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Fabrication of Ti/Polymer Biocomposites for Load-Bearing Implant Applications

J.F. Wang, X.Y. Liu^{*} and B. Luan

Integrated Manufacturing Technologies Institute, National Research Council Canada, 800 Collip Circle, London, ON N6G 4X8, Canada

Abstract

This paper presents a two-step method for the fabrication of Ti/polymer biocomposites. In the first step, a porous titanium substrate was produced by powder compaction and sintering. The porosity and pore structure of the substrate were controlled by varying the sintering process parameters. In the second step, high-density polyethylene (HDPE) or polyurethane (PU) was impregnated into the porous titanium substrate to form Ti/polymer biocomposites with the assistance of a hydraulic pressure. Ti/polymer composites with the polymer volume fraction varying from 21% to 37% have been successfully fabricated. Suitable impregnation parameters such as temperature, pressure and holding time for HDPE and PU were determined.

Keywords: porous Ti; Ti/polymer composites; sintering; polymer impregnation.

^{*} Corresponding author, Tel: +1-5194307042, Fax: +1-5194307064, Email: xingyang.liu@nrc.gc.ca

1. Introduction

The use of titanium for load-bearing implant applications can be tracked back to 1951 [1]. Nowadays, titanium alloys have been widely used as dental and orthopedic implant materials [2] due to their excellent biocompatibility combined with high specific strength and high corrosion resistance. However, the elastic modulus of titanium (110GPa) is much higher than that of cortical bones (10-30GPa), which can leads to bone resorption over time and eventually the loosening of implants [3-6]. This phenomenon, termed “stress-shielding induced bone resorption”, is one of the main factors necessitating revision surgery. To address the concerns related to the stress-shielding effect, considerable amount of research has been devoted to the development of new implant materials with bone-matching modulus, such as polymer based composites [7-11], carbon-carbon composites [12] and metastable β -Titanium alloys [13-14], for the fabrication of permanent implants. Although the polymer-based composites can be designed to have a similar elastic modulus to that of natural bones, their fatigue resistance and fracture toughness are inferior to that of the natural bones. The metastable β -Titanium alloys show promising mechanical strength and significantly lower elastic modulus (55 GPa for Ti-35Nb-7Zr-5Ta) than that of the conventional titanium alloys, but the elastic modulus is still higher than that of the natural bones.

An alternative approach to reducing the elastic modulus of orthopedic implants is to use porous materials, because the elastic modulus of porous materials can be tailored by controlling the porosity level and pore characteristics [15]. It has been demonstrated that sintered titanium compacts with around 30% porosity [16-17] have an elastic modulus close to that of human cortical bones. However, the introduction of porous structures leads to degradation of the

mechanical strength of the materials due to the structural defects and the stress concentration around the pores. Additionally, porous titanium is more susceptible to corrosion than solid titanium due to the much greater surface area exposed to the aqueous corrodent [18].

Since metals have excellent mechanical properties and polymers have low elastic modulus, the combination of a metal with a biocompatible polymer can potentially form a biocomposite with bone-matching modulus along with satisfactory mechanical strength. In addition, the filling of the pores with a polymer will effectively reduce the exposed area to the environment and hence reduce corrosion tendency of the porous materials. To date, however, little work has been reported on metal matrix composites for load-bearing implant applications.

The objectives of this study are to produce porous titanium parts with controlled porosity by a powder metallurgy (P/M) method, and to develop a method for the integration of biocompatible polymers, such as high-density polyethylene (HDPE) and polyurethane (PU), into porous titanium to form a composite with interpenetrating networks.

2. Experimental Methods

2.1 Powder compaction and sintering

Commercially pure titanium powders (provided by Atlantic Equipment Engineers, USA) with a purity of greater than 99.7% and an average particle size of 20 μm were used in this study. The particles have an irregular shape, as shown in Figure 1. The powders were uniaxially pressed at 105 MPa in a die with a diameter of 12.7mm for 5 minutes. The height of the cylindrical green compact was approximately 7 mm. The green compacts were pressurelessly sintered in a vacuum of 10^{-3} Pa. The sintering temperature was varied from 1000°C to 1300°C and the

sintering time from 1 hr to 12 hr, respectively. The density of the sintered samples was determined from the measured weight and volume.

2.2 Characterization

The average porosity (P) of the samples was calculated by using the following equation:

$$P = (1 - \rho_c / \rho_{Ti}) \times 100$$

Where ρ_c and ρ_{Ti} were the density of the porous compacts and the density of the solid titanium (4.51 g/cm³), respectively. Cross-section scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) was used for microstructural and compositional analyses at different locations of the composites and different stages of processing.

2.3 Impregnation of biocompatible polymers

HDPE and PU were chosen as the impregnation materials in this study due to their good biocompatibility and long history of being used as implant materials. The HDPE polymer, with a density of 0.95 g/cm³ and a melting point of 129 °C, was provided by ExxonMobil Chemical. The polyurethane resin with a density of 1.15 g/cm³ and a melting point of 196-215 °C was provided by Bayer Corporation. The impregnation of sintered Ti compacts with HDPE or PU polymer was conducted in a hydraulic-assisted impregnation device schematically illustrated in Figure 2. Solid pellets of HDPE or PU resin were placed on top of the sintered Ti compact inside the die. After the die was heated to the impregnation temperature (160 °C - 200 °C for HDPE, 260 °C for PU), a hydraulic pressure varying from 35 MPa to 105 MPa was applied to force the molten polymer flowing into the pores of the sintered titanium. The holding time under pressure was between 3-5 minutes.

3. Results and discussion

3.1 Fabrication of porous Ti substrates

Figure 3 shows the effect of sintering temperature and sintering time on the porosity level of the sintered titanium compacts. With the sintering temperature increased from 1000 °C to 1300 °C for a sintering time of 1 hour, the porosity level decreased from 37% to 10%. The increase in sintering time from 1 hour to 12 hours at 1000 °C led to the porosity decrease from 37% to 21%. Previous work has shown that porous Ti materials with a porosity level inside this range will have an elastic modulus close to that of cortical bones [16-17].

Since the fabrication of Ti/polymer composites by impregnation requires the porous titanium have an open pore structure, the pore characteristics of the sintered titanium materials were examined. Figure 4 shows the pore structures of the sintered samples with different porosity levels. The pores were open and interconnected to form a three-dimensional network for the compacts with porosity greater than 25%. Some isolated pores were observed for the compacts with porosity less than 25%. The formation of the sintering necks among powders and neck growth with the sintering temperature were observed. For the compacts sintered at relatively low temperatures and hence with high level of porosities (28-35%), the pores featured irregular shapes with sharp corners, as shown in Figure 4 (a) and (b). With increasing in the sintering temperature and consequently reduced porosities, the contours of the pores became smoother (Figure 4 (c) and (d)). Since lower porosity and smooth pore contours are favored for high mechanical strength, and an appropriate porosity level is required for bone-match elastic modulus and impregnation processing, the optimal porosity level of the porous titanium materials need s to balance the two requirements.

3.2 Impregnation of the sintered titanium with a polymer

The cross-section SEM/EDS studies on different locations of the composites from top surface to the middle and to the bottom surface were conducted and confirmed the uniform dispersion of the polymer in Ti matrix. Figure 5 shows the typical microstructure of sintered titanium and titanium/polyethylene composite fabricated by impregnating HDPE resin into the sintered titanium samples at a temperature of 200°C using hydraulic assisted impregnation. The SEM micrographs revealed clear differences in surface morphology between the as-sintered sample and the impregnated sample. A porous structure with interconnected pores was observed in the as-sintered sample (Figure 5 (a)), while the existence of polymer in the areas between titanium regions was evident in the impregnated sample (Figure 5 (b)). Compositional analysis of the polymer areas between titanium regions by EDS revealed that the major composition in these areas was carbon (Figure 5 (c)). This is consistent with the fact that HDPE contains only carbon and hydrogen, demonstrating that HDPE has been successfully impregnated into the porous titanium matrix.

Polymer impregnation is commonly used for filling the pores in porous castings and P/M parts. Normal impregnation processes are capable of eliminating mainly the macroporosity (pore size $>125\text{ }\mu\text{m}$). For removing microporosity (pore size $<125\text{ }\mu\text{m}$), process modifications or the use of low-viscosity resins are needed [19]. Successful impregnation of the compacts with microporosity, especially when the pore size is less than $50\text{ }\mu\text{m}$, is still a technical challenge in terms of the selection of suitable resins (low viscosity for penetration and low surface tension for wetting and adhesion) and the establishment of suitable processing parameters. Impregnation of

sintered porous Ti materials containing very small pores with biocompatible polymers such as HDPE and PU is even more challenging due to the high viscosity of the polymers in the liquid state, and the small pore size (with an average pore width of about 10 μm) existing in the sintered compacts. These results demonstrate that, with the use of a hydraulic assisted system, high viscosity polymers, such as HDPE and PU, could be impregnated into porous Ti materials with a pore size as small as 10 μm .

To further confirm the complete impregnation of the titanium matrix with HDPE or PU, the theoretical density of the completely impregnated composites were calculated and compared with the measured values. The following equation was used for the calculation of the theoretical density of the completely impregnated composites:

$$\rho_c = \rho_{\text{Ti}} \times F_{\text{Ti}} + \rho_{\text{polymer}} \times F_{\text{polymer}}$$

where ρ_c , ρ_{Ti} and ρ_{polymer} are the density of the composite, Ti and the polymer, respectively; F_{Ti} and F_{polymer} are the volume fractions of the Ti matrix and the polymer, respectively. The comparison of the measured densities of the Ti/HDPE and Ti/PU composites with the corresponding calculated densities for the composites with complete polymer impregnation is shown in Figure 6. It can be seen that the measured densities of the composites agreed well with that of the theoretical calculations, indicating that the pores in the sintered compacts were completely filled by the polymers.

Figure 7 and Figure 8 show typical microstructures of the Ti/HDPE and Ti/PU composites produced by impregnating sintered titanium materials with 21% and 37% porosity, respectively. The pictures show clearly the uniform dispersion of polymer phase in Ti matrix. It can be seen

that for the compacts with 37% porosity, all pores have been filled with the polymer and zero porosity was achieved after impregnation. For the compacts with a porosity of 21%, however, some small pores were left unfilled and about 2% porosity was left after impregnation. This is due to the facts that some pores were isolated so that polymers could not flow into these pores.

Since the melting point of HDPE is around 137°C, it is expected that a wide range of processing temperature can be used for the impregnation of HDPE. A systematic study showed that impregnation of HDPE could be successfully performed in the temperature range of 160 - 200 °C. In contrast, the suitable impregnation temperature range for PU is 240 – 260 °C, due mainly to its higher melting point (196-215°C).

Further investigation also revealed that for small sintered Ti compacts, an impregnation pressure as low as 14 MPa is sufficient to produce complete impregnation, giving a wide processing pressure window for the impregnation of various sintered porous Ti materials.

4. Conclusions

Powder compaction and solid state sintering was employed to fabricate porous titanium materials with the porosity controlled by varying the sintering temperature and time. The pores were interconnected and more irregular in shape when the sintering temperature is relatively low. The pore contours became smoother with increase in sintering temperature. The total number of pores decreased with the increase in sintering temperature and time. The average pore size, however, did not show obvious change with sintering temperature, and remained at about 10 µm when the sintering temperature was varied between 1000 °C and 1300 °C.

A hydraulic assisted impregnation procedure was established for the fabrication of Ti/HDPE and Ti/PU composites with the polymer volume fraction ranging from 21% to 37%. A uniform polymer dispersion in Ti matrix were successfully achieved by the established impregnation technique. The impregnated polymers form an interpenetrating network with the Ti matrix. The suitable impregnation temperature range is 160-200°C for PE and 240-260°C for PU, respectively. A hydraulic pressure as low as 14 MPa is sufficient for the full impregnation of small Ti samples.

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Figure Captions

Figure 1. SEM micrograph of the titanium powders.

Figure 2. Schematic illustration of the device setting-up for hydraulic assisted impregnation.

Figure 3. The effect of sintering temperature and sintering time on the final porosity of the sintered Ti compact.

Figure 4. SEM surface images show the pore structures of the sintered titanium samples with different porosity levels (a) 35%, (b) 28%, (c) 20%, (d) 14%.

Figure 5. SEM micrographs of (a) as-sintered titanium sample, (b) titanium/HDPE composite, and (c) locations of EDS compositional analysis on both the matrix (points 1&2) and the polymer (points 3&4).

Figure 6. Comparison of the measured and the calculated densities for the Ti/HDPE and Ti/PU composites.

Figure 7. SEM micrographs of the Ti/HDPE composites (a) 21% porosity before impregnation, 2% after impregnation (b) 37% porosity before impregnation, zero% after impregnation.

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