Rare Metal Materials and Engineering
Volume 50, Issue 12, December 2021
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Wang Hongxing, Zhang Yan, Wu Canhui, et al. Effect of Gd Addition Amount on Microstructure and Properties of Zn-1.2Cu-1.2Mg Zinc Alloy[J]. Rare Metal Materials and Engineering, 2021, 50(12): 4282-4287.

ARTICLE

Effect of Gd Addition Amount on Microstructure and Properties of Zn-1.2Cu-1.2Mg Zinc Alloy

Wang Hongxing[1,2], Zhang Yan[1,2], Wu Canhui[1,2], Lu Qianyi[1,2], Liu Longlong[1,2], Xue Yajun[1,2]

[1] School of Material Science and Engineering, Nanjing Institute of Technology, Nanjing 211167, China; [2] Advanced Structural Materials and Application Technology of Jiangsu Province, Nanjing 211167, China

Abstract: The microstructure, immersion corrosion behaviour in simulated body fluid and mechanical properties of Zn-1.2Cu-1.2Mg-xGd (x=0, 0.1, 0.25, 0.5, wt%) alloys were studied. The results show that the microstructure of zinc alloy is mainly composed of Zn solid solution and Mg_2Zn_{11} intermetallic compound. When Gd addition content is 0.5wt%, the $GdZn_{12}$ intermetallic compound appears. The microhardness of zinc alloy increases with the increase of Gd addition content, and when the addition content of Gd is 0.5wt%, the microhardness reaches maximum, 1530 MPa. The tensile strength increases first and decreases afterwards, and when the Gd addition content is 0.25wt%, the zinc alloy has high tensile strength. Zinc alloy with 0.1wt% Gd addition content has the lowest corrosion rate.

Key words: zinc alloy; mechanical property; corrosion; Gd addition amount

As a new biodegradable metallic material, zinc has attracted more and more attention. Compared with magnesium and iron, zinc has the advantages of low melting point, good formability, etc. More importantly, the degradation rate of zinc in simulated body fluid is slower than that of magnesium and faster than that of iron, and more in accordance with the requirement of human body implant than other metals[1]. However, the poor mechanical properties and slow degradation rate of zinc are not suitable for the clinical application of stent implantation. Alloying can improve the mechanical properties of the alloy and change the degradation rate[2]. So far, it has been reported[3-7] that the addition of Mg, Cu, Ca, Mn and Ag in pure zinc can improve the mechanical properties to meet the application requirements of stent implantation materials. The Zn-Cu alloy has acceptable cytotoxicity to human endothelial cells and obvious antibacterial effect, so it can be used as an implantable stent, but the slow degradation rate is not suitable for medical application, as reported in Ref. [8]. It is reported[9] that the degradation rate of Zn-Cu binary alloy can be increased by adding Mg element, but it is still far from the standard of corrosion rate of biodegradable metallic stent materials.

As an alloying/microalloying element, rare earth metals have been found useful in the development of new biodegradable magnesium alloys or in the improvement of strength and the regulation of degradation rate[10-13]. For example, Mg-Y[14], Mg-Gd[15], Mg-Dy[16] and other new magnesium alloys[17] have been developed. At present, the effect of rare earth metals on the microstructure, corrosion behavior and biocompatibility of zinc alloys is seldom studied[18,19]. The results of Li et al[18] showed that the degradation rate of Zn alloy can be increased by adding Sr. Tong et al[20] found that zinc alloys containing Ge have good blood compatibility and are beneficial to the improvement of cell activity. Gd is harmless to human body, and plays the role of refining grain size and improving strength of magnesium alloy[21]. In this work, the effect of Gd addition amount on the microstructure, mechanical properties and corrosion resistance of Zn-1.2Cu-1.2Mg alloy was studied.

1 Experiment

Pure Zn (99.9wt%), pure Mg (99.9wt%), pure copper

Received date: December 19, 2020
Foundation item: Jiangsu Key Laboratory of Advanced Structural Materials and Applied Technology Open Fund (ASMA201706); Science and Technology Innovation Fund for College Students of Nanjing Institute of Engineering (TB202002053)
Corresponding author: Wang Hongxing, Ph. D., School of Material Science and Engineering, Nanjing Institute of Technology, Nanjing 211167, P. R. China, Tel: 0086-25-86118274, E-mail: wanghx@njit.edu.cn

(99.9wt%) and master alloy Mg-30Cd were used as raw materials, Zn-1.2Cu-1.2Mg-*x*Gd (*x*=0, 0.1, 0.25, 0.5, wt%) alloys were prepared by melting in a graphite crucible with a resistance furnace and poured into a metal mold at 150 °C. The metallographic examination was carried out by Olympus GX51 metallographic microscope, and the composition (wt%) of metallographic corrosion agent was CrO_3:Na_2SO_4:H_2O=20:1.5:100.

The microstructure, corrosion surface morphology and tensile fracture surface morphology of the alloy were analyzed by JSM-6380LV scanning electron microscope (SEM) equipped with energy spectrum analyzer (EDS). The phase composition of alloy was analyzed by X-ray diffractometer (Bruker d 8advance) with Cu target, tube current 40 mA, tube voltage 40 kV, testing range from 10° to 90°, and scanning speed 10°/min. The mechanical properties were analyzed by material testing machine (Zwick/Roell Z030, Germany) at room temperature and drawing rate of 1 mm/min. Three samples were tested under the same conditions. The microhardness of alloy was measured by FM700 microhardness tester. Test conditions are as follows: pressure head load 1 N, loading time 15 s. The microhardness was tested at ten different locations of the alloy sample, and then averaged.

The corrosion behavior of zinc alloy was studied by electrochemical workstation (Parstat 2273) and simulated body fluid immersion test. In the electrochemical process, a three-electrode system was adopted, with saturated calomel electrode (KCl) as reference electrode, platinum plate as auxiliary electrode and sample as working electrode. The corrosive medium was 3.5wt% NaCl solution. The test area of the working electrode was 1 cm^2. The open circuit potential was tested for 3600 s, and then the polarization curve was measured at the scanning rate of 5 mV/s and the voltage of -1600 to -400 mV. The self-corrosion current was calculated by extrapolation of polarization curve and the self-corrosion potential was calculated by ASTM-G102-89[16]. Immersion tests were carried out in Hank's solution according to ASTM-G31-72[22]. The immersion test conditions were as follows: the immersion solution was simulated body fluid (SBF) and pH value was 7.3~7.4. The immersion temperature was 37±0.5 °C and the time was 720 h. The ratio of sample surface area to immersion solution volume was 1 cm^2:50 mL. The samples were cleaned by ultrasonic wave and dried after soaking. The sample mass before and after soaking was measured by balance with an accuracy of 0.1 mg. The average corrosion rate was calculated as follows: corrosion rate (μm/a) $=KW/(DTA)$, where the coefficient $K=8.76\times10^7$, W is the weight loss (g), A is the sample area exposed to solution (cm^2), T is the exposure time (h) and D is the density of the material (g/cm^3).

2 Results and Discussion

2.1 Effect of Gd addition amount on morphology and microstructure

As shown in the metallographic photographs of Fig.1a, 1c, 1e and 1g, the microstructure of Zn-1.2Cu-1.2Mg-*x*Gd(*x*=0, 0.1, 0.25, 0.5, wt%) alloys consists mainly of light-colored dendrite and dark-colored structure, the size and content of dendrite decrease with the increase of Gd addition content. The results of EDS analysis show that the Zn content is 97.94at% and Cu content is 2.06at% in the light-colored dendrite. The light-colored dendrite is Zn solid solution containing Cu, as shown in Fig.1i. The dark-colored structure contains Zn, Cu and Mg, with contents of 91.76at%, 1.64at% and 6.60at%, respectively, as shown in Fig.1.

With the addition of Gd, the microstructure labeled by “O” appears in Fig. 1h containing Zn (92.29at%) and Gd (7.71at%), which is different from the area labeled by “M” and “N” in Fig.1b. The XRD pattern of Fig.1l shows that the light-colored dendrite is Zn solid solution and the dark-colored structure is intermetallic compound of Mg_2Zn_{11}. When the Gd addition content is 0.5wt%, the $GdZn_{12}$ is found in the XRD pattern of zinc alloy. As shown in Fig.1b, 1d, 1f and 1h, the dark-colored structure in Fig.1a, 1c, 1e and 1g appears as a lamellar structure. It also shows that the microstructure is a eutectic structure composed of Zn and Mg_2Zn_{11} intermetallic compound. Part of dendrites break off and a large number of fine, more evenly distributed grains appear at 0.25wt% Gd addition, as shown in Fig.1f. The dendrite is basically broken, and the fine grains show segregation with 0.5wt% Gd addition, as shown in Fig. 1h. The microstructure is refined and the tendency of dendrite growth is reduced with reasonable addition content of Gd. Segregation occurs and the amount of dendrite structure increases slightly with excessive Gd addition.

2.2 Effect of Gd addition amount on corrosion resistance

Fig.2 shows the corrosion morphology and EDS analysis of corrosion products of Zn-1.2Cu-1.2Mg-*x*Gd (*x*=0, 0.1, 0.25, 0.5) zinc alloys in Hank's solution. From Fig.2a~2d, the corrosion morphology of the alloy surface is affected by the addition content of Gd in zinc alloy. Serious local corrosion occurs on the alloy surface without Gd addition, and corrosion pits appear when the local corrosion products are separated from the surface. Protruding corrosion products appear on the local surface and local corrosion occurs at 0.1wt% Gd addition content. With the increase of Gd addition content to 0.25wt%, the granular corrosion products are uniformly covered on the surface, showing uniform corrosion. With the increase of Gd addition content to 0.5wt%, the corrosion surface of the sample is smooth and full of corrosion cracks.

The EDS analysis of corrosion product shows that O, Ca and P elements are rich in the corrosion products of alloy surface with 0.25wt% Gd addition content, which are 39.83at%, 25.34at% and 24.37at%, respectively. While, the contents of O, Ca and P elements are 11.22at%, 5.86at% and 9.45at% in corrosion products with 0.5wt% Gd addition, and Ca and P are the components of Hank's solution. According to Ref. [23, 24], the corrosion products may be composed of $Zn(OH)_2$ and $Ca_3(PO_4)_2$.

Fig. 3 shows the polarization curve and corrosion rate of Zn-1.2Cu-1.2Mg-*x*Gd (*x*=0,0.1,0.25,0.5) alloy. As can be seen

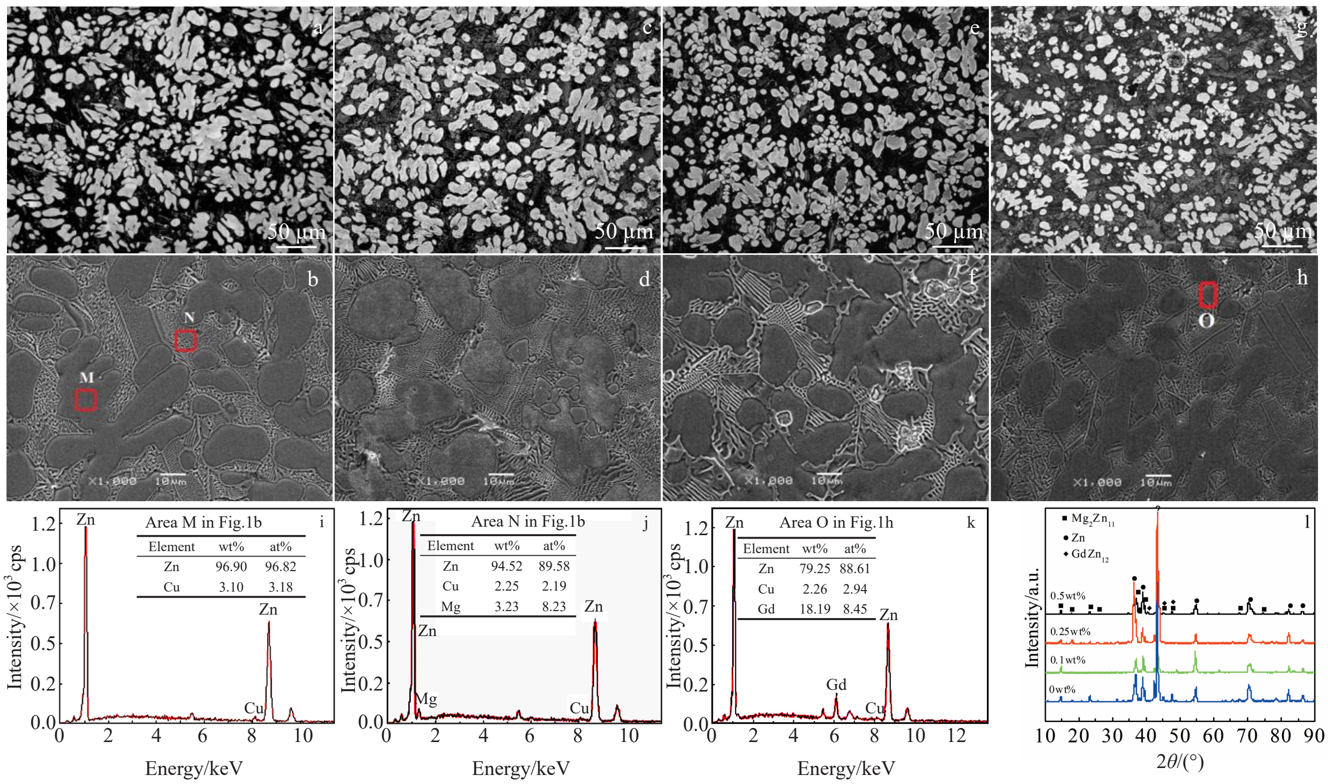

Fig.1 Optical images (a, c, e, g), SEM images (b, d, f, h) and XRD patterns (l) of Zn-1.2Cu-1.2Mg-*x*Gd alloys: (a, b) 0wt%, (c, d) 0.1wt%, (e, f) 0.25wt%, and (g, h) 0.5wt%; EDS spectra corresponding to the area marked by M in Fig.1b (i), N in Fig.1b (j) and O in Fig.1h (k)

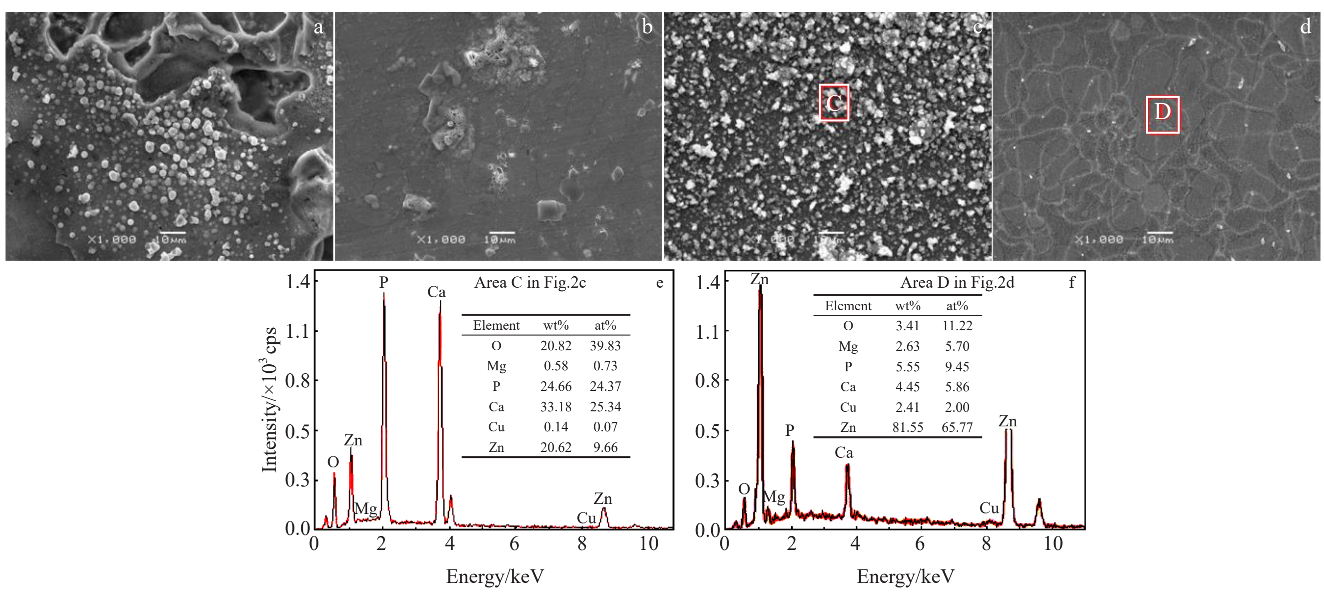

Fig.2 SEM images of corrosion morphology (a~d) and EDS results of degradation products (e, f) of Zn-1.2Cu-1.2Mg-*x*Gd alloys: (a) 0wt%, (b) 0.1wt%, (c) 0.25wt%, and (d) 0.5wt%

from Fig.3a, the corrosion resistance of alloy is improved with Gd addition. When Gd addition amount is 0.1wt%, it shows better corrosion resistance, and the self-corrosion potential and current density are -1.221 V and 1.258 μA/cm^2, respectively.

According to surface corrosion morphology in Fig. 2a~2d, the samples with 0.1wt% and 0.5wt% Gd addition amount may form a dense and adhesive corrosion product, which acts

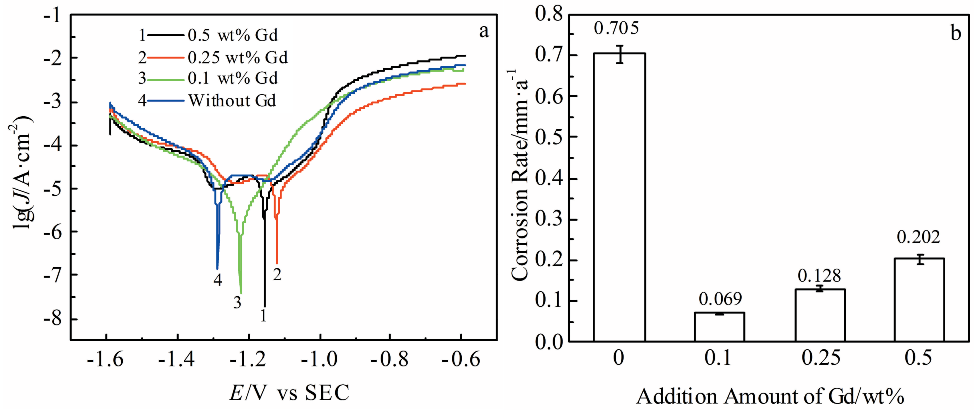

Fig.3 Polarization curves (a) and corrosion rate (b) of studied alloys

as a barrier layer and slows down the corrosion of the alloy. However, the surface corrosion products of as-cast samples with 0.25wt% Gd addition amount are loose porous, and the bonding force with the base metal is weak. In the process of immersion, the corrosion products form on the alloy surface, then fall off, exposing a new surface, and the base metal is continuously corroded. It can be seen from Fig. 3b that the corrosion rates of the alloys are 0.705, 0.069, 0.128 and 0.202 mm/a with the increase of Gd addition content, which are consistent with the corrosion process of zinc alloy.

2.3 Effect of Gd addition amount on mechanical properties

Fig.4 shows the tensile strength and hardness (Fig.4a) and stress-strain curves (Fig. 4b) of Zn-1.2Cu-1.2Mg-*x*Gd (*x*=0, 0.1, 0.25, 0.5, wt%) zinc alloy. From Fig. 4a, the average microhardness of zinc alloy increases with increasing the addition content of Gd, from 1350 MPa (without Gd addition) to 1530 MPa (with 0.5wt% Gd addition), and the tensile strength increases at first and then decreases. When the addition content of Gd is 0.25wt%, the tensile strength and elongation of zinc alloy reach the maximum value, 228 MPa and 0.46%, respectively.

From Fig.4b, zinc alloy with 0.25wt% Gd addition amount shows better mechanical property compared with other zinc alloys. The tensile strength is very sensitive to the grain size of the alloy. According to Hall-Petch relation, $\sigma_s = \sigma_0 + Kd^{-1/2}$, ($\sigma_s$ is yield strength, K is constant, d is grain size), the smaller the grain size, the higher the tensile strength. When Gd addition content is 0.25wt%, the grain size of zinc solid solution is obviously refined and the effect of fine grain strengthening is remarkable, while small size $GdZn_{12}$ intermetallic compounds may play a role of precipitation strengthening. When Gd addition content is 0.5wt%, $GdZn_{12}$ intermetallic compound with larger size is formed, which causes the matrix to be cleaved and the tensile strength and plasticity of the alloy decrease.

Fig. 5 shows the tensile fracture morphologies of Zn-1.2Cu-1.2Mg-*x*Gd (*x*=0, 0.1, 0.25, 0.5, wt%) zinc alloy at room temperature. It can be seen that the fracture surface of zinc alloy is mainly composed of cleavage surface, which is a typical brittle cleavage fracture feature. With the increase of Gd addition content to 0.25wt%, the grain size of dendritic solid solution zinc in the alloy decreases significantly, resulting in a gradual decrease in the cleavage surface size, showing high tensile strength and growth rate. When the addition content of Gd element is 0.5wt%, the size of $GdZn_{12}$ increases significantly, the crack expands between the second phase and the matrix, and irregular shape section appears in the fracture, which result in a rapid

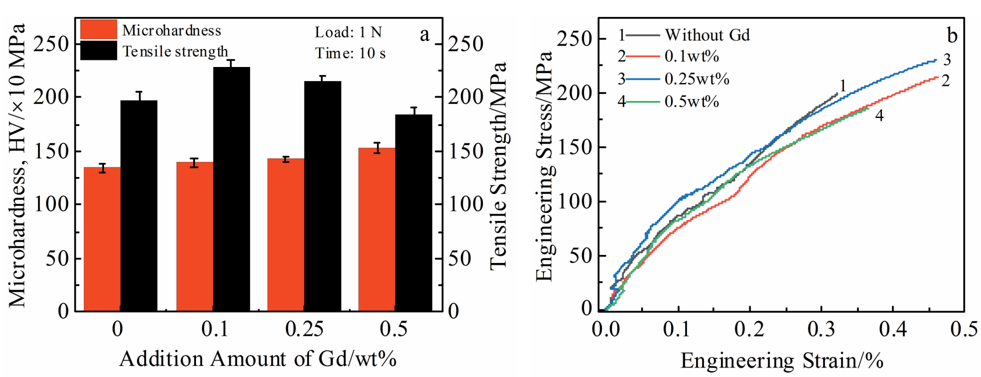

Fig.4 Microhardness and tensile strength (a) and stress-strain curves (b) of studied alloys

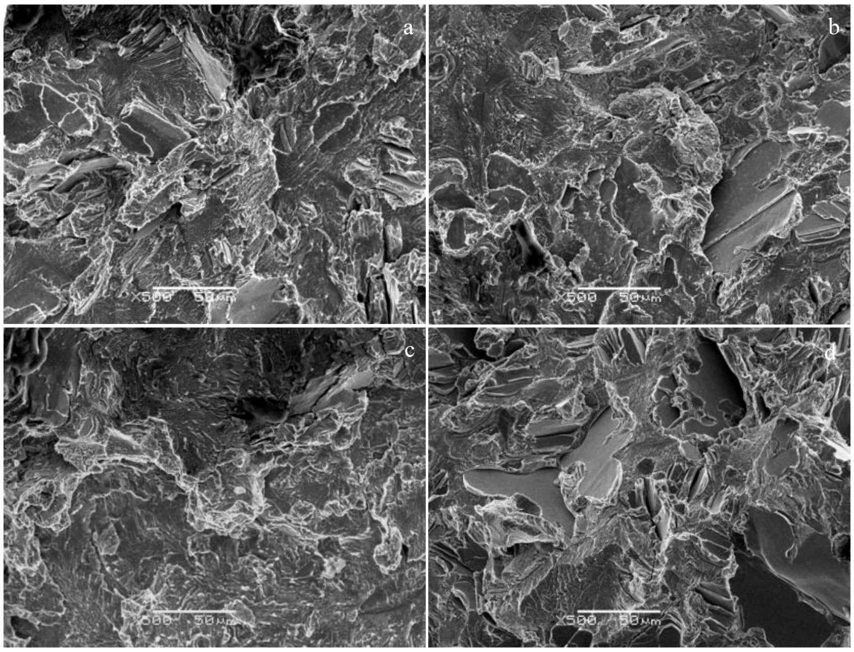

Fig.5 Tensile fracture morphologies of zinc alloy with different addition amount of Gd: (a) 0wt%, (b) 0.1wt%, (c) 0.25wt%, and (d) 0.5wt%

decrease in the tensile strength of the alloy.

3 Conclusions

1) The microstructure of zinc alloy is mainly composed of Zn solid solution and Mg_2Zn_{11} intermetallic compound. When Gd addition amount is 0.5wt% , the $GdZn_{12}$ intermetallic compound appears.

2) The microhardness of zinc alloy increases with the increase of Gd addition amount, but the tensile strength increases at first and then decreases. When Gd addition amount is 0.25wt%, the mechanical properties of the alloy are the best, and the tensile strength and elongation are 228 MPa and 0.46%, respectively. After Gd is added, the corrosion resistance of the alloy is improved. The alloy with 0.1wt% Gd addition amount has the smallest mass loss in simulated body fluid, which is 0.069 mm/a.

References

1 Seitz J M, Durisin M, Goldman J *et al. Advanced Healthcare Materials*[J], 2015, 4: 1915

2 Sun Y, Kong M X, Jiao X H. *Transactions of Nonferrous Metals Society of China*[J], 2011, 21: 252

3 Murni N S, Dambatta M S, Yeap S K *et al. Materials Science and Engineering C*[J], 2015, 49: 560

4 Tang Z B, Niu J L, Huang H *et al. Journal of the Mechanical Behavior of Biomedical Materials*[J], 2017, 72: 182

5 Zou Y L, Xia Chen Z, Chen B. *Material Letters*[J], 2018, 218: 193

6 Sotoudeh Bagha P, Khaleghpanah S, Sheibani S *et al. Journal of Alloys and Compounds*[J], 2018, 735: 1319

7 Sikorajasinska M, Mostaed E, Mostaed A *et al. Materials Science and Engineering C*[J], 2017, 77: 1170

8 Niu J L, Tang Z B, Huang H *et al. Materials Science and Engineering C*[J], 2016, 69: 407

9 Lin S, Wang Q L, Yan X H *et al. Material Letters*[J], 2019, 234: 294

10 Liu P, Jiang H T, Cai Z X *et al. Journal of Magnesium and Alloys* [J], 2016, 4: 188

11 Chen Y A, Wang Y, Gao J J. *Journal of Alloys and Compounds* [J], 2018, 740: 727

12 Geng Z W, Xiao D H, Chen L. *Journal of Alloys and Compounds* [J], 2016, 686: 145

13 Wang F, Xiao W L, Liu M W *et al. Vacuum*[J], 2019, 159: 400

14 Peng Q, Huang Y, Zhou L *et al. Biomaterials*[J], 2010, 31: 398

15 Hort N, Huang Y, Fechner D *et al. Acta Biomaterialia*[J], 2010, 6: 1714

16 Yang L, Huang Y D, Peng Q M *et al. Materials Science and Engineering B*[J], 2011,176: 1827

17 Yang D H, Chen X H, Xu X Y *et al. Rare Metal Materials and Engineering*[J], 2020, 49(1): 1

18 Li H F, Xie X H, Zheng Y F *et al. Scientific Reports*[J], 2015, 5: 10 719

19 Li H F, Yang H T, Zheng Y F *et al. Materials and Design*[J], 2015, 83: 95

20 Tong X, Zhang D C, Zhang X T *et al. Acta Biomaterialia*[J], 2018, 82: 197

21 Yang M B, Guo T Z, Li H L. *Materials Science and Engineering A*[J], 2013, 587: 132

22 ASTM. *Standard Practice for Laboratory Immersion Corrosion Testing of Metals*, *Annual Book of ASTM Standards*, G31-72[S].

2004
23 Tang Z B, Huang H, Niu J L *et al*. *Materials and Design*[J], 2017, 117: 84
24 Liu X, Sun J, Zhou F *et al*. *Materials and Design*[J], 2016, 94: 95

Gd添加量对Zn-1.2Cu-1.2Mg锌合金组织和性能的影响

王红星[1,2]，张　炎[1,2]，吴灿辉[1,2]，鲁千怡[1,2]，刘龙龙[1,2]，薛亚军[1,2]
(1. 南京工程学院 材料科学与工程学院，江苏 南京 211167)
(2. 江苏省先进结构材料与应用技术重点实验室，江苏 南京 211167)

摘　要：研究了Zn-1.2Cu-1.2Mg-*x*Gd（*x*=0，0.1，0.25，0.5，质量分数，%）锌合金微观组织、在模拟体液中的腐蚀行为和力学性能。结果表明，锌合金组织主要由Zn固溶体和Mg_2Zn_{11}金属间化合物组成。当Gd添加量为0.5%时，形成了$GdZn_{12}$化合物。锌合金的硬度随Gd添加量的增加而增加，在0.5% Gd添加量时，硬度达到最大值为1530 MPa。在0.25% Gd添加量时锌合金具有高的抗拉伸强度，而在0.1% Gd添加量时锌合金具有最低的腐蚀速率。

关键词：锌合金；力学性能；腐蚀；Gd添加量

作者简介：王红星，男，1971年生，博士，南京工程学院材料科学与工程学院，江苏 南京 211167，电话：025-86118274，E-mail：wanghx@njit.edu.cn