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ROHAYA ABDUL MALEK

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LIST OF ABBREVIATIONS

Co	Cobalt
Ti	Titanium
Au	Aurum / Gold
Fe	Ferum / Iron
Ag	Argentum / Silver
Pt	Platinum
Co-Cr	Cobalt-Chromium
Mo	Molybdenum
Al	Aluminium
Cu	Copper
Zn	Zink
Mg	Magnesium
ASTM	American Society of Testing Materials
Ltd	Limited
W	Tungsten
C	Carbon
Si	Silica
P	Phosphorous
S	Sulphur
N	Nitrogen
Bo	Boron
HCP	Hexagonal close packed
FCC	Face centred cubic
HAP	Hydroxyapatite

$Ca_{10}(PO_4)_6(OH)_2$	Hydroxyapatite (HAP)
O	Oxygen
OH	Hydroxide
Ca	Calcium
P/M	Powder metallurgy
$Cr_{23}C_6$	Chromium carbide
$Ca_2P_2O_7$	Calcium phosphate
B_4C	Boron carbide
Si_3N_4	Silicon nitride
NaCl	Sodium chloride
SBF	Simulated body fluid
SEM	Scanning Electron Microscopic
EDS	Energy Dispersive Spectrocopy
XRD	X-ray Diffraction
CuKα	Cuprum Kα target
rpm	rotational per minute
F-75	Co-Cr-Mo alloy
Eq	Equation
D_o	Initial diameter
D_f	Final diameter
T_o	Initial thickness
T_f	Final thickness
W_a	Weight of sample in dry condition
W_b	Weight of sample when it is suspended in the water
W_c	Weight of sample after it is taken out of the water when the pores are filled with water
SiC	Silica carbide

USA	United States of America
UK	United of Kingdom
d_{av}	Average grain size
ℓ	Length of the line
N_{av}	Average number of grains in one line
P	Load
d	Diameter of indentation
W	Weight
W_x	The following weight
W_0	Initial weight
A	Area of composite
T	Time of immersion
D	Density
k	Constant for corrosion rate
mpy	mil per year
r.t	room temperature

LIST OF SYMBOLS

%	Percentage
Wt.%	Weight percent
α	Alpha
g / mol	gram per mol
g / cm^3	gram per centimeter cubic
˚C	Degree Celsius
GPa	Giga Pascal
MPa	Mega Pascal
E	Elastic modulus
μm	Micrometer
K / min	Kelvin per minute
kV	Kilo volt
mA	Milliamphere
θ	Theta
deg / min	Degree per minute
g	gram
rpm	rotation per minute
mm	Millimeter
˚C / min	Degree Celsius per minute
mL	Milliliter
N	Newton
cm^2	centimeter square
ρ	Density

Kesan Penambahan HAP Terhadap Sifat-Sifat Aloi F-75 yang Dihasilkan Melalui M/S untuk Aplikasi Biobahan

ABSTRAK

Aloi Co-Cr-Mo (ASTM F-75) secara amnya digunakan kerana mempunyai sifat-sifat mekanikal, kehausan yang baik, rintangan kakisan dan juga kebolehserasian. Untuk mendapatkan kesamaan kimia dan pembentukan ikatan antarafasa di antara biobahan implan dan tisu hidup; penambahan Hidroxyapatit (HAP) diperlukan. Kajian ini telah memfokuskan penyelidikan terhadap aloi F-75 yang digabungkan dengan HAP melalui teknik metalurgi serbuk. Kesan penambahan HAP dalam julat antara 2 dan 10 % berat terhadap kebolehserasian, sifat fizikal dan mekanikal telah dikaji. Semasa proses pemadatan, tekanan 500MPa dikenakan dengan menggunakan mesin tekanan eka-paksi. Semua sampel dibakar di dalam relau tiub pada 1100˚C dalam atmosfera argon. Sampel-sampel tersebut dihasilkan dengan dimensi tinggi 5mm dan garispusat 19mm. Untuk menganalisa keputusan, sampel rujukan (aloi F-75 tanpa HAP) dan komposit-komposit telah dibandingkan. Semua sampel diuji untuk menentukan pengecutan, saiz butiran, ketumpatan pukal, keliangan ketara, kekerasan mikro dan ujian kakisan. Untuk kebolehserasian (ujian kakisan), semua sampel direndam dalam larutan simulasi bendalir badan 0.9% sodium klorida pada suhu 37˚C selama 6 minggu. Setiap selang 48 jam, pengurangan berat per luas direkodkan. Dengan penambahan HAP, komposit-komposit didapati kurang mengecut dan didapati saiz butiran semakin membesar jika dibandingkan dengan sampel rujukan. Saiz butiran terbesar diperolehi pada komposit 10 % berat HAP (32.56µm) manakala saiz butiran terkecil diperolehi pada sample rujukan (21.43µm). Keputusan ini berkadarsongsang kepada nilai pengurangan ketumpatan pukal dan kekerasan mikro. Keputusan keliangan ketara menghampiri 30% diperolehi dengan peningkatan jumlah HAP. Keputusan yang tinggi untuk keliangan ketara diperlukan untuk tujuan pertumbuhan tulang. Bagi mikrostruktur analisis, mikrostruktur komposit menunjukkan terdapat gumpalan HAP dan liang-liang bertaburan di atas permukaan komposit. Manakala, ujian kebolehserasian menunjukkan kadar kakisan meningkat akibat pertambahan HAP kecuali pada komposit yang mengandungi 2% berat HAP yang mempunyai kadar kakisan paling rendah iaitu 2.53ipt berbanding dengan komposit yang lain. Kemungkinan-kemungkinan yang menyumbangkan berlakunya peningkatan kadar kakisan dengan pertambahan jumlah HAP adalah wujudnya pembentukan serangan am dan kakisan bopeng di antara matrik dan larutan elektrokimia yang digunakan. Selain itu, pembentukan lapisan apatit boleh dilihat dengan jelas pada permukaan komposit seperti yang dijangkakan. Berdasarkan ujian yang telah dilakukan, komposit yang mengandungi 6% berat HAP menunjukkan keputusan yang menarik bagi keliangan ketara dan rintangan kakisan yang boleh dikaitkan dengan keperluan aplikasi biobahan.

The Effect of HAP Addition on Properties F-75 Alloy Fabricated via P/M For Biomaterial Applications

ABSTRACT

A Co-Cr-Mo (ASTM F-75) alloy is generally used because of their mechanical properties, good wear and corrosion resistance as well as biocompatibility. In order to obtain chemical similarity and interfacial bond form between implanted biomaterials and living tissue, addition of Hydroxyapatite (HAP) is required. This study has focused on a research on F-75 alloy mixed with HAP fabricated by powder metallurgy (P/M) technique. The effect of HAP addition ranging between 2 and 10 wt.% on biocompatibility, physical and mechanical properties were examined. During compaction, 500MPa of pressure was applied using uniaxial press machine. The samples were sintered into tube furnace at 1100˚C in argon atmosphere. The samples with dimensions of approximately 5mm in thickness and 19mm in diameter were produced. To analyse the result, the reference sample (F-75 alloy without HAP powder) and composites were compared. All the samples were tested to determine shrinkage, grain size, bulk density, apparent porosity, microhardness and corrosion test. For biocompatibility (corrosion test), all samples were immersed into simulated body fluid of 0.9% sodium chloride solution at 37˚C in 6-week duration. Every interval of 48 hours, the weight loss per area was recorded. By increasing amount of HAP, it is noticed that the composites were less shrink and grain size getting larger compared to the reference sample. The largest grain size was obtained for composite consists of 10 wt.% of HAP (32.56μm) meanwhile the smallest grain size was obtained for reference sample (21.43μm). These results are inversely proportional to the decreasing value of bulk density and microhardness. The result of apparent porosity closely to 30% is obtained due to the increasing amount of HAP. Higher result of apparent porosity is required for bone ingrowth purposes. For microstructure analysis, the composites microstructure showed agglomeration of HAP and pores scattered on the composite surface. Meanwhile, biocompatibility test has indicated that the corrosion rate are increasing due to addition of HAP except for composite that consists of 2 wt.% of HAP which has the lowest corrosion rate among others (2.53mpy). The possibilities that contribute to the increasing of corrosion rate as a function of HAP addition are; the formation of general attack and pitting between matrix and electrochemical solution used. Besides, the formation of apatite layer can be clearly seen on the composite surface as predicted. According to the results, composite contains 6 wt.% of HAP shows an interesting result for apparent porosity and corrosion resistance that can be correlated to the requirement of biomaterial applications.

CHAPTER 1

INTRODUCTION

1.1 Research introduction

A biomaterial can be defined as any material used to make devices to replace a part or a function of the body in a safe, reliable, economic and physiologically acceptable manner. According to Park & Lakes, 2007, biomaterial also can be defined as a synthetic material used to replace part of living system or to function in intimate contact with living tissue. A variety of devices and materials is used in the treatment of disease or injury. The examples are sutures, tooth fillings, needles, catherers, bone plate, etc.

The major metals used in medical applications today include stainless steels, cobalt-based alloys and commercially pure titanium and its alloys (Gradzka-Dahlke & Dabrowski, 2008). According to research carried out by Katz et al., 2004 and Park & Lakes, 2007; cobalt-based is superior to stainless steels in corrosion resistance. There are four types of Co-based recommended by American Society of Testing Materials (ASTM), 2003 as surgical implant applications: (a) cast CoCrMo alloy (F-75); (b) wrought CoCrWNi alloy (F-90); (c) wrought CoNiCrMo alloy (F-562) and (d) wrought CoNiCrMoWFe alloy (F-563).

The F-75 alloy is considered to be biocompatible material and widely used for orthopedic applications such as hip and knee joint replacements. The cast alloy contains 28 wt.% Cr and 6 wt.% Mo (balance Co). The F-75 alloy demonstrates the most useful balance in strength, fatigue and wear along with resistance to corrosion. F-75 alloy has better corrosion resistance because it contains higher weight percentage chemical compositions of Co and Cr among other implant metals.

In order to form biocompatible materials, a bioactive addition has to be added into fabrication of F-75 alloy which is Hydroxyapatite, (HAP). HAP has calcium and phosphorus ratio (Ca/P) of 1.67. The significant of Ca/P ratio is, the lower Ca/P ratio larger are the acidity and solubility of the mixture. The characteristic element of Ca and P is their ability to bond with living bone though formation of HAP interface layer (Siriphannon et al., 2002). Among the calcium compounds, HAP is the most important since it is found in natural hard tissues as mineral phase (Park & Lakes, 2007). According to Koo, 2008 and Ramesh et al., 2008; they also supported that HAP material is being applied in many areas of denstistry and orthopaedics because of its excellent osteoconductive and bioactive properties.

At least three methods of manufacture can be used to make Co-Cr-Mo implants. They are precise (lost wax) casting, hot forging and powder metallurgy (P/M). Among these, P/M offers interesting technological solutions in the range of obtaining new exploitative materials. A P/M part is conventionally made by compactions a lubricated metal powder in a die to the desired shape followed by sintering at protective atmosphere.

Simple and complex parts with densities typically ranging between 80 and 90% of theoretical and having the finished dimensions are produced at high production rates.

The P/M industries have expanded more rapidly than those using the conventional process and widely used for a variety of products. This is mainly due to the outstanding advantages such as facility of components manufacture, material utilization and economical advantages for large production. The other advantages include energy saving, the possibility of producing near net shape products of complex geometries and high strength, use of re-cycled metals, less noise and no toxic fumes or pollutants.

1.2 Problem statement

Co-Cr-Mo (F-75) alloy which is the most biocompatible metal is proposed to mix with HAP to improve mechanical properties and corrosion resistance. Currently, the mechanical properties of F-75 are superior to bioceramics, other ceramics and glasses (Salman et al., 2009). In order to develop high bioactive performance of biomaterials for bone replacements, composites consisting of HAP and F-75 are considered among the most promising groups of biomaterials such as Ti and its alloy and stainless steel. Titanium alloy is seldom used in tribiological contact situation mainly because of their poor wear resistance. The stainless steel is recommended rather for short-term implants due to lower corrosion resistance.

Living in the area of life control and prolongation, artificial implants of HAP, $Ca_{10}(PO_4)_6(OH)_2$ are very popular in hard-tissue restorations because they accelerate bone growth around the implant. In particular, HAP has received considerable attention as an implant material over the past two decades due to its excellent biocompatibility. Ceramics of pure HAP cannot be suggested for use in heavy-loaded implants such as artificial bones or teeth. They can be used at non-loading applications. To increase their properties in implant materials, the combination of metal and HAP are necessary.

There are no researches have been made with regard to investigating the optimum weight percentage of HAP that can be mixed into composites. However, Gradzka-Dahkle & Dabrowski, 2008 have used calcium pyrophosphate with Ca/P ratio of 1.0 and they recommended that 10 wt.% of calcium pyrophosphate has improved the properties of implant materials in their research.

From the previous study conducted by Marti, 2000 and Gradzka-Dahkle & Dabrowski, 2008, commonly casting and wrought Co-Cr-Mo were used to fabricate implant materials. Cast Co-Cr-Mo alloy exhibits extremely high wear resistance and moderately strong but with limited ductility. Cast microstructures exhibit large grains, severe chemical inhomogeneity and interdendritic shrinkage porosity. The wrought Co-Cr-Mo alloys are harder and stronger than the cast composition and with similar level of ductility. However, Evan & Gregson, 1998 reported that P/M technique offers interesting technological solutions in the range of obtaining exploitative materials. The P/M process offers several advantages including chemical homogeneity and fine-scale microstructures. On the other hand, it can control the porosity and produced simple and complex parts.

1.3 Research objectives

i) To fabricate composite F-75 with HAP via P/M technique.

ii) To identify the optimum weight percentage of HAP to be used in composite fabrication.

iii) To study the effect of HAP addition to the microstructures and properties of F-75 alloy for biomaterial applications.

iv) To investigate the effect of HAP addition to the corrosion resistance of the composites.

1.4 Scope of research

This research consists of three phases which are (a) Phase 1-The characterisation of raw materials; (b) Phase 2- The fabrication of compact F-75 alloy in addition of HAP using P/M technique and (c) Phase 3 - Physical, mechanical and biocompatibility testing of composites.

In Phase 1, the characterisation of raw materials for F-75 alloy and HAP were conducted before the fabrication of composites. It was done by using SEM analysis, particle size analyser and XRD analysis.

Phase 2 was done according to the P/M technique which consists of mixing, compressing and finally sintering. A range between 2 and 10 wt.% of HAP was added into F-75 alloy. F-75 alloy without HAP acts as a reference sample. Each of composites mixture weighed 8g and deposited into a mold. A uniaxial press machine with pressure of 500 MPa was used to compress the composites. These green bodies were then sintered in carbolite tube furnace at 1100˚C in argon atmosphere.

The physical, mechanical and biocompatibility testing of each composite were carried out. For physical testing, shrinkage determination, microstructure analysis, bulk density, apparent porosity and grain size determination were done. The mechanical testing was microhardness test and lastly biocompatibility testing of composites (corrosion test). The corrosion test was done in 6-week duration at constant temperature of 37˚C. The composites were immersed in simulated body fluid of 0.9% NaCl solution. Fig. 1.1 shows the flow chart for the production of F-75 mixed with HAP.

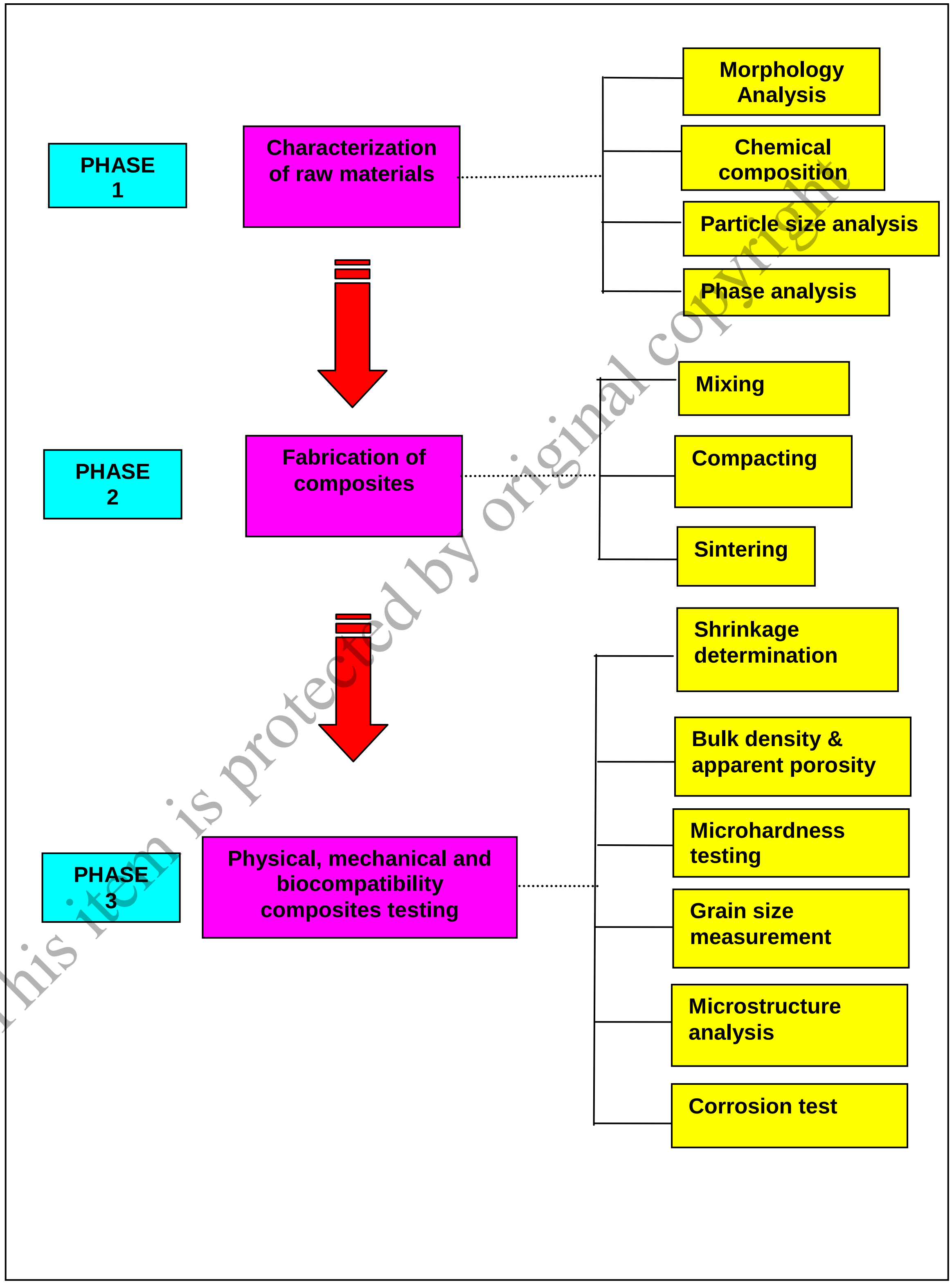

Figure 1.1: The flow chart for the production of F-75 alloy powder mixed with HAP