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Current development of creep-resistant magnesium cast alloys: A review

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Abstract

The low creep resistance has been one of the major issues of Mg alloys, which limited their wider industrial applications in the past decades. It has been reported that the inherent creep resistance of Mg should be higher than that Al. Hence, it is highly likely that the low creep resistance of Mg alloys was attributed to the effects of alloying elements rather than Mg itself. In order to systematically understand the effects of alloying elements on the creep behaviours of cast Mg alloys and therefore to develop new alloys with higher creep resistance, the present work reviews the major creep-resistant Mg systems that were developed and successfully commercialized for applications at different temperatures. Because the majority of commercial Mg alloys are used as cast, this review focuses on cast alloys.

Keywords

Magnesium alloys; Creep resistance; Microstructure; Metallography

1. Introduction

Owing to the light weight, abundance and good castability, magnesium (Mg) alloys have attracted increasing interest from researchers and engineers who are pursuing weight reduction in engineering applications [1, 2]. High specific strength and stiffness, damping capacity, and good machinability are other advantages of Mg alloys [3, 4]. Mg alloys are especially valuable to automotive and aerospace industries as the benefits to energy conservation and higher fuel efficiency through weight reduction. The worldwide primary magnesium production (excluding U.S.) in 2015 was up to 972,000 metric tons [5]. Magnesium cast alloys in particular, have comprised 85-90% of all Mg alloy products due to their advantages over wrought alloys in terms of their cost [6, 7].

Despite these merits, the relatively low creep resistance at elevated temperature of Mg alloys is regarded as the key challenge that limits their wider

applications in automotive and aerospace industries because some critical components are used at a temperature above 175 °C [8-11]. The automobile powertrain system is one potential application for cast Mg alloys, however, only a small fraction of powertrain components is currently made of magnesium alloys [3, 12], and aluminium alloys are still the predominated materials used in powertrain systems.

There is no ascertainable evidence confirming the reasons for the lower creep resistance of Mg alloys than Al alloys. Work by Murayama and co-workers [13] showed a better inherent creep resistance of Mg alloys than Al alloys. In this work, the creep rates of an HCP (hexagonal close-packed) Mg-3mol%Al alloy with solid solution treated were reported to be lower than that of solid solution treated Al-3mol%Mg alloy that has FCC (face centred cubic) crystal structure. The better creep resistance of the Mg alloys was attributed to a fewer number of independent basal slip systems and higher intrinsic stress (the Peierls-Nabarro stress) in HCP structure. Thus, it seems that the low creep strength of Mg alloys is more likely due to the solute additions rather than Mg itself. The influences of alloying elements on the creep behaviour of alloys are multiple and diverse. They can either directly promote creep strength by introducing grain boundary reinforcement, by solid solution strengthening and/or precipitation hardening, by increasing the eutectic temperature and by solute dragging in the matrix [14]. In the last couple of decades, substantial progress has been made in addressing the issues associated with the low creep strength of Mg alloys. The present work reviews the current progress in developing creep-resistant Mg alloys and the influence of alloying additions on creep behaviours.

2. Creep-resistant Mg-Al based alloys

2.1 Low creep resistance of Mg-Al-Zn/Mn alloys

Aluminium (Al) was reported to be the most favourable solute to be added into magnesium for improving the strength and castability of the magnesium alloys [7]. In the early 20th century, Mg-Al-Zn based alloys (AZ series) were developed and commercialized extensively in Germany [15]. Later, the addition of manganese was found enhancing the corrosion resistance of Mg-Al based alloys [16]. Thus, the Mg-Al-Zn/Mn system has been the basis of most commercial Mg alloys in the current market. These alloys offer a good combination of mechanical properties, reasonable corrosion resistance, low cost and high castability when compared with other Mg alloy systems. Typical commercial alloys include the AZ91 (Mg-9Al-0.7Zn), AZ61 (Mg-6Al-0.7Zn), AM50 (Mg-5Al-0.4Mn) and AM60 (Mg-6Al-0.4Mn) [1-10]. These commercial alloys are mainly served at room temperature and in high pressure die-castings (HPDC) owing to the need for high productivity and cost effectivity in industry

production. Typical applications included 3C (computer, communication, and consumer electronics) products and automotive components, like computer housing, instrument panel beams, transfer cases, annual transmission case, steering components and various housings brackets [9]. However, they can only be used at room temperature because of the dramatical loss of the strength and the creep resistance at operating temperature over 393K (120 °C).

Although various merits are contributed by Al addition to Mg, the low creep resistance of these commercial alloys is known to be associated with Al through investigation of creep mechanism of alloys. Creep deformation can be divided into three stages, which are primary creep, steady state creep and tertiary creep. But the steady state stage is the most significant one being widely investigated. Generally, the dominant creep mechanism of alloy can be empirically identified by two values, creep stress exponent n and activation energy, Q_c , calculated from an empirical equation for steady state creep strain rate (or secondary creep rate) as a function of temperature and applied stress. The equation is expressed as

$$\dot{\epsilon}_s = A \left(\frac{\sigma}{E}\right)^n \exp\left(-\frac{Q_c}{kT}\right) \quad (1)$$

where A is a constant, σ is applied stress, E is Young's modulus, k is Boltzmann's constant and T is absolute temperature. Therefore, stress exponent n can be obtained by plotting $\log \dot{\epsilon}_s$ against $\log \sigma$, and activation energy for steady state creep can be obtained by plotting $\ln \dot{\epsilon}_s$ against $1/T$. Generally, $n=1$ and $Q_c \sim 92 - 135 \text{ kJ/mol}$ is corresponded to diffusional creep, $n=2$ is related to grain-boundary sliding and dislocation creep is associated with value of n from 3 to 7, of which $n=3$ indicates solute drag creep and 5-7 indicates dislocation climbing and gliding as dominated mechanism [17-23].

Studies of the creep behaviour of Mg-Al based alloys have revealed that dislocation climbing and grain boundary sliding are the two main mechanisms dictating the creep process [9, 22-27]. It was reported by Agnew et al. [24] that diffusion controlled dislocation climbing was responsible for the creep of the AM60 alloy as $n = 4$ under applied stresses of 20-60 MPa at 180 °C. Asl et al. [26] indicated that a mixed mode of dislocation climb mechanism and grain boundary effects contributed to the overall creep behaviour of AZ91 under applied stresses of 48-96 MPa at 200 °C. Roodposhti and co-workers [27] also concluded that grain boundary sliding and dislocation climb dominated the creep mechanism of AZ91 at low and higher stresses, respectively. The creep mechanism does not closely related to the manufacturing processes of the alloy. It's widely accepted that the root cause for poor creep resistance of the AM and the AZ series is the low thermal stability of the secondary phase, $\text{Mg}_{17}\text{Al}_{12}$ [7-14, 25, 28]. Not only has $\text{Mg}_{17}\text{Al}_{12}$ a low melting temperature (458 °C), but the Mg- $\text{Mg}_{17}\text{Al}_{12}$ eutectic

structure is also associated with a low eutectic temperature (437 °C). Hence, the intermetallic compound can be readily softened and/or coarsened when the temperature is above 120 °C, promoting grain boundary sliding and migration during the creep process. Coarsened $\text{Mg}_{17}\text{Al}_{12}$ precipitates provide less inhibition to dislocation climb. In addition, segregation of Al solutes along grain boundaries is also considered that can increase the local homologous temperature and hence preferentially soften grain boundaries at elevated temperature [29].

In summary there is no evidence indicating that the host Mg intrinsically has low creep resistance, but rather, it is dependent on other alloy constituents. As such it is possible to increase the high-temperature creep resistance of Mg alloys through careful solute selections. In terms of the applications and manufacturing process, the common strategies to improve the creep resistance of Mg alloys include two approaches [10]. One is to modify the AZ91 alloy through small additions of other alloying elements to enhance the creep resistance of components that can be produced through HPDC. Another is to develop entirely new alloys that are ageing hardenable and can be used as cast or wrought alloys.

2.2 Enhanced Mg-Al based alloys by further additions

The Mg-Al system is considered to be irreplaceable in many HPDC applications due to its good castability and low cost. In such situations it is preferable to modify the Mg-Al based alloys in order to enhance their creep resistance. The effects of solutes on the creep behaviours have been investigated, including Si [30], Ca [31], Sr [32], rare-earths (REs) [33, 34] and/or their combined effect [35, 36]. The increased creep resistance is attributed to grain boundary reinforcement or pinning effect by thermally stable intermetallic particles, or to the strengthening of Mg matrix by solid solution and/or precipitation hardening. As a result, several commercialized creep-resistant Mg-Al based alloys, such as AS, AE, AX, AJ and MRI series, were developed over recent decades.

2.2.1 Si, Bi and Sb additions

Mg-Al-Si series alloys were developed and commercialised as creep-resistant alloys by Volkswagen in the 1970s. Typical alloys, including AS21 (Mg-2Al-1Si) and AS41 (Mg-4Al-1Si), were used at temperatures up to 150 °C with enhanced creep resistance compared with the AZ91 and AM60 alloys. Fig.1 presents the normalized creep rate at a range of applied stress and temperatures in comparison between AZ91 and AS alloys [37]. Both of AS21 (Fig.1b) and AS41 (Fig.1c) were recorded to have lower creep rate than AZ91 (Fig.1a). Furthermore, the AS41 alloy exhibited better creep performance than AS21 in all tested conditions. The enhancement of creep strength was attributed to the formation of fine Mg_2Si particles

along the α -Mg grain boundaries during the creep process, which inhibited grain boundary sliding [38, 39]. In addition, the low Al content in the AS series alloys reduced the fraction of $Mg_{17}Al_{12}$ phase, which as discussed in Section 2.1, has a negative effect on the creep resistance. A reduction of this phase also contributed to the higher creep resistance in the Si-containing alloys. Zhang [38] investigated the creep behaviour of the die-cast AS21 alloy under compression at 150 °C and determined the creep stress exponent that was about 5, suggesting a creep mechanism dominated by dislocation climb. The research also indicated that creep under an applied stress of 90 MPa was significantly suppressed, but higher levels of stress led to tertiary creep due to the breakage of Mg_2Si intermetallic particles. Mazraeshahi and co-workers [40] studied 0.8~1.6wt.% Si-containing AZ61 alloys and determined that the creep stress exponent was within the ranges of 4 to 7 and 10 to 14 for low and high stress levels, respectively. This verified the dislocation climb and power-law breakdown as the dominant creep mechanisms in this group of Mg alloys.

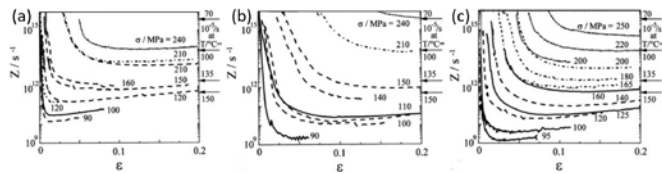


Figure 1 Normalized creep rate $Z = \dot{\epsilon} \exp Q/RT$ at a range of constant stresses σ and temperatures for (a) AZ91; (b) AS21; (c) AS41 [37].

Mg_2Si has a high melting point of 1085 °C, high hardness and low coefficient of thermal expansion [41]. However, its strengthening effect is extremely limited in the die cast products due to the fast cooling, which suppressed its formation. Slow cooling during solidification leads to the formation of coarse Chinese script Mg_2Si precipitates, which create more crack sources and damages the mechanical properties [42]. Subsequently, additions of Ca, P, Sb and Sr were reported to modify the morphology of the Chinese script Mg_2Si phase. Kim et al. [43] indicated that additions of Ca and P led to the formation of $CaSi_2$ and $Mg_3(PO_4)_2$ particles, acting as nucleants for Mg_2Si precipitates and refining the Mg_2Si particles. Srinivasan et al. [44, 45] also reported that minor addition of Sb or Sr resulted in the change of Mg_2Si morphology from massive Chinese script to fine polygonal, which improved creep properties of the alloys.

Bismuth (Bi) and antimony (Sb) have similar strengthening effect in Mg-Al based alloys. Work by Yuan et al. [46] illustrated that small additions of both Bi and Sb gave rise to noticeable improvements in yield strength and creep resistance of the AZ91 alloy at elevated temperatures up to 200 °C. Table 1 lists the minimum tensile creep rate of a few AZ91 alloys with and without Bi/Sb additions at various temperatures. Significant reductions in creep rate can be seen after

addition of Bi/Sb, and Sb in particular. Bi and Sb additions enabled the formation of thermally stable rod-shape Mg_3Bi_2 and Mg_3Sb_2 particles. Such particles not only impeded the grain boundary sliding, but also refined the $Mg_{17}Al_{12}$ precipitates in the as-cast microstructure and suppressed discontinuous precipitation of the $Mg_{17}Al_{12}$ during aging process. Additionally, it's noticed that the potency of intermetallic particles to improve creep resistance of Mg-Al based alloys is closely related to their melting points. The AZ91 alloy containing Mg_3Sb_2 (melting temperature of 1228 °C) was reported to have higher creep resistance than alloys containing Mg_2Si (melting temperature of 1085 °C) and Mg_3Bi_2 (melting temperature of 823 °C) [45, 46]. Hence, additions of Si, Bi and Sb have been recognized as an effective approach to develop low cost Mg alloys with improved creep resistance in comparison with other creep-resistant Mg-Al based alloys. In addition, it is worth pointing out that although additions of Si, Bi and Sb can promote the formation of intermetallic particles with higher melting temperatures and thermal stability, dislocation climb is considered as the dominated creep mechanism of the AZ91 based Mg alloys within particular ranges of temperature and applied stress. $Mg_{17}Al_{12}$ phase is still the major precipitates in Mg-Al based alloys [46]. Thus, the increment in creep resistance of those alloys is moderate. Srinivasan and co-workers' results [45] showed that additions of 0.5% Si and/or 0.2% Sb to AZ91 alloys led to a significant reduction of creep rate at 150 °C, however, the improvement in creep resistance at a temperature up to 200 °C was marginal.

Table 1 Minimum tensile creep rate (s^{-1}) of Mg-9Al alloys at a stress of 50 MPa [46].

Alloy	Minimum creep rate (s^{-1}) at an applied stress of 50 MPa		
	150 °C	175 °C	200 °C
AZ91	5.0×10^{-8}	3.4×10^{-7}	2.5×10^{-6}
AZ91+2.0Bi	9.6×10^{-9}	6.8×10^{-8}	5.4×10^{-7}
AZ91+0.4Sb	4.7×10^{-9}	3.5×10^{-8}	2.9×10^{-7}
AZ91+1.0Bi+0.4Sb	3.1×10^{-9}	2.3×10^{-8}	1.9×10^{-7}

2.2.2 Rare earth elements additions

The formation of more thermally stable intermetallic compounds with Mg cannot suppress the formation of $Mg_{17}Al_{12}$, which may continuously promote the grain boundary sliding and migration. Thus, comparing with the AZ series alloys, the improvement of creep resistance in AS alloys is limited. Moreover, a minimum Al content is required in the AS series to ensure the good castability for HPDC. Hence, an alternative approach to develop creep-resistant Mg-Al based alloys is to add alloying elements that have higher chemical affinity to Al than to Mg. These additions are supposed to chemically react with Al, which not only leads to the formation of intermetallic compounds

hindering grain boundary sliding, but also suppresses the formation of the $Mg_{17}Al_{12}$ phase. Rare earth elements (REs) can meet such requirements. In order to reduce the cost of HPDC parts, Ce-rich mischmetal alloys are commonly used, which mainly comprises of Ce, La and Nd [47]. Addition of mischmetal into Mg-Al based alloys enabled the development of AE series commercial alloys in the last century, including AE41 (Mg-4Al-1RE), AE42 (Mg-4Al-2RE) and AE44 (Mg-4Al-4RE). These alloys exhibited superior creep resistance over AS and AZ alloys [1]. Fig.2a illustrates the variation of creep strains of these three AE/AS series alloys compared to the AZ91 alloy with time at 150 °C/50 MPa condition. The 100 hours creep strain of the AE42 was almost 10 times lower than that of the AZ91 alloy.

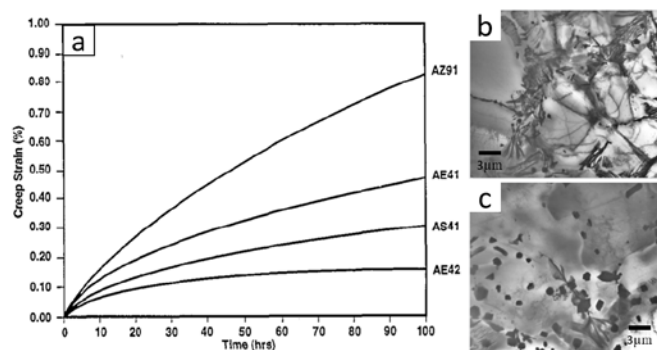


Figure 2 (a) Tensile creep strain at 150 °C / 50 MPa of Mg-Al HPDC alloys; TEM micrographs of the AE42 specimen tested at (b) 150 °C and (c) 175 °C (reproduced from [49, 52]).

The improved creep resistance of RE-containing Mg-Al based alloys is attributed to the reduction of $Mg_{17}Al_{12}$ fraction and the presence of lamellae $Al_{11}RE_3$ (or Al_4RE) phase, as an interdendritic microstructure, and small amount of Al_2RE phase [48-50]. The AE42 has been a benchmark of Mg-Al based alloy with good properties at elevated temperature and better corrosion resistance, as shown in Fig.2a. Dieringa et al. [51] calculated the true stress exponent n of AE42 for both tensile and compressive creep within the temperature range from 150 °C to 240 °C. The n -values were within a range of 3 to 6. The results implied the predominant creep mechanism as dislocation gliding and climbing. However, the application of this type of alloys was limited to temperatures below 150 °C because of the sharp loss of creep strength above this temperature [48, 52, 53]. The reasons for creep failure of the AE series alloy at higher temperatures are controversial. Powell et al. [52] reported different microstructures of AE42 alloy after creep tests at 150 °C and 175 °C, as shown in Fig.2b and 2c. The increased volume fractions of Al_2RE phase and the $Mg_{17}Al_{12}$ phases in an AE42 sample after long-term creep test at 175 °C were detected through XRD analysis. The authors suggested that the decomposition of $Al_{11}RE_3$ into Al_2RE during creep testing, releasing Al atoms that subsequently formed $Mg_{17}Al_{12}$ phase, and lowering the creep resistance of the

alloy. However, more recent work on AE42 by Zhu et al. [54] did not observe the decomposition of $Al_{11}RE_3$ intermetallic compound after two-week ageing at 200 °C and considered that the subsequent formation of $Mg_{17}Al_{12}$ phase was due to the supersaturation of Al solute in the die-cast Mg matrix. These two controversial results on the decomposition of $Al_{11}RE_3$ phase may be related to the different experimental conditions. Powell and co-authors' work [52] were done at crept samples and investigation by Zhu et al. [54] was conducted at aged samples. Hence, it is reasonable to deduce that the stress at high temperature could promote the decomposition of the $Al_{11}RE_3$ phase. Thus, further investigation is worthwhile.

By increasing the content of RE, the AE44 alloy was developed targeting at applications at higher temperatures. This alloy has been used to make engine cradle of GM Corvette [55]. Rzychon et al. [50] observed neither change in the fraction of $Al_{11}RE_3$ nor the formation of $Mg_{17}Al_{12}$ in the die-cast AE44 alloy after annealing at 175 °C for 3000 h. Thus, even at 200 °C, the alloy still showed a low secondary creep rate $\dot{\epsilon}$ as $5.72 \times 10^{-10} s^{-1}$ under 60 MPa, and only 0.13% of creep strain after 120 hours. Furthermore, replacement of Ce-rich mischmetal with either La [47] and/or Nd [56] was found to further improve the creep properties of the die-cast AE alloys. Higher thermal stability of $Al_{11}La_3$ and $Al_{11}Nd_3$ than that of $Al_{11}RE_3$ (majority is $Al_{11}Ce_3$) was considered to be responsible for the improved creep resistance. Furthermore, the combined effect of REs and Ca (or Sr) on creep properties were also investigated [57-61]. Dargusch et al. [57] reported that 1 wt.% addition of Sr to die-cast AE42 alloy led to the improvement of creep strength and yield strength with decrease in ductility at high temperatures. Companion paper by Dargusch et al. [58] observed an additional thermally stable phase, Mg_8Al_4Sr , which reinforced the grain boundaries and also reduced the supersaturation of Al solute in the Mg matrix. In addition, combined additions of Ca and Sr to AE41 alloy [59, 60] exhibited even better compressive creep resistance due to the further reduction in volume fraction of the $Mg_{17}Al_{12}$ phase, which promoted the hindering effect of Al-RE, Al-Ca and Al-Sr intermetallic compounds to dislocation climb and grain boundary sliding. But, the reverse effect of addition of Ca on creep resistance of AE44 alloy was observed by a most recent work [61]. The authors suggested that the shrink of $(Mg, Al)_2Ca$ phase lattice and denuded zones near grain boundaries contributed to the deteriorated creep resistance of the alloy.

More recently, Mn addition was found to be effective in increasing the creep resistance of the AE alloys through strengthening the Mg matrix. Generally, it's considered that small Mn addition has negligible influence on mechanical properties, but it may improve the corrosion resistance. Increasing the Mn addition to 0.3-0.5 wt.% was reported to significantly impede creep

deformation of a die-cast AE43 alloy at 150 °C and 175 °C, as shown in Fig.3 [62]. As increasing the Mn addition level from 0 to 0.3 wt.%, the creep strain was significantly reduced at the test conditions. But further additions to 0.5wt.% showed very marginal effect. The minimum creep rate of the alloy was decreased by at least three orders of magnitude at both 150 °C/90 MPa and 175 °C/75 MPa when 0.5wt.% Mn was added. Zhu and co-workers [62] suggested that the dynamic precipitation of nano-scaled Al-Mn particles contributed to the noticeable strengthening effect, which overwhelmed the softening effect from $Mg_{17}Al_{12}$ precipitates. This result indicates an alternative approach to develop new creep-resistant Mg-Al alloys by offering the possibility of strengthening Mg matrix by precipitation hardening, which previously is not an available option to HPDC Mg-Al alloys due to their weak ageing responses.

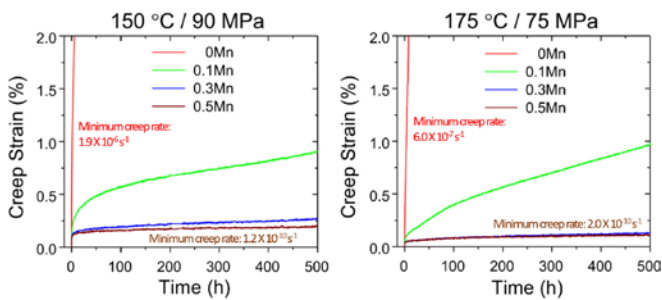


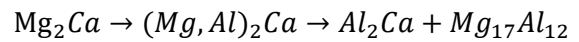
Figure 3 Creep curves of the Mg-4Al-3La alloy with Mn additions at 150 °C /90 MPa and 175 °C /75 MPa (reproduced from [62]).

2.2.3 Alkaline elements additions

Addition of REs can effectively improve the creep resistance of Mg-Al based alloys. However, rare earth elements are also associated with higher cost. Alkaline elements, such as Ca and Sr, are alternatives to REs to improve the creep properties of Mg-Al alloys in order to minimize the cost. Like REs, additions of alkaline elements consume Al solutes, forming more stable intermetallic phases, which effectively suppress the grain boundary sliding and dislocation movements [63]. A number of alkaline elements containing creep-resistant alloys have been developed and commercialized. This includes the Mg-Al-Ca (AX) series [64], Mg-Al-Sr (AJ) series [65] and Mg-Al-Ca-Sr (MRI) series [66]. These alloys exhibited creep strength superior to the AS alloys and AE42, and some even comparable to A380 aluminium alloy at 175 °C [67]. However, Mg-Al alloys with Ca additions were associated with a few casting defects, such as cold shuts, hot cracking and die sticking, particularly when the Ca addition was in between 1wt.% and 2wt.% [68]. Compared to AX series, AJ alloys (Mg-Al-Sr) were reported to exhibit good casting quality [69].

Fig.4a presents creep properties of the Mg-Al-Ca (AX) alloys and AE42 at a range of temperatures and applied stresses. AX alloys evidently had superior creep resistance than AE42 at both 150 °C and 175 °C. It can

be seen that the AX52 alloy had a slightly lower secondary tensile creep rate than AX53 alloy, but 0.15 wt.% addition of Sr enabled the decrease in secondary tensile creep rate of the AX53 alloy. Luo et al. [67] also investigated the creep mechanism of the AX53 alloy. Stress exponent n was calculated as 1.5 (<70 MPa) and 8.5 (> 70 MPa), and creep activated energy Q_c was calculated as 40 (< 150 °C) and 120 kJ/mol (> 150 °C), respectively. The results suggested that grain boundary sliding dominated the creep under 150 °C and 70 MPa, otherwise dislocation climbing was predominant mechanism. The formation of compounds and precipitates in the AX alloys depends on the mass ratio of Ca to Al. An early study [70] suggested that Al_2Ca with C15 structure formed when Ca/Al ratio was below 0.8. Higher Ca/Al ratio led to the formation of Mg_2Ca with C14 structure. Later research [71] indicated a formation sequences of the intermetallic compounds with a decrease in the Ca/Al ratio, which was listed below:



Micrographs of the Al_2Ca with C14 structure and $(Mg, Al)_2Ca$ with C36 structure are presented in Fig.4b and 4c. Al_2Ca phases presented along the α -Mg grain boundaries were considered as the major contributor to creep resistance of the AX51 alloy (Mg-5Al-0.8Ca), while the eutectic phase, $(Mg, Al)_2Ca$, was considered to be responsible for the improved creep resistance of the AX52 and AX53 alloys [72]. In addition, the saturated Ca solute in the die-cast AX alloys might also contribute to strengthen the α -Mg matrix by both solid solution strengthening and precipitation hardening. Disk-shaped Al_2Ca precipitates were observed in an AXJ530 HPDC alloy after ageing for 1 hour, as presented in Fig.5a [73]. The crystallographic orientation relationship between the precipitate and the matrix phase was reported as: $\{111\}_{C15} // (0001)_{\alpha}$, $[01\bar{1}]_{C15} // [0\bar{1}10]_{\alpha}$. As the Al_2Ca precipitated on the basal plane of the Mg matrix, they effectively impeded the dislocation gliding on non-basal planes and therefore improved the creep strength, particularly when a high-volume fraction of the precipitates was obtained.

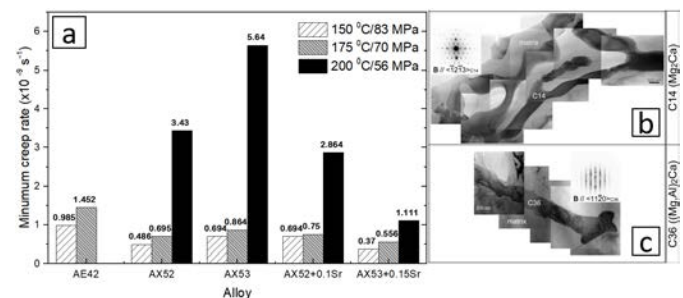


Figure 4 (a) Secondary tensile creep rates of the Mg-Al-Ca alloys and AE42 alloy. (b, c) Bright-field TEM micrographs of compounds Mg_2Ca and $(Mg, Al)_2Ca$ (reproduced from [67, 76]).

The effect of Barium (Ba) addition on improving creep resistance of AX alloys was also investigated. Dieringa and co-workers [74, 75] developed a patented alloy called DieMag422 with a nominal composition of Mg-4Al-2Ca-2Ba (wt.%). It showed one order of magnitude lower steady-state creep rate than that of the AE42 at 200 °C. Ba was rarely used as alloying element in Mg. But, the additional Mg-Al-Ba phases were considered as beneficial phases contributing to the creep resistance of the DieMag422 alloy [75]. Homma and co-workers [76] reported that minor addition of Mn was able to enhance creep resistance of the AX22 alloy. The minimum creep rate ($\dot{\epsilon}_s$) of AX22 alloy with 0.3 wt.% Mn addition was reduced by one order of magnitude at 175 °C/200 °C and 50 MPa. The author [76] suggested that Mn addition did not influence the number density of Al₂Ca precipitates but increased the volume fraction of GP zones and the solid solubility of Ca in Mg matrix. However, such GP zones in Mg-Al-Ca alloy were not observed previously. Highly likely, both the precipitation and solid solution strengthening may corporately contribute to the higher creep strength in the Mn-containing AX series alloys.

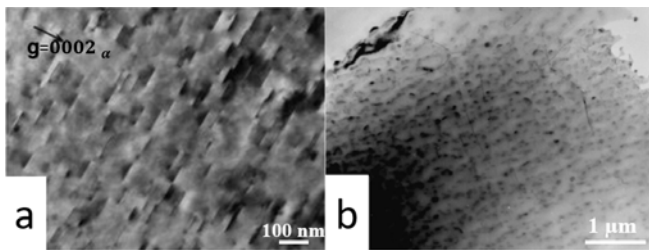


Figure 5 Dynamic precipitates detected in (a) AXJ530 and (b) MRI 230D HPDC alloys (reproduced from [73,80]).

As mentioned above, minor addition of Sr in Mg-Al-Ca based alloys resulted in a further improvement in creep resistance, which led to the development of AXJ alloys and another series, MRI alloys. MRI alloys were developed in Dead Sea Magnesium and Volkswagen AG [77]. Unlike the AX alloys, MRI alloys contain higher additions of Al but lower Ca content, of which typical alloys are MRI153 (Mg-8Al-1Ca-0.3Sr) and MRI230 (Mg-6.5Al-2Ca-1Sn-0.3Sr) [78]. MRI153 alloy was developed through modification of the AZ91 by replacement of the Zn with Ca, slightly lowering the Al content and microalloying with Sr. This alloy exhibits better castability, higher strength and creep resistance at elevated temperatures [79]. Combined additions of Ca (1 wt.%) and Sr (0.3 wt.%) enable the formation of stable intermetallic phase, (Mg, Al)₂Ca, which was reported to be effective in improving elevated temperature performance of AZ91 under 150°C. The MRI230D alloy was designed for the automotive powertrain applications with high creep resistance at temperature up to 190 °C [77]. The creep behaviour of AE, AX alloys and the MRI alloys at 150 °C and 90 MPa are exhibited in Fig.6. At the testing condition of 150 °C and 90 MPa, both MRI230D and

AXJ530 alloy had superior creep behaviour to other Mg-Al based alloys, and they were creep-resistant comparable to the A380 Al alloy. In comparison, MRI153A showed less creep resistance which was similar to AE42. Amberger et al. [80] examined the microstructure of MRI230D and concluded that the high creep resistance of this alloy was attributed to the formation of highly connected secondary phases (Al₂Ca) along grain boundaries, which were able to effectively shield load from the softer α -Mg matrix. The authors termed such microstructure as high interconnectivity of intermetallic compounds, which contributed to the high creep resistance of the alloys, whereas alloys containing disconnected intermetallic compounds (low interconnectivity) exhibited lower creep resistance. Furthermore, creep-induced precipitates Al₂Ca was also detected and attributed to the improvement of creep resistance in MRI 230D. Fig.5b presents the TEM morphology of dynamic precipitates Al₂Ca detected in MRI 230D alloy. Mondal et al. [81] investigated compression creep behaviour of MRI230D HPDC alloy at the stress ranged from 60 MPa to 120 MPa and temperatures of 175 and 200 °C. The work determined the stress exponent as 5.1 and hence summarized dislocation climb as the dominant creep mechanism.

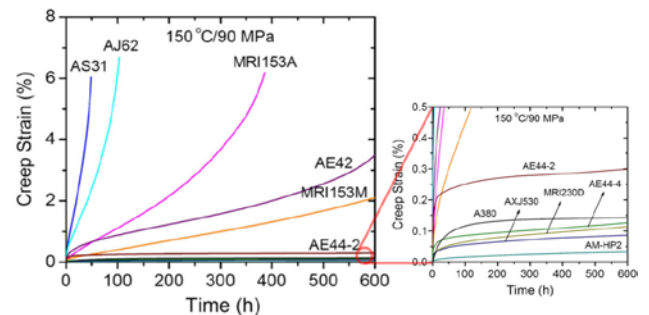


Figure 6 Creep curves of MRI alloys in comparison with other Mg-Al alloys and A380 aluminium alloy at 150 °C /90 MPa (reproduced from [78]).

AJ series HPDC alloys offer the good properties in terms of strength, ductility, creep, castability and cost. Hence, the benchmark AJ alloy, AJ62 (Mg-6Al-2Sr), were used in the production of BMW I6 crankcase [82]. Table 2 lists the creep strain of AJ alloys in comparison with other Mg-Al alloys at 150 °C and 200 hours [65]. The four alloys (AS41, AE42, AJ52x and AJ62x) exhibit similar creep resistance at an applied stress of 50 MPa, but AJ52x and AJ62x alloys evidently keep lower creep strain than others when the applied stress was up to higher level, of 70 MPa. The microstructure of AJ alloys is dependent on the Sr/Al ratio. When the ratio is below 0.3, lamellae Al₄Sr eutectic phase forms, whereas above this ratio massive Mg-Al-Sr ternary intermetallic compounds appear. Kunst et al. [83, 84] conducted the investigation to the creep mechanism of AJ62 and AJ63 HPDC alloy. They [83] determined the stress exponent $n = 9$ and activation energy Q_c of 92 kJ/mol for AJ63 HPDC alloy within the stress ranging from 35 MPa to

90 MPa at 150-175 °C. They concluded that the grain boundary diffusion was the dominated creep mechanism while the high stress exponent n indicated dislocation gliding was involved in creep under the tested conditions. As to AJ62, the stress exponent n and activation energy Q_c were calculated as 8 and 147 kJ/mol under the stress range of 35-90 MPa at 150-175 °C [84]. The authors suggested that dislocation climb with additional strengthening effect by Mg-Al-Sr ternary particles led to the increase in the stress exponent. However, the chemical composition of the ternary intermetallic compound were not ultimately verified and has been ever reported as $Mg_{13}Al_3Sr$, $Mg_{11}Al_3Sr$ and Mg_9Al_3Sr [65, 84, 85]. Nevertheless, such ternary compounds were not stable and subjected to decompose into α -Mg and Al_4Sr at temperatures over 175 °C. In addition, it was found that Sr solute did not provide further strengthening to α -Mg matrix of die-cast alloys due to its limited solubility in Mg. However, TEM observation confirmed that the matrix of the AJ62 was reinforced by the existence of Al-Mn intermetallic particles within the grains [84].

Table 2 Tensile and compressive creep strains of AJ alloys in comparison with other Mg-Al alloys at 150 °C for 200 h [65].

Alloys	Creep strain (%) at 150 °C for 200 h	
	Tensile test at 50 MPa	Compressive test at 70 MPa
AZ91D	2.7	21
AS41	0.05	6.13
AE42	0.06	2.16
AJ62x	0.05	1.73
AJ52x	0.04	0.24

2.3 Section summary

In summary, modification of the Mg-Al based alloys has been a common approach to improve the creep resistance of Mg alloys, particularly for the high pressure die cast Mg products. Fig.7 compares the creep strength of a number of commercialized Mg-Al based HPDC alloys with the A380 aluminium alloy. In terms of the creep strength, AS alloys showed poor creep resistance and was only marginally better than AZ91. While MRI230D and AXJ530 alloys were particularly of interest as they exhibited the highest values among all the Mg-Al die-cast alloys and comparable to the A380 alloy at 175 °C. The better creep resistance of these two alloys is most likely attributed to the extra strengthening from creep-induced or dynamic precipitates as mentioned in Fig.5a and 5b [73, 80]. Pekguleryuz & Celikin [3] summarized creep mechanisms for AS, AE, AX, and AJ alloys. Grain boundary sliding and migration were considered as the dominating creep mechanism at low stress levels and low temperatures (under 50 MPa and 175 °C). At high stress and temperatures, dislocation climbing and gliding promoted the creep. In addition, particle reinforced cross-slip was also identified during creep at

70 MPa and 200 °C in an AJ51 alloy [86]. Additions of Si, Ca, Sr and REs are supposed to improve the creep strength of Mg-Al alloys in different degrees through formation of either Al-containing or Al-free thermally stable intermetallic compounds along grain boundaries, inhibiting the grain boundary sliding. Their strengthening effects generally are associated with several factors, including the thermal stability, morphology, interconnectivity of intermetallic compounds, etc. The presence of higher thermally stable secondary phases will give rise to the better grain boundary reinforcement. However, coarsening phase like Mg_2Si is reported to adversely degrade mechanical properties even though it has a high melting point. Further refinement on the morphology always provide with improvement in creep properties. Additionally, high interconnectivity of intermetallic phases has been demonstrated to effectively shield load from Mg matrix [80]. Figs. 8 presents SEM images showing microstructure of five die-cast Mg-Al based alloys, which have various creep properties according to Fig.7. In comparison with AZ91, AS21 and AE42, the intermetallic phases along the matrix of AXJ530 and MRI230D were much finer and interconnected, hence attributing to higher creep resistance than others.

Despite such advantages, the formation of these high-melting temperature compounds has resulted in the reduction in the solid solution strengthening effect due to the consumption of solutes. Furthermore, ageing hardening is invalid to increase the creep strength, because the HPDC alloys are not heat treatable and the intermetallic compounds with high-melting temperatures cannot be dissolved into the α -Mg matrix during solid solution treatment, which corresponds to limited ageing response. The solid solution strengthening of the saturated Al solute in α -Mg is very limited and the precipitation strengthening of $Mg_{17}Al_{12}$ precipitates at elevated temperature is also very marginal. Hence, dislocations across the α -Mg matrix still readily climb or cross slip. As shown in Fig. 4a, a remarkable increase in creep rate of Mg-Al-Ca alloys occur once the temperature is over 175 °C. Hence, the applications of the Mg-Al based alloys are limited below 200 °C at present. For higher temperature applications, Mg-RE based alloys were developed.

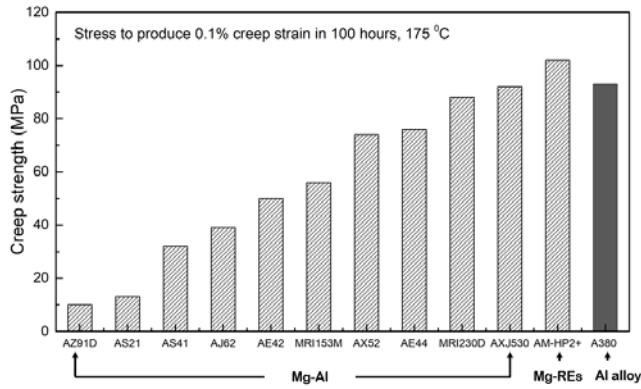


Figure 7 Creep strength of commercial Mg die-cast alloys to produce 0.1% creep strain in 100 hrs, at 175 °C (reproduced from [67, 87]).

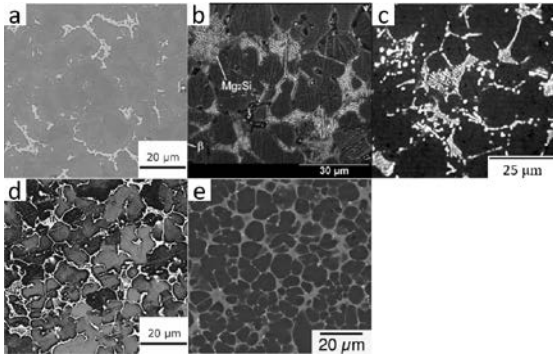


Figure 8 Morphology of intermetallic phases of die-cast (a) AZ91 alloy; (b) AS21 alloy; (c) AE42 alloy; (d) MRI230D alloy and (e) AXJ530 alloy (reproduced from [38, 52, 73, 80]).

3. Mg-REs based alloys

The key point of modification of Mg-Al based alloys for improving creep resistance is to arrest the Al atoms through addition of other solutes that have high affinity with Al to inhibit the formation of $Mg_{17}Al_{12}$. However, so far research has shown that the increment is limited and the alloys can only be used below 175 °C. Another approach to develop creep resistant Mg alloys is to develop Al-free alloys. They are normally associated with high ageing response and can be used after gravity casting to minimize the cost. For higher temperature applications, several Mg-Th based alloys were developed by Magnesium Elektron Ltd., such as the HK31 and HZ32 alloys [10]. They were reported to have good creep resistance at temperatures up to 350 °C, which was attributed to the ordered precipitates formed during ageing. However, the radioactivity of Th restricted its usage in Mg alloys. Previous research has been focused on lanthanide series elements and yttrium. In terms of the number of valence electrons of the REs, REs-containing Mg alloys are categorized into two groups [3, 10]. The first is the Ce group (La-Eu) with two valence electrons and the second is the Y group (Y and Gd-Lu) with three valence electrons. Elements in the Y group have a higher solid solubility in Mg than those in the Ce group, and alloying of Mg with solutes in the Y group leads to better ageing response resulting from the formation of metastable coherent precipitates [88-90]. Up until now, the highest elevated temperature performance of Mg alloys has been achieved through

addition of solutes in Y group, such as Y and Gd. Unfortunately, the excessive cost of this type of REs has limited the industry applications of Mg alloys containing the Y group alloying elements to gravity castings. Compared with the Y group, metals in the Ce group are generally lower cost and there is the potential to use these elements to produce creep-resistant alloys for HPDC. Although technically not belonging to either the Y group or the Ce groups, Scandium (Sc) has also been widely investigated in the attempt to develop creep-resistant Mg alloys and promising results have been found (covered more details in Section 3.4).

3.1 Mg-REs based alloys for HPDC

Although Mg-Al based alloys are attractive to HPDC due to their high castability, as previously established it is the Al solute that is the major cause of low creep resistance. To completely eliminate the negative influence of Al, Elektron Ltd in UK successfully developed a number of non-Al containing HPDC Mg alloys, of which the MEZ (Mg-2.5RE-0.3Zn-0.3Mn) alloy is the benchmark, exhibiting good creep resistance superior to AE42 (Mg-4Al-2REs) at 175 °C [53, 91]. Fig.9 shows the creep curves of both the MEZ and AE42 alloys in tension and compression creep tests. At lower temperature and stress (150°C and 70 MPa), the creep behaviours of both alloys were very close. However, at higher temperature and/or higher stress (175°C and 80/100 MPa), the MEZ showed improved creep resistance. It was considered that the $Mg_{12}RE$ intermetallic compound that formed in the interconnected eutectic structure along grain boundaries was responsible for the better creep resistance than AE42 since $Mg_{12}RE$ was more stable than $Al_{11}RE_3$ [91]. The dominant creep mechanism was determined as dislocation climbing at 150 and 175 °C at stress levels below 70 MPa ($n= 5.5$ and 7.2 respectively). Higher stress levels resulted in the power law break down [53].

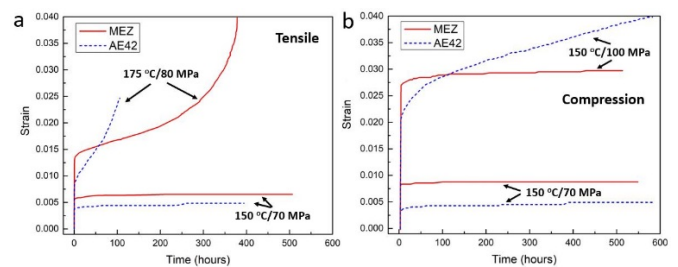


Figure 9 Creep curves of the MEZ and AE42 alloys at 150 °C / 70 MPa and 175 °C / 80 MPa in (a) tension and (b) compression (reproduced from [53]).

Further studies have verified that the RE saturated solid solution also plays important roles in improving creep resistance of Mg alloys. Unlike Al, strengthening effect on creep resistance by REs, i.e. Gd, Y and Nd, in solid solutions has been widely reported [10, 13, 92, 93]. As stated above, REs have been added into Mg-Al based alloys, but their solute strengthening to creep strength was limited since the majority of the added REs was

consumed by formation of RE-Al intermetallic compounds. In Al-free Mg alloys, Zhu et al. [94, 95] concluded that the degree of supersaturation of RE solutes in the α -Mg matrix was a predominated factor that determined the creep strength of Mg-RE based die cast alloys. It was reported that Mg-2.5RE-0.6Zn HPDC alloy with addition of Nd-rich REs had lower primary creep rates but similar secondary creep rate with the alloy containing La-rich REs. The higher solubility of Nd (0.63 at.%) than La (0.04 at.%) in Mg was considered as the major contributor to the higher creep resistance [94]. The same group [95] compared the creep resistance of Mg-Nd, Mg-Ce and Mg-La die-cast alloys and found that the creep strength was closely related to the solid solubility of the RE solute. Fig.10a presents the tensile creep curves of three Mg-REs HPDC alloys tested at 177 °C and 90 MPa. The highest solid solubility of Nd corresponded to the highest creep resistance among these three systems, followed by Mg-Ce and Mg-La alloys. Figs.10 (b-g) are the microstructures of the Mg-REs alloys before and after creep tests. Mg-Nd alloy, which showing the highest creep resistance, contained the lowest fraction of intermetallic compounds but denser dynamic precipitates after creep testing. Whereas, the Mg-La alloy with the lowest creep strength contained the highest amount of secondary phases and no dynamic precipitation was observed. Hence, solution strengthening and/or dynamic precipitation, rather than grain boundary pinning effect, may govern the creep strength of Mg-REs based die-cast alloys. Based on these results, a new AM-HP2+ (Mg-La-Ce-Nd-Zn) HPDC alloy was developed [96]. Compared with the MEZ alloy, the AM-HP2+ alloy exhibited better creep resistance within the temperature range from 150 °C to 200 °C. In addition to the effect of the interconnected $Mg_{12}RE$ secondary phases, supersaturated Nd solute within α -Mg matrix provided either solid solution strengthening or dynamic precipitation strengthening (Mg_3Nd) during the creep process at high temperatures [78, 96]. More recently, the role of Zn addition in strengthening creep properties of Mg-REs HPDC alloy was verified by Choudhuri et al. [97]. It was reported that micro-alloying Zn in Mg-Nd HPDC alloy extended creep lifetime by 600% and reduced minimum creep rate by one order of magnitude. The author clarified that the increments in creep life were primarily attributed to the increase in vacancy diffusion barrier, which caused by the strengthened interplanar bond stiffness in alloy due to the presence of both Zn and Nd. Besides, the formation of new Zn-stabilized γ'' precipitates on basal planes and reduction in activated cross-slip caused by Zn solutes were complementary mechanisms enhancing creep performance of the alloy. As shown in Fig.7, the creep strength of the AM-HP2+ is higher than all other Mg-Al HPDC alloys and even greater than the A380 aluminium alloy at 175 °C.

However, dynamic precipitation are not positive to creep resistance of Mg-REs HPDC alloy in all case. Zhu and co-workers [78] considered that solid solution strengthening played a more important role than dynamic precipitates in creep strength of Mg HPDC alloys if the precipitate phase was not thermally stable and coarsened rapidly during prolonged creep process. Furthermore, Gravras et al. [98] found that, after solid solution treatment, Mg-0.45La-1.18Y (at.%) HPDC alloy exhibited an order of magnitude lower secondary creep rate than the Mg-0.45La-0.63Nd (at.%) alloy at 177 °C/90 MPa even though the dynamic precipitation was only observed in the latter alloy. Moreover, as shown in Figs.11, the Mg-0.45La-1.18Y alloy after peak aging at 160 °C showed no increment but slightly decrease in creep resistance at 177 °C/90 MPa. Precipitates in this Mg-La-Y alloy should be thermally stable since the alloy did not over aged until 1700 hours, but such thermally stable precipitates still couldn't give rise to a better creep resistance. The results implied that the solid solution strengthening by Y solute may be sufficient to achieve high creep resistance for the alloy and additional ageing may be unnecessary. A recent work by Abaspour et al. [99] suggested that the effect of short-range order (SRO) of solute in Mg solid solution governed the creep behaviour of this type of alloys. Details about the SRO is reviewed in Section 3.2.2 below.

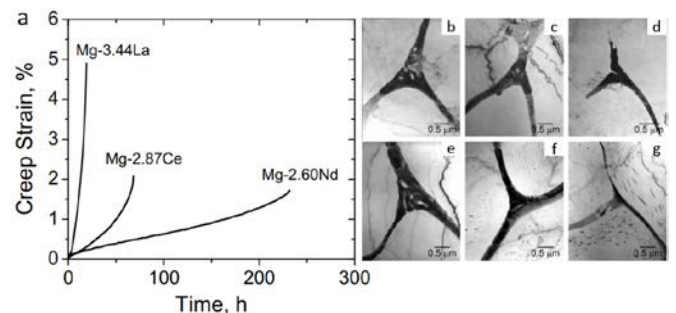


Figure 10 (a) Creep curves of Mg-REs HPDC alloys at 177 °C/90 MPa. (b-g) Corresponded TEM micrographs of microstructures of Mg-La (b and e), Mg-Ce (c and f) and Mg-Nd (d and g) before and after creep test (reproduced from [95]).

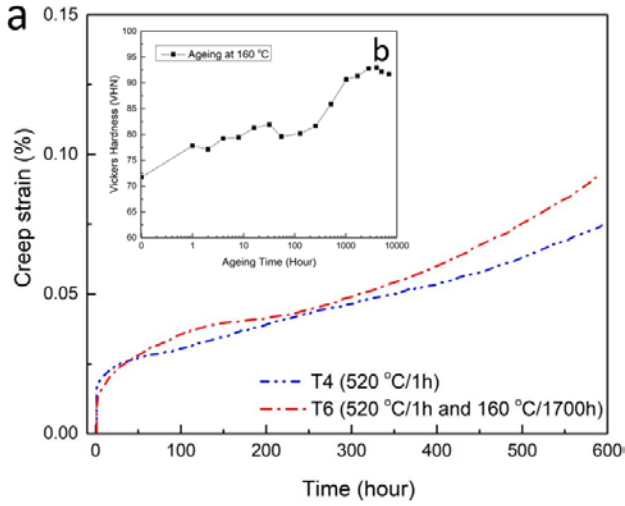


Figure 11 (a) Creep strain comparisons of T4 (520 °C/1h) and T6 (520 °C/1h and 160 °C/1700h) for Mg-0.45La-1.18Y(at.%) alloy tested at 177 °C and 90 MPa. (b) Ageing curve of Mg-0.45La-1.18Y alloy at 160 °C (reproduced from [98]).

3.2 Mg-(Y group) based alloys for gravity casting

The high solid solubility of gadolinium (Gd) and the similar element yttrium (Y) in Mg provides high potency to effectively improve creep resistance of Mg alloys. In addition, although neodymium (Nd) belongs to Ce group, it has a similar potency to Gd and Y to achieve remarkable ageing response and has been extensively used with Y group REs to develop creep-resistant Mg alloys. The maximum solid solubilities in Mg are 4.53 at.% for Gd and 3.40 at.% for Y and 0.63 at.% for Nd at their eutectic temperatures, respectively [100]. In comparison with Al and Zn solutes, the solid solution strengthening by Gd and Y are much higher. Table 3 lists the solid solution strengthening rates of these four solutes [101]. Suzuki et al. [93] also reported that the creep resistance of Mg-0.2 at.% Y alloy was one order of magnitude higher than Mg-3at.% Al alloy, as shown in Figs.12a. Maruyama et al. [13] figured the higher solid solution strengthening effect as the major cause of the largely higher creep strength of Mg-Y than Mg-Al. Based on those merits, Mg-(Y-group) based alloys were widely designed as heat-treatable alloy in gravity casting for achieving good mechanical and creep performance.

Table 3 Solid solution strengthening rates for Y, Gd, Zn and Al atoms in Mg. δ is misfit parameter for atomic size; η is for shear modulus and ϵ is interaction parameter [101].

Solut e	Misfits			Strengthening rate		
	δ	η	ϵ	dH_p/dC	$d\sigma/dC^{1/2}$	$d\sigma/dC^{2/3}$
Y	+11 %	0.40 4	1.8 1	13.2	737	1249
Gd	+11 %	0.24 7	1.7 8	14.0	683	1168
Zn	- 17%	0.86 7	2.8 5	9.0	578	905
Al	- 14%	0.41 9	2.2 8	3.3	118	198

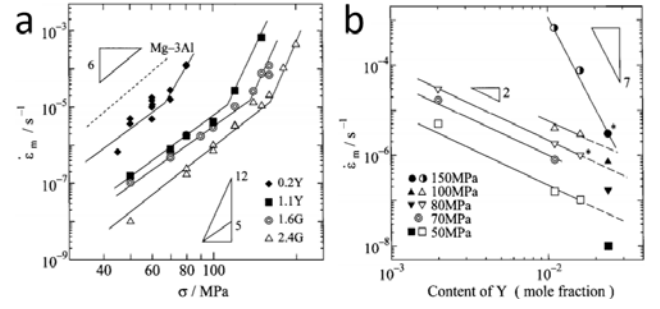


Figure 12 (a) Stress dependence of minimum creep rate of Mg-Y binary alloys in comparison with Mg-Al alloy at 277 °C. Concentration is in mole fraction. (b) Concentration dependence of minimum creep rate of Mg-Y binary alloys at 277 °C. Solid marks indicate the presence of dense precipitates in alloys [93].

3.2.1 Precipitation hardening

Generally, the metastable coherent precipitates with high thermal stability formed after incubation time are responsible for the good precipitation strengthening of Mg-REs alloy, such as $Mg_{24+x}Y_5$ in aged Mg-Y binary alloys [10]. Suzuki et al. [93] identified the stress exponent n for Mg-Y alloys as 5 at low stress levels and power-law breakdown ($n = 12$) at high stress levels, indicating the dislocation climb as predominated creep mechanism as presented in Fig.12a. Also, Fig.12b reveals that heat-treated Mg-Y alloys containing precipitates exhibited remarkable reduction in minimum creep rate in a range of stress levels at 277 °C. The combined addition of Zn was reported able to promote the formation of the $Mg_{24+x}Y_5$ precipitates through decreasing the Y solutes in matrix [102]. In addition, Suzuki et al. [103] found that Zn addition reduced the stacking fault energy of Mg, which contributed to an improvement in creep resistance of Mg-Y alloys. Moreover, the ageing response of Mg-Y alloys can also be increased by Nd additions, which led to further improvement of the creep resistance. Based on these outcomes, benchmarked WE series alloys were developed and have become the most important Mg-REs alloy used in aerospace and automotive applications. The typical alloys are the WE43 (Mg-4Y-2Nd-1-Hf-0.6Zr) and WE54 (Mg-5Y-2Nd-2Hf-0.6Zr). Fig.13 compares the creep strength of WE gravity casting alloys and Mg HPDC alloys. It illustrated the good creep resistance of the T6-treated WE43 and WE54 alloy, which are unachievable by the current HPDC Mg alloys. Wang et al. [104] studied the creep mechanism of the aged WE43 alloy at temperatures ranging from 150 °C to 250 °C and stresses ranging from 30 to 300 MPa. The stress exponent n was about 4-5 with the range of temperatures over 200 °C and stress below 100 MPa while the stress exponent increased to 10 below 200 °C and above 200 MPa. The activation energy was determined to be 118.7 kJ/mol at temperatures from 150 °C to 200 °C and 232.9 kJ/mol from 200 °C to 250 °C. The results suggested that dislocation climbing

controlled the mechanism for low temperature creep and shifted to cross-slip at higher temperatures.

During ageing, the precipitation process in WE alloys involved in the evolution of metastable β'' phase with ordered $D0_{19}$ structure, metastable based-centred orthorhombic (bcbo) β' , face-centered cubic β_1 and equilibrium β [105]. At peak ageing condition, the β' ($Mg_{12}NdY$) and β ($Mg_{14}Nd_2Y$) plate precipitates form on $\{1\bar{1}00\}_\alpha$ planes as shown in Fig.14a. The precipitates were oriented on the prismatic planes and distributed in interlocking triangular arrangement, hence can effectively hinder the basal dislocation slip and rise creep resistance of the WE alloys. But those precipitates were subject to coarsening at temperatures over 200 °C, resulting in the reduction in creep resistance [104, 106]. A most recent work by Kang et al. [107] further clarified that the thermal stability of β'' and β' precipitates depended on the initial temperature of aging treatment. The peak-aged WE43 alloy at 250 °C showed superior creep resistance to the peak-aged alloy at 225 °C since initial precipitates in former were more thermally stable.

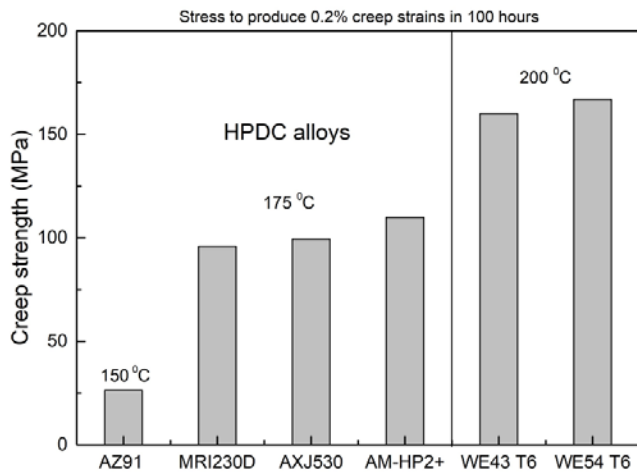


Figure 13 Creep strength of selected Mg alloys to produce 0.2% creep strains in 100 hours (reproduced from [10, 78]).

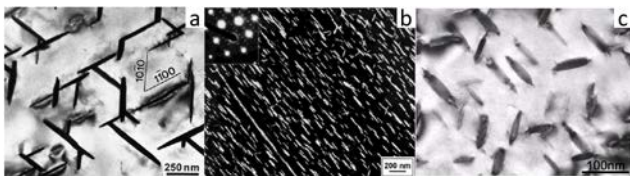


Figure 14 TEM micrographs showing (a) *bcbo* β' precipitates in peak-aged WE54 alloys at 250 °C [106]; (b) *bcbo* β' precipitates in Mg-15Gd alloy annealed up to 330 °C [109]; (c) *bcbo* β' precipitates in Mg-10Gd-3Y-0.4Zr alloy peak aged at 250 °C for 16 hours [115].

In addition to Y, Gd has also been found to be very effective in improving the creep resistance of Mg alloys. The higher solid solubility enabled higher additions of Gd up to 20 wt.%. Fig.15 displays the minimum creep rate of the WE alloys in comparison with Mg-Gd binary alloys tested at 200 °C and 60 MPa. Binary Mg-Gd alloys after aging exhibited better creep resistance than

WE43. The precipitation sequence of the Mg-Gd binary alloys is similar to the Mg-Y-Nd based (WE) alloys. At peak aged stage, the base centred orthorhombic (bcbo) Mg_7Gd β' plates precipitate on $\{1\bar{2}10\}_\alpha$ prismatic planes and display in triangular morphology as shown in Fig.14b [109]. It is believed that the Mg_7Gd β' plates are responsible for the excellent creep resistance of the Mg-15wt.%Gd alloy. During ageing at higher temperatures, the β' plates were known to transfer to equilibrium Mg_5Gd β plates. But unlike the β ($Mg_{14}Nd_2Y$) precipitates in the WE alloys, the stable Mg_5Gd β plates could still effectively hinder dislocations movement during creep at 300 °C and 60 MPa. However, such precipitation hardening of binary Mg-Gd alloys could only be achieved when the Gd content was over 10 wt.% and little precipitation response was found in Mg-Gd alloys with Gd content below 10 wt% [105, 109]. The poor precipitation hardening response of dilute Mg-Gd alloy is also demonstrated in Fig.15. Mg-10Gd alloy after aging treatment (T6) has a marginal effect on suppressing creep while the creep rate of aged Mg-15Gd alloy is noticeably reduced when compared with the as-cast alloy.

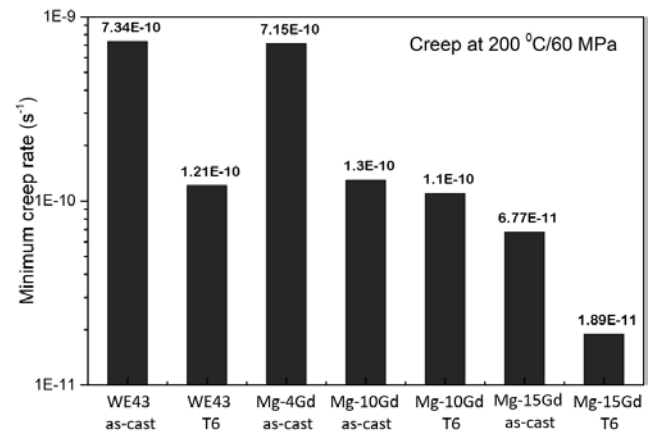


Figure 15 Comparison of secondary creep rates of Mg-Gd binary alloys (reproduced from [10, 108]).

To further improve the performance of RE-containing Mg alloys, the combined effects of Gd and Y were also widely investigated. The addition of Y into Mg-Gd alloys produced similar microstructure as the WE54 alloy, together with remarkable ageing response resulted from the triangular arrangement of β' and β precipitates in the alloy at T6 condition, as shown in Figs.14c. Accordingly, a number of Mg-Gd-Y-Zr alloys (Zr was used to refine the as-cast grains) with high strength and high creep resistance have been developed and patented mostly in China due to its rich REs resource [110-114]. For example, the Mg-8Gd-4Y-0.8Zr alloy [111] achieved a better creep resistance than WE54 at applied stress of 100 MPa and temperatures from 250 °C to 300 °C. The Mg-12Y-5Gd-2Zn-0.5Zr alloy exhibited a creep rate that was one order of magnitude lower than that of WE54 when the creep test was done at 300 °C and 50 MPa [113]. The stress

exponent and activation energy were determined in the range of 3.7-5.2 and 160-240 kJ/mol, for the Mg-Gd-Y-Zr alloys (30-120 MPa and 250 °C-300 °C) [111, 114]. Hence, dislocation creep was considered as the dominant creep mechanism in the test conditions. It was believed that higher thermal stability of the β' phase was responsible for the higher creep resistance of the Mg-Gd-Y-Zr alloys in comparison with the WE54 [115]. However, those concentrated Gd and Y containing Mg alloys did have high creep resistance. But, they also suffered from the high cost and increased density (7.89 gm/cm³ for Gd and 4.5 gm/cm³ for Y vs 1.74 gm/cm³ for Mg). This limited their wider applications.

In order to reduce the usage of REs, a progress in Mg research was to add Mn and Sc into the Mg-Gd or Y alloys. Typical alloys include Mg-5Gd-0.3Sc-1Mn and Mg-4Y-1Sc-1Mn alloys [116]. The formation of additional disk-like fine Mn₂Sc basal precipitates was considered as the major cause for higher creep resistance even with lower REs content, because Mn₂Sc precipitates were more thermally stable than cbco β' Mg-REs precipitates, at least up to 350 °C. Table. 4 lists the secondary (steady-stage) creep rates of various Mg-Gd and Mg-Y based alloys. Both the as-cast Mg-5Gd-0.3Sc-1Mn and Mg-4Y-1Sc-1Mn alloys had a lower creep rate than the T6-treated WE43 and Mg-Gd binary alloy. A recently patented alloy developed by Pan's team [117], Mg-4Y-0.5Sc-1Mn-0.6Zn, was reported having higher creep resistance. The peak-aged alloy had a minimum creep rate that was one order of magnitude lower than the Mg-4Y-1Sc-1Mn alloy as shown in Table.4. In addition, Zn additions, up to 2wt.%, were also found to noticeably improve the age hardening response and the creep strength of the Mg-Gd alloy [118, 119]. A later relevant work [120] identified the formation of metastable basal Mg-Gd-Zn precipitates γ'' and γ' , contributing to the strengthening effect. Further trace addition of Ca up to 0.6wt.% into Mg-11.6Gd-1.2Zn alloy was reported that reduced the minimum creep rate by around 50% when creep at 250 °C and 110 MPa [121]. Besides refined Mg5Gd precipitates formed on the prismatic planes and the extra dense basal GP zones were detected. They worked as strong obstacles for movement of basal dislocations. Additionally, the LPSO phases were likely stabilized by trace Ca addition as well.

Table 4 Minimum creep rates of various magnesium alloys at 300 °C and 30 MPa [116, 117].

Alloy (wt.%)	Minimum creep rate (s ⁻¹)
WE43 T6	1.10×10^{-6}
Mg-15Gd T6	4.39×10^{-7}
Mg-4Y-1Sc-1Mn as-cast	6.62×10^{-8}
Mg-5Gd-0.3Sc-1Mn as-cast	2.49×10^{-8}
Mg-4Y-0.5Sc-1Mn-0.6Zn T6	8.62×10^{-9}

In all of the creep-resistant Mg-(Y group) alloys discussed above, the high creep strength resulted from the formation of highly stable precipitates that are homogeneously distributed in the α -Mg matrix after heat treatment. It is believed that these stable precipitates can effectively hinder the dislocation movement at high temperatures, and hence decreasing the creep rate. However, these alloys, especially Mg-Gd alloys, contain high contents of REs in order to achieve a high fraction of the metastable precipitates. High level additions of Y, Gd and Nd are associated with two issues. As previously eluded to, these issues include the high cost and the increased density of the alloys, which reduces the appeal for lightweight magnesium alloys. Therefore, it is of commercial interest to explore creep-resistant Mg alloys with significantly lowered RE content. Introduction of complementary precipitates to low Gd or Y containing Mg alloys, e.g. by Mn, Sc and Zn as stated above, is a promising approach. Recently, the exploitation of solid solution strengthening effect of Y group elements on Mg alloys has attracted increasing interests of researchers and is another potential approach.

3.2.2 Solid solution strengthening

In most non-ferrous alloys, including Mg alloys, additions of solutes form substitutional solid solutions which generally lead to limited solid solution strengthening. Hence, precipitation strengthening and strain hardening are commonly used to improve the strength of these types of metallic materials. However, as mentioned above, Gavras and co-workers' recent work [98] showed that the HPDC Mg-La-Y alloy had a much lower secondary creep rate than the Mg-La-Nd alloy even though the latter was associated with dynamic precipitation strengthening effect. Lower creep rates were also reported for the Mg-La (~1 at.%) Nd, Gd & Y HPDC alloys as solid solution treated than aged [98]. In 2014, Lentz et al. [122] suggested that solid solution strengthening of Mg by Y and Nd was more effective than precipitation strengthening of Mn and Ce. Hence, it is reasonable to consider that precipitation strengthening does not always lead to the optimal creep resistance. Solid solution strengthening effect of Y, Gd and Nd may result in better creep strength than the precipitation strengthening for Mg alloys in some cases.

It is generally accepted that solid solution strengthening of alloys arising from the elastic interaction between the strain field of solutes and dislocations [123]. Gao et al. [101] concluded that elastic interactions failed to explain the high solid solution effect of Y and Gd. They pointed out that based on the classical model, the calculated misfit parameters, ϵ , of Zn and Al solutes were larger than that of Y and Gd (listed in Table 3) yet the strengthening rate of Zn and Al in Mg was lower than Y and Nd. The authors [101] suggested that the valency effect was responsible

for the abnormal solid solution strengthening effect of Y and Gd. Unfortunately, there is still a lack of direct evidence confirming this assumption. Another assertion was raised recently through a thermodynamic analysis based on the enthalpy of mixing by Abaspour et al. [99]. It was considered that the higher strengthening effects of dilute Y, Gd and Nd solutes in Mg was attributed to the relatively high tendency for developing short range order (SRO) in solid solutions. More importantly, it has been clarified that SRO can curtail the cross slip and suppress dynamic recovery, therefore introduced athermal forest hardening to high-temperature strength and creep resistance of alloys. The tendency of solutes in Mg to develop SRO was ranked in a descending order as [99]:

$$Y, Gd > Nd, Ca > Zn, Ag, Sn > Al > Sb, Sr$$

Y and Gd were suggested having the highest potency on developing SRO and therefore significantly increasing the creep resistance of Mg alloys, followed by Nd. Later, research from the same group [124, 125] experimentally verified the above hypothesis in terms of the compression and stress relaxation behaviours using binary Mg-M (M denotes the solutes) alloys that were just solid solution treated. It was found that the stress relaxation resistance at 180 °C was consistent with the order forming the SRO of solutes. At the same addition level of about 1 at.%, Gd, Y, Nd and Ca containing Mg binary alloys exhibited superior strength and stress relaxation resistance at elevated temperatures as shown in Fig.16. Mo et al. [126] subsequently developed a number of Mg-3Gd-2Ca (wt.%) based creep-resistant alloys based on this outcome. Due to the comparable effect of Ca solute to REs in producing SRO as predicted, 2 wt.% Ca was added to replace the high addition level of Gd in the published alloy Mg-6Gd-2Zn-0.6Zr alloy [118]. The as-solution treated Mg-3Gd-2Ca based alloys showed compatible compression strength and an improved stress-relaxation resistance at 180 °C compared with Mg-6Gd-2Zn-0.6Zr alloy. This work not only provided with evidence supporting the SRO effect in Mg solid solution, but also indicated a potential approach using Ca to replace more expensive REs in the development of lower-cost and lighter creep-resistant Mg alloys.

However, due to the lack of direct microstructural evidence verifying this hypothesis, other researchers argued this SRO assumption. Nie et al. [127] presented results demonstrated a structural relationship between the solute clusters having short-range order formed in Mg-Nd and Mg-Y alloys and the subsequent GP zones. As this type of SRO was considered as unstable and disappeared in long-term ageing, it was unable to contribute to the creep resistance. Matsuoka and co-workers [128] also only observed the short-range order solutes cluster in the early stages of aging in a Mg-Gd-Y alloy using HAADF-STEM. Hence, the SRO

hypothesis needs further investigation. But, previous studies [124-126] indicated that solid solution strengthening of dilute Y, Gd and Nd solutes may play a more important role than precipitation strengthening in improvement of the creep resistance of Mg alloys. This offers an alternative approach to develop low REs-containing creep-resistant cast Mg alloys.

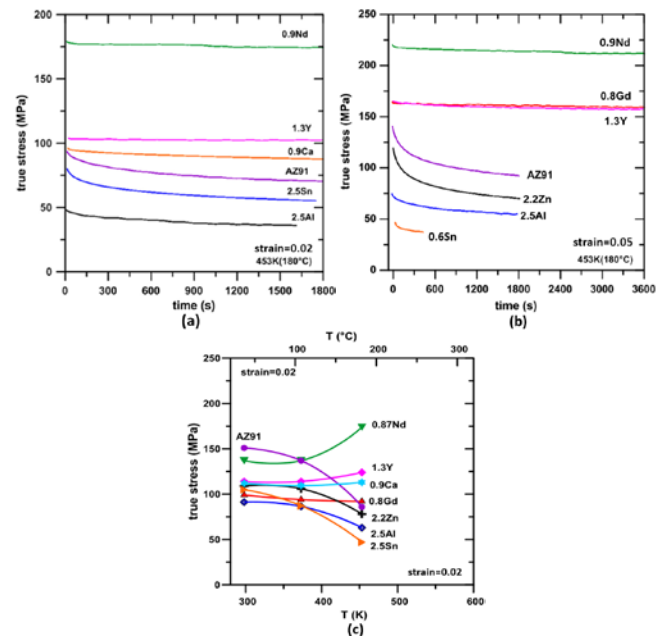


Figure 16 Stress relaxation behaviour of binary Mg alloys at 180 °C at an applied strain of (a) 0.02; (b) 0.05. The flow stress of alloys as a function of the temperature for applied compressive strain of 0.02 (c). The figure preceding each solute is its concentration in at.% (reproduced from [124, 125]).

3.3 Mg-(Ce group) based alloys for gravity casting

Cast Mg-Ce alloys with Ce content ranging from 0.06 to 6 wt.% were extensively investigated and reported in the 1950s to 60s [129, 130]. Mg₁₂Ce intermetallic compounds were considered as the major strengthening phase. In the early 2000s, it was found that Mn addition could enhance the creep resistance of Mg-Ce alloys through promoting the precipitation response. Weiss et al. [131] investigated the creep of Mg-1.7RE (Ce rich)-0.3Mn alloy at 190-210 °C and 50-60 MPa, and reported that the secondary creep rate of Mg-2Ce-0.3Mn alloy was an order of magnitude lower than the AE42 and AS21 alloys at T6 condition. The determined activation energy was 240-250 kJ/mol, suggesting the cross slip dominating the creep. The observed intergranular β Mg₁₂Ce precipitates were considered as the major cause of the high creep strength. Celikin et al. [132] further stated that the β Mg₁₂Ce precipitates in the Mg-Ce-Mn alloys were refined by dynamic co-precipitation of α-Mn, which might serve as nucleant for Mg₁₂Ce. In addition, like the Mg-(Y group) alloys, the precipitation process of Mg-(Ce group) alloys also lacks GP zones, but semi-coherent and then incoherent precipitates could form in subsequent ageing process [10]. As the solid solubility of Ce group

elements in Mg alloys is lower than the Y group elements, the former is not as effective as the latter in improving the creep strength through precipitation hardening. Hence, apart from Nd, Ce group elements are normally used for the purpose of providing extra intermetallic compounds' locking effect on grain boundary in precipitation hardenable alloys. A Ce-rich REs containing Mg alloy, AM-SC1 alloy (Mg-1.7Nd-1REs-0.5Zn-0.5Zr) has been developed and commercialized for high temperature applications, such as the engine block material for the USCAR MPCC project V6 petrol engine [133]. Fig.17a records the creep strain of AM-SC1 in a range of temperatures and stresses. Bettles and co-authors [134] studied the AM-SC1 alloy and proposed that the high creep strength of this alloy resulted from the combined effects of the discontinuous $Mg_{12}REs$ ($Mg_{12}Ce$ and $Mg_{12}La$) particles that distributed along grain boundaries, and the very fine Zn-Zr interfacial precipitates. They hindered the boundary sliding and dislocation emission, respectively. Fig.17 (b-d) present the microstructure of AM-SC1 at T6 condition, including the $Mg_{12}REs$ particles and Zn-Zr precipitates by TEM [134].

In addition, the Mg-Nd based alloy, EV31 alloy (Elektron 21) [135] with nominal composition of Mg-3Nd-1Gd-0.3Zn-0.5Zr (wt.%), was developed to replace the WE43 alloy for aerospace applications. This new Mg-Nd-Gd based alloy has high strength and creep resistance, essentially achieved by precipitation strengthening. The precipitation process in the alloy aged isothermally at 200 °C has been found to be: $\beta'''(D019) \rightarrow \beta'(cbco) \rightarrow \beta(fcc)$ [136]. Fig.18a and 18b presents and compares the creep behaviour of WE43 and EV31 at 200-300 °C and 90-150 MPa at peak-aged condition [137]. EV31 alloy maintained good creep resistance in comparison to WE43 at a temperature of 200 °C and 90 MPa but it lost the resistance and crept rapidly when suffered a higher temperature or applied stress. WE43 however exhibited good creep-resistant performance until temperature reached to 300 °C. Overall, EV31 appears to be as suitable replacement for WE43 in applications under 200 °C, however, studies of the creep mechanism of the EV31 alloy is very limited at present. Katsarou et al. [138] investigated the compression creep behaviour of as-cast EV31 and determined the stress exponent n of as 4.2 in tests between 70 MPa and 200 MPa at 240 °C. They suggested that rate-controlling mechanisms were dislocation climb and glide. Han et al. [139] fully investigated the creep behaviour of a similar alloy with composition of Mg-2.5Nd-1.8Gd-0.2Zn-0.4Zr and concluded that grain boundary sliding was dominant mechanism at temperatures below 225 °C and in the stress range of 60-120 MPa. Otherwise, dislocation climbing led to the creep over 225 °C. In addition, there were also several patented alloys with lower REs additions, including the Mg-Nd-Zr and Mg-Nd-RE

based alloys. They were claimed having good creep resistance at temperatures over 175 °C [140, 141]. But, no detailed information and actual applications of these alloys have been found yet.

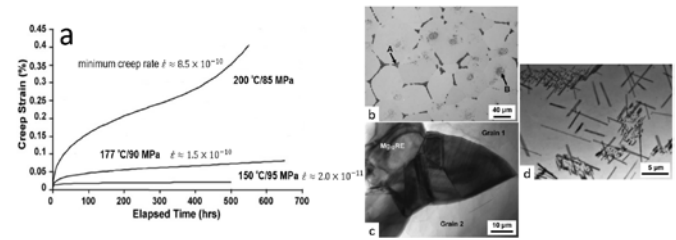


Figure 17 (a) Tensile creep curves of AM-SC1 with the grain size of 45 μm ; (b) Optical micrograph of AM-SC1 in the T6 condition; (c) TEM image of a $Mg_{12}RE$ particle at triple point of grain boundary, and (d) TEM image of a portion of a cluster of Zn-Zr intermetallic precipitates (reproduced from [134]).

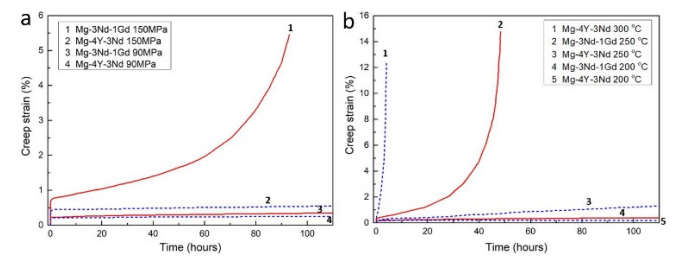


Figure 18 (a) Tensile creep curves of peak-aged WE43 and EV31 alloys tested under 200 °C; (b) Tensile creep curves of peak-aged WE43 and EV31 alloys tested at 90 MPa and 200-300 °C (reproduced from [137]).

3.4 Mg-Sc-Mn alloys for gravity casting

Like Y, scandium (Sc) is also classified as a RE-similar element. But it does not belong to any group since Mg-Sc is the only peritectic system among the Mg-RE alloys. Trace additions of Sc and Mn were known to significantly improve the creep resistance of a number of Mg alloys due to the formation of additional precipitates [62, 76, 116, 132]. Thermodynamics-based analysis by Abaspour et al. [99] suggested that in addition to Th, Mn and Sc were effective solutes to produce noticeable age hardening against creep by thermally stable, internally ordered precipitates. However, individual addition of either Sc or Mn into pure Mg had little effect on the creep resistance. Binary Mg-Sc alloys exhibited weak age-hardening response owing to the low diffusivity of Sc in Mg. Moreover, the Mg-Sc precipitates on the basal plane contributed marginally to the precipitation hardening [10, 142, 143]. Binary Mg-Mn alloys showed remarkably high creep resistance compared with pure Mg at temperatures up to 450 °C, but this increase in creep strength was limited to low stresses (below 15 MPa) [129, 130, 144]. The higher creep strength of Mg-Mn binary alloys was attributed to the precipitation of α -Mn on the basal plane of Mg and/or on the prism plane [144-146].

However, combined additions of Sc and Mn lead to a significant improvement of creep resistance in Mg. Fig.19a shows the creep curves of Mg-Sc-Mn based alloys and the WE43 alloy, which are extracted from Mordike and co-authors' work [143]. The result illustrated evidently higher creep resistance of Mg-Sc-Mn alloys than that of WE43 at a high temperature of 350 °C. The secondary creep rate of the T5 Mg-6Sc-1Mn (wt.%) alloy was two orders of magnitude lower than the T6 WE43 alloy. It was believed that the fine Mg₂Sc spherical precipitates were responsible for the enhancement of the creep strength as this type of precipitates were dense and stable at temperatures up to 350 °C, as presented in Fig.19b. Thus, it is reasonable to conclude that the Mn₂Sc precipitates are associated with higher potency to improve the creep strength at elevated temperatures than the metastable cobe β' in Y subgroup Mg alloys. Additionally, the Mg-Sc-Ce-Mn alloy, it exhibited the best creep behaviour among those alloys in Fig.19a. Creep activation energy of Mg-Sc-Ce-Mn alloy was 161 kJ/mol and the stress exponent n was 10, indicating cross-slip dominated creep at 350 °C and 30 MPa [143]. Further enhancement was mainly accounted to the change in morphology of Mn₂Sc precipitates from spherical to basal discs, as displayed in Fig.19c. As the basal discs were more effective than spherical particles in terms of impeding dislocations cross-slip or non-basal slip, the Mn₂Sc morphological change resulted from the Ce addition led to a higher creep strength.

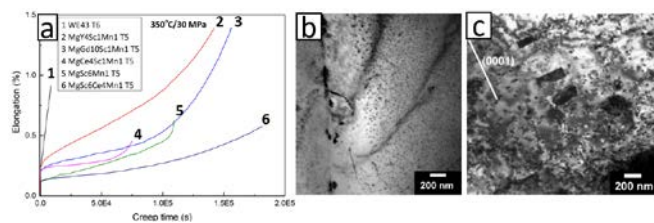


Figure 19 (a) Creep behaviours of Mg-Sc-Mn based alloys and the WE43 at 350 °C and 30 MPa; (b) TEM micrographs of fine spherical precipitates Mn₂Sc in Mg-Sc-Mn alloy; (c) TEM micrographs of fine basal disc-like precipitates Mn₂Sc in Mg-Sc-Ce-Mn alloy (reproduced from [143]).

4. Other low-cost creep-resistant Mg alloys

As stated in Section 3, Mg-REs based alloys have superior performance at elevated temperatures compared with Mg-Al based alloys. However, the high cost of REs lifts the price of Mg-RE based alloys which limits their industry applications. Hence, researchers and engineers are seeking alternative approaches in developing low cost creep-resistant Mg alloys that can be produced through gravity casting and are heat treatable. A number of Mg systems have been investigated, including Mg-Zn, Mg-Sn, Mg-Ca and Mg-Sr-Mn. They exhibited more or less potential to be used at elevated temperature. Further research is needed in order to exploit new alloys and associated processes to

achieve sufficient creep strength required for engineering applications.

4.1 Mg-Zn based alloys

In the past decades, Mg-Zn based alloys have attracted continuous interests of researchers and engineers due to their good age hardening response and castability. In addition, grain refinement of cast Mg-Zn based alloys can be achieved through addition of Zr, which is unavailable to Mg-Al based alloys due to reaction between Al and Zr [147, 148]. Hence, Mg-Zn system has been one of the most commonly used Mg systems in addition to Mg-Al and Mg-REs. Boehlert and Knittel [149] investigated the creep behaviour of Mg-4.1wt% Zn alloys at 150 °C with applied stresses between 30 to 50 MPa. Creep stress exponent was measured as 4.2, indicating that dislocation climb dominated the creep. Alizadeh et al. [150] also pointed out that creep behaviour of both as-cast and aged Mg-4Zn alloy within the temperature range from 150 °C to 250 °C was dominated by dislocation climb, which relied on both lattice and dislocation pipe diffusion at high and low stress regimes, respectively. Generally, ageing of Mg-Zn alloys leads to improvement of creep resistance due to the formation fine Mg₄Zn₇ (also known as Mg₂Zn₃) precipitates. The majority of Mg₄Zn₇ precipitates adopts a rod-like morphology with the rod direction parallel to [0001]_α, which provides effective precipitation hardening and leads to improved creep strength of the Mg-Zn based alloys [151, 152].

The addition of 1 wt.% mischmetal results in the development of ZE41 (Mg-4Zn-1REs-0.6Zr), which is one of the most-used commercial Mg alloys in gravity casting applications owing to its low cost and good castability. However, the alloy showed very moderate strength and creep resistance at elevated temperature, which was slightly better than AZ91 alloy. Creep strength of ZE41 at 0.2% creep strain and 200 °C, was only 50 MPa, but it was up to 160 MPa for the T4 WE43 alloy [153]. Further enhancement of creep strength of the Mg-Zn based alloys can be achieved by Cu addition through promoting aging response as the result of higher solid solubility of Zn due to the increased eutectic temperature. This led to the development of ZC series (Mg-Zn-Cu) alloys by MEL [6, 154, 155]. The ZC63 (Mg-6Zn-3Cu-0.5Mn alloy) can be used up to 150 °C after gravity casting. The ZC62 alloy was available to HPDC and was reported to have better ambient and high temperature properties than AS21 [154]. However, the addition of Cu was associated with the deleterious corrosion effect in Mg alloys, and subsequently, has been replaced with Ca.

Minor addition (0.1 wt.%) of Ca in the Mg-4wt.%Zn alloy led to refinement and homogeneous distribution of the rectangular rod like β'_1 Mg₄Zn₇ and hexagonal tablets β'_2 MgZn₂ [156]. Fig.20 schematically shows the morphologies of the β'_1 and β'_2

phases. Precipitates are not only refined and denser in Mg matrix, their orientation of rod-shaped β'_1 are less restricted which leads to more effective inhibition of dislocations. Subsequently, a reduced creep rate and an extensive steady-state creep region at 150 °C was observed in the Ca-modified alloy compared with the Mg-4wt.%Zn alloy without Ca [156]. Increasing Ca content led to the development of a new type of creep-resistant Mg alloys, i.e. Mg-Zn-Ca based alloys. In 1999, Horie et al. [157] reported that alloys containing less than 4 wt.% Zn and more than 0.5 wt.% Ca showed improved creep properties below 200 °C. The alloy Mg-2Zn-1Ca (wt.%) exhibited minimum creep rates in the order of 10^{-9} s^{-1} at 64 MPa and within a temperature from 150 °C to 175 °C. The creep resistance was attributed to the thermally stable intermetallic compounds $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ and/or Mg_2Ca along grain boundaries in the as-cast microstructure [158]. A study about the creep behaviour of the as-cast Mg-4wt.%Zn-0.5wt.%Ca alloy revealed that dislocation climb was the rate-controlling mechanism in both low and high stress regime [159]. Gao et al. [160] confirmed the improvement of creep resistance of the Mg-Zn-Ca alloy after aging hardening. Pan's team [161] investigated the effect of Ce, Sn and Gd additions on creep resistance of as-cast Mg-3.8Zn-2.2Ca alloy and found that Ce particularly improved creep behaviour of Mg-Zn-Ca alloy than others. In addition, a dilute alloy Mg-1Ca-1Zn-0.6Zr after aging exhibited a better yield strength and creep resistance than AZ91 at temperatures up to 150 °C and 90 MPa applied stress. The minimum creep rate of the Mg-1Ca-1Zn-0.6Zr alloy was about two orders of magnitude lower than that of AZ91 in a range of stress levels. $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ and Zn-Zr precipitates were reported to be responsible for the strengthening effect in the alloy [160, 162].

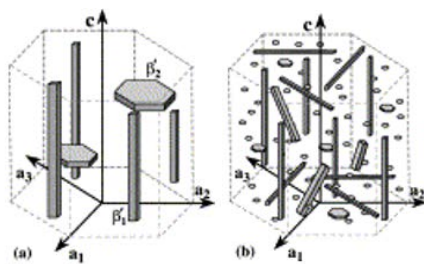


Figure 20 Schematic illustration of the β'_1 and β'_2 precipitates and habit planes in Mg matrix for (a) Mg-4wt.%Zn; (b) Mg-4wt.%Zn-0.35wt.%Ca after ageing [156]

4.2 Mg-Sn alloys

Mg-Sn based alloys have been considered as a relatively new type of creep-resistant alloys designed in recent years. Sn has a high solid solubility of 3.35 at.% in Mg at eutectic temperature and low solubility at room temperature. The Mg-Sn intermetallic compound, Mg_2Sn , formed in Mg-Sn alloy system has a melting temperature of 770 °C, which is much higher than that of the $\text{Mg}_{17}\text{Al}_{12}$ in Mg-Al alloys. Hence, Mg-Sn alloys potentially have good high-temperature performance.

Mg-Sn based alloys are therefore likely to be a more effective alloy system than Mg-Al based alloys to achieve high creep resistance through precipitation hardening. The Mg-Sn system is also a possible alternative to the age-hardenable Mg-REs system. Research by Liu et al. [163] on the Mg-(1-10) wt.% Sn alloys illustrated that the indentation creep performance of as-cast Mg-10Sn alloy was superior to that of the AE42 at 150 °C due to the high volume fraction of Mg_2Sn phase. Fig. 21 shows the variations of indentation creep rate of Mg-Sn alloys containing different amounts of Sn with time. For the purpose of comparison, the creep behaviour of the AE42 alloy is also plotted. As can be seen, the indentation creep rate decreased with an increase in the Sn content. The indentation creep behaviour of the AE42 alloy was close to the Mg-Sn alloy containing 7 wt.% Sn and it was overtaken by Mg-10wt.% Sn alloy. Wei et al [164] examined compressive creep behaviour of an as-cast and aged Mg-5wt.%Sn alloy at low stress levels from 25 MPa to 35 MPa and temperatures from 150 °C to 200 °C. The measured stress exponent n was 6.3 and the activation energy Q_c was 86.1 kJ/mol. This indicated the dislocation climb controlled mechanism for low-stress creep of the alloy. Much higher creep resistance was observed in the aged alloy than as-cast alloy owing to the presence of depressively distributed Mg_2Sn precipitates with both plate and lath shaped morphology, as shown in Fig.21b and 21c. Nevertheless, the precipitation effect in Mg-Sn binary alloys is moderate when compared with the Mg-REs alloys with metastable *cbco* precipitates. A study on precipitation of Mg-Sn alloys recently confirmed that Mg_2Sn precipitates in binary Mg-Sn alloys were relatively coarsened and in lath shape, paralleled to the basal planes of Mg matrix [165]. This precipitate configuration was regarded as less effective in suppressing dislocation movement [105]. In addition, Huang and co-workers [166] found that the moderate creep resistance was attributed to the segregation of Sn along the dendritic and grain boundaries, which is similar to Al solutes, promoting the grain boundary sliding at high temperature creep deformation. Hence, compared with the Mg-REs alloys, lower strength and creep resistance were obtained in aged Mg-Sn alloys.

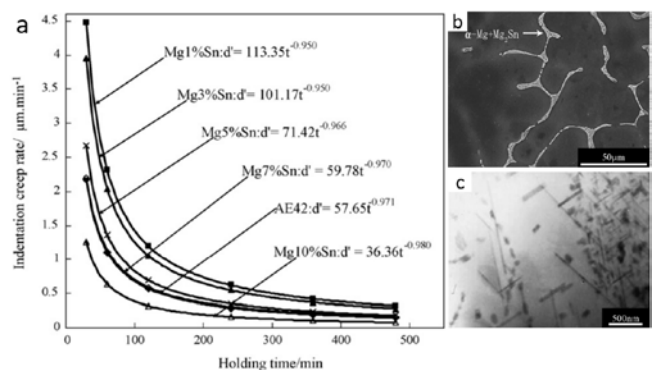


Figure 21 (a) Indentation creep rates of as-cast Mg-Sn alloys in comparison with the AE42 alloy at 150 °C [163]. (b) SEM

micrograph of as-cast Mg-5Sn alloy; (c) TEM micrographs of aged Mg-5Sn alloy [164].

Na, Zn and Al were found as promising solutes to further improve the ageing response of Mg-Sn based alloys even though the actual mechanisms might vary [165, 167-169]. Micro-alloying of an Mg-1.3at.%Sn alloy with 0.13 at.% Na refined the Mg₂Sn precipitates and led to increase in the hardness by 2.7 times [165]. In addition, adding 1.0 at.% Zn also changed both the morphology and orientation relationship (OR) of Mg₂Sn precipitates with Mg matrix, and therefore significantly enhanced the age response. Three types of precipitates with various shapes and ORs to Mg matrix were observed and 140% increment of hardness after peak ageing was exhibited in the Mg-1.3Sn-1.2Zn (at.%) T6 alloy [167]. Further enhancement was also reported in an alloy that contained both Zn and Na. The promoted aging hardening effect subsequently led to the improvement in creep properties of Mg-Sn based alloys. Gibson et al. [168] investigated the tensile creep behaviours of the Mg-Sn-Zn(-Na) alloys at a stress of 60 MPa and a temperature of 177 °C. The alloy containing both Zn and Na had a secondary creep rate that was 4 orders of magnitude lower than the Mg-Sn binary alloys. The creep behaviour of this alloy was also comparable to the dilute Mg-REs alloys as listed in Table 5.

Furthermore, Al addition was reported having ability to significantly increase the peak hardness values and shorten the time to reach peak hardness in the Mg-2.2Sn-3Al-0.5Zn (at.%), TAZ alloy [169]. This alloy can also be regarded as a Sn-modified AZ31 alloy. Unfortunately, the actual strengthening mechanism is not clear. Further addition of 0.1at.% Na into this alloy resulted in peak aged hardness of the alloy over 100 HV, which would not be achievable in the current Mg alloys without REs [170]. Fig.22a shows ageing curves of a few Mg-Sn based alloys at various temperatures. Fig.22b and 22c presents the refined nanometre-scale Mg₂Sn precipitates on the basal plane. It can be seen that combined additions of Al, Zn and Na effectively increased the ageing response of this type of alloy. However, further research is needed to explore the creep performance of the alloys at elevated temperatures.

In addition, an alloy series of Mg-Sn-Ca is of special interest as it offered good corrosion and creep resistance over Mg-Al based alloys. Particularly, the Mg-3Sn-2Ca alloy exhibited creep performance comparable to the benchmark AE42 alloy [171]. The minimum tensile creep rate of Mg-3Sn-Ca and AE42 at 175 °C/80 MPa was 2.04E-08 s⁻¹ and 1.95E-08 s⁻¹, respectively. Hence, Mg-Sn-Ca series was regarded as a potential creep-resistant alloy that can be used in casting [171, 172]. However, most current research so far has focused on the as-cast alloys [173-178]. It has been considered that the high creep resistance of the as-cast Mg-Sn-Ca alloys was ascribed to the presence of

highly thermal-stable phases, including CaMgSn and/or Mg₂Ca depending on the Ca content [175-177]. The major drawback of this alloy was the coarse primary CaMgSn phase, which lowered the mechanical properties of the alloys. A number of work by Pan's group in CCMg [178-180] reported that minor additions of Ce, Y or Gd were able to refine the CaMgSn phase and therefore to improve the mechanical and creep properties.

Table 5 Experimentally measured secondary tensile creep rates of aged Mg-Sn based alloys and Mg-REs HPDC alloys [168].

Alloy (at. %)	Secondary creep rates (s ⁻¹) 177 °C/60MPa
Mg-1.3Sn	8.2 × 10 ⁻⁵
Mg-Sn-1Zn	2.5 × 10 ⁻⁶
Mg-Sn-1 Zn-0.1Na	2.2 × 10 ⁻⁹
Mg-0.62 La	2.1 × 10 ⁻⁸
Mg-0.51Ce	1.2 × 10 ⁻⁹
Mg-0.45Nd	3.5 × 10 ⁻¹⁰

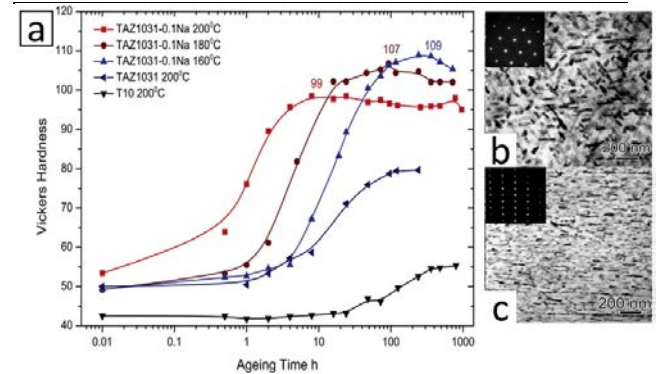


Figure 22 (a) Aging curves of Mg-Sn based alloys with additions of Al, Zn and Na; (b, c) TEM micrographs of Mg-10Sn-3Al-1Zn-0.1Na alloy peak aged at 200 °C along the [0001], [112̄0] zone axis [170].

4.3 Mg-Ca alloys

Ca is considered as the most effective non-REs solute that can significantly improve the creep resistance of various Mg systems through the formation of thermally stable intermetallic compounds in the alloy at elevated temperatures. This resulted in the development of a number of creep-resistant Mg alloys, including the AX series, Mg-Zn-Ca and Mg-Sn-Ca alloys [72, 157, 171]. On the other hand, unlike the Mg-REs, Mg-Sn and Mg-Zn systems, the low solid solubility of Ca in Mg (only 0.82at.%) limits the precipitation hardening response in Ca-containing Mg alloys. Nevertheless, effective solid solution strengthening effect by dilute Ca has been suggested in several studies [125, 126]. As stated in Section 3.2.2, the tendency of Ca solutes for developing SRO in solid solutions is comparable to those of REs. Abaspour and co-authors' work [124] also confirmed that Ca solute effectively prevented stress relaxation, which was comparable with the Y, Gd and Nd at elevated temperatures. Figs.16c shows the variation of the flow stress at 0.02% strain with testing temperature. It can be seen that Mg-0.9at.%Ca alloy has more stable

performance at elevated temperature than other low-cost alloys, including Mg-2.2at.%Zn, Mg-2.5at.%Al, Mg-2.5at.%Sn and even Mg-0.8at.%Gd [124]. This implies that there is high potential to develop low cost creep-resistant Mg alloys using Ca because the market price of Ca is much lower than Y, Nd and Gd. Furthermore, the recent work [126] on the new Mg-3Gd-2Ca based alloys illustrated that Ca solute played a similar role as Gd solute in contributing to the high-temperature strength and creep resistance. This provides a potential approach to reduce REs addition in creep-resistant Mg alloys by exploitation of Ca's promising solid solution strengthening effect. Nevertheless, a reduction in castability due to the Ca addition is also an issue of Mg-Ca alloys that requires further attention.

4.4 Mg-Sr-Mn alloys

Mg-Sr-Mn (JM series) is a new system initially developed by Celikin et al. [181, 182] since 2012 that has been drawn a lot of attentions. In this alloy system, it is considered that dynamic precipitation makes the major contributions to the creep resistance in gravity casting Mg alloys. The addition of Sr leads to the formation of interconnected intermetallic phases that reinforce the grain boundaries. The utilization of the features of manganese, high solubility and peritectic nature in Mg-Mn, promote the formation of α -Mn precipitates that strengthen the matrix [181]. Typical alloys include JM51H (Mg-5wt.%Sr-1.25wt.%Mn) and JM52 (Mg-5wt.%Sr-2wt.%Mn). Fig.23a presents the tensile creep behaviours of the as-cast JM51H and JM52 alloys tested at 200 °C/50 MPa. Although those two alloys had similar primary creep behaviour, the JM51H alloy exhibited both longer period of steady-state creep and lower minimum creep rate than the JM52 alloy. Celikin et al [181] suggested that a higher Mn amount in JM52 alloy possibly promoted coarsening of the α -Mn precipitates that dynamically precipitated in the $Mg_{17}Sr_2$ phases during isothermal holding, as shown in Fig.23(b and c). As a result, lower creep strength were expected. Their subsequent publication [182] investigated the creep mechanisms through determination of the activation energy Q_c for JM51H and JM52 with a temperature range from 150 °C to 225 °C at 50 MPa. It was found that the dominated mechanism for JM52 shifted from pipe diffusion to dislocation climb at 175 °C and that of JM51 shifted to cross-slip at 200 °C. Further 0.5wt.% Ce addition into the JM52 alloy and the JM32 alloy was reported, which resulted in a significant reduction in the minimum creep rate by about three orders of magnitude at 200 °C/50 MPa [183, 184]. The dynamic co-precipitates $Mg_{12}Ce/\alpha$ -Mn were also identified as obstacles that can effectively impede the basal and prismatic slip and dislocation climb during creep [184].

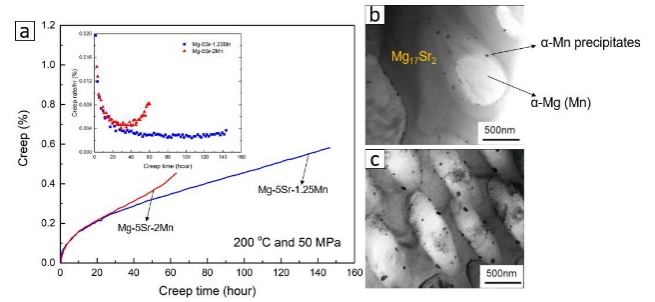


Figure 23 (a) Tensile creep curve and creep rates of Mg-5Sr-1.25Mn and Mg-5Sr-2Mn as-cast alloy tested at 200 °C and 50 MPa; TEM bright-field images of (b) Mg-5Sr-1.25Mn and (c) Mg-5Sr-2Mn upon isothermal holding at 225 °C for 150 h (reproduced from [178]).

5. Future of creep-resistant cast Mg alloys

As mentioned above, in the past decades, a number of creep-resistant cast magnesium alloys have been developed and commercially used in industries [1, 9, 10]. However, compared with other structural cast Mg alloys, such as the AZ series alloys, the market of creep-resistant Mg alloys is relatively small. This is attributed to the unsatisfied performance compared with Al alloys and steels and to the high costs, particularly the RE-containing Mg alloys, such as WE54. Hence, development of new creep-resistant cast Mg alloys with better performance and lower cost will be the future of this type of alloys.

Creep-resistant cast Mg alloys generally target at applications in automotive, aerospace and defence industries where weight reduction is one of the key concerns. Powertrain components are typical examples. Owing to the unique advantages of HPDC Mg alloys, AZ91 and AM60 has offered the same functionality as the A380 aluminium alloy for low-temperature and structural applications, such as body and chassis of vehicles, but with significant weight reduction [185]. However, powertrain components, such as transmission cases and engine block with operation temperatures up to 200 °C, require specific Mg alloys with high creep resistance. It has been considered that powertrain sector has been one of the most potential and constantly growing market for creep-resistant cast Mg alloys since 2000 [186]. In addition, this type of alloys also have potential to be used in aeronautics and military industries, these two sectors also require weight reduction of components, which still retain high mechanical and creep properties at high temperatures [187, 188].

In order to fulfil potential applications, more effort and progress on development of creep-resistant Mg alloys are necessary. For automotive powertrain, a number of HPDC alloys were successfully developed but the creep properties are still not adequate for widely replacing the use of Al alloys. BMW hybrid crankcase for instance was produced partially using AJ62 as crankcase shell while AlSi17Cu4Mg alloy was used to produce inner block in order to counter the low creep

resistance of Mg alloys [82]. To further improve creep resistance, development of new alloy system is becoming less possible as HPDC is sensitive to castability and alloying elements are limited. Strengthening by minor additions, such as Mn addition in Mg-Al-Ca alloy [76] and Zn addition in Mg-RE alloy [97], may receive more concern for improving creep resistance of such type of alloy in the future. Furthermore, although the usage is limited, Mg alloys by gravity casting still have a chance for automotive applications since they can offer higher performance, such as AM-SC1. But the commercial interest requires development of creep-resistant alloys in gravity casting with reducing REs concentrations or based on other low-cost alternative system. Most of low-cost alternatives currently suffer from insufficient creep resistance as Mg-REs based alloys, Mg-Sr-Mn is one of few novel alloys successfully developed since 2010 [183]. As to aerospace and military industries, in which the demand of high performance usually overwhelms the cost, concentrated Mg-REs based alloys with improved high temperature mechanical properties thus may find some specific applications. Potential alloys are Elektron alloys, Mg-Y-Gd-Zr alloys and etc.

In addition, there are also several fundamental challenges related to creep-resistant Mg alloys. This includes the actual creep mechanisms of Mg alloys at different temperatures and stresses, and the roles of REs in improvement of the creep resistance. Besides effective precipitation hardening by REs additions, some researchers recently [99, 124-126] believe that the short-range order in Mg-REs solutions plays key and crucial role in improvement of creep resistance of Mg-REs alloys. Hence, to clarify address these challenges, further studies are needed.

6. Summary

Based on existing literature, the dominated creep mechanisms in typical cast Mg alloys tested at stresses ranging from 20 to 120 MPa and at temperatures of 100 °C – 350 °C have been summarized in Fig. 24. It can be seen that the creep mechanisms in Mg alloys varies with testing conditions and alloy systems. At relatively low temperatures and low stress levels, especially for the Mg-Al HPDC alloys that creep at temperatures from 100 °C to 175 °C, grain boundary sliding (GBS) and diffusion are the dominating creep mechanisms. In AM-SC1 alloys, GBS is also the major cause of creep at higher stress [134] as shown in Fig. 24. At a low applied stresses of about 20-40 MPa, grain boundary diffusion is also responsible for the creep of Mg-Sc-Mn gravity casting alloys tested at a high temperature of 300 °C [142]. Dislocation climbing normally dominates the creep of most Mg alloys at moderate temperatures (~150 °C-250 °C) and moderate to high stress (~60 MPa-120 MPa). Non-basal slip, such as cross-slip, usually causes creep of alloys at relatively high

temperature but low stress. At stresses closed to the yield strength, a combination of dislocation gliding and climbing promote creep deformation. For instance, AS21 alloy crept at 150 °C/70-100 MPa as shown in Fig.24, dislocation climbing and gliding are dominating since the stress is already over yield strength of the alloy [38].

Additions of solutes generally increase the creep resistance of cast Mg alloys based on several mechanisms at the same time. In Mg-Al based alloys, the major effect of solute additions is to introduce thermal stable intermetallic compounds and/or reduce the amount of Mg₁₇Al₁₂ phase to reinforce grain boundaries. The solutes in this group include Si, Bi, Sb, REs (La, Ce and Nd) and alkaline elements (Ca and Sr). Another group of solutes, such as Y, Gd, Nd, Sc and Mn, are added to produce strong precipitation strengthening to impede dislocation processes during creep, and therefore improve the creep resistance of Mg alloys. In addition, Zn, Ca and Sn in Mg can also form stable precipitates to strengthen the alloys in some extent. Additions of Y, Gd, Nd and Ca promote short range order in some solid solution treated Mg alloys. This type of short range order is also considered as a major factor that contributes to higher creep strength.

The currently available creep-resistant cast Mg alloys can be categorized into three groups. The first is the Mg-Al based alloys mainly for HPDC applications at temperatures below 200 °C. This includes AE, AX, MRI series alloys etc. The second group, Al-free Mg-RE based alloys, can achieve high creep strength and low creep rate at higher temperatures but their high cost, together with higher density, is a major concern. Typical alloys in this group are the WE alloys and Mg-Sc-Mn alloys. The third group of low-cost cast Mg alloys includes Mg-Zn, Mg-Sn, Mg-Ca and Mg-Sr-Mn based alloys. They are associated with lower cost and have ongoing challenges to further improve their creep resistance.

In order to widen the applications of cast Mg alloys, new low cost and high performance alloys will be required. Based on this review, in addition to the REs (Y, Gd and Nd), promising candidate alloy elements worthy of ongoing investigation include Ca, Sn and Mn.

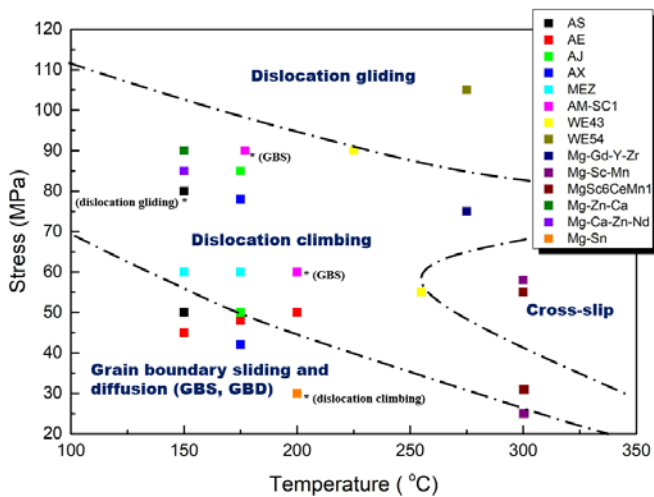


Figure 24 Rate-controlled creep mechanism map for magnesium alloys in a range of stresses and temperatures. * indicates the specified creep mechanism not fitted in the regime.

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