An Overview of Hydroxyapatite Coated Titanium Implants

Pankaj Vikas Rattan¹, T.S. Sidhu², Manoj Mittal³

¹Dept. of Mech. Engg., Amritsar College of Engineering and Technology, Amritsar -143 001, Punjab, India ²Shaheed Bhagat Singh College of Engineering and Technology, Ferozepur -152 004, Punjab, India ³Aryabhatta Group of Institutes, Barnala - 148 101, Punjab, India ¹Corresponding author E- mail: akshatrattan@gmail.com

Abstract - Hydroxyapatite [(HA), Ca_{10} (PO₄)₆ (OH)₂] is the main mineral component of bone and teeth. It has favorable osteoconductive and bioactive properties that is necessary for the early bone formation and fixation .HA being identified as the major mineral constituent of hard tissue, plays a vital role in orthopedic applications. One of its major applications is as a covering material for titanium and other metals used in implants. Main metallic biomaterials are stainless steel; Co based alloys, titanium and its alloys. Amongst the metallic biomaterials titanium and its alloys are getting much attention for use as biomaterials due to their excellent specific strength, corrosion resistance and above all good biocompatibility. Pure titanium and Ti-6AL-4V are still the most widely used biomaterials for biomedical applications among the titanium alloys. This article briefly reviews the hydroxyapatite coated titanium implants and its effects on the performance of the implants.

Keywords: Hydroxyapatite, Implants, Titanium, Biomaterials

I. INTRODUCTION

Bioactive ceramics and coatings for clinical applications in bone repair and replacements are represented by Bioglass, Hydroxyapatite [(HA), Ca_{10} (PO₄)₆ (OH)₂] and HA coated Ti-6AL-4V coatings. These biocompatible ceramics and coatings have a common characteristic in that they bond chemically and integrate well with living bone tissues [1].

Hydroxyapatite $[(HA), Ca_{10} (PO_4)_6 (OH)_2]$ is a bioactive material that has been applied in many prosthetic applications, mainly as a porous material for optimal bone in growth. Clinical tests have proved that HA is compatible with the tissues of vertebrates, making it an attractive bioimplant material [2].

However, it is severely limited by the intrinsic poor mechanical properties which can lead to instability and unsatisfactory duration of the implant in the presence of body fluids and local loading [3].

One solution to this problem is to use HA as a surface coating on a bio-inert metallic substrate e.g. titanium, Ti-6AL-4V and stainless steels. Biocompatible ceramic coatings on metals are used to take advantage of the bioactive properties of the ceramic and the mechanical properties of the metallic substrate [4].

II. DEPOSITION OF HA (TECHNIQUES USED)

The main property of any metallic biomaterial is the good mechanical strength, little or no cytotoxic metals in its composition, very good corrosion resistance, good plasticity and biocompatibility. All the properties mentioned are necessary for a biomaterial to be used as implant. The common biomaterials used are stainless steel, Co based alloys and titanium and its alloys. Titanium alloys are light and have very high strength to weight ratio. They possess good biocompatibility, outstanding mechanical properties, excellent resistance to corrosion in physiological environment and good formability. These properties make titanium alloys as the good candidate for the dental and orthopedic applications. However bone does not bond directly to these materials as they get covered with fibrous tissue after implantation, which keeps them isolated from the surroundings. In order to enhance the bone bonding ability, osseointegration and biocompatibility of titanium alloys its surface needs to be altered. Therefore, bioactive surface treatment i.e. bioactive surface modification is in general applied to titanium alloys for biomedical applications in order to improve their biocompatibility. For that many phosphate calcium ceramics and Hydroxyapatite are mainly coated on the surface of titanium alloys. In general, formation of Hydroxyapatite is finally targeted [5].

HA can be coated on the titanium by the process like plasma spraying, Sol-gel, sputtering, ion implantation etc. Plasma spraying technique is a popular method of depositing HA on titanium alloys like Ti-6AL-4V. HA coated implants with plasma spraying shows good bond strength as against uncoated implants. The coated implants provide earlier and stronger fixation [6].

However there are processing problems associated with this technique. Plasma spraying parameters such as spraying current, gun transverse speed influences the characteristics of the composite coatings. When high level of current is used the structure becomes less porous and splatted [7, 8].

On the other hand Sol-gel is time consuming and requires post processing annealing, but ion implantation has found the applications better than the plasma spraying and Sol-gel techniques [9].

Biomimetic technique to deposit HA coating on titanium alloys has found interest of researchers. With the use of 5X times concentrated simulate body fluids solution and soaking the titanium alloy substrate for different periods of time with and without use of Cao-Sio2 based glass, as a possible source of nucleating agent of apatite formation, various characterization techniques characterization techniques reveals the deposition of hydroxyapatite coating. But formation of HA coating is faster and better if soaked directly into the solution for few days. Coating developed by both the methods shows poorly crystallized structure [10].

Another method to implant Hydroxyapatite on the surface of titanium is by providing bioactive spots on the surface of the titanium mechanically. This is mainly due to the reason that the fixation of the implant to living bone is still developing, mainly because titanium and some of its alloys are not able to bond chemically. Stable fixation of titanium implants can be provided by bioactive spots on the surface by implanting the super plastic titanium alloy (Ti-4.5 Al-3V-2 Fe-2Mo) at 17 MPa and 1203k to obtain Ti-alloy-HA hybrid. HA granules can be mechanically held on the surface of the alloy, suggesting the possibility of the HA implantation for the surface modification of the orthopedic implants. The HA implanted pure titanium implant is considered good and favorable for the dental and orthopedic implants. The implanted HA ceramics are expected to bond to bone much faster than pure titanium resulting in faster initial fixation of the implant [11].

HA can also be deposited on the titanium substrate using micro blasting technique. HA deposited on the titanium via micro blasting of the surface directly with a HA particulate grit and using a novel coincident (Co blast) process, whereby alumina grit and HA dopent are blasted onto the surface together, reveals that Co blast surface is biocompatible and it promotes the formation of good quality lamellar bone. Also Co blast surface provide early stage osseointegration of metallic implants [12].

III. BIOLOGICAL AND MECHANICAL RESPONSE OF HA COATED TITANIUM

To enhance the mechanical properties of the HA/Ti-6AL-4V composites Hot Isostatic Pressing (HIP) can be used. The latter can offer the combined bioactive property of HA with the excellent mechanical properties of titanium alloys, for biomedical implants and prosthesis. Plasma spraying is used to obtain HA/ Ti-6AL-4V composite coating. The HIP of plasma sprayed composite coatings of Ti-6AL-4V improves properties like micro hardness and adhesion strength [13].

Different surface finishing of the Ti-6AL-4V alloy and of Hydroxyapatite coating has various effects on the performance of the alloy when it actually perform in simulated physiological solution under direct and alternating electrochemical current. Vaccum plasma spraying process shows increase of passive and corrosion current densities of the metallic substrate [14].

Pure titanium and its alloys such as Ti-6AL-4V occupy almost of the market of titanium biomaterials [8]. They show a high resistance to corrosion in the environment of physiological fluids and a good biocompatibility, in particular with hard human tissues. A passive oxide film (primarily Tio₂) protects the surface of titanium and its alloys against pitting corrosion and crevice corrosion. In order to improve the biocompatibility of titanium and its alloys calcium ion implantation founds to be very good alternative process and this also proves to be advantageous for the growth of the bone tissue. But it shows different results when it is studied for corrosion resistance of the metallic substrates. Its results confirmed the biocomtability of both calcium ion implanted and non implanted titanium under experiment. When electrochemically examined calcium ion implantation shows positive results for corrosion resistance, but undergoes pitting corrosion during its polarization. This aspect is of great importance for the materials to be used as implants [1 5].

The biocompatibility of calcium ion incorporated Ti-6AL-4V alloy implants using a Ca containing solution can be examined when produced by hydrothermal treatment. A considerable apatite deposition was observed on all surfaces of the Ca-incorporated samples. Cell viability, removal torque forces and bone –to- implant contact values increases with Ca-incorporation when treated and untreated Ti-6AL-4V implants are compared [16].

The coating thickness of Hydroxyapatite plays a vital role on the performance of the titanium alloy Ti-6AL-4V. The effect of coating thickness on the fatigue behavior of Hydroxyapatite coated Ti-6AL-4V shows that as the coating thickness increases fatigue resistance decreases, it shows no effect on fatigue resistance as the thickness decreases [17].

When grooved titanium implants are used, the addition of HA coating significantly improves the biological fixation. Groove depth plays a vital role in fixation, as groove depth of 1mm give significantly better fixation than 2mm. Also HA coated grooved titanium implants shows better fixation than traditional beeds coated porous surfaces [18].

Bonding of bone to plasma sprayed hydroxyapatite coatings cannot be explained on the basis of a mechanical interlocking bond alone. Insights into the mechanism of bone bonding at the ultra structural level could lead to improvements in the design of HA coatings. Results of Plasma Sprayed Hydroxyapatite (PSHA) coated titanium alloy (6%Al-4%V) indicates that PSHA coating crystallinity influences the timing of apatite deposition [19].

The biological properties of titanium depend on its surface oxide film. Many processes are used to modify the surface morphology and properties of titanium dental implants. Dental implant biocompatibility can be increased by increasing surface roughness and decreasing contact angle. Surface roughness and wet ability of implants influences the removal torque of dental implants [20].

Composite coatings can also be applied on the titanium alloys to enhance the mechanical and biological properties of the implants. Likewise hydroxyapatite –zirconia composite coatings can be applied on to the Ti-6AL-4V substrate with the plasma spraying process. The results show degradation of HA increases with the increase in the plasma arc current and also the ZrO₂ influences the decomposition of HA [21].

Another composite coating of hydroxyapatite and Titania can be applied successfully by plasma spraying process on titanium substrate, which shows that TiO_2 has positive effect on the biological and mechanical properties of HA-related coatings [22].

IV. FAILURE OF BIOIMPLANTS

The titanium alloys are known for their application in biomedical devices such as hip prosthesis and bone plates since many decades. Alloys such as Ti-6AL-4V are most widely used for bioimplants. Many bioimplants fails due to the fretting fatigue. Surface modifications can enhance the life of the biomedical titanium alloys. This can offer resistance against fretting damage. PVD Ti coatings and plasma nitriding are some of the processes that prove to be effective in minimizing friction and delaying failure of materials [23].

The poor bonding strength between HA and Ti has been of concern to the orthopedics. To overcome this, a composite coating of HA/Ti, prepared by atmospheric plasma spraying on Ti-6AL-4V alloy substrate, shows good results. The addition of Ti enhances the mechanical properties of the coatings. The bonding strength of HA/Ti composite coating proves to be higher than the HA coatings alone. Adhesive strength also shows positive results. Bioactivity of HA/Ti composite proves to be good [24].

Another problem that coatings on implants have to deal with is the decrease in interfacial shear strength due to the development of residual stresses. It directly affects the success of implantation and long term stability. This can be overcome by using Fluoriditated Hydroxyapatite coatings. It has attracted much attention as promising coating to replace pure HA ion implant surface. Sol-gel method is best suited for this type of coatings due to its homogeneous composition, low cost and ease of operation [25].

V. CONCLUSIONS

- 1. Titanium alloy (Ti-6AL-4V) is the most widely used alloy for the implant material.
- 2. Ion Implantation technique to deposit HA on titanium has been found to be a better option than Sol-gel, Plasma spraying and sputtering techniques.
- 3. Coating thickness plays a vital role on the performance and life of titanium alloys used as implants.
- 4. Implants fail due to the fretting fatigue, poor bonding strength between HA and Ti and due to the residual stresses developed in the coatings.

References

- Gu.Y.W., Khor.K.A. and Cheang.P.(2004), "Bone-like apatite layer formation on hydroxyapatite prepared by spark plasma sintering (SPS)", *Biomaterials.*, Vol.25, pp 4127–4134.
- [2] Yip.C.S., Khor.K.A., Loh.N.L. and Cheang.P.(1997), "Thermal spraying of Ti-6AL-4V / hydroxyapatite composites coatings : powder processing and post spray treatment", *Journal of Material Processing Technology*, Vol.65, pp 73-79.
- [3] Li.H., Khor.K.A. and Cheang.P. (2002), "Titanium dioxide reinforced hydroxyapatite coatings deposited by high velocity oxy-fuel (HVOF) spray", *Biomaterials*, Vol. 23, pp 85–91.
- [4] Haman.Jeannie D.,Lucas Linda C.and Crawmer Daryl.(1995), "Characterization of high velocity oxy-fuel combustion sprayed hydroxyapatite", *Biomaterials*, Vol.16, pp 229-237.
- [5] Niinomi Mitsuo.(2003) "Recent research and development in titanium alloys for biomedical applications and healthcare goods",*Science and Technology of Advanced Materials*, Vol. 4 ,pp 445–454.
- [6] Oonishi H., Yamamoto M., Ishimaru H., Tsuji E., Kushitani S., Aono M. and Ukon Y.(1989), "The effect of hydroxyapatite coating on bone growth into porous titanium alloy implants, *Journal of Bone Joint Surgery*, Vol. 71(B), pp 213-216.
- [7] R.Heleno., N. S Wagner. and Branco J. R. T.(2009), "Performance Evaluation of Hydroxyapatite Coatings Thermally Sprayed on Surgical Fixation Pins", *Key Engineering Materials*, Vol.396-398,pp 69-75.
- [8] Quek C.H., Khor K.A.and Cheang P.(1999), "Influence of processing parameters in the plasma spraying of hydroxyapatite/ Ti-6Al-4V composite coatings", *Journal of Materials Processing Technology*, Vol. 89-90, pp 550-555.
- [9] Rautray.Tapash R., Narayanan .R. and Han Kim Kyo.(2011), "Ion implantation of titanium based biomaterials", Progress in Materials Science, Vol. 56, pp 1137–1177.
- [10] Bharati S, Sinha M.K.and Basu D. (2005), "Hydroxyapatite coating by biomimetic method on titanium alloy using concentrated SBF", *Buletin. Material. Science*, Vol. 28, pp 617–621.
- [11] Teraoka K., Nonami T., Doi Y., Taoda H., Naganuma K., Yokogawa Y.and Kameyama T.(2000), "Hydroxyapatite implantation on the surface of pure titanium for orthopedic implants", *Materials Science* and Engineering, Vol. 13, pp 105–107.
- [12] Hare Peter O'., Meenan Brian J., Burke George A., Byrne Greg., Dowling Denis.and Hunt John A. (2010), "Biological responses to hydroxyapatite surfaces deposited via a co-incident micro blasting technique", *Biomaterial*, Vol. 31, pp 515–522.
- [13] Khor K.A., Yip C.S. and Cheang P.(1997), "Post-spray hot isostatic pressing of plasma sprayed Ti-6AI-4V/hydroxyapatite composite coatings", *Journal of Materials Processing Technology*, Vol. 71,pp 280-287.
- [14] Cabrini M., Cigada A., Rondelli G.and Vicentini B.(1997), "Effect of different surface finishing and of hydroxyapatite coatings on passive and corrosion current of Ti6Al4V alloy in simulated physiological solution", *Biomaterials*, Vol. 18, pp 783-787.
- [15] Krupa D., Baszkiewicz J., Kozubowski J.A., Barcz A., Sobczak J.W., Bilinski A., Lewandowska-Szumiel M. and Rajchel B .(2001), "Effect of calcium-ion implantation on the corrosion resistance and biocompatibility of titanium", *Biomaterials*, Vol.22, pp 2139-2151.
- [16] Park Jin-Woo., Park Kwang-Bum.and Suh Jo-Young. (2007), "Effects of calcium ion incorporation on bone healing of Ti6Al4V alloy implants in rabbit tibiae", *Biomaterials*, Vol. 28, pp 3306–3313.
- [17] Lynn A.K. and DuQuesnay D.L.(2002)," Hydroxyapatite-coated Ti-6Al-4V Part 1: the effect of coating thickness on mechanical fatigue behavior", *Biomaterials*, Vol.23, pp 1937–1946.
- [18]. Hayashi K., Mashima T.and Uenoyama K.(1999), "The effect of hydroxyapatite coating on bony in growth into grooved titaniumimplants", *Biomaterials*, Vol.20, pp111-119.
- [19] Porter A.E., Hobbs L.W., Rosen V. Benezra.and Spector M.(2002), "The ultra structure of the plasma-sprayed hydroxyapatite–bone interface predisposing to bone bonding", *Biomaterials*, Vol.23, pp 725–733.

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- [20] Elias Carlos Nelson., Oshida Yoshiki., Lima José Henrique Cavalcanti. and Muller Carlos Alberto.(2008), "Relationship between surface properties (roughness, wettability and morphology) of titanium and dental implant removal torque", *Journal of Mechanical behavior of biomedical materials*, Vol.1, pp 234-242.
- [21] Lim V.J.P., Khor K.A., Fu L.and P. Cheang. (1999), "Hydroxyapatitezirconia composite coatings via the plasma spraying process", *Journal* of. Materials Processing Technology, Vol. 89-90, pp 491-496.
- [22] Lu Yu-Peng., Li Mu-Sen ., Li Shi-Tong., Wang Zhi-Gang. and Zhu Rui-Fu.(2004), "Plasma-sprayed hydroxyapatite+titania composite bond coat for hydroxyapatite coating on titanium substrate", *Biomaterials*, Vol. 25, pp 4393–4403.
- [23] Vadiraj Aravind.and Kamaraj M.(2007), "Effect of surface treatments on fretting fatigue damage of biomedical titanium alloys", *Tribology International*, Vol.40, pp 82–88
- [24] Zheng Xuebin., Huang Minhui.and Ding Chuanxian.(2000), "Bond strength of plasma-sprayed hydroxyapatite/Ti composite coatings", *Biomaterials*, Vol.21, pp 841- 849.
- [25] Zhang S., Wang Y.S., Zeng X.T., Cheng K., Qian M., Sun D.E., Weng W.J. and Chia W.Y. (2007), "Evaluation of interfacial shear strength and residual stress of sol-gel derived fluoridated hydroxyapatite coatings on Ti6Al4Vsubstrates", *EngineeringFractureMechanics*, Vol.74, pp 1884–1893.