Preparation of a Highly Oleophobic Magnesium Alloy AZ31 Surface with Hierarchical Structure and Fluorination

Jonghyeon Jeong and Woonbong Hwang

ABSTRACT: Wettability is an important surface property owing to its useful characteristics such as self-cleaning, antifrosting, and anticorrosion. In particular, an oleophobic surface, which can overcome the limitation of the anti fouling performance of a hydrophobic surface, is a considerably valuable research subject. Magnesium alloys are widely used in various industrial fields owing to their superior mechanical performance; however, a technology that is applicable for surface modification has been limited due to their chemical properties. In this study, a new method to prepare a highly oleophobic magnesium alloy AZ31 surface is introduced; this method involves applying a hierarchical structure and fluorination. The hierarchical structure was formed via two-step anodization and magnesium hydroxide formation, and a self-assembled monolayer (SAM) coating method was applied to fluorinate the surface. This hierarchical structure with low surface energy can reduce the contact area between the surface and droplets, thereby decreasing the adhesive force. Contact angles were measured using various test liquids to evaluate the oleophobic surface, and all test liquids, including rapeseed oil (35.0 mN/m), were repelled by the surface.

1. INTRODUCTION

The wetting properties of material surfaces have been widely studied because of their potential for various applications. It is known that the surface wettability varies depending on the surface structure and surface energy. The Wenzel model shows that the surface wettability increases as the surface roughness increases. Therefore, if the surface roughness is sufficiently high, the surface can be fully wetted by water. In addition, the Cassie−Baxter model states that a proper surface structure and proofing agent provide superhydrophobic characteristics that prevent the surface from getting wet. Based on this model, many studies related to various fields such as self-cleaning, antifrosting, antifouling, and anticorrosion have been conducted by making use of superhydrophobic properties realized through surface structure and surface energy modification.

However, a simple superhydrophobic surface cannot repel liquids with a relatively low surface tension, such as oil. In this case, the surface may be easily contaminated by other materials that are entangled with wet oil, resulting in the loss of superhydrophobic properties of the surface. This has led to the development of oleophobic surfaces with repulsion not only for water but also for liquids with low surface tension. In the case of an initially developed oleophobic surface, an air layer was formed in the lower part of the structure in the form of a column having a wider top area than the lower part, thereby preventing the penetration of the liquid. Thus, a droplet is supported by a columnar structure, and the contact area between a liquid and surface is drastically reduced. Accordingly, the adhesion force between the surface and the liquid is also greatly reduced. However, to manufacture such a special structure, anisotropic etching through a special system is required. Therefore, several studies have been conducted to reduce the adhesion force as much as possible through a relatively easy method. Consequently, many methods to fabricate oleophobic surfaces using anodization and chemical etching on the surfaces of various metals, such as aluminum, copper, zinc, and titanium, have been published.

However, research on the oleophobic surface of magnesium has not progressed, even though magnesium is widely used in aerospace, automotive, and electronics industries owing to its many advantages such as low weight, high ductility, specific rigidity, and specific strength. The reason for this is the high electrochemical reactivity of magnesium. Moreover, anodization, chemical etching, etc., which can be applied to other metals to form various structures, do not form a special structure on the magnesium surface that can increase the
roughness sharply. Thus, the existing studies on superhydrophobic magnesium surfaces focus on increasing the repulsive force against liquids by forming particles on the surface or covering the film layer; however, in this way, the repulsive force against a solution having low surface tension is limited.

In this study, we introduce a new fabrication method to realize a highly oleophobic magnesium surface on the magnesium alloy AZ31, using two-step anodization, magnesium hydroxide particle formation, and silane coating process, as shown in Figure 1. While the large-scale wall-shape structure acts as a support for a droplet, the flake-like small-scale structures dramatically reduce the contact area between the surface and droplet, thereby dramatically reducing the adhesion. In this way, a surface that can repel various solutions with low surface tension is realized.

2. RESULTS AND DISCUSSION

When a surface has a complex structure, in the general case, a liquid can permeate through gaps in the structure and the surface is completely wet. Under certain circumstances, however, the air layer is trapped under the liquid, and they form a complex interface between the surface, liquid, and air. At this time, the liquid can be repelled by the surface and does not get wet. This complex phenomenon is generally described by the Cassie–Baxter (CB) model. According to the CB model, the apparent contact angle $\theta_{\text{CB}}$ is given by the following equation:
where $\theta_i$ is the intrinsic contact angle on the flat surface and $f_s$ is the contact area fraction of the solid. According to eq 1, the large intrinsic angle and the small contact area with the surface can lead to a high apparent contact angle. It is necessary to form a complex structure on the surface and lower the surface energy to realize that. By forming a complex structure on the surface, it is possible to secure a gap between the structures in which an air layer can exist. In addition, the decrease of the surface energy can lead to an increase of the repulsive force of the surface against the liquids, so it is possible to allow the air layer to be formed instead of the liquid permeating into the gap between the secured structures.

In this research, two-scale hierarchical structure is formed to make the gap between structures. To form the hierarchical structure, two processes were applied: anodization for large-scale structure and magnesium hydroxide particle formation for small-scale structure. Figure 2 shows the anodized AZ31 surface by timeline. The AZ31 specimen connected to the anode loses electrons, forms magnesium ions, and carves the surface of the specimen. Some of these magnesium ions react with the hydrogen carbonate and hydroxide ions dissolved in the electrolyte to form magnesium carbonate precipitates. In addition, magnesium ions react with the hydroxide ions formed at the cathode to form magnesium hydroxide precipitates. A series of reactions that occur during anodization is as follows

\[
\begin{align*}
\text{Mg} & \rightarrow \text{Mg}^{2+} + 2e^- \quad \text{(Anode)} \\
\text{H}_2\text{O} + 2e^- & \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{(Cathode)} \\
\text{Mg}^{2+} + \text{HCO}_3^- + \text{OH}^- & \rightarrow \text{MgCO}_3 + \text{H}_2\text{O} \quad \text{(4)} \\
\text{Mg}^{2+} + 2\text{OH}^- & \rightarrow \text{MgOH}_2
\end{align*}
\]

In the first anodization step, the anodization started partially and spread out from the starting points; therefore, the anodized surface exhibits an irregular structure, as shown in
grows. Repeating this process, the magnesium hydroxide structure and the cracks grow; hence, the specimen to form new magnesium hydroxide (eqs 8 and 9). By with hydroxide group on the surface of the magnesium and water in the aqueous solution, and the nuclei combine crystal nuclei are formed by the reaction of magnesium ions in an autoclave, the magnesium specimen reacts with water and forms magnesium oxide. Then, the magnesium oxide reacts with water to form the initial magnesium hydroxide (eqs 6 and 7). Meanwhile, MgOH+ forms hydrogen gas and magnesium oxide. Then, the reactions of (2), (3), and (5). After 5 min of the second anodic oxidation step, the cracks that can be seen in Figure 2a grow wide, and a sunken lowland is formed if the second anodization time reaches 10 min, as shown in Figure 2b,c. In particular, wall-like structures are formed as a recessed area is formed, and the wall-like structures reduce the contact area between the droplet and the surface. However, the contact area, especially the top side of the structure that is directly in contact with the droplet, is still large. In addition, the top area can be widened after magnesium hydroxide formation; therefore, the anodization was conducted for 20 min to reduce the area. As shown in Figure 2d, the wall structure was thinned due to considerable anodization, and increasing the anodization time did not produce a significant difference in the structure. Therefore, the anodization time of 20 min was selected as the optimized time.

After two-step anodization, magnesium hydroxide particles are formed on the surface. When the magnesium sulfate solution containing a magnesium specimen is heated to 180 °C in an autoclave, the magnesium specimen reacts with water and forms hydrogen gas and magnesium oxide. Then, the magnesium oxide reacts with water to form the initial magnesium hydroxide (eqs 6 and 7). Meanwhile, MgOH+ crystal nuclei are formed by the reaction of magnesium ions and water in the aqueous solution, and the nuclei combine with hydroxide group on the surface of the magnesium specimen to form new magnesium hydroxide (eqs 8 and 9). By repeating this process, the magnesium hydroxide structure grows.

Figure 3 shows the images of the AZ31 surfaces on which magnesium hydroxide particles form for 30, 60, 90, and 120 min. Figure 3a shows the result of the 30 min formation. It can be seen that almost no magnesium hydroxide is formed as a whole, and a small magnesium hydroxide seed is formed in the low zone of the surface and the bottom of the wall structure. When the reaction time is increased to 60 min, magnesium hydroxide is still not widely formed as a whole, but the magnesium hydroxide seed grows, and the particle formation proceeds to the lowland region and the wall that are not yet formed (Figure 3b). As can be seen in Figure 3c, when the reaction occurred for approximately 90 min, most of the surface was covered with magnesium hydroxide particles, but the particles were not completely formed on the top of some wall structures. When the particle formation time increased to 120 min (Figure 3d), it was confirmed that magnesium hydroxide was completely formed over the entire surface of the specimen. It can be seen from Figure 3e–h that the magnesium hydroxide particles grew in size with increasing reaction time. The grown magnesium hydroxide particles can greatly reduce the contact area with the droplets, thereby reducing the adhesion force, helping the droplets to fall off the surface easily.

Surface fluorination is also indispensable for reducing the contact area between the surface and droplets. Without surface energy modification, the droplets penetrate into the gaps of the structure, resulting in a wide contact area. Therefore, the surface formed by the structure has oleophilic properties, and when the droplet touches the surface, it can be seen that it spreads very widely as if absorbed by the paper. By performing fluorination on the surface, the repulsive force of the structure against the droplets is increased to form air layers instead of droplets between the structures, thereby minimizing the contact area between the droplets and the surface.

Surface fluorination is achieved by a self-assembled monolayer (SAM) method.51,52 When 1H,1H,2H,2H-perfluoro-
odecyldichlorosilane (FDTS) comes into contact with magnesium hydroxide, Cl ions bound to Si of FDTS can react with the OH ions of magnesium hydroxide to form the Si–O–Mg bonds (Figure 4a). In addition, when the FDTS in which Cl is bound to Si is converted to OH comes into contact with magnesium hydroxide on the surface, the Si–O–Mg bond is formed and water is produced as a byproduct (Figure 4b). The newly produced water again replaces Cl bonded to Si of another FDTS with OH, which then combines with the OH group of another magnesium. By repeating this process, each OH group on magnesium hydroxide is combined with FDTS, but the opposite side of FDTS is composed of −CF2 or −CF3; therefore, no reaction occurs. In this way, the single-molecule coating of FDTS on the magnesium structure surface is possible, and the thickness of the coating is very thin, below 1.4 nm. Therefore, it is possible to form a large number of fluorine groups on the surface to lower the surface energy without affecting the surface structure.

Figure 5 shows the X-ray photoelectron spectroscopy (XPS) analysis before and after surface fluorination with SAM coating.

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c01225)

**Figure 5.** XPS spectra of the hierarchically structured surface before and after fluorination.

The source is Al Kα, and the phase shift is calibrated by the C 1s binding energy of 284.5 eV. In the spectrum of the samples before and after fluorination, the peaks of the binding energies of approximately 1304 and 530 eV can be seen in common, which are the values of Mg 1s and O 1s, respectively, constituting the surface structure. In addition to the common peak, the surface after fluorination can be seen to have a binding energy of approximately 685 eV, indicating that the content of −CF2 and −CF3 bound to the surface by the SAM coating increased. By this surface energy modification, the surface energy can be lowered, and the oleophobic surface can be realized with the structure formed above.

The oleophobic surface produced by two-step anodization, magnesium hydroxide formation, and fluorination was tested for the repellency of various solutions. Four kinds of liquids were used for this test: DI water (72 mN/m), glycerol (62.5 mN/m), ethylene glycol (48.2 mN/m), and rapeseed oil (35.0 mN/m). For the untreated AZ31, the surface showed hydrophilic and oleophilic properties due to the oxide layer consisting of magnesium oxide and magnesium hydroxide on the surface. Therefore, droplets could not maintain their hemispherical shape and spread widely, as shown in Figure 6a. On the other hand, in the case of the oleophobic surface, the droplets did not spread on the surface and remained spherical owing to the low surface energy and surface, as shown in Figure 6b. To confirm this quantitatively, the contact angle between the droplet and surface was measured. As shown in Figure 6c, the contact angles were over 150° for all of the droplets at 120 min of the formation of magnesium hydroxide throughout the structure. When the magnesium hydroxide formation time was less than 60 min, the contact angles were similar because magnesium hydroxide was partially formed only at the lower and side portions of the structure. The contact angle is increased under the 90 and 120 min condition in which much magnesium hydroxide is formed at the upper end of the structure as compared to in the lower 60 min condition.

However, the tendency of the contact angle with water is different from the general oleophobic surface using other materials. In general, the contact angle is proportional to the surface tension of a droplet when fluorination is applied to the surface. However, this oleophobic surface shows that the contact angle of water is lower than that of oil. In the case of water, a droplet maintains a high contact angle at the first contact with the surface, but it gradually spreads over time, and the contact angle gradually decreases. However, this trend does not appear for oil, and further study is needed to explain the difference between water and oil behavior.

### 3. CONCLUSIONS

In this study, we developed a method to impart highly oleophobic properties to the surface of magnesium alloy AZ31. This was achieved by two-step anodization, magnesium hydroxide formation, and surface fluorination. A two-scale hierarchical structure was formed by creating a small-scale magnesium hydroxide structure on a large-scale structure by anodization. Subsequently, the contact area between the droplet and surface was minimized by lowering the surface energy using the SAM coating of FDTS. The oleophobic surface exhibits sufficient repellency for various solutions with low surface tension as well as for water. Magnesium has many restrictions in forming the surface structure by etching, anodization, etc. because of its high chemical reactivity compared to those of other metals. The successful formation of a hierarchical structure on the magnesium surface is expected to provide new opportunities for future magnesium surface studies.

### 4. EXPERIMENTAL SECTION

#### 4.1. Materials

Magnesium alloy AZ31 foil (1 mm thickness) was purchased from Alfa Aesar. The common
Sulfuric acid solution (70%), potassium hydrogen carbonate (99%), sodium hydroxide (99%), anhydrous magnesium sulfate (99.5%), and n-hexane (95%) were purchased from SAMCHUN Chemical, Korea. 1H,1H,2H,2H-Perfluorodecyltrichlorosilane (96%) was also purchased from Alfa Aesar.

4.2. Preprocessing. The 1 mm thick magnesium alloy foil was prepared with a width of 25 mm and a height of over 25 mm because a 25 × 25 mm² area of the foil was anodized. The prepared foil was polished by dipping it in a 1.5 M sulfuric acid solution for 10 s and further wiping it quickly. Subsequently, the wiped foil was dipped in 0.05 M sulfuric acid for 5 min to remove the remaining foreign materials. Then, the foil was rinsed with deionization (DI) water and dried.

4.3. Anodization to Form Large-Scale Structures. The prepared magnesium foil was anodized twice. A 0.01 M potassium hydrogen carbonate solution was used as the electrolyte for the first anodization step. Before anodization, the electrolyte was aged by anodizing a dummy AZ31 foil under a constant current density of 0.24 A/cm² at 25 °C for 80 min. Then, the preprocessed foil was anodized under the same conditions, except 30 min of anodization time. The first anodized foil was rinsed with DI water.

The rinsed foil was anodized once more using a 1 M sodium hydroxide solution as the electrolyte. The foil was anodized under a constant current density of 0.32 A/cm² at 25 °C for 20 min. Further, the anodized foil was also rinsed with DI water and dried.

4.4. Magnesium Hydroxide Formation for Small-Scale Structures. An autoclave was filled with 0.005−0.01 M of magnesium sulfate solution up to approximately 70% of the autoclave volume. Subsequently, the anodized foil was placed in an autoclave. The autoclave was heated to 180 °C for 30, 60, 90, and 120 min. Then, the heated autoclave was cooled by water, and the AZ31 foil was rinsed with DI water and dried.

4.5. Surface Energy Modification by Fluorination. The AZ31 foil was immersed in n-hexane-based 0.1 vol% of 1H,1H,2H,2H-perfluorodecyltrichlorosilane solution for 30 min. Next, the foil was rinsed with n-hexane and dried.

4.6. Characterization. The surface structure was observed by field emission scanning electron microscopy (FE-SEM; SU6600, Hitachi, Japan). The surface elemental composition was analyzed using a X-ray photoelectron spectrometer (XPS; VG scientific ESCALAB 250, UK). The contact angles of various droplets were measured using a contact angle measurement equipment (SmartDrop, FemtoFAB, Korea). The contact angles were measured at five different points on the specimen, and the average values were used.

Table 1. Elemental Composition of Magnesium Alloy AZ31

| element | Mg | Al | Zn | Mn | Si | Cu | Ni | Fe |
|---------|----|----|----|----|----|----|----|----|
| wt %    | balance | 2.5−3.5 | 0.6−1.4 | 0.2−1.0 | 0.1 | 0.05 | 0.005 | 0.005 |

The detailed elemental composition of AZ31 is shown in Table 1. The performance of superhydrophobic surfaces and lubricant-infused fibrous membranes with improved hemocompatibility, anticoagulation, and anti-fouling performance. Colloids Surf., A 2020, 585, 124087.

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Author

Jongyeon Jeong — Department of Mechanical Engineering, POSTECH, Pohang 37673, Republic of Korea

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c01225

Author Contributions

J.J. conducted all experiments and research studies under the supervision of W.H. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

SAM, self-assembled monolayer; FE-SEM, field emission scanning electron microscopy; XPS, X-ray photoelectron spectrometer; FDTS, perfluorodecyltrichlorosilane

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Author Information

Corresponding Author

Woonbong Hwang — Department of Mechanical Engineering, POSTECH, Pohang 37673, Republic of Korea; orcid.org/0000-0001-9072-9732; Phone: +82-54-279-2174; Email: whwang@postech.ac.kr; Fax: +82-54-279-5899
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