https://doi.org/10.1007/s41230-019-8117-7

Single and double aging treatments on Mg97Zn1Y2 alloy

***Di-qing Wan, Ying-lin Hu, Hou-bin Wang, Shu-ting Ye**
School of Material Science and Engineering, East China Jiaotong University, Nanchang 330013, China

Abstract: The development of magnesium alloys was limited due to the low absolute strength and poor corrosion resistance. It was found that the optimal performance could not be achieved in some alloys by a single quenching and aging treatment, but could be achieved after a graded aging or multiple-stage aging heat treatment. The Mg97Zn1Y2 alloy was prepared and subjected to single and double aging treatments. Single aging was carried out at 250 ºC for 6 to 15 h. For double aging, the first step was performed the same as the single aging. The second step was performed at 350 ºC for 12 h. The microstructure and properties of the alloy with single and double aging were analyzed by means of hardness measurement, optical microscopy, scanning electron microscopy, X-ray diffraction, and polarization curve measurements. Results show that the precipitated nanoscale phases are formed during aging, and evenly distributed in the matrix. Compared with the single aging treatment, the hardness and corrosion resistance of the alloy are further improved due to the double aging treatment.

Key words: single aging; double aging; Mg97Zn1Y2 alloy; LPSO phase

CLC numbers: TG146.22 **Document code:** A **Article ID:** 1672-6421(2019)01-046-07

Magnesium alloy has a hexagonal close-packed crystal structure, which fascinates scholars because of its low density, high specific strength and elastic modulus, and high recycling efficiency [1-5]. The requirements for saving energy and environmental protection have promoted the rapid growth of magnesium alloy applications. However, the development of magnesium alloys was limited due to the low absolute strength and poor corrosion resistance [6-7]. To improve the strength and corrosion resistance of an alloy, the alloying and heat treatment methods are important [8-9].

It was found that the optimal performance could not be achieved in some age-hardening alloys by a single quenching and aging treatment. However, a good performance could be achieved after a graded aging or multiple-stage aging heat treatment [10-11]. Recently, the multiple-stage aging heat treatment (interrupted aging temperature or T6I6) has been developed. Oh-ishi et al. [12] studied the transformation mechanism of precipitated phases of Mg-Zn and Mg-Zn-Al alloys during multiple-stage aging. Compared with single aging, the morphology and distribution of the precipitates changed significantly after double aging. Graded aging can cause an alloy to undergo nucleation at the pre-aging temperature of the first-stage, and slowly grow at the subsequent aging temperature. The alloy obtains higher mechanical properties in a relatively short time, thereby improving the heat treatment efficiency of the alloy. Compared with the traditional single-aging treatment, the tensile strength, elongation, and hardness of the alloy are improved after double aging [13-15].

Mg-Y-Zn alloys were selected for many studies due to the long-period stacking ordered (LPSO) structure [16-17]. This alloy is a currently promising casting magnesium alloy, but the size of the LPSO phase in the magnesium alloy is coarse under conventional casting conditions. The strengthening effect of the LPSO phase is strongly related to the size and morphology of the LPSO phase, and the coarse LPSO phase decreases the mechanical properties of the alloy [18-19]. Thus, the aging treatment has a great effect on the microstructure of the alloy, and therefore, affects the properties of the alloy. In this study, the effects of the single and double aging treatments on the microstructure and properties of the Mg97Zn1Y2 alloy reinforced by the LPSO phase were studied.

***Di-qing Wan**
Male, born in 1981, Ph.D. He is mainly engaged in the research of high strength magnesium alloys.
E-mail: divadwan@tom.com ; divadwan @163.com.
Received: 2018-09-06; Accepted: 2018-12-26

1 Experimental procedure

The Mg97Zn1Y2 alloy was prepared by commercially pure Mg (99.95wt.%) and Zn (99.9%), with Mg-25wt.%

Y master alloys in a resistance furnace under a protective SF_6+CO_2 mixed gas. The metals were placed in a clean crucible preheated at 720 ºC for 5 min. The melt was stirred for approximately 10 min, and then poured into a steel mold with a length of 140 mm, width of 30 mm, and height of 30 mm. Samples were cut from the same horizontal plane, parallel to the bottom surface of the casting alloy. All the samples were solution-treated at 520 ºC for 8 h, and then aged at 250 ºC for different aging times (6 h, 9 h, 12 h, and 15 h). Finally, the samples were water-quenched at room temperature for the single treatment samples. The double-aged samples were further treated at 350 ºC for 12 h after single treatment before they were water-quenched at room temperature.

The microstructure of the alloys was observed using an optical microscope (OM, COOLPIX-4500) and a scanning electron microscope (SEM, JSM6701F). Phase analysis was conducted by means of X-ray diffraction (XRD, Siemens D5000), using monochromatic Cu-Kα radiation with 0.05º step length. The scanning range was 20º to 80º.

Hardness was measured using a microhardness tester (HXD-1000TMB/LCD) with a load of 0.5 kgf and a loading time of 12 s. In the testing process, five indentations were made to provide an average hardness value. Electrochemical polarization was conducted in a three-electrode cell on an electrochemical workstation (CHI660A) using a scanning rate of 5 $mV{\cdot}s^{-1}$. The dynamic polarization curves were measured after open-circuit immersion for 1 h in 3.5% NaCl aqueous solution.

2 Results and discussion

2.1 Microstructure of Mg97Zn1Y2 alloy in as-cast and solid solution states

It can be seen from Figs. 1(a) and 1(c) that the microstructure of Mg97Zn1Y2 alloy consists of the dendritic α-Mg matrix and intergranular compound. The secondary phases with a white irregular blocky shape are distributed at the grain boundary. In the solidification process, Zn and Y atoms are excreted to the solid-liquid interface, so that the solute enriches in the front of the solid-liquid interface, resulting in the formation of a constitutional supercooling zone. Moreover, Y and Zn as surface active elements can effectively reduce the critical nucleation radius. So, the α-Mg phase is firstly crystallized and then the secondary phase is formed during solidification. Many studies [20-23] have shown that the secondary phase in the Mg97Zn1Y2 alloy is Mg12ZnY (LPSO phase).

According to the related studies [24-25], to maximize the dissolution of the secondary phase and uniformly diffuse the

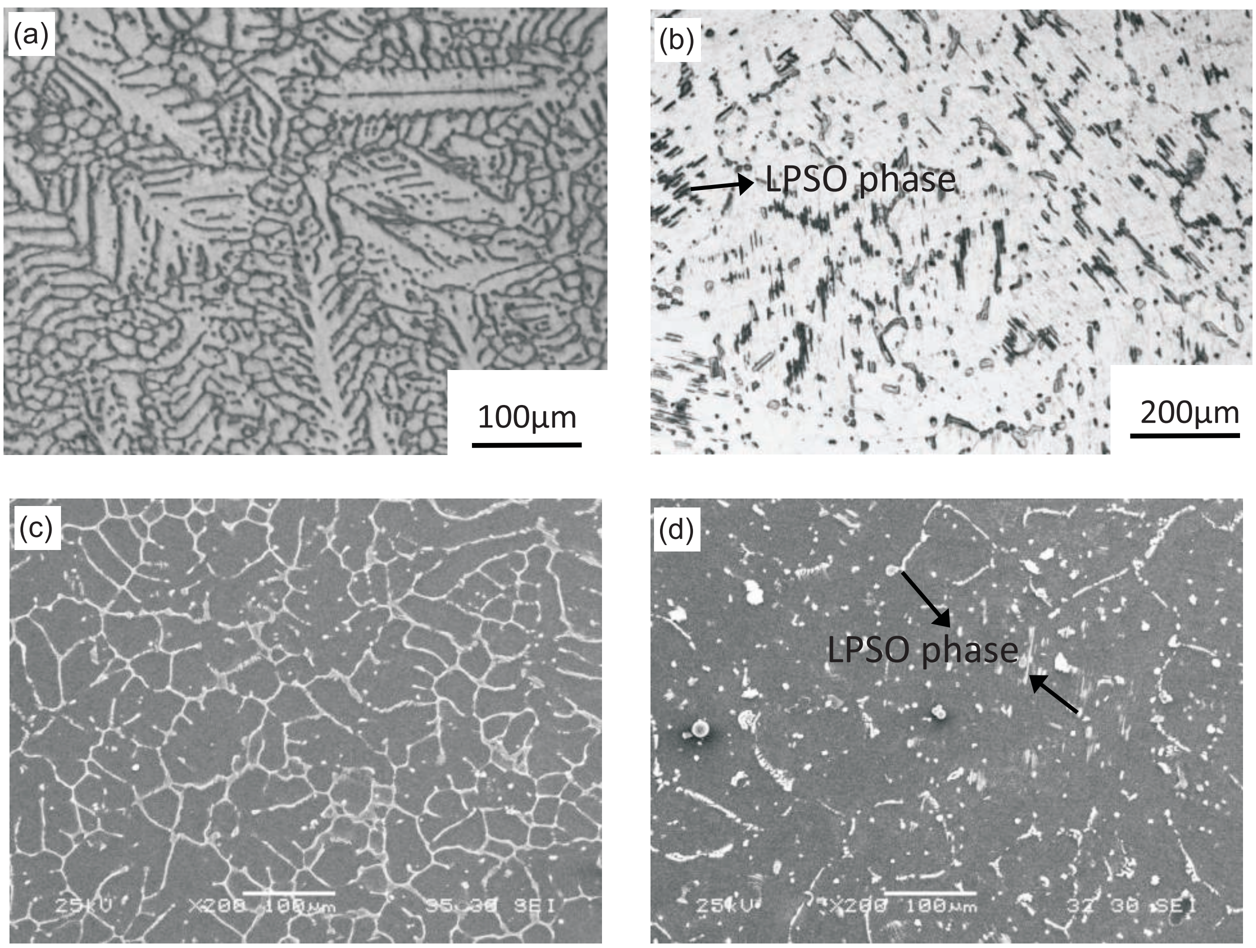

Fig. 1: Microstructures of Mg97Zn1Y2 alloy: (a) OM image of as-cast Mg97Zn1Y2 alloy, (b) OM image of Mg97Zn1Y2 alloy after solid solution (520 ºC/8 h), (c) SEM image of as-cast Mg97Zn1Y2 alloy, (d) SEM image of Mg97Zn1Y2 alloy after solid solution (520 ºC/8 h)

secondary phase into the matrix in the form of solid solution atoms, the solid solution temperature was set at 520 ºC and the solution time was 8 h. During the solution process, the coarse dendrites are gradually fused and the secondary phases (LPSO phases) at the grain boundary are partially dissolved, as shown in Figs. 1(b) and (d).

2.2 Microstructure and properties of single aged Mg97Zn1Y2 alloy

2.2.1 Microstructure of Mg97Zn1Y2 alloy after single aging treatment

Figure 2 shows the XRD analysis results of the Mg97Zn1Y2 alloy with the single-aging treatment at 250 ºC for 6, 9, 12, and 15 h. The microstructure after the aging treatment is composed of α-Mg matrix and Mg12ZnY phase. With an increase in aging time, the diffraction intensity of the precipitated Mg12ZnY phase increases slightly. Compared with the as-cast Mg97Zn1Y2 alloy, a small amount of lamellar LPSO (nanoscale) phases precipitated in the alloy after aging treatment. The volume fraction of the LPSO phase precipitate in the matrix increases with an increase of aging time, as shown in Fig. 3.

2.2.2 Hardness of Mg97Zn1Y2 alloy after single aging treatment

As shown in Fig. 4, the hardness of the alloy firstly increases and then decreases as the aging time increases. The Vickers hardness of the as-cast Mg97Zn1Y2 alloy is 63.5 HV, and the hardness of the alloy after single aging at 250 ºC for 12 h is up to 88.4 HV. At the beginning of the aging, the Zn and Y atoms in the supersaturated solid solution are constantly aggregated at the crystal planes of the solid solution, so that the lattice of the solid solution region is distorted and the hardness of the alloy increases. With an increase of the aging time, Zn and Y atoms continue to segregate, and the LPSO phase gradually

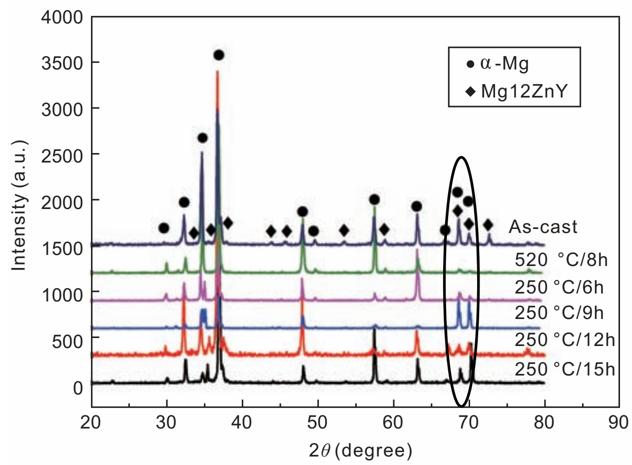

Fig. 2: XRD analysis of Mg97Zn1Y2 alloy with single aging treatment

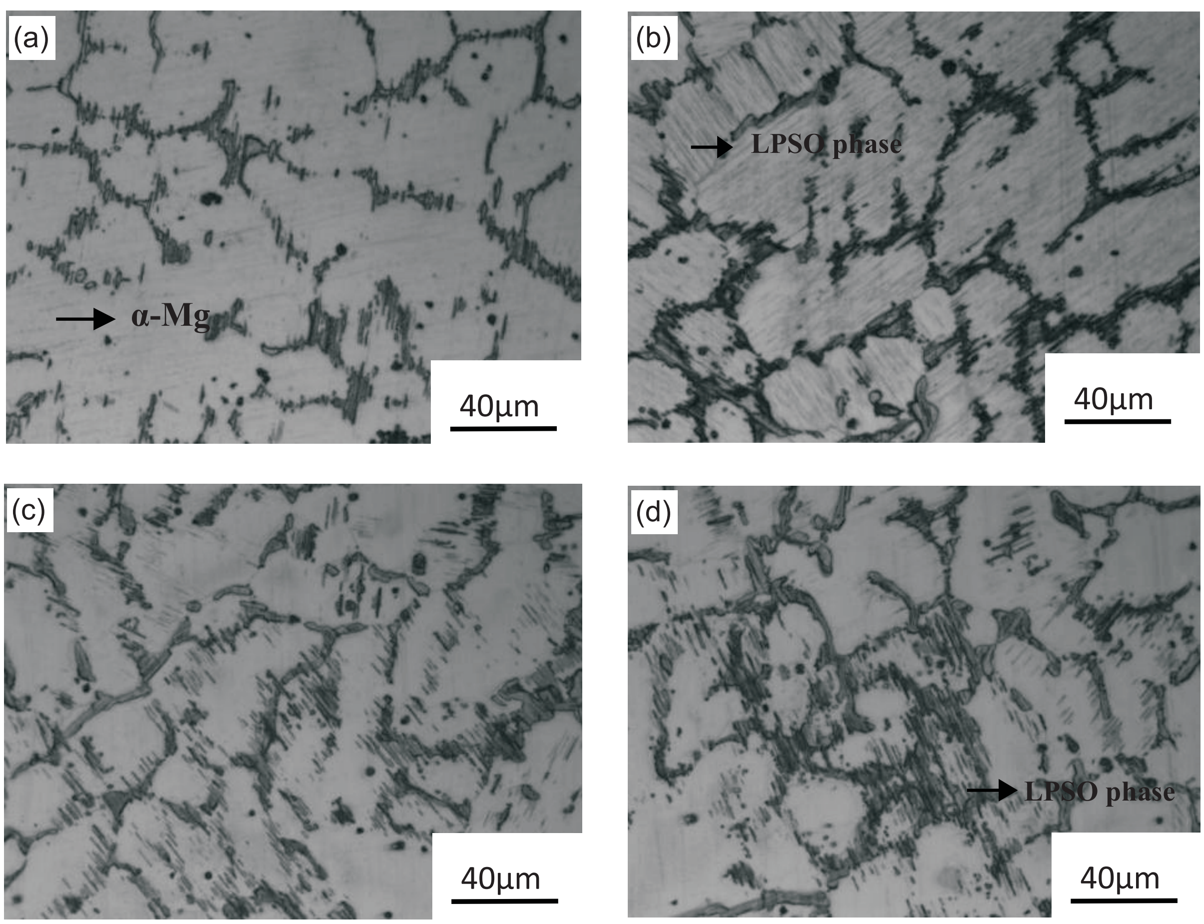

Fig. 3: Microstructures of Mg97Zn1Y2 alloy after single aging treatment at 250 ºC for different times: (a) 6 h, (b) 9 h, (c) 12 h, (d) 15 h

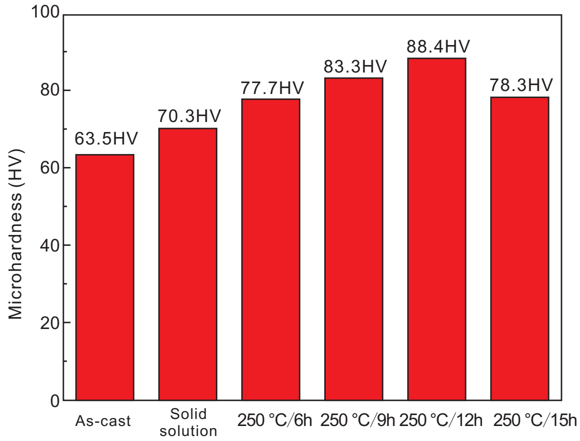

Fig. 4: Hardness of Mg97Zn1Y2 alloy with single aging treatment

precipitates in the form of a lamellar or strip structure. A large number of precipitations greatly hinder the movement of dislocations. The dislocations cannot easily pass through a precipitated phase, so the bending turns around to form a dislocation ring. Therefore, the hardness of the alloy is further improved. However, when the aging time is further increased to 15 h, the hardness of the alloy decreases compared with the alloy after single aging at 250 ºC for 12 h, which may be due to the over aging resulting in the coarsening of LPSO phase.

2.2.3 Corrosion resistance of Mg97Zn1Y2 alloy after single aging treatment

When immersed in 3.5% NaCl solution, the self-corrosion potentials of the single-aging alloys are -1.551V, -1.502V, -1.498V, and -1.488V, corresponding to an aging time from 0 to 12 h, as shown in Fig. 5. The corrosion resistance of the alloy is closely related to the corrosion potential. According to thermodynamics theory, the self-corrosion potential (E_{corr}) is used to characterize the corrosion tendency of an alloy. The lower the self-corrosion potential, the more susceptible the alloy is to corrosion. Figure 5 shows that the corrosion resistance of the alloy increases with an increase of aging time. The corrosion resistance of the alloy that was aged for 12 h is the best.

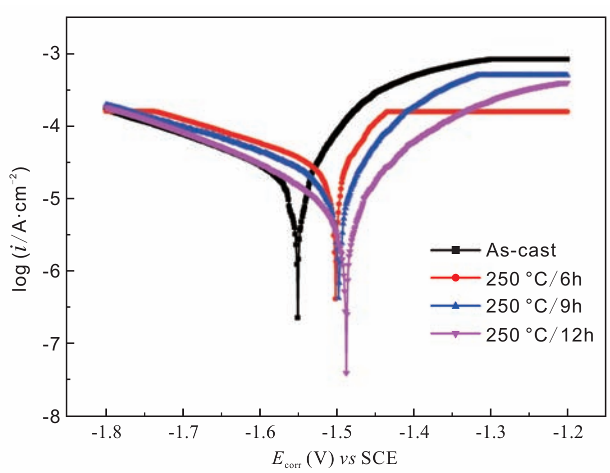

Fig. 5: Potentiodynamic polarization curves of Mg97Zn1Y2 alloy after single aging treatment

As shown in Fig. 3, the grain size of the alloy after aging treatment is small and distributed uniformly, and the precipitated secondary phase is evenly distributed in the matrix. The microstructure of the alloy changes from a discontinuous to a continuous network structure during the aging treatment, and the volume fraction of the precipitated LPSO phases increases with the increased aging time. The LPSO phase plays an important role in the corrosion process: the LPSO phase has good corrosion resistance, the network-like structure can suppress the penetration of the corrosion solution, and thus the corrosion is retarded on the LPSO phase [7,10]. Therefore, the structure and size of the precipitated LPSO phase can affect the corrosion resistance of the alloy.

2.3 Microstructure and properties of double aged Mg97Zn1Y2 alloy

2.3.1 Microstructure of Mg97Zn1Y2 alloy after double aging treatment

In the double-aging treatment, the specimens were firstly aged at 250 ºC for different aging times (6 h, 9 h, 12 h and 15 h), followed by a second-aging at 350 ºC for 12 h. Figure 6 shows the microstructure of the Mg97Zn1Y2 alloy after the double-aging treatment. The dispersed and fine secondary phase further precipitated in the matrix and grain boundaries during the double-aging process. The volume fraction of the secondary phase increases compared with that of the single-aging alloy, which improves the hardness and strength of the alloy. In addition, the size of the precipitated phase at the grain boundary increases after the double aging, and blocky-shaped secondary phases form at the grain boundary. Taking the alloy (250 ºC /12 h+350 ºC /12 h) as an example, the phase composition of the alloy does not change. It is still composed of α-Mg and Mg12ZnY phases (Fig. 7). Compared to the alloy with the single aging treatment, the intensity of the diffraction peak of the α-Mg phase is weakened. The Mg12ZnY phase diffraction peak intensity increases slightly due to the increase in the volume fraction of Mg12ZnY phase, precipitated in the double aging alloy.

2.3.2 Hardness of Mg97Zn1Y2 alloy after double aging treatment

Figure 8 shows the hardness of the double aged alloy. The hardness of the alloy after double aging (250 ºC/12 h+350 ºC /12 h) is up to 91.6 HV. During the double aging, the alloy undergoes concentration fluctuations for nucleation in the single-aging step, so that when the second-step aging is carried out, the LPSO phase is further precipitated on the basis of stable nuclei. The dispersed fine LPSO phase distributed in the matrix and grain boundary and the volume fraction of the LPSO phase increases compared with the single aged alloy, which cause an increase in the hardness of the alloy. The hardness of the Mg97Zn1Y2 alloy after double aging (250 ºC /15 h+350 ºC /12 h) is decreased compared with the alloy after single aging (250 ºC /15 h) because the alloy is over aged after a single stage aging treatment, and softened after the double aging treatment.

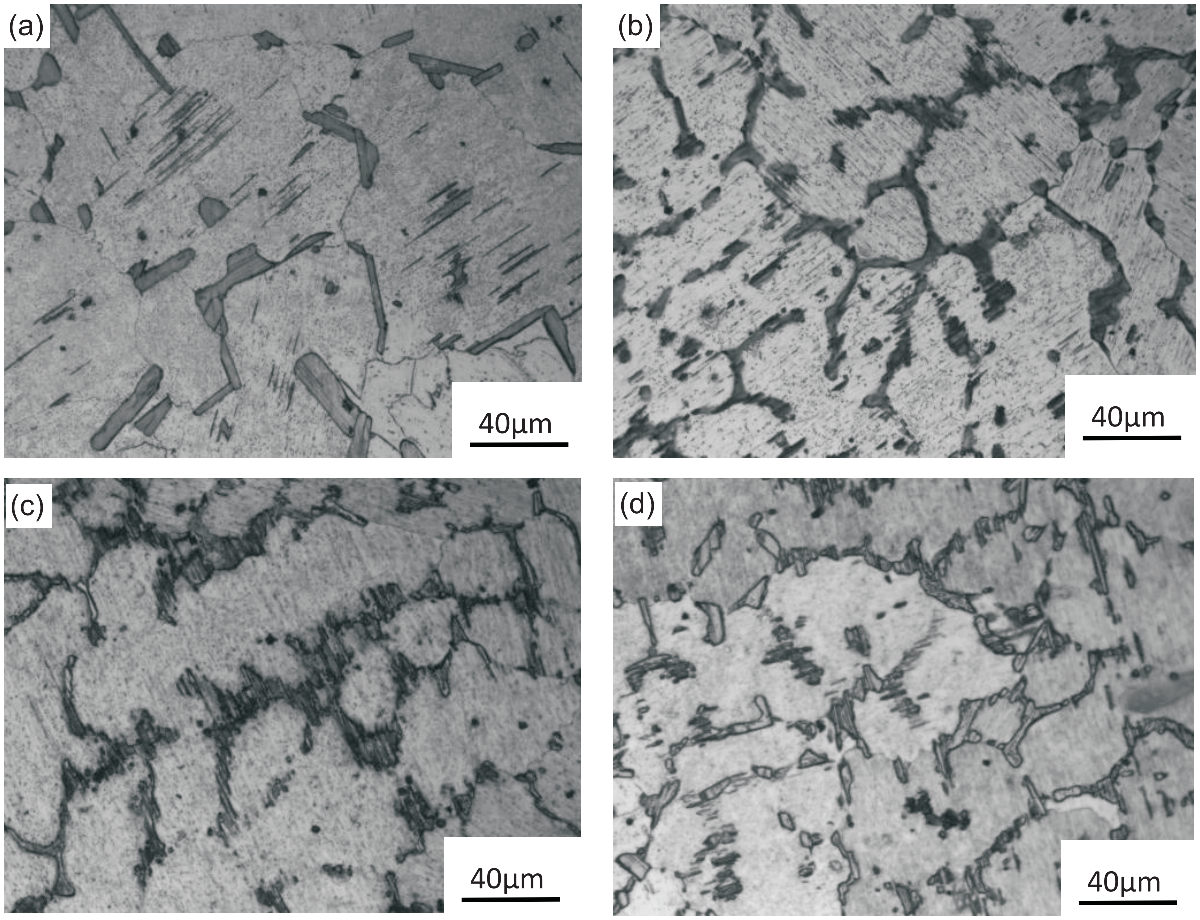

Fig. 6: Microstructures of Mg97Zn1Y2 alloy after double aging treatment: (a) 250 ºC/6 h+350 ºC/12 h, (b) 250 ºC /9 h+350 ºC/12 h, (c) 250 ºC/12 h+350 ºC/12 h, (d) 250 ºC /15 h+350 ºC/12 h

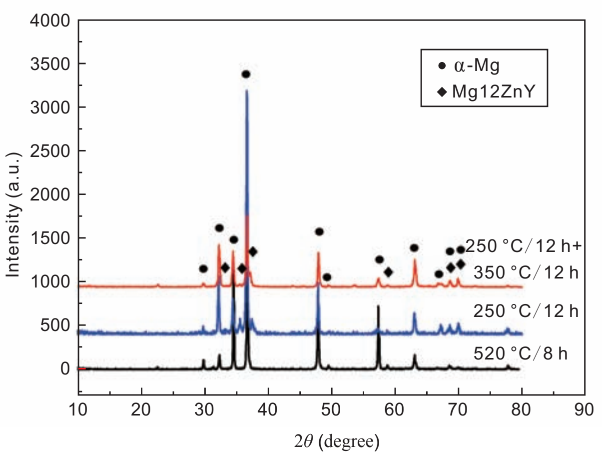

Fig. 7: XRD analysis of Mg97Zn1Y2 alloy with double aging treatment

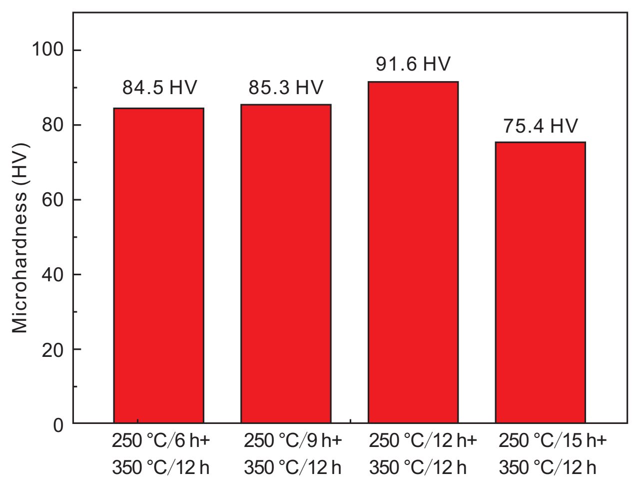

Fig. 8: Hardness of Mg97Zn1Y2 alloy after double aging treatment

2.3.3 Corrosion resistance of Mg97Zn1Y2 alloy after double aging treatment

When immersed in 3.5% NaCl solution, the self-corrosion potentials of the double aging alloys are -1.476V, -1.483V, -1.511 V, and -1.404 V, corresponding to the first-step aging time from short to long, as shown in Fig. 9. Compared with the single aged alloy, the corrosion resistance of the alloy with double aging was improved. The corrosion resistance of the alloy (250 ºC/15 h + 350 ºC/12 h) is the best. When the alloy is aged at 350 ºC, the precipitates are gradually coarsened and a network-like structure can be formed. In addition, the further precipitation of the dispersed fine LPSO phase leads to an increase in the volume fraction of the LPSO phase in the alloy. Many fine LPSO phases are distributed in the matrix, so that the matrix is isolated and the corrosion at the matrix can be effectively suppressed during the corrosion process, thereby further improving the corrosion resistance of the alloy.

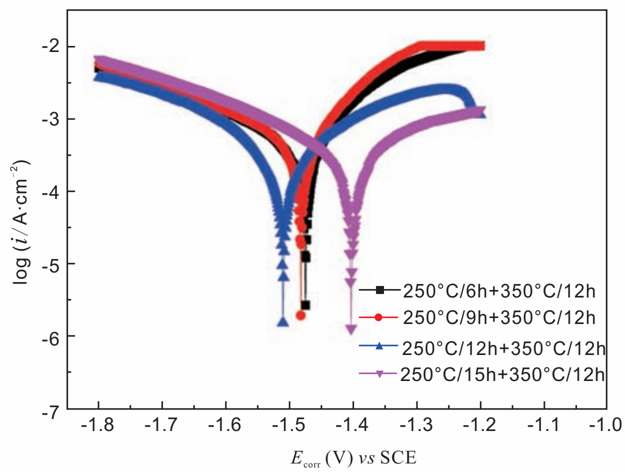

Fig. 9: Potentiodynamic polarization curves of Mg97Zn1Y2 alloy after double aging treatment

2.4 Discussion

The aging treatment is a very effective way to improve the performance of an alloy. After the solution treatment, the grains are coarsened, and the secondary phases are partially dissolved into the alloy. Because the Y-rich phase is difficult to dissolve even at a high temperature, there are still many secondary phases at the grain boundary even after the solid solution treatment for 8 h. However, those secondary phases are spheroidized under the action of the solid solution, and the network structure is destroyed. In addition, with the Y and Zn atoms dissolved into the matrix, lattice distortion can be generated.

In general, in the double aging process, the first-step aging is set at a lower temperature to obtain a great dispersion of precipitates; the second-step aging is set at a higher temperature to promote the secondary phase precipitation from the solid solution, to grow into a certain size. In the first-step aging process, solute atoms may segregate with an increase of aging time. A small number of lamellar precipitates appear in the region of the incomplete-solid solution, and a large number of precipitates appear in the complete-solid solution region. In the second-step aging process, the precipitated phase is further precipitated and coarsened.

For the Mg97Zn1Y2 alloy, a supersaturated solid solution is formed because a large amount of solute has dissolved into the matrix after the solution treatment. As the alloy aged at 250 ºC, the hexagonal close-packed crystal structure of Mg produces a stacking layer, and the solid solution of Zn and Y atoms can be used to fill the stack of layers. The dislocations generated by lattice distortion provide an additional stress field, which promotes the diffusion of atoms and the nucleation and growth of the LPSO phase. When the aging time is short, most of the solute atoms remain in the solid solution state in the matrix, and a small amount of atoms are migrated by diffusion. Therefore, the amount of precipitation of the second phase in the alloy is small and the distribution of the second phase is uneven during the aging process.

When the alloys were aged at 350 ºC, the Y and Zn atoms that are dissolved in the matrix are precipitated again to fill the staggered layer, to form the nucleation of a fine LPSO phase. This LPSO phase is precipitated further. Then the precipitated Y and Zn solid solution atoms diffuse toward the nucleus along with the thermal motion of the atoms, which promotes the growth of the LPSO phase, thereby forming a LPSO phase aggregation region in the matrix.

Compared with the single aging alloy, the hardness of the double aging alloy increases except one (250 ºC/15 h+350 ºC/12 h), which decreases slightly, as shown in Fig. 10. After the single aging treatment, the alloy (250 ºC/15 h) is over aged due to the excessive aging time. For the alloy (250 ºC/15 h + 350 ºC/12 h), the LPSO phase is further precipitated after the second-step aging treatment, but the softening is improved, so that the hardness of alloy decreases.

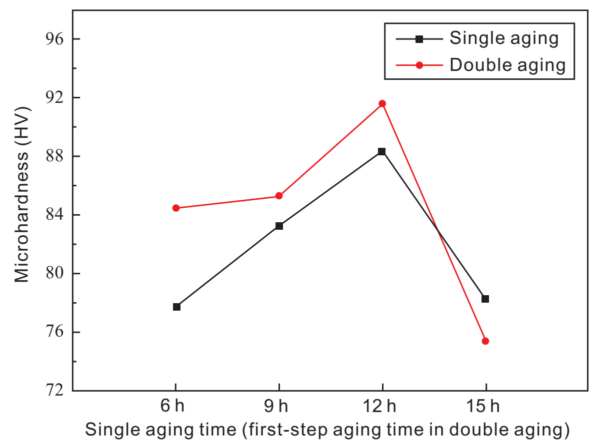

Fig. 10: Vickers hardness of Mg97Zn1Y2 alloy after single and double aging treatment

3 Conclusions

The effects of single and double aging treatments on the microstructure and properties of the Mg97Zn1Y2 alloy were studied, and the following results are obtained.

(1) Compared with the single aging treatment, the secondary phase is further precipitated and coarsened after the double aging treatment.

(2) The hardness of the single aged alloy increases to 88.4 HV due to the age hardening. After the double aging treatment, the second phase is further precipitated and distributed evenly, so that the hardness of the alloy further increases up to 91.6 HV.

(3) After the double aging treatment, the corrosion resistance of the alloy is further improved because of the further precipitation of the LPSO phase.

References

[1] Ando D, Sutou Y, Koike J. Internal microstructure observation of enhanced grain-boundary sliding at room temperature in AZ31 magnesium alloy. Materials Science and Engineering: A, 2016, 666: 94–99.

[2] Rashad M, Pan F S, Lin D, et al. High temperature mechanical behavior of AZ61 magnesium alloy reinforced with graphene nanoplatelets. Materials & Design, 2016, 89: 1242–1250.

[3] Feng H, Liu H P, Cao H, et al. Effect of precipitates on mechanical and damping properties of Mg-Zn-Y-Nd alloys. Materials Science and Engineering: A, 2015, 639: 1–7.

[4] Nagaraj M Chelliah, Ram Kumar, Harpreet Singh, et al. Microstructural evolution of die-cast and homogenized AZ91 Mg-alloys during dry sliding condition. Journal of Magnesium and Alloys, 2017, 5: 35–40.

[5] Mironov S, Onuma T, Sato Y S. Microstructure evolution during friction-stir welding of AZ31 magnesium alloy. Acta Materialia, 2015, 100: 301–312.

[6] Li C Q, Xu D K, Zeng Z R, et al. Effect of volume fraction of LPSO phases on corrosion and mechanical properties of Mg-Zn-Y alloys. Materials & Design, 2017, 121: 430–441.

[7] Miao H W, Huang H, Shi Y J, et al. Effects of solution treatment before extrusion on the microstructure, mechanical properties and corrosion of Mg-Zn-Gd alloy in vitro. Corrosion Science, 2017, 122: 90–99.

[8] Srinivasan A, Huang Y, Mendis C L, et al. Investigations on microstructures, mechanical and corrosion properties of Mg-Gd-Zn alloys. Materials Science and Engineering: A, 2014, 595: 224–234.

[9] Wang S D, Xu D K, Chen X B, et al. Effect of heat treatment on the corrosion resistance and mechanical properties of an as-forged Mg-Zn-Y-Zr alloy. Corrosion Science, 2015, 92: 228–236.

[10] Mousavi Anijdan S H, Kang D, Singh N, et al. Precipitation behavior of strip cast Al-Mg-0.4Sc-0.15Zr alloy under single and multiple-stage aging processes. Materials Science and Engineering: A, 2015, 640: 275–279.

[11] Santhosh R, Geetha M, Saxena V K, et al. Studies on single and duplex aging of metastable beta titanium alloy Ti-15V-3Cr-3Al-3Sn. Journal of Alloys and Compounds, 2014, 605: 222–229.

[12] Oh-ishi K, Hono K, Shin K S. Effect of pre-aging and Al addition on age-hardening and microstructure in Mg-6wt% Zn alloys. Materials Science and Engineering A, 2008, 496 (1/2): 425–433.

[13] Wang Y, Dai S, Chen F, et al. Influence of single and double aging treatment on microstructures and mechanical properties of cold rolled Ti-30Nb-5Ta-6Zr alloy. Materials Science and Technology, 2014, 30: 189–195.

[14] Zhu S Z, Luo T J, Yang Y S. Improving mechanical properties of age-hardenable Mg-6Zn-4Al-1Sn alloy processed by double-aging treatment. Journal of Materials Science & Technology, 2017, 11: 1–15.

[15] Xu C, Zheng M Y, Xu S W, et al. Improving strength and ductility of Mg-Gd-Y-Zn-Zr alloy simultaneously via extrusion, hot rolling and ageing. Materials Science and Engineering: A, 2015, 643: 137–141.

[16] Fang Xiaogang, Wu Shusen, Lv Shuli, et al. Microstructure evolution and mechanical properties of quasicrystal-reinforced Mg-Zn-Y alloy subjected to ultrasonic vibration. Materials Science and Engineering: A, 2017, 679: 372–378.

[17] Kawamura Y, Kasahara T, Izumi S, et al. Elevated temperature Mg97Y2Cu1 alloy with long period ordered microstructure. Scripta Materialia, 2006, 55: 453–456.

[18] Hagihara K, Kinoshita A, Fukusumi Y, et al. High-temperature compressive deformation behavior of Mg97Zn1Y2 extruded alloy containing a long-period stacking ordered (LPSO) phase. Materials Science and Engineering: A, 2013, 560: 71–79.

[19] Hagihara K, Kinoshita A, Sugino Y, et al. Effect of long-period stacking ordered phase on mechanical properties of Mg97Zn1Y2 extruded alloy. Acta Materialia, 2010, 58(19): 6282–6293.

[20] Hagihara K, Kinoshita A, Fukusumi Y, et al. High-temperature compressive deformation behavior of Mg97Zn1Y2 extruded alloy containing a long-period stacking ordered (LPSO) phase. Materials Science and Engineering: A, 2013, 560: 71–79.

[21] Jin Q Q, Shao X H, Hu X B, et al. New polytypes of long-period stacking ordered structures in a near-equilibrium Mg97Zn1Y2 alloy. Philosophical Magazine Letters, 2017, 97: 180–187.

[22] Wan Diqing, Li Zhumin, Zhou Xinjian. Microstructure and Damping of Mg97Zn1Y2 Alloy with or without Solid Solution Treatment. Rare Metal Materials and Engineering, 2016, 45: 1245–1248. (In Chinese)

[23] Mitsuhiro O, Shuhei T, Masafumi M, et al. Mechanical properties and failure characteristics of cast and extruded Mg97Y2Zn1 alloys with LPSO phase. Materials Science and Engineering: A, 2016, 652: 14–29.

[24] Zhu Y M, Morton A J, Nie J F. The 18R and 14H long-period stacking ordered structures in Mg-Y-Zn alloys. Acta Materialia, 2010, 58(8): 2936–2947.

[25] Gröbner J, Kozlov A, Fang X Y, et al. Phase equilibria and transformations in ternary Mg-rich Mg-Y-Zn alloys. Acta Materialia, 2012, 60(17): 5948–5962.

This research was financially supported by the National Natural Science Foundation of China (Grant No. 51665012) and the Jiangxi Province Science Foundation for Outstanding Scholarship (Grant Nos. 20171BCB23061, 2018ACB21020).