Materials Letters 172 (2016) 202–206

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Silicon oxycarbide/titanium dioxide fibers with wrinkle-like surface by electrospinning

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ARTICLE INFO

Article history:
Received 16 October 2015
Received in revised form
26 February 2016
Accepted 27 February 2016
Available online 2 March 2016

Keywords:
Fiber technology
Surfaces
Silicon oxycarbide
Titanium dioxide
Electrospinning

ABSTRACT

Silicon oxycarbide/titanium dioxide ($SiOC/TiO_2$) fibers have been prepared from tetrabutyl titanate modified polyhydromethylsiloxane through electrospinning and pyrolysis. The $SiOC/TiO_2$ fibers, which are hydrophobic with water contact angle of 130°, own wrinkle-like surface rising from anisotropic volume shrinkage during the pyrolysis. X-ray photoelectron spectroscopy, X-ray diffraction and transmission electron microscopy are exploited for characterization on the obtained polytitanosiloxane gel fibers and the ceramic fibers. The results indicate that the gel fibers are converted to ceramic fibers consisting of amorphous silicon and titanium oxycarbide glass by pyrolysis at 1000 °C, and further decomposed into cristobalite-SiO_2, brookite-TiO_2 and trace of TiC nanoparticles embedded in amorphous phase at 1300 °C.

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1. Introduction

Multicomponent $SiOC/TiO_2$ composites exhibit remarkably improved thermal stability, oxidation and creep resistance, and mechanical property compared with Ti–free SiOCs because of the covalent bonding between nonstoichiometric excess carbon and titanium or/and the increased overall bonding strength of the constituent elements by addition of titanium [1–3]. Recently, the preparation and characterization of $SiOC/TiO_2$ composites, as well as the influence of titanium content on their structures and properties were explored for enhanced high-temperature stability, which should provide fundament for possible applications in the high temperature field of energy, environment and transportation as thermal and environmental protection barriers [4–6].

Yet few papers concerned with the preparation of $SiOC/TiO_2$ fibers due to complex but critical requirements on the solution for fiber spinning including precursor chemistry, viscosity and rheology. SiO_2/TiO_2 and $SiC(O)/TiO_2$ fibers were prepared from silicon and titanium alkoxides by sol-gel process [7] or from titanium alkoxide modified polysilanes by melt-spinning [8,9] followed by pyrolysis in argon. The strength of such $SiOC/TiO_2$ fibers was markedly higher (tensile strength: 3 GPa, Young's modulus: 220 GPa) [8] than that of conventional sol–gel derived TiO_2 and SiO_2 fibers (< 1 GPa), and can even retain high strength after heat-treating above 1200 °C in the air [8], superior than traditional SiC and carbon fibers. Therefore $SiOC/TiO_2$ fibers have been considered as novel reinforcement materials of high performance ceramic matrix composites. Moreover, they show tailored electrical conductivities (specific resistance 10^7–10^{-1} Ω cm [8]) controlled by the carbon amount in the fibers, which further expands their use as microwave absorbable or permeable materials. Particularly, SiOCs incorporated with TiO_2 can find applications in telecommunications, photonics and catalysis fields utilizing the semiconductor and photocatalyst properties of TiO_2 [10,11]. Hojamberdiev et al. [12] prepared mesoporous $SiOC/TiO_2$ composite by introducing TiO_2 powders into polysiloxane precursor followed by pyrolysis and explored its potential in the removal of organic dyes from contaminated water. The results showed $SiOC/TiO_2$ exhibited higher adsorption and photocatalytic activities of methylene blue when compared with pure TiO_2 because of their high surface area and unique mesoporous structure.

Compared with conventional methods, electrospinning is an effective route to prepare ceramic fibers with diameter down to a few nanometers or with complex architectures. SiOC fibers have been successfully fabricated by a combination of electrospinning and sol–gel process [13] or directly electrospun from polysilanes

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http://dx.doi.org/10.1016/j.matlet.2016.02.150
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[14,15]. Recently, preparation of polymer-derived microfibers including SiOC and SiCNO with specific nanostructures (such as, luffa-like [14] or bead-like [16]) has attracted extensive attention, since such unique microfibers exhibit super-hydrophobicity, self-cleaning, oil-uptake capacity and supporting catalysts capacity [14,16]. To the best of our knowledge, preparation of SiOC/TiO_2 fibers with dual micro- and nanostructures has not been reported previously. SiOC/TiO_2 fibers with wrinkle-like surface are generated in this study by electrospinning titanium modified polyhydromethylsiloxane utilizing the anisotropic volume shrinkage during the pyrolysis. The fibers exhibit unique hydrophobicity, and their pyrolysis behavior, chemical structure and microstructure are investigated.

2. Material and methods

Polyhydromethylsiloxane (PHMS, $Me_3SiO[SiHMeO]_nSiMe_3$, MW: ~3500, Kaihuasantai, China) and tetrabutyl titanate (TBT,Ti$(O(CH_2)_3CH_3)_4$, Jiangtian, China) were selected as polytitanosiloxane (PTSO) precursor, polyvinylpyrrolidone (PVP, [–CH$(NCH_2CH_2CH_2CO)CH_2–]_n$, MW: ~6000, Jiangtian, China) as spinning reagent and ethanol as solvent. In a typical synthesis, PHMS (4.00 g), TBT(1.70 g), PVP (1.00 g) and ethanol (7.60 g) were mixed by magnetic stirring for 30 min to give out a transparent viscous solution, and the mole ratio of Ti of TBT and Si of PHMS was about 0.1. The viscosity of PTSO/PVP solutions is 175 cp measured with a viscometer (Brookfield DV-II, USA) at 25 °C using a rotating velocity of 20 r/min. Subsequently, the solution was loaded into a 5-ml-syringe equipped with a stainless steel needle. The electrospinning parameters were as working voltage of 10 kV, feeding at the rate of 0.4 mL/h, working distance of 10 cm and with aluminum plate as collector. After the spinning process, the as-spun PTSO gel fibers were heated at 50 °C for 5 h for further crosslinking, and then converted to SiOC/TiO_2 ceramic fibers by pyrolysis at 1000 °C or 1300 °C in flowing argon for 1 h.

The PTSO and SiOC/TiO_2 fibers was analyzed by X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Fisher Scientific), scanning electron microscopy (SEM, s4800, Japan), transmission electron microscopy (TEM, Tecnai G2F20, Philips) connected with EDS, X-ray diffractometer (XRD, Rigaku D/max 2500v/pc), and thermogravity analysis (TGA, Netzsch STA 449F3). Contact angle measurement was performed on a standard goniometer (DSA100, KRUSS, Germany) using the static method and repeated on 3 samples. A constant drop volume of 5 μL was used corresponding to the diameter of ~2 mm.

3. Results and discussion

TBT functions not only as crosslinking agents between the Si–H of PHMS and Ti–OBu of TBT but also as catalysts for the condensation reactions of siloxanes [4,17] yielding three-dimensional polysiloxane network. Therefore no additional catalyst or crosslinker is needed in this system to ensure the integrity and the shape of electrospun PTSO fibers during pyroylsis. The PTSO fibers are white and flexible, and transform to black SiOC/TiO_2 ceramic fibers by pyrolysis at > 1000 °C in argon. TGA analysis (Fig. 1a) shows the organic-inorganic conversion is completed at ~1000 °C, and the total weight loss is 34.2 wt% corresponding to ceramic yield of 65.8 wt%. There are three stages of weight loss: (1) 3 wt% below 150 °C resulting from the releasing of alcohol and water; (2) 17 wt% between 150 and 450 °C mainly due to thermal degradation and evaporation of the PVP; and (3) 14 wt% between 450

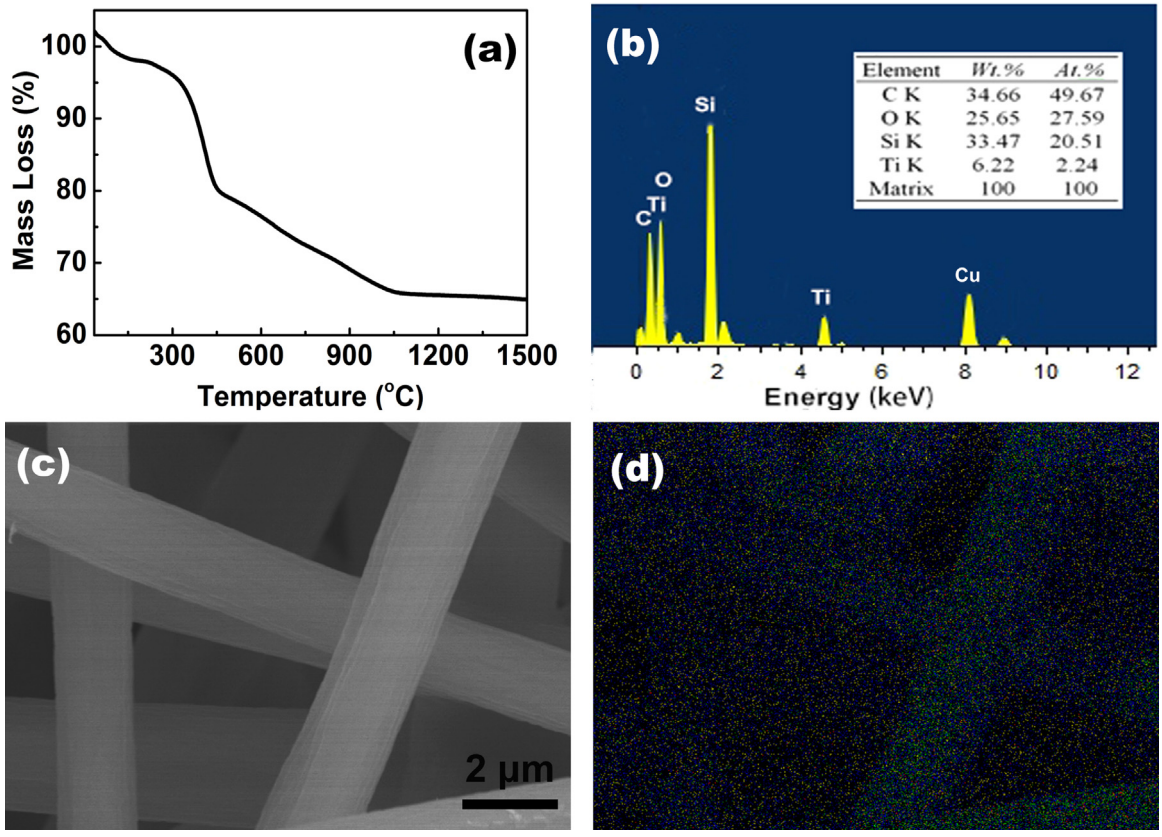

Fig. 1. (a) TGA curves of PTSO fibers in flowing argon, SiOC/TiO_2 fibers: (b) EDS spectrum, (c) SEM image and (d) elemental mapping (blue: Si, green: O, red: C and yellow: Ti). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

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