Most commonly used metallic biomaterials for plasma sprayed hydroxyapatite coatings

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Abstract.
In load bearing implants metallic biomaterials have the first preference in orthopedic surgery because of their good mechanical properties which satisfied the prerequisite of human cortical bone. However metallic implants have limitations of poor wear resistance and release of metal ions resulting in to implant failure. To overcome these limitations hydroxyapatite based coatings on metal substrate can be used. The application of hydroxyapatite coating with the second reinforcement improve the fatigue strength of composite coatings. In this paper, commonly used metallic biomaterials for application of hydroxyapatite based composite coatings are discussed. Plasma spray coating technique with variable process parameters has been considered for this review. Presently plasma spray technique is commonly used for application of HA coatings in medical industry.

Keywords: Metallic biomaterials; Hydroxyapatite; Plasma spray technique; Process parameters.

1. Introduction:

Recently a lot of research is being carried out pertaining to biomedical engineering as far as artificial joint assembly is concerned. Orthopedic biomaterials have the largest market share as compared to all other biomaterials. The load bearing prostheses such as hip-knee, Glenohumeral referred as shoulder and Ginglymus referred as elbow joint prostheses are most active area of joint replacement in the current scenario. Near about five lakhs and more hip and knee joint surgery replacement are being performed per year in the world [1]. The possibility of this number is increases day by day as the population ages. Orthopedic biomaterial implants and fixing accessories are generally made of metals, ceramics or their composites. *In vivo*, longevity and performance of these load bearing units is still a big challenge for scientist, engineers and researchers. For reduction of wear rates and biocompatibility of orthopedic implants, ceramic surface modification process offers the excellent benefits. Bones are the load bearing parts of human body. Good mechanical and tribological properties are initial requirement of bone to prevent the failures like cracking, fracture, wear loss, aseptic loosening etc.

The artificial bones must have good fracture toughness on the application of high and cyclic loading during movement and action of the limbs. Poor fracture toughness results in poor wear resistance leading to wear loss during the movement and action of limbs. Generally, 80 % of bioimplant devices/ prosthesis in the medical industry are made from metal biomaterials [2, 3]. Nevertheless, the metallic biomaterials have the poor bio-function capability and the low adhesion strength between the substrate and coating layer [4]. Metallic biomaterials are especially used in the manufacturing of knee joint prosthesis, hip joint prosthesis, dental implants, surgical instruments, etc. Schematic of an orthopedic load bearing metallic hip and knee implant prosthesis is shown in figure 1 [5].

![Figure 1. a) Hip Implant Prosthesis, b) Knee Implant Prosthesis [5]](image)

1.1 Agreeable properties of artificial bioimplant material:

Following properties are essential for artificial orthopedic assembly to survive *in vivo* for 15 to 20 years in the living organism.

1. Good mechanical characteristic such as high fatigue resistance, hardness, elastic modulus, strength. Artificial...
bioimplant material resist deformation when subjected to cyclic load during normal walking, jogging and stumbling. Natural bone assembly such as hip and knee joints sustain the three to eight time’s load of the body weight of human being [6].

2. Good tribological properties such as high wear resistance, low friction and low surface roughness value for high surface finish. Low wear resistant biomaterial generates the wear debris when it slides against the bone tissue and articulating surface of bone assembly. This wear debris when comes in contact with living tissues or cells causes inflammation or allergy resulting in revision surgery [7].

3. High chemical corrosion resistance for bioactive, bioinertness and biodegradable artificial bioimplant material. Metal ions are released in case of low corrosion resistant biomaterials resulting in harmful and toxic reactions.

4. Good biocompatibility and Osseointegration properties. Biomaterials should give positive response to bone cells. Biomaterials should have good bone–tissue compatibility without any toxic effect. In vivo bone forming cells such as osteoblasts and fibroblasts shows excellent growth and proliferation on biomaterials. Implant biomaterials must prove its biocompatibility in terms of viability, proliferation and differentiation. Osseointegration ability is very decisive for orthopedic biomaterials for determining the life-time of the implants. Adhesion of fibroblast on biomaterials surface plays an important role in Osseointegration [8].

### 2. Types of metallic alloys for artificial bioimplant material:

The mechanical and tribological performance of metallic bioimplant make them more reliable and exceptional candidate for orthopedic applications. Generally metallic biomaterials and devices are used for the replacement of hard tissue like artificial knee and hip joint, bone screw, bone plates, dental implant and shoulder replacement. Several types of orthopedic implant biomaterials and alloys system with their physical and chemical characteristic have been studied in the research carried out in biomedical field. Out of this only a few biomaterials are presently used for orthopedic bioimplant surgery. This review paper is focused on selected biomaterials which are in great demand and are used in current scenario.

1. **STAINLESS STEEL ALLOYS:**

   Stainless steel was first biomaterial introduced in a total hip arthroplasty. This system has seen high generation of wear debris and high friction coefficient resulting in osteolysis and loosening of the implant. This system has number of variation over the years by modifying the surface properties for long longevity and service life. AISI 316L grade is most commonly used material in orthopedic application. The letter L in the designation signifies low carbon content. This grade is largely used in the manufacturing of surgical instruments, stents and fracture fixation parts. Some studies have reported allergic reactions due to presence of nickel content in the chemical composition of stainless steel. To avoid this allergic reaction, nitrogen ion implantation surface modification technique is employed. An Attempt has already been made by researchers to develop nickel free stainless steel without compromising on its physical properties [9].

2. **COBALT ALLOYS:**

   Implant loosening or failure is a common factor affecting the total hip and knee replacement. Cobalt alloys possess high wear resistance, strength and ductility and its wear resistance is higher than stainless steel and titanium alloys. In artificial hip assembly, the femoral head is subjected to high cyclic load resulting in wear. Femoral head made from cobalt alloys exhibit good tribological properties when in contact with articulating liner. In our research study it was found that the specific wear rate and coefficient of friction of Co- Cr-Mo alloys is lower as compared to other metal alloys. Wrought cobalt alloys have high strength as compared to cast cobalt alloys so wrought cobalt alloys are in more demand. These alloys are used in dental implant, hip and knee assembly, heart valves etc. Carbides play an important role in strengthening of the cobalt alloys. Low carbon cobalt alloys have more wear resistance as compared to high carbon cobalt alloys. Modulus of elasticity of cobalt alloy is twice that of the titanium alloy. Elastic modulus of cortical bone is generally in the range of 15-25 GPa [10]. Mismatch in the modulus of elasticity between bone and implant surfaces may cause stress shielding resulting in revision of surgery.

3. **TITANIUM ALLOYS:**

   Over a past decade titanium alloys have been selected as a biomaterial for the replacement of hard tissue damaged like knee and hip joints, bone plates, fracture fixation etc. It is most commonly used in femoral stem part of hip prosthesis. The high resistance, good biocompatibility and Osseointegration of titanium alloys makes it suitable for this application. Torsional stiffness and modulus of elasticity of titanium alloys is closer to the human critical bone. This helps in reducing the stress shielding of bone. Titanium alloys are not suitable for femoral head because of their poor tribological properties. However, the strength to weight ratio of titanium alloys is higher as compared to other metallic alloys. The less weight of medical device or implant is one of most important criteria in design of artificial prosthesis in recent scenario. Several surface modification techniques were investigated to improve properties of
titanium alloys. Thermal coating process is found to be most promising technique for coating titanium alloy bioimplant. In the present market, noncemented press fit stems are generally used for younger patients. This press fit stem is coated with bioceramic such as hydroxyapatite (HA) nano powder. Titanium press fit stem have good stability as compared to cemented stem. In cemented press fit stem, early failure or degradation of cement leads to poor stability resulting loosening of implants [11]. Table 1 summarizes the most commonly used metallic bioimplant materials for the orthopedic application.

Table 1. Comparison of orthopedic Metallic biomaterials in terms of their advantages, disadvantages, applications, Major alloying elements and density [11, 12, 13]

| Orthopedic biomaterials | Stainless steels | Cobalt alloys | Titanium alloys |
|-------------------------|------------------|---------------|----------------|
| Advantage               |                  |               |                |
| 1. Very low cost.       |                  |               |                |
| 2. Commercially available. |                |               |                |
| 3. Formed metal oxide sometimes act as lubricating agent. | | | |
| Disadvantage            |                  |               |                |
| 1. High coefficient of friction. | | | |
| 2. Poor wear resistance. |                  |               |                |
| 3. Poor corrosion resistance. |            |               |                |
| 4. Moderate biocompatibility and Osseointegration. | | | |
| 5. Wear generation leads to aseptic loosening. | | | |
| 6. High Elastic modulus. |                  |               |                |
| 7. Presence of Ni in some cobalt alloys causes allergy. | | | |
| Application             |                  |               |                |
| 1. Artificial Hip joint assembly (Femoral head of hip, stem part of hip prosthesis, acetabular cup). | | | |
| 2. Artificial knee joint assembly (Knee femoral component, Tibial component). | | | |
| 3. Medical surgical instruments. | | | |
| 4. Fracture plates and fixation. | | | |
| | 1. Artificial Hip joint assembly (Femoral head of hip, acetabular cup). | | |
| 2. Dental implants. | | | |
| 3. Artificial knee joint assembly (Knee femoral component, Tibial base plate). | | | |
| Major chemical contents/All oying elements | | | |
| Fe-Iron (Balance) | Co-Cobalt (Balance) | Ti-Titanium (Balance) |
| Cr-Chromium | Cr-Chromium | Al-Aluminum |
| Ni-Nickel | Mo-Molybdenum | V-Vanadium |
| Mn-Manganese | Fe-Iron | Nb-Nubian |
| Mo-Molybdenum | Ni-Nickel | C-Carbon |
| C-Carbon | Density | In between | In between | In between |
| (g/mm³) | 7.98x10⁻³ to 10.5x10⁻³ | 8.3x10⁻³ to 11.4x10⁻³ | 4.43x10⁻³ to 6.5x10⁻³ |

Table 2. Comparison of mechanical properties of orthopedic metallic biomaterials with cortical bone and HA bioceramic material [14].

| Material       | Tensile Strength (MPa) | Compressive Strength (MPa) | Elastic Modulus (GPa) | Fracture toughness (MPa. m⁰.⁵) |
|----------------|------------------------|----------------------------|-----------------------|-------------------------------|
| Ti-alloys      | 780 -1050              | 450 -1850                  | 110                   | 40 -70                        |
| Titanium (Ti-6Al-4V) | 345                  | 250-600                    | 117                   | 60                            |
| Stainless Steel | 540 -1000             | 1000                       | 200                   | 55- 95                        |
| Cobalt alloys  | 600 -1795             | 500 -1900                  | 200 - 230             | 70- 90                        |
| Cortical Bone  | 50 -160               | 130 -180                   | 15 - 25               | 2- 12                         |
| Hydroxyapatite (HA) | 40 - 300             | 300 - 900                  | 80 -120               | 0.6-1                         |
2.1 pie chart: % of bone mineral content:

To improve the Osseointegration and biocompatibility of bioimplant prosthesis HA ceramic has been used in last few years. The best suitable candidate for these coating are HA \([\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]\) due to its Osseointegration, biocompatibility and osteoconductive properties [15]. HA also shows the antimicrobial effect. HA is nothing but a calcium phosphate based ceramic and this offers physiological environment and surface for new bone growth and integration. HA is a clinically proved and acceptable ceramic whose chemical composition is same as human bones. It is largely accepted in the orthopedic industry by virtue of its inherent biological properties. Generally medical metallic implants are coated with HA. HA shows the brittle nature and low fracture toughness resulting in rapid wear and sometimes earlier fracture of artificial implant bone. From table no 2 it is evident that the fracture strength of HA is less than the fracture strength of human cortical bone. HA coating is applied to especially metal substrate for improving strength and fatigue resistance of implant coating in load bearing application. Hence there is a need to improve the mechanical and tribological properties of HA coated artificial implants without compromising on its biocompatibility. Various surface coating methods have been developed for deposition of HA on metallic surface. Thermal coating methods are mostly preferred because melting point of HA is very high approximately 1614°C [16].

The most important factor during the surface modifications or consolidation is to maintain good dispersion of HA throughout the surface of implant. To control the porosity of HA coating is another important consideration because maintaining some degree of porosity and proper distribution of HA imparts good tribological, mechanical properties. Porosity helps in new bone formation (cell/tissue growth) and integration on implant surface. Appropriate degree of porosity is desirable property for orthopedic bioimplant material. Since 21st century, HA is used as a bioceramic material on orthopedic implant. Improvement of HA based coatings on the metal substrate is necessary for the future scope of human being real life application. Laser surface alloying was first technique used for HA coating on bioimplant metal substrates. Thermal spray HA coating is widely used to improve the Osseointegration and to control the healing process of metallic bioimplant prosthesis. The surface properties of base material is changed by using the surface modification technique. The surface modification can improve the tribological, mechanical and biological properties of bioimplant prosthesis. Table 3 shows the comparison of Weight % Constituents of cortical bone with HA bioceramic.

| Weight % Constituents | Cortical Bone | Hydroxyapatite (HA) |
|-----------------------|--------------|---------------------|
| Ca                    | 24.5         | 39.6                |
| P                     | 11.5         | 18.5                |
| Ca/P ratio            | 1.65         | 1.67                |
| Na                    | 0.7          | Trace               |
| K                     | 0.03         | Trace               |
| Mg                    | 0.55         | Trace               |
| CO3\(^{-2}\)          | 5.8          | -                   |

Researcher recommended HA bioceramic powder not only because of its similar weight % of different elements with natural bone but also by considering its \(\textit{in vivo}\) performance. Different studies were carried out on the \(\textit{in vivo}\) performance of HA composite implant coatings [18].

2.2 Need of second reinforcement:

It was investigated that the HA coated bioimplant suitable for the load bearing prosthesis. Tsui et al. coated HA on the Ti6Al4V substrate by using the plasma spray technique. They have reported that HA composite shows excellent adhesion strength at the interface between the HA and Ti6Al4V surface. They have also reported good phase stability and chemical purity [19]. Fracture strength of HA 1 MPa.m\(^{0.5}\) was reported which is less than the cortical bone 2 MPa.m\(^{0.5}\). Hence to improve the fracture toughness of HA based bioimplant composites researcher suggested need of second phase reinforcement.
3. Composite fabrication technique:

Various fabrication techniques have been investigated systematically to form the HA based bioimplant composites prosthesis. Due to high melting temperature of HA, most of processes have used elevated temperature for solidification. Challenge with these techniques is to control the dissociation of HA to other phases. During these processes HA powder experiences high temperature. These high temperature results in thermal decomposition of HA into new phases such as tri-calcium phosphate (TCP), β-tri-calcium phosphate (β-TCP) and tetra-calcium phosphate (TTCP). For maintaining the mechanical strength of bioimplant composites it is necessary to control the dissociation of HA bioceramic. The phase purity of HA is one of the essential requirement of bioimplant coatings. As per biomedical BS ISO standard, 5% dissociation of HA in other non HA phases is allowed during the thermal composite technique. The composite fabrication technique is categorized in to two groups based on the application of bioimplant composite. The classification of composite is shown in figure 3 [20].

Various composite fabrication process are ineffective and failed to satisfy the mechanical, tribological and biological properties of HA coatings. The main reason of failures are decomposition of HA powder particles, weak adhesion/bonding strength between the implant and coating, overheating of metal substrates and Cytotoxicity related issues. Plasma spray process has ability to address all of the above issues and to produce coating satisfying all requirement such as purity phase of HA, good adhesion/bond strength, good wear resistance, good biocompatibility, good bioceramic etc. [21].

3.1 Plasma spray technique:
Plasma spray technique is generally used for coating of metallic implants such as stainless based alloys, Cobalt based alloys and titanium based alloys. For coating of metallic biomaterials plasma spray technique is US Food and Drug Administration (FDA) approved technique [22]. This process has been used in industry for many years for coating of bioceramic on metal substrates because of its high degree of flexibility, high production coating rates, low porosity and excellent bond strength. This process is commonly used for application of bioceramic HA coating. In plasma spray technique only bioceramic powders are exposed to high temperature not metallic substrate. Hence there is no chance of changing the physical and chemical properties of metallic substrate due to high heating. In the plasma spray process, the bioceramic powders in nanosize or micron size are fed in to hot plasma flame by the plasma carrier gas. This bioceramic powder is exposed to very high temperature and melted in a hot plasma. This melted bioceramic powder is driven towards the metallic substrates to form a coating. In plasma sprayed coatings generally the splats and lamellar microstructure are observed due to the layer by layer deposition of molten bioceramic powder on the metallic substrates. This technique is suitable to produce uniform thickness of bioceramic coating on the metallic substrates. Low plasma velocity in the plasma spray process results in to larger size of splot morphology whereas at high plasma velocity results in smaller size of splats morphology. In plasma spray process the degree of melting of bioceramic particle depends on the temperature of hot plasma flame, plasma velocity and size of bioceramic particle.

In a recent study HA coating with (002) orientation was fabricated on titanium alloy by using the atmospheric plasma spraying technique. For the coating 60 mm working distance was maintained with spray current 40 ampere.
The result demonstrates that (002) oriented coating improves the Osseointegration and mechanical properties [23]. Chou & Chang examined the microstructure of two different composite coatings on titanium alloy substrate. The composite coatings were plasma sprayed HA coating and plasma sprayed HA-10 wt % ZrO2. They found that addition of second phase ZrO2 improves the wear resistance and fatigue strength of coatings. Various investigators closely examined the in vivo behaviour and its biocompatibility of plasma sprayed HA coating on titanium alloys. Plasma sprayed HA coating on Ti-6Al-7Nb alloy resulted in better osseointegration and osseoconduction ability of coating [24]. Thian et al. reported silicon-HA based composite coating can be used for artificial knee-hip implants. They deposited silicon-HA films on titanium alloy substrate and observed denser and crack free coating [25]. As compared to only HA coating, the plasma sprayed HA-CNT (Carbon nanotube) coating showed excellent improvement in terms of wear resistance, hardness and fracture strength [26]. Therefore, plasma spray technique is an efficient process for application of HA coating reinforced with second phase CNT on metal substrates. Kaleem et al. stated that reinforcement of ceramic as a second phase helps in improving mechanical properties of HA based bioimplant composite coatings. Addition of Al2O3 in HA based composite by using plasma spray showed tremendous improvement in bending strength and fracture toughness [27]. Reduction in decomposition of HA phases in to other phases has been observed on using HA-ZrO2 composite coatings with plasma spray technique. Jorge et al. reported that the hybrid composite (HA- Al2O3-CNT) showed threefold increase in the fracture strength than the HA coatings. These hybrid coatings result in to the lower adhesion (attachment) but have the higher proliferation rate [28]. Similar to hybrid composite coatings, ebrahimi et al. carried out research study using HA- Al2O3 and HA-SiO2 nano-composites on titanium alloy substrate. Results revealed that bi-layered plasma coating improved the cytotoxicity and proliferation rate with wettability of composites as compared to HA coating [29]. Figure 5 (a) and 5 (b) shows [30] the plasma sprayed HA coating and HA-CNT composite coating on Ti-6Al-4V substrate. Figures clearly indicate the typical splats and lamellar structure.

Figure 5. a) HA coating, b) HA-CNT composite coating [30].

Anstis equation was used for calculating fracture toughness. The equation [31] as follow:

$K_{IC} = 0.016 \left( \frac{E}{H} \right)^{0.5} \frac{P}{c^{1.5}}$  \hspace{1cm} (1)

Where $K_{IC}$ is the fracture toughness, $E$ is the modulus of elasticity, $H$ is the harness of coating, $P$ is the applied load and $c$ is the radial crack length.

Evans and Marshall suggested the model for brittle ceramic material. This model computed the wear volume loss of brittle ceramic material. The wear volume loss is a combined function of the fracture strength, hardness and modulus of elasticity. The proposed equation [32] as follows.

$V = p^{1.125}K_{IC}^{-0.5}H^{-0.625} \left( \frac{E}{H} \right)^{0.8} S$  \hspace{1cm} (2)

Where $V$ is the wear volume, $P$ is the normal applied load, $H$ is the hardness, $E$ is the modulus of elasticity and $S$ is the total travelling distance by specimen on wear track.

3.2 preparation of metallic substrates for plasma spray process:

Researchers have used various surface techniques as a part of substrate preparation prior to plasma spray process. The processes are chemical etching, Micro roughing and grit blasting. Out of this grit blasting is a standard process and mostly used for preparation of bioimplant metallic substrates for HA coating. In plasma process grit blasted prepared metal surface is used for the good adhesion of implant coating. Generally, Al2O3 ceramic powder in micron size is used for grit blasting. Most preferred blasting angle was 750 and blasting pressure is in the range of 5 to 7 bar which has been identified by Amada and Hirose for grit blasting process [33]. The grit angle is responsible for the surface roughness of sample/substrates and this surface roughness improves the adhesion strength of plasma sprayed coatings. After the grit blasting, mostly ultra-sonic cleaning process was used to remove some of the grit particles that are embedded during the grit blasting.
3.3 Process parameters/variables used for plasma process technique:

The quality of bioimplant coating is largely dependent on the selection of optimum process parameters in the plasma spray technique. Spraying process parameters influence the mechanical and morphological properties of bioimplant coating. User or operator can directly control the primary parameters before or during the plasma process. Secondary parameters depend on the primary parameters. The list of parameters for plasma spray process is mentioned in table 4.

| Primary Parameters/Variables for plasma spray process | Secondary Parameters/Variables for plasma spray process |
|------------------------------------------------------|--------------------------------------------------------|
| Bioceramic powder particle microstructure             | Temperature of plasma flame                           |
| Bioceramic powder particle chemical composition       | Velocity of plasma flame                              |
| Bioceramic powder injection angle used                | Plasma flame dwell time                               |
| Plasma forming gas                                   | Bioceramic powder particle velocity                   |
| Flow rate of plasma forming gas                       | Bioceramic powder particle melting                    |
| Plasma power/Current (Power = Current x Voltage)      | Bioimplant substrate temperature                      |
| Carrier gas/Carrier gas flow rate                     | Bioceramic particle quench rate/Development of stress |
| Working spray distance                                | Plasma spray coating thickness                        |

Considering the all above mentioned parameters in table 4 during the plasma spray process is not possible which is not economically accepted or plausible. So in the experimental design (DOE) it is required to select some specific important primary parameters. DOE is a desirable tool that furnish appropriate information on the basis of optimized number of experiments. Researcher have already shown the advantage of DOE while studying the plasma spray coatings technique for alumina, aluminum nitride and Zirconia materials. In few research studies, DOE tool was successfully implemented to HA coatings applied using plasma spray technique. Xiaomei et. al. recently investigated that the process parameters had significant effect on bioceramic HA coating. The morphology and phase purity of HA coatings is greatly influenced by varying spray distance and current in the plasma spray technique [35]. Larger spraying distance tend to increase the dwell time of inflight particle in the plasma flame. So due to this the velocity of particle reduces resulting in complete melting of HA powder particles leading to decomposition of HA phases. The parameters that have significant effect on the HA based bioceramic coatings during plasma process includes plasma power/Current, powder Particle Size, working spray distance, powder feed rate, plasma Forming Gases and powder Carrier Gas [36].

4. Conclusion/summary:

The different types of most commonly used metallic biomaterials used in orthopedic surgery were reviewed in detail in this paper. The common deposition/modification technique such as plasma spray was evaluated on the basis of process parameters. The different process parameters of plasma spray technique that affects the quality of final coating were discussed. The following conclusions are drawn from this review.

1. The metallic biomaterials such as stainless steel alloys (316L), Titanium alloys (Ti-6Al-4V), Cobalt alloys (Co-Cr-Mo) are used globally and extensively in the world due to their superior mechanical properties.
2. The mechanical and tribological properties of bioceramic coatings can be maintained by selecting the proper functional metallic biomaterials, proper fabrication coating technique and proper selection of process parameters.
3. Plasma spray technique is the commercially accepted method for fabrication of HA coating in orthopedic medical industry. A small change in process parameters can immensely affect the properties of coatings.
4. It researches out that the second phase reinforcement in HA based composite coating imparts better wear resistance, fracture toughness and biochemical properties as compared to HA coating.

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