Effects of solution treatment on yield ratio and biocorrosion behaviour of as-extruded Mg–2·7Nd–0·2Zn–0·4Zr alloy for cardiovascular stent application

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Biodegradable magnesium alloy with proper yield strength, high ultimate strength and elongation is a potential candidate for cardiovascular stent. Nevertheless, magnesium alloy with high ultimate tensile strength always exhibits high yield strength, which is not suitable for the plastic deformation of cardiovascular stent during implantation. Solution treatment was conducted on the as extruded Mg–2·7Nd–0·2Zn–0·4Zr alloy in order to reduce the high yield ratio, and the biocorrosion behaviour of the alloy was also evaluated in artificial plasma. The results show that the grains of the alloy grow, and the second phase reduces with increasing solution treatment temperature. The yield strength decreases gradually, and the ultimate tensile strength still keeps a high level due to the remarkable workhardening. The yield ratio of the alloy reduces from 92 to 57%. The corrosion resistance of the alloy after solution treatment is improved slightly when the temperature is $<475^\circ$C.

Keywords: Biodegradable magnesium alloy, Yield ratio, Biocorrosion behaviour, Solution treatment

Introduction

Biodegradable stents were described as 'fulfilling the mission and stepping away'[1] and 'they do their job and disappear'.[2] During the last decade, biodegradable magnesium stents have been developed and investigated as alternatives for the currently used permanent cardiovascular stents because of its low thrombogenicity and well known biocompatibility.[3] Magnesium is an essential trace element and has a high systemic toxic level, which is about 7–10 mmol L^{-1} serum.[4] It is also a structural constituent of the tissue and essential element in the living organism.[3] Magnesium alloys AE21 were first implanted into coronary artery of pigs as cardiovascular stents by Heublein *et al.*[5] The results showed that no stent caused major problems during implantation or showed signs of initial breakage in the histological evaluation and there were no thromboembolic events; nevertheless, AE21 alloy degradation occurred faster than the expected rate. The first successful implantation of a biodegradable metal stent in human was performed in the left pulmonary artery of a preterm baby with a congenital heart disease.[6] Implantation of a biodegradable magnesium stent was performed in a hybrid procedure when the baby weighed 1·7 kg. Reperfusion of the left lung was established and persisted throughout the 4 month follow-up period, during which the gradual degradation process of the stent was completed. Despite the small size of the baby, the degradation process was clinically well tolerated. The mechanical and degradation characteristics of the magnesium stent proved to be adequate to secure reperfusion of the previously occluded left pulmonary artery. Biodegradable stents with different diameters may help develop new strategies in the therapy of vessel stenosis in paediatric patients.

The implantation of cardiovascular stent is balloon expanded: stent is manually crimped to the balloon catheter; after positioning at the predetermined implantation site, the stent is expanded to sustain the vessel. The stent undergoes twice plastic deformation during the implantation process. The stent with lower yield strength (YS) is prone to expand with low expansion pressure and prevents from acute recoiling after releasing pressure of the balloon, while the stent with higher ultimate tensile strength (UTS) is good for sustaining vessel. Therefore, materials for cardiovascular stents with low YS, but high UTS and elongation are expected.

Mg–Nd–Zn–Zr alloy is a promising biodegradable magnesium alloy for cardiovascular stents and bone implants due to higher mechanical properties and better corrosion resistance than WE43 and AZ31 alloys.[7,8] Particularly, the corrosion mode of the Mg–Nd–Zn–Zr alloy is uniform corrosion, which is desired for

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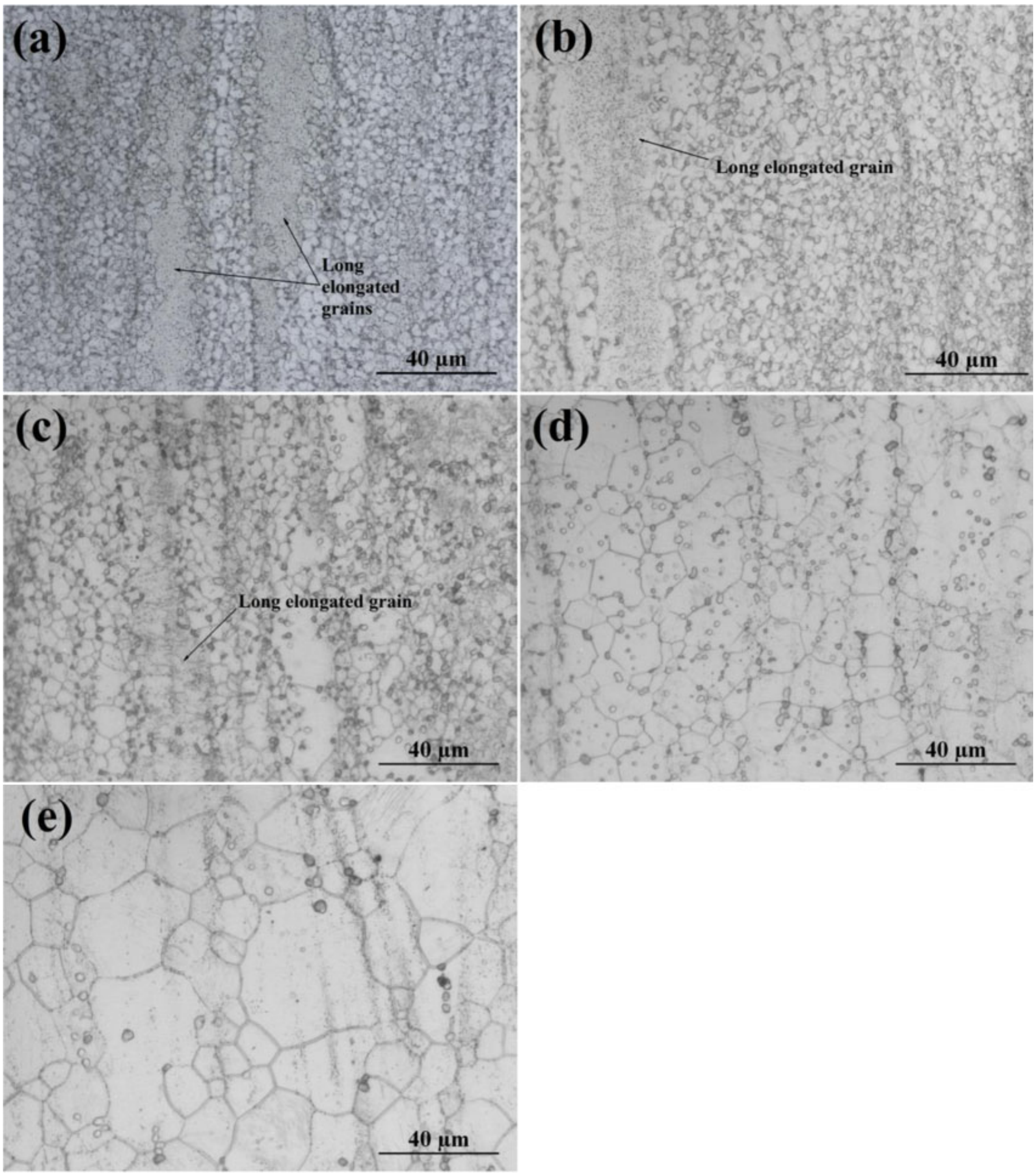


a E; *b* S425; *c* S450; *d* S475; *e* S500

1 Optical images of Mg–2·7Nd–0·2Zn–0·4Zr alloy

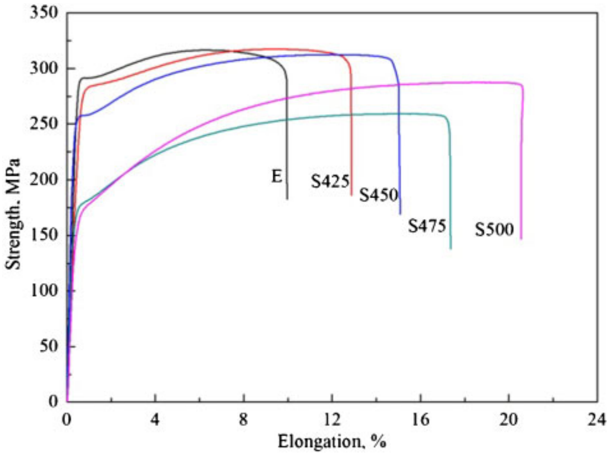
biodegradable materials.[9] Previous studies showed that high strength of magnesium alloys could be achieved by hot extrusion.[7,9] Nevertheless, the yield ratio of the as extruded alloys was >0·95. It means that YS is closer to UTS, which suggests that the stent can be easily recoiled and even fractured during expanding the stent. Therefore, in this study, solution treatment was conducted to adjust the mechanical properties of the as extruded Mg–Nd–Zn–Zr alloy with high yield ratio, and corrosion resistance in artificial plasma (AP) of the alloy was also evaluated for cardiovascular stent application.

Experimental

The Mg–2·7Nd–0·2Zn–0·4Zr (wt-%) alloy was extruded at 320°C with an extrusion ratio of 8 and extrusion speed of 2 mm s^{-1}. The as extruded rods were solution treated at 425, 450, 475 and 500°C for 1 h respectively and then quenched into water. The as extruded alloy was denoted as E and those heat treated at different temperatures were denoted as S425, S450, S475 and S500 accordingly.

Specimens for microstructure observation were cut parallel to the extrusion direction, polished to a mirror surface, etched with acid solution (10 mL acetic acid, 4·2 g picric acid, 70 mL ethanol and 10 mL distilled water) and then observed by optical microscopy. Tensile test was conducted at room temperature with a strain rate of $1{\cdot}7\times10^{-3}$ s^{-1}, and three samples of the alloy at each condition were tested and the results were the averaged.

Specimens with dimension of Ø20×3 mm were polished for biocorrosion behaviour test. Corrosion behaviours of the alloy were evaluated by immersion test including hydrogen evolution and mass loss experiments according to ASTM G31-72. The AP, composed of NaCl (6·8 g L^{-1}), $CaCl_2$ (0·2 g L^{-1}), KCl (0·4 g L^{-1}), $MgSO_4$ (0·1 g L^{-1}), $NaHCO_3$ (2·2 g L^{-1}), Na_2HPO_4



2 Tensile curves of Mg–2·7Nd–0·2Zn–0·4Zr alloy

(0·126 g L^{-1}), NaH_2PO_4 (0·026 g L^{-1}) and glucose (1·0 g L^{-1}), was used as the immersion solution. The pH value was adjusted to 7·4 with NaOH or HCl solution before experiments, and the temperature was kept at 37±0·5°C during experiments. The ratio of SBF volume to the specimen surface area is 30 mL cm^{-2} according to ASTM G31-72. The AP was renewed every 24 h, and the immersion test lasted for 120 h. The hydrogen volume was recorded before renewing the AP. After the immersion test, the corrosion products were removed in a chromic acid solution (200 g L^{-1} Cr_2O_3+10 g L^{-1} $AgNO_3$). The corrosion rate of the alloy was calculated by the weight loss. Three samples of the alloy at each condition were tested, and the results were averaged.

Results and discussion

Figure 1 shows the optical images of the alloy under different conditions. The microstructure of the as extruded alloy is inhomogeneous, which consists of fine grains, long elongated grains and precipitated phase, as shown in Fig. 1*a*. The fine grains are the results of the dynamic recrystallisation during hot extrusion, while the long elongated grains arose from previous unextruded structures that have survived dynamic recrystallisation. The long elongated grains are beneficial to YS but detrimental to the elongation of magnesium alloys according to published works.[9–12] The precipitated phase located in both grain boundaries and grains is $Mg_{12}Nd$ according to previous studies.[9,13] After solution treatment, the grains of the alloy grow apparently with increasing temperature (Fig. 1*b–e*). The precipitated phase is dissolved into the matrix gradually during solution treatment, and thus, it becomes less with increasing the temperature. In addition, the long elongated grains can be still observed in S425 and S450, but cannot be observed in S475 and S500, which can be attributed to the static recrystallisation of the long elongated grains.

Mechanical properties

Figure 2 shows the tensile curves of the Mg–2·7Nd–0·2Zn–0·4Zr alloy under different conditions, and the average data were listed in Table 1. It is visible that the as extruded alloy (E) exhibits high YS and UTS, and the yield ratio is 92%. The YS of the alloy decreases gradually with increasing the solution treatment temperature; the UTS of the E, S425 and S450 is close; and those of the S475 and S500 drop slightly. Therefore, heat treatment plays an effective role on decreasing the yield ratio. Moreover, the elongation of the alloy is improved with increasing the temperature, which is also good for the application of cardiovascular stent.

The growth of the grains and the reduction of the second phase are the main reasons for the decrease in the YS. However, the UTS of the alloys does not decrease apparently, which suggests a significantly workhardening. Generally, a basal slip system can be easily activated, which accelerates the accumulation of dislocation during plastic deformation, which is the origin of workhardening.[10] However, the highest dislocation density of the as extruded alloy (E) has almost reached the critical level, which restricts further dislocation accumulation and workhardening. Therefore, E exhibits scarcely any workhardening during tensile testing. However, the static recrystallisation occurred during solution treatment, the microstructure became more homogeneous and the dislocation density decreased, which is beneficial to the workhardening. Consequently, the remarkable workhardening occurs with increasing the solution treatment temperature. Additionally, for the reduction or elimination of the long elongated grains, even the grains grow and the elongation of the alloy is improved significantly with increasing the temperature.

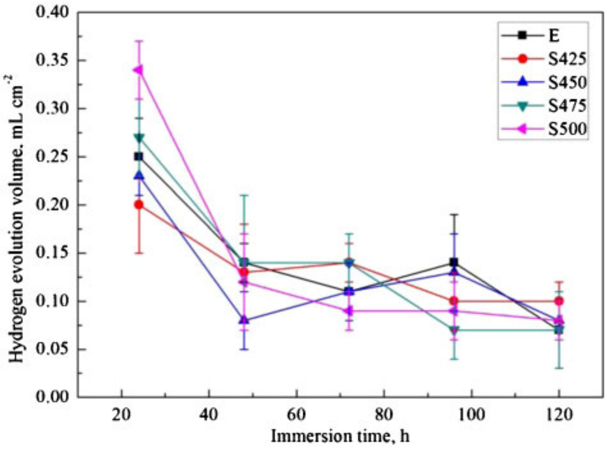
Biocorrosion behaviour

Figure 3 shows the hydrogen evolution of the Mg–2·7Nd–0·2Zn–0·4Zr alloy under different conditions. Generally, the most hydrogen is generated during the first 24 h for the alloy and then it decreases with increasing immersion time. The reason may be that the thickness of the corrosion layer on the surface of the alloy becomes thick with increasing the immersion time, which can prevent matrix from exposing in AP and thus stifles corrosion to some extent. It is a little difficult to distinguish the corrosion rate of the alloy under different conditions from Fig. 3. The total hydrogen evolution of E, S425, S450, S475 and S500 after 120 h immersion is 0·71, 0·67, 0·63, 0·69 and 0·72 mL cm^{-2} respectively. Therefore, the solution treatment on the as extruded alloy shows a slight improvement on corrosion resistance when the solution treatment temperature is <475°C.

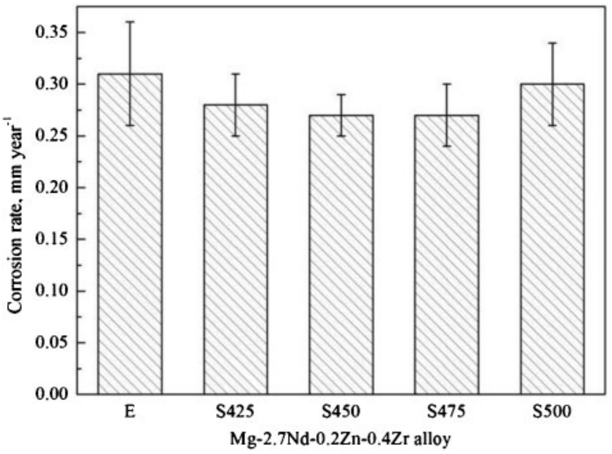
Figure 4 shows the biocorrosion rate of the Mg–2·7Nd–0·2Zn–0·4Zr alloy immersed in AP for 120 h, which is calculated by mass loss. It shows that the corrosion rate of the alloy decreases and then increases slightly, which is similar to the results of hydrogen evolution test. The corrosion behaviour of the alloy is influenced by grain sizes and the amount and distribution of the second phase. Fine grains result in better corrosion resistance of the magnesium alloys, and the second phase, which is nearly continuous over matrix, can act as a barrier on corrosion.[14–16] In the present study, on the one hand, the grains grow obviously with

Table 1 Mechanical properties of Mg–2·7Nd–0·2Zn–0·4Zr alloy

Specimen	YS/ MPa	UTS/ MPa	Yield ratio/%	Elongation/ %
E	291 ± 9	317 ± 10	92 ± 0·5	9·7 ± 3·4
S425	267 ± 14	322 ± 2	83 ± 4·1	11·4 ± 4·3
S450	255 ± 10	313 ± 16	81 ± 1·3	14·9 ± 2·1
S475	178 ± 3	268 ± 4	66 ± 0·1	18·7 ± 0·8
S500	163 ± 9	287 ± 2	57 ± 2·7	25·1 ± 4·9



3 Hydrogen evolution volume of Mg–2·7Nd–0·2Zn–0·4Zr alloy immersed in AP for 120 h



4 Biocorrosion rate of Mg–2·7Nd–0·2Zn–0·4Zr alloy immersed in AP for 120 h

increasing the temperature; thus, it plays a negative role on the corrosion resistance. On the other hand, the reduction of the discontinuous second phase plays a positive effect on the corrosion resistance due to the reduction of galvanic corrosion. The slight difference of the corrosion rate compared with the as extruded alloy is the result of the competition between the grain sizes and the amount of the second phase. When the grain growth is not obvious, the reduction of the second phase dominates the corrosion resistance, so the corrosion rate decreases. When the grain growth is obvious with high solution treatment temperature, the negative effect of grain sizes on the corrosion resistance of the alloy governs the corrosion resistance; therefore, the corrosion rate of the alloy increases accordingly.

Conclusions

The effects of solution treatment on the microstructure, yield ratio and biocorrosion behaviour of the Mg–2·7Nd–0·2Zn–0·4Zr alloy were studied. The results showed that the grains grew and the second phase decreased with increasing the solution treatment temperature. The long elongated grains were eliminated in S475 and S500 due to the static recrystallisation. The yield ratio of the alloy was reduced from 92 to 57% effectively, and the elongated was improved from 9·7 to 25·1%, which is desired for cardiovascular stent. The grain growth and reduction of the second phase were attributed to the decrease in YS, and workhardening was attributed to the high UTS. Biocorrosion resistance of the alloy in AP was improved slightly when the temperature is <475°C. Proper solution treatment process of magnesium alloy can be chosen based on the results of this study.

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