

Two main and a new type rare earth elements in Mg alloys: A review

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Abstract. Magnesium (Mg) alloys stand for the lightest structure engineering materials. Moreover, the strengthening of Mg alloys in ductility, toughness and corrosion predominates their wide applications. With adding rare earth elements in Mg, the mechanical properties will be improved remarkably, especially their plasticity and strength. A brief overview of the addition of rare earth elements for Mg alloys is shown. The basic mechanisms of strengthening Mg alloys with rare earth elements are reviewed, including the solid solution strengthening, grain refinement and long period stacking ordered (LPSO) phase. Furthermore, the available rare earth elements are summarized by type, chemical or physical effects and other unique properties. Finally, some challenge problems that the research is facing and future expectations of rare-earth Mg alloys are stated and discussed.

1. Introduction

Magnesium (Mg) alloys are considered to be utilized in automobile, electronics and aerospace industry due to their high specific strength, casting formability, performance of resistance shielding, damping shock absorption and etc. However, in contrast to the traditional steel or aluminum materials, they have not been widely accepted by consumer. Their commercial products are mainly fabricated by die casting. Compared with cast products, the wrought Mg alloys only have a small market which the proportion is less than 5%, because of their low ductility or toughness and poor corrosion which will limit their wide applications in several fields [1]. So, it is extremely significant for researchers to improve the formation and corrosion resistance of Mg alloys.

The properties and applications of Mg alloy and pure Mg are perplexed by these two main problems above. It is necessary for researchers to find some effective methods to solve these problems. Usually, there are two kinds of methods: i) fabrication and processing; ii) alloying, which can achieve these goals. In the past centuries, researchers have investigated many different kinds of methods for fabrication and processing of Mg alloys, such as powder metallurgy [2], friction stir processing [3], equal channel angular pressing (ECAP) [4] and etc. Except of the traditional casting method, almost all the fabrication processing which mentioned above can refine the microstructure grain, and lead the Mg alloy to high ductility, elongation, yield strength in the Hull-Petch equation, even the superplasticity [5]. On the other hand, the common adding alloy elements are Zn, Zr, Al, Li, Ca, Ag, Mn, and rare-earth elements [6] and etc. Recently, a large number of researchers have investigated many different kinds of rare-earth elements and find out effects of these elements which can refine the crystal particles, enhance the creep and corrosion resistance at elevated temperature and improve the mechanical properties due to the presence of second phase in microstructure. Rare-earth elements are located at the third subgroup (IIIB) in the periodic table, and their chemical properties are similar because of the common structures of peripheral electrons, as well as the similar structures of secondary electrons. So,



the solubility of rare earth element in Mg matrix is higher than any other normal element, which can lead the formation of more second phases, and then the mechanical properties of Mg alloy can be improved by leaps and bounds. For instance, in Mg-Zn-Y-Zr system alloys with different processing methods, Bae et al. reported a maximum elongation of 780% in a hot rolled Mg-3.0Zn-0.5Y-1.5Zr (wt.%) alloy at 450°C and a strain rate of $5 \times 10^{-4} \text{ s}^{-1}$ [7]. Moreover, Tang et al. reported that an ECAP Mg-5.8Zn-1.0Y-0.48Zr alloy exhibited an elongation of 800% at 350°C and $1.7 \times 10^{-3} \text{ s}^{-1}$ [8]. Because of the presence of icosahedral quasi-crystal $\text{Mg}_3\text{Zn}_6\text{Y}$ (I phase) and $\text{Mg}_3\text{Zn}_3\text{Y}_2$ (W phase) which can result in refinement of grains, both of them have achieved the superplasticity on rare-earth Mg alloys [7]. Xu et al. produced Mg-8.2Gd-3.8Y-1.0Zn-0.4Zr alloy with ultra-high yield strength of 426 MPa and ultimate strength of 517 MPa by large-strain hot rolling and aging [9]. However, disadvantages of the rare-earth Mg alloys is that the high cost and natural resource scarcity of rare-earth elements, especially for heavy rare-earth elements, make their large-quantity usage (usually ~10 wt.%) unpractical in industry applications. In contrast, the advantage of high specific strength of Mg alloys compared with Al alloys gradually losses due to the increased density of the rare-earth Mg alloys [10]. In this regard, the developments of low-cost, rare-earth Mg alloys with high strength and ductility are strongly desired.

In this review, the strengthening effects of common rare-earth elements on Mg alloy were critically stated. Furthermore, the future and development of rare-earth Mg alloys was proposed.

2. Types and affections of rare-earth elements in magnesium alloys

2.1 Gadolinium

Gd is used to increase the elevated temperature strength of Mg-alloy and improve the microstructure of alloys. It is worth noting that Gd shows higher solubility in Mg compared with other rare earth elements. This can provide simultaneous solid solution hardening and precipitation strengthening, and the later could enhance thermal stability of the microstructure in Mg alloys.

According to the research of Du et al. [11], the α -Mg and Al_2Gd phase will be formed in AZ21-Gd alloy. With the addition of Gd increasing, the size and number of α -Mg phase will be decreased while the size and number of Al_2Gd phase will be increased. When the addition of Gd approaches to 3.5 wt.%, the number of intermediate phase will also be increased, especially around grain boundaries or grain boundaries. Also the elevated tensile strength and yield stress of the alloy increases with increasing addition of Gd. Then, Reba Mahmud et al. [12] investigated Mg-9Gd-4Y-0.4Zr alloy in the temperature range of 573-773K by shear punch testing which shows that m value, strain rate sensitivity index, increases with increasing temperature from 0.22 at 623K to 0.4 at 723K and then decreases to 0.32 with a further increase in temperature. And the lattice diffusion accommodated grain boundary sliding can be considered as the dominant deformation mechanism of the material in the superplastic region. In addition, M. Sarebanzadeh et al. [13] investigated Mg-3Gd-1Zn alloy processed by ECAP (equal-channel angular pressing) with SPT method, which demonstrated that the microstructure was refined with the average grain size of 1.7 μm and the Mg_5Gd and $\text{Mg}_3\text{Gd}_2\text{Zn}_3$ particles were detected which can act as grain growth inhibitors during superplastic deformation along with particle strengthening. And the microstructure is showed by Fig.1.

However, Yang et al. [14] pointed out that Gd acts as grain refinement strengthening and grain boundary strengthening, which improves tensile properties of AM50 Mg alloy. But, Gd improves the plastic deformation properties and reduces the toughness at the same time. AM50Gd1 Mg alloy is also quasi-cleavage fracture. So, it could draw a conclusion that Gd improves the tensile strength, but reduces the deformation capacity of AM50 Mg alloy.

Apart from improving the strength and ductility, some literatures point that the creep and corrosion resistance [15] of Mg alloy also can be increased remarkably with adding Gd.

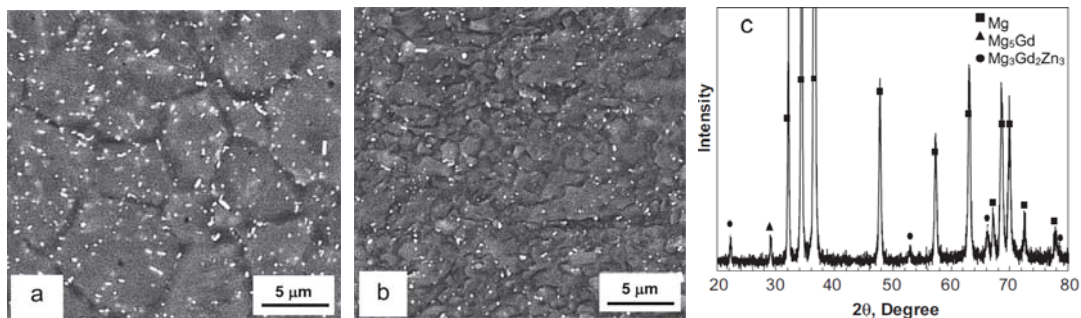
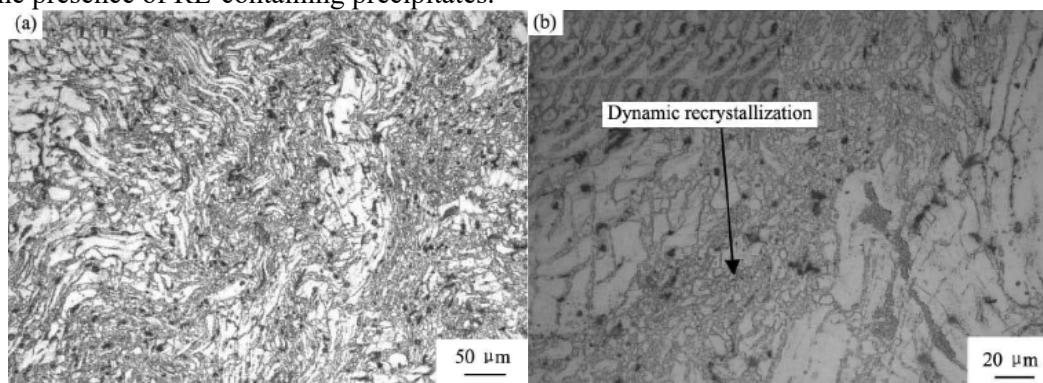


Fig. 1. SEM images of the material for (a) extruded and (b) ECAP conditions and (c) the corresponding XRD pattern indicated in the image [13]

2.2 Yttrium

According to the result of simulation, the lattice structure of Y is similar to that of Mg, which meets the similar dissolve mutually theory. So, the effect of Y is to improve elevated temperature plasticity and the creep resistance of Mg alloys. For ZK60 alloy, the addition of rare-earth element Yttrium (Y) into it can remarkably improve the mechanism properties at elevated temperature and ductility, because of the formation of ternary Mg-Zn-Y phase with high thermal stability [16]. Li et al. [17] investigated Mg-4Zn-1Y alloy for discovering the tensile properties and evolution of microstructure. Although it is not similar to that of Xie et al. [16], the tensile strength and elongation of as-cast alloy were 125.22MPa and 8.2% respectively and those of extruded alloy were 254.94 MPa and 17.9%, which means the tensile properties including strength and elasticity and plasticity were all improved greatly, which microstructure is showed in Fig.2 [17]. With addition of Y element, especially in the Mg-Zn-RE alloy as ZK60, it is significant to form two kinds of phase, *e.g.*, I-phase ($\text{Mg}_3\text{Zn}_6\text{Y}$) and W-phase ($\text{Mg}_3\text{Zn}_3\text{Y}$), and the eutectic temperature are 450°C and 510°C, respectively [18]. Rosalie et al. [19] suggested that Mg-Zn-Y alloy can be quasicrystal-strengthened by I-Phase which is icosahedral quasicrystal structure with high hardness, high strength and low surface energy. I-phase can refine the microstructure and increase elongation by dynamic recrystallization and the dissevered effect between matrix and I-Phases decreases as I-Phases are spheroidized through hot extrusion.

Recently, mixing Y and Gd into Mg alloy has been the mainstream measure of improving the mechanism properties, such as Mg-10Gd-3Y-0.5Zr alloy [20] with maximum strain value of 18% while that of traditional Mg alloy is ~12.3%. It can be explained that the reciprocal action of Y and Gd affect significantly the deformation behavior of the extruded Mg alloys by predominantly suppressing the twinning due to the finer grain size, the relatively more random crystallographic texture, and the presence of RE-containing precipitates.



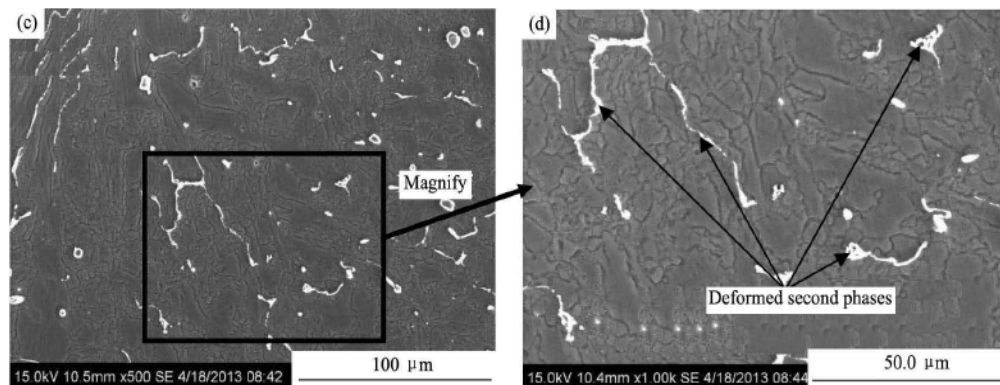


Fig. 2. OM (a, b) and SEM (c, d) of microstructure of cross section of extruded Mg-4Zn-1Y alloy[17]

2.3 Dysprosium

Up to now, the addition of Dysprosium (Dy) is reported few. But, its effects are also significant and have special properties in common, because of the similar size between Dy and Y in atom order of magnitudes. Both of them will have the similar effecting mechanism. The group of Yang et al. [21] have investigated that the tensile strength of the alloy with the addition of Y decreased while increased in the alloys with the single addition of Dy. Compound add two RE elements made the increasing of the tensile strength, yield strength and elongation of alloy, which increase 5.3%, 17.1% and 177.4% compared ZK60 alloy without RE element. And Guangli Bi et al. [22] studied the deformation of an extruded Mg-2Dy-0.5Zn (at%) alloy under uniaxial tensile test at 300°C with $3 \times 10^{-5} \sim 3 \times 10^{-1} \text{ s}^{-1}$, which exhibited a quasi-superplastic deformation with an elongation of 105% at 300 °C with $3 \times 10^{-5} \text{ s}^{-1}$ due to the formation of the LPSO phase which can improve the deformation and dislocation of the grain boundary slip.

3. Summary and future perspectives

Except of the rare earth elements above, there are also many other kinds of alloying elements, such as neodymium (Nd), promethium (Pm), ytterbium (Yb) and etc., which are also investigated in other kinds of Mg alloys [23]. Three difficulties towards application are still remaining to be solved. Firstly, the high cost of the rare earth elements, like Dy, Pm and Yb, which can only be used in research and not be utilized in engineering. Relatively low-cost rare element, *e.g.*, scandium (Sc), needs to be developed with the similar effect for replacement of the high-cost ones needs to be developed with the similar effect for replacement of the high-cost ones [24]. Secondly, in order to realize some specific properties, the content of rare earth element needs to be paid attention for mass producing. Thus, the main target is to improve the mechanical properties of Mg alloys with little content ($\sim 1 \text{ wt.}\%$) of rare earth element.

It is necessary to search for the alloying mechanism between rare earth element and Mg alloy in order to develop the most optimal ratio of alloy in Mg alloys. Researchers have also turned to investigate some effective processing method, such as equal-channel angular pressing (ECAP), rapidly solidified powder metallurgy (RSPM), hydrostatic extrusion (HE), friction stir processing (FSP), severe torsion straining (STS) and etc. Each of them has its own exotic point which can be utilized in different conditions. In consequence, there are three main problems waiting to be improved: i) high cost of elements; ii) processing method of Mg-RE alloy and iii) changing the role of rare element in Mg.

Recently, with the development rare earth elements adding Mg alloy, they have been widely accepted by more and more people, and their application will be expanded. The high strength, heat resistant and corrosion resistant of rare earth Mg alloys will not only increase the applications in recent automobile, communications, electron industry and etc. but also can promote and exploit new fields for rare earth Mg alloys. It is significant for researchers to complete the existing rare earth Mg alloys

which mentioned above. For Mg alloys and rare earth Mg alloys, it will be enormously facilitate the development of these materials.

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