The partial isothermal section of the Mg-Er-Si Ternary System at 500°C

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Abstract— The partial isothermal section of the Mg-Er-Si ternary system in the Mg-Corner at 500°C has been studied through the equilibrated alloy method by using X-ray diffraction analyses and scanning electron microscopy assisted with energy dispersive spectroscopy of X-ray (SEM-EDS). There is convincing evidence for three compounds which have been clarified to be existing in equilibrium with the α-Mg solid solution at 500°C, i.e. Mg2Si, Er2MgSi2 and Er5Mg24. The results show that the partial isothermal section in the Mg-Corner consists of four single phase regions, five two-phase regions: α-Mg+Er5Mg24, α-Mg+Mg2Si, Mg2Si+Er2MgSi2, α-Mg+Er2MgSi2 and Er5Mg24+Er2MgSi2 and two three-phase regions: α-Mg+Er5Mg24+Er2MgSi2 and α-Mg+Mg2Si+Er2MgSi2. The homogeneity ranges of Mg solid solution as well as the solid solubilities of the intermediate phases at 500°C are reported. The phase of Er5Mg24 (cI58-Mn-type), Mg2Si (cF12-CaF2-type) and Er2MgSi2 have been mainly studied.

1. INTRODUCTION
Magnesium alloys are very attractive materials for the transport industry due to their low weight, high strength and satisfactory biocompatibility and biodegradation [1-4]. Adding alloy elements can improve the properties and refine the structure of magnesium alloy, which is an important topic currently [5-8]. Mechanical properties of Mg-based alloys are inadequate, especially high temperature
mechanical properties of magnesium alloy restricts the wide application. Si element is widely studied as an additive element of magnesium alloy [9-12]. Si and Mg can form the compound of Mg2Si, which is an effective strengthening phase with low density, high hardness and high melting temperature (1085°C). Adding Si element is beneficial to the fluidity of liquid by the addition of Si to the magnesium alloys [13-15]. Moreover, silicon element is very cheap, which can reduce the cost of magnesium alloy, but will appear in the crystal structure of Chinese characters like Mg2Si, the mechanical properties are deteriorating, brittle increasing. Therefore, it is necessary to add a small amount of Y, Ce and Sr etc. to improve the morphology of Mg2Si phase, improve the heat resistance and the mechanical properties [16-18].

The beneficial effect of rare earth on non-ferrous materials is the most obvious in magnesium alloys. In the Mg-RE magnesium-based alloys, RE has a greater solubility, has a good solid solution hardening and aging strengthening. The RE has the function of refining crystalline, purifying the melt, improving corrosion resistance and improving the thermal stability of the mechanical properties of the alloy, etc. [19-22]. Rare earth elements like Gd, Y and Sm can further optimize the microstructure and properties of alloys, by forming strengthening intermetallic compounds, inhibiting precipitation some of the less stable phase at elevated temperatures [23-25]. Among the many rare earth elements, Er has been proved to be an effective strengthening element which can be explained by the precipitation of nanometric L12 dispersoids and so on [26-28]. We have studied the phase transition in the magnesium rich of the Mg-Er-Si ternary system at 300 and 400°C, and these data have been published in the Journal of Phase Equilibria and Diffusion [29]. In order to better study its phase equilibrium and phase transformation at higher temperature, we also studied the phase transition in the 500°C.

2. EXPERIMENT
In this work, there are seven alloys prepared by melting. High purity Mg (99.99 mass%) ingots, Er (99.99 mass%) ingots, Er-8.53 mass% Si and Mg-30 mass% Er master alloy were used as raw materials to prepare these samples. The nominal compositions were shown in Table 1. All samples were prepared by induction melting with the semi-sealed graphite crucible under high purity argon, were sealed into steel tube for homogenization treatment with a high-purity argon atmosphere in the vacuum atmosphere steel furnace and annealed at 500°C for 500h, and finally quenched into liquid nitrogen. The microstructures and compound composition of the Mg-Er-Si alloys were carried out by a TESCAN VEGAII SEM equipped with an Oxford INCA 350 EDS, the x-ray fluorescent (LAB CENTER XRF-1800 CCDE), the phase analysis of the treated alloys were determined by X-ray diffraction on the Rigaku D/MAX-2500PC diffractometer with Cu Ka radiation, and a high tension of 40 kV and 200 mA.

| Code | Nominal comp.(at.%) Mg; Er; Si | Nominal comp.(wt.%) Mg; Er; Si | Equilibrium phase constituent at 500°C |
|------|------------------------------|------------------------------|--------------------------------------|
| #1   | 91.60; 6.00; 2.40            | 67.52; 30.44; 2.04           | Mg / Er2MgSi                        |
| #2   | 91.11; 3.76; 5.12            | 74.13; 21.05; 4.81           | Mg / Mg2Si                         |
| #3   | 91.41; 1.71; 6.81            | 82.32; 10.60; 7.09           | Mg / Mg2Si                         |
| #4   | 93.83; 1.14; 5.03            | 87.29; 7.30; 5.41            | Mg / Mg2Si                         |
| #5   | 94.59; 4.00; 1.41            | 76.44; 22.24; 1.32           | Mg / Er2MgSi2 / Mg2Si              |
| #6   | 93.58; 2.79; 3.63            | 80.00; 16.41; 3.59           | Mg / Er2MgSi2 / Mg2Si              |
| #7   | 95.92; 1.75; 2.33            | 86.68; 10.88; 2.43           | Mg / Er2MgSi2 / Mg2Si              |
3. RESULTS AND DISCUSSION

The microstructure and phase equilibria of the typical ternary Mg-Er-Si alloys were measured, the following are detailed analysis of SEM-BSE, EDS and XRD, and gradually build the phase relation in the Mg-corner of Mg-Er-Si at 500°C.

The BSE images of ×500, ×2000 times and the XRD pattern of the #1 sample held at 500°C are shown in Fig.1. There are apparently two phases, which is located in the Mg+Er2MgSi2 two-phase region. According to EDS analysis and XRD analysis (Fig.1a-c), the dark is Mg phase, the white block is Er2MgSi2 phase. With the temperature increasing the grey laths phase of Er5Mg24 almost disappeared (shown in Fig.1a), this can be seen from the XRD data of the #1 sample, the Er5Mg24 phase of #1 samples at 300°C has a clear diffraction peak. The standard diffraction data of the Er5Mg24 phase, the most intense diffraction peak is at 2θ of 33.84°, and the second strongest peak for the peak position at 2θ of 19.30° and 11.1°, where do not appear clearly diffraction peak of the #1 sample at 500°C (shown in Fig.1c). With the temperature range from 300 to 500°C increasing the grey laths phase of Er5Mg24 almost disappeared, By the XRD cannot make the accurate detection of trace phase, so cannot confirm Er5Mg24 phase does not exist at 500°C, merely state the fact that the content of Er5Mg24 phase in the #1 alloy is less at this temperature.

Figure 1. BSE image and X-ray diffraction of alloy #1 held at 500°C for 500h: (a) ×500, BSE image; (b) ×2000, BSE image; (c) X-ray diffraction of alloy #1

Fig.2 are ×500 times SEM pictures and XRD diffraction analysis image for the #2, #3 and #4 samples at 500°C respectively, these samples composed of three different components are all located in the two-phase region of α-Mg+Mg2Si. Combined with the EDS analysis, Fig.2a is the microstructure picture of #2 alloy, the dark is the α-Mg matrix phase; the average composition of gray bulk phase in three samples are respectively for Mg:67.19 at.%, Si: 32.81 at.%, Er:0.00 at.%; Mg: 64.68 at.%, Si: 35.32 at.%, Er: 0.00 at.%; Mg:66.26 at.%, Si: 33.74 at.%, Er: 0.00 at.%, so it can be judged Mg2Si phase. And there are some small white particles, it is proved that is the unmelted Er elements, and trace of Er2MgSi2. As a result, the composition of these three alloys deviates from the predetermined position, the position is shifted in the direction of higher Mg content. Through the above experimental analysis, these three samples are made of black α-Mg matrix and gray Mg2Si phase. Which confirmed the presence of two-phase region (α-Mg+Mg2Si) in the Mg-Er-Si ternary system at 500°C.
In the three-phase region of $\alpha$-Mg+$\text{Mg}_2\text{Si}+\text{Er}_2\text{MgSi}_2$, #6 and #7 alloys were held at 500°C for 500h, respectively. Their microstructures of SEM images with 2000 times (Fig.3a-b) and XRD diffraction (Fig.3c) are illustrated in Fig.3, combined with EDS component analysis, the black is: Mg:97.58 at.%, Si:2.42 at.%, Er:0.00 at.%, it can be judged that the phase of $\alpha$-Mg matrix; the white block of Er$_2$MgSi$_2$ phase is Er: 38.59 at.%, Mg: 21.83 at.%, Si: 39.58 at.%. The size of Mg$_2$Si phase too small and cannot accurately measure composition by the energy spectrum. The same method to analyze #7 sample (Fig.3b), the composition of the dark phase is Mg: 99.99 at.%, Si: 0.01 at.%, Er: 0.00 at.%, so it is $\alpha$-Mg matrix phase; component of white block is Er: 39.23 at.%, Mg: 21.22 at.%, Si: 39.55 at.%, the ratio value of Er: Mg: Si is 2:1:2, so the Er$_2$MgSi$_2$ phase. According to the analysis above, we prove the existence of the $\alpha$-Mg+$\text{Mg}_2\text{Si}+\text{Er}_2\text{MgSi}_2$ three-phase region. In order to further confirm the result mentioned above, analyze the map scanning analysis of the #6 alloy, as shown in Fig.3d. Mg, Er and Si element in different place of #6 alloy were measured with EDS map scanning analysis. From the image we can further confirm the black area is the $\alpha$-Mg matrix, containing trace of Er and Si.
elements; white region where the bulk phase contains mainly Er and Si element, it also contains a small amount of Mg, as Er$_2$MgSi$_2$. After the above analysis of #6 and #7 alloys can confirm the existence of the α-Mg+Mg$_2$Si+Er$_2$MgSi$_2$ three-phase region of Mg-Er-Si ternary system at 500°C.

According to the experiment analysis above of every alloy, the phase relation of Mg-rich corner at 500°C is consequently constructed in the Mg-Er-Si system, as shown in Fig.4. The nominal compositions point of each alloy are marked with an asterisk (★) in the Fig.4. As can be seen from Fig.4, the partial isothermal section of Mg-Er-Si ternary system in the Mg-corner 500°C has five two-phase regions, and two three-phase regions. Combined with EDS analysis also measured the solubility of some phases at 500°C, as follows: the solubility of Si element in α-Mg is 2.42 at. %, Er element is 2.35 at. %; the solid solubility of Si in the Mg$_2$Si phase is: 32.81-33.34 at. %, Er$_2$MgSi$_2$ is 20.00-22.11 at. % Mg, the balance solubility of Er$_5$Mg$_{24}$ phase could not be accurately measured.

Figure 4. The phase relation in the Mg-corner of the Mg-Er-Si at 500°C

4. CONCLUSIONS

The partial isothermal section of the Mg-Er-Si ternary system at 500°C was systemically investigated through the equilibrated alloy method by using X-ray diffraction analyses and scanning electron microscopy assisted with energy dispersive spectroscopy of X-ray (SEM-EDS), the phase equilibria transformation diagram was constructed for the Mg-Er-Si ternary system at 500°C. There is convincing evidence for four compounds have been clarified to be existing in equilibrium with the α-Mg solid solution at 500°C, i.e. Mg$_2$Si, Er$_2$MgSi$_2$, Er$_5$Mg$_{24}$ and Er$_2$Mg$_{24}$Si$_2$. The partial isothermal section in the Mg-Corner consists of four single phase regions, five two-phase regions: Mg$_2$Si+Er$_2$MgSi$_2$, α-Mg + Er$_5$Mg$_{24}$, α-Mg + Er$_2$Mg$_{24}$Si$_2$, α-Mg + Mg$_2$Si and Er$_5$Mg$_{24}$ + Er$_2$MgSi$_2$; and two three-phase regions: α-Mg + Er$_2$Mg$_{24}$Si$_2$ + Er$_5$Mg$_{24}$ and α-Mg + Er$_2$Mg$_{24}$Si$_2$ + Mg$_2$Si. The homogeneity ranges of Mg solid solution as well as the solid solubilities of the intermediate phases at 500°C are given.

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