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Development of New Types of Magnesium Alloys Containing Sr or RE Elements

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Abstract: The latest research results on new types of magnesium alloys containing strontium or rare earth elements are reviewed. Special attentions are paid to the alloying design, microstructure and properties controlling, the influence of minor addition of Sr and RE on the microstructure and properties of existing magnesium alloys. Some new types of magnesium alloys containing Sr or RE are introduced and discussed.

Introduction

In recent years, magnesium alloys are increasingly used in automobile, aeronautical and aerospace industries because of their low density and good damping property, etc. But their poor elevated temperature properties, especially creep resistance, limit their wider application, which are attributed to low melting point that is in the range from 470 °C to 650 °C related to their compositions. For instance, both of the existing AZ and AM series magnesium alloy can not be used for important transmission parts in the automobile because their strength will decrease dramatically when the working temperature is more than 120°C[1~4]. Poor plasticity and corrosion resistance are another two barriers on the way of magnesium alloy application. Currently more and more attentions are drawn to develop new type of magnesium alloy through alloying and microalloying with the expection to improve the properties of the existing magnesium alloys. Some researches have shown that Sr and RE have advantage to increase high temperature strength and creep resistance of Mg based alloys. The present paper overviewed the researches of new type magnesium alloys containing Sr and RE in the aspects of alloy design, microstructure control as well as the relationship between microstructure and properties.

Development of new type magnesium alloys containing Sr

Development of new type Mg-Al-Sr based alloys

Design and mechanical properties of the new type Mg-Al-Sr based alloys. AJ (Mg-Al-Sr) alloy is a representative alloy series in the heat-resistant Mg alloys containing Sr[5~7]. The high creep resistance of Mg-Al-Sr is attributed to the formation of heat-stable alloy phases due to the addition of Sr. It was reported that divorced A1-Sr eutectic and Mg-Sr-A1 would form when 1.2% of Sr was added into Mg-5%Al alloys; when Sr was increased to 1.8%, lamellar Mg-A1-Sr eutectic formed instead. Sr containing phases mainly distributed along grain boundaries and were more heat-stable than $Mg_{17}A1_{12}$. With the appearance of Sr containing phases and decrease of less heat-stable $Mg_{17}A1_{12}$, better creep resistance of the alloy then could be expected[1].

Noranda from Canada is one of the leading companies in developing Mg-Al-Sr heat-resistant magnesium alloys. Some new type alloys like AJ50X, AJ52X and AJ62X through adding various amount of Sr into the AM50 commercial magnesium alloy have been developed. Bai from China also tried to develop several kinds of Mg-Al-Sr alloys, namely AJC411, AJC511, AJC611 and AJC711 by adjusting the contents of Al and Ca. The chemical composition and tensile properties of some newly developed Mg-Al-Sr alloys are listed below for comparison.

Table.1 Compositions and tensile properties for part new type Mg-Al-Sr based alloys [8~14]

Alloys	Composition, wt%					Tensile properties			
	Al	Sr	Mn	Ca	Mg	$\sigma_{0.2}$ /MPa	σ_b /MPa	δ /%	Temp.
AJ50X	5	0.5	0.2-0.3	-	Bal.	125	194	6.0	RT
						88	108	4.6	175□
AJ52X	5	2.0	0.2-0.3	-	Bal.	145	202	4	RT
						103	148	15	175□
AJ62X	6	2.4	0.2-0.3	-	Bal.	140	232	7	RT
						106	144	21	175□
AJC411	3.8-4.2	0.8-1.2	0.3-0.5	0.8-1.2	Bal.	98	143	1.6	RT
						86	120	2.1	175□
AJ42	4	2	0.3	-	Bal.	114	161	5.1	RT
						97	136	9.8	175□
AJC421	4	2	0.3	1	Bal.	88	131	1.2	RT
						91	122	1.6	175□
AJC511	4.8-5.2	0.8-1.2	0.3-0.5	0.8-1.2	Bal.	101	134	1.3	RT
						87	124	2.7	175□
AJC611	5.8-6.2	0.8-1.2	0.3-0.5	0.8-1.2	Bal.	104	140	2.2	RT
						95	133	3.1	175□
AJC711	6.8-7.2	0.8-1.2	0.3-0.5	0.8-1.2	Bal.	112	152	3.0	RT
						92	138	4.9	175□

Microstructure and properties controlling for the new type Mg-Al-Sr based alloys . The Sr/Al ratio is thought as to be important to control the microstructure of Mg-Al-Sr alloys. Pekguleryuz[11~12] reported that Mg-Al-Sr alloys showed different microstructures according to various Sr/Al ratio. For a Sr/Al ratio below about 0.3, the Al_4Sr and/or $Mg_{17}Al_{12}$ phases were found in the microstructure (Fig.1a and Fig.1b). When the Sr/Al ratio was higher, a new ternary Mg-Al-Sr compound was observed. When the Sr/Al ratio was very low, there was an insufficient amount of Sr to bind all Al atoms and the excess Al would form the $Mg_{17}Al_{12}$ phase. These results were confirmed by Parvez et al[10] who investigated 22 alloys from the Mg-Al-Sr system. They found that Al_4Sr and Mg solid solution were the dominating phases.

In China, Bai et al [13] investigated the microstructures and mechanical properties of the AJC411-711 alloys. The research results indicated that in the AJC411 alloy thin lamellar eutectic Mg_2Ca, coarse eutectic $(Mg,Al)_2Ca$ and a bulky ternary Mg-Al-Sr phase were observed at grain boundaries (Fig.2). With increase of Al content, the volume fraction of the Mg_2Ca and Mg-Al-Sr phase decreased and that of the coarse $(Mg,Al)_2Ca$ phase increased. Both of strength and ductility increased with the increase of Al concentration in the alloys studied at 175 and 200°C respectively. Under the condition of 175°C/70MPa, the AJC611 and AJC511 alloys showed best creep resistance among prepared alloys. In addition, Bai et al[14] investigated the effect of extrusion on microstructures, mechanical and creep properties of Mg-4Al-2Sr (AJ42) and Mg-4Al-2Sr-1Ca (AJC421) alloys, and found that after hot extrusion, the intermetallics were converted into band structure and eutectic phases were crushed into small blocks. However, the creep resistances of both alloys were obviously reduced after extrusion deformation.

Zuzanka et al[15] investigated the deformation behaviour of the ternary magnesium alloy Mg-5Al-0.6Sr (AJ50) in uniaxial tension tests at temperatures between 20 and 300°C, and found that the yield stress as well as the maximum stress of the alloy was very sensitive to the testing temperature (Fig.1).

Effects of minor Sr on the microstructure and properties of magnesium alloys

The research results obtained by Lee et al[16~19] found that the grain size of pure magnesium and magnesium alloys with low Al content could be reduced by adding minor Sr, but the refinement efficiency for magnesium alloys with high Al content was not obvious. In addition, Zeng et al[20] reported that the refinement efficiency of Sr to AZ31 magnesium alloy was effected by cooling rate. For a given Sr adding amount, the grain size of AZ31 alloy decreased with the increasing of cooing rate (Fig.2).

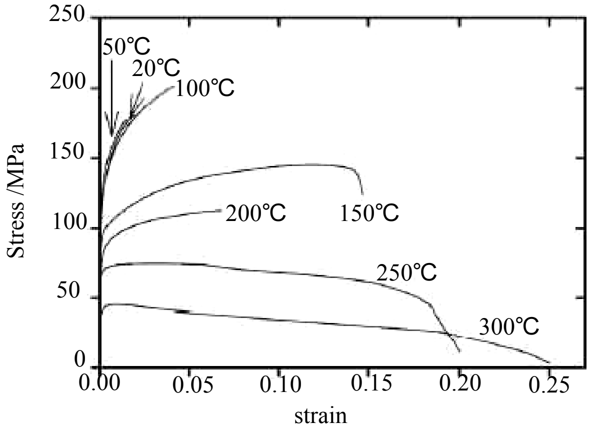

Fig.1 Stress-strain curves of AJ50 alloy at various temperature[15]

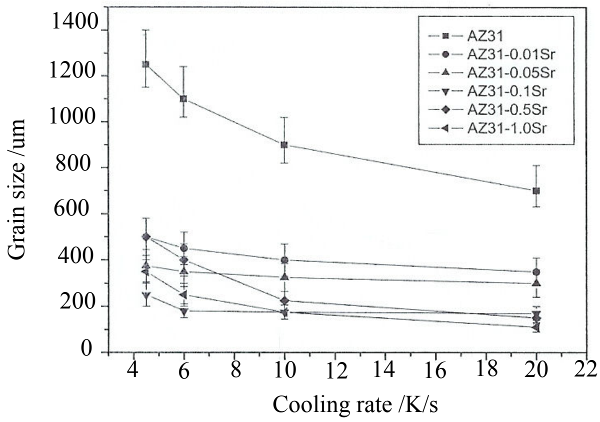

Fig.2 Effects of cooling rate on the grain size of AZ31+xSr alloys[20]

In addition, Zhao et al[21] investigated the microstructure, tensile properties and creep behavior of Mg-5Al based alloys with Sr and Ti additions. The results indicated that small additions of Sr mainly dissolved into $Mg_{17}Al_{12}$ particles and increased their thermal stability and creep strength.

Recent research showed that Sr was also beneficial to improve the microstructure and/or properties of containing-Si magnesium alloys[22~31]. According to the research results obtained by the authors in this paper, adding 0.06%Sr to Mg-6Al-1Zn-0.7Si magnesium alloy could result in morphology transformation of Mg_2Si phases from the coarse Chinese script shape to small block shapes (Fig.3). Similar result was obtained by Yuan et al[24]. In addition, Nam et al[22] also found that the modification efficiency of Sr to Mg_2Si phase in the microstructure of containing-si magnesium alloys was better than that of Sb element.

Chen and co-workers[32] found that the effects of Al-Sr and Mg-Sr master alloys with different states on the refinement to magnesium alloys were very obvious. For example, the refinement efficiency of Mg-10Sr master alloy to AZ31 alloy was higher than that of the Al-10Sr master alloy (Fig. 4), and the states of Mg-Sr or Al-Sr master alloys were also important to obtain ideal refinement efficiency. For the Mg-10Sr master alloys, the refinement efficiency of solution treated Mg-10Sr master alloy was higher than that of the conventional casting, rolled and rapid solidification master alloys. The difference of refinement efficiency possibly related to the morphology and distribution of the second phases in the microstructures of Mg-10Sr master alloys (Fig.5).

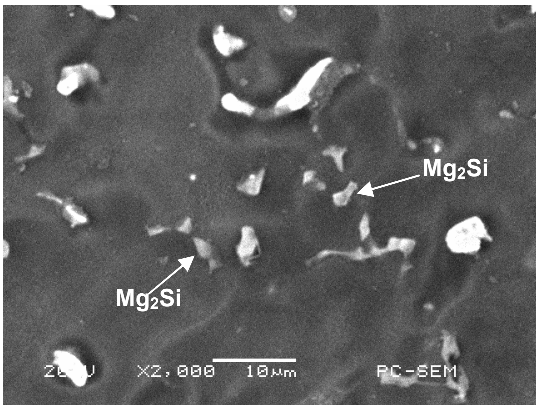

Fig.3 SEM images of Mg-6Al-1Zn-0.7Si alloy containing 0.06%Sr

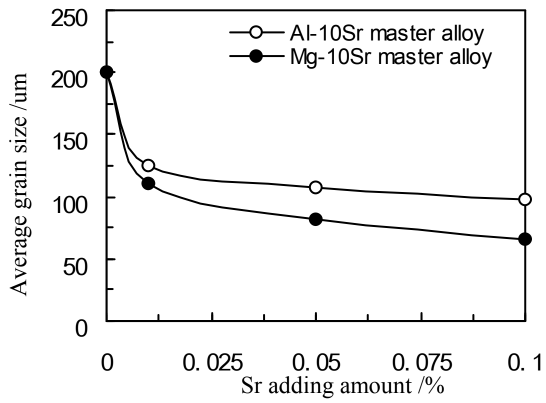

Fig.4 Effect of Sr adding amount on grain sizes of AZ31 alloy

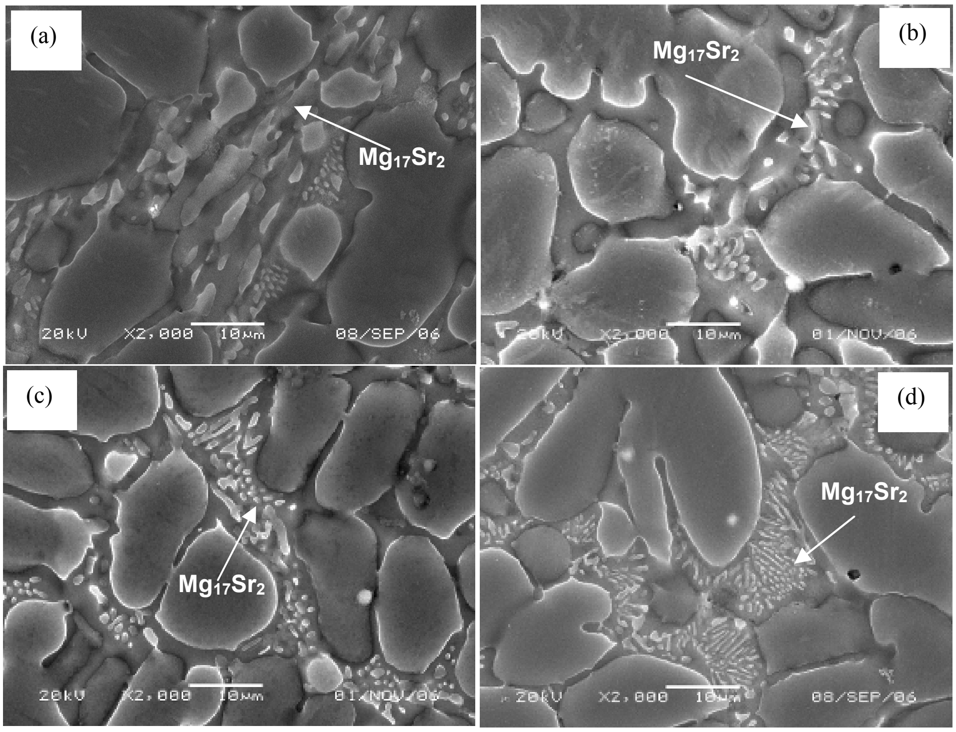

Fig.5 Microstructures of Mg-10Sr master alloys with different states
(a):Conventional casting state; (b): Rolled state; (c):Solutionized state;
(d): Rapid solidification state

Development of new type magnesium alloys containing RE

Since 1937 when the first new type Mg-Ce alloy was reported, rare earth elements have received great attention. In the early period, Cerium (Ce), Lanthanum (La), Neodymium (Nd) and Yttrium (Y) are added into the magnesium alloys as either major or minor alloy elements. Recently, more rare elements like Scandium (Sc), Gadolinium (Gd), Dysprosium(Dy), Didymium (Di), Terbium(Tb) are used along or as mixture with other rare elements to further improve corrosion resistance and mechanical properties by refining the microstructure or forming finer and more stable alloy phases[33]. As a result, some new type of Mg-RE alloys has appeared; improved properties are also obtained for some traditional magnesium alloys because of minor addition of new type rare earth elements.

Development of New type Mg-RE alloys

Mg-Sc based alloys. The Mg-Sc system is a promising Mg-RE alloy system[34]. Ternary Mg-Sc-Mn and quaternary Mg-Sc-Ce-Mn, are most representative ones in Mg-Sc system.

Buch et.al.[35] prepared two types of Mg-Sc alloys using the squeeze casting technique: Mg-6Sc-1Mn and Mg-15Sc-1Mn. The materials showed a fine cast structure with a cellular microstructure and pronounced segregation of Sc. Microstructural examination showed that Mn_2Sc precipitated on the grain boundaries and in the Mg-Sc solid solution, in the as cast condition as well as in the T5 condition. The alloys exhibited a strong annealing response due to the formation of Mn_2Sc precipitates. The UTS of the new alloys was somewhat lower than the corresponding values for the conventional alloy WE43 (Fig.6a) whereas the TYS was comparable to that of WE43 for higher Sc contents (Fig.6b). Although the alloys showed a low elongation to fracture due to a strongly localized plastic deformation, they showed excellent creep properties particularly at high temperatures and low stresses.

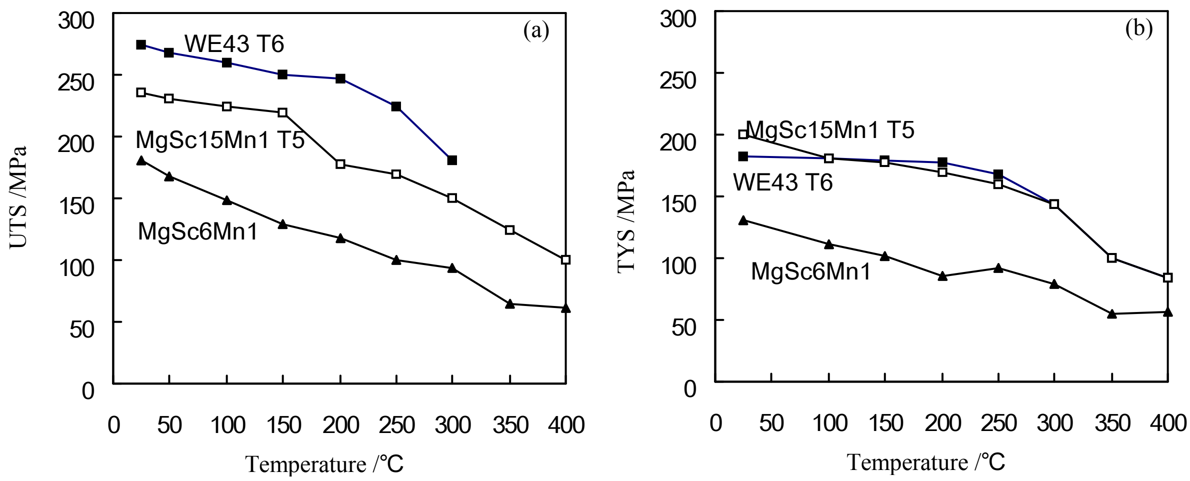

Fig.6 Tensile properties of the alloys in the as-cast and in T5-condition as a function of temperature in comparison to the WE43 alloy in T6 condition: (a) UTS; (b) TYS

Moedike et.al[34] reported that when Ce was added in Mg-Sc-Mn system, fine discs phases parallel to the basal planes of the a-Mg matrix would form, which had a stronger effect on the cross-slip of basal dislocation or non basal slip and consequently increased the creep resistance.

Mg–Tb-Nd based alloys. Neubert et.al [36] attempted to develop a new Mg-RE alloy by substituting yttrium in the WE43 alloy by terbium. They compared the microstructure, thermal stability and mechanical properties of Mg-Y-Nd-Zr (commercial WE43) and Mg-Tb-Nd alloys. The results indicated that the creep resistance of both alloys was similar at elevated temperatures (473K) but the minimum creep rate of WE43 at 623K was lower than that of the Mg-Tb-Nd alloy as a result of more stable microstructure. However, the corrosion rate of the Mg-Tb-Nd alloy was high..

Mg-Dy-Nd system. Magnesium alloys containing dysprosium and neodymium are recently found to exhibit higher strength than the conventional WE type alloys at high temperature. Unfortunately, the microstructure and the alloy phases which contribute to the above mentioned properties are not fully understood yet. Some primary results about second phases have been reported[37,38].

Effects of minor RE on the microstructure and properties of magnesium alloys

Effects of Ho on Mg–Al system alloys. According to Lunder et al[37], $Mg_{17}Al_{12}$ phase is nobler than the matrix and would leads to micro-galvanic corrosion when the grain size is large and the distance between adjacent $Mg_{17}Al_{12}$ phase phases is far. Many researchers tried to decrease the amount of $Mg_{17}Al_{12}$ phase and reduce the potential difference between $Mg_{17}Al_{12}$ phase and the matrix by addition of RE elements. Lunder and Nisancioglu et al [36] found that the $Al_{11}Mm_3$ (Mm, a mixture of rare earth metals) intermetallic phase in AE42 magnesium alloy was nobler than pure Mg. However, its micro-galvanic corrosion was not severe since the $Al_{11}Mm_3$ phase behaved as a passive cathode over a wide pH range. Rosalbino et al . studied the effect of Er addition on the corrosion behavior of Mg-Al alloy. They believed that the incorporation of Er in $Mg(OH)_2$ lattice was responsible for the improved corrosion behavior of Mg-Al-Er alloy.

Recently, Zhou et.al [39] investigated the corrosion behavior of two types of Mg-9Al-Ho alloys compared with that of Mg-9Al, an equivalent to the commercial AZ91D alloy. The results showed that the corrosion rate of alloys with 0.24wt.% or 0.44 wt.% Ho addition was only one ninth of the alloy without Ho addition. Furthermore, Ho addition also caused the formation of Ho-containing intermetallic phases, which generally contained Ho, Al, Mg and Mn and they were easily oxidized and passivated. Besides, Ho addition reduced the Fe concentration in the deposited phases and the fraction of $Mg_{17}Al_{12}$ phase in alloys. As a result, the cathodic role of the deposited phases was drastically weakened and the micro-galvanic corrosion was obviously suppressed.

Effects of Nd on Mg–Sn alloys. Mg-Sn binary alloys have much narrower solidification temperature compared with Mg-Al and Mg-Zn binary alloys. As a result, the casting defects such as dispersed shrinkage and hot tearing in Mg-Sn alloys are less severe than in Mg-Al and Mg-Zn alloys. The solubility of Sn in α-Mg solid solution also drops sharply when temperature decreases, which provides a fundamental basis for improving the mechanical properties of these alloys through ageing. In addition, intermetallic phase Mg_2Sn in Mg-Sn alloys has a much higher melting point (770°C) than the $Mg_{17}Al_{12}$ phase (462°C) in Mg-Al alloys. Mg–Sn based alloys are therefore likely to be more creep resistant at elevated temperatures, especially when their properties are further improved by rare earth elements, than Mg-Al based alloys.

Neodymium has a greater solid solubility and solid solution strengthening effect than praseodymium. In addition, adding didymium (Nd–Pr mixed metal) is more attractive than adding pure neodymium from a cost point of view. Recently Liu et.al [40] studied the effect of didymium (neodymium–praseodymium mixed metal, neodymium: praseodymium = 3:1) on the microstructure and mechanical properties of a permanent-mould cast Mg-5wt%Sn alloy. The research indicated that the didymium addition to the Mg-5 wt%Sn alloy resulted in the formation of a feather-shaped $Sn_x(Nd,Pr)_y$ phase mainly on the grain boundaries, and gave rise to grain refinement when the addition was below 2 wt% (Fig.23). The tensile strength and elongation of the alloys were improved with the addition of didymium, and optimum mechanical results were attained at an addition of 2.0 wt% didymium, where the UTS increased by 26.9% and the elongation by 7.7%.

Summary

It is exited to see that a lot of work concerning magnesium alloys containing Sr or RE has been carried out at various level and some positive results have been obtained. It is undoubted that the magnesium alloys containing Sr or RE are very promising. However, there is still a hard way to go to put these new type alloys into application.

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