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Preparation and heat-insulating property of the bio-inspired ZrO_2 fibers based on the silk template

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Abstract

Natural silk fibers were used as the template to prepare biomorphic ZrO_2 fibers. Silk fibers were first immersed into a $Zr(NO_3)_4$ solution and then sintered in air at high temperatures to produce the final ZrO_2 fibers. Their microstructures, phases, synthesis process, infrared absorption spectra and thermal conductivity were analyzed. The results show that these synthesized fibers retained the morphologies of silk faithfully. These ZrO_2 fibers also obtained the ability of absorbing infrared from the silk, so that they possessed better heat-insulating property than the traditional ZrO_2 fibers.

Keywords: C. Thermal conductivity; D. ZrO_2; Fibers; Silk

1. Introduction

In industry, zirconia (ZrO_2) fiber is usually used as a heat insulator due to its good heat-insulating property. It has been made into the lining of various furnaces, heat-insulating layer in the spacecrafts and aircrafts, diaphragm in the fuel cells, insulating materials in the atomic energy reactors, etc. These days, ZrO_2 fibers can be fabricated mainly by the precursor methods, such as the sol–gel method, the hybrid method, the immersion method, etc. [1–4]. Through these methods, fibrous precursor is obtained first by spinning the solution or collosol that contains zirconic ion. Then ZrO_2 fibers are got by sintering the precursor in air or oxygen. It is obvious that the shapes of these ZrO_2 fibers were completely artificially controlled.

Recently, ceramics mimicking the bio-structures of natural tissues have attracted increasing interest. In comparison to synthetic materials, natural materials such as bamboo, wood, cotton, etc., possess intricate and graceful microstructures formed in a long-term evolution process. Researchers have used these bio-structures as templates to fabricate desired ceramics such as SiC, TiC, Al_2O_3, SnO_2, etc., that retained the micro-morphologies of their original counterparts [5–12]. Results show that natural bio-structures can play an important role in obtaining new ceramic materials with excellent properties. These ceramics may be used for molecular screens, filters, catalyst support, thermal insulation materials, gas-sensing materials, electromagnetic shielding materials, far-infrared radiation materials, etc. The method of using the bio-templates provided a new and effective way to fabricate the materials with excellent properties.

Silk is an animal fiber made by silkworms. Fig. 1 shows the pod and the microstructure of the silk fibers. The main component of the silk is protein. A pile of silk has an excellent heat-insulating property, so it is often made into quilts. In the present work, we just select silk as a natural template to prepare biomorphic ZrO_2 fibers. Their microstructures, phases, synthesis process, infrared absorption spectra and thermal conductivity were investigated. We hope this method could provide a new and handy way to fabricate ZrO_2 fibers with an excellent heat-insulating property.

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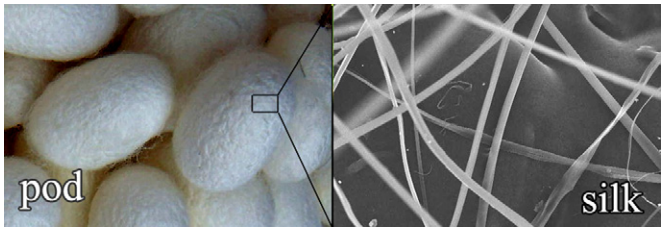

Fig. 1. Images of the pod and microstructure of the silk fibers.

2. Experimental

2.1. Sample preparation

Three groups of silk fibers were first immersed into three $Zr(NO_3)_4$ solutions with different concentrations for 10 min. Their concentrations are 5%, 10%, and 15% with the solvent of water. Then, they were taken out and dried at 70 °C for 12 h. Finally, they were placed in an oxidation furnace and sintered at 800 °C for 2 h. Thus, the silk templates were removed and ZrO_2 fibers were obtained.

2.2. Characterization

The microstructures of the materials were observed by using a scanning electronic microscope (SEM, JSM-6380, JEOL, Japan). The phases of the materials obtained in this study were identified by an X-ray diffractometer (XRD, Cu-Kα, RigakuX 2038, Japan). The immersed silk and the original silk without immersing in solution were analyzed with a thermogravimetric analyzer (TG-DSC, SDT Q600, TA Instruments, US) in air. The temperature ranged from room temperature to 1000 °C. The heating rate was 20 °C/min. The Fourier transform infrared (FTIR) was carried out to the silk and the biomorphic ZrO_2 (obtained by soaking in the 10% solution) by a spectrometer (Magna 560, Nicolet Instrument Corporation, US) in the wave number region 4000–500 cm^{-1}. The samples of FTIR were made by mixing the materials with the KBr pellet, which was followed by pressing disk. To compare with the biomorphic fibers, the FTIR of the ZrO_2 fiber made by the traditional sol–gel method was also measured.

2.3. Thermal conductivity

The thermal conductivities of the ZrO_2 fibers (obtained by soaking in the 10% solution) were measured by the steady-state plate diathermometer. Its thermal conductivity at 100 °C was detected by J60 diathermometer (Shanghai Diathermometer Company, China) and those at 500 and 1000 °C were detected by PBD-02P diathermometer (Luoyang Institute of Refractories Research Co. Ltd., China). The apparent densities of the specimens are 0.096 g/cm^3.

3. Results and discussion

3.1. Microstructures

Fig. 2 shows the full-scale photo of the ZrO_2 derived from silk. It can be seen that this pile of material is composed of fibers, which indicates that the ZrO_2 got the fibriform shape of silk.

Fig. 3a–c shows the microstructures of the ZrO_2 fibers obtained by soaking in the solutions with different concentrations. These fibers retain the original fibrous silk morphology well, as compared with the microstructure of the silk in Fig. 1. The diameters of the ZrO_2 fibers are in the range 10–15 μm. The conformations of these ZrO_2 fibers are controlled by nature, which is different from the traditional oxide fibers.

Fig. 4a and b shows the morphology of the silk fibers and the biomorphic ZrO_2 fibers. The surface of the ZrO_2 fiber is not as smooth as the silk. There are lots of scraggly rumples on its surface, which was formed during the decomposition of the $Zr(NO_3)_4$. It should be noted that many hollow ZrO_2 fibers were found by the microscope. From the arrows in Fig. 4b, it can be seen obviously that the fibers are hollow. This is because that the $Zr(NO_3)_4$ solute only covered the surfaces of the silk fibers after we immersed the silk into the solution and dried it. Then during heating, the solutes on the surfaces decomposed and turned into ZrO_2 in situ, which was followed by removal of silk templates at higher temperature. Hence, after the silk is removed, the hollow fibers as shown in Fig. 4b can be obtained.

From Fig. 3, it can also be seen that the continuity of the fiber after soaking in the solution of higher concentration is better than that of lower concentration. The fibers in Fig. 3a and b have some ruptures and are a little shorter, but the fibers in Fig. 3c are longer. This is because that more $Zr(NO_3)_4$ solute covered the surface of the silk fibers

Fig. 2. Full scale photo of biomorphic ZrO_2.

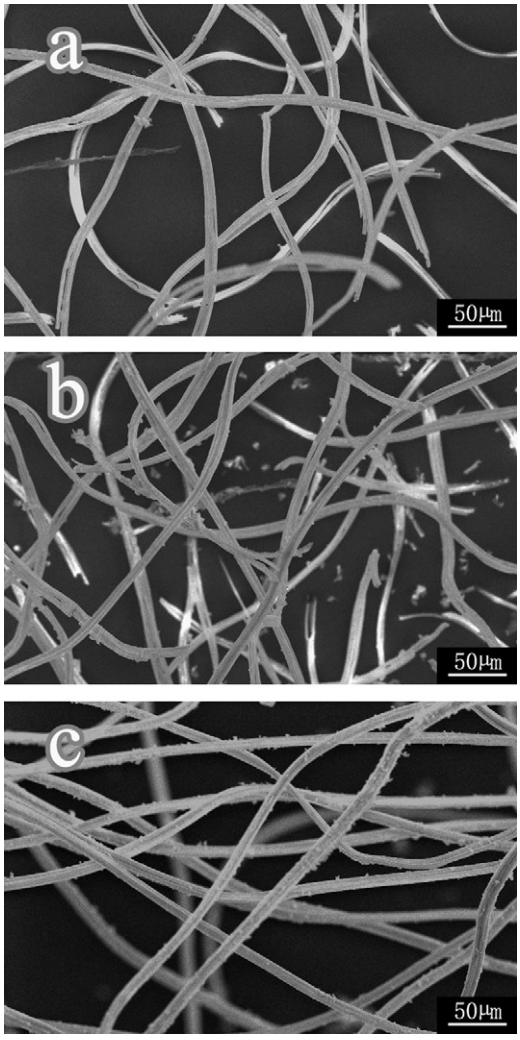

Fig. 3. SEM images of biomorphic ZrO_2 fibers obtained by soaking in the solutions with different concentrations: (a) 5%, (b) 10%, and (c) 15%.

after soaking in the solution of higher concentration. Then, more ZrO_2 formed and covered the silk after sintering. Thus, this ZrO_2 fiber was stronger to keep the shape of silk more perfect when the silk-template was removed. Therefore, their continuity was improved with the increasing concentration.

3.2. XRD

The XRD pattern of the material derived from silk was shown in Fig. 5. The XRD pattern shows that the component of these biomorphic fibers is monoclinic ZrO_2. The average crystallite size of the biomorphic ZrO_2 is 19.40 nm, which was calculated according to the Scherrer equation.

3.3. TG-DSC

Fig. 6a shows the TG-DSC thermogram of the original silk without immersing in the solution. There is a remarkable weight lost between 300 °C and 685 °C, with some

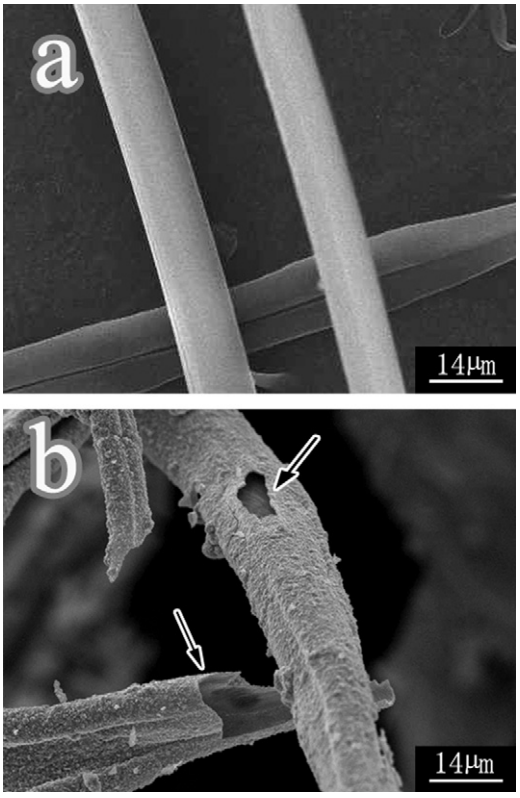

Fig. 4. Morphology of the silk fibers (a) and the hollow ZrO_2 fibers (b).

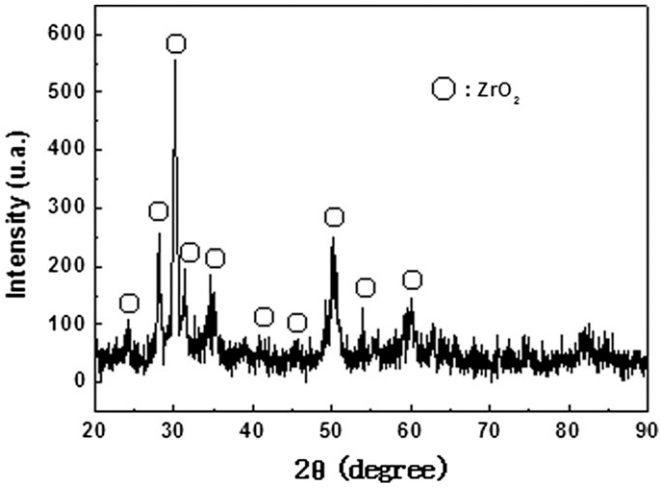

Fig. 5. XRD pattern of ZrO_2 derived from silk.

exothermic peaks being found at 395, 594 and 677 °C. This is due to the decomposition and burning of the silk. Researchers found: silk is composed of two regions: the crystal region and the amorphous region [13]. Since the amorphous region is not as stable as the crystal region, the amorphous region can decompose and burn at lower temperature, as compared to the crystal region. Therefore, the exothermic peak at 395 °C is attributed to the burning of the amorphous region, and the peaks at 594 and 677 °C

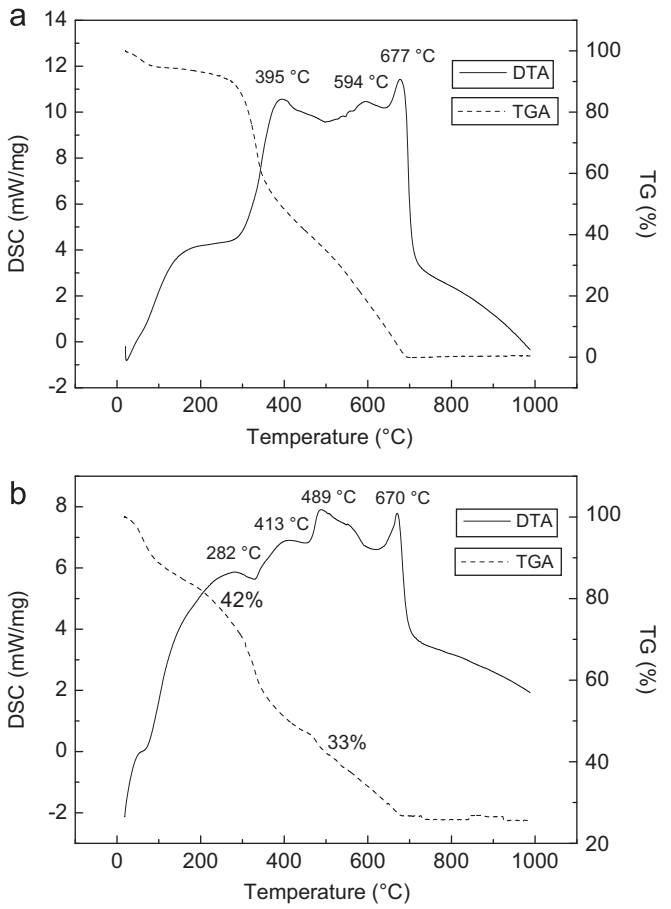

Fig. 6. TG-DSC thermograms of the original silk (a) and the immersed silk (b).

are attributed to the crystal region. Above 700 °C, the weight no longer goes down, but there are still no more than 0.5% residual materials. These remains may be the incomplete decomposed silk.

Fig. 6b shows the TG-DSC thermogram of the immersed samples below 1000 °C. As shown in this figure, there is an exothermic peak at 282 °C before the decomposition of the silk, corresponding to about 42% weight loss. It can be attributed to the decomposition of $Zr(NO_3)_4$ to form ZrO_2. The decomposition of $Zr(NO_3)_4$ was according to the following chemical reaction: $Zr(NO_3)_4 \longrightarrow ZrO_2 + NO_2 + O_2$. There is another 33% weight loss between 340 and 680 °C, with three exothermic peaks being found at 413, 489, and 670 °C. This is due to the decomposition and burning of the silk. Compared to the original silk, the beginning of the decomposition and burning of the immersed silk was remitted to the higher temperature. It may be because of two reasons. One reason is that the silk here was covered with the insulating ZrO_2 that could slow the heat transfer from outside to the silk inside. The other reason is that the oxygen was difficult to penetrate the covering ZrO_2 so that the burning of the silk need higher temperature.

From the TG-DSC thermogram, it can be known that the fabrication process of these biomorphic fibers can be separated into two steps: one is the formation of biomorphic ZrO_2 fibers, and the other is the removal of their silk templates. Since the ZrO_2 formed before the removal of the silk-template, the fibrous morphology of the silk could be retained to this ZrO_2.

3.4. FTIR spectra

Fig. 7 shows the contrast FTIR spectra of the silk, biomorphic ZrO_2 (obtained by soaking in the 10% solution), and traditional ZrO_2. The absorption peaks for the silk sample at 3440, 2920 and 2850, 1660, 1590 and 1450, 1380, 1260, and 1090 cm^{-1} correspond to the N–H in amine, C–H in methene, C═O in carboxyl and C═C in olefin, C═C in arene, C–H methyl, C–O in carboxyl, and C–N in amine. It is obvious that the absorption spectrum of the biomorphic ZrO_2 fiber made from the silk is similar to that of the silk. Most of the peaks of the silk sample emerged in the spectrum of biomorphic ZrO_2, which indicates that the ZrO_2 from silk inherited the good ability of absorbing infrared from the silk. This may be due to the incomplete decomposed silk included in the biomorphic fibers. However, these peaks did not emerge in the spectrum of the traditional ZrO_2 fibers. There are little absorption peaks in its spectrum. It indicates that its ability of absorbing infrared is not as good as the biomorphic ZrO_2 fibers.

3.5. Thermal conductivity

Fig. 8 shows the thermal conductivities of the biomorphic ZrO_2 obtained by soaking in the 10% solution. Fig. 8 also shows the thermal conductivities of the traditional ZrO_2 with the same apparent density (0.096 g/cm^3) as biomorphic ZrO_2, which were summarized in a review article by Hu et al. [14]. It can be seen that the thermal conductivities of the biomorphic ZrO_2 are lower than that of the traditional ZrO_2, especially when the detecting temperature is 500 °C and 1000 °C. It indicates that this

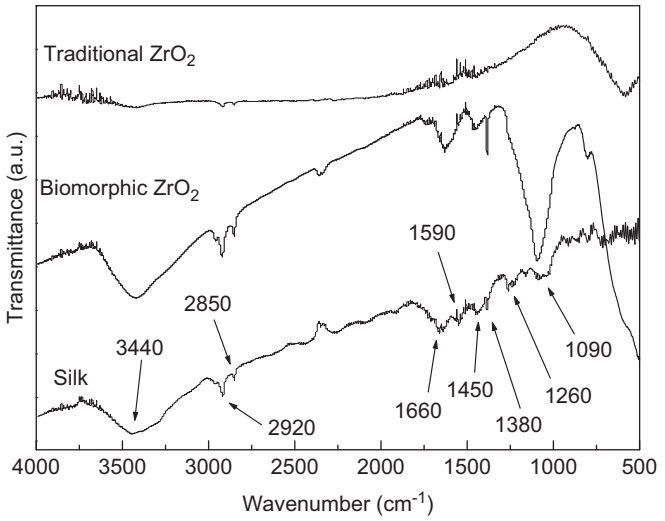

Fig. 7. FTIR spectra of the silk, biomorphic ZrO_2 and traditional ZrO_2.

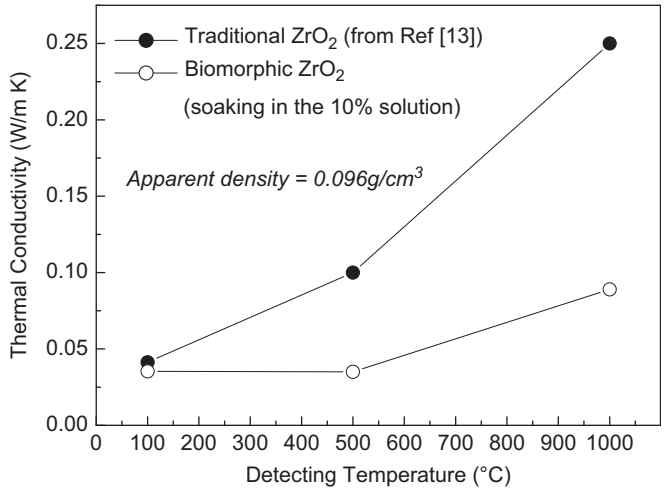

Fig. 8. Thermal conductivities of the biomorphic ZrO_2 and traditional ZrO_2.

kind of ZrO_2 fibers has a much better heat-insulating property than the traditional ZrO_2 fibers. This may be due to two reasons.

One reason is that the hollow ZrO_2 fibers shown in Fig. 4b can prevent the convection of air and heat radiation more efficiently. Since the same apparent densities of these ZrO_2 fibers were used for the test of thermal conductivity, the contents of the air in the specimens were the same. If there were a large number of hollow fibers in the specimen, the air would be divided into more rooms and every room would have smaller volume. Thus, the convection of the air in the specimen would be restricted in each tiny room, and the convection in a wide range would become more difficult. At the same time, the more tiny rooms in the fibers can also cause the shorter mean free path of the photon, which made the heat radiation more difficult.

The other reason is that the incomplete decomposed silk made the biomorphic ZrO_2 fibers inherit the ability of absorbing infrared from the silk, as shown in Fig. 7. It is known that the silk has an excellent heat-insulating property. One of the reasons is that the silk can prevent the heat loss by absorbing the infrared that radiates inside the matter. Now this ability was left behind to the biomorphic fibers, which helped the biomorphic ZrO_2 fibers possess better thermal-insulating property than the traditional ZrO_2.

In Fig. 8, the thermal conductivities of these fibers increase with the rising of the detecting temperature. However, the increment speed of the biomorphic ZrO_2 exhibits much slower than that of the traditional ZrO_2. At low detecting temperature and small temperature gradient, the heat transfer in the fibers was caused mainly by heat transmittance. With the increasing of the detecting temperature and the temperature gradient, the heat radiation and convection of air would become the dominant means for heat transfer gradually. The hollow fibers could keep these two means not progressing too fast, so that the biomorphic ZrO_2 had the lower increment speed of the thermal conductivity.

4. Conclusions

This study provided a new method to fabricate high heat-insulating ZrO_2 fibers by using natural silk fibers as a bio-template. The processing principle of bio-template technologies was to treat the silk fibers with an inorganic solution and then to sinter at high temperature to form biomorphic ceramics. The ZrO_2 fibers retained the basic fibrous silk morphology well. Compared to the traditional ZrO_2 fibers, the biomorphic ZrO_2 has a better heat-insulating property because of its hollow structure and good ability of absorbing infrared that descended from the silk. The treatment by the solutions with different concentration can influence their crystal structures and has an effect on the continuity of ZrO_2. The fabrication process of biomorphic ceramic included the formation of ZrO_2 and removal of their silk templates. Since it is different from the traditional fibers with their structures obtained artificially, this method of using bio-template could provide a new idea for designing of heat-insulating fiber.

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