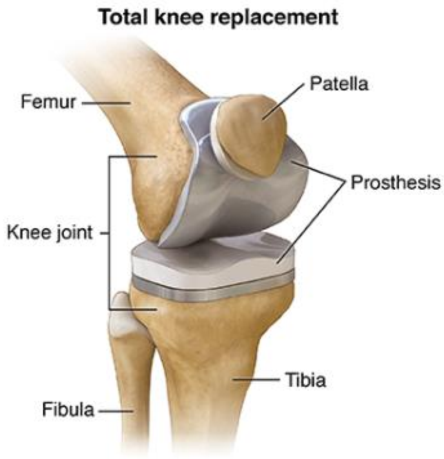

Fig 1.4: Total knee replacement

1.5.1.2 Partial Knee Replacements

In partial knee replacements, only sections of the knee are replaced rather than the entire knee, keeping much of the original biological tissue intact and functional. Typically, patients who proceed with a partial knee replacement are those who have osteoarthritis concentrated in a given region, rather than the entire knee. One major advantage of a partial knee replacement is that recovery time is cut down significantly, as well as the knee function feels much more natural than what patients experience with a total knee replacement. However, since there is a chance that disease may spread to the other compartments which are still biologically intact, there is an increased chance that follow-up surgery may be required.

1.5.2 Parts of Knee Implant

1.5.2.1 Tibial component: The flat part that attaches to the top of the resurfaced shin bone at the front of the leg (Tibia). This part is usually made of metal platform with a polyethylene insert. This part is usually made of softer metal, like titanium alloy.

Fig 1.5: Tibial Tray

1.5.2.2 Femoral component: The largest, curved part that attaches to the end of the resurfaced thighbone (Femur). This part comes in various metal options or ceramic.

Most commonly, this part is made of cobalt-chromium alloys which are most durable since this part engages in the most movement.

Fig 1.7: Femoral component

1.5.2.3 Patellar component— A dome-shaped piece that replaces the damaged kneecap that rubs against thighbone. This part is only used in some knee replacement surgeries and is made of polyethylene.

Fig 1.8: Patellar component

Chapter 2
Literature review

It presents review of the past work covering aspects of development of functionally grade material for biomedical application and on Micro Plasma transferred arc additive manufacturing process. It also presents summary of review of the past work, identified research gaps, the objectives of the present research work and the research methodology used to meet the research objectives.

2.1 Past work on functionally grade material for biomedical application

Dimic et al. (2015) examined metallic ion release and cytotoxicity of Co-30Cr-5Mo cast alloy as the initial phase of biocompatibility evaluation. They conducted three *in-vitro* tests namely he colorimetric methyl-thiazol-tetrazolium (MTT) test, the dye exclusion test (DET) and the agar diffusion test (ADT) for determination of the viability of human (MRC-5) [ISO 10993-5] and animal (L929) [ISO 7405] fibroblast cells. Chromium, the main alloying element in Co-Cr-Mo alloys, is added to advance the formation of a stable passive oxide layer that contributes to corrosion resistance, while molybdenum is also frequently added to increase alloy resistance to pitting corrosion and crevice corrosion. The released metallic ions from dental materials could diffuse into mucosal tissue or could be distributed throughout the human body and cause adverse biological effects, depending on the ion type and concentration. The main factors affecting metallic ion release from dental materials are the quantity and quality of the saliva, plaque, pH value, temperature and presence of proteins. Additionally, the physical and chemical properties of food and liquids as well as oral health conditions have great influences on ion release.

Mohammed et al. (2017) done assessment of metal ion toxicity, cellular viability, and deoxyribonucleic acid damage induced by orthodontic appliances. They stated that it is difficult to assess the exact level of metals that produce toxicity or cellular damage since metal toxicity is governed by various factors. The corrosion of an alloy releases free ions from the metals which may have significant influence on surrounding tissues, such as toxicity, allergy, mutagenicity, and carcinogenicity.

Wei et al. (2018) investigated the spatial distribution of microstructures of a Co-Cr-Mo alloy rod fabricated by Electron Beam Melting (EBM) method along built height. Biomedical Co-Cr-Mo (CCM) alloys have been widely used as orthopedic implants, such as artificial knee and hip joints, owing to their high biocompatibility, good mechanical properties, and superior wear and fatigue resistances. These alloys generally contain minor elements such as carbon, nitrogen, and other impurity elements conforming to the ASTM F75, F799, and F1537 standards. The doping of these elements on the alloys can improve the mechanical properties through secondary-phase strengthening.

Nova et al. (2017) studied the influence of alloying elements on the mechanical properties of a cobalt- based alloy produced with powder metallurgy. The standard Co-Cr-Mo alloy and Co-Cr-Mo alloy with various alloying elements, specifically Nb, Si, Ti in an amount of 5 % mass fraction, were prepared using mechanical alloying followed by the compacting method called spark-plasma sintering. The influences of the alloying elements on the microstructure as well as mechanical and tribological properties were observed. Based on the obtained results, the Co-Cr-Mo-Nb alloy seems to be most suitable because the addition of niobium greatly improved the wear resistance. However, it is necessary to perform many other tests, especially the tests of corrosion resistance and biocompatibility.

Hinuber et al. (2010) studied leading caused for revision surgery in case of hip and knee replacement which becomes critical to increase the lifetime of a hip and knee replacement to minimize the number of revision surgery. One of the primary issues impeding orthopedic implants longevity is the high wear rate of commonly used material wear couples such as Co_{28}-Cr_6-Mo/ultra-high molecular weight polyethylene (UHMWPE) and Ti6-Al-4V/UHMWPE found in orthopedic implants replacement. They showed that there is evidence that wear debris especially UHMWPE particles, lead to wear particle induced aseptic loosening. Wear products from metallic implants have also been shown to be harmful to the surrounding tissue. Co and Cr ions are toxic or even carcinogenic and have been shown to promote inflammation and reduced cell activity.

Hazlehurst et al. (2013) evaluates the stiffness characteristics of square pore Co-Cr-Mo cellular structures manufactured using laser melting technology to improve the stress shielding characteristics of orthopedic implants. Additive layer manufacturing process provides a capability to produce orthopedic implants with tailored mechanical properties. Orthopedic implants manufactured from biomedical alloys such as titanium and cobalt chrome have routinely been used for clinical use in all forms of joint arthroplasty. Post operatively, the load transfer into host bones can be reduced by the insertion of such stiff fully dense metallic implants that exhibit homogeneous and isotropic behavior. The change to the loading environment causes a phenomenon known as stress shielding. This can promote premature implant loosening and the need for revision surgery through a loss in periprosthetic bone density. A reduction in implant stiffness can reduce stress shielding and offer improved implant longevity.

T. Matkovic et al studied the structure, hardness and corrosion behavior of Ti-Co- Cr alloys. Titanium alloys have an elastic modulus of 100-120 GPa, only about half that of 316 stainless steel (200 GPa) or Co-Cr-Mo alloy (210 GPa). The key problem, though, is the mismatch of the elastic modulus of the titanium implant and bone (10-30 GPa). Pure titanium exhibits an allotropic transition $\alpha \rightarrow \beta$ at 883 °C. The elastic modulus of the α-hcp phase (100-120 GPa) is higher than that of the β-bcc phase (60-80 GPa). The design of full or partial β-type Ti-alloys by adding some strong β-phase forming elements (Nb, Ta, Mo, Zr) or some β-phase improving elements (Cr, Fe, Sn) can obviously reduce the elastic modulus. When the elastic modulus is reduced, the strength of the titanium alloy is decreased. Some alloying elements (Co, Cu, Ni) can be used to strengthen the alloys. Optical microscopy shows that most of the as-cast Ti-Co-Cr alloys have multi-phase microstructures. The results of XRD-analysis indicate that the crystal structures of as-cast Ti-Co-Cr alloys are mainly complex, sensitive to the composition of the alloys, and consistent with the microstructural examinations. The results of the hardness measurement reveal the strong influence of the alloy chemistry and microstructure on the hardness values.

N M S Abd Malek et al(2015) evaluated the structural stiffness of porous cellular structure of cobalt chromium allow. Cobalt (Co) in Co-Cr-Mo alloys exhibits high corrosion resistance and has excellent wear resistance which makes Co, often employed as artificial joints and body implants. Co also shows stability of allotropic transformation at room and elevated temperatures. In biomedical applications, Co-Cr-Mo alloys (ASTM F75) were much preferred to be used in human since they are free of Nickel (Ni). Ni element is well known as highly toxic element.

Félix A. España. et al(2009) studied that metals are bioinert and have a considerably higher stiffness than natural bone which significantly reduces the implant's in vivo lifetime. Short life of current THR(Total hip replacement) implants is generally due to the aseptic loosening of the implant, which occurs due to (i) mismatch of the Young's modulus between bone (10–30 GPa) and metallic implant materials (110

GPa for Ti and 248 GPa for Co-Cr-Mo alloy) leading to stress-shielding, (ii) poor interfacial bond between the host tissue and the implant due to bioinert surface, (iii) wear induced osteolysis and aseptic loosening in metal-on-polymer implants, and (iv) absence of high recoverable strain (~ 2%) as well as hysteresis similar to natural bone. In order to increase the vivo lifetime of metal implants one can reduce (i) effective modulus of the implant to match that of bone (ii) increase the interfacial bond between the living cells and implant material via compositional or structural modification. Another serious concern limiting the life of THR is relatively high wear rate of ultra-high-molecular-weight polyethylene (UHMWPE) liner leading to osteolysis and aseptic loosening. Therefore, there is a growing interest in wear-resistant metal/alloy coatings for THR because of their excellent toughness coupled with high wear resistance. So improved fixation and increased longevity are still important performance criteria in the development of orthopedic prostheses, which mandates the development of innovative designs and use of advanced manufacturing techniques.

2.2 Past work on Micro Plasma transferred arc additive manufacturing process

Sawant et.al investigated wear characteristics of stellite coating on AISI 4130 steel substrate using micro- plasma transferred arc powder deposition process. From studies it was found that travel speed of worktable is the most important parameter affecting wear characteristics of stellite coating. Microstructural analysis, energy- dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) patterns revealed that the produced stellite coating had a lamellar structure consisting of α-Co and ε-Co phase, chromium- rich carbides ($Cr_{23}C_6$ and Cr_7C_3) and tungsten – containing compound (W_2C) which responsible for imparting the higher hardness and wear resistance to the stellite coating.

Sawant and Jain et al investigated additive manufacturing aspects of Ti-6Al-4V by micro plasma transferred arc powder deposition (μ - PTAPD) process in continuous and dwell – time mode. They concluded that dwell – time deposition yielded higher effective wall width (EWW), deposition efficiency (DE), yield strength, ultimate strength, microhardness, surface straightness, lower strain, wear volume and friction coefficient and smaller lamellar width.

2.3 Conclusion from the past work

By studying the relevant past work, we have concluded the following points:

- Alloying elements (Co, Cu, Ni) can be used to strengthen the alloys.
- The design of full or partial β-type Ti-alloys by adding some strong β-phase forming elements (Nb, Ta, Mo, Zr) or some β-phase improving elements (Cr, Fe, Sn) can obviously reduce the elastic modulus
- Cobalt (Co) in Co-Cr-Mo alloys exhibits high corrosion resistance and has excellent wear resistance which makes Co, often employed as artificial joints and body implants.
- Metals are bioinert and have a considerably higher stiffness than natural bone which significantly reduces the implant's in vivo lifetime.
- Short life of current THR(Total hip replacement) implants is generally due to the aseptic loosening of the implant, which occurs due to (i) mismatch of the Young's modulus between bone (10–30 GPa) and metallic implant materials (110 GPa for Ti and 248 GPa for Co-Cr-Mo alloy) leading to stress-shielding.
- μ-PTA powder deposition process has Low power and concentrated heat source hence low thermal distortion and smaller heat affected zone as compared to other arc-based deposition processes.
- Also Good metallurgical bonding between multi-layered deposition.
- Higher energy concentration with better thermal efficiency as compared to arc-based deposition processes.

2.4 Identified research gap

- No work has been reported on development of functionally graded materials (FGM) having properties similar to that of human bone by micro-plasma transferred arc deposition (μ-PTAPD) process.
- No work has been reported on use of Co-Cr-Ti powder for orthopedic implants and its in-vitro biocompatibility evaluation and mechanical characterization.
- No work has been reported on manufacturing of knee implant by μ-PTAPD process

2.5 Objectives of present research work

- Investigation of porous structure and mechanical properties of additive layer manufactured Co-Cr-Ti alloy for biomedical applications.
- Static load analysis of knee implant component using finite element analysis.

2.6 Research methodology

Relevant Literature review

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Deposition of Co-Cr-Ti powder by U-PTA Process

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Evaluation and Characterization of deposited Co-Cr-Ti alloy

- Optical microscopy
- XRD analysis
- Microhardness
- SEM analysis
- Biocompatibility Test

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Modelling and static load analysis of knee implant

- Designing CAD model of Tibial tray and femoral component
- Stress and Strain analysis by FEA

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Result Analysis

Chapter 3

Experimental Procedure

Our objective is to characterize the additive layer manufactured Co-Cr-Ti allow for biomedical implants. This chapter describes the experimental procedure and explains the experimental apparatus. For deposition we used μ-PTAPD process developed by Dr Mayur Sawant. It gives a detailed view into μ-PTAPD process and its process parameters. For characterization of our alloy we performed numerous experiments such as optical microscopy, Scanning electron microscopy for detailed view of the micro structure, X- ray diffraction for the phase analysis and composition. The mechanical testing such as tensile test to calculate the young modulus and yield strength of the material and micro hardness test to calculate the hardness of the material was also performed.

3.1 Experimental setup of μ-PTAPD

Deposition of Co-Cr-Ti powder by μ-PTAPD process – In powder-based AM processes, the major advantage is in terms of flexibility in powder deposition rate, flexibility of mixing of different deposition materials, attainment of higher deposition rate and better metallurgical bond between the deposition and substrate materials as well as easy availability of the deposition materials in powder form. μ-PTAPD process uses very low current in the range of 0.1 to 20 A to generate a pilot arc between non-consumable tungsten electrode (connected to negative terminal of DC power supply unit) and the constricting nozzle housed in a deposition head. This ionizes the inert gas (argon) forming its precisely controlled and focused micro-plasma arc which forms melt pool on the substrate surface by melting the deposition material delivered as powdered stream. When the powder contacts the melt pool it is absorbed into melt pool and creates deposition layer.

Experimental Apparatus – The Experimental apparatus of µ-PTAPD process Consists of (i) power supply unit and torch for micro-plasma, (ii) in-house designed and developed powder feeding system, (iii) in-house developed deposition head.

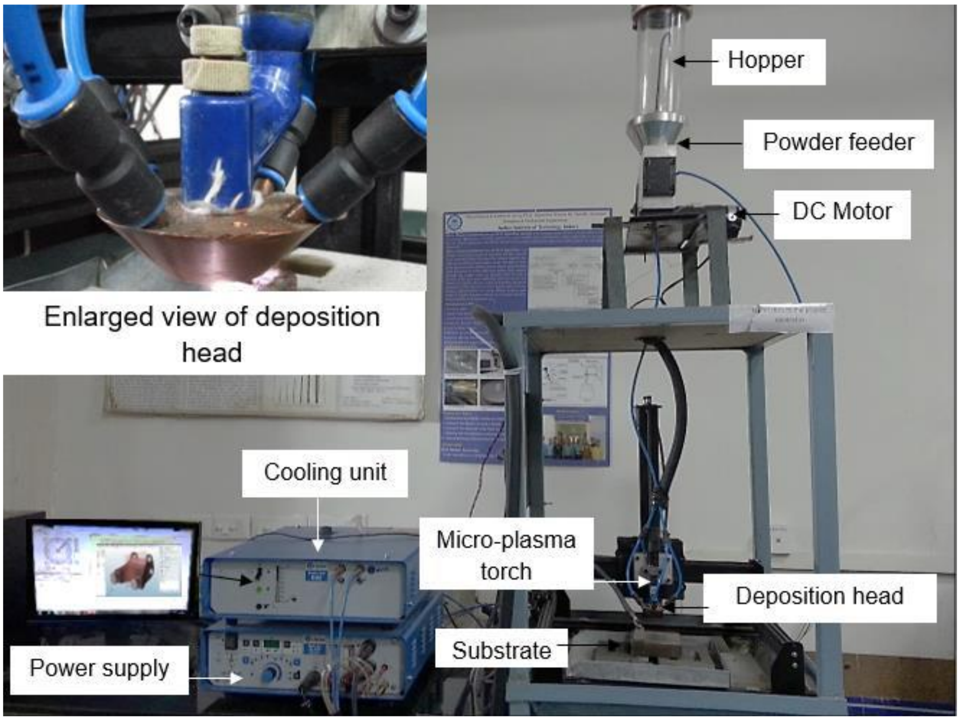

Fig 3.1: Photo of experimental apparatus

Power Supply: Power supply unit for micro-plasma (Dual Arc 82-HFP from Pro-Fusion Inc. USA) was used as power source in the experimental apparatus. It can supply DC power up to 440W with current varying from 0.1 to 20 with increments of 0.1 at a constant voltage of 22volts.

Powder Feeding System: This consists of a hopper, shaft, DC motor and a power supply unit for DC motor. The powder will be stored in the hopper which will be supplied to the deposition head with the help of a pressurized argon gas with constant flow rate of 0.5Nl/min. This system can store powder of particle size ranging from 20-200µm.The powder we will be using is having a particle size of 50 µm and a mesh size of 270 in U.S. Std. Sieve.

Deposition Head and Micro Plasma torch: The deposition head consists of a micro plasma torch and four nozzles at a feed angle of 46 degrees to supply powder to micro plasma torch for the deposition purpose. The orientation and positioning of these nozzles are so important as this effects the efficiency of the deposition process. The micro-plasma torch (PLT100 series) consisted of tungsten electrode, constricting nozzle, gas lens and gas guiding insert.

3.2 Process parameters of μ-PTAPD

It is important to understand different process parameters and their respective functions during actual deposition in order to develop the process. Various process parameters related to micro-plasma power supply and deposition process affect the performance of the μ-PTAPD process.

Micro-plasma power '*P' (W)*: It is product of the current and DC voltage supplied for the generation of the plasma. The supply of higher power will result in the production of higher heat thus more powder will be melted resulting in more heat effected zone. There will be improper metallurgical bonding between the layers if low power is supplied due to the partial melting of powder. So Ideal values for plasma power should be selected to ensure a proper deposition process.

Plasma gas flow rate 'F_p' (Normal liter per minute, Nl/min)**:** It is rate at which the plasma forming gas is supplied. The high-power plasma is produced by the pilot arc by ionizing this plasma gas. This also maintains a continuous directional flow of the high-power plasma towards the substrate thus forming a good deposition.

Shielding gas flow rate 'F_s' (Normal litre per minute, Nl/min)**:** It is rate at which shielding gas supplied to protect the melt pool from atmospheric contamination. If ample amount of shielding gas is not supplied, then this will create imperfections in the deposited bead. So ideal value should be chosen for the flow rate to avoid the above-mentioned problems.

Powder mass flow rate '*f*' (gram per minute): The rate at which powder is supplied to the deposition head for the deposition processes. This decides whether the deposition has good metallurgical bonding or not. But choosing ideal value for the flow rate is dependent on two parameters micro plasma power and the travel speed.

Travel speed '*T'* (mm/min)**:** It is the relative speed between the deposition head and the substrate material. Sometimes, deposition head is provided the required movement and the substrate remains stationary and, in some case, vice-versa. It also governs the rate by which a particular deposition is taking place. The travel speed significantly affects the cooling rate and microstructure of the deposition.

Stand-off distance '*X*' (mm): It is the distance between exit of the deposition head and top surface of the substrate on which deposition is taking. Higher value of this parameter will increase the gap between the deposition head and the surface of the substrate leading to stopping of the processes. Low value of this will decrease the amount of melted powder that can be added to the deposition process. So ideal value should be chosen.

3.3 Criteria for Selection of Materials for Orthopedic Applications

Table 3.1 : Criteria for selection of material for orthopedic applications.

Requirements	**Consequences of not fulfilling**
Biocompatibility	Response of human body Adverse effects in the Immune system
Higher Corrosion Resistance	Releasing non-compatible metallic ions Allergic reactions
Modulus of Elasticity similar to that of bone	Loosening and Failure of Implant, Stress Shielding Effect Severe Inflammatory Response, Destruction of Healthy Bones
Adequate Strength	Implant failure, Pain to patient and revision surgery
Higher Wear Resistance	Generation of wear debris which can mix with blood
Longer Fatigue Life	Mechanical Failure of the Implant Need of revision surgery
Osseointegration	Inadequate Integration between Implant and Bones leading to loosening of the implant

Biocompatibility refers to the property of biological tissue of living organisms to react to nonliving materials. Generally, it refers to the compatibility between the material and the host, including histocompatibility and blood compatibility. Lack of biocompatibility between the implant and the body may lead adverse effects on the immune system.

A biomedical implant is required to have **Higher corrosion resistance.** Corrosion of the implants will result in releasing of non-compatible metallic ion into the human blood which can result in allergic reactions.

The **Modulus of Elasticity similar to the bone** is required in the biomedical implant. High difference in the modulus of elasticity will not properly distribute the load of the body on the implant and the bone. Thus in most cases critical stresses on the bone are redistributed on the implant, which results in weakening of the bone and this phenomenon is called stress shielding effect.

The Biomedical implant should have **Adequate Strength** to sustain the load of human body. Improper strength will result in failure of the implant and revision surgeries. Also a major issue in medical implants is mixing of the wear debris with the blood which can be very harmful to the human body. Thus the biomedical implant should also have **Higher Wear Resistance.**

Osseointegration is the direct structural and functional connection between living bone and the surface of a load-bearing artificial implant. The min pore size for proper Osseointegration should be 100 μm

3.4 Chemical Composition of selected material

The chemical composition of the Co-Cr-Ti alloy and the substrate for this study is shown in table 3.2(a) and 3.2(b).

Table 3.2(a) : Composition of Co-Cr-Ti alloy

Elements	Al	Fe	C	Ni	Mn	Cr	Mo	**Ti**	Co
Mass (wt %)	<0.1	<0.75	<0.35	<0.5	<1	29	6	**2,4,6**	Bal.

Table 3.2(b) : Composition of Substrate (AISI 4130 alloy steel)

Elements	C	Ni	Cr	Mo	V	Mn	Si	P	Fe
Mass (wt %)	0.3	0.5	0.8	0.15	0.1	0.6	0.15	0.04	Bal.

3.5 Characterization of Deposited material

3.5.1 Optical microscopy

Optical microscopy is a technique employed to closely view a sample through the magnification of a lens with visible light. Optical microscopy is a technique employed to closely view a sample through the magnification of a lens with visible light. For optical microscopy we started the experiment by polishing the samples with appropriate silicon carbide papers. Then etching of the surface was done using the following reagent: 50ml HCl, 5 ml HNO_3, 50ml H_2O heated at 50^oC. Then the surface was looked under an inverted optical microscope at 50x and 100x magnification.

3.5.2 SEM

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties.

3.5.3 XRD Analysis

X-ray powder diffraction analysis, by way of the study of the crystal structure, is used to identify the crystalline phases present in a material and thereby reveal chemical composition information. Identification of phases is achieved by comparison of the acquired data to that in reference databases. For the scan the 2 theta angle was taken from 20^o to 90^o and the step size was 0.02. The dwell time was 2 seconds.

3.6 Mechanical testing of deposited material

3.6.2 Micro Hardness test

Microhardness Testing is a method of determining a material's hardness or resistance to penetration when test samples are very small or thin, or when small regions in a composite sample or plating are to be measured. For our experiment the Vickers hardness test was performed. The test was performed by applying controlled pressure for a standard length of time, with a square-based diamond pyramid indenter. The applied load was 300gm and dwell time was 15 seconds.

3.6.2 Static load analysis

The static load analysis was done on the models prepared of the Total Knee replacement. Solid works was used to create a 3D model of the TKR which are shown in the Fig 3.2 and Fig 3.3 . The material Properties considered in the FEA are shown in table 3.3. A standard mesh was used to generate the mesh in which the element size is taken as 4mm. Total number of nodes and elements present in the mesh are 12498 and 6964. respectively.

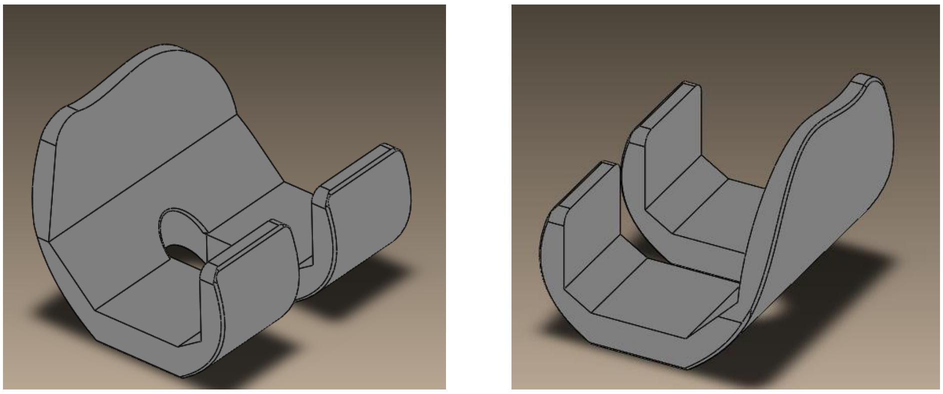

Fig 3.2: Model of the femoral component

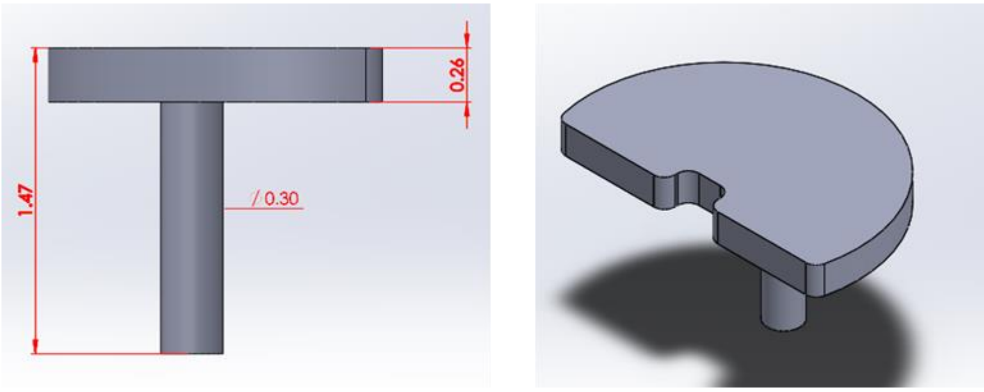

Fig 3.3: Model of the Tibial component

Table 3.3: Properties of material

Materials	**Properties**			
	Density (gm/cm^3)	**Young's Modulus (GPa)**	**Yield Strength(MPa)**	**Poisson's Ratio**
Co-Cr-Ti	8.29	225	525	0.3

3.7 Biocompatibility Test

Cytotoxicity evaluation was performed using 3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium bromide (MTT) assay. The HeLa cells were seeded in 96-well plate with seeded density 1x10 4 cells per well and allow to adhere for 24 h at 37 ° C in a 5% CO2 incubator. The three samples (2%, 4% and 6% titanium) was incubated in 1 mL of media after sterilization at 37 ºC for 24 h. The treatment of different concentration was given after removal of culture media and incubated with fresh media containing titanium at different concentrations (16.6, 33.3, 66.6 and 106.6 µL) were added over the cells in triplicate and were incubated for 24 h for evaluation of cellular cytotoxicity.

After 24h of the incubation the media was removed, and fresh media containing MTT at final concentration of 0.5 mg/mL was added over the cells and allow to incubate for 4 h. At the end, the MTT media was removed and the insoluble formazan crystals synthesized by the viable cells were dissolved in 200 µL DMSO. . Cells not treated with titanium considered as blank, and the relative viability of the cells against the blank was calculated.

Chapter 4

Results and Discussions/ Analysis

This chapter compiles different experimental results and analysis obtained from different experiments mentioned in the previous chapter. Our objective is to characterize the alloy deposited by μ-PTAPD process. We start the experiment by finding the process parameters of the μ-PTAPD process for deposition of the alloy. After deposition, appropriate polishing and diamond polishing we study the cross section under optical microscope, Scanning electron microscope to determine the microstructure of our alloy. In addition to this XRD analysis was also performed to get understanding of the composition and different phases in Co-Cr-Ti alloy. For mechanical testing, the results and tensile test and micro hardness test is also given in this chapter.

4.1 Process parameters

Table 4.1: Process parameters

Process parameters	**Range for pilot experiment**	**Value identified for main experiment**
Plasma power (W)	110-440	412; 423; 435
Powder mass flow rate (g/min)	0.6-5	1.8; 3.0; 3.8
Travel speed of nozzle (mm/min)	40-200	47; 85;130
Stand –off distance (mm)	5-12	9
Plasma gas flow rate (normal liter/min)	0.1-0.5	0.3
Shielding gas flow rate (normal liter/min)	3.0-8.0	3.6

Pilot were carried out depositing single-layer single track of Co-Cr-Ti alloy on AISI 4130 steel substrate by varying micro-plasma power, powder mass flow rate, travel speed of the worktable, stand-off distance, plasma gas flow rate and shielding gas flow rate. Table 4.1 presents the range for the pilot experiments and the values identified for the main experiments. It was observed that the minimum value of 412 W micro plasma power was required to melt Co-Cr-Ti powder during the deposition process. Therefore the values selected were 412, 423 and 435 W. The powder mass flow rate and the standoff distance values were identified for the experiment because it allowed smooth powder feeding operation to the melt pool. At higher speed of the work table discontinuous tracks were observed whereas at low speed excessive heat affected zones was observed, therefore travel speed of 47 to 130 mm/min was selected. Plasma gas flow rate of 0.3 Nl/min was found to be sufficient to transfer the micro-plasma arc toward the substrate, whereas the shielding gas flow rate of 3.6 Nl/min was found sufficient.

4.2 Deposition of Cr-Co-Ti alloy by µ-PTAPD

Using the above mentioned process parameters, we deposited single-layer single track of Co-Cr-Ti alloy on AISI 4130 steel substrate. Fig 4.1, 4.2, 4.3 shows the images of the deposited material.

Fig 4.1: Photo of Deposition with 2% Ti FGM

Fig 4.2: Photo of Deposition with 4% Ti FGM

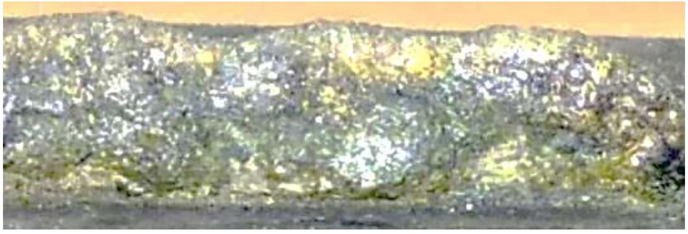

Fig 4.3: Photo of Deposition with 2% Ti FGM

4.3 Characterizing the deposited material

The samples of depositions using µ-PTAPD process were prepared for characterization by cutting the depositions along the depositions height on the wire electric discharge machining machine. The samples were then hard mounted, and polished using silicon carbide paper up to grit size P2000, and etched in a solution containing 10ml HCl, 1 ml HNO_3 and 10 ml of H_2O. The prepared samples were then studied under an optical microscope and scanning electron microscope to study the microstructure.

4.3.1 Microstructure

The optical microscopy of the alloy were done to see the microstructure of deposited material. The images were captured at two magnifications 50x and 100x. After studying the microstructure of each sample we conclude the following:

4.3.1.1 Microstructure of FGM with 2% Ti

By observing the microstructure of Co-Cr-Ti alloy with 2% Ti we conclude that the grains is made of cobalt rich matrix made up of $CoTi_2$ and the grain boundary is is made up of chromium carbide laminar phases such as Cr_7C_3. Here we can also observe finer formation of chromium carbide phases in the grain boundaries which gives it higher value of microhardness.

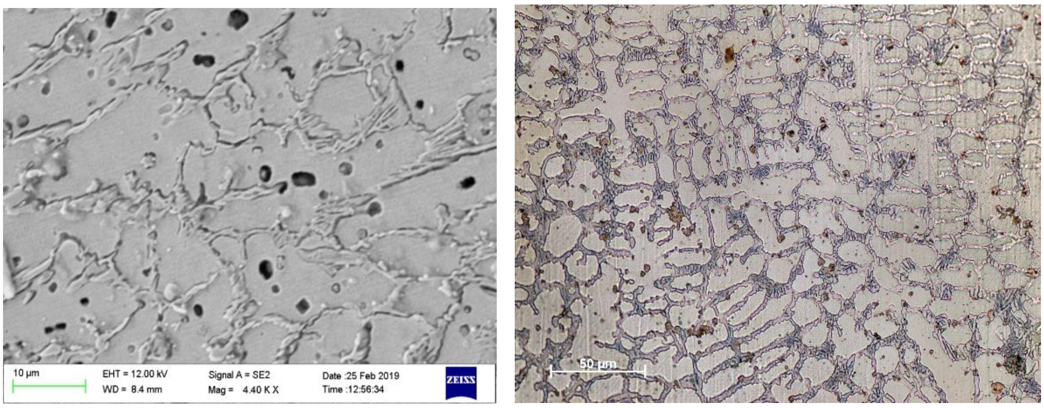

Fig 4.4: Optical microscopy and SEM images at 50x and 100x of 2% Ti alloy

4.3.1.2 Microstructure of FGM with 4% Ti

Similarly to the microstructure of 2% Ti allow, we can observe the cobalt rich matrix and also fine formation of chromium carbide laminar phases. Here also the porosity in the structure can be observed but its density is a bit lower than that of the 2% Ti alloy.

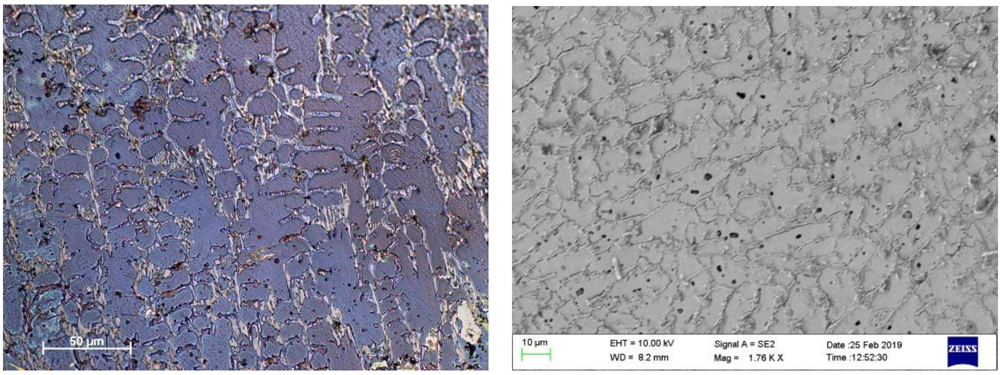

Fig 4.4: Optical microscopy and SEM images at 50x and 100x of 4% Ti alloy

4.3.1.2 Microstructure of FGM with 6% Ti

In the microstructure of the 6% Ti alloy, we can observe that there is coarse formation of the chromium carbide laminar phases. The porosity in the microstructure is also negligible.

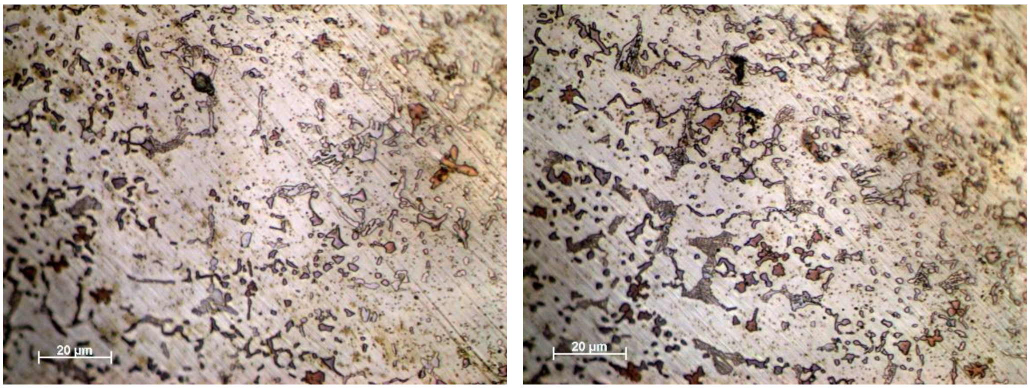

Fig 4.4: Optical microscopy images at 50x and 100x of 6% Ti alloy

4.3.2 XRD Analysis

The XRD analysis was done to identify the different phases present in the microstructure. Fig 4.5 shows the graph of 2 theta vs intensity. XRD pattern of different phases of multi -track deposition of Co-Cr-Ti alloy revealing the presence of the cobalt phases and carbides such as chromium carbide phase of M_3 and M_6 i.e. Cr_7C_3, $Cr_{23}C_6$ and tungsten carbide W_2C.

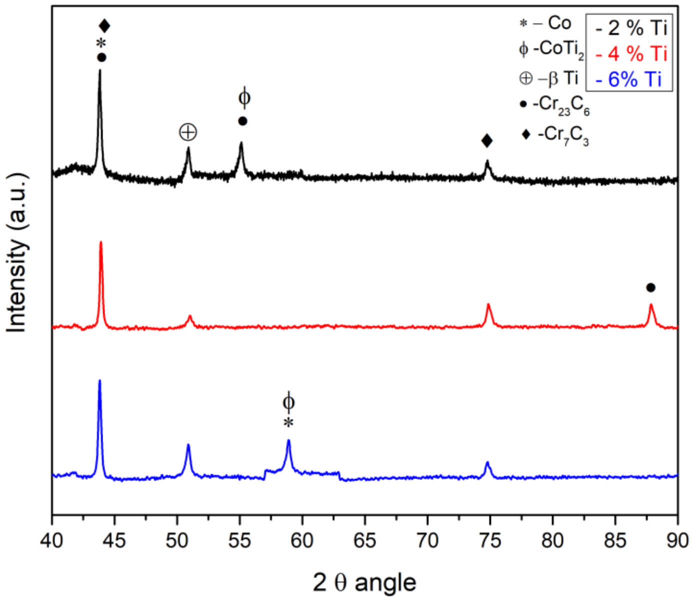

Fig 4.5: Xrd analysis graph

4.4 Mechanical testing of the deposited Material

4.4.1 Microhardness

The microhardness test was done using the Knoop and Vickers microhardness test. Fig 4.6 shows the microhardness profile of Co-Cr-Ti with varying the Ti composition with 2%, 4%, 6%. It can be observed that the microhardness value of for 4% his higher than 2% and 6% because of variation of finer and coarse cobalt based carbides precipitation. It is because finer carbides gives higher value of microhardness whereas coarse carbide gives lesser value. Also it can be observed that due to high amount of porosity the microhardness value of 2% is the lowest.

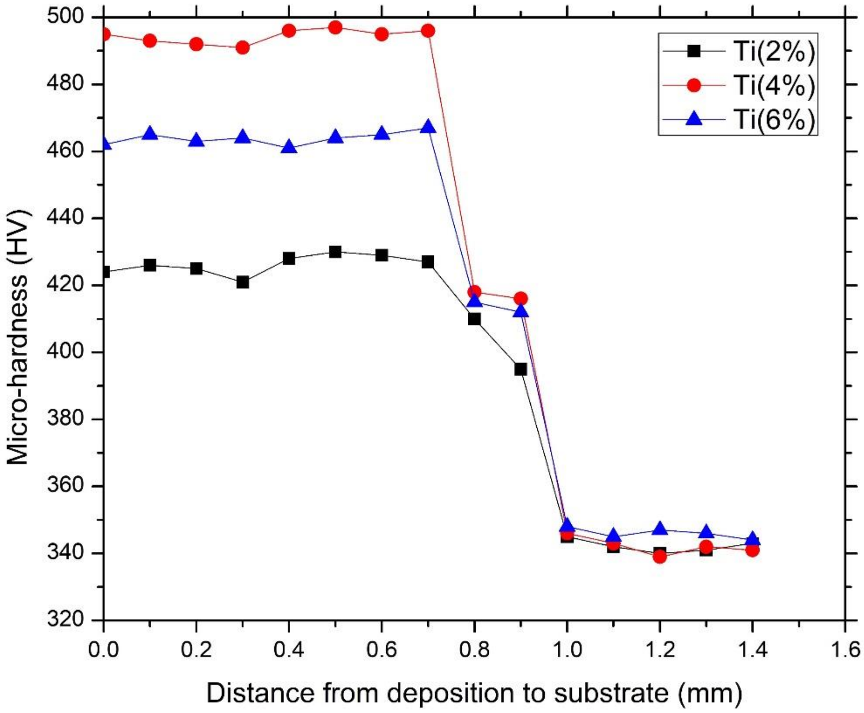

Fig 4.6 : Microhardness profile of the FGM with varying Ti %

4.4.2 Static Load analysis

The static load analysis of the total knee replacement model using physical properties of cobalt alloy Co-Cr-Ti material has been conducted and based on infinite element analysis; developed von mises stress and deformation values have been obtained. The FEA was done using three different loads of 250N, 350N, 450N considering the different age group, sex, and height. The comparison of developed von Mises stresses and the maximum deformation has been made with the allowable strength of the Co-Cr-Ti materials and it has been found that the selected materials satisfied the safety criteria. The distribution of stress and deformation in the TKR model has been shown in the Fig 4.7(a,b,c) . If the deformation is more than this, it may cause displacement or loosening of hip joint prosthesis.

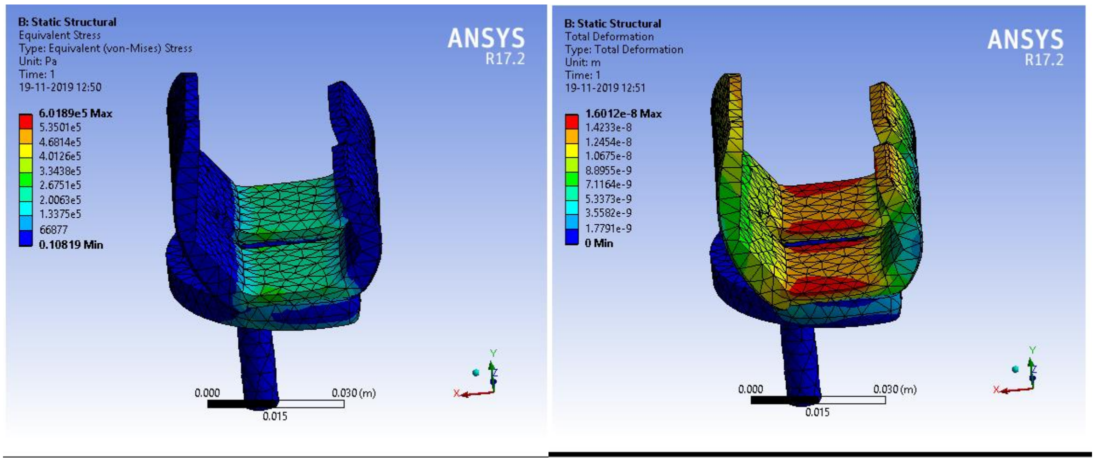

Fig 4.7(a): Von Mises stresses and deformation at 250N

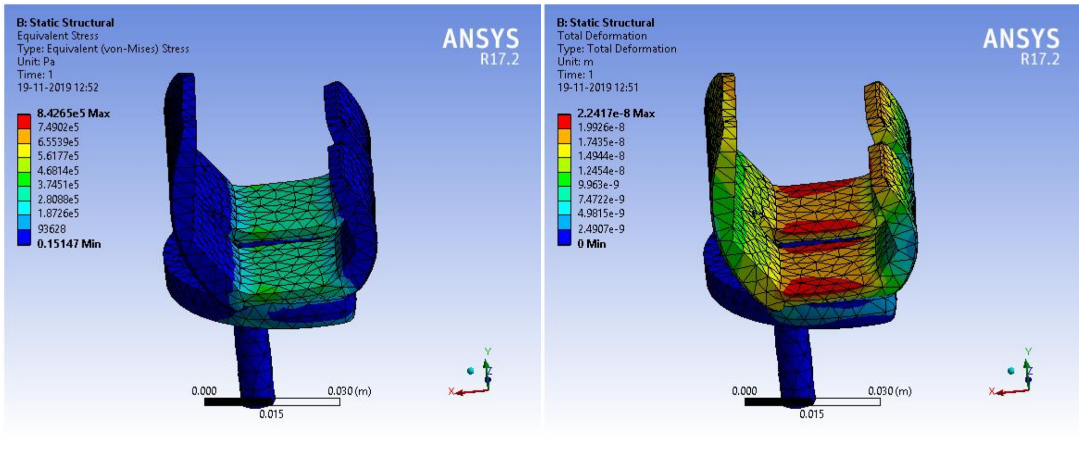

Fig 4.7(b): Von Mises stresses and deformation at 350N

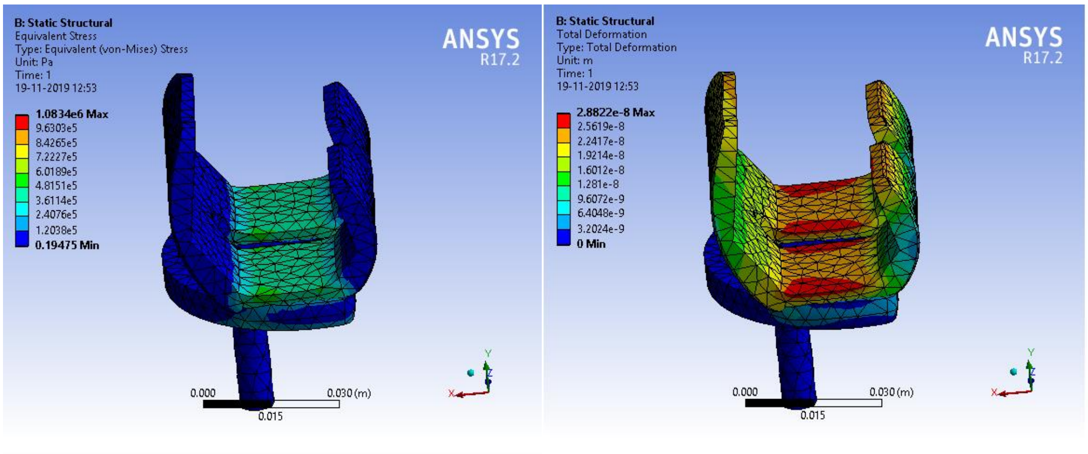

Fig 4.7(c): Von Mises stresses and deformation at 350N

4.5 Biocompatibility Test

The biocompatibility test was done using the human cervical cancer (HeLa) cell line. . The three samples (2%, 4% and 6% titanium) was incubated in 1 mL of media after sterilization at 37 ºC for 24 h. The treatment of different concentration was given after removal of culture media and incubated with fresh media containing titanium at different concentrations (16.6, 33.3, 66.6 and 106.6 µL). After 24h of the incubation the media was removed, and fresh media containing MTT at final concentration of 0.5 mg/mL was added over the cells and allow to incubate for 4 h. . Cells not treated with titanium considered as blank, and the relative viability of the cells against the blank was calculated .

The graph in Fig 4.8 compares between the cell viability and media concentration. In each case, it can be seen that more than 80% of cell survived the biocompatibility test. The Human cervical cancer (HeLa) cell showed excellent adhesion and spreading on the surface of the Co-Cr-Ti alloy.

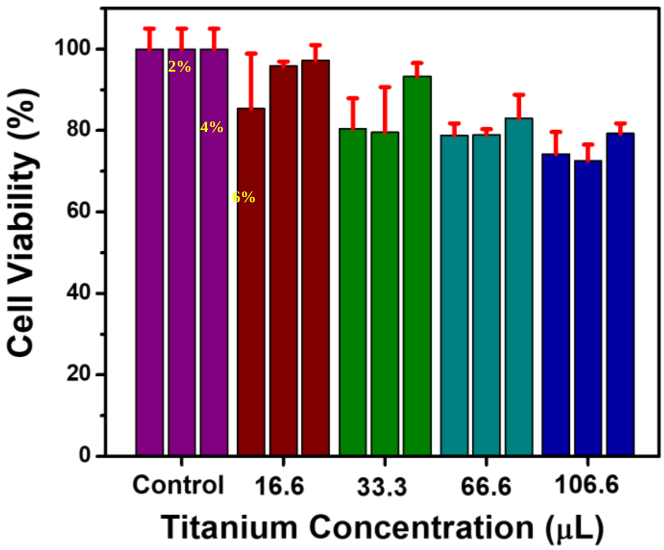

Fig 4.8 : Variation of cell viability with media percentage

Chapter 5

Conclusions and Scope for Future Work

The main objective of this chapter is to draw interfaces or conclusions based on the different experimental results. The aim of this project was development of functionally grade material Co-Cr-Ti alloy and in- vitro biocompatibility assessment for biomedical application. For this the substrate material AISI4130 steel and deposition metallic powder Co-Cr-Ti was used. The process parameter for deposition of Co-Cr-Ti were plasma power of (412 W, 423 W and 435 W), powder mass flow rate (1.8 g/min, 3 g/min and 3.8 g/min), Travel speed of nozzle (47 mm/min, 85 mm/min and 130 mm/min), standoff distance of 9 mm, Plasma gas flow rate of 0.3 normal liter/min and shielding gas flow rate of 3.6 normal liter/min were used.

5.1 Conclusion

A series of experiments have been carried out to development of functionally grade material Co-Cr-Ti alloy and in- vitro biocompatibility assessment for biomedical application. The deposition of Co-Cr-Ti was done on substrate of AISI 4130 steel with different process parameter for micro-plasma transferred arc deposition process. Deposited samples were cut with Wire Electro Discharge Machining (WEDM). Microstructural evaluation of the Co-Cr-Ti alloy was carried out to understand the nature of microstructure. Micro hardness values of substrate and deposited material for different percentages of Titanium (2%, 4% and 6%) were measured. X-ray Diffraction (XRD) analysis was done to analyze the different phase present in the multi -layer deposition. Static load analysis was done to estimate the von misses stress for different loads of 250 N, 350 N and 450 N by considering different age group. The following major conclusions or inferences can be drawn from the obtained results and their analysis:

- Optical microscopic images of cross section of multi -layer track deposition of Co-Cr-Ti alloy reveal that Titanium with 2 % and 6% content had non uniform porosity whereas Titanium 4% content had uniform porosity which reduces the hardness value of the deposition. Based on Microscopic evaluation, there were Cobalt rich matrix was spread over the area whereas at the grain boundaries laminar phase of chromium carbide were found which increase the hardness of deposited material.

- The microhardness profile of Co-Cr-Ti alloy deposition showed that the microhardness of Co-Cr-Ti alloy deposition is much higher than the substrate for all the values of Ti content in the deposition. Titanium with 2 % and 6% content had lower value of hardness as compare to Titanium 4% content because of non- uniform porosity, and the less carbide phase present in the deposition which reduces the hardness value of the deposition
- XRD pattern of different phases of multi -track deposition of Co-Cr-Ti alloy revealing the presence of the cobalt phases and carbides such as chromium carbide phase of M_3 and M_6 i.e. Cr_7C_3, $Cr_{23}C_6$ and tungsten carbide W_2C.
- The result of MTT assays showed that examined Co-Cr-Ti alloy with titanium content in the different quantity of 2%, 4% and 6 % did not exhibit cytotoxic effect in Human cervical cancer (HeLa) cell line. The Human cervical cancer (HeLa) cell showed excellent adhesion and spreading on the surface of the Co-Cr-Ti alloy. Based on in-vitro biocompatibility examination, It could be concluded that Co-Cr-Ti alloy is a biocompatible material that could safely be used in biomedical application.
- Von Misses stress, strain, and displacement distribution is attained from static load analysis results are within the satisfactory range, but if the static applied load was increased to values more than 450N the von mises stress, strain development and displacement of knee implant are directly proportional with the static applied load so the risk proportion of artificial knee prosthesis damage will increase.

5.2 Scope of future work

Present work was the first attempt to development of functionally graded material (FGM) of Co-Cr-Ti using μ-PTAPD process as an alternative to the existing AM processes for different metallic materials therefore, there is plenty scope for future research in this area as mentioned below:

- The present study was done on development of functionally graded material (FGM) of Co-Cr-Ti using μ-PTAPD process with variation of Titanium content from 2%, 4% and 6%. It can be extended as per the need for different biomedical application.
- A future attempt can be made to carry out the test for different substrate for the same functionally graded material to observe the effect of process parameter on the deposition.
- An investigation may be done to establish the mechanical simulation model experimentally.

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