



Surface microstructurization of a sputtered magnesium thin film via a solution–immersion route

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ARTICLE INFO

Article history:

Received 16 October 2009

Accepted 17 November 2009

Available online 24 November 2009

Keywords:

Magnesium
Thin film
Sputtering
Surface
Microstructure

ABSTRACT

Surface microstructurization is one of the important procedures to fabricate a superhydrophobic surface of materials. Thus, this study was focused on the modification of the surface microstructure of magnesium materials to tailor its wettability. Bias magnetron sputtering was used to prepare magnesium thin films. In the deposition process, a relatively dense magnesium film was obtained using the bias voltage of 200 V. A solution–immersion method was subsequently applied to modify the surface of the magnesium thin film. A honeycomb-like layer, mainly composed of $\text{Mg}(\text{OH})_2$, was formed on the film's surface after the surface modification. Accordingly, this route provides a basis for the following surface functionalization of magnesium materials.

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1. Introduction

In recent years, magnesium and magnesium-base materials have received much attention owing to their potential use as structural materials [1,2], biomaterials [3,4], sacrificial anode materials [5,6] and hydrogen storage materials [7,8]. However, extensive applications of magnesium and magnesium-base materials have been limited by their poor corrosion resistance.

Surface plays an important role in controlling some properties of materials, such as wettability, corrosion and catalysis. In order to reduce the corrosion of magnesium materials, one of the effective ways is to avoid the immersion in aqueous solutions and a superhydrophobic surface seems possible to perform this function. Because both surface free energy and surface microstructure are key factors to influence the wettability of a surface, a traditional way to obtain a superhydrophobic surface is usually performed as follows: the substrate is first modified to obtain a rough microstructured surface and then is coated with low-surface energy materials. Chemically, the wettability of a flat solid surface is governed by the free energy of the surface material and a fluorinated surface has the lowest free energy. Even so, the contact angle (CA) of water on such a flat surface is no more than 120° [9,10]. It is known that the wettability of a surface can be amplified by its roughness. Thus, it is necessary to fabricate a rough microstructured surface in the preparation of a superhydrophobic surface. So far, many kinds of microstructured surfaces have been created. For example, Xu [11]

used a solution–immersion process to build a hierarchical structure on copper substrate to perform the function of superhydrophobicity. In this study, we attempted to fabricate a rough microstructured surface on a sputtered magnesium film using a simple solution–immersion method.

2. Experimental

A DC magnetron sputtering system was performed to prepare magnesium films on as-polished silicon substrates and glass substrates in this study. Substrates were ultrasonically washed in pure alcohol for 5 min before they were sent into the vacuum chamber. When the base pressure of the chamber was below 2.66×10^{-3} Pa, the magnetron sputtering source was used to prepare Mg films with Ar as sputtering gas. The specific parameters are shown as follows: Ar flux of 40 sccm, sputtering current of 2 A and deposition of 60 min. In this series of experiments, negative bias voltage was applied at pulse mode with frequency of 350 kHz and its value was chosen as 50, 100, 200 and 300 V for investigation, respectively. After magnesium films were obtained, they were immersed into 3.5 wt.% sodium chloride solution for 30 min at room temperature (RT) for surface modification.

Field emission scanning electron microscope (FESEM) was performed to characterize the surface morphology and cross section morphology of the obtained Mg films. X-ray diffraction meter (XRD) with Cu $K\alpha$ radiation was used to study the crystal structure of these films. After surface modification, FESEM was applied to observe the surface and cross section morphology of the modified surface layer. X-ray diffraction meter (XRD) and X-ray photoelectron spectrometry (XPS) were performed to identify the phase structure and the chemical state of the elements in the surface layer, respectively.

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3. Results and discussion

Fig. 1 shows the surface and the cross section morphologies of sputtered magnesium thin films. With the increase of bias voltage from 50 V to 200 V, the obtained magnesium coating became dense gradually. But, the film turned looser again when the value of bias voltage reached 300 V. Fig. 2 presents the XRD patterns of magnesium thin films prepared under different bias voltages. When applied bias voltage was 50 V, there were three peaks, (002), (102) and (103), occurred in the XRD pattern of Mg film. The (002) texture was gradually strengthened with the increase of bias voltage. In the process of thin films deposition, when bias voltage is applied to substrate, energetic Argon ions are introduced to bombard the surface of the growing thin film. The higher the applied bias voltage is, the higher the energy of Argon ion is. Thus, the energy of deposition atoms is enhanced, which improves their diffusion ability. So, the quantity of the pores between columns is reduced as a result of the enhancement of the deposition atoms' diffusion ability. But, the re-sputtering effect will be also gradually enhanced with the increase of bias voltage, which eventually induces the film to become loose again.

From the result of SEM observation, it was found that the Mg film prepared at bias voltage of 200 V was relatively dense. Thus, the film prepared at bias voltage of 200 V was used as a template in order to reduce the effect of substrate in the following immersion process. Fig. 3 shows the surface morphology and the cross section morphology of the modified layer on Mg surface. Combined with the observation of the surface and the cross section, it can be found that this modified layer presented a honeycomb-like structure, which also indicates that a microstructured layer was successfully obtained by this facile method. Fig. 4 (a) shows the XRD patterns of Mg film after immersion. By comparison, it can be found that this modified layer mainly consisted of $\text{Mg}(\text{OH})_2$. XPS with Argon ions etching was further used to investigate the modified layer. The aim of Argon ions etching was to investigate the chemical state of the elements within

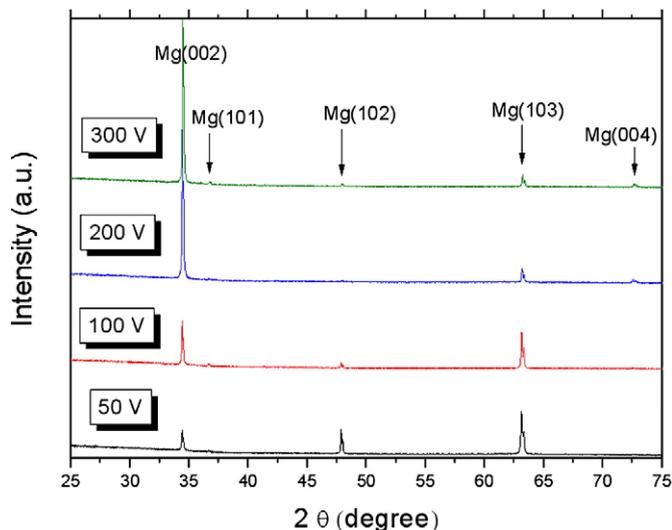


Fig. 2. XRD patterns of magnesium films prepared at different bias voltages.

the modified layer. The high resolution XPS spectra of Mg 2p and O 1s were shown in Fig. 4 (b). After 10 min Ar ions etching, Mg 2p peak was slightly shifted to a lower position in the XPS spectra. For O 1s peak, an obvious difference occurred in the curves between the original surface and the etched surface. In the curve of the original surface, the peak can be deconvoluted into two peaks whose binding energy correspond to $\text{Mg}(\text{OH})_2$ and MgCO_3 . In the curve of the etched surface, the peak can be deconvoluted into two peaks whose binding energy correspond to MgO and $\text{Mg}(\text{OH})_2$. By comparison, it can be found that the content of $\text{Mg}(\text{OH})_2$ turned lower with the occurrence of MgO at the investigated depth of the modified layer. But, there is no distinct

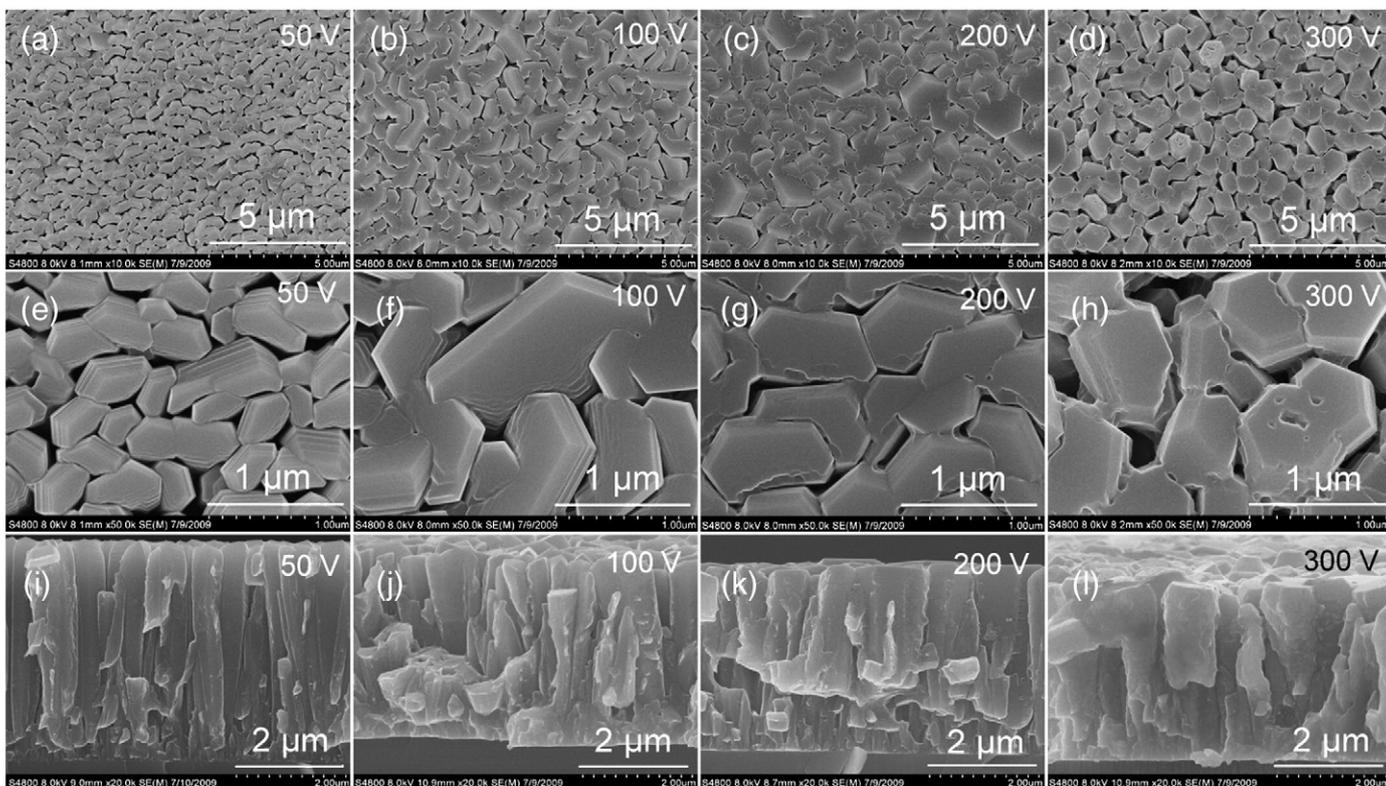


Fig. 1. Surface morphologies (a–h) and cross section morphologies (i–l) of Mg films prepared at different bias voltages.

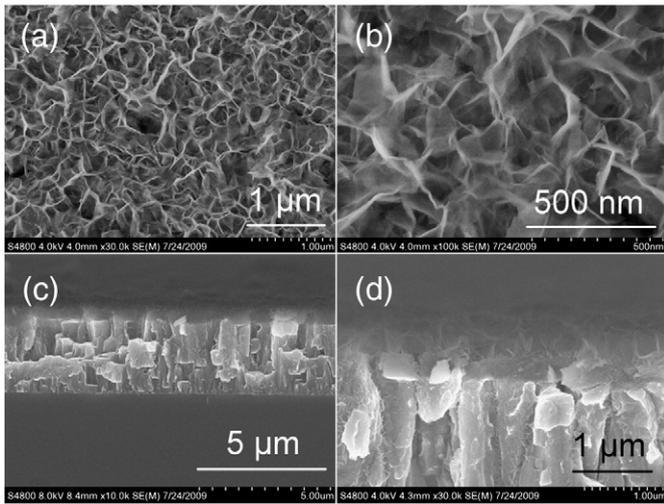


Fig. 3. Low and high magnification SEM images of the modified layer on Mg film prepared at bias voltage of 200 V: (a) and (b) surface morphology and (c) and (d) cross section morphology.

signal of MgO occurred in the XRD spectra, which is probably due to the very small content of MgO within the modified layer. Therefore, combined with the result of XRD, it can be determined that this modified layer was mainly composed of $\text{Mg}(\text{OH})_2$ with a small quantity of MgO.

Generally, the fabrication of a rough microstructured surface is a very necessary process to obtain a superhydrophobic surface. As depicted above, a facile solution-immersion method was successfully used to obtain a microstructured surface on magnesium thin film. Actually, this idea is inspired from the corrosion study of magnesium alloy. For pure magnesium materials, the corrosion product film, $\text{Mg}(\text{OH})_2$, is spontaneously formed in aqueous solution and its formation process will be accelerated with the existence of Cl^- . XPS with Ar ions etching as a traditional method has been used for the characterization of corrosion product of magnesium for a long time [12,13]. But, up to now, there is a lack of methods to observe the cross section of the corrosion product effectively because the magnesium substrate is very difficult to be split. In order to overcome this difficulty, we deposited Mg film on Si substrate in this study. Because the cleavage of silicon substrate was easy to be accomplished, the cross section of Mg film after corrosion was successfully observed. That is to say, this paper also provides a new

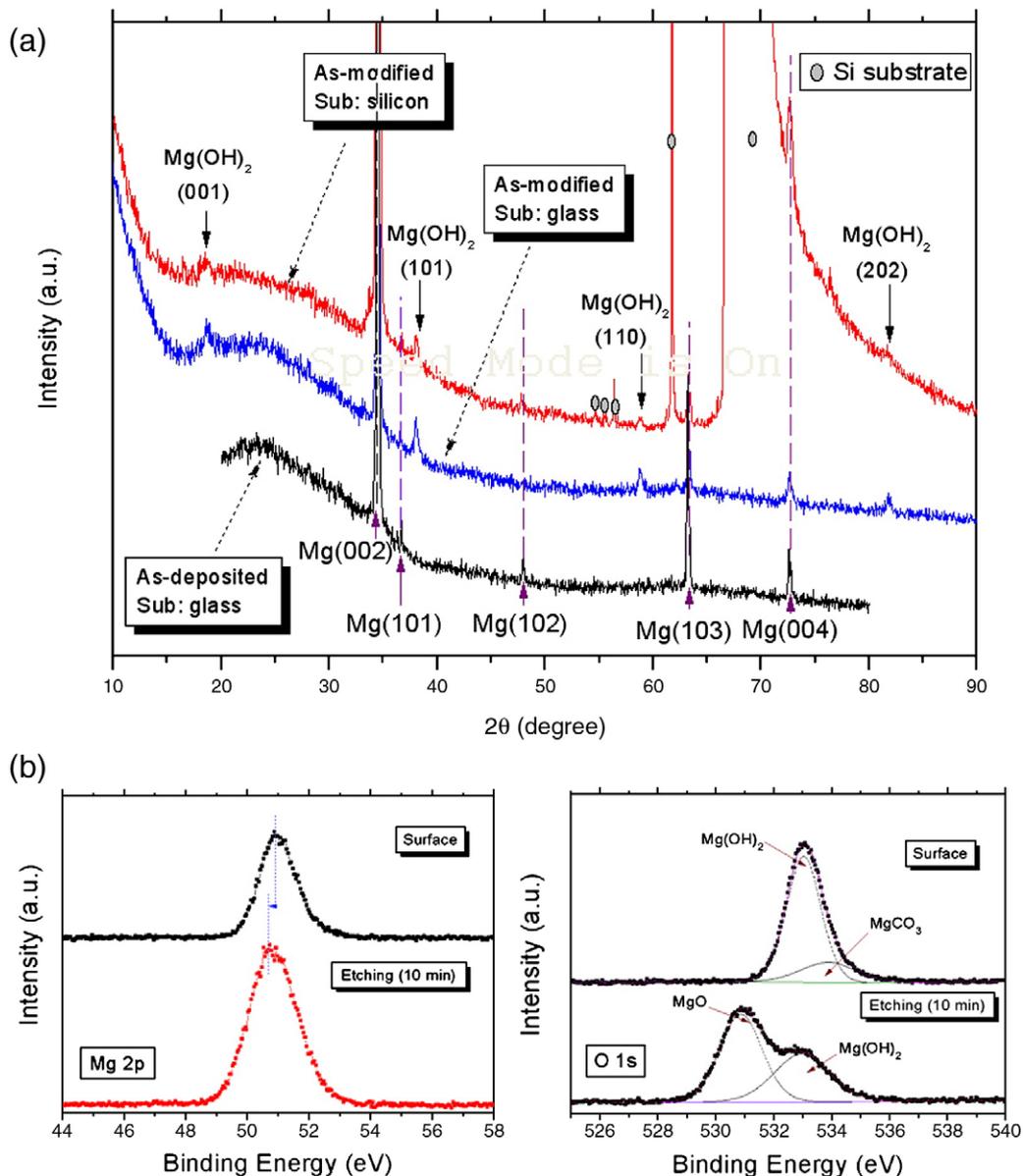


Fig. 4. (a) XRD patterns of Mg film before and after modification and (b) high resolution XPS spectra of the modified layer on Mg film.

and facile technique to study the cross sections of corrosion products formed on magnesium and magnesium-base materials.

4. Conclusions

A facile solution-immersion method was used to modify a sputtered magnesium film's surface. A honeycomb-like layer, mainly composed of $Mg(OH)_2$, was formed on its surface after 30 min of immersion in NaCl solution. This route provides a good basis for the following surface functionization of magnesium materials.

Acknowledgements

This study was supported by China Postdoctoral Science Foundation (grant no. 20080430694), Shanghai Postdoctoral Scientific Program

(grant no. 08R214156) and Zhejiang Province Key Technologies R & D Program (grant no. 2008C21055).

References

- [1] Fu P, Peng L, Jiang H, Chang J, Zhai C. *Mater Sci Eng A* 2008;486:183–92.
- [2] Fu P, Peng L, Jiang H, Zhang Z, Zhai C. *Mater Sci Eng A* 2008;486:572–9.
- [3] Ibasco S, Tamimi F, Meszaros R. *Acta Biomater* 2009;5:2338–47.
- [4] Zhang E, Xu L, Yang K. *Scripta Mater* 2005;53:523–7.
- [5] Yu B, Uan J. *Scripta Mater* 2006;54:1253–7.
- [6] Lee M, Kim J, Oh J, Yang J, Baek S. *Surf Coat Technol* 2008;202:5590–4.
- [7] Pranevicius L, Milcius D, Templier C. *Int J Hydrogen Energy* 2009;34:5131–7.
- [8] Siviero G, Bello V, Mattei G, Mazzoldi P. *Int J Hydrogen Energy* 2009;34:4817–26.
- [9] Wu X, Zheng L, Wu D. *Langmuir* 2005;21(7):2665–7.
- [10] Xiu Y, Zhu L, Hess DW, Wong CP. *Nano Lett* 2007;7(11):3388–93.
- [11] Xu W, Liu H, Lu S, Xi J, Wang Y. *Langmuir* 2008;24(19):10895–900.
- [12] Santamaria M, Di Quarto F, Zanna S, Marcus P. *Electrochim Acta* 2007;53:1314–24.
- [13] Liu M, Zanna S, Ardelean H, Song G, Atrens A. *Corros Sci* 2009;51:1115–27.