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Short communication

Zirconium nitride (ZrN) fibers prepared by carbothermal reduction and nitridation of electrospun PVP/zirconium oxychloride composite fibers

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ABSTRACT

Zirconium nitride (ZrN) fibers were synthesized by carbothermal reduction and nitridation of composite fibers obtained by electrospinning. The structure and morphology of ZrN fibers were characterized by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM). After calcinations at 1600 °C, the surface of ZrN fibers with average diameter about 500 nm is rough but the continuous microstructure was still maintained by the connection of irregular fine particles. The diameter of ZrN crystalline was in the range of 100–500 nm. Both X-ray diffraction (XRD) and Raman spectroscopy analysis indicated that the zirconium nitride fibers have a NaCl-structure cubic cell and the better crystallinity of grains.

1. Introduction

In recent years, with high-temperature strength and corrosion resistance, metal nitrides have found an increasing number of applications in increasing the hardness and improving the wear and corrosion resistance of materials [1–3]. As a transition-metal nitride having a NaCl-structure [4], zirconium nitride (ZrN) can be used as wear resistant, friction reducing coatings for machine tools [5], and a diffusion barrier in integrated circuits [6] because of its metallic behavior, extreme hardness, high melting points, remarkable chemical resistance, high-temperature strength and low-temperature superconductivity. Moreover, it has been proposed as a solar control coating for windows due to its optical properties [7]. The films of ZrN have been prepared on various substrates by several methods, such as chemical vapor deposition (CVD) [8], physical vapor deposition (PVD) techniques [9], ion beam assisted deposition [10] and reactive dc magnetron sputtering [11], and were widely deployed for the thermometer coatings in cryogenic work and the gate electrode in MOS transistors [12,13].

One-dimensional systems exhibit novel physical and chemical properties that can be exploited in optics, catalysis and data-storage devices. The properties of better electrode [14], higher luminescence efficiency [15] and superior mechanical toughness [16] have been demonstrated for the fiber materials. There are several preparation methods to obtain fiber materials, such as supercritical fluid solution-phase approach [15], laser ablation [15], laser-heated pedestal growth (LHPG) [17], carbon nanotube-confined reaction [18] and ion beam irradiation [19]. As a simple and versatile technique, electrospinning has been widely used for the fabrication of polymer nanofibers with exceptional length, uniform diameter, and diversified compositions [20,21]. The ceramic nanofibers can also be obtained by electrospinning mixture solutions of ceramic precursors and polymers, which were subjected to calcinations in order to remove polymer matrixes [22,23]. In this work, ZrN fibers were synthesized by a high-temperature carbothermal reduction and nitridation process using electrospun PVP/zirconium oxychloride composite fibers as a precursor at 1600 °C for 5 h in N_2 atmosphere. Compared with the other synthetic methods, the fabricated technique used in this work processes the virtues including simplicity, low cost and absence of template. Such a strategy might be extended to the preparation of other nitride fibers.

2. Experimental

$ZrOCl_2{\cdot}8H_2O$ (99%, Sinopharm Chemical Regent Co., Ltd.) was used as starting materials for the synthesis of the ZrN fibers. Due to the good solubility in alcohol and water and the compatibility with nitrates, poly(vinyl pyrrolidone) (PVP, Sinopharm Chemical Reagent Co., Ltd.) was acted as the polymeric component of the composite.

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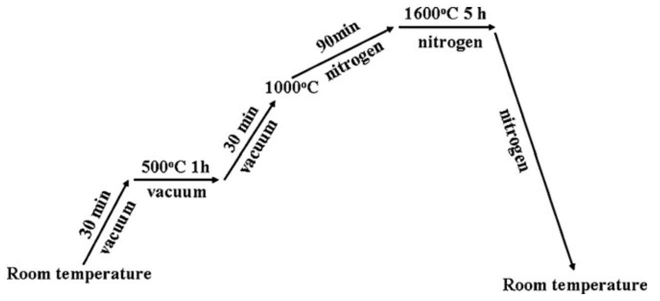

Fig. 1. The calcination schedule of the electrospun composite fibers.

The composite fibers were prepared as follows. 13.0764 g $ZrOCl_2{\cdot}8H_2O$ was dissolved into the 10 ml solvent including 7.5 ml de-ionized water and 2.5 ml ethanol. Then the 5 g PVP was added into the solution. Subsequently, the mixture was magnetically stirred at room temperature for 3 h until the PVP was completely dissolved and a viscous homogeneous solution of PVP/zirconium oxychloride composite was formed. The solution was drawn into a hypodermic syringe and then ejected from the conductive stainless steel capillary with a voltage of 30 kV. The distance between the capillary and the collector was 15 cm. The collector was coated with an aluminium foil. The composite fibers were collected on the aluminium foil to form non-woven mats. This fiber mat was dried at 100 °C for 12 h, and then heated up to 1600 °C for 5 h in three stages according to the schedule shown in Fig. 1. The composite fibers were first carbonized in vacuum for 1 h at 500 °C. With the increasing of temperature to 1000 °C, the N_2 was provided as nitrogen source and carbon was used as the reducing agent. These fibers were heated at 1600 °C for 5 h for carbothermal reduction and nitridation.

TG–DTA was performed on a thermoanalyzer (Mettler, TGA/SDTA851) in N_2 atmosphere with a heating rate of 10 °C/min. X-ray diffraction (XRD) patterns were collected on a Shimadzu/XRD-6000 diffractometer with Cu Kα radiation. Raman spectra were recorded on a Renishaw invia instrument. The morphology of the ZrN fibers was analyzed by the scanning electron microscope (JSM-5600LV, JEOL) and transmission electron microscopy (TEM, Tecnai G220 S-Twin, FEI)

3. Results and discussion

3.1. Thermoanalysis

The thermal behavior of the composite fibers under flowing nitrogen is shown in Fig. 2. The weight loss of about 10% in the range of 50–200 °C could be attributed to the evaporation of moisture and trapped solvent (ethanol) from the precursor. The 40% weight loss between 300 and 500 °C is believed to originate from the decomposition of nitrates and the carbonization of PVP. The peaks at about 107 and 400 °C in the DTA curves corresponding to weight losses are endothermic, implying that the precursor fibers involve slow decomposition and carbonization without the combustion of carbon below 500 °C in nitrogen. No weight loss above 500 °C was observed, indicating complete carbonization of organic components in the composite.

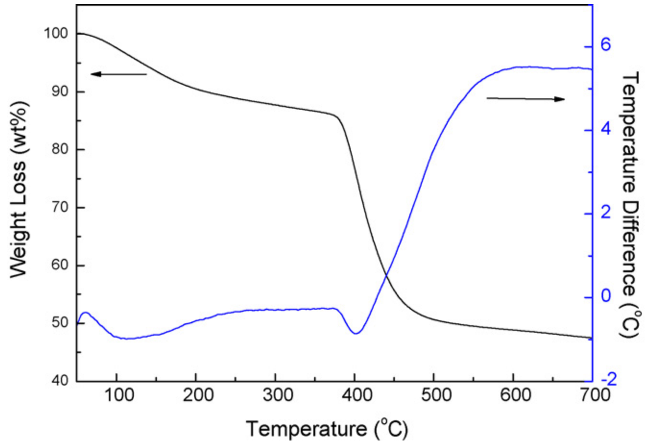

Fig. 2. The TG–DTA curves of the composite precursor fibers.

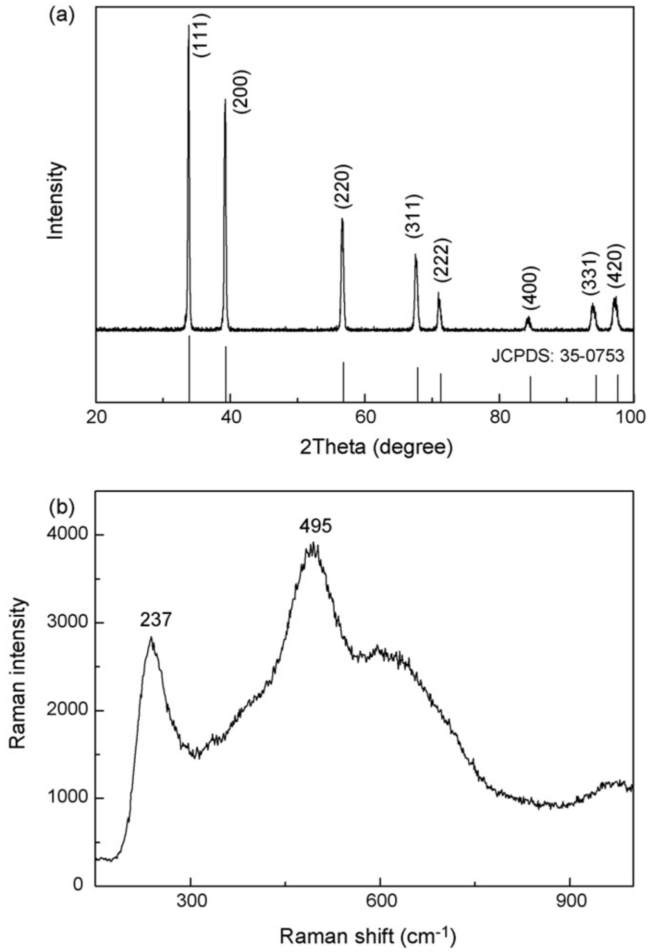

Fig. 3. XRD pattern (a) and the Raman spectrum of the ZrN fibers (b).

3.2. Crystal structure development of ZrN fibers

Fig. 3a shows the X-ray diffraction patterns of the ZrN fibers after calcination at 1600 °C. It is noted that all of the diffraction peaks in the XRD pattern match well with the cubic ZrN phase (JCPDS 35-0753, space group: *Fm*3*m* (2 2 5)). No other peaks are found, indicating the ZrN crystalline with cubic NaCl-structure has been successfully synthesized. The sharp diffraction peaks implies the better crystallinity of ZrN grains. The PVP in composite fibers had been completely carbonized after heat treatment at 500 °C for 1 h in vacuum. Therefore, the carbonization of the fibers was further carried out at 1600 °C for 5 h in N_2 atmosphere, the ZrN fibers are formed via the reaction (1) [24]:

$$2ZrO_2(s) + 4C(s) + 2N_2(g) \rightarrow 2ZrN(s) + 4CO(g) \qquad (1)$$

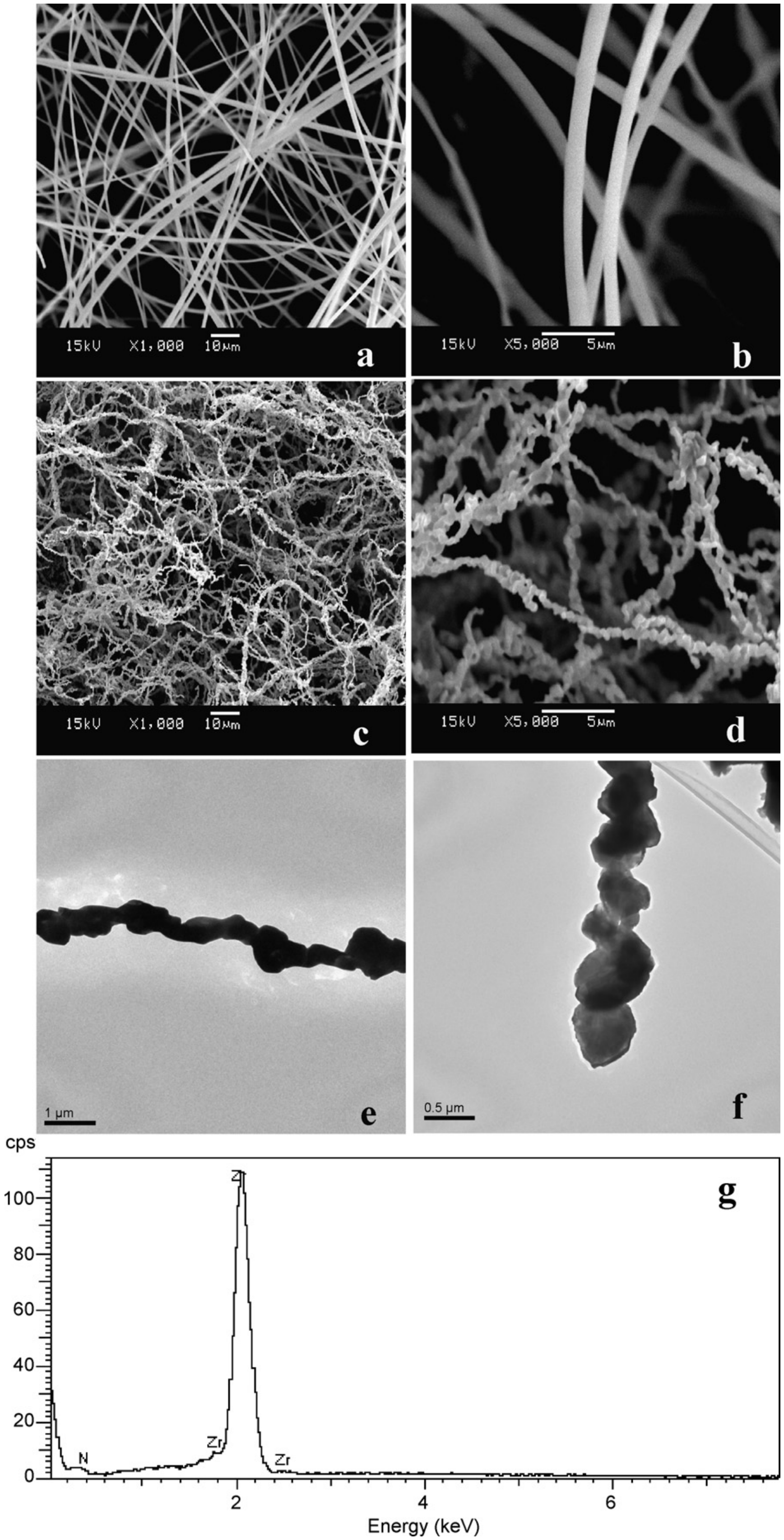

Fig. 4. (a and b) SEM images of the composite precursor fibers. (c and d) SEM images and (e and f) TEM images of ZrN fibers after heating treatment at 1600 °C. (g) EDS pattern in the ZrN fibers sample.

Table 1
EDS quantitative analysis for ZrN fibers

Element	Weight ratio (%)	Atomic ratio (%)
N	13.02	49.37
Zr	86.98	50.63

The Raman spectra are in accordance with the XRD results. As shown in Fig. 3b, the spectrum of ZrN is dominated by two strong peaks at 237 and 495 cm^{-1}. It has been reported in Ref. [25] that the peak in the range of 150–260 cm^{-1} and the peak at about 500 cm^{-1} are due to the disorder induced single acoustic phonons and the disorder induced scattering from optic phonons, respectively. The frequencies of these features are supported by the results of neutron scattering [26] and tunneling experiments [27].

3.3. *Microstructure of the fiber*

Fig. 4(a) and (b) shows the SEM micrographs of the electrospun composite fibers in the amorphous state with different magnifications. The surface of randomly oriented fibers is very smooth and uniform, which is attributed to the high PVP content. The average diameter of these fibers is about 1 μm and the length could reach several millimeters. The electrospinning process is an important step for the fabrication of precursor fibers. The ZrN fibers are obtained by the carbothermal reduction of these precursor fibers. After carbonization and nitridation at 1600 °C, the cubic ZrN phase with yellow-gold color was obtained, moreover, the surface of ZrN fibers coarsen due to the removal of PVP and crystallization of ZrN. The ZrN fibers have a diameter of about 500 nm, which is smaller than the electrospun composite fibers because of shrinkage when the organic components were removed. As shown in Fig. 4c and d, a well-defined fiber texture is still maintained by the connection of irregular fine particles, indicating that the composite fibers constitute a structure-directing template during the calcining.

The structure and morphology of the ZrN fibers were further characterized by the transmission electron microscopy. Fig. 4e and f clearly shows that the diameter of the ZrN fibers is about 500 nm which is in accordance with the SEM observation. The surface of the calcined fibers is rough due to the crystallization of ZrN. TEM also shows that the ZrN fibers structure is kept by the connection of irregular fine particles and the diameter of ZrN crystalline is in the range of 100–500 nm. A quantitative analysis by energy-dispersive spectroscopy (EDS) (Fig. 4g) shows the elements of Zr and N and the result for quantitative analysis is presented in Table 1. It shows that the atomic ratio of Zr:N is 1.008:1.033 which gives good agreement with the ZrN phase composition.

4. Conclusion

In summary, direct electrospinning was used in this work to prepare the PVP/zirconium oxychloride composite fibers. After carbonization and nitridation in N_2 atmosphere at 1600 °C for 5 h, the polycrystalline ZrN fibers with diameters of about 500 nm have been successfully prepared. This fiber structure is kept by the connection of irregular fine particles and the diameter of ZrN crystalline is in the range of 100–500 nm.

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