Fabrication of Porous Biomorphic C–TiC and TiO_2 from Sea Wool Sponges

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Porous C–TiC biomorphic ceramic was derived from sea wool sponges by simple infiltration and heat treatment methods. During annealing, the sponge was converted to carbon templates, and it reacted with the infiltrated Ti-contained metal–organic solution to form C–TiC. The porous structure of sea wool sponge was retained in the final C–TiC product. Hollowed TiO_2 scaffold was also produced by postannealing of the as-prepared C–TiC ceramic in air.

The inherent porous, hierarchical and sophisticated structures exhibited by many biological organisms could provide biological templates for the syntheses of biomorphic materials with lightweight, large specific surface area, and high permeability. This article reports the fabrication of biomorphic C–TiC and TiO_2 ceramics and described how the biotemplating techniques could bring together the intrinsic properties and the potential functions of the final products. TiC has attracted great deal attentions because of its relatively high electrical conductivity, and corrosion and wear resistance when compared with other ceramics; while TiO_2 is well known for its utilization as catalyst in photochemical and biochemical reactions.[1]

The fabrication methods[2] of biomorphic materials from organic biomaterials generally include biotemplating to obtain carbon templates, infiltration of reactants, and reactive heat treatment. Some common difficulties in these methods are the slow infiltration and low conversion rates. In many cases, repeated infiltration in vacuum might make slight improvement. Alternative templates such as egg-shell membrane[3] or electrospun polymer fibers[4] could obtain better infiltration rate because of their porous microstructures, but they are either difficult to be prepared from natural materials or require pretreatment before use. In contrary, organic sea wool sponge is abundant in nature, and it has excellent absorbance which provides an alternative and economic solution for easy infiltration.

Sea wool sponges (from Crabtree and Evelyn) were washed and dried at 100 °C for 4 h. They were then immersed in titanium(IV) bis(ammonium lactato) dihydroxide solution (TALH, Sigma Aldrich) for 2 min and dried again. The samples were heated at temperatures between 900 and 1500 °C for 6 h in Ar atmosphere. In postannealing processing, the samples were further annealed at temperatures between 400 and 1000 °C in air from 2 to 15 h. The samples were characterized by scanning electron microscopy (SEM, LEO 1450VP), transmission electron microscopy (TEM, Philips CM120), both equipped with energy dispersive X-ray spectrometry (EDS). Phases of the samples were determined by X-ray diffractometry (XRD, Huber with Cu Kα source).

Figure 1a reveals the microstructure of a fresh sponge. It had a macroporous network with solid strut (see inset). The samples annealed at 1500 °C for 6 h is presented in Figure 1b. The typical networklike structure of sponge was retained in all samples after annealing. A TEM image of fragments from a sample annealed at 1500 °C is shown in Figure 1c. The microdiffraction pattern with zone axis of [110] (inset of Figure 1c) showed that these fragments were crystalline TiC. The results of the EDS analysis (not shown) of the fragments also revealed that they contained Ti and C. Figure 2 shows the XRD patterns of the samples annealed in Ar. For the samples annealed below 1200 °C, peaks in the patterns indicated that the sample contained TiC_xO_y, Ti_3O_5 (asterisked in Figure 2) and Ti_2O_3 phases. When the sample was annealed at 1400 °C, the peaks in the pattern corresponded only to the TiC_xO_y phase. These TiC_xO_y peaks shifted slightly to lower angles as the annealing temperature increased. In the pattern of sample annealed at 1500 °C, only peaks corresponding to TiC phase were found.

Figure 3a shows the SEM images of the samples after the postannealing in air at 450 °C for 15 h. The hierarchical pore network of sponge was retained, but both solid and hollow struts were observed (see insets, enlarged from the circled regions). The EDS results (not shown) showed that there was over 90 atom % of C in the center of the solid strut and that the rest were Ti and O. Figure 3b shows a TEM image of fragments of the struts. EDS (not shown) revealed strong signals of Ti and O in these fragments. The selected area electron diffraction pattern (inset of Figure 3b) indicated that these fragments were

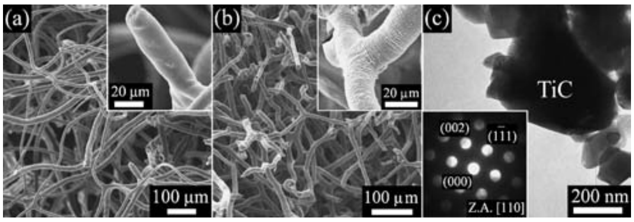

Figure 1. SEM images of (a) fresh sponge; (b) infiltrated sponge annealed at 1500 °C for 6 h in Ar, and (c) TEM image of a fragment from (b) and (inset) its microdiffraction pattern.

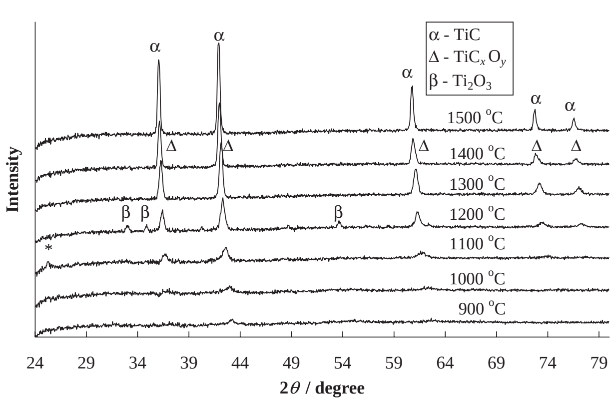

Figure 2. XRD patterns of infiltrated wool sponge annealed at different temperatures for 6 h in Ar.

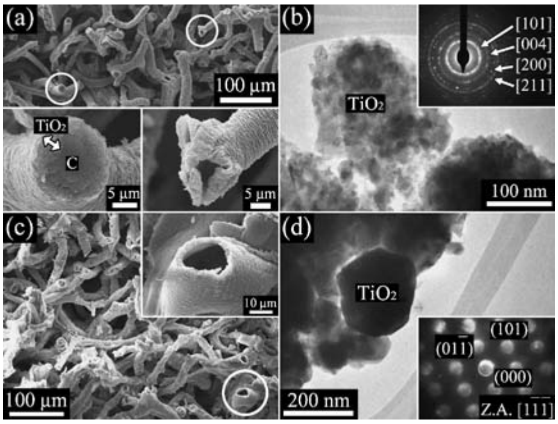

Figure 3. (a) SEM and (b) TEM images of the samples after postannealing at 450 °C for 15 h in air; (c) SEM and (d) TEM images of the samples after postannealing at 1000 °C for 2 h in air.

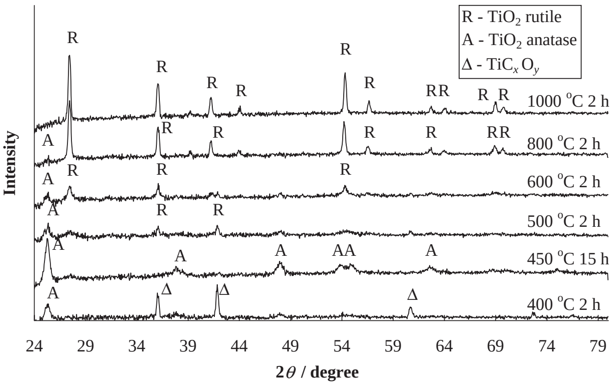

Figure 4. XRD patterns of the samples after postannealing in air at different temperatures and durations.

polycrystalline anatase (A–TiO_2).

When postannealing of the sample was performed at 1000 °C for 2 h in air, the macroporous network structure of sponge was still retained (Figure 3c); however, only hollow struts were found. Fragments taken from the struts were examined by TEM (Figure 3d). EDS (not shown) showed that it contains Ti and O. The microdiffraction pattern with zone axis of $[1\bar{1}\bar{1}]$ (inset of Figure 3d) indicated that they were crystalline rutile (R–TiO_2). Figure 4 shows the XRD patterns of the samples after postannealing in air. For the samples annealed at 400 °C for 2 h, peaks corresponding to TiC_xO_y and A–TiO_2 were observed. In pattern of sample annealed at 500 °C, these peaks became weak and new peaks indexed as R–TiO_2 appeared. The peaks of R–TiO_2 became dominant when the annealing temperature increased. For the sample annealed at 1000 °C, only strong peaks of R–TiO_2 were found. It is worth to mention that rich anatase samples would be obtained under prolonged postannealing at 450 °C in air. Its XRD pattern is also shown in Figure 4 for comparison (second from the bottom).

In the annealing process, the TALH solution in the wool sponge was decomposed into TiO_2.[5] The abundance of C in the sample converted TiO_2 to TiC_xO_y at 900 °C:

$$TiO_2(s) + (2 + x - y)C(s) \rightarrow TiC_xO(s) + (2 - y)CO(g) \quad (1)$$

The intermediate phases Ti_3O_5 and Ti_2O_3, which found in the samples annealed below 1200 °C (see Figure 2), suggested that reaction might not be completed.[6] When the annealing temperature was raised to above 1300 °C, the peak positions of the TiC_xO_y in the XRD pattern were found shifting to the lower angles, indicated that the lattice parameter was increased, and it was probably due to the substitution of C for the O atoms in the TiC_xO_y phase. The reduction process to the TiC product was completed in the samples after the sample was being annealed at 1500 °C, and this result was also reported by Shin et al.[7]

In the postannealing treatment at 400 °C in air, TiC was converted to TiC_xO_y and a small amount of anatase TiO_2. Several other works[8,9] also obtained similar results:

$$2TiC(s) + (y/2 + 1)O_2(g) \rightarrow TiO_2(s\text{,anatase}) + (2 - x)CO_2(g) \quad (2)$$

By increasing the postannealing temperature beyond 500 °C, TiC_xO_y was further oxidized to TiO_2. At the same time, an irreversible phase transformation from anatase to rutile also occurred.[10] From Figure 3, the diameter of the struts was found to be about 15 µm. The reaction described by eq 2 would have taken place within a few micron depth from the surface of the struts, and large amount of C could still be found in the center of the strut as shown in Figure 3a. In the postannealing treatment at higher temperature, C was allowed to diffuse outward and further oxidized to form CO_2 until it was completely exhausted from the core region, and a hollow TiO_2 scaffold was produced.

In conclusion, biomorphic C–TiC ceramics with the original sea wool sponge structure retained are successfully produced by infiltration of diluted TALH solution and annealing at 1500 °C for 6 h in Ar. During a single annealing process, the sponge was pyrolyzed and formed C–TiC composites with TiO_2 produced by the thermal decomposition of TALH. By postannealing the TiC sample at temperature of 450 °C for 15 h, anatase type C–TiO_2 composites was obtained, and R–TiO_2 hollow scaffold was produced after annealing at 1000 °C for 2 h. The sea wool sponge has been converted to a potential effective catalyst with hollow TiO_2 strut-network.

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