Research Progress of Heat Resistant Magnesium Alloys

Xiaomin Wang\textsuperscript{1*}, Yang Su\textsuperscript{1}, Lili Guo\textsuperscript{1}, Yan Liu\textsuperscript{1}, Honggang Li\textsuperscript{2} and Hailin Ren\textsuperscript{2}

\textsuperscript{1}Liaoning Key Laboratory of Chemical Additive Synthesis and Separation, School of Materials Science and Engineering, Yingkou Institute of Technology, Yingkou, 115014, China
\textsuperscript{2}Department of Mechanical and Power Engineering, Yingkou Institute of Technology, Yingkou, 115014, China
*Corresponding author email: ty.com.cn@126.com

Abstract. Magnesium alloy has extremely excellent properties and is known as "21st Century Green Engineering Material". This article mainly introduces the influence of the heat resistance and comprehensive performance of the three series of Mg-Al, Mg-Zn and Mg-RE heat-resistant magnesium alloys after adding rare earth elements, alkali metal elements and other elements. Three development directions of improving the heat resistance of magnesium alloys are prospected. These are: 1. Using cheap alloy elements (such as Ca, Si, etc.) to replace rare earth elements of the heat-resistant magnesium alloy, 2. Titanium element is added to improve heat-resistant magnesium alloy’s mechanical properties and its strength, 3. The new casting process and processing technology are used to improve the heat-resistant magnesium alloy’s properties. This article aims to provide technical reference for the development of my country's magnesium alloy industry.

1. Introduction
Magnesium and its alloy are the lightest structural metal material used in industry today, which is known as "green metal of the 21st century". The alloy plate has broad development prospects in various fields such as automotive, electronics and medical products, and has attracted wide attention and attention from scholars. It has gradually become an important material selection for replacing aluminum alloy, steel and engineering plastics [1]. In recent years, people's environmental awareness and energy conservation awareness have improved, and the application of magnesium alloy in the automotive industry and the electronics industry has also developed rapidly. Magnesium alloy is a biodegradable material, but due to the characteristics of excessive degradation speed and uneven corrosion, the hardness is relatively difficult to process, which greatly restricts the application of the alloy. Thus, magnesium alloys are limited to a small number of structural components of vehicles and transportation vehicles. How to improve the heat resistance of magnesium alloy has become a hot topic of scholars at home and abroad. At present, different thermal resistance magnesium alloy material is obtained by adjusting the alloy element proportion and combining with advanced forming technology [2].

This paper introduces the influence of Mg-Al heat resistant alloy, Mg-Zn heat resistant alloy, Mg-RE heat resistant alloy and other elements on these three heat resistant alloys [3].

2. Mg-Al Based Heat-Resistant Magnesium Alloys
Mg-Al based heat-resistant magnesium alloy is divided into two categories: one is a modified magnesium alloy based on Mg-Al-Zn in AZ system, usually calcium, antimony, silicon, barium, rare
earth elements are added to change the structure of the alloy or form a stable second phase at high temperature to improve heat resistance; the other is based on Mg-Al alloy, with calcium, silicon, such as Mg-Al-Si, Mg-Al-Ca and Mg-Al-RE alloy [4].

3. Modified AZ-based Magnesium Alloys
Mg-Al-Zn alloy mainly improves its heat resistance by controlling the content of adding zinc and aluminum elements and adding a very small amount of Bi, Si, Ca, RE. The impact on alloy properties includes the following aspects [5-7].

1)Bi: can refine the grains by adding Bi elements to produce a hexagonal stable Mg3Bi2 precipitate phase in the magnesium matrix, which enhances the comprehensive performance relative to the alloy. Bi element can effectively prevent the precipitation of β phase and improve the performance of heat-resistant magnesium alloy.

2)Si: Si element is added to the AZ-series magnesium alloy, Mg2Si phase is formed in the alloy which can improve the heat-resistance of the AZ magnesium alloy, mainly due to its high elastic modulus, close density and matrix, low expansion coefficient and high melting point.

3)Ca: Ca has a refinement effect on the β phase and branching crystal, increasing the content of Ca elements in the alloy, will produce a thermal stable Al2Ca phase and reduce the Mg17(Al, Sb)12 phase content, and enhance the high temperature of the alloy.

4)RE: addition of rare earth elements can reduce the Mg17Al12 precipitation phase content to refine its microtissue, while improving the high temperature tensile ability and creep of the Al11RE3 phase, and have little effect on the room temperature tensile strength of the alloy.

4. Mg-Al-Si Based Heat-Resistant Magnesium Alloys
Mg-Al-Si based heat-resistant magnesium alloy has excellent high-temperature performance and low-cost characteristics, and is one of the most promising alloys in high-temperature anti-creep magnesium alloy. Adding suitable Mg2Si elements to the alloy for stable phase can improve its high temperature creep resistance. The phase is characterized by high melting point, high elastic modulus, close density and matrix, and low coefficient of expansion, which ensures stability at 300°C. Nowadays, the composition design and microtissue control of the system of alloy have been widely concerned by scholars at home and abroad. The most typical research results are the AS21 and AS41 alloys developed by Volkswagen enterprises. AS21 alloy aluminum content, resulting in less β phase, strong high temperature creep resistance, but poor room temperature. AS41 alloys have better tensile and yield strength and toughness and higher high temperature creep compared to AZ91 and AM60 alloys. Today, the alloy is used in the automobile engine crankcase widely, clutch piston and other [8].

Mg-Al-Si series high-temperature creep resistant magnesium alloy has broad development prospects and has many substantial studies at home and abroad, but has defects in comprehensive mechanical properties and casting properties. The metamorphism of Chinese Mg2Si phase by the solid reinforcement, micro alloy, and electromagnetic mixing and silicon addition remains to be considered. It is promising to control the optimization process of Mg2Si phase. At the same time, promoting the next development of the system of alloy in the automobile field is the main research content in the future [9].

5. Mg-Al-Ca based Heat-Resistant Magnesium Alloys
In the 1960s, the Mg-Al alloy improved its heat resistance by adding an amount of Ca elements. In recent years, foreign scholars have developed AX51 magnesium alloy with Al3Ca as the strengthened phase, whose corrosion resistance and creep strength are similar to AZ91D and AE42 alloys, but it is prone to thermal cracking and adhesive mold during casting. It was found that casting defects, creep strength and corrosion resistance were improved when calcium reached 2% or an amount of Sr was added [10].

In order to reduce costs, rare earth elements, such as calcium, are replaced with low price elements, so the new Mg-Al-Ca-RE heat-resistant magnesium alloy was emerged. The products are mainly composed of MR1153 alloy (developed by Volkswagen) and ACM522 alloy (developed in Japan).
The test showed that the MRI153 alloy can long-term operate in 150°C and 50~80MPa environments without changing the design conditions and casting conditions in the production of original automotive driving parts. The alloy performs better than AE42, AS21 and AZ91D under the same conditions, and can be used to prepare the original parts of automobile oil chassis and gearbox housing. Mg-Ca, Al-Ca, Al-Ce equivalent of alloys can enhance heat resistance and creep resistance of ACM522 alloy. At 150°C, 0.1% and A384 creep strength of 100 MPa, is 9 times of AZ91D and about 1.67 times of AE42; high fatigue strength and corrosion resistance, but high cost, low impact strength and poor ductility. The addition of 2% Ca elements causes thermal cracking, as these defects greatly reduce the application width of the alloy [11-12].

Fig. 1[13] is the change in microtissue of alloy of cast alloy Mg-Al-Ca-RE heat resistant magnesium alloy in Ca element content from 1%~5% (a~e). When calcium content is 1%, the tissue is mainly uneven large Mg17Al12 phase and intermittent mesh Al2Ca phase in Figure 1 (a); 2%, the tissue is mainly gradually continuous Al2Ca phase in Figure 1 (b); after 1%, the large phase area gradually continuous, only partial intermittent in Figure 1 (c); after 4%, the precipitate phase completely changes to grid continuous tissue in Figure 1 (d); finally 5% calcium content, the phase presents a sheet structure, and some stable skeleton in Figure 1 (e). Specific microstructure is as shown.

**Figure 1. Microstructure of Mg-Al-xCa-RE (x=1,2,3,4,5) alloy**

6. **Mg-Al-RE based Heat-Resistant Magnesium Alloys**
   At the end of the 20th century, to increase the creep properties of the Mg-Al heat-resistant magnesium alloy, a 1% mixture of rare earth was generally added and optimal when the content of Al was lower than 4%. Al and rare earth elements in the alloy form Al-RE compounds with high thermal stability, reducing the synthesis of the β phase, but due to the pinning of the compound in the crystal boundary causes slower diffusion and improved heat resistance. The AE series of alloys developed AE42 have the best heat resistance, operate in high temperatures and get [14] in the automotive industry. Slow cooling causes a thick compound to only die cast when casting. Rare earth consumption is too large, high cost, low content of Al elements, and rare earth elements will also consume Al elements, resulting in poor alloy mobility and poor casting performance of [15].

7. **Mg-Zn based Heat-Resistant Magnesium Alloys**
   Mg-Cu-Zn alloy has good high temperature performance and is widely used in the automotive parts manufacturing industry. Through the study, when the Zn element is less than 4.5%, adding over 0.5% of the Ca elements can improve creep resistance and high temperature stability within 167 °C. Park et al. found that the MCZZ alloy with Zr or Ca elements had poor heat resistance than MCZC.
The compounds are Mg-Co-Zn and Mg-Ca phases. After aging treatment at 150°C for 1h, many fine Mg-Zn-Co-Ca quaternary precipitates are produced, which can realize precipitation strengthening [16-17]. By controlling the ratio of Zn to Al, AZ magnesium alloys are added Zn to form ZA alloys, such as ZA104, ZA124 and ZA144. The Mg32(Al,Zn)49 phase has a melting point of 535°C, and its melting point, thermal stability and high temperature creep properties are better than those of Mg17Al12 phase. At the same time, the creep resistance of AZ91 is weaker than that of ZA series alloy. The casting property and corrosion resistance of ZA124 alloy are higher than that of AS41 alloy, and the creep property at high temperature is similar, but the alloy has some disadvantages such as low elongation and poor toughness. The creep resistance of Mg-Al-Zn alloy can be enhanced by adding Ca or Sr, especially the effect of adding Ca is better [18].

8. Mg-Zn-Al based Heat-Resistant Magnesium Alloys

Mg-Zn-Al heat resistant magnesium alloys have the characteristics of low cost and good comprehensive mechanical properties. By adjusting the ratio of Zn to Al, MgZn and MgGal two-phase heat-resistant magnesium alloys can be obtained and the high temperature creep property can be improved. With the increase of Zn content in the alloy, solid solution strengthening can be achieved and products with high strength and creep resistance can be obtained. Low melting point, poor performance at high temperature and easy slip at grain boundary can cause poor creep resistance of AZ91 series heat-resistant magnesium alloys at high temperature. The Mg32(Al,Zn)49 phase [20] (Fig. 3) is more resistant to high temperature than the Mg17Al12 phase [19] (Fig. 2) by reducing the Al content and increasing the Zn content of the alloy. The results show that when the amount of Al is less than 8%, the content of Zn is directly proportional to the tensile strength and inversely proportional to the tensile strength. When above 8%, the tensile strength and elongation have little relation with Zn element, but have relation with Al element. The elongation is directly proportional to the content of Al, and the tensile strength is inversely proportional. Zn and Al contents have different effects on the casting properties of the alloys. The alloys with different Zn contents are in the castable crack zone (< 1%), hot crack zone (> 1%), castable zone and brittle zone (Zn content is greater than hot crack zone). Therefore, the selection of appropriate Zn/Al content ratio is one of the reasons for obtaining perfect comprehensive properties of the alloy [21-22].

![Figure 2](image1.png)

**Figure 2.** TEM microstructure (a, b), SEM microstructure (c) and EDS image (d) of Mg17Al12 phase

![Figure 3](image2.png)

**Figure 3.** SEM microstructure of Mg32(Al,Zn)49 phase
9. Effect of Zn and Al contents on Mg-Zn-Al Heat-resistant Magnesium Alloys

The empirical analysis shows that Al and Zn are the main components of Mg-Zn-Al heat-resistant magnesium alloys, and the proper proportion of Al and Zn will directly affect the properties of the alloys. The influence of Zn/Al ratio on this series of alloys is shown in Table 1[23]:

| Alloy        | Zn/Al ratio | Phase composition            |
|--------------|-------------|------------------------------|
| Mg-3Al-0.5Zn | 1/6         | α-Mg+Mg_{17}Al_{12}          |
| Mg-3Al-1Zn   | 1/3         | α-Mg+Mg_{17}Al_{12}          |
| Mg-8Al-4Zn   | 1/2         | α-Mg+Mg_{17}Al_{12}+Mg_{32}(Al,Zn)_{49} |
| Mg-3Al-3Zn   | 1           | α-Mg+Mg_{32}(Al,Zn)_{49}+MgZn |
| Mg-3Al-5Zn   | 5/3         | α-Mg+Mg_{32}(Al,Zn)_{49}+MgZn |
| Mg-3Al-7Zn   | 7/3         | α-Mg+Mg_{32}(Al,Zn)_{49}+MgZn |
| Mg-2Al-8Zn   | 4           | α-Mg+Mg_{32}(Al,Zn)_{49}+MgZn |

Zeng X. et al. [24] studied the influence of Al and Zn ratio on the mechanical properties and microstructure of the ternary heat-resistant magnesium alloy. They found that the magnesium matrix and β phase, MgZn phase and Mg_{32}(Al,Zn)_{49} phase at the grain boundary edge were the main microstructure of the alloy. Alloy elements less general high temperature strength is low, high strength of general alloy elements, the alloy will be at room temperature or high temperature with the increase of its element plasticity shows a downward trend.

Yang M. et al. [25] studied the effect of Zn/Al ratio on the as-cast microstructure and solidification of this series of alloys and found that when the ratio of Zn/Al is less than 2, the main components are magnesium matrix and Mg_{32}(Al,Zn)_{49} phase. When the ratio increases, the structure of the second phase decreases, and the discontinuous compound gradually replaces the continuous network compound. When the ratio exceeded 2, MgZn phase formed in addition to the original tissue, and the dispersed granular phase gradually replaced the continuous reticular tissue as the main body.

The results show that the content ratio of Zn to Al has a serious effect on the mechanical properties and microstructure of the alloy. Therefore, further research on this problem is needed.

10. Microstructure Modification of Mg-Zn-Al Magnesium Alloys

The ratio of Zn to Al in Mg-Zn-Al magnesium alloys plays a guiding role in the design of the alloys. However, the crystallization temperature of Mg-Zn alloy is much higher than that of Mg-Zn-Al alloy, and the temperature difference of 290 °C greatly affects the foundry property. Researchers have tried to improve the properties of the alloy by refining grain size, micro alloying and heat treatment. It is found that calcium; strontium and rare earth elements have a good effect on the microstructure and mechanical properties of the alloys. Magnesium alloys with high Zn content have good solution strengthening properties, so heat treatment has good effects on the room temperature, high temperature and microstructure of the alloy [26-28].

11. Ca and Sr

Yang. et al. [29] cast Mg-5Zn-3Al-0.2Mn alloy with sand mold. When the Ca content reaches 0.43%, it mainly consists of α-Mg matrix and Mg-Zn-Al-Ca complex phase. When the Ca content reaches 0.95%~1.8%, Al₂Ca phase is increased on the basis of 0.43%Ca element formation. In terms of mechanical properties, the increase of Ca decreases at room temperature, but can be improved at 350°C solution treatment and 17h quenching. The yield strength and tensile strength of the alloy increase with the increase of Ca element. Zhang et al. [30] found that Ca and Sr can enhance the high temperature creep strength of Mg(8~14)Zn(2~6)Al alloy, and Ca has a better ability than Sr [31].

12. RE

Wang. et al. [32] researched the effect of 0.5%~1.5% rare earth elements on the microstructure of Mg_{5}Zn_{9}Al_{0.3}Mn alloy. They found that the phases of the alloy are mainly α-Mg, Mg_{32}(Al,Zn)_{49} phase
and Al₂Mg₅Zn₂Re phase. The semi-continuous meshwork compounds adsorbed by grain boundary gradually decompose into particles, and the Mg-Zn-Al alloy exists scattered. The rod-like or needle-like compounds at grain boundaries are proportional to the amount of rare earth elements added. The grain size is the smallest when rare earth elements account for 1.5% of the total element content. The addition of rare earth elements can improve the microhardness and mechanical properties of the alloy. Wang et al. [33] found that when rare earth elements were added to Mg₈Zn₄Al₀.₁₃Mn alloy, the shading damping of the alloy would be reduced, and the optimal high temperature performance could be obtained when the rare earth content was appropriate [34].

13. Heat Treatment
Wang et al. [35] studied the microstructure, microstructure, mechanical properties and damping properties of rare earth modified alloys and analyzed the effects of heat treatment. They found that the comprehensive mechanical properties of the alloys could be significantly improved after aging at 345°C for 12 hours and at 175°C for different times. When the optimal aging is 8 h, the buckling strength increases by 36% and 19%, the tensile strength increases by 33% and 8%, respectively, at room temperature and 155°C, and the damping is greatly improved [36]. The Mg-Zn-Al heat-resistant magnesium alloy has good creep resistance, but has casting defects and poor comprehensive properties, which seriously restricts the application and development of the automobile industry. The further development of the Mg-Zn-Al heat-resistant magnesium alloy is also paid attention to. The effect of Al/Zn ratio, microalloying and heat treatment on the microstructure of Mg-Zn-Al alloys is not consistent, which is also a major factor hindering the application of Mg-Zn-Al alloys. The future research direction is mainly to continue to deepen on the original basis, so as to improve the comprehensive application performance of the alloy, so that it can adapt to more harsh conditions [37-39]. The main heat treatment process of the alloy is shown in Fig. 4[40].

14. Mg-RE Based Heat-Resistant Magnesium Alloys
Rare earth elements can hinder the movement of grain boundaries, slow down the agglomeration between phase boundaries and improve the performance of heat-resistant magnesium alloys. Changing the lattice parameters reduces the formation of concentrated defects. In addition, the sizes of magnesium atoms and rare earth elements are similar, which can form a very strong precipitation strengthening phase. At 200°C, Mg-RE is the main magnesium alloy [41].

15. Mg-Sc
Sc can improve the high temperature performance of magnesium alloy. Mg-Sc series alloys have better heat resistance. The addition of elements such as cerium and manganese can improve the high-temperature strength of the alloy, and obtain excellent thermally stable particles Mg-Sc phase [42] (Figure 5) and Mg-Ce phase [43] (Fig. 6), so that it has better performance. Even better than WE series
alloys. The creep rate of alloy T5 is much slower than that of WE43 at 30MPa and 350°C, and cerium can improve the high temperature creep.

16. Mg-Y
Y’s solid solubility can reach 12% in magnesium, which is proportional to the temperature change. When the magnesium alloy contains Y element, solid solution strengthening is improved and precipitation strengthening is aged. As a result, scholars have developed many Mg-Y-RE series heat-resistant magnesium alloys [44]. Among them, WE54 alloy can work stably at 300°C and has become the most prominent heat-resistant alloy in commercial applications. The alloy is mainly formed by adding Y, Nb and Ge elements to a magnesium matrix. The WE43 alloy is obtained by controlling the content of Nb and Y elements. This alloy has good initial properties and can work stably at 250°C, but has slightly lower high-temperature strength. It is mainly used in automobile and aircraft gearbox housings. Zn alloy elements can effectively improve the creep resistance, and low manufacturing cost. Adding Y and Mn to Mg-Y alloy [45] (microstructure shown in Fig. 7) can also obtain Mg-4Y-1Sc-1Mn alloy with higher creep resistance than WE43 alloy [46].

![Figure 5. Microstructure of Mg and Mg-xSc(2,5,10) alloy](image1)

![Figure 6. Microstructure of Mg-xCe(x=0.5,1,5,10) alloy](image2)

![Figure 7. Microstructure of Mg-xY(x=0.5,1,5,10) alloy](image3)

17. Mg-Gd, Mg-Dy and Mg-Sm
Researchers found that Mg-Gd alloy [47] has high mechanical properties at room temperature and high temperature. The obtained Mg9.3Gd4.8Y0.6Mn alloy has good tensile strength at room temperature and 35°C, reaching 450 MPa and 160 MPa respectively. The alloy can adapt to high temperature environment, but the high content of rare earth elements restricts the application of the alloy. Recently, scholars have added Mn and Sc to the alloy at 300°C, 40Mpa the lowest creep rate of Mg5GdMnSc alloy is only one grade lower than that of WE54. Scholars have found that: if there are gadolinium and dysprosium elements in the alloy, Mg6Gd (Dy)3NdZr alloy can be obtained, which has better heat resistance than WE54. Sm element has strong solid solution strengthening property. After solution heat
treatment and artificial aging, the room temperature and high temperature properties of Sm element are similar to WE43.

18. Summary and Prospect
Three kinds of heat-resistant magnesium alloys introduced in this paper are mainly realized by adding alloying elements and improving the manufacturing process. Due to the introduction of expensive rare earth elements, the cost of the alloy will increase and its application will be greatly limited. Therefore, how to reduce the cost of heat-resistant magnesium alloy by replacing rare earth elements with cheap alloy elements (Ca, Si, etc.) while keeping the heat resistance of the alloy unchanged will become one of the further research directions of scholars.

In addition, some scholars found that adding titanium to magnesium alloy can improve the mechanical properties and strength of the alloy. Therefore, improving the mechanical properties and strength of heat-resistant magnesium alloy from the perspective of adding titanium is also the development direction of heat-resistant magnesium alloy in the future.

Thirdly, the comprehensive properties of heat-resistant magnesium alloy can be further improved by improving the casting process and processing technology.

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