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Alloying Elements of Magnesium Alloys: A Literature Review

Nouha Loukil

Abstract

Magnesium alloys are the lightest structural metal. The lightness is the main reason for the interest for Mg in various industrial and clinical applications, in which lightweight structures are in high demand. Recent research and developments on magnesium Mg alloys are reviewed. A particular attention is focused on binary and ternary Mg alloys consisting mainly of Al, Zn, Mn, Ca and rare earth (RE) elements. The effects of different alloying elements on the microstructure, the mechanical and the corrosion properties of Mg alloys are described. Alloying induces modifications of the microstructural characteristics leading to strengthening mechanisms, improving then the ductility and the mechanical properties of pure Mg.

Keywords: magnesium alloy, alloying element, strengthening, mechanical properties

1. Introduction

Magnesium alloys are the lightest structural metal view to the very low density of 1.74 g/cm^3 and designed as Green Structure Metal [1]. Taking into account its very negative potential (-2.34 V), Mg is a reducing agent and is able to combine with oxygen, sulfur and halogen compounds. This reducing power finds its interest in the production of sacrificial anodes that prevents corrosion. Meanwhile, this reducing agent constitutes a major barrier to the use of Mg as a structural material. In addition to this undesirable property, poor wear resistance of pure Mg hinders its use for different applications.

That's why, pure Mg is combined with other metal elements to improve their properties even at high temperatures, namely manganese, aluminum, zinc, silicon, copper, zirconium and rare-earth metals. Mg alloys, non-ferrous material, are characterized with low density, high ductility, strength and acceptable corrosion resistance.

The lightness is the main reason for the interest in the civil and military transport sector for Mg, in which lightweight structures are required. When compared with metallic structure namely, aluminum Al and iron Fe, the density of Mg is much lower than those of these metals [2]. In reverse, Mg exhibits similar specific mechanical properties, mainly excellent castability and machinability compared to a metal which is durable [3, 4]. When used as alloying element in metallic material, Mg enhances the mechanical properties of Aluminum and the malleability of the iron.

Compared to that of metallic structures, Mg alloys show higher weight/strength ratio. They possess an elastic modulus of 45 GPa and tensile strength of 160–365 MPa [5]. Based on the above reasons, Mg alloys have been widely used in the aerospace industry, mechanic manufacture and automotive industry. Indeed, the replacement

in the three major components (body, power train and chassis) of a vehicle by Mg alloys lead to weight reduction of 20–70% [6].

Mg alloys provides an excellent property of damping vibration and heat dissipation property which is an important factor for different automobile and aerospace industries. As well known, the vibration is a kind of loss and affects the efficiency of the vehicle.

Special attention is paid to Mg-based materials for clinical applications (orthopedic applications, critical wounds ...) owing to its density that is very close to that of human bone (1.75 g/cm^3), higher specific strength and low elastic modulus. Furthermore, Mg is biocompatible as it is essential for several biological reactions and as a co-factor for enzymes.

Quite opposite to the conventionally used metallic materials such as stainless steel and Ti alloys that exhibit stress shielding and metal ion releases, Mg is biodegradable. That is to say, Mg entirely degrades in the human body preventing then the need for second surgical procedure to remove the implants material [7]. This has received a widespread attention from the scientific and medical community [8]. However, the biodegradability of implanted Mg alloys is hindered by an accelerated degradation rate in chloride-abundant environments like human body [9]. Generally, the period of bone remodeling is about 3 to 6 months. To be wary of this suggestion, the rate of degradation must be controlled by suitable surface modification in order to enhance the duration of effectiveness of the implantable material.

Researchers have been working on synthesis and characterization of Mg-based biomaterials with a variety of composition in order to control the degradation rate of Mg that leads to a loss of mechanical properties and contamination in the body. The alloying elements affect the characteristics and performance of Mg alloys.

This paper is a comprehensive review that compiles the recent literature on the important alloying elements and their impacts on the properties of Mg alloys.

2. Designation and types of Mg alloys

According to the addition elements, Mg alloys are designated in different ways. Alloys are designated by letters corresponding to their main addition elements followed respectively by the percentage of each element. The American Society for Testing and Materials ASTM developed a method to designate Mg alloys which are named by their main alloying elements. The first two letters indicate the alloying elements used in the greatest quantity. One or two letters are followed by numbers which represent the percentage by weight of the elements rounded to the nearest whole number. The ASTM code for alloying elements is as follows, aluminum is designated by the letter A, zinc by the letter Z, manganese by the letter M, silicon by the letter S, yttrium by the letter W, zirconium by the letter K, silver by the letter Q, thorium by the letter H. The most common families are: AZ (example AZ31), AM (example AM60), AS (example AS41), WE (example WE43) and AE (example AE42). For instance, AZ91 Mg alloy contains 9% of Al and 1% of Zn and the rest by pure Mg.

Based on the process of operation, Mg alloys can be categorized into two groups: cast alloys and wrought alloys.

2.1 Cast Mg alloys

Cast alloys are basically made by pouring the molten liquid metal into a mold, within which it solidifies into the required shape. Depending on the chemical composition, there are two groups of cast Mg alloys [10].

The first group includes Mg-Al alloys in which Al amount does not exceed 10% with an addition of Zn and Mn. These alloys are characterized by a low cost of manufacture. Indeed, this criterion is recommended for the industrialization and the commercialization of high performance of Mg alloys. The most commonly used is AM50 alloy mainly for die casting, and AZ91 for sand and die casting method. Meanwhile, their disadvantage is a low operating temperature-below 120 °C. The aging hardenability of these Mg-Al based alloys, such as AM60 alloy, is relatively poor. That's why, these alloys are prepared by high pressure die casting with relatively high cooling rate. The strength, the castability, the workability, the corrosion resistance and the weldability of these commercial AZ91 and AM60 alloys are not satisfying, but can be improved by introducing alloying elements. For instance, AZ91 alloy's strength is relatively high; however, its ductility is not so good due to the high Al content. Whereas, AM60 alloy has high ductility, but its strength is relatively low. Various alloying elements such as Ce, Nd, Y, Si, Ca, Ti, B, Sr., Sb, Bi, Pr have been used to enhance the operating temperature and the mechanical properties of modified AZ91 alloy [11]. Among these alloying elements Ce, Nd, Y, Bi and Sb are effective to improve the tensile properties of AZ91 alloy. For the modified AM60 alloys, various alloying elements, Ti, Nd, Sn and Ce elements are relatively effective to further enhance the mechanical properties of AM60 alloy. For instance, the tensile strength of 280 MPa and elongation of 11% could be obtained [12].

The second group of alloys is free from Al, but containing mostly Zn, rhenium RE and Y with an addition of Zr. Such alloys are recommended for high temperature until 250 °C, but the cost of their production increases due to the cost of alloy additions. The common commercial WE43 and WE54 alloys can be cast by sand casting process with a low cooling rate. Accordingly, the mechanical properties are further improved by solution and aging treatment. These alloys are largely used as sand castings. The strength of WE54 is basically attained via precipitation strengthening. Depending on the aging temperature and time, the precipitating sequence in WE alloys has been reported to involve the formation of phases β'' , β' , and β . The equilibrium β phase is isomorphic to the Mg_5Gd phase and is identified as a $Mg_{14}Nd_2Y$ phase [13].

The mechanical properties of the cast alloys are determined on poured test bars according to standard ASTM procedures.

2.2 Wrought alloys

Wrought alloys are destined to mechanical working, such as forging, extrusion and rolling operations to shaping. Al, Mn and Zn are also the main alloying elements. Wrought alloys of Mg are sorted into heat treatable and non-heat treatable alloys. The use of wrought Mg alloys is limited less than 10%. This is due to the poor cold workability of the hexagonal close packed (HCP) crystal structure of Mg, generating low formability at room temperature. New Mg alloys have been developed to enhance their strength by modifying the existing alloy [14] or by grain refinement. It was also reported that advanced processing, such as hot extrusion, rolling, forging are able to refine the microstructure and improve the mechanical properties of Mg alloys. Many commercial wrought Mg alloys have been developed, such as AZ system, ZK system... Compared with wrought Mg alloys, casting Mg alloys have economical advantages due to their shorter processing cycle. Therefore, casting Mg alloys obtain more incremental use of almost 90% of total application products.

Based on literature data, new Mg alloys with high strength can be developed when modified the present commercial cast and wrought alloys [15] by strengthening mechanisms: alloying, grain refinement, precipitation and texture

strengthening effect. To overcome the weakness of pure Mg, different elements have to be alloying with pure Mg to obtain Mg alloys with desired mechanical properties. Mg alloys shows an excellent specific strength and stiffness with dimensional stability due to its hexagonal crystal structure and to its atomic size (about 320 nm). Much progress has been achieved in strengthening of Mg alloys through solid solution strengthening using different alloying elements. The effects of such elements on the microstructure and mechanical properties are described.

2.2.1 Aluminum

Mg alloys including Al are called Mg-Al binary alloys. Al is the most widely used alloying element of Mg alloys as structural materials [16]. Indeed, Al improves the tensile strength, the ductility and the castability of Mg alloys at temperature not exceeding 120 °C [17]. If the amount of Al varies from 1 to 9%, the grains size of Mg-Al alloys decreases, increasing accordingly the micro-hardness [18]. Zheng et al. [18] demonstrated that the average grain size of Mg-Al alloy falls from 3097 μm to 111 μm if Al amount increases from 1% to 9%. **Figure 1** shows the influence of the addition of Al on the size of α -Mg dendrites for Mg-Al binary alloys. It can be seen that with 1% of Al to pure the structure of Mg, α -Mg dendrites are transformed from columnar to equiaxial (**Figure 1**). With higher Al amount, α -Mg dendrites become more developed and the dendrite arms become finer [18]. According to Mg-Al binary alloy phase diagram [19], α -Mg dendrite firstly precipitates during the solidification process, and then expels the redundant Al solute. In fact, this precipitation releases latent heat, causing an increase of the melt temperature ahead of the solidification interface. It decreases the degree of super-cooling, and suppresses the growth of α -Mg dendrites, leading to the grain refinement [18]. When Al exceeds 2%, an eutectic microstructure involving α -Mg and $\text{Mg}_{17}\text{Al}_{12}$ will be formed along the grain boundaries. The $\text{Mg}_{17}\text{Al}_{12}$ phase improves the corrosion potential and reduces the corrosion rate [20]. However, the $\text{Mg}_{17}\text{Al}_{12}$ phase has a relatively low melting temperature (437 °C), giving arise to the microstructure instability over 120 °C. This occurrence related to the grain boundary sliding explains the degradation of the mechanical properties of Mg-Al alloys at elevated temperatures [21]. Moreover, the micro-hardness of the α -Mg matrix increases from 36.3 HV to 50.1 HV. This

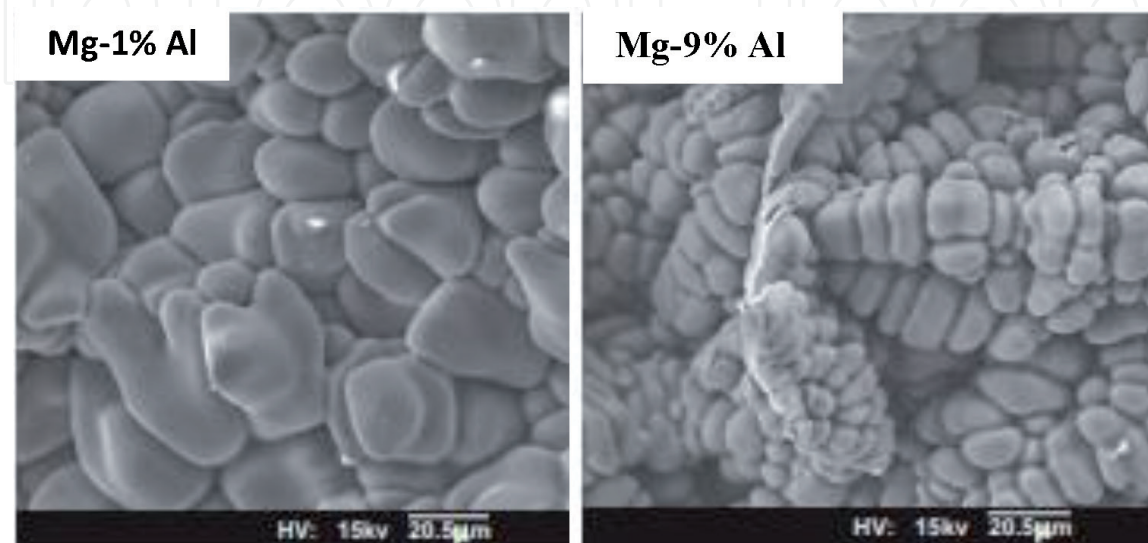


Figure 1. Size and morphology of α -Mg dendrites of Mg-Al binary alloys with various Al amount [18].

increase is recognized to solution strengthening caused by Al solubilized in the α -Mg matrix.

The most popular alloys are Mg-Al-Zn (AZ) and Mg-Al-Mn (AM) as Zn improves the ambient temperature mechanical properties and Mn enhances the creep resistance of alloys [22].

2.2.2 Zinc Zn

Zinc is added in Mg alloys to enhance the tensile properties. Zinc decreases the weldability property [23]. Above 1% of Zn, it provides strengthening to Mg by solid solution [24]. If zinc is added in higher amount, the Mg alloy presents hot cracking and lower ductility [23]. In addition, micro porosity of sand casted Mg alloys is observed with an Al amount ranging from 2% to 10%. The dissolution of Zn in Mg diminishes its reducing power, improving then its oxidation resistance [25]. The corrosion rate of Mg-Zn alloys decreases with increasing Zn in Mg matrix. For instance, the corrosion rate of Mg-3%Zn alloy is 34.6% lower than that of pure Mg compact. Zhang et al. [26] reported that 6% of Zn diminishes the corrosion rate of the Mg alloy for implant applications.

The micro structural analysis indicates smaller grain size at higher Zn content. The reason for the grain sizes refinement is recognized to close-packed hexagonal structure of both Mg and Zn metals. The diffusion rate of Zn atoms in Mg matrix is fast, favoring an easier diffusion into Mg matrix and forming Mg solid solution or intermetallic compounds. **Figure 2** shows surface scanning micrographs of Mg-Zn alloys with various Zn content. The phases present in Mg-Zn alloys depend on the Zn amount. **Figure 2** shows some white phase along the Mg grain boundary. This white phase increases with higher Zn content, hindering both the movement of the grain boundary and the grain growth [27]. For instance, Mg-3%Zn alloy is mainly composed of α -Mg phase, whereas Mg-4%Zn alloy is composed of α -Mg and MgZn₂ phases [27]. The micro-hardness for different Mg-Zn alloys continuously increases with increasing Zn content. For illustration, the micro-hardness HV of Mg-3%Zn alloy is about 45% higher than those of pure Mg samples.

Mg-Zn based alloys are the most popular wrought Mg alloys with good room temperature strength and ductility. Recent researches attempt to develop new type wrought Mg-Zn alloys using the addition of alloying elements including RE (rare earth), non-toxic Ca, Sn and Mn to optimize the properties of Mg-Zn alloys at room and high temperatures. Mg-Zn-Zr (ZK) is the strongest system owing to good strength and elongation at room temperature.

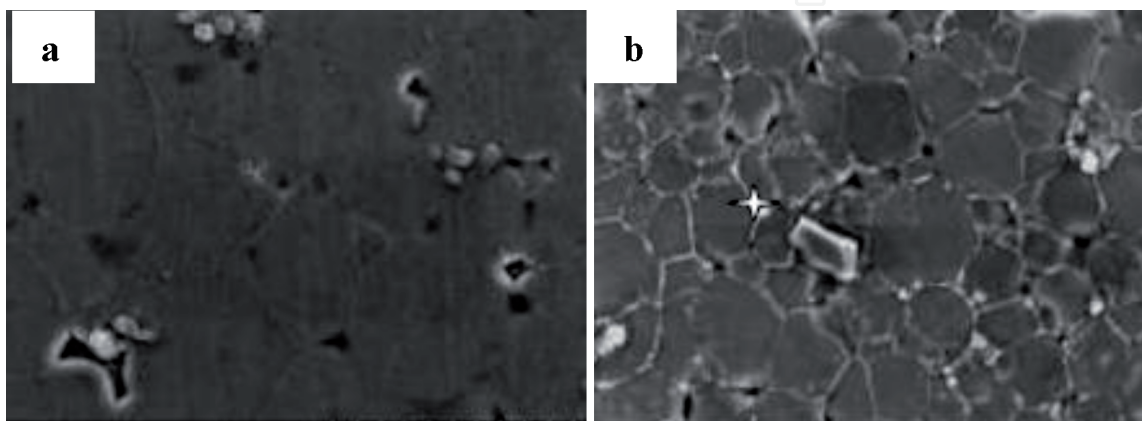


Figure 2.
SEM images of Mg-Zn alloys with different Zn contents: (a) 1% Zn and (b) 4% Zn [27].

The use of Mg-Zn alloys in medical applications as bio degradable materials is one of the research areas [28]. It is well known that the adding element Zn is one of the indispensable trace elements in the human body that promotes the growth, stimulates healing and participates in enzyme synthesis.

2.2.3 Manganese

The alloying element Mn improves the corrosion resistance of Mg alloy and limits the presence of harmful cathodic impurities such as Fe, Ni by the formations of intermetallic compound As matter of fact, such impurities lead to galvanizing oxidation of Mg [29]. Mn combines with impurities in order to moderate the corrosion of Mg-Al alloys. In the presence of Al and Fe, adding Mn produces an intermetallic phase $Al_8(Mn,Fe)_5$ that moderate the corrosion rate caused by Fe [30]. Until now, the exact Mn content addition required to counter-act the detrimental effect of the Fe impurity are still unknown.

With Al, the limit of solubility of Mn in the solid solution of Mg decreases, the strengthening by solid solution induced by Mn remains limited. That's why, the addition of Mn does not improve the mechanical properties of Mg. When investigated the effect of adding Mn into Mg-Gd alloys, Zhao et al. [31] demonstrated that the strength of alloys gradually increases while the ductility deteriorates. The main reasons are related to the combination of fine-grained strengthening, precipitation strengthening and texture strengthening [31]. In this regard, Cho et al. [32] stated that Mn refines grains of Mg-4Zn-0.5Ca alloy. This occurrence is due to the solute at the S/L interface aggregates in presence of Mn element, resulting different degrees of structural overcooling. Based on the biosafety to the human body, Mn can be accepted by the human body [32].

2.2.4 Ca

Incorporating Ca in Mg alloys can improve the mechanical properties and the corrosion behavior of Mg-Ca alloys. Ca is considered as an alloying element to develop Mg alloys for biomedical applications owing to their good biocompatibility.

As well known, Ca accelerates the bone growth. Moreover, cytocompatibility evaluation results indicated that Mg-1%Ca alloy induces no toxicity to human cells. In this regard, Li et al. [33] investigated the biodegradability within bone of Mg-Ca alloys with various Ca amounts ranging from from 1 to 20%. It was reported that 20% of Ca content makes Mg alloy very brittle.

Mg-Ca alloys with 0.6–1% Ca were reported to exhibit good mechanical properties and corrosion resistance [34]. The elongation of Mg-Ca alloy samples decreases with rising Ca content.

Previous studies suggested that Mg-Zn-Ca alloy system is a promising candidate for biodegradable implants in biomedical applications. With the increase of Ca content, the yield strength of Mg-Zn-Ca alloy increases. The addition of Ca to Mg-6%Zn alloy inhibits dynamic recrystallization and grain growth. Microstructural results indicate that Mg-Zn-Ca alloys consist of α -Mg matrix and $Ca_2Mg_6Zn_3/Mg_2Ca$ intermetallic phase mainly distributed along grain boundary [35].

High Ca content improves mechanical properties, while it is detrimental to corrosion resistance due to the micro-galvanic corrosion acceleration [36]. Literature data revealed that Mg-5%Zn-1%Ca exhibits excellent corrosion resistance and good biocompatibility.

2.2.5 Yttrium Y

Generally, the addition of Yttrium (Y) aims to improve elevated temperature plasticity and the creep resistance of Mg alloys. Wu et al. [37] studied the mechanical properties of pure Mg and binary Mg-Y alloys. They demonstrated that the elongation is proportional with the Y content, but the strength decreases. Adding Yttrium to Mg-Zn alloys is effective to weaken and change the basal texture of wrought Mg alloys [38].

When added to the cast alloy ZK60, the mechanical properties and ductility are enhanced at elevated temperature. This is ascribed to the formation of ternary Mg-Zn-Y phase with high thermal stability [39]. Meanwhile, alloys containing yttrium are expensive.

2.2.6 Rare earths RE elements

The rare Earths elements are common incorporating elements in Mg alloys. A large number of rare-earth elements have been investigated and proven to successfully refine the crystals and to enhance the creep and the corrosion resistance at elevated temperatures required for automobile engineering. Due to their high solubility in Mg, RE elements strengthen Mg alloys either by solid solution strengthening or precipitation hardening mechanisms [36]. For instance, the addition of RE elements to Mg-Al alloys accelerate the formation of the thermally stable $(\text{Mg,Al})_x\text{RE}_y$ phases to improve the high temperature mechanical properties of wrought Mg alloys.

Depending on the chemical composition, various amounts of precipitates can be observed. **Figure 3** exhibits small precipitates containing Mg, Zn and O in Mg-1.5Zn (**Figure 3a**), while precipitates in the RE-containing alloys consist of Mg, Zn and RE elements [27]. The amount of precipitates of Mg-1.5Zn-0.2Gd alloys are more than Mg-1.5Zn alloy, leading to smaller grain size of this alloy. Compared with other rare earth elements, Gd shows higher solubility in Mg, allowing simultaneous solid solution hardening and precipitation strengthening, enhancing then the thermal stability of the microstructure in Mg alloys [27]. Yang et al. [39] pointed out that Gd acts as grain refinement and grain boundary strengthening. In this regard, Liu et al. [40] reported that Mg-1.5Zn-0.2Gd alloy exhibits higher plasticity with the elongation of 27%. Meanwhile, Gd simultaneously reduces the toughness [36]. These Mg alloy systems containing large amounts of rare-earth for solid solution strengthening result high costs for many practical applications.

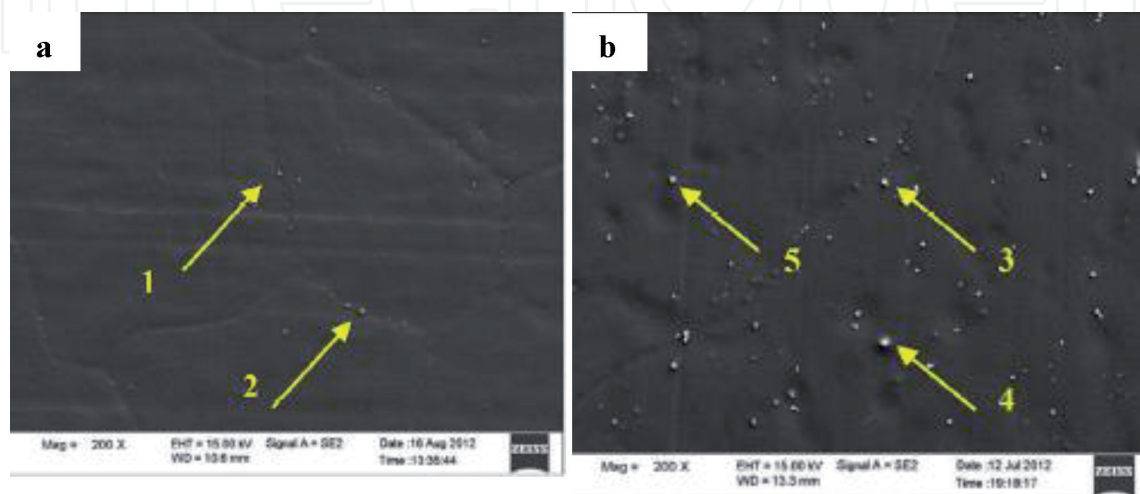


Figure 3. Microstructural (SEM) of Precipitates in Mg alloy (a) Mg-1.5%Zn; (b) Mg-1.5%Zn-0.2%Gd [27].

3. Conclusion

The attractive properties of Mg alloys include light weight, high specific strength, excellent castability and machinability However, these alloys have limited formability, limiting their industrial application. Strengthening of Mg alloys via the introduction of solid solution atoms and grain refinement additives are effective approaches. Much progress has been achieved in the development of high strength Mg alloys through solid solution strengthening using various types of solute atoms. Researchers incorporated various alloying elements such as Al, Zn, Ca, Mn and RE elements in Mg matrix. The chemical composition of Mg alloys affects the microstructure and then improves the mechanical properties and corrosion resistance.

The most commercial are the casting magnesium alloys such as AZ91, AM60 and WE43 due to their low cost. Meanwhile, the Mg alloy systems containing rare-earth and noble metal elements for solid solution strengthening result high costs. The heat treatment and the grain refinement via severe plastic deformation methods represent new approach to further strengthening of Mg alloys.

Conflict of interest

The authors declare no conflict of interest.

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