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Preparation of ZrO_2-CaO fiber by using a chemical solution process

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Abstract In this work, chemical solution derived Ca-doped zirconia fiber has been prepared by using calcium- and zirconium-naphthenate. Fibrous ZrO_2-CaO was drawn from a sticky mixture. Dried gel fibers were finally annealed at 1000°C for 1 h in argon. 91 mol%ZrO_2 - 9 mol%CaO fiber consisted of tetragonal, monoclinic and $CaZrO_3$ phases after annealing at 1000°C. On the other hand, samples annealed at 500°C consisted of almost tetragonal single phase. Homogeneous fibers surface at 500°C became rougher after 1000°C-annealing. The sample annealed at 1000°C with relatively rough surface structure showed a high Calcium phocphate forming ability.

Key words Zirconia fiber, Calcium phosphate

1. Introduction

Pure zirconia has a monoclinic form at temperature lower than 1000~1200°C, but can be stabilized in a tetragonal or cubic form with different dopants, mainly CaO and Y_2O_3 [1-5].

Stabilized ZrO_2 has various applications such as engineering and biomaterials. And if these materials were made to fiber form, it could be used for potential uses in industrial areas [6, 7]. Many works reported the preparation of Y_2O_3- and CaO-doped ZrO_2 fibers prepared by chemical solution process [7-9].

The chemical solution process has been used as an alternative method to prepare ceramic powder, thin films, and fiber. This method often allows the crystallization of metastable phase at relatively lower temperatures where long-range diffusion required for the crystallization of the stable phase or the phase separation can not occur [5, 10].

Generally, in the chemical solution method, the pores and cracks were easily recognized in the product owing to volatilization of organics. At present, available data are limited for the surface properties of ZrO_2-CaO fiber, which could be crucial to the performance of application, in spite of synthesis of metastable phase by chemical solution process would be possible also in the ZrO_2-CaO system.

The aim of the present work has been to analyze the crystal growth and surface morphology of ZrO_2-CaO fiber. Special attention was given to the evaluation of surface topology to use biological application.

2. Experimental Procedure

ZrO_2-CaO fibers were prepared with starting solution from mixture of zirconium- and calcium-naphthenates (Soekawa Rika Co., Ltd., Tokyo, Japan) in toluene. Precursor solutions with 9 mol% Ca are fabricated by mixing zirconium- and calcium-naphthenates. This mixture was dried in a dry oven at 80°C for five days to achieve an appropriate viscosity for drawing of fiber. When the sol became sufficiently sticky, spinnability tests were conducted by pulling fibers from the sticky sol with a glass bar. Then the sol fiber was placed back into the dry oven at 30°C until they became gel fiber. Gel fiber was converted to ZrO_2-CaO fiber by annealing at 1000°C for 1 h in argon.

X-ray diffraction (XRD, Rigaku Co., D-Max-1200, Japan) patterns of ZrO_2-CaO fiber were obtained with a CuKα X-ray source at room temperature. The morphology of the fiber was investigated by using field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Fourier transform infrared spectrophotomether (FTIR, FTS-60, BIO-RAD Digilab, U.S.A.) in the transmission mode with a 4 cm^{-1} resolution was chosen to

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monitor the spectral evolution of the chemical structure of the fiber.

All atomic force microscope (AFM) measurements described here were performed with a NanoScope Multimode™ SPM (Scanning Probe Microscope) from Digital Instruments, U.S.A., which was operated with the TappingMode (non-contact) imaging technique to prevent damage to the fiber and to provide optimal image and data quality. The resonant frequency of the silicon probe was ~260 kHz, and the scan rate and tip velocity were 1.0 kHz and 20 μm/s, respectively. The AFM images were collected in at least three different regions on the surface of each sample. The root mean square (RMS) roughness and the power spectral density (PSD) curves used throughout this paper were calculated from selected AFM scans with Nanoscope off-line analysis software.

The *in vitro* formation of calcium phosphate (CaP) was evaluated by immersing the annealed fiber in 15 m*l* SBF for 1 day. The simulated body fluid (SBF) was prepared by dissolving NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$ and Na_2SO_4 in deionized water. To this solution, 50 mM tris-(hydroxymethyl) aminomethane $[(CH_2OCH_3)CNH_2]$ and 45 mM hydrochloric acid (HCl) were used as buffering agents to maintain the pH of SBF at 7.25 at 36.5°C.

The *in-vitro* test was performed in a constant temperature-circulating bath (Model 90, Poly Science, U.S.A.) at a temperature of 36.5°C. After immersion, the sample was removed from the SBF, carefully rinsed with distilled water, and dried at room temperature. Energy dispersive X-ray spectrometer (EDS) was chosen to evaluate composition of the surface after immersion in SBF.

3. Results and Discussion

Figure 1 shows XRD patterns of ZrO_2-CaO fibers annealed at 500°C and 1000°C. XRD analysis showed that the fiber annealed at 1000°C was present as a mixture of tetragonal, monoclinic and $CaZrO_3$ phases. The fibers, which were annealed at 1000°C, showed the tetragonal peaks, such as (111), (200), (220) and (311) reflections at about $2\theta = 30.1\sim30.3°$, $35.1\sim35.4°$, $50.1\sim50.5°$ and $59.5\sim60°$ (JCPDS Card 17-0923) and the monoclinic phases, such as (-111), (111), (220) and (022) reflections at $2\theta = 28.15\sim28.18°$, $31.4\sim31.45°$, $49.21\sim49.36°$ and $50.11\sim50.26°$ (JCPDS Card 37-1484) and other diffraction peaks corresponding to $CaZrO_3$. On the other hand, samples annealed at 500°C consisted of almost tetragonal single phase.

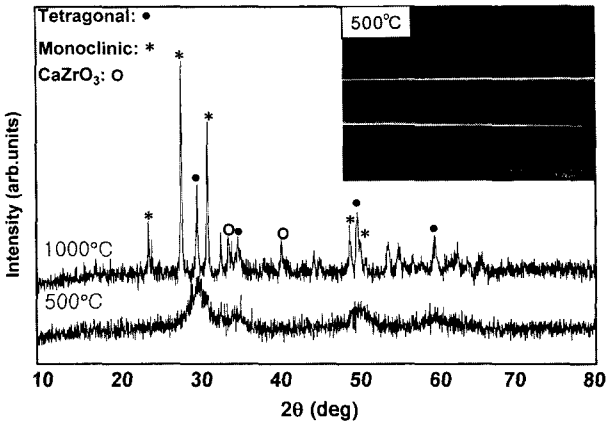

Fig. 1. XRD patterns of the samples annealed at 500°C and 1000°C and FE-SEM image of 500°C-annealed sample.

In the case of ZrO_2 prepared by chemical solution process, the crystalline species precipitating first was tetragonal or cubic, at low temperature, while monoclinic phase was firstly appeared in ZrO_2 prepared by conventional melting process. This was explained by that the tetragonal and cubic having a high-temperature stability was stable at low temperature, since starting materials used in chemical solution process was sufficiently fine to react during heat treatment [11].

Furthermore, the FE-SEM image of the fractured cross section of the sample annealed at 500°C showed that the shape of the fiber is of circular-type without fusion of fibers. The mean diameter of the fiber is about 50~60 μm.

The FTIR spectra for the samples after annealing at 500°C and 1000°C was shown in Fig. 2. In the samples annealed at 500°C, the wide band at around 3000~3500 cm^{-1} corresponds to the OH group of water and the

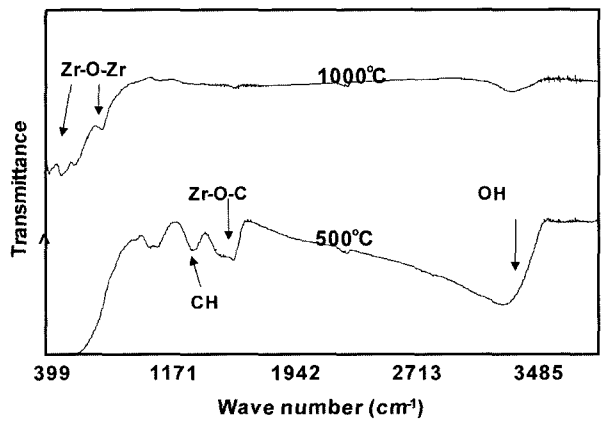

Fig. 2. FTIR spectra for the samples annealed at 500°C and 1000°C.

bands at around 1400~1600 cm^{-1} to the asymmetric stretching of the Zr-O-C bond exhibited [12, 13]. This suggests that carbon from the organics does not pyrolyze completely and may instead dissolve into the ZrO_2 crystal for the sample annealed at low temperature, i.e., 500°C. As increase with annealing temperature to 1000°C, the spectra of the densified fiber show that the vibration corresponding to the Zr-O-C and OH bonds disappears almost completely. From previous reports [14, 15], as increase with strain in ZrO_2 product, i.e., quantity of the monoclinic phase increased, number or intensity of the absorption mode at below 800 cm^{-1} could be increased. In this work, newly formed peaks, at around 435 cm^{-1} and 510 cm^{-1} corresponding to tetragonal and at around 615 cm^{-1} and 750 cm^{-1} corresponding to monoclinic, were visible in the sample annealed at 1000°C [14].

Surface morphology of the fiber after annealing was investigated by FE-SEM and AFM. Figure 3 shows that, for the sample after annealing at 1000°C, a fine grain structure became evident, while it is difficult to identify clear surface structure at 500°C. At 1000°C, plenty of 3-dimentional growth can be found on the surface of the fiber.

In order to more clearly elucidate surface roughness of the fiber, roughness analysis was performed. Figure 4 shows the AFM images (10×10 μm^2) of the samples after annealing at 500°C and 1000°C. Generally, in previous work using an AFM, most surface roughness were obtained by line profiles. In this work, however, in order to obtain more exact roughness data, we performed area scanning (5×5 μm^2). Five analyses at different area per each sample were done. The smoothness of the surface of fiber after annealing at 500°C is relatively high. However, fiber annealed at 1000°C showed comparatively rough surface structure. We assume that increase of the surface roughness may be inducted by crystal growth of the fiber, resulting in increase of RMS roughness.

In biological applications, a general trend of the varying surface topography and its relation to *in vitro* bioactivity is shown in previous works [17]. The rougher the surface of the biomaterials, the better the bioactivity. However, as far as we know, there has been little information on the surface topography and roughness of chemical solution derived ZrO_2 - CaO fibers. In this study, FE-SEM and EDS analysis were performed on the sample after immersion for 1 day. As shown in Fig. 5, adsorbed crystals on sample annealed at 1000°C were identified after immersion.

The calcium and phosphate ions required for hydroxy apatite generation on the surface were derived from the SBF. This was indicated by the formation of CaP on fiber [See Fig. 5]. As clearly shown in Fig. 5, the sample annealed at 1000°C with relatively rough surface structure showed a high CaP forming ability.

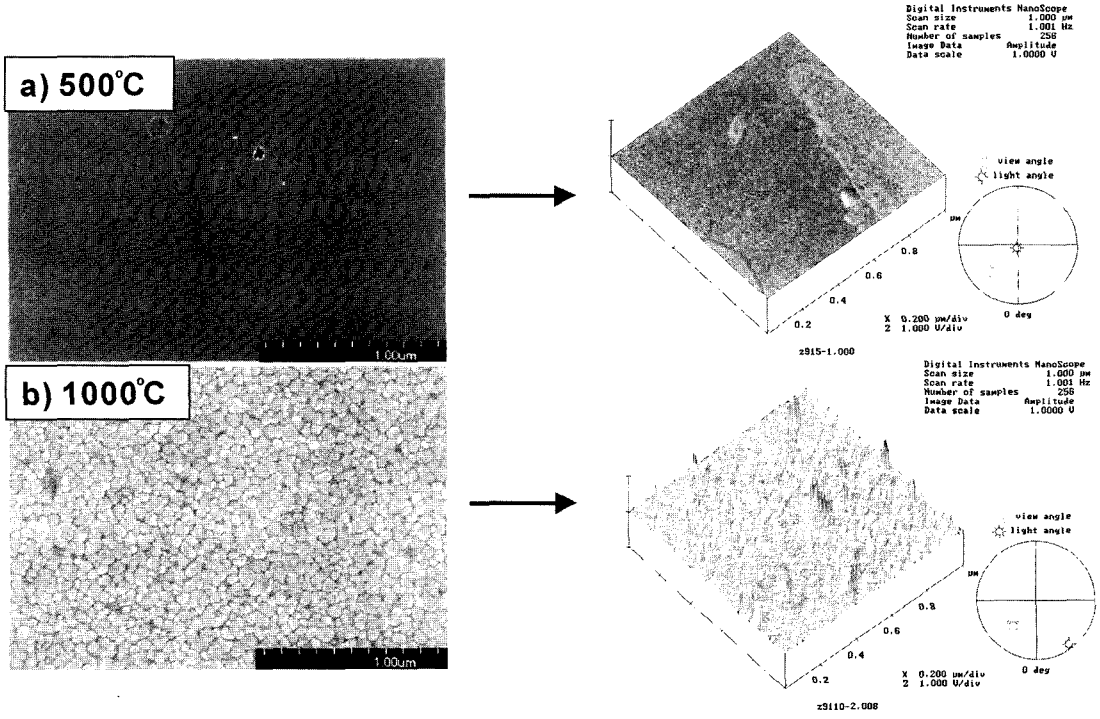

Fig. 3. FE-SEM images and AFM surface plots (1 μm×1 μm) of the free surface of the samples annealed at 500°C (a) and 1000°C (b).

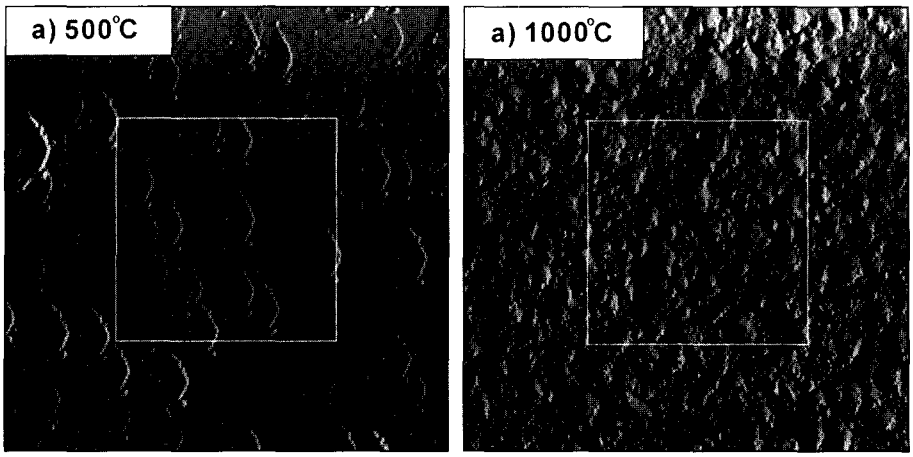

Fig. 4. AFM top-view images (10 μm×10 μm) and surface roughness of the samples annealed at 500°C (a) and 1000°C (b).

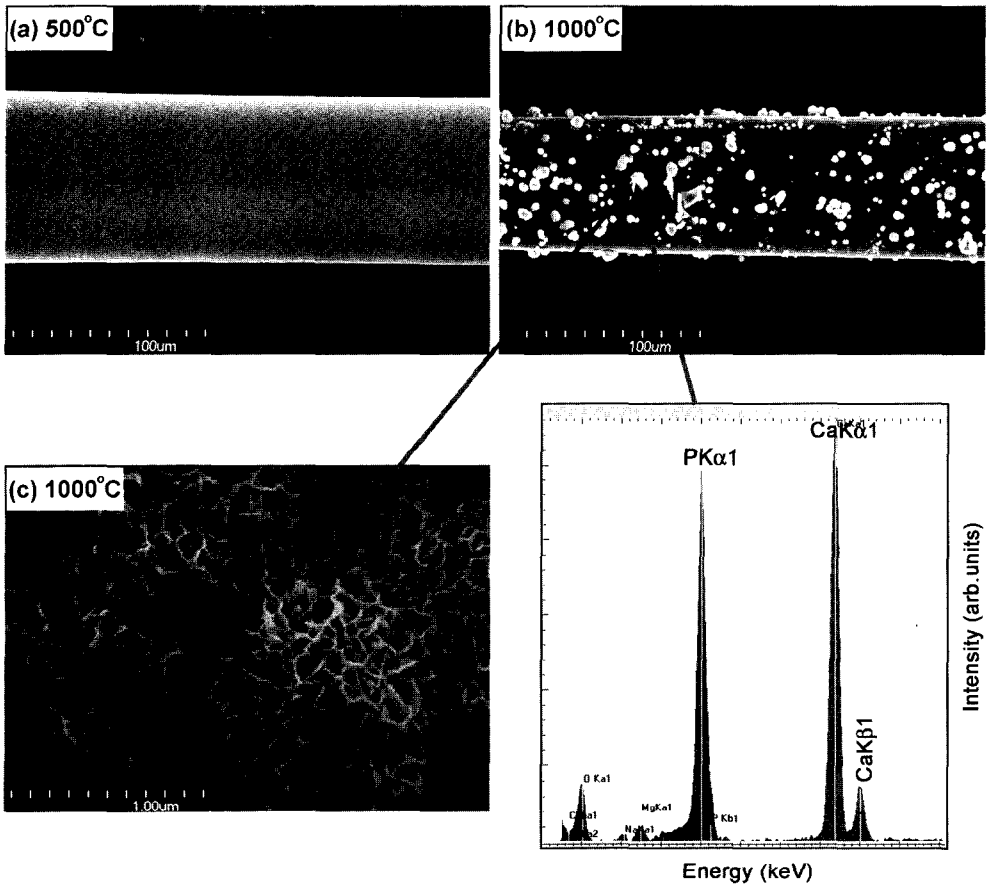

Fig. 5. FE-SEM and EDS spectra of the samples annealed at 500°C (a) and 1000°C (b) and (c) after immersion in SBF.

In our work, we assumed that relatively rough surface structure was probably responsible for CaP forming ability of sample.

4. Conclusions

Chemical solution derived Ca-doped zirconia fiber has been prepared by using calcium- and zirconium-naphthenate. Fibrous ZrO_2-CaO was drawn by using a sticky mixture. 91 mol%ZrO_2 - 9 mol%CaO fiber consisted of tetragonal, monoclinic and $CaZrO_3$ phases after annealing at 1000°C. Surface roughness of the sample with a fine grain structure after annealing at 1000°C showed relatively rough surface. We can obtain relationship between surface roughness and CaP formation ability of

the sample.

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