Corrosion Degradation Behavior of Forged Mg-Zn-Zr/-Y Alloy in Simulated Body Fluid

Chunhua Ma1,2,3,a*, Dongguang Xu4,5,6, Hao Yang6,6, Zhiguo Zhong7,8,9, Zhiwen Lu9,10,e

1Material Science and Engineering Institute Chongqing University, Chongqing 400044, China
2,4,7,9Institute of Mechanical and Electrical Engineering, Nanyang Normal University, Nanyang 473061, China
3,8,10Henan Rare-earth Alloy Material Engineering and Engineering Research Center, Nanyang 473061, China
5,6Institute of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, China

a*Corresponding Author e-mail: sdmach@126.com, b-e-mail: xdg0325@126.com, c-e-mail: yanghaony@126.com, d-e-mail: zhongzhiguo1978@126.com, e-e-mail: lzw@nynu.edu.cn

Abstract—The corrosion degradation rate of pure magnesium and forged Mg-Zn-Zr/-Y magnesium alloy was compared by static immersion corrosion weight loss experiment and electrochemical corrosion experiment at constant temperature (37±0.5°C) and room temperature (25±1°C) SBF to simulate the corrosion degradation rate in body fluids. The results show that the corrosion resistance of magnesium alloy can be improved by adding Zn, Zr, Y compared with pure magnesium. The results of static immersion corrosion test and electrochemical corrosion test of forged Mg-Zn-Zr-Y show that the corrosion resistance of magnesium alloy can be improved by adding Zn, Zr, Y element. The average corrosion rate of the forged Mg-Zn-Zr-Y alloy was 0.62mm/a by weight loss method after 240 h immersion corrosion in SBF at 37 ± 0.5 °C, and the corrosion resistance of forged Mg-Zn-Zr-Y alloy was better than Mg-Zn-Zr alloy.

1. INTRODUCTION

Biomedical magnesium alloy is an ideal biomedical metal implant material [1-4]. In recent years, due to its advantages in biomechanical compatibility, biocompatibility, biodegradability and economic applicability, magnesium alloy as a kind of new biocompatible degradable implant has been widely concerned by large number of biomaterial research scholars at home and abroad [5-9]. However, the biomedical magnesium alloy has a problem of excessive corrosion in the physiological environment of the human body [10-12], so that the mechanical integrity and mechanical properties are lost before the bone healing or vascular occlusion is restored, resulting in treatment failure and possibly causing other adverse reactions [13-17]. Therefore, it is extremely urgent to develop high-strength, high-toughness, high-corrosion biomedical magnesium alloys as soon as possible and to apply them to clinical work as
early as possible [18]. Yang Min et al [19] designed the newly Mg-3Zn-0.2Ca alloy exhibiting the good combination of mechanical performance and corrosion resistance for biomedical application.

Han Shaobing et al [20] studied the corrosion performance of Mg-2Y-xZn-0.4Zr alloy for degradable vascular stent in simulated human body fluid (SBF solution). The results show that the addition of Zn element makes the alloy grain refinement resistant to the alloy. Corrosion performance has a certain effect, but it is not the main factor. The corrosion resistance of the alloy is mainly determined by the W phase and the I phase. The I phase improves the corrosion resistance of the alloy and the W is likely to have an adverse effect on the corrosion resistance of the alloy. Song Yingwei et al [21, 22] studied the corrosion behavior of the forged Mg-Zn-Y-Zr alloy. The experimental study concluded that the corrosion process of the alloy can be divided into three stages: galvanic corrosion, filament corrosion and pitting corrosion. Zhang Yacong et al [23] studied the corrosion behavior of Mg-Zn-Y-Zr alloy in NaCl solution. The results show that the second phase and Zn content in Mg-Zn-Y-Zr alloy can significantly affect the corrosion resistance of magnesium alloy. Therefore, this work chooses pure magnesium, forged Mg-5Zn-0.5Zr alloy and forged Mg-5Zn-0.5Zr-Y. The alloy is the research object, and its corrosion degradation behavior in Simulating human body fluids (SBF solution) is studied, and its biological clinical application value.

2. EXPERIMENT

The experimental materials used pure magnesium and forged magnesium alloy sheets provided by Luoyang Maige Magnesium Co., Ltd., the purity of pure magnesium sheets was 99.98 wt.%, and the nominal composition of forged magnesium alloy sheets was Mg-5Zn-0.5Zr (Mg-5.46Zn-0.58Zr, mass fraction, %) and Mg-5Zn-0.5Zr-Y (Mg-5.39Zn-0.54Zr-0.73Y, mass fraction, %), made by alloy ratio-melting-slab-rolling-forging production process. The actual chemical composition of pure magnesium and forged magnesium alloy sheets is shown in Table 1.

The simulated human body fluid is a SBF (Simulated Body Fluid) solution, and its chemical composition is shown in Table 2. According to the ASTM-G31-72 immersion test standard [24], the ratio of the sample surface area to the SBF simulated solution volume is 1 cm²: 30 mL.

| Material          | Chemical composition (wt. %) |
|-------------------|------------------------------|
| Pure magnesium    | Mg  ≥99.98, Zn  - , Zr  - , Y ≤0.0016, Si  ≤0.0002, Mn  ≤0.0004, Ni  ≤0.0014, Cu  ≤0.0005 |
| Forged Mg-Zn-Zr alloy | balance 5.46, 0.58, 0.0945, 0.1771, 0.0010, 0.0206, 0.0684, 0.1373 |
| Forged Mg-Zn-Zr-Y alloy | balance 5.39, 0.54, 0.73, 0.0905, 0.1368, 0.0010, 0.0256, 0.0684, 0.1319 |

| NaCl, CaCl₂, KCl, Na₂HPO₄·12H₂O, MgSO₄·7H₂O, MgCl₂·6H₂O, NaHCO₃ | 8.00, 0.14, 0.4, 0.06, 0.06, 0.10, 0.35 |

The alloy sample was cut into small pieces of Φ20 mm×3 mm by an electric spark cutting machine, and a hole of Φ3 mm was drilled near the edge to facilitate threading to suspend the sample in the simulated body fluid. First, use 240#, 600#, 1000#, 2000#, 3000# sandpaper to sequentially grind, and then polish the surface of the alloy sample to no scratches and bright. The diameter and thickness of the specimen were measured with a 0-150 mm vernier caliper and the surface area was calculated.

The alloy sample with the measured surface area is numbered in a 100 mL small beaker, then ultrasonically cleaned with acetone and absolute ethanol for 10 min, blown dry air with a blower, and then weighed on an electronic balance with an accuracy of 0.1 mg, after the backup. According to the
ratio of surface area of the alloy sample to the volume of the solution, the addition amount of the SBF solution is determined. The sample is immersed in a 250 mL beaker containing SBF solution, and then placed in a constant temperature water bath and covered with tin foil to prevent the simulated body fluid from evaporating too quickly. The constant temperature water bath is set at 37°C.

In order to more realistically simulate the human body fluid environment, the SBF solution needs to be replaced every 24 hours to make its pH not exceed 8. The soaking period was 6 h, 1 d, 2 d, 3 d, 5 d, 7 d and 10 d. After the immersion was completed, the sample was ultrasonically cleaned with chromic acid solution in hot water at 80°C for 10 min to remove surface corrosion products, then washed and dried, and weighed again on an electronic balance to calculate the mass loss before and after corrosion. In order to ensure the accuracy of the experimental results, three parallel samples were tested for each component alloy, and the average value was taken under the premise of small error.

In this experiment, the microstructure and surface corrosion morphology of the alloy were observed by ZEISS Sigma 500 FESEM field emission scanning electron microscope produced by Zeiss, Germany. The surface of the alloy was analyzed by OXRORD X-max EDS spectrometer manufactured by Oxford Instruments.

The corrosion rate is calculated by the following formula [25]:

\[ R_c = \frac{(K \times \Delta m)}{\rho AT} \]  

In the formula: \( R_c \) is the average corrosion rate of the sample, mm/a; \( K = 8.76 \times 10^4 \); \( \rho \) is the density of the metal, the density of the alloy sample is 1.74 g/cm³; \( \Delta m \) is the mass of the loss (\( \Delta m = m_0 - m_1 \), \( m_0 \) is the weight before corrosion of the sample, \( m_1 \) is the weight after corrosion of the sample), mg; \( A \) is the area of the sample, cm²; \( T \) is the time of corrosion, h.

The electrochemical test instrument is a CHI660D electrochemical workstation. The three-electrode system is used in the test. The working electrode is a magnesium alloy sample (pure magnesium and forged Mg-Zn-Zr-Y magnesium alloy). The reference electrode is saturated. The calomel electrode, the auxiliary electrode is a Pt electrode. Electrochemical test sample preparation method: The sample was made into a square body of 10 mm × 10 mm × 2 mm by a wire electric discharge machine, and the other faces of the square body were wrapped with epoxy resin, and only the exposed area was 1cm². Test surface, the surface was ground by 240#, 600#, 1200#, 2000#, 3000# sandpaper before the experiment, and then polished to a bright surface without scratches. The surface of the sample was sequentially treated with acetone and absolute ethanol in an ultrasonic cleaner. The mixture was washed for 10 minutes, then air-dried and then tested, and each component was tested for three parallel samples. SBF simulated body fluid with corrosive medium at room temperature (25±1°C).

The alloy sample was placed in a SBF simulated body fluid at room temperature (25±1°C) for 30 minutes, and the open circuit potential test was performed immediately. The test was performed before the potentiodynamic polarization curve test to ensure that the potential before the test was stable. Value, test time is 3600 s. After the open circuit potential test is completed, the AC impedance spectrum test is performed. The applied voltage is a sinusoidal AC voltage of 10 mV above the open circuit potential. The test frequency scan range is 0.1 Hz-100 kHz and the amplitude is 0.005 V/s. The test method of the potentiodynamic polarization curve is a potentiodynamic scanning method. The scanning range of the potentiodynamic polarization curve is ±0.1 V, the scanning rate is 5mV/s, and three parallel samples are measured in each group. The results are taken as the average of three measurements, and the Tafel polarization curve is drawn according to the experimental data.

3. RESULTS AND DISCUSSION

3.1. alloy immersion weight loss experiment

Fig.1 shows the weight loss and corrosion rate curves of the forged Mg-Zn-Zr-Y alloy in SBF simulated body fluid at 37±0.5°C constant temperature. After soaking for 24 h, the weight loss of magnesium alloy is only about 0.006 g. It can be seen from the figure that the weight loss of magnesium alloy increases with time, and the corrosion rate begins to decrease after soaking for 72 h.
3.2. open circuit potential test

Fig. 2 shows a plot of open circuit potential versus time for pure magnesium and forged Mg-Zn-Zr/-Y magnesium alloy in room temperature (25 ± 1°C) SBF simulated solution. The soaking time is 3600 s.

It can be seen from Fig. 2 that in the SBF simulated solution, the forged Mg-Zn-Zr alloy rapidly shifts to the positive direction in the early stage of immersion, and then fluctuates in a small range around the relatively stable value as the immersion time is prolonged. At 1500s, the open circuit potential is stable at -1.541V; the open circuit potential of the forged Mg-Zn-Zr-Y alloy shows a rapid rising trend before 200 s, and then becomes a slow rise, but with the immersion time, the extension of the open circuit potential gradually stabilizes after the start of 3200s. The reason for the decrease in potential may be due to the destruction of the Mg(OH)₂ protective film formed on the surface of the alloy, and finally due to the formation of the new film and the dissolution of the old film. When the equilibrium is reached at 3400 s, the open circuit potential is stable at -1.55 V.

After soaking for 1 hour, the open circuit potential values of the forged Mg-Zn-Zr/-Y magnesium alloy studied in the test were basically stable. According to the electrochemical principle, the more positive the open circuit potential value, the smaller the corrosion tendency, and the more negative the open circuit potential value, the greater the corrosion tendency. It can be seen from Fig. 2 that the open circuit potential of the forged Mg-Zn-Zr alloy and the Mg-Zn-Zr-Y alloy in the SBF simulated solution is higher than that of pure magnesium, which can explain the corrosion tendency of the Mg-Zn-Zr/-Y alloy is less than that of pure magnesium.
3.3. Electrochemical impedance spectroscopy test

Fig. 3 shows the AC impedance spectra of pure magnesium and forged Mg-Zn-Zr-Y magnesium alloy in SBF simulated solution. It can be seen that the AC impedance spectrum of the alloy is mainly composed of a high-medium frequency capacitive arc and a short low frequency sense anti-arc composition. The high-medium frequency capacitive arc-resistance is mainly caused by the charge transfer reaction between the corrosion film layer on the surface of the alloy and the electric double layer between the corrosive media. The existence of low-frequency induction arc resistance generally indicates the occurrence of pitting corrosion.

Makar [26] studied the relationship between the high-frequency capacitive reactance half-ring and the corrosion rate on the Nyquist spectrum of magnesium alloys. It was found that the analysis results of most Nyquist curves are consistent with the mass loss corrosion rate, that is, the size of the high-frequency capacitive reactance half-ring. It can indicate the strength of corrosion resistance of the alloy. The larger the radius, the smaller the corrosion rate, the better the corrosion resistance of the alloy. It can be clearly seen from Fig.3 that the tolerant arc radius of the forged Mg-Zn-Zr-Y alloy is the largest in the SBF simulated body fluid compared with the pure magnesium and forged Mg-Zn-Zr alloy. It has the best corrosion resistance.

![Figure 3](image.png)

Figure 3. The nyquist diagram of pure magnesium and forged Mg-Zn-Zr-Y magnesium alloys at 25±1°C in SBF simulated solution

3.4. Dynamic potential polarization curve test

It can be seen from Fig.4 that there is a distinct "passivation inflection point" in both the pure magnesium and the forged Mg-Zn-Zr-Y alloy in the anode region, but in the forged state Mg-Zn-Zr-Y Before the "passivation inflection point" of the alloy, the corrosion current of Mg-Zn-Zr-Y increases with the increase of corrosion potential very slowly; after the "passivation inflection point" of the forged Mg-Zn-Zr-Y alloy, The Mg-Zn-Zr-Y corrosion current increases sharply within a small range of corrosion potential variations, indicating that the corrosion product layer of the Mg-Zn-Zr-Y alloy begins to crack.
Figure 4. Potentiodynamic polarization curves of pure magnesium and forged Mg-Zn-Zr/-Y magnesium alloys in SBF simulated solution

It can be seen from Table 3 that the self-corrosion current density \( I_{\text{corr}} \) of the forged Mg-Zn-Zr-Y alloy is 2.512, and the self-corrosion current density \( I_{\text{corr}} \) of the forged Mg-Zn-Zr alloy is 3.162. The self-corrosion current of Mg-Zn-Zr-Y alloy is lower than that of pure magnesium, indicating that Mg-Zn-Zr/-Y alloy is more resistant to corrosion than pure magnesium, while Mg-Zn-Zr-Y alloy has the lowest self-corrosion current density, which indicates that Mg-Zn-Zr-Y alloy has better corrosion resistance than Mg-Zn-Zr alloy, which is consistent with the results of electrochemical impedance spectroscopy.

| Solution                | Alloy          | \( E_{\text{corr}} \) (V/cm²) | \( I_{\text{corr}} \times 10^{-6} \) (A/cm²) |
|------------------------|---------------|-------------------------------|---------------------------------------------|
| SBF simulated body fluid | Pure magnesium | -1.661                        | 31.623                                      |
|                        | Forged Mg-Zn-Zr alloy | -1.388                        | 3.162                                       |
|                        | Forged Mg-Zn-Zr-Y alloy | -1.415                        | 2.512                                       |

3.5. Analysis of Corrosion Mechanism of Forged Mg-Zn-Zr/-Y Alloy

When magnesium and magnesium alloys are immersed in the corrosive medium of SBF simulated body fluid, the corrosion process is mainly the electrochemical reaction between magnesium and water. The total corrosion reaction equation is:

\[
\text{Mg} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2\uparrow \quad (2)
\]

It contains the following step-by-step reactions:

Anode reaction:

\[
\text{Mg} \rightarrow \text{Mg}^{2+} + e^- \quad (3)
\]

Cathodic reaction:

\[
\text{H}_2\text{O} + e^- \rightarrow \text{H}_2 + \text{OH}^- \quad (4)
\]

Generate corrosion product reaction:

\[
\text{Mg}^{2+} + \text{OH}^- \rightarrow \text{Mg(OH)}_2 \quad (5)
\]

Fig.5 reveals a scanning photograph of the surface morphology of the forged Mg-Zn-Zr/-Y alloy after immersion in a constant temperature SBF simulated solution at 37±0.5°C for 6h, 1d, 2d and 3d. It can be seen from the figure that the addition of Zr and Y elements significantly changes the corrosion morphology of the magnesium alloy and enhances the corrosion resistance of the magnesium alloy. Due to the galvanic phenomenon between the second phase and the substrate, pitting occurs and different degrees of local corrosion occur inside the substrate.
Fig. 5 shows the scanning photograph of the surface morphology of the forged Mg-Zn-Zr/-Y alloy after soaking in SBF simulated solution for 6h, 1, 2 and 3 days. It can be seen that the corrosion pit is in the shape of a nest, and the substrate preferentially forms a corrosion pit. It can be seen from the corrosion morphology of Fig. 5 that the surface of the alloy is only partially corroded, indicating that the corrosion type of the magnesium alloy is pitting. It can be seen from the figure that the forged state Mg-Zn-Zr-Y has contiguous corrosion pits, and the Fig. 5(b1) is an internal corrosion diagram for 1 day. It can be seen from the figure that typical pitting occurs in the alloy. The pits, and microcracks in the corrosion products, are caused by the dry cracking of the corrosion products of the corrosion products during the drying process. It can be seen that many large and deep pitting pits appear on the surface of the alloy, and the pitting pit will be enlarged due to the generation of H₂.

![Figure 5. SEM Analysis at 37±0.5℃ Constant-temperature SBF Simulated Solution for Different Time of Forged Mg-Zn-Zr/-Y alloy for (a-a1) 6h; (b-b1) 1d; (c-c1) 2d; (d-d1)3d](image)

3.6. Conclusions
(1) The results of static immersion test of forged Mg-Zn-Zr/-Y show that the addition of Zn, Zr and Y can improve the corrosion resistance of magnesium alloy compared with pure magnesium. The average corrosion rate of the forged Mg-Zn-Zr measured by the weight loss method is 0.62 mm/a, and the corrosion resistance of the forged Mg-Zn-Zr-Y alloy is better than that of Mg-Zn-Zr alloy.

(2) From the point of view of electrochemical corrosion, compared with pure magnesium, the open circuit potential of the forged alloy tends to decrease the positive eclipse current, and the high-frequency capacitive anti-arc also increases, so the corrosion resistance of the forged Mg-Zn-Zr-Y alloy is enhanced and the corrosion rate is reduced.

(3) From the macroscopic and microscopic corrosion morphology, the black corrosion product adheres to the alloy surface, and the alloy loses its original metallic luster. The SEM morphology shows that the corrosion products are all lamellar cracked structures, most of which are relatively flat, and typical pitting pits appear. With the addition of Zn, Zr, and Y elements, the number of grain boundaries increases, making the degree of corrosion worse. The precipitated phase of the forged Mg-Zn-Zr-Y alloy acts to hinder the corrosion propagation and is beneficial to the improvement of the corrosion resistance of the alloy.

ACKNOWLEDGMENT
This work is supported by the Science and Technology Key Projects of Henan Province, China (172102210425); the Natural Science Foundation of Henan Province, China (162300410207).

REFERENCES
[1] Zhengjie Lin, Zhao Ying, Zhang Zhixiong, Xi Yanfei and Yeung Kelvin. Rare Metal Materials and Engineering[J], 2018, 47, pp. 403-408.
[2] Aliyari Sh, S. M. Fatemi, S. M. Miresmaeili. Transactions of Nonferrous Metals Society of China[J], 2019, 29(9), pp. 1842 -1853.
[3] Anna Carangelo, Annalisa Acquesta, Tullio Monetta, Journal of Magnesium and Alloys[J], 2019, 2(7), pp. 216
[4] Cai Changhong, Renbo Song, Erding Wen, et al. Materials & Design[J], 2019, 182, pp. 1-11.
[5] Aboudzadeh Neda, Changiz Dehghanian, Mohammad Ali Shokrgozar. Transactions of Nonferrous Metals Society of China[J], 2018, 28(9), pp. 1745-1754.
[6] Ali Murad, M. A. Hussein, N. Al-Aqeeli. Journal of Alloys and Compounds[J], 2019, 792, pp. 1162-1190.
[7] Bommala Vijay Kumar, Mallarapu Gopi Krishna, Ch Tirumala Rao. Journal of Magnesium and Alloys[J], 2019, 7(1), pp. 72-79.
[8] Bao Lei, Qichi Le, Zhiqiang Zhang and Esling, Claude. Materials Letters[J], 2019, 235, pp. 189-192.
[9] Nabiyouni Maryam, Theresa Brückner, Huan Zhou, Gbureck, Uwe and Bhaduri, Sarit B. Acta Biomaterialia[J], 2018, 66, pp. 23-43.
[10] Mohedano M., B. J. C. Luthringer, B. Mingo, Feyerabend, F., Arrabal, R., et al. Surface and Coatings Technology[J], 2017, 315, pp. 454-467.
[11] Jin Weihong, Guomin Wang, Abdul Mateen Qasim, Mo Shi and Ruan Qingdong, et al. Surface and Coatings Technology[J], 2019, 357, pp. 78-82.
[12] Du Wenbo, Ke Liu, Ke Ma, Wang Zhaohui and Li Shubo. Journal of Magnesium and Alloys[J], 2018, 6(1), pp. 1-14.
[13] Zhang Jian, Haiyan Li, Wu Wang, Huang Hua and Pei Jia. Acta Biomaterialia[J], 2018, 69, pp. 372-384.
[14] Chen Xiao-Bo, Chuanqiang Li and Daokui Xu. Bioactive Materials[J], 2018, 3(1), pp. 110-117.
[15] Roche V., G. Y. Koga, T. B. Matias, Kiminami C. S. and Bolfarini C. et al. Journal of Alloys and Compounds[J], 2019, 774, pp.168-181.
[16] Henderson Hunter B., Vidhya Ramaswamy, Alexander E. Wilson-Heid, Kesler Michael S., Allen Josephine B., et al. Journal of the Mechanical Behavior of Biomedical Materials[J], 2018, 80, pp. 285-292.
[17] Heakal Fakiha El-Taib, Amira M. Bakry. Materials Chemistry and Physics[J], 2019, 234, pp. 224-236.
[18] Wenzhao Zhang, Sun Yi, Xu Chunxiang, Zhang Jinxian, Jia Qinggong, et al. Rare Metal Materials and Engineering[J], 2019, 48(07), pp.2244-2250.
[19] Min Yang, Liu Debao, Zhang Runfang and Chen Minfang. Rare Metal Materials and Engineering[J], 2018, 47(01), pp. 93-98.
[20] HAN Shaobing, JIA Changjian, ZHAO Bing, XU Chunxiang, HANG Jinxian, et al. FOUNDRY TECHNOLOGY[J], 2017, 38(05), pp. 1001-1003.
[21] Song Yingwei, Dayong Shan, Rongshi Chen and Han En-Hou. Corrosion Science[J], 2010, 52(5), pp. 1830-1837.
[22] Song Yingwei, Dayong Shan, Rongshi Chen and Han En-Hou. Surface and Coatings Technology[J], 2010, 204(20), pp. 3182-3187.
[23] Yacong Zhang, Wang Jincheng and Lv Wenquan. Acta Meallurgica Sinica[J], 2011, 47(09), pp. 1174-1180.
[24] Standard A. Standard practice for laboratory immersion corrosion testing of metals[J]. American Society for Testing and Materials G31-72.
[25] American Society for Testing and Materials. Standard practice for laboratory immersion corrosion testing of metals. Annual book of ASTM standards, PA, USA, 2004.
[26] Makar G L Kruger J. Corrosion of magnesium[J]. International Materials Reviews, 1993, 38(3), pp. 138-153.