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Rheological properties of commercially pure titanium slurry for metallic foam production using replica impregnation method

Anchalee Manonukul [a,*], Makiko Tange [b], Pathompoom Srikudvien [a], Nipon Denmud [a], Paiboon Wattanapornphan [a]

[a] National Metal and Materials Technology Center (MTEC), 114 Thailand Science Park, Paholyothin Rd., Klong Nung, Klong Luang, Pathumthani 12120, Thailand
[b] Taisei Kogyo (Thailand) Co., Ltd., Room INC2D-409, Innovation Cluster 2 Building, Tower D, 141 Thailand Science Park, Paholyothin Rd., Klong Nung, Klong Luang, Pathumthani 12120, Thailand

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ABSTRACT

Open-cell titanium foam can be produced by the sacrificial polymer foam impregnation method. It is important to control and understand the rheological properties of titanium slurry for the commercial production of titanium foam. The effects of titanium solid loading, binder (PVA) content and dispersing agent (Dolapix) content on the viscosity of titanium slurry were studied. The results show that the viscosity of titanium slurry is dependent on titanium solid loading and PVA content but independent on Dolapix content. However, Dolapix is required to prevent rapid sedimentation. The optimum titanium slurry composition is 75 wt.% of titanium powder, 1.5 wt.% of PVA, 1.0 wt.% of Dolapix and 22.5 wt.% of water. It was used to produce titanium foam with a porosity level of 84%, 0.47 wt.% of carbon content and 0.3 wt.% of oxygen content. From the compression test, Young's modulus of the titanium foam is 0.58 GPa, the plateau stress is 10 MPa and the densification strain is 78%. The good mechanical properties were achieved because there was limited contamination from organic compounds or from the atmosphere during sintering.

1. Introduction

Due to their high strength-to-weight ratio, high corrosion resistance and superior biocompatibility, titanium and its alloys have been widely used in several industrial applications including aerospace components, automotive components, sport equipment and medical implants. Titanium and its alloys have also become common materials for load-bearing implants [1,2]. Although, titanium has lower modulus of elasticity than other biocompatible metal e.g. stainless steel 316LVM, its modulus of elasticity is still significantly higher than bone. The mismatch in the modulus of elasticity can cause stress shielding effect, bone resorption and implant loosening. Porous titanium or titanium foam has been introduced not only to reduce the modulus of elasticity closer to bone, but the open-cell porous structure can also promote ingrowth of new tissue and the transport of the body fluid [2]. For example, porous titanium has been used as implants for hip joint, dental work and lumber interbody fusion.

Because of the high reactivity and high melting point of molten titanium, the common fabrication method for porous titanium is the powder metallurgy route, for example sintering titanium powder with foaming agent, sintering titanium powder with powder space holder and replica impregnation methods. The sintering of titanium powder with foaming agent method can produce an open-cell foam with non-uniform foam structure and moderate level of porosity of 50–70% [3]. It is noted that human cancellous bone has a porosity of approximately 75% and a pore size from 100 to 600 μm [4]. Different foaming agents can be used, e.g. H_2O_2 [5] or TiH_2 [6]. Different space holders can also be used, e.g. carbamide [7–9], NaCl [10], magnesium [11] and tapioca starch [12]. Although the sintering of titanium powder with a powder space holder method can produce both closed-cell and open-cell structure, it is difficult to achieve very high porosity. For the replica impregnation method, polymer foam is used as a template for impregnation. Titanium powders are mixed with water and binder into titanium slurry, which will be used to impregnate the open-cell polymer foam template. After drying, the polymer foam and binder are removed by pyrolysis and the titanium powder framework sintered. The titanium foam will replicate the structure of the polymer foam. Hence, it is possible to produce highly porous open-cell titanium foam with a uniform cell structure similar to the polymer foam.

To achieve titanium foam with good mechanical properties, there are several parameters, e.g. the size and morphology of titanium powder [4], the type and size of polymer foam, the binder [13] and the sintering condition that need to be carefully controlled. To achieve titanium foam with an acceptable open-cell structure, the properties of the slurry, especially rheological properties are highly important and these also require exact control. The rheology of the slurry affects the thickness and uniformity of the titanium layer coated on struts of the polymer foam, the openness of the cell, and the ability to retain shape after the polymer foam is removed. There are several factors that can

* Corresponding author. Tel.: +66 2 564 6500x4570; fax: +66 2 564 6403.
E-mail address: anchalm@mtec.or.th (A. Manonukul).

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influence the rheology of slurry, e.g. solid loading, binder type, binder molecular weight, binder content, dispersing agent content, particle size, particle size distribution, particle shape, pH value of slurries, shear rate, temperature and the presence of air bubbles [4,14,15].

Ti–6Al–4V slurry using 75 wt.% solid loading with five-organic components, which are polyethylene glycol 4000, methylcellulose, ammonia (25% solution), 1-octanal and Dolapix, has been investigated [4]. It was found that smaller powder size with spherical shape is beneficial for the preparation of Ti–6Al–4V slurry. In addition, at least two organic components, which decompose at different temperatures, have the advantage to maintain the shape after polymer foam is removed. TiH_2 slurry using 75 wt.% solid loading with two-organic components, which are k-carrageenan (polysaccharide), and Dolapix or Dispex has also been studied [16]. It was found that Dispex is effective in dispersing the suspensions, while Dolapix did not avoid flocculation. Dolapix appeared to be effective for Ti–6Al–4V but was not for TiH_2 slurry. The previous studies [4,16] show that an organic component can have different effects on the rheological properties of different metal powder slurries. In addition, there was no previous systematic study on the rheological properties of pure titanium slurry especially with only two-organic components, which are polyvinyl alcohols (PVA) as a binder and Dolapix as a dispersing agent. The objectives of this works are the understanding of each component on the rheological properties and also identification of the optimal titanium slurry formulation for commercial production of titanium foam with good compressibility and high strength.

2. Materials and experimental procedures

2.1. Materials

Commercially pure titanium powder readily available in the market was used in this work. The chemical composition of the powder as shown in Table 1 reveals some traces of Fe, H, N, C and O. This satisfies the general specification of the titanium powder, which is 99.7% minimum purity. The powder size distribution is 22.94 μm (D_{50}). SEM showed that the powder shape is spherical as expected for gas atomised powder and that all powder sizes observed were below 45 μm (Fig. 1). In addition, some micrometre size powders were observed, which tended to adhere to larger powders. It is noted that the powder with the particle size range from 20 to 40 μm is recommended for titanium slurry [4]. The measured density of the powder is 4.49 g/cm^3.

There were two organic components used in this experiment, which were PVA and Dolapix. PVA was the main binder to increase the viscosity of the liquid and Dolapix acted as a dispersing agent. It has been reported previously that a single-binder component is not practical [4]. This work attempts to use the lowest number of binder components possible with commercial production in mind. The viscosity of PVA at 4% aqueous solution, 20 °C is 25–31 cP. Dolapix is carboxylic acid solution with approximately 65% active matter. It is also free from alkali with a pH of approximately 7. Dolapix is commonly used in combination with PVA, polysaccharides, cellulose derivatives and polymer dispersions.

2.2. Preparation and analysis of titanium slurry

PVA and Dolapix were dissolved in water at 90 °C using magnetic stirrer for 90 min. Subsequently, commercially pure titanium powder was added and mixed for 10 min at 90 °C using electronic mixer. The rheological property of titanium slurries was measured by a viscometer using Brookfield Engineering Labs DV-II + viscometer at a speed of 30 rpm with a spindle SC4-29 at 25 °C. For each batch of titanium slurry, the rheology tests were repeated twice. In addition, sedimentation tests were also performed on 3 batches of slurries as shown in Table 2. The sedimentation tests were also repeated twice for each batch. Sedimentation rate was measured in 10 ml glass tube by the comparison of the height of the sediment powder over 2 h.

Table 1
Chemical compositions of commercially pure titanium (wt.%).

Fe	H	N	C	O	Ti
0.033	0.005	0.009	0.005	0.113	Balance

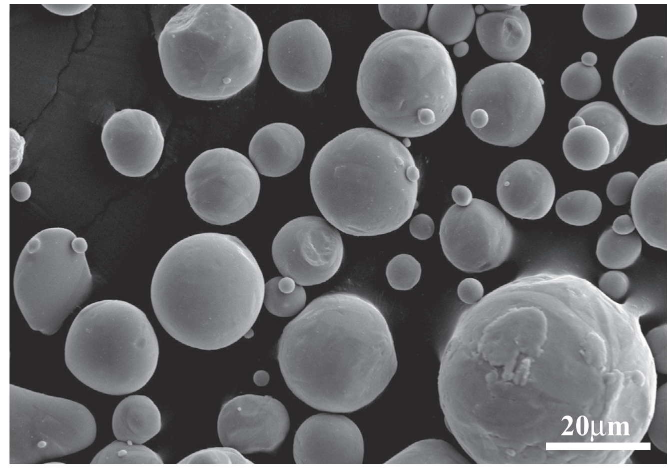

Fig. 1. SEM micrograph of commercially pure titanium powder.

2.3. Effects of solid content

The effects of solid content on the viscosity of titanium slurry were studied using several batches of titanium slurry with 1.0 wt.% of PVA, 1.0 or 2.0 wt.% of Dolapix and varied solid loading of titanium powder from 65 to 80 wt.%.

2.4. Effects of binder

The effects of binder (PVA) on the viscosity of titanium slurry were investigated using several batches of titanium slurry with 75 wt.% of titanium powder, 1 wt.% of Dolapix and varied concentration of PVA from 1.0 to 2.5 wt.%.

2.5. Effects of dispersing agent

The effects of dispersing agent (Dolapix) on the viscosity of titanium slurry were studied using several batches of titanium slurry with 75 wt.% of titanium powder, 1.0 or 1.5 wt.% of PVA and varied concentration of Dolapix up to 2.0 wt.%. In addition, the sedimentation tests were carried out for 3 batches of titanium slurry with 75 wt.% of titanium powder, 1.0 wt.% of PVA and varied concentration of Dolapix (1.0, 1.5 and 2.0 wt.%).

2.6. Preparation of porous titanium foam

In this work, a reticulated polyurethane (PU) foam was used as a sacrificial template. The PU foam has a pore size of 35 ppi (pore per linear inch). Fig. 2 shows a three-dimensional optical view of the PU foam

Table 2
Sedimentation results of titanium slurries with varied wt.% of Dolapix.

No.	Ti (wt.%)	PVA (wt.%)	Dolapix (wt.%)	Water (wt.%)	Sedimentation test (mm/h)
1	75	1		Balance	10
2	75	1	1	Balance	8
3	75	1	2	Balance	2.8