Materials and Design 44 (2013) 555-565

Contents lists available at SciVerse ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes





Development of a new magnesium alloy ZW21

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ARTICLE INFO

Article history: Received 22 May 2012 Accepted 14 August 2012 Available online 30 August 2012

Keywords: A. Non-ferrous metals and alloys E. Mechanical F. Microstructure

ABSTRACT

A new magnesium alloy named ZW21 has been developed through orthogonal experiment method and the effects of heat treatment on the alloy's tensile properties have also been investigated. The results indicate that the alloy only has one Mg–Zn–Y(Nd) phase of Mg₃Zn₃(Y, Nd)₂ (named W phase) and has higher mechanical properties, lower cost and lighter weight compared with the other congeneric alloys. Its microstructure is composed of small equiaxed dendrites and interdendritic discontinuous net-like eutectic structures. The eutectic structures appear in divorced W phase laths in the thin regions between the dendrites and in regular W + α -Mg lamellar structures in the triangle regions. The eutectic structures, especially the W phase, with such distribution are harmful to the tensile properties and thus proper heat treatment can improve its properties through changing the W phase distribution. Solution treatment at 250 °C for 4 h (T₄ treatment) improves the ultimate tensile strength from 210 MPa to 243 MPa. The fracture modes of the as-cast, T₄- and T₆-treated alloys all obey the quasi-cleavage regime. The fracture of the as-cast alloy belongs to a mixed mode of intergranular and transgranular forms, but those of the T₄- and T₆-treated alloys follow the transgranular mode due to the relatively high bonding strength between the grains.

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1. Introduction

As the lightest metallic structural materials, magnesium alloys are attracting more and more attention due to their great application potential in the fields of automobile and aerospace [1]. Unfortunately, the mechanical properties of the commonly used magnesium alloys are relatively low and cannot match the requirements in many application conditions. Thus, the present status is still far away from the target that some traditional metallic alloys such as aluminium alloys and ferrous alloys can be substituted by magnesium alloys as many as possible. However, it has been reported that wrought Mg-Zn-Y alloys exhibit significantly improved mechanical properties at room temperature as well as at elevated temperatures [2]. A Mg₉₇Y₂Zn₁ (in mol%) alloy produced by rapid solidified powder metallurgy exhibits a yield stress of more than 610 MPa and elongation of 5% at room temperature and a yield strength more than 380 MPa at 200 °C [3]. As-cast monolithic Mg-Zn-Y alloys have yield stress from 180 to 480 MPa at room temperature, depending on their compositions [4]. So Mg–Zn–Y system is an ideal candidate for developing high performance magnesium alloys.

The existing investigations have intensively studied the Mg– Zn–Y alloys from composition, as-cast microstructure, rolled or extruded microstructure, annealed microstructure and their effects on mechanical properties [2–13]. But there are still two great shortages in the present status. First, the study on the composition is not enough and the optimal composition corresponding to a specific mechanical property has not been determined. It is well known that Nd, Zr, Sn and Ca are the most commonly-used alloying elements in magnesium alloy. But the existing investigations have mainly focused on the effects of one of alloying elements (such as Y, Zn, Zn/Y ratio, Nd or Zr) on microstructure and mechanical properties and the other two elements of Sn and Ca have been rarely added in the Mg-Zn-Y alloys [4,5,7,13-19]. Of course, the interactions between the alloying elements have not been considered. In addition, the Zn contents of most of the investigated alloys are not lower than 4% and always around 6% (all percentages in this paper refer to mass percentage if without particularly noted) [2–13]. This undeniably increases the densities of the alloys and leads the most important advantage of magnesium alloys, light weight, to loss to some degree. Second, the effects of ternary equilibrium Mg-Zn-Y phases on mechanical properties have not been comprehensively studied. Generally, there are three kinds of ternary equilibrium phases in the Mg-Zn-Y system alloys, i.e. I-phase (Mg₃Zn₆Y, icosahedral quasicrystal structure, quasi-periodically ordered), W-phase (Mg₃Zn₃Y₂, cubic structure) and Z- or X-phase (Mg₁₂ZnY) [3]. The Ior Z-phase is closely bonded with the Mg matrix and can effectively retard the basal slip, and then strengthens the alloy greatly [2,3–9,11–13]. But for the W-phase, the existing investigations

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^{0261-3069/\$ -} see front matter @ 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.matdes.2012.08.040

indicate that it easily cracks during tensile testing and the interfaces of W/matrix are not coherent because of the limited symmetry of these phases, and thus the W phase containing alloys have relatively low mechanical properties [4,13,14–18]. However, some investigations indicate that the W phase is beneficial for improving mechanical properties. For examples, the W phase can increase the ductility [4]; When the volume fraction of W phase is between 11.2% and 17.5%, the alloys have superior strength due to the strong bonding interface between W phase and Mg matrix [19]; the alloys containing W + Z phases always exhibit higher comprehensive mechanical properties than those containing unique I or Z phase [15,16]. That is to say that there is a dispute for the effects of W phase on the mechanical properties.

Therefore, in this study, alloying elements that are added into Mg–Zn–Y alloys were first selected based on the existing studies. Then an optimal composition of an Mg–Zn–Y–Zr–Nd–Sn–Ca alloy with high comprehensive as-cast mechanical properties (taking the product of ultimate tensile strength (UTS) and elongation as the parameter for evaluating the comprehensive mechanical properties) is obtained through orthogonal experiments. The results indicate that this alloy only contains one Mg–Zn–(Y, Nd) phase, W phase, which implies that the W phase is not always a harmful phase in Mg–Zn–Y alloys. Finally, heat treatment experiments were carried out to investigate the effects of heat treatment on the microstructure and tensile properties of this alloy.

2. Selection of alloying elements and experimental procedure

2.1. Selection of alloying elements

Precipitation strengthening is the most important principle for improving mechanical properties of alloys. The elements with the precipitation strengthening role all have a common characteristic that their solubilities in Mg matrix always reduce as temperature decreases. In magnesium alloys, the solubility of Zn decreases from 6.2% at Mg–Zn binary eutectic temperature to less than 2% at 100 °C [20]. During ageing, numerous small and dispersive rod like MgZn' phase will precipitate in the Mg matrix of solutionized Mg– Zn alloys and a significant strengthening can be produced [13]. As described above, the Zn content in magnesium alloys is always higher than 4% and mostly around 6% [2–13]. To comprehensively verify the effects of Zn content on microstructure and mechanical properties and then obtain its optimal content, the content range is expanded and chosen within the extent of 2–7% in this work.

Zr element is usually used as a grain refiner in Mg–Zn alloys. The Zr solubility in liquid magnesium is very small and only 0.58% at the peritectic temperature, so Zr particles firstly crystallize during solidification [21]. Due to their same crystal structure and similar lattice with Mg matrix, they can act as the substrates of heterogeneous nucleation to refine Mg grains through a peritectic reaction [20,21]. It can be expected that the Zr particles may coarsen and settle when the Zr content is too high, and then the number of the effective substrates is decreased. In view of the solubility (0.58%) in liquid magnesium [21] and the contents (0.16–0.86%, but most of them are focused within 0.4–0.6%) in the investigated alloys [3–7,13–19], the Zr content in this work is selected within the range of 0.3–0.8%.

The element of Y is the necessaries for forming the ternary phases of I, W and X. In addition, Y can refine Mg–Zn–Zr alloys because its partition coefficient is less than 1 and thus the atoms can hider the growth of grains and form constitutional undercooling to accelerate nucleation [22,23]. So Y is a kind of commonly-used alloying element in Mg–Zn–Zr alloys. In the studied alloys, the Y content has a wide range of 0.5–7%, but is always in the extent

of 3–5% in most of the alloys [2–19,22,23]. Therefore, the Y content in this work is selected within 1–5%.

Nd has similar roles to Y in Mg–Zn–Zr alloys [22,23]. In addition, when two or more kinds of rare earth elements are added, the interaction between them can reduce their solubilities in Mg matrix and change the precipitation kinetics of supersaturated Mg solution, and then an additional strengthening can be obtained [22–24]. So Nd is also selected as an alloying element in this work. In the studied Mg-RE or Mg–Zn–Y–Zr alloys, the content of Nd is generally less than 5% [22–24], so its content is controlled within the range of 0.5–4.5% in this work.

The element of Sn does not only improve the castability of magnesium alloys, but also more importantly can form Mg₂Sn precipitates during solution-ageing treatment to enhance mechanical properties [25]. So this element is also selected as an alloying element to add into the Mg–Zn–Y–Nd–Zr alloys. It can be expected that the main alloying elements in this work include Zn, Y and Nd, Sn is only a micro-alloying element. In view of the Sn containing Mg–Al and Mg–Zn alloys, the Sn content is normally less than

Table 1

Selected alloying elements and their content ranges.

Content range	Allo	Alloying element								
(wt.%)	Zn	Zr	Y	Nd	Sn	Ca	Mg			
	2- 7	0.3- 0.8	1– 5	0.5- 4.5	0.5- 2.5	0.05- 0.25	Balance			

Table 2

Factor	level	table	of	the	orthogonal	tests.
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Level	Factor (wt.%)							
	A(Zn)	B(Zr)	C(Y)	D(Nd)	E(Sn)	F(Ca)		
1	2	0.3	1	0.5	0.5	0.05		
2	3.5	0.5	2	1.5	1	0.1		
3	5	0.6	3	2.5	1.5	0.15		
4	6.5	0.7	4	3.5	2	0.2		
5	7	0.8	5	4.5	2.5	0.25		

able 3				
Results	of	the	orthogonal	tests.

Testing serial number	UTS (MPa)	Elongation (%)	PUE (MPa·%)
A1B1C1D1E1F1	210	17.75	3727.5
A1B2C2D2E2F2	168	5	840
A1B3C3D3E3F3	154	4.5	693
A1B4C4D4E4F4	171	2.75	470.25
A1B5C5D5E5F5	131	0.75	98.25
A2B1C2D3E4F5	139	4.75	660.25
A2B2C3D4E5F1	125	3	375
A2B3C4D5E1F2	158	1.5	237
A2B4C5D1E2F3	228	0.1	22.8
A2B5C1D2E3F4	186	6.5	1209
A3B1C3D5E2F4	154	1.75	269.5
A3B2C4D1E3F5	200	6	1200
A3B3C5D2E4F1	168	2.25	378
A3B4C1D3E5F2	187	5.5	1028.5
A3B5C2D4E1F3	200	5	1000
A4B1C4D2E5F3	171	2	342
A4B2C5D3E1F4	225	6.5	1462.5
A4B3C1D4E2F5	171	2	342
A4B4C2D5E3F1	151	2	302
A4B5C3D1E4F3	210	8.25	1732.5
A5B1C5D4E3F2	155	0.75	116.25
A5B2C1D5E4F3	154	2.5	385
A5B3C2D1E5F4	156	2.5	390
A5B4C3D2E1F5	160	2	320
A5B5C4D3E2F1	167	0.25	41.75

3% [25–29]. So in this work the Sn content is controlled within 0.5–2.5%.

Ca can reduce the oxidation of magnesium alloy melts and always is used in ignition proof magnesium alloys [30]. In addition, Ca has significant grain refinement and thus improves mechanical properties such as yield strength, hardness and creep resistance [30–32]. Especially, 0.2% Ca has good effect on improving UTS and yield strength of Mg–Zn–RE alloys [33]. The Ca content thereby is preliminarily determined in the range of 0.05–0.25%.

Based on the above discussion, it can be summarized that for the Mg–Zn–Y–Zr alloys studied in this work, the other three ele-

Table 4

Means of parameters and	d corresponding ranges
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Mean	Factor								
of SEP	A(Zn)	B(Zr)	C(Y)	D(Nd)	E(Sn)	F(Ca)			
<i>K</i> ₁	1165.800	1023.100	1338.400	1414.560	1349.400	964.850			
K_2	500.810	852.500	638.450	617.800	303.210	555.438			
K ₃	775.200	408.000	678.000	777.200	704.050	695.883			
K_4	836.200	428.710	458.200	460.700	725.200	760.250			
K_5	250.600	816.300	415.560	258.350	446.750	524.100			
Range (R)	915.200	615.100	922.840	1156.210	1046.190	440.750			



Table 5				
Supplemental	tests	and	the	results.

ments of Nd, Sn and Ca are also selected as alloying elements. In view of the status of this alloy system and applications of Nd, Sn and Ca elements in magnesium alloys, the content ranges of Zn, Y, Zr, Nd, Sn and Ca are preliminarily selected and are shown in Table 1.

2.2. Experimental procedure

To obtain the optimal contents of these alloying elements mentioned above, orthogonal experimental method was applied. As discussed above, six alloying elements are selected, i.e., the orthogonal experiment has six factors. The setting range values of each factor are divided into five levels as shown in Table 2. That is to say that the various factor level values are used in $L_{25}(5^6)$ orthogonal table.

The alloys were prepared using Mg, Zn, Sn and Ca pure metals, and Mg-30Zr, Mg-30Y and Mg-30Nd master alloys. During melting, a JDMJ refining agent and a special covering agent for Mg-RE alloys were employed. The prepared melts were finally poured into a permanent mould with a cavity of 16 mm diameter at 710-720 °C. For a structural material, its UTS and elongation are the two most important mechanical properties. So the product of the UTS and elongation (PUE) was used as the parameter for evaluating the alloys' mechanical properties. According to the ASTM test standard [34], the casting rods were machined into tensile bars with a gauge of 40 mm and a diameter of 8 mm. The tensile tests were carried out on a universal testing machine at a strain rate of $1.67 \times 10^{-3} \text{ s}^{-1}$. The average of at least three tests was taken as the final mechanical properties for each alloy. According to the PUE values, an optimal composition that corresponds to the maximum PUE value was obtained. The optimized alloy was named according the specification of ASTM [35].

Some casting rods with the optimal composition were prepared according to the melting procedure mentioned above and used to study the effects of solution and age heat treatments on the microstructures and tensile properties of the alloy. Based on the existing investigations on Mg–Zn–Y alloys [2,8–11], the solution temperature of 525 °C and age temperature of 250 °C were employed respectively. All of the heat treated rods were water-quenched and then machined into tensile bars with the same dimensions to the above as-cast alloys. Also the average of at least three bars was taken as the mechanical properties of each of the heat treated alloys.

Alloy number	Content (v	wt.%)			UTS (MPa)	Elongation (%)	PUE (MPa·%)		
	A(Zn)	B(Zr)	C(Y)	D(Nd)	E(Sn)	F(Ca)			
1	0	0.3	1	0.5	0.5	0.05	117	6.25	731.25
2	3.5	0.3	1	0.5	0.5	0.05	173	7	1211
3	6.5	0.3	1	0.5	0.5	0.05	145	3.5	507.5
4	2	0	1	0.5	0.5	0.05	81	2	162
5	2	0.2	1	0.5	0.5	0.05	135	2.5	337.5
6	2	0.5	1	0.5	0.5	0.05	181	11.25	2036.25
7	2	0.7	1	0.5	0.5	0.05	184	10.75	1978
8	2	0.3	0	0.5	0.5	0.05	199	6	1194
9	2	0.3	0.3	0.5	0.5	0.05	186	14.25	2650.5
10	2	0.3	0.5	0.5	0.5	0.05	192	15.75	3024
11	2	0.3	3	0.5	0.5	0.05	192	9	1728
12	2	0.3	1	0	0.5	0.05	185	11.13	2059.05
13	2	0.3	1	0.3	0.5	0.05	190	12.25	2327.5
14	2	0.3	1	1	0.5	0.05	176	8.25	1452
15	2	0.3	1	2	0.5	0.05	162	5.58	903.96
16	2	0.3	1	0.5	0	0.05	192	11.13	2136.96
17	2	0.3	1	0.5	1	0.05	134	4.5	603
18	2	0.3	1	0.5	0.5	0	138	5.25	724.5
19	2	0.3	1	0.5	0.5	0.15	174	15.42	2683.08

Metallographic specimens were cut from the as-cast and heat treated rods, and finished and polished by standard metallographic technique [36]. The as-cast and solutionized specimens were etched by an aqueous solution containing picric acid, acetic acid and ethanol. The aged specimens were etched by an aqueous solution containing nitric acid. Then they were observed by an optical microscope (OM) or/and a scanning electron microscope (SEM). The phase constituents of the alloys were examined by an X-ray diffractometer (XRD) and the compositions of some phases were analyzed by an energy disperse spectroscopy (EDS) or electron



Fig. 2. (a) OM, and (b) and (c) SEM micrographs of the as-cast ZW21 alloy.

probe microanalyzer (EPMA). The as-cast specimen was examined by a differential thermal analyzer (DTA) in a heating rate of $10 \,^{\circ}$ C min⁻¹. The fracture surfaces and their side-views were also observed on the SEM and OM respectively.

3. Results and discussion

3.1. Composition optimization

Table 3 shows the results of the orthogonal tests. It shows that the PUE is up to a maximum value of 3727.5 MPa.% when the parameters are combined in $A_1B_1C_1D_1E_1F_1$. The average PUE values of various factor levels (i.e., means of the PUE) are calculated and listed in Table 4 in K₁₋₅. According to the larger-the-better characteristic of orthogonal test, it can be concluded that the optimum parameter combination of the PUE is $A_1B_1C_1D_1E_1F_1$. The ranges of the factors are also listed in Table 4. It implies that Nd has the largest effect on the PUE and Sn takes the second place. Y and Zn have similar effect and take the third and fourth place respectively. The effects of Zr and Ca are quite small, which implies that their content variations cannot significantly influence the tensile properties. The reasons of the alloying element effects on the mechanical properties will be discussed in elsewhere.

The results mentioned above shows that the composition corresponding to the level 1 in Table 2 is the optimum composition. The PUE response chart of various factor levels is shown in Fig. 1, which



Fig. 3. XRD diffractogram of the ZW21 alloy.



Fig. 4. EDS analysis of the interdendritic phase marked by cross A in Fig. 2c.



Fig. 5. (a) Back scattered electron image of the ZW21 alloy, (b) Mg map, (c) Zn map, (d) Y map, (e) Nd map, (f) Zr map, (g) Sn map and (h) Ca map.



Fig. 6. DTA curve of the ZW21 alloy.

indicates that the PUE values all decrease with increasing the alloying element contents. That is to say the minimum contents within the selected composition ranges are their optimum contents. So it can be expected that the resulting combination of $A_1B_1C_1D_1E_1F_1$



Fig. 7. Variations of UTS and elongation with solution time.

may not represent the real optimum composition and the contents of some elements may be lower than these values.

Therefore, a set of supplementary experiments has been designed. Based on the compositions of $A_1B_1C_1D_1E_1F_1$, the content of one element decreases from a given value to zero and the contents of the other elements remain unchanged. The detailed experimental scheme is shown in Table 5. The results including UTS, elongation and PUE are also listed in Table 5. It indicates that the decreases of the element contents cannot further enhance the mechanical properties. So it can be reasonably concluded that the combination of $A_1B_1C_1D_1E_1F_1$ is the final optimum combination, i.e., the optimum composition should be Mg–2Zn–1Y–0.5Nd–0.3Zr–0.05Ca. According to the specification of ASTM [35], this alloy is named ZW21.

3.2. Microstructure and solidification process

Fig. 2 shows the microstructure of the optimized alloy of ZW21. It reveals that its microstructure is composed of small equiaxed dendrites (the grain size is about 50 μ m) and the net-like interdendritic eutectic structures (Fig. 2a). From the SEM micrograph shown by Fig. 2b, it can be seen that the distribution of one phase (in white) in the eutectic structures is not continuous and it exists in discontinuous laths in the thin regions between the dendrites and in pools in the triangle regions. The pool-like structures are always in regular lamellar form (Fig. 2c).

The result from XRD shows that the alloy only contains two phases, α -Mg and W (Mg₃Zn₃Y₂ [3]) (Fig. 3). In view of the microstructure, it can be expected that the primary dendrites should be the α -Mg and the interdendritic white phase (in Fig. 2b and c) may be the W phase. As discussed above, Nd has similar behavior to Y in Mg–Zn alloys and Nd can partially replace Y in the ternary Mg–Zn– Y phases [22,23]. The EDS analysis indicates that the Zn/(Y + Nd) atomic ratio of the white phase (shown by cross A in Fig. 2c) is close to 3:2 (Fig. 4). In addition, the available investigations propose that Mg–Zn–Y(Nd) alloys should include two phases of α -Mg and W when the Zn/(Y + Nd) ratio (in weight) is in the range of 0.85–2.05 [2,3]. In the present work, the ratio of the ZW21 alloy is 1.33 and is just within this range. So it can be concluded that the ternary Mg–Zn–Y phase (i.e., the white phase in Fig. 2b and c) is the W phase and its composition should be Mg₃Zn₃(Y, Nd)₂ (see Fig. 4).

Fig. 5 gives the back scattered electron image and the alloving element maps of the ZW21 alloy. It shows that the primary grains belong to typical equiaxed dendrites (Fig. 5a) and the white interdendritic phase is rich in Zn, Y and Nd elements (Fig. 5c-e), which is consistent to the above discussion that the white dendritic phase is the Zn, Y and Nd riched W phase. The white particle in the center of the grain shown in Fig. 5a may be the nucleus of this grain and Fig. 5f reveals that this particle is rich in Zr. As discussed above, the firstly crystallized Zr particles during solidification can act as the nucleation substrates of primary α -Mg grains [20,21]. So it can be proposed that the white particle is exactly the nucleation substrate of the grain and is the elemental Zr particle. Sn and Ca exist in the form of interdendritic particles (Fig. 5g and h), which is in accordance with the available results that the extra Sn and Ca can form eutectic Mg₂Sn phase and Ca-rich brittle phase in interdendritic regions respectively besides some of them dissolve in the α -Mg phase [25,27,30,31,33,37]. Due to the amounts of these phases are very limited, the XRD does not detect their existence under its sensibility.

The result from DTA shows that there are two endothermic peaks at 513.1 °C and 648 °C respectively (Fig. 6), which implies that two structures or phases melt at the two temperatures respectively. As discussed above, the microstructure of the ZW21 alloy indicates that it mainly consists of primary α -Mg dendrites and interdendritic eutectic structures and one phase of the eutectics is the W phase. Generally, one phase of eutectics is always its primary phase for an alloy. In addition, the amounts of Mg₂Sn and Carich intermetallics are very little. So the interdendritic eutectics of the ZW21 alloy should mainly consist of the eutectic constituents of Mg-Zn-Y(Nd) ternary alloy, i.e., the W phase and α -Mg phase. Therefore, it can be expected that the first endothermic peak at 513.1 °C corresponds to the melting of the eutectic W and α -Mg phases and the start melting temperature is at 505.75 °C (Fig. 6); the second peak at 648 °C is related to the melting of the primary α -Mg phase that starts from 593.58 °C. The melting temperatures of the W and primary α -Mg phases are very close to those proposed by the existing investigations [3,5].



Fig. 8. Microstructures of the ZW21 alloys solutionized at 525 $^\circ\text{C}$ for (a) 4 h and (b) 16 h.



Fig. 9. XRD diffractograms of the ZW21 alloy solutionized at 525 °C for 4 h.

Based on these analyses, the solidification process of the ZW21 alloy can be proposed: firstly, the primary α -Mg phase begins crystallizing at about 648 °C, and then the residual melt solidifies through an eutectic reaction of L \rightarrow W + α -Mg at about 513.1 °C. Together with the microstructure shown by Fig. 2, it can be found that the α -Mg phase grows into the equiaxed dendrites (Fig. 2a). But for the eutectic structures in the thin regions between the dendrites, the eutectic α -Mg preferentially grows on the surfaces of the primary α -Mg dendrites and only the W phase is left in a discontinuous net form (Fig. 2b), i.e., the eutectic structures in these regions belong to devoiced eutectics. As for those in the large-sized triangle regions, they often appear in a regular lamellar morphology (Fig. 2c). The distribution of W phase in such forms is consistent with the result from previous investigations [3,19].

3.3. Effects of heat treatment on microstructure and mechanical properties

For the Mg–Zn–Y alloys, the existing investigations only involve the effects of thermalmechanical processing such as rolling and extrusion on the microstructures and/or mechanical properties, and the study on the traditional heat treatment behaviors has not been found [2,8–12]. Furthermore, all of these investigations almost have focused on the I- or Z-phase containing alloys. Only one paper involves a W-phase containing alloy: the effects of forging processing and subsequent solution, solution plus ageing and ageing treatments on the microstructure (particular grain size) and mechanical properties of ZK60-Y alloy have been studied [13]. So it is necessary to verify the heat treatment behaviors of the ZW21 alloy.

Fig. 7 gives the variations of UTS and elongation of the ZW21 alloy with the solution time at 525 °C. It shows that both the UTS and elongation sharply increase during the initial period and reach the maximum values of 223 MPa and 26.5% respectively when it is solutionized for 4 h. Then the properties decrease and tend to relatively constant values after 40 h. Compared with the as-cast alloy, the UTS and elongation of the alloy solutionized for 4 h are increased by 6% and 50% respectively. So it can be concluded that a proper solution treatment can improve the tensile properties of the ZW21 alloy, especially the elongation.

The result from metallographic observations shows that the interdendritic structures gradually reduce and have completely disappeared when the alloy is solutionized for 4 h and a microstructure with small polygonal grains is obtained (Fig. 8a). As discussed above, the interdendritic structures are the α -Mg+W eutectics, especially the devoiced eutectic W phase. Namely, the W phase can dissolve through solution treatment although it has quite high thermal stability (its melting is about 513 °C as shown by Fig. 3, being very close to 510 °C proposed by Xu et al. [19]). The XRD result also shows that the diffraction peaks of W phase have disappeared at this time (Fig. 9). A previous investigation indicates that the big bulk W phase has almost completely decomposed when a forged ZK60-Y alloy are solutionized for 2.5 h at 500 °C [13]. So it can be concluded that the improvement of mechanical properties should be attributed to solution strengthening resulted from the dissolution of W phase. Fig. 2b shows that the eutectic W phase distributes in a discontinuous net-like form in



Fig. 10. Fractographs of the ZW21 alloys solutionized at 525 °C for (a) and (b) 0 h (as-cast), (b) and (c) 4 h.

the interdendritic regions. The previous investigations indicate that the W phase is guite fragile and the distribution with discontinuous net-like form can easily lead its structures to crack during tensile testing and then impair the alloy's tensile properties [4,13]. Namely, the W phase structures with such distribution are the weak points of the as-cast alloy. If this distribution form can be changed into a dispersive distribution form through heat treatment, the alloy's mechanical properties should be improved. This standpoint is the main reason why the heat treatment behavior of the alloy is carried out in this work. Therefore, it can be expected that the tensile properties will be gradually improved with the decrease of the interdendritic W phase amount during solution treatment. In other words, the decrease of the W phase's harmfulness is another reason that the tensile properties are improved besides the solution strengthening. When the solution is further proceeded, the main phenomenon is the grain growth, which can be clearly seen through comparing Fig. 8a and b. The obvious grain growth is also found for the forged ZK60-Y alloy during solution at 500 °C [13]. So it can be expected that the grain growth is the main factor that leads the tensile properties to decrease when the ageing time is over 4 h. The result also shows that the grain size basically does not change after being aged for 40 h, so the tensile properties tend to constant values after this time.

For the as-cast alloy, the fracture surface exerts a relatively fine microstructure (Fig. 10a) and is composed of small-sized cleavage facets and fine dimples (Fig. 10b), which means that its fracture belongs to quasi-cleavage regime. The side-view of the fracture surface reveals that the propagation of cracks along the interdendritic regions (marked by A in Fig. 11a) can be frequently seen besides across the primary α -Mg dendrites. Considering the fragile characteristic of the interdendritic W phase and its net-like distribution, it can be expected that the cracks may preferentially initiate from the W phase or other defects such as inclusions and porosities, and then develop along the interdendritic W phase and across the primary dendrites. A previous investigation showed that cracks were always found in the W phase and the interface debonding of W/ α -Mg was not seen [19]. In addition, W phase can be frequently seen on the fracture surfaces of W-phase containing alloys [13,19]. That is to say the cracks propagate in the W phase structures, but not along the W/α -Mg interfaces. Fig. 10b also shows that there are some deep cracks in the fracture surface (marked by arrows), which should correspond to the deep grooves (marked by B in Fig. 11a) resulted from partial debonding of neighboring dendrites. According to the results from Xu et al. [19], this partial debonding is also due to the W phase fracture, but not the debonding of W/α -Mg interfaces. Based on this standpoint, it can be expected that solution treatment can reduce the debonding tendency of neighboring grains due to the bonding strength improvement resulted from the dissolution of interdendritic W phase. This is the other one reason that the solution treatment can increase the tensile properties besides the solution strengthening. So as shown by Fig. 11b, cracks always develop across the grains for the alloy solutionized for 4 h, and propagate along the grain boundaries at only some local small-sized sites (marked by B). As discussed above, all of the W phase has completely dissolved at this time and its harmfulness to the mechanical properties disappears. In addition, the solution treatment also homogenizes the grains' composition, and thus their deformation harmony is simultaneously improved. So cracks can steadily traverse the grains and the large-sized cleavage facets are formed (Fig. 10c). The large-sized facets should correspond to the straight edges across the grains as shown by Fig. 11b. Also due to the composition homogenization, the grains have good toughness and the resulted facet surfaces are not so smooth and some plastically deformed wrinkles are always on them (Fig. 10d). In addition, dimples can also be clearly seen (Fig. 10c). These imply that the



Fig. 11. Side-views of the fracture surfaces of (a) as-cast ZW21 alloy and (b) solutionized ZW21 alloy for 4 h at 525 °C.

solution treatment does not change the alloy's fracture regime and it still obeys the quasi-cleavage fracture. Similarly, the deep wedge-shaped grooves (marked by A in Fig. 11b) that form from the local debonding of neighboring grains also correspond to the deep cracks in Fig. 10d (marked by arrows). When the solution time is over 4 h, as described above, some grains fantastically grow up, which leads the tensile properties to decrease. Based on the above discussion, it can be reasonably to understand why the alloy



Fig. 12. Variations of UTS and elongation with ageing time.

solutionized for 4 h has the highest properties. In addition, it can be concluded that the solution treatment for 4 h at 250 °C is appropriate for the ZW21 alloy.

To verify the effect of ageing treatment on the alloy's tensile properties, the alloy solutionized for 4 h at 525 °C is aged for different times at 250 °C. Fig. 12 gives the variations of the tensile properties with the ageing time. It shows that the elongation decreases all the time, but the decrease amplitude is reduced after 8 h. The UTS first sharply increases and then continuously decreases after 24 h. For the alloy aged for 24 h, the UTS is up to 243 MPa and

16% higher than that of the as-cast alloy. The elongation is 34% higher although it is decreased compared with that of the solution-ized alloy.

The metallographic observation indicates that lots of fine precipitates form throughout the matrix during the initial ageing period (Fig. 13a) and then they gradually evolves into flower-shaped structures in the grains (Fig. 13b). Fig. 13c shows that each petal of the flower-shaped structures is composed of fine particles. The XRD result indicates that only W phase forms during ageing



Fig. 13. Microstructures of the solutionized ZW21 alloys aged at 250 $^\circ C$ for (a) 2 h, (b) and (c) 24 h.



Fig. 14. XRD diffractogram of the solutionized ZW21 alloy aged at 250 °C for 24 h.



Fig. 15. Fractographs of the solutionized ZW21 alloy aged at 250 °C for 24 h.



Fig. 16. Side-view of the fracture surface of solutionized ZW21 alloy aged for 4 h at 250 $^{\circ}\text{C}.$

(Fig. 14), which means that the precipitates are the W phase particles. Driving by decreasing the interfacial energy of W/α -Mg, the W particles may coarsen and agglomerate into the flower-shaped structures. So it can be expected that the precipitate strengthening from the formation of fine W phase particles is the main reason that leads the UTS to increase. Simultaneously, the elongation decreases due to the deformation harmony of grains becomes bad as the W phase particles precipitate. But it is surprised that the UTS does not reach its maximum value when the W particles dispersively distribute in the grains, but does when they agglomerate into the flower-shaped structures at 24 h. This should be that the grain boundaries are the preferential sites for forming W precipitates and the precipitates at these sites must weaken the bonding strength between the grains due to their fragile characteristic. So when they agglomerate to the insides of the grains, the bonding strength is improved and thus the UTS is enhanced. The results indicate that the general morphology of the flower-shaped structures do not change obviously as the time is further prolonged. But the W phase precipitates should further coarsen and agglomerate, and thus the UTS then decreases when the time is over 24 h. As for the formation of the flower-shaped structures, the details will be discussed in elsewhere. The result from Xu and co-workers indicates that no obvious W phase precipitates during ageing of the solutionized ZK60-Y alloys at 180-225 °C [13]. This may be attributed to the different composition and low ageing temperature.

It can be expected that the propagation directions of cracks during tensile tests will change frequently due to the obstruction of the W phase precipitates, so the cleavage facet size is relatively small and the microstructure on the fracture surface is quite fine (Fig. 15a). Comparing Figs. 15b and 10d, it can be seen that the facets are clearly smaller for the alloy aged for 24 h. In addition, the bonding strength between the grains is quite high because there are no W phase precipitates to agglomerate at the grain boundaries and the grain debonding is rarely found (Fig. 16). Namely, the cracks also propagate across the grains during tensile test.

Table 7

Compositions a	and	densities	of	the	ZW21	and	other	congeneric	all	loy	S
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Alloy	Density (g/cm ³)	Composition (wt.%)					
		Zn	Zr	RE	Mn	Sn	Ca
ZW21	1.79	2	0.3	1.5	-	0.5	0.05
ZM1	1.82	3.5-5.5	0.5-1.0	-	-	-	-
ZM2	1.85	3.5-5.0	0.5-1.0	0.75-1.75	-	-	-
ZM4	1.82	2.0-3.0	0.5-1.0	2.5-4.0	-	-	-
ZE41	1.85	3.5-5.0	0.4-1.0	0.75-1.75	0.15	-	-

Summarily, the interdendritic net-like W phase in the as-cast ZW21 alloy is harmful to its tensile properties. But the tensile properties can be improved by heat treatment through changing the W phase distribution. Solution treatment can lead the W phase to dissolve into the α -Mg grains and thus improve the properties, especially the elongation. Subsequent ageing treatment can further enhance the UTS because of precipitate strengthening of the W phase particles, but decrease the elongation. The fracture of the as-cast alloy belongs to quasi-cleavage regime and the heat treatments do not change this regime. For the as-cast alloy, cracks not only propagate along the interdendritic W phase structures, but also across the primary dendrites. However, cracks always develop across the grains for the T₄-(solutionized for 4 h at 525 °C) and T₆-treated (subsequently aged for 24 h at 250 525 °C) alloys due to no W phase at the grain boundaries.

3.4. Features of the alloy

Table 6 gives the tensile properties of the ZW21 alloy and other commonly-used Mg–Zn–RE alloys [38,39]. It shows that the UTS (210 MPa) of the as-cast ZW21 alloy is comparative to those of ZE10A, ZE41, ZM1 and ZM7 alloys and obviously higher than those of the other alloys. The elongation (17.75%) is greatly higher than those of all of the listed alloys. Both the UTS and elongation can be further improved by proper heat treatments. That is to say the ZW21 alloy has relatively excellent mechanical properties.

Table 7 lists the compositions and densities of the ZW21 alloy and other congeneric alloys [38,39]. It can be found that the concentration of RE (including Y and Nd) of the ZW21 alloy is equivalent to or lower than those of the other alloys. This means that the cost of this alloy is comparative to or lower than those of the other alloys. In addition, its density is smaller because its Zn content is the lowest, which implies that this alloy can more reflect the superiority of magnesium alloys, light weight. So we can say that the ZW21 has three advantages compared with the other congeneric alloys, such as higher mechanical properties, lower cost and lighter weight.

4. Conclusions

Taking the PUE as the parameter for evaluating comprehensive mechanical properties, the contents of Zn, Zr, Y, Nd, Sn and Ca in a magnesium alloy are optimized through orthogonal experiment method, and then the effects of solution treatment and subsequent ageing on microstructure and tensile properties of the optimized alloy are investigated. The following conclusions have been concluded.

Tensile properties of	of the ZW21	alloy and	other	congeneric	alloys

Table C

Alloy	ZW21			ZE10A	ZE41	ZM1	ZM2	ZM3	ZM4	ZM6	ZM7
UTS (MPa)	210	223	243	200	200	205	165	105	120	180	205
Elongation (%)	17.75	26.5	23.75	12	3	2.5	1.5	1.5	2	1	3
State	As-cast	T_4	T ₆	As-cast	As-cast	T_1	T_1	As-cast	As-cast	As-cast	T_4

- (1) A new magnesium alloy named ZW21 has been developed. The alloy has only one Mg–Zn–Y(Nd) ternary phase of W (Mg₃Zn₃(Y, Nd)₂). It has higher mechanical properties (UTS of 210 MPa and elongation of 17.75%), lower cost and lighter weight compared with the other congeneric alloys.
- (2) The microstructure of the alloy is composed of small equiaxed dendrites and interdendritic discontinuous net-like eutectic structures. The eutectic structures exist in divorced W phase laths in the thin regions between the dendrites and in regular W + α -Mg lamellar structures in the triangle regions.
- (3) T_4 treatment can improve the tensile properties, especially the elongation (26.5%). T_6 treatment can further increase the UTS (243 MPa), but decrease the elongation. However, the elongation is still 34% higher than that of the as-cast alloy although it is decreased by the T_6 treatment compared with that of the solutionized alloy.
- (4) The fracture of the alloy obeys the quasi-cleavage regime and the T_4 and T_6 heat treatments do not change this regime.
- (5) The fracture of the as-cast alloy belongs to the mixed mode of intergranular and transgranular forms, but those of the T₄and T₆-treated alloy follow the transgranular mode due to good bonding strength between the grains.
- (6) The interdendritic discontinuous net-like eutectic W phase in the as-cast alloy is harmful to the tensile properties, but this harmfulness can be weakened or eliminated by proper heat treatments. To improve the elongation, it can be solutionized at 525 °C for 4 h and to enhance the UTS, it can be subsequently aged at 250 °C for 24 h.

Acknowledgements

The authors wish to express thanks to financial support from the National Basic Research Program of China (Grant No. G2010CB635106), the Program for New Century Excellent Talents in University of China (Grant No. NCET-10-0023) and the Program for Hongliu Outstanding Talents of Lanzhou University of Technology.

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