Influence of solid-solution treatment on microstructure, mechanical property and corrosion behavior of biodegradable Mg-Zn-Ca alloy

Xuan Nam Ly, S Yang and Y Qin
School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

E-mail: yangsen@njust.edu.cn

Abstract. The influence of solid-solution treatment on microstructure, mechanical property and corrosion behavior of Mg-Zn-Ca alloy was studied in the present investigation by SEM, tensile test, electrochemical and immersion test. The results show that the microstructure of Mg alloys after solid solution treatment significantly changed, a large number of the second phase (Ca2Mg6Zn3, Mg2Ca) dissolved into the α-Mg matrix reaching a supersaturated state, and the grains size was bigger than before solid solution treatment; the mechanical properties were obviously improved. In particular the tensile strength of 0.5wt.% Ca of Mg alloy reached 220MPa and the ductility reached 16.6%. Compared with the as-cast Mg alloys, the corrosion potential after solid-solution treatment slightly shifted negative, but the corrosion current density significantly decreased. After solid solution treatment, the surface corrosion was not serious and the result of weight gain was lower compared with those of the as-cast Mg alloys.

Keywords: Mg-Zn-Ca alloy, solid-solution treatment, microstructure, corrosion behavior

1. Introduction
Magnesium alloys with a low density, the elastic modulus closest to that of the human bone than other traditional metallic alloys. In addition, magnesium alloys have a excellent biocompatibility, degradability, making it a promising candidate in bone implant [1]. However, the as-cast magnesium alloys serving as implant materials are limited due to their quick corrosion rate and poor dispersion strengthening [2]. Heat treatment can improve the performances of magnesium alloys through changes their microstructure, relief of the defect in the process of cast [3-5]. The solid-solution treatment can make the microstructure of magnesium alloys more homogeneous than that of as-cast Mg alloys, resulting in influence on the mechanical property, corrosion performance of the alloy. The effect of solid-solution treatment on corrosion and electrochemical mechanisms of Mg-15Y alloy in 3.5 wt.% NaCl solution was investigated by Zhang [6], the results indicated that the E_{corr} and corrosion rate of as-cast samples were both lower than those of solid solution-treated samples, and both increased with increment of solid solution-treated time and the corrosion resistance of Mg-15Y sample gradually deteriorated with immersion time increasing. Chen [7] was investigated the effect of heat treatment (T5, T6) on the biodegradable property of ZK60 alloy, the results showed that both the mechanical properties and degradation behavior were improved after T5 treatment due to the formation of small and uniformly distributed MgZn phases, but T6 treated samples were severely corroded due to the
formation of large amounts of second phases accelerating the corrosion rate owing to the galvanic corrosion.

In the research, Mg-Zn-Ca alloys with different Ca content were prepared, and then studies the influence of solid-solution treatment on mechanical property and corrosion behavior of magnesium alloys.

2. Experimental

The magnesium alloys were prepared from pure magnesium (99.95%), high purity zinc (99.99%) and Mg-30%Ca intermediate alloy (mass fraction) through smelting in a graphite crucible in a resistance furnace protected by flux. The melt was held at 720°C for 10 min and casted at 690°C into a steel mold. The final compositions of Mg alloys are given in Table 1.

The samples were cut from the as-cast ingot to solid-solution treatment, which were carried out at 445°C for 12h in the air with protected by carbon powders, and then quenched into water at room temperature.

Table 1. Chemical composition of the as-cast magnesium alloys in wt.%

| Design alloy            | Analyzed composition (wt.%) |
|-------------------------|-----------------------------|
|                         | Zn  | Ca  | Fe  | Al  | Si  | Cu  | Mn  | Mg   |
| Mg-5.0Zn-0.5Ca          | 6.52| 0.46| 0.056| 0.03| 0.035| 0.021| 0.015| Bal  |
| Mg-5.0Zn-1.0Ca          | 5.62| 0.98| 0.031| 0.045| 0.118| 0.02  | 0.016| Bal  |
| Mg-5.0Zn-2.0Ca          | 5.46| 1.90| 0.026| 0.022| 0.049| 0.028 | 0.018| Bal  |

Microstructure observation was conducted on an Olympus GX41 optical microscope (OM) and a XQUANTA-200 scanning electronic microscope (SEM), and the phase constitutions were analyzed by a X-Ray diffraction (XRD, Bruker D8-Advance). The samples for mechanical testing look like dog-bone is shown as figure 1, and tensile rate is 0.6 mm/min.

Figure 1. Schematic of tensile specimen.

The electrochemical testing was carried out using specimens with 1cm² of working area exposed in Hank’s solution at 37°C. The measurement system using a three-electrode configuration of the Zennium electrochemical workstation, with a platinum electrode as the counter, a saturated calomel as a reference and the samples as the working electrode. For all measurement a voltage scan rate was 10 mV/s from -3V_sce to -0.5V_sce.

Table 2. Chemical composition of Hank’s solution (g/L).

| Compounds                | Content |
|--------------------------|---------|
| NaCl                     | 8.00    |
| KCl                      | 0.40    |
| Na2HPO4·12H2O            | 0.12    |
| KH2PO4                  | 0.06    |
| CaCl2                    | 0.14    |
| NaHCO3                   | 0.35    |
| MgSO4·7H2O               | 0.20    |
The immersion test was performed using samples with only one side of 1cm² exposed in Hank’s solution at 37 °C, this working surface is ground with SiC papers up to 1200 grit, and then finely polished up to 0.5μm diamond powder liquid and cleaned by alcohol and dried in air. The samples were immersed in 120 ml Hank’s solution after weighed, and Hank’s solution is refreshed every 24 h. The samples are removed from Hank’s solution and dried in drying box and is weighed after immersed for 24 h, 48 h and 72 h, respectively.

3. Results and discussions

3.1. Microstructure

Figure 2. Optical micrograph (OM) of the magnesium alloys.

(a) OM of Mg-5Zn-0.5Ca alloy before(a) and after(b) solid solution treatment
(b) OM of Mg-5Zn-1.0Ca alloy before(c) and after(d) solid solution treatment
(c) OM of Mg-5Zn-2.0Ca alloy before(e) and after(f) solid solution treatment
The optical micrograph of the magnesium alloys are shown in figure 2. It can be seen that the microstructure of Mg alloys consisted of Mg matrix phase and the second phases, which distributed on grain interior and grain boundary. After solid-solution treatment, a lot of intragranular spherical secondary phases and the strip-like second phases at grain boundaries were dissolved into \( \alpha \)-Mg matrix phase, the grains of Mg alloys obviously grow up and their size was significantly increased. The average grain size is increased from 104\( \mu \)m to 197\( \mu \)m for Mg-5Zn-0.5Ca alloy, from 86\( \mu \)m to 189\( \mu \)m for Mg-5Zn-1Ca alloy and from 65\( \mu \)m to 178\( \mu \)m for Mg-5Zn-2Ca alloy, respectively.

Figure 3 shows the X-ray diffraction patterns of as-cast Mg alloys. It can be seen that Mg alloys was mainly composed of \( \alpha \)-Mg matrix phase and \( \text{Ca}_2\text{Mg}_6\text{Zn}_3 \) phases, and a new phase of \( \text{Mg}_2\text{Ca} \) was detected with the increase of Ca content. The Mg alloys after solution treatment at 445 °C for 12 h had similar phase constitutions to the corresponding as-cast Mg alloys, but the number of second phases are decreased quickly due to dissolved into the \( \alpha \)-Mg matrix reached a supersaturated state.

![Figure 3. The XRD patterns of Mg alloys after solid solution treatment.](image)

3.2. Mechanical properties

![Figure 4. Tensile curves of the magnesium alloys at room temperature.](image)
The stress-strain curves of the as-cast Mg alloys and after solid-solution treatment obtained from the tensile test are shown in figure 4. After solid-solution treatment, the yield strength ($\sigma_{YS}$) of magnesium alloys is slightly reduced compared with that of as-cast Mg alloys due to the grain size of Mg alloys is bigger than before; but the ultimate tensile strength ($\sigma_{UTS}$) and elongation ($\varepsilon$) of Mg alloys were significantly improved, the results are attributed to the microstructure of Mg alloys is more homogenous than that of as-cast Mg alloys and could be effectively decreased the defects in the cast process. In addition, the solid-solution treatment could improve the mechanical properties of as-cast Mg alloys through the second phases which reinforcement the $\alpha$-Mg matrix phase during tensile test. It can also be seen from the table 3 that after solid-solution treatment $\sigma_{UTS}$ of 220.7 MPa and $\varepsilon$ of 16.6% are obtained in the Mg alloy of 0.5wt.% Ca, compared with those of the corresponding as-cast Mg alloy improved 18.5% and 66.7%, respectively.

Table 3. Data of Mg alloys for tensile test.

| Alloy        | Status     | $\sigma_{YS}$ / MPa | $\sigma_{UTS}$ / MPa | $\varepsilon$ / % |
|--------------|------------|---------------------|----------------------|------------------|
| Mg-5Zn-0.5Ca | As-cast    | 72.0                | 186.2                | 9.96             |
|              | Solid-Solution | 70.1                | 220.7                | 16.6             |
| Mg-5Zn-1.0Ca | As-cast    | 75.8                | 160.3                | 7.55             |
|              | Solid-Solution | 69.3                | 183.1                | 8.3              |
| Mg-5Zn-2.0Ca | As-cast    | 78.9                | 131.4                | 4.1              |
|              | Solid-Solution | 71.2                | 158.3                | 6.56             |

3.3. Electrochemical results

The Tafel curves from electrochemical test of the magnesium alloys samples are shown in figure 5, and the corresponding electrochemical parameters are summarized in table 4. It can be seen that the corrosion potential ($E_{corr}$) of as-cast Mg alloy had a little changed, but significantly increase in the corrosion current density ($I_{corr}$) can be observed with increasing Ca content. The result shows that the corrosion resistance of as-cast Mg alloys is deteriorated with the increase of Ca. Compared with the as-cast Mg alloys, after solid solution treatment the corrosion potential of Mg alloys slightly shifted negative, but the corrosion current density is significantly decreased (show in table 4). With the addition of Ca, the number of second phases ($Ca_2Mg_6Zn_3, Mg_2Ca$) will increase, which beneficial to the formation of more micro-galvanic coupling between $\alpha$-Mg matrix phase with the second phases. After solid-solution treatment the microstructure of Mg alloys is more homogenous than before and a large amount of second phases dissolved into the $\alpha$-Mg matrix phase which can decrease probability and activity of micro-galvanic corrosion, resulting in significantly improved the corrosion resistance of Mg alloy.

Figure 5. Tafel curves of magnesium alloys in electrochemical test.
Table 4. Data of magnesium alloys for electrochemical test.

| Alloy         | Ecorr/V | Icorr/(μA/cm²) | As-cast | Solid-Solution |
|--------------|---------|----------------|---------|----------------|
| Mg-5Zn-0.5Ca | -1.421  | 48.27          | 35.15   |
| Mg-5Zn-1.0Ca | -1.467  | 56.25          | 44.98   |
| Mg-5Zn-2.0Ca | -1.479  | 84.55          | 55.17   |

3.4. Electrochemical results

Figure 6. Surface morphologies of Mg alloys in immersion test for 3 days after cleaning the corrosion products. Morphologies of as-cast(a) and solution treated(b) Mg-5Zn-0.5Ca alloy samples; Morphologies of as-cast(c) and solution treated(d) Mg-5Zn-1.0Ca alloy samples; Morphologies of as-cast(e) and solution treated(f) Mg-5Zn-2.0Ca alloy samples.

The surface morphologies of Mg alloys from immersion test which were carried out in Hank’s solution at 37°C for 3 days after cleaning the corrosion products are shown in figure 6. It can be seen
that the surface morphologies of Mg alloys have been appeared a lot of holes, which deduce that the corrosion characteristic of Mg alloys was started from pitting corrosion, which along surface direction and depth direction constantly grew up at the same time. With the increase of Ca content, the surface morphologies of Mg alloys observed more big holes, and the corrosion on the surface is more serious than that of low Ca content of Mg alloy as shown in figure 6 (a), (c), (e). After solid-solution treatment, the grain of as-cast Mg alloys is obviously grown up and a lot of the second phases dissolved into the $\alpha$-Mg matrix, which beneficial to reduce the formation of micro-galvanic coupling and could be effectively impede the corrosion pits growth up during the immersion process (shown in figure 6(b), (d), (f)). In the word, the corrosion resistance of Mg alloys was improved by suitable solid solution treatment.

Figure 7 shows that the weight-gain curves of Mg alloys after immersed in 37°C Hank’s solution for different times. The corrosion of Mg alloys in the Hank’s solution is combined result of forming the corrosion product film on the surface and a dissolution process [8]. It can be seen from the figure 7 that the weight-gain of Mg alloys increased with increasing immersion time, and the result of weight-gain of Mg alloys after solid-solution treatment is lower than that of as-cast Mg alloys. The FT-IR patterns of the precipitates on the surface of before and after solid-solution treatment of the Mg-5Zn-0.5Ca alloy in Hanks’ solution for 3 days are show in figure 8, we can seen that the precipitates layer contains hydroxyl radical (OH$^-$) and phosphate radical (PO$_4^{3-}$) suggesting that the dissolved metal ions (Mg and Ca ions) combine with ions in the Hank’s solution (OH$^-$ and PO$_4^{3-}$ ions), magnesium hydroxide is formed, Mg and Ca ions combine with the PO$_4^{3-}$ forming Mg- and Ca- containing phosphates and HA, which to improve the biocompatibility of Mg alloy.
4. Conclusions

The as-cast Mg alloys is mainly composed of $\alpha$-Mg matrix and the Ca$_2$Mg$_6$Zn$_3$ phase, and a new phase of Mg$_2$Ca is appeared with increasing Ca content. After solid-solution treatment at 445°C for 12h, the Mg alloys had similar phase constitutions to the corresponding as-cast Mg alloys, but a large number of second phases dissolved into the $\alpha$-Mg matrix reached a supersaturated state, the grain of Mg alloys obviously grew up and the average grain size is increased from 104µm to 197µm for Mg-5Zn-0.5Ca alloy, from 86µm to 189µm for Mg-5Zn-1Ca alloy and from 65µm to 178µm for Mg-5Zn-2Ca alloy, respectively.

After solid-solution treatment, the yield strength ($\sigma_{YS}$) of Mg alloys is slightly reduced compare with that of as-cast Mg alloys, but the ultimate tensile strength ($\sigma_{UTS}$) and elongation ($\varepsilon$) of Mg alloys were significantly improved; $\sigma_{UTS}$ of 220.7 MPa and $\varepsilon$ of 16.6% are obtained in the Mg alloy of 0.5wt.% Ca, compared with those of the corresponding as-cast Mg alloy improved 18.5% and 66.7%, respectively.

The corrosion resistance of Mg alloy is significantly improved by suitable solid-solution treatment. The precipitates layer on the surface of solid-solution treated Mg alloys after immersed in Hank’s for 3 days contains Mg- and Ca- containing phosphates and HA, which have a good biocompatibility.

References
[1] Li N and Zheng Y 2013 J. Mater. Sci. Technol. 29 489-502
[2] Staiger M P, Pietak A M, Huadmai J and Dias G 2006 Biomaterials 27 1728-34
[3] Liu C L, Xin Y C, Tang G Y and Paul K. Chu 2007 Mater. Sci. Eng. A 456 350-7
[4] Zhou W, Shen T and Aung N N 2010 Corr. Sci. 52 1035-41
[5] Feliu Jr S, Samaniego A, Barranco V, El-Hadad A A, Llorente I and Adeva P 2014 Corr. Sci. 80 461-72
[6] Zhang X, Zhang K, Li X G, Deng X, Li Y J, Ma M L and Shi Y 2012 J. Rare Earths 30 1158-67
[7] Chen J, Tan L and Yang K, 2016 Bioactive Mater
[8] Liu D, Liu Y, Huang Y, Song R and Chen M 2008 Prog. Natur. Sci. Mater. Inter. 24 452-7