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# Titanium compacts with controllable porosity by slip casting of binary powder mixtures

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Titanium compacts with tailored porosity and pore size were fabricated by slip casting of binary powder mixtures, followed by debinding and vacuum sintering. Two different particles sizes (avg. 14 μm & avg. 56 μm) of pure titanium hydride–dehydride powder were used in six volume ratios (0:100, 20:80, 40:60, 60:40, 80:20 & 100:0). The packing density and sintering behaviour of the titanium compacts were characterised, in terms of porosity, pore size analysis, tensile properties and gas permeability. A theoretical model predicted that the green density reaches a maximum when the volume fraction of fine particles is 0.35. It was found that although experimental results showed similar behaviour there was no well-defined maximum green density. The sintered compacts showed that an increase in the volume fraction of fine powder particles reduced the porosity, permeability level and pore size, and increased the tensile properties. The relationship between permeability and porosity level was non-linear and this was caused by the differences in pore diameters in the compacts. The capillary tube model was used to discuss the relationship between the permeability, pore diameter and porosity. Using this information, a graded porosity compact was designed and fabricated by slip casting.



## 1. Introduction

Porous titanium (Ti) is attractive for both structural and biomedical applications owing to its good strength-to-weight ratio, excellent corrosion resistance, large specific surface area and good bio-compatibility. A number of techniques have been developed to fabricate Ti products with tailored porosity, such as partial sintering of powder [1], sintering using a temporary space holder [2,3], and creep expansion of trapped argon or hydrogen gas [4–7]. To form a more complex shape, the green body or sintered component often has to be machined, which increases production costs [3,8]. Recently, fabrication techniques using a powder slurry for casting into near net shape porous Ti products have emerged as attractive approaches. These include freezing casting [9, 10], gel casting [11,12], slip casting [13–15] and tape casting [16]. However, research has rarely focused on using a slurry composed of a mixture of coarse and fine powder particles to control the porosity, pore size, permeability and mechanical properties of the porous Ti compacts.

The effect of the particle size distribution on packing density and sintering behaviour of compacts has been described in a number of publications [17–19]. The advantages of using coarse powder particles in the process include low material cost and limited sintering shrinkage. Smith and Messing [20] investigated the green density and sintered density for a mixture of 5 μm and 0.5 μm alumina powder by using the press and sinter method. The highest sintered density occurs with the 100% fine powder particles, even though it showed the lowest green packing density. This is because when the small particles constitute the bulk of the structure, large particles generate stresses that inhibit densification [17].

Robertson and Schaffer [21] have summarised some general observations applicable to Ti powder; firstly, for a bimodal powder mixture, the maximum green packing density in which the fine particles occupy the cavities between the coarse particles, occurs when the powder mixture contains 20–30 vol.% of fine particles mixed with coarser particles an order of magnitude larger in size; secondly, the higher driving force from the finer particles leads to an increased sintered density and this usually increases monotonically as the content of fine particles increases.

This study investigates the effect of a mixture of coarse and fine powder particles on the slip casting process for Ti. A detailed investigation of packing density, porosity, permeability, pore size and tensile properties was undertaken on Ti compacts prepared from binary powder mixtures.

## 2. Experimental procedure

### *2.1. The slip casting process*

Commercially available Ti powders (purity: 99.95%; Xi'an Baode Powder Metallurgy Co., Ltd., China), with two different particle sizes

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produced by the hydride/dehydride (HDH) process, were used in this study. These had average particle sizes of 14 μm and 56 μm, as shown in Fig. 1, with oxygen contents of 0.32 wt.% and 0.28 wt.%, respectively. In the slip casting process, Dolapix CE 64 (Zschimmer & Schwartz GmbH Co., Germany) was used as a dispersant, polyvinyl alcohol (Sigma-Aldrich, US) as a binder and polyethylene glycol (Fluka Chemie GmbH, Germany) as a plasticiser.

For all the experiments, the slurry was composed of 77 wt.% of HDH Ti powder, 0.8 dry weight percent (dw.%) of binder, 0.8 dw.% of plasticiser, and 0.3 dw.% of dispersant with a balance of distilled water. The powder volume ratios between coarse and fine HDH Ti powder used in this investigation were 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100. The mixed slurries were cast into plaster moulds with a rectangular cavity of 40 mm × 10 mm × 20 mm. The slip cast compacts were then removed from the plaster moulds and dried over 24 h at 40 °C in an oven, followed by debinding at 320 °C for 2 h under an argon flow of 150 ml/min. Three sintering temperatures of 1000 °C, 1100 °C and 1200 °C were studied with a 2 hour holding time during sintering.

### 2.2. Characterisation

To analyse the homogeneity of the powder particle size distribution in a mixed slurry composed of coarse and fine powder particles, samples from a long rectangular slip cast compact (100 × 20 × 10 $mm^3$) were taken at three different locations (top, middle & bottom) as illustrated in Fig. 2. The particle size distribution of each powder was determined using a Malvern MasterSizer machine with low angle laser light scattering (LALLS). Powders were dispersed ultrasonically in water.

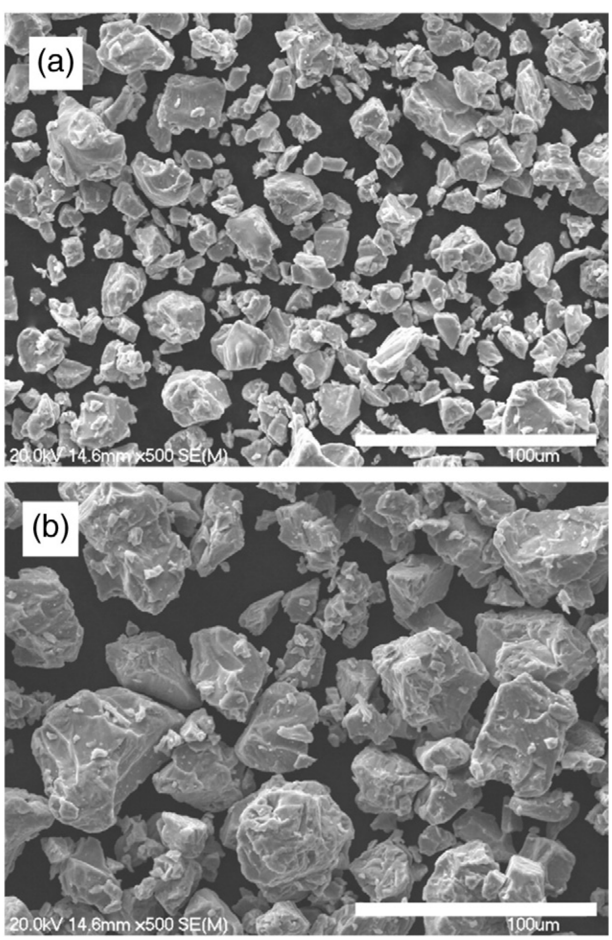


**Fig. 1.** SEM image of HDH Ti powders; (a) an average particle size of 14 μm; (b) an average particle size of 56 μm.

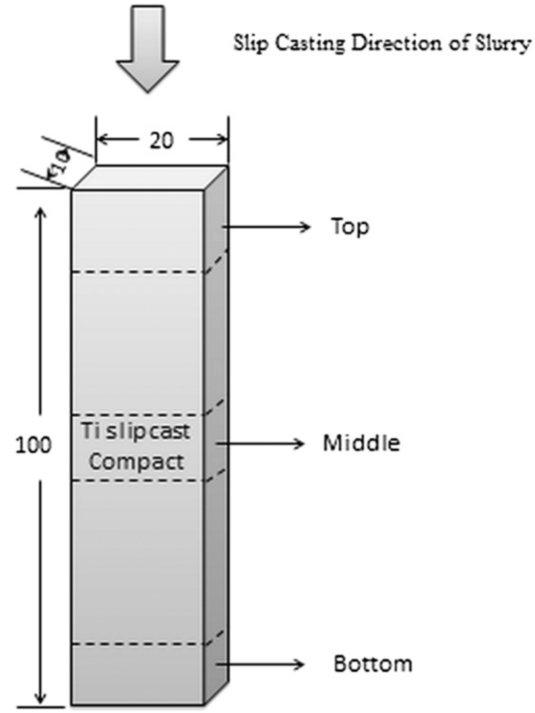


**Fig. 2.** An illustration of the location of samples taken from a green compact.

For all the slip cast compacts, except for that made from the 100 vol.% of coarse powder, the green packing density was averaged using a mass/volume equation from three green rectangular compacts (40 mm × 20 mm × 10 mm). Because of the effect of gravity on the sedimentation rate of the coarse Ti powder, it was difficult to obtain a slip cast green compact composed of 100% coarse Ti powder. Therefore, in this case the green density was measured by pouring the slip into a 10 ml cylinder and drying out the water in a 50 °C oven. The same mass/volume equation was used to obtain the green density. The total porosity and the open porosity in sintered Ti compacts were measured by the Archimedes method by vacuum impregnating them overnight with distilled water. The permeability was analysed by a pore size distribution analyser (GaoQ Functional Materials Ltd., China). The samples for testing had a circular shape with a diameter of 20 mm and a thickness of 2 mm, which were wire electric discharge machined from the large rectangular compact (40 mm × 20 mm × 10 mm). These samples were also ground and fine polished to remove the blockage in the pores caused by machining. Optical microscopy and image analysis software (Image-Pro Plus) were used to measure the average pore size and maximum pore size in polished cross sectional microstructures. The samples were also chemically etched using Kroll's reagent to observe the microstructure. Dumbbell shaped specimens for tensile testing were wire electric discharged machined from sintered rectangular compacts (gauge length of 10 mm with a 2 mm × 2 mm square cross section). An Instron tensile testing machine, with a crosshead speed of 0.05 mm/min was used in the tensile testing. For each test condition, three tensile specimens were prepared. The tensile fracture surfaces were examined using a Hitachi S4000 scanning electron microscope (SEM). The oxygen and carbon contents of the sintered samples were analysed by Leco combustion techniques.

## 3. Results

### 3.1. Particle size distribution

The slip casting process requires stable slurries. In a bimodal powder where there is an unstable suspension, because of the