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The development of porous titanium products using slip casting

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ABSTRACT

An optimized titanium slurry was developed from 43 vol.% of titanium powder, 0.3 dw.% of dispersant, 0.8 dw.% of plasticizer and 0.8 dw.% of binder, mixed with a balance of distilled water, which produced a viscosity of 40 cP. It was then poured into a plaster mold to form compacts with a green density of 45%. Thermal debinding was carried out at 320 °C with an argon flow for 2 h, followed by vacuum sintering different samples at 1000 °C and 1200 °C for 0.5 h, respectively. The porous sintered compacts had satisfactory tensile strength with some plastic deformation. The increase in oxygen and carbon content during processing was minor. An X-ray diffraction pattern showed pure alpha titanium peaks without any indication of contamination from organic additives. The results from this investigation suggested that slip casting is a potentially low-cost, simple production route for manufacturing porous titanium products.

1. Introduction

It is well known that porous titanium products have many potential applications due to their good strength-to-weight ratio, excellent corrosion resistance and high surface area. There are a broad range of applications for porous titanium, including medical implants, sandwich cores in structural applications, chemical filters and acoustic absorbers. Pure titanium has a strong chemical affinity to oxygen and therefore has poor high temperature oxidation resistance at temperatures at above 400 °C. Also, too high an interstitial oxygen content results in embrittlement. Because of the high surface area of porous titanium, a powder metallurgy route which allows the forming process to be carried out at lower temperatures to reduce the possibility of contamination is therefore a promising way to fabricate porous titanium products.

A variety of powder metallurgy approaches, which can be found in the literature, have been developed to fabricate titanium products with tailored porosity. Wen et al. (2001) reported a fabrication process for open-cellular titanium foams by mixing titanium powders with space-holders, followed by cold compaction, burning out the space-holders and sintering. This method is capable of creating products with a large portion of open pores in an interconnected structure, which are created by the space-holders after burning out. However, it is limited by the high cost of molding dies, the limited complexity of the compact shape and a variable density gradient. Chen et al. (2009) employed powder injection molding (PIM), mixing titanium powders with space holders, to produce porous titanium compacts with porosity in the range of 42.4–71.6 vol.%. PIM can be used to fabricate complex shapes, but the cost of molds and the problem of variable density gradient are important issues. In addition, a relatively large amount of binder is required for PIM, which raises concerns about binder residuals after the debinding stage, especially in the case of titanium.

Researchers have been using ceramics' techniques to fabricate near-net-shape porous titanium products and this has emerged as an attractive approach. Chino and Dunand (2008) developed directional freeze casting of an aqueous titanium slurry, followed by ice sublimation and powder sintering. Titanium foams with aligned and elongated pores were created from this technique. Rak and Walter (2006) obtained a porous titanium sheet with a thickness of 370 μm by tape casting a mixture of titanium and a titanium hydride slurry. Erk et al. (2008) demonstrated the feasibility of a gel casting process to fabricate porous titanium in complex shapes. A unique porous titanium screw for implant applications was fabricated with a 20 vol.% porous core and a higher porosity near the surface. Neirinck et al. (2009) presented slip casting of a mixture consisting of a slurry of titanium and titanium hydride powder to form a green compact through absorption of solvent by plaster mold, followed by sintering. However, safety is a major concern with this process due to the high reactivity of titanium hydride powder.

Slip casting is a conventional near-net-shape ceramics technique that is commonly used to manufacture dinnerware and sanitaryware. It is a filtration process in which a solvent based powder slurry is poured into a plaster mold, creating capillary forces as a result of the porosity and these absorbs the solvent from slurry.

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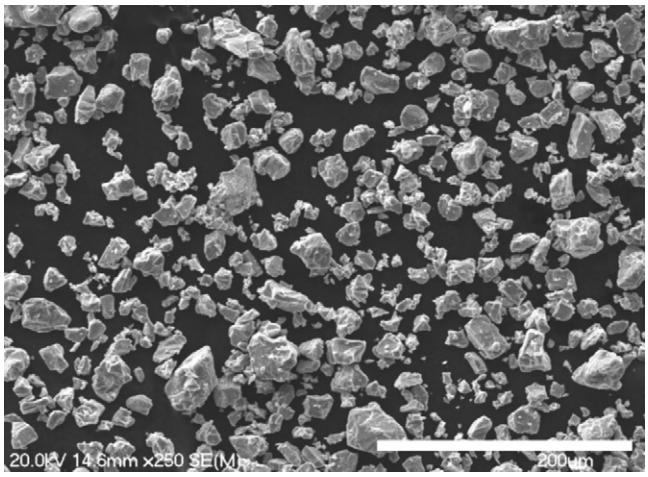

Fig. 1. SEM image of HDH Ti powder.

Over a period, the powder compact will be formed in the mold. Viscosity is a critical parameter in slip casting. This process involves binder, plasticizer and dispersant for controlling the viscosity of slurry. Asthana et al. (2006) indicated that both too high or too low a viscosity slurry yields poor quality sediment.

A solvent is an important component to make a slip in the slip casting, which offers a media for powder interactions and the interaction between the powder and organics additives. Although an organic solvent is commonly used as a dispersion media in colloidal processing due to its excellent compatibility with organic additives, water is emerging as an alternative because it is environmentally friendly, low cost and safe. Metal powder–water systems have been employed in colloidal processing by some researchers. Sánchez-Herencia et al. (2001) demonstrated colloidal processing using aqueous nickel powder suspensions to produce porous or dense compacts, which consist of a 77 wt.% solids loading, 0.5 wt.% carrageenan acting as a gelling agent on cooling with a balance of deionized water. Takeda and Minagawa (1990) developed a stainless steel slurry to produce dense compacts from slip casting process, which contains 82.7 wt.% powder, 0.3 wt.% ammonium alginate as a binder and the balance of water.

In the present work, we demonstrate that porous titanium compacts can be produced from a water based titanium slurry using a slip casting approach. This opens up a simple and low cost manufacturing route for porous titanium production. An important aim was the optimization of the water based titanium slurry formulation to minimize the content of organic additives. A lower organic additive content reduces the probability of carbon contamination in the sintered titanium products. Of interest were the mechanical properties of compacts sintered to give different porosity levels.

2. Experimental methods

2.1. Raw materials

As starting materials, commercially available titanium powders (purity: 99.95%; Xi'an Baode Powder Metallurgy Co. Ltd., China) produced by the hydride/dehydride (HDH) process were used in this study (Fig. 1). The powder had a surface area of 0.30 m^2/g measured by nitrogen adsorption using the BET equation and a mean particle size of 14 μm measured using laser analysis (Mastersizer, Malvern, UK). Dolapix CE64 (DP64; Zschimmer & Schwartz GmbH Co., Germany) made from carboxylic acid, with a density of 1.2 $g\,cm^{-3}$ was used as a dispersant to obtain a stable slurry. Polyvinyl alcohol (PVA, mw. 13,000; Sigma–Aldrich, US) and polyethylene glycol 400 (PEG400; FlukaChemie GmbH, Germany) were used as the binder and plasticizer, respectively. The choice of these two chemicals was based on their low decomposition temperature so that the reaction with titanium powders at high temperature is minimized.

2.2. The slip casting process

The aim was to fabricate rectangular and tubular compacts using slip casting. A high density polyethylene (HDPE) plastic jar was used to ball mix all the components, including water. The speed of the roller used for ball mixing was kept at a constant 120 rpm until degassing. The sequences of adding each component into the jar are described below. Initially, distilled water was mixed with the dispersant in the jar for 2 h, followed by additions of the titanium powder with further mixing for 24 h. Then, the binder and plasticizer were added and mixed for another 16 h. The final step was to degas the slurry using a low rotation speed at less than 10 rpm for 6 h. The well-mixed slurry was poured into a plaster mold with a plaster to water ratio of 1.53, to form green compacts. The plaster mold used for casting the rectangular compact had a cavity 40 mm long, 20 mm high and 10 mm wide and the mold for casting the tubular compact had a cavity 40 mm in diameter and 70 mm high, with an inner cylindrical mandrel (Ø20 mm). The green cast was dried in the mold overnight, and was then transferred to an oven at 40 °C for one day prior to debinding.

The slurry formulation was investigated with respect to solids content level, dispersant, binder and plasticizer concentrations. From a previous study, Xu et al. (2012) reported that an optimum amount of dispersant for this type of titanium slurry system was 0.3 dry weight percent (dw.%). To obtain the optimum solids content level, the viscosities of slurries prepared at different solids loadings (15, 21, 29, 40, 43 and 47 vol.%) with an addition of 0.3 dw.% of dispersant were measured using a viscometer (Brookfield Digital Viscometer, LVTDV-II) operating in the range of 12–60 rpm. To determine the optimum amount of binder and plasticizer, viscosity of slips, green strength and green density of green compacts were investigated. The green strength of compacts was evaluated from a three point bending test carried out using an Instron tensile testing machine with a cross-head speed of 0.05 mm/min. Before testing, each slip cast rectangular part (40 mm × 20 mm × 10 mm) was sliced into rectangular bars with a 6 mm × 6 mm square cross section and a 24 mm span. The green densities of compacts were averaged using a mass/volume equation from three green rectangular compacts (40 mm × 20 mm × 10 mm) for each binder concentration (0.6–1.2 dw.%).

Thermogravimetrical (TG) analysis were performed on the DP64, PVA and PEG400 components to determine their thermal properties in order to optimize the debinding temperature. The debinding work was carried out in a horizontal tube furnace with a heating rate of 1 °C/min and a controlled argon flow rate of 150 ml/min.

The debound compacts were placed on a molybdenum plate with a thin layer of BN coating and sintered under high vacuum (3×10^{-3} Pa). Different samples were heated at 7 °C/min to sintering temperatures of 1000 °C and 1200 °C respectively for 0.5 h, followed by a controlled cooling ramp at 5 °C/min to 650 °C and then furnace cooling down to room temperature, whilst keeping the high vacuum conditions.

2.3. Characterization

The sintered density of compacts for both rectangular and tubular shapes, previously vacuum impregnated with distilled water, was measured using the Archimedes method. The results were averaged from two sintered rectangular compacts and one tubular sintered compact. Open porosity was calculated as the percentage