Study on Micro-arc Oxidation of Mg-Zn-Y-Nd-Ca Magnesium Alloys

Yuelai Dai*, Yulei Li, Juan Lv, Jingwei Li
Inner Mongolia Metallic Materials Research Institute, Ningbo, 315103, China
*Corresponding author’s e-mail: dyl@norincogroup.com.cn
daiyuelai_1988@126.com

Abstract. To solve the problem of rapid degradation of magnesium alloy implanted in human body, the surface of magnesium alloy was modified by micro-arc oxidation treatment. In order to improve the comprehensive mechanical properties and corrosion resistance of magnesium alloy materials, a new type of Mg-Zn-Y-Nd-Ca degradable magnesium alloy materials was formed by adding a certain proportion of rare earth elements Y and Nd, as well as Zn and Ca. A micro-arc oxidation layer containing Ca, P and Si was formed on the surface of magnesium alloy by secondary micro-arc oxidation. The surface of the micro-arc oxidation film was covered by sol-gel technology to reduce the micro-crack and micro-pore structure of the film and improve the corrosion resistance of the film in the human body simulation liquid.

1. Introduction
Magnesium alloys have attracted wide attention as medical degradable implant materials due to their biodegradability and good mechanical properties[1]. Traditional biometallic materials such as 316L stainless steel, cobalt-chromium alloy and titanium alloy cannot decompose by themselves after being implanted into human body, resulting in many adverse reactions and side effects[2]. However, the rapid degradation rate of magnesium alloy limits its clinical application. The corrosion resistance was improved by alloying and micro-arc oxidation treatment on the alloy surface.

The properties of micro-arc oxidation coatings are affected by many factors, including the composition of magnesium alloy, electrolyte composition and electrical parameters. Liang et al. compared the effects of different electrolyte systems on the properties of micro-arc oxidation coatings on the surface of AM50 magnesium alloy[3]. Cai et al. prepared phosphorus film and silicon film on the surface of AZ91D magnesium alloy, and the experiment found that the silicon film had higher corrosion resistance than the phosphorus film[4].

2. Composition design of magnesium alloy
In this paper, Mg-Zn-Y-Nd-Ca magnesium alloy is taken as the research object, and the flux covering method is adopted to melt the magnesium alloy material. The addition of rare earth elements Y and Nd has a great effect on the micro-structure of magnesium alloys. Firstly, both elements can combine with magnesium to form binary phase, which becomes the core of heterogeneous nucleation of magnesium matrix.

Secondly, during the solidification process, Y and Nd gather in the front edge of the alloy to form a component of super cooling, which impedes the growth of the magnesium matrix, refine the as-cast micro-structure of the magnesium alloy, and improve the comprehensive mechanical properties of the
alloy. The addition of Zn element can enhance the mechanical properties of magnesium alloy by solution strengthening[5]. The addition of Ca element can refine the grain[6]. The element addition is mainly in the form of magnesium - master alloy in the melting process of magnesium alloy. Mg master alloys are mainly Mg-20%Y, Mg-20%N, Mg-12%Zn and Mg-30%Ca, and the composition of the final Mg-Zn-Y-Nd-Ca magnesium alloy is shown in Table 1.

Table 1 Composition of Mg-Zn-Y-Nd-Ca magnesium alloy (wt%)

|   | Y    | Nd   | Ca  | Zn  | Mg   |
|---|------|------|-----|-----|------|
|   | 3.5~4.2 | 2.4~2.7 | 0~0.6 | 0.5 | Balance |

3. Preparation and technological parameters of micro-arc oxidation electrolyte

The basic components of micro-arc oxidation electrolyte are mainly potassium hydroxide, ammonium hydrogen fluoride, glycerol, hydrogen peroxide and so on. Formulations for electrolytes containing calcium and phosphorus and electrolytes containing silicate are shown in Table 2 and Table 3, respectively.

Table 2 Chemical composition of calcium-phosphate electrolyte

| Constituent | C₃H₇CaO₆P·H₂O | (NaPO₃)₆ | KOH | NH₄HF₂ | C₃H₈O₂ | H₂O₂ | N(CH₂CH₂OH)₃ |
|-------------|----------------|----------|-----|--------|--------|------|---------------|
| Concentration | 7.00g/L | 7.50g/L | 4.5g/L | 7.0g/L | 5.0mL/L | 7.5mL/L | 5.0mL/L |

Table 3 Chemical composition of silicate electrolyte

| Constituent | NaSiO₃·9H₂O | KOH | NH₄HF₂ | C₃H₈O₂ | H₂O₂ | N(CH₂CH₂OH)₃ |
|-------------|-------------|-----|--------|--------|------|---------------|
| Concentration | 15g/L | 5.0g/L | 7.0g/L | 5.0mL/L | 7.5mL/L | 5.0mL/L |

The process parameters used in the process of micro-arc oxidation, such as positive and negative voltage, oxidation time and duty cycle, are closely related to the thickness of the oxidized ceramic layer, the size and number of micro-pores, as well as the composition and phase composition of the film. Therefore, it is necessary to select reasonable process parameters. Constant pressure mode is used in the test, and the specific parameters are shown in Table 4.

Table 4 Electrical parameters setting of the prepared micro-arc oxidation film

| Forward voltage (V) | Negative voltage (V) | Oxidation time (min) | Duty ratio (%) | Pulse frequency (Hz) |
|---------------------|---------------------|----------------------|---------------|---------------------|
| 400                 | 50                  | 10                   | 40            | 1000               |

4. Preparation of micro-arc oxidation layer

Electrolytic liquid systems commonly used in micro-arc oxidation of magnesium alloys include single electrolytic liquid system and composite electrolytic liquid system. Single electrolytic liquid system mainly includes silicate, phosphate and silicate composition[7].

Preparation of micro-arc oxidation coatings containing calcium and phosphorus. The pretreated magnesium alloy is connected to the positive electrode of the power supply with an aluminum wire, and the stainless steel container containing calcium and phosphorus electrolyte is poured into the container to be connected to the negative electrode of the power supply. The magnesium alloy sample is placed in the center of the stainless steel container to open the circulating cooling system. Turn on the micro-arc oxidation power supply and carry out the micro-arc oxidation experiment according to the set electrical parameters. At the end of the experiment, the samples were taken out, washed several times in deionized water and anhydrous ethanol, and dried to obtain the samples with micro-arc oxidation layer.

Preparation of micro-arc oxidation films containing calcium, phosphorus and silicon. The dried micro-arc oxidation film samples containing calcium and phosphorus are connected to the positive pole of the power supply, and the stainless steel container containing silicate electrolyte is poured into the container to connect to the negative pole of the power supply, and the magnesium alloy samples are placed in the center of the stainless steel container to open the circulating cooling system. Turn on the micro-arc oxidation power supply and carry out the micro-arc oxidation experiment according to the set parameters. After the end of the experiment, the samples were taken out, washed several times in...
deionized water and anhydrous ethanol, and then dried in a blast oven at 35°C for 3h to obtain the samples with calcium, phosphorus and silicon as micro-arc oxidation film.

The thickness of the films containing Ca and P is between 20 and 28μm, while the films containing Ca and P and Si are between 30 and 41μm. Figure 1 shows the microscopic images of the micro-arc oxidation films containing calcium phosphorus and calcium phosphorus silicon. There are micro-pores of different sizes in the two kinds of films. The micro-pores of the films containing Ca, P and Si are 2-5μm in diameter, while those containing Ca, P and Si are relatively small, about 1-2μm in diameter.

![Figure 1 Microscopic image of micro-arc oxidation film](image)

There are no obvious micro-cracks on the surface of the micro-arc oxidation film, and the micro-cracks mainly exist in the interior of the film. The formation process of the film layer is through local inward growth rather than uniform growth on the surface [8]. The presence of micro-pores and micro-cracks has a certain effect on the corrosion resistance of magnesium alloys.

5. Sol-gel technology

Micro-arc oxidation surface treatment can greatly improve the surface characteristics of the alloy, such as hardness, corrosion resistance, wear resistance and adhesion to the matrix. However, at the same time, the existence of micro-pores and micro-cracks in the micro-arc oxidation ceramic film reduces the protective power of the micro-arc oxidation film to the body. In order to improve the protective characteristics of the micro-arc oxidation film on the surface of magnesium alloy, it is necessary to seal the pores of the film. After immersion in the sol, a sol gel film appears on the surface of the micro-arc oxidation film. However, the sol-gel film did not completely cover the micro-pores of the micro-arc oxidation film after one and two times of dipping and pulling. With the increase of the number of dipping and pulling, the micro-pores of micro-arc oxidation are basically sealed. The magnesium alloy without micro-arc oxidation treatment, the magnesium alloy with Ca-P-Si film, and the sealed magnesium alloy were immersed into human body fluid for 3d, 6d, 12d, and 18d respectively. The weight loss rates were shown in Table 5, Table 6, and Table 7 respectively. Micro-arc oxidation film can effectively reduce the corrosion rate of magnesium alloy in human body fluid simulation, and sol-gel technology can make the micro-arc oxidation film have a lower corrosion rate.

| Table 5  | Weight loss rate of Mg-Zn-Y-Nd-Ca magnesium alloy immersed in simulated body fluids |
|----------|---------------------------------------------------------------------------------------------------|
| Time     | 3d | 6d | 12d | 18d |
| Weight loss(%) | 1.06 | 2.03 | 5.27 | 8.43 |

| Table 6  | Weight loss rate of composite film containing Ca-P-Si in simulated body fluid immersion |
|----------|---------------------------------------------------------------------------------------------------|
| Time     | 3d | 6d | 12d | 18d |
| Weight loss(%) | 0.64 | 1.22 | 2.35 | 3.27 |

| Table 7  | Weight loss rate of sol-gel treated composite film in simulated body fluid immersion |
|----------|---------------------------------------------------------------------------------------------------|
| Time     | 3d | 6d | 12d | 18d |
| Weight loss(%) | 0.22 | 0.51 | 1.25 | 2.14 |
6. Conclusion
The Mg-Zn-Y-Nd-Ca magnesium alloy was used as the matrix, and the micro-arc oxidation film containing Ca, phosphorus and silicon was obtained by secondary micro-arc oxidation on the basis of micro-arc oxidation film containing Ca, phosphorus and silicon. On the basis of the micro-arc oxidation film containing Ca-P-Si, a composite film was prepared on the surface of the film by sol-gel technology to seal the micro-cracks and micro-pores in the film, and effectively reduce the degradation rate at the early stage of soaking.

Acknowledgments
This study was supported by Zhejiang Basic Public Welfare Research Project of China under Grant No.LGF19E010001; Natural Science Foundation of Ningbo, China(No.2018A610059).

References
[1] Li X, Liu X, Wu S, Yeung K W K, Zheng Y, Chu P K. Design of magnesium alloys with controllable degradation for biomedical implants: From bulk to surface[J]. Acta Biomaterialia, 2016, 45: 2-30.
[2] Gordon J. Mcdougall, Partricia Dobson, Pauline Smith, Alison Blake, Derke Stewart. Assessing potential bioavailability of raspberry anthocyanins using an in vitro digestion system[J]. Agric. Food Chem. 2005,53: 5896-5904.
[3] Liang J, Srinivasan P B, Blawert C, Stormer M, Dietzel W, Electrochemical corrosion behavior of plasma electrolytic oxidation coatings on AM50 magnesium alloy formed in silicate and phosphate based electrolytes[J]. Electrochimica Acta, 2009,54(14):3842-3850.
[4] Cai Q, Wang L, Wei Bo, Liu Q. Electrochemical performance of microarc oxidation films formed on AZ91D magnesium alloy in silicate and phosphate electrolytes[J]. Surface and Coatings Technology, 2006,200(12-13):3727-3733.
[5] Yamasaki Y, Yoshida Y, Okazaki M, et al. Action of FGMgCO 3 Ap-collagen composite in promoting bone formation[j]. Biomaterial, 2003, 24(27): 4913-4920.
[6] Ilich J Z, Kerstetter J E. Nutrition in bone health revisited: a story beyond calcium[J]. Journal of the American College of Nutrition, 2000, 19(6): 715-737.
[7] Sankara Narayanan T 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.
[8] Gu Y, Bandopadhyay S, Chen C, Ning C, Guo Y. Long-term corrosion inhibition mechanism of microarc oxidation coated AZ31 Mg alloys for biomedical applications[J]. Material & Design, 2013,46: 66-75.