1 INTRODUCTION

Commercially pure Titanium (Ti 12) and Ti-6Al-4V (Ti 31) are the most suitable metallic materials as dental and medical implants because these materials exhibit good mechanical properties and corrosion resistance\(^1\). However vanadium in Ti-alloys may dissolve and form harmful metal ions which have been detected in tissue close to the titanium implant\(^2,3\). Materials of good biological properties show high rate of bone growth and high corrosion resistance in high chloride containing body fluid environment. Corrosion of implant material causes minute corrosion products to accumulate in adjacent tissues and stimulate allergy in patients.

The efficiency of metallic implants for biomedical applications can be improved by coating with biocompatible materials. Bioconductive material hydroxyapatite \([\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2, \text{(HA)}]\) is widely used as coating on the surface of the metals or alloys because they chemically connect the metal/alloy implant and bone. Due to its similarity to CaP minerals found in bone tissues, HA promotes chemical osteointegration through formation of light bond with bone. Specifically, the biocompatibility of HA and osseoconductivity behaviour of this ceramic material were confirmed and employed in medicine for more than twenty five years\(^4\).

It is found that there is significant difference between coated implants and uncoated implants in both amount of bone growth and strength with which bone adheres to implants. Stimulation of bone growth was particularly high in the case of implants coated with HA. At molecular level it has been shown that CaP ceramic acts as a substrate which facilitates cell differentiation and collagen deposition, as well as CaP precipitation\(^5\). The local increase in the concentration of calcium and phosphate causes
intense calcification and establishes a gradient of bone cell proliferation. Because of this advantageous property, hydroxyapatite-coated prosthesis could better overcome the interfacial gap between the metal/alloy implant and existing bone, thus increasing the surgical tolerance limits. Strong interfacial bond between coated metal/alloy and the bone is crucial to prevent micro movement at the metal-tissue interface and consequential failure of prosthetic device\(^6\). Furthermore, it is assumed that CaP coating protects the metal substrate from corrosion dissolution, which invariably leads to poor osteointegration.

HA coatings have been applied by variety of methods: dip coating\(^7,8\), electrophoretic deposition\(^9,10\), hot isostatic pressing\(^7\), ion beam sputtering\(^11\), ion-beam dynamic mixing\(^12\), plasma spraying\(^13\), conventional flame spraying\(^14,15\), and high velocity oxy-fuel (HOVF) combustion spraying\(^16\). Among these, plasma spray appears to be most favourable in terms of chemical control, biocorrosion resistance\(^17,18\), process efficiency\(^2\) and degree to which the surface fatigue resistance is reduced\(^19\).

Plasma spraying\(^20,21\) is considered as the suitable and cost-effective surface treatment process for various uses, e.g. mechanical protection (abrasion and wear), chemical barrier (corrosion, aggressive chemicals intrusion preservation), thermal shield, or, as in the case of hydroxyapatite coatings, used as a substitute for biological tissues. In plasma-sprayed coatings, the hot gas jet created by plasma arc expands, entrains powder particles, heats the particles, and accelerates them towards the substrate, where they impact, deform, and solidify to form a coating. The high degree of particle melting and relatively high particle velocity of plasma lead to higher deposit densities and bond strength compared to most flame and electric arc spray coatings. The high
droplet/substrate adhesion is achieved due to the high particle velocity and deformation that can occur on impact. The inert gas plasma jet, ignoring ambient air mixing effects, contributes to lower oxide content than other thermal spray processes.

Close control of the standoff distance, particle heating, and particle velocity produces lower-oxide-content microstructures. Some oxides will always be present in air plasma sprayed (APS) coatings. The spray processes are characterized by rapid solidification. Such rapid rates of cooling produce a wide range of material states from amorphous to metastable. Two structures are generally present within a coating: splat structures and intrasplat structures. Porosity is another important coating feature that strongly influences coating properties. Porosity creates poor coating cohesion and allows for higher wear and corrosion rates. Porosity is generally associated with a high number of unmelted and or resolidified particles that become trapped in the coating. Poor splat or particle cohesion leads to premature coating cracking, delamination, or spalling. In medical and dental implant prosthesis porosity is intentionally included. The porosity allows bone matter to grow into the coating, which accelerates patient healing and shortens recovery time.

However the layers deposited by plasma spray process have several disadvantages, e.g. micro-cracks, poor adhesion between the coating and substrate, phase changes due to high temperature exposure, non-uniformity in the coating density, and improper microstructural control, which could result in the failure of the implanted structure\textsuperscript{22}.

The ideal HA coating for orthopedic and dental implants would be one with low porosity, strong cohesive strength, good adhesion to the substrate, high degree of
crystallinity and high chemical purity and phase stability. Amorphous HA tend to dissolve rapidly in physiological environment, so the coating with low crystallinity quality become weak and may promote inflammatory response. The most common level of crystallinity in HA coating for biomedical use\textsuperscript{23} is about 60-70\%. Materials for medical and dental applications form a huge market, in volume as well as diversity. Depending on the specific application, different materials are used. In some applications osseointegration behaviour is the deciding factor, whereas for some material in contact with blood the prevention of platelet adhesion and subsequent clotting is the main focus. For example endosseous implants initially come into contact with blood. Thus, the nature of interaction between the blood and implanted endosseous implants may influence bone healing events in the peri-implant healing compartment. Furthermore, mechanical properties like wear, hardness and elastic modulus can have important influence on biocompatibility. In the present investigation studies were conducted to the following questions:

i. Does the HA coated metal substrates modulate platelet activity?

ii. Does the coated surface have influence on the cell viability?

At present, the plasma spray process is still partly stochastic, influenced by a large number of parameters, no matter whether they are controlled (powder used, settings of plasma spray systems, substrate materials used) or fully random. With the advancement of technology and plasma spray gun design\textsuperscript{20}, average coating densities and bond strengths are increasing, average coating oxide contents are decreasing. The powder injection geometry and conditions strongly influence the degree of particle heating/melting, thereby controlling coating porosity and oxide inclusion levels. The
distributions of gas temperature and velocity in plasma jets range widely with anode/cathode design, power, arc-gas flow rate, and gas composition.

Typical plasma jet uses argon together with another secondary (auxiliary) gas. Argon-only plasmas create relatively low-energy plasma. Nitrogen on the other hand, is one of the hottest plasma gases. Argon/helium mixtures are very often used. Helium increases the thermal conductivity of the plasma stream, increasing the heating capability of the plasma. Argon/hydrogen mixtures provide increased enthalpy over argon/helium due to the diatomic structure of hydrogen and its high collisional cross section related to its low mass.

The properties of the coatings are controlled by regulating various plasma spray parameters. Some basic parameters include power, current, distance between nozzle and substrates, plasma work gas rate and feed rate. The plasma working gas composition remains same during plasma spray process and is not generally a basic parameter that is changed during coating process. However it is considered to be an important parameter that has influence on coating properties. For example argon mixed with hydrogen gives good coating. But without hydrogen, the powder particles bounce back from the flame instead of entering it. This is because of the high velocity and viscosity of the argon gas. Plasma work gas composition also influences the thickness of the coating. For example nitrogen as carrier gas results in thicker coating as compared to the use of argon gas. Therefore, one can expect the plasma gas composition also to play a major role on the properties of HA coating.

A strict plasma control is required to optimize the property of the coating. Many investigators have studied various processing parameters to understand the phase
constitution, porosity, degree of crystallinity, OH content, microstructure and surface roughness of HA coating by regulating the basic spray parameters.

It was therefore planned to study the effect of plasma working gas composition on HA coating keeping in mind the basic parameters of plasma spray technique. The coatings were made on Ti and Ti-6Al-4V metal substrates. The plasma gas compositions selected in the present study were argon, nitrogen, argon/hydrogen, and nitrogen/hydrogen. The primary objectives of the study are:

1. To study the microstructure of substrate metal Ti and Ti-6Al-4V after plasma coating and to compare with as received metal.
2. Microstructural characterization of plasma coated HA on Ti and Ti-6Al-4V in different plasma working gas composition.
3. To study the porosity, diffusion, Ca-P ratio, crystallinity, surface roughness, and microhardness of HA coating.
4. Biological evaluation of HA coating

**THESIS LAY OUT:**

Following this introductory chapter, a detailed literature survey on the concept of heat treatment of commercially pure titanium and Ti-6Al-4V, followed by plasma spray technique, surface coating material HA and the biological effect of the coating is presented in chapter 2. Recent studies carried out on various parameters used in plasma coating and their effect on physical, chemical and biological effects were also reviewed in the survey. The survey also briefly mentions various in vivo and in vitro biocompatibility studies carried out on HA plasma coating.
The third chapter describes the materials and experimental methods used in the investigation. It contains the substrate metal composition, heat treatments, mechanical properties, HA composition, plasma coating of HA on Ti 12 and Ti 31 samples in various plasma gas compositions. A brief description of various tests employed to characterize the microstructure, chemical, mechanical and biological properties of plasma sprayed HA coating. Results are presented in chapter 4, while the chapter 5 presents the discussion on these results. The major conclusions drawn from the present investigations are summarized in chapter 6.