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Morph-Genetic Materials Derived from Plants

Di Zhang^a, Binghe Sun^a, Tongxiang Fan^a, Zhiqiang Li^a, Guoding Zhang^a and Toshihiro Okabe^b

^a State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University, Shanghai, 200030, P.R. China Fax: +86-21-62822012, E-mail: <u>zhangdi@sjtu.edu.cn</u>

^b Industrial Research Institute of Aomori Prefecture, Hirosaki, 036-8363, Japan

Abstract

Natural materials become more and more attractive in the field of materials design for their intrinsic hierarchical structure. Based on their unique character, a simple route is developed to produce inorganic morph-genetic ceramics through infiltration with various organic or inorganic impregnant and by sintering at high temperatures. In this paper, the fabrication process, microstructure and pore-size distribution of resulting morph-genetic materials are discussed.

Keywords: plant; morph-genetic materials; microstructure; XRD; SEM

1. INTRODUCTION

Recently, there has been an increasing interest in the fabrication of multi-scale structures at different length scales with template techniques ^[1-6]. Artificial templates synthesized with organic molecule are currently used to produce highly three-dimensional uniform porous materials ^[7-16]. The basic idea of these methods is to use sol-gel processing to deposit inorganic materials at the exterior of mono-disperse templates. The size of products obtained with these methods is, however, largely limited in general, and processing is also complex, so these materials have found little practical applications. In comparison to synthetic materials, natural materials such as cotton, jute, bamboo, etc, exhibit a multi-scale built anatomy, developed and optimized in a long-term

evolution process, and are cheap, abundant, renewable and of environment consciousness ^{[17-22}].

Here wood is utilized as bio-template to produce inorganic morph-genetic materials. This process consists essentially of pyrolyzing the natural fibers coated with the impregnant and can be applied to the formation of a variety of inorganic morph-genetic materials with biological structure.

2. EXPERIMENTAL

2.1 Morph-genetic ceramics synthesis

Wood was used as templates for the preparation of morph-genetic ceramics. Methyl organic silicone resin and tetrabutyl titanate were used as impregnant, respectively. The fabrication process of morph-genetic ceramics was summarized in **Fig. 1**.





2.2 Characterization

The phases of morph-genetic ceramics were identified X-ray diffractometer (XRD, Cu-K by α Rakaku-D/maxAIIIX). To characterize the morphology of the morph-genetic ceramic, Scanning Electron Microscopy (SEM) was used. The HITACHI S-520 SEM was operated at 20kV. The sample in epoxide resin was cut into sheets. The thin foil was prepared using Gatan argon ion-milling machine and studied by Transmission Electron Microscopy (TEM). The TEM H800 was operated at 200kV and High Resolution TEM (HRTEM, H9000) was operated at 300kV.

For porous materials, the surface area and the pore size distribution were measured with mercury intrusion method (AutoPoreIV 9510, Micromeritics).

3. RESULTS AND DISCUSSION





3.1 Morph-genetic SiC/C ceramic

Fig. 2 shows the typical X-ray diffraction patterns of the fraxinus mandshurica after infiltrating with methyl organic silicone resin, drying and sintering from 800 to 1400°C in a vacuum furnace. β -SiC can be obtained through the reaction between charcoal and silicon compound at 1400°C.



Fig. 3 SEM images of C-template and SiC/C (a: carbon preform; b: morph-genetic ceramics)

Fig. 3-a shows the original microstructure of pyrolytic fraxinus mandshurica at 650 °C . The fraxinus mandshurica structure composed of cells and vessels is in a hierarchical form and. some small pores are distributing on the vessel wall. Fig. 3-b shows the SEM photograph of fraxinus mandshurica specimen sintered at 1400°C in a vacuum furnace after the treatment with methyl organic silicone resin. The structure of fraxinus mandshurica could be retained very well in the products and the pores in the specimen are not completely filled with reactant.

Fig. 4-a shows the TEM images of morph-genetic SiC/C ceramics obtained at 1400°C. It can be found in Fig. 4-a that the SiC layer was formed from the surface of the wood vessel walls where impregant deposited. In addition, there are a few amount of unreacted carbon distributed in the inner layer of porous ceramics. From HRTEM observations images of crystalline SiC (Fig. 4-b), it can be known that the crystallinity of SiC obtained at 1400°C is quite high.^[23]



Fig. 4 TEM images of morph-genetic SiC/C ceramic (a: bright filed image; b: HRTEM and corresponding SAD)



Fig. 5 Pore-size distributions of specimens (a: carbon preform b: morph-genetic SiC/C ceramics)

Fig. 5-a shows that the charcoal from fraxinus mandshurica before infiltration exhibits hierarchically porous structure from nanometer to millimeter. **Fig. 5-b** shows the pore-size distribution of specimen after infiltrating methyl organic silicone resin and sintering at 1400 °C . From comparison of pore-size distribution between charcoal and morph-genetic SiC/C ceramic, it can be seen that the pore-size distribution has changed a little after infiltration, the hierarchically porous structure of the original template retains well in the obtained morph-genetic porous ceramic.



Fig. 6 XRD patterns of morph-genetic ceramics obtained at various temperatures after infiltration

3.2 Morph-genetic TiC/C ceramic

The typical X-ray diffraction patterns of the morph-genetic materials after the treatment of tetrabutyl titanate infiltration, drying and firing at various temperatures are shown in **Fig. 6**, which demonstrates that the tetrabutyl titanate was firstly decomposed to different type titania. The titanium carbide (TiC) in morph-genetic ceramic was formed at 1400°C through the reaction of charcoal with titania.

Fig. 7-a shows the SEM photograph of the pine charcoal by firing at 650°C in a vacuum furnace. The cellular texture of pine consists of regular cells and tracheids, many of which exhibit a uniform structure. Fig.7-b shows morph-genetic porous TiC/C ceramics obtained at 1400°C in a vacuum furnace after the treatment of tetrabutyl titanate. The texture of pine is retained very well in the products without filling of pores with impregnant. It is obvious that the impregnant was deposited in the cellular wall and the reaction between TiO₂ and carbon template had taken place there.^[24-25]



Fig. 7 SEM images of morph-genetic ceramic specimens
 (a: Charcoal fired at 650°C; b: Specimen fired at 1400°C after the treatment with tetrabutyl titanate infiltration;
 c: Specimen after the removal of residual carbon)



Fig. 8 SEM images of (a) Al₂O₃ fibers and (b) SnO₂ fibers derived from cotton fibers

According to different functional requirements, natural materials such as wood, bamboo, rice husk, cotton, coconuts, etc. with different cellular structure can be selected to produce morph-genetic materials with different morphology. This process is also being applied to oxide ceramics, such as Al₂O₃, SnO₂ and ZnO, at our group (see Fig. 8) ^[26]. In addition, based on the porous character of some natural plants, there is a further possibility of compounding the resulting morph-genetic materials with molten metal or polymer to produce morph-genetic composites with interpenetrating networks ^[27-29]. In this way, the morph-genetic materials will be endowed with new use values.

4. SUMMARY

The results presented here show that it is possible to obtain inorganic morph-genetic materials with the intrinsic morphology of plant fibers through the template technique. The hollow structure will be beneficial in the application of heat preservation materials, and the high specific surface area will be helpful when used as catalysis carrier or adsorption materials etc. This approach of fabrication with creative and biological conception is simple and economical compared with conventional methods and may offer significant improvement in performance over traditional designs and conventional fabrication processes.

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