Formation of Unstabilized and Yttria Stabilized ZrO₂ Fibers from a Suspension of Monodispersed ZrO₂

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Abstract
Unstabilized and yttria stabilized ZrO₂ fibers were prepared from a monodispersed ZrO₂ particles derived from hydrolysis of Zr(OBu)₄. Unstabilized ZrO₂ fibers with 71 to 151 μm of width and yttria stabilized ZrO₂ fibers with 96 to 214 μm of width, were formed by drying the ethanol suspension of monodispersed ZrO₂ particles with 116 nm in mean diameter. The morphology of the ZrO₂ fibers were plate like and consisted of densely packed ZrO₂ nano particles. The preparation conditions affected the fiber width. This was due to the lower concentration of ZrO₂ particles in suspension, or the higher drying temperatures, which gave the narrower fiber width. The mean particle size of the 5 mol% Y₂O₃ doped ZrO₂ fiber heat treatment at 1473 K was 0.14 μm and the fiber showed 11.0 GPa on the Vickers Hardness Test.

Key-words : Zirconia fiber, Fiber formation, Zirconia sol, Self-arrange particles, Vickers hardness

1. Introduction
Zirconium dioxide is one of the most important ceramics because it has high melting point, high toughness, ion conductivity and high chemical stability. Zirconium dioxide is widely used for electronic and sensor materials or structural materials. It is well known that the performance of ZrO₂ ceramics depends on their shape and microstructure. Therefore, the synthesis, forming and sintering of ZrO₂ have been widely studied.¹,² Zirconia fibers have been manufactured in commercial scale by pyrolysis and oxidation of precursor salt at high temperatures.³ However, there are few reports on synthesis of ZrO₂ fibers consisted of nano particles. If ZrO₂ fibers with fine microstructure and nano particles were prepared, the performance of mechanical and electrical properties of ZrO₂ is expected to be improved. Therefore, development of a new method for the preparation of ZrO₂ fibers with fine microstructure is an important. The present authors have developed a simple and low temperature method to prepare SiO₂ fibers⁴ and TiO₂ fibers⁵ consisted of nano size particles. In this study, the formation of unstabilized and yttria stabilized ZrO₂ fibers was investigated by applying the similar method to that of SiO₂ and TiO₂ fibers, and the effects of the preparation conditions on the morphology, microstructure, crystal phase and mechanical properties of the fibers were investigated.

2. Experiments
Monodispersed ZrO₂ particles were synthesized by hydrolysis of Zr(OBu)₄.⁶ An aqueous HCl solution diluted with ethanol was added to the ethanol solution in which Zr(OBu)₄ was dissolved and the mixed solution was agitated. When the reaction was carried out with HCl catalyst, the reaction solution became turbid in ten seconds to generate ZrO₂ particles. The solution was reserved for 24 h, and then ZrO₂ particles were washed with ethanol by centrifuging to remove impurities such as unreacted Zr(OBu)₄ and HCl. The ZrO₂ particles were re-dispersed in ethanol. Experimental conditions for the synthesized of ZrO₂ particles were as follows: [Zr(OBu)₄] = 0.01 mol, [H₂O] = 0.1 mol, [HCl] = 4 × 10⁻⁵ mol, [EtOH] = 200 ml and reaction temperature: 298 ± 1 K. Under this condition, ZrO₂ particle with 116 nm in average diameter (CV (coefficient of variation) = 18%) was formed and used for fiber formation. The suspension of the ZrO₂ powder was diluted with ethanol by a ultra-sonication to prepare 1.0 to 3.0 mass% particle suspension. The suspensions were then dried in a borosilicate glass test tube (inner diameter = 15 mm) at 341 to 361 K in a drying oven.

For the preparation of yttria stabilized zirconia fiber, yttrium hexahydrate was used for Y₂O₃ source. Yttria stabilized ZrO₂ fibers were prepared by using the monodispersed ZrO₂ synthesized as described above. The monodispersed ZrO₂ particles were suspended in ethanol in which 6 to 20 mol% YCl₃ dissolved, and the suspensions were then dried at 351 K in a borosilicate glass test tube (inner diameter = 15 mm) in a drying oven. The concentration of YCl₃ (6 to 20 mol%) added is corresponding to 3 to 10 mol% of Y₂O₃ for the ZrO₂. The fibers obtained were calcined in air at temperatures between 373 to 1673 K for 1 h. The morphology and microstructure of the fibers prepared were investigated by SEM and an optical microscopy. To obtain the fiber width distributions, 100 samples of fibers were randomly chosen and their width were measured. The crystal structures of the fibers were investigated by XRD (Cu Kα). The lattice parameter was calculated from the diffraction angles, using the silicon powder as an internal standard. Vickers microhardness measurements had been performed using a MVK–E III microhardness apparatus (Akashi, Japan). The yttria stabilized ZrO₂ fibers were mounted in resin and applied 0.98 N of loading and 15 s contact time.

3. Results and discussion
3.1 Preparation of unstabilized ZrO₂ fibers

Figure 1 shows the formation of ZrO₂ fibers on the surface of a glass test tube after drying 2 mass% suspension of monodispersed ZrO₂ at 351 K in the test tube. The fiber generation mechanism is considered to be same as those in SiO₂ and TiO₂ fibers, which have already reported elsewhere.⁴,⁵ The length
of fiber prepared was about 10 to 15 mm. The SEM photographs of ZrO$_2$ fiber generated from 2 mass% suspension are shown in Fig. 2. The morphology of the fiber was a plate like shape. From the photograph, it is obvious that particles were densely packed to form the fiber. The upper surface of the fiber was smooth and flat, but the side face was rough and broken surface concerning the formation mechanism of the fibers. The effects of the preparation conditions on fiber width distribution were investigated with emphasis on suspension concentration and drying temperature. The average width of fibrous ZrO$_2$ prepared from 1.0, 2.0 and 3.0 mass% suspensions was 71, 90 and 151 $\mu$m at 351 K of drying temperature, respectively, and variation coefficient was 18, 16 and 20%, respectively. The fiber width became wider when the particle size became large in preparation of fibers. However, they crystallized into tetragonal and monoclinic phases at around 673 K. The crystal phase became monoclinic completely at 1173 K. The particle size of ZrO$_2$ at 673 K was 116 nm. Therefore, the tetragonal phase appeared at 673 K is metastable phase due to fine particle size.\textsuperscript{7,8}

3.2 Preparation of yttria stabilized ZrO$_2$ fibers

The yttria stabilized ZrO$_2$ fibers were prepared at 351 K by drying the monodispersed ZrO$_2$ suspensions in which YCl$_3$ was added. The effect of the YCl$_3$ concentration on fiber width distribution was investigated. The average width of fibers prepared from the suspensions added 0, 10, and 20 mol% of YCl$_3$ was 90, 96 and 214 $\mu$m, respectively, indicating that the fiber width became wider when the YCl$_3$ concentration increased as shown in Fig. 5. Authors reported that the fiber width became wider when the particle size became large in preparation of SiO$_2$ and TiO$_2$ fibers.\textsuperscript{4,5} The monodispersed ZrO$_2$ particles were coated with YCl$_3$ by addition of YCl$_3$/EtOH solution. The particle size of YCl$_3$ coated ZrO$_2$ increase with increase YCl$_3$ concentration. Therefore, the increase in the fiber width by addition of YCl$_3$ is attributable to the increase of particle size. Figure 6 shows XRD patterns of (a) 3 mol% yttria doped ZrO$_2$ fiber and (b) 5 mol% yttria doped ZrO$_2$ fiber heat-treated at various temperatures. The as-prepared fibers were amorphous as same as the case of unstabilized ZrO$_2$ fibers. However, they crystallized into tetragonal for 3 mol% Y$_2$O$_3$ doped ZrO$_2$ and cubic for 5 mol% Y$_2$O$_3$ doped ZrO$_2$ at around 773 K depending on Y$_2$O$_3$ concentration. It is considered that YCl$_3$ is deposited homogeneously on the surface of various temperatures. Although the as-prepared fibers were amorphous, they crystallized into tetragonal and monoclinic phases at around 673 K. The crystal phase became monoclinic completely at 1173 K. The particle size of ZrO$_2$ at 673 K was 116 nm. Therefore, the tetragonal phase appeared at 673 K is metastable phase due to fine particle size.\textsuperscript{7,8}
Fig. 5. Effect of YCl\(_3\) concentration on fiber width of as-prepared ZrO\(_2\) fibers. ZrO\(_2\) concentration = 2 mass%, drying temperature = 351 K.

Fig. 6. XRD patterns of (a) 3 mol% Y\(_2\)O\(_3\) doped ZrO\(_2\) fibers and (b) 5 mol% Y\(_2\)O\(_3\) doped ZrO\(_2\) fibers heated at various temperatures. Measured at room temperature.

Fig. 7. Effect of heat-treatment temperature on Vickers hardness of Y\(_2\)O\(_3\) stabilized ZrO\(_2\) fibers. Loading weight = 0.98 N, contact time = 15 s.

Fig. 8. Effect of heat-treatment temperature on microstructure of 5 mol% Y\(_2\)O\(_3\) stabilized ZrO\(_2\) fibers. (a) 1273 K, (b) 1473 K, (c) 1673 K.

ZrO\(_2\) particles by evaporation of ethanol during the drying process for fiber formation and then Y\(_2\)O\(_3\) doped ZrO\(_2\) solid solution was formed by calcination at temperatures above 773 K. In the phase diagram of ZrO\(_2\)–Y\(_2\)O\(_3\) system, crystal phase became tetragonal mono phase at 3 mol% of Y\(_2\)O\(_3\) content and it becomes tetragonal-cubic mixed phase above 5.5 mol% of Y\(_2\)O\(_3\) content.\(^9\) In this experiments, mixed phases were not observed. In this study, Y\(_2\)O\(_3\) dissolved into ZrO\(_2\) at low temperatures compared with the case of Y\(_2\)O\(_3\) stabilized ZrO\(_2\) by solid state reaction previously reported.\(^10\) The lattice parameter of 8 mol% Y\(_2\)O\(_3\) doped ZrO\(_2\) fiber heated at 1673 K for 1 h was \(d_a=0.5143\) nm. It was larger than lattice parameter of \(d_a=0.5139\) nm of 8 mol% Y\(_2\)O\(_3\) doped ZrO\(_2\) reported by Pfoertsch and McCarthy.\(^11\)

3.3 Vickers hardness of yttria stabilized ZrO\(_2\) fiber

The mechanical property of the yttria stabilized ZrO\(_2\) fiber formed was evaluated by measuring of Vickers hardness. The effect of heat treatment temperature on Vickers hardness of the fibers is shown in Fig. 7. The Vickers hardness of the fibers increased with increased doped Y\(_2\)O\(_3\) concentration. However, the Y\(_2\)O\(_3\) concentration dependence and temperature dependence of the hardness are changed with heat-treated temperature. The Vickers hardness of fiber shows a maximum at 1473 K of heat treatment temperature. The average Vickers hardness of 5 mol% Y\(_2\)O\(_3\) doped ZrO\(_2\) fibers was 5.3, 11.0 and 4.7 GPa for 1273, 1473 and 1673 K of heat treatment temperature, respectively. The Vickers hardness are significantly influenced by the microstructure of fiber. The mean grain size of the 5 mol% Y\(_2\)O\(_3\) doped fibers heat treatment at 1273, 1473 and 1673 K were 0.13, 0.14 and 0.59 \(\mu m\), respectively as shown in Fig. 8. Although pores were observed in the fibers heated at 1273 K, pores decreased by the progress of sintering and disappeared at 1473 K. The highest Vickers hardness value of the fiber heated at 1473 K is considered to be due to the fine microstructure with fine particle size and high density of the fiber. The Vickers hardness of 8 mol% Y\(_2\)O\(_3\) doped ZrO\(_2\) bulk ceramics heat-treated at 1773 K for 2 h was 11.0 GPa reported by Šomiya and Akiba.\(^2\) The Vickers hardness of 8 mol% Y\(_2\)O\(_3\) doped ZrO\(_2\) fiber heat-treated at 1473 K for 1 h was 10.6 GPa.
4. Summary

Unstabilized and yttria stabilized ZrO\(_2\) fibers were able to prepare from suspensions of monodispersed ZrO\(_2\) particles. Monodispersed ZrO\(_2\) particles with 116 nm of diameter were prepared by hydrolysis of Zr(OBu)\(_4\) in ethanol with hydrochloric acid as catalyst. Unstabilized ZrO\(_2\) fibers with 71 to 151 \(\mu\)m of width and Y\(_2\)O\(_3\) stabilized ZrO\(_2\) fibers with 96 to 214 \(\mu\)m of width were formed by drying the ethanol suspensions of the monodispersed ZrO\(_2\) particles. The effects of preparation conditions on morphology, microstructure, crystal phase and mechanical property of fibers were investigated. The fibers have a plate like shape and were consisted of densely packed nano particles. The unstabilized ZrO\(_2\) fibers crystallized into metastable tetragonal and monoclinic phase at 673 K and transformed into monoclinic phase at 1173 K. Stabilized ZrO\(_2\) fibers became cubic phase by heating at 773 K, when 5 mol\% Y\(_2\)O\(_3\) was added. Mean particle size in the 5 mol\% Y\(_2\)O\(_3\) doped ZrO\(_2\) fiber heat-treated at 1473 K was 0.14 \(\mu\)m and the fiber showed 11.0 GPa of the Vickers hardness. The present method provides Y\(_2\)O\(_3\) stabilized ZrO\(_2\) fiber with fine microstructure to be prepared. The performance of mechanical and electrical properties of Y\(_2\)O\(_3\) stabilized ZrO\(_2\) is expected to be improved. The new application such as fiber reinforcement materials, oxygen sensor etc. is expected.

References

11) Pfoertsch, McCarthy, Penn State University, ICDD Grant-in Aid (1977).