Preparation of superhydrophilic alumina films by hydrothermal processes using an organophosphorous compound

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Superhydrophilic alumina films were successfully fabricated by a hydrothermal reaction of nanofibrous alumina films in a nitrilotris(methyleneephosphonic acid) (NMP) aqueous solution at 180°C for 6 h. The films showed superhydrophilicity not only as prepared but also after a boiling water resistance test, indicating that they had good durability. The alumina films were phosphorylated wholly in a hydrothermal condition only at 180°C for 6 h. Phosphate moieties were present both at the surface and inside the films and a micro-structure with a serrated morphology was observed over the entire film surface. Whole phosphorylation of the alumina films resulted in good durability in the boiling water resistance test. Other films were phosphorylated partially at 160°C for 6 h and at 180°C for 4 h. The micro-structure with a serrated morphology was observed partially at the film surface. This morphology corresponded to the degree of phosphorylation. These results indicate that the phosphate moieties present on and in the films and the micro-structure of the films produced superhydrophilicity.

Key-words : Superhydrophilicity, Alumina, Phosphorylation, Hydrothermal treatment

1. Introduction

Surface functions concerning water behavior, such as hydrophilicity, hydrophobicity and sliding properties of water droplets, are of significant scientific and technological interest because of their potential for many applications.1–10 Hydrophilic and superhydrophilic surfaces and films have been developed in the last two decades. Ultraviolet irradiation of TiO2 films has been shown to induce superhydrophilicity. TiO2-based hydrophilic materials have been actively studied, and the number of research papers concerning such materials has increased dramatically over the last two decades.2,4,5

Hydrophilicity, however, is maintained only during UV irradiation and decreases once irradiation is removed. There are demands for superhydrophilic surfaces and films that can keep their hydrophilicity even in a dark environment. Durable superhydrophilic surfaces and films are also required for industrial applications. Such materials could be applied to devices used in various environments without UV light, for example, antifogging mirrors on cars and in bathrooms.

Different types of superhydrophilic metal and metal oxide surfaces have been prepared by several methods.5,9–8) Anodic aluminum oxide films with a honeycomb-like and a bird’s-nest-like micro-structured surface were prepared by anodizing aluminum foils.5 Alumina with a nanowire surface was fabricated by anodization.5,9 Titanium hydrothermally treated with phosphoric acid formed micro-structured Ti₂O(PO₄)₂(H₂O)₂ at the surface.5,9 Aluminum fluoride and oxyaluminum fluoride were prepared by treating aluminum with a XeF₂ gas.9,10 All these materials showed superhydrophilicity.

However, to the best of our knowledge, there is only one reported study concerning the durability of superhydrophilic films.9 A superhydrophilic surface was prepared by hydrothermal treatment of a molybdenum plate in a HNO₃ solution. The surface was reported to maintain its superhydrophilicity for 105 days in air at room temperature.9

Preparation of alumina nanomaterials with a detailed nanostructure and their industrial application have attracted widespread attention in recent years. Some of the authors of this paper reported the preparation of an alumina nanofiber sol with a novel length of ca. 1400 nm and a boehmite structure, and also the fabrication of several types of alumina films including free-standing, transparent and flexible ones.9–13 Nitrilotris(methyleneephosphonic acid) (NMP) has been used to modify inorganic metal and metal oxide surfaces.10,13 Adhesive bonding of an aluminum alloy has been improved by anodizing the material with NMP.14 Modified crystalline BaTiO₃ nanopowders were synthesized with NMP for the purpose of stabilizing their water dispersion property.15 The ³¹P NMR spectrum showed significant evidence of strong interactions between phosphate ions and the surface of the nanopowders.15

Phosphate ions are one of the hydrophilic groups16,17 as well as OH – or COOH ions.16,17 Matsuda et al.17 prepared a new proton conductor, PbMg₁₋ₓH₂y(PO₄)ₓyH₂O (x = 0.00–0.18), and analyzed its crystal structure by Rietveld refinement with multi-profile analysis using X-ray and neutron diffraction data. They pointed out that there was a strong affinity between phosphate ions and H₂O.

AlPO₄ crystals have been synthesized using Al₂O₃, P₂O₅ and an organic template such as tripropylamine by a hydrothermal process.20 Therefore, it is reasonable to think that an alumina film can be converted to aluminum phosphate by a hydrothermal process using an organic phosphate. On the basis of these
findings, we have designed a process for preparing a new type of superhydrophilic film in which an alumina film is treated with NMP in a hydrothermal condition. The results of this work demonstrate that durable superhydrophilic alumina films can be prepared by a hydrothermal reaction using nanofibrous alumina films in a NMP aqueous solution. The composition and morphology of the films were analyzed to identify the origins of their superhydrophilicity and clarify their hydrothermal processes.

2. Experimental procedure

A mixed solution of a nanofiber (ca. 4 nm in diameter and 1400 nm in length) alumina sol (1.0 g) and H2O (19.0 g) adjusted to a pH of 1 with HCl was coated on alkali-free glass substrates (AF-45, Shott) by a spin coating technique. Hardened alumina films were obtained by applying UV irradiation to the coated films for 10 min using a high-pressure mercury lamp (H1000L, Toshiba Lighting & Technology Corp.). The alumina films were hydrothermally treated as follows to obtain superhydrophilic surfaces. The films (50 mm × 25 mm) were dipped in 1 wt % NMP aqueous solutions (80 mL; pH 1) and the solutions were heated in autoclaves at 100–180°C for 2–6 h. After the hydrothermal treatment, the films were washed with water and dried in air.

The water droplet contact angle of the films was measured using an automatic Kyowa DM-501 contact angle meter and water droplets of 2 μL. The surface components of the samples were evaluated by Fourier transform infrared (reflection absorption) spectroscopy [FT-IR(RAS)] using a PerkinElmer Spectrum One spectrometer. The surface compositions of the films were analyzed by X-ray photo spectrometry (XPS) using a PHI 1600/3057 XPS instrument with incident X-ray radiation (Mg Kα1,2 = 1253.6 eV). The vacuum pressure was approximately 6.7 × 10⁻⁷ Pa. Narrow multiplex scans were recorded with 29.35 eV pass energy and a 0.1 eV step size. The measurements were made at 75° take-off angles with respect to the sample surface. The surface morphology of the samples was evaluated by field-emission scanning electron microscopy (FE-SEM) using a JEOL JSM-6500F SEM.

3. Results and discussion

The film surfaces were transparent after being treated at 100–150°C for 2–6 h, at 160°C for 2–4 h and at 180°C for 2–4 h (Table 1). The surfaces, however, were opaque after being treated at 160°C for 6 h and at 180°C for 4–6 h because small particles adhered to the films during the hydrothermal processes (Table 1). The surfaces were slightly opaque or transparent after the particles were wiped off.

The water droplet contact angles of the films were evaluated immediately after the hydrothermal treatment and all the values were under 10° (closed triangles in Fig. 1), indicating that all the films were superhydrophilic.

Boiling water resistance is a typical durability test in industrial applications. Test samples are generally immersed in boiling water for 1 h and their properties are then evaluated. If there is no or little change in the properties before and after the test, the materials are regarded as having good durability. This durability test was used in this study. After the test, the contact angles of films treated at 150°C for 4–6 h, at 160°C for 6 h and at 180°C for 2–6 h were less than 10° (open squares in Fig. 1). However, the films which had been treated at 100°C for 2–6 h, at 150°C for 2 h and at 160°C for 2 h showed larger contact angles (open squares in Fig. 1).

After the test, the films were kept for 7 days in an ambient environment. The contact angles of the samples are also shown in Fig. 1 (closed circles). Only the film hydrothermally treated at 180°C for 6 h showed a small contact angle of 10°, whereas that of the other samples increased. The superhydrophilicity of the former sample was maintained even after the boiling water resistance test and elapsed time of 7 days. These results indicate that the hydrothermal treatment of the alumina film in a NMP aqueous solution at 180°C for 6 h imparted superhydrophilicity that was maintained after the durability test, indicating that the film had good durability. The relationship between durability and the surface components will be discussed later.

The surface components of the samples after the hydrothermal treatment was evaluated by FT-IR(RAS). The spectrum of the samples treated at 180°C for 6 h (Fig. 2) showed an absorbance at 1129 cm⁻¹ (triangle), which was absent in the spectra of the samples treated at 180°C for 2 and 4 h and the alumina film.

![Image](image_url)

**Table 1.** Film surface morphology after being treated at 100–180°C for 2–6 h by hydrothermal processes

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○: transparent, ×: opaque.

![Image](image_url)

**Fig. 1.** Water droplet contact angles of samples prepared by a hydrothermal process at 100–180°C for 2–6 h as prepared, after undergoing a boiling water resistance test and after 7 days following the test.

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**Fig. 2.** FT-IR(RAS) spectra of samples after the treatment at 180°C for 2–6 h and alumina film before the treatment.
before the treatment (Fig. 2). This absorbance was ascribed to phosphate ions.23) When the alumina films were treated at 160°C for 6 h, the spectrum of the films showed an absorbance at 1136 cm⁻¹, whereas the films treated at the same temperature for 4 h or less did not show the absorbance (not shown). These results indicate that phosphate ions were present at the film surfaces after the treatment at 160 and 180°C for 6 h.

Surface compositions of the films before and after the hydrothermal treatment at 180°C for 6 h were also analyzed by XPS. The Al 2p and P 2p XPS spectra of the samples are shown in Figs. 3 and 4, respectively. The Al 2p XPS spectra of the films before and after the treatment (Fig. 3) showed peaks at 73.6 and 74.8 eV, respectively. The former peak was assigned to Al₂O₃, whereas the latter one was ascribed to AlPO₄ because the Al 2p peak of AlPO₄ is reported to appear at 74.5–75.0 eV.23) The P 2p XPS spectrum of the film after the treatment showed a peak at 133.2 eV, whereas the peak was absent in the case of the film before the treatment (Fig. 4). The peak was ascribed to PO₄ ions.24)

The XPS depth profile of the film after the treatment was also evaluated and is shown in Fig. 5. The film thickness was calculated as the SiO₂ sputter depth. Phosphate denoted as the P 2p spectrum was present not only on the film surface but also inside the film, indicating that phosphorylation proceeded throughout the entire alumina film in this experimental condition.

The surface morphology of the samples before and after the hydrothermal treatment at 160 and 180°C was evaluated by FE-SEM. The FE-SEM surface images before the treatment and those after the treatment at 180°C for 2–6 h are shown in Fig. 6. The film surface before the treatment [Fig. 6(a)] was flat and showed microfibers consisting of aggregated alumina nanoparticles. The films after the treatment at 180°C for 2 h [Fig. 6(b)] showed flat surfaces without any microfibers but with a nano-level fine micro-structure. The film after the treatment for 4 h, however, showed two types of surface, one of which was flat with a nano-level fine micro-structure [A in Fig. 6(c)] and the other was micro-structured [B in Fig. 6(c)], similar to that after the treatment for 6 h. The micro-structured surface appeared to be higher than the flat one. The film after the treatment for 6 h showed a micro-structure with a serrated morphology.

The FE-SEM images of the films after the treatment at 160°C for 2 and 6 h showed surfaces similar to those after the treatment at 180°C for 2 and 4 h, respectively (not shown). It is inferred that the alumina films reacted with NMP in a similar process at both 160 and 180°C in the hydrothermal conditions.

Chemical analysis of the films after the hydrothermal processes was carried out by EDS. The EDS results for the film after the treatment at 180°C for 6 h [Fig. 6(g)] showed a peak at 2.0 keV which was ascribed to P.25) This result supported the FT-IR(RAS) and XPS findings. The EDS results for the micro-structured area of the film after the treatment at 180°C for 4 h showed a shoulder at 2.0 keV [Fig. 6(f)], but the flat area of the film showed no peak at 2.0 keV [Fig. 6(e)]. These results indicated that the micro-structured area was phosphorylated, but the flat area was not.

Na₂[(HO₂PCH₂)₃NH]·5H₂O was reported to decompose at temperatures over 225°C in an ambient atmosphere.26) That reported finding and the FT-IR(RAS) and FE-SEM results suggest that NMP decomposed under the hydrothermal condition at temperatures of 160°C or higher in this study.

The thickness of the films after the treatment at 180°C for 6 h was calculated from cross-sectional images of the films (Fig. 7) to be 420 nm. The thickness of the film treated at 180°C for 2–4 h was not calculated because the boundary between the film and the substrate could not be distinguished clearly. A cross-sectional image of the film before the treatment was not measured because of the halation that occurred at the edge of the glass substrate under the FE-SEM measurement conditions used. Because of that halation, the film thickness before the treatment was estimated to be less than approximately 30 nm. The film thickness increased and the surface morphology changed during the hydrothermal processes.

An alumina film was hydrothermally treated in H₂O of pH 1 without NMP at 180°C for 6 h. A FE-SEM surface image after the treatment [Fig. 8] showed hemisphere-like pores of ca. 0.5–1 μm in size, but the thickness was not calculated because the boundary between the film and the substrate could not be distinguished clearly. This revealed that the alumina dissolved into the solvent during the treatment. Tadanaga et al.,27,28 prepared...
Fig. 6. FE-SEM surface images of (a) alumina film before hydrothermal treatment, (b) sample after treatment at 180°C for 2 h, (c) sample after treatment at 180°C for 4 h and (d) sample after treatment at 180°C for 6 h. EDS results for (e) flat area (A) of film after treatment at 180°C for 4 h, (f) micro-structured area (B) of film after treatment at 180°C for 4 h and (g) surface of film after treatment at 180°C for 6 h.

Fig. 7. Cross-sectional FE-SEM images of sample treated at 180°C for 6 h.

Fig. 8. FE-SEM surface image of alumina film hydrothermally treated in H₂O (pH 1) at 180°C for 6 h without NMP.
micro-structured, i.e., flowerlike, alumina films by immersing sol–gel derived alumina films in boiling water. Presumably, aluminum dissolved in water and was deposited on alumina, resulting in the formation of a flowerlike morphology, although the authors did not mention the mechanism involved. Chen and Xiang\(^{[5]}\) prepared \(\gamma\)-AlOOH whiskers from amorphous and crystalline hydrated alumina by a hydrothermal process. They reported that the amorphous precursor dissolved faster than the crystalline one and formed whiskers. On the basis of these findings, aluminum phosphate presumably formed in the hydrothermal process as follows. Aluminum dissolved in water when alumina films were heated in an autoclave at temperatures of 160°C or higher for 2 h or more. Aluminum ions reacted with phosphate ions derived from NMP and aluminum phosphate formed when the films were treated at 160°C for 6 h and at 180°C for 4–6 h. It was deposited on the substrate heterogeneously. Only when treated at 180°C for 6 h the alumina film was phosphorylated wholly, resulting in the formation of a thick, micro-structured film. However, when treated at 160°C for 6 h and at 180°C for 4 h, the films were phosphorylated partially, resulting in the formation of both the micro-structured and flat surfaces. The change in the data in Fig. 1 can be explained in terms of the durability test process and the stability of aluminum phosphate. Durability tests in this study were carried out in two steps. First, the films were immersed in boiling water. This step examined the stability of aluminum phosphate. If aluminum phosphate is stable, it will remain on and in the film and the contact angle of the film will be small. The second step was the storage of the films in an ambient atmosphere for 7 days. Sol–gel derived metal oxide films show small water droplet contact angles immediately after preparation by firing or immersion in boiling water. Their contact angles increase after storage in an ambient atmosphere.\(^{[20,21]}\) The reason is explained as follows. Large amounts of M–OH moieties are present on the metal oxide film surfaces immediately after firing or immersion in boiling water, resulting in small contact angles. However, two M–OH moieties associate to form M–O–M during the elapsed storage time, resulting in large contact angles. The films were not phosphorylated when they were treated under 150°C, at 160°C for 2–4 h and at 180°C for 2 h. The contact angles of the films increased during storage. Because the films treated at 160°C for 6 h and at 180°C for 4 h were phosphorylated partially, their contact angles increased during storage. However, only the film treated at 180°C for 6 h was phosphorylated wholly, and its contact angle remained small after the boiling test and storage. The superhydrophilic films in this study had a micro-structured surface similar to the honeycomb-like,\(^{[2]}\) bird’s nest-like,\(^{[5]}\) nanowire-like\(^{[6]}\) and strawberry-like\(^{[7]}\) structures reported for other superhydrophilic metal and metal oxide films of aluminum\(^{[5,6]}\) and molybdenum.\(^{[9]}\) The relationship between superhydrophilicity on rough surfaces and the water droplet contact angle has been discussed on the basis of Wenzel’s model.\(^{[22]}\) According to this model, the contact angle \(\theta\) on a rough surface can be described as follows.\(^{[22]}\)

\[
\cos \theta = r \left( \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{SV}} \right) = r \times \cos \theta
\]

In this equation, \(\theta\) denotes the contact angle on a smooth solid surface, \(\gamma_{SV}\), \(\gamma_{SL}\) and \(\gamma_{SV}\) represent interfacial surface tensions of solid–gas, solid–liquid and liquid–gas interfaces, respectively, and \(r\) is the roughness factor that is defined as the ratio of the actual area of a rough surface to the geometrically projected area and is greater than unity. Contact angles on rough surfaces are smaller than those on flat ones. The micro-structured surface in this study promoted small contact angles, resulting in superhydrophilicity.

### 4. Conclusion

Nanofibrous alumina films reacted with NMP under hydrothermal conditions. The surface properties of slightly opaque or transparent films were evaluated. The composition and morphology of the films were analyzed by FT-IR(RAS), XPS, FE-SEM and EDS. These analyses revealed that aluminum phosphate formed on and inside the alumina films in a hydrothermal condition only at 180°C for 6 h, whereas it formed partially under the conditions of 160°C for 6 h and 180°C for 4 h. A micro-structure with a serrated morphology formed over the whole film surface when the film was treated at 180°C for 6 h, whereas the morphology formed partially under the conditions of 160°C for 6 h and 180°C for 4 h. This morphology corresponded to the degree of phosphorylation. It is concluded that superhydrophilic alumina films were fabricated by the hydrothermal process using nanofibrous alumina films and an NMP aqueous solution. It is also concluded that phosphate moieties at the surface and inside the films and the micro-structured film surface produced superhydrophilicity.

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### References