Materials Letters 193 (2017) 42–45

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

# Ultrafast fabrication of superhydrophobic surfaces on engineering light metals by single-step immersion process

Takahiro Ishizaki [a,*], Sou Kumagai [b], Mika Tsunakawa [b], Takuya Furukawa [b], Kae Nakamura [b]

[a] *Materials Science and Engineering, College of Engineering, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, 135-8548, Japan*
[b] *Materials Science and Engineering, Graduate School of Engineering and Science, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, 135-8548, Japan*

ARTICLE INFO

*Article history:*
Received 22 November 2016
Accepted 13 January 2017
Available online 16 January 2017

*Keywords:*
Magnesium alloy
Alminum alloy
Superhydrophobicity
Immersion process
Anticorrosion

ABSTRACT

Superhydrophobic surfaces were successfully fabricated on magnesium alloy AZ31 and aluminum alloy Al6061 by an easy and ultrafast single-step immersion process. The treated surfaces were composed of myristic acid and cerium oxide, and showed a static water contact angle of more than 150°. The shortest process time for fabricating superhydrophobic Mg and Al alloys were found to be 60 and 15 s, respectively. The anticorrosion resistance of the superhydrophobic AZ31 was estimated by potentiodynamic polarization curve measurements. The polarization curve measurements revealed that the superhydrophobic AZ31 improved the anticorrosion resistant performance of magnesium alloy AZ31.

## 1. Introduction

The control of wettability on solid surfaces is one of the most important technologies from a viewpoint of industrial applications. Superhydrophobic surface means a surface showing a water contact angle of more than 150° and a sliding angle of less than 10° [1]. Nature creates many living organisms that exhibit superhydrophobic properties such as lotus leaf [2] and legs of water strider [3]. The superhydrophobic properties are created by a combination of dual structures at nano- and micrometers scales and coverage of wax-like materials on them. The special micro-nano-binary structures increase the surface roughness and minimize the contact area between the surface and liquid.

Mg and Al alloys are light metals and the greatest advantage of these metals is their light weight, which has made it possible to achieve energy savings in automobiles, ships, trains and airplanes through their use [4,5]. However, the light metals offers a much lower corrosion resistance. The corrosion reaction occurs by contacting the light metals with water and environmental humidity [6]. To suppress their contact, superhydrophobic coating would be one of the most suitable technologies because it would inhibit considerably their contact, resulting in improvement of the corrosion resistance [7]. Thus, various methods including the sol-gel process [8], electrodeposition [9,10], electrospinning [11], hydrothermal technique [12], chemical vapor deposition [13], spray coating [14] to fabricate superhydrophobic surface on various metal surfaces such as steel, copper, zinc, aluminum, and magnesium [15–18], have been developed to improve their corrosion performances. However, most of these methods are costly and time-consuming, and often multi-step processes. Thus, the development of an economical, easy, and rapid surface treatment method for fabricating superhydrophobic coating on the metals to improve the corrosion resistance is highly desirable. Guo et al. fabricated a superhydrophobic surface by immersing zinc or copper substrate into an aqueous solution of 0.1 M $CuCl_2$ and 1 M HCl at room temperature, followed by modifying octadecanethiol and revealed that the fabricated zinc surface showed a water contact angle of 160° and copper mesh had oil absorption ability [19]. Although this method realized to impart superhydrophobicity to metal surfaces in very short time, the process is multi-step. From a viewpoint of industrial application, fabricating superhydrophobic surface on metal surfaces at single step is highly desirable.

In this letter, we report a simple and ultrafast one-step immersion process at room temperature for fabricating superhydrophobic surfaces on engineering light metals, which was successfully applied to Mg and Al alloys.

## 2. Experimental procedures

Magnesium alloy AZ31 (composition: 2.98% Al, 0.88% Zn, 0.38% Mn, 0.0135% Si, 0.001% Cu, 0.002% Ni, 0.0027% Fe, and the rest is Mg) and aluminum alloy Al6061 with a size of 10 × 10 × 1.5 mm were used as the substrates. Each substrate was ultrasonically

---

* Corresponding author.
*E-mail address:* ishizaki@shibaura-it.ac.jp (T. Ishizaki).

http://dx.doi.org/10.1016/j.matlet.2017.01.050
0167-577X/© 2017 Elsevier B.V. All rights reserved.

cleaned in absolute ethanol for 10 min. Solution A was prepared by introducing 5.03 g of myristic acid into 100 mL of ethanol. Solution B was also prepared by introducing 1.15 g of cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) into 100 mL of ultrapure water. The solution A and B was mixed at the volume ratio of 7:3. The mixed solution's pH were adjusted to be 2 using nitric acid. The cleaned Mg alloy substrates were immersed for 1 to 30 min in the mixed solution at the room temperature. After the immersion, the AZ31 substrate was extracted from the solution and dried with inert $N_2$ gas. The Al alloy substrate was also immersed in the mixed solution at the volume ratio of 7:3 for 10 to 60 s at the room temperature. After the immersion, the Al6061 substrate was extracted from the solution and dried with inert $N_2$ gas.

The surface morphologies of the obtained samples were observed by field emission scanning electron microscopy (FE-SEM; JSM-7610, JEOL Corp.). The composition of the samples was quantitatively determined using energy dispersive X-ray analysis (SEM-EDX) and X-ray photoelectron spectroscopy (XPS, JPS-9010MC). All binding energies in the spectra were corrected using standard binding energy of C 1s peak (284.6 eV) as reference.

Static water contact angles of the fabricated surfaces were estimated with a contact angle meter (Kyowa Interface Science, DM-501) based on a sessile drop measuring method with a water drop volume of 2 μl. The measurements were conducted in air at 298 K. The water contact angles were measured at different five points and were averaged. The dynamic water contact angles of the superhydrophobic surfaces were determined using ultrapure water that was added and withdrawn from the drop, respectively. Their measurements were conducted in air at room temperature.

All electrochemical measurements were performed in a 5.0 mass% NaCl aqueous solution at room temperature using a computer-controlled potentiostat (Princeton Applied Research, VersaSTAT$^3$). Potentiodynamic polarization curves were measured at a scanning rate of 0.5 mV/s from −100 to +800 mV with respect to the open circuit potential (OCP) after the immersing the film coated AZ31 into the NaCl solution for 30 min. The film coated on the AZ31 magnesium alloy and a platinum plate were employed as the working and counter electrodes, respectively. An Ag/AgCl-saturated electrode was used as a reference.

## 3. Results and discussions

The static water contact angles on the treated AZ31 Mg alloy surfaces as a function of immersion time are shown in Fig. 1(a). The water contact angle of the AZ31 Mg alloy surface after immersion for 1 min were found to be more than 150°, showing superhydrophobic surface. The corresponding photo of the water droplet on the superhydrophobic AZ31 is shown in the inset of Fig. 1b. The static water contact angle values are almost kept constant to be in the ranges of 150 to 156° despite of the immersion time. The advancing and receding water contact angles of the sample surfaces treated for 1, 3, 5, 10, and 20 min were estimated to be 153.4 and 146.1°, 151.2 and 143.9°, 150.3 and 145.5°, 151.8 and 143.2°, and 153.5 and 149.4°, respectively. Water contact angle hysteresis for all samples are found to be less than 10°. The surface morphology of the AZ31 Mg alloy surface after immersion for 1 min are shown in Fig. 1b. The SEM image shows that the surface

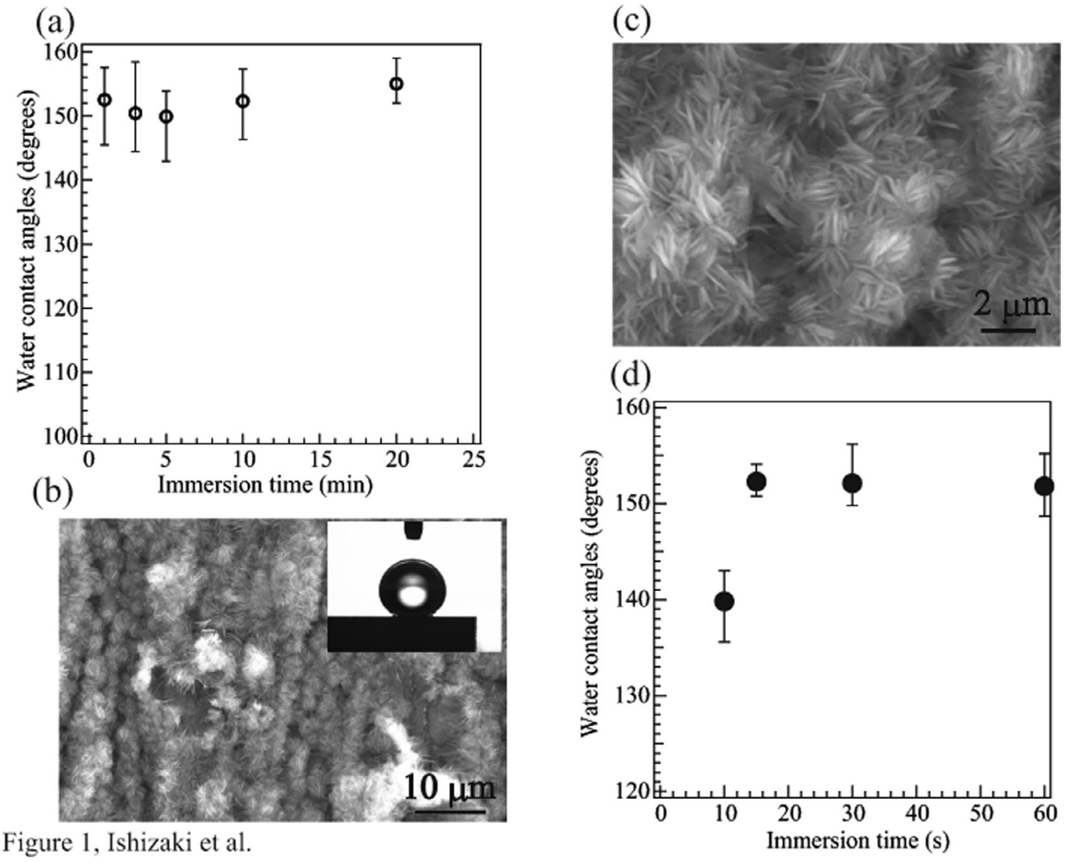

**Fig. 1.** (a) Static water contact angles of the treated AZ31 surface as a function of immersion time. (b) SEM image of the superhydrophobic AZ31 treated for 1 min. The inset shows a photo of the water droplet on the superhydrophobic AZ31 treated for 1 min. (c) SEM image of the enlarged version of (b). (d) Static water contact angles of the treated Al6061 surfaces as a function of immersion time.