Formation of Unstabilized and Yttria Stabilized ZrO_2 Fibers from a Suspension of Monodispersed ZrO_2

Kenji SHIDA and Yoko SUYAMA

Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060, Nishikawatsu-cho, Matsue-shi, Shimane 690–8504

単分散ジルコニア懸濁液からのジルコニア及びイットリア安定化ジルコニア繊維の形成

志田賢二・陶山容子

島根大学大学院総合理工学研究科, 690–8504 島根県松江市西川津町 1060

Unstabilized and yttria stabilized ZrO_2 fibers were prepared from a monodispersed ZrO_2 particles derived from hydrolysis of $\text{Zr}(\text{OBU})_4$. Unstabilized ZrO_2 fibers with 71 to 151 μm of width and yttria stabilized ZrO_2 fibers with 96 to 214 μm of width, were formed by drying the ethanol suspension of monodispersed ZrO_2 particles with 116 nm in mean diameter. The morphology of the ZrO_2 fibers were plate like and consisted of densely packed ZrO_2 nano particles. The preparation conditions affected the fiber width. This was due to the lower concentration of ZrO_2 particles in suspension, or the higher drying temperatures, which gave the narrower fiber width. The mean particle size of the 5 mol% Y_2O_3 doped ZrO_2 fiber heat treatment at 1473 K was 0.14 μm and the fiber showed 11.0 GPa on the Vickers Hardness Test. [Received December 8, 2005; Accepted May 18, 2006]

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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 the performance of ZrO_2 ceramics depends on their shape and microstructure. Therefore, the synthesis, forming and sintering of ZrO_2 have been widely studied.^{1),2)} Zirconia fibers have been manufactured in commercial base by pyrolysis and oxidation of precursor salt at high temperatures.³⁾ However, there are few reports on synthesis of ZrO_2 fibers consisted of nano particles. If ZrO_2 fibers with fine microstructure and nano particles were prepared, the performance of mechanical and electrical properties of ZrO_2 is expected to be improved. Therefore, development of a new method for the preparation of ZrO_2 fibers with fine microstructure is an important. The present authors have developed a simple and low temperature method to prepare SiO_2 fibers⁴⁾ and TiO_2 fibers⁵⁾ consisted of nano size particles. In this study, the formation of unstabilized and yttria stabilized ZrO_2 fibers was investigated by applying the similar method to that of SiO_2 and TiO_2 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 ZrO_2 particles were synthesized by hydrolysis of $\text{Zr}(\text{OBU})_4$.⁶⁾ An aqueous HCl solution diluted with ethanol was added to the ethanol solution in which $\text{Zr}(\text{OBU})_4$ 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 ZrO_2 particles. The solution was reserved for 24 h, and then ZrO_2 particles were washed with ethanol by centrifuging to remove impurities such as unreacted $\text{Zr}(\text{OBU})_4$ and HCl. The ZrO_2 particles were re-dispersed in ethanol. Experimental conditions for the synthesized of ZrO_2 particles were as follows: $[\text{Zr}(\text{OBU})_4] = 0.01 \text{ mol}$, $[\text{H}_2\text{O}] = 0.1 \text{ mol}$, $[\text{HCl}] = 4 \times 10^{-5} \text{ mol}$, $[\text{EtOH}] =$

200 ml and reaction temperature: $298 \pm 1 \text{ K}$. Under this condition, ZrO_2 particle with 116 nm in average diameter (CV (coefficient of variation) = 18%) was formed and used for fiber formation. The suspension of the ZrO_2 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 Y_2O_3 source. Yttria stabilized ZrO_2 fibers were prepared by using the monodispersed ZrO_2 synthesized as described above. The monodispersed ZrO_2 particles were suspended in ethanol in which 6 to 20 mol% YCl_3 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 YCl_3 (6 to 20 mol%) added is corresponding to 3 to 10 mol% of Y_2O_3 for the ZrO_2 . 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 microscope. 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 $\text{K}\alpha$). 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 ZrO_2 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 ZrO_2 fibers

Figure 1 shows the formation of ZrO_2 fibers on the surface of a glass test tube after drying 2 mass% suspension of monodispersed ZrO_2 at 351 K in the test tube. The fiber generation mechanism is considered to be same as those in SiO_2 and TiO_2 fibers, which have already reported elsewhere.^{4),5)} The length

Fig. 1. Monodispersed ZrO_2 suspension (a) and formation of ZrO_2 fiber (b).

Fig. 2. SEM photographs of unstabilized ZrO_2 fiber. (a) appearance, (b) surface ①, (c) surface ② ZrO_2 concentration = 2 mass%, drying temperature = 351 K.

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 ① of the fiber was smooth and flat, but the side face ② 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 μm at 351 K of drying temperature, respectively, and variation coefficient was 18, 16 and 20%, respectively. The fiber width became wider when the concentration of ZrO_2 particles in the suspension was high. The average width of fibrous ZrO_2 prepared from 2 mass% ZrO_2 suspension was 104, 90 and 74 μm for 341, 351 and 361 K of drying temperature, respectively, showing the narrower fiber width with the higher drying temperature as shown in Fig. 3. It was found that the fiber width was possible to control by the preparation conditions. Figure 4 shows XRD patterns measured at 300 K of ZrO_2 fibers heat-treated at vari-

Fig. 3. Effect of drying temperature on fiber width. ZrO_2 concentration = 2 mass%.

Fig. 4. XRD patterns of unstabilized ZrO_2 fibers heated at various temperatures. Measured at room temperature.

ous 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.^{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 μm , 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.^{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_2O_3 doped ZrO_2 and cubic for 5 mol% Y_2O_3 doped ZrO_2 at around 773 K depending on Y_2O_3 concentration. It is considered that YCl_3 is deposited homogeneously on the surface of

Fig. 5. Effect of YCl₃ concentration on fiber width of as-prepared ZrO₂ fibers. ZrO₂ concentration = 2 mass%, drying temperature = 351 K.

Fig. 6. XRD patterns of (a) 3 mol% Y₂O₃ doped ZrO₂ fibers and (b) 5 mol% Y₂O₃ doped ZrO₂ fibers heated at various temperatures. Measured at room temperature.

ZrO₂ particles by evaporation of ethanol during the drying process for fiber formation and then Y₂O₃ doped ZrO₂ solid solution was formed by calcination at temperatures above 773 K. In the phase diagram of ZrO₂-Y₂O₃ system, crystal phase became tetragonal mono phase at 3 mol% of Y₂O₃ content and it becomes tetragonal-cubic mixed phase above 5.5 mol% of Y₂O₃ content.⁹⁾ In this experiments, mixed phases were not observed. In this study, Y₂O₃ dissolved into ZrO₂ at low temperatures compared with the case of Y₂O₃ stabilized ZrO₂ by solid state reaction previously reported.¹⁰⁾ The lattice parameter of 8 mol% Y₂O₃ doped ZrO₂ 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% Y₂O₃ doped ZrO₂ reported by Pfoertsch and McCarthy.¹¹⁾

3.3 Vickers hardness of yttria stabilized ZrO₂ fiber

The mechanical property of the yttria stabilized ZrO₂ 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 Y₂O₃ concentration. However, the Y₂O₃ 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% Y₂O₃ doped ZrO₂ fibers was 5.3, 11.0 and

Fig. 7. Effect of heat-treatment temperature on Vickers hardness of Y₂O₃ stabilized ZrO₂ fibers. Loading weight = 0.98 N, contact time = 15 s.

Fig. 8. Effect of heat-treatment temperature on microstructure of 5 mol% Y₂O₃ stabilized ZrO₂ fibers. (a) 1273 K, (b) 1473 K, (c) 1673 K.

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% Y₂O₃ doped fibers heat treatment at 1273, 1473 and 1673 K were 0.13, 0.14 and 0.59 μm, 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% Y₂O₃ doped ZrO₂ bulk ceramics heat-treated at 1773 K for 2 h was 11.0 GPa reported by Sōmiya and Akiba.²⁾ The Vickers hardness of 8 mol% Y₂O₃ doped ZrO₂ 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 $\text{Zr}(\text{OBU})_4$ in ethanol with hydrochloric acid as catalyst. Unstabilized ZrO_2 fibers with 71 to 151 μm of width and Y_2O_3 stabilized ZrO_2 fibers with 96 to 214 μm 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_2O_3 was added. Mean particle size in the 5 mol% Y_2O_3 doped ZrO_2 fiber heat-treated at 1473 K was 0.14 μm and the fiber showed 11.0 GPa of the Vickers hardness. The present method provides Y_2O_3 stabilized ZrO_2 fiber with fine microstructure to be prepared. The performance of mechanical and electrical properties of Y_2O_3 stabilized ZrO_2 is expected to be improved. The new application such as fiber reinforcement materials,

oxygen sensor etc. is expected.

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