Plasma Spray: A Proposed Augmentation to Achieve Better Orthopedic Coating For Industrial Application

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Abstract— Hydroxyapatite (HAp) has widely been used as bone substitutes and as coatings on metallic prostheses because of its good biocompatibility and bioactivity. In order to improve its bioactivity further, HAp has been doped with zinc. It also increases the mechanical strength of implants. In this paper, zinc-doped HAp powder is synthesized through wet chemical method and the as-prepared powder is coated on titanium alloy through plasma spray process. The obtained powder is physically characterized using XRD and FTIR. The average Crystallite size is estimated by applying Scherer’s formula to the powder XRD pattern, which is found to be 31nm to 39nm. The crystallinity of the powder is also determined from the XRD pattern. The microstructure of the coating is observed using SEM image which confirms the coating to be a porous one. The adhesion strength, hardness and the crack propagation behavior of the coating is evaluated using ASTM C-633 standard; Vicker’s hardness testing and three point bending test respectively. The result shows that zinc doped HAp Coating exhibits higher mechanical strength. Few augmentations are proposed in this paper for the production of good quality Ca-HAp coating on orthopedic implants, emphasizing on the methods in current commercial use. Industrial practice with regards to cleanliness and characterization received special attention in this article.

Index Terms- Plasma spray, Ca-HAp, Coating

I. INTRODUCTION

There is a well recognized need of cement less fixation of metallic implants in orthopedic surgery. This promotes bone bonding with surrounding tissues and enables proper load transfer to prevent stress shielding. Few special metals and alloys (Titanium and Ti6Al4V alloy, surgical grades of stainless steel and cobalt chromium alloy) have been established for fabrication of artificial implants (prostheses) including orthopedic and dental devices because of their favorable mechanical and biological properties [1]. The primary stability of these implants requires extensive use of different bone cements. However, the use of polymethylmethacrylate or other polymer based bone cements to improve implant fixation can result in the deterioration of the adjacent cell or tissues due to necrosis because of excess heat generation during setting of cement [2]. To solve this problem and to improve the performance of metallic implants, they are coated with a bioactive material. A bioactive coating with good adhesion to the metal bond and interracially to the surrounding bone accelerates the stabilization of the implant and extends its life expectancy [3]. Especially preferred bioactive materials are however the ones having a chemical composition and crystal structure similar to those of the mineral constituents of bone tissues like Ca-phosphates. The human bone and teeth are mineralized tissues. The major sub phase of the mineral consists of submicroscopic crystals of an apatite of calcium and phosphate, whose crystal structure is very similar to calcium HAp that promotes bone formation which is necessary for implant Osseo integration. This property of Osseo integration is needed to minimize damages to surrounding tissues and to increase the implant efficiency [4]. HAp is used for bone replacement both as bulk or coating [3].

Biological and physicochemical properties of HAp can be improved by the substitution with ions usually present in natural apatites of bone. Most natural apatite’s are non-stoichiometric because of the presence of minor constituents such as captions (Mg$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Na$^+$, Sr$^{2+}$) or anions (HPO$^{4-}$ or CO$_3^{2-}$). Trace ions substituted in apatite’s can have effect on the lattice parameters, the crystallinity, and other physical properties of apatite’s [5]. Synthesis of Zn substituted HAp is of major interest because biological tissues like bone and teeth are composed with HAp containing zinc. Zinc is present in small amount in the enamel of human teeth and in bone. This element is probably the most important element in medicine because of its role in as much as 200 enzymes [6]. In order to improve the bioactive properties of HAp, it is doped with zinc. Zn$^{2+}$ ions substitute for Ca$^{2+}$ cations in the HAp
structure. HAp doped with 5% of Zn dissolves more rapidly than pure HAp or HAp doped with low concentrations of Zn [7]. Zinc plays an important role in proliferative effects on osteoblastic cells apart from inhibiting osteoclastic resorption. Zinc-substituted calcium phosphate has thus received considerable attention. The present study has focused on the effect of zinc doping on the microstructure of Zn-HAp coating on titanium implant by using plasma spray technique. This technique is being used for last one decade or so and it is giving good result as far as the performance of implants in long range of time domain is concerned [8]. The present article reviews the process, its efficacy, further scope and limitations particularly in context with the growing need of quality healthcare products in the Indian and south east Asian market.

II. MATERIALS AND METHODS

A. Powder Preparation and Characterization

The zinc doped HAp powder was prepared by wet precipitation route 5 wt% of Zinc Oxide was incorporated into the Calcium Hydroxide suspension and an aqueous solution of \( \text{H}_3\text{(PO)}_4 \) was added drop by drop to a solution of Ca(OH)\(_2\). The powder in the “as-prepared” condition did not flow freely, and it was not suitable for Plasma spray. Therefore, the powder was made free flowing before plasma spray. The phase composition of the powder was analyzed by X-ray diffraction (XRD) (Philips PW1710, The Netherlands) using monochromatic Cu K\(_\alpha1\) radiation at 55mA and 40 kV. The degree of crystallinity and the crystallite size of the as-sprayed Zn doped HAp powder was evaluated from the XRD data. The crystallinity (Xc) of the samples were determined with the following expression:

\[
X_c = \left(1 - \frac{V_{112/300}}{I_{300}}\right)
\]

where, \( V_{112/300} \) is intensity of hollow between the planes (112) and (300) reflections and \( I_{300} \) is the intensity of (300) reflection. [9]. The Fourier transformed infrared (FTIR) spectrum of the powder was recorded in the 400–4000cm\(^{-1}\) range by a spectrometer (Perkin-Elmer, Model: 1615, U.S.A.) in the transmission mode.

B. Substrate Preparation

In the present work, titanium alloy was taken as the metallic substrate. The substrates were shaped into strips of 110mm by 13mm by 4mm size. Prior to coating, the flat parallel ground substrate strips were blasted with 250 µm alumina grits of grit size 60 at a blasting angle of 90 degree with 100 psi pressure for 3 min. to roughen the Ti substrate surface to an average roughness (Ra) of ~6 µm. This step was followed by ultrasonic cleaning of the substrates using sequentially AR-grade acetone, ethanol, and deionized water.

C. Plasma Spraying

Plasma Spraying was carried out using a commercial machine 3 MB Sulzer Metco 40 kW system. The input current was fixed at 400 A. High purity Nitrogen (N\(_2\)) gas was used as the carrier gas or the primary gas for generation of plasma and Hydrogen (H\(_2\)) as the secondary gas for shielding. Plasma arc voltage was kept at 80V during spraying. A water cooling unit was used to cool the copper anode arrangement. Primarily, an arc is produced between tungsten cathode and copper anode, and it transfers to a continuous current path. The details of the process parameters are given in Table I. Due to high potential difference; a Pilot arc is initiated between tungsten cathode and continuous water cooled copper anode. Primary gas, i.e., plasma gas (N\(_2\)) is passed between the cathode and anode, and it ionizes. Now this ionized Nitrogen gas provides a continuous current path for the main transferred plasma arc. In our experiments, Hydrogen was used as the secondary gas, i.e., the shielding gas to protect from oxidation. Hot and partially molten externally fed powder was flown by the N\(_2\) gas pressure, and it stuck layer by layer on the substrate in the form of splats. Subsequently, the splats were air cooled for the development of coating. TiO\(_2\) was used as bond coat, it increases the bond strength and the coating life as well [10], [11].

**Table I. Parameters for plasma spraying process**

<table>
<thead>
<tr>
<th>Plasma spraying parameters</th>
<th>N(_2)/50/75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary gas/Flow rate (SLPM*)/Pressure (psi)</td>
<td>N(_2)/50/75</td>
</tr>
<tr>
<td>Secondary gas/Flow rate (SLPM)/ Pressure (psi)</td>
<td>H(_2)/7.5/75</td>
</tr>
<tr>
<td>Input current (Amp)</td>
<td>400</td>
</tr>
<tr>
<td>Voltage (Volt)</td>
<td>80</td>
</tr>
<tr>
<td>Standoff distance or Spray distance (mm)</td>
<td>125</td>
</tr>
<tr>
<td>Average size of powder (µm)</td>
<td>53-90</td>
</tr>
<tr>
<td>Feed rate (kg/hr) [low feed rate]</td>
<td>1.5</td>
</tr>
</tbody>
</table>
The phase purity and crystallinity of the as-sprayed Zn doped HAp coating on the Titanium is being analyzed by XRD. The FTIR spectra of the coating were recorded. To collect the spectra of the coating, the sample was prepared by scratching an extremely thin layer from the coating surface using a fine-pointed scalpel. These fragments were then mixed with dried potassium bromide (KBr) powders at a concentration of around 1wt%. The coating structure was examined using a Lucia 4.21 Nikon optical microscope. Hardness Test was carried out using a Vicker’s diamond indenter on an automated hardness tester (Model No-LV-700AT, LECO Co, MI). During the hardness test, a load of 3Kgf was applied on the sample for the hardness at five different locations. The average of these readings was computed, reported. The microstructure characterizations of the coating were carried out by scanning electron microscopy (SEM; JEOL JSM-6480 LV). The bonding strength of the coatings was evaluated in accordance with ASTM C633 using an Instron-type universal test machine at a crosshead speed of 0.5 mm/min. The purpose of adhesion strength tests is to understand the adhesion effect of Zn doped HAp Coating and substrate. Two identical cylindrical Titanium rod of approx 5 mm in diameter and 25 mm in length was grit blasted and attached to the surface of the coating using quick set epoxy resin as the adhesive and equal amount of hardener was mixed with it. The assembled samples were placed in an oven at 120 °C for 2 h for thermal curing [12]. The deformation and crack propagation behavior of the Zn doped HAp coating was investigated by simple three-point bending tests with the same machine under displacement controlled mode keeping the coated surface of the titanium bars in the same tensile side (Fig. 8). The doped sample was tested keeping the span length between the two rollers at 75 mm. The cross head speed was kept at 0.5mm/min. The Bending stress for both samples was computed, reported. D. Coating Characterization

The obtained XRD patterns of 5 wt% of Zn doped HAp powder was presented in Fig 1. The XRD calculated. The obtained FTIR patterns of 5 wt% of Zn doped HAp powder clearly shows the presence of the most prominent peak at 20 angle of ~31.7°C, corresponding to HAp (2 1 1) plane. Presence of this sharp peak suggests that the presence of 5 wt% ZnO as dopant did not alter the phase purity of crystalline HAp. Fig 2 shows the XRD of the Zn doped HAp coating. Apparently the XRD of Coating is similar with the powder XRD but Table II reveals decreased level of crystallinity in case of coating which might be a result of induced new phases by a high temperature during plasma spraying.

### Table II. Lattice parameter, Volume & Crystal Size of Zn doped HAp Powder

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percentage of Crystallinity</th>
<th>Lattice parameters (a and c)</th>
<th>Unit cell volumes (V)</th>
<th>Crystal size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5wt%Zn doped HAp Powder</td>
<td>88.123%</td>
<td>9.4178, 6.8850</td>
<td>1581.0270</td>
<td>31-39</td>
</tr>
<tr>
<td>Zn doped HAp Coating</td>
<td>77.79%</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The obtained FTIR patterns of 5 wt% of Zn doped HAp powder is presented in Fig 3, which shows bulge shaped peak at 3573 cm⁻¹ and 669 cm⁻¹ ensures the stretching vibration of OH⁻¹ ion. The bands formed at 1082, and 965 cm⁻¹ are characteristic bands of phosphate stretching vibration and the peaks at 1030, 562, 604 cm⁻¹ also reveals the presence of phosphate group. From these measurements, the powder is proved to be HAp. However, the
presence of a couple of minor peaks could possibly be attributed to the absorption of moisture and also of CO$_2$. The data on FTIR spectra of Zn doped HAp coating is shown in Fig.4. The band at around 964 cm$^{-1}$ and 965 cm$^{-1}$ in Zn doped powder and the coating 1043 cm$^{-1}$ & 1047 cm$^{-1}$, was the characteristic of non degenerate symmetric stretching of the PO$_4^{3-}$ group in HAp. It was also interesting to note that the characteristic bending band for OH$^1$ occurred at 636.5 cm$^{-1}$ in doped HAp powder, but it disappeared in the as-sprayed coating, thereby suggesting the presence amorphous phase in the as-sprayed coatings. This was earlier reported by other researchers [13], it was also observed in the present work. The band at 3571 cm$^{-1}$ has been referred as a stretching band of OH$^1$ in literatures. This information also suggests that a dehydroxylation occurred in the Zn doped HAp coating of present work. Thus, the overall observations of the FTIR spectra corroborated well with the XRD data.

![FTIR of Zn doped HAp Powder](image1)

**Fig 3.** FTIR pattern of 5% Zn doped HAp Powder [16]

![FTIR of Zn doped HAp Coating](image2)

**Fig 4.** FTIR pattern of Zn doped HAp Coating [16]

The Optical Microscopic Image of the cross section of the Zn doped HAp coated sample is shown in Fig 5 and it can clearly be seen that the coating is dense and have a very good contact with the substrate. The thickness measured shows that for TiO$_2$ Bond coat, the thickness was ~ 0.267 mm ± 0.0336 and that of Zn doped HAp Coating~ 0.623 mm ± 0.0521. We measured the thickness of the bond coat as well as the coating for both the cases at number of locations along the length of contact. It revealed a very much uniform coating thickness.

![Cross-sectional optical micrograph image of Zn doped HAp Coating](image3)

**Fig 5.** The cross-sectional optical micrograph image of Zn doped HAp Coating [16]

The hardness of Zn doped HAp coating was measured from Vicker's hardness test and it is found to be 300.9 ± 63.85, which is quite higher than the hardness value of pure HAp as reported by the other paper [14]. It means zinc incorporation increases the mechanical strength of the coating which is an important aspect from mechanical point of view. The SEM micrographs of as-deposited HAp coatings shown in Fig 6 describe that the coating was mainly composed of accumulated splats of elliptical and spheroidal shapes. Typical intra-splat and inter-splat pores are shown in Fig 6. (a) [the small arrows indicate the pores]. Some large pores found on the inter particle boundaries which may have originated during solidification of particles from un/semi-molten state. The SEM image fig 6 (b) shows larger portions of the coatings exhibit flattened regions which might have been formed during solidification of molten species that have fused together in lumps. No cracks are observed on the surface.
The bonding strength of the coating was evaluated as ~9.768 MPa which is within the wide range of values (~2-30 MPa) reported in the literature of coating [15] (due to lack of samples the experiment could not be repeated). After the bonding strength test, the fractographs are shown in Fig 7. The failure modes of the coating involved both cohesive failure zones ($F_{co}$) where fracture occurred in between the ceramic splats themselves and adhesive failure zones ($F_{ad}$) where fracture occurred in between the ceramic splats and substrate. Bonding strength was strongly dependent on the mode of fracture. More of adhesive failure was likely to promote good adhesion between the coating and the substrate [15]. Bonding strength of Zn doped HAp coating is higher than that of Pure HAp coating as reported in the thesis [16]. It means that zinc incorporation has increased the adhesion strength.

The typical load versus load-point displacement plots for the Zn doped HAp Coated sample is shown in Fig.9. Stress developed at the coated sample was calculated according to the following equation [17]

$$\sigma = \frac{3PL}{2wt^2}$$

Where $P$ is the applied load, $L$ is the span length, $w$ is the width and $t$ is the total thickness of the Zn doped HAp coated sample. It should be noted that the calculation of the stress assumes the coating-substrate composite system as a single material [17]. The value of stress developed at the Zn doped HAp coated sample during the initiation of crack was 447.64 MPa and at the time of failure was 509.45 MPa. Under similar test condition, pure HAp sample showed that the crack initiation and the failure of the Pure HAp coated sample occurred at much lower load as reported earlier [16].
IV. INDUSTRIAL COATING

A. Coating quality aspect from application point of view

The virtues of plasma spray coating have made it popular among orthopedic surgeons as well as researchers. As a result the demand of coated dental and orthopedic implants has increased with time. But as far as high quality of coating (in terms of safe and prolonged lifetime) is concerned, there are still a lot of areas to address.

In case of a nicely coated Acetabular cup as shown in fig 10, the edges of the protrusions and the edge of the cups are coated uniformly. The roundness of coating is ensured even after the removal of the screws attached at the top. The color of the metallic part near the coating does not suffer change due to excess heating. As the on-job temperature was properly optimized. Minor marks of masking tapes could not be seen on the metallic implant surfaces after their removal. No scratch was formed on the surfaces.

B. Use of Bond Coat

Bond coats improve the adhesion strength in case of bioceramic coatings. It also prevents direct contact between substrate and coating since this is thought to catalyze the thermal transformation of HAp towards tri- or tetra calcium phosphate or even non-biotolerant CaO [10], [11]. It reduces the release of metal ions from the substrate to the surrounding living tissue that has been shown to induce massive hepatic degeneration in mice and impaired development of human osteoblasts, it reduces the thermal gradient at the substrate/coating interface caused by the rapid quenching of the molten particle splats that leads to deposition of amorphous HAp with a concurrent decrease in resorption resistance and hence reduces the in vivo performance, i.e. longevity of the implant. It prevent a steep gradient in the coefficients of thermal expansion between substrate and coating that promotes the formation of strong tensile forces in the coating giving rise to crack generation, chipping and/or delamination, as well as cushion damage by cracking and delamination of the coating initiated by cyclic micro motions of the implant during movement of the patient in the initial phase of the healing process [21]. Thus, it is highly desirable to engineer the substrate/ HAp coating interface in such a way that by application of a suitable thin biocompatible bond coat layer the advantages addressed above can be realized. In the commercially available HAp coated implants no bond coat
is used. As of now no such implant failure is reported. However, it is widely reported that use of bond coat in between the surface of implant and coating helps in increasing the bond strength [22]. But the use of bond coat in implant is not in practice. It is an area where a thorough study is still awaited.

C. Some technical suggestions

Surface roughness of coating should be checked with the help of roughness gauge. Bond strength should be measured following ASTM C633 standard. Masking is very important while coating. Metal Masking can be an option which will reduce the problems such as scratches on the metallic surface during removal of masking, overheated metal zone etc. and it will give uniform and even edge. Before coating and after blasting, proper cleaning of implant surface is a must. If ultrasonic cleaning in acetone is done it can be beneficial. Dry Ultrasonic cleaning after HAp coating is highly recommended. If the coating is done manually, uniform thickness is a major issue which needs precise control. A properly designed fixture can be used to achieve an even coating thickness. After the material has been coated the characterization techniques are to be followed. Often during industrial practice, only the thickness is checked but the roughness and the bond strength should also be checked. The parameters for Plasma coating of HAp on different material are different. An optimized set of parameters can be beneficial for better utilization of power and efficient coating. There should be some controlled study in pilot level so as to optimize all the operation parameters like power, powder feed rate, table movement, speed and angle of rotation of the sample holders.

In the plasma spraying process many inter-dependent variables influence the properties of coatings and their performance in practical service. As far as the performance of HAp coatings deposited onto prosthesis shafts is concerned, the following properties appear to play a major role i.e. the Crystal phase composition that renders the coatings more or less biocompatible & porosity that may influence kinetics of osteointegration. These micro structural features depend, in turn, on the parameters of plasma spray processing [23]. Hence an optimized parameter can be beneficial for better utilization of power and less wastage of powder. Powder utilization can be controlled by using different Fixtures for different types of implant. These jigs and fixtures should be carefully designed so as to maximize powder utilization and ensure uniform coating. It will also help in holding the samples and developing a uniform thickness of coating by rotating the object in three dimensions. The plasma spray parameters should be optimized to control the thickness. This can be done by a detailed study of the parameters. Care should be taken to avoid coating on masking. Otherwise while removing the masking, cracks can be formed (see fig 11). Apart from all these, some soft interventions are also needed. Industrial workers should be well trained to put masks or the wax cover with utmost precision, to maintain cleanliness. The environment should be free from dust. Workers should wear clean gloves. Plasma room should be clean. An overall cleanliness should be maintained while handling the implants.

Fig 11. Coating Defects [16]

D. Cost and Efficiency

The machines required for plasma spray coating are Blasting machine, ultrasonic cleaner, Plasma Spray Machine. Instruments required for Characterization are thickness-gauge, profilometer and UTM for bond strength checking. All these machines together demand a huge investment. But once done, the ever expanding market can appreciably cut down the pay-back period. Before we end, it would not be irrelevant to reiterate that cement less fixation of biomedical implants has come into picture with great promise. The success of this approach solely depends on efficacy of coating technique on orthopedic components like stem, cup, plates, screws etc. Recent trends show that with increasing popularity of cement less fixation, Plasma spray technology is going to be explored to a great extent in next few decades. For this, proper design augmentation, better characterization techniques and cleanliness are
some of the major tasks lying ahead. But all these should be done at an industrially affordable cost so that the coated implant can reach the end users at a reasonable price.

V. CONCLUSION
The major observations as evident from the study are as follows:

- Zn doped HAp powder could be developed and coated on Titanium substrates successfully. The necessary optimization of Plasma spray process parameters were done so as to generate a thin layer as required various biomedical applications.
- The FTIR of Zn doped HAp coating verifies that dehydroxylation takes place during plasma Spray process.
- The thickness of the coating and bond coat produced on Titanium were found to be very thin as desired. For HAp coating a uniform thickness (less than 1 mm) could be maintained along the total length of the specimen.
- SEM micrographs reveal the formation of mixed splats and good amount of porosity with no cracks on the surface.
- It was observed that hardness of Zn doped HAp coating was substantially higher than that of undoped HAp coated sample as reported by other researcher under similar experimental condition.
- The cracks initiating load in Zn doped HAp coating was higher than pure HAp coating as reported by other researcher under similar experimental condition.
- The adhesion strength of coating increases with the incorporation of zinc into HAp.

VI. ACKNOWLEDGEMENT
We acknowledge the support from the School of Bioscience and Engineering Department, the IFGL Bioceramics Ltd. and the Mechanical Dept. of IIT Kharagpur.

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Abhijit Chanda completed his Bachelor’s in Mechanical Engineering from Jadavpur University, WB, India, in 1991 followed by Masters in Mechanical Engineering from Calcutta University in 1994. He completed his PhD in 2002 from Jadavpur University. He has 50 journal publications under his name and has authored three engineering textbooks. Currently he is the Joint Director of School of Bio Science and Engineering, Jadavpur University, India.