Synthesis and microstructure analysis of morph-genetic materials

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Abstract Based on the unique character of the natural materials, three types of wood were selected as bio-template. Through infiltrating with various organic or inorganic impregnants, followed by sintering at high temperature, morph-genetic SiC/C, TiC/C ceramics were produced. Observing the microstructure under the SEM and the TEM, the morph-genetic ceramics were shown to retain the intrinsic porous structure of the original wood template, and the resultant was distributed mainly on the surface layer of the cellular wall. The synthesis process had little effect on the hierarchical structure with a wide range from nanometer to micron.

Keywords: natural materials, morph-genetic materials, microstructure, pore-size distribution.

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Biological systems are characterized by their sensitivity, their high degree of flexibility, their ability to adapt to changing environments, and their high degree of reliability. These design features offer a great range of possibilities for research seeking to derive engineering principles from natural systems by adapting these principles for the improvement of man-made systems. Thus, bionics based on the natural models and natural optimization is developed[1−9]. In recent years, the materials designed with creative and biological conception are of increasing interest. Natural materials, such as wood, jute, diatom, scale, etc. are widely used as bio-templates to produce inorganic ceramic, and the final materials exhibit good performance in electric conduction, thermal conduction, friction and adsorption properties. These results demonstrate that these materials show significant improvement in performance over traditional designs and fabrication methods[10−17]. Meanwhile, it was reported that molten silicon, liquefied wood, metal and magnetic materials could be compounded with bio-template to fabricate composites, which were endowed with new use values, such as high strength, wearing resistance, anti-damping and thermal insulating properties[18−26].

Here, three types of wood were utilized as bio-templates to prepare SiC/C and TiC/C porous ceramics based on their intrinsic multidimensional and hierarchical structure. After processing with organic or inorganic solution, wood templates were subsequently sintered at high temperature to produce the ceramic structure. The final products were produced. The final products were called morph-genetic materials. The process of conversion of biological templates into morph-genetic materials was called morph-genetic process.

1 Experiment procedure

1.1 Morph-genetic materials synthesis

Three types of wood (white pine, walnut and fraxinus mandshurica) were utilized as templates for the preparation of morph-genetic ceramics. Methyl organic silicone resin (solid content: 27.5%—32.5%, solvent: isopropyl alcohol) and tetrabutyl titanate (content: >98%, density: 0.999—1.003 g/mL) were used as impregnant, respectively. After drying at 80℃ for 24 hours, the wood specimens were first changed to carbon preform at 650℃ after 2 hours. The morph-genetic ceramics were subsequently produced by infiltrating the carbon preform with impregnant. It was then sintered in vacuum furnace at various temperatures. The fabrication process of morph-genetic ceramics was summarized in fig. 1.

1.2 Characterization

The phases of morph-genetic ceramics were identified by X-ray diffractometer (XRD, Cu-Kα, Rakaku-D/maxAⅢX). To characterize the morphology of the morph-genetic ceramic, Scanning Electron Microscopy (SEM) was used. The HITACHI S-520

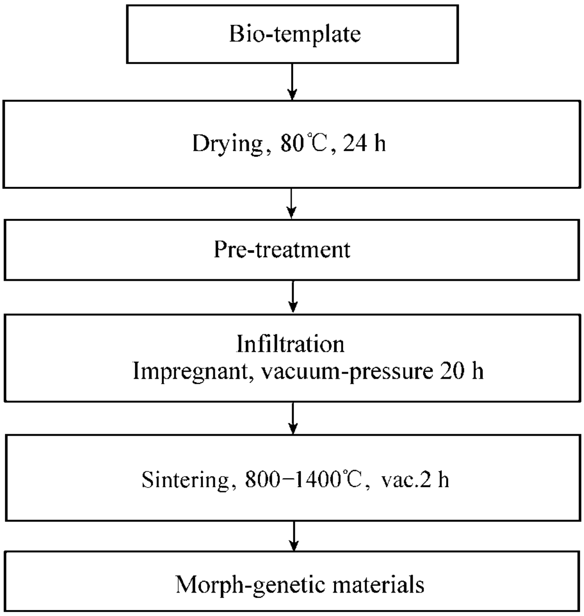

Fig. 1. Flow chart of the fabrication process.

SEM was operated at 20 kV. 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) and HRTEM (H9000) were respectively operated at 200 and 300 kV.

In order to investigate the effect of infiltration on the pore-size distribution of morph-genetic ceramics, the samples (5 mm×5 mm×10 mm) were studied using the mercury intrusion method (AutoPore IV 9500, Micromeritics). Working pressures covered the range from approximately 0.6 to 60000 psia.

2 Results and discussion

2.1 SEM observation

It is known that the biological structure of wood is mainly composed of tracheid vessels and is characterized by natural hierarchical architectural scales ranging from nanometer to micron. The wood is generally pyrolyzed in advance. The pyrolysis of wood into the carbon preform involves an anisotropic shrinkage, and an increasing porosity. This makes the wood for infiltration easier.

Fig. 2 shows respectively the SEM photographs of carbon preform, the morph-genetic SiC/C ceramics, and the morph-genetic TiC/C ceramics obtained with three types of wood. It is shown in fig. 2(a) that the cellular textures of woods with different morphologies consist of regular cells and tracheids. The original textures of wood are retained essentially in the morph-genetic ceramic structures after 1400℃ sintering without filling of pores with resultant as shown in fig. 2(b) and (c).

2.2 XRD analysis

The typical X-ray diffraction patterns of the morph-genetic materials after the various treatments of impregnant infiltration, hydrolysis, drying and by firing at various temperatures are shown respectively in fig. 3.

It is shown in fig. 3(a) that the methyl organic silicone resin first decomposed to amorphous silicon compounds, and β-SiC was obtained through the *in-situ* reaction between carbon preform and silicon compounds at 1400℃[26,27]. In the process of morph-genetic TiC/C ceramics, the tetrabutyl titanate was first decomposed to anatase-type with a small amount of rutile-type titania at 800℃. And then anatase-type titania was converted completely into rutile-type titania with temperature increasing to 1200℃. The titanium carbide (TiC) in morph-genetic ceramics was formed at 1400℃ through the reaction of carbon preform with titania[28,29].

2.3 TEM observation

Fig. 4 shows the TEM images of morph-genetic SiC/C ceramic and its corresponding selected area electron diffraction (SAD) after 1400℃ sintering. The black sections in fig. 4(a) are SiC. It is known from the SAD of SiC in fig. 4(b) that a large number of

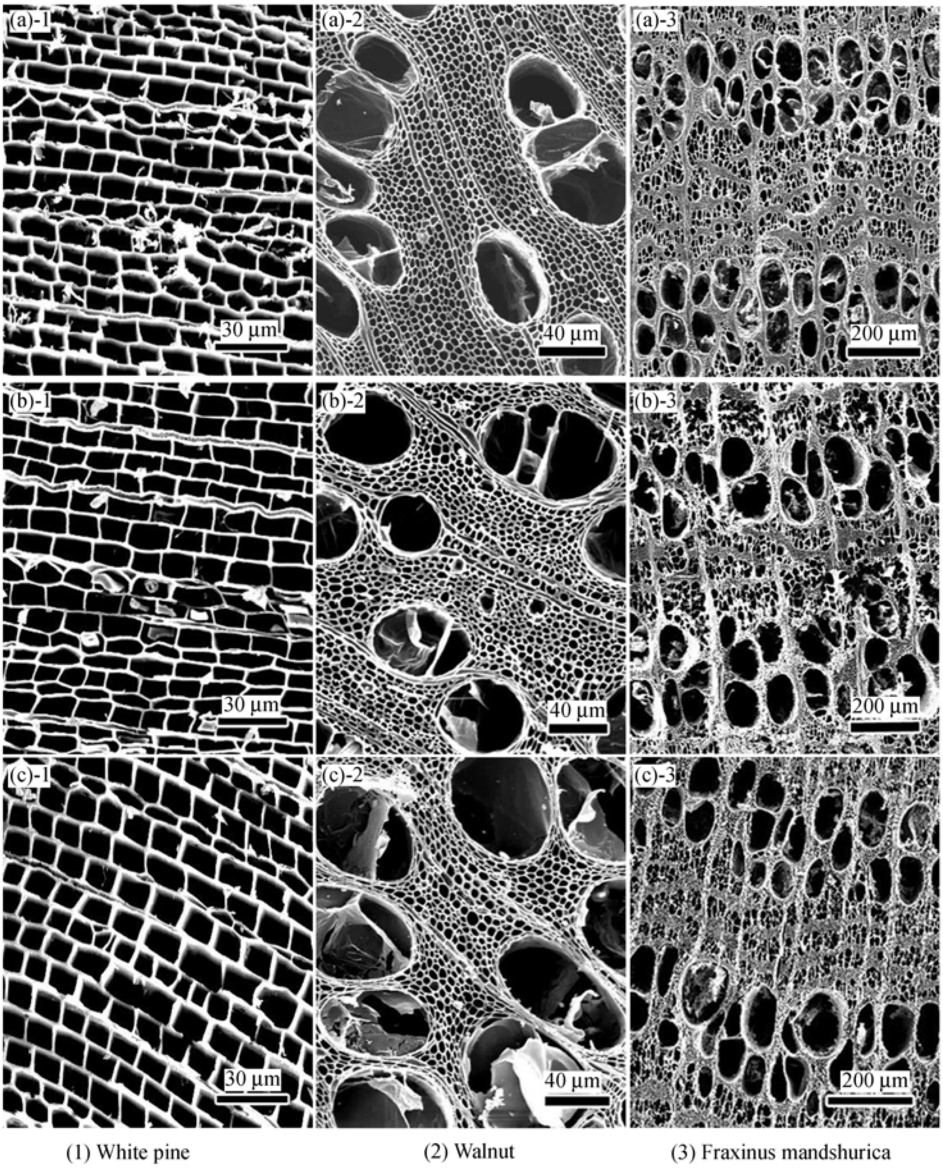

Fig. 2. SEM images of wood preform before and after infiltrating and sintering. (a) Carbon preform; (b) SiC/C; (c) TiC/C.

faults exist in the crystalline SiC, and it can be further proved from the HRTEM image of SiC in fig. 5(a). It is shown in fig. 4(a) that the methyl organic silicone resin first deposited on and within the cellular wall of carbon preform. Then *in-situ* reaction took place between silicon compounds and carbon preform in 1400℃. Therefore, the SiC is distributed mainly in the surface layer of carbon vessel wall where the methyl organic silicone resin deposited[27]. There is still remnant carbon distributed in the inner layer of porous ceramic as shown in fig. 4(a). It is stated in fig. 4(c) that the remnant carbon in

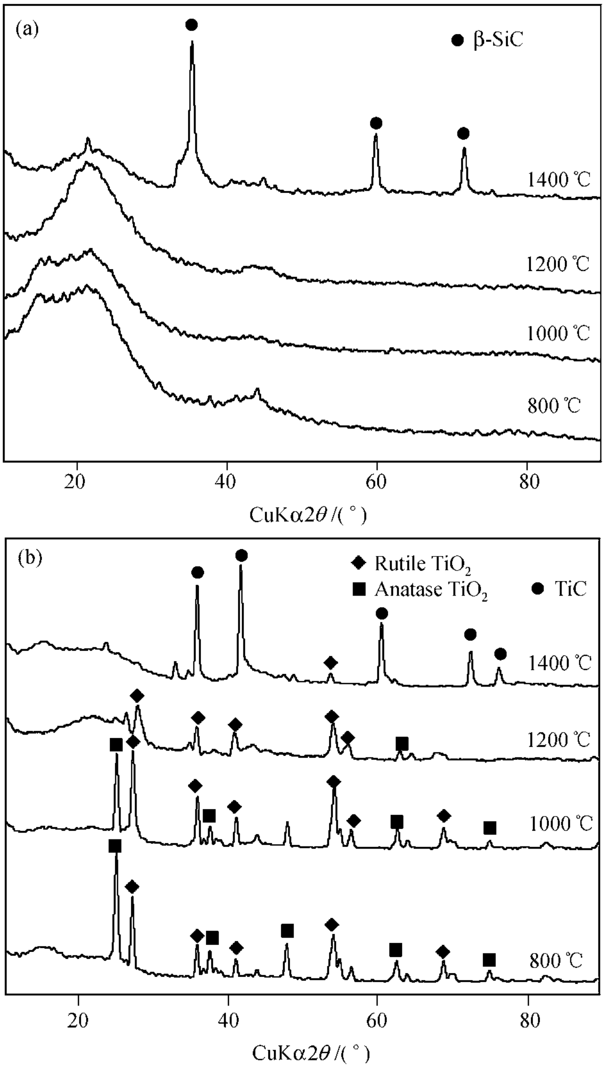

Fig. 3. XRD patterns of morph-genetic ceramics obtained at various temperatures. (a) SiC/C ceramic; (b) TiC/C ceramic.

SiC/C ceramic is still amorphous after sintering at 1400℃. However, the degree of order of residual carbon in morph-genetic ceramic increases significantly, and it forms banding arrays in short range as shown in fig. 5(b).

It can be known in fig. 6(a) that TiC in TiC/C morph-genetic ceramic is also distributed in the surface layer of carbon vessel, and a large amount of unreacted carbon is remaining. From HRTEM and SAD study of TiC shown in fig. 6(b) and (c), the crystallinity of TiC formed by the reaction of the impregnant with the carbon preform in the cell wall is quite high, and it exhibits an integrated and sharply defined diffraction pattern[28].

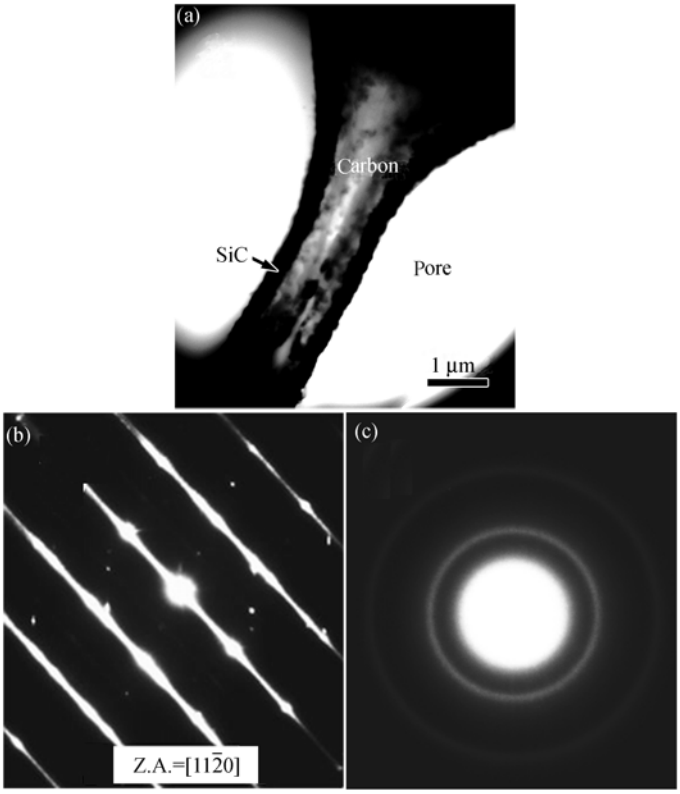

Fig. 4. TEM images of SiC/C morph-genetic ceramic and its corresponding SAD. (a) SiC/C; (b) SAD of SiC; (c) SAD of carbon.

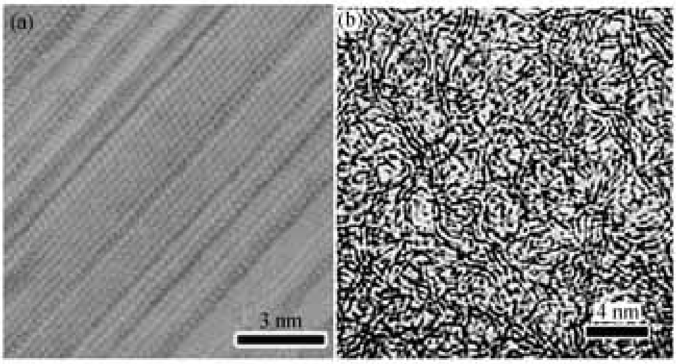

Fig. 5. HRTEM images of (a) SiC and (b) carbon in morph-genetic SiC/C ceramic.

2.4 Pore-size distribution

Fig. 7 shows respectively the pore-size distribution of the carbon preform and the morph-genetic SiC/C ceramic after 1400℃ sintering.

As shown in fig. 7, both the carbon preform and the morph-genetic SiC/C ceramic exhibit hierarchical porous structure from nanometer to micron. Comparing the pore-size

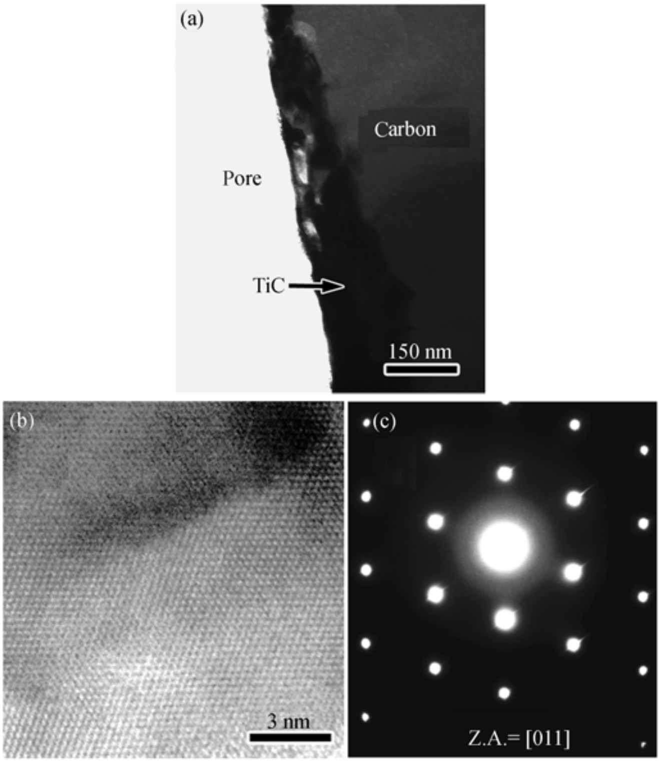

Fig. 6. TEM images of TiC/C morph-genetic ceramic and its corresponding SAD. (a) TiC/C; (b) HRTEM of TiC; (c) SAD of TiC.

distribution peak of morph-genetic ceramic with the pore-size distribution peak of carbon preform, the peak varies slightly with the synthesis process. The original structure of wood is retained essentially in the morph-genetic SiC/C ceramic. And new pore-size distribution peak in the range of 10—50 nm appears in the morph-genetic ceramic as shown in fig. 7(b). It may be caused by the morphological change of the vessel wall. Here the results demonstrate that the structure of wood is replicated very well in the final morph-genetic SiC/C ceramics. The porous structure is not completely filled with the reactant[27].

3 Conclusions

Natural material like wood is successfully utilized as a bio-template for preparing morph-genetic materials. It maintains the original structure of bio-templates. The hierarchical pore structure of wood template in the range from nanometer to micron scale level is kept well in the final morph-genetic porous ceramic. Based on the unique intrinsic structure of natural materials, to develop the structural-functional designs or processing approaches with creative and biological conception may offer significant improvement in performance over traditional designs and synthetic methods.

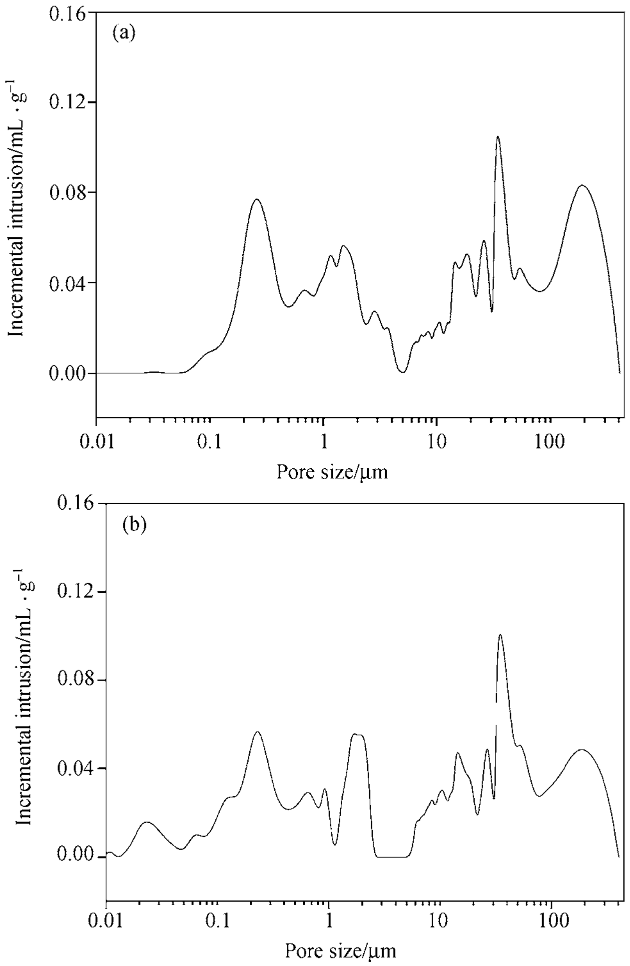

Fig. 7. Pore-size distribution of SiC/C ceramic and its corresponding carbon preform. (a) Carbon preform; (b) SiC/C ceramic.

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References

1. Mann, S., Hannington, J. P., Williams, R. J. P., Phospholipid vesicles as a model system for biomineralization, Nature, 1986, 324: 565—567.
2. Clegg, W. J., Kendall, K., Alford, N. M. et al., A simple way to make tough ceramics, Nature, 1990, 347: 455—457.[DOI]
3. Mann, S., Molecular tectonics in biomineralization and biomimetic materials chemistry, Nature, 1993, 365: 499—505. [DOI]
4. Fiona, C. M., Vanessa, J. W., Duncan, L. N. et al., Synthesis of inorganic nanophase material in supramolecular protein cages, Nature, 1991, 349: 684—687. [DOI]

5. Fritz, M., Belcher, A. M., Radmacher, M. et al., Flat pearls from biofabrication of organized composites on inorganic substrates, Nature, 1994, 373: 49—51. [DOI]
6. Heuer, A. H., Fink, K. J., Laraia, V. J. et al., Innovative materials processing strategies: a biomimetic approach, Science, 1992, 255: 1098—1105.
7. Yao, K. D., Shen, F., Biomemitic design of biomaterials, Chinese Engineering Science, 2000, 2(6): 16—20.
8. Li, H. D., Feng, Q. L., Cui, F. Z. et al., Biomimetic research based on the study of nacre structure, J. Tsinghua University, 2001, 41(4-5): 41—47.
9. Zhang, G. S., Biomineral material and biominetic material engineering, Mineral Resources and Geology, 2002, 16(2): 98—102.
10. Patel, M., Padhi, B. K., Titania fibres through jute fibre substrates, J. Mater. Sci. Lett., 1993, 12: 1234—1235.
11. Greil, P., Lifka, T., Kaindl, A., Biomorphic cellular silicon carbide ceramics from wood: I. Processing and Microstructure, J. Eur. Ceram. Soc., 1998, 18(14): 1961—1974. [DOI]
12. Sieber, H., Kaindl, A., Greil, P., Biostructure derived ceramics, Ceramic Engineering and Science Proceedings, 2000, 21(4): 53—60.
13. Shin, Y., Liu, J., Chang, J. H. et al., Hierarchically ordered ceramics through surfactant templated sol-gel mineralization of biological cellular structures, Adv. Mater., 2001, 13(10): 728—732.
14. Okabe, T., Saito, K., Hokkirigawa, K., New porous carbon materials, woodceramics: Development and fundamental properties, J. Porous Mater., 1996, 2: 207—213.
15. Hokkirigawa, K., Okabe, T., Saito, K., Wear properties of new carbon materials: Woodceramics, J. Porous Mater., 1996, 2: 229—235.
16. Kano, M., Momota, M., Okabe, T. et al., Specific heat capacity of new porous carbon materials: Woodceramics, Thermochimica Acta, 1997, 191: 175—177. [DOI]
17. Shibata, K., Okabe, T., Saito, K. et al., Electromagnetic shielding properties of woodceramics made from wastepaper, J. Porous Mater., 1997, 4: 269—275. [DOI]
18. Wang, X. C., Tian, J., Composite mechanism of ceramic-wood, Chinese Journal of Materials Research, 1995, 10(4): 435—440.
19. Xie, X. Q., Zhang, D., Fan, T. X. et al., Woodceramics composites with interpenetrating network, Chinese Journal of Materials Research, 2002, 16(3): 259—262.
20. Hirose, T., Fujino, T., Fan, T. X. et al., Effect of carbonization temperature on the structural changes of woodceramics impregnated with liquefied wood, Carbon, 2002, 40(5): 761—765. [DOI]
21. Singh, M., Salem, J. A., Mechanical properties and microstructure of biomorphic silicon carbide ceramics fabricated from wood precursors, J. Eur. Ceram. Soc., 2002, 22: 2709—2717. [DOI]
22. Qiao, G. J., Ma, R., Cai, N. et al., Microstructure transmissibility in preparing SiC ceramics from natural wood, J. Mater. Proc. Tech., 2002, 120: 107—110. [DOI]
23. Zhang, D., Fan, T. X., Sun, B. H. et al., Microstructure and properties analysis of composites based on woodceramics, Key Eng. Mater., 2003, 249: 31—36.
24. Oka, H., Hojo, A., Seki, K. et al., Wood construction and magnetic characteristics of impregnated type magnetic wood, J. Magnetism and Magnetic Mater., 2002, 239: 617—619. [DOI]
25. Nagasawa, C., Kumagai, Y., Urabe, K. et al., Electromagnetic shielding particleboard with nickel-plated wood particles, J. Porous Mater., 1999, 6: 247—254. [DOI]
26. Kpewkob, A. Ⅱ., Silicon Organic Compounds and Application, Bei jing: Industrial Publishing Company of China, 1962, 11, 204.
27. Zhang, D., Sun, B. H., Fan, T. X. et al., Morph-genetic materials derived from plants, Trans MRS-J, 2004, in press.
28. Sun, B. H., Fan, T. X., Zhang, D. et al., The synthesis and microstructure of morph-genetic TiC/C ceramics, Carbon, 2004, 42: 177—182. [DOI]
29. Sun, B. H., Fan, T. X., Zhang, D., Production of morph-genetic TiC/C ceramic, Materials Letters, 2004, 58: 798—801. [DOI]