FABRICATION OF POROUS TITANIUM-HYDROXYAPATITE COMPOSITE VIA POWDER METALLURGY WITH SPACE HOLDER METHOD

M.Y. Zakaria[1], A.B. Sulong[1], M.I. Ramli[1], B. Ukwueze[1], W.S.W. Harun[2] and R.L. Mahmud[3]

[1]Department of Mechanical and Materials Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia 43600 Bangi, Selangor, Malaysia.

[2]Green Research of Advanced Materials Laboratory (Grams Lab), Human Engineering Group, Faculty of Mechanical Engineering, Universiti Malaysia Pahang, 26600, Pekan, Pahang, Malaysia.

[3]MAJU Saintifik Sdn. Bhd., No. 35G, Jalan Mutiara Subang 1, Taman Mutiara Subang 47500 Subang Jaya, Selangor, Malaysia.

Corresponding Author's Email: [1]mohdyusuf@siswa.ukm.edu.my

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ABSTRACT: The porous structure of metals has been attracting a growing interest, particularly the use of titanium for bone implants as it promotes cell growth and matches the elastic modulus of the human bone. A porous titanium-hydroxyapatite (Ti-HA) composite was successfully fabricated through the powder metallurgy route using the space holder method. Ti, HA and NaCl space holder were mixed with a binder system consisting of palm stearin (PS) and low-density polyethylene (LDPE). The mixture was later put through a hot press process at a pressure of 20 bars and a temperature of 150 °C. The binders were removed in a two-step process; solvent and thermal de-binding, followed by sintering in a high vacuum furnace at 1300 °C for 5 hours holding time. The Ti-HA at the ratio of 9:1 possessed the best compressive strength and the strength was in the range of 2-70 MPa, which is the range for the trabecular bone of humans. The XRD analysis revealed the existence of a new β-TCP phase due to the decomposition of the HA at a high temperature which resulted in biocompatibility, thereby, indicating a promising prospect for the use of the material in medical implants in the future.

KEYWORDS: *Titanium Ti6Al4V; Hydroxyapatite; Space Holder; Powder Metallurgy; Porous*

1.0 INTRODUCTION

Titanium and its alloys have attracted researchers to develop a new generation of implant materials due to their mechanical properties, high resistance to corrosion, and biocompatibility [1-2]. However, the mismatch of mechanical properties between titanium and natural human bone has resulted in the phenomenon of stress shielding which has become a major drawback for titanium implants [3]. This drawback has opened up fresh research opportunities for the development of a novel material as well as a new manufacturing technique to solve this issue. Various methods have been proposed, one of which is the introduction of a second material, such as hydroxyapatite, to reduce the mismatch in the mechanical properties because hydroxyapatite is a bioceramic material that is brittle but possesses similar properties to the human bone [4]. Furthermore, the introduction of a porous structure can also reduce the mismatch in the mechanical properties because the porosity of titanium is strongly related to its mechanical properties [5-6]. Moreover, the porous structure can facilitate cell growth and act as a form of transportation for body fluids [7].

Early developments in the incorporation of titanium and hydroxyapatite involved coating techniques. Hydroxyapatite acts as a coating material for titanium implants [8, 9]. Plasma spray (PS) and electrodeposition (ED) are among the coating techniques used for the coating of HA to the titanium substrate [10-11]. Then, the coating technique shifts towards a composite coating to enhance the properties of the coating and its biocompatibility [12-18]. However, the main downside of the coating technique is the possibility of the coating peeling off from the titanium substrate over time because the coating is prone to degradation and wear [19]. Later, titanium and hydroxyapatite are successfully formed into a composite by the powder metallurgy route, such as powder compaction and powder injection moulding (PIM) [20-21]. A recent study showed that by applying the space holder method to the powder metallurgy process, a porous titanium structure can be produced [22-26]. For a porous titanium fabricated by space holder method, its porosity is obtained by adding a certain amount of space holder materials and then removing them before sintering, leaving new pores behind in the structure. Commonly used space holder materials are starch, saccharose, polymethyl-methacrylate (PMMA), magnesium (Mg) and sodium chloride (NaCl) [27]. Sodium chloride space holder material is one of the potential materials because it is easy to dissolve which helps in the removing process, less costly and has good biocompatibility [28]. Porous titanium-hydroxyapatite composite is successfully produced by PIM using a similar approach [29]. However, the porous titanium-hydroxyapatite composite prepared by PIM is not being extensively studied because researchers are focusing more on the binder system and are limited to one composition only. Therefore, this study focused on the incorporation of titanium and hydroxyapatite as well as on producing a porous structure through powder metallurgy route.

2.0 METHODOLOGY

2.1 Materials

Gas atomized titanium Ti6Al4V powder, with an average particle size of 19.6 µm, was obtained from TLS Technik GmbH, Germany, and hydroxyapatite (HA) powder, with average size of 5.3 µm, was obtained from Sigma Aldrich, as shown in Figures 1 (a) and (b), respectively. Sodium chloride (NaCl) was chosen as the space holder material due to its low cost and high solubility. The average powder sizes and morphologies are summarized in Table 1 and Figure 1, respectively. Meanwhile, the binder system consisted of low density polyethylene (LDPE) and palm stearin, with a melt temperature of 111.42°C and 54.58°C, respectively. The composition of the binder is given in Table 2.

Table 1: Powder size

Material	Size (d50) (µm)
Titanium (Ti6Al4V)	19.61
Hydroxyapatite (HA)	5.3
Sodium Chloride (NaCl)	381.39

Table 2: Binder system

Type of binder	Content (wt.%)	Melting temperature (°C)
LDPE	40	54.58
Palm stearin	60	111.42

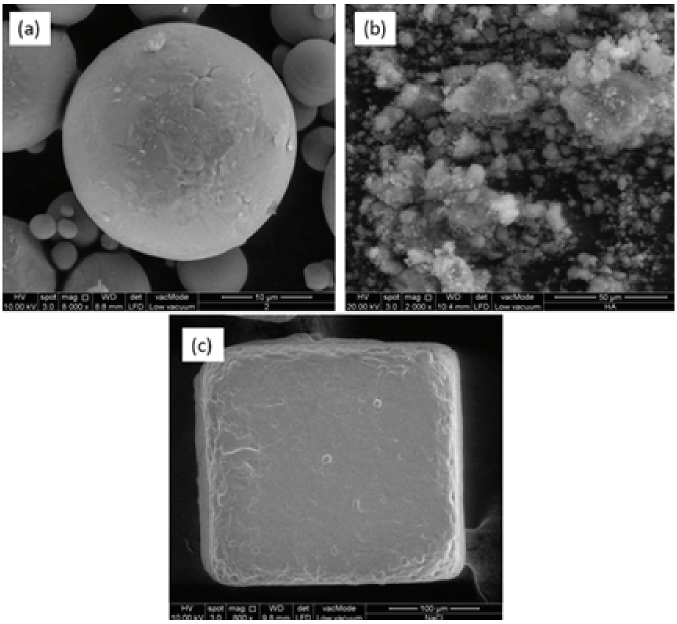

Figure 1: SEM image for (a) Ti6Al4V, (b) Hydroxyapatite and (c) Sodium chloride

2.2 Feedstock preparation

Ti6Al4V and HA powder were dry mixed at a ratio of 9:1 for the powder weight percentages with a solid loading of 78 vol.% using a dry ball mill at a rotational speed of 100 rpm for 3 hours. The binder system consisted of LDPE and palm stearin at a ratio of 4:6, and 20 % of the space holder was mixed into the powder mixture using a Brabender mixer at 150°C and a rotational speed of 40 rpm for 90 minutes. These steps were repeated for different compositions of titanium-hydroxyapatite at ratios of 8:2, 7:3 and 6:4.

2.3 Fabrication of green, brown and sintered parts

The green part was produced by the hot press process using a cylindrical mould at 150°C and a pressure of 20 bars for 2 minutes. Then, the NaCl space holder was leached out in water at 60°C for 5 hours. Meanwhile, the binders were removed thermally at 500°C in an argon environment at a heating rate of 5°C/min to produce the brown part. Later, the brown part went through the sintering process at 1300°C for 5 hours of holding time at a heating and cooling rate of 3°C/min in a vacuum [29].

2.4 Characterization

The densities of the green and sintered parts were obtained based on the Archimedes' principle. Meanwhile, the compressive strength of the sample was measured using a Zwick/Roell testing machine with a 100-kN load cell. The microstructure of the sample was observed using a Hitachi TM1000 scanning electron microscope (SEM). The XRD analysis was determined using D8 Advance model of the Bruker AXS Germany.

3.0 RESULTS AND DISCUSSION

3.1 Effect of the addition of HA on the density

The physical changes to the sample throughout the entire process can be observed in Figure 2, where pores started to appear at the surface after the debinding and sintering processes. This result indicated that the NaCl space holder was successfully removed through water leaching method at 60°C. The image from the scanning electron microscope (SEM) revealed that the composite was porous which also influenced its density. Figure 4 shows the effect of the addition of HA on the densities of the green and sintered parts. The density decreased with an increase in the HA content up to 40 wt.% for both the green and sintered parts. This phenomenon occurred due to the fact that HA powder possesses a lower density than titanium. Meanwhile, the density of the sintered part was slightly higher than that of the green part due to the debinding and sintering processes. The binder was removed during the debinding stage, whereas the titanium was diffused during the sintering stage.

Figure 2: Physical observation of (a) green part, (b) brown part and (c) sintered part

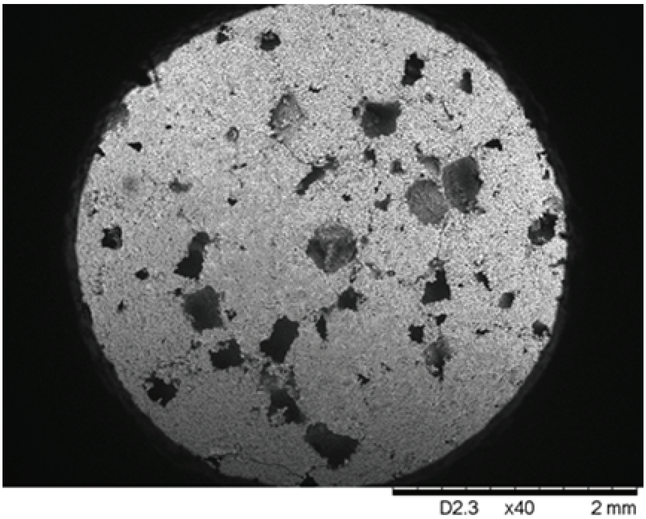

Figure 3: Porous structure at the surface of the sintered part

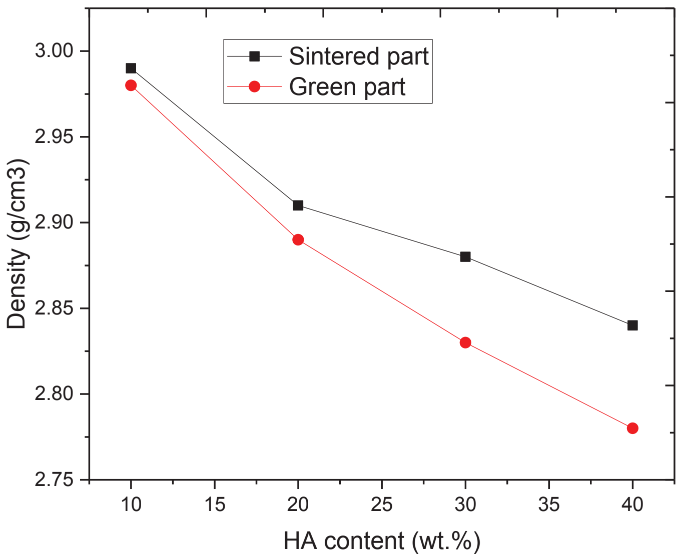

Figure 4: Effect of the addition of HA on the density

3.2 Effect of the addition of HA on the compressive strength

The trend continued with a decrease in the compressive strength of the sintered part when the HA content increased, as shown in Figure 5. While the Ti-HA ratio of 9:1 possessed the best compressive strength of 22.4 MPa, the lowest compressive strength of 6.11 MPa was obtained at a Ti-HA ratio of 6:4. This behaviour indicated that the incorporation of HA into the titanium reduced its strength due to the fact that HA is a brittle, bioceramic material. Thus, by controlling the amount of HA, the strength of the Ti-HA composite can be tailored to suit the application. For this study, the compressive strength was within the range of that of trabecular human bone, 2-70 MPa [30-31]. Moreover, the compressive strength behaviour was also influenced by the porous structure of the Ti-HA composite where the localized stress occurred at the pores area as shown in Figure 3. Nevertheless, balancing the porosity and HA content is the key to obtain the desired mechanical properties of the porous Ti-HA composite because both of them are greatly related.

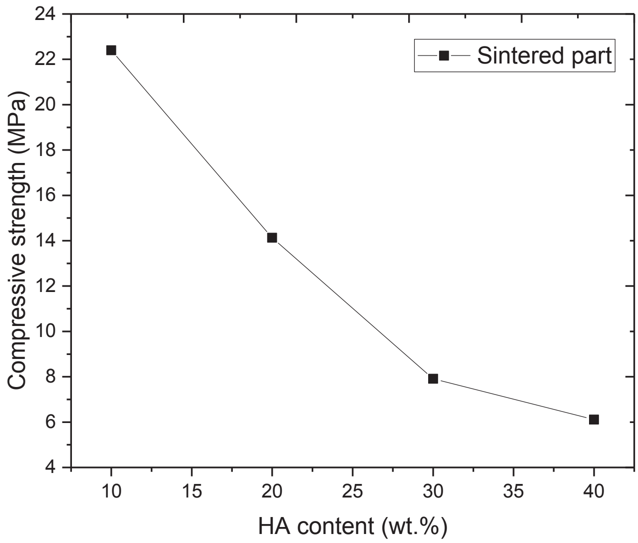

Figure 5: Effect of the addition of HA on the compressive strength

3.3 XRD analysis of the sintered part

Figure 6 shows the XRD spectrum of the green and sintered parts of the Ti-HA composite at a ratio of 9:1. The sintering was carried out for 5 hours in a high vacuum environment at a sintering temperature of 1300°C. The XRD spectrum for the green part indicated the existence of titanium and HA elements and the absence of contamination. However, after the sintering process, only the titanium peak could be observed as the major peak with some other new phases being discovered. The major peak of the HA diminished due to the decomposition of HA at a high temperature during the sintering process with the existence of the new β-TCP phase. β-TCP, known as beta-tricalcium phosphate, is an osteoconductive material with good biocompatibility, making it suitable for the promotion of new bone formation and for use in implant applications [32]. Moreover, at 1300°C, the composite became thicker as a result of the necking of the titanium, as shown in Figure 7.

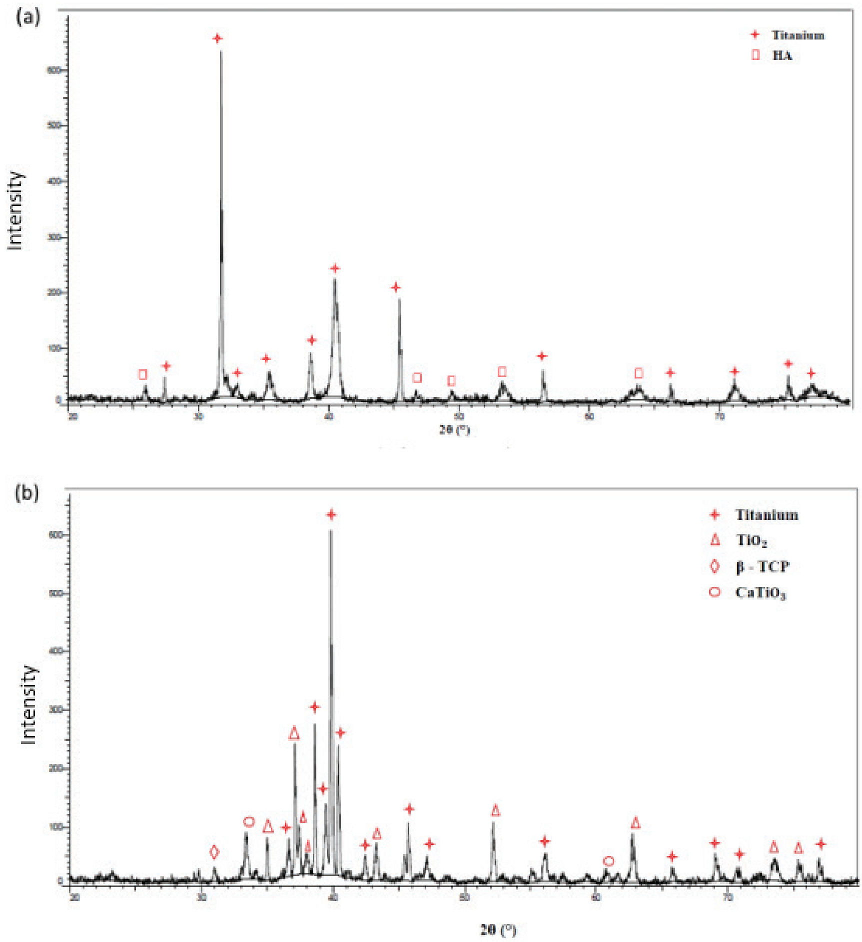

Figure 6: XRD spectrum for Ti-HA at a ratio of 9:1 for (a) green and (b) sintered parts

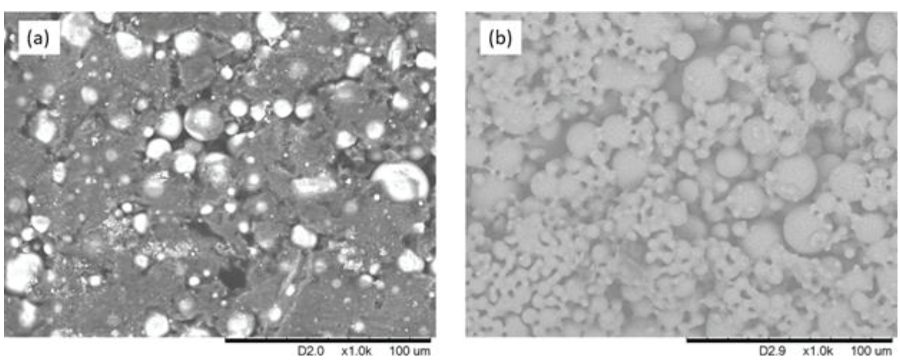

Figure 7: SEM image for (a) green and (b) sintered parts

4.0 CONCLUSION

Porous titanium (Ti6Al4V)-hydroxyapatite (HA) has been successfully fabricated through the powder metallurgy route with the space holder method. The mechanical properties of the porous Ti-HA composite are reduced with an increase in the HA content. The highest compressive strength of 22.4 MPa is achieved for the Ti-HA composite at a ratio of 9:1. The XRD spectrum reveals the existence of a new β-TCP phase, indicating that the composite has good biocompatibility properties. The newly-developed porous Ti-HA composite has great potential for use in implant applications and further studies are necessary to obtain its optimal pore characteristics as well as its biocompatibility performance.

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