# EVALUATING THE SURFACE PROPERTIES OF HA COATING ON TITANIUM-ALUMINUM SUBSTRATE

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To my beloved father and mother Faramarz Karandish and Susan Ghaffari

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## ABSTRACT

Hydroxyapatite (HA) is the main structural component in natural bone. Due to its excellent biocompatibility and bioactivity, it can be used for biomedical application as a coating layer for metallic implants. It is reported that it helps the formation of chemical bonding at the HA/bone interface. It also works as a protective layer against ion release from a metallic prosthesis. In this project, HA bioactive coatings were prepared via sol-gel method on Ti-Al-Nb substrate. Although sol-gel is simple to control the chemical composition and able to coat on the complex-shape implants, massive cracks of HA sol-gel coated layer on implants are still remain as a major issue. Cracks can be minimized by changing the viscosity, composition or variation in heat treatment procedure. In this research, Na<sub>3</sub>PO<sub>4</sub> and CaCl<sub>2</sub>were used as biocompatible additives for preparing the sol-gel. The sol-gel solution was centrifuged at two different speeds (1000 and 3000 rpm) to remove excessive water contents to a desired viscosity. Substrates were then dipped into sol-gel at 3 m/s for 20 sec and dried at room temperature for 72hrs. They were sintered at 500°C, 600°C and 700°C for 15 and 45 minutes. It is found that increasing of sintering temperature and time from 500°C to 600°C and from 15 to 45 minutes respectively, the hardness value of sintered HA has increased significantly. However, there is a decrease in HA hardness value when it was sintered at 700°C. Surface characteristics have been analyzed by FESEM and AFM equipments. The AFM results show that surface roughness of the Ti-Al-Nb coated with HA decreases when sintering temperature is increased from 500°C to 600°C. However it is concluded that sintering temperature above 600°C for HA coating on Ti-Al-Nb results in massive cracks and worse surface roughness. Moreover, the effect of HA coated layer on corrosion behavior of metallic substrates was evaluated which results better corrosion resistance of HA coated Ti-Al-Nb substrate compare to uncoated substrate.

## ABSTRAK

Hydroxyapatite (HA) adalah komponen utama dalam struktur tulang semulajadi. Oleh kerana kekuatan dari segi Bio-serasi dan bio-aktiviti, ia boleh digunakan dalam pelbagai aplikasi bioperubatan seperti sebagai lapisan salutan untuk implant logam. Banyak laporan menyatakan bahawa, ia dapat membantu pembentukan ikatan kimia sebagai pengantara HA dengan tulang. Ia juga bertindak sebagai lapisan pelindung terhadap pembebasan ion dari proses prosthesis logam. Dalam projek ini, salutan bioaktif HA disediakan dengan kaedah rumusan gel pada substrat Ti-Al-Nb. Walaupun sol-gel adalah mudah untuk mengawal komposisi kimianya dan ia mampu menyaluti implant pada rekabentuk yang kompleks, keretakan besar HA pada lapisan rumusan gel pada implant masih menjadi isu utama. Keretakan dapat dikurangkan dengan mengubah kelikatan, kandungan atau perubahan dalam prosedur rawatan haba. Dalam kajian ini, Na<sub>3</sub>PO<sub>4</sub> dan CaCl<sub>2</sub> telah digunakan sebagai bahan tambahan bio-serasi untuk menyediakan rumusan gel. Larutan rumusan gel (sol-gel) dipisahkan pada tiga kelajuan yang berbeza (1000 dan 3000 rpm) untuk mengeluarkan kandungan air berlebihan untuk menghasilkan kelikatan yang dikehendaki. Substrat kemudiannya dicelup ke dalam sol-gel pada 3m/selama 20 saat dan dikeringkan pada suhu bilik selama 72 jam. Kemuadian disinter pada 500°C, 600°C dan 700°C selama 15 dan 45 minit. Prosess ini menunjukkan peningkatan suhu dan masa pensinteran dari 500°C kepada 600°C dan dari 15 hingga 45 minit masing-masing, dapat meningkatkan nilai kekerasan HA tersinter yang ketara. Walau bagaimanapun, terdapat penurunan dalam nilai kekerasan HA ketika disinter pada suhu 700°C. Ciri-ciri kehalusan permukaan dianalisa dengan menggunakan FESEM dan peralatan AFM. Keputusan analisa diperoleh dari AFM menunjukkan bahawa nilai kehalusan permukaan salutan Ti-Al-Nb dengan lapisan salutan HA menurun, pada suhu pensinteran meningkat antara 500°C ke 600°C. Justeru, dapat disimpulkan bahawa, keputusan proses pada suhu pesinteran melebihi 600°C untuk lapisan HA pada Ti-Al-Nb menyebabkan keretakan ketara dan juga menyebabkan kehalusan permukaan bertambah teruk. Tambahan, kesan lapisan salutan HA pada substrat logam dinilai dan didapati bahawa substrat logam bersalut lapisan HA adalah lebih baik daripada substrat logam tanpa salutan dari segi tindakbalas kakisan.

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## **CHAPTER 1**

## INTRODUCTION

## 1.1 Introduction

Biomaterials are used in medical devices, particularly in those applications that the device either is temporarily inserted or permanently implanted in the body. The material selection requirements are determined by the specific device application. For soft tissue device applications, the materials are typically implanted into soft tissue to redefine the tissue. In orthopedic and dental applications, the materials are components of structural implants to repair bony defects [1].

Polymers, metals, ceramics, and natural macromolecules are some examples of different type of material which are manufactured to be suitable as a medical device that comes into intimate contact with proteins, cells, tissues, and organ systems. These days, composite materials are finding applications in orthopedic and dental implants. Bioactive ceramic coatings for orthopedic and dental implant applications have been used to encourage bony attachment. Stainless steel, titanium (Ti) and its alloys, Co-Cr-Mo alloys are widely used as orthopedics and dental implants. However, these materials have to be bio inertness and non-toxicity. Hydroxyapatite (HA) and glass-ceramics (GC) are bioactive and are directly bonded to bone, whereas titanium (Ti) and its alloys which are bio inert do not bond directly but has close contact with bone. These materials have already been used clinically, indicating that they are biocompatible. Moreover, it is not clear which material is the most favorable to the cells of the host tissue and what occurs in the cells and at the material interface of bone-bonding and non-bonding materials [2].

Ti and its alloys have many advantages, such as excellent biocompatibility, corrosion resistance, and desirable physical and mechanical properties. In addition, high strength to weight ratio, good fracture toughness and low modulus are other significant properties of Ti and its alloys. Biocompatibility is related to the behavior of biomaterials in various contexts. The term refers to the ability of a material to perform with an appropriate host response in a specific situation. The ambiguity of the term reflects the ongoing development of insights into how biomaterials interact with the human body and eventually how those interactions determine the clinical success of a medical device [3].

The corrosion of biomaterials is a clinical issue. In spite of the recent innovative metallurgical and technological advances and remarkable progress in the design and development of surgical and dental materials, failures do occur. Thermodynamic driving forces are one of the causes of corrosion (oxidation and reduction) reactions. The thickness of the coating can be the other causes of corrosions. Resistance to corrosion is critically important for a surgical material because corrosion can lead to roughening of the surface, weakening of the restoration and liberation of elements from the metal and alloys. Liberation of elements can produce discoloration of adjacent soft tissues and allergic reactions in susceptible patients [4].

Therefore metals which are using as a biomaterial in the human body should have a high corrosion resistance. A general way to protect metals from corrosion is coatings, by this way the desired properties of the substrate (mechanical strength) to be coated through the chemical modification of the coatings (biocompatibility) will be obtained.

Bioactive materials, including bioactive glasses, bioactive glass-ceramics, bioactive calcium phosphate ceramics and bioactive composites and coatings, bond to living tissues. A bioactive material is a specific biological response at the interface of the material which results in the formation of a bond between the tissues and the material [5]. The implant-tissue interfacial reactions and bonding mechanisms of the different bioactive materials are divided into two types of bioactivities, osteoproductive bioactivity and osteoconductive bioactivity, due to different rates and mechanisms of implant-tissue interfacions [6].

A bioactive surface coating is capable bonding to support to surrounding bone. One of the main mineral components of bone is HA and its synthetic form is extensively used as biomaterials for reconstruction of the skeleton due to the lack of local or systemic toxicity together with its osteoconductive properties [6].

Hydroxyapatite  $(Ca_5(PO_4)_3OH)_2$  is a form of calcium phosphate used in the chromatographic separation of biomolecules. Sets of five calcium doublets (C-sites) and pairs of –OH containing phosphate triplets (P-sites) are arranged in a repeating geometric pattern. Repeating hexagonal structures can be seen in electron micrographs of the material. Space-filling models and repeat structure from Raman spectroscopy have also been constructed. Hydroxyapatite has unique separation properties and unparalleled selectivity and resolution [7]. It often separates proteins shown to be homogeneous by electro-phoretic and other chromatographic techniques. Applications of hydroxyapatite chromatography include the purification of different subclasses of monoclonal and polyclonal antibodies, antibodies that differ in light chain composition, antibody fragments, isozymes, super coiled DNA from linear duplexes, and single-stranded from double stranded DNA.

Various HA (hydroxyapatite) coating techniques are available, such as plasma spray, sputtering, electrolysis, sol-gel systems. These differ in terms of chemical and physical properties of the formed layer consequently.

The sol-gel technique offers a low-temperature method for synthesizing materials that are either totally inorganic in nature or both inorganic and organic. The process, which is based on the hydrolysis and condensation reaction of organometallic compounds in water solutions, offers many advantages for the fabrication of coatings, including excellent control of the stoichiometry of precursor solutions, ease of compositional modifications, customizable microstructure, ease of introducing various functional groups or encapsulating sensing elements, relatively low annealing temperatures, the possibility of coating deposition on large area substrates, and simple and inexpensive equipment. Within the past several years, a number of developments in precursor solutions, coating processes and equipment have made the sol-gel technique even more widespread [8].

In this project HA coating on Ti-Al-Nb substrates with sol-gel technique is obtained to optimize the biocompatibility and corrosion resistance of the implants. Moreover, the HA layer is expected to develop the bioactivity during the initial stage of following implantation.

## **1.2 Problem Statement**

Titanium and its alloys as biomedical implants have to be bio inertness and non-toxicity due to this fact that releasing of metal ions into the tissue can cause inflammatory. In spite of hydroxyapatite has been studied by many researchers for improving osteoblast properties, but a crack free HA coating has not being reported on Ti-Al based implant material. Corrosion behavior of a coated Ti-Al is also very limited available in the literature. In addition, surface characteristics of the coating layer play an important role in the functioning of biomaterial. Therefore characterization of the coating layer by different techniques is of great interest.

## 1.3 Objectives of the Research

Based on the Problem statement of the project, this study was mainly focused on hydroxyapatite coating on Ti-Al-Nb substrate. The aims of this research are:

- 1. To determine the feasible parameters for a crack free HA coating on Ti-Al-Nb substrate.
- 2. To analyze the surface integrity of the HA coated layer on Ti-Al-Nb substrate.
- 3. To evaluate the effect of heat treatment on micro hardness of HA coated substrates.
- 4. To compare the corrosion behavior of Ti-Al-Nb substrate before and after HA sol-gel coated at crack free condition.

#### **1.4** Scopes of the Research

The scopes of this project were limited on the following:

- 1. Titanium Aluminum alloy was used as the substrate material.
- 2. Sol-gel method was employed for coating HA on the substrate.
- 3. Centrifuging sol-gel solution was varied from 1000 to 3000 rpm
- Sintering temperature and soaking time of HA were varied from 500°C, 600°C and 700°C at 15 and 45 minutes respectively.
- 5. Potentiodynamic test with tafel graph was used to characterize corrosion behavior.

#### **1.5** Organization of thesis

The organization of thesis reports the content of each chapter.

Chapter 1 includes the introduction about research, problem statement, scope and objective of research.

Chapter 2 includes the literature reviewed about the biomaterials differences, preparation, useful coating methods, required characteristics, and different available tests on the biomaterials.

Chapter 3 is focused on the method of research which is used in this study, in addition the equipments and facilities that is utilized in the research is introduced.

Chapter 4 relates to results and discussion about the Ti-Al-Nb coated with Hydroxyapatite.

Finally the chapter 5 is discussed the conclusions and future research opportunity suggestions of this research.

#### REFERENCES

- 1. Puleo DA, Nanci A. Understanding and controlling the bone–implant interface, *Biomaterials*, 1999, 11–21.
- 2. Block MS, Finger IM, Fontenot MG, Kent JN, Loaded hydroxyapatitecoated and grit-blasted titanium implants in dogs, *Int J Oral Maxillofac Implants*, 1989, 219–25.
- 3. Considerations for the Biocompatibility Evaluation of Medical Devices, Kammula and Morris, *Medical Device & Diagnostic Industry*, 2001.
- 4. HENCH, L. L., SPLINTER, R. J., ALLEN, W. C. & GREENLEE, T. K. Jr, Bonding mechanisms at the interface of ceramic prosthetic materials, 1972, 117-141.
- 5. GROSS U., KINNE R., SCHMIT H. J., STRUNZ V., The response of bone to surface active glass/glassceramics. CRC, *Res. Biocompat*, 1988.
- 6. E. Dolinski, Purification of a Fusion Protein by Ceramic Hydroxyapatite Chromatography, *Second International Conferences on Hydroxyapatite and Related Products*, San Francisco, CA 2001.
- Huang Yuhong, Zheng Haixing, Forsyth Ian, Application of Functional Ceramic and Hybrid Nanostructure Coating Fabrication via Sol-Gel Processes with Ultrafine and Nano Powders, 2000, 29-31.
- Joseph D. Bronzino, *The Biomedical Engineering Handbook*, 2nd edition, Vol-1, 2000, 540-663.
- 9. Erlin Zhang, Dongsong Yin, Liping Xu, Lei Yang, Ke Yang, Microstructure, mechanical and corrosion properties and biocompatibility of Mg-Zn-Mn alloys for biomedical application, *Materials Science and Engineering*, 2009, volume (29), 987-993.
- 10. Tetsuya Tateish, *Biomaterials in Asia*, In Commemoration of the 1st Asian Biomaterials, 978-981, 2002.
- 11. Anthony Atala, *Principles of Regenerative Medicine*, 952-965, 2007.
- 12. Y. R. Yoo, H. H. Cho, S. G. Jang, K. Y. Lee, H. Y. Son, J. G. Kim, Y. S. Kim, Effect Of Co Content On The Corrosion Of High Performance

Stainless Steels In Simulated Biosolutions, *Key Engineering Materials*, 2007, 585-588.

- 13. U Kamachi Mudali, T M Sridhar and Baldev Raj, Corrosion of bio implants, 601-637, 2003.
- 14. L. Hench and E. C. Ethridge, *Advanced Biomedical Engineering*, 5-35 1975.
- 15. K. Hayashi, *Biomaterial Science*, Tokyo, 215-236, 1993.
- 16. Y. Mu, T. Kobayashi, M. Sumita, A. Yamamoto, and T. Hanawa, *Biomedical Material*, 49-138, 2000.
- 17. H-Y. Lin and J. D. Bumgardner, Orthopaedic Research, 22-54, 2004.
- Bordiji, K., Joazeua, J., Mainard, D., Payan, E., Delagoutte, J. and Netter,
  P. , Evaluation of the effect of three surface treatment on the biocompatibility of 316L stainless steel using human differentiated cells, *Biomaterials and tissue engineering*, 1996, 491-500.
- Hasting,G.W and D.F. Williams., *Mechanical Properties of Biomaterials*, John Wiley & Sons, 1980.
- 20. Lee, Y.S. Jeong, S.Y. Park, S.Y. Jeong, H.G. Kim, C.R. Cho., *Current Applied Physics*, 528-533, 2009.
- Kim HM, Miyaji F, Kokubo T, Nakamura T. Preparation of bioactive Ti and its alloys via simple chemical surface treatment. *J Biomed Mater Res.* 1996, 409-417.
- 22. Narayanan R, Seshadri SK, Kwon TY, Kim KH. Calcium phosphatebased coatings on titanium and its alloys, *J Biomed Mater Res*, 2008, 279-299.
- Carpenito-Moyet, L. J. Nursing Care Plans and Documentation: Nursing Diagnosis and Collaborative Problems, *Lippincott Williams and Wilkins*, 2008.
- 24. Perry, C. R., Court-Brown, C. M. Mastercases, *Orthopaedic Trauma*, Thieme, 1999.
- 25. Amin, A. K.; Sales, J. D., Brenkel, I. J., Current Orthopaedics, 2006, 16-22.
- J. Wendelboe, A. Hegmann, K. Briggs, J. Cox, C. Portmann, A. Gildea, J. Gren, L. Lyon, *American Journal of Preventive Medicine* 2003, 290-295.

- 27. A. Campbell, A. Fryxell, G. E. Linehan, *Journal of Biomedical Materials Research*, 1996, 111-118.
- L. Schlossberg, G. D. Zuidema, Johns Hopkins University. School of Medicine, *The Johns Hopkins Atlas of Human Functional Anatomy*; JHU Press, 2004.
- 29. J. Katta, , Z. Jin, E. Ingham, J. Fisher, *Medical Engineering and Physics* 2008, 1349-1363.
- 30. J. Epinette, M. T. Manley, Fifteen Years of Clinical Experience with Hydroxyapatite Coatings in Joint Arthroplasty, *Springer*, 2004.
- 31. S Nag, R Banerjee, HL Fraser, *Materials Science and Engineering*, 357-362, 2005.
- 32. E Eisenbarth, D Velten, M Muller, R Thull. and J Breme, *Biomaterials*, 5705-5713, 2004.
- M. Geetha, A.K. Singh, R. Asokamani, K. Gogia, Ti based biomaterials, the ultimate choice for orthopaedic implants, *Progress in Materials Science*, 2008.
- 34. R. Boyer, G. Welsch, and E.W. Collings: Materials Handbook, *Titanium Alloys, ASM*, Materials Park, OH, 1994, 483-636.
- Standard Specification for Wrought Titanium 6Al 4V ELI Alloy for Surgical Implants, ASTM Designation F136-82, ASTM, Philadelphia, PA, 1994, 19-20.
- Standard Specification for Wrought Titanium 6Al 7Nb Alloy for Surgical Implants, ASTM Designation F1295-92, ASTM, Philadelphia, PA, 1994, 687-89.
- 37. Toshikazu Akahori, Mitsuo Niinomi, Kei-Ichi Fukunaga, And Ikuhiro Inagaki, effects of microstructure on the short fatigue crack initiation and propagation characteristics of biomedical a/b titanium alloys, *metallurgical and materials transactions*, 2000, 1949-1958.
- N. Figueira, T.M. Silva, M.J. Carmezim, J.C.S. Fernandes, Corrosion behaviour of Ni-Ti alloy, *Electrochimica Acta*. 2009, 921–926.
- 39. Qiu Q, Vincent P, Lowenberg B, Sayer M, Davies JE. *Bone growth on sol-gel calcium phosphate thin films in vitro*. Cells Mater, 1993.
- 40. Haddow DB, James PF, Van Noort R. Characterization of sol-gel surfaces for biomedical applications. *J Mater Sci Mater Med*, 1996.

- 41. Bai, A., Leiner, D. and Cypin, M., Oxidation of Titanium and Its Alloys, Metallurgia, Moscow, 1970.
- 42. Z.Z. Zyman, V.I. Glushko, On the layered structure of condensed titanium films on the surfaces with adsorbed water, Poverkhnost 1987 86-92.
- 43. J. Delecrin, S. Szmuckler-Moncler, G. Daculsi, J. Rieu, Ultrastructural, crystallographic and chemical analysis of different calcium phosphate plasma coatings before implantation, *Bioceramics*, Oxford, UK, 1991, 311-315.
- 44. J.F. Kay, Bioactive surface coatings for hard tissue biomaterials, Handbook of Bioactive Ceramics, Boca Raton, FL, USA, 1990, 111-122.
- 45. J.G.C. Wolke, , C.P. Klein, K. de Groot, Plasma- sprayed hydroxylapatite coatings for biomedical applications, *Thermal Spray Research and Applications*, Proceedings of the Third National Thermal Spray Conference, Long Beach, CA, USA, 1990, 413-417.
- 46. J. Weng, X. Liu, X. Zhang and Z. Ma, *Amorphous structure of coatings* phase and morphological hydroxyapatite, 2005.
- 47. Orlovski, V.P., Ezhova, Zh.A., Sukhanova, G.E. and Rodicheva, G.V., Synthesis and structural transformations of hydroxyapatite, *Transactions* of the Fourth World Biomaterials Congress, Berlin, Germany, 1992, 522-531.
- 48. F.G. Zakirov, E.A Nikolaev, *Pumping and Hermetization in the Electrovacuum Production*, Vysshaia shkola, Moscow, 1983.
- 49. C.E. Wen, W. Xu, W.Y. Hu, P.D. Hodgson. Acta Biomaterialia, 2007, 403-410.
- 50. R. Narayanan, SK. Seshadri, TY. Kwon, KH. Kim. Calcium phosphatebased coatings on titanium and its alloys. *J Biomed Mater Res B*, 2008, 279-299.
- 51. HM Kim, F Miyaji, T Kokubo, T Nakamura. Preparation of bioactive Ti and its alloys via simple chemical surface treatment *J Biomed Mater Res*, 1996, 409-417.
- 52. M Wei, HM. Kim, T. Kokubo, JH. Evans, Optimising the bioactivity of alkaline-treated titanium alloy, *Material Science Eng.*, 2002, 125-134.

- 53. Wolke JGC, van der Waerden JPCM, Schaeken HG, Jansen JA. In vivo dissolution behavior of various RF magnetron-sputtered Ca-P coatings on roughened titanium implants. *Biomaterials*, 2003, 2623-2629.
- Ban S, Maruno S. Morphology and microstructure of electrochemically deposited calcium phosphates in a modified simulated body fluid. *Biomaterials*, 1998, 1245-1253.
- 55. Dirk W. Schubert, Thomas Dunkel; Spin coating from a molecular point of view, its concentration regimes, influence of molar mass and distribution, *Materials Research Innovations*, 314-318, 2003.
- 56. Narushima T, Ueda K, Goto T, Masumoto H, Katsube T, Kawamura H, Ouchi C, Iguchi Y. Preparation of calcium phosphate films by radiofrequency magnetron sputtering. *Mater Trans.* 2005, 2246-2252.
- 57. Strnad Z, Strnad J, Povýšil C, Urban K. Effect of plasmasprayed hydroxyapatite coating on the osteocconductivity of commercially pure titanium implants. *Int J Oral Maxillofac Implants*, 2000, 483-490.
- Shiohama Y, Fukuzato H, Yutani K, Shiratori N, Ito M. Release of Ca ion and pH values from heat treated spherical hydroxyapatite powder for bone filling material. *J Jap Oral Implantology*, 2003, 390-399.