Influence of solution treatment on microstructure, mechanical and corrosion properties of Mg-4Zn alloy

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Abstract

The solution treatment parameters, mechanical properties and corrosion behavior of binary Mg-4Zn alloy were investigated. The results showed that after the solution treatment at 335 °C for 16 h, Mg-4Zn alloy had an ultimate tensile strength of 184.13 MPa and elongation of 9.43%. Furthermore, the corrosion resistance was evaluated by electrochemical measurements and immersion tests in 3.5% NaCl solution. The results revealed that the corrosion current density of the solution treatment Mg alloy was 11.2 μA/cm², it was lower than 15.8 μA/cm² for the as-cast Mg alloy under the same conditions, which was greatly associated with the micro-cathode effect of the second phases.

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Keywords: Solution treatment; Magnesium alloy; Mechanical property; Corrosion behavior

1. Introduction

Magnesium alloys have attracted great attention as medical implant material and devices due to their low density, perfect biocompatibility and close mechanical properties to natural bone [1–3] and it is also naturally found in the human body, where it plays essential roles in metabolic pathway [4–7]. Various magnesium alloys have been researched as biodegradable materials, such as AZ31, AZ91, AE21, WE43, LAE442 and so on [8,9]. Unfortunately, most of the reported biomedical magnesium alloys contain aluminum and/or rare earth elements. Many researches [10–13] have shown Al is harmful to neurons and osteoblasts and also associated with dementia and Alzheimer’s disease. The administration of RE could lead to hepatotoxicity [14]. Song explored several Mg alloys, pointing out that Zn, Ca and Mn could be appropriate element for biomedical application [6]. It was also found that zinc was one of the most abundant nutritionally essential elements in the human body and had basic safety for biomedical application [12]. Therefore, Zn-containing Mg alloys have been paid more attention and developed as promising biomaterials.

However, the application of Mg alloys has been limited due to their high corrosion rate at physiological conditions and their fast biodegradation before the new tissue has adequately been healed [15]. The early researches [16–21] have indicated that the poor corrosion resistance of Mg alloys mainly results from two reasons: The first is the intrinsic dissolution tendency of magnesium, which is only weakly inhibited by corrosion product films; the second is the presence of second phases acting as local cathodes and thus causing local micro-galvanic to accelerate corrosion [15]. The effect of second phases on the corrosion resistance of Mg alloys has been investigated widely [22–27], especially for the AZ91 Mg alloys. The second phases usually act as cathodes to accelerate corrosion, while they may act as barrier against corrosion if they are in the form of continuous network along grain boundaries. In general, heat treatment is the most effective method to adjust the second phases, corresponding to change in the properties of Mg alloys [23]. In this paper, the most suitable parameter of solution treatment is discussed and the effects of solution treatment on mechanical and corrosion properties of Mg-4Zn alloy as a degradable biomaterial are investigated to clarify the role of second phases in the corrosion mechanism.

2. Experimental

Ingots with nominal alloy compositions of Mg-4wt%Zn alloy were prepared with pure magnesium (99.99 wt%) and pure zinc (99.99 wt%) in an electronic resistance furnace under
the protection of CO\textsubscript{2} and 0.8% SF\textsubscript{6} mixture gas. The alloying melt was held at 730 °C for 30 minutes to homogenize, and cast as ingots at 690 °C into a graphite mold. The chemical compositions of the alloy were measured by inductively coupled plasma atomic emission spectrum (ICP-AES) apparatus.

Specimens cut from the ingots were first solution treated with different times, then quenched into water. The temperature of solid solution was determined by the Mg-Zn binary phase diagram \cite{28} and DSC analysis. Microstructures of specimens for different heat treatment times were observed with an optical microscope (OM). Vickers hardness testing was taken using 100 g load and holding time of 10 s, not fewer than 5 points were taken in each specimen. Tensile tests were performed at room temperature and a constant cross-head speed of 1 mm s\textsuperscript{-1}. Three specimens were used for same test conditions to ensure the reproducibility of data.

Samples for electrochemical test were cut from the ingots and mounted by epoxy resins with an exposed area of 1 cm\textsuperscript{2}. The surface was grinded by 600–2000# SiC papers. The polarization test was carried out at room temperature in a beaker containing 3.5%NaCl solution using a standard three electrode configuration: the saturated calomel as a reference, a platinum electrode as the counter and the sample as the working electrode. In the polarization tests, the working electrode was first immersed in NaCl solution for 5 minutes and then the polarization curve was measured at a scanning rate of 0.5 mV/s.

Immersion tests were also carried out according to ASTM-G31-72 \cite{23} and the ratio of surface area to solution volume was 1 cm\textsuperscript{2}:20 mL. Samples were removed for characterization after 4 h, 12 h, 24 h and 48 h of immersion in 3.5%NaCl solution, rinsed with distilled water and dried in air. The solution was refreshed at 12 h intervals to ensure the solution concentration unchanged. The corrosion products were cleaned with chromate acid (200 g/L CrO\textsubscript{3} and 10 g/L AgNO\textsubscript{3}) for 1–2 minutes without removing any amount of metallic Mg, then washed with distilled water and alcohol, dried in air. The surface morphology after immersion was observed using scanning electron microscopy (SEM).

3. Results and discussion

3.1. The optimum solution treatment parameters

The optical microstructure and XRD results of the as-cast Mg-4Zn alloy are shown in Fig. 1. It can be seen that there were two main phases in the as-cast samples, namely, the matrix α phase and the second phases MgZn, precipitating along the grain boundary.

The DSC curves of the Mg-4Zn alloy are shown in Fig. 2, the second phases dissolve at 346 °C and exist steadily below 329 °C. So the solid solution treatment temperature was...
determined at 335 °C in consideration of the furnace temperature fluctuation.

The curve of micro-hardness variation of the Mg-4Zn alloy for solution treatment at 335 °C with time is shown in Fig. 3. The hardness values are increased as solution time and reached a peak at 16 h, then the hardness started to decrease gradually. The change of the hardness can be explained through the microstructures during the solution treatment which are shown in Fig. 4. It can be seen from Fig. 4a and b that the microstructures contain a large number of second phases and the second phases become more dissolved into the Mg matrix with the increasing solution time (Fig. 4c). By a solution time of 16 h, the second phases are dissolved completely (Fig. 4d) and the alloy has a supersaturated single phase. There is a noticeable coarsening tendency of the grains in the following time (Fig. 4e and f) compared with that of the original microstructure. As a result, the optimum solution parameter should be 335 °C for 16 h for the Mg-4Zn alloy in the experiments.

3.2. The effect of solution treatment on the mechanical properties

The tensile properties of the as-cast Mg-4Zn alloy in comparison with solution treatment Mg alloy are summarized in Table 1. The ultimate tensile strength (UTS) and elongation of the as-cast Mg alloy are 156.93 MPa and 7.38%, respectively. However, after the solution treatment, the UTS and elongation increased to 184.13 MPa and 9.43%, respectively. The enhancement of UTS is due to the solution strength effects of the alloying elements. Besides, Zn dissolving into Mg matrix will decrease the stacking fault energy of the matrix, which leads to the change of plastic deformation mechanism, i.e., cross slip is difficult to happen and twins will appear to adjust plastic deformation [29]. Thus, the solution treatment will enhance the UTS and elongation at the same time.

The SEM micrographs of the fracture surface of the Mg-4Zn alloy are illustrated in Fig. 5. The fracture surface consists of cleavage planes for the as-cast Mg-4Zn alloy (Fig. 5a), which is in accordance with its lower elongation of 7.38%, so the fracture mold of as-cast Mg-4Zn alloy is quasi-cleavage. For the alloy subjected to solution treatment at 335 °C, the fracture surface contains dimples and tear ridges (Fig. 5b), which is in accordance with its higher elongation of 9.43%. But the fracture mold is also quasi-cleavage.

3.3. The effect of solution treatment on corrosion properties

The polarization curves of the as-cast Mg alloy and solution treatment Mg alloy in 3.5% NaCl solution are shown in Fig. 6. The corrosion parameters obtained from the polarization curves are listed in Table 2. It can be seen that the corrosion potential shifts toward nobler direction and the corrosion current density of solution treatment Mg alloy is 11.2 μA/cm², lower than that of the as-cast Mg alloy.
of the as-cast Mg alloy (15.8 μA/cm²), which is related with the second phases in the as-cast alloys.

The corrosion morphologies of the as-cast and as-solution treatment specimens of the Mg-4Zn alloy are observed to further clarify the effect of the second phases by immersion test in 3.5% NaCl solution, which are shown in Figs. 7 and 8, respectively. In the early stage of immersion, a large number of hydrogen bubbles were evidently arising from the surface of the as-cast specimens indicating a fast rate of corrosion, compared to the solution treatment ones. After 4 h, the as-cast specimens were covered with corrosion products shown as Fig. 7a, while only a small area of solution treatment specimens was covered with corrosion products (Fig. 8a). As the immersion time increased, corrosion products were observed on all samples. With the immersion time increased to 48 h, there were a large number of deep pits as indicated by arrows shown in Figs. 7d and 8d, respectively. However, the quantity and depth of the corrosion pits in the as-cast samples present a much larger scale compared with that in the solution treatment ones and these corrosion pits suggested that localized corrosion attacks happened during the immersion process. It was noted that the corrosion products were found on the bottom of beaker containing the as-cast specimens after immersion for 12 h.

### Table 2
Electrochemical parameters of Mg-4Zn alloy.

<table>
<thead>
<tr>
<th>State</th>
<th>E_{corr} (V)</th>
<th>I_{corr} (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast</td>
<td>−1.709</td>
<td>15.8</td>
</tr>
<tr>
<td>Solid solution</td>
<td>−1.685</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Fig. 4. Optical images of Mg-4Zn alloy during different solution time: (a) 4 h, (b) 8 h, (c) 12 h, (d) 16 h, (e) 20 h, (f) 24 h.

Fig. 5. Typical fracture and SEM images: (a) as-cast, (b) 335 °C solid solution.
As confirmed in the microstructure characterization of the as-cast and as-solution treatment specimens, the significant difference in microstructure between them is the second phases. In general, the second phases have nobler potential than the Mg matrix, so they may act as micro-cathode and the Mg matrix as the anode, resulting in galvanic corrosion. For the as-cast Mg-4Zn alloy in this experiment, the second phase particles MgZn can be regarded as the cathode sites and Mg matrix as the micro anode site. Thus, a lot of reactions happened on the surface of the samples, which resulted in an accelerated corrosion. Meanwhile, as to the solution treatment Mg-4Zn alloy, all the second phase particles were dissolved in the Mg matrix and less local reactions happen, so the sample surface experiences a uniform corrosion, resulting in a lower corrosion rate.

4. Conclusion

This work has been concerned with the solution treatment parameters, mechanical and corrosion properties. The main results can be summarized as follows.

(1) The Mg-4Zn alloy was fabricated with high-purity raw materials and though DSC analysis, micro-hardness testing and microstructure observation, the optimum solution parameter is 335 °C for 16 h.

(2) The UTS and elongation of the solution treatment Mg-4Zn alloy were about 184.13 MPa and 9.43%, respectively. The fracture mold of the Mg-4Zn alloy was quasi-cleavage and it was not changed by solution treatment.

(3) The corrosion resistance of solution treatment samples is superior to the as-cast ones. The corrosion morphologies and immersion testing as well as electrochemical measurements proved that the corrosion resistance is strongly associated with the second phases, which act as the micro-cathodes to accelerate the corrosion of Mg matrix.
Fig. 8. SEM micrographs of solid solution Mg–4Zn alloy. (a) 4 h; (b) 12 h; (c) 24 h; (d) 48 h.

References