2 LITERATURE REVIEW

2.1. Titanium and Ti-6Al-4V

Commercially pure (CP) titanium and titanium alloys have wide range of applications in aerospace, energy, chemical and automotive industries. Some of the titanium alloys are excellent materials for biomedical use, especially as orthopedic and dental alloys. The most important characteristic features of these biomedical titanium and its alloys are high strength, low density, excellent corrosion resistance and the best biocompatibility among metallic materials. The Ti-6Al-4V alloy, originally having been developed as construction alloy for aircraft industry, belongs to the most significant alloys within the implant alloys for hard tissue replacement.

2.1.1. Crystal structure and alloy types

Titanium is an allotropic element; that is, it exists in more than one crystallographic form. At room temperature, titanium has hexagonal close-packed (hcp) crystal structure, which is referred as “alpha” (α) phase. On heating this structure transforms to a body-centered-cubic (bcc) crystal structure, called “beta” (β) phase at 882.5° C. Alloying elements can act to stabilize either α or β phase. Through the use of alloying additions, β phase can be sufficiently stabilized to coexist with α at room temperature. This fact forms the basis for the creation of titanium alloys that can be strengthened by heat treatment.

It is common to classify commercial titanium alloys into 3 categories (α, α + β, and β) according to their position in a pseudo - binary section through α-β isomorphous phase diagram, schematically shown in Fig. 2.1.
Classifying titanium alloys by their constitution ($\alpha$, $\alpha + \beta$, and $\beta$) is convenient but misleading. Therefore they are further classified in five, not three, classes of titanium alloys, depending on the microstructure and chemistries involved\(^3\). They are:

i. Alpha alloys, which contain neutral alloying elements (such as tin) and/or alpha stabilizers (such as aluminium, oxygen) only and are not heat treatable.

ii. Alpha + beta alloys, which generally contain combination of alpha and beta stabilizers and are heat treatable to various degrees.

iii. Beta alloys, which are metastable and contain sufficient beta stabilizers (such as molybdenum, vanadium) to completely retain the beta phase upon quenching, and can be solution treated and aged to achieve sufficient increase in strength.

iv. Near-alpha (Super alpha).


These classes denote the general type of microstructure after processing. An alpha alloy forms no beta phase. A near-alpha (or super alpha) alloy forms only limited beta phase on heating, and so it may appear microstructurally similar to an alpha alloy at lower temperatures. An alpha-beta alloy consists of alpha and retained or transformed beta. A (metastable) near-beta or beta alloy tends to retain the beta phase on initial cooling to room temperature, but it precipitates secondary phases during heat treatment.

2.1.2. Effects of alloying elements

Alloying elements generally can be classified as alpha or beta stabilizers. Alpha stabilizers such as aluminium and oxygen, increase the temperature at which $\alpha$ phase is stable. Beta stabilizers such as vanadium and molybdenum, result in stability of the $\beta$
phase at lower temperatures. This transformation temperature from $\alpha + \beta$ or from $\alpha$ to all $\beta$ is known as $\beta$ transus temperature. Beta transus is defined as the lowest equilibrium temperature at which material is 100% $\beta$. The $\beta$ transus is critical in deformation processing and in heat treatment.

Below the $\beta$ transus temperature, titanium is a mixture of $\alpha + \beta$ if the material contains some $\beta$ stabilizers; otherwise it is all $\alpha$ if it contains limited or no $\beta$ stabilizers. The $\beta$ transus is important, because the processing and heat treatment often are carried out with reference to some incremental temperature above or below the $\beta$ transus. Alloving elements that favour the $\alpha$ crystal structure and stabilize it by raising the $\beta$ transus temperature include aluminium, gallium, germanium, carbon, oxygen, and nitrogen.

Two groups of elements stabilize the $\beta$ crystal structure by lowering the transformation temperature. The $\beta$ isomorphous group consists of elements that are miscible in the $\beta$ phase, including molybdenum, vanadium, tantalum, and columbium. The other group forms eutectoid systems with titanium, having eutectoid temperatures as much as 333°C below the transformation temperature of unalloyed titanium. The eutectoid group includes manganese, iron, chromium, cobalt, nickel, copper, and silicon.

Two other elements that often are alloyed in titanium are tin and zirconium. These elements have extensive solid solubilities in $\alpha$ and $\beta$ phases. Although they do not strongly promote phase stability, they retard the rates of transformation and are useful as strengthening agents. The effects and ranges of some alloving elements used in titanium are indicated in Table 2.1.\(^{35}\)
In summary, the transformation temperature is strongly influenced by:

- The interstitial elements oxygen, nitrogen, and carbon (alpha stabilizers), which raise the transformation temperature.
- Hydrogen (beta stabilizer), which lowers the transformation temperature.
- Metallic impurity or alloying elements, which may either raise or lower the transformation temperature.

Ti-6Al-4V is an alpha + beta alloy that is heat treatable to achieve moderate increase in strength. It has high strength at low moderate temperatures, light weight and excellent corrosion resistance. It immediately and spontaneously forms a stable, continuous, tightly adherent oxide film upon exposure to oxygen in air or water. This accounts for the excellent corrosion resistance in a variety of media.

2.2 Microstructure development

Microstructure of titanium alloys usually are developed by heat treatment or processing followed by heat treatment. Structural changes invariably are achieved through production of beta phase in some amount and the subsequent changes as β transforms. In all-alpha alloys, microstructural change is limited to grain refinement and, possibly, to grain shape.

2.2.1. Ti-6Al-4V microstructure

One of the most widely used titanium alloy is an alpha-beta type containing 6% Al and 4% V. The addition of aluminium for strength and vanadium for beta stabilization produces a mixture of alpha and beta phases that results in reasonable ductility
accompanying the higher strength. This alloy can be solution-treated to produce retained phase that is subsequently aged to improve the alloy properties. The aging treatment results in decomposition of retained metastable beta phase, producing finely divided mixture of alpha and beta phases. The properties of this alloy are developed by relying on the refinement of grains upon cooling from the β region, or α + β region, and subsequent low-temperature aging to decompose martensite formed upon quenching. When this alloy is slowly cooled from the β region, α begins to form below β transus, which is about 980° C. The α forms in plates, with a crystallographic relationship to the β in which it forms. The α plates form with their basal (close-packed) plane parallel to a special plane in the β phase. Upon slow cooling, a nucleus of α forms and, because of the close atomic matching along this common plane, the α phase thickens relatively slowly perpendicular to this plane but grows faster along the plane. Thus, plates are developed. Since in a given β grain there are six nonparallel growth planes, then a structure of α plates is formed consisting of six nonparallel sets.

The formation process of Widmanstatten microstructure is shown schematically in Fig. 2.2. It uses a constant-composition phase diagram section at 6% Al to illustrate the formation of α upon cooling. The microstructure consists of parallel plates of α delineated by the β between them. Where α plates formed parallel to one specific plane of β meet plates formed on another plane, a high-angle grain boundary exist between the α crystals and etches to reveal a line separating them. This microstructural morphology, consisting of these sets of parallel plates which have formed with a crystallographic relationship to the phase from which they formed, is called a Widmanstatten structure.
Upon cooling rapidly, β may decompose by a martensite reaction, similar to that pure titanium, and form a Widmanstatten pattern. The structure present after quenching to 25° C depends upon the annealing temperature. Different types of martensite may form, depending upon the alloy chemistry and quenching temperature. These are designated as $\alpha'$ and $\alpha''$. Upon quenching from above the β transus (about 980° C), the structure is martensitic ($\alpha'$ or $\alpha''$) with a small amount of β (although in some alloys the β has not been observed).

Presence of some β in the structure after quenching from above β transus is due to the fact that the temperature for the end of the martensite transformation, $M_f$, is below room temperature (25° C) for this alloy. That is because vanadium is a β stabilizer, and the addition of 4% V to a Ti-6% Al alloy is sufficient to place the $M_f$ below 25° C. Thus, upon quenching to 25° C, not all the β is converted to $\alpha'$ or $\alpha''$.

### 2.2.2. Influence of heat treatment on the microstructure of CP Ti and Ti-6Al-4V

Titanium and titanium alloys are heat treated for the following purposes:

- To reduce residual stresses developed during fabrication, a process called stress relieving.
- To produce acceptable combination of ductility, machinability, and dimensional and structural stability, especially in alpha-beta alloys under less stringent processing rules than those used to generate optimum strength or special property combinations, a process called annealing.
- To increase strength by means of a process that combines solution treatment and aging.
• To optimize special properties such as fracture toughness, fatigue strength, and high-temperature creep strength.

The response of titanium and titanium alloys to heat treatment depends on the composition of the metal and, by extension, upon the metal’s characterization as alpha, alpha-beta, beta, near-alpha, and near beta. Not all heat-treating cycles are applicable to all titanium alloys, because the various alloys are designed for different purposes. For example Ti-6Al-4V is designed for high strength at low-to-moderate temperatures. Actual heat-treat cycles for each alloy vary. Any heat treatment at temperatures above 427° C should provide the titanium with an atmospheric protection that prevents pickup of oxygen or nitrogen and alpha case formation. The protection also prevents possibility of undesirable scale formation.

Unlike most of higher strength alloys, many α alloys also can be extensively cold rolled, but α alloys are seldom used in recrystallized conditions. This is because cold worked titanium has little strength advantage since it has very low work hardening and because cold worked material has reduced ductility which constraints the subsequent component manufacturing options. Annealing can be done in a continuous annealing oven. The microstructure of α alloys after processing consists of recrystallized α grains with dispersed β phase. This β phase is present because there always is a small amount of iron present in all grades of CP titanium. Iron has low solubility in α phase and it therefore is subjected to form the β phase, either during solidification or subsequent cooling. This β phase remains stable down to room temperature. Smaller grain sizes can be used to increase the yield strength as described by Hall-Petch relationship when higher strength is desired36.
Grain growth can occur during continued annealing once recrystallization is complete, but the β phase reduces the grain growth and enhances the ability to process material with reproducible grain sizes\textsuperscript{37, 38}. The properties of α titanium alloys depend on composition (i.e. oxygen content for CP titanium) and on processing history, because this controls the grain size and preferred orientation. By comparison to α + β and β alloys, the properties of α titanium alloys have more direct composition dependence. In general, the sheet products show a continuous variation of the yield strength and elastic modulus between longitudinal and transverse direction\textsuperscript{39}. This variation is due to the crystallographic texture always present in α titanium alloys.

In the α + β alloys three distinctly different types of microstructures can be obtained by changing thermo-mechanical processing route: fully lamellar structures, fully equiaxed structures, and bi-modal (duplex) microstructures containing equiaxed primary α (α\textsubscript{p}) in a lamellar matrix α + β\textsuperscript{40}.

2.2.3. Heat treatment of Ti-6Al-4V

Ti-6Al-4V alloy in five different heat treatment conditions is examined\textsuperscript{41}.

i. Annealed (this is the starting state of the alloy, which is rolled with a reduction degree not less than 60% at temperatures in the α + β field, followed by recrystallization anneal at 800° C for two hours);

ii. Furnace cooling, with a cooling rate of 0.5° C/s, after β-homogenization at 1100° C;
Fig. 2.1 Schematic pseudo-binary section through α - β isomorphous phase diagram\textsuperscript{34}
Table 2.1 Ranges and effects of some alloying elements used in titanium

<table>
<thead>
<tr>
<th>Alloying elements</th>
<th>Range (approx.) wt.%</th>
<th>Effect on structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>2 to 7</td>
<td>Alpha stabilizer</td>
</tr>
<tr>
<td>Tin</td>
<td>2 to 6</td>
<td>Alpha stabilizer</td>
</tr>
<tr>
<td>Vanadium</td>
<td>2 to 20</td>
<td>Beta stabilizer</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2 to 20</td>
<td>Beta stabilizer</td>
</tr>
<tr>
<td>Chromium</td>
<td>2 to 12</td>
<td>Beta stabilizer</td>
</tr>
<tr>
<td>Copper</td>
<td>2 to 6</td>
<td>Beta stabilizer</td>
</tr>
<tr>
<td>Zirconium</td>
<td>2 to 8</td>
<td>Alpha and beta strengthener</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.2 to 1</td>
<td>Improves creep resistance</td>
</tr>
</tbody>
</table>
Fig. 2.2 Schematic illustration of formation of Widmanstatten structure in a Ti-6Al-4V alloy.
i. water quenching after β-homogenization at 1100° C;

ii. Water quenching after homogenization in α + β region at 850° C; and

iii. Water quenching after homogenization in α + β region at 850° C, followed by ageing at 650° C for 20 hours.

The phase composition of the Ti-6Al-4V alloy after different heat treatments is mainly α-phase, with a small amount (5wt. %) of β-phase in the annealed condition. There is also small amount of retained β-phase after furnace cooling from β-region. During slow cooling, the diffusional redistribution of the alloying elements leads to enrichment of β phase with β stabilizer (V). As a result, a small amount of β phase remains stable at room temperature\(^{42,43}\).

2.3. Biomedical applications

The use of titanium in biomedical field is well-established because titanium fulfills the property requirements better than any competing material such as stainless steels, Co-Cr-alloys, CP niobium, and CP tantalum\(^44\). The properties which are of interest for biomedical applications are corrosion resistance, biocompatibility, bioadhesion (bone ingrowth), modulus of elasticity (should be close to that of bone which is in the range of 10-30 GPa), fatigue strength, and good processability including joining and casting. Especially the excellent corrosion resistance and biocompatibility make titanium the material of choice. Even the price of titanium which is normally the drawback for its application, is only slightly higher as compared to the Co-Cr alloys and to the types of stainless steel used. Compared to CP niobium and CP tantalum the price of titanium is much lower.
There are numerous medical devices using titanium materials, e. g. bone plate screws, hip joint implants, stents, heart valves, and various other kinds of fixtures in the dental area. Three groups of titanium (CP titanium, α + β titanium alloys, and β alloys) are used in biomedical area. Traditionally, CP titanium and Ti-6Al-4V alloys were the first titanium materials used for biomedical applications and even today these two materials are used in most applications. Because of the suspicion of long term toxicity problems with vanadium, the α + β alloys Ti-5Al-2.5Fe and Ti-6Al-7Nb were developed in 1980’s. These two alloys have similar microstructure and properties as the Ti-6Al-4V alloy. Then in 1990’s, a similar variety of β titanium alloys were developed, mainly because of the higher fatigue strength and lower modulus of elasticity as compared to α + β titanium alloys. These two properties are important for the application of hip joint implants. If higher strength is required for an implant, then either the Ti-6Al-4V alloy or the Ti-6Al-7Nb alloy is used.

To facilitate bioadhesion (bone ingrowth) the surface of the finished implant is very important. In general bone ingrowth behaviour improves with increasing roughness of the stem surface. Various finishing methods are used like machining, etching, blasting with Al₂O₃, porous coatings, plasma spraying. One popular surface treatment is plasma spraying of hydroxyapatite (main component of bone tissue) as bioactive coating of titanium implant.
2.4. Plasma assisted thermal spray processes

Plasma, the fourth state of matter, has been extensively used for a large number of thermally assisted surface engineering processes. Solid materials when heated transform into various states as follows:

Solid → Liquid → Gas → Plasma

With the increasing temperature, solid transforms to liquid and liquid to gas. Further increasing temperature results in the transformation of the third state of matter i.e., gas atoms to charged particles and the material enters the plasma state. Plasma, the fourth state of matter, normally consists of neutral atoms, positive ions, and free electrons. Plasma is produced by transferring energy into a gas until the energy level is sufficient to ionize the gas, allowing the electrons and ions to act independently of one another. The plasma state is achieved when, under an electric field, currents can be sustained as the free electrons move through the ionized gas. Once the energy input is removed, the electrons and ions recombine, releasing heat and light energy. It has been estimated that nearly 98% of the visible universe exist in the form of plasma. Common man-made plasmas include neon and fluorescent tubes and bulbs. The plasmas under consideration in this review are less common and are part of a class called thermal plasmas or plasma arcs.

In plasma spray technique a DC electric current is struck between two electrodes, while a stream of gases pass through this arc. This results in an ionized high temperature gas. A large gaseous expansion occurs as a result of the increase in gaseous temperature, thereby causing the carrier gas stream pass through the arc at a
speed approaching the speed of sound. Coating powder is suspended in the carrier gas stream and is propelled by the stream of ionized gas on to the substrate. The particles striking the surface get flattened to form thin platelets. These adhere to substrate surface which can be kept below 500° C, eliminating metallurgical changes in base material\textsuperscript{50,51}. Deposited material will possess a different microstructure compared to wrought material microstructure due to the nature of deposition which is incremental and the gaseous atmosphere in which it is built up. Plasma beam is also used to spray refractory carbides, hydroxyapatite and oxides to give a uniform coating to get hard and wear resistant surface. Here non transferred arc (NTA) is used. In NTA tungsten electrode is negative; while water cooled copper nozzle is positive. Transferred arc (TA) gives higher temperature than NTA which will permanently alter the base material. The setup is as shown in Fig. 2.3.

2.4.1. Equipment\textsuperscript{20}

Plasma arc spray systems consist of components similar to other thermal spray systems. The main components are:

- Gas supply
- Gas Hoses
- Gas regulators for plasma and powder carrier gases
- Gas flow controls
- Plasma arc spray gun comprising a torch body, anode/nozzle, cathode, gas ring, and powder injector
- Electrical controls for arc current and voltage
• Direct-current power supply, typically a constant-current type
• High-frequency RF spark arc ignition source
• Water cooling circuit
• Feedstock delivery: powder feeder
• Water-cooled power cables
• Hoses/cables
• Safety interlocks and console purging

2.4.1.1. Plasma spray gun\textsuperscript{20}

Gun designs vary widely. Some differentiating characteristics are:

• Plasma generator: dc versus RF
• Operating power levels: 20, 40, 80, 120, and >200 kW
• Gas velocity: subsonic versus supersonic
• Arc stabilization: gas or water, axial or vortex flow
• Powder injection: internal axial, internal radial or external radial

Powder-injection geometry and conditions strongly influence the degree of particle heating/melting, thereby controlling coating porosity and oxide inclusion levels. The combination of carrier gas flow rate and powder-port diameter determine the carrier gas velocity, which determines the carrier gas injection velocity and in part, the trajectory. Particle velocities combine with particle mass to directly control particle momentum; this determines the path, or trajectory, that an injected particle takes into and through the plasma jet.
Fig. 2.4 illustrates the various trajectories that particle distribution may follow. Each trajectory shown represents extremes in particle heating, and this affects the average condition of the particles on impact (liquid or solid + liquid). As smaller-diameter particles do not have enough momentum to penetrate the hottest portion of the jet core, so they do not get heated as long as the larger ones. High carrier gas flows (velocity) may force larger particles to follow a low trajectory that passes through the jet to the opposite side of the plasma. This would result in decreased heating and possibly cause a buildup of powder on the nozzle bore.

2.4.2. Plasma gas composition

The distribution of gas temperature and velocity in plasma jets depend on anode/cathode design, power, arc-gas flow rate, and gas compositions. Typical plasma jet use argon together with another secondary (auxillary) gas. Argon-only plasmas create relatively low energy-plasma, which is related to its ionization potential and thermal heat capacity. Nitrogen on the other hand, is one of the hottest plasma gases; however, it is also a reactive gas and has some material limitations. Argon/helium mixtures are very often used, with 20 to 50 vol% helium. Helium increases the thermal conductivity of the plasma stream, increasing the heating capability of the plasma. Argon/hydrogen mixtures are also commonly used, with hydrogen additions of approximately 5 to 15%. Argon/hydrogen plasmas provide increased enthalpy over argon/helium due to the diatomic structure of the hydrogen and its high collisional cross section related to its low mass. In a dc plasma arc, gas heating is sufficient to generate core plasma temperature exceeding 20,000° C, depending on the gas properties and its electrical breakdown characteristics. Fig. 2.5 plots energy content, or enthalpy, of the gases as a
function of temperature. Note that the diatomic gases, nitrogen and hydrogen, have higher enthalpies for a given excitation temperature, which is related to the dissociation of their molecular structure, followed by ionization.

- \( \text{N}_2 + \text{E} = 2\text{N} \)
- Diatomic molecule of nitrogen + energy gives 2 free atoms of nitrogen
- \( 2\text{N} + \text{E} = 2\text{N}^+ + 2\text{e}^- \)
- 2 free atoms of nitrogen + energy gives 2 nitrogen ions and 2 electrons

The reverse process provides most of the energy for heating the spray material without a dramatic drop in temperature:

- \( 2\text{N}^+ + 2\text{e}^- = 2\text{N} + \text{E} \)
- \( 2\text{N} = \text{N}_2 + \text{E} \)

Common plasma gas combinations, in the ascending order of enthalpy are:

- Argon (Ar)
- Argon/helium (Ar/He)
- Argon/hydrogen (Ar/H\(_2\))
- Nitrogen (N\(_2\))
- Nitrogen/hydrogen (N\(_2\)/H\(_2\))

Plasma flames for thermal spraying can produce temperatures around 7,000 to 13,000 K, far above the melting temperature (and vapour temperature) of any known material. The extreme temperature of the plasma is not the only reason for the effective heating
properties. If for example helium gas is heated to around 13,000 K without plasma forming, it would have insufficient energy for normal plasma spraying. Nitrogen on the other hand heated to 10,000 K going through dissociation and ionization forming a plasma is an effective heating media for thermal spraying, being able to supply about six times more energy than an equal volume of helium at 13,000 K. The plasma is able to supply large amounts of energy due to the energy changes associated with dissociating molecular gases to atomic gases and ionization which occur with little change in temperature.

Nitrogen and hydrogen are diatomic gases (two atoms to every molecule). These plasmas have higher energy contents for a given temperature than the atomic gases of argon and helium because of the energy associated with dissociation of molecules.

Argon and Helium are monoatomic gases (the atoms don't combine to form molecules). These plasmas are relatively lower in energy content and higher in temperature than the plasmas from diatomic gases.

**Nitrogen** is a general purpose primary gas used alone or with hydrogen as secondary gas. Nitrogen also benefits from being the cheapest plasma gas. Nitrogen tends to be inert to most spray materials except materials like titanium.

**Argon** is probably the most favoured primary plasma gas and is usually used with a secondary plasma gas (hydrogen, helium or nitrogen) to increase its energy. Argon is the easiest of these gases to form plasma less aggressive towards electrode and nozzle hardware. Argon is a noble gas and is completely inert to all spray materials.
Hydrogen is mainly used as a secondary gas; it dramatically affects heat transfer properties and acts as anti-oxidant. Small amounts of hydrogen added to the other plasma gases dramatically alters the plasma characteristics and energy levels and is thus used as one control for setting plasma voltage and energy.

Helium is mainly used as a secondary gas with argon. Helium is a noble gas and is completely inert to all spray materials and is used when hydrogen or nitrogen secondary gases have deleterious effects. Helium imparts good heat transfer properties and gives high sensitivity for control of plasma energy. It is commonly used for high velocity plasma spraying of high quality carbide coatings where process conditions are critical.

2.4.3. Surface roughening

The clean substrate surface is made rough in order to increase the effective surface area and to improve adhesive bonding of the sprayed deposit. The surface roughness is increased by abrasive grit blasting, machining or rough grinding. The grit blasting is the most commonly used practice of surface roughening. In this process, the substrate surface is blasted with compressed air jets carrying the abrasive grits. The angular particles of chilled cast iron or ceramic are used as grits. The grits of 16-60 mesh size are used for metal substrates and 60-100 mesh for plastics. For ceramic substrates hard ceramic grits are used. For thin substrates, fine grits (25-120 mesh) and for thick coatings, coarse grits (18-25 mesh) are recommended. The compressive residual stress on the grit blasted surface improves fatigue resistance of the component. With rougher surface finishes, the coating adherence improves. The best adhesive bond is associated with roughness dimension comparable to 3/4th of the diameter of the particles sprayed.
2.5. Coating structure and properties$^{21,52}$

Important thermal spray coating features, which combine to determine the properties of a coating, include the lamellar or layered splat structure, entrapped unmelted or resolidified particles, pores, oxide inclusions, grains, phases, cracks, and bond interfaces. Many overlapping splats (impacted droplet/particle formed during thermal coating is known as splat) solidify and adhere to one another to form a continuous coating layer. Thus the splat is the basic structure of building block of thermal spray coatings. Splats are created when the accelerated, molten particles impact a prepared surface. The arriving droplets are generally spherical, and on impact with substrate surface they spread over and fill the underlying interstices. The droplet becomes flattened, a disc like structure which, when polished in cross section reveals the characteristic lamellar structure.

Thermal spray processes are also characterized by rapid solidification. As the relatively small individual particles impact the more massive substrate, their heat is liberated quickly. Such rapid cooling rates produce a wide range of material states, from amorphous to metastable. Therefore two structures will be generally present within a coating known as splat structures and intrasplat structures. Within the splats, the rapid solidification of thermal spray creates grain sizes less than 5 µm and prevents many materials from achieving equilibrium phases, resulting in anisotropic coating properties.

Thermal spray coatings are used to address an ever-increasing variety of surface needs. The importance of the properties is based on the intended coating function. The coating characteristics such as porosity, splat cohesion, and oxide content all have
significant bearing on these properties. Bonding of the coating to the substrate and cohesion between consecutive splats is affected, in rough order, by:

- Residual stresses within the coating
- Melting and localized alloying at the contact surfaces between particles and between the substrate and adjoining particles
- Diffusion of thermal species across the splat boundaries
- Atomic-level attractive forces (van der Waals forces)
- Mechanical interlocking

2.6. Plasma coating materials

Generally, materials that are suitable for thermal spray processing are stable at elevated temperatures. Materials that decompose or sublime tend to be poor candidates for coatings. Thus, most metals, intermetallics, alloys, all forms of ceramics, cements and some polymers are sprayable by one or more thermal spraying processes. The spraying material is usually supplied in powder, wire or rod form. Coating applications are many such as: wear coatings, thermal insulations, corrosion resistance, abradable and abrasive coating, electrical conducive coatings, insulating coating, dimensional restoration coatings, polymer coatings and medical coatings.

Medical coatings are divided into two categories: bioactive and biocompatible. Both coating types are used for implant prostheses. Biocompatible coatings are typically porous titanium applied to titanium alloys; new bone tissue grows into the porosity and secures the implant. Bioactive coatings are typically some form of calcium phosphate,
including tricalcium phosphate and hydroxyapatite. These coatings emulate the characteristics of natural bone such that new bone growth attaches to the implant and eventually resorbs – that is, replaces the coating. Both types of coatings are intended to speed patient recovery and extend usable implant life. Dental implants and other orthopedic devices are also coated in this way.

2.6.1. Hydroxyapatite

Apatites are a structural type for compounds of general formula $M_{10}(XO_4)_6Y_2$ rather than specific compounds. In general, they are known to be capable of accommodating a wide variety of modifications and combinations of substitutions of ions and groups within the apatite lattice. However, the term “apatite” has been extensively used to represent the calcium phosphates, $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$, where $\text{X} = \text{F}^-, \text{OH}^-$, or $\text{Cl}^-$. Apatites are thermodynamically the most stable phases among calcium phosphates and therefore, can be considered as the probable end product in many reactions.

Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is used as a model for inorganic component of bones and teeth. However, apatites as they occur in biological tissues, mineral formations and laboratory products can incorporate a wide variety of impurities and are seldom found in pure stoichiometric form. The most common form is hexagonal and its crystal structure has been described$^{53}$ in the space group $\text{P6}_3/m$ (No. 176) with lattice parameter $a = b = 9.432$ nm and $c = 6.881$ nm, $z = 12$. 
2.6.1.1. Bioactive hydroxyapatite

Any material incorporated into a human organism has to abide by certain properties that will assure that there are no negative interactions with living tissue. Hydroxyapatite is a biocompatible material. It is also a bioactive material. It shows positive interaction with living tissue that includes also differentiation of immature cells towards bone cells. In contrast to bioinert materials there is chemical bonding to the bone along the interface, thought to be triggered by the adsorption of bone growth-mediating proteins at the biomaterials surface. Hence there will be a biochemically-mediated strong bonding. The bond between a metallic titanium alloy implant and bone tissue is mediated by a so-called contact osteogenesis. Bone tissue will be uni-directionally growing towards the interface and “bony on-growth” occurs that is able to transmit compressive loads. However the actual loads the interface is subjected to during movement of the patient contain also strong tensile and shear components that have to be taken care of.

In the clinical practice in many cases a bioactive hydroxyapatite layer is provided that will allow a bonding osteogenesis that through “bony in-growth” will be able to transmit these tensile and shear forces. Here two ossification fronts develop, one growing from the bone towards the implant and another growing from the implant towards the bone. Bioactive hydroxyapatite coating will elicit a specific biological response at the interface of the implant material by control of its surface chemistry through adsorption of non-collagenous proteins. This will result in the eventual
establishment of a strong and lasting osseoconductive bond between living tissue and biomaterial. The advantages of bioactive coating include

- The prevention of fibrous capsule of connective tissue surrounding the implant.
- Fast bone apposition rates through preferential adsorption of proteins.
- Bonding osteogenesis providing a continuous and strong interface between implant and tissue that is able to transmit not only compressive but also tensile and shear loads.
- Accelerated heating compared to implants without bioactive coating, as well as
- Reduced release of titanium ions to surrounding tissue thus minimizing the perceived risk of a cytotoxic response. In one such study\(^5\) a plasma-sprayed hydroxyapatite coating on porous titanium layer covering the titanium alloy surface showed improved interfacial bond strength compared to uncoated porous titanium.

2.6.2. Hydroxyapatite coating by plasma spray

Of many techniques used for implant surface modification, plasma spraying is one of the commercially accepted methods for producing HA coating. It is well known that thin coatings below about 50 µm will be rather quickly resorbed \emph{in vivo}. Therefore 100-150 µm thick coatings are desired for long-term stable coating. According to the performance requirements of plasma sprayed coatings, the essential properties required for specific application are shown in Table 2.2.
Fig. 2.3 Plasma torch

Fig. 2.4 Plasma jet particle trajectories
Fig. 2.5 Enthalpy values of typical plasma spray gases as a function of temperature\textsuperscript{58}
Table 2.2 Performance requirements of bioceramic hydroxyapatite coating

<table>
<thead>
<tr>
<th>Property</th>
<th>Requirement</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating thickness</td>
<td>50 µm</td>
<td>Coating &lt; 50 µm will be resorbed</td>
</tr>
<tr>
<td>Coating thickness</td>
<td>200 µm</td>
<td>Upper limit for maintenance of sufficient strength</td>
</tr>
<tr>
<td>Porosity/roughness</td>
<td>100 – 200 µm</td>
<td>Minimum porosity for ingrowth of bone tissue</td>
</tr>
<tr>
<td>HA content</td>
<td>&gt; 95%</td>
<td>Minimum purity for biocompatibility</td>
</tr>
<tr>
<td>HA content</td>
<td>&gt; 98%</td>
<td>Chemical stability</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>&gt; 90%</td>
<td>Increasing resorption with decreasing crystallinity</td>
</tr>
<tr>
<td>Adhesion strength</td>
<td>&gt; 35 MPa</td>
<td>Prevention of spalling</td>
</tr>
</tbody>
</table>
Plasma spray has been used as a major technique in applying hydroxyapatite \([\text{Ca}_{10}(\text{PO}_4)_{6}(\text{OH})_2]\) coating onto metal implants to improve implant fixation and bone growth\(^{25,26,59,60}\). However, due to extremely high temperature of plasma flame and the rapid cooling rate, the phase and structure of HA coatings are greatly changed from those of feed stock. Deposition parameters can lead to different phase composition, crystal structure and microstructure\(^{25,61,62}\). This results in the alteration of two major coating properties: mechanical and dissolution behaviour. For example different phases have demonstrated different solubility\(^{63,64}\) and Young’s modulus\(^{65}\). Therefore to obtain HA with predictable properties and performance for important applications, the phase, structure and microstructure of HA should be designed for practical purposes. To achieve this both spray parameters and feed stock HA should be optimally controlled.

Important performance criteria of plasma sprayed hydroxyapatite coatings are:

1. Adhesion to the metal substrate. This depends crucially on the microstructural features of the coatings. These are porosity, degree of deformation of spray particle splats, the presence of micro and macro cracks, as well as residual stresses at the coating-substrate interface, and

2. Biochemical resistance against aggressive body fluids. This depends on the crystallinity of the hydroxyapatite, the nature and the amount of thermal dehydroxylation, decomposition (tricalcium phosphate, tetracalcium phosphate, (CaO) products, as well as the presence of amorphous calcium phosphate\(^{66}\).
However, high adhesion strength requires high plasma enthalpy that in turn causes increased thermal decomposition of hydroxyapatite and low biochemical resistance. To solve this problem, a compromise is needed. Optimization of coating performance can be achieved principally by three routes:

1. Control of plasma spray parameters.
2. Microstructural engineering of spray powders prior to deposition.
3. The application of the bioinert bond coats\textsuperscript{67}.

Even then thermal decomposition of hydroxyapatite in the extremely hot plasma jet is inevitable owing to its incongruent melting at 1570° C\textsuperscript{59}.

The thermal decomposition of hydroxyapatite in the plasma jet occurs in four steps:

\begin{align*}
\text{Step 1:} & \quad \text{Ca}_{10}\text{(PO}_4\text{)}_6\text{(OH)}_2 \longrightarrow \text{Ca}_{10}\text{(PO}_4\text{)}_6\text{(OH)}_{2-2x}\text{O}_x\text{□}_x + x \text{H}_2\text{O} \\
& \quad \text{(hydroxyapatite)} \quad \text{(oxyhydroxyapatite)}
\end{align*}

\begin{align*}
\text{Step 2:} & \quad \text{Ca}_{10}\text{(PO}_4\text{)}_6\text{(OH)}_{2-2x}\text{O}_x\text{□}_x \longrightarrow \text{Ca}_{10}\text{(PO}_4\text{)}_6\text{O} + (1 - x) \text{H}_2\text{O} \\
& \quad \text{(oxyhydroxyapatite)} \quad \text{(oxyapatite)}
\end{align*}

\begin{align*}
\text{Step 3:} & \quad \text{Ca}_{10}\text{(PO}_4\text{)}_6\text{O} \longrightarrow 2 \text{Ca}_3\text{(PO}_4\text{)}_2 + \text{Ca}_4\text{(PO}_4\text{)}\text{O} \\
& \quad \text{(oxyapatite)} \quad \text{(tricalcium phosphate)} \quad \text{(tetracalcium phosphate)}
\end{align*}

\begin{align*}
\text{Step 4:} & \quad \text{Ca}_4\text{(PO}_4\text{)}_2\text{O} \longrightarrow 4 \text{CaO} + \text{P}_2\text{O}_5 \quad \text{or} \quad \text{Ca}_3\text{(PO}_4\text{)} \longrightarrow 3 \text{CaO} + \text{P}_2\text{O}_5 \\
& \quad \text{Ca}_4\text{(PO}_4\text{)}_2\text{O} \quad \text{Ca}_3\text{(PO}_4\text{)}
\end{align*}
Previous studies \(^{25,61,68}\) in this field usually reported on the coating crystallinity and its effect on dissolution and mechanical property. However due to the existence of different forms of crystalline HA; i.e. unmelted, recrystallized, dehydroxylated, and their variations within the coating, crystallinity alone may not reflect the coating quality. In addition, microstructural features such as the sub-microstructure features, pores, cracks and splat boundaries also influence the coating quality and these have not been investigated in detail \(^{25,26,60-69}\).

Hydroxyapatite is preferred for its ability to interact with living bone, resulting in improvements of implant fixation and faster bone healing. It is capable of interacting with surrounding bone and produces direct attachment of implant to bone without interposed fibrous tissue layer because of the presence of free calcium and phosphorous compounds at the surface \(^{70}\). The relationship between plasma spray operational parameters and microstructure of HA coating and powder particles sprayed into water showed that electric power influences in the most decisive way the crystalline phase composition of coating \(^{70}\). The fraction of plasma forming gas has second most important effect on the content of crystal phase in coatings. Finally the carrier gas flow rate plays the least important role in the phase composition of the coatings.

Variation in the material properties of HA coating has an effect on the bone bonding mechanism and the rate of bone formation \(^{64,71,72}\). Both the Ca/P ratio and the crystallinity of calcium phosphate coating are important parameters that influence its dissolution characteristics. It was found that the calcium phosphate film with Ca/P ratio of 1.5 has an extremely low dissolution rate even in the amorphous state. Osteoblasts
were more attached on calcium phosphate coated sample by 20% and approximately 40% improvement in proliferation were observed\textsuperscript{73}.

The method of applying HA coating and the chemical composition play major roles in coating morphology and in vivo bone response\textsuperscript{74}. Overgaard et al.\textsuperscript{75} suggested that HA coating crystallinity is an important factor in biological response and resorption. Plasma sprayed HA morphology has been shown to be dependent on proximity to metallic substrate, with region adjacent to the substrate exhibiting reduced crystallinity\textsuperscript{76}. Thin plasma spray HA layers have been reported to be more amorphous and these result in premature coating dissolution and resorption\textsuperscript{77}. Svehla et al.\textsuperscript{78} found plasma coated implants were superior to grit-blasted implants with respect to fixation and on growth.

Endosseous implants initially come in contact with blood. Thus, the nature of interactions between blood and implanted endosseous implants may influence subsequent bone healing events in the peri-implant healing compartment. The activation of platelets both in contact with an implant surface, and in bulk healing compartment can be regulated as function of implant surface microtexture\textsuperscript{79}. Kikuchi et al.\textsuperscript{80} concluded that: calcium (Ca) and phosphate (PO\textsubscript{4}) containing surfaces of increasing surface microtopographical complexity exhibited increasing platelet activation regardless of the presence of Ca and PO\textsubscript{4} in the surface. They also concluded that surface microtopography is responsible for platelet activation rather than presence of Ca and PO\textsubscript{4} in the surface.

Platelet adhesion is an initial, crucial and complex matter even for inhibiting blood loss upon vascular injury. Activation and adhesion of platelets also play a
fundamental role in the development of thrombosis. Many methods have been developed to measure and study adhesion of platelet in plasma with standard laboratory equipment\textsuperscript{81-83}. The relationship between the surface state and biocompatibility of a material is of topical concern in the development of biomaterials. The main problem of mechanical heart valves is their thrombogenicity.

Life time anticoagulation therapy is necessary to minimize the risk of thromboembolic complications. Huang et al.\textsuperscript{84} found that, when a titanium oxide layer with a rutile structure is formed on a titanium matrix, the blood compatibility is improved, and is better than that of low temperature isotropic pyrolytic carbon. In similar studies less platelet adhesion was observed in samples with titanium oxide layer indicating improved blood compatibility\textsuperscript{85-88}. Platelet adhesion of titanium coated with apatite investigated in real time using cone and plate type viscometer and fluorescence labeled platelets showed suppressed platelet adhesion compared with those on untreated titanium. Titanium metal coated with apatite is superior to commercially pure titanium metals in terms of platelet adhesion\textsuperscript{88}. This suggests that apatite coated samples would exhibit thromboresistance.