Fabrication of Superhydrophobic Surface on Magnesium Alloy

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A stable biomimetic superhydrophobic surface on magnesium alloy was fabricated by microarc oxidation pretreatment and followed by chemical modification based on lotus effect. The as-prepared surface showed an interesting micro- and nanoscale binary structure, exhibiting a good superhydrophobic property with a water contact angle larger than 150° and a water sliding angle less than 8°.

Over the past decade considerable progress has been made in the development of biomimic superhydrophobic surfaces with a water contact angle (CA) larger than 150° and a water sliding angle (SA) less than 10° based on lotus effect.[1–4] Lotus leaf exhibits water repellency and self-cleaning characteristics by inducing water droplet to rest on it, but roll when it is tilted slightly and do so with advancing and receding contact angles.[5] The numerical results have implicated that an appropriate surface roughness, which could trap air in the surface, lowering the surface free energy, is the main cause of rendering this effect.[1–10] Accordingly, it is essential to increase the surface roughness to provide direct pathways for fabrication of superhydrophobic surfaces based on lotus effect.[11]

In our previous papers,[1] we have successfully fabricated the superhydrophobic surfaces on aluminum, aluminum alloy and copper substrates by means of various wetting chemical reactions. Magnesium alloy as a kind of excellent engineering material has an attractive application in the aerospace, automotive and communication fields. Magnesium has even been suggested for use as an implant metal because of its low weight and inherent biocompatibility.[12] To the best of our knowledge, a superhydrophobic magnesium alloy has not yet been reported. Herein, we present a facile and cost-effective fabrication process of a superhydrophobic surface on magnesium alloy by means of microarc oxidation pretreatment, followed by chemical modification. In this way, a hierarchically rough structure (micro- and nanoscales) is created.

With the aim of obtaining a high repellence to water, the method employed is as follows: The Mg–Zn alloy blocks (mass fraction: Zn 3.0–5.5%, Cu 0.1%, impurity 0.3%, balance Mg) with a size of 25 mm × 14 mm × 12 mm were ground to an average surface roughness of $Ra \approx 0.18\,\mu\text{m}$, cleaned with a detergent solution, and then washed with distilled water. The microarc oxidation process was conducted in alkaline phosphate electrolyte under bipolar pulsed electrical source. The samples were coated in the electrolytic solution for 30 min at a constant current density. Coated samples were flushed with water after the treatment and dried in warm air. The coated sample was then immersed in 0.5 M aqueous acrylic acid solution at $80 \pm 3\,^\circ\text{C}$ for around 2 h, modified with poly(dimethylsiloxane) vinyl terminated (PDMSVT) (containing 1 wt % 184 curing agent) by means of drop coating, and annealed at around 120 °C for about 2 h. The detailed fabrication process is shown in the Supporting Information.

Figure 1 shows the SEM images of the magnesium alloy surface after microarc oxidation and the resulting surface, respectively. Figure 1a shows the morphology of the oxide film after microarc oxidation treatment, revealing a porous microstructure and a relatively uniform surface appearance (left and right images of Figure 1a). Figure 1b shows the morphology of the resulting surface on oxide film after chemical modification. It is clear that many islands with average diameters of 20–70 µm are distributed uniformly across the surface (Figure 1b left). The right image of Figure 1b is the subsurface images at ×500 magnification, implying the subsurface is composed of nanoconvexities with average diameters of 200–400 nm in arrays on the islands. The superhydrophobicity is believed to be due to the presence of cooperative binary structures at micro- and nanometer scales formed on the resulting surface, which reduces the surface free energies, regardless of the effect of lower surface energy materials.[1–3]

The XRD pattern of the oxide film surface (Figure 2a) shows strong peaks around 42 and 62° indexing to (200) and (220) of magnesium oxide, respectively, and only a few weak peaks corresponding to the element magnesium were also observed in the surface, indicating that the elemental magnesium on the surface is almost changed into magnesium oxide by microarc oxidation process. The case has changed a lot after the coated sample was immersed into 0.5 M aqueous acrylic acid solution. The characteristic peaks of the resultant product became stronger and transferred. The strong peaks at around 32 and 37° indexing to (100) and (101) of magnesium organic compound are attributed to the chemical reaction between magnesium oxide and acrylic acid, which also causes the considerately surface roughness (as shown in Figure 1b). In a word, the XRD analysis proved that magnesium organic compound had been produced with a simple route. It is noted that, if the magnesium alloy substrate was not treated with microarc oxidation prior to the immersion, the

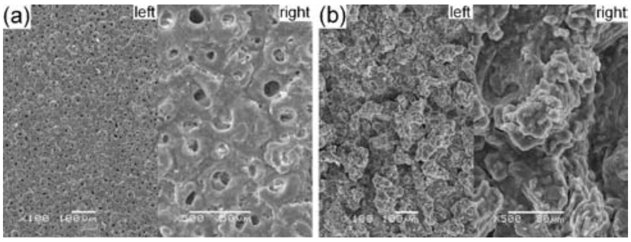

Figure 1. The SEM images of the magnesium alloy surface after microarc oxidation (a) and the resulting surface (b) showing good superhydrophobic properties.

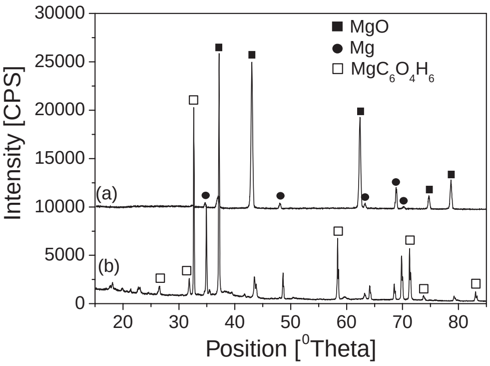

Figure 2. XRD patterns of (a) magnesium alloy and (b) the microroughness film on magnesium alloy substrate immersed into 0.5 M aqueous acrylic acid solution at 80 ± 3 °C for about 2 h after being treated with microarc oxidation.

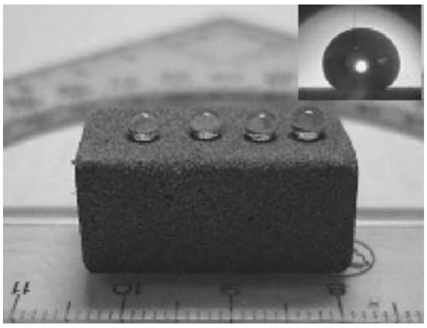

Figure 3. Photograph of a few water droplets with weight of all about 10 mg on the resulting surface onto magnesium alloy substrate to demonstrate superhydrophobicity and the water contact angle of about 155 ± 1.6°.

binary-scale structure surface roughness could not be achieved when the magnesium alloy substrate was directly immersed in aqueous acrylic acid solution, indicating the process of microarc oxidation pretreatment is very vital to fabricate the resulting superhydrophobic surface.

The superhydrophobicity of the above as-prepared surface was then investigated by probing the contact angle via the sessile drop and tilting-plate measuring methods. Prior to the immersion, the water contact angle of the surface after treatment with microarc oxidation was measured to 51 ± 1.6°, and the sliding angle is more than 90°, indicating hydrophilicity and a larger contact hysteresis (see Supporting Information). However, when the sample was immersed into aqueous acrylic acid solution and modified with PDMSVT, the water contact angle of the as-prepared surface added up to 155 ± 1.6° and the sliding angle was less than 8° (see Supporting Information), shown in Figure 3, indicating the contact type between the water droplet and the resulting surface is Cassie model, not Wenzel model.[13,14] The high water contact angle and low sliding angle of the resulting surface indicate that the water droplets do not penetrate into the grooves but rather are suspended on the resulting surface. The difference of wettability of the surface before and after being treated with aqueous acrylic acid solution is attributed to the formation of nanoscale structure for the resulting surface, resulting in a dual-scale structure. McCarthy and Gao[15] believed that the dual length-scale topography affects the kinetics of contact line recession by lowering the transition-state energy between metastable states and showed the reasons that dual-length scales are important for superhydrophobicity: one involving the kinetics of droplet movement; another involving the thermodynamics of wetting. Thereby, in our research herein, the distinguishable hierarchical micro- and nanostructures developed by microarc oxidation pretreatment, followed by wetting chemical reaction and chemical modification should be responsible for the formation of the final superhydrophobicity with a high contact angle and a small water contact angle hysteresis.

In conclusion, we have successfully developed a facile and cost-effective method to fabricate a superhydrophobic surface on magnesium alloy substrate. This superhydrophobic surface is expected to be important in those fields such as preventing containment, anticorrosion and biocompatibility.

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16 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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