Y_2O_3 AND CaO ZIRCONIA AS REINFORCEMENT FOR HYDROXYAPATITE BIOCOMPOSITE

ZAW LINN HTUN

UNIVERSITI SAINS MALAYSIA

2016

Y_2O_3 AND CaO ZIRCONIA AS REINFORCEMENT FOR HYDROXYAPATITE BIOCOMPOSITE

by

ZAW LINN HTUN

Thesis submitted in fulfilment of the requirements for the degree of Master of Science

September 2016

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitles "Y_2O_3 and CaO Zirconia as Reinforcement for Hydroxyapatite Biocomposite". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

Name of Student: Zaw Linn Htun Signature:

Date: 29th, August, 2016

Witness by

Supervisor: Prof. Dr. Ahmad Fauzi Mohd Noor Signature:

Date: 29th, August, 2016

ACKNOWLEDGEMENTS

Firstly, I gratefully acknowledge financial support from Japan International Cooperation Agency (JICA), ASEAN University Network/ Southeast Asia Engineering Education Development Network (AUN/SEED-Net) for giving me the opportunity to undertake this research work.

I cherish this chance to express my deepest thankfulness to my supervisor Prof. Dr. Ahmad Fauzi Mohd Noor and co-supervisor, Dr. Nurazreena Ahmad for their support, patient, motivation, guidance and inspiration to accomplish this research project. I also would like to thank my advisor, Prof. Dr. Mitsugu TODO at Division of Renewable Energy Dynamics, Research Institute for Applied Mechanics, Kyushu University, for his valuable comment and suggestions.

I would like to convey my appreciation to Prof. Dr. Zuhailawati Bt. Hussain, Dean of SMMRE (School of Materials and Mineral Resources Engineering), for her concern and valuable helps during my study. I am also grateful to University Sains Malaysia (USM) for offering an opportunity for me to study MSc in bioceramics with adequate research facilities, great supports from administrative, academic and technical staffs. I would like to express my special thanks to all lecturers for their innovative teaching.

I like to express my gratitude to all of my friends, local students as well as international ones, studying in School of Materials and Mineral Resources Engineering, USM. I really appreciated in knowledge sharing, taking care each other

and making activities together during my study, and it will make me unforgettable in my life.

I would like to take this opportunity to convey my gratitude to all of my teachers starting from Primary School until now, especially Daw Aye Aye Myint, Assoc. Prof. Dr. Lwin Lwin Than, Assoc. Prof. Daw Lian Tial and Prof. Dr. Aye Aye Thant. Their enthusiasm and words of encouragement facilitated me to reach this height. This thesis is dedicated to them.

Finally, it is the time to describe my endless thanks to my beloved parents; U Maung Maung and Daw Aye Myint for supporting and encouraging me to try my best. Thanks for always being there for me during the good and the bad. Most of all, thanks a million for always believing in me, even when I fail to believe in myself. I am being one of the happiest people and so lucky to have you.

Thank you indeed.

Zaw Linn Htun

August 2016

TABLE OF CONTENTS

CHAPTER THREE : MATERIALS AND METHODOLOGY

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

%	Percentage
<	Less than
>	Greater than
≈	Approximately
°	Degree
°C	Degree Celsius
°C/min	Degree Celsius per minute
cm	Centimetre
h	Hour
L	Litre
m	Metre
min	Minute
mL	Millilitre
mm	Millimetre
rpm	Revolution per minute
wt %	Weight percent
nm	Nanometre
g	Gram
λ	Wavelength
θ	Theta (Angle)

LIST OF ABBREVIATIONS

Al_2O_3	Alumina
BCP	Biphasic Calcium Phosphate
c-ZrO_2	Cubic Zirconia
Ca	Calcium
CaF_2	Calcium Fluoride
CaO	Calcia
CaO-ZrO_2	Calcia Stabilized Zirconia
CaP	Calcium Phosphate
CDA	Calcium Deficient Apatite
CeO_2	Ceria
EDX	Energy Dispersive X-ray
FAp	Fluorapatite
FESEM	Field Emission Scanning Electron Microscope
FSZ	Fully Stabilized Zirconia
HAp	Hydroxyapatite
ICDD	International Centre for Diffraction Data
JCPDS	Joint Committee on Powder Diffraction Standards
MgO	Magnesia
MOR	Modulus of Rupture
MPa	Megapascal
m-ZrO_2	Monoclinic Zirconia
PSZ	Partially Stabilized Zirconia
SBF	Simulated Body Fluid

SEM	Scanning Electron Microscope
SiC	Silicon Carbide
TEM	Transmission Electron Microscopy
TTCP	Tetra Calcium Phosphate
t-ZrO_2	Tetragonal Zirconia
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
Y_2O_3	Yttria
Y_2O_3-ZrO_2	Yttria Stabilized Zirconia
ZrO_2	Zirconia
ZrO_2/HAp	Zirconia Reinforced Hydroxyapatite Biocomposite
α-TCP	Alpha Tricalcium Phosphate
β-TCP	Beta Tricalcium Phosphate

ZIRKONIA Y_2O_3 DAN CaO SEBAGAI PENGUAT DALAM BIOKOMPOSIT HIDROKSIAPATIT

ABSTRAK

Biokomposit hidroksiapatit diperkuat zirkonia (ZrO_2/HAp) telah difabrik untuk menambahbaik kekuatan dan keliatan patah bioseramik HAp tunggal. Y_2O_3-ZrO_2 dan CaO-ZrO_2 komersial dipilih sebagai bahan penguat untuk matrik HAp. Sampel ZrO_2/HAp telah dihasilkan dengan cara konvensional pemprosesan seramik, iaitu melibatkan pencampuran serbuk, pemadatar dan persinteran. Pemprosesan sampel dimulakan dengan pencampuran atau pengisaran-pencampuran untuk membandingkan kehasilan kedua-dua sistem ini. Hasil sifat fizikal dan mekanikal adalah lebih baik dengan penggunaan cara pengisaran-pencampuran. HAp yang diperkuatkan sebanyak 5 bt% Y_2O_3-ZrO_2 komersial yang seterusnya ditambah dengan berlainan amaun CaF_2 amaun (1, 3, 5, 7 and 9 bt%) sebagai pembantu sinter dalam biokomposit ZrO_2/HAp. Sampel dipadat dengan mampatan ekapaksi sebanyak 90 MPa. Sampel kemudian disinter pade suhu 1050°C sehingga 1250°C dalam udara selama 5 jam. Semakin tinggi amaun CaF_2 digunakan, semakin besar kemungkinan fasa HAp dikekalkan. Kekuatan lentur dan keliatan patah optima dicapai ialah 61.10 MPa dan 1.15 $MPa.m^{1/2}$ selepas penambahan 3 bt% CaF_2 (komposit 5YZH-3CF). Dengan ini, 3 dan 5 bt% CaF_2 dipilih sebagai amaun optima. Dalam bahagian kedua, penambahan 5 dan 10 bt% CaO-ZrO_2 dalam HAp dibanding dengan Y_2O_3-ZrO_2 dari segi kesan kekuatan dan keliatan. Amaun CaF_2 yang terpilih sebelum ini juga ditambah ke biokomposit CaO-ZrO_2/HAp. Sifat mekanikal biokomposit CaO-ZrO_2/HAp adalah lebih baik daripada optima HAp tunggal, iaitu kekuatan lentur dan ketahanan lentur ialah 54.77 MPa dan 1.33 $MPa.m^{1/2}$ dengan ketumpatan 3.14 gcm^{-3}. Bahagian terakhir

adalah pengujian bioaktiviti biokomposit HAp diperkuat Y_2O_3 dan $CaO-ZrO_2$. Pembentukan lapisan apatit dijumpai di atas permukaan sampel terpilih menandakan bioserasi dan potensi keupayaan pembentukan tulang.

Y_2O_3 AND CaO ZIRCONIA AS REINFORCEMENT FOR HYDROXYAPATITE BIOCOMPOSITE

ABSTRACT

Zirconia reinforced hydroxyapatite (ZrO_2/HAp) biocomposites were fabricated to improve the strength and fracture toughness of monolithic HAp. Commercial Y_2O_3-ZrO_2 and CaO-ZrO_2 were selected as the reinforcement for the HAp matrix. The ZrO_2/HAp samples were produced by conventional ceramic processing route. The samples were initially produced by pure mixing as well as milling-mixing system. Better physical and mechanical properties were observed from milling-mixing. 5 wt% of commercial Y_2O_3-ZrO_2 was used to reinforce HAp and various amount of CaF_2 (1, 3, 5, 7 and 9 wt%) were added to the ZrO_2/HAp biocomposite as sintering aid. Samples were compacted with a uniaxial pressure of 90 MPa. The samples were then sintered from 1050°C to 1250°C for 5 hours. The optimum flexural strength of 61.10 MPa and fracture toughness of 1.15 MPa.$m^{1/2}$ was achieved by 3 wt% of CaF_2 addition. From this study, 3 and 5 wt% of CaF_2 were selected as optimum addition. Subsequently, 5 and 10 wt% of CaO-ZrO_2 were incorporated to HAp to improve the strength and toughness of the HAp as compared with Y_2O_3-ZrO_2 addition. The selected amounts of CaF_2 were also added to CaO-ZrO_2/HAp biocomposites. The mechanical properties of CaO-ZrO_2/HAp biocomposite were found to be better than the optimum properties of monolithic HAp. The biocomposite achieved better flexural strength of 54.77 MPa with higher density 3.14 gcm^{-3} and fracture toughness of 1.33 MPa.$m^{1/2}$. The bioactivity test on both Y_2O_3 and CaO-ZrO_2 reinforced HAp biocomposites revealed the formation of apatite layer on the surfaces, indicating the biocompatibility and potential bone forming ability.

CHAPTER ONE

INTRODUCTION

1.1 Background

Biomaterials are generally based on the groups of materials such as metals, polymers, and ceramics (Park & Lakes 2007; Hermansson 2014). Biomaterials based ceramics, also known as bioceramics, are found within all the classical ceramic families such as traditional ceramics, special ceramics, glasses, glass-ceramics, coatings, and chemically bonded ceramics (Hermansson 2014). Bioceramics can be classified into bioinert, bioactive and resorbable bioceramics (Hench 1991). Depending on the applications, type of bioceramics can be selected. For instance, hard tissue and bone replacements are synthesized mainly from bioactive ceramics such as dense non-porous bioglass, ceravital and hydroxyapatite (HAp) (Best et al. 2008).

HAp, however, is the most largely used material than the others primarily because of its compositional and biological similarity to human bone, biocompatibility, bioactivity and osteoconduction characteristic (Jun et al. 2003; Sadjadi et al. 2010). It possesses exceptional biocompatibility and unique bioactivity, and it will form an artificial bone-like structure with the surrounding bone tissue when implanted (Hench & Wilson 1993). The reason for using hydroxyapatite as a bone substitute material is because the major constituent of bone is HAp and natural bone is approximately 70% hydroxyapatite by weight and 50% hydroxyapatite by volume (Shors & Holmes 1993; Vasconcelos 2012). HAp is frequently used for reconstruction and replacement of damaged bone or tooth zones in plastic and dental surgeries as well as in coatings on dental and orthopaedic implants (Muster 1992; An et al. 2012; Oyefusi et al. 2014). Metals coated with hydroxyapatite have also been introduced as artificial bones. The hydroxyapatite coating will assist the surrounding tissue to bond firmly with the implant while the metal provides the strength for the artificial bone (Oonishi 1991; Mohseni et al. 2014; Pylypchuk et al. 2015).

Hydroxyapatite is reported as a low soluble basic calcium phosphate with Ca/P ratio of 1.67 (Daniel Arcos 2014). It has consistent bioactive properties and therefore is well suited as a calcium phosphate coating for total joint arthoplasty and total knee arthoplasty. As a result of its biocompatible, nontoxic, and capable of bonding directly to bone, HAp possesses true osteointegration (Epinette 1999). However, although HAp offers high biocompatibility, relatively low density, high compressive strength and high hardness, application of HAp as a load bearing implant is limited because of its brittleness, relatively low mechanical properties and a high dissolution rate in body fluid. Hence, the necessity of reinforcement to HAp without hampering its biocompatibility plays a crucial role (Balani et al. 2009).

Based on this understanding, the development of biocomposite materials is attractive as the advantage properties of two or more types of materials can be combined to suit better physical and mechanical properties of the matrix (Raucci et al. 2016). The introduction of bioinert ceramics with better properties as reinforcement into HAp ceramic is one effective way in producing a biocomposite with acceptable strength in order to sustain the cyclic loading. Bioinert ceramics are chosen to enhance the properties of bioactive HAp because it can maintain their physical and mechanical properties while being implant in human body. Alumina (Al_2O_3), zirconia (ZrO_2) and