CHARACTERISATION OF PLASMA-SPRAYED FISH SCALE HYDROXYAPATITE/YTTRIA STABILIZED ZIRCONIA BIOCERAMIC ON TITANIUM ALLOYS FOR MEDICAL IMPLANTS

By

ANENE FRANKLIN AMAECHI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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DEDICATION

This thesis is solely dedicated to my lovely wife and daughter, my dear parents and my brothers.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chairman : Associate Professor Ts. Che Nor Aiza Jaafar, PhD
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Hydroxyapatite (HA) coating on metallic implants have been extensively used in orthopaedic applications to improve on the tissue-implant interactions, enhance their biocompatibility and functionality without altering the implant's substrate properties. However, currently the expensive synthetic HA is widely used for coating of implants leading to the high cost of implants. Hence, the present research has explored the potentials of an inexpensive and halal natural biogenic HA derived from fish scales (FsHA) and FsHA doped with yttria stabilised zirconia (YSZ) bioceramic as an alternative coating material on Ti-6Al-4V and Ti-13Nb-13Zr titanium alloys. In this research, the effect of post coating heat treatment at 750 ^{o}C on plasma sprayed FsHA and FsHA/YSZ coating materials were investigated. Spray dry technique was used to produce the fine FsHA powders while plasma spray technique was applied in the coating process on the surface of Ti alloys substrates. The FsHA and FsHA/YSZ powders used as feedstock for the plasma spray coating were examined by x-ray diffraction (XRD) technique, fourier transform infra-red (FTIR) and scanning electron microscopy/energy dispersive x-ray (SEM/EDX). Meanwhile the physicomechanical and bioactivity tests were conducted on the coated substrates to study their mechanical properties, corrosion resistance, wettability, in vitro bioactivity in simulated body fluid (SBF) and in vitro cytotoxicity. The results of the research showed that the crystallinity of the FsHA/YSZ powders was above 96%, the least crystallinity of the plasma sprayed coatings was 65.7% while the crystallinity of the heat-treated FsHA coatings was about 85%. From SEM analysis, the microstructure of the plasma sprayed coatings revealed fine lamellar with partially melted and unmelted FsHA particles as well as fine micro cracks along with evenly dispersed ZrO_2 particles within the coating matrix of the FsHA/YSZ coatings. Post-coating treatment led to much denser and finer lamellar morphology with more cracks. It was observed that plasma sprayed

FsHA coatings on both alloys produced rougher surfaces (4.316 and 4.215 µm) than heat treated coatings (3.881 and 3.916 µm). Plasma sprayed FsHA/20 wt.% YSZ coatings on both Ti alloys recorded the highest hardness values (558.5 and 536.9 Hv) compared to their undoped coatings (459 and 467.8 Hv). Further improvement in hardness strength for heat treated coated Ti alloys gave the maximum hardness values (631 and 651.6 Hv), respectively for doped coatings of FsHA/20 wt.% YSZ on both substrates. Similarly, YSZ doping of FsHA improved the adhesion strengths, wettability and coefficient of friction (CoF) of doped coatings. Additionally, the corrosion resistance of both alloys was significantly improved up to 80% (9.48 and 9.97 mmpy) with the deposition of FsHA/YSZ bioceramic coatings compared to their uncoated substrates (169.37 and 128.0 mmpy). Bioactivity evaluation of the plasma sprayed and post coating heat treatment indicated all the surfaces of the coatings were covered with well grown apatite layers after 21 days immersion in SBF solution. Besides, the in vitro cytotoxicity test of the coating demonstrated good cell viability (more than 95%) which indicated the FsHA/YSZ coated Ti alloys were proven to be biocompatible. Therefore, it can be concluded that the coating materials produced from this research work are suitable for biomedical applications.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
segagai memenuhi keperluan untuk ijazah Doktor Falsafah

KARAKTERISASI BIOSERAMIC SISIK IKAN HIDROKSIAPATIT/ZIRKONIA YANG DISTABILKAN DENGAN YTTRIA YANG DISEMBUR PLASMA KE ATAS ALOI TITANIUM UNTUK IMPLAN PERUBATAN

Oleh

ANENE FRANKLIN AMAECHI

Oktober 2022

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Salutan hidroksiapatit (HA) pada implan logam telah digunakan secara meluas dalam aplikasi ortopedik untuk memperbaiki interaksi implant-tisu, meningkatkan bioserasi dan kefungsiannya tanpa mengubah sifat substrat implan. Walau bagaimanapun, sekarang ini, HA sintetik banyak digunakan secara meluas sebagai bahan salutan implan yang membawa kepada kos implan yang tinggi. Jadi, penyelidikan yang dijalankan ini telah menerokai potensi biogenik HA semulajadi yang murah dan halal yang diperoleh daripada sisik ikan (FsHA) dan juga FsHA yang didopkan dengan bioseramik yttria stabilized zirconia (YSZ) sebagai bahan salutan alternatif pada Ti-6Al-4V dan Ti-13Nb -13Zr aloi titanium. Dalam penyelidikan ini, kesan rawatan haba pada suhu 750 ^{o}C ke atas bahan salutan FsHA dan FsHA/YSZ yang disembur plasma telah dikaji. Teknik semburan kering telah digunakan untuk menghasilkan serbuk FsHA yang halus manakala teknik semburan plasma pula digunakan dalam proses salutan pada permukaan substrat aloi Ti. Serbuk FsHA dan FsHA/YSZ yang digunakan sebagai bahan suapan untuk salutan semburan plasma telah diperiksa dengan menggunakan teknik pembelauan sinar-x (XRD), spektroskopi Fourier inframerah (FTIR) dan mikroskop elektron imbasan / tenaga pembelauanan sinar-x (SEM/EDX). Sementara itu, ujian fizikmekanikal dan bioaktiviti telah dijalankan ke atas substrat bersalut untuk mengkaji sifat mekaniknya, rintangan kakisan, kebolehbasahan, bioaktiviti *in vitro* dalam cecair badan yang disimulasikan (SBF) dan sitotoksisiti *in vitro.* Keputusan dari penyelidikan yang dijalankan ini menunjukkan bahawa kehabluran serbuk FsHA/YSZ adalah melebihi 96%, kehabluran paling sedikit bagi salutan semburan plasma ialah 65.7% manakala kehabluran salutan FsHA yang dirawat haba adalah sekitar 85%. Daripada analisis SEM, strukturmikro salutan semburan plasma mendedahkan lamelar halus dengan partikel FsHA yang separa cair dan tidak cair serta retakan mikro halus bersama-sama dengan partikel ZrO_2 yang

tersebar secara sekata di dalam matriks salutan FsHA/YSZ. Rawatan salutan lanjut membawa kepada morfologi lamelar yang lebih padat dan halus dengan lebih banyak rekahan. Ianya dapat dilihat iaitu salutan FsHA yang disembur plasma pada kedua-dua permukaan aloi menghasilkan permukaan yang lebih kasar (4.316 and 4.215 µm) daripada salutan yang dirawat haba (3.881 and 3.916 µm). Salutan plasma FsHA/20 berat.% YSZ yang menyalut kedua-dua aloi Ti mencatatkan nilai kekerasan tertinggi (558.5 dan 536.9 Hv) berbanding salutan tidak terdop (459 dan 467.8 Hv). Peningkatan kekuatan kekerasan selanjutnya untuk aloi Ti bersalut dirawat haba berlaku dengan nilai kekerasan maksimum (631 dan 651.6 Hv), masing-masing untuk salutan terdop FsHA/20 berat.% YSZ pada kedua-dua bahan substrat. Begitu juga, FsHA yang didop YSZ telah meningkatkan kekuatan lekatan, kebolehbasahan dan pekali geseran (CoF) salutan terdop. Tambahan pula, rintangan kakisan kedua-dua aloi telah meningkat dengan ketara sehingga 80% (9.48 and 9.97 mmpy) dengan pemendapan salutan bioseramik FsHA/YSZ berbanding substrat yang tidak bersalut (169.37 and 128.0 mmpy). Penilaian bioaktiviti ke atas penyembur plasma FsHA/YSZ yang disembur dan rawatan haba selepas salutan menunjukkan semua permukaan salutan telah ditutupi dengan lapisan apatit yang tumbuh dengan baik selepas 21 hari rendaman di dalam larutan SBF. Di samping itu, ujian sitotoksisiti *in vitro* bahan salutan menunjukkan perkembangan sel yang baik (lebih daripada 95%) yang menunjukkan bahawa aloi Ti bersalut FsHA/YSZ ini terbukti mempunyai sifat bio serasi. Maka, ianya dapat disimpulkan bahawa bahan salutan yang dihasilkan daripada kerja penyelidikan ini adalah sesuai untuk kegunaan bioperubatan.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision.
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AM	Additive Manufacturing
DMLS	Direct Metal Laser Sintering
EBM	Electron Beam Melting
EDX	Energy Dispersive X-ray Spectroscopy
FsHA	Fish scale Hydroxyapatite
FTIR	Fourier Transform Infrared Spectroscopy
HA	Hydroxyapatite
JCPDS	Joint Committee of Powder Diffraction Society
PBF	Powder Bed Fusion
PBS	Phosphate Buffered Saline
PSD	Powder Size Distribution
SBF	Simulated Body Fluid
SEM	Scanning Electron Microscopy
SLM	Selective Laser Sintering
XRD	X-ray Diffraction
YSZ	Yttria Stabilized Zirconia

CHAPTER 1

INTRODUCTION

1.1 Background of the Research

The major factors driving the increased demand of orthopedic medical devices are the increasing rate of musculoskeletal diseases and osteoporosis, traumatic and sports injuries and increasing geriatric population. Reports have it that the global market size of orthopedic devices in 2019 was USD 53.44 billion and by 2027 it is projected to increase to USD 68.51 billion (Fortune business insights, 2020) while published report by United Health Foundation 2019 (UHF), stated that more than 300,000 adults aged 65 and above are estimated to be hospitalized each year for hip fractures. Similarly, the American academy of orthopedic surgeons reported that about 6.8 million patients with orthopedic injuries seek medical attention each year in the USA. Meanwhile the National Institute of Health (NIH) reported that more than 53 million people in the United States are estimated to have osteoporosis and are susceptible to higher risk of this disease due to the low bone to mass density (Medgadget, 2020).

One of the very important properties of metal alloys in use in orthopedic applications is the Young's modulus. Implants with higher modulus than the human bone results in inadequate stress transfer to bone which causes implant loosening and failure after some years (Geetha et al., 2005). This is one of the demerits of α + β Ti alloys like the Ti-6Al-4V alloy with high modulus of 110 GPa far more than the bone modulus of 18-30 GPa and contains Al that has been associated with long-term alzheimer disease while V has potential toxicity and adverse reactions in the body (Zaffe et al., 2004; Rao et al., 1996). This has led to the recent adoption of low modulus (40-60 GPa) β-Ti alloys with alloying elements such as Nb, Zr, Mo, Ta and Fe instead of Al and V elements (Hao et al., 2006; Kuroda et al., 1998).

Biomaterials possess good biological properties that are exploited in drug delivery, tissue engineering, cardiovascular devices, orthopedic and dental applications (Park and Bronzino, 2003). These materials are grouped into four major categories such as ceramics, polymers, metals and its alloys and natural materials (Sheikholeslam et al., 2017; Jaganathan et al., 2014; Langer et al., 2003). The human body which is made up of several parts degenerates as a result of many factors such as aging, diseases and accidents, hence, appropriate treatment is required. Biomaterials, like replacement implants for the hips, knees, shoulders, elbows and dental structures, can be used to replace the damaged body components (Aherwar et al., 2016). Metallic alloys such as Co-Cr alloys, 316L stainless steel and Ti-based alloys are the major biomaterials used in fabrication of these implants (Aherwar et al., 2016; El-Zayat et al., 2013; Uhthoff et al., 1981).

Commercially pure (CP)-Ti and Ti-6Al-4V alloy are the mostly used titanium-based alloys among the metallic alloys in orthopedic implants production due to their good biocompatibility and mechanical properties (Singh and Dahotre, 2007). Nevertheless, failures of these implants have been reported after long-term due to many factors like fatigue, wear, corrosion and higher modulus compared to the human bone (Geetha et al., 2009). Hence, development of enhanced biomaterials with improved toughness, resistance to wear and corrosion that can serve long-term in vivo is imperative. Vanadium contained in Ti-6Al-4V alloy has been reported to be toxic when released in the body which led to Ti-6Al-7Nb alloy gaining prominence in biomaterials application as Nb does not cause inflammation and allergic reactions when released in the body and stabilizes the β-phase like vanadium (De Assis et al., 2006; Venkatarman and Sudha, 2005; Khan et al., 1999). In addition, Ti-6Al-7Nb alloy has been noted to have higher biocompatibility and corrosion resistance in physiological solutions than Ti-6Al-4V alloy (Kobayashi et al., 1998). In contrast, Ti-6Al-4V alloy have higher resistance to wear than Ti-6Al-7Nb alloy with double phase microstructure (Fellah et al., 2014).

Researchers have posited that the best way to improve the life span of implants is by coating their surfaces with a bioceramic that promotes the adhesion of the inorganic component of bone hydroxyapatite (HA) with formula [$Ca_{10}(PO_4)_6(OH)_2$] (Renganathan et al., 2018). Bone consists of inorganic and organic components which offer strength, toughness and flexibility properties. The organic component comprises the glycoproteins, fibrillin, proteoglycans and collagen while HA is the inorganic component (Ghosh et al., 2018). For decades, HA has been used as a bioactive bone substitute material mainly as ceramics, cements, coatings and biocomposites in biomedical applications (Rey et al., 2009; Eichert et al., 2008; Xue et al., 2006). HA mainly used as dental prosthetics and bone grafting material is a mineral form of calcium apatite which can naturally be fabricated from bovine bone, coral, eggshells and fish bone. Other bioactive materials used in implant coating include carbonated hydroxyapatite (CHA), oxyhydroxyapatite (OHA), alkaline phosphate (ALP), fluoridated hydroxyapatite (FHA), tricalcium phosphate (TCP), oxyapatite (OA) and calcium phosphate (CaP) (Surmenev et al., 2014).

Materials for coating of orthopedic implants must exhibit high cohesive strength, minimal porosity, high adhesion strength, high crystallinity and phase stability (Epple and Surmenev, 2013; Surmenev, 2012). HA coating on Ti alloy implants is one of the most developed and efficient surface treatments that optimize the good mechanical properties of Ti with the bioactivity of HA (Deram, 2003). Implants are expected to remain intact after implantation for 15-20 years. Unfortunately, corrosive body fluids such as blood and other body fluid constituents like proteins, sodium, plasma, water, chlorine, and amino acids can adversely affect the biomechanical integrity of implants. Hence, an implant should possess high corrosion resistance to limit the dissolution of its surface oxide films that may introduce toxic ions in the body and induce the implants failure (Cachinho and Correia, 2008). The excellent biocompatibility and osteoconductivity of HA with human body fluid favours early bonding between bone tissues and the surface of the implant (Suchanek and Yoshimura, 1998; De Bruijn et al., 1995).

Despite the excellent properties of HA, their poor mechanical properties like low tensile strength, brittleness, fretting fatigue, toughness, poor impact resistance and adhesive strength have limited their use in some load bearing applications (Grootde et al., 1998). Significant improvement on the mechanical properties of HA has been reported with their reinforcement with metal powders or bioinert ceramics. Zirconia has been widely used as a biomaterial in implant and prostheses productions due to their biocompatibility in addition to good strength (Kohorst et al., 2012; Piconi and Maccauro, 1999). Similar to Zirconia, reinforcement with yttria stabilized zirconia (YSZ) is often used due to their biocompatibility, good toughening properties during crack-particle reactions and high strength (Chou et al., 2002). Enhanced mechanical properties have been reported with plasma coated HA/YSZ and HA/ZrO_2 than the HA (Chou and Chang, 2002; Fu et al., 2002) while Singh et al., (2013) reported improved resistance to corrosion with plasma coated HA + SiO_2 composite on 304 AISi alloy.

Some researchers reported the influence of HA coatings modified with other elements or compounds such as strontium (Sr), silicon (Si), Zirconia (ZrO_2), yttria stabilized zirconia (YSZ) and silica (SiO_2) on their biological properties (Nguyen et al., 2019; Ong et al., 2015; Singh et al., 2013; Balamurugan et al., 2008). Nguyen et al., (2019) reported that coating with calcium phosphate doped strontium improved cell attachment and proliferation on Ti medical devices for bone regeneration. Ong et al., (2015) reported good osteoconductivity with HA and silicate CaP coatings on porous Ti alloys. Similarly, Balamurugan et al., (2008) reported that synthetic HA doped with 3-5 wt.% silicon improved osteoblast growth by increasing cell growth density as well as improved osteoblast activity and differentiation. Addition of 1-10 wt.% strontium to HA was reported to favour proliferation of osteoclast and their production inhibition whereas carbonate-substituted HA was reported with enhanced osteogenesis (Spence et al., 2009; Capuccini et al., 2008). Piconi et al., (2016) reported that coating of the metallic ball head of a metal-polyethylene bearings in the hip arthroplasty with ceramics such as titanium nitride (TiN), titanium niobium nitride (TiNbN), zirconium nitride (ZrN), monoclinic zirconia (ZrO_2) and silicon nitride (SiN) enhanced their wear properties.

Plasma spray technique is one of the most commercially adopted techniques for HA coating owing to its advantages of high uniform rates of deposition, simplicity and low substrate temperature (Fernandez et al., 2004). Plasma coating involves production of an ionized gas (plasma) in which HA powder is injected, partially melted and projected to splat on a substrate at a controlled distance from the spaying gun (Fernandez et al., 2004). Despite the merits of coating ceramics such as HA, ZrO_2, HA/SiO_2 on Ti alloys, some drawbacks have also been reported. Firstly, the existence of significant difference in thermal expansion of ceramics and Ti alloys often induce thermal stresses that can result in formation of cracks at the coating interface layers and compromise the adhesion strength of the coatings (Renganathan et al., 2018). Also, the coating strength can be adversely affected by the chemical reactions at the interface between the ceramic and the alloy substrate (Renganathan et al., 2018).

1.2 Problem Statements

Ti-based alloy implants have been reported to fail in long-term owing to many factors like corrosion, fatigue, wear, mismatch of Young's modulus with bone (Geetha et al., 2009). One of the methods to improve the life span of implants is to coat their surfaces with a bioceramic that promotes the formation and adhesion of hydroxyapatite HA [$Ca_{10}(PO_4)_6(OH)_2$], the inorganic component of bone (Renganathan et al., 2018). However, the expensive synthetic HA is the mostly used bioceramic in coating of implants leading to high cost of implants. Hence, it's pertinent to find an economical and natural HA as an alternative coating material for implants.

Natural HAs unlike synthetic HA is non-stoichiometric due to the presence of trace elements such as Na, Zn, Mg, K, Si, Ba, F and CO_3 which makes it similar to the chemical composition of human bone (Akram et al., 2014). The presence of these trace elements in natural HAs mimic the apatite produced from human bone and plays a vital role in the regeneration of bone as well as accelerate the process of bone formation (Doostmohammadi et al., 2011). HA extracted from fish scales using calcination method have Ca/P ratios in the range of 1.62 to 1.71 which is close to the stoichiometric Ca/P ratio of 1.67 for synthetic HA and contains trace elements such as Mg, Sr, Na, and K (Mohd Pu'ad et al., 2019). Natural HA from fish scales offers the best alternative to synthetic HA since it is halal and their properties are similar to synthetic HA in addition to being inexpensive (Zainol et al., 2012). Also, despite the excellent properties of HA, their poor mechanical properties such as poor impact resistance and adhesive strength have limited their use in some load bearing applications (Grootde et al., 1998). Hence, HA was toughened with YSZ which has proven to improve their mechanical properties (Chou and Chang, 2002).

Many coating techniques such as sol-gel deposition, pulse laser deposition (PLD), chemical vapour deposition (CVD), aerosol deposition, electrophoretic deposition (EPD) and plasma spraying techniques have been used in coating bioceramics on metallic implants (Ben-Nissan et al., 2015; Duta et al., 2013; Hahn et al., 2009; Wang et al., 2009; Choy, 2003). Among all the coating techniques, plasma spraying technique is the most commercially adopted technique for coating of HA on metallic implants. This is due to its advantages of high deposition rates, enhanced corrosion and wear resistance, process simplicity and economic viability (Fernandez et al., 2004). The potential of fish scale HA (FsHA) as a coating material for Ti alloy implants has not been explored by researchers thus this study was carried out to investigate the physicochemical, mechanical and bioactivity properties of plasma sprayed FsHA/YSZ bioceramic on Ti-6Al-4V and Ti-13Nb-13Zr alloys for medical implants. Above all, this research determined the potentials of FsHA as an economical coating material for metallic implants.

1.3 Objectives of the Research

The aim of this research is to develop an inexpensive and eco-friendly bioceramic coatings on Ti-6Al-4V and Ti-13Nb-13Zr alloys with fish scale HA (FsHA) and FsHA toughened with YSZ using plasma spraying technique for biomedical applications.
The main objectives of the research are as follows:

1. To formulate and evaluate the FsHA and FsHA/YSZ bioceramic coatings on Ti-6Al-4V and Ti-13Nb-13Zr alloys produced from plasma spraying technique.
2. To characterize the surface (surface roughness and porosity), hardness properties (microhardness and adhesion strength) and morphology of FsHA coatings on Ti-6Al-4V and Ti-13Nb-13Zr alloys.
3. To examine the effects of FsHA coating toughened with YSZ on morphology, surface and hardness properties of the Ti-6Al-4V and Ti-13Nb-13Zr alloys.
4. To investigate the corrosion resistance, wettability, cytotoxicity and bioactivity of the FsHA and FsHA/YSZ coatings on the Ti-6Al-4V and Ti-13Nb-13Zr alloys.
5. To analyse the post coating heat treatment effects on the physicochemical and biomechanical properties and corrosion resistance of the plasma sprayed FsHA and FsHA/YSZ coatings on Ti-6Al-4V and Ti-13Nb-13Zr alloys.

1.4 Scope and Limitations of the Research

The scope of this research includes the production of FsHA from tilapia fish scale using spray drying technique and to produce FsHA powder modified with 10-20 wt.% YSZ. The characterization of the powders such as particle size distribution (PSA), fourier-transform infrared spectroscopy analysis (FTIR), X-ray diffraction analysis (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) were performed. After characterization, the FsHA/YSZ powders were used as feedstock for plasma spraying on Ti-6Al-4V and Ti-13Nb-13Zr alloys and subsequently heat treatment was carried out on the plasma sprayed coatings. This was followed by the characterization of the coatings using FTIR, XRD and SEM-EDX analyses. The determination of their surface properties (surface roughness, porosity, and wettability), mechanical properties (microhardness and adhesion strength), corrosion resistance and biological properties (in vitro bioactivity and cytotoxicity) were also performed.

The limitations of this research include:

1. The titanium alloy plates (Ti-6Al-4V and Ti-13Nb-13Zr alloys) used as substrates in this research were not produced from this research.
2. This research was only conducted on sample characterization upto in vitro bioactivity and cytotoxicity.
3. The heat treatment of the coated samples was limited at 750 ℃ for one hour only due to the reported minimal in vitro dissolution of HA coatings heat-treated at 800 ℃ for 1 hour (Kweh et al., 2002).
4. This research did not involve in vivo experiments.

1.5 Significance of the Research

Titanium alloys remain the most used alloys in orthopaedic applications due to their excellent mechanical properties and good resistance to corrosion. However, to enhance their biological properties, implants manufactured from Ti alloys are coated with bioinert ceramics. Among the ceramics, HA has remained the most preferred as an implant coating material. The major reasons for biomedical implants coating with HA are to improve on the tissue-implant interactions, enhance their biocompatibility and functionality without altering the implant's substrate properties. Among all the coating techniques, plasma spraying technique is the most commercially adopted technique for coating of HA on metallic implants due to its advantages of high deposition rates, enhanced corrosion and wear resistance, process simplicity and economic viability. The use of HA in coating metallic implants can easily compensate for the non-bioactivity of the metal alloys. Similarly, new bone development is improved with coating of metallic implants with HA due to the formation of strong interface between the coating and host tissue (Sadat-Shojai et al., 2013; Song et al., 2008).

Also, HA coating on metallic alloys acts as a corrosion control film against aggressive body fluids and the dissolution rate of the metallic ions are suppressed by the films, thereby minimizing leaching occurrence (Zhong et al., 2015). Above all, the lower dissolution rate of HA in body fluid makes it an excellent choice as a coating material for metallic implants among other ceramics. Despite the indispensable nature of HA and its high demand as an implant coating material, synthetic HA has remained the major source of HA for this application. Hence, the present study will utilize a low cost and abundant natural HA produced from fish scale as a coating material. Fish scales have been reported to contain 40-50% of inorganic materials known as HA and have been the best alternative source of HA due to low manufacturing cost and safety (Zainol et al., 2012). Additionally, FsHA is noted to exhibit similar biological properties in comparison to synthetic HA. Also, FsHA is non-stoichiometric due to the presence of trace elements such as Mg, Na, Zn, Si etc, which makes it similar to the chemical composition of human bone (Akram et al., 2014; Milovac et al., 2014). In spite of the cheap processing cost of FsHA compared to the cost of synthetic HA, the potentials of FsHA as an implant coating material has not been explored thus far by researchers. Finally, this research will try to achieve in two fonts, firstly improved FsHA coatings on Ti alloys with similar properties to that of synthetic HA coatings, thereby reducing the cost of implants. Secondly, this research will mitigate the global environmental pollution by the useful conversion of biowaste and significantly increase the economy of waste-to-wealth sector.

1.6 Outlines of the Thesis

This thesis is divided into five major chapters that explicitly covers the whole study. Chapter 1 explains the background of the study, biomaterials (types, properties and applications), HA (synthetic and biogenic HA, properties and applications) and plasma spraying technique. Also, presented in chapter 1 is the problem statements, aim and objectives of the research, scope and limitations and significance of the research.

Chapter 2 presents in first part, the recent literatures on biomedical applications of titanium alloys and a comprehensive review of titanium and its alloys, their classifications, surface treatments, mechanical properties, corrosion resistance, biocompatibility and porosity. On the second part, the chapter explicitly dealt on ceramic coating of Ti alloys, hydroxyapatite (HA), types, merits and demerits of HA as a coating material for implants, modification of HA with other bioceramics, modification with yttria stabilized zirconia (YSZ), spray drying technique, different HA coating techniques and characterization and properties of HA coatings.

Chapter 3 outlined the methodology used in achieving the objectives set for this research work which aims to develop an inexpensive and eco-friendly bioceramic coatings on Ti-6Al-4V and Ti-13Nb-13Zr alloys with fish scales HA (FsHA) and FsHA toughened with YSZ for biomedical applications. The methods include production of FsHA from fish scale slurry, addition of 10-20 wt.% YSZ and ball milling, characterization of the powders (particle size analysis (PSA), FTIR, XRD, SEM-EDX), FsHA/YSZ plasma coating and their heat treatments, characterization of the coatings, determination of surface coating properties (surface roughness, porosity, and wettability), evaluation of their mechanical properties (microhardness and adhesion strength), corrosion resistance and their biological properties (in vitro bioactivity and cytotoxicity).

In chapter 4, the results of the experimental work of the research are presented and discussed. Firstly, the characterization results such as scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX), particle size distribution, fourier-transform infrared spectroscopy (FTIR), X-ray diffraction of the yttria stabilised zirconia (YSZ), fish scale hydroxyapatite (FsHA) and FsHA modified with (10-20 wt.%) YSZ powders as well as the titanium alloy substrates (Ti-6Al-4V and Ti-13Nb-13Zr) used are presented and discussed. Then followed by the results of the surface, hardness and bio-corrosion of the plasma sprayed FsHA and FsHA/YSZ coatings. The influence of different wt.%

YSZ addition on FsHA and the heat treatment effects on surface, hardness and bio-corrosion of FsHA coatings were explicitly explained. Thirdly, the wettability and bioactivity in simulated body fluid (SBF) of the plasma sprayed and heat-treated FsHA/YSZ coatings were equally discussed. Finally, the biocompatibility and cell culture results of the plasma coatings were diligently discussed.

Lastly, chapter 5 summarizes the major findings of the research with respect to the objectives of the research. Also, recommendations and suggestions on future studies on the development of FsHA coating using different coating techniques and FsHA modified with different bioinert ceramics are presented.

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