Effect of Ce on Microstructure and Mechanical Properties of AZ91 Magnesium Alloy

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Abstract. In this paper, gravity casting experiments were used to prepare AZ91-xCe alloys, and the effects of Ce addition on the mechanical properties and structure of the AZ91-xCe alloy were analyzed. X-ray diffractometry and metallurgical microscopy were used to characterize the phase composition and microstructure of the experimental alloy, and the strength and hardness of the alloy were tested and analyzed. Results show that the addition of a small amount of Ce generates a high melting point, thermally stable Al₄Ce, and reduces the porosity of the alloy. The tensile strength and yield strength of the AZ91-xCe alloy have been significantly improved under joint strengthening of multiple mechanisms of fine-grain strengthening, precipitation strengthening, and solid solution strengthening. By comparing and observing the mechanical properties and microstructures of alloys with different Ce concentrations, it was concluded that at a Ce content of 0.5%, the overall performance of the alloy is optimal. Compared to the AZ91 alloy, the tensile strength was increased by 29% and the yield strength was increased by 34%.

1. Introduction

As one of the most abundant elements in the earth's crust, magnesium has a density of only 1.738 g/cm³ at 20°C, which is the lightest metal among commonly used structural materials [1]. Simultaneously, magnesium is characterized by good strength, low manufacturing cost, and non-toxicity, and is a metal material with great development potential. However, the chemical properties of magnesium are more active, and the surface of magnesium will react with oxygen at room temperature, so the corrosion resistance of magnesium is not optimal [2]. If pure magnesium is used directly as a structural material, its strength and hardness do not meet the necessary requirements [3]. In practical applications, different alloying elements are added to magnesium to achieve improved properties via alloying. This method is more common and also a very effective strengthening method. Through grain refinement, deformation strengthening, alloying, and heat treatment, the introduction of a particle reinforcement phase and magnesium alloy composite methods can significantly improve the properties of magnesium alloys [4].

Rare earth elements are elements of the third subgroup of the periodic table, and their extranuclear electron arrangement is relatively special. The particularity of the outer orbital electrons enables rare earth elements to show special properties, especially in the strengthening of magnesium alloys [5]. After the rare earth elements are melted into the magnesium alloy matrix, they produce grain refinement and solid solution strengthening effects, improve the microstructure of the magnesium alloy, and thereby change the mechanical properties. Compared with magnesium, rare earth elements...
are more likely to react with oxygen. Rare earth elements can also react with other oxides, such as MgO, in molten magnesium alloys to generate rare earth oxygen that can be precipitated, which has a purifying effect on magnesium alloys. Current research on the influence and law of Ce on die-cast magnesium alloy is imperfect.

Chaubey et al. [6] performed room temperature compression tests to study the mechanical properties and structures of as-cast Mg90Al10-xCex alloys. Minglin He et al. [7] discussed the effects of Ce rare earth elements on the structures and properties of ZK60 magnesium alloys and showed that the microstructure of Ce-containing alloy samples has a higher degree of recrystallization and more uniform and fine grains. Wei Jin et al. [8] discussed the effects of Ce on the properties and structure of AM60 magnesium alloys. The results show that when the Ce content in the as-cast AM60 alloy is 1%, the alloy TS, elongation, hardness, and other properties are improved to varying degrees. At present, some progress has been made in the research on the structure and mechanical properties of Ce-containing magnesium alloys. However, there are few reports on the effects of Ce on AZ91 magnesium alloys. Therefore, based on previous research, this article specifically studies the effects of adding a single rare earth element, Ce, on the microstructure and hardness of AZ91 magnesium alloys. It also provides a basic theoretical basis for further development of new magnesium alloy materials.

2. Experimental

2.1. Materials

In this experiment, Ce was added to the base alloy AZ91 magnesium alloy to prepare AZ91D-xCe (x = 0%, 0.3%, 0.5%, 0.7%, 1%). By comparing the mechanical properties and microstructural morphology of AZ91-xCe alloys with different compositions, the effects of different Ce contents on the properties and structure of AZ91 alloy were analyzed. The composition of the experimental alloy to be prepared is shown in Table 1. Controlling the content of other elements in the experimental raw materials is intended to obtain alloy materials with excellent properties. The raw materials used in the preparation of the alloy in this experiment and their purity are shown in Table 2.

| Table 1. Composition of AZ91-xCe alloys |
|-----------------|-----|-----|-----|-----|-----|
| Alloy number    | Al  | Zn  | Ca  | Ce  | Mg  |
| 1               | 7.6 | 0.5 | 2.0 | 0   | Bal.|
| 2               | 7.6 | 0.5 | 2.0 | 0.3 | Bal.|
| 3               | 7.6 | 0.5 | 2.0 | 0.5 | Bal.|
| 4               | 7.6 | 0.5 | 2.0 | 0.7 | Bal.|
| 5               | 7.6 | 0.5 | 2.0 | 1.0 | Bal.|

| Table 2. Experimental materials and main technical indicators |

| Raw materials      | Materials name                 | Technical index            |
|--------------------|--------------------------------|-----------------------------|
| AZ91D magnesium    | MG-8.68Al-0.63Zn-0.22Mn        |
| master alloy       | Ce: 18%-22%                    |

Figure 1. is the experimental flow chart. The crucible resistance furnace was selected to melt the magnesium alloy raw materials required for the gravity casting experiment, and the melt is directly poured into the designated mold to obtain an ingot. The whole process must be carried out under SF6 protective gas.
2.2. Microstructural analysis

Using wire cutting technology, 0.5 cm thick samples were taken on the casting alloys, and metallographic samples were made by an inlaying machine. Roughly grind the metallographic sample with 240#, 600#, 1000# sandpaper, respectively, until the surface of the metallographic sample is smooth and flat without obvious scratches. 1000# sandpaper was used to grind the surface of the alloy sample. The grinded sample was polished on the P-1 polishing machine until there was no obvious tailing and other defects on the surface of the metallographic sample. Figure 2. shows the metallographic sample after inlay polishing. Figure 3. shows the Keller reagent preparation test bench. The self-prepared Keller reagent (95% H2O, 2.5% HNO3, 1.5% HCl, 1% HF) were used to corrode and clean the surface of the sample with alcohol and water. Then the surface was ambiently air dried. An MJ2 upright metallographic microscope was used to observe and analyze the microstructure of the sample, and an X-ray diffractometer was used to analyze the phase of the test alloy.
2.3. Performance experiments

According to the calculation, the indentation surface pressure divided by the acceleration of gravity is the required Vickers hardness value. Formula (1) is the calculation of Vickers hardness.

\[ HV = \frac{F}{gS} = C \frac{2F \sin \alpha}{d^2} = 0.189 \frac{F}{d^2} \]

In the formula: \( F \) is the test force; \( S \) is the surface area of the indentation; \( \alpha \) is the top angle of the diamond indenter; \( d \) is the arithmetic average of the indentation diagonal dimensions \( d_1 \) and \( d_2 \); \( g \) is the acceleration of gravity.

A wire cutting machine was used to cut a 5 mm thick alloy, then the sample was ground, polished, and cleaned, and a digital intelligent hardness tester was used to measure the sample hardness. The average of three points was taken to analyze the hardness. The shape and size of the tensile specimen are shown in Figure 4 and Figure 5. In ambient room temperature conditions, select a universal testing machine to perform a tensile test on the tensile specimen. After the stretching process was over, the tensile strength of the casting was measured based on the relevant experimental data, and tensile performance was discussed.
3. Results

3.1. X-ray diffraction phase analysis
A ProCAST software material calculation module was used to simulate the thermodynamic parameters of AZ91-xCe alloys under five different Ce contents. The phase composition of the alloy when the Ce contents were 0, 0.5%, and 1.0% are shown in Figure 6 from the data, it can be seen that the AZ91 alloy contains an $\alpha - Mg$ phase and $\beta - Mg_{17}Al_{12}$ phase. After Ce was added, a new binary alloy rare
earth phase was formed.

The X-ray diffraction pattern (XRD) of the AZ91-xCe alloy is shown in Figure 7. Figure 7 (a) is a comparative chart of XRD patterns of three alloys with different Ce contents, and Figure 7 (b–d) are XRD patterns of the three different alloys, respectively. It can be seen that all three alloys contain an \( \alpha - Mg \) phase and \( \beta - Mg_{17}Al_{12} \) phase. Ce-containing alloys also contain an \( Al_4Ce \) phase, and when the Ce content increases, the phase content also increases. After adding Ce, the \( \beta \) phase diffraction peak intensity decreased, and \( Al_4Ce \) diffraction peak appeared. With the increasing Ce content, the \( Al_4Ce \) diffraction peak intensity increases.

3.2. Metallographic analysis

Figure 8(a–c) are the microstructural diagrams of as-cast alloy samples. Combining the phase diagrams of Mg-Al and Mg-Al-Zn alloys, it was speculated that the matrix structure \( \alpha - Mg \) solid solution is in the microstructure of the AZ91 magnesium alloy, and the coarse structure around the grain boundaries is \( \beta - Mg_{17}Al_{12} \) phase. There is also a small amount of continuous eutectic structure along the grain boundary as the \( \alpha - Mg \) and \( \beta - Mg_{17}Al_{12} \) mixed phase, and they are distributed in a semi-continuous network or block.

3.3. Analysis of the mechanical properties of the alloy

Table 3. Mechanical property data of AZ91-xCe alloys

| Alloy number | Ce content (%) | UTS (MPa) | YS (MPa) | EF (%) | HV     |
|-------------|----------------|-----------|----------|--------|--------|
| 1           | 0              | 130       | 90       | 1.56   | 58.8   |
| 2           | 0.3            | 145       | 98       | 1.66   | 64.6   |
| 3           | 0.5            | 168       | 115      | 1.98   | 66.3   |
| 4           | 0.7            | 138       | 120      | 1.78   | 62.6   |
| 5           | 1.0            | 145       | 109      | 1.88   | 56.6   |

Table 3 shows the tensile strength (UTS), yield strength (YS), and elongation to failure (EF) data of experimental alloys with different Ce contents.

![Microstructure of AZ91-xCe alloys ((a) x = 0; (b) x = 0.5; (c) x = 1.0)](image-url)
Figure 9 shows the hardness test results of alloys with different Ce contents. Compared to the hardness of AZ91, which is 58.8, the hardnesses of alloys with Ce contents of 0.3%, 0.5%, and 0.7% were increased to 64.6, 66.3 and 62.2 respectively. When the Ce content is 1.0%, the hardness of the alloy is lower than that of AZ91 alloy. It is speculated that the Ce content is too high and the internal rare earth phase is excessively concentrated.

4. Discussion

4.1. Alloy performance simulation calculation
When selecting component materials, the Young's modulus of elasticity is an important reference, and this parameter is often used in engineering technical design. As shown in Figure 10(a), the curves of different Ce content basically overlap, which shows that the Young’s moduli of alloys with different Ce contents are insignificant. It can be seen from Figure 10(b) that when the temperature is 30°C–450°C, the thermal conductivity of AZ91 alloy is stronger than that of Ce-containing alloy, but the difference is not large and the effect can be ignored. After the temperature exceeds 450°C, the thermal conductivity curves of several alloys with different compositions are approximately the same. Therefore, it is believed that the Ce content has little effect on the thermal conductivity of the alloy.
Figure 10 (c) shows the relationship of material density with respect to temperature. With increasing temperature, the density of the five different composition alloys all showed a decreasing trend. Due to the addition of Ce, the density of the alloy increases with increasing Ce content. The density of AZ91-1Ce alloy is the highest, and the density is greater than that of AZ91 alloy. Figure 10 (d) is the graph of Poisson's ratio versus temperature. Poisson's ratio is the absolute value of the ratio of the transverse and axial strains when the material is under unidirectional tension or compression. Poisson's ratio is also called the transverse deformation coefficient, which characterizes the elastic constant of the material when transversely deformed. It can be seen that with increasing temperature, the Poisson’s ratios of the five alloys with different contents all show an increasing trend, but the difference between them is not obvious. Figure 10 (e) is the curve of the enthalpy of the material with respect to temperature. It can be seen that the enthalpy shows an increasing trend with increasing temperature. However, the changes in enthalpy of several alloys with different Ce contents were negligible. It can be seen that Ce content has little effect on the performance of alloy enthalpy.

4.2. Effect of Ce content on the AZ91 alloy

When the alloy is solidified, the insoluble Ce accumulates at the solid-liquid interface, which reduces the diffusion of Mg to a certain extent. The added Ce reacts with Al to form an $\text{Al}_3\text{Ce}$ eutectic phase. This has a negative impact on the migration of grain boundaries and a certain effect on grain growth inhibition.

It can be seen from Figure 10 (b) that when 0.5% Ce is added, the as-cast structure of the AZ91 alloy is significantly refined. A large area of the eutectic structure begins to decompose, and the network of $\beta - Mg_7Al_12$ evolves into dispersed particles or bone shapes. New rare earth phases with needle-like arrangement are also found in the grain boundaries and within the grains, and the refinement effect is the most significant at this time. Observing Figure 10 (c), the rare earth content gradually increases, the dispersed $\beta$ phase gradually becomes coarser, and its size begins to increase while the distribution becomes uneven.

The main principle of using the intercepting method to count grains is to intercept the grains through a certain length of straight line to calculate the average grain size and use the Image J auxiliary software to measure and calculate the average grain size. Figure 11 shows the average grain size of alloys with different Ce contents. The average grain size of the AZ91 alloy is $125 \mu m$. After 0.3% Ce was added, the average grain size was reduced to $65 \mu m$; after 0.5% Ce was added, the average grain size was reduced to $37 \mu m$; when the addition amount was 0.7%, the grain size was $46 \mu m$; and when 1% Ce was added, the average grain size of the alloy was $54 \mu m$. When the Ce content was 0.5%, the grain size was the smallest, which was reduced by 70.4% compared with AZ91 alloy. Overall, after adding Ce, the average grain size was significantly reduced, which means that the rare earth element Ce has a significant effect on the grain refinement of the alloy.
The main mechanism of Ce refinement of the alloy structure is that the rare earth element Ce and Al element in the alloy can form a second phase with a relatively high melting point. During the solidification of the alloy, these newly produced rare earth phases will crystallize at the grain boundaries. The crystallization temperature gradually decreases, and the dispersed second phase can be used as the heterogeneous nucleation center of the matrix phase, or it can be pushed to the front of the interface to hinder the growth of the dendritic structure.

Since the crystal structure of the magnesium alloy is hexagonal close-packed, it contains less slip systems, so the grain size plays a decisive role in the influence of the strength of the magnesium alloy. According to previous analysis, with increasing Ce content, the grains of the alloy are refined, and a second phase containing rare earth is formed in the alloy structure, which allows the Mg-Al compound to be uniformly distributed on the matrix grain boundary while improving the alloy hardness.

Additionally, the formed Al-Ce rare earth phase will consume a portion of the Al element in the matrix, which causes the $\beta$ phase in the alloy structure to gradually change from a continuous network distribution along the grain boundary to a smaller island with a reduced number. This phenomenon also leads to increased hardness.

In summary, the addition of cerium can improve the mechanical strength and elongation of the alloy. Especially with 0.5% Ce loading, the optimization effect on the mechanical properties of the alloy is most obvious.

Through experimental analysis, the effects of rare earth cerium on the mechanical properties of AZ91 alloy were summarized as follows:

1. The addition of Ce significantly improves the microstructure of the alloy and reduces the average grain size inside the alloy. The hindrance of dislocation movement increases, which hinders the crack growth and plays an important role in improving the strength of the alloy. After the grain structure is refined, the number of grains around each grain increases, and the possibility of the deformation occurring inside the grains being coordinated to its surroundings is increased. This strengthening method is fine-grain strengthening.

2. There is a phase with lower thermal stability inside the AZ91 alloy. The addition of Ce forms dispersed $Al_4Ce$, a high melting temperature thermally stable phase, in the grain boundaries and grains, thereby reducing the number of $\beta - Mg_{17}Al_{12}$ phases. Therefore, it has a certain pinning effect on the movement of the surrounding grains at high temperatures, which also hinders the movement of dislocations at the grain boundaries at high temperatures, and has a better dispersion strengthening effect, that is, the method of precipitation strengthening.

3. The solid solubility of Ce in magnesium is only 0.09%, and a small part of Ce is solid-dissolved in the matrix structure, which makes the lattice distortion stress field distributed around the magnesium atoms. The interaction between the stress field and the dislocation stress field hinders the movement of grain boundary dislocations while increasing the strength of the alloy. This is a solid solution strengthening method.

The combined effects of fine-grain strengthening, precipitation strengthening, and solid solution strengthening mechanisms have improved the tensile strength and properties of the alloy to a certain extent. However, this improved performance is not linear with cerium loading. After the Ce content in the alloy exceeds a certain level, the rare earth phases are concentrated in the alloy. This also makes the rare earth compound phase structure coarse, where there may be a risk of stress concentration and a reduction in tensile properties. In addition, when the rare earth element content is too high, the dispersion strengthening effect of the thermally stable phase in the alloy is suppressed, and the mechanical properties of the alloy are reduced accordingly.

5. Conclusions

Alloys with different Ce contents were studied, the mechanical strength, elongation, and hardness of the alloy were tested, the microstructures were observed and the average grain size was obtained, and the following conclusions were obtained:

1. A small amount of Ce was added to the AZ91 as-cast alloy to form a thermally stable $Al_4Ce$
phase with a high melting point, the internal porosity of the alloy structure was reduced, the average grain size was reduced, and the grains were refined.

(2) The three strengthening mechanisms of internal fine-grain strengthening, precipitation strengthening, and solid solution strengthening work together to improve the mechanical properties of the alloy. When the loading of cerium was 0.5%, the tensile strength increased by 29.2%, the YS increased by 34.4%, and the comprehensive mechanical properties and microstructure were optimized.

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