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Preparation and characterization of morph-genetic C/TiN composites from filter paper

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Abstract Morph-genetic C/TiN composites with cable-like structure was prepared from filter paper template through the surface sol–gel process and carbothermal nitridation reaction. The resulting materials have a hierarchical structure originating from the morphology of cellulose paper. The C/TiN composites formed the core-shell microstructure, the core is graphitic carbon, and the shell is TiN nanocoating formed by carbothermal nitridation reduction of titania with the interfacial carbon in nitrogen atmosphere. Scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction, and transmission electron microscope were employed to characterize the structural morphology and phase compositions of the final products.

Introduction

Advanced ceramic materials such as titanium nitride, TiN, have gained much attention because of its high-temperature strength, extraordinary hardness, stability to corrosion, thermal shock resistance, and thermal conductivity, combining with some materials to form composites can improve properties of the materials and even can reveal novel applications [1–3]. These attractive properties enable it to be used as diffusion barriers in microelectronics [4], as hard, protective coatings for cutting tools, and as crucibles in metal smelting [5–7]. Generally, TiN was prepared via the reaction of metal titanium with nitrogen or ammonia at temperatures above 1073 K [8, 9] or nanosized titania nitrified in flowing ammonia gas at 973–1373 K [10, 11]. However, research intensity focus on the synthesis of TiN powder, publications relating to TiN nanocoating synthesis with carbothermal nitridation method are very scarce.

In the recent years, the biotemplating technology has been developed for conversion of naturally grown plant structures in biomorphic, high-porous ceramics with undirected pore morphologies in the micrometer range [12–15]. This technology offers a possibility to use the large variety of nature materials to produce microcellular ceramics, composites and nanocoatings, which are so far difficult to manufacture by conventional techniques. The coating of a template results in hollow replication as opposed to a negative copy or true replication [16]. Sol–gel chemistry applied to three-dimensional (3-D) materials allows homogeneous coating of complex structures [17]. Huang and Kunitake [18–20] have shown replication of multiscale materials with outstanding precision (tens of nanometers) while maintaining stability on the macroscale using templates that are abundant in nature, low cost, and environmentally benign, such as simple paper, cotton, and cloth. The procedure used was a repeated surface sol–gel process [21–23]. This resulted in a subnanometer-thick layer coating the morphologically complex template surface. The natural cellulose fibers possess surface hydroxyl groups, and provide a suitable vehicle for the surface sol–gel process. However, the previous related studies focus on the preparation of oxides using template-directed synthesis, there is not report about the preparation of nitrides from filter paper through the surface sol–gel process and carbothermal nitridation reaction.

In the present work, we report a novel method for preparing C/TiN composites from filter paper by using the

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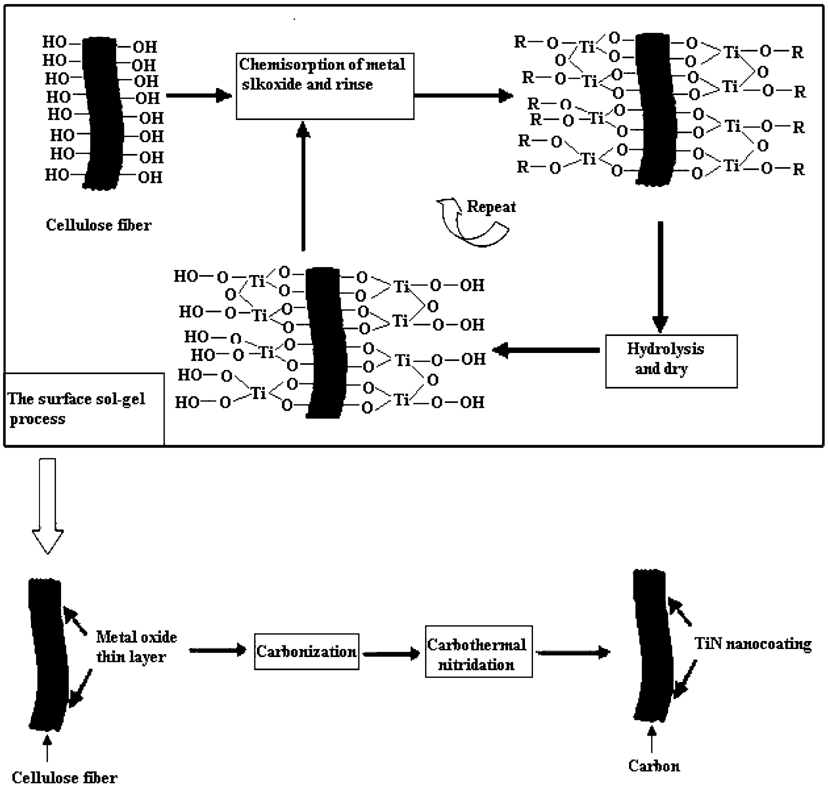

Fig. 1 Representative illustration of C/TiN composites synthesis from filter paper

surface sol–gel process and carbothermal nitridation reaction. The structural morphology and crystalline phase of the final products are investigated by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and transmission electron microscope (TEM).

Experimental

A piece of commercial filter paper was placed in a suction filtering unit, and was washed by suction filtration of ethanol, follow by drying with air flow. Ten milliliters of titanium *n*-butoxide solution was then passed through the filter paper slowly within 2 min, two 20-mL portions of ethanol were immediately filtered to remove the unreacted metal alkoxide, and 20 mL of water was allowed to pass through to promote hydrolysis and condensation. Finally, the filter paper was drying in flowing air. By repeating this filtration/deposition cycle, thin titanium gel layers covered the surface of the cellulose fibers. The dried filter paper/titanium gel composite was placed in alumina boat and carbonized in a horizontal tube furnace at desired temperatures (about 1073 K) for one hour with slow heating rates. The whole treatment was preformed in N_2 atmosphere, and carbon/titania composites were formed in the end of carbonization. Carbothermal nitridation reduction of the as-prepared carbon/titania composites was carried out in an atmosphere furnace (High Multi 10000, Fijidempa Co. Ltd.). The flowing nitrogen pressure was maintained 0.6 MPa in the whole reactive procedure. The samples were firstly heated to 1473 K with a heating rate of 10 K/min, then, heated at rate of 2 K/min to the final sintering temperature 1773 K with 2 h holding time, finally, cooled down to room temperature in nitrogen. The processing scheme for manufacturing of C/TiN composites using filter paper as template is described in Fig. 1.

The morphology and quantitative elemental analyses of the resulting products and the initial filter paper were observed and characterized by SEM (Hitachi, S-2700) equipped with an EDX spectrometer. XRD was carried out on a D/MAX-RA X-ray diffractometer to determine the crystalline phases formed during the carbothermal nitridation reduction. The microstructure of the produce was observed by transmission electron microscope (TEM, JEM-200CX, Japan Electron Co).

Results and discussion

SEM analysis

SEM photograph of the original filter paper is shown in Fig. 2a. It can be seen that filter paper have a fibrillar

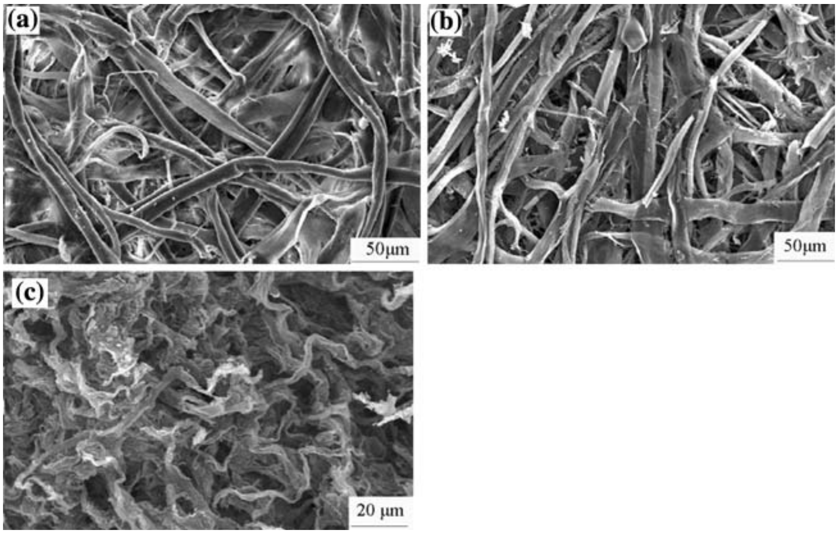

Fig. 2 SEM micrographs the samples (**a**) filter paper; (**b**) C/TiO_2 composites; (**c**) morph-genetic C/TiN composites.)

microstructure, show disorderly arrangement without any direction. Single fiber possesses strip or strap structure with sizes of 5–20 μm in radial direction and about 0.5–5 mm in axial direction. Figure 2b shows the SEM photographs of the C/TiO_2 composites specimens fabricated by above mentioned the surface sol–gel process which is fit for prepare ultrathin nanometer-thick gel film on the substrate and the carbonization process which only change organic cellulose into inorganic carbon. The carbon core completely retained the original morphology of filter paper except a homogeneous shrinkage in all directions, and titania nanocoating on the carbon core was too thin to distinguish from the surface of carbon in low magnified SEM image. Therefore, the morphology of C/TiO_2 composites was a little shrinkage compared to the filter paper. The resultant C/TiN composites still kept the core-shell microstructure, as shown in Fig. 2c; the core was graphitic carbon, and the shell was TiN nanocoating formed by carbothermal nitridation reduction of titania with the interfacial carbon in nitrogen atmosphere. Whereas, the higher temperature not only lead to carthermal nitridation reaction take place but also increase the ratio of shrinkage compared to C/TiO_2 composites specimens. These C/TiN composites were composed of irregular micrometer cables and nanometer cables, originated from cellulose microfibers and nanofibers respectively. From the observations it is concluded that the original structure of the filter paper can be replicated in the resulting morph-genetic C/TiN composites. During the conversion their microstructure is neither destroyed nor altered, only a homogeneous shrinkage in all directions takes place.

The corresponding EDX spectrum of the C/TiN composites shown in Fig. 3 indicates that the sample consist of C, N and Ti. Moreover, the quantitative analysis shows that their average atomic ratio approximates to C:N:Ti $\approx$ 3.5:1:1.

XRD analysis

The XRD patterns of the as-produced C/TiN composites is shown in Fig. 4. The one broad diffraction band of carbon (0002) is observed, indicating that the carbon core is amorphous. The previous study showed that the crystallinity of the carbon increased to a more graphitic-like microstructure with the increase of reactive temperature [24]. All of the peaks can be indexed to cubic TiN with a lattice constant of a = 0.4243 nm, which is in good agreement with the JCPDS card No. 38-1420. The broadening nature of the peaks indicates that the sample is composed of nanocrystallites, and the average size of the

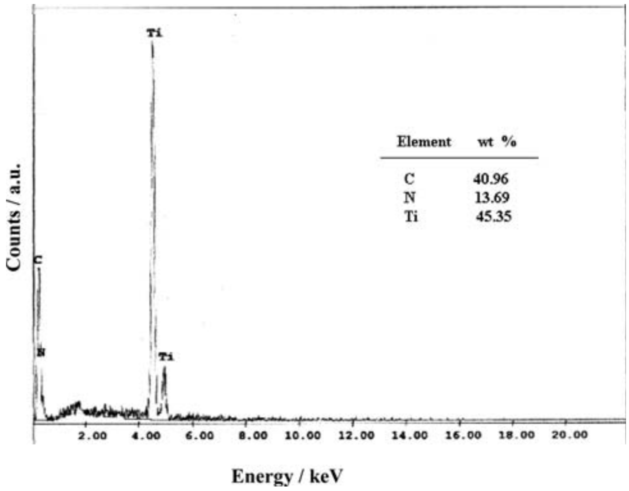

Fig. 3 EDX spectrum of the morph-genetic C/TiN composites

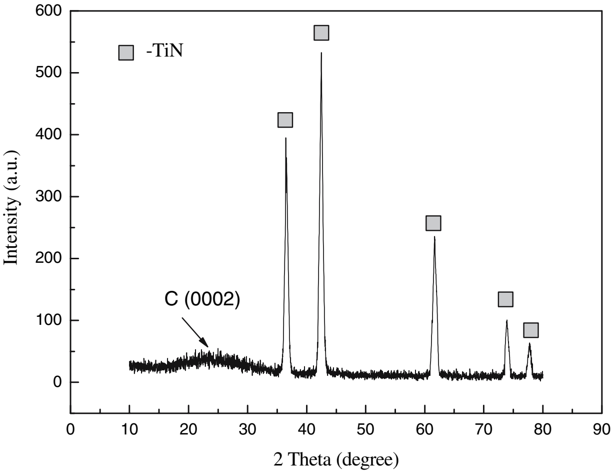

Fig. 4 XRD patterns of the as-produced C/TiN composites

particles is about 30 nm calculated by the Debye–Scherrer equation. The same result is also confirmed by the observation of transmission electron microscopy.

TEM analysis

The filter paper is composed of broken fibers, the exposed strands including microfibrils and their bundles with diameters ranging from 10–30 nm up to several micrometers. The resulting C/TiN composites retained the original shape of the filter paper. Figure 5 shows typical TEM images of carbon core with well-dispersed TiN nanocoating. The mean diameter and standard deviation of TiN nanoparticles were estimated from this TEM images, as d = 24 nm and σ = 8 nm, respectively. These values are similar to those estimated from the XRD results.

Formation mechanism of C/TiN composites

Preparation of TiN using carbothermal reduction and nitridation of TiO_2 is a well-known process [25–27]. TiO_2 reacts with C in nitrogen atmosphere according to the following overall equation:

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

Researchers have observed a minor amount of CO_2 in the effluent gas, which does not exclude the following possibility:

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad (2)$$

$$C(s) + CO_2(g) \rightarrow CO(g) \qquad (3)$$

TiN may also be formed by reacting TiO_2 with CO. The corresponding reaction can be written as

$$TiO_2(s) + 2CO\ (g) + 1/2N_2(g) \rightarrow TiN\ (s) + 2CO\ (g) \qquad (4)$$

It is assumed that TiN does not appear to form in one single step. The phase diagram suggests that the loss of oxygen from the TiO_2 structure leads to the formation of oxygen-deficient magneli phases, namely Ti_nO_{2n-1} with 10 ≥ n ≥ 4. Experimentally, a reaction sequence involving the formation various titanium-rich phases, such as Ti_3O_5 and Ti_4O_7 was observed by many researchers. In an ambient nitrogen atmosphere, the reaction sequence that occurs to the different transient phases formation can be written as

$$\begin{aligned} TiO_2(\text{anatase}) &\rightarrow TiO_2(\text{tutile}) \rightarrow Ti_5O_9 \rightarrow Ti_4O_7 \\ &\rightarrow Ti_3O_5 \rightarrow TiN \end{aligned}$$

The carbothermal nitridation process involves many steps. The most important is diffusion of the nitrogen gas into the pores of the carbon template followed by reductive decomposition of TiO_2 with C to intermediate oxygen-deficient magneli phases and subsequently react with carbon to form TiN. However, limiting factor for the grade of conversion of the biomorphic carbon into C/TiN cables is the diffusion of the reactants carbon, nitrogen gas and titania through the steadily growing TiN layer. The thicker is the layer, the slower is the diffusion. Therefore, in order

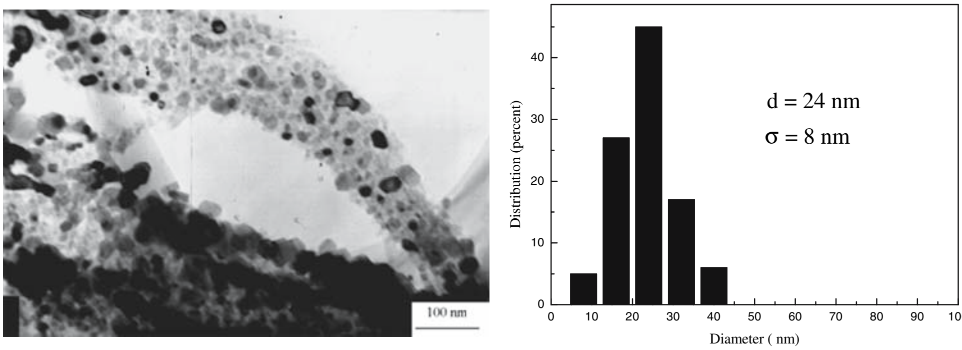

Fig. 5 TEM images of the C/TiN composites and histogram of TiN nanoparticles

to obtain a complete conversion of the titania, we adopted higher nitrogen pressure in the whole reactive process.

Conclusion

We prepared morph-genetic C/TiN composites from filter paper by the surface sol–gel process and carbothermal nitridation reaction. SEM, EDX, XRD and TEM studies show that the as-prepared C/TiN composites maintained the original morphology of paper template, and it were made up of irregular micrometer cables and nanometer cables. These cables were novel core-shell microstructure, the core was graphitic carbon, and the shell was TiN nanocoating formed by carbothermal nitridation reduction of titania with the interfacial carbon in nitrogen atmosphere. We have demonstrated a facile approach towards fabrication of amorphous carbon core with covered TiN nanocoating. The facile, economical fabrication process allows for ready extension to the preparation of various carbon-based functional materials with nitride nanocoating, such as electrodes for fuel cells.

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