Influence of heat treatment and hot extrusion on the microstructure and tensile properties of rare earth modified Mg-Zn based alloy

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Abstract. In the present paper, the Mg-Zn-Y-Nd alloy was prepared by casting, heat treatment and hot extrusion. The microstructure and mechanical properties of the alloys were tested by OM, SEM, TEM and tensile test. The results showed that the Mg3Zn2Y3 phase is the main strengthening phase and forms the eutectic structure with α-Mg matrix in the as cast alloy. The strengthening phases semi-continuously connect and separate the α-Mg matrix into cell structure. The average grain size of the as cast alloy is about 60 μm. The heat treatment promotes the solid solution of the strengthening phase and precipitation of small particles inside grain. Compared with the as cast alloy, the heat treatment increases grain size a little and mechanical properties more than 30%. The hot extrusion refines the grain and strengthening phase, which increase the mechanical properties significantly. Moreover, the great deformation by the hot extrusion results in the ultrafine structure and abundant of crystal defects. The intersection of micro-twins lead to the special region with nanometer size.

1. Introduction

Magnesium (Mg) alloys have attracted great attention as the light weight structural materials owing to their high specific strength, low density, ease of recycling and good damping, which can be applied in many fields, including implants, hand tools, sports equipment, automobiles, aerospace applications and electronic equipment [1-4]. Moreover, the recent research exhibited that the clinic trial of coronary stent made by rare earth doped Mg alloy exhibited good therapeutic effect without thrombosis, which demonstrated the good application prospect of Mg based implant [5]. However, the hexagonal close-packed (HCP) crystal structure of Mg limited the number of initiation slip systems during deformation at relative low temperature, which resulted in the poor deformability of Mg alloy [6]. The poor ductility and low strength of Mg alloy handicapped its wide application. To conquer these shortcomings of Mg alloy, many methods had been applied [7-9]. Alloying and thermal processing had been thought as the efficient method to improve the mechanical properties of Mg alloy at room and high temperature.

Recently, the investigations [10-12] on biomedical magnesium alloys revealed that the addition of Zn could improve its mechanical properties and corrosion resistance with little influence on its biocompatibility, because the Zn is the essential element of the human body. Then a series of new magnesium alloys for biomedical application were developed [13-15]. The research of Zhang et al. [10] exhibited that Zn addition in Mg could increases the mechanical performance and biocompatibility, and the Mg-6Zn (wt.%) alloy was the best choice. But the mechanical properties of Mg-Zn alloy is not
high enough, because of the low proportion of strengthening precipitate and coarse grain [16,17]. Previous researches [18,19] exhibit that the rare earth could increase the strength of the alloy by enhancing grain boundary. The Cheng et al. studied the minor Y doped Mg alloy and exhibited that the minor Y addition could increase the impact toughness more than one times by changing the deformation mode from twinning to dislocation slip [20]. Kula et al. investigated the deformation behavior of the Mg-Y alloy and revealed that the Y addition could change the fracture mode by improving the dislocation movement [21]. The research of Li et al. investigated the Nd doped Mg-Zn-Zr alloy and exhibited that the Nd presence would increase the strength of the alloy obviously [22]. And moreover the precipitation by the aging treatment improved the strength of the alloy further. The recent investigations [23, 24] on the Y and Nd modified Mg based alloy exhibited that the formation of intermetallic phase was beneficial to the corrosion resistance and strength. Though the addition of Y and Nd could increase the strength of the Mg alloy, however their low solid solubility in Mg matrix promoted them to segregate along the grain boundary during solidification, which was detrimental to the ductility. The research of Liu et al. fabricated the WE54 alloy by severe plastic deformation and revealed that the great deformation could refine the microstructure and redistribute the precipitates, which improved the high temperature mechanical properties obviously [25]. The study of Li et al. exhibited that the great processing deformation and precipitates would improve the mechanical properties synergistically [26]. Though the severe thermal processing could refine microstructure and increase mechanical properties of Mg alloy, its application was limited due to its size limitation. Especially to the tube processing, the hot extrusion was still the main method. Based on the future application of Mg alloy in biomedical implant, the conventional extrusion processing was still needed to study accordingly. Therefore, in the present research, the Mg-Zn-Y-Nd alloy was fabricated by casting and hot extruded. Its microstructure evolution and mechanical properties were investigated simultaneously.

2. Experimental procedure
The Mg-4Zn-1.2Y-0.5Nd alloy (wt.%, Mg-Zn-Y-Nd for short) used in the present study was prepared from pure magnesium (99.9%), Zn (99.9%), Mg-25%Y and Mg-25%Nd master alloys using an electric resistance heating furnace in an SF$_6$ and CO$_2$ atmosphere with ratio of 99:1. The molten alloy was poured into a cylindrical metal mould with a diameter of 100 mm. Some ingots were investigated at as-cast state, the others were solid solutioned at 720 K for 8 h and quenched in water. The sample for hot extrusion was heated at 700 K for 4 h and then hot extruded with an extrusion ratio of 8:1. Before the hot extrusion, the extrusion mould was heated to 500 K.

The specimen for microstructure observation and tensile test were cut from the alloys with different state, respectively. Microstructural characterizations of all samples were carried out on optical microscope (OM) and scanning electron microscopy (SEM). Phase analysis was carried out by transmission electron microscopy (TEM). The samples for transmission electron microscope (TEM) observation were cut from the alloys with different state and prepared by the conventional method. TEM observation was performed by a JEM-2010 transmission electron microscope operated at 200 kV. The tensile tests were conducted using the SANS-CMT5105 tensile testing machine at room temperature with a strain rate of $1 \times 10^{-3}$ s$^{-1}$.

3. Results and discussion
Microstructure of the as-cast Mg-Zn-Y-Nd alloy is shown in figure 1. Clearly, it is mainly composed of α-Mg and strengthening phase along the grain boundary, as shown in figure 1 (a). The strengthening phases semi-continuously connect with each other and exhibits net shape, which is helpful to the strength. The α-Mg matrix is separated by the strengthening phase and forms the cell structure. The statistical analysis on the microstructure shows that the average grain size is about 60 μm. Further observation on the strengthening phase exhibits that the coarse strengthening phase is composed of eutectic structure, as shown in figure 1 (b). The white strengthening phase and the black α-Mg phase align alternately. The EDS test reveals that the white strengthening phase is rich of Mg,
Zn and Y. According to the recent researches [27, 28], the white phase may be the I phase or W phase, whose morphology would influence the mechanical properties of the alloy obviously.

**Figure 1.** (a) Optical microscopy of the as cast alloy, (b) SEM back-scattered electron images showing the eutectic structure along the grain boundary.

In order to confirm the white strengthening phase, TEM has been applied to analyze the precipitates. TEM observation on the as cast Mg-Zn-Y-Nd alloy shows that there are fine eutectic structure, as shown in figure 2 (a). Two kinds of phases exhibit rod or lamella shape and package with each other. The selective area electron diffraction (SAED) pattern reveal that the strengthening phase is Mg$_3$Zn$_2$Y$_3$ phase, which has the face-centered cubic crystal structure with lattice parameter a = 0.6833 nm and the space group of Fm3m, as shown in figure 2 (b). Though no orientation relationship is found between the Mg$_3$Zn$_2$Y$_3$ phase and α-Mg matrix, the interface dislocation is found in the TEM observation. Based on the lattice parameters of Mg$_3$Zn$_2$Y$_3$ phase and α-Mg phase, there would be great difference between these phase. Moreover, the Mg$_3$Zn$_2$Y$_3$/α-Mg eutectic structure is the final solidification region, which would result in great element segregation and increase the crystal misfit along phase interface [29-31].

**Figure 2.** (a) Bright field TEM image of α-Mg and Mg$_3$Zn$_2$Y$_3$ eutectic structure (arrow indicates the interface dislocation), (b) SAED pattern of Mg$_3$Zn$_2$Y$_3$ phase.

Due to the detrimental effect of the coarse strengthening phase, the heat treatment is carried out to solid solute them. The microstructure of the heat treated Mg-Zn-Y-Nd alloy is exhibit in figure 3. Clearly, the heat treatment promote the solid solution and decrease the amount and size of the Mg$_3$Zn$_2$Y$_3$ strengthening phase, as shown in figure 3 (a). The coarse and semi-continuously distributed Mg$_3$Zn$_2$Y$_3$ strengthening phase has been change into small one and the distribution is irregular. The original coarse one results in relative big phase in the heat treated alloy. The grain boundary become clear and the strengthening phase is mainly distributed along grain boundary. In addition, there are a lot of small precipitates inside grain. TEM observations on the heat treated alloy reveal that there are two dual-scale precipitates, as shown in figure 3 (b). The big one with hundreds nanometer is mainly
along the grain boundary and the small one with scores of nanometers is mainly in grain. Further observation on the precipitate in the grain exhibits that small precipitates have two kinds of shape: lamella and rectangle, as shown figure 3 (c). These precipitates with different shape mingle with each other inside grain. The TEM observation on the precipitates adjacent to grain boundary reveals that small precipitates influence the crystal structure, as shown figure 3 (d). The edge dislocation can be observed on the interface of precipitates, which indicates the difference between the precipitate and the α-Mg matrix [32, 33].

![Image](image_url)

**Figure 3.** (a) Microstructure of the solid soluted alloy, (b) TEM image of residual precipitating phase, (c) High resolution TEM image showing the nanoscale precipitate along the phase boundary.

The microstructure of hot extruded Mg-Zn-Y-Nd alloy is shown in figure 4. It can be found that the hot extrusion changes the microstructure greatly. Compared with the as cast and heat treated alloy, the hot extrusion refine the grain obviously, as shown in figure 4 (a). The hot extruded alloy exhibits typical dual-scale crystal structure. The relative fine grains exhibits the strip distribution along the extrusion direction. The relative coarse grain is almost surrounded by the fine grains. Moreover, the Mg₃Zn₂Y₃ strengthening phases are fragmented into small ones and semi-continuously distributed along the extrusion direction as the strip shape. The cooperation of fragmented strengthening phase and extrusion promotes the refinement of the microstructure further [34-36]. The observation on the cross section of the hot extruded alloy exhibits that the Mg₃Zn₂Y₃ strengthening phases mainly distribute along the grain boundary and form the semi-continuous annular shape, as shown in figure 4 (b). Such a morphology should be ascribed to the original microstructure of as cast alloy. Though the heat treatment promotes the solid solution of the precipitates, it exceeds the solid solubility of the α-Mg matrix. The nonequilibrium state will be broken and the precipitation would be prior to occur in the region which has coarse Mg₃Zn₂Y₃ strengthening phases. The statistical analysis on the microstructure shows that the average grain size of the hot extruded alloy is about 20μm.
TEM observation on the hot extruded alloy reveals that the hot extrusion refines the microstructure greatly, as shown in figure 5. Along the fine grain region, the ultrafine structure with about hundreds nanometer is observed, as shown in figure 5 (a). Based on the Moreover, it also finds that there are great amount of crystal defects such as dislocations, micro-twins and stacking faults in the ultrafine structure. These crystal defects always traverse the whole ultrafine structure and some ones have intersected with each other. The detailed observation on the lamellar structure finds that they are composed of micro-twins and stacking faults, as shown in figure 5 (b). According to the recent investigations [37-39], the great deformation would lead to the coexistence of micro-twins and stacking faults. In addition, the formation of these crystal defects would generate the barrier to restrict the movement of dislocation, which is helpful to the strength. Moreover, the intersection of the micro-twins results in the special region, as the arrows indicated. The atom array is really different from the micro-twins and related with the thickness of the micro-twins.

The tensile properties of the Mg-Zn-Y-Nd alloy with different states are shown in figure 6. Clearly, with the heat treatment and hot extrusion, the mechanical properties of the alloy increase greatly. The strength and ductility of the heat treated alloy are more than 30% higher than that of the as cast alloy. However, the hot extrusion increases the strength and ductility about two times of the as cast alloy. According to the recent researches [23, 40], the mechanical properties of alloy is related with the microstructure greatly. The matrix with fine microstructure and well distributed strengthening phase would increase the strength and ductility simultaneously. In the present study, the heat treatment promotes the solid solution of strengthening phase and eliminates the bulk precipitate, which could contribute to the ductility. Moreover, the solid solution and ultrafine precipitate are also beneficial to the strength. Though the grain coarsening during heat treatment influences the mechanical properties, the heat treated alloy is still possesses better strength and ductility than the as cast alloy. In the hot extruded alloy, the
extrusion refines the microstructure and the strengthening phase significantly, which contributes to the strength and ductility simultaneously [40, 41]. Though the strengthening phases still prefer to segregate along grain boundary, their small size could exert little influence on the synergistically deformability of the alloy. Therefore, the hot extrude alloy possesses the best mechanical properties.

**Figure 6.** Mechanical properties of the Mg-Zn-Y-Nd alloy with different states at room temperature.

### 4. Conclusions

1) In the as cast Mg-Zn-Y-Nd alloy, the Mg$_3$Zn$_2$Y$_3$ phase is the main strengthening phase and forms the eutectic structure with α-Mg matrix. The strengthening phases semi-continuously connect and separate the α-Mg matrix into cell structure. The average grain size of the as cast alloy is about 60 μm.

2) The heat treatment promotes the solid solution of the strengthening phase and precipitation of small particles inside grain. Compared with the as cast alloy, the heat treatment increases grain size a little and mechanical properties more than 30%.

3) The hot extrusion refines the grain and strengthening phase, which increases the mechanical properties significantly. Moreover, the great deformation by the hot extrusion results in the ultrafine structure and abundant of crystal defects. The intersection of micro-twins lead to the special region with nanometer size.

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### References

[1] Li C Q, Xu D K, Wang B J, Sheng L Y and Han E H 2016 *J Mater. Sci. Technol.* **32** 1232

[2] Liu Z, Wang Y and Wang Z G 2000 *J. Mater. Res.* **14** 449

[3] Li Z J, Gu X N, Lou S Q and Zheng Y F 2008 *Biomaterials* **29** 1329

[4] Mordike B L and Ebert T 2001 *Mater. Sci. Eng. A* **302** 37

[5] Haude M, Ince H, Abizaid A, Toelg R, Lemos P A, Birgelen C, Christiansen E H, Wijns W, Neumann FJ, Kaiser C, Eeckhout E, Lim S T, Escaned J, Garcia-Garcia H M and Waksman R 2016 *Lancet* **387** 31

[6] Yi S B, Davies C H J, Brokmeier H G, Bolmaro R E, Kainer K U and Homeyer J 2006 *Acta Mater.* **54** 549

[7] Li C Q, Xu D K, Wang B J, Sheng L Y, Qiao Y X and Han E H 2017 *Sci. Rep.* **7** 40078

[8] Valle J A, Carreno F and Ruano O A 2006 *Acta Mater.* **54** 4247
[9] Feng B, Xin Y C, Guo F L, Yu H H and Liu Q 2016 Acta Mater. 120 379
[10] Zhang S X, Zhang X N, Zhao C L, Li J N, Song Y, Xie C Y, Tao H R, Zhang Y, He Y H, Jiang Y and Bian Y J 2010 Acta Biomater. 6 626
[11] Qin H, Yaochao Zhao Y C, An Z Q, Cheng M Q, Wang Q, Cheng T, Wang Q J, Wang J X, Jiang Y, Zhang X L and Yuan G Y 2015 Biomaterials 53 211
[12] Xu L P, Ye G N, Zhang X N, Zhao C L, Li J N, Song Y, Xie C Y, Tao H R, Zhang Y, He Y H, Jiang Y and Bian Y J 2010 Acta Biomater. 6 1743
[13] Cipriano A F, Sallee A, Tayoba M, Alcaraz M C C, Lin A, Guan R, Zhao Z and Liu H 2017 Acta Biomater. 48 499
[14] Zhao X, Shi L L and Xu J 2013 Mater. Sci. Eng. C 33 3627
[15] Zhang Y, Huang X F, Ma Z D, Li Y, Guo F, Yang J C, Ma Y and Hao Y 2017 Mater. Sci. Eng. A 686 93
[16] Xu D K, Tang W N, Liu L, Xu Y B, Han E H 2007 J. Alloys Comp. 432 129-134.
[17] Sheng L Y 2016 Strength Mater. 48 107
[18] Sheng L Y, Yang F, Guo J T and Xi T F 2014 Trans. Nonferrous Met. Soc. China 24 673
[19] Cheng J, Mu Y L, Zu G Y and Yao G C 2017 Mater. Design 120 379
[20] Kula A, Jia X, Mishra R K and Niewczas M 2017 Int. J. Plasticity 92 96
[21] Li H Z, Lv F, Liang X P, Qi Y L, Zhu Z X and Zhang K L 2016 Mater. Sci. Engi. A 667 409
[22] Liu L, Yuan F, Zhao M, et al. 2017 Mater. 10 477
[23] Shuai C, Yang Y, Peng S, et al. 2017 J. Mater. Sci.-Mater. M. 28 130
[24] Liu X, Chen R and Han E 2008 Mater. Sci. Eng. A 497 326
[25] Li C Q, Xu D K, Yu S, Sheng L Y and Han E H 2017 J Mater. Sci. Technol. 33 475
[26] Wang S D, Xu D K, Wang B J, Sheng L Y, Han E H and Dong C 2016 Sci. Rep. 6 29471
[27] Sheng L Y, Yang F and Xi T F 2015 Appl. Mech. Mater. 727 111
[28] Sheng L Y, Du B N, Lai C, Guo J T and Xi T F 2017 Strength Mater. 49 109
[29] Sheng L Y, Yang F, Xi T F, Zheng Y F and Guo J T 2012 Intermetallics 27 14
[30] Sheng L Y, Yang F, Guo J T and Xi T F 2014 Trans. Nonferrous Met. Soc. China 24 673
[31] Sheng L Y, Yang F, Xi T F, Lai C and Ye H Q 2011 Compos. Part B-Eng. 42 1468
[32] Sheng L Y, Guo J T, Ren W L, Zhang Z X, Ren Z M and Ye H Q 2011 Intermetallics 19 143
[33] Sheng L Y, Yang F, Xi T F, Guo J T and Ye H Q 2012 Mater. Sci. Eng. A 555 131
[34] Sheng L Y, Xi T F, Lai C, Guo J T and Zheng Y F 2012 Trans. Nonferrous Met. Soc. China 22 489
[35] Sheng L Y, Yang F, Guo J T, Xi T F and Ye H Q 2013 Compos. Part B: Eng. 45 785
[36] Zhang W, Du K, Chen X Q, Sheng L Y and Ye H Q 2016 Philos. Mag. 96 58
[37] Sheng L Y, Guo J T, Xi T F, Zhang B C and Ye H Q 2012 Prog. Nat. Sci.: Mater. Int. 22 231
[38] Sheng L Y, Zhang W, Guo J T, Wang Z S, Ovcharenko V E, Zhou L Z and Ye H Q 2009 Intermetallics 17 572
[39] Li C Q, Xu D K, Zeng Z R, Wang B J, Sheng L Y, Chen X B and Han E H 2017 Mater. Design 121 430
[40] Li C Q, Xu D K, Wang B J, Sheng L Y, Qiao Y X and Han E H 2017 Sci. Rep. 7 40078