HYDROXYAPATITE COATING ON STAINLESS STEEL 316L USING INVESTMENT CASTING TECHNIQUE

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Mechanical Engineering)

Faculty of Mechanical Engineering
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JANUARY 2016

I dedicate this thesis to my lovely parents, wife, and sons

ACKNOWLEDGEMENTS

It is with immense gratitude that I acknowledge the consistent support, encouragement, guidance and help of my supervisor Prof. Dr. Mohd Hasbullah Idris and my co-supervisor Prof. Ir. Dr. Mohammed Rafiq bin Dato' Abdul Kadir for their valuable suggestions, advice and motivation throughout this project. Indeed, this thesis would not have been possible without their continued helpful supervisions.

I would like to take this opportunity to extend my thanks to all my colleagues in Cast Metal Group and the staff in Foundry and Materials Science laboratories for their help and assistance in the course of conducting the experiments and fulfilling the requirements of this thesis.

Finally, I owe my deepest gratitude to my parents, wife and sons for their love, patience and many sacrifices.

ABSTRACT

Decades of research had found that the use of hydroxyapatite (HA) could promote osseointegration and increase the mechanical stability and strength of the metallic implant. Currently, medical implants are produced by machining, metal forming and casting particularly investment casting technique. Comparatively, the investment casting technique is more practical to mass produced implant due to its simplicity, superior surface finish, relatively cheap process, capability to produce complex and near-net shape implants. Investment casting technique provides a single stage processing technique in producing coated implant i.e. HA coated on the cast implant. In this respect, the possibility of applying HA layer during casting for implant substrate using investment casting was explored. Previous studies used paint brush in applying HA layer onto the internal cavity of the ceramic mould. However, the layer thickness was inconsistence which affects the quality of the HA layer coated on the casting and impractical for small and complex shapes components. In this study, medical grade 316L stainless steel (316L-SS) was coated with HA using investment casting technique by pouring molten 316L-SS into a HA coated ceramic mould at temperature of 1650°C in argon gas. The coated samples were sintered in a furnace at four different temperatures (600, 800, 1000 and 1200°C) for 1 hour. The as-cast and sintered HA coated samples were characterised using scanning electron microscopy, energy dispersive x-ray spectroscopy and x-ray diffraction analysis. Results showed that the as-cast samples produced good HA coating bond, formed amorphous phases and complex calcium-chromium oxide (CaCrO) layer at the interface between HA and 316L-SS. Sintering process was conducted to recrystallise and improve the properties of the as-cast HA coating. The results confirmed that crystallinity and purity of the coating increased with increasing sintering temperature whilst Ca/P ratio and porosity decreased. Increasing sintering temperature from 600 to 800ºC did not significantly alter the crystallinity and purity. The crystallinity and purity recorded at that temperature range were 57.35% - 58.55% and 61.80% - 63.21% respectively. This temperature range was considered insufficient to re-crystallise and purify the coating to an acceptable value for implant applications. Increased of sintering temperature from 1000 to 1200ºC increased the crystallinity from 73.52% - 74.47% and purity from 61.80% - 81.8%. Simultaneously, the Ca/P ratio and porosity were reduced to 1.51 and 14.14% respectively which is acceptable to human body. Sintered as-cast specimen at 1000ºC immersed into Simulated Body Fluid (SBF) solution showed increased in Ca/P ratio with increasing immersion time indicating that the coating was bioactive.

ABSTRAK

Penyelidikan sejak beberapa dekad telah mendapati bahawa penggunaan *hydroxyapatite* (HA) boleh menggalakkan *osseointegration* dan meningkatkan kestabilan mekanikal dan kekuatan pada implan logam. Pada masa ini, implan perubatan dihasilkan dengan kaedah pemesinan, pembentukan logam dan tuangan terutamanya teknik tuangan pelaburan. Secara perbandingan, teknik tuangan pelaburan adalah lebih praktikal untuk implan yang dihasilkan secara banyak kerana proses tersebut ringkas, kemasan permukaan yang unggul, proses yang agak murah, keupayaan untuk menghasilkan bentuk kompleks dan bentuk implan yang hampir tepat. Teknik tuangan pelaburan menyediakan pemprosesan satu peringkat untuk menghasilkan implan bersalut contohnya salutan HA pada tuangan implan. Dalam hal ini, kemungkinan untuk mengaplikasikan lapisan HA semasa penuangan logam pada substrat implan menggunakan teknik tuangan pelaburan telah diteroka. Kajian terdahulu menggunakan berus cat untuk mengaplikasikan lapisan HA pada rongga dalam acuan seramik. Walaubagaimanpun, ketebalan lapisannya tidak konsisten yang memberi kesan kepada kualiti lapisan HA yang terbentuk pada tuangan dan ia tidak praktikal digunakan pada komponen yang kecil dan berbentuk kompleks. Dalam kajian ini, keluli tahan karat gred perubatan 316L (316L-SS) telah disalut dengan HA menggunakan teknik tuangan pelaburan dengan menuang logam 316L-SS ke dalam acuan seramik bersalut HA pada suhu 1650°C dalam gas argon. Sampel bersalut disinter dalam relau pada empat suhu yang berbeza (600, 800, 1000 dan 1200°C) selama 1 jam. Sampel bersalut HA yang dituang dan yang disinter telah dicirikan menggunakan mikroskop elektron imbasan, tenaga serakan x-ray spektroskopi dan analisis pembelauan x-ray. Keputusan menunjukkan sampel hasil tuangan menghasilkan ikatan salutan HA yang baik, membentuk fasa amorfus dan lapisan kalsium kromium oksida (CaCrO) yang kompleks pada antara muka HA dan 316L-SS. Proses pesinteran telah dijalankan untuk penyusunan semula hablur dan menambah baik ciri-ciri lapisan HA hasil tuangan. Keputusan mengesahkan bahawa penghabluran dan ketulenan lapisan meningkat dengan peningkatan suhu pesinteran manakala nisbah Ca/P dan keliangan berkurang. Meningkatkan suhu sinter dari 600 ke 800ºC tidak mengubah penghabluran dan ketulenan secara berkesan. Penghabluran dan ketulenan yang direkodkan pada julat suhu tersebut adalah 57.35%-58.55% dan 61.80%-63.21% masing-masing. Julat suhu ini dianggap tidak memadai untuk penyusunan semula hablur dan penulenan lapisan kepada nilai yang diterima bagi penggunaan implan. Peningkatan suhu pesinteran dari 1000 kepada 1200ºC meningkatkan penghabluran daripada 73.52%-74.47% dan ketulenan dari 61.80%-81.8%. Pada masa yang sama, nisbah Ca/P dan keliangan telah dikurangkan kepada 1.51% and 14.14% masing-masing dimana dapat diterima oleh tubuh manusia. Spesimen yang disinter pada suhu 1000ºC yang telah direndam di dalam larutan *Simulated Body Fluid* (SBF) menunjukkan peningkatan nisbah Ca/P dengan peningkatan tempoh rendaman yang menunjukan bahawa salutan adalah bioaktif.

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LIST OF ABBREVIATIONS

ASTM	-	American Society for Testing and Materials
BS	-	British Standard
EDS	-	Energy Dispersive X-ray Spectroscopy
ISO	-	International Organization for Standardization
SEM	-	Scanning Electron Microscopy
XRD	-	X-ray Diffraction

LIST OF SYMBOLS

cm^3	-	Cubic centimetre
g	-	Gram
K	-	Thermal conductivity
lit	-	Litre
m^2	-	Square metre
min	-	Minute
ml	-	Millilitre
mm	-	Millimetre
wt.%	-	Weight percentage
µm	-	Micrometre
°	-	Degree
°C	-	Centigrade degree

CHAPTER 1

INTRODUCTION

1.1 Background of the Research

An implant is a man-made medical device manufactured to replace a missing biological structure, support a damaged biological structure, or enhance an existing biological structure (Vedula, 2015). Currently, medical implants are produced by machining, metal forming and casting particularly investment casting technique. Comparatively, the investment casting technique is more practical to mass produced implant due to its simplicity, superior surface finish, relatively cheap process, capability to produce complex and near-net shape implants (ASM Handbook, 2008). The paramount important in implant device is that the material must be biocompatible such that it is not toxic and harmful to human body.

The materials especially metals currently widely accepted for implant devices are titanium and cobalt and its alloys and stainless steels, which not only have excellent biocompatibility but at the same time possess good mechanical properties (Paital and Dahotre, 2009). Other metallic biomaterials such as magnesium and iron based alloys as biodegradable materials are widely applied temporary implants i.e. cardiovascular, paediatric, orthopaedic and dental applications. It serves as structural mechanical support for a limited duration and diminishes gradually being adsorbed or resorbed by physiological metabolic reaction (Hermawan et al, 2010).

Further requirement of medical implant is that, it has the capability to promote tissue growth. The used of the aforementioned metals alone could not fulfill such requirement. Decades of research had found that the use of Hydroxyapatite (HA) could promote osseointegration (new bone formation), increase the mechanical fixation and mechanical stability of the metallic implant (Acton, 2013). HA can be applied as a layer on the surface of the implant (coating) or acts as bone filler.

In recent decades, plasma spraying (Kweh, 2000; Sun, 2003 and Heimann, 2006) is currently one of the most widely methods used for coating metallic implant with HA. Even though, plasma spraying of HA is a simple process, high deposition rate, low substrate temperature, variable coating porosity, and variable phase and structure (Shi, 2006). Its major problem is it high temperature during spraying (up to 10000ºC) alters the HA and also metal substrate phases, causing the dehydroxylation, decrease crystallinity and phase decomposition into a mixture of HA. Other coating processes proposed to coat HA on substrate are electrophoretic deposition (Boccaccini *et al*., 2010; Van, 1999 and Besra, 2007), sputtering (Ozeki, 2002; Yang, 2005 and Hao, 2011), dip coating (Mavis, 2000; Aksakal, 2008 and Shibli, 2008), sol-gel (Brinker, 1991; Weng, 1998 and Liu, 2001), hot pressing and hot isostatic pressing (Atkinson, 2000; Onoki, 2006 and 2011). These techniques have been used to improve the quality of HA coating since they are low temperature process techniques. However, low adhesion strength and relatively non-uniform layer of coatings are the disadvantages limiting these techniques although they have high deposition rate and low process cost (Shi, 2006).

All these techniques require two preparation processes; preparation of the implant part (substrate) and coating process, such that the implant is either prepared by machining or metal forming and finally coated with HA using the coating processes as mentioned earlier. Investment casting technique provides a single processing in producing the coated implant i.e. HA coated on the cast implant. In view of these procedures, the possibility of applying HA layer during casting for implant substrate using investment casting is an alternative promising method. The concept is by applying HA layer onto the inner wall of the ceramic mould cavity with the desired thickness and pouring of molten metal into it. During solidification, the HA particles that are coated on the cavity of the ceramic mould react with the molten metal and creates a mechanical bonding between them. As a result, porous HA layer formed on the surface of substrate, promotes bioactive implant part and at the same time eliminates the post procedure for HA coating. This method promises an improvement to the manufacturing of implant as well as meeting the bioactivity requirement of high loading implant applications such as hip prostheses and dental implant.

In this research, stainless steel implant grade 316L (316L-SS) ASTM F-745 and HA powder was used as the biometallic implant and coating material respectively. The research covered issues on quality of HA coated on the cavity of the ceramic mould, interaction between HA-molten metal during casting and effect of post-heat treatment subjected to phase transformation of the coating. The coating bioactivity was also evaluated in vitro test by immersing specimens into Simulated Body Fluid (SBF). However, the main aim in this research was to establish the procedure in coating of HA by investment casting technique and evaluating the quality the properties of the HA coating.

1.2. Problem Statement

Published reports regarding HA coating using investment casting technique are limited and not extensive. Previous studies reported the coating of HA on titanium and cobalt based alloys. Sohmura *et al*. (2001) were the first researchers to propose such technique, where medical grade titanium was poured into investment and graphite moulds coated with HA to produce implants coated with HA. Other researchers have also reported developing HA and biphasic calcium phosphate (BCP) coating on cobalt based alloys using the technique, in addition to investigating the effect of pre-heating mould and post sintering process on the enhancement of bioactive implants (Escobedo, 2006; Almanza, 2006 and Minouei, 2011). The researchers reported coating of the cavity of ceramic mould with water moisturised HA using a paintbrush before assembling the moulds. The use of paintbrush to coat the mould cavity maybe applicable to simple and non-delicate part but may be difficult when used on complex shape and small implants. Furthermore, the thickness and consistency of HA adhered to the ceramic mould cavity are also of concern. The possibility of using dipping to coat HA onto the mould cavity could be used to overcome these problems. This method is likely to be more practical and applicable for coating of complex shape and small implant. Other aspects that have to be considered are effects of viscosity of HA mixture, coating thickness, HA binder, and sintering temperature.

Medical grade 316L-SS has been used in implant application which offers several advantages such as high corrosion resistance when implanted in the human body, low cost and ease of manufacturing compared to titanium and cobalt based alloys. For decades, this material has been successfully employed as implant, which requires it to be in contact with soft and hard tissues (Narushima, 2010). However, no study has been reported pertaining to the use of 316L-SS as substrate coated with HA using investment casting technique. Based on that facts, there is a need to explore into investigating how HA could be coated onto the 316L-SS substrate, evaluating the performance of the coating as well as investigating its bioactivity once coated through casting process.

1.3. Objectives of the Research

The main aim of this research was to produce an ever ready HA coated medical grade 316L-SS using investment casting technique. The following specific objectives in this study are:

1. To study the effect of sintering temperature on the properties of HA powder.
2. To investigate the effect of HA slurry viscosities on the quality of HA coated on ceramic shell mould by dipping method.
3. To investigate the effect of mould firing and casting temperatures on the properties of HA coating.
4. To study the effect of sintering temperatures on the properties of coating.
5. To study the effect of different immersion duration on the bioactivity responses of the coating.

1.4. Scope of the Research

The research was conducted within the following limits:

1. The biometallic material used in this research was 316L-SS of medical grade.
2. The investment casting processes followed the ASM (2008) standard procedures. Refractories slurry used was zircon flour and colloidal silica as the binder.
3. The sintering temperature investigated was at 600, 800, 1000 and 1200ºC for the duration of 1 hour.
4. In-vitro bioactivity immersion test used Kokubo solution for the duration of 7, 14, 21 and 28 days.
5. Properties investigated to establish the effect of sintering temperature includes crystallinity, purity, porosity, Ca/P ratio and bioactivity of the coated HA.

1.5. Significant of the Research

This research provides an alternative approach to coating of biomedical ceramic hydroxyapatite (HA) onto metallic implant using a widely acceptable technique for implant manufacture-investment casting technique. Current approaches used in embedding biomedical ceramics are by producing the implant by investment casting technique and using other coating techniques such as plasma spray, high velocity oxygen fuel (HVOF), sol gel, electrodeposition etc. However, with the finding of this research, a more practical and time saving approach could be developed through a single process in embedding the biomedical ceramics onto implants.

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