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ORIGINAL PAPER

Ti6Al4V/Wollastonite Composite Through Powder Injection Molding Process For Bone Implant Application

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INTRODUCTION

Titanium and its alloy (Ti6Al4V) have been successfully used widely since the year of 1940 for medical applications, aerospace and chemical industries (Callister and Rethwisch, 2014). The advantages of using titanium in medical applications are biocompatibility and high mechanical properties (Ye *et al.*, 2009). However, Ti6Al4V is a bio-inert materials which cannot supplies biological elements for fixation to the surrounding tissues after the implantation process (Nakahira and Eguchi, 2001). In order to improve the bioactivity of alloy, bioceramic was added. Wollastonite (W) is a bioceramic materials have recently received an interest because of its bioactivity properties. This bioceramic materials have an ability to stimulate body tissues for repairing process and bone ingrowth(Fiocco *et al.*, 2015). The wollastonite contains of CaO and SiO_3 were found to bond to living bond and have bioactive properties (De La Casa-Lillo *et al.*, 2011). The combination of both Ti6Al4V and W can have produced high mechanical properties and biocompatible which can be used in bone implant applications.

Powder injection molding (PIM) is a combination from plastic injection and powder metallurgy process. This PIM can produces high mechanical properties product, high density, complex shapes (Huang *et al.*, 2003). This process consists of four main steps which are mixing, injection molding, debinding and sintering. There is no previous report using PIM process to produce Ti6Al4V/W composite. The most common process used is coating (Li *et al.*, 2015; Sharma *et al.*, 2009).

In this study, palm stearin (PS) were used and a based binder to produce a Ti6Al4V/W feedstock. Palm stearin has a good properties, low cost and wide availability. PS is a fraction of palm oil which have the decomposition temperature of 200-500 °C (Foudzi *et al.*, 2013). This temperature is higher than injection temperature and below the sintering temperature of Ti6Al4V/W composite which make it suitable use as a binder. PS in binder system will act as surfactant and lubricant to facilitate the feedstock to inject and removed from the mold (Arifin *et al.*, 2015; Omar *et al.*, 2012). The main objective in this study is to analyze the rheological properties of the Ti6Al4V/W feedstock and to produce the sintered part with no defects.

MATERIALS AND METHOD

Materials

Gas-atomized Ti6Al4V with an average size of 19.6 µm was purchased from TLS Tecknik GmbH & Co, Germany. Wollastonite with an average size of 8.7 µm was purchased from CNPC Powder Material Co., Ltd., China as shown in Fig. 1 (a) and (b). A binder system used in this study consists of 60 wt.% palm stearin and 40 wt.% of polyethylene (Arifin *et al.*, 2015).

Feedstock preparation

Powder loading were obtained from critical powder volume percentage (CPVP) analysis and 2% below CPVP value is taken which is 61.0 vol.% (German and Bose, 1997). 80 wt.% of Ti6Al4V and 20 wt.% of W were mixed together with the binder system using Brabender mixer at 150 °C with constant speed of 25 rpm for 2h. The prepared feedstock were granulated at room temperature (Raza *et al.*, 2015).

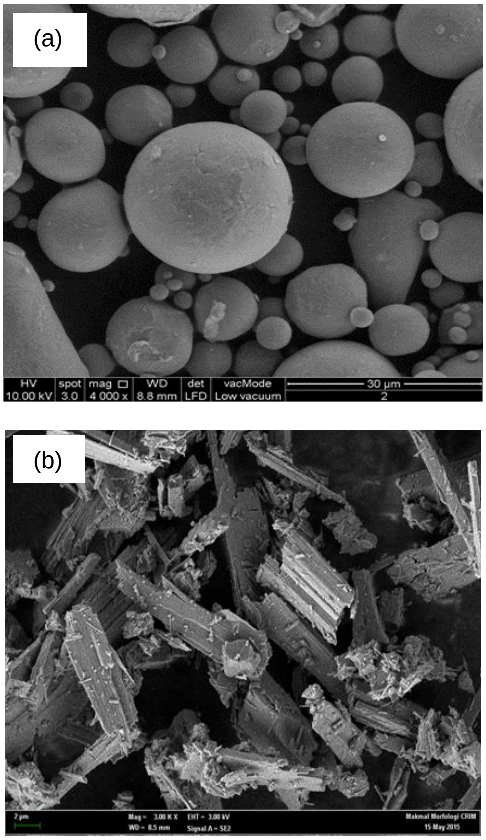

Fig. 1. Scanning electron microscope (SEM) micrograph of (a)Ti6Al4V powder.

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Rheological properties characterization

The rheological test was carried out using Shimadzu CFT-500D capillary rheometer with 1.0 mm diameter of die. Three different temperature were used: 130, 150 and 170 °C based on highest melting point temperature of binder which is PE with load of 20, 30, 40 and 50 kN. The graph of viscosity against shear rate was plotted. Based on Power Law equation (Eq. 1), the flow behavior index of the feedstock can be analyzed.

$$\eta = K\gamma^{n-1} \quad (1)$$

Where η is the viscosity, K is the constant, γ is the shear rate and n is the flow behavior index of the feedstock. The activation energy (E) of the feedstock have been determined using Arrhenius's equation (Eq. 2).

$$\eta = \eta_o \exp(E/RT)$$
(2)

Where η_o is the viscosity at a reference temperature, E is the activation energy, R is the gas constant and T is the temperature in Kelvin. The activation energy was obtained by calculate the slope of the graph plotted of $\ln\eta$ versus 1/T.

Injection molding of feedstock

The granulated feedstock was molded using DSM Xplore injection molding machine. The parameters used: molding temperature, 130 °C; mold temperature, 40 °C, pressure, 12 bar; and injection time 12 s.

Debinding and sintering of greem parts

The binder system was removed in two steps debinding which are solvent extraction and thermal debinding. Solvent extraction was carried out in heptane solution at 60 °C for 6 h to extract palm stearin. Then, the sample were transferred to thermal debinding step to remove the remaining polyethylene. In thermal debinding, the sample were heated at 500 °C for 1 h holding time at a heating rate of 5 °C/min in argon atmosphere (Raza *et al.*, 2012). The debound parts were sintered at 1200 °C, heating rate of 3 °C/min for 3 h in high vacuum furnace (VAC-TEC VTC 500 4TSF).

RESULTS AND DISCUSSION

The CPVP analysis were carried out as a reference to determine the powder loading of the feedstock. Fig. 2 shows that the CPVP graph of torque against time. The CPVP value was obtained from the highest peak of torque where all the particles were packed closely together and all the remaining spaces in between the particles was filled by the binders. The CPVP value obtained was 63.0 vol.%. Based on R. M. German and A. Bose (1997), the optimum powder loading value is 2-5% below the critical powder volume percentage (CPVP) (German and Bose, 1997). Thus, 61.0 vol.% were chosed.

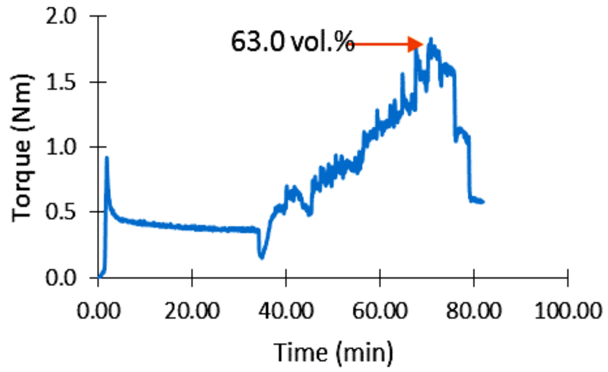

Fig.2. CPVP graph of torque againts time.

In PIM, the feedstock must have a pseudoplastic flow behavior which is the viscosity decrease with increasing shear rate (Abdullah *et al.*, 2011). Fig. 3 shows graph of viscosity against shear rate based on variable temperatures of 130, 150 and 170 °C. It was clearly shows that the viscosity of the feedstock decrease when the shear rate increase. This happened due to the reduction of friction between binders and the friction between powder and binder.

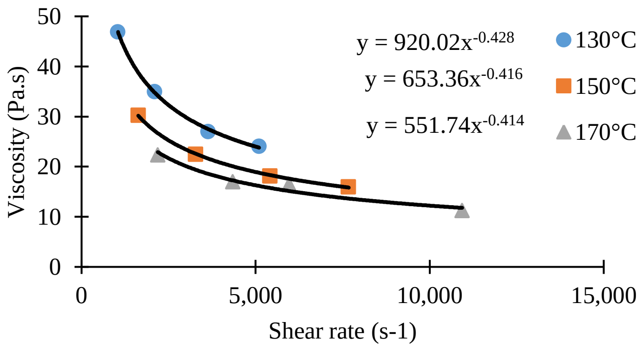

Fig. 3. Graph of viscosity againts shear rate for 61.0 vol.% of powder loading.

The flow behavior index, n for all the temperatures of 130, 150 and 170 °C were 0.57, 0.58 and 0.59 respectively which exhibit the pseudoplastic behavior and suitable for PIM process (Karatas *et al.*, 2004).

The activation energy, E (kJ/mol) were measured to determine the sensitivity of the feedstock towards the pressure and the change of temperatures. The feedstock with small E value is preferable since less defects on the green part will be produced due to low sensitivity toward pressure and temperature changes. Fig. 4 shows the graph of activation energy for 61.0 vol.% feedstock. The E value measured was 15.45 kJ/mol. By comparing to the previous research, the E value obtained for this Ti6Al4V/W feedstock were smallest which indicate that it is suitable for injection molding process and can produce the green part with no defects such as distortion and cracks.

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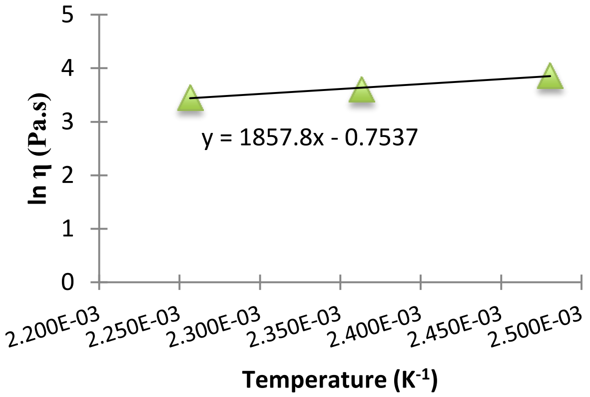

Fig. 4. Graph of activation energy for 61.0 vol.%

Debinding process were carried out on the green part to remove the binder system. There were two-steps debinding process used to reduce the time required for removing both palm stearin and polyethylene from the sample before sintering process. In the first step of debinding which also known as solvent debinding, the sample was immersed in heptane solution at 60°C for 6h to remove palm stearin that have been successfully done on previous research by (Foudzi *et al.*, 2013) and (M.A. Omar and I. Subuki., 2007). When the palm stearin removed, voids were formed between the particles. Its function as capillary paths and holes for the remaining binder which is higher molecular weight to be removed in the next thermal debinding stage without damage the samples (Thian *et al.*, 2001). Fig. 5 shown the percentage removal of palm stearin against time. It was shown that at 6 h, more than 95.0% of palm stearin were successfully removed.

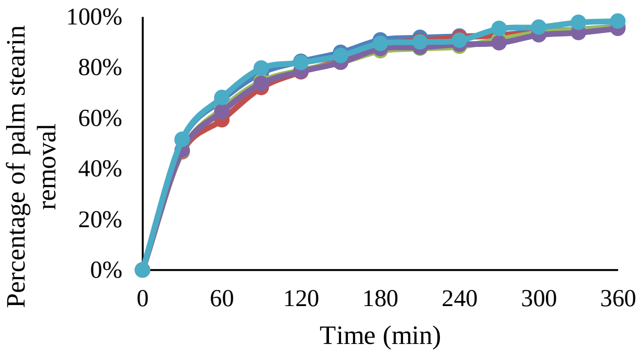

Fig. 5. Graph of percentage removal of palm stearin againts time.

Fig. 6 shows the SEM micrograph of debound parts with less binders surround the particles of Ti6Al4V/W samples after thermal debinding stage. In this stage, the PE usually decomposed through chain depolymerization. This higher molecular weight of PE will break into lower molecular weight and thus can be removed in gaseous form. The remaining binder system in the debound part was used to sustain its shape prior to sintering process (Foudzi *et al.*, 2013).

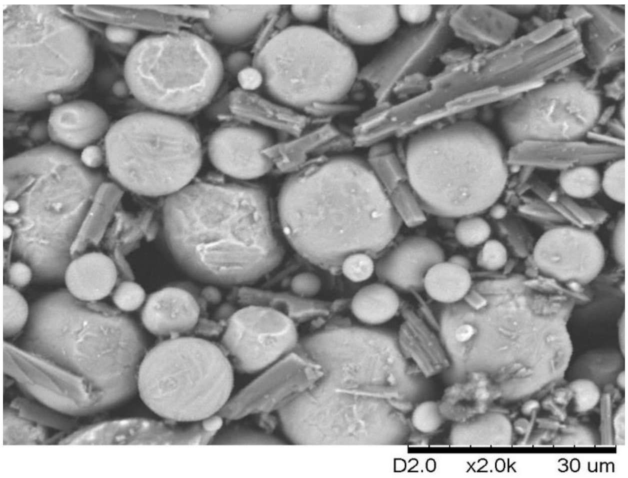

Fig. 6. SEM micrograph of debound part for 61.0 vol.% powder loading

The sintering process were conducted at a temperature of 1200 °C for 3 h with heating rate of 3 °C/min. Fig. 7 shows the comparison of the green part, debound part and sintered part for Ti6Al4V/W composite. The green part and debound part had similar dimensions while shrinkage happened on the sintered part. This is due to the presence of voids after the binder system removed from green part which cause the diffusion and solidification of the powder during the sintering process. The sintered part was successfully produced with no defects.

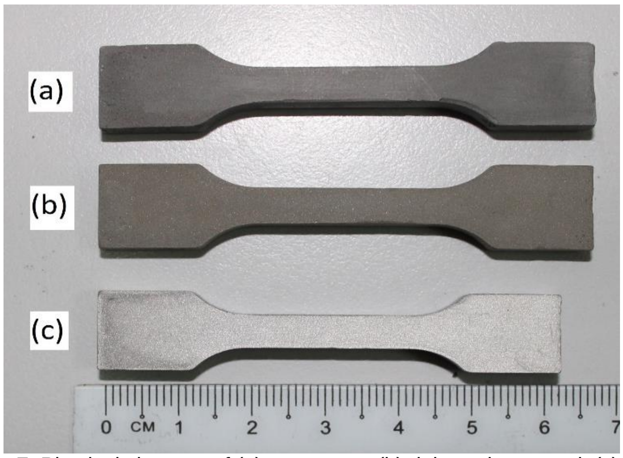

Fig. 7. Physical changes of (a) green part, (b) debound part, and, (c) sintered part for 80 wt.% Ti6Al4V/ 20 wt.% W.

Morphological analysis were conducted on the surface of the sintered part as illustrated in Fig. 9. The particles of the powder diffused with one another through the necking process. It can be seen that the pores were located in intergranular regions. The pores indicates that the temperature is still not sufficiently high for mass transport by diffusion for both wollastonite and Ti6Al4V. Hence, only short range connections were happened by liquefied Ti6Al4V/W composite particles that are in contact (Suwanprateeb *et al.*, 2009).

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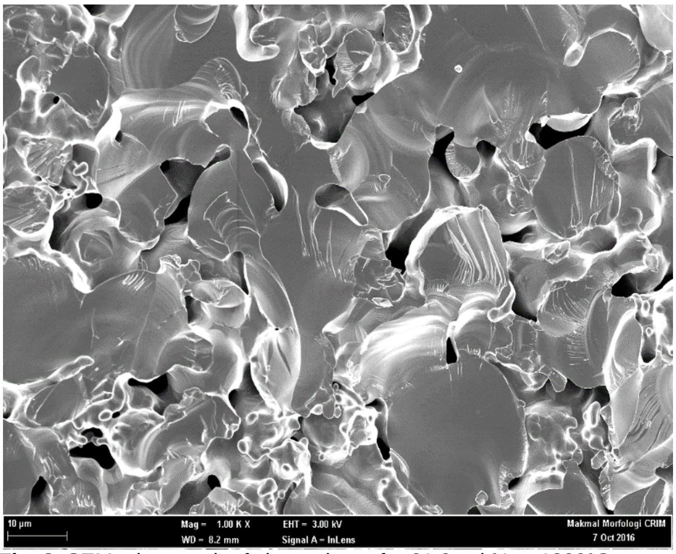

Fig. 8. SEM micrograph of sintered part for 61.0 vol.% at 1200°C.

Cellular viability test was conducted on the sintered sample using Presto Blue™ reagent. This test is use to evaluate the viability and proliferation of the cells. It is also use to measure the cytotoxity of the sample (Xu *et al.*, 2015). Fig. 11 shows the graph of cellular viability of Ti6Al4V/W composite. It was shown that from day 1 to day 4, the absorbance rate increase. This indicates that the cell proliferation increase. From day 4 to day 7, the absorbance slightly increase, which is shows the cell growth and viable.

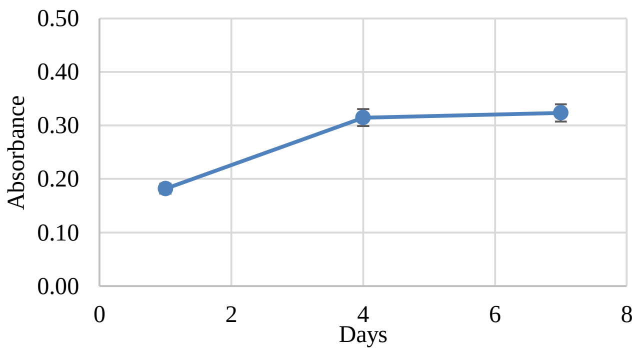

Fig. 9. Graph of viability test for Ti6Al4V/W composite.

CONCLUSION

The flow behavior of Ti6Al4V/W feedstock for 61.0 vol.% powder loading was pseudoplastic behavior and the flow behavior index was in the range of injectability index which is suitable for powder injection molding process. The activation energy shows that the feedstock is less sensitive towards the pressure and temperature changes that can produce the sample with less defects during the injection molding process. The binder system was successfully removed from the green body using two-steps debinding process. The sintered part produce was no major defects. Sintering at 1200°C shows diffusion between the particles. The viability test shows that the Ti6Al4V/W composite are viable and non-toxic.

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