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Quantitative analysis of rare earth elements in Mg–Zn–RE(Ce, Y, Gd)–Zr alloy

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Abstract

The solid solution amount of rare earth elements and the mass fraction of compounds were measured by low-temperature phase separation technology, the existing forms of rare earth elements in ZK-RE (Ce, Y, Gd) alloy were quantitatively studied, and the difference of solid solution ability of rare earth elements and the factors affecting the number of rare earth compounds were analyzed. The experimental results show that the solid solution amount of rare earth elements mainly depends on their addition amount, Zn and RE inhibit each other’s solid solution amount, and the order of solid solution amount (wt%) of rare earth elements with the same addition amount is GD > Y > Ce. Rare earth elements are mostly distributed in Mg–Zn–RE compounds, and the increase of rare earth content is helpful to form more Mg–Zn–RE compounds. With the same content of elements, the order of mass fraction of Mg–Zn–RE compounds is ZK-Ce system > ZK-Y system > ZK-Gd system. The order of solid solution ability of rare earth elements is Gd > Y > Ce, and the amount of solid solution directly affects the initial element content of compound precipitation in the remaining melt. The influence of Zn/Ce ratio in the residual melt of ZK-Ce alloy is shown in the number of rare earth compounds, while the Zn/Y(Gd) ratio in the residual melt of ZK-RE(Y, Gd) alloy determines the type and number of rare earth compounds.

1. Introduction

Magnesium alloy, as the lightest commercial metal structural material, has a great application prospect in automobile and other industries [1–3], but there are still many problems in mechanical properties [4–6], deformation workability [7], and corrosion resistance [8]. Therefore, many methods have been used to improve the properties of magnesium alloy [9–11], among which the addition of rare earth elements can not only make magnesium alloy show more excellent mechanical properties [12–14], but also make magnesium alloy show unique functionality [15, 16]. It is found that rare earth elements mainly exist in the form of solid solution and intermetallic compounds in magnesium alloy, and the mechanical properties of the alloy can be improved by solid solution strengthening and second phase strengthening. On this basis, the researchers found that the distribution of rare earths in different forms is also an important factor affecting its function [13, 17, 18].

Mg–Zn–RE–Zr magnesium alloys have been widely used in practice because of their good mechanical properties and thermal deformation properties [1, 19–21]. For Mg–Zn–RE–Zr magnesium alloy, α-Mg solid solution containing rare earth is precipitated at first in the solidification process, and rare earth compounds are mainly formed in the residual melt after the crystallization of primary α-Mg solid solution is basically finished. The formation order of the main constituent phases of this alloy provides conditions for the effective solid solution of rare earth elements. If the solid solution data of rare earth can be obtained, it is possible to further analyze the amount of rare earth compounds. In related studies, the amount or content of rare earth is often used as a variable to analyze its influence on properties. For example, the yield strength (YS) and ultimate strength...
(UTS) of extruded Mg–Zn–Zr alloy can be significantly improved by adding different content of Ce, which is due to the grain refinement effect of Ce and the formation of Ce(Mg₁₋ₓZnₓ)₁ phase [22], while adding different content of La can promote dynamic recrystallization (DRX). The alloy shows excellent yield strength and ultimate tensile strength [23]. Adding Yb element can form dispersed nano-scale precipitates, resulting in a denser and more uniform protective film, significantly improving the bio-corrosion resistance of the tested alloy [19]. Adding Y and Gd element can form various types of Mg–Zn–RE ternary compounds, which can make the alloy show excellent mechanical properties [24, 25]. Although the above research has made clear the strengthening effect of rare earth elements, it is still impossible to directly discuss the specific quantity and properties of rare earth elements. Therefore, a quantitative understanding of the distribution of rare earth elements in magnesium alloy will be helpful to the in-depth study of rare earth alloying.

In conclusion, the representative rare earth elements Ce, Y and Gd were selected to be added to the experimental alloy. The solid solution amount of rare earth elements in Mg–Zn–RE–Zr as-cast alloy was measured by low temperature phase separation method, and the difference of solid solution ability of different rare earth elements was compared, and the influence of alloy composition on solid solution amount of rare earth elements was studied. At the same time, the morphology and structure of rare earth compounds were analyzed, and the number of rare earth compounds was calculated according to the solid solution data. The reason why rare earth affects the microstructure of the alloy is analyzed and discussed from the perspective of the change of solid solution content of elements.

### 2. Materials and methods

On the basis of Mg–3Zn-0.5Zr alloy and Mg–6Zn-0.5Zr alloy, rare earth elements Ce, Y and Gd are added with the designed contents of 0.5 wt%, 1.0 wt% and 1.5 wt% respectively, so as to form the experimental Mg–Zn–Zr–RE alloy with different Re and Zn contents. Pure magnesium was melted with Mg–Zn, Mg–RE and Mg–Zr master alloy under the protection of slag, and ϕ210 mm ingot was prepared by semi-continuous casting method. The actual chemical composition of ingot was determined by Optima7000 spectrometer, and the detection results of rare earth and Zn elements are shown in Table 1. Samples were cut at 1/2 radius of the same ingot height for solid solution determination and microstructure analysis.

The chemical method was used to separate the as cast and homogenized alloys at low temperature. The solid solution in the alloy reacted with the solution and dissolved into the solution, while the compound phase remained in the solution. The phase separation solution used was methanol as solvent, ammonium benzoate, 2,2′-bipyridine, salicylic acid and dioxane as solutes, which were used as surface passivator, complexing agent of Zn ion, inhibitor of hydrolysate and chemical inhibitor of magnesium alloy. The chemical solution can be used to separate the solid solution and compound of Mg–Zn alloy accurately. The solid and liquid were separated by centrifugation and membrane filtration. The liquid phase was used to determine the content of Zn and Gd in solid solution, and the solid phase was used for phase identification and morphology observation of compounds.

The element content of the reaction solution following solid phase separation was analyzed using an Optima 7000 inductively coupled plasma emission spectrometer (ICP-OES), and the solid solution amount of elements was determined using the decomposed solid solution amount. The mass fraction of the compound phase was determined using the Value K technique of x-ray diffraction, and the phase composition of the separated solid phase was studied using a D/Max 2500/PC x-ray diffractometer (XRD). The morphology and micro-area composition of the metallographic sample and the separated solid phase of the alloy were observed using an HITACHI-SU8220 scanning electron microscope (SEM).

The formation energy of alloying elements doped into Mg lattice is estimated using the CASTEP module in Material Studio, and the solid solution capacity of various elements is discussed from the standpoint of solid solution energy change. The heat of formation of the binary system is calculated using the Miedema heat of

| Table 1. The measured contents of RE and Zn in the experimental alloys (wt%). |
|-----------------|-------|-----|-----------------|-------|-----|-----------------|-------|
| Alloy code      | Zn    | Ce  | Alloy code      | Zn    | Y   | Alloy code      | Zn    |
| ZK31-Ce0.5      | 2.60  | 0.62| ZK31-Y0.5       | 2.93  | 0.49| ZK31-Gd0.5      | 2.95  |
| ZK31-Ce1.0      | 3.04  | 0.94| ZK31-Y1.0       | 2.95  | 0.95| ZK31-Gd1.0      | 3.11  |
| ZK31-Ce1.5      | 3.18  | 1.33| ZK31-Y1.5       | 2.90  | 1.25| ZK31-Gd1.5      | 2.94  |
| ZK61-Ce0.5      | 5.41  | 0.53| ZK61-Y0.5       | 5.76  | 0.39| ZK61-Gd0.5      | 5.56  |
| ZK61-Ce1.0      | 5.90  | 1.06| ZK61-Y1.0       | 5.66  | 0.95| ZK61-Gd1.0      | 5.75  |
| ZK61-Ce1.5      | 5.56  | 1.41| ZK61-Y1.5       | 5.99  | 1.30| ZK61-Gd1.5      | 5.47  |

The Zn content of ZK31 is 3.20 and that of ZK61 is 5.86.
formation model, the excess Gibbs free energy of the ternary system is calculated using the Guozhi Zhou model, the activity interaction coefficient between Zn and RE in solid solution is calculated using the definition of activity interaction coefficient of solution, and the influence of Zn on solid solution of RE is analyzable.

3. Results and discussion

3.1. Solid solution amount of rare earth elements and Zn
Table 2 shows the data of solid solution amount of RE and Zn elements, and figure 1(a) displays the trend that the solid solution amount of rare earth increases with the increase of its content in the alloy, which shows that increasing the content of rare earth can obtain greater solid solution. However, under the same element content, the solid solution of Gd is the highest, followed by Y, and the solid solution of Ce is obviously lower, that is, the order of solid solution of rare earth elements in the experimental alloy is Gd > Y > Ce. In figure 1(b), the solid solution amount of Zn decreases with the increase of rare earth content. When the rare earth element content is the same, the solid solution amount of Zn in ZK-Ce alloy is the highest, while that in ZK-Gd alloy is the lowest, that is, the order of solid solution amount of Zn in each alloy system is ZK-Ce > ZK-Y > ZK-Gd. According to the determination results of solid solution content of Zn and RE, it is found that they show opposite changing trends, which indicates that Zn and RE inhibit each other in the process of solid solution.

3.2. Morphology and types of rare earth compounds
The experiment alloy mainly consists of α-Mg matrix phase and intermetallic compound phase, as shown in the SEM photo of typical alloy microstructure shown in figure 2. Energy spectrum analysis shows that the above compounds are mainly Mg-Zn-RE ternary compounds containing Mg, Zn and RE, that is, the forming compound is another existing form of rare earth, but the distribution range of elements in the compound is wide. The morphology of rare earth compounds is also different. The compounds in ZK-Ce alloy structure are mainly arranged in grain boundaries in a granular way, while the separated solid phase is in a state where small particles with smooth appearance adhere to each other. The compounds in ZK-Y and ZK-Gd alloy structures are mostly strip-shaped, and cross-linked in parallel at wide grain boundaries, while the separated solid phases are overlapped with each other and have parallel concave stripes on the surface. In addition, Mg–Zn compounds

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**Table 2. The solid solution amount of RE and Zn elements.**

| Alloy code | Ce   | Zn   | Alloy code | Y   | Zn   | Alloy code | Gd   | Zn   |
|-----------|------|------|------------|-----|------|------------|------|------|
| ZK31-Ce0.5 | 0.093 | 0.978 | ZK31-Y0.5  | 0.103 | 1.322 | ZK31-Gd0.5 | 0.132 | 1.358 |
| ZK31-Ce1.0 | 0.137 | 0.940 | ZK31-Y1.0  | 0.241 | 1.289 | ZK31-Gd1.0 | 0.263 | 1.241 |
| ZK31-Ce1.5 | 0.142 | 0.936 | ZK31-Y1.5  | 0.474 | 1.135 | ZK31-Gd1.5 | 0.573 | 0.924 |
| ZK61-Ce0.5 | 0.043 | 2.902 | ZK61-Y0.5  | 0.081 | 2.613 | ZK61-Gd0.5 | 0.121 | 2.589 |
| ZK61-Ce1.0 | 0.078 | 2.413 | ZK61-Y1.0  | 0.207 | 2.415 | ZK61-Gd1.0 | 0.211 | 2.576 |
| ZK61-Ce1.5 | 0.101 | 2.147 | ZK61-Y1.5  | 0.239 | 2.280 | ZK61-Gd1.5 | 0.321 | 2.045 |

The solid solution of Zn in ZK31 is 1.421 and that in ZK61 is 2.974.
were detected in some alloy isolates, while Zn-Zr compounds were found in all alloys, and the Zn/Zr atomic ratio was between 0.5 and 2.

Figure 3(a) shows the XRD comparative analysis results of solid phase separation product of typical alloys and corresponding alloys. The XRD results of solid phase separation product show clearer diffraction peaks, which is beneficial to the calibration and analysis of rare earth compounds. Figures 3(b)–(d) show the XRD spectra and phase calibration results of solid phases separated from all experimental alloys, which are mainly Mg-Zn-RE ternary rare earth compounds. The rare earth components in the ZK-Ce alloy system are mostly (Mg, Zn)\textsubscript{12}Ce, which is in line with previous studies [26, 27]. With the increase of Ce content, the diffraction peak intensity of (Mg, Zn)\textsubscript{12}Ce phase in the alloy gradually increases, reflecting that the number of (Mg, Zn)\textsubscript{12}Ce phase increases, and the main peak slightly shifts to a high angle when the alloy composition is different, indicating the atomic ratio of the compound phase. ZK-Y alloy and ZK-Gd alloy have the same type of compounds. Rare earth compounds mainly include Mg\textsubscript{3}Y\textsubscript{2}Zn\textsubscript{3} (Mg\textsubscript{3}Gd\textsubscript{2}Zn\textsubscript{3}) and Mg\textsubscript{3}YZn\textsubscript{6} (Mg\textsubscript{3}GdZn\textsubscript{6}), which are W phase and I phase, respectively. Among them, Mg\textsubscript{3}YZn\textsubscript{6} (Mg\textsubscript{3}GdZn\textsubscript{6}) is icosahedral quasicrystal phase, which is also consistent with the research conclusions of many researchers. The relative intensities of W-phase and I-phase diffraction peaks in different ZK-Y alloy and ZK-Gd alloy are obviously different, which indicates that the ratio of them varies with the change of rare earth and Zn contents in the alloys. In addition, Mg\textsubscript{11}Zn\textsubscript{25}
was detected in the isolate of ZK61-Y0.5 alloy, while Mg$_2$Zn$_3$ was detected in ZK61–0.5Gd alloy, but no obvious diffraction peak of Zn-Zr compound was found in the diffraction spectra of all alloy isolates.

Three typical experimental alloys in figure 2 were selected for TEM analysis, and the calibration results of phase selected area electron diffraction (SAED) are shown in figure 4. The calibration results of ZK61-Ce1.5 alloy in figure 4(a) show that the phase is (Mg, Zn)$_{12}$Ce phase, and the atomic percentages of Mg, Zn and Ce elements are 50.13%, 42.18% and 7.7%, respectively, which are close to the results of EDS analysis of solid phase separation. The calibration results of ZK61-Y1.5 alloy include two phases. The diffraction pattern in figure 4(b) shows an obvious five-time rotational symmetry relationship. The position marked by the arrow is the axis of symmetry, and the ratio of distances between points in the reciprocal direction is the same. Therefore, it is identified as icosahedral quasicrystal Mg$_3$YZn$_6$ phase. The calibration results in figure 4(c) show that the phase is Mg$_6$Y$_2$Zn$_3$ phase with face-centered cubic structure. There are also two phases in the calibration results of ZK61-Gd1.5 alloy. The phase in figure 4(d) shows an obvious five-time rotational symmetry, the position marked by the arrow is the axis of symmetry, and the ratio of distances between points in the reciprocal direction is the same, so it is determined to be icosahedral quasicrystal Mg$_6$GdZn$_6$ phase, and the calibration results in figure 4(e) show that the phase is face-centered cubic Mg$_6$Gd$_2$Zn$_3$ phase. The calibration result of diffraction pattern proves the accuracy of XRD analysis result of solid phase separation.

3.3. Quantity and proportion of rare earth compounds

Rare earth compounds are formed in the late solidification stage of the alloy and mainly distributed at the grain boundary of the alloy. Metallographic observation shows that the number of compounds at grain boundaries increases with the increase of RE and Zn content. As the RE in the experimental alloy mainly exists in the form of solid solution and compound, the amount of rare earth compounds can be calculated according to the difference between RE content and solid solution amount. However, because (Mg, Zn)$_{12}$Ce in ZK-Ce alloy system contains Zn with uncertain proportion, the calculation of its mass fraction needs to consider the amount of Zn in the compound. On the other hand, ZK-Y alloy and ZK-Gd alloy have W phase and I phase with different element stoichiometry at the same time, so the mass ratio of the two phases is calculated by XRD spectrum of the separated solid phase and K value method, and then the mass fraction of each phase and the total mass fraction of the two phases are calculated according to the amount of rare earth existing in the compound. The calculation
results of the mass fraction of rare earth compounds in each experimental alloy and the mass fraction ratio of W phase to I phase in ZK-Y alloy and ZK-Gd alloy are shown in table 3.

Figure 5 shows the change of the total mass fraction of rare earth compounds in experimental alloys with the content of RE and Zn. It can be seen that all experimental alloy systems show a trend that the mass fraction increases with the increase of the content of RE and Zn. At the same time, at the same content of RE and Zn, the mass fraction of ZK-Ce alloy compound is the largest, while that of ZK-Gd alloy compound is the smallest. In table 3, the calculation results of the mass fraction ratio of W phase to I phase in ZK-Y and ZK-Gd alloy systems show that the ratio increases with the increase of RE content and decreases with the increase of Zn content.

Figure 4. TEM images of typical alloy compounds and calibration results of diffraction patterns. (a) ZK61-Ce1.5, (b)–(c) ZK61-Y1.5, (d)–(e) ZK61-Gd1.5.

Figure 5. The change of the total amount of RE compounds with content of RE in the experimental alloys.
Figure 6 shows the calculation results of rare earth compounds in ZK-Y and ZK-Gd alloys respectively. The change trend of W phase and I phase content in ZK-Y alloy is opposite. Increasing the content of Y alone is beneficial to the formation of W phase, while the formation of I phase decreases while the number of W phase increases. Increasing the content of Zn alone is more beneficial to the formation of I phase, and the increase of Zn is beneficial to the increase of the total amount of rare earth compounds. The amount of W phase in ZK-Gd alloy and I phase in ZK31-Gd alloy show similar change trend with the change of alloy composition, while the content of I phase in ZK61-Gd has no obvious change trend with the increase of Gd content, and the amount of I phase formed in ZK-Gd alloy is obviously less than that in ZK-Y alloy. The above experimental results show that the effects of RE (Y, Gd) and Zn content on the formation of rare earth compounds are similar. There are more I phases in ZK-Y alloy, more W phases in ZK-Gd alloy and more compounds in ZK-Y alloy than ZK-Gd alloy.

3.4. Discussion

3.4.1. Difference of solid solution amount of rare earth elements and influence of Zn element

Because different rare earth elements have different solid solution abilities in experimental alloys, this difference must correspond to the different alloy energy changes caused by solid solution. Therefore, in this paper, the energy change caused by doping rare earth elements into Mg crystal lattice is calculated by using the first principles to illustrate the solid solution ability of rare earth elements. Table 4 shows the lattice constant, total energy and formation energy of the optimized $3 \times 3 \times 3$ supercell model calculated by first principles. The results show that the lattice constant and energy state of the supercell change after the rare earth atom replaces one Mg atom in the supercell. As far as energy is concerned, the energy of supercell containing Gd decreases, while the energy of supercell containing Y and Ce increases, and the order of supercell energy is $Mg_{53}Ce_1 > Mg_{53}Y_1 > Mg_{53}Gd_1$. However, the formation energies of supercells are all negative, indicating that all three rare earth elements can replace Mg to form solid solutions, but the energy changes of the system caused by a supercell are different, and the order of energy decrease is $Mg_{53}Gd_1 > Mg_{53}Y_1 > Mg_{53}Ce_1$. The above energy changes show that among the three rare earth elements involved in this study, Gd is the easiest to be solid-dissolved in Mg, followed by Y and Ce is the most difficult.

As RE and Zn were dissolved in Mg at the same time in the experiment, a $3 \times 3 \times 3$ supercell model of Mg-Zn-RE was established. In the model, rare earth atoms were fixed at the lowest energy position, and the energy change of solid solution containing RE and Zn elements was calculated, which showed the promotion or inhibition effect of elements in forming solid solution. Table 5 shows the calculation results of Mg-Zn-RE (Ce, Y, Gd) supercell, in which the formation energy of $Mg_{52}Zn_1Gd_1$ is the lowest and that of $Mg_{52}Zn_1Ce_1$ is the highest.
Therefore, it is extremely difficult for Ce atoms to dissolve into the matrix, showing the worst solid solution ability. The formation energy of Zn atoms dissolved in Mg53Zn1 supercell is lower than that of Y, which indicates that Zn is easier to dissolve in solid solution, resulting in the decrease of the solid solution number of Y atoms, which shows the inhibition effect on Y solid solution. Although the formation energy of Gd atoms dissolved in supercell decreases, the reduction range is small, and the solid solution of Gd may still be inhibited by the solid solution of Zn.

The activity mutual coefficient of elements is a thermodynamic parameter that characterizes the nature and degree of interaction between two solute components in the system. The mutual repulsion or attraction between the positive and negative reaction components indicates that each other’s activity is increased or decreased, so it can be used to analyze the decrease or increase of the actual solubility of components caused by interaction. Table 6 shows the activity interaction coefficients between RE and Zn in the solid solution of Mg-Zn-RE (Ce, Y, Gd) alloy system. It can be seen that the activity interaction coefficients between Zn and various RE elements are all positive, which indicates that Zn and RE mutually repel each other in the solid solution and improve each other’s activity, which leads to that when RE and Zn are dissolved in Mg at the same time, they will reduce each other’s actual solubility.

3.4.2. Influencing factors of rare earth compound quantity
In ZK-Ce alloy, because the (Mg, Zn)12Ce phase is formed in the remaining melt after the crystallization of primary α-Mg solid solution is basically finished, the content of Ce and Zn in the remaining melt should be the fundamental reason that affects its quantity. Figure 7 is the calculation result of Zn/Ce mass ratio and compound content in ZK-Ce alloy residual melt. The change trend of Zn/Ce mass ratio in residual melt is opposite to that of (Mg, Zn)12Ce phase. The higher Zn/Ce mass ratio in residual melt, the less (Mg, Zn)12Ce phase is formed. The content of elements in the remaining melt (that is, the difference between the initial addition amount of elements and the amount of solid solution) increases as their respective contents increase, and its value is related not only to the content of the two elements in the alloy, but also to Ce’s solid solution ability. As a result, the amount of (Mg, Zn)12Ce is the result of a complex interaction between alloy composition and solid-solution properties of alloy elements.

The amount of rare earth compounds in ZK-Y and ZK-Gd alloys increases with the increase of RE and Zn content, and the contents of W phase and I phase are also affected by the alloy composition. Since the rare earth compounds in these two alloy systems are mainly formed after the crystallization of α-Mg solid solution is basically finished, the contents of Y, Gd and Zn in the remaining melt are the main reasons that affect the number of compounds and their two-phase ratio. The mass fraction of rare earth compounds increases with the

| Supercell       | Lattice constant    | Axial ratio | Total lattice energy E/eV | Forming energy Ef/eV |
|-----------------|---------------------|-------------|---------------------------|---------------------|
| Mg54            | 3.2092              | 5.2105      | 1.6058                    | -52593.24           |
| Mg53CE1         | 3.2411              | 5.2097      | 1.6074                    | -51566.32           |
| Mg53Y1          | 3.2329              | 5.1912      | 1.6056                    | -51812.82           |
| Mg53GD1         | 3.2374              | 5.1932      | 1.6041                    | -54656.97           |

| Supercell       | Total lattice energy E/eV | Forming energy Ef/eV |
|-----------------|---------------------------|---------------------|
| Mg53Zn1         | -53329.10                 | -14.188             |
| Mg53Zn1Zn1      | -54068.99                 | -14.263             |
| Mg53Zn1Ce1      | -53366.04                 | -13.333             |
| Mg53Zn1Y1       | -52548.70                 | -14.249             |
| Mg53Zn1Gd1      | -55398.01                 | -14.465             |

| ε°C | ε°Zn | ε°Gd |
|-----|------|------|
| 18.348/T | 26.023/T | 26.023/T |

Table 4. Lattice constants and energy situation of supercell.

Table 5. Lattice constants and energy situation of supercell.

Table 6. The activity interaction coefficient between of RE and Zn.
increase of RE and Zn content in the remaining melt, which corresponds to the amount of RE and Zn that the remaining melt can provide to participate in the formation of compounds. It can be seen that the content of RE and Zn in the remaining melt at the end of crystallization of primary $\alpha$-Mg solid solution of ZK-Y and ZK-Gd alloy basically affects the number of rare earth compounds and the ratio of W phase to I phase, but the content of RE and Zn in the melt at this time is also related to alloy composition and solid solution characteristics of alloy elements. The above analysis results can give the following enlightenment: when the alloy composition is determined, all factors that affect the solid solution of RE and Zn elements will affect the amount of RE and Zn elements involved in the formation of rare earth compounds, thus affecting the amount of rare earth compounds in the alloy. Figure 8 shows the calculation results of the mass ratio of Zn/RE and the number of rare earth compounds in the remaining melt. The decrease of the mass ratio of Zn/RE will lead to the increase of the number of rare earth compounds in the alloy. It can be seen that high Zn content or low RE content in the alloy is not conducive to the formation of rare earth compounds.

3.4.3. Effect of rare earth content on compound types
From the respective formation trends of W phase and I phase, the larger the Zn/RE mass ratio in the residual melt, the smaller the two phases, which is beneficial to the formation of W phase, while the larger the Zn/RE mass ratio, the larger the two phases, which is beneficial to the formation of I phase, which corresponds to the requirement of the element ratio of RE and Zn in W phase and I phase on the Zn/RE mass ratio of residual melt. In figure 9, with the increase of Zn/Y ratio (wt%) in ZK-Y alloy, the number of I phases gradually increases and the corresponding number of W phases gradually decreases. When Zn/Y (wt%) is 3.85, the proportions of W phase and I phase are the same; when Zn/Y (wt%) is higher than 3.85, the proportions of I phase increase, which can be used to judge the types and quantities of compounds in the alloy. The change trend of W phase and I phase content in ZK-Gd alloy is similar to that of ZK-Y alloy. The increase of Zn/Gd ratio (wt%) is more conducive to the formation of I phase. When Zn/Gd ratio (wt%) is 10.44, the ratio of W phase and I phase is the...
same. When it is greater than this value, more I phase will be formed. The above analysis results provide a reference for adjusting and controlling the composition of rare earth compounds in Mg–Zn–RE(Y, Gd)–Zr alloy, and contribute to the design of new high-strength magnesium alloy.

4. Conclusion

1. The increase of rare earth elements in Mg–Zn–RE(Ce, Y, Gd)–Zr alloy is beneficial to the increase of its solid solution amount, and the order of solid solution amount of rare earth elements is GD > Y > Ce with the same addition amount. The increase of Zn is beneficial to the increase of its own solid solution, but not conducive to the increase of the solid solution of rare earth elements.

2. The increase of rare earth content can promote the increase of the number of compounds, and the order of mass fraction of compounds in alloys with the same composition is ZK-Ce system > ZK-Y system > ZK-GD system. The effects of Y, Gd and Zn contents on the formation of rare earth compounds are similar. There are more I phases formed in ZK-Y alloy, more W phases formed in ZK-Gd alloy and more compounds formed in ZK-Y alloy than ZK-Gd alloy.

3. The formation energy findings of Mg53RE1 demonstrate that the order of rare earth element solid solution ability is GD > Y > Ce, which is compatible with the solid solution amount test results. Rare earth elements and Zn elements repel each other during solid solution, according to the interaction coefficient between formation energy and activity of Mg52Zn1RE1. The element content and the interaction between elements both impact the quantity of rare earth elements in solid solution.

4. The content of alloying elements in the remaining melt has a direct influence on the types and quantities of Mg-Zn-RE ternary compounds. The lower the Zn/Ce ratio (wt%) in the residual melt of ZK-Ce alloy, the better the formation of (Mg, Zn)12Ce phase. The Zn/Y(Gd) ratio (wt%) in the remaining melt of ZK-Y(Gd) alloy not only affects the number of compounds, but also affects the types of compound phases.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.
Conflict of interest statement

The authors declare that they have no conflict of interest.

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