Use of a Naphthalene-Based Binder in Injection Molding
Net-Shape Titanium Components of Controlled Porosity

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We have recently developed a naphthalene-based binder system for use in powder injection molding (PIM) of ceramic and metallic materials. The use of a binder that can be removed via sublimation offers several unique advantages relative to the typical thermoplastic and/or thermoset binders employed in PIM. One of these is that essentially no volume change takes place during debinding. This offers a relatively facile method of introducing porosity into a net-shape part of potentially complex geometry. In the study described in this paper, the effects of powder loading and subsequent isostatic compaction on the size and amount of porosity in the components produced by this technique were investigated. In general, it was found that the amount of porosity is inversely proportional to the initial concentration of metal powder in the PIM feedstock. Likewise, average pore size displays a similar relationship with powder loading.

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1. Introduction

The development of porous titanium has received a great deal of interest from the medical community, particularly for its application in orthopedic and dental implants and appliances.\textsuperscript{1–3} From the standpoint of materials compatibility and biomedicine design, titanium alloys display an excellent combination of properties, including high specific strength, low density and lightweight feel, excellent corrosion resistance, and biocompatibility.\textsuperscript{4,5} These translate into significant clinical advantages in terms of reduced time of recovery and rehabilitation and improved patient comfort, making titanium a nearly ideal material for use in bone reinforcement and replacement products.\textsuperscript{5} However, the extent and quality of bone growth that takes place within a given porous metal implant is dependent not only on the base material but also on other key factors, which include the nature of the porosity (e.g. size, shape, and interconnectedness of pores),\textsuperscript{6,7} the stability and degree of micromotion between the implant and bone,\textsuperscript{8} the type of bone into which the implant is introduced (i.e. trabecular or cortical),\textsuperscript{9} and the presence of gaps between the implant and bone surface.\textsuperscript{9,10} Ideally the substitute bone material should display excellent osteoconductance, with a high degree of open porosity to facilitate cell integration as rapidly as possible. Previous research has shown that good bone ingrowth can be achieved with pore sizes ranging from 50–125 \( \mu \)m, though larger interconnected fenestrations are generally needed to provide space for the vascular tissue that is required to continue mineralized bone ingrowth.\textsuperscript{11,12}

There are a number of processing techniques that exist for producing porous metallic products, including: powder metallurgy methods such as loose powder-sintering, slurry foaming, burnout of porous organic scaffolds infiltrated with metal powder, and powder injection molding using burnable spacer agents;\textsuperscript{13} compaction of metallic fiber; combustion synthesis techniques;\textsuperscript{14} solid-gas eutectic solidification;\textsuperscript{15} and sputter deposition or electrodeposition on a three-dimensional reticulated organic foam.\textsuperscript{16,17} The use of powder injection molding (PIM) is particularly intriguing because it offers a net-shape method of fabrication, a feature which is attractive for several reasons: (1) production costs can potentially be reduced and (2) greater control over surface microstructure can be established. The latter is suspected to be a key factor in promoting more rapid and complete osseointegration.\textsuperscript{18} PIM is a well-established method of fabricating small-to-moderate size metal components. The process is derived from plastic injection molding and is comprised of four main steps: (1) mixing of metal powder with a polymer binder to form the feedstock, (2) melting of the feedstock mixture followed by pressure injection into a mold, (3) binder removal via heat treatment, solubilization, or catalytic decomposition, and (4) sintering or densification.\textsuperscript{19} The use of easily removed fugitive phases in the feedstock mixture and control of the de-binding and/or sintering heat treatments are two possible methods of tailoring porosity in this processing technique.\textsuperscript{20}

Work conducted on titanium powder injection molding (Ti-PIM) in the early 1980s utilized thermoplastic- and/or thermoset-based binders of the type employed in other metal injection molding processes, with these materials constituting 40–50 vol % of the feedstock and downstream binder removal taking place via thermal pyrolysis.\textsuperscript{21,22} More recently, binders have been designed that are soluble in water or organic solvents and/or contain a catalyst that facilitates in-situ decomposition.\textsuperscript{23} We have developed an alternate approach that uses an aromatic compound as a combination solvent/binder and thus requires only a fraction of the traditional binder material as a minor additive.\textsuperscript{24} The advantage of aromatics such as naphthalene, anthracene, and pyrene is that they melt at relatively low temperatures and can be completely removed by sublimation under reduced pressure at temperatures well below their melting point. Additionally, we have found that the use of this type of binder offers a potential means of tailoring pore size and concentration in the final sintered product. In this paper, we discuss the effects of binder concentration on the density, average pore size, and elastic modulus of as-sintered specimens fabricated by PIM using a naphthalene-based feedstock.
2. Experimental Methods

Pure titanium was chosen for study in this investigation because of its well-established use in biomedical devices. Commercial purity titanium hydride powder (TiH\textsubscript{2}; Titanium Systems, Inc.) was used as the source material to mitigate concerns with oxygen contamination. Prior studies suggest that during thermal decomposition (around 350°C or higher, depending on the ambient atmosphere), the hydrogen from TiH\textsubscript{2} reduces oxygen impurities to form metallic titanium, although the mechanisms for this are not well understood.\textsuperscript{25,26} The characteristics of the TiH\textsubscript{2} powder employed are reported in Table 1 and its distinctive angular morphology is shown in Fig. 1. The binder system that was used contained 93 vol % naphthalene (Aldrich Chemical Co.), 6 vol % ethylene vinyl acetate (EVA, Microthene MU 763-00; Equistar Chemicals LP) to improve green strength, and 1 vol % stearic acid (Aldrich Chemical Co.) as a powder surfactant and lubricant. Details of how this formulation was established have been previously reported.\textsuperscript{27} A 50/50 combination of mold release agents Dow Corning DC 20 and Miller-Stephenson Teflon\textsuperscript{TM} was applied to the mold cavities prior to feedstock injection to aid in removing the molded parts.

Cylindrical Ti-PIM tensile bars were fabricated via the process outlined in Fig. 2. The feedstock mixing and injection molding parameters that were employed are given in Table 2. Feedstock formulations of TiH\textsubscript{2} powder and premixed binder were prepared by shear mixing at 358 K using Haake mixer equipped with Brabender blades. Mixing was conducted at 50 min\textsuperscript{-1} for 15 min, which prior characterization indicated would ensure good uniformity.\textsuperscript{27} The resulting slurry was then transferred to an extruder and charger to form solid 3 mm diameter by 10 mm long pellets that were used as the feedstock material in our experiments. Molded bars were fabricated by feeding the material into the heated barrel of a 20 MPa injection molder (Crystal Alloy Injectors USA, Minneapolis, MN). The barrel temperature was maintained at an external temperature of 408 K, which was found to be hot enough internally to keep the feedstock sufficiently fluid, and the molten slurry was injected under maximum pressure into an aluminum mold. The mold contained two cylindrical dogbone-shaped cavities (ASTM E8) each connected on end to a central 4 mm diameter injection port.

As molded, the tensile specimens measured 5 mm dia \times 40 mm long through the gage length body and 15 mm dia. \times 7.62 mm long at each grip end with a 0.8 mm radius at the gage to grip (shoulder) transitions. As will be discussed the naphthalene was removed via sublimation during a vacuum drying step. In select cases,
specimens underwent uniform room temperature compaction in a cold isostatic press (CIP) under a hydrostatic pressure of 103 MPa. Final removal of the remaining binder and subsequent sintering were conducted in a single-step heat treatment run. Specimens were placed onto a pre-reduced zirconia setter plate, and heat treated in a refractory metal furnace (front loading SinterMaster, Thermal Technology, Inc., Santa Rosa, CA) under a set of conditions determined from previously reported thermal analysis experiments: heat in Ar/2.75% H\textsubscript{2} at 1 K/min to 648 K; hold at 648 K for 3 h; heat at 1 K/min to 1023 K, turn off the gas flow, and begin pulling a vacuum on the heating chamber while holding at 1023 K for 3 h; continue heating in 1.33 × 10\textsuperscript{-3} Pa vacuum at 5 K/min to a final soak temperature of 1373 K and hold for 4 h; followed by argon assisted convective cooling to room temperature.

Density measurements of the green and sintered specimens were conducted by simple geometric and mass measurements, as well as by the Archimedes technique using distilled water as the displacement medium. The microstructures of the sintered samples were characterized on polished cross sections using an Olympus BX60 optical light microscope and a JEOL JSM-5900 LV scanning electron microscopy (SEM; JEOL USA, Inc., Peabody, MA) equipped with an Oxford Energy Dispersive X-ray Spectrometer (EDS) system (Oxford Instruments, UK). Quantitative combustion analyses using the American Society for Testing and Materials standard ASTM D5373 were performed on the raw TiH\textsubscript{2} powders and the as-sintered titanium PIM components at Wah Chang Corporation (Albany, OR) to determine the nitrogen, carbon, and oxygen contents prior to and after PIM processing. Tensile testing was conducted using an Instron model 4465 test unit (Instron Corporation, Canton, MA) according to the conditions specified by ASTM E8. A constant crosshead speed of 0.25 mm/min was employed.

### 3. Results

As reported in Table 3, seven different feedstock loadings were prepared using the method described above. After injection molding, the specimens were grouped into three batches, each of which was exposed to a different temperature during drying in 2.67 Pa vacuum: 333, 343, or 353 K. Mass measurements were taken at periodic intervals during the sublimation process. Shown in Fig. 3 is an example set of mass loss curves for specimens prepared from a feedstock initially containing 62 vol % TiH\textsubscript{2}. As expected, the rate of naphthalene sublimation increases significantly with increasing temperature. In addition, over the range of feedstock loadings considered in the study, a slight increase in sublimation rate was observed as the powder loading was reduced. As will be discussed, this is likely related to the larger average pore sizes found in materials with lower loadings. Based on the mass loss data, specimens used in subsequent experiments were vacuum heat treated at 353 K to minimize the time for naphthalene sublimation.

In addition to mass, the length and gage diameter of the bars were measured after complete removal of the naphthalene. As shown in Fig. 4, specimen volume remains constant through the debinding process. The mass loss data plotted in this figure equates directly to the binder loading of the feedstock, as seen by comparing with Table 3. That is, because the binder is primarily composed of naphthalene, the phase which sublimes during vacuum drying, the resulting mass loss should display a 1:1 correlation with feedstock loading. However, the relationship between volume change and feedstock loading is more surprising. With many thermoplastic and thermoset binder systems, binder removal is often accompanied by substantial part swelling or shrinkage, which must be accounted for in the design of the PIM mold and in the subsequent sintering schedule. The issue is particularly problematic if the change in volume does not occur uniformly, which is often the source of

<table>
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<th>Volume Fraction of TiH\textsubscript{2} Powder</th>
<th>Mass % Powder</th>
<th>Mass % Binder</th>
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<tr>
<td>50</td>
<td>80.6</td>
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cracking and/or distortion in PIM produced components. However, this does not appear to occur in the naphthalene-based process.

It is suspected that the mechanism responsible for this is analogous to that observed in supercritical drying; a technique which is used to synthesize extremely low density aerogel materials from colloidal sols because solvent evaporation takes place with virtually no commensurate change in material volume. The phenomenon is typically attributed to the low surface energies intrinsic to supercritical fluids. Consequently, as the fluid is removed through pores in the drying body, it exerts very little capillary or collapsing force on the remaining solid and subsequent causes little change in the bulk volume of the solid during drying. Similarly, the process of sublimation also involves low surface energies in the vaporizing “solvent”. The effective result is less distortion and a more porous structure in the green part. The latter characteristic can be problematic if one wishes to attain high density in the final sintered component, but can be potentially exploited to achieve parts containing a controlled amount of porosity.

Because volume remains constant during the debinding process, the densities of the completely debound parts increase monotonically with powder loading as shown in Fig. 5. The relationship between green density and feedstock loading for the unpressed parts can be described using a simple rule-of-mixtures correlation:

\[
\rho_{\text{part}} = \rho_{\text{pore}} V_{\text{pore}} + \rho_{\text{powder}} V_{\text{powder}}
\]

where \( \rho_{\text{part}} \) is the density of the green part, \( \rho_{\text{pore}} \) is the density of the gas within the pore space (effectively zero), and \( \rho_{\text{powder}} \) is the density of the powder used in the injection molded part. \( V_{\text{pore}} \) and \( V_{\text{powder}} \) represent the volume fraction of porosity and powder (which is equal to feedstock loading), respectively. Equation (1) can be rearranged, yielding the 1:1 correlation between the theoretical density of the molded part and the initial feedstock loading that is observed in Fig. 5 for the unpressed components:

\[
\rho_{\text{th}} = \frac{\rho_{\text{part}}}{\rho_{\text{powder}}} = V_{\text{powder}} = \text{feedstock loading}
\]

where \( \rho_{\text{th}} \) is the green density of the part represented as a percentage of the full density of the starting material, in this case TiH₂.

Subsequent isostatic compaction of the specimens causes the curve to move higher green densities, with the greatest effect observed at lower feedstock loadings. In the as-sintered condition, a similar relationship is exhibited between density and initial feedstock loading, as seen in Fig. 6. In both the isostatically pressed and unpressed specimens, sintered density exhibits a monotonic increase with feedstock loading out to a TiH₂ concentration of \( \sim 67 \text{ vol\%} \). That is, lower powder loadings in the feedstock, and therefore lower green densities and less particle-to-particle contact within the specimen, will yield greater porosity and lower density in the final sintered body; a finding that agrees with results typically obtained in powder pressing studies.

Shown in Fig. 7(a) is an optical image of a sintered Ti-PIM tensile bar fabricated from feedstock initially containing 50 vol\% TiH₂. The specimen was not isostatically pressed prior to sintering. XRD and EDAX analyses indicate that the material is essentially pure \( \alpha \)-Ti, which is consistent with the slow cooling rate that the specimen experienced after sintering. A set of macropores, on the order of 200–300 \( \mu \text{m} \) in size is readily apparent in the material. In prior studies, the low number density of large-sized voids indicated that they were remnants from the occasional air bubble in the original molten feedstock. However, the greater number density of large-scale pores observed in the material in Fig. 7(a) suggests that their formation is directly related to the material’s low green density and presumably results from a greater average spacing distance between powder particles due to the large volume fraction of binder in the original as-molded specimen. A second set of much smaller voids is also observed. These are an order of magnitude finer in size (\( \sim 10–30 \mu\text{m} \)) and likely arise due to the volume shrinkage associated with the sintering process.

The micrograph shown in Fig. 7(b) is of a specimen fabricated from feedstock containing 67 vol\% TiH₂ and was isostatically pressed prior to sintering. Like the specimen in Fig. 7(a), this sample is also composed solely of \( \alpha \)-Ti, but contains almost no large-scale pores. There are also fewer fine-scale sintering pores and those observed exhibited a measurably smaller average size, on the order of 3–5 \( \mu \text{m} \) in diameter. The apparent difference in these two microstructures suggests that both the amount and size of the porosity in PIM components fabricated using a naphthalene-based binder can be regulated through control of feedstock loading and
by the use of cold isostatic pressing after molding. Further evidence for this is found by measuring pore size as a function of feedstock loading in both the isostatically pressed and unpressed specimens.

Estimates of the average pore size were made on select specimens from a series of cross-sectional optical micrographs using image analysis software (SigmaScan, Systat Software, Inc.). The results are presented in Table 4 as a function of initial feedstock loading. As expected, the use of isostatic compaction leads to smaller pore sizes on average at each powder loading. In general for both the pressed and unpressed samples, a larger average pore size was observed in specimens fabricated with a lower TiH₂ powder loading in the original feedstock. Similar trends between pore size and sintered density have been reported for ceramic powder compacts prepared by uniaxial cold-pressing.32) The pore sizes found in the unpressed specimens and the isostatically pressed specimens prepared with lower loading feedstocks fall within the range generally considered acceptable for good bone ingrowth. It is anticipated that the use of larger-scale fugitive phases, possibly particulates of a higher temperature aromatic such as pyrene or an inorganic such as ammonium hydrogen carbonate, would allow appropriately sized fenestrations to be incorporated if desired.

Shown in Fig. 8 is a plot of elastic modulus as a function of porosity for these specimens. Included for comparison is a straightline representation of the data obtained by Oh et al.,33) and a correlation between modulus and porosity for titanium predicted by the Halpin–Tsai equation,34) which is an empirical correction for a simple rule-of-mixtures description for the modulus of a two-phase material (where in this case one phase is the titanium matrix, the other is pores):

\[ E_{\text{part}} = \left( \frac{1 + \xi \eta V_{\text{pore}}}{1 - \eta V_{\text{pore}}} \right) E_{\text{matrix}} \]  

(3)

where

\[ \eta = -\frac{1}{\xi} \]  

(4)

and

\[ \xi \sim 2 \]  

(5)

while \( E_{\text{part}} \) is the resulting modulus of the porous component and \( E_{\text{matrix}} \) is the modulus of fully dense titanium. Note that the approximation in eq. (5) is adapted from Whitney.35) Although the Halpin-Tsai equation accurately predicts the monotonic decrease in modulus with increasing porosity, the slope that fits the observed data in Fig. 8 better matches the results obtained by Oh et al.,33) as well as those of Ledbetter.36) One of the key problems with the fully dense metallic implant materials in use today is their high elastic moduli. The resulting mismatch with neighboring bone can cause resorption of the bone, ultimately leading to failure of the implant.37) Although good progress has been made with low rigidity titanium alloy compositions,38) an alternate method of overcoming this issue is to incorporate porosity into the implant material and thereby reduce its stiffness in the manner shown in Fig. 8.
respect to the size and amount of porosity. The largest pores enveloping an inner core that appears to be graded with a

Fig. 9 Cross-sectional microstructure of a specimen prepared from feedstock initially containing 62 vol % TiH₂ powder. After molding ~50 wt % of the naphthalene was removed by sublimation, the specimen was isostatically pressed, the remaining naphthalene was sublimed, and the specimen was sintered.

In all of the specimens discussed above, the naphthalene was completely removed prior to carrying out additional processing, i.e. sintering or isostatic pressing and sintering. However, the possibility of only partially removing the naphthalene was also considered in the study. In this case, a sample fabricated from feedstock containing 62 vol % TiH₂ was vacuum treated at 353 K for 3 h, long enough to sublime ~50% of the naphthalene according to Fig. 9. It was anticipated that the majority of the remaining naphthalene would be retained in the central portion of the specimen. The sample was then isostatically pressed, after which the remaining naphthalene was sublimed prior to sintering under the previously described conditions. A cross-sectional optical micrograph of the resulting material is shown in Fig. 9. As can be seen, a dense outer rim measuring approximately 250 µm thick forms over the axisymmetric specimen, enveloping an inner core that appears to be graded with respect to the size and amount of porosity. The largest pores are found directly in the center of the sample and measure 100 µm or larger in size. In an approximate fashion, the microstructure is suggestive of the cancellous and compact tissue found in natural bone. Work is continuing on this concept to determine the extent of microstructural gradation that can be incorporated into the material and examine the resulting effect on elastic modulus and other mechanical properties.

4. Conclusions

From this study on the use of naphthalene-based PIM in fabricating porous titanium components we conclude the following:

- The amount of porosity in the sintered parts is inversely proportional to the initial powder loading in the PIM feedstock. The relationship between porosity and feedstock loading can be modified by incorporating a separate isostatic pressing step after molding, which results in higher densities at each feedstock concentration vis-à-vis the unpressed components.
- Similarly, the average size of the pores observed in the sintered specimens was found to increase with reduced powder loading. Thus, in order to maximize component density and minimize average pore size, high feedstock loadings should be employed. Conversely if increased porosity and pore size are desired, a lower powder loading can be used in the feedstock.
- The elastic modulus of these materials is inversely proportional to the concentration of inherent porosity.
- By partially removing the naphthalene binder prior to isostatic pressing and eventual sintering, a microstructure that displays gradation in both the amount and size of porosity can be achieved. This technique allows a dense outer skin to be formed over a porous central core and may have potential application as a more tailored bone replacement material.

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