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Short communication

Preparation of porous TiO_2 by a novel freeze casting

Linlin Ren [a,b], Yu-Ping Zeng [a,*], Dongliang Jiang [a]

[a] *Shanghai Institute of Ceramics, Chinese Academy of Science and State Key Laboratory of High Performance Ceramics and Superfine Microstructure, 1295 Dingxi Road, Shanghai 200050, China*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100049, China*

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Abstract

Highly porous and open interconnected pore structural TiO_2 were prepared by a novel freeze casting method. In the experiment, the well-dispersed aqueous slurries were first frozen, and then dried at a reduced vacuum. Since the sublimation of ice crystals developed in the freezing process, the green bodies with highly porous were obtained. The phase composition and the microstructure of the sintered samples were characterized by XRD, SEM, porosity and the pore size distribution was measured by mercury porosimetry. The results demonstrated that the PVA concentration in the slurries remarkably affect the microstructure of TiO_2 ceramics. The pore morphology of TiO_2 ceramics with 3 wt.% polyvinyl alcohol (PVA) addition was dendritic, and however, the pore morphology of TiO_2 ceramics with 6 wt.% PVA addition changed into columnar. The reason for the variation of the pore morphology was ascribed to the effect of the PVA gelation on the growth behavior of the ice crystals.

Keywords: A. Freeze casting; B. Porous; D. TiO_2

1. Introduction

Porous materials, due to their large surface area and high porosity, were widely used in many fields, such as catalyst supports, separation filters, and absorbents [1,2]. So far, a lot of methods are employed to fabricate porous ceramic materials, including polymer foams dip coating [3], the foaming of ceramic powder slurry [4,5], the pyrolysis of ceramic precursors [6,7], the firing of ceramic powder compacts [8,9], etc. Each of these methods has its own merits and drawbacks, and the key issue is still to control the pore's morphology and the pore size of porous materials.

Freeze casting technique is a good processing for fabrication of porous ceramics. It can produce porous materials with controllable porosity and open interconnected pores. Especially, the pore morphology and the pore size can be tailored in a certain range by altering the parameters in the processing easily, such as slurry concentration, freezing temperature and cooling rate. Moreover, freeze casting is an environment friendly method. In the preparation process, ceramic slurries with different solid loadings are first frozen, and then the frozen bodies are dried in a lyophilizer to sublimate the frozen medium, finally, the porous samples are obtained by sintering the green bodies at different temperatures. So far, aqueous [10–12] and non-aqueous [13–15] slurries have been successfully used to fabricate porous materials by freeze casting.

Due to the peculiarity of freeze casting, porous ceramics prepared by this method have the characteristics of high porosity, well-controlled pore morphology, open interconnected pore structure, etc. These advantages endow these porous ceramics with large surface area, making them to be a preferential candidate as catalyst support, even as catalyst itself. So in the present work, freeze casting technique was utilized to fabricate porous TiO_2, and the effect of PVA concentration on the pore structure was also investigated.

2. Experimental procedure

TiO_2 powder (98.4 wt.% purity, Shanghai Xinrun Co. Ltd., China) with the particle size of 100–200 nm was used as starting material. The initial crystal phase was anatase. First, TiO_2 powder was mixed with a small amount of dispersant ammonium polyacrylate (NH_4PAA, BK Guiulini Chemic Representative Office, Ladenburg, Germany) in deionized water, ball-milled in plastic jars for 24 h with zirconia balls as medium, and polyvinyl alcohol (PVA, Shanghai Chemical Reagent Corp., China) was

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* Corresponding author. Tel.: +86 21 5241 5203; fax: +86 21 5241 3903.
E-mail address: yuping-zeng@mail.sic.ac.cn (Y.-P. Zeng).

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then added to the slurry. After ball-milled for another 24 h, the well-dispersed and stable slurries were obtained. The as-received slurries were de-aired, and then poured into the rectangular rubber molds. The freezing of the slurries was carried out in a cold chamber, where the temperature was −18 °C. After 10 h, the completely frozen samples were stripped out of the molds, and quickly transferred into the vacuum chamber of the lyophilizer (Shanghai Zhongke Biomedicine High-tech Develop Co. Ltd.), the frozen TiO_2 samples were dried under a reduced vacuum for ~15 h. Due to the sublimation of the ice crystal, the porous green bodies were received. Then the samples were sintered in a muffle furnace at 1000 °C for 1 h, the heating and cooling rate of 5 °C/min was used.

In order to investigate the effect of PVA concentration on the microstructure of the samples, the solid loadings of the slurries were fixed to 60 wt.%, 3 wt.%, 6 wt.% PVA (based on powder) were added to the slurries, respectively. The compositions of the slurries were listed in Table 1. Hereinafter, sample 1 and sample 2 were used to denote the samples with the addition of 3 wt.% and 6 wt.% PVA, respectively.

The microstructure of porous TiO_2 samples was characterized by scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan) observation, phase composition was identified by X-ray diffraction (D/Max 2550VX, Rigaku, Tokyo, Japan), porosity and pore size distribution were measured by mercury porosimetry (Model PoreSizer 9320, Micromeritics, US).

3. Results and discussion

Fig. 1 shows the XRD patterns of initial TiO_2 powder and the porous TiO_2 sample sintered at 1000 °C for 1 h. Compared with starting phase, the crystal phase of the sintered sample has partially transformed to rutile, but the predominant phase is still anatase, which can be estimated by the intensity ratio of the peaks at 25.3° and 27.4°, corresponding to the characteristic peaks of anatase and rutile, respectively. The high temperature is helpful to promote the phase transformation of TiO_2 from anatase to rutile.

Fig. 2 shows SEM images of porous TiO_2, with cross-section parallel and perpendicular to the ice growth direction. (a) 3 wt.% PVA, parallel; (b) 3 wt.% PVA, perpendicular; (c) 6 wt.% PVA, parallel; and (d) 6 wt.% PVA, perpendicular. The image (a) exhibits the typical dentritic pores in sample 1, and the image (b) shows that the pores have higher connectivity compared with sample 2. From the images (c) and (d), it can be seen that the porous TiO_2 consist of parallel channels, which align along the ice growth direction and distribute homogeneously in the whole sample. The pore morphology is columnar, and the mean pore diameter is about 1.5 μm. The TiO_2 wall is also consist of pores, which are from the stacking of particles and the binder removal of PVA additives.

Table 1
The composition of TiO_2 slurries

Slurry composition	Concentration (wt.%)	
	Sample 1	Sample 2
TiO_2	60	60
H_2O	37.6	35.8
NH_4PAA	0.6	0.6
PVA	1.8	3.6
Based on powder	3	6

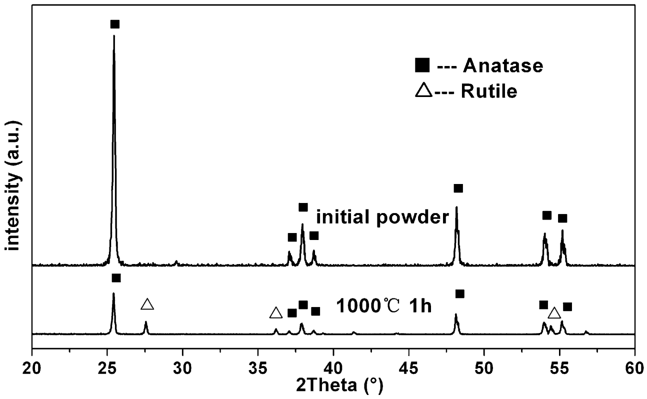

Fig. 1. XRD patterns of TiO_2 (1) initial powder and (2) sintered at 1000 °C for 1 h.

Since ice crystals sublimation, the resultant pores and their morphologies are the replica of the ice crystals. Fig. 3 shows the sketch for the growth process of the ice crystal. In the freezing process, the samples together with the rubber mold were put into the cold chamber, since the rubber container has a lower heat conductivity coefficient, so there is a temperature gradient from the top of the slurry to the bottom of slurry. Therefore, ice crystals began to nucleate and grow from the surface of the slurry to the bottom of the slurry, along with the direction of the temperature gradient. At the same time, the ceramic particles and PVA were expelled from the moving ice front.

The two kinds of TiO_2 samples were fabricated at the same experimental conditions, and the difference was only the PVA concentration in the slurries. So the reasonable explanation for the different pore morphology between the two samples should be attributed to the variation of PVA concentration in the slurries, which had great effect on the growth manner of ice crystals. In the process of nucleation and growth of the ice crystal, ceramic particles together with PVA were expelled from the freezing front. Since PVA had polymeric long chain configuration, at relative high temperature, the PVA chains moved freely in the water. With the temperature decrease, PVA chains lost fluidity and became gelation, and the viscosity of the slurry increased accordingly. Once the temperature is below 0 °C, the phase separation of slurry happened, and the slurry would develop to two phases, one was ice crystal, another was PVA-wrapped TiO_2 particles. During phase separation, the migration of the water molecular had remarkable effect on the size and morphology of the ice crystals. With the increase of PVA concentration, the gelled PVA increased the migration resistance of water, consequently, resulting in the small ice size and different ice morphology. Therefore, the variation of the pore morphology with the change of PVA concentration was accountable. In this experiment, with the variation of PVA concentration from 3 wt.% to 6 wt.%, the pore size of the porous TiO_2 decreased and the pore morphology also changed from dendritic to columnar.

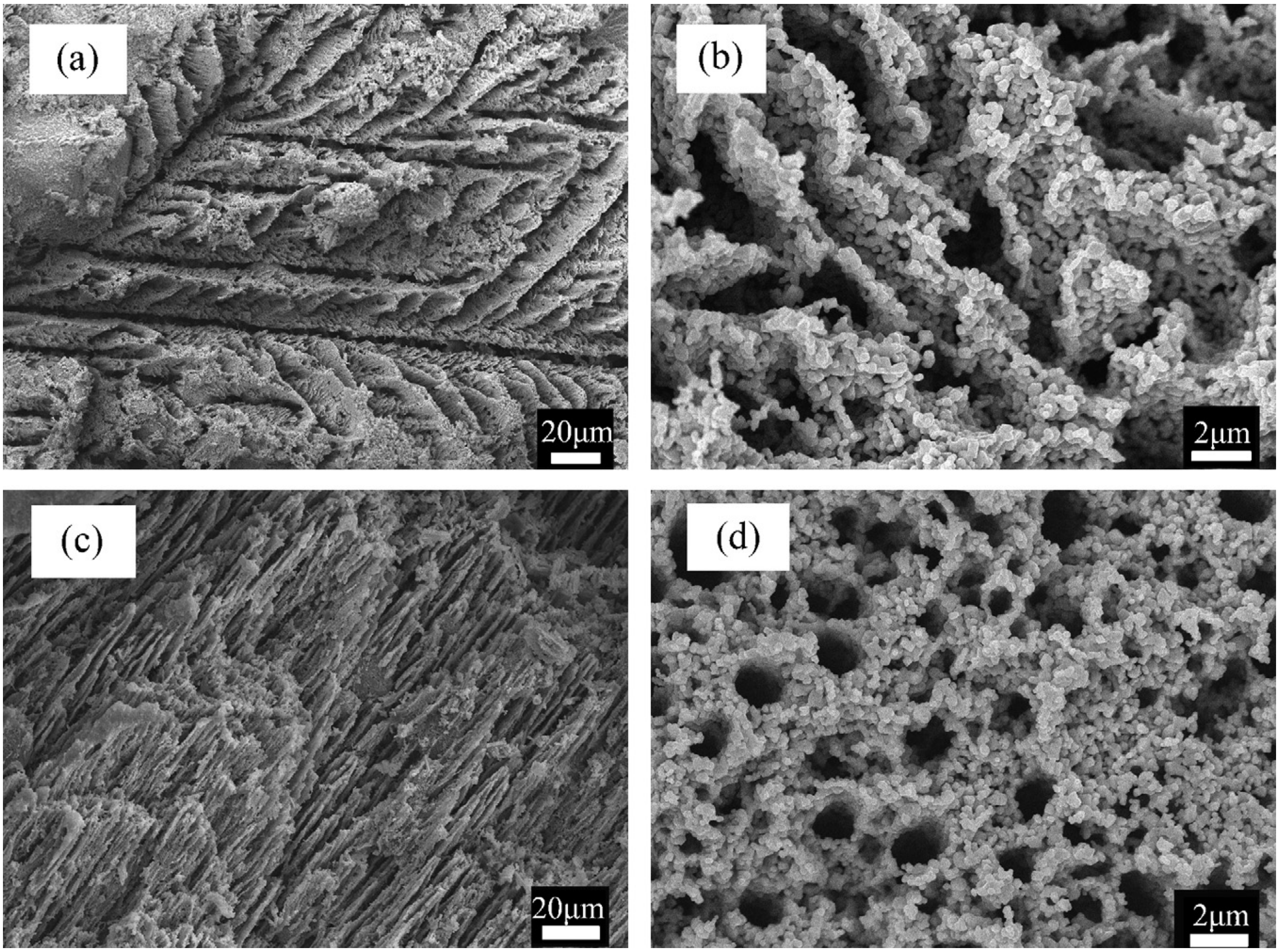

Fig. 2. SEM images of porous TiO_2 with cross-section parallel and perpendicular to the ice growth direction. (a) 3 wt.% PVA, parallel; (b) 3 wt.% PVA, perpendicular; (c) 6 wt.% PVA, parallel; and (d) 6 wt. PVA, perpendicular.

Fig. 4 shows the pore size distribution of TiO_2 samples (a) 3 wt.% PVA and (b) 6 wt.% PVA. Both the curves exhibit bimodal distribution of the pore size. There are two obvious peaks in each curve, the small pores at 0.44 μm in curve (a) and 0.36 μm in curve (b) are corresponded to the particle stacking and binder removal pores on the porous TiO_2 walls, and the big pores at 2.64 μm in curve (a) and 0.91 μm in curve (b) are ascribed to the sublimation of the ice crystals. The results show that the sample 2 with addition of 6 wt.% PVA has smaller pore size than sample 1 with addition of 3 wt.% PVA, and this further validates the PVA concentration greatly affects the pore size of the porous TiO_2. The porosities measured for sample 1 and sample 2 are 56.99% and 60.39%, respectively.

The pore structure is a replica of the morphology of the ice crystal. Therefore, the pore's morphology of TiO_2 can be tuned by controlling the growth manner of the ice crystal. Besides modifying the concentration of the additives, the microstructure

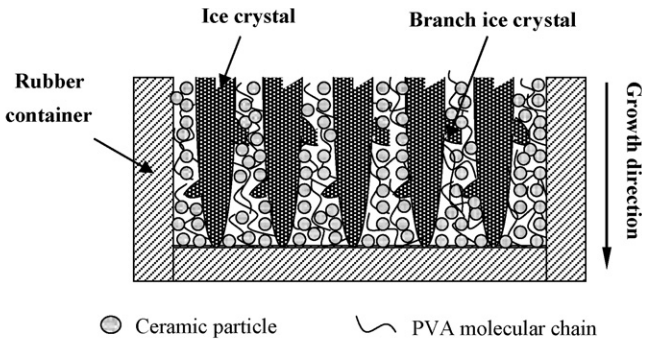

Fig. 3. The sketch for the growth process of the ice crystals.

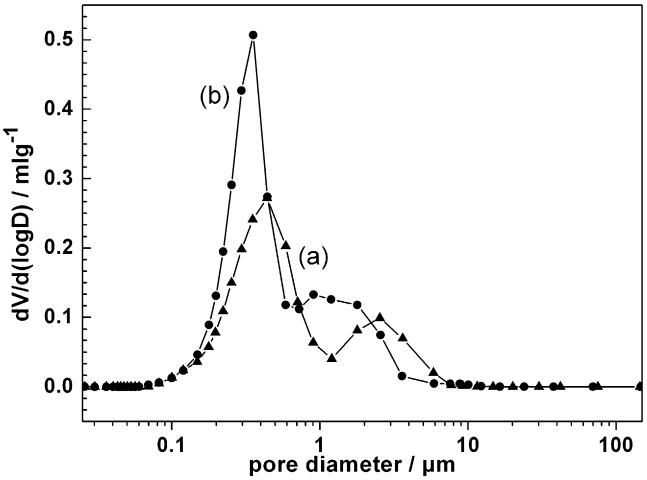

Fig. 4. Pore size distribution of TiO_2 samples (a) 3 wt.% PVA and (b) 6 wt.% PVA.

of porous materials can also be modulated by slurry concentration, freezing temperature, cooling rate, etc.

4. Conclusions

Highly porous and open interconnected pore structural TiO_2 samples were prepared by novel freeze casting. The results showed that PVA concentration notably affected the microstructure of the samples, and the reason was attributed to the PVA gelation phenomena at freezing process, which influenced the growth manner of the ice crystal. When the PVA concentration changed from 3 wt.% to 6 wt.% (based on powder), the growth manner changed from dentritic to parallel columnar, so the pore morphology resulted from the sublimation of the ice crystals was also varied accordingly. The pore size exhibited bimodal distribution for both samples, and the porosities measured for sample 1 and sample 2 are 56.99% and 60.39%, respectively. XRD pattern showed the crystal phase had partially transformed from anatase to rutile when the samples were sintered at 1000 °C for 1 h.

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