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Fabrication of a hierarchical aluminum oxide surface with micro/nanostructures via a single process and its application as a superhydrophobic surface: Simple sintering method with an aluminum microsized powder

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ABSTRACT

In this study, a hierarchical aluminum oxide surface with micro/nanostructures was fabricated via a single pressureless sintering method. About 70-μm-thickness pile of aluminum powder (i.e., sub-10-μm) was laid on a sapphire substrate with an area of 10 × 10 mm^2, and the substrate was placed in the middle of the furnace. Using a working temperature of 900 °C, 1-, 2-, 4-, 6-, and 8-h sintering processes were performed. After this process, a plate with a micro-spherical shape similar to the initial morphology of the laid aluminum powder was formed via adhesion between the aluminum powders. In addition, needle-like nanorods were formed at the surface of the plate. Therefore, an aluminum oxide surface with hierarchical micro/nanostructures was fabricated. In addition, a mechanism was proposed to explain the fabrication process. Several types of experiments with varying temperatures, atmospheres, purging times, and substrates were performed to confirm the proposed mechanism. Finally, with the aid of a simple hydrophobic surface treatment, a superhydrophobic surface with low hysteresis was fabricated.

1. Introduction

Recently, a superhydrophobic surface with self-cleaning characteristics has received much attention in industrial and scientific research fields. The self-cleaning effect typically comes from the superhydrophobic surface, which has a water contact angle larger than 150° and a sliding angle for water of less than 10°. In general, the superhydrophobic surface has hierarchical structures with micro- and nanostructures and a hydrophobic outer surface layer. The hierarchical structures of the micro- and nanostructures enhance the hydrophobic chemical characteristic of the surface, and these morphologies are found in nature, such as in the lotus leaf [1].

To fabricate a superhydrophobic surface, many techniques have been proposed as follows: chemical vapor deposition [2], the electrospinning method [3–5], liquid flame spraying [6,7], the sol–gel technique [8,9], the self-assembly method [10,11], and the spray coating technique [12–14]. In addition, for the metal surface with the superhydrophobic characteristic, electrochemical deposition [15], plasma treatment [16], and etching techniques [17–19] are primarily employed by researchers.

Among several industrial metals, aluminum oxide (Al_2O_3) is a very important material due to its light weight and good corrosion resistance. A facile fabrication method for hierarchical structures of Al_2O_3 would be a promising technique to fabricate superhydrophobic surfaces with the aid of a hydrophobic coating. Several studies have investigated the fabrication of superhydrophobic surfaces using aluminum via dislocation-selective chemical etching [17], a boiling technique to form boehmite (AlOOH) [18], and the adoption of an AAO (anodized aluminum oxide) surface [20]. However, no studies of the fabrication of hierarchical aluminum oxide surfaces with micro/nanostructures using a single process have been reported.

In this study, a hierarchical aluminum-oxide surface with micro/nanostructures was fabricated using a single pressureless sintering process. Next, we proposed a mechanism for our technique that was confirmed verified by the results from several experiments. Finally, with the aid of a simple hydrophobic treatment process, a superhydrophobic surface was fabricated using our aluminum oxide specimen, which has a hierarchical structure.

2. Materials and methods

2.1. Materials

For the raw material, sub-10-μm aluminum (Al) powder (ALCO Engineering Co., Korea) was used. For the aluminum powder suspension, triple distilled water was prepared using a water purification system (MEGAPLUS I, PURE SCIENCE, Korea). For the heating process, a horizontal tube furnace (LTF-15/75/610, LENTON, United Kingdom) was

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used. In addition, high-purity nitrogen gas (N_2, 99.999%) was used as an inert atmosphere during the heating process. The impurities of used high-purity nitrogen gas are O_2, H_2O, CO, CO_2 and CH_4. Each impurity amount was reported via official certification and depicted in Table 1. For the experiment where the atmosphere was changed, a nitrogen–oxygen mixed gas (N_2:O_2 = 99:1, 98:2, 96:4, and 92:8) was prepared. In addition, a sapphire wafer (C-plane) (2SCS, iNexus Inc., Korea) and quartz wafer (2500, iNexus Inc., Korea) that were 10 × 10 mm^2 (L × W) were prepared for the substrate on which the aluminum powder suspending solution was poured.

2.2. Fabrication process of the plate with micro/nanostructures using a pressureless sintering method

As shown in Fig. 1(a), using 45 ml of triple distilled water and 5 g of aluminum powder, a suspending solution was prepared by stirring for 5 min with a glass rod. Immediately, 0.2 ml of the aluminum powder suspending solution was poured on the sapphire and dried in a vacuum desiccator for 1 day to completely evaporate the triple distilled water. After drying, the prepared specimen was laid in the middle of a horizontal tube furnace, as shown in Fig. 1(a) and (b). After the purging process (flow rate = 500 cm^3/min) using nitrogen gas for 30 min, the furnace was heated with a heating rate of 5 °C/min. When the furnace reached 900 °C, the temperature was maintained for the specified time. Next, the furnace was cooled at a rate of −5 °C/min. During the entire process, the nitrogen flow rate was maintained at 500 cm^3/min to provide an inert atmosphere.

2.3. Observation of surface characteristics using SEM and EDS

The morphology of the sintered specimens was observed via FE-SEM (field emission scanning electron microscope, S-3000N, Hitachi, Japan), and the atomic composition ratios were determined by EDS (energy dispersive X-ray spectroscopy, S-3000N, Hitachi, Japan). In this study, calibration sample was not used. However, EDS was analyzed at the area of 675 ± 53 μm^2 to eliminate the roughness effect. The accuracy of EDS results was assumed as 1%, because there is no calibration sample used, therefore, the depicted error in this manuscript could be said as an estimation.

2.4. Surface modification using a hydrophobic treatment

The fabricated specimens were treated with trichloro(1H, 1H, 2H, 2H-perfluorooctyl) silane, which has hydrophobic characteristics. First, a tiny open capsule with 10 μl of trichloro(1H, 1H, 2H, 2H-perfluorooctyl) silane was placed in a small air-tight container. Next, the fabricated specimen was laid apart. After the container was sealed, the container was placed on a hot plate at 80 °C for 12 h.

2.5. Measurement of the contact angle and sliding angle

For the measurement of the water (also olive oil and hexadecane) contact angle and sliding angle, the center of the fabricated specimen was selected and measured with 5 μl of triple distilled water (also olive oil and hexadecane) using a contact angle meter (SDL110TEZ, Femtofab Co., Ltd., Korea). The water (also olive oil and hexadecane) contact angle was measured three times for each specimen.

Table 1
Impurity amount in high-purity nitrogen gas (99.999%): specifications and results by official certification analysis.

Components	Specifications	Result of analysis
O_2	<1.00 ppm	<0.80 ppm
H_2O	<1.00 ppm	<0.70 ppm
CO	<0.10 ppm	<0.10 ppm
CO_2	<0.10 ppm	<0.10 ppm
CH_4	<0.10 ppm	<0.10 ppm
The others	–	–

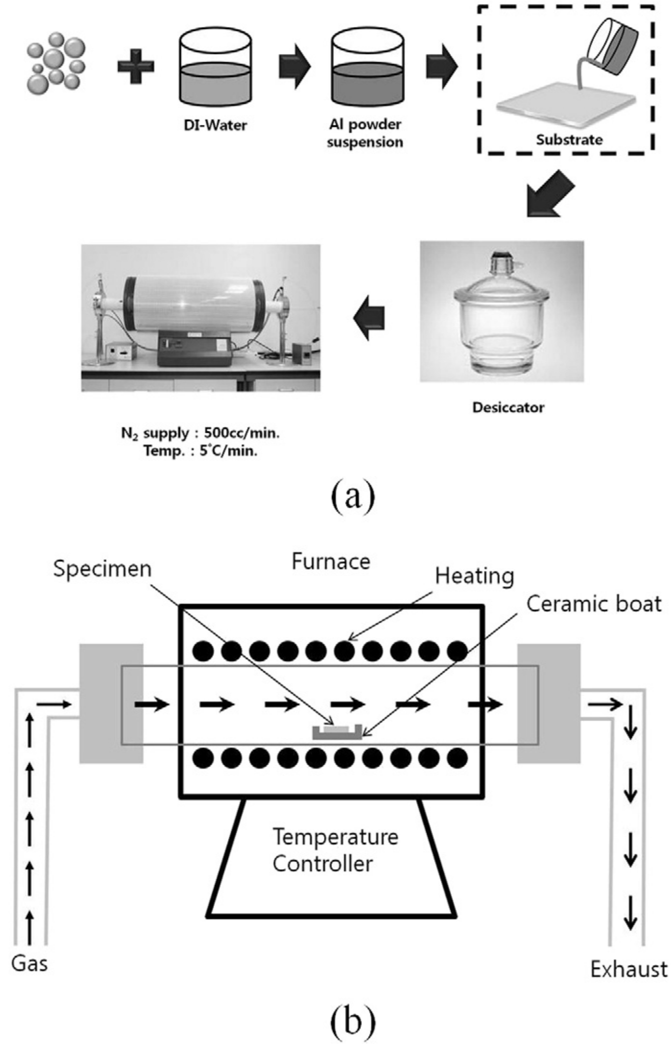

Fig. 1. (a) Schematic representation of the sintering experiment and (b) the high-temperature horizontal tube furnace system.

2.6. 3M tape test of surface after hydrophobic treatment

For the taping test was implemented using 3M tape [21,22]. 3M tape was adhered on the fabricated specimens and detached. After detaching, water contact angles was measured and compared with the original specimens.

3. Results and discussion

3.1. Fabrication of a hierarchical aluminum oxide surface with micro/nanostructures

First, the aluminum powder was laid on top of the sapphire substrate, and this specimen was place in a furnace. The maximum temperature was set to 900 °C and the temperature was maintained for 1, 2, 4, 6, and 8 h. As shown in Fig. 2, the aluminum powders adhered to each other to form a plate with a microsized spherical surface morphology. In addition, at the surface of the fabricated specimen, needle-like nanorods were generated. Therefore, a hierarchical surface with a micro/nanostructure was fabricated via a simple process. In addition, as the heating time was increased, the nanorods grew longer. Therefore,