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## FABRICATION OF POROUS Ti BY THERMAL DECOMPOSITION AND SINTERING OF PMMA/TiH<sub>2</sub> POWDER COMPACT

### WYTWARZANIE POROWATEGO TYTANU PRZEZ ROZKŁAD TERMICZNY I SPIEKANIE WYPRASEK PMMA/TiH<sub>2</sub>

Porous Ti with controlled pore structure was fabricated by thermal decomposition and sintering process using TiH<sub>2</sub> powders and Polymethylmethacrylates (PMMA) beads as pore forming agent. The beads sizes of 8 and 50 μm were used as a template for fabricating the porous Ti. The TiH<sub>2</sub> powder compacts with 20 and 70 vol% PMMA were prepared by uniaxial pressing and sintered for 2 h at 1100°C. TGA analysis revealed that the PMMA and TiH<sub>2</sub> were thermally decomposed at about 400°C forming pores and at about 600°C into metallic Ti phase. The porosity increased with increase in the amount of PMMA addition. Also, the microstructure observation showed that the pore size and shape were strongly dependent on the PMMA shapes.

*Keywords:* Porous Ti, PMMA powders, Thermal decomposition of TiH<sub>2</sub>, Pore structure

#### 1. Introduction

Porous materials are currently the subject of intensive work due to excellent properties such as small specific weight, large specific surface area and high permeability. These characteristics have made diverse applications of porous materials, including separation filters, catalyst supports and energy absorbers [1-3]. In this field, application models underline the control of the pore structure (shape and orientation) as well as the porosity and pore size.

Porous materials with controlled pore characteristics have been produced by several ways such as partial sintering of powder compacts, sacrificial fugitives as pore forming agents, replica templates and mold casting in gas atmosphere [4]. Among them, the process of sacrificial fugitives is useful particularly for obtaining desired pore morphologies and high porosity, because the porosity, pore shape and size can be easily controlled by the amount, shape and size of the pore forming agents [5,6]. In this regard, porous ceramics such as SiC, Si<sub>3</sub>N<sub>4</sub> and ZrO<sub>2</sub> have been successfully developed by mixing of pore forming agents with solid powder and burning out them during sintering process [6-8]. However, in case of metal system the use of pore forming agents such as polymer beads and starch would be expected to cause oxidation of metal powder by the decomposition of them. For a wider application of sacrificial fugitives process to porous metal systems, a new approach to inhibition of oxidation may be necessary.

In order to fabricate porous Ti without oxygen contamination, unique processing by using titanium hydride (TiH<sub>2</sub>)

as the source for the formation of metallic Ti via hydride decomposition and Polymethylmethacrylates (PMMA) powder as pore forming agents is proposed in the present study. Also, the effect of the size and amount of PMMA on the pore characteristics is analyzed based on the observed microstructure.

#### 2. Experimental

Angular TiH<sub>2</sub> powders of 99% purity with an average particle size of 15 μm (MTIG Co., Korea) were used as the source materials of Ti. Fig. 1 shows the typical TiH<sub>2</sub> powders used in the experiment. PMMA (Sigma-Aldrich Inc., USA) with spherical particles of 8 and 50 μm were employed as pore forming agent. The TiH<sub>2</sub> powders with 20 and 70 vol% PMMA were wet ball-milled in highly pure ethanol for 10 h. The milled powder mixtures were dried and uniaxially pressed into cylindrical compacts of 10 mm in diameter and 7 mm in length under a pressure of 30 MPa. The powder compacts were heat-treated at 400°C to decompose the pore forming agent and at 600°C to convert the TiH<sub>2</sub> to metallic Ti. Then the treated samples were sintered at 1100°C for 2 in hydrogen atmosphere.

To determine the conditions of the decomposition process, the PMMA and TiH<sub>2</sub> powders were subjected to thermogravimetry analysis (TGA, Shimadzu, Japan) during heat-up to 600°C with 10°C/min in Ar atmosphere. Phase identification of the samples was performed by X-ray diffraction (XRD, Rigaku Denki Co., Japan). Microstructure of

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the powders and sintered Ti was observed with scanning electron microscopy (SEM, JEOL Co., Japan).

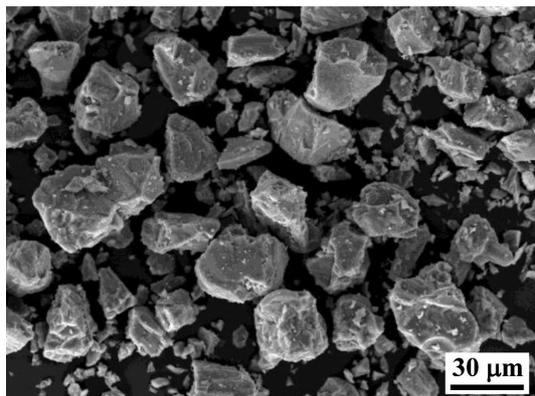


Fig. 1. SEM image of  $\text{TiH}_2$  powder

### 3. Results and discussion

Typical micrographs of the powder mixtures using different amount of PMMA are shown in Fig. 2. In the ball-milled  $\text{TiH}_2$ -20 vol% PMMA powder mixture (Fig. 2(a)), the homogeneous distribution of PMMA powders with size of 8 mm was observed. Conversely, the powder mixture with 70 vol% PMMA exhibited relatively inhomogeneous mixing between powders to the increased PMMA content.

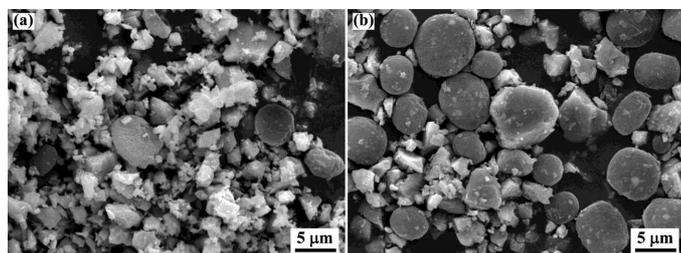


Fig. 2. SEM images of ball-milled powder mixture with (a) 20 vol% PMMA and 70 vol% PMMA

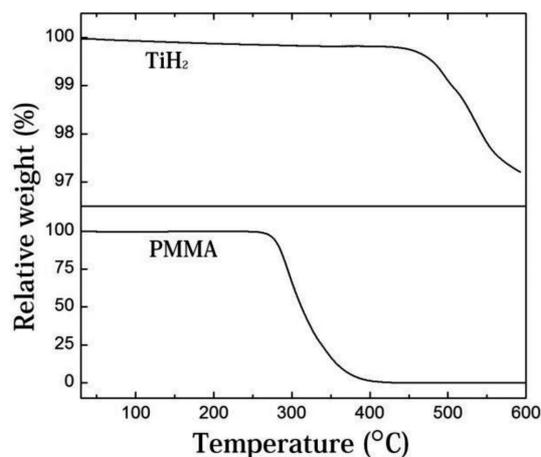


Fig. 3. TGA curves for PMMA and  $\text{TiH}_2$  powders, obtained at a scanning rate of  $10^\circ\text{C}/\text{min}$  in air

TGA investigation on the decomposition behavior of PMMA and  $\text{TiH}_2$  carried out from room temperature to  $600^\circ\text{C}$ . Fig. 3 exhibits typical TGA curves scanned at a heating rate

of  $10^\circ\text{C}/\text{min}$  in Ar atmosphere. The curve of PMMA powder shows a weight loss at a temperature range between  $260$  and  $400^\circ\text{C}$ , and finally it reaches a relative weight of 0%. This result is suggested that PMMA is an ideal template to produce porous structure. In case of  $\text{TiH}_2$  powder, sharp decrease in TGA curve was observed at  $460^\circ\text{C}$ . In order to analyze the phase change relating to the weight loss of  $\text{TiH}_2$ , XRD analysis was carried out. Fig. 4 shows the XRD patterns of the initial and heat-treated  $\text{TiH}_2$  powders, respectively. The heat-treated powder was composed entirely of Ti phase. Considering the XRD result and thermal decomposition behavior of  $\text{TiH}_2$  reported in [9,10], it is suggested that the weight loss is mainly due to the evolution of  $\text{H}_2$  resulting from the dehydrogenation of  $\text{TiH}_2$  to metallic Ti.

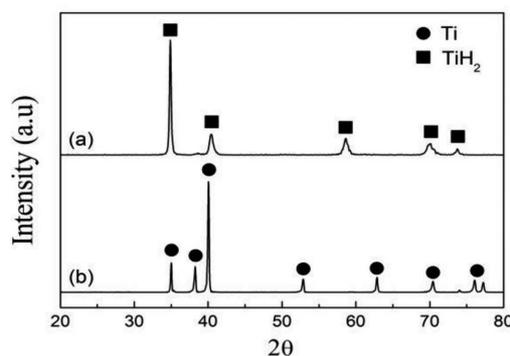


Fig. 4. XRD patterns of the  $\text{TiH}_2$  samples (a) before and (b) after heat-treatment in hydrogen atmosphere

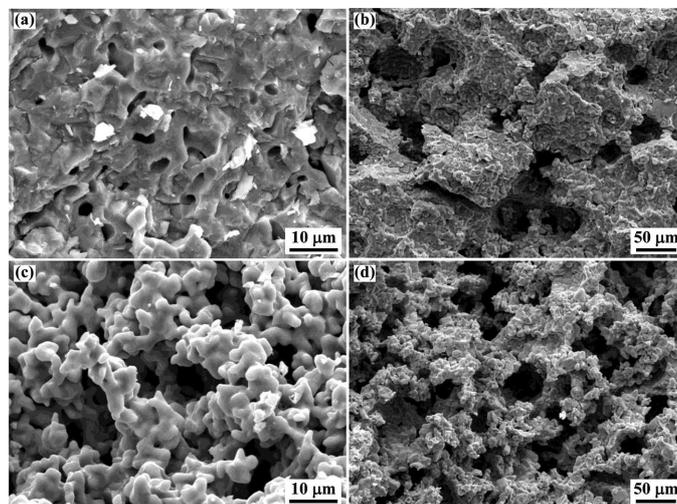


Fig. 5. SEM images of the porous Ti, sintered at  $1100^\circ\text{C}$  for 2 h with PMMA contents of 20 vol% (a and b) and 70 vol% (c and d). The left and right images show the initial PMMA sizes of 8 and  $50\ \mu\text{m}$ , respectively

Figure 5 shows the SEM micrographs of porous Ti specimens with different size and content of PMMA spheres, sintered at  $1100^\circ\text{C}$  for 2 h. It is observed that the pore size and shape were strongly dependent on the initial PMMA powders. Also, it is clear that closed cells with macropores were formed for Ti specimens with 20 vol% PMMA, as shown in magnified image (Fig. 6). In contrast, the specimens with 70 vol% PMMA showed the open cellular structure with partially interconnected micropores. In the sintered specimens with

20 vol% PMMA, the spherical macropores with the range in size from 10 to 50  $\mu\text{m}$  are generated from decomposition of PMMA during sintering. In case of micropores, it is explained that they are the result of partial sintering of the Ti powders [11]. The present results suggest that the variations in the size and content of PMMA spheres are an efficient way to control the pore structure.

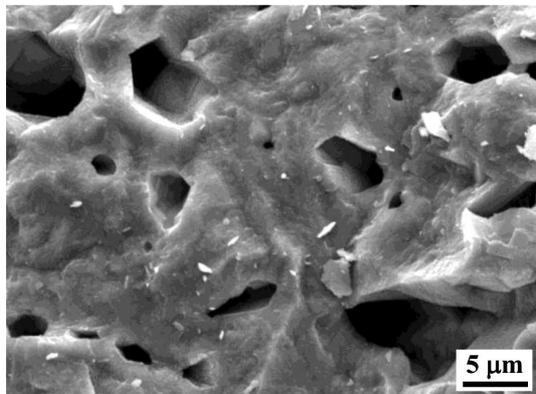


Fig. 6. Magnified image of the porous Ti produced with an initial PMMA content of 20 vol% and size of 50  $\mu\text{m}$

#### 4. Conclusions

Porous Ti with controlled pore structure was fabricated from the powder mixture of  $\text{TiH}_2$  as the source for the formation of metallic Ti and PMMA as pore forming agents by thermal decomposition and sintering process. TGA and XRD analysis showed that the PMMA and  $\text{TiH}_2$  were thermally decomposed at about 400°C forming pore and at about 600°C forming Ti phase by the dehydrogenation of  $\text{TiH}_2$ , respectively. Microstructural observation for the sintered specimens

revealed that the pore size and shape were strongly dependent on the initial PMMA powders. Also, closed cells were formed for Ti specimens with 20 vol% PMMA, whereas the specimens with 70 vol% PMMA showed the open cellular structure with partially interconnected micropores. The pore formation was explained by the decomposition of PMMA and partial sintering of the Ti powders. These results indicated that the use of  $\text{TiH}_2$  and variations in the size and content of PMMA spheres are a promising method of fabricating porous Ti with controlled the pore structure.

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