DESIGN AND CONSTRUCTION OF A COATING REACTOR FOR R.F. THERMAL PLASMA SYSTEM

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DESIGN AND CONSTRUCTION OF A COATING REACTOR FOR R.F. THERMAL PLASMA SYSTEM

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ABSTRACT

DESIGN AND CONSTRUCTION OF A COATING REACTOR FOR R.F. THERMAL PLASMA SYSTEM

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Thermal plasma is a common method of surface coatings applied in a number of applications; aerospace, automotive and medical. Among them, medical application is probably the most critical as the coating should satisfy a number of requirements. Although D.C. plasma is the most common method used in coatings in general, R.F. plasma has its advantages, namely an extremely clean deposition condition as no electrode is involved in the process. In this study, a coating reactor was designed and constructed which can be used with an R.F. plasma system. The system, as is, consists of an induction plasma torch with the required generator and control units, a nanopowder reactor, a powder collector and a scroll vacuum pump. The coating unit is designed such that it will replace the nanopowders reactor and will fit between the torch and the powder collector. The coater has a double wall cylindrical chamber of 460 mm in diameter and 860 mm in length. The chamber is water-cooled via water circulation between the double wall. It comprises a manipulator which allows the movement of substrate in three dimensions namely -200 < x < 200, -100 < y < 100 and -75 < z < 75 mm. The coating chamber as designed was tested with HA coating of Ti-6Al-4V. Coating was applied with 18-20 kW power loading. The particle feeding rate was in 1 to 18 g/min and the stand-off distance was varied between 80-130 mm. Coatings obtained were compared with a conventional HA coated medical
implant in terms of both morphology and the phase make-up. It was found that HA coatings obtained with R.F. thermal plasma had Ca/P ratio of 1.80 or higher. This value is higher than Ca/P=1.67 which is the target value in plasma spraying. High value of Ca/P is a sign of thermal decomposition caused probably by a long residence time in the plasma. It is therefore concluded that power loading should be kept low so as to produce HA coating with an acceptable Ca/P ratio or alternatively the coating may be achieved by suspension plasma spraying.

*Keywords:* Thermal plasma spraying, Coating chamber, Hydroxyapatite, Hydroxyapatite coatings, Implants.
ÖZ

R.F. TERMAL PLAZMA SİSTEMİ İÇİN KAPLAMA REAKTÖRÜ
TASARIMI VE ÜRETİMİ

Yıldırım, Hatice Gözde
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Temmuz 2017, 52 sayfa


Yapılan değerlendirmede, ideale yakın az fazlı, Ca/P =1.67, oranında hidroksiapatit kaplamaların elde edilebilmesi için plazmanın daha düşük güç değerlerinde çalıştırılması veya hidroksiapatit parçaçıkların üretece süspansiyon olarak beslenmesi ile elde edilebileceği sonucuna varılmıştır.

**Anahtar kelimeler:** Termal plazma spreyleme, Kaplama reaktörü, Hidroksiapatit, Hidroksiapatit kaplama, Medikal implant.
Dedicated to my family,
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CHAPTER 1
INTRODUCTION

A variety of techniques can be used for coating. These are sol-gel, dip coating, ion beam deposition, pulsed laser deposition, magnetron sputtering and thermal plasma spraying. The most common and suitable method for many purposes is thermal plasma spraying. It provides coating thicknesses between 20-200 micron which is wider in range than most of the other coating techniques. The method is applicable to a variety of application areas in automotive, aerospace, medical etc. Plasma spraying may be based on D.C. plasma or R.F. plasma. D.C. plasma has the advantage that the torch is rather small and can be manipulated around the substrate which is quite advantageous for the coating process. The use of R.F. plasma torch despite its advantages is less common since the torch is stationary because of the nature of how plasma is generated.

Stainless steel, cobalt-chromium alloy and titanium alloys are quite common as implant material. Titanium alloys, especially Ti-6Al-4V is the most popular due to their high strength, toughness and good corrosion resistance. In addition, Ti alloys, as the other alloys, are coated with ceramics that have chemical similarities with bone such as calcium phosphates so as to improve their bioactivity. Among of them, hydroxyapatite is the most common. Hydroxyapatite (HA) coatings on metallic implants enable faster and better hard tissue implant fixation and biointegration due to intrinsic osteoconductive nature of hydroxyapatite.

This study deals with design and construction of a coating reactor for R.F. thermal plasma system. The study is made up of three parts. In the first part, a commercial hip implant was studied with regard to its structural characteristics. The second part deals with the design and construction of a thermal plasma coating chamber. This part deals with modification of an existing R.F. plasma which comprises a
nanopowder reactor. Here in this part, coating chamber was designed in such a manner that it would replace the nanopowder reactor. The third part deals with the results of preliminary experiments carried out using the coating chamber in which Ti-6Al-4V substrates were coated with hydroxyapatite.
CHAPTER 2

LITERATURE REVIEW

2.1. Surface Coating of Hip Implants

Total hip replacement consists of three parts. These are the acetabular component fitted into the hip socket, the femoral head and the femoral prothesis within the femur, Figure 2.1.

![Components of a hip replacement](image)

**Figure 2.1** Components of a hip replacement.

Since 1960s, metallic materials have been used as medical implants, especially for hip implants. Materials used are stainless steel, cobalt chromium alloys and titanium alloys. The most important requirement is that base metal should be suitable in terms physical properties and non-toxicity, Table 2.1. It is also important that the materials should promote the growth of natural tissues.

2.1.1. Substrate

Cobalt chromium alloys have been extensively used in biomedical applications. ASTM F75 standard specify the requirements for CoCrMo alloys used in the surgical implants. They have been used in medical applications because of their superior mechanical properties and corrosion resistance (Ayu et al. 2017 and Co et al. 2016).
Table 2.1 Young’s modulus of the materials used in medical applications (Arifin et al. 2014).

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless Steel (316L)</td>
<td>190</td>
</tr>
<tr>
<td>CoCrMo</td>
<td>210-253</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>116</td>
</tr>
<tr>
<td>Natural Bone</td>
<td>15-30</td>
</tr>
</tbody>
</table>

Pure cobalt has a hexagonal structure (hcp) at room temperature and it transforms to face centered cubic (fcc) structure at 400°C by adding the alloying elements such as chromium. Thus the structure which is fcc at elevated temperatures (and often dendritic) transforms slowly into hexagonal structure. In addition, the alloy contains some carbides as reported by Giacchi et al. (2010), Opris & Liu (2007), Ren et al. (2016).

Alternatively, titanium alloys can be used as the implant material. Titanium alloys can be divided into three groups: α-, (α+β)-, and β-type alloys. Of these, the alloys used as medical implants are of (α+β) two-phase alloys. Tensile strength of the titanium alloys is around 1400 MPa at room temperature. In addition to all these, titanium alloys have high corrosion resistance.

As seen in Table 2.1, the elastic modulus of Ti-6Al-4V, an (α+β) alloy, is lower than stainless steel and CoCrMo alloy. It is close to the elastic modulus of the natural bone. Unfortunately titanium and titanium alloys have poor biocompatibility. It is therefore necessary to coat Ti alloys with a material with properties that are close to those of the bone (Arifin et al. 2014).

2.1.2. **Hydroxyapatite (HA)**
Calcium phosphate ceramics attracted considerable interest because their structure and chemistry are analogous with the calcified tissue in human body. They have been extensively utilized in orthopedic, dental applications, periodontal treatment,
There are a number of calcium phosphate compounds which can be categorized according to their crystal structure, chemical composition and Ca/P ratios. These compounds as given by Carayon & Lacout (2003) are listed in Table 2.2. Of these, hydroxyapatite is the compound most similar to the human bones.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Phase</th>
<th>Chemical Formula</th>
<th>Chemical Definition</th>
<th>Ca/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCPA</td>
<td>Monetite</td>
<td>CaHPO$_4$</td>
<td>Dicalcium Phosphate Anhydrous</td>
<td>1.00</td>
</tr>
<tr>
<td>DCPD</td>
<td>Brushite</td>
<td>CaHPO.2H$_2$O</td>
<td>Dicalcium Phosphate Dihydrate</td>
<td>1.00</td>
</tr>
<tr>
<td>OCP</td>
<td>-</td>
<td>Ca$_8$H$_2$(PO$_4$)$_6$.5H$_2$O</td>
<td>Octocalcium Phosphate</td>
<td>1.33</td>
</tr>
<tr>
<td>α-TCP</td>
<td>-</td>
<td>α-Ca$_3$(PO$_4$)$_2$</td>
<td>α-Tricalcium Phosphate</td>
<td>1.50</td>
</tr>
<tr>
<td>β-TCP</td>
<td>Whitlockite</td>
<td>β-Ca$_3$(PO$_4$)$_2$</td>
<td>β-Tricalcium Phosphate</td>
<td>1.50</td>
</tr>
<tr>
<td>OHA</td>
<td>-</td>
<td>Ca$_{10}$(PO$_4$)$_6$(OH)$_2-2xO_x$</td>
<td>Oxyhydroxyapatite</td>
<td>1.67</td>
</tr>
<tr>
<td>OA</td>
<td>-</td>
<td>Ca$_{10}$(PO$_4$)$_6$O</td>
<td>Oxyapatite</td>
<td>1.67</td>
</tr>
<tr>
<td>HA</td>
<td>-</td>
<td>Ca$_{10}$(PO$_4$)$_6$(OH)$_2$</td>
<td>Hydroxyapatite</td>
<td>1.67</td>
</tr>
<tr>
<td>TTCP</td>
<td>-</td>
<td>Ca$_4$(PO$_4$)$_2$O</td>
<td>Tetracalcium Phosphate</td>
<td>2.00</td>
</tr>
</tbody>
</table>

The chemical formula of HA is Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ with the Ca/P ratio of 1.67. According to Dorozhkin (2010, 2011) the unit cell of HA comprises Ca, PO$_4$ and OH$^-$ ions arranged in apatite structure, Figure 2.2. Thus HA has hexagonal crystal structure with the Hermann-Mauguin space group notation of P6$_3$/m. The dimensions of the unit cell are $a = b = 9.43$ Å and $c = 6.89$ Å (Yashima et al. 2003).

2.1.2.1. Thermal Behaviour

Temperature in thermal plasma are normally quite high and can reach to temperatures $> 10000$ K. If the HA powder particles are exposed to these high temperatures, they decompose to different phases. Therefore, HA coatings can contain many phases each with a different crystal structure, chemical composition and morphology as compared to the original powder fed into the system. In order to
obtain a sound coating with the desired phases and composition, the effects of exposure to high temperatures on the depositing phases and their morphology must be thoroughly understood. According to Carayon and Lacout (2003) heating of HA in plasma torches leads sequentially to 1) evaporation of water, 2) dehydroxylation and 3) decomposition.

Figure 2.2 Structure of Hydroxyapatite (Yashima et al. 2003)

Hydroxyapatite is highly water-absorbant material. Water can stay both on the surface of the powder and trapped within the pores. When HA is heated, the first change to occur is that water will evaporate and move out of hydroxyapatite. At elevated temperatures, the structure experiences “dehydroxylation”, i.e. hydroxyapatite looses its OH⁻ (hydroxyl) group progressively. According to Carayon and Lacout (2003) dehydroxylation reaction may be written as:

\[
\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\square_x + x\text{H}_2\text{O} \tag{eqn. 1}
\]

(hydroxyapatite) → (oxyhydroxyapatite)
\[
\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2\ldots2x} \xrightarrow{\text{Oxyhydroxyapatite}} \text{Ca}_{10}(\text{PO}_4)_6\text{O}_x \xrightarrow{\text{Oxyapatite}} \ \\
(1-x)\text{H}_2\text{O}
\]
(Eqn. 2)

Where □ is vacancy and x < 1

Oxyhydroxyapatite (OHA), which is a by-product, deficient of hydroxyl ion, is formed in the first step in this process. It consists of a bivalent oxygen ion, and a vacancy substitute for two monovalent OH- ions of HA, which means that there are many vacancies in the structure (Sridhar, 2010). Apart from these, there is another possible product which might be produced after dehydroxlation reaction, called oxyapatite. However, Heimann (2006) claimed that oxyhydroxyapatite and oxyapatite have tendency towards transformation to hydroxyapatite when they are exposed to a water-containing environment.

Before the critical temperature is reached, HA sustains its lattice structure during dehydroxylation process and hydrated again upon cooling. However, when the critical temperature is exceeded, the dehydroxylation reaction will become irreversible. This phenomenon is known as decomposition. As a result of these decomposition reactions, other calcium phosphates; e.g. β-tri-calcium phosphate (β-TCP) or/and tetra-calcium phosphate (TTCP) may evolve. The reactions leading to the formation of β-tri-calcium phosphate (β-TCP) and tetra-calcium phosphate (TTCP) are given below (Sridhar et al. (2003), Heimann (2006)). As shown below both phases later transform into calcium oxide.

\[
\text{Ca}_{10}(\text{PO}_4)_6\text{O}_x \xrightarrow{\beta} 2\text{Ca}_3(\text{PO}_4)_2 (\beta) + \text{Ca}_4(\text{PO}_4)_2\text{O}
\]
(Eqn. 3)

(oxyapatite) → (tricalcium phosphate) + (tetracalcium phosphate)

\[
\text{Ca}_3(\text{PO}_4)_2 \rightarrow 3\text{CaO} + \text{P}_2\text{O}_5
\]
(Eqn. 4)

(tricalcium phosphate) → (calcium oxide) + (phosphorus pentoxide)

\[
\text{Ca}_4(\text{PO}_4)_2\text{O} \rightarrow 4\text{CaO} + \text{P}_2\text{O}_5
\]
(Eqn. 5)

(tetracalcium phosphate) → (calcium oxide) + (phosphorus pentoxide)
There is an overall agreement about the reaction mechanisms during the thermal decomposition of HA. However, it is still doubtful at what temperatures these reactions take place. According to Deram et al. (2003), Heimann (2006) and Sridhar et al (2003), this is probably due to the uninstant nature of the reactions which could take place over a wide range of temperatures. The reaction temperature is determined by many factors including the process environment and composition of HA. Various techniques are available for the determination of the reaction temperatures; Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD) and Differential Thermal Analysis (DTA).

Because of the uncertainty mentioned above, rather than a specific temperature, a range of temperatures are reported. As an example, Heimann (2006) and Sridhar et al (2003) reported that the evaporation of water from hydroxyapatite occurs over a wide temperature range, namely, from about 25°C and 600°C. The total weight loss of absorbed water is reported to be as high as 6.5 wt %. Table 2.3 shows reactions and the range of corresponding temperatures as they occur from room temperature to 1730°C.

### Table 2.3 Thermal effects on hydroxyapatite adapted from Carayon & Lacout, (2003), Dorozhkin, (2012), Heimann, (2006).

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation of absorbed water</td>
<td>25 – 600°C</td>
</tr>
<tr>
<td>Decarbonation</td>
<td>600 – 800°C</td>
</tr>
<tr>
<td>Dehydroxylation of HA forming partially dehydroxylated (OHA) or completely dehydroxylated oxyapatite (OA)</td>
<td>800 – 900°C</td>
</tr>
<tr>
<td>HA decomposes to form β-TCP and TTCP</td>
<td>1050 – 1400°C</td>
</tr>
<tr>
<td>β-TCP is stable</td>
<td>&lt; 1120°C</td>
</tr>
<tr>
<td>β-TCP is converted to α-TCP</td>
<td>1120 -1470°C</td>
</tr>
<tr>
<td>Melting temperature of HA</td>
<td>1550°C</td>
</tr>
<tr>
<td>Melting temperature of TTCP, leaving behind CaO</td>
<td>1630°C</td>
</tr>
<tr>
<td>Melting of TCP</td>
<td>1730°C</td>
</tr>
</tbody>
</table>
2.1.2.2. Requirements in HA

The main application area of HA-coated implants is orthopedics and dentistry. This is because the cementless nature of the system combines good mechanical properties like strength with the ease of fabrication. Also, hydroxyapatite increases the biocompatibility of the implant significantly. When the HA coated implant is implanted to the body, it establishes physical bond with the bone and as a result, an excessive interfacial strength is obtained in a short while. All these arises because the structure and composition of the HA is very similar to human bones. The main parameter which determines the performance of the implant is stability and adherence of the interfaces; implant-HA interface and HA-bone interface. In both interfaces, the nature of coating with its properties affect the bondings that are established (Dorozhkin, 2012).

Sridhar (2010) studied the interaction between hydroxyapatite and the tissue. The results are summarised in Figure 2.3. Bonding begins with covering the HA coatings by tissues, Figure 2.3(a). During this process, collagens have position between the coating and tissues, Figure 2.3(b). Proteins were then adsorbed by the coating surface. Calcium phosphate compounds are capable of doing this, but hydroxyapatite among them has the most important role in terms of adsorbing proteins with a high capacity. Figure 2.3(c) shows the calcification following the adsorption which occurs at the interface, with bone minerals. As the implant integrates with the body, the bonding zone decreases down to 0.05–0.2 μm, Figure 2.3(d). Thus, hydroxyapatite coatings are very important to provide biocompatibility to improve osseointegration.

Features such as high purity, phase stability, high level of crystallinity as well as low porosity and the good adherence to implant are essential requirements for hydroxyapatite. Amorphous hydroxyapatite, i.e. low degree of crystallinity, in the coating may dissolve rapidly in body fluid so it will not be desirable. The chemical content of the coating must promote bone growth with quickly integrating the implant to the body (Dorozhkin (2010) and Shepherd et al. (2012)).
2.2 Thermal Plasma Spraying of Hydroxyapatite

Surface coating is very common practice in many sectors of the industry. For medical applications, a variety of methods are available (Dorozhkin, 2012). These are sol-gel technique, dip coating, ion beam deposition, pulsed laser deposition, magnetron sputtering and thermal plasma spraying. They are chosen depending on the specific application. Thermal plasma spraying is very common in medical applications.

There are two alternatives in thermal plasma; DC plasma and RF plasma. Schematics of these two methods are given in Figure 2.4. DC plasma torches are widely used to produce coatings resistant to wear, corrosion and high temperature. For example, plasma-sprayed coatings provide turbine blades to resist up to 1200°C and also provide wear-resistance to prosthetic implants (Boulos, 1991).

The DC torches are usually operated at atmospheric pressure. The torch contain anode, cathode, a structure that allow the injection plasma-forming gas into the gap between the electrodes, Figure 2.4.

Argon or nitrogen are used as the plasma gas. The plasma is usually initiated by a high voltage pulse applied to the electrode generating an electric arc between the cathode and anode. The plasma temperature reaches very high values (e.g. > 10000 K), which ionizes the flowing gas (Boulos, 1991). Power levels of the DC torches
cathode and anode. The plasma temperature reaches very high values (e.g. > 10000 K), which ionizes the flowing gas (Boulos, 1991). Power levels of the DC torches can be between 10 and 100 kW, currents: 250 -1000 A, the voltage: 30 and 100 V. Normally gas flow rates are between 20 and 150 slpm (standard liters per minute). Ar, and N₂ are most common, though when needed He, H₂, O₂, and mixtures of them could also be used as plasma gas (Pablo et al. 2006).

Figure 2.4 Schematics of a DC plasma (left) and an inductively coupled RF plasma-spraying system (right).

Figure 2.4 shows a schematic drawing of a radio frequency (RF) plasma torches. They have no electrodes so they are cleaner than DC torches as they have no contaminations arising from the electrodes. Plasma is produced by the energy provided with an RF power generator through the electromagnetic field of the induction coils. The R.F. plasma has high enthalpy, large plasma volume with low gas velocity. Thus when powders are injected into the plasma they have long residence time which would allow melting of the particles and sometime to partial evaporation (Boulos, 1991).
RF plasma torches comprise an inner quartz tubes, inside of which central (plasma) gas is maintained. Outside the tube a sheath gas is maintained so as to protect the torch from the high temperature of the plasma. The other units of the torches, injection probes and induction coils are also water-cooled to protect them against high temperature.

The frequency range in R.F. plasma is typically between 200 kHz to 40 MHz. The power ranges from 15 kW to up to 60 kW for most cases, though examples do exist where the power is high as 1.0 MW (Boulos, 1991).

One of the main difference between R.F. plasma and D.C. plasma is related to the torch. In the case of R.F. plasma, due to induction coils, the torch is normally stationary. Thus during coating, only substrate can be manipulated so as to produce a uniform coating. This is in contrast to D.C. plasma torch which due to its simpler structure, can be manipulated also. This ability of manipulation provides a considerable advantage during coatings as not all substrates are easy to manipulate.

The particles are fed to the plasma torch with a carrier gas. As the particles contact with the plasma, they are partially melted due to high temperature. They accelerate towards the metallic substrate, they re-solidify and create a characteristic coating morphology consisting of splats, voids and some porosity on the substrate.

HA coatings of medical implants using D.C. plasma were carried out by Lu et al. (2002), Sun et al. (2003), Carayon et al. (2003), Cizek & Khor, (2012), Inagaki et al. (2003), Inagaki et al. (2006), Roy et al. (2011), Hasan et al. (2013), Tomaszek et al. (2007) and Jaworski et al. (2010).

Sun et al. (2003) investigated plasma sprayed hydroxyapatite coatings in terms of their microstructure. They concluded that the crystallinity of the coating decreases both as the plasma power increases. Hydroxyapatite particles melt completely or partially because of high plasma temperature. For this reason, hydroxyapatite may
decompose to other phases. This results in a typical lamellar structure with splat formation.

Cizek & Khor (2012) studied the effects of in-flight temperature and velocity of hydroxyapatite powder particles on the coatings. Hydroxyapatite powder used in the coating were spherical and approximately 40μm in size. Six combinations of the system parameters were selected; low, medium and high in-flight velocities at different temperatures. It was found that the calcium oxide (CaO) content decreased as the temperature increased and also tetra-calcium phosphate (TTCP) phase was present in the coatings obtained with high plasma temperature. Calcium pyrophosphate (CPP) phase were also observed in some of the coatings. They concluded that the in-flight velocity was the most effective parameter controlling the morphology of the coating followed by the plasma temperature. In this study, contrary to the general expectation, with high plasma temperature hydroxyapatite powder yielded coatings with well defined splat formation and whereas at low temperature the coating was more of bulk type.

Lu et al. (2002) investigated the stand-off distance and the power loading in D.C. plasma coating of implants. Hydroxyapatite was 10-20 μm in size. Hydroxyapatite coatings were prepared with the stand-off distances of 80, 120, 160 and 200 mm at plasma power of 30 kW and 40 kW. The stand-off distance was not very effective on the phase make up of hydroxyapatite coating prepared with 30 kW. However, the case was different with 40 kW. They observed that the crystallinity of the coating increased with increased stand-off distance at 40 kW.

Carayon & Lacout (2003) carried out a detailed investigation of D.C. coatings as it influences Ca/P atomic ratio in the coatings. They observed that hydroxyapatite decomposes during the plasma spraying; amorphous phase formed in addition to phases such as tricalcium phosphate (TCP), tetracalcium phosphate (TeCP), calcium oxide (CaO) and oxyhydroxyapatite (OxyHA). A number of plasma sprayed hydroxyapatite coatings were analyzed and the Ca/P ratio of these coatings were determined with values that varied from 1.50 and 1.67.
HA coatings of implants with R.F. plasma were investigated by Inagaki et al. (2003), Inagaki et al. (2006), Roy et al. (2011), Hasan et al. (2013).

Roy et al. (2011) prepared hydroxyapatite coatings on Ti substrate with normal and supersonic plasma nozzles at different plate powers and working distances. Their analyses showed that the normal plasma nozzle cause phase decomposition and high amorphous calcium phosphate formation. Coatings prepared with supersonic nozzle, on the otherhand, retained the crystallinity and the phase purity of hydroxyapatite because of short residence time. Using supersonic nozzles, they also studied the power loadings and different working distances as given in Table 2.4.

**Table 2.4** Experimental parameters used in the effect of type of nozzle on experiments (Roy et al. 2011).

<table>
<thead>
<tr>
<th>Experimental Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (kW)</td>
<td>22, 25, 28</td>
</tr>
<tr>
<td>Working distance (mm)</td>
<td>90, 110, 130</td>
</tr>
<tr>
<td>Central gas flow rate (slpm)</td>
<td>25 Ar</td>
</tr>
<tr>
<td>Sheath gas flow rate (slpm)</td>
<td>60 Ar + 6 H₂</td>
</tr>
<tr>
<td>Carrier gas flow rate (slpm)</td>
<td>10 Ar</td>
</tr>
</tbody>
</table>

Working distance had significant influence on phase decomposition, while plate power had no significant effect. The phase decomposition in the coating at working distance of 90 mm was more than that of the coatings at 110 and 130 mm. Therefore, it is concluded that the type of nozzle, working distance as well as power are all influential on the crystallinity of the coating.

Hasan et al. (2013) carried out a similar study dealing with the stand-off distance and power. The coatings were prepared with different powers, from 20 to 40 kW and stand-off distance range from 8 to 16 cm, Table 2.5. The increase in power which was made together with the increase in the stand-off distance decreased crystallinity
and reduced the fraction of HA in coatings. The coatings in addition to HA contained β-tricalcium phosphate (β-TCP), tetra-calcium phosphate (TCP) and calcium oxide (CaO). In addition, with increased power the coatings were smooth.

**Table 2.5** Experimental parameters used in the effect of power and stand-off distance experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (kW)</td>
<td>20, 30, 40</td>
</tr>
<tr>
<td>Working distance (mm)</td>
<td>80, 110, 160</td>
</tr>
<tr>
<td>Primary gas flow rate (Ar) (slpm)</td>
<td>50</td>
</tr>
<tr>
<td>Secondary gas flow rate (He) (slpm)</td>
<td>6, 9, 12</td>
</tr>
<tr>
<td>Carrier gas flow rate (Ar) (slpm)</td>
<td>3</td>
</tr>
</tbody>
</table>

Inagaki et al. (2003) prepared three different coatings. These are hydroxyapatite coating on its own, Ti coating followed by HA coating and coating with HA+Ti composite powder. The bond strength was under 5 MPa for pure hydroxyapatite coating. This value was 23 MPa for Ti coating followed by HA coating. The value was highest with composite coating which had a value of 40 MPa. They also examined the bond strength with different powers ranging from 11 kW to 27 kW. The bond strength was highest at 17 kW where HA/Ti composite coating yielded a bond strength of 50.2 MPa.

In a similar study, Inagaki et al. (2006) investigated composite coating; HA and Ti on Ti substrate with R.F. plasma with powers from 10 to 30 kW. The parameters used are given in Table 2.6. The feeding of the HA and Ti powders was controlled by two feeders. The coating produced was rich in Ti at the bottom close to the substrate and was HA-rich at the top. The bond strength of the coating was better (40–65 MPa) when sprayed with plasma gas containing Ar+N₂ compared to that with Ar+O₂. They also observed that Ti coatings without HA contained titanium nitride and titanium dioxide as well as Ti due to spraying with Ar+N₂ and Ar+O₂. Different morphologies were observed in the coatings depending on the plasma gas compositions, Ar+N₂ and Ar+O₂.
Table 2.6 Experimental parameters used in effect of gas composition experiments (Inagaki et al. 2006).

<table>
<thead>
<tr>
<th>Experimental Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma power (kW)</td>
<td>10-27</td>
</tr>
<tr>
<td>Plasma frequency (Mhz)</td>
<td>4</td>
</tr>
<tr>
<td>Plasma gas</td>
<td>Argon+1-6 % oxygen or argon+1-6% nitrogen</td>
</tr>
<tr>
<td>Flow rate of plasma gas (L/min)</td>
<td>50</td>
</tr>
<tr>
<td>Feed rate of Ti power (g/min)</td>
<td>0.15-0</td>
</tr>
<tr>
<td>Feed rate of HA powder (g/min)</td>
<td>0-0.1</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Argon</td>
</tr>
<tr>
<td>Flow rate of carrier gas (L/min)</td>
<td>5</td>
</tr>
<tr>
<td>Spray distance (cm)</td>
<td>28-35</td>
</tr>
</tbody>
</table>

Tomaszek et al. (2007) tried to improve multilayer coatings on the titanium substrate by using suspension plasma spraying. In this method, rather than feeding the powder precursors, the coating is achieved by feeding the powders suspended in a suitable solution. Firstly, hydroxyapatite was coated on the TiO$_2$ coated substrate. The coatings were gradually changed from pure TiO$_2$ to pure HA at the top. The results showed that suspension plasma spraying enhanced the interfacial strength with TiO$_2$ coating. When the coatings were prepared with high power rates, e.g. 40 kW, less pores and better cohesion were observed. However, this has led to decomposition of hydroxyapatite into α-TCP, β-TCP, TTCP and CaO.

Jaworski et al. (2010) investigated suspension plasma sprayed TiO$_2$ and hydroxyapatite coatings as well as their multilayer coatings on stainless steel and titanium substrates. The total coating thickness was between 10 and 150 μm. The
suspensions in the distilled water, ethanol and their mixtures were used in the process. Suspension was fed to the system via peristaltic pump. The injection of suspension was carried out by using an atomizer injector or a continuous stream one. Anatase and rutile was found in the titanium oxide coating. Hydroxyapatite coatings consist of HA, \(\alpha\)-TCP, \(\beta\)-TCP and amorphous calcium phosphate (ACP). The rapid cooling in the coating caused the formation of amorphous calcium phosphate.

As seen in the literature, R.F. and D.C. plasma are widely used for hydroxyapatite coating. Functional and biocompatible coatings which have desired properties can be produced with either of these methods. However, R.F. plasma system has no electrode like D.C. plasma so R.F. plasma is more preferable in terms of producing a clean coatings. In addition, it appears that suspension plasma spraying is better than the conventional coatings because it enhances interface strength especially with the use intermediate layer.
CHAPTER 3

CHARACTERIZATION OF HYDROXYAPATITE COATED A HIP IMPLANT

This part deals with a characterization of a commercially produced hydroxyapatite coated implant. The implant which was sprayed via R.F thermal plasma was characterized with respect to the intermediate layer and the coating.

Figure 3.1 The total hip implant.

3.1 Implant

A photograph of a hip implant characterized in this study is shown in Figure 3.1. With exception of Co-Cr substrate, two different regions could be identified on the implant. These are i) coating-white in colour and ii) a dark circular region which appear as intermediate layer, Figure 3.2.

The implant was cut longitudinally with electrical discharge machining (EDM) yielding a slice approximately 5 mm in thickness. A macro photograph of a cross-section of the slice is shown in Figure 3.2(c). Here the coating appears as the outer layer over the base metal.
3.1.1. Intermediate layer

SEM images of the intermediate layer are shown in Figure 3.3. It is seen that the structure comprises different structural sizes; some are micron or submicron in size.

The cross-sectional view of the slice taken from the implant is shown in Figure 3.4. The coating belongs to intermediate layer in this structure. Measurement over the intermediate layer yielded values varying between 80 and 100 μm.

EDS analysis from intermediate layer is given in Figure 3.5, the intermediate layer contains titanium, nitrogen and oxygen. However, the quantitative analyses of nitrogen and oxygen cannot be conducted in EDS systems. Therefore, it can be concluded that the system contains these elements, but their amounts cannot be known with this technique.
Intermediate layer was also examined with EDS mapping, Figure 3.6. This shows that the intermediate layer is titanium. Oxygen seems to be concentrated in specific regions, Figure 3.6(c), implying that titanium is partially oxidized.

**Figure 3.4** Cross-sectional SEM images of intermediate layer.

**Figure 3.5** EDS result for intermediate layer.
Figure 3.6 EDS mapping in the cross-section of the implant (coating layer was removed).

Refined x-ray diffraction pattern of the intermediate layer is given in Figure 3.7. The peaks of titanium (Ti) and titanium nitride (TiN) were observed. The main phases are Ti and TiN. The structure is hexagonal and the lattice parameter of Ti is $a: 2.96 \, \text{Å}$ and $c: 4.69 \, \text{Å}$.

Figure 3.7 Refined x-ray diffraction patterns of the intermediate layer.

3.1.2. Coating

The surface morphology of the coating, as examined with SEM, is shown in Figure 3.8. The morphology is typical of implants that are coated with plasma spraying. Thus the coating revealed individual splat formation as well as partially melted spherical particles with occasional presence of pores in the overall structure.
The cross-sectional view of the slice taken from the implant is shown in Figure 3.9. The coating layer is clearly visible in this structure. Measurement over the coating yielded values varying between 120 and 200 μm the average being 162.2 ± 39.7μm.

EDS analysis of the coating is given in Table 3.1. As seen in the table the elements present comprise Ca and P. The quantities is such as to yield Ca/P ratio of 1.67, the value expected from medical grade hydroxyapatite.

In order to determine the “structural” size of coating, a cross-sectional SEM image was analyzed with a square grid of 20, 30 and 40 microns. As shown in Figure 3.10, the structural size shows a closer matches with a 30 micron grid. Thus the structural
size of the coating is close to 30 microns which is also probably the size of spraying powder.

Table 3.1 Atomic percentage of elements for surface coating.

<table>
<thead>
<tr>
<th>Element</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>62.61</td>
</tr>
<tr>
<td>P</td>
<td>37.39</td>
</tr>
</tbody>
</table>

Figure 3.10 Square grids of size 20, 30 and 40 micron, superimposed on the coatings.

Qualitative phase analysis has yielded phases of hydroxyapatite (Ca$_5$(PO$_4$)$_3$OH), β-tricalcium phosphate (β-Ca$_3$(PO$_4$)$_2$) and tetracalcium phosphate (Ca$_4$(PO$_4$)$_2$O). Rietveld refinement of the pattern, shown in Figure 3.11, showed that the coating
was predominantly hydroxyapatite. The weight fraction of hydroxyapatite was 86.3 \%, this was followed by tetracalcium phosphate (13.7 \%) and a trace amount of $\beta$-tricalcium phosphate (0.04 \%), Table 3.2.

![Refined XRD patterns of the coating at Maud.](image)

**Table 3.2** Weight fraction of phases according to refinement results for coating.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Phase 1 (HA)</th>
<th>Phase 2 (TeCP)</th>
<th>Phase 3 ((\beta)-TCP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight fraction of phase</td>
<td>0.86</td>
<td>0.14</td>
<td>Trace (0.0004)</td>
</tr>
</tbody>
</table>

### 3.1.3. Summary

The implant was characterized with respect to the coating. Microscopic examination showed presence of intermediate layer between the base metal and the coating. The intermediate layer is mainly Ti. Cross-sectional observation showed that coating thickness of intermediate layer varies from 80 to 100 \(\mu\)m. Characterization of the coating layer showed a coating structure where the particles making up the coatings were approximately 30 micron in size. EDS results showed that the coating material is hydroxyapatite with Ca/P ratio of 1.67. The total coating thickness is 160 \(\mu\)m of which 80-100 \(\mu\)m was intermediate layer and 60-80 \(\mu\)m were the coatings.
CHAPTER 4

DESIGN AND CONSTRUCTION OF A THERMAL PLASMA COATING CHAMBER

Thermal plasma system used in this study was an R.F. 30 kW system (Tekna Plasma System Inc.) which incorporated nanopowder reactor, Figure 4.1. The system includes the following principal components; RF (radio frequency) generator with Faraday cage, Tekna’s PL-35 induction plasma torch, nanopowder reactor, powder collectors, cyclone, nanopowder collector and vacuum unit. The system also include closed circuit deionized water, gas control console, touch screen operator interface.

Figure 4.1 Schematic of the induction thermal plasma system with nanopowder reactor.
4.1 Construction of a Coating Reactor

The present system shown in Figure 4.2(a) has an integrated nanopowder reactor shown separately in Figure 4.2(b). The system is quite versatile and could be used together with a coating reactor or with a spheroidization unit.

In order to construct a sustainable coating reactor, it is necessary to comply with two reference points. These points are shown in Figure 4.2(b) on the existing nanopowder reactor. Reference point T is the point where the torch is located and reference C is the connection to the nanopowder collector.

![Figure 4.2](image)

Figure 4.2 The photographs showing (a) the induction plasma system and (b) nanopowder reactor.

A coating unit that was constructed is shown in Figure 4.3. The coating unit consists of the coating chamber, a manipulator attached to the chamber, one bottom collector and one cyclone.

Technical drawing of coating chamber is given in Figure 4.4. The chamber was constructed with 304 stainless steel due to its good corrosion resistance and easy welding. The chamber together with other parts had a double-wall construction so as to allow the circulation of cooling water during the coating operation. The wall thickness was 1.5 mm with the a spacing of 5 mm totalling to 8 mm.
Figure 4.3 Schematics of the coating unit (a,b).

The basic dimensions of the reactor were 460 mm in diameter and 860 mm in length, Figure 4.4. The chamber had a door at the left hand side as shown in Figure 4.5, which had an O-ring seal of diameter 400 mm. On the right handside, the coating chamber had a the manipulator attached to it. There are two viewing ports, one of them is on the reactor door and the second one is front edge, as seen in Figure 4.4.

Figure 4.4 Technical drawings of the coating chamber with basic dimensions.
Figure 4.5 View the coating unit with some dimensions.
The collectors are shown in Figure 4.6. The coating chamber had a conical portion which connects the chamber to bottom collector. The purpose of this collector is to collect particles not attached to substrate that come together with aerosol flow. The gas stream makes a 90° turn at the collector which leaves behind particles that are relatively coarse.

The second bottom collector is connected to a cyclone unit with a double walled pipe. In the cyclone unit, aerosol flow is forced to make 180° turn leaving behind particles that are relatively fine. Aerosol flow is then fed to the powder collection unit before it is discharged to atmosphere via a scroll pump.

![Figure 4.6 The photograph of the bottom collectors and cyclone collector, respectively.](image)

**Water cooling**

The coating unit has a water cooling system connected to the existing thermal plasma system. Details of connections are shown in Figure 4.7. Firstly, cooling water taken from 1 inch hose typically with a pressure of 18 bar, splits into two ½ inch lines. One of these lines are connected at the bottom of the coating chamber and the other is connected to cyclone and the manipulator. Where necessary ½ inch line was then split into two 3/8 inch lines before being fed to the connectors. The return lines are constructed with the same approach.
Figure 4.7 Water flowline to reactor and from reactor.

Manipulator

The manipulator that was attached to a coating chamber is shown in Figure 4.8. The manipulator incorporates three stepping motors and provides movement in x, y and z direction. These would allow movements of \(-200 < x < 200\), \(-100 < y < 100\) and \(-75 < z < 75\) mm. The manipulator had limit switches for its safe operation. The manipulator has a changable substrate holder. The stage is driven to the intended coordinates by the Mach3 programming.

Figure 4.8 Manipulator.

The components described above are put together to form the complete coating chamber. This chamber as integrated into the existing thermal plasma system is shown in figure 4.9.
Figure 4.9 Coating chamber together with the thermal plasma system.
In this section, coating experiments carried out as trial experiments were described. A total of three groups of experiments were carried out. These were experiments related to the feed rate of powder and carrier gas, adjustments of coating thickness by multiple pass and experiments related to stand-off distance.

5.1 Experimental

Sample preparation for microscopical examination followed standard procedure. Morphology was examined via FEI NanoSEM 430 scanning electron microscope (SEM). Where necessary, chemical analysis was carried out with EDS analysis.

Structural characterization was carried out by X-ray diffraction using BRUKER Diffractometer with Cu Kα radiation. The system was operated at 40 kV and 30 mA. Data was collected at a rate of 0.1°/min. The XRD patterns were refined with Rietveld Analysis using the software Maud (Lutterotti 2011).

5.2 Substrate

Ti substrate material was a 3 mm thick plate. Microscopic images of substrate are given in Figure 5.1. EDS analysis of the plate is given in Table 5.1. According to this analysis, the substrate has composition of Ti, 7.11wt % Al and 2.59 wt % V. Due to uncertainty in EDS analysis, this composition will be referred to as Ti-6Al-4V.

X-ray diffraction pattern taken from the substrate is given in Figure 5.2. The Rietveld analysis showed that the substrate is a two phase material, the major phase is hexagonal with the lattice parameters of Ti a: 2.92 Å and c: 4.67 Å. The minor phase has bcc crystal structure with the lattice parameter of a: 3.16 Å.
Before coating, the substrate was prepared using a procedure adapted from Deligianni et al. (2001) and Balza et al. (2013). Thus the plates were sandblasted using 100-150 μm alumina particles applied to the plate at an angle of 75° angle. The treatment was carried out for 40-45 seconds with 0.6 MPa air pressure. After the
sandblasting, the plates were cleaned ultrasonically in ethanol for 10 minutes. They were then washed with deionized water.

5.3 Coating Powder

Coating powder was a medical grade HA powder (Eurocoating, Italy) 99.9 % pure. Particle size distribution of the powder is shown in Figure 5.3. This yielded d(0.5) value of 27 micron.

![Figure 5.3 Particle size distribution of coating powder hydroxyapatite.](image)

XRD pattern of the coating powder is given in Figure 5.4. The pattern comprises peaks that are compatible with hydroxyapatite (HA). There are also two small peaks arising from a CaO. The amount of CaO is quite small (0.4 %). Structural parameters determined from Rietveld refinement of the pattern is given in Table 5.2.

<table>
<thead>
<tr>
<th>Weight fraction</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyapatite</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>a=9.42</td>
</tr>
<tr>
<td></td>
<td>c=6.87</td>
</tr>
</tbody>
</table>

5.4 Trial Experiments with the Coating Chamber

Parameters varied in this work were powder feed rate, carrier gas feed rate, multipass coating and the stand-off distance. In all experiments, thermal plasma was operated
under standardized conditions, with parameters given in Table 5.3.

Figure 5.4 Refined XRD pattern of the coating powder at Maud.

Table 5.3 Standardized parameters used in the all experiments.

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Central gas</strong> (Ar) (slpm)</td>
<td></td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td><strong>Sheath gas</strong> (Ar+H₂) (slpm)</td>
<td></td>
<td>60+6</td>
<td>60+6</td>
<td>60+6</td>
<td>60+6</td>
</tr>
<tr>
<td><strong>Plate travel velocity</strong> (mm/min)</td>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

5.4.1. Feed Rate of Powder and Carrier Gas

Experiments carried out to examine the effect of feed rate and carrier gas is summarized in Table 5.4. As seen in the table, a total of four experiments were carried out. First, the coatings were prepared with different powder feed rate (experiment 1, 2 and 3). Then, carrier gas flow rate was modified (i.e experiment 3 and 4). In all experiments the substrate velocity and the stand-off distance were the same, Table 5.4. The substrate were coated in the middle portion of the plate (4 cm by 4 cm) and passed underneath of the torch twice; forward and backward.

SEM images of the cross-section of coated substrate are given in Figure 5.5. It is seen that with a feeding rate of 1 g/min, the coating is rather thin with a thickness of
5-6 micron, Figure 5.5(a). With a faster feed rate (6 g/min), the coating thickness increases substantially reaching values of 10 and 20 μm, Figure 5.5(b).

Table 5.4 Parameters used in the experiments powder feed rate and carrier gas.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Powder feed rate (g/min)</th>
<th>Carrier gas (Ar) (slpm)</th>
<th>Power (kW)</th>
<th>Stand-off distance (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>5</td>
<td>20.1</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>5</td>
<td>19.2</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
<td>5</td>
<td>19.2</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>18</td>
<td>7</td>
<td>20.4</td>
<td>10</td>
</tr>
</tbody>
</table>

It should be noted that the coating formed is well bonded with a feed rate of 1 g/min. This is not the case with 6 g/min where the interface seems to be separated. This is even worse when the feed rate was increased to 18 g/min, Figure 5.5(c).

The experiment reported above were carried out with Ar carrier gas where the flow rate was 5 slpm. For the purpose of examining the effect of carrier gas, the flow rate was increased to 7 slpm. This experiment however was not successful, Figure 5.6. The coating did not seem to adhere to the surface. This is probably because hydroxyapatite did not melt completely because of the high passage rate of powder through the torch.

EDS results obtained from the coatings are given in Table 5.5. As seen in the table, the elements present comprise Ca and P. The quantities are such that Ca/P ratio range from 1.80 to 2.71. It should be noted that lowest value is obtained with fast delivery, i.e, with high flow rate of carrier gas. The value of Ca/P=1.80 is higher than the targeted value of Ca/P=1.67. This implies that powders stay too long in the plasma whereby causing the decomposition of HA.
Figure 5.5 Cross-sectional SEM images of HA-coated Ti-6Al-4V plate for a) experiment 1 (low feed rate), b) experiment 2 (medium feed rate) and c) experiment 3 (high feed rate).

Figure 5.6 The photographs of the HA-coated Ti-6Al-4V plate with high carrier gas.

Typical XRD pattern of the coated sample is given in Figure 5.7. Here some of the peaks come from the substrate underneath. Eliminating the Ti peaks, here the pattern, unlike that reported in Figure 5.4 consist of many phases; the coating consists of tetracalcium phosphate (TeCP) (Ca₄(PO₄)₂O), β-tricalcium phosphate (β-Ca₃(PO₄)₂), α-tricalcium phosphate (α-Ca₃(PO₄)₂), calcium oxide (CaO) and hydroxyapatite (Ca₅(PO₄)₃OH), Table 5.6.
Table 5.5 Ca/P atomic ratio determined from EDS analysis of coatings.

<table>
<thead>
<tr>
<th>Experiment 1 (low feed rate)</th>
<th>Experiment 2 (medium feed rate)</th>
<th>Experiment 3 (high feed rate)</th>
<th>Experiment 4 (high carrier gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.59</td>
<td>2.54</td>
<td>2.5</td>
<td>1.68</td>
</tr>
<tr>
<td>2.52</td>
<td>2.61</td>
<td>3.06</td>
<td>1.98</td>
</tr>
<tr>
<td>1.88</td>
<td>2.17</td>
<td>2.56</td>
<td>1.73</td>
</tr>
<tr>
<td>Ca/P</td>
<td>1.99 ± 0.477</td>
<td>2.44 ± 0.240</td>
<td>2.71 ± 0.307</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>3.06</td>
<td>1.80 ± 0.164</td>
</tr>
</tbody>
</table>

Figure 5.7 Rietveld refired XRD pattern of coating obtained with high powder feed rate.

5.4.2. Adjustment of coating thickness: multiple pass

Normally coating involves a multiple pass operations. So as to see the effect of multiple pass, separate experiments were carried out in which coatings were obtained in three and four passes. Powder feed rate was 6 g/min and the carries gas flow rate was 5 slpm, Table 5.7. The other parameters were the same as those reported in Table 5.3.

Table 5.6 Weight fraction of phases present in the coating obtained with high powder feed rate.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Weight fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyapatite (Ca$_5$(PO$_4$)$_3$OH)</td>
<td>0.196</td>
</tr>
<tr>
<td>Tetracalcium phosphate (TeCP)</td>
<td>0.08</td>
</tr>
<tr>
<td>β-tricalcium phosphate (β-Ca$_3$(PO$_4$)$_2$)</td>
<td>0.27</td>
</tr>
<tr>
<td>α-tricalcium phosphate (α-Ca$_3$(PO$_4$)$_2$)</td>
<td>0.07</td>
</tr>
<tr>
<td>Calcium oxide (CaO)</td>
<td>0.12</td>
</tr>
<tr>
<td>Titanium (Ti)</td>
<td>0.26</td>
</tr>
<tr>
<td>TiV</td>
<td>0.004</td>
</tr>
</tbody>
</table>
Table 5.7 The parameters used in the multiple pass experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder feed rate (g/min)</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Carrier gas (Ar) (slpm)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stand-off distance (cm)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Power (kW)</td>
<td>19.8</td>
<td>19.2</td>
</tr>
</tbody>
</table>

Figure 5.8 Cross-sectional SEM images of HA-coated Ti-6Al-4V plate with a) three passes and b) four passes.

Typical micrographs taken from the cross-sections of the coatings obtained with a multi-pass treatment are shown in Figure 5.8. It is seen that coatings are quite thin with thicknesses varying from 8 and 27 micron. Ca/P values obtained from EDS analysis are reported in Table 5.8. The values are similar to those reported above.

Table 5.8 Ca/P atomic ratio determined from EDS analysis of coatings.

<table>
<thead>
<tr>
<th>Ca/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 5 (3 passes)</td>
</tr>
<tr>
<td>1.98</td>
</tr>
<tr>
<td>Ca/P</td>
</tr>
</tbody>
</table>
5.4.3. Stand–off distance

Distance between the torch and the substrate is referred to as the stand-off distance and this is the most crucial parameter of coating. This distance in the present work was measured from the bottom face of the torch and had a value of 8, 10 and 13 cm. Other parameters of coatings are summarized in Table 5.9. Coatings were applied to the mid portion of the travelling substrate in two-passes.

With stand-off distance of 13 cm, the coatings did not adhere to the substrate, Figure 5.10. The coating obtained from closer stand-off distance of 10 and 8 cm were better, as could be seen in SEM images shown in Figure 5.9. The best result was obtained with 8 cm stand-off distance where the coatings had a thickness of approximately, 80-90μm.

<table>
<thead>
<tr>
<th>Table 5.9 Parameters used for stand-off distance experiments.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment</strong></td>
</tr>
<tr>
<td><strong>Powder feed rate</strong> (g/min)</td>
</tr>
<tr>
<td><strong>Stand-off distance</strong> (cm)</td>
</tr>
<tr>
<td><strong>Power</strong> (kW)</td>
</tr>
<tr>
<td><strong>Carrier gas</strong> (Ar) (slpm)</td>
</tr>
</tbody>
</table>

**Figure 5.9** Cross-sectional SEM images of HA-coated Ti-6Al-4V plate with stand-off distance a) 8 cm and b) 10 cm.
Ca/P ratio determined from EDS analysis of coatings obtained with different stand-off distances are given in Table 5.10. As seen in the table Ca/P ratio varies from 2.76 to 2.1. With increased stand-off distance, the Ca/P ratio decreases, though the value is still higher than the target value of 1.67.

Table 5.10 Ca/P atomic ratio determined from EDS analysis of coatings.

<table>
<thead>
<tr>
<th>Ca/P</th>
<th>Experiment 7 (low distance, 8 cm)</th>
<th>Experiment 8 (medium distance, 10 cm)</th>
<th>Experiment 9 (high distance, 13 cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.03 2.78 2.48</td>
<td>2.5 3.06 2.56</td>
<td>2.21 2.27 1.81</td>
</tr>
<tr>
<td>Ca/P</td>
<td>2.76 ± 0.277</td>
<td>2.71 ± 0.307</td>
<td>2.1 ± 0.251</td>
</tr>
</tbody>
</table>

Figure 5.10 The photographs of the HA-coated Ti-6Al-4V plate with high stand-off distance, 13 cm.
CHAPTER 6

CONCLUSIONS

Thermal plasma is a common method of surface coatings applied in a number of applications; aerospace, automotive and medical. Among them, medical application is probably the most critical as the coating should satisfy a number of stringent requirements; Ca/P ratio: 1.67, high crystallinity, high bond strength at the interface.

The present work deals with radio-frequency (RF) thermal plasma spraying. The RF plasma, has the disadvantage that the torch, unlike D.C. plasma is normally stationary and can not be manipulated around the substrate. The advantage of R.F. plasma is that since no electrodes are involved extremely clean coating is possible without contamination.

In this study, a thermal plasma equipment normally designed for the synthesis of nanopowders, was modified for the coating purposes. Therefore, a coating chamber was designed and constructed which could be used interchangeable with the nanopowders reactor in the existing system. The coater has a double wall cylindrical chamber of 460 mm in diameter and 860 mm in length. The chamber is water-cooled via water circulation between the double wall. It comprises a manipulator which allows the movement of substrate in three dimensions namely -200 < x < 200, -100 < y < 100 and -75 < z < 75 mm. Thus the chamber would allow a stand-off distance of 150 mm.

A preliminary study was carried out using the coating chamber in which Ti-6Al-4V was coated with HA powder. The study has shown that the best coating was obtained when the hydroxyapatite was fed to the plasma at the lowest feed rate. Since most coatings could easily be separated from the substrate, it was concluded that it is
necessary to apply an intermediate coating between the substrate and hydroxyapatite coating for better adhesion.

The Ca/P ratio in the current experiments were all higher than 1.67, target value that could be reached with nearly pure HA. The coatings obtained in the present work, in addition to HA, included additional phases such as tricalcium phosphate (TCP), tetracalcium phosphate (TeCP), β-tricalcium phosphate (β-Ca$_3$(PO$_4$)$_2$), α-tricalcium phosphate (α-Ca$_3$(PO$_4$)$_2$) and calcium oxide (CaO).

Lastly it may be stated that the low stand-off distance and the low feed rate are best for adhesion but these conditions negatively effect the Ca/P ratio. This implies that the powders stay too long in the plasma, i.e. the residence time is too long. A reduction in power or increased flow rate of plasma gas would reduce the residence time and could improve the Ca/P ratio. Other alternative would be the use of suspension plasma spraying where the exposure to high temperature may be controlled in a more efficient way.
REFERENCES


APPENDICES

APPENDIX A

A CHARACTERIZATION OF A CoCr ALLOY USED AS MEDICAL IMPLANT

This appendix comprises a characterization study carried out on a hip implant procured from Dinamik Travma Medikal. The implant as procured had coatings on it. Here only the base metal will be characterized.

Microscopic images of base metal are given in Figure A.1. The base metal has dendritic structure with grains noticeable at the edge.

![Microstructure of the base metal.](image)

Figure A.1 Microstructure of the base metal.

Figure A.2 shows the composition taken from matrix. According to EDS analysis the matrix has a composition of Co-61.28 %, Cr-29.97 %, Mo-7.41 % and Si-1.35 %. Occasionally the matrix has a second phase particles that are rich in Si content.

The base metal was also characterized by X-ray diffraction using BRUKER Diffractometer with copper Kα radiation. X-ray diffraction pattern taken from the base metal is given in Figure A.3. The pattern as refined with Rietveld analysis...
showed that the base metal is hexagonal with the lattice parameters of CoCr: a: 2.56 Å and c: 4.15 Å.

**Figure A.2** Microstructure and EDS analysis of the base metal. The base metal has a composition of Co, Cr, Mo and Si. Note that the base metal also has second phase particles which are richer in their Si content.

**Figure A.3** X-ray diffraction pattern of the base metal.