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Journal of the European Ceramic Society 29 (2009) 1387–1391

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Synthesis of ceramic nanotubes using AAO templates

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Received 6 June 2008; received in revised form 12 September 2008; accepted 13 September 2008
Available online 25 October 2008

Abstract

In this paper, the metal aluminum oxide ceramic nanotubes (M–Al–O, M = Zn, Mg and Ba) were synthesized by the use of porous anodic aluminum oxide (AAO) template. Metal oxide nanotubes were firstly formed from the thermal decomposition of respective nitrates within the pores of AAO templates. Then M–Al–O nanotubes were synthesized through the solid-state chemical reaction between the metal oxide nanotubes and AAO. TEM observation shows that the as-prepared samples are nanotubes and XRD measurement reveals that M–Al–O nanotubes (M = Zn, Mg and Ba) are crystalline in nature with spinel structure.

Keywords: AAO template; Metal oxides; Ceramic nanotubes

1. Introduction

During the past few years, materials of nanometer-scale have attracted much more interest because of their unusual properties compared to the bulk counterparts. The study of metal aluminum oxide (M–Al–O) ceramics compound nanostructures is meaningful since they can be used in catalysts,[1] pigment,[2] and luminescent materials.[3] Although considerable studies have reported the fabrication of M–Al–O ceramic nanoparticles,[4–6] there are only a few examples of M–Al–O ceramic nanotubes. One-dimensional nanostructures such as nanowires and nanotubes can serve as building blocks and components for many novel functional applications,[7] so the fabrication of ceramic nanotubes is a challenge that has outstanding technological consequences.

The template method, especially those based on porous anodic aluminum oxide (AAO) membrane, is a simple and effective strategy in the synthesis of one-dimensional nanostructures. Many researchers have prepared nanowires and nanotubes by chemical vapor deposition methods,[8–10] sol–gel technique[11–13] and electrodeposition approach[14–20] assisted with AAO membranes. In the general fabrication process, the AAO membrane acts as template to control the morphology of the prepared materials. To our knowledge, Al_2O_3 can react with a variety of other oxide materials (such as ZnO, MgO and BaO) to form ceramic compounds through solid-state chemical reaction.[21–23] It is reasonable to imagine that the AAO membrane serves as reactant to synthesize one-dimensional ceramic nanostructures. In this paper, we report a novel synthetic method to prepare M–Al–O (M = Zn, Mg and Ba) ceramic nanotubes with AAO membranes by successive thermal treatment in air at 450 °C for 1 h and at 680 °C for 26 h. With calcination treatment at 450 °C, the AAO membrane acts only as a template in the formation of the metal oxide nanotubes. Then long time calcination treatment at 680 °C stimulates the reaction between the AAO membrane and the metal oxide nanotubes, the M–Al–O nanotubes are formed.

2. Experimental

2.1. Preparation of AAO membrane

High purity aluminum foil (purity 99.99%) was annealed at 500 °C for 5 h in air and degreased with acetone. The as-treated foil was direct current (DC) anodized in 0.3 mol/L $H_2C_2O_4$ aqueous solution under a constant voltage of 120 V at 0 °C for 90 min. The remaining aluminum substrate was removed in 0.1 mol/L $CuCl_2$ solution. After anodization, the foil was immersed into 6 wt% phosphoric acid for approximately 60 min to widen the pores. Finally, the template was rinsed with distilled water for many times.

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doi:10.1016/j.jeurceramsoc.2008.09.011

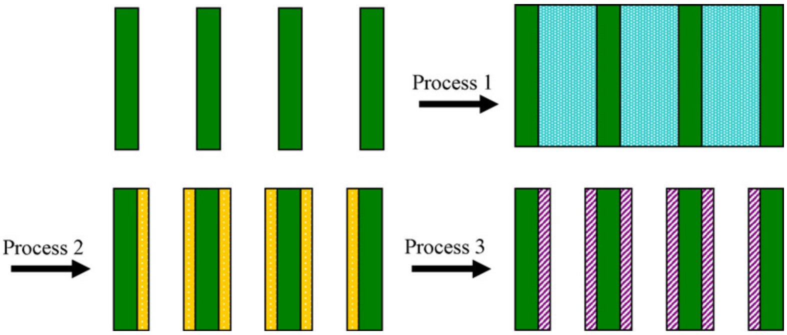

Fig. 1. A typical process to generate M–Al–O ceramic nanotubes using AAO template.

2.2. *Synthesis of metal aluminum oxide ceramic (M–Al–O) nanotubes*

The preparation process of M–Al–O nanotubes mainly involves three steps, as schematically shown in Fig. 1.

The powders of nitrate (Zn, Mg and Ba) were respectively dissolved in glycol with the help of magnetic stirrer. The AAO membranes were immersed in the precursor solutions and sonicated for 5 min (Process 1). Subsequently, the AAO membranes were heated from room temperature up to 450 °C in air with a heating rate of 100 °C/h and held at 450 °C for 1 h. After the AAO membranes were cooled down to room temperature, excess products on the AAO surfaces were carefully wiped off with laboratory tissue. Such "dip-anneal-dip" process was repeated 3 cycles (Process 2). The as-treated AAO membrane was calcinated from room temperature up to 680 °C in air with a heating rate of 100 °C/h and held at 680 °C for 26 h to obtain the M–Al–O ceramic nanotubes (Process 3).

2.3. *Characterization of nanotubes*

The surface morphology of AAO membrane was analyzed by scanning electron microscope (SEM, Philips, XL30). The phase structures of the nanotubes were investigated by a rotating X-ray diffractometer (XRD, Philips X'pert) with Cu Kα radiation ($\lambda = 1.542$ Å).

To investigate the morphologies of the as-synthesized nanotubes, the AAO template was removed selectively by treating the sample with 6 mol/L NaOH aqueous solution at 60 °C. The suspension was carefully diluted with de-ionized water for several times and then dropped onto copper grids coated with a thin carbon film for transmission electron microscope (TEM, JEOL, JEM-100S) study. Note that NaOH contaminations were still present, this was particularly obvious from TEM figures.

3. Results and discussions

Fig. 2 shows a typical surface morphology of AAO template after pore widening. The thickness of template is about 100 μm and the average diameter of pores is about 100 nm.

During the calcination treatment of nitrate-filled template at 450 °C, the glycol was removed from the pores and the nitrate decomposed into the metal oxides, oxygen and NO_2 gas.[24] The metal oxides grew within the AAO pores to form nanotubes.[25] The related decomposition reactions in our experiments can be expressed as follows:

$$Zn(NO_3)_2 \rightarrow ZnO + NO_2\uparrow + O_2\uparrow$$

$$Mg(NO_3)_2 \rightarrow MgO + NO_2\uparrow + O_2\uparrow$$

$$Ba(NO_3)_2 \rightarrow BaO + NO_2\uparrow + O_2\uparrow$$

The TEM images of these metal oxide nanotubes are shown in Fig. 3a–c, respectively. The diameter of the nanotubes is about 100 nm, as shown in the TEM images, corresponds to the pore size of the AAO template. The wall thickness of these nanotubes is about 5 nm, which relates with the times of the "dip-anneal-dip" process.[26]

Fig. 4 shows the XRD patterns of the as-prepared samples. The peaks can be identified as ZnO (JCPDS77-2364), MgO (JCPDS75-0576) and BaO (JCPDS01-0746) respectively in addition to the background diffraction of amorphous Al_2O_3. The intensity of the peaks decreased with a peak broadening with the result of nanoscale character and poor crystallization.

The above process resulted in the formation of metal oxide/alumina core-shell structure within the AAO template. Such a core-shell structure provided a large interface area for the diffusion process.[27,28] Hence, the subsequent calcination treatment excited the solid-state chemical reaction between the pre-formed metal oxide nanotubes and AAO membranes,

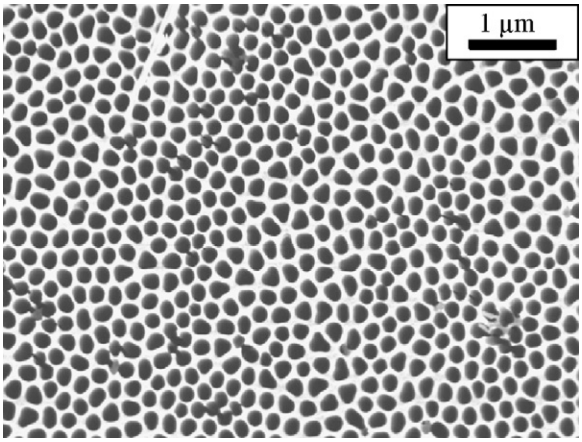

Fig. 2. SEM image of a blank AAO membrane.

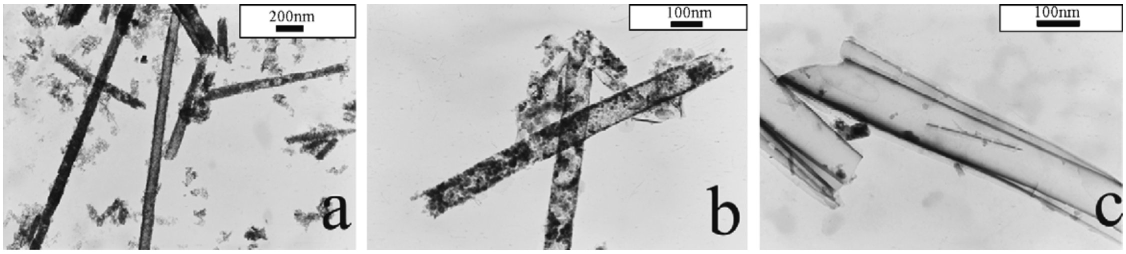

Fig. 3. The TEM images of metal oxides nanotubes (a) ZnO; (b) MgO; (c) BaO.

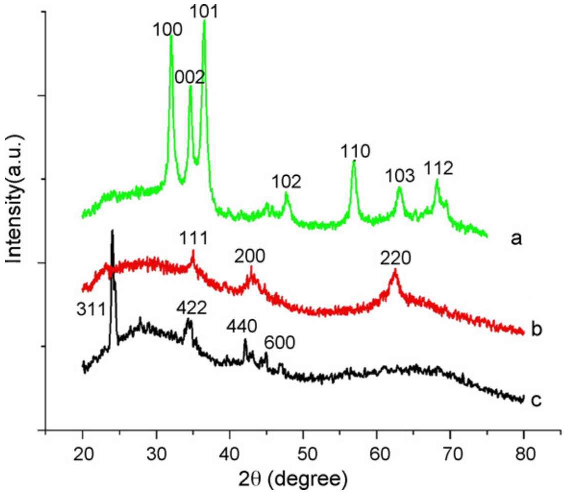

Fig. 4. XRD patterns of as-prepared metal oxide nanotubes: (a) ZnO; (b) MgO; (c) BaO.

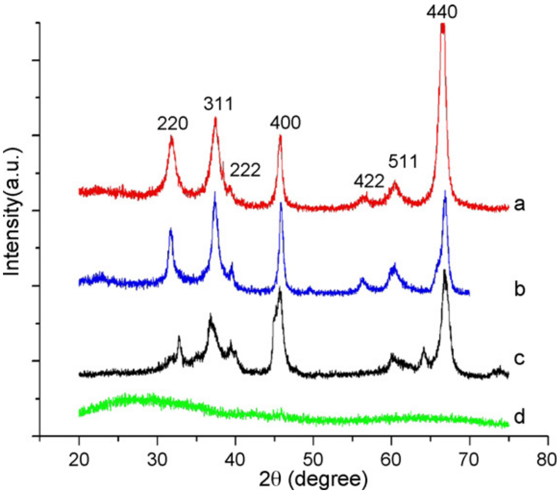

Fig. 6. XRD patterns of products calcinated at 680 °C for 26 h. (a) Mg–Al–O, (b) Zn–Al–O, (c) Ba–Al–O, (d) blank AAO membrane.

which finally resulted in the formation of M–Al–O ceramic nanotubes.

High temperature calcination treatment might result in a transition from amorphous to crystallization of AAO. Previous research shows the AAO remain amorphous up to 800–850 °C when transition phase alumina (γ-Al_2O_3) appeared.[29,30] If the AAO has the crystalline structure, dissolving AAO in the alkaline or acid solution will be very difficult. Therefore, we chose 680 °C to calcine the AAO template with the metal oxide nanotubes inside, after which the AAO templates keep in the state of amorphous. The TEM micrographs of the as-synthesized ceramic nanotubes are shown in Fig. 5a–c, respectively.

The XRD patterns of the ceramic nanotubes and a blank AAO membrane are shown in Fig. 6. The XRD pattern of the blank membrane (Fig. 6d) shows that the AAO template is amorphous even after calcination at 680 °C for 26 h. Comparing to the standard XRD data, the peaks of three as-synthesized products (Fig. 6a–c) are similar to the $Al_{2.144}O_{3.2}$ phase (JCPDS79-1558), which can be indexed to spinel structure (space group Fd3m).

For further interpretation of the reaction process, we focused on the study of the formation of Zn–Al–O nanotubes. The AAO template with the ZnO nanotubes inside was calcinated at different condition. The treated samples were analyzed with XRD.

Fig. 7 shows the XRD patterns of the dissimilar products within the AAO under the different calcination conditions. Decomposition of the zinc nitrate at 450 °C for 1 h resulted to the formation of zinc oxide nanotube (Fig. 7c). This ZnO was used as precursor in the next step to synthesize aluminate nanotubes. Fig. 7b is the XRD pattern of the sample heated at 640 °C for 7 h. The diffraction peaks can be identified as ZnO (JCPDS77-2364) and spinel $ZnAl_2O_4$ (JCPDS71-0968) which shows that part of the ZnO has been changed to $ZnAl_2O_4$ in this period. The formation of $ZnAl_2O_4$ can be attributed to the solid-state reaction of ZnO and Al_2O_3.[31,32] The chemical reactions can be

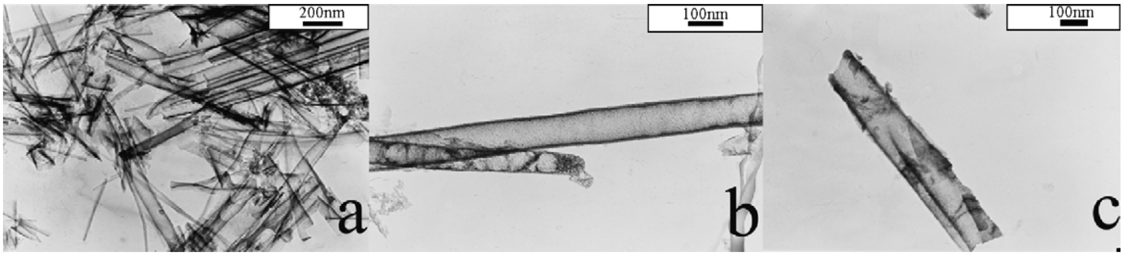

Fig. 5. TEM images of the metal aluminum oxide ceramic nanotubes. (a) Zn–Al–O; (b) Mg–A–O; (c) Ba–Al–O.

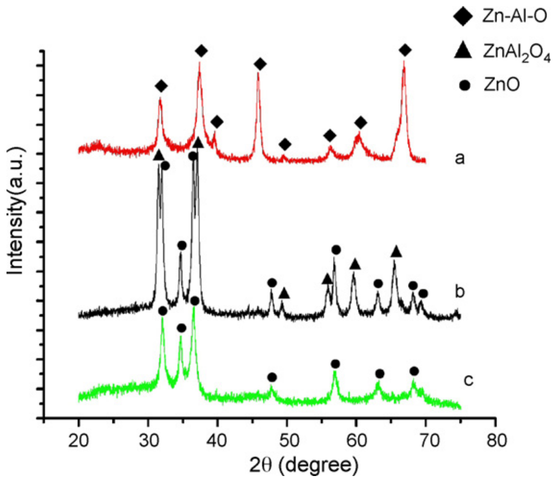

Fig. 7. XRD patterns of the samples prepared at different conditions (a) 680 °C for 26 h, (b) 640 °C for 7 h, (c) 450 °C for 1 h.

expressed as:

$$ZnO + Al_2O_3 \rightarrow ZnAl_2O_4$$

Because the nanotubes-AAO nanocomposite offers excessive amount of Al_2O_3, there is no enough opportunity to convert all of Al_2O_3 to aluminate. As calcining time was sufficiently long, Zn^{2+} had a tendency to diffuse from $ZnAl_2O_4$ to Al_2O_3 and brought some vacancies to the spinel structure of $ZnAl_2O_4$. The vacancies of $ZnAl_2O_4$ were partially filled up by Al^{3+} cation (to satisfy the valences of Al^{3+} and Zn^{2+}). For the above cause, the cubic symmetry of the spinel structure was change into the defect structure and led to non-stoichiometric phase (Zn–Al–O).

Fig. 7a is the XRD pattern of the sample heated at 680 °C for 26 h. It can be found that the ZnO phase disappeared completely and a non-stoichiometric phase appeared. This non-stoichiometric phase presents very similar diffraction patterns with $ZnAl_2O_4$ because they share the same spinel cubic structure with minor difference in the lattice parameter ($ZnAl_2O_4$: $a_0 = 8.08$ Å, Zn–Al–O: $a_0 = 7.97$ Å). From the energy dispersion spectrum (EDS) study, the atomic ratio of Zn/Al element in the final product is about 0.31, which is smaller than the case of stoichiometric $ZnAl_2O_4$ (Zn/Al = 0.5).

As shown above, spinel MAl_2O_4 can be regarded as the intermediate product in the formation of M–Al–O spinel nanotubes by solid-state reaction between the metal oxide and alumina. AAO membrane acts as template and reactant during the calcination process. The method reported here is simple and efficient for the fabrication of M–Al–O (M = Zn, Mg and Ba) ceramic nanotubes. This method requires low calcination temperature and so can be easily introduced for the preparation of other ceramic nanotubes.

4. Conclusions

Assisted with AAO templates, we report a novel synthetic method to prepare oxide ceramic nanotubes through solid-state chemical reaction between metal oxides (ZnO, MgO and BaO) and AAO membrane. A defect spinel crystal phase of M–Al–O is formed at 680 °C for 26 h. The formation process is regarded as the further diffusion of Zn ions into aluminum membrane through the intermediate product. This method reported here can be extended to other metal aluminum oxide ceramic nanotubes.

Acknowledgments

This work was supported by programs NSFJS (No. BK2006111), NCET (07-0430) and National Basic Research Program of China (2007CB936302).

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