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CHARACTERIZATION OF HYDROXYAPATITE/TI6AL4V COMPOSITE POWDER UNDER VARIOUS SINTERING TEMPERATURE

Amir Arifin[a,b]*, Abu Bakar Sulong[a], Norhamidi Muhamad[a], Junaidi Syarif[a]

[a]Department of Mechanical and Materials Engineering, Universiti Kebangsaan Malaysia, Selangor, Malaysia
[b]Department of Mechanical Engineering, Sriwijaya University, 30662 Indralaya, Sumatera Selatan, Indonesia

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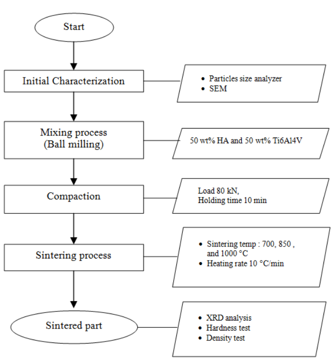
*Corresponding author
amir@unsri.ac.id

Graphical abstract



Abstract

Hydroxyapatite (HA) has been widely used in biomedical applications due to its excellent biocompatibility. However, Hydroxyapatite possesses poor mechanical properties and only tolerate limited loads for implants. Titanium is well-known materials applied in implant that has advantage in mechanical properties but poor in biocompatibility. The combination of the Titanium alloy and HA is expected to produce bio-implants with good in term of mechanical properties and biocompatabilty. In this work, interaction and mechanical properties of HA/Ti6Al4V was analyzed. The physical and mechanical properties of HA/Ti6Al4V composite powder obtained from compaction (powder metallurgy) of 60 wt.% Ti6Al4V and 40 wt.% HA and sintering at different temperatures in air were investigated in this study. Interactions of the mixed powders were investigated using X-ray diffraction. The hardness and density of the HA/Ti6Al4V composites were also measured. Based on the results of XRD analysis, the oxidation of Ti began at 700 °C. At 1000 °C, two phases were formed (i.e., TiO_2 and $CaTiO_3$). The results showed that the hardness HA/Ti6Al4V composites increased by 221.6% with increasing sintering temperature from 700°C to 1000°C. In contrast, the density of the composites decreased by 1.9% with increasing sintering temperature.

Keywords: Hydroxyapatite, Ti6Al4V, sintering temperature, density, hardness

Abstrak

Hidroksiapatit (HA) telah digunakan secara meluas dalam aplikasi bioperubatan kerana mempunyai sifat bioserasi yang unggul. Walau bagaimanapun, HA mempunyai sifat mekanik yang rendah dan hanya terhad untuk implant dengan beban yang rendah. Titanium adalah bahan yang biasa digunakan dalam implan kerana mempunyai kelebihan dalam sifat mekanik tetapi kurang dalam sifat bioserasi. Gabungan aloi Titanium dan HA dijangka dapat menghasilkan bio-implan dengan sifat mekanik yang baik serta mempunyai sifat bioserasi yang unggul. Dalam kajian ini, interaksi dan sifat-sifat mekanik HA/Ti6Al4V dianalisa. Sifat-sifat fizikal dan mekanik serbuk komposit HA/Ti6Al4V yang diperoleh melalui kaedah pemadatan dengan komposisi 60 wt.% Ti6Al4V/40 wt.% HA, pensinteran pada suhu yang berbeza di udara telah dijalankan dalam kajian ini. Interaksi daripada serbuk campuran telah dianalisa menggunakan pembelauan sinar-X. Kekerasan dan ketumpatan bagi komposit HA/Ti6Al4V juga dianalisa. Berdasarkan keputusan analisis XRD, pengoksidaan Ti bermula pada 700 °C. Pada 1000 °C, dua fasa telah dibentuk (iaitu, TiO_2 dan $CaTiO_3$). Hasil kajian menunjukkan bahawa kekerasan komposit HA/Ti6Al4V meningkat sebanyak 221,6% dengan peningkatan suhu pensinteran daripada 700°C ke

1000°C. Sebaliknya, ketumpatan bagi komposit menurun sebanyak 1.9% dengan peningkatan suhu pensinteran.

Kata kunci: Hidroksiapatit, Ti6Al4V, suhu pensinteran, ketumpatan, kekerasan

1.0 INTRODUCTION

In the first period of medical implant research, the researchers only consider "non-toxic criteria" for implant materials that will be used for the human body [1]. Today, the criteria for implant material that are used in the human body have changed with the addition of the necessary requirements. An implant material, beside non-toxic also expected to encourage the growth of cells that can accelerate the healing period the patient [2]. Moreover, in term of mechanical properties the implant material should be close to the bone properties [3, 4].

Hydroxyapatite (HA) or [$Ca_{10}(PO_4)_6(OH)_2$] is a calcium phosphate ceramic that is used as a bioactive material for many applications in the biomedical field [5]. Moreover, HA has similar to the bone in chemical structure [6]. Therefore, HA has excellent in biocompatibility and has ability to encourage growth of the cell [7]. HA forms a real bond with the surrounding bone tissue when implanted in the human body [8, 9]. One of the weaknesses of HA is in term of mechanical properties. HA cannot be used for heavily loaded implants, such as artificial teeth or bones. medical applications of HA are limited in certain place; unloaded implants, powders, coatings, and low-loaded porous implants [10-12].

Titanium (Ti) and its alloys have low density, high-strength mechanical properties, and corrosion resistance in a large number of environments. Thus, Ti and its alloys are widely used in manufacturing watches, medical devices, dental parts, and sporting goods [13] . Titanium in medical application has poor in biocompatibility compared to HA, combination of both is expected to produce implant materials with excellent mechanical properties and biocompatibility. Generally, HA has been developed widely as material deposit on metallic medical implants. the presence of HA in metallic implant is believed to enhance biocompatibility [14].

Several problems in the HA-Ti system need to be addressed, such as its sintering mechanism, the mechanical properties of the resulting composites, and the decomposition of HA at high temperatures [3, 15-17]. Moreover, in sintering metal-ceramic, common problems is occurring the crack on sintered part. It is occur usually due to differences in thermal coefficient of both materials that giving rise to residual stress [18-20]. The main objective of this study is to analyze mechanical properties and interactions between HA and Ti alloy under various sintering temperatures.

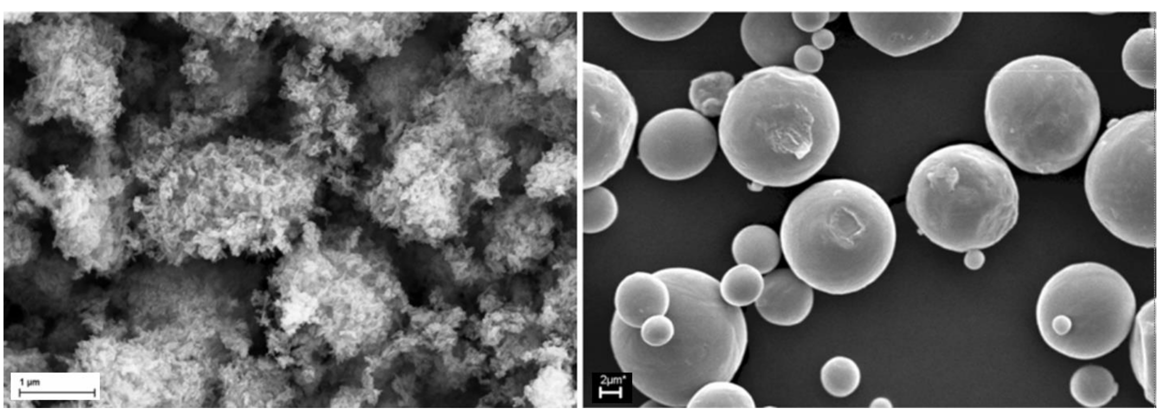


Figure 1 Scanning electron micrograph of; (a) Hydroxyapatite powder and (b) Ti6Al4V

2.0 MATERIAL AND METHOD

HA powder (5 µm; Sigma-Aldrich Co.) and Ti6Al4V powder (25 µm; TLS Technik GmbH & Co.) were used, as shown in Figure 1, respectively. 50 wt.% HA and 50 wt.% Ti6Al4V powder were mixed by ball milling machine with a hard steel ball for 0.5 h. The mixture was compacted using a Universal Testing Machine with a load of 80 kN and the pressure held for 10 min. Green compacts were sintered at 700 °C, 850 °C, and 1000 °C in air at a heating rate of 10 °C/min. As a control, another sample was prepared by mixing the powders at 25 °C for 0.5 hour without sintering.

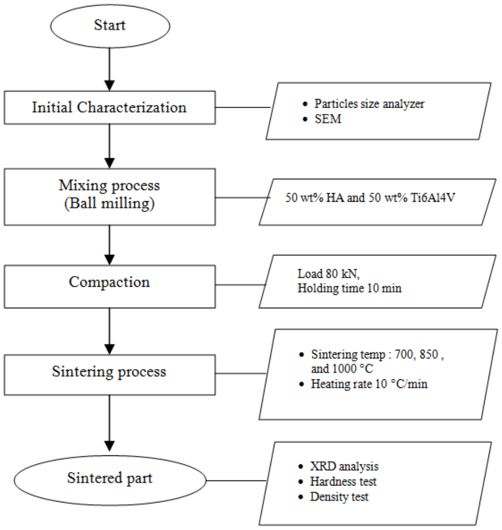


Figure 2 Flowchart of experiment

The different phases of the samples were identified by X-ray diffraction (XRD) with 2θ ranging from 20° to 70°. The hardness and density of the samples were measured using the Vickers method and Archimedes' principle, respectively. Figure 2 showed the detail of experiment.

3.0 RESULTS AND DISCUSSION

Figure 3 illustrates the surface hardness of the samples obtained from Vickers hardness tests. The hardness value increase from 165.16 HV at sintering temperature 700 °C up to 612.6 HV at 1000 °C. The increasing of the hardness value is 221.6% in range sintering temperature 700 °C to 1000 °C. Forming TiO_2 phase has played important role for increasing surface hardness value at 700 °C ~ 850 °C.

At temperature 850 °C until 1000 °C, hardness value was increasing significantly. It was believed due to increasing the intensity of TiO_2 phase. Moreover, the reaction between TiO_2 and HA results in $CaTiO_3$ at higher temperatures [21].

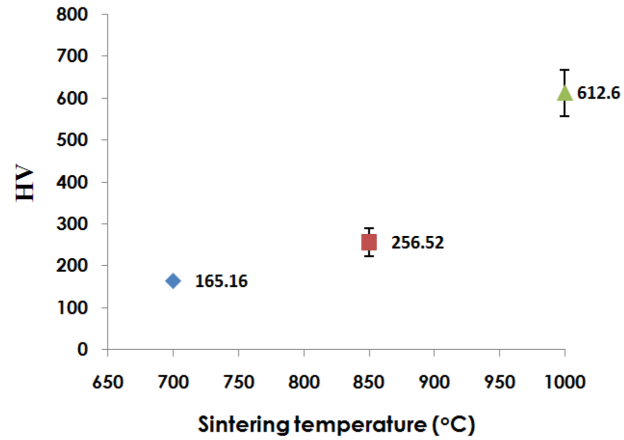


Figure 3 Hardness of sintered part at 700 °C, 850 °C and 1000 °C

The Increase in the hardness value of sintered part has strong correlation with increased sintering temperature, which due to diffusion and densification rate of HA/Ti6Al4V increases. Other researchers have reported this phenomenon that hardness value of composite HA /Ti6Al4V tend to increase at sintering process 1000 °C to 1300 °C [10].

The theoretical density of the mixed powder is 3.8 gr/cm^3. As shown in Figure 4, the maximum density was obtained at 700 °C. The density decreased by 1.9 % from 700 °C to 1000 °C. In atmosphere condition, the hydroxylation of HA was begin at 900 °C [6]. However, dehydroxylation and decomposition of HA in composite HA/Ti are accelerated with the presence of Ti [22]. The rate of density reduction from 700 °C to 1000 °C was not significant. The reduction of density of sintered part occurs due to water adsorption and decomposition.

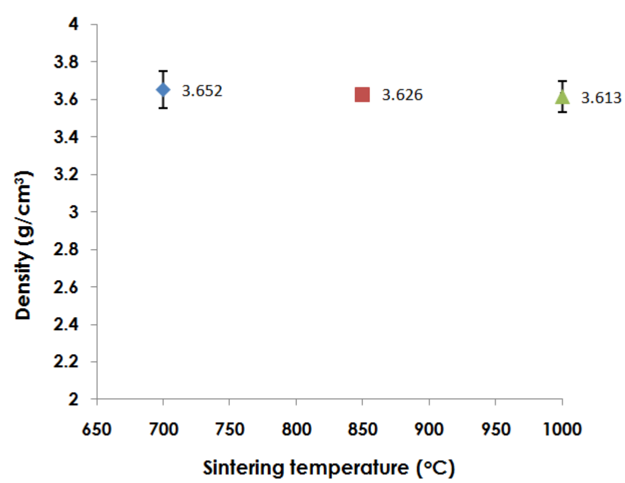


Figure 4 Density of sintered part at 700 °C, 850 °C and 1000 °C

Figure 5 shows the SEM of composite HA/Ti6Al4V under various sintering temperatures. Some cracks was observed on sintered part especially on sintering temperature 850°C and 1000 °C as shown on Figure 5 (b) and (c). Residual stress is common phenomena in composite structure; somehow, it is encouraging of crack on material if the difference of coefficient thermal of material quite large. On the composite HA/Ti6Al4V, the cracks may occur due to differences in coefficient thermal expansion of HA and Ti6Al4V (Ti6Al4V ± 8.5×10^{-6}/K; HA ± 11.6 $\times10^{-6}$/K).The intensity of TiO_2 peak tend to increase with the increase of sintering temperature as an indication of the oxidation processes. In composite HA/Ti6Al4V, the occurring of many crack due to HA is very weak, moreover the crack easily deflected when facing Ti particle. This phenomenon as indication that interfaces bonding between HA and Ti is weak [19]. If the interface bonding both of material strong enough, the occurring of cracks can be reduced due to the energy can be absorb by deformation plastic of Ti particle [23].

XRD pattern of mixture between angle ranges 20-70 under different sintering temperatures are shown on Figure 6. Control powder was HA and Ti6Al4V powder which were mixed for 0.5 hour without sintering process. The XRD result showed that XRD pattern clearly visible in the right position. In addition, no phase oxides are formed in control powder.

On sintering temperature 700 °C, main peak of titanium at 2Θ 40.6° did not appear. Other hand, XRD pattern showed a peak characteristic of Ti_2O at 2Θ 40.3°. In addition, peak of TiO_2 on 2Θ 27.6° was found in this pattern as indication oxidation of titanium. Increasing intensity of peak TiO_2 as indication process oxidation of titanium was found on sintering temperature 850 °C. However, reflections of Ti_2O were not emerging in this temperature as hint almost completely oxidized [21]. Whereas at a sintering temperature 1000 °C: XRD pattern of HA disappeared.

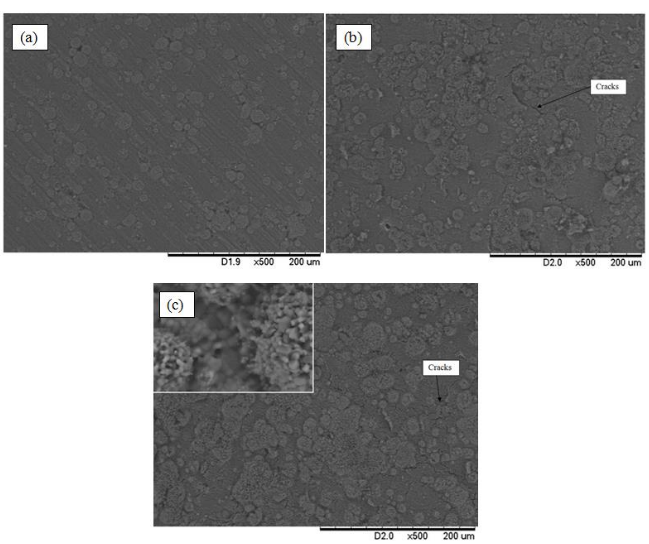


Figure 5 SEM of composite HA/Ti under various sintering temperature (a) 700 °C; (b) 850 °C and (c) 1000 °C

However, the emerging pattern of calcium titanate ($CaTiO_3$) that was due to reaction between HA and TiO_2. Another author reported that TiO_2 and $CaTiO_3$ was observed as main phase on sintered part of HA/Ti [14, 21]. Commonly, In sintering process of HA/ Ti6Al4V under vacuum conditions, TiO_2 will always occur due to the interaction of the Ti and O ions derived from HA [24].

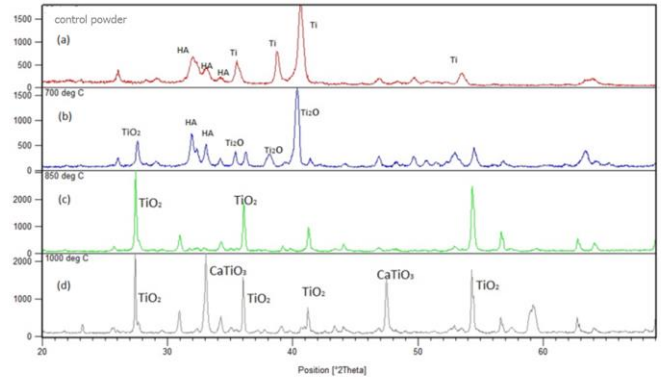


Figure 6 XRD analysis of HA/Ti6Al4V composites; (a) control powder, (b) 700 °C, (c) 850 °C and (d) 1000 °C

4.0 CONCLUSION

Based on the hardness and density result, increasing the sintering temperature has significant effect in improving the hardness and density of HA/Ti6Al4V composite. This phenomenon occurs due to the increased rate of diffusion and densification of the powders. In the sintered part was observed cracks that occur due to residual stress arising from the difference coefficient of thermal HA and Ti6Al4V and low interfaces bonding of HA/Ti.

The studies of interaction physical and mechanical properties of HA/Ti6Al4V structure shows that under various sintering temperature, oxidation of titanium has appeared on 700 °C. Based on XRD result. The intensity of TiO_2 peak tend to increase with the increase of sintering temperature as as an indication of the oxidation processes during sintering process. At 1000 °C, two phases were formed (i.e., TiO_2 and $CaTiO_3$). The density of the HA/Ti6Al4V composites decreased due to dehydroxylation and decomposition of HA. The highest hardness of the composites was achieved at sintering temperature 1000 °C, possibly because of the formation TiO_2 and $CaTiO_3$. Some crack has observed on the sintered part

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