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Biomorphic TiN/C ceramics prepared by reduction–nitridation of charcoal/titania composite

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Abstract Porous titanium nitride ceramics with a biomorphic microstructure were manufactured at 1400 °C by carbothermal reduction and nitridation of charcoal/titania composites under high concentration nitrogen atmospheres. These composites were prepared from beech-derived charcoal impregnated with titania sol by vacuum/pressure infiltration process. The formation mechanism of TiN was analyzed. The results show that the nitridation is based on gas–solid reaction among TiO (s), N_2 (g), C (s) or CO (g). Under higher nitrogen pressure, the nitridation reaction was complete and porous TiN/C ceramics obtained. The phase composition and microstructure of as-obtained porous TiN/C ceramics were characterized by X-ray diffraction and scanning electron microscopy. Experimental results show that the resultant porous TiN/C ceramic had the same external and internal forms of the original wood that consists of cubic phase TiN.

Introduction

The template-directed method has been widely used to synthesize a variety of materials in the inorganic synthesis. Recently, bio-templates, such as wood [1, 2], bamboo [3], cellulose fiber [4, 5], filter paper [6–8], virus [9], bacteria [10, 11], eggshell membrane [12], have been applied to the synthesis of novel hierarchical and complex microstructure materials. Among these, woods with natural growth plant structure make them as ideal bio-templates to produce ceramics materials. The microstructure features of wood range from mm (growth ring structure) via μm (tracheidal cell palterns, macro- and micro-fibril cell wall textures) down to nm scale (molecular fiber and membrane structures of cell walls) [13]. In the finally products, the original structure of plant is retained, but replaced by other component.

In the synthesis of woodceramics, the key process—infiltration of carbon preform derived from wood can be performed via different route. First, infiltration of carbon perform derived from wood with liquid reactants such as Si or other metallic or non-metallic melts offers a versatile processing scheme to produce wood ceramics [13, 14]; second, infiltration with gaseous metal to from highly porous SiC [15, 16], Al_2O_3 [17] ceramics; third, infiltration of metal alkoxides or oxide sols into charcoal to yield SiC [18], TiC [19, 20], ZrC/C [21],TiO_2 [22, 23], Al_2O_3 [24], Y-doped ZrO_2 [25] biomorphic ceramics.

In the previous works, many scientists paid attention to the fabrication of carbide, oxide, but few attempted the preparation of nitride such as silicon nitride, titanium nitride, aluminum nitride, zirconium nitride with wood template. TiN is an interesting materials to try to be prepared from wood templates. TiN ceramics show attractive attributes such as high hardness, good electrical conductivity and high melting-point (2927 °C), making them promising candidates for application as coatings on

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cutting tools, self-heating crucibles, high-temperature heterogeneous catalysis, and so on [26].

Currently, the most popular method for synthesizing the titanium nitride is the carbothermal reduction of TiO_2. The conversion of the bio-carbon templates into TiN after carbothermal reduction nitridation of TiO_2 is shown in the following equation:

$$TiO_2 + 2C + 1/2N_2 \rightarrow TiN + 2CO \qquad (1)$$

Since both TiC and TiN are products of carbothermal reduction of TiO_2. It should be possible to establish conditions wherein one set of special condition favours one over the other. In this work, a novel approach was developed to fabricate the morphgenetic TiN/C ceramics with hierarchical micro-morphologies and well-oriented pore structures from biologically derived templates, using sol–gel and carbothermal reduction nitridation of TiO_2/C composite under high nitrogen atmosphere.

Experimental procedure

Beech was used as wood templates for fabrication of biomorphic TiN ceramics. Rectangular (about 10 × 10 × 5 mm) specimens of beech wood were shaped, dried at 120 °C for 1–2 days. Titania sol was prepared from Tetrabutyl titanate ($Ti(OC_4H_9)_4$), acetylacetone ($CH_3COCH_2COCH_3$) and distilled water at a suitable molar ratio of $Ti(OC_4H_9)_4$:$CH_3COCH_2COCH_3$:H_2O = 1:0.5:1 by a sol–gel process.

Samples were placed in a self-made vessel equipment described in reference [18]. The vessel was evacuated and held for 3 h, and then backfilled with titania sol. After that, the pressure in the vessel was raised to a high atmosphere pressure of 1.0 MPa with overnight. The titania sol contained in wood was gelled and dried at 130 °C for 12 h to remove other solvents. The pyrolysis was performed in a carbon-heated furnace, which was continuously flushed with nitrogen. The furnace was heated at 800 C for 2 h at a rate of 5 min^{-1}, resulting in titania/charcoal composites. In order to increase the titania content in charcoal/titania composites, the treatment procedure of impregnation, gelling and drying was repeated several times.

Carbothermal reduction and Nitridation of the as-prepared titania/charcoal composites was carried out in a graphite furnace (High multi-5000 Fijidempa Co.Ltd., Osaka, Japan) at different temperature under a high purity nitrogen gas (99.999%, 0.5 MPa) for 2–4 h. During the sintering, the nitrogen gas was made to flow directly toward the samples to supply enough nitrogen for the reactions, by using specially designed accessory for the furnace [27]. Figure 1 outlines the experiment procedure.

Crystalline phases and Lattice parameter were determined by X-ray diffraction (XRD) analysis (D/MAX-2400X, Rigaku Co., Tokyo, Japan). Lattice constant values α_0 could be extrapolated at each crystal plane where α and $\cos^2\theta$ have linear relationship as below:

$$\alpha = \alpha_0 + k' \cos^2 \theta$$

The morphological changes of the starting material during the transformation of the titania/carbon material into TiN ceramic were observed and analyzed by scanning electron microscopy (SEM, JSM-35C). Thermodynamic analysis for the formation of the TiN phases were calculated according to the thermodynamic data in the literature [28, 29].

Results and discussion

Thermodynamic and kinetic analysis of reduction–nitridation

The nitridation temperature of the TiO_2/C depends not only on the phase, grain size and crystallinity of the

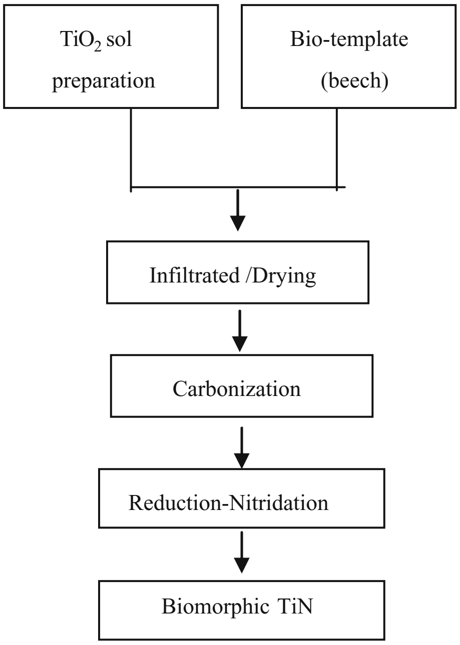


Fig. 1 Processing scheme of manufacturing Biomorphic TiN ceramic from beech wood

TiO_2 and the carbon, but also the nitrogen partial pressure (P_{N_2}) and carbon monoxide partial pressure (P_{CO}). Moreover, the reaction system for the carbothermal nitridation reduction is complex. It is probable that carbonization reactions of titania would occur under the conditions used. Besides reaction (1), the reactions that could occur are as follows:

$$TiO_2 + 3C \rightarrow TiC + 2CO \tag{2}$$

$$TiC + 1/2N_2 \rightarrow TiN + C \tag{3}$$

The Gibbs free energy change of reactions (1), (2) and (3) as a function of temperature for various nitrogen partial pressure (P_{N_2}) and various carbon monoxide partial pressure (P_{CO}) can be written as

$$\Delta_r G_{T,P}(1) = \Delta_r G^0_T(1) + RT\ln\left(\frac{P^2_{CO}}{\sqrt{P_{N_2}}}\right)\,(\mathrm{kJ\,mol^{-1}})$$

$$\Delta_r G_{T,P}(2) = \Delta_r G^0_T(2) + RT\ln(P^2_{CO})\,(\mathrm{kJ\,mol^{-1}})$$

$$\Delta_r G_{T,P}(3) = \Delta_r G^0_T(3) - RT\ln\left(\sqrt{P_{N_2}}\right)\,(\mathrm{kJ\,mol^{-1}})$$

To simplify the calculations, the partial pressure of CO is assumed to be 0.1 MPa (P_{co} = 0.1 MPa). Based on experience data, the partial pressure of N_2 is set to 0.5 MPa $(P_{N_2} = 0.5\,\mathrm{MPa})$. Figure 2 shows the free Gibb's energy $(\Delta_r G_{T,P})$ plots as function of the temperature for the formation of TiN. According to the change in the free Gibb's energy, the pure TiN was obtained between 1418–1552 K (1145–1279 °C). Due to high nitrogen pressure, Reaction (3) is thermodynamically favourable below 2031 K (1758 °C) in the system. Therefore, not TiC but TiN was formed after sintering under the conditions used.

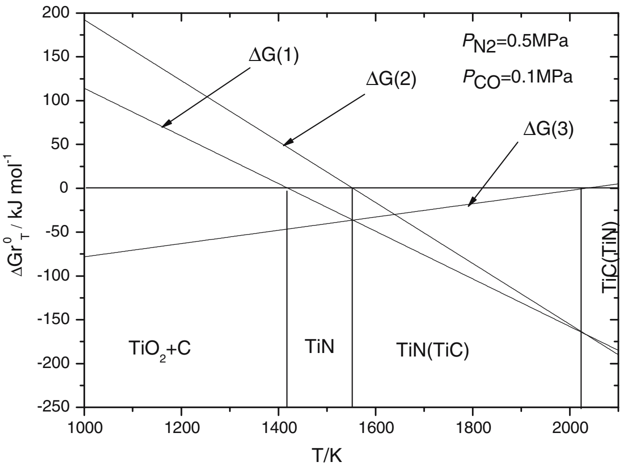


Fig. 2 $\Delta_r G_{T,P}$ of reactions (1)–(3) as a function of reaction temperature T when \raster="_"$P_{N_2} = 0.5\,\mathrm{MPa}$ and P_{co} =0.1 MPa

In kinetic analysis, vacuum/pressure infiltration process and flowing nitrogen gas sintering yields a better distribution of titania within the carbon templates and improves the contact area between TiO_2, N_2 and C. Hence, the kinetic barrier of reactions is lowered, resulting in low reaction temperature and short reaction time.

XRD analysis

Figure 3 shows the X-ray diffraction (XRD) patterns of the samples in different stage of the process. It can be seen that two broad peaks centred around 2θ = 22° and 44° in Fig. 3a suggest that charcoal is amorphous. Peaks due to anatase TiO_2 phases are observed when the native wood infiltrated with titania sol was carbonized at 800 °C for 2 h in nitrogen atmosphere, indicating after carbonization the as-infiltrated TiO_2 was crystallized into anatase structure (Fig. 3b). The phase transformation from anatase to rutile at 1200 °C and titanium nitride phase formed when the nitridation temperature was 1200 or 1400 °C (Fig. 3c). The intensity of peaks due to TiN phases in the XRD patterns increases significantly with increasing sintering temperature, whereas the intensity of peaks due to residual free carbon disappears. Well-crystallized TiN was obtained when charcoal/titania composite are sintered at 1400 °C for 4 h (Fig. 3d). The lattice parameter

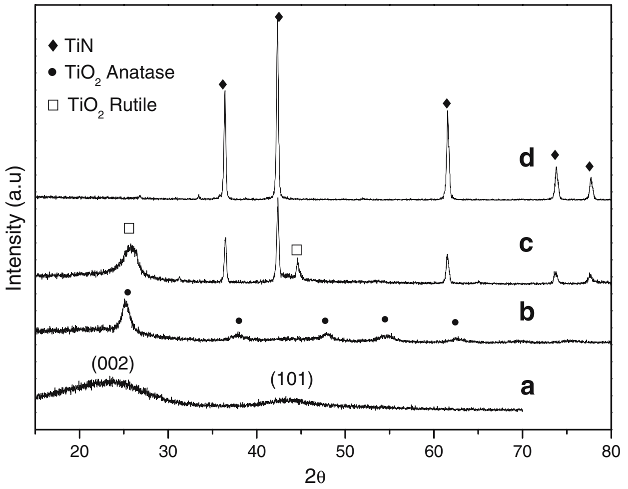


Fig. 3 XRD analysis of the C_B template, charcoal/titania composite after pyrolysis and TiN ceramic samples after nitridation and sintering. (a) C_B template (b) 800 °C, infiltration charcoal, (c) TiN, 1200 °C, 0.5 MPa, 2 h (d) TiN, 1400 °C, 0.5 MPa, 4 h (the samples were ground into powders for XRD measurement)

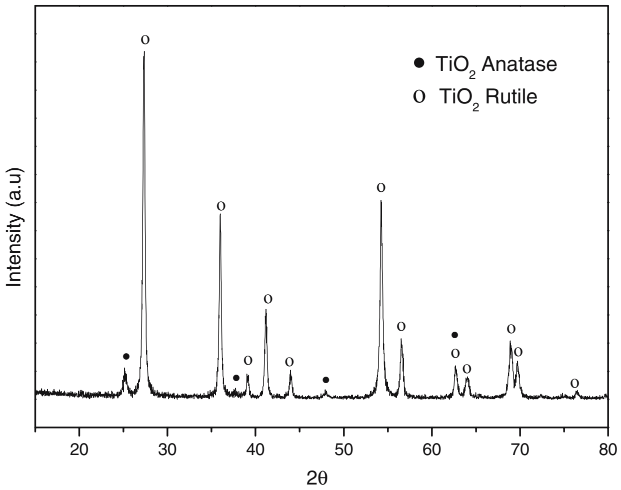


Fig. 4 XRD pattern of biomorphic TiN ceramics after firing at 560 °C in air for 2 h

obtained for the cubic phase of TiN after nitridation and sintering was $\alpha_{0,\mathrm{TiN}}$ = 0.4243 nm. This values are close to that of titanium nitride (0.42414 nm) and far away from that of titanium carbide (0.43274 nm).

Figure 4 demonstrates that TiN in the biomorphic TiN/C ceramic was oxidized completely into TiO_2 during the process of burning off the residual carbon at 560 °C for 2 h. Since the amount of Ti was keep constant during this processing, the content of TiN in the biomorphic TiN/C ceramic can be calculated form the content of TiO_2 oxidized from TiN. It is about 55% after infiltrating and sintering once.

Microstructure characterization

Figure 5 shows the cellular microstructures of biocarbon template from beech wood. The morphology of the pyrolysed beech is characterized by larger-diameter pores (20–50 μm) as well as small-sized cells (around 5–10 μm). After the pyrolysis, the wood pieces retained their shape, but loss in weight and decreased in size. A mean massive weight loss of ~75% and linear shrinkages of ~30% in the radial direction and ~20% in the axial direction occurred in all samples. Despite the changes in porosity and anisotropic shrinkage the porous macro- and micro-structure of the carbonized wood is retained after pyrolysis with high precision. None of them fractured due to the heating rates are crucial controlled.

SEM images of the titania sol-infiltrated and pyrolysed titania/charcoal composites are shown in Fig. 6.The original structure of wood can still be seen, but the pore are filled with dried TiO_2 gel, as the number of infiltrations increased, the amount of TiO_2

Fig. 5 SEM micrographs of beech wood char. The samples without infiltration were pyrolyzed at 800 °C/2 h in N_2 atmosphere (**a**) cross-sections perpendicular to axial direction, and (**b**) cross-sections parallel to axial direction, (100×)

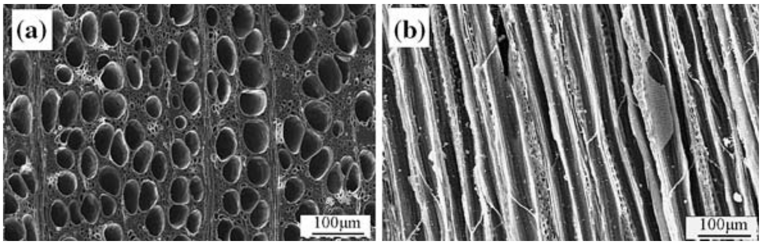
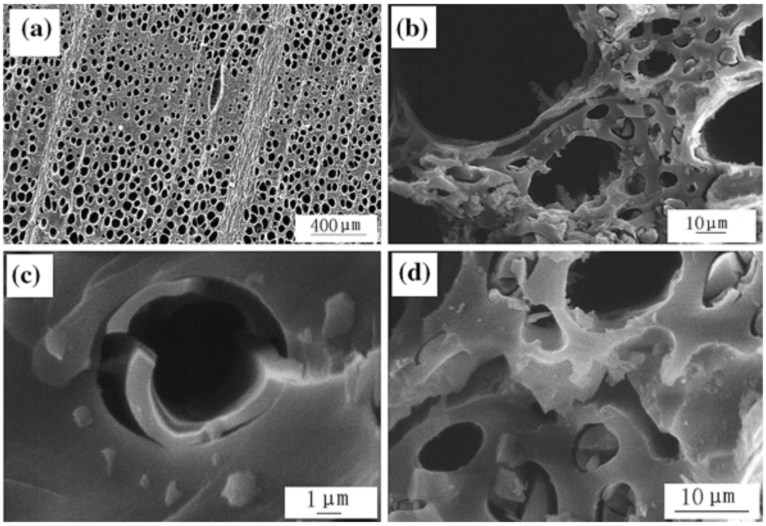


Fig. 6 SEM micrographs of TiO_2/C composites from beech when the infiltration procedure is carried out three times, (**a**) a low-magnification image and (**b**) small pores (**c**) a large pore (**d**) macro-cracks in the sample with weight gain of more that 60%



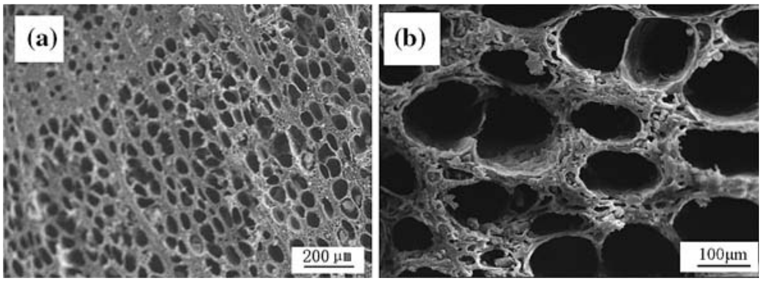


Fig. 7 SEM micrographs of Biomorphic TiN ceramics obtained from C/TiO_2 composites after reduction–nitridation at 1400 °C, 4 h, 0.5 MPa (**a**) low-magnification image of TiN ceramic and (**b**) high-magnification image of TiN ceramic. (**a**), (**b**)cross-sections perpendicular to axial direction

sol deposited increased, eventually some of the pores are filled up. In some cases, Small pores in beech wood are completely filled with TiO_2 gel (Fig. 6b), while some large pores seem to be coated with the titania gel (Fig. 6c). Yet, a few regions of the beech were not filled with TiO_2 gel (Fig. 6b). Figure 4d shows the macro-cracks of sample with a high weight gain (>60%) in carbonization process. Thus the time of infiltration procedure before carbonization should be repeated no more than three times.

The microstructures of the beech-derived Biomorphic TiN ceramic after reduction–nitridation proceeding are shown in Fig. 7. The gas–solid reaction among TiO, N_2 and carbon occurred and the TiN specimen maintains the microstructural features of biocarbon template (Fig. 7a). The porosity increased slightly due to the release of the carbon via CO(g) evaporation (produced mainly by reactions (6) and (8)).The main microstructural features of the biocarbon template were well reproduced by biomorphic TiN ceramic. Upon further treatment at 1400 °C for 4 h, infiltration titania gel is nearly completely changed into TiN ceramics. The complete nitrided specimen was brown in colour.

Formation mechanism of TiN ceramics

In the infiltration-reaction, the titania reacted with the carbon and nitrogen gas to form titanium nitride (TiN). The formation mechanism of TiN ceramics will be described detailed below.

It has been shown that under the experimental condition of the present work, the tetrabutyl titanate was firstly decomposed to anatase-type titania, Then, it converted into rutile-type titania with temperature increasing to 1200 °C [20]. The reactions are shown in Eqs. 4 and 5

$$\mathrm{Ti(OC_4H_9)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_4H_9(OH)} \tag{4}$$

$$\mathrm{Ti(OH)_4 \rightarrow TiO_2 + 2H_2O} \tag{5}$$

The Eq. 1 is the sum of a more complex set of reactions. When the temperature reaches 1400 °C, at the initial stage of the reactions is the reduction of TiO_2 to lower metal oxide (TiO).

$$\mathrm{TiO_2(s) + C(}s\mathrm{) \rightarrow TiO(s) + CO(g)} \tag{6}$$

$$\mathrm{TiO_2(s) + CO(g) \rightarrow TiO(s) + CO_2(g)} \tag{7}$$

In our experiments, the carbothermal reduction was carried out in flowing nitrogen gas atmosphere, The higher the nitrogen flowing rate, the more the CO gas carried out by the flowing nitrogen gas and the lower the thermodynamic onset temperature which favours the forming of TiN. Thus under high nitrogen gas flowing, the following reactions can take place.

$$\mathrm{TiO(s) + C(s) + 1/2N_2(g) \rightarrow TiN(s) + CO(g)} \tag{8}$$

$$\mathrm{TiO(s) + CO(g) + 1/2N_2(g) \rightarrow TiN(s) + CO_2(g)} \tag{9}$$

The TiO from Eqs. 6 and 7 reacts with biocarbon and nitrogen gas to product TiN(s) nuclei heterogeneously on the surfaces of carbon template through Eq. 8. As soon as TiN forms on carbon template, the growth process via Eq. 8 could be slowed down by either the solid diffusion of carbon or the diffusion of CO and N_2 gases molecules through TiN layer, the continuing growth of TiN could result only through Eq. 9. Since a significant amount of carbon remains in the material, any CO_2 produced will be consumed by Eq. 10 to form CO gas, which keeps the CO/CO_2 ratio high enough to make the reduction of TiO possible by gas phase CO.

$$\mathrm{CO_2(g) + C(s) \rightarrow 2CO(g)} \tag{10}$$

Conclusion

The morph-genetic TiN/C ceramics was obtained at 1400 °C for 4 h in a flowing nitrogen atmosphere (0.5 MPa) by infiltration with tetrabutyl titanate, and reaction sintering through carbothermal reduction–nitridation using beech wood as the starting materials. It exhibited a good replica of integral cellar structure of original wood template. The result TiN ceramic is composed of cubic titanium nitride. The degree of nitridation in porous TiN ceramic prepared is controllable by sintering temperature and flowing nitrogen atmosphere. Consequently, this technique provided its promising application for other nitride woodceramics preparation.

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