Development of Bioactive Ceramic Coating on Titanium Alloy substrate for Biomedical Application Using Dip Coating Method

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Abstract. Bioactive apatite, such as hydroxyapatite ceramic (HA), \([\text{Ca}_{10}(\text{PO}_4)_{6}(\text{OH})_2]\) has been extensively investigated for biomedical applications due to its excellent biocompatibility and tissue bioactivity properties. Its bioactivity provides direct bonding to the bone tissue. Because of its similarity in chemical composition to the inorganic matrix of bone, HA is widely used as implant materials for bone. Unfortunately, because of its poor mechanical properties, this bioactive material is not suitable for load bearing applications. In this study, by the assistance of dip-coating technique, HA coatings were deposited on titanium alloy substrates by employing hydrothermal derived HA powder. The produced coatings then were oven-dried at 130˚C for 1 hour and calcined at various temperature over the range of 200-800˚C for 1 hour. XRD measurement showed that HA was the only phase present in the coatings. However coatings calcined at 800˚C comprised a mixture of HA and tri-calcium phosphate (TCP). FTIR measurement showed the existence of hydroxyl, phosphate, and carbonate bands. PO\(_4\) band became sharper and narrower with the increased of calcination temperature. FESEM observation showed that the coating is polycrystalline with individual particles of nano to submicron size and has an average particle size of 35 nm. The thickness of the coating are directly proportional with the viscosity of coating slurry. It was shown that the more viscous coating slurry would produce a thicker ceramic coating. Mechanical properties of the coating were measured in term of adhesion strength using a Micro Materials Nano Test microscratch testing machine. The result revealed that the coating had a good adhesion to the titanium alloy substrate.

1. Introduction

The need to introduce man-made materials into the treatment of the human body has prompted a wave of research into the field of biomaterials. A major challenge in biomaterials field is to enhance the interface between biomaterial implants and the living tissue surrounding them. Some researchers in the field of orthopedic biomaterials direct their focus on the fabrication and enhancement of bioactive properties of calcium phosphate-based compounds, in particular towards the use of hydroxyapatite (HA). On the other hand, the number of patients requiring and receiving biomedical implants to
correct skeletal or dental defects and heal diseases is constantly increasing. Large demand exists for load-bearing hip, knee and dental implants and also for bone replacement.

Biomedical materials in use today include metals and alloys, ceramics, synthetic polymers, biologically derived substances, and composites[1]. They are used to repair, restore, or replace damaged or diseased tissue in artificial organs, tissues or in prostheses. It is of foremost importance that the implanted device not only restores the desired function to the body but continues to do so for the lifetime of the patient. When orthopaedic implants fail after certain period of time, revision surgery becomes necessary where it is far more complicated than the original replacement surgery. Thus, affirms the need to promote long implant lifetime where the implant should be integrated quickly with the human body by the way of bonding with the surrounding bone [2]. Biomedical materials can be divided into three main categories based on the tissue response. However, there is no single biomaterial that is best for all implants and all patients [1].

Hydroxyapatite has excellent chemical and biological affinity with host hard tissue due to the chemical and compositional similarity between natural bone and HA[3,4]. Studies have shown that HA shows no toxicity, no inflammatory response, no pyrogenic response, promotes formation of osseous tissue, facilitates in bone-implant bonding, and does not result in fibrous tissue formation between the implant and the bone [1-4]. Although HA is a stable phase, HA alone is not favoured is a nonbiodegradable bone-replacement materials which would not be replaced by bone as it degraded. Furthermore, due to its brittleness and low fracture toughness [5], its application is constrained to non-load bearing area only.

Therefore, the incorporation of metal such as manganese [6], magnesium [7], and many others into the apatite structure has been of great interest as it improves the mechanical properties of bones. Another way to utilize the bioactive characteristics of HA is by depositing a bioactive coating on metallic implants that enhances the adherence of the metal to the bone and protects the metal from corrosion by the body fluids. Thus, the concept of coating metal implant surfaces with HA ceramic coating would combine the excellent bioactivity and biocompatibility of HA with the good mechanical properties of metal alloys[7].

Bioactive coatings are substances that are added to the surface of an implant to promote and to enhance biological fixation. In other word, it is used to modify the surface of the implant material and to create new surfaces with totally different properties with respect to the substrate. The CaP family has a variety of compounds, many of which are used in biomedical applications. The stability of CaP compounds is controlled by the ratio of calcium to phosphorous, the temperature at which they are processed, the amount of water present, as well as the pH of the surrounding environment.

Adhesion strength between the coating and the substrate is a critical factor in successful implantation and long-term stability of any coated implant. The most commonly used methods employed to evaluate adhesion strength of hydroxyapatite on metal alloys include tensile test (pull-out test) and scratch test. Scratch testing is frequently used to assess the behaviour of thin films under the influence of an applied load. In particular, scratch testing can be used to assess coating adhesion to determine when the failure mode is occurring.

2. Experimental Procedures

2.1 Preparation of HA powder
The HA powder was prepared via a hydrothermal method involving simple chemical reaction. Using calcium oxide, \((\text{CaO})\), ammonium di-hydrogen phosphate, \((\text{NH}_4\text{H}_2\text{PO}_4)\) as the raw materials for calcium and phosphorus, respectively, while distilled water was used as solvent. The mixture was heated and stirred at 86-92°C under stirring condition until all water fully evaporated. The produced powder then was oven-dried at 120°C and calcined at different temperatures of 200°C to 800°C for 1 hour.
2.2 Preparation of HA coating slurry
HA powder together with starch as binder and water as solvent were used to prepare the coating slurry. Meanwhile, titanium alloy Ti–6Al–4V was used as the substrate. The slurry preparation involves mixing and stirring the HA powder with starch and water until a stable solution was produced for coating purposes. In this study, three different compositions of coating slurries were prepared. The composition of slurry was manipulated by varying the amount of water at 8, 10 and 12 grams, while the amount of HA powder and starch were fixed at 5 g and 0.5 g respectively. The details are as tabulated in Table 1.

Table 1: Parameter of Coating Slurry

| Composition | Water (g) | HA powder (g) | Starch (10% of HA) (g) | Stirring time (hrs) |
|-------------|----------|---------------|-------------------------|---------------------|
| 1           | 8        | 5             | 0.5                     | 24                   |
| 2           | 10       | 5             | 0.5                     | 24                   |
| 3           | 12       | 5             | 0.5                     | 24                   |

2.3 Preparation of titanium alloy substrate

Titanium alloy substrate (Ti–6Al–4V) was used for hydroxyapatite ceramic coating. The Ti–6Al–4V is usually preferred in load bearing bone implant applications due to its higher strength and fatigue resistance. The titanium alloy sheet was cut into small pieces with the size of 8 mm (w) X 8 mm (l) X 1 mm (h) using Electro discharge machine (EDM Wirecut). Then the sheets were abraded using emery paper grit 400. Prior to the coating process, all the samples were cleaned ultrasonically with acetone, ethanol, and distilled water, respectively, for 10 minutes and dried at 80˚C.

2.4 Dip Coating Process

The coating process was performed electronically using a special dip-coating apparatus) at a constant dipping and withdrawn rates of 1 mm/s. Dipping and pulling were done at a constant speed without any rapid shaking. The coated substrate then, they were oven-dried at 130˚C for 1 hour to form a white coating layer before calcination process at temperatures of 200, 400, 600 and 800˚C for 60 minutes with the heating–up rate kept at 10˚C/min.

2.5 Characterization Techniques

The purity and phase compositions of the HA coating were analyzed by using X-ray diffractometer (XRD). Fourier transform infrared (FTIR) spectroscopy was used to identify typical hydroxyapatite chemical groups. Analyses were performed in the range of 380 to 4000 cm⁻¹, with a Perkin Elmer (Spectrum 1000 model) equipment. In the meantime, hydroxyapatite coatings microstructure were evaluated by means of Field Emission Scanning Electron Microscope (FESEM). At the same time, Micro Materials Nano Test micro scratch testing machine was used to measure the adhesion strength of the produced coating.

3. Results and Discussion

3.1 XRD analysis of HA coatings at different calcination temperatures
Figure 1 shows the XRD patterns of HA coatings at different calcination temperature on titanium alloy substrate at 200, 400, 600 and 800°C. Until 600°C, the XRD result showed that HA was the only phase present which is in agreement with the standard JCPDS file No. 09-0432 for hydroxyapatite. Meanwhile at 800°C, a β–tricalcium phosphate phase (β–TCP) (JCPDS 09-0169) [9], was identified in the hydroxyapatite coatings. It was a mixture, comprising hydroxyapatite and tricalcium phosphate phases. It is known that the presence of β-TCP phase is the result of high calcination temperature of calcium deficient-HA. XRD results also established that with the use of a commercially cheap raw material, it is possible to produce hydroxyapatite coating using a simple dip-coating technique.

3.2 FTIR analysis of HA coatings at different calcination temperature

Meanwhile, Figure 2 shows the FTIR analysis of titanium alloy substrates at different calcination temperatures. It is observed that the OH band of HA coating for calcination at 200°C was much more intense compared to other calcination temperatures. It was also observed that at higher temperatures, the OH band, at around 2900-3700 cm⁻¹, disappeared. The spectrum also revealed that PO₄ band became sharper and narrower, indicating an increase in crystallinity of HA coatings upon the increment of calcination temperatures. It was also observed that at 800°C, the TCP phases appeared suppressing the HA phases. This is in agreement with XRD result as in Figure 1. The presence of carbonate group in the HA coatings was also observed. This was probably due to the fact that depositions were performed in open atmosphere. For this reason, carbonate was incorporated into the coating due to CO₂ presence in the environment, which had reacted with OH⁻ present in solution or atmospheric humidity.
3.3 Morphology observation of HA coatings at different calcination temperature
The microstructure of HA coating at different calcination temperatures is shown in Figure 3 below. Observation showed that the produced HA coating was extraordinarily polycrystalline with nano-size primary particles. The size of the particles tended to increase as the calcination temperatures increased. It was conditional that as the calcination temperatures increased, the coatings would be more densified due to the coarsening of crystallite size. This was contributed by the fusion of the particles with one another as the spherical aggregates melted.

![Figure 3: FESEM morphology of HA coating at different calcination temperatures; (a)200 ºC, (b)400 ºC, (c)600 ºC, (d) 800 ºC.](image)

3.4. Particle size of HA coating
The particle size of HA coatings was calculated by applying Scherer’s equation in XRD analysis and Nano-sizer. The obtained result was summarized in Table 2 below. It was observed that the particle size for HA powders increased from 24nm to 64nm (xrd) and 298nm to 2327nm (nanosizer) with increasing of temperature from 200°C to 800°C.

| Calcination Temperatures °C | XRD analysis of coating(Scherer’s equation) (nm) | Nano–sizer analysis (nm) |
|----------------------------|-----------------------------------------------|--------------------------|
| 200                        | 24                                            | 298                      |
| 400                        | 19                                            | 305                      |
| 600                        | 32                                            | 648                      |
| 800                        | 64                                            | 2327                     |

3.5. Thickness of HA ceramic coating
The thickness of the ceramic coating was measured by using FESEM. It was shown that the more viscous coating slurry would produce a thicker ceramic coating. The average thickness and cross section view of the coating are as shown in Table 3 and Figure 4 respectively.

| Water contents | Thickness of ceramic coating |
|----------------|----------------------------|
| 8g water       | 135.7μm                    |
| 10g water      | 52.6 μm                    |
| 12g water      | 12.8μm                     |

Table 4: Measurement variation of ceramic coating

Figure 4: Thickness of ceramic coating at different viscosity; a) 8g water, b) 10g water and c) 12g water.

3.5. Scratch test of HA ceramic coating
Scratch test is one of widely used, fast, and effective methods to obtain the critical loads that are related to adhesion properties of coating. The strength of coating is influenced by a number of factors. These include substrate surface roughness, calcination temperature, deposition method, post heat treatment condition and many others. In this study, the HA coatings were subjected to a series of scratch test measurements using a Micro Materials Nano Test microscratch testing platform with a 200 μm spherocnical diamond indenter. The data recorded during scratch testing included the penetration depth, failure load and displacement. In this study the scratch analyses were done in term of two different measurement parameters as shown in Table 4.
The data during scratch testing is recorded include the penetration load, distance and depth. The result of the scratch analysis are as tabulated in Table 5, while the scratch track were observed using SEM. For example, in Measurement 1, the minimum load at which cohesive failure occurs is called the first critical load \( L_{c1} \), which is 2.45 mN appears at the distance of 40.7μm with the suddenly decreasing of the depth to 2274 nm. From Table 5 also, it is observed that for Measurement 1 (comparison between 8g water), the penetration distance of (ii), was higher than (i). Thus it is deduced that high temperature produced denser coatings. Figure 5 shows the differences of these two coating parameters.

### Table 5: Comparison of failure values in the ceramic coating

| Measurement | Condition                      | Penetration distance, (μm) | Penetration load, (mN) | Penetration depth, (nm) |
|-------------|--------------------------------|----------------------------|------------------------|-------------------------|
| 1           | Variation in calcination temperature | 40.7                       | 2.45                   | 2274                    |
| 2           | Variation in thickness of coating slurry | 70.6                       | 2.41                   | 5747                    |
| (i)8g       | 200                             |                            |                        |                         |
| (ii)8g      | 400                             |                            |                        |                         |
| (iii)10g    | 600                             |                            | 1.18                   | 42.9                    | 1193                    |
| (iv)12g     | 600                             |                            | 0.63                   | 28.6                    | 957                      |

![Figure 5: Scratch images for 8g water calcined at (a) 200°C and (b) 400°C.](image)

The comparison between scratch test at different thickness of coating slurry but same calcination temperature is shown in Figure 6. The scratch track for less viscous coating slurry (b) was almost unseen due to the thin ceramic coating. The penetration load and distance before failure occurred was also very little compared to the more viscous coating slurry (a). It was also observed that penetration distance of (a) was higher than (b). Thus it is concluded that the less viscous slurry would produce less density of coating.

![Figure 6: Scratch images for (a) 10g water and (b) 12g water after calcination at 600°C.](image)
Conclusion
A simple, cheap and good repeatability dip-coating technique was employed to deposit hydroxyapatite coatings on titanium alloy Ti–6Al–4V substrate. XRD and FTIR results showed that HA was the only phase present in the coating. However at higher temperature, TCP phases appeared suppressing HA phases forming biphasic calcium phosphate (BCP). From FESEM observation, it was obvious that the produced HA coating was extraordinarily polycrystalline with nano-size primary particles. However, from the scratch test analysis, it was revealed that the produced coating exhibited poor bonding strength although throughout various HA coating analyses, a pure and fine HA coating was produced. Moreover the coating exhibited surface cracked probably due to the shrinkage occurring during the drying and thermal processes. On contrary, this study had shown that the use of dip coating method for deposition of HA coating is simple; having good flexibility for various shapes of medical implant materials with high production rates.

References

[1] N. Patel and P. Gohil, “A review on biomaterials: scope, applications & human anatomy significance,” Int. J. Emerg. Technol. Adv. Eng., vol. 2, no. 4, pp. 91–101, 2012.
[2] T. Szatkowski, A. Kolodziejczak-Radzimska, J. Zdarta, K. Szwarc-Rzepka, D. Paukszta, M. Wysokowski, H. Ehrlich, and T. Jesionowski, “Synthesis and Characterization of Hydroxyapatite,” Physicochem. Probl. Miner. Process., vol. 51, no. 2, pp. 575–585, 2015.
[3] S. Jafari, M. M. Atabaki, and J. Idris, “Comparative study on bioactive coating of Ti-6Al-4V alloy and 316 L stainless steel,” Assoc. Metall. Eng. Serbia AMES, vol. 18, no. 2, pp. 145–158, 2012.
[4] Hench, L.L. and Wilson, J. (1993). An Introduction to bioceramics. Advanced series in Ceramics. Singapore; New Jersey: World Scientific.
[5] Tan, C. Y., Ramesh S., Khalid KA., Abou-El-Hossein, M. Hamdi, and Sopyan, I. (2006). The effect of MnO2 on the sinterability of hydroxyapatite. Proceeding of the International Conference on Manufacturing and Materials Processing, ICMM, Kuala Lumpur, Malaysia.
[6] Mayer, I, Cuisinier, F.J.G., Popov, I., Schleich, Y., Gdalya, S., Burghaus, O. and Reinen, D. (2006). Phase Relations Between β-Tricalcium Phospahte and Hydroxyapatite with Manganese (II): Structural and Spectroscopic Properties. Eur. J. Inorg. Chem, 1460.
[7] Toibah, A.R., Sopyan, I., Hamdi, M. and Ramesh, S. (2008). Development of Magnesium-Doped Biphasic Calcium Phosphate through Sol-Gel Method. IFMBE Proceedings, 21, 314–317.
[8] M. A. Hussein, A. S. Mohammed, and N. Al-Aqeeli, “Wear characteristics of metallic biomaterials: A review,” Materials (Basel). vol. 8, no. 5, pp. 2749–2768, 2015.
[9] Kazuhiko, K., Hironobu, S., Tamoyuki, Y. (2008) Local environment analysis of Mn ions in β-tricalcium phosphate, Journal of the Ceramic Soc. of Japan. 116, 108-110.