



Preparation and corrosion resistance of superhydrophobic coatings on AZ31 magnesium alloy

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Abstract: In order to improve the corrosion resistance of the Mg alloys, the superhydrophobic coatings on AZ31 Mg alloy were prepared by a two-step process of micro-arc oxidation treatment and superhydrophobic treatment in stearic acid ethanol solution. The effects of voltages, frequencies and treatment time on the contact angle of the superhydrophobic treated sample were investigated. The results showed that with increasing the voltage, frequency and treatment time, all of the contact angles of the superhydrophobic treated sample increased first, and then decreased, reaching the maximum values at 350 V, 1000 Hz and 5 min, respectively. The optimal superhydrophobic coating was mainly composed of MgO and Mg₂SiO₄ phases, with the pore diameter of ~900 nm, the thickness of ~6.86 μm and the contact angle of 156.96°. The corrosion current density of the superhydrophobic AZ31 sample decreased by three orders of magnitude, and the amount of hydrogen evolution decreased by 94.77% compared with that of the AZ31 substrate sample.

Key words: superhydrophobic coating; AZ31 magnesium alloy; micro-arc oxidation; corrosion resistance; biomedical application

1 Introduction

Magnesium and its alloys possess the advantage of high specific strength and specific stiffness, excellent damping and shock absorption capacity, strong electromagnetic shielding and heat-conducting property and easy to machining and recycling, especially for the elastic modulus and density mostly similar to that of the natural bone, biodegradability and excellent biocompatibility, which make the magnesium alloys become promising candidates for orthopedic and cardiovascular implants [1–3]. However, the Mg alloys usually corrode rapidly in body fluid, which will cause them to degrade so rapidly that they cannot maintain the mechanical support before the bone tissue is recovered completely [4,5]. Moreover, accumulation of the hydrogen bubbles in gas pockets adjacent to the implant will cause a delay in healing of the wound and lead to

necrosis of tissues, even cause death of a patient [6]. Surface treatment of deposition of a coating is a viable option to improve and control the corrosion rate of Mg alloys [4]. Among these surface treatment methods, preparation of the superhydrophobic coatings on the Mg alloys is one of the research hotspots [7–9]. The superhydrophobic surfaces have been widely used in clothing and weaving, biomedicine, liquid transport, daily products and packaging, construction, transportation and microanalysis due to their unique properties of anti-corrosion, waterproof, oil proof, acid proof, anti-snow, anti-freeze, anti-pollution, self-cleaning and antibacterial, etc [10,11]. Moreover, the superhydrophobic surfaces also possess excellent blood compatibility [12,13]. Generally, metal materials can obtain superhydrophobic coatings through building up the micro/nano surface structure and then grafting the low surface energy chemicals. The micro/nano surface structure can be obtained by etching, template, electropinning, sol-gel,

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electrodeposition, anodic oxidation and hydrothermal treatment [11,12], etc. The low surface energy chemicals contain fluorocarbon resin (polytetrafluoroethylene), organic silicon resin (polydimethylsiloxane), fluoro-siloxane resin (fluoroalkyl silane) and long-chain polymer (stearic acid), etc [11].

Micro-arc oxidation (MAO), also named as plasma electrolytic oxidation (PEO), is a high voltage plasma-assisted anodic oxidation process involved in thermochemistry, plasma chemistry and electrochemical reactions, widely employed to prepare ceramic coatings on valve metals (Al, Mg, Ti and their alloys) [4,14,15]. Previous studies demonstrated that the micro/nano order rough and porous ceramic coatings could be prepared by MAO on the Mg alloys to improve their bioactivity, corrosion resistance, wear resistance and biocompatibility [4]. The micro/nano porous structure prepared by MAO also can be used as the micro/nano surface structure of superhydrophobic coating. Recently, many superhydrophobic coatings have been constructed on the Mg alloys through the MAO treatment [13,16–18]. However, most of them only focused on the study of the performance of the superhydrophobic coatings, while the influence factors of the superhydrophobic coatings formation were rarely investigated. It is well known that the MAO is a multifactor-controlled process and the process parameters can greatly influence the surface morphologies of MAO coatings on Mg alloys [4,14]. Therefore, the superhydrophobic coatings were prepared by a two-step process of MAO treatment and immersion in stearic acid ethanol solution in this work, and the effects of the process parameters (voltage, frequency and treatment time) on the contact angles of the coatings were investigated. The surface and cross-sectional morphologies, phase composition, potentiodynamic polarization curves and H_2 evolution behavior of the superhydrophobic coatings were also studied.

2 Experimental

2.1 Sample preparation and micro-arc oxidation

Commercially available AZ31 Mg alloys were cut into $d16\text{ mm} \times 3\text{ mm}$ as the substrate materials. The cut AZ31 Mg alloys were successively polished with SiC paper from 100# to 2000#, and then ultrasonically cleaned with acetone and distilled water, respectively. The polished sample was as an anode while the wall of the stainless steel container was used as the cathode. A 10 kW homemade pulsed bipolar power supply was employed to prepare MAO coatings on AZ31 Mg alloys. The MAO treatment was carried out in an aqueous solution of $Na_2SiO_3 \cdot 9H_2O$ and NaOH with the concentrations of 15 and 5 g/L, respectively. In this work, the constant voltage mode was used and the detail

MAO process parameters are listed in Table 1. During the experiment process, the electrolyte solution was stirred and cooled below 35 °C. The coated samples were flushed with distilled water after the treatment and dried in air at room temperature.

Table 1 Process parameters of micro-arc oxidation treatment

Anodic voltage/V	Negative voltage/V	Frequency/Hz	Treatment time/min	Duty cycle (anodic/negative)/%
250, 300, 350, 400, 450	10	50, 500, 1000, 2000, 3000	2, 5, 10, 15, 30	45/45

2.2 Superhydrophobic treatment of micro-arc oxidized samples

The micro-arc oxidized samples were immersed in 10 g/L stearic acid ethanol solution at room temperature for 3 h and subsequently heated in drying oven at 120 °C for 1 h.

2.3 Characterization

The surface and cross-section morphologies of the MAO coatings were observed by a scanning electron microscope (SEM, FEI QUANTA250, USA). The phase composition of the MAO coated sample was analyzed by X-ray diffraction (XRD, D8 ADVANCE, Germany) using a $Cu\ K_{\alpha}$ radiation. The pore size and thickness of the MAO coated sample were measured from SEM images by the image analysis software of Nano Measurer 1.2. The static water contact angles (WCAs) of the superhydrophobic treated samples were measured by an optical contact angle meter (DSA 100, Krüss, Germany) with a computer-controlled liquid dispensing system at ambient temperature. The volume of the droplet was 3 μL and at least five points were tested for each sample, and the contact angles were reported as average values $\pm$ standard deviation.

2.4 Corrosion resistance

The potentiodynamic polarization test was employed to evaluate the corrosion resistance of the samples in simulated body fluid (SBF) solution at $(37 \pm 1)^\circ\text{C}$ through the electrochemical analyzer (CHI650D, China). The electrochemical measurement was conducted using a conventional three-electrode electrochemical cell with a saturated calomel electrode (SCE) as the reference, a Pt foil as the auxiliary electrode and the samples with the area of 1 cm^2 as the working electrode. The polarization scan rate was controlled at 1 mV/s.

The hydrogen evolution test was also employed to evaluate the corrosion resistance of the samples. The samples were perpendicularly immersed in the

(37 ± 0.5) °C SBF solution, in which the ratio of solution volume to the surface area of samples was 0.2 mL/mm^2 and the SBF solution was refreshed every 2 days to maintain the ionic concentrations. The schematic diagram of hydrogen collection device is shown in Fig. 1. A funnel was inverted and put at the bottom of the beaker, and then an inverted measuring cylinder was connected the bottom of the funnel to collect the gas, in which all of the containers were plastic products. During the measurement process, the hydrogen generated in the corrosion process was imported into the inverted measuring cylinder through the funnel, and the decline value of the funnel liquid level was the amount of hydrogen evolution.

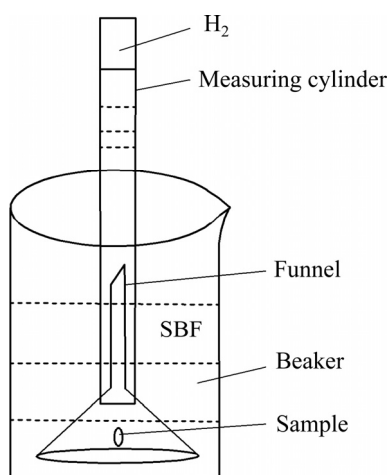


Fig. 1 Schematic diagram of hydrogen collection device

3 Results and discussion

3.1 Effect of process parameters on contact angles

Figure 2 shows the relationship between anodic voltages and the contact angles of the superhydrophobic treated samples, in which the treatment time is 5 min and the frequency is 500 Hz. It can be seen that with increasing the anodic voltages the contact angles increase first, reaching the maximum value at 350 V, and then decrease. The average contact angle of the sample prepared at 250 V is only 118.1° , and it increases from 151.7° for 300 V to the maximum value of 154.7° for 350 V. As further increasing the voltages, the contact angle rapidly decreases to 119.9° for 450 V. The anodic voltages have remarkable influence on the wettability of the superhydrophobic treated samples, because the surface uniformity of MAO coatings greatly depends on the voltages [19]. When the voltage is too low ($<300 \text{ V}$), the MAO coating is so thin that it cannot completely cover the polished scratches distributed over the surface of the sample, which results in the non-uniformity of the MAO coatings [4]. On the other hand, some oversized pores, even many micro-cracks, can be observed on the

surface of MAO coating as the applied voltage is too high ($>350 \text{ V}$), which also deteriorates the uniformity of the MAO coatings [20]. Therefore, the nonuniform coatings are adverse to the formation of superhydrophobic surface, leading to the decrease of the contact angles of superhydrophobic treated samples. When the voltage ranges from 300 to 350 V, the contact angles are larger than 150° , which can meet the preliminary requirement of the superhydrophobic surface.

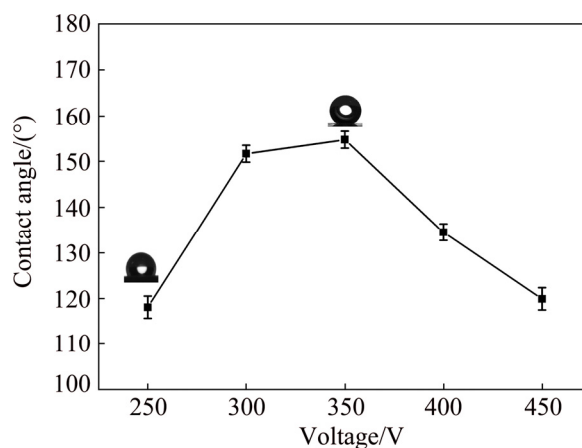


Fig. 2 Effect of voltage on contact angle of superhydrophobic treated sample

The effects of frequencies on the contact angles of the superhydrophobic treated samples are shown in Fig. 3, in which the voltage is 300 V and the treatment time is 5 min. With increasing the frequency, the contact angle increases first, and then decreases, reaching the maximum at 1000 Hz. The average contact angle of the sample prepared at 50 Hz reaches 146.3° , and it gradually increases to 154.0° with increasing the frequency to 1000 Hz. Further increasing the frequency, the average contact angle gradually decreases, lower than 150° . The effects of frequencies on the contact angles of the superhydrophobic treated samples are much smaller

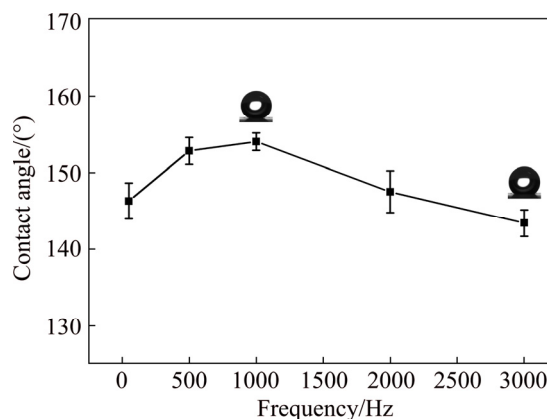


Fig. 3 Effect of pulse frequency on contact angle of superhydrophobic treated samples

than that of the voltages. The contact angles of the superhydrophobic treated samples can be higher than 150° as the frequency ranges from 500 to 1000 Hz.

Figure 4 shows the effect of treatment time on the contact angles of superhydrophobic treated samples, in which the voltage is 350 V and the frequency is 1000 Hz. With increasing the treatment time, the contact angle increases first, and then decreases, reaching the maximum at 5 min. The average contact angle of the sample prepared at 2 min is 153.78° , and it increases to 156.96° when the treatment time prolongs to 5 min. Further prolonging the treatment time, the contact angle gradually decreases to 133.45° for 30 min. Based on the above-mentioned results, the optimal preparation process of the MAO superhydrophobic coatings is the voltage of 350 V, the frequency of 1000 Hz and the treatment time of 5 min, and the maximum average contact angle of the superhydrophobic treated samples is 156.96° .

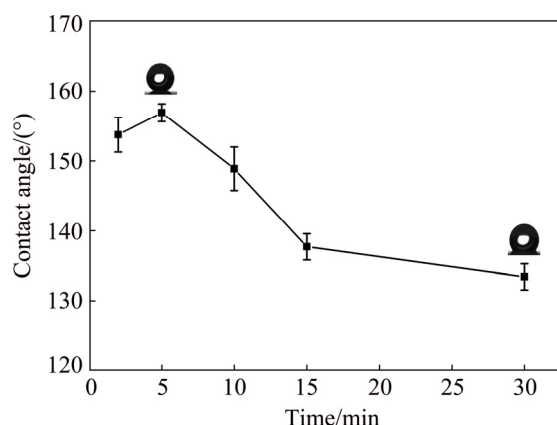


Fig. 4 Effect of treatment time on contact angle of superhydrophobic treated samples

3.2 Microstructure and phase composition of MAO coating

Figure 5 shows the surface and cross-sectional morphologies of the MAO coatings prepared with the optimal process parameters. The MAO coating exhibits uniform but rough and porous microstructure. The circular crater-like pores with an average pore size of 900 nm are randomly distributed throughout the surface, which is formed when the molten oxide and gas bubbles are thrown out of the micro-arc discharge channels [21,22]. Commonly, the morphologies of the MAO coatings are not changed after the superhydrophobic treatment [13,23]. It can be seen from Fig. 5(b) that the thickness of the MAO coating is uniform with the average thickness of $6.86\ \mu\text{m}$. No distinct discontinuity and defects between the coating and the substrate can be detected, indicating the interface bonding of the coating and the substrate is well and the coating can be tightly adhered to the substrate. Moreover, there are no apparent pores and cracks defects distributed

over the cross-section of the coating, which is beneficial to improving the corrosion resistance of AZ31 Mg alloy substrate.

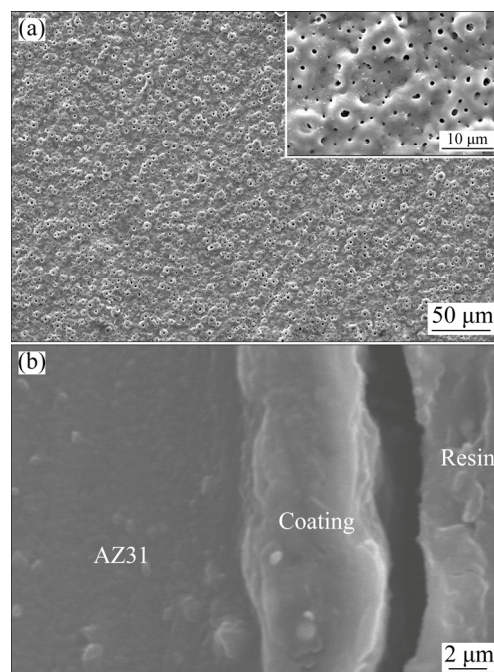


Fig. 5 Surface (a) and cross-sectional (b) morphologies of micro-arc oxidized AZ31 Mg alloys

The XRD patterns acquired from the MAO coated sample prepared with the optimal process are depicted in Fig. 6, the uncoated Mg alloy substrate as the control. The diffraction peaks of MgO and Mg_2SiO_4 phases are detected except the diffraction peaks of AZ31 Mg alloy substrate, which illustrates that the MAO coating is mainly composed of MgO and Mg_2SiO_4 phases. During the MAO process, the Mg substrate is in situ oxidized and forms MgO ceramic phase through the thermal chemical reaction, electrochemical reaction and plasma chemical reaction [14]. At the same time, SiO_3^{2-} will

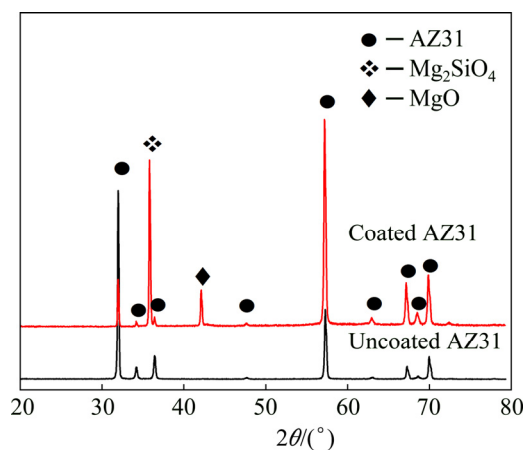


Fig. 6 XRD patterns of MAO coated and uncoated AZ31 alloys

transfer and gather near the positive electrode under the electric field effect. During the plasma discharging process, SiO_3^{2-} will further react with MgO and the Mg_2SiO_4 phase generates finally.

According to the references [13,20,24,25], the metallic samples treated by MAO would form a large number of OH groups on the surface. The OH groups react with stearic acid through dehydration self-assembling reaction when the micro-arc oxidized Mg alloy samples are immersed in the stearic acid ethanol solution. Then, the low surface energy stearic acid film is grafted on the micro-arc oxidized AZ31 Mg alloy surface through the above-mentioned self-assembling reaction. The combination of the stearic acid low surface energy film and the hierarchical micro/nano-scale MAO structure, the superhydrophobic surface on AZ31 Mg alloy is very likely achieved. In the present work, whether forming the superhydrophobic surface is mainly depend on the microstructure of the MAO coatings, such as uniformity, surface roughness and pore size, which is controlled by the MAO process parameters. According to the influence rules of the process parameters on the contact angles of the superhydrophobic treated samples, the MAO voltage has the greatest influence on superhydrophobic characteristics of AZ31 Mg alloys, the treatment time is the second and the frequency is the least. It is well known that the pore size and thickness of the MAO coatings increase with increasing the voltage and time, while the surface uniformity of the coatings deteriorates [20,26]. On the other hand, the pore size and thickness of the MAO coatings decrease with increasing the frequencies [27]. Furthermore, the number of the OH groups is also an influence factor for the formation of superhydrophobic surface, and the coatings cannot form the superhydrophobic surface when the number of OH groups distributed over the surface of MAO coatings is insufficient [28]. The relationship among the number of the OH groups, MAO process parameters and the contact angles of the superhydrophobic surface should be detailedly investigated in the future. In conclusion, the MAO coating prepared with the voltage of 350 V, treatment time of 5 min, frequency of 1000 Hz, the possessing thickness of 6.86 μm and the pore size of 900 nm, is more favorable for forming the superhydrophobic surface in this work.

3.3 Corrosion resistance of superhydrophobic sample

The potentiodynamic polarization curves of AZ31 substrate, MAO coated AZ31 sample and superhydrophobic AZ31 sample in the SBF solution are shown in Fig. 7, and the results of corrosion tests extracted from the polarization curves using Tafel extrapolation are shown in Table 2. It is clear that the corrosion resistances of both MAO coated and

superhydrophobic treated samples are improved compared with that of the uncoated AZ31 substrate, which can be observed by a shift of the whole polarization curve towards the region of lower current density and the higher potential. According to Table 2, the corrosion potential of the MAO coated AZ31 sample is shifted in the noble direction by 45 mV relative to the uncoated AZ31 sample, while the corrosion current density is two orders of magnitude lower than that of the uncoated AZ31 sample. Especially, the corrosion potential of the superhydrophobic AZ31 sample is shifted in the noble direction by 100 mV relative to the uncoated AZ31 sample, while the corrosion current density is three orders of magnitude lower than that of the uncoated AZ31 sample. Therefore, the corrosion resistance of the superhydrophobic samples is the greatest and that of the AZ31 substrate is the lowest, while the MAO coated sample is in between.

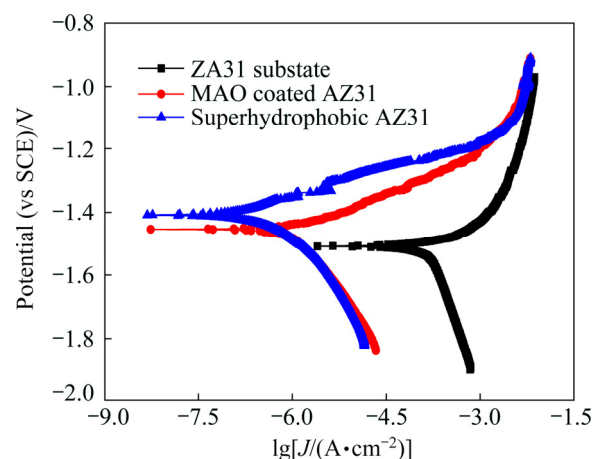


Fig. 7 Potentiodynamic polarization curves of AZ31 substrate, MAO coated and superhydrophobic samples in SBF solution

Table 2 Results of corrosion tests from potentiodynamic polarization curves

Sample	φ_{corr} (vs SCE)/V	J_{corr} (A·cm ⁻²)
AZ31 substrate	-1.509	4.21×10^{-4}
MAO coated AZ31	-1.454	1.13×10^{-6}
Superhydrophobic AZ31	-1.409	2.35×10^{-7}

Figure 8 shows the corrosion hydrogen evolution curves of the AZ31 substrate, MAO coated AZ31 sample and superhydrophobic AZ31 sample in the SBF solution. With increasing the immersion time, the amount of hydrogen evolution of the samples increases. The amount of hydrogen evolution of the AZ31 substrate is the largest, and that of the superhydrophobic AZ31 sample is the least, while the MAO coated sample is in between. The amount of hydrogen evolution of the AZ31 sample is relatively small before being immersed in the SBF solution for 50 h, and then linearly increases, which

indicates that the passive film on the AZ31 alloy surface is broken after being immersed in SBF solution for 50 h. There is little amount of hydrogen evolution of the MAO coated sample before being immersed in the SBF solution for 150 h, and it begins to linearly increase as the immersion time increases to 200 h, indicating that the MAO coating has been local failure. Almost no hydrogen releases for the superhydrophobic AZ31 sample within 225 h of immersing in the SBF solution, and then a small amount of hydrogen begins to appear with a linear increase, indicating that local failure occurs at the superhydrophobic coating after being immersed in SBF solution for 225 h. The amount of hydrogen evolution is 58.418, 8.483 and 3.052 mL/cm² for AZ31 substrate, MAO coated AZ31 sample and superhydrophobic AZ31 sample after immersed in the SBF solution for 300 h, respectively. The MAO coated sample can decrease the hydrogen evolution by 85.47% compared to the AZ31 sample, and the superhydrophobic sample can decrease by 94.77%. Therefore, the superhydrophobic coating can greatly decrease the amount of hydrogen evolution, and delay the time for the vast hydrogen evolution, which can avoid the hazard of the accumulation of the hydrogen bubbles when the Mg alloys implant the human body [4,6].

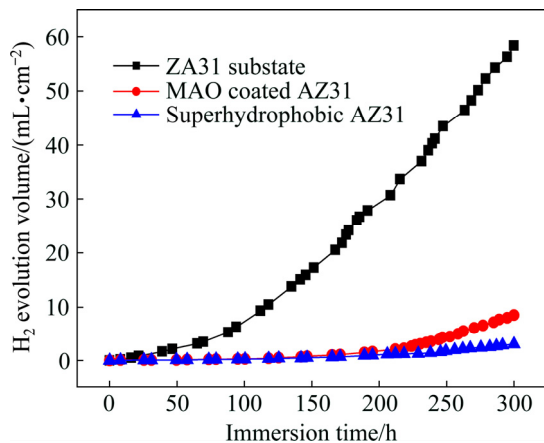


Fig. 8 Hydrogen evolution curves of AZ31 substrate, MAO coated and superhydrophobic samples in SBF solution

The MgO/Mg₂SiO₄ ceramic coating is formed on the AZ31Mg alloy after MAO treatment, which is the reason for the improvement of the corrosion resistance of the MAO coated sample. The superhydrophobic coating is formed through the superhydrophobic treatment for the MAO coated sample, which is consistent with the superhydrophobic model of Cassie–Baxter and can form the “solid–gas–liquid” three phases coexistence compound contact interface [29]. This compound contact interface can greatly decrease the contact area between the corrosive medium and the surface of sample, and impede and isolate the sample to further corrode, which

can effectively improve the corrosion resistance of the sample. Therefore, compared with the MAO coated sample the superhydrophobic surface can further improve the corrosion resistance and reduce the amount of the hydrogen evolution.

4 Conclusions

1) Micro-arc oxidation was carried out on the AZ31 Mg alloys in the silicate solution, and the maximum contact angle of the coated sample could reach 156.96° after superhydrophobic treatment in the stearic acid ethanol solution.

2) With increasing the voltage, treatment time and frequency, all of the contact angles of the superhydrophobic treated samples increased first, and then decreased. The voltage had the greatest influence on the contact angles of the superhydrophobic treated samples, and the frequency was the least, while the treatment time was in between.

3) The MAO coating was composed of MgO and Mg₂SiO₄ phases. The thickness of the MAO coating was about 6.86 μm. The circular crater-like pores with the average pore size of 900 nm were randomly distributed throughout the surface, which provided the hierarchical micro/nano-scale for the superhydrophobic surface.

4) The superhydrophobic surface greatly improved the corrosion resistance of the AZ31 Mg alloy in the SBF solution, delayed the hydrogen evolution and reduced the amount of the hydrogen evolution.

References

- [1] STAIGER M P, PIETAK A M, HUADMAI J, DIAS G. Magnesium and its alloys as orthopedic biomaterials: A review [J]. *Biomaterials*, 2006, 27: 1728–1734.
- [2] ZHENG Yu-feng, GU Xue-nan, WITTE F. Biodegradable metals [J]. *Materials Science and Engineering R*, 2014, 77: 1–34.
- [3] CUI Lan-yue, XU Ji, LU Na, ZENG Rong-chang, ZOU Yu-hong, LI Shuo-qi, ZHANG Fen. In vitro corrosion resistance and antibacterial properties of layer-by-layer assembled chitosan/poly-L-glutamic acid coating on AZ31 magnesium alloys [J]. *Transactions of Nonferrous Metals Society of China*, 2017, 27: 1081–1086.
- [4] TSN S N, PARK I S, LEE M H. Strategies to improve the corrosion resistance of microarc oxidation (MAO) coated magnesium alloys for degradable implants: Prospects and challenges [J]. *Progress in Materials Science*, 2014, 60: 1–71.
- [5] HORNBERGER H, VIRTANEN S, BOCCACCINI A R. Biomedical coatings on magnesium alloys—A review [J]. *Acta Biomaterialia*, 2012, 8: 2442–2455.
- [6] SONG G. Control of biodegradation of biocompatible magnesium alloys [J]. *Corrosion Science*, 2007, 49: 1696–1701.
- [7] LIU Y, XUE J Z, LUO D, WANG H Y, GONG X, HAN Z W, REN L Q. One-step fabrication of biomimetic superhydrophobic surface by electrodeposition on magnesium alloy and its corrosion inhibition [J]. *Journal of Colloid and Interface Science*, 2017, 491: 313–320.
- [8] MUNRO J G, CAMPBELL J. Mimicking the hierarchical surface topography and superhydrophobicity of the lotus leaf on magnesium

- alloy AZ31 [J]. Materials Letters, 2017, 189: 271–274.
- [9] ZHANG F, ZHANG C L, SONG L, ZENG R C, LI S Q, CUI H Z. Fabrication of the superhydrophobic surface on magnesium alloy and its corrosion resistance [J]. Journal of Materials Science and Technology, 2015, 31: 1139–1143.
- [10] XUE C H, JIA S T, ZHANG J, MA J Z. Large-area fabrication of superhydrophobic surfaces for practical applications: An overview [J]. Science & Technology of Advanced Materials, 2010, 11: 033002.
- [11] LIU K, TIAN Y, JIANG L. Bio-inspired superoleophobic and smart materials: Design, fabrication, and application [J]. Progress in Materials Science, 2013, 58: 503–564.
- [12] YANG Y, LAI Y K, ZHANG Q Q, WU K, ZHANG L H, LIN C J, TANG P F. A novel electrochemical strategy for improving blood compatibility of titanium-based biomaterials [J]. Colloid Surface B, 2010, 79: 309–313.
- [13] JIANG J Y, XU J L, LIU Z H, DENG L, SUN B, LIU S D, WANG L, LIU H Y. Preparation, corrosion resistance and hemocompatibility of the superhydrophobic TiO_2 coatings on biomedical Ti–6Al–4V alloys [J]. Applied Surface Science, 2015, 347: 591–595.
- [14] YEROKHIN A L, NIE X, LEYLAND A, MATTHEWS A, DOWEY S J. Plasma electrolysis for surface engineering [J]. Surface & Coating Technology, 1999, 122: 73–93.
- [15] WANG Y, YU H J, CHEN C Z, ZHAO Z H. Review of the biocompatibility of micro-arc oxidation coated titanium alloys [J]. Materials & Design, 2015, 85: 640–652.
- [16] CUI Xue-jun, YANG Rui-song, LIU Chun-hai, YU Zu-xiao, LIN Xiu-zhou. Structure and corrosion resistance of modified micro-arc oxidation coating on AZ31B magnesium alloy [J]. Transactions of Nonferrous Metals Society of China, 2016, 26: 814–821.
- [17] LIANG J, GUO Z G, FANG J, HAO J C. Fabrication of superhydrophobic surface on magnesium alloy [J]. Chemistry Letters, 2007, 36(3): 416–417.
- [18] GNEDENKOV S V, EGORKIN V S, SINEBRYUKHOV S L, VYALIY I E, PASHININ A S, EMELYANENKO A M, BOINOVICH L B. Formation and electrochemical properties of the superhydrophobic nanocomposite coating on PEO pretreated Mg–Mn–Ce magnesium alloy [J]. Surface & Coatings Technology, 2013, 232: 240–246.
- [19] GU Y H, XIONG W M, NING C Y, ZHANG J. Residual stresses in microarc oxidation ceramic coatings on biocompatible AZ31 magnesium alloys [J]. Journal of Materials Engineering and Performance, 2012, 21: 1085–1090.
- [20] XU J L, XIAO Q F, MEI D D, TONG Y X, ZHENG Y F, LI L, ZHONG Z Z. Microstructure, corrosion resistance and formation mechanism of alumina micro-arc oxidation coatings on sintered NdFeB permanent magnets [J]. Surface & Coatings Technology, 2017, 309: 621–627.
- [21] GUO H F, AN M Z. Growth of ceramic coatings on ZA91D magnesium alloys by micro-arc oxidation in aluminate–fluoride solutions and evaluation of corrosion resistance [J]. Applied Surface Science, 2005, 246: 229–238.
- [22] DUAN H P, DU K Q, YAN C W, WANG F H. Electrochemical corrosion behavior of composite coatings of sealed MAO film on magnesium alloy AZ91D [J]. Electrochimica Acta, 2006, 51: 2898–2908.
- [23] WANG Zhong-wei, SU Yong-liang, LI Qing, LIU Yan, SHE Zu-xin, CHEN Fu-nan, LI Long-qin, ZHANG Xiao-xu, ZHANG Peng. Researching a highly anti-corrosion superhydrophobic film fabricated on AZ91D magnesium alloy and its anti-bacteria adhesion effect [J]. Materials Characterization, 2015, 99: 200–209.
- [24] HAN Y, CHEN D H, SUN J F, ZHANG Y M, XU K W. UV-enhanced bioactivity and cell response of micro-arc oxidized titania coatings [J]. Acta Biomaterialia, 2008, 4: 1518–1529.
- [25] XU J L, XIAO Q F, MEI D D, ZHONG Z Z, TONG Y X, ZHENG Y F, LI L. Preparation and characterization of amorphous SiO_2 coatings deposited by micro-arc oxidation on sintered NdFeB permanent magnets [J]. Journal of Magnetism and Magnetic Materials, 2017, 426: 361–368.
- [26] XU Ji-lin, LIU Fu, LUO Jun-ming, ZHAO Lian-cheng. Effects of anodic voltages on microstructure and properties of plasma electrolytic oxidation coatings on biomedical NiTi alloy [J]. Journal of Materials Science and Technology, 2013, 29: 22–28.
- [27] ZOU Bin, LÜ Guo-hua, ZHANG Gu-ling, TIAN Yu-ye. Effect of current frequency on properties of coating formed by microarc oxidation on AZ91D magnesium alloy [J]. Transactions of Nonferrous Metals Society of China, 2015, 25: 1500–1505.
- [28] BOINOVICH L B, GNEDENKOV S V, EMELYANENKO A M, EGORKIN V S, PASHININ A S, SINEBRYUKHOV S L. Mg alloy treatment for superhydrophobic anticorrosion coating formation [J]. Surface Innovations, 2013, 1(3): 162–172.
- [29] MOHAMED A M A, ABDULLAH A M, YOUNAN N A. Corrosion behavior of superhydrophobic surfaces: A review [J]. Arabian Journal of Chemistry, 2015, 8: 749–765.

AZ31 镁合金表面超疏水涂层的制备及耐蚀性

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摘要: 为提高镁合金的耐蚀性, 通过微弧氧化和硬脂酸乙醇溶液疏水处理两步法在镁合金表面制备超疏水涂层。考察微弧氧化电压、频率和时间对疏水处理试样接触角的影响。结果表明: 随着微弧氧化电压、频率和时间的增加, 疏水处理试样的接触角均先增大后减小, 分别在 350 V、1000 Hz 和 5 min 时获得最大值。最佳超疏水涂层主要由 MgO 和 Mg_2SiO_4 相组成, 其表面微孔直径为~900 nm, 厚度为~6.86 μm , 接触角高达 156.96°。超疏水试样的腐蚀电流密度较基体降低 3 个数量级, 而氢气析出量较基体降低 94.77%。

关键词: 超疏水涂层; AZ31 镁合金; 微弧氧化; 耐蚀性; 生物医学应用

(Edited by Xiang-qun LI)