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Electrospun fabrication, excellent high-temperature thermal insulation and alkali resistance performance of calcium zirconate fiber

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ABSTRACT

$CaZrO_3$ (CZO) precursor fibers were prepared by sol-gel method and electrospinning technique from solutions which contained aqueous precursors of calcium and zirconium ions and polyethylene oxide. The crystallization of CZO fibers was a concurrent process with the decomposition of organics. The evolution process was characterized by Fourier transform infrared (FT-IR) and Raman spectra, thermogravimetry and differential scanning calorimetry (TG/DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The heat-conducting property and high temperature stability of fibers were characterized by the measurements of thermal conductivity and heating permanent linear change, respectively. The fibers were treated in NaOH solution at 80 °C to characterize the alkali resistance. The results showed that CZO fibers had the lower thermal conductivity than the other reported forms of CZO materials, and they possessed excellent stability up to 1100 °C with thermal shrinkage less than 1.2% and excellent corrosion resistance to alkalis. Hence, CZO fiber could be used as a suitable corrosion resistant refractory material for high-temperature thermal insulation.

1. Introduction

Calcium zirconate ($CaZrO_3$, CZO) is a kind of compound with the highest CaO content and most stable in $CaO\text{-}ZrO_2$ system, with an orthorhombic perovskite structure of slightly deformed [ZrO_6] and [CaO_8] polyhedra at low temperatures. It undergoes a polymorph transformation from orthorhombic-CZO to cubic-CZO at 1750 °C and melts at 2340 °C [1]. Owing to the low loss tangent, high dielectric constant with the low temperature coefficient, it can be used in multilayer ceramic capacitors and dielectric resonators, especially for microwave applications [2]. CZO additions have been observed to greatly improve the dielectric constant and temperature coefficient of capacitance (TCC) behavior in $BaTiO_3$-based capacitors [3]. CZO also attracts much attention because that undoped CZO is a p-type semiconductor in air. When doped with oxides such as $A1_2O_3$, Y_2O_3 and MgO or with a small excess of ZrO_2 or CaO, it becomes predominantly an oxygen-ion conductor [4,5]. Moreover, it can be used as sensors for monitoring oxygen, humidity and hydrogen [1]. CZO can be an effective heterogeneous base catalyst for the manufacture of biodiesel, and it has a high durability of catalytic activity [6].

Due to the high melting point, excellent thermal and chemical stability, and good thermal shock resistance [7], CZO has been widely used as one of refractory materials [8]. The comparatively lower thermal conductivity than yttria stabilized zirconia (YSZ), renders it to be a convenient candidate for some thermal barrier coating applications [9]. CZO could prevent accretion growth through the formation of liquid phases at the inclusion refractory interface to improve the clogging of submerged entry nozzles (SENs) and tundish well nozzles in the continuous casting of aluminum-killed steels [10]. The good corrosion behavior of the 80% MgO and 20% $CaZrO_3$ (wt%) materials supported their use as a matrix in magnesia chrome-free bricks for the burning zone of rotary cement kilns [11]. Owing to the excellent corrosion resistance to alkalis, CZO was evaluated as a crucible material and identified that it was a suitable corrosion resistant refractory material for titanium alloy melts, especially for the alloy Ti_6Al_4V [12].

Several methods have been used for the fabrication of CZO such as solid-state reactions [13–15], co-precipitate method [5,16,17], sol-gel method [18], molten salt [19] and high-energy ball milling [20]. All above-mentioned methods focus on producing powders, dense ceramics, and ceramic nanopowders. Over the past decade, one-dimensional (1-D) nanostructured materials have made rapid development and received a high degree of attention because of their interesting applications such as adsorption, catalysis, and electronics [21,22]. Refractory fiber is a kind of 1-D materials with many advantages of light weight, good heat stability, low thermal conductivity, small specific heat, and resistance to mechanical vibration. The superiorities of fiber

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morphology and CZO itself high melting point, low thermal conductivity, good alkali resistance would give CZO ceramic fibers some more advantages in high-temperature thermal insulation applications. Among the many methods employed to prepare refractory fibers, electrospinning technique is one of the most widely applied methods due to its simplicity, low cost, and high yield [23].

Recently, the preparation and preliminary high-temperature-test of CZO fibers by the centrifugal spinning technique have been reported by our group [24]. Compared to centrifugal spinning, the fibers fabricated by electrospinning are exceptionally long in length, small and uniform in diameter, which makes the fibers have good mechanical properties, low thermal conductivity and excellent temperature resistance. To our knowledge, no results have been reported about the fabrication of CZO ceramic fibers by electrospinning. In the paper, the CZO ceramic fibers were prepared by using the electrospinning technique, and the parameters in the preparation process were explored. The evolution process of the precursor fibers to polycrystalline fibers was discussed in detail. Meanwhile, the variation of microstructures of CZO ceramic fibers heat-treated at different temperatures was analyzed. Finally, the thermal conductivity, high-temperature stability and alkali resistance of fibers were also provided and discussed.

2. Experimental procedure

2.1. Materials

Basic zirconium carbonate ($Zr(OH)_2CO_3{\cdot}nH_2O$, BZC, $ZrO_2 \geq 40\%$, Zibo Guangtong Chemical Co., Ltd.), glacial acetic acid (CH_3COOH, ≥ 99.5%, Shandong Luzhong Chemical Co., Ltd.), anhydrous methanol (CH_3OH, ≥ 99.5%, Shandong Luzhong Chemical Co., Ltd.), calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$, CN, ≥ 99.0%, Tianjin Guangcheng Chemical Co., Ltd.) and polyethylene oxide (PEO, Mw ~ 1,000,000, Aladdin, Shanghai, China) were used as starting materials without further purification.

2.2. Preparation of CZO fibers

BZC (10.000 g) was mixed with 5.000 g glacial acetic acid in anhydrous methanol with stirring at 65 °C until the solution became clear, that would form the linear polymers polyaceticzirconium (abbreviated as PEZ). Then 9.569 g CN and 0.116 g PEO were added to the above solution and stirred until the solution became transparent. The resulting solution was formulated to 54 g with anhydrous methanol and the viscosity of the sol was 15 mPa·s at 25 °C. This was a new system to prepare CZO, which was much simpler than our previously reported method [24]. Precursor fibers were obtained by using the electrospinning technique. The effect of process parameters on fiber morphology and diameter were studied. The parameters were optimized with the voltage of 14 kV, the distance of 20 cm between needle and collector and the flow rate of 1.5 mL/h with the environmental temperature and humidity of 28 °C and 35%, respectively. Subsequently, the precursor fibers were heat-treated in air with the established heat treatment schedule. A slow heating rate of 1 °C/min from room temperature up to 600 °C was hoped to remove the organics gradually, and then heat-treated to desired temperatures with a heating rate of 2 °C/min. The fibers were held for 1 h at desired temperatures and then cooled down to room temperature naturally.

2.3. Thermal conductivity

The fibers heat-treated at 1000 °C were grinded with 2% PEO aqueous solution and infused in a mold to obtain a sheet (4 mm × 4 mm × 1 mm) under a uniaxial press of 8 MPa for 30 s. The sheet was heat-treated at 800 °C to completely remove the PEO. The thermal conductivity was measured by using a NETZSCH LFA457 instrument (LFA457, NETZSCH, Germany), and the value at each point was the average of triplicate analysis with standard derivation less than 0.01 W/(m K).

2.4. High temperature stability

The fibers heat treated at 1000 °C were collected into a beaker with 40 mL 1 wt% PEO aqueous solution and stirring to get a fiber suspension solution, and PEO was used as binder to keep the board form. Infuse fiber suspension solution in a sand core funnel then vacuum filtrate to get a board. The board was heated at 1000 °C to completely remove the PEO. The as-prepared board was held for 24 h at different temperatures in a furnace. Before the measurement of the heating permanent linear change, the fiber board was cut into several ones with the typical dimensions of 20 mm × 20 mm × 3 mm. Four platinum wires were inserted in each sample on the surface of the diagonal 2–3 mm from the edge as the mark, the distance between each two platinum wires was about 15 mm. The distance before (L_0) and after (L_1) heat-treating between each two platinum wires was measured, and then the permanent changes (L_c) in all directions of the sample could be calculated using the following formula.

$$L_c = \frac{L_1 - L_0}{L_0} \times 100\%$$

2.5. Alkali-resistance

The fibers heat treated at 900 °C were soaked in NaOH solutions with a concentration of 1 or 2 mol/L to characterize the alkali resistance. The treating time ranged from 1 to 24 h. In order to accelerate alkali activity, the solutions were kept at 80 °C in an oven. Before the treatment, all the fibers were washed using acetone in order to clean the fiber surface. After the treatment, the fibers were separated by centrifugation. Then the fibers were dried after washing thrice with distilled water, removing the residual chemical softly.

2.6. Physicochemical measurements

Fourier-transformation infrared (FT-IR, ALPHA-T, Bruker, Karlsruhe, Germany) spectrum recorded in the region 4000–400 cm^{-1} was measured with an RT-DLATGS spectrometer using the KBr pellet method. The thermal behaviors of precursor fibers were studied by thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses using an SDT Q600 V8.3 Build 101 thermal analyzer instrument, ranging from room temperature to 800 °C at a heating rate of 10 °C/min in air. Raman spectrum was measured on a LabRAM HR800 spectrometer equipped with a CCD detector at room temperature and a 632.8 nm laser as excitation. The X-ray diffraction (XRD) data for fibers treated at different temperatures were collected on a Bruker D8 advance X-ray diffractometer at 40 kV and 100 mA with Cu Kα (λ = 1.540598 Å) radiation in the range of 10–80° with a step size of 0.02°. The morphologies and microstructures of the fibers were characterized using scanning electron microscopy (SEM, S-4800, Hitachi, Japan) at an accelerating voltage of 7 kV instrument with an energy-dispersive X-ray spectroscopy (EDS). In order to enhance the conductivity, the samples were gold coated using ion sputter (E-1045, Hitach, Japan) before taking SEM. The density and porosity of the sheets were measured by the Archimedes method.

3. Results and discussion

3.1. Formation of the precursors

Fig. 1 showed the FT-IR spectra of CN, PEZ and PEZ + CN, and the assignments of the spectrum for CZO precursor fiber were listed in Table 1. In the spectrum of precursor fibers, the spectral data of pure PEZ were reported in Ref [25]. The bands at 1567 cm^{-1} was attributed