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Fine-structured patterns of porous alumina material fabricated by a replication method

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Abstract

Porous alumina materials with three-dimensional fine-patterning over multiple length scales were fabricated from mixed slurry of polyvinyl alcohol (PVA) and alumina nanosized particles in water by a replication method. The mixed slurry was then filled in a silicon mold with different pattern sizes and dried at room temperature. After the drying, the PVA and alumina dried film were detached from the mold. Through burn-out at various sintering temperatures, alumina porous materials with dot, hole and line and space patterns as small as sub-micrometer in size were successfully fabricated. The results demonstrated possibilities to produce porous inorganic materials with various compositions and structures with a facile approach and a simple method.
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Keywords: Replication; Ceramics patterning; Alumina; Polyvinyl alcohol; Shrinkage

1. Introduction

The ability to fabricate high precision micro- to nanoscale structures in a wide variety of materials is of crucial importance for the advancement of microtechnology, nanotechnology and nanoscience.[1–3] For example, developing micrometer and sub-micrometer architecture for functional ceramics is expected to promote the industrialization of ceramic nanotechnology.

Numerous studies have been centered on developing novel methods and processes to fabricate fine-structured ceramic patterns. Although several ceramic patterning methods have been developed during the last decades, techniques that can pattern ceramics are very limited.[4–10] Most commonly used approaches for patterning ceramic surfaces were the hard-lithography techniques, that in many cases are time-consuming, expensive, and low-resolution techniques. This is due in part to the refractory nature of ceramics and the difficulty in etching such materials.[11] For instance, when ceramic patterns are to be prepared by sputtering, one of top-down methods, it is difficult to avoid etching processes in order to lift off the patterns. This may lead to severe problems such as sidewall redeposition, contamination, and structural damage.[12]

Furthermore, nanoimprint lithography (NIL) using nanoscale molds, first reported by Chou,[13,14] is recognized as a promising candidate for nanolithography in the next generation. However, the disadvantage of this technique involves expensive and complex processes. The main reason for the expense of the nanoimprint equipment is that the nanoscale molds need to be hardened by thermal and photonic treatments after imprinting.

On the other hand, by bottom-up methods, difficulties also exist in precisely controlling the shape, size, and relative position of the nanocomponents.[15] Recently, a sol–gel method was applied for the patterning of TiO_2 and ZnO.[16] However, this process required both silicon and polymer molds. Furthermore, the complicated chemical process yielded hazardous wastes. Thus, much simple processes to fabricate patterned ceramics have been awaited.

In this study, we attempted to fabricate sub-micron sized porous alumina materials using a simple method combining, the advantages of the use of polyvinyl alcohol (PVA) polymer material and alumina (Al_2O_3) nanosized particles, without using expensive equipments and complicated chemical processes. We

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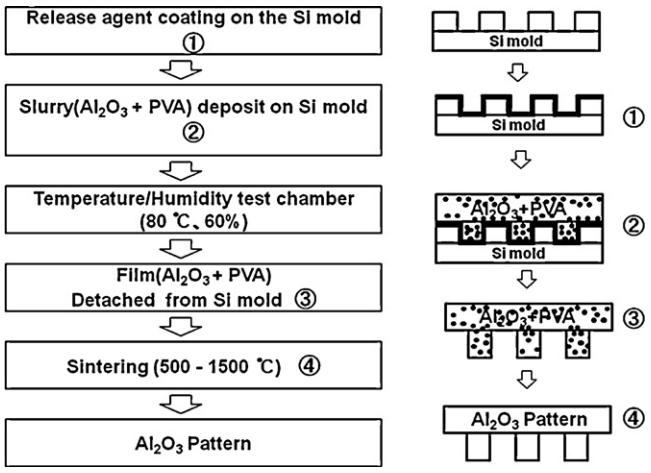

Fig. 1. A schematic drawing of the experimental procedure for the replication process.

used PVA as a binder for the formation of alumina suspensions in aqueous solutions. Al_2O_3 nanosized powder was chosen because of its optical and electrical properties, and its high chemical and mechanical stability.[17] PVA polymer materials offer several advantages, including low toxicity, low cost, high Young's modulus, and solubility in water.[18] Furthermore PVA has already been widely used as a low cost binder in the commercial production of ceramics.[19]

2. Experimental procedure

The critical steps in our patterning scheme are shown schematically in Fig. 1. A Si mold (25 mm × 25 mm × 1 mm), which was fabricated using a conventional electron-beam lithography and a dry etching process, was obtained from a commercial vendor (Kyodo International, Co. Ltd., Japan). The mold contained various patterns such as line and space (L&S), dots, and holes, with a pattern size ranging from 1 μm to 50 μm. PVA (average degree of polymerization = about 500, Wako Pure Chemical Industries, Co. Ltd., Japan) and alumina nanoparticles (TM-300D, γ-alumina, 10 nm; Taimei Kagaku, Co. Ltd., Japan) were used as raw materials.

Firstly, PVA and alumina nanoparticles were mixed in water and ball-milled using zirconia balls (diameter of 5 mm) for 24 h. The content of Al_2O_3 was in the range of 3–15 wt%, where PVA content was fixed at 3 wt%. The surface of the Si mold was coated with a release agent (HD-1100, HARVES Co. Ltd., Japan) to allow the dried film of the PVA–alumina slurry to be detached from the mold. The PVA–alumina slurry was then filled to cover the patterned silicon mold and dried. The drying process was carried out in a temperature/humidity test chamber (KCL-2000, EYELA Co. Ltd., Japan) maintained at a temperature of 80 °C with the relative humidity of 60% to minimize the distortion of the film. The dried film was then detached from the Si mold by peeling. The patterned films were sintered at various temperatures ranging from 500 to 1500 °C for 1 h in air.

The size and surface morphology of the alumina patterns were observed using a scanning electron microscope (SEM, JSM-6700F, JEOL, and Japan) and a violet laser scanning microscope (VK-9700, Keyence, Japan) with a capability to measure the height and width. Phase identification was carried out by X-ray diffraction (XRD, RINT 2500, Rigaku, Japan) using Cu-Kα radiation.

3. Results and discussion

Preliminary work showed that for PVA concentrations greater than 5 wt%, the PVA powder partially remained undissolved in the slurry. For PVA concentrations less than 2 wt%, no alumina patterns were formed due to low binding strength. Thus, the content of PVA was fixed at 3 wt%.

To optimize the fabrication method, the relative quantities of PVA, alumina and water were then varied as shown in Table 1. The patterns were partially formed when the alumina contents were less than 3 wt% or more than 15 wt% owing to the insuffi-

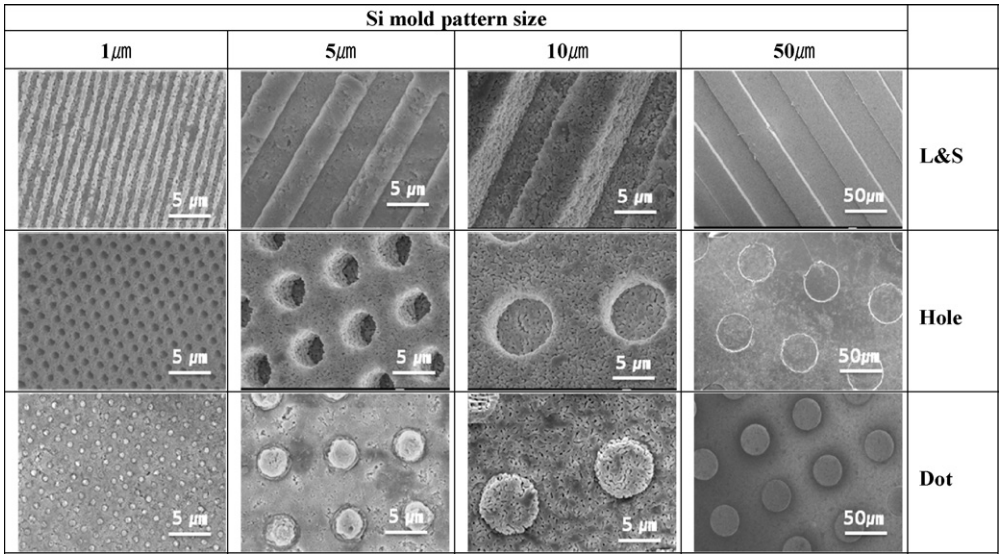

Fig. 2. Scanning electron micrographs of fine-structured alumina by imprinting of various pattern shapes and sizes.

Table 1
Optimization of the mixing ratios of the alumina slurry.

Sample number	PVA (wt%)	Al_2O_3 (wt%)	H_2O (wt%)	Remark
1	3	3	94	Partial film formation
2	3	6	91	Formation of film
3	3	9	88	
4	3	12	85	
5	3	15	82	Partial film formation

Table 2
Shrinkage of patterned alumina as a function of sintering temperature.

Temperature (°C)	Pattern width of alumina (μm)	Pattern width of Si mold (μm)	Shrinkage (%)	Pattern height of alumina (μm)	Pattern height of Si mold (μm)	Shrinkage (%)
500	9.3	10.0	6.9	9.5	10.0	5.0
1000	8.4	10.0	15.8	7.9	10.0	21.0
1200	7.7	10.0	22.6	7.9	10.0	21.0
1500	6.8	10.0	32.4	5.8	10.0	42.4

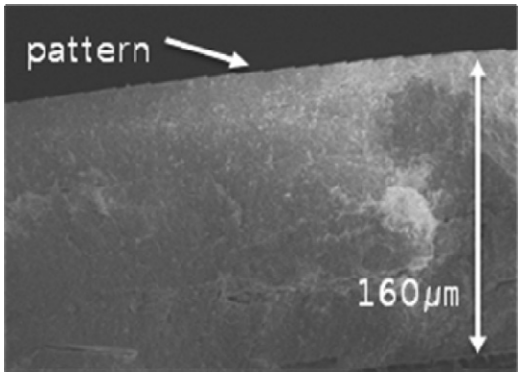

Fig. 3. Scanning electron micrograph of cross-section of patterned alumina.

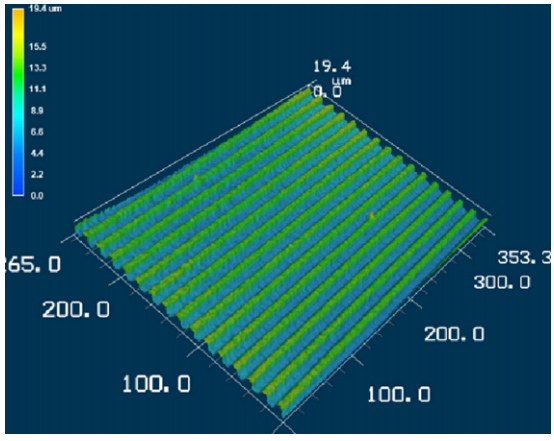

Fig. 5. 3D surface morphology of sintered alumina patterns.

ciency of particles connection or binding strength, respectively. Accordingly, optimized alumina patterns were fabricated with the PVA content of 3 wt% and the alumina contents of 6–12 wt%.

Fig. 2 shows the scanning electron micrographs of alumina sintered at 1500 °C following the replication of a Si mold. Various Si mold patterns were successfully replicated on the surface of alumina with L&S, hole and dot appearance. The lateral pattern sizes were similar and slightly smaller than those of the molds. The cross-section of patterned alumina using a mold with 10 μm L&S patterns is shown in Fig. 3. The thickness of whole alumina body was observed to be 150–200 μm and no cracks were found.

Although the patterns were successfully transferred, the patterned alumina samples were found to shrink in size following the sintering process. Enlarged scanning micrographs for patterned alumina replicated using 1 μm molds are shown in Fig. 4. Sub-micron-sized alumina patterns, which were smaller than the molds, were successfully formed.

The amount of volumetric shrinkage was estimated by using a violet laser scanning microscope. 3D surface morphology of the patterned alumina sample replicated using a 10 μm mold is shown in Fig. 5. From this morphology and the mold size, shrink-

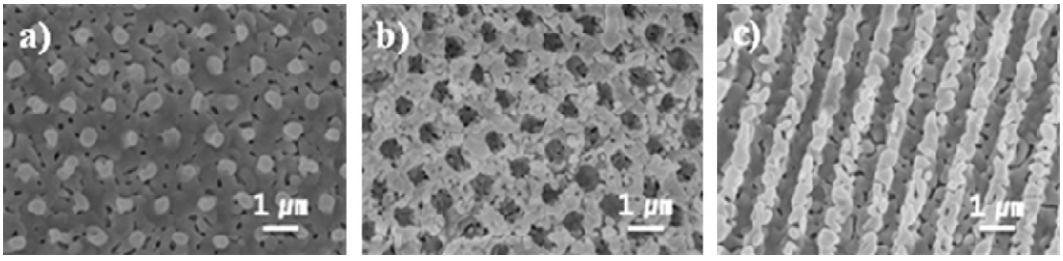

Fig. 4. Scanning electron micrographs of sub-micron alumina patterns, with a) dot, b) hole and c) line and space.

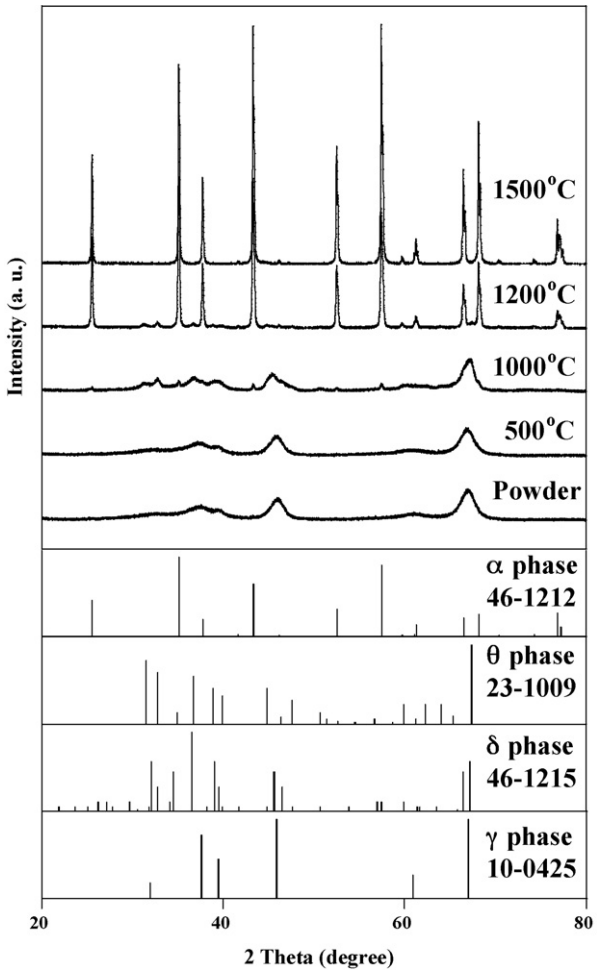

Fig. 6. XRD patterns of the alumina patterns sintered at different temperatures.

age was calculated. Results for all patterned alumina samples are summarized in Table 2. Following the sintering process, the patterns were found to shrink by as much as 5–42%. Shrinkage was found to increase with increasing the sintering temperature. The shrinkage effect can be a technique to produce the sub-micron-sized alumina patterns from a micron-sized Si mold.

X-ray diffraction patterns of the raw powder and sintered alumina are shown in Fig. 6. For the raw powder, all peaks were broad and the peak positions were matched to those for γ-Al_2O_3. After the sintering at 500 °C, the XRD pattern was not changed significantly. For samples sintered at 1000 °C, new peaks at about 31° and 32° appeared. These may correspond to those for θ-Al_2O_3. Furthermore, faint α-Al_2O_3 peaks were also seen at 35°, 43° and 57°. This indicated that this sample was of α- and θ-Al_2O_3. With increasing temperature to 1200 °C, the α-Al_2O_3 peaks became stronger and those for θ-Al_2O_3 were still observed. At 1500 °C, all peak positions matched to those for α-Al_2O_3. Thus, this sample was of α-Al_2O_3.

From XRD patterns (Fig. 6), phase change was observed. During the θ-Al_2O_3 and α-Al_2O_3 transformation in sintering of γ-Al_2O_3 powders, it was reported that α-Al_2O_3 nuclei form within the ultrafine θ-Al_2O_3 matrix, but rapidly grow to produce α-Al_2O_3 colonies.[20] As a result of the low intrinsic nucleation density and the volume reduction accompanying the phase transformation due to the lower specific volume of α-Al_2O_3 (0.251 and 0.276 cm^3/g for α-Al_2O_3 and θ-Al_2O_3, respectively[21]), the colonies recede from the matrix to form a network of pore channels.

Enlarged scanning electron micrographs of sintered alumina at 500–1500 °C are shown in Fig. 7. An exothermic burning process of the PVA occurs in the range of 150–450 °C and the process results in the formation of pores.[22] Pore and grain sizes were increased with increasing temperature. It is also expected

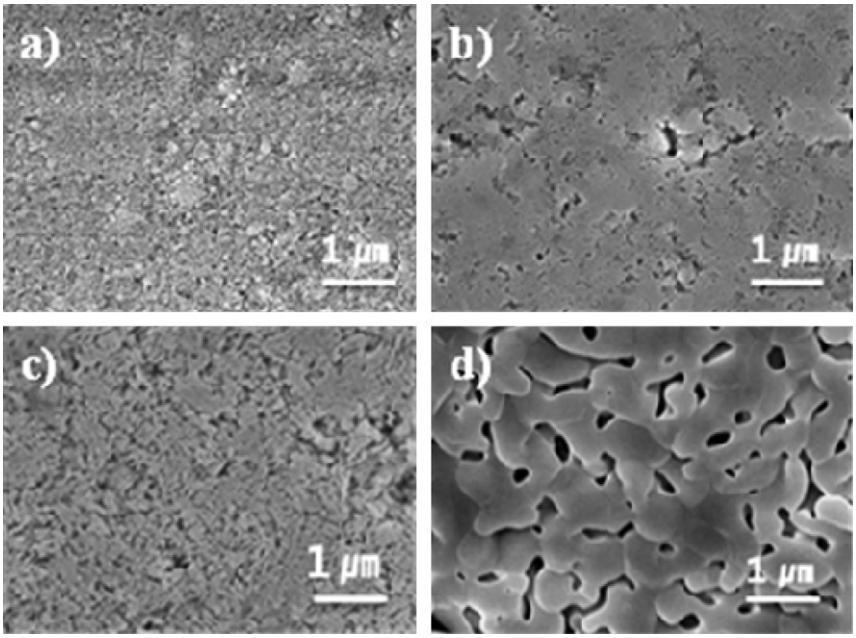

Fig. 7. Scanning electron micrographs of the alumina patterns sintered at a) 500 °C, b) 1000 °C, c) 1200 °C and d) 1500 °C. Grain growth was confirmed for the sintered product at 1500 °C. Fine pores were observed for the sintered products from 500 °C to 1200 °C.

that not only phase change but also pore size and shape may be changed by increasing the sintering temperature in the present samples. Thus, it is likely that microstructure in the patterned alumina can be controlled by adjusting parameter such as the sintering temperature.

In the present research, it was found that heat-treatment of replicated PVA–alumina slurry using a Si molds enabled us to fabricate porous sub-micron-sized alumina samples. It is also expected that using this method, various products including catalysts, super-water-repellent, heatproof materials, and microelectronics can be fabricated in a simple process.

4. Conclusions

Micron and sub-micron-sized alumina patterns containing nanosized pores were successfully fabricated by a simple process using PVA–alumina slurry and a Si mold. The shrinkage in the sintering was found to be used as a technique to fabricate sub-micron-sized patterns from micron-sized Si molds. This versatile technique seems to offer the advantages of simplicity and low production cost, and it is capable of facilitating the design of complex patterns involving many applications ranging from catalysts, super-water-repellent, heatproof materials, and microelectronics.

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