Preparation of zirconia fiber based on akund template

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Abstract. Zirconia fiber is widely used in the field of fire resistance and heat insulation because of its excellent thermal insulation performance. In this study, the hollow plant fiber, akund, was used as template to prepare zirconia fibers with hollow structure. SEM, XRD, mercury porosimetry, and TG-DSC were used to characterize the microstructure, phase and crystal structure, pore size distribution, and formation process of the zirconia fiber. The analysis shows that the hollow structure restricted the air flow and was conducive to the improvement of thermal insulation performance. Yttria doping made the phase of zirconia fiber stable. Lower heat treatment temperature made the grain size smaller. The concentration of impregnating solution can influence on the fiber morphology.

1. Introduction

Among the common metal oxides, zirconia (ZrO₂) has the highest thermal stability, the lowest thermal conductivity, and the highest melting point (2715 °C), so it is widely used in the field of thermal barrier coating or refractory parts [1-6]. At present, most of the refractory ceramic fiber made by traditional technology is solid structure. The porosity of the solid fiber is low, which is not conducive to the further improvement of the thermal insulation performance [7]. The researchers found that there were a series of plant fibers with micron-level hollow structure, and the akund fiber is one of them. The hollow structure can lock the air in a narrow space and reduce the heat convection of air. Therefore, hollow plant fibers will have better thermal insulation performance than solid fibers [8].

In the field of material preparation, biological template method has become an important research direction. It aims to prepare advanced materials that retain the complex microstructure of biology [9]. Researchers have prepared many kinds of materials that retain biological characteristics [10-17]. In this study, we will take the hollow structure of the akund as the template to prepare the hollow ZrO₂ fiber with the biological structure. The effects of preparation parameters on the ZrO₂ fiber, the pore-size distribution of ZrO₂ fiber, and the process of inheriting the hollow structure of plant fiber template were studied.

2. Experimental procedure

The akund was immersed in a solution composed of zirconium oxychloride (ZrOCl₂•8H₂O) and yttrium nitrate (Y(NO₃)₃•6H₂O), in which the mass fraction of ZrOCl₂•8H₂O is 1–10 wt%, and the yttria doping content is 2–8 mol% (calculated according to the final ZrO₂ and Y₂O₃ content). After fully immersed in the solution, the fibers were taken out, squeezed, and dried at 60 °C for 12 hours. Then, the dried fibers were heated to a certain temperature (750, 1000, and 1250 °C) at a heating rate of 3 °C/min and kept warm for 2 h. Thus, ZrO₂ fibers with hollow tubular structure were prepared after...
cooling in the furnace. The mass fraction of the solution, the mole fraction of doped Y$_2$O$_3$, and the heat treatment temperature are shown in table 1.

Field emission scanning electron microscopy (FESEM, quant 250 FEG) was used to observe the hollow structure and continuity of ZrO$_2$ fibers. The phase composition of ZrO$_2$ fibers was characterized by X-ray diffraction (XRD, Bruker-AXS D8 Advance) to analyze the influence of yttria content and temperature on the crystal structure. The pore size distribution of ZrO$_2$ fibers was measured by mercury porosimeter (MIP, POREMMASTER GT-60, QUANTACHROME). TG-DSC (METTLERTGA/DSC1) was used to analyze the decomposition and crystallization temperature of the material during the heat treatment process. The heating rate of the test process is 20 °C/min, and the temperature range of the test is from room temperature to 1200 °C.

### Table 1. Preparation parameters of ZrO$_2$ fiber.

| Sample No. | Concentration of ZrOCl$_2$·8H$_2$O (wt%) | Yttria doping content (mol%) | heat treatment temperature (°C) |
|------------|----------------------------------------|---------------------------|-------------------------------|
| No.1       | 1                                      | 4                         | 1000                          |
| No.2       | 5                                      | 4                         | 1000                          |
| No.3       | 10                                     | 4                         | 1000                          |
| No.4       | 5                                      | 8                         | 1000                          |
| No.5       | 5                                      | 2                         | 1000                          |
| No.6       | 5                                      | 4                         | 750                           |
| No.7       | 5                                      | 4                         | 1250                          |

3. Results and discussion

Calotropis gigantea, a plant of the genus Calotropis in Asclepiadaceae. It is mainly distributed in the tropics and subtropics. The main components of akund include 69% cellulose, 23% lignin, and 3.8% ash. The diameter of a single fiber is about 20 μm. It has a hollow tubular structure, with a hollowness of about 90%. Figure 1 shows a series of fiber pictures of akund. The hollow structure at the fiber section can be seen clearly from Figure 1c [18-19].

![Figure 1](a: fruit; b: morphology of fibers; c: morphology of hollow structure).

Figure 2 shows the micro morphology of ZrO$_2$ fibers prepared using different concentrations of solution, yttria doping content of 4 mol%, and heat treatment temperature of 1000 °C. In general, the ZrO$_2$ fibers kept the natural morphology and hollow structure of akund. Figs. 2a–c are low magnification SEM photos. It can be seen that the fibers prepared at low concentration (1 wt%) have more curls and breakage, which is because the wall of the fiber tube is too thin due to too little solute. The fiber prepared at medium concentration (5 wt%) has better continuity and less bending degree, as shown in Figure 2b. The fibers made at high concentration (10 wt%) are relatively straight, but there is obvious adhesion phenomenon, as shown in Figure 2c. Figs. 2d–f show the cross-section of fibers. It can be seen clearly that the fiber replicated the hollow structure of akund. Compared with the traditional solid fiber, the hollow structure is more conducive to limit the flow of air. Therefore, the
analysis show that the ZrO$_2$ fibers based on the akund template had better thermal insulation performance.

Figure 2. The morphology of ZrO$_2$ fibers prepared with different concentrations of impregnation solution (a, d: 1 wt%; b, e: 5 wt%; c, f: 10 wt%).

Figure 3a shows the XRD patterns of ZrO$_2$ fibers prepared at different heat treatment temperatures (750, 1000, 1250 °C), ZrOCl$_2$$\cdot$8H$_2$O concentration of 5 wt%, yttria doping of 4 mol%. The fibers obtained at these three temperatures are all composed of tetragonal and cubic ZrO$_2$. With the increasing of heat treatment temperature, the half peak width of ZrO$_2$ peak is narrowing, which means the grain growth. The smaller the grain size at lower temperature means that there are more grain boundaries, so that the conduction of phonon is not smooth. Therefore, the smaller the grain size is, the better the thermal insulation performance is [20]. Figure 3b is the XRD pattern of ZrO$_2$ fiber prepared by different doping contents of yttria (2, 4, and 8 mol%), ZrOCl$_2$$\cdot$8H$_2$O concentration of 5 wt%, and heat treatment temperature of 1000 °C. It can be seen that with the increase of yttria doping content, ZrO$_2$ changed from monoclinic phase (m-ZrO$_2$) to tetragonal phase (t-ZrO$_2$) and then to cubic phase (c-ZrO$_2$).

Figure 4a shows the pore size distribution of the hollow ZrO$_2$ fiber and the traditional solid ZrO$_2$ fiber. The main pore size of the hollow fiber is far lower than that of the solid fiber. The pore size of hollow fiber is mainly between 8–64 μm, while that of solid fiber is more than 64 μm. Generally, the smaller the inner pore diameter of the porous material with the same apparent density is, the better the thermal insulation performance is [21].
Figure 3. XRD patterns of ZrO$_2$ fiber based on akund template (a: different heat treatment temperature; b: different yttria doping content).

Figure 4b shows the TG-DSC curves of the precursor after soaking in impregnating solution and drying. It can be seen that the heat treatment is divided into four processes, the first of which is from room temperature to about 130 °C, corresponding to the loss of water adsorbed by the precursor fiber, with a mass loss of 15.20%. The second process is about 130–311 °C, which corresponds to the loss of crystal water in the solute attached to the fiber surface. This process has a mass loss of about 19.04%. The third process is 311–600 °C, which is mainly the combustion and decomposition of the fiber, the decomposition of solute, and the initial formation of ZrO$_2$ crystal. This process is accompanied by 44.56% mass loss. The last process is above 600 °C, corresponding to the phase transformation and crystal growth of ZrO$_2$, with a mass loss of 2.3%.

Figure 4. a: Pore size distribution of hollow and solid ZrO$_2$ fiber; b: TG-DSC curve of the precursor fiber after soaking in ZrOCl$_2$ solution and drying.

4. Summary
In this paper, we prepared hollow ZrO$_2$ fiber with natural structure by using akund as the template. The obtained ZrO$_2$ fiber kept the shape of the template fiber, and presented a hollow structure. The analysis show that the hollow structure divided the space into smaller parts, restricted the air flow, and was conducive to the improvement of the fiber's thermal insulation performance. Yttria doping made the phase of zirconia fiber stable, which could avoid the volume change in the process of phase transformation. Lower heat treatment temperature made the grain size smaller. When the concentration of impregnating solution was too small, the fiber had more breakage. When the concentration of
Impregnating solution was too high, the fiber would stick. So the concentration of impregnating solution should be moderate.

5. References

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