YAG/Al$_2$O$_3$/ZrO$_2$ composite fibers of core-shell structure prepared by electrospinning

Ling He$^{a,b}$, Shuang Cao$^{a,b}$, Wensheng Li$^{a,b}$, Qizheng Dong$^{a,b}$ and Weimin Sun$^{a,b}$

$^a$State Key Laboratory of Advanced Processing and Recycling of Nonferrous Metals, Lanzhou University of Technology, Lanzhou, China; $^b$School of Materials Science and Engineering, Lanzhou University of Technology, Lanzhou, China

ABSTRACT
As the performance of each component is complementary, the performance of alumina-based as the performance of each component is complementary, the performance of alumina-based-composite fiber is much better than single-component fiber. However, it is difficult to prepare composite fiber is much better than single-component fiber. However, it is difficult to prepare as the performance of each component is complementary, the performance of alumina-based as the performance of each component is complementary, the performance of alumina-based-composite fiber is much better than single-component fiber. However, it is difficult to prepare composite fiber is much better than single-component fiber. However, it is difficult to prepare composite fiber was successfully prepared by electrospinning method. The effects of spinning process parameters on structure and the morphology of composite fibers were studied, such as applied voltage, tip-collector distance, polymer concentration, etc. The result showed the YAG/Al$_2$O$_3$/ZrO$_2$ composite fibers with a smooth surface and an average diameter of 250 nm were obtained when the polymer concentration was applied voltage was 25 kV, the tip-collector distance was 16 cm, calcination and the temperature was 1300°C. It was also found YAG/Al$_2$O$_3$/ZrO$_2$ composite fibers were single crystal with core-shell structure and then the formation mechanism of fiber was studied.

1. Introduction

Alumina (Al$_2$O$_3$) zirconia (ZrO$_2$) and yttrium aluminum garnet (YAG) exhibit optimal chemical compatibility and similar thermal expansion coefficients.

Al$_2$O$_3$: 8.4×10$^{-6}$–6K$^{-1}$, ZrO$_2$: 7.5×10$^{-6}$–6K$^{-1}$, along with high melting points and excellent oxidation resistance and they could complement each other in performance. A number of studies have reported that the YAG/Al$_2$O$_3$ (ZrO$_2$) composites as reinforced materials showed good mechanical property and stability, such as YAG/Al$_2$O$_3$ binary system [1–3], Al$_2$O$_3$/ZrO$_2$ binary system [4,5] and YAG/Al$_2$O$_3$/ZrO$_2$ ternary system [6,7]. All these researches found that YAG/Al$_2$O$_3$ (ZrO$_2$) composites are superior to the individual components for metal-based reinforcement. During recent decades, more studies have focused on the alumina-based composite fibers due to the advantages of large aspect ratio, favorable mechanical, physical, chemical properties and excellent ability to combine as reinforcing agents [8]. For instance, Pan L., and Li W [9] reported the preparation of YAG/Al$_2$O$_3$ fibers by electrospinning technology. In another study, the YAG/Al$_2$O$_3$ [10,11] composite fibers were formed by the sol-gel method. These composite fibers exhibit more high strength and creep resistance than the single component fiber. J. H. Lee [12] prepared YAG/Al$_2$O$_3$/ZrO$_2$ ternary eutectic fibers by micro-drawing. The hardness and tensile strength of the fibers reached 17.4 GPa and 1100 MPa respectively, which showed the mechanical properties are superior to the binary systems. The diameter of the fibers prepared by these methods ranges from a few microns to tens of microns and it is difficult to obtain smaller diameters and controllable morphology. As far as we know, there was shortage of research on the fabrication of ternary composite fibers with controllable morphology.

Electrospinning technology has been widely used as a simple and versatile method for preparing ultra-thin polymer fibers and ceramic fibers with diameters from tens of nanometers to microns [13–17]. The morphology and property of the fibers depend on the properties of the materials and the electrospinning parameters, including the polymer concentration, applied voltage, and tip-to-collector distance. The fibers prepared by electrospinning represent the characteristics of continuity, controllable diameter and morphology, high aspect ratio, etc.

In this study, YAG/Al$_2$O$_3$/ZrO$_2$ composite fibers were synthesized by electrospinning method. The process parameters effect on structure and morphology.
were studied in detail, and the formation mechanism of the fibers was researched.

2. Materials and methods

The projection of the liquidus surface for the Al2O3-ZrO2-Y2O3 system was shown in Figure 1 [18]. In this study, the ternary stable eutectic E4 has been selected for reporting the raw.

The molar ratio of the eutectic composition of material ratio. Correspondingly, polyvinyl alcohol (PVA), aluminum nitrate (Al(NO3) 3·9H2O, 99.00%), yttrium oxide (Y2O3, 99.99%), citric acid (C6H8O7·H2O, 99.50%), zirconium oxychloride (ZrOCl2·8H2O, 99.00%), and nitric acid (HNO3) were used as raw materials. PVA was used as a gel, whereas deionized water and ethanol C2H5OH (A.R.) were used as solvents. A specific amount of PVA (8 ~ 10 wt. %) particles was dissolved in deionized water while stirring, followed by heating to 90°C in a thermostatically controlled water bath to obtain the PVA sol with specific viscosity. Y2O3 was dissolved in concentrated nitric acid, and Al(NO3)3·9H2O, C6H8O7·H2O, ZrOCl2·8H2O, and C2H5OH were added to the PVA sol. The homogeneous precursor sol was subsequently stirred using magnetic stirrer for 4 h.

Precursor fibers were prepared by electrospinning method. The selected electrospinning parameters were as follows: the tip-collector distance maintained at 14 ~ 20 cm, applied 8~10 wt. % voltage maintained at 15 ~ 30 kV, polymer concentration maintained atand feeding rate of the precursor sol of about 1.0 mL/h. The precursor fibers were subsequently collected and dried at 80°C for 3 h in a drying oven, followed by heating to 500°C for 4 h in a muffle furnace for removing C and H. Afterward, the samples were respectively calcined at 900°C, 1000°C, 1100°C, 1200°C, 1300°C, or 1350°C for 5 h under nitrogen atmosphere. The heating rate was 5°C/min before 900°C and 1°C/min after 900°C.

The phase of YAG/Al2O3/ZrO2 composite fibers determined by X-ray diffraction analysis IR spectra were (XRD BRUKER, AXS, Germany) using CuKα radiation (λ = 1.54178Å). recorded as on FT-IR spectrometer ( Nicolet, Waltham, MA) after mixing the sample with KB recorded as on FT-IR spectrometer (Nicolet, Waltham, MA) after mixing the sample with KB. The diameter and surface morphology of the samples were characterized using field emission scanning electron microscope (SEM, JEM 6700 F) at an accelerating voltage of 5 kV. The crystal structure of the sample was characterized using Transmission Electron Microscope (TEM, TECNAL G2).

3. Results and discussion

3.1. Spinning process

The effect of spinning process parameters on spinning phenomenon was shown in Table 1.

A small working distance led the solvent does not have sufficient time to evaporate completely so that the fiber diameter was larger. The distance during 16 cm to 18 cm, spinning process tends to be stable and the fibers with uniform diameters can be obtained. If the tip-collector distance was too large, because at larger distances electric field strength was decreased and the fiber jet became too small and unstable, it was easy to form the larger diameter fibers. Overall, the optimal tip-collection distance was 16 cm.

When the applied voltage was lower than 15 kV, it was hard to spin any fibers. As the applied voltage
increased to 20 kV, spinning process was slow and few beads were found on the surface of the precursor fibers. On further increasing the voltage to 25 kV, the average diameter of the fibers was found to be less than 1 µm with a smooth and cohesionless surface. At a voltage of 30 kV, the diameter of the precursor fibers became large, this was because the fast spinning process led to adhesion between the precursor fibers. Therefore, 25 kV was confirmed to be the optimum applied voltage.

It was hard to spin any fibers when the PVA concentration was below 8 wt. %, and only a great number of beads on the collector were observed. At the PVA concentration was 8 wt. %, precursor fibers were produced. As the PVA concentration was enhanced to 10 wt. %, the diameter of the precursor fibers was found to decrease and the surface was smooth and uniform. On further increasing the PVA concentration, the spinning became difficult and the precursor fibers diameter increases. This was because the large viscosity leads to incomplete fiber tensile refinement. Hence, the optimal PVA content was 10 wt. %. From this point onwards, the spinning has been performed by taking the PVA concentration of 10 wt. %, applied voltage of 25 kV and tip-collector distance of 16 cm.

The effect of spinning process parameters on the diameter of the precursor fibers was shown in Figure 2.

| Process parameters | Spinning process | Morphology |
|--------------------|------------------|------------|
| Tip-collector distance | Spinning difficulty | Coarse fiber |
| 14 cm | | |
| 16 cm | Suitable speed | Smooth and even |
| 18 cm | Suitable speed | Coarse fiber |
| 20 cm | Spinning difficulty | Coarse fiber |
| Applied voltage | Spinning difficulty | Droplets |
| 15 kV | | |
| 20 kV | Slow spinning | Fine fibers |
| 25 kV | Suitable speed | Fine fibers |
| 30 kV | Spinning difficulty | Coarse fiber |
| PVA content | Spinning difficulty | Droplets |
| 8 wt. % | | |
| 9 wt. % | Slow spinning | Coarse fiber |
| 10 wt. % | Suitable speed | Smooth and even |
| 11 wt. % | Slow spinning | Droplets |
| 12 wt. % | Spinning difficulty | Droplets |

**Figure 2.** Effect of spinning process parameters on the diameter of precursor fiber (a) tip-collection distance, (b) applied voltage, (c) PVA concentration.
The diameter range of the precursor fibers was 0.9 ~ 1.15 µm, with the change of the applied voltage, as shown in Figure 2(b). The diameter range of the precursor fibers was 0.8 ~ 1.7 µm, with the change of the applied voltage, as shown in Figure 2(c). Overall, the diameter of the precursor fibers could be controlled between 0.8 ~ 2.7 µm.

### 3.2. Phase and morphology analysis

Figure 3(a) showed the XRD patterns of the YAG/Al2O3/ZrO2 composite fibers annealed from 900°C to 1350°C for 5 h, respectively. The diffraction peaks of the c-ZrO2 phase were observed after calcining the sample at 900°C, which indicated that the ZrO2 phase appears first. When the sample was calcined at 1100°C, the diffraction peaks of θ-Al2O3, YAIo3 (YAP) phases and the c-ZrO2 phase can be observed. All the peaks can be well indexed to the phase of YAG/Al2O3/ZrO2 after processing at 1300°C, which can be assigned to the standard database of the YAG (JCPDS No. 33–0040), α-Al2O3 (JCPDS No. 46–1212) and c-ZrO2 (JCPDS No. 42–1164) phases. No peaks from any other phase of impurities were found. When the calcination temperature reaches 1350°C, there was no phase transition, only the intensity of the peak increases than 1300°C. Figure 3(b) showed the Rietveld refined XRD data of 1350°C fired sample. Among the samples, the YAG phase was 49.44 wt. %, the Al2O3 phase was 31.54 wt. % and the ZrO2 phase was 19.01 wt. %. The molar ratio for Al/Zr/Y was noted to be 72/11/17. Conforming to the molar ratio of eutectic composition Consideration of energy saving, the calcination temperature of precursor fiber was 1300°C.

Figure 4 showed the FT-IR spectra of the precursor YAG/Al2O3/ZrO2 composite fibers before and after calcination at different temperatures, respectively. The broad absorption peak which near 3500 cm−1
can be attributed to the O–H vibrations of water and PVA [19].

Peaks located at 1320 cm⁻¹ ~ 2940 cm⁻¹ corresponded to the stretching vibration of C–C, C–O and C–H in PVA [20–25]. The absorption peaks from 800 cm⁻¹ to 1090 cm⁻¹ were attributed to the absorption peak caused by the influence of the adjacent group of M-O-M (M for Y, Al and Zr) [26], and this structure ensures the spinnability of the precursor sol. When the sample was calcined, the absorption peak representing the inorganic substance appeared. The broad absorption peaks in the lower wavenumber range (400 ~ 1000 cm⁻¹) evinced the presence of Al–O (792 and 698 cm⁻¹), Y–O (721 and 571 cm⁻¹), and Zr–O (452 cm⁻¹) [27]. When the sample was heated at 1100°C, absorption peaks were representing Al–O, Y–O, and Zr–O, indicated the presence of ZrO₂, β-Al₂O₃ andYAIO₃ phase in the sample which is consistent with XRD data. The second Y-O absorption peak appeared in the spectrum of sample heated at 1200°C, which is caused by the Y having two lattice positions in the YAG, indicated the appearance of the YAG phase in the sample. By 1300°C, the absorption peak at 2925 cm⁻¹, 2845 cm⁻¹, and 1397 cm⁻¹ represented the crystal character absorption peaks of the ZrO₂ phases, YAG phases and FTIR analysis with wave numbers and bonds as shown α-Al₂O₃ phases, respectively [28,29]. In Table 2. Table 2 showed that with the increase of temperature, the characteristic peaks representing organic matter disappears and the characteristic peak representing Al–O, Y–O, and Zr–O gradually appears, which proves that the composite fiber was gradually formed.

The FT-IR spectra confirmed that the precursor fibers were calcined at 1300°C to form the YAG/Al₂O₃/ZrO₂ composite fibers. Figure 5 showed the SEM images of precursor fibers and YAG/Al₂O₃/ZrO₂ composite.

Figure 5(a) showed that the diameter distribution of the fibers calcined at 1300°C for 5 h. precursor fibers was uniform and no adhesion occurs, indicated that the appropriate. Due to the decomposition of PVA and evaporation of water during annealing, the diameter of the YAG/Al₂O₃/ZrO₂ composite fibers electrospinning parameters have been selected.

As showed in Figure 5(b), when the fibers were calcined at became smaller, about 250 nm. different, indicated that the distribution of ternary components was regular. After further heating, the fiber surface has no obvious change as showed in Figure 5(c), indicated that the fiber surface grows completely at 1200°C In addition, the surface of the composite fibers was smooth and the distribution of fiber diameter was uniform, with no obvious fibers agglomeration. The results showed that YAG/Al₂O₃/ZrO₂ composite fibers with excellent morphology were successfully prepared. (b) calcined at Figure 5. SEM images of YAG/Al₂O₃/ZrO₂ composites fibers (a) precursor; 1200°C for 5 h; and (c) calcined at 1300°C for 5 h.

Figure 6(a) presented a typical TEM image of the YAG/Al₂O₃/ZrO₂ composite fibers. It can be seen that the composite fibers with an average diameter of 250 nm were composed of fine closely linked nanoparticles with a homogeneous diametrical distribution along the axial direction. Figure 6(d) showed the

| Table 2. FTIR analysis with wave numbers and bonds. |
|-----------------------------------------------|
| Temperature (°C) | Wave number (cm⁻¹) | Bond precursor |
|----------------|-------------------|----------------|
| 1100           | 3293 ~ 3500       | O–H           |
|                | 1320 ~ 2940       | C=C, C–O, C–H |
|                | 800 ~ 1090        | M–O–M         |
| 1200           | 3293 ~ 3500       | O–H           |
|                | 929               | Al–O          |
|                | 571               | Y–O           |
|                | 452               | Zr–O          |
| 1300           | 2925              | ZrO₂ characteristic peaks |
|                | 2845              | YAG characteristic peaks |
|                | 1397              | Al₂O₃ characteristic peaks |
|                | 792, 698          | Al–O          |
|                | 721, 571          | Y–O           |
|                | 452               | Zr–O          |
3.3. Growth mechanism of YAG/Al2O3/ZrO2 fibers

During the preparation of the precursor sol, the metal inorganic salts dissolved in water through the solvation reaction to form hydrated ions \([\text{M (H2O)}\text{n}]^{z+}\) (M for Y, Al and Zr, Z is the valency of M ions). The hydrated ions were hydrolyzed under certain conditions (as showed in Figure 7) so that the metal ions existed in different forms as sol. Moreover, the large number of hydroxyl groups on the long PVA chains underwent condensation reactions with the hydroxyl groups on the hydrates of the inorganic ions in the sol system to form the organic-inorganic hybrid chains with high molecular weight.

The precursor YAG/Al2O3/ZrO2 composite fibers were subsequently obtained from the precursor sol by high voltage electrostatic action. The heat treatment destroyed the PVA molecular bonds in the precursor fibers and shortened the distance between Y3+, Al3+, and Zr4+ leading to the oxide crystallization. The spacing between the ZrO2 and Al2O3 phases was noted to be smaller than the spacing between the ZrO2 and YAG phases. Therefore, the interface energy between the ZrO2 and Al2O3 phases was low, and the ZrO2 and Al2O3 phases tended to combined growth during the eutectic growth process [30]. With the increase of calcination temperature, the ZrO2 phase first appeared, and then the Al2O3 phase and the ZrO2 phase were grown combine. The two phases interlaced and distributed axially forming core, the YAG phase distributed on both sides of the axial direction forming the shell, which was consistent with the TEM findings. The core-shell structure fibers were a new type of functional fiber with better properties than core or shell material, which realized the functionalization of fibers [31,32]. The corresponding fiber generation mechanism was showed in Figure 8.
Figure 6. (a) TEM image of YAG/Al2O3/ZrO2 fibers; (b) EDS spectra corresponding to A; (c) EDS spectra corresponding to regions B; (d) HRTEM image of YAG/Al2O3/ZrO2 fibers; (e) SAED patterns of the composite fibers.

Figure 7. Schematic diagram of solvation reaction.
4. Conclusions

In this study, we have successfully prepared single crystal YAG/Al2O3/ZrO2 composite fibers with core-shell structure by electrospinning and can control the morphology of the fibers. The core-shell structure fibers can hinder crack propagation in composites material, which broadens the application of YAG/Al2O3/ZrO2 composite materials. The study of fiber structure provides theoretical support for subsequent experiments.

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Disclosure of potential conflicts of interest

No potential conflict of interest was reported by the author(s).

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