

# Preparation of yttria-stabilized zirconia fibers from a zirconia sol and their properties

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Yttria-stabilized zirconia (YSZ) fibers various widths ranging from 36 to 66  $\mu\text{m}$  of width were prepared by a drying process at 363 K from a zirconia sol containing 4 mol % yttria with 40 nm of primary particle size. The effects of preparation method on the crystal phase, microstructure and electrical properties of the obtained YSZ fibers were investigated. The obtained fibers were heat-treated at 1473 K for 1 h. The grain size and relative density of the fiber were 126 nm and 97%, respectively. The oxygen ion conductivity of the fiber showed heat-treated at 1473 K is 0.18 S/cm at 1273 K, which is the same as 8 YSZ bulk ceramics.

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## 1. Introduction

Yttria stabilized zirconia ( $\text{Y}_2\text{O}_3$ -stabilized  $\text{ZrO}_2$ ) is widely used owing to its excellent properties such as a high melting point, high strength, and good oxygen ion conductivity etc.<sup>1)</sup> Currently, fibrous zirconia is applied to make molded insulations such as a fiber boards and cloths because of the low thermal conductivity and excellent heat-resistivity. As a special application, zirconia fiber can be used to heat elements utilizing conductivity at high temperature.<sup>2)</sup> Many preparation methods for zirconia fibers have been developed, such as pyrolysis of a polymer containing zirconium salt and zirconia powder, and a spinning method for a gel prepared by a sol-gel method have been developed.<sup>3-8)</sup> However, these methods require high temperature from 673 to 873 K to form fibers. Moreover, stack gas scrubbers are needed because hazardous gases are generated in the thermal decomposition processes.

In the last decade, numerous amounts of reports on nanoparticle preparation have been published.<sup>9)</sup> These nanoparticles are expected as building blocks for nano-structured materials with good performance. Many researchers are making great effort to obtain controlled assembly of the nano-blocks and eventually to obtain materials with well controlled micro- and nano-structure. It is well known that the stable colloid of nanoparticles can make a homogeneous and close packed particle layer by self assembly.<sup>10)</sup> Here, we are focusing on the homogeneity in the self assembled nanoparticle layer films, and have been succeeded in applying the layer for homogeneous ceramic fibers such as silica and taitania by utilizing spontaneous crack generation during drying process.<sup>11-12)</sup> Comparing to the conventional sol-gel process or plastic mold process, this method has several advantages: simplicity in process, easiness in optimization, binder-less, and high green density. Furthermore, this process can use nanoparticles on the

market, as far as they maintain high colloidal stability. Adding to the silica and taitamia, recently, the authors have further reported that unstabilized zirconia and yttria-stabilized zirconia (YSZ) fibers with fiber widths of 71–214  $\mu\text{m}$  can be formed through a drying process at temperature between 341 and 361 K from a sol that includes zirconia with an average particle size of 116 nm synthesized through the hydrolysis of zirconium alkoxide.<sup>13)</sup> However, in our previous studies, some important properties including oxygen ion properties were not well investigated. Furthermore, this unique process, which giving high green density under a strain may affects sintering behavior. Therefore, in the present study, 4 mol % YSZ fibers were prepared from a commercial based zirconia sol containing 4 mol % yttria. The commercial-based sol was employed in this study for easier application in industry. The morphologies, microstructures, thermal behavior, crystal types, and oxygen ion conductivities of the obtained 4 mol % YSZ fibers were investigated.

## 2. Experiments

### 2.1 Preparation of YSZ fiber

The yttria-stabilized zirconia sol (YSZ sol, ZRYS4<sup>TM</sup>) produced by Nyacol Nano Technologies, Inc. (USA) was used in order to prepare 4 mol % YSZ fibers. The sol contains 20 mass % of zirconia as well as 4 mol % yttria, a stabilizing agent. According to SEM observation, shape is spherical and the primary zirconia particle in the sol is 30–40 nm in size. The particle size distribution of the zirconia sol was about 91–182 nm ( $D_{50} = 132$  nm), measured by Dynamic Light Scattering method (Nikkiso, Nanotracer Wave-UT151), its suggested particles formed secondary particle by aggregate. The sol is a monodispersed suspension with high dispersibility. The sol was diluted with distilled water to reduce the zirconia concentration to 2–10 mass % and was then ultrasonically dispersed. The 35 ml of sol was then put into a polypropylene vessel (inner diameter = 40 mm, height = 55 mm, volume = 70 ml), and dried at 363 K in a incubator for 12 h to form YSZ fibers. The obtained fibers were heat-treated at 673 to 1473 K in air for 1 h (heating rate 10 K/min).

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## 2.2 Evaluation of the fiber properties

After the preparation, the properties of the YSZ fibers were evaluated. The average fiber width was estimated based on the widths of about 100 as-prepared fibers randomly selected by an optical microscope. The microstructures of were observed by scanning electron microscope (FE-SEM, JEOL JSM-7600F). The crystal phase of the heat-treated fibers was identified by powder X-ray diffraction method (XRD, RIGAKU RINT-2000). Density was measured by Archimedes' method in degassed distilled water at room temperature. The relative densities of the fibers have been calculated using the theoretical density of 4 mol % YSZ to  $6.05 \text{ g/cm}^3$ .<sup>14)</sup> The electrical property of the fiber was investigated by oxygen ion conductivity. There are few report measurement of electrical properties of fibrous zirconia. The measurement applied the measuring method of the zirconia bulk body.<sup>15)</sup>

The oxygen ion conductivity was measured at temperatures from 873 to 1273 K in air by using an impedance analyzer (Solatron 1260) over the frequency range of 20 Hz to 1 MHz. A platinum paste was applied to both ends of the fiber that was later fired at 1273 K in air for 30 min to form the platinum electrodes. Only the fibers heat-treated at 1273 and 1473 K for 1 h obtained 6 mass % sol were used for the oxygen ion conductivity measurement.

## 3. Results and discussion

### 3.1 Formation of YSZ fiber

In this study, YSZ fibers were successfully obtained by using commercially based YSZ sol the same as using alkoxide derived zirconia sol.<sup>10)</sup> The fibers were generated on wall of the polypropylene vessel bottom. **Figure 1** shows the morphology of the as-prepared fibers formed from a 6 mass % sol. The fibers are pale white in color and approximately 10 mm in length. The YSZ fibers were formed by solidification of zirconia sol at 363 K. It was observed that the behavior of fiber formation varied depending on the zirconia sol concentration. When the sol concentration was 2 mass %, zirconia particles precipitated as a film on the vessel internal wall. YSZ fibers were formed when the sol concentration was above 4 mass %. The authors have reported the fiber formation mechanism from sols (monodispersed particles) of silica and taitania in detail.<sup>11),12)</sup> Fibers are formed only when sol concentration exceeds a certain value, or else films are formed. In the present study, the minimum sol concentration for fiber formation was found to be 4 mass % for ZRYS4™. **Figure 2** shows the schematic representative of fiber formation mechanisms. The fiber forms in the following steps: (1) formation of closely packed homogeneous zirconia film; (2) generation of cracks by shrinking of the film; (3) formation of fibers by propagation of the cracks. As described in the our previous reports,<sup>11)</sup> the colloidal suspension makes self-assembled particle film on the vessel wall during drying, and the fibers were generated by spontaneous crack generation and propagation during drying of the particle film. In this kind of process, the crack generation rate is affected by the mechanical strength of the film and tensile stress generated during drying. The mechanical strength of the film is determined by the particle interaction and film thickness. If the film was too thin with high strength, crack could not be generated and particle films are obtained rather than fibers. In the current case, the YSZ particle size and film thickness was almost the same with the previous study (alkoxide derived zirconia).<sup>13)</sup> The tensile stress is considered to be almost the same. Therefore, the requirement of higher concentration for fiber formation can be attributed to higher film strength, probably

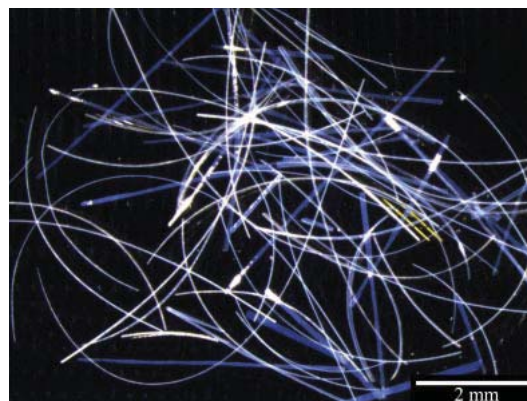


Fig. 1. (Color online) Photograph of as-prepared YSZ fiber. Sol conc.: 6 mass %, Drying temp.: 363 K.

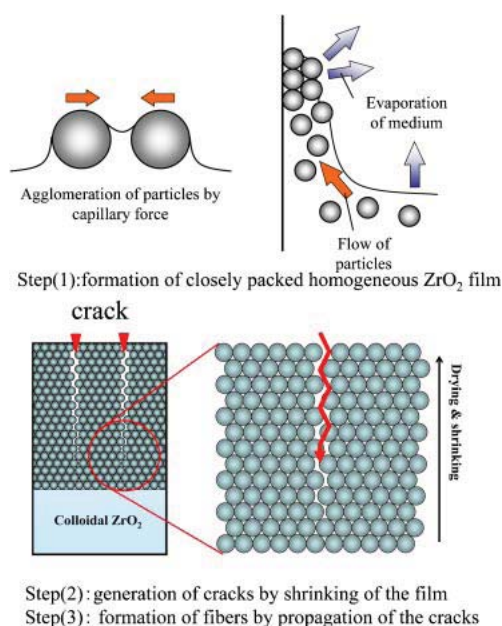


Fig. 2. (Color online) Schematic representation of fiber generation mechanisms.

caused by the dispersant in the colloid solution, particle morphology or packing density.

An optical micrograph of fiber formed from a 6 mass % sol is shown in **Fig. 3**. The fiber widths are almost uniform  $46 \mu\text{m}$  in average. **Figure 4** shows the effect of sol concentration on fiber width. The average width for the fibers prepared from 4, 6 and 10 mass % of sol concentration were 36, 46 and  $66 \mu\text{m}$ , respectively. The increasing tendency of fiber width with sol concentration can be observed. This phenomena was similar with our previous study. The thicker (i.e., higher strength) film requires higher tensile stress by making spacing of cracks larger.

### 3.2 Thermal properties of YSZ fiber

**Figure 5** shows the TG-DTA curves of the as-prepared YSZ fibers. The TG-DTA curves of the samples showed an endothermic peak along with 8% of weight loss at temperatures below 43 K, corresponding to the thermal dehydration and/or evaporation of physically adsorbed water. A sharp exothermic peak with 10% of weight loss was observed at the temperature between 513 and 703 K, indicating the decomposition of some

organic materials (i.e. dispersant agent) following up on the crystallization of yttria stabilized zirconia.<sup>16,17</sup> This crystallization temperature agrees well with XRD results.

The XRD spectra for the 4 mol% YSZ fibers heat-treated at various temperatures are shown in Fig. 6. The as-prepared 4 YSZ fiber reveals an amorphous-like monoclinic structure. Cubic phase can be observed for the fibers heat-treated at above 673 K showed. Crystallinity increased with increase of heat treatment temperature. Except for the cubic phases, some tetragonal phases also existed as evidenced by the asymmetry and slight broadening of the peak in the spectra. According to the equilibrium phase diagram for zirconia-yttria system reported by R. Ruh et al., it is considered that a mixture of tetragonal and cubic phase is obtained temperature above at 773 K.<sup>18,19</sup>

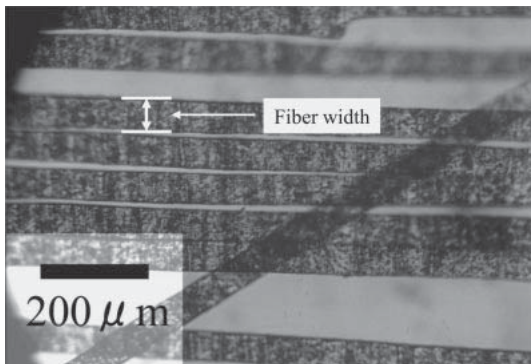


Fig. 3. Optical micrograph of as-prepared YSZ fiber. Sol conc.: 6 mass %, Drying temp.: 363 K.

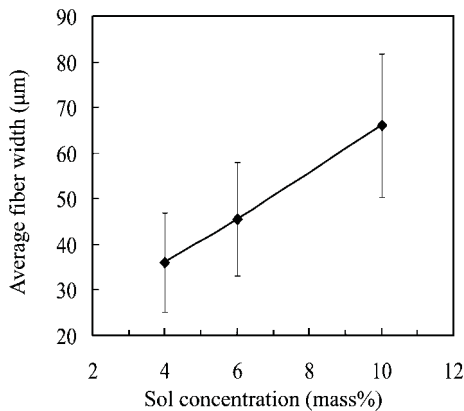


Fig. 4. Effect of sol concentration on fiber width. Drying Temp.: 363 K. The error bars represent standard deviations.

### 3.3 Microstructures of YSZ fibers

The SEM photographs of the as-prepared fiber generated from a 6 mass% sol are shown in Fig. 7. The fiber was a rectangular shape. The thickness of the fiber was under 100 μm. From the photograph, it is obvious that zirconia particles were densely packed to form the fiber. The upper surface of the fiber was smooth and flat while the side face was rough.

Figure 8 shows the SEM images of the microstructures of fibers heat-treated at 1273 and 1473 K, respectively. The fiber heated at 1273 K consists of grain 54 nm in diameter and some pores. At 1473 K, the grain size is 126 nm, indicating the grain

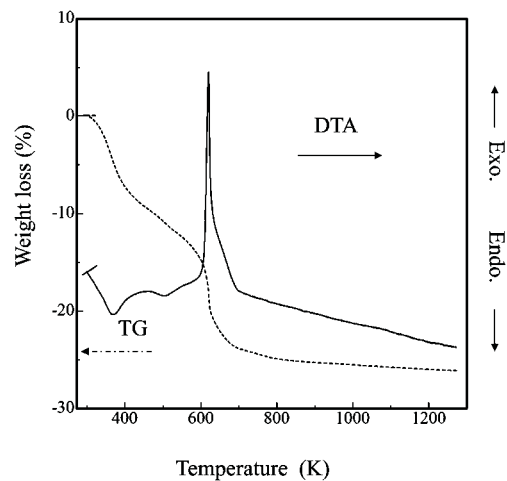


Fig. 5. TG-DTA curve of the as-prepared YSZ fibers.

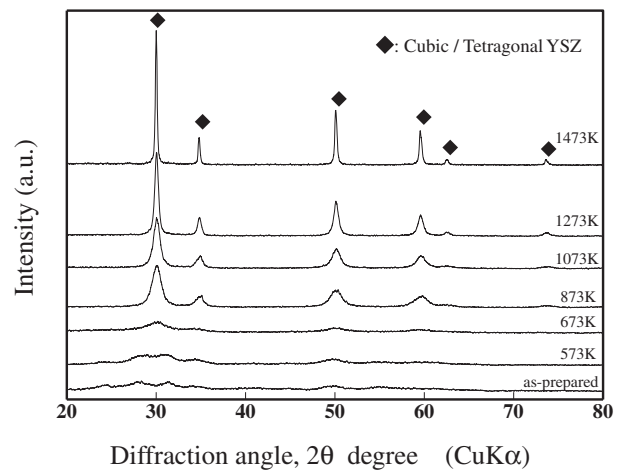


Fig. 6. XRD patterns of YSZ fibers heated at various temperatures. Measured at room temperature.

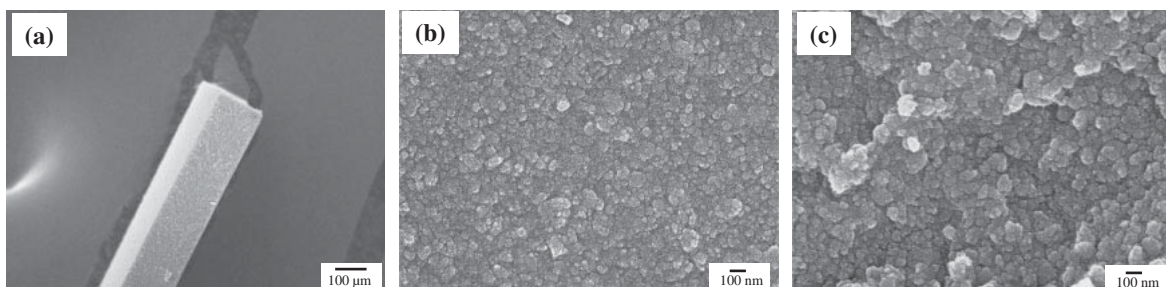


Fig. 7. SEM micrographs of as-prepared fiber. Sol conc.: 6 mass %, Drying temp.: 363 K.

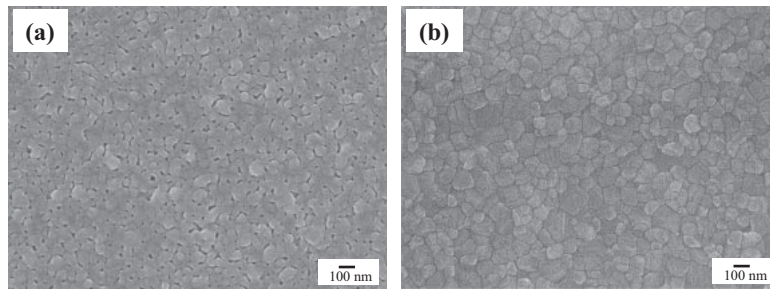


Fig. 8. Effect of heat-treatment temperature on microstructure of YSZ fiber (a) 1273 K and (b) 1473 K.

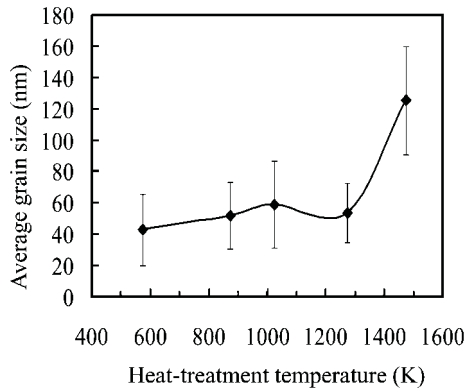


Fig. 9. Effect of heat-treatment temperature on grain size of YSZ fiber. The error bars represent standard deviations.

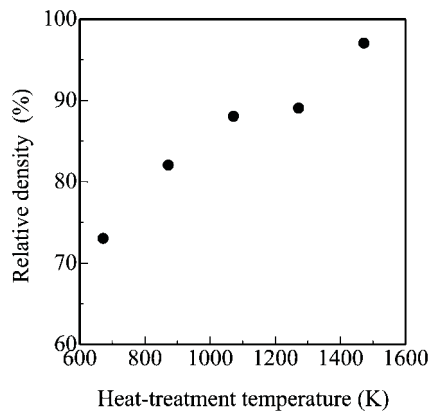


Fig. 10. Effect of heat-treatment temperature on relative density of YSZ fiber.

growth at this temperature. Additionally, pores are disappearing and the dense microstructure is found. **Figure 9** shows the change of grain size with temperature of heat treatment. The average particle size is 43 nm in the fibers heat-treated at 573 K. Although the particle size does not change up to 1273 K, it significantly increases to as large as 126 nm by 1473 K. This is due to grain growth caused by progress of sintering. **Figure 10** shows the variation of relative density of fibers with heat treatment temperature. The relative density of the fibers was as high as 74% just after the drying at 373 K. The relative density increases gradually up to 1273 K, above which it increases abruptly and reaches 97% at 1473 K. This densification behavior of 4 mol% YSZ fibers found in this study coincides with that of 8 mol% YSZ bulk reported by M. C. Stein et al.<sup>20</sup> In case of ordinary YSZ bulk sintered body, it has been reported the relative density reaches 95% or more after sintering at 1673–1773 K

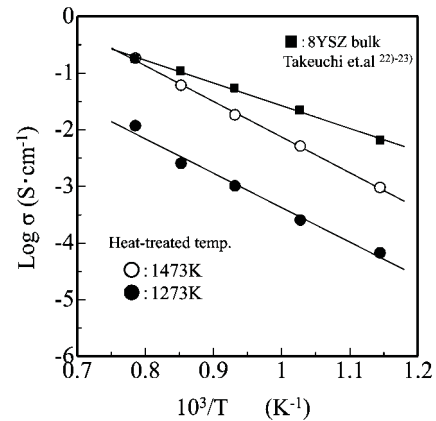


Fig. 11. Arrhenius plots of the oxygen ion conductivities of YSZ fiber.

for 2–4 h. In the present study, YSZ fiber with high density is obtained at lower temperatures by 773 K than that of YSZ bulk sintered body. The small particle size of the initial zirconia as well as the unique microstructure of the as-prepared fibers in which the monodispersed zirconia particles are closely packed by self-assembly are considered to be the reason. Therefore, it is concluded that from the above that, 4 mol% YSZ fibers with fine grain sizes, dense and homogeneous microstructure can be obtained at lower temperatures with the method developed in the present study than the conventional method.

### 3.4 Oxygen ion conductivity of YSZ fibers

YSZ fibers attract scientific and practical interest due to the excellent oxygen ion conductivity. However, studies on the electrical properties of fibrous zirconia are limited, where those of bulk and thin film are widely investigated.<sup>15</sup> A semicircular plot is obtained in the measurement frequency range from 20 Hz–1 MHz. The resistance,  $R$ , is calculated from the  $-Z''_{\max}$  value on the plot by Eq. (1);

$$R = 2 \times (-Z''_{\max}) \quad (1)$$

The oxygen ion conductivity,  $\sigma$ , is calculated by Eq. (2)

$$\sigma = (1/R)(L/S) \quad (2)$$

where,  $L$  and  $S$  are the length and cross-sectional area of sample fiber, respectively.

**Figure 11** shows the Arrhenius plots of the oxygen ion conductivities of the YSZ fibers heat-treated at 1473 and 1274 K. The oxygen ion conductivity of the fiber heat-treated at 1473 K is 0.18 S/cm, higher than 0.012 S/cm that of 1273 K heat-treated fiber at 1273 K. The relative densities of the fibers heat-treated at 1473 and 1273 K are 97 and 88%, respectively. This suggests that the fiber heat-treated at 1473 K has higher oxygen ion con-

ductivity because of the denser structure. It is already known that oxygen ion conductivities of YSZ change with yttria concentration, 8 mol% of yttria results in the highest oxygen ion conductivity for bulk zirconia.<sup>21)</sup> Takeuchi et al. reported that the oxygen ion conductivity of the 8 mol% YSZ bulk prepared by SPS method is 0.18 S/cm at 1273 K.<sup>22),23)</sup> The fibers prepared in the present study gave the same value, 0.18 S/cm with only 4 mol% of yttria. Furthermore, comparison of 4 mol% YSZ fiber and 8 mol% YSZ bulk will also change the value of activation energy. The preparation method, starting materials, crystal phase and microstructure as well as the shape, i.e. fiber, in the present study are considered to be the reason.

#### 4. Summary

YSZ fibers with various widths ranging from 36 to 66  $\mu\text{m}$  were prepared from a commercial-based zirconia sol containing 4 mol% yttria. The effects of morphology and microstructure on the oxygen ion conductivities of the YSZ fibers were investigated. The conductivity of the fiber heat-treated for 1 h at 1473 K (average grain size: 126 nm, relative density: 97%) is 0.18 S/cm at 1273 K, which is higher than the oxygen ion conductivity 0.012 S/cm of the fiber heat-treated at 1273 K for 1 h (average particle size: 54 nm, relative density: 88%). The electrical property of the YSZ fiber heated at 1273 K was same to the conventional 8 mol% YSZ bulk material at 1273 K. This suggests that the fiber heat-treated at 1473 K has a higher oxygen ion conductivity because it has a denser microstructure. Formation of YSZ fiber with fine microstructure has been carried out from commercial zirconia sol (ZRYS4<sup>TM</sup>) under mild condition.

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