

On the exceptional creep resistance in a die-cast Gd-containing Mg alloy with Al addition

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Abstract

Over the past few decades, aluminium (Al) has been considered to be beneficial for castability but detrimental for the creep resistance of magnesium (Mg) alloys. However, an excellent creep resistance has been achieved in a die-cast Mg_{3.5}RE(La,Ce,Nd)_{1.5}GdMnAl alloy, with a super low steady-state creep rate (SCR) of $1.25 \times 10^{-10} \text{ s}^{-1}$ at 300°C/50MPa. Compared with the counterpart Al-free Mg_{3.5}RE(La,Ce,Nd)_{1.5}GdMn alloy, the SCR decreased by 73%. The synthetic effect of Al, Gd and Mn induced a novel thermally stable (TS) AlMnGd ternary short-range order (SRO, 0–2nm)/cluster (2–10nm) in the Mg matrix. After creep at 300°C/50MPa for 400 hours, the AlMnGd SRO was still observed, and the AlMnGd clusters were under 10nm and coherent with the Mg matrix, without a unit cell structure. The AlMnGd SRO/clusters were massively observed for pinning dislocations, which was the main reason for the improvement in the creep resistance in contrast to the counterpart Al-free alloy. The TS Mg₁₂RE(La,Ce,Nd) network at the grain boundaries (GBs) impeded dislocation mobility, which also played an important role for the creep resistance compared to the traditional die-cast Mg-Al-based alloys. Under the critical conditions of 300°C and 50–80MPa, the creep still satisfied the power law, and the dominant creep mechanisms were SRO/cluster drag dislocation gliding, associated with GB diffusion. This work provides clear evidence for the long-term existence of some SRO/clusters in Mg alloys under critically high temperatures and stresses. Moreover, the utilising of AlMnGd SRO/cluster can be a novel approach for designing heat-resistant Mg alloys with the sync boost of castability.

Key words: Magnesium alloy; Creep; Short-range order; Cluster; Mechanism.

1. Introduction

Magnesium (Mg) alloys are excellent candidate materials for lightweight structures in the automobile, aerospace, rail and other industries when compared to steel and aluminium (Al) alloys [1–3]. Over the past few decades, one of the beneficial applications of magnesium alloys is the manufacturing of powertrain components, operating at the elevated temperatures of 150–200 °C [4–6]. Recently, this advancement has focused on the die-castable components in small internal combustion engines (SICE), used in machinery such as powered tools, drones and unmanned aerial vehicles, with a working temperature capable of reaching 200–300 °C, and where the creep resistance is a major challenge [7,8].

In the past, for Mg alloys, Al was considered beneficial for castability, but it was found to be detrimental for creep resistance at elevated temperatures [6,9,10]. The most widely used die-cast Mg alloys are Mg-Al-based alloys, such as AZ91, AM50 and AM60 because these Al-rich alloys have good die castability [11]. Unfortunately, the AZ and AM series die-cast Mg alloys are not suitable for elevated applications above 120 °C due to the formation of a thermally unstable $Mg_{17}Al_{12}$ phase that is unbeneficial to creep resistance [12,13]. Considerable efforts were made to improve the creep resistance of the Al-rich die-cast Mg alloys via the addition of Si, Sr, Ca, Sn and rare earth (RE) to restrain the formation of $Mg_{17}Al_{12}$ [6,14]. The representative alloys are Mg-3Al-Si (AS31, compositions in the text are in wt.% unless specified) [15], Mg-Al-Sr (AJ62, AJ52) [16], Mg-8Al-1Ca-Zn (MRI153A) [17], Mg-4Al-1.2Ce-0.6La-0.4Nd (AE42) [18], Mg-8Al-1Ca-Sr (MRI153M) [19], Mg-4Al-2.5Ce-1.2La-0.5Nd (AE44) [14], Mg-6.5Al-2Ca-1Sn-Sr (MRI230D) [20,21] and Mg-4.5Al-3.5Ca-Sr (AXJ530) [22]. Moreover, the creep resistance at 150 °C/90 MPa for the above-mentioned die-cast Mg-Al-based alloys increased gradually [14]. However, the improved die-cast Mg-Al-based alloys can generally only work at the elevated temperatures of 150–175 °C due to a significant increase in the creep rate when the temperature surpasses 175 °C [6,9]. It is generally believed [14] that the formation of thermally unstable or non-interconnected Al-rich compounds such as Al_4Sr , Al_2Ca and $Al_{11}RE_3$ at the grain boundaries (GBs) restrict the die-cast Mg-Al-based alloys from working at higher temperatures. For die-cast Mg-Al-based alloys, the creep was dominated by grain boundary sliding (GBS) at low temperatures and applied stresses, while the dominant creep mechanisms could shift to dislocation climbing and cross-slip with the increase of temperatures to 150–175 °C [9,23].

One effective approach to improve elevated creep resistance is to develop Al-free die-cast Mg-RE alloys. The benchmarks are the La, Ce and/or Nd rich Mg-2.5Nd-0.3Zn-0.3Mn (MEZ) [24] and Mg-1.7La-1.0Ce-1.0Nd-0.45Zn (AM-HP2+) alloys [10,14]. The RE content in die-cast Mg-RE alloys was usually set within 4 wt.% as a high RE resulted in brittleness [6,10,25]. This restricted the die-cast Mg-RE alloys from working at higher temperatures, that is above 200 °C. It was thought [10] that the formation of thermally stable and interconnected $Mg_{12}RE$ compounds at the GBs benefited the creep resistance in Al-free die-cast Mg-RE alloys, and the addition of Al has been well reported for a deteriorating creep resistance in die-cast Mg-RE(La,Ce,Nd) alloys [10,26]. Further investigations disclosed that solute atoms and dynamic precipitation in the Mg matrix played important roles for creep resistance [27,28]. However, there is still intense debate about the effects of the solute atoms and precipitation on creep resistance [6]. The Mg-0.45La-1.2Y alloy was found to have a higher creep resistance in a solid solution state than in a solid solution and peak-aged condition, even though precipitates only existed in the Mg matrix of the aged alloy before creep [29]. The development of a short-range order (SRO) and cluster of solute atoms in the Mg matrix that could hinder dislocation movement was viewed as the dominant creep mechanism in this alloy system [30], but the SRO and cluster of solute atoms were considered as unstable and disappeared after ageing and/or creep for a while in certain experiments [31,32].

Generally, the creep resistance of Mg alloys can be enhanced by the formation of thermally stable and interconnected compounds at the GBs [26,33], the solid solution of solute atoms [27,30,34] and/or the thermally stable precipitates [13,35,36] in the Mg matrix. However, the existing die-cast Mg alloys for elevated applications go to two extremes of Al-rich and Al-free alloys. The Al-rich Mg alloys have a good castability. However, most of the atoms that are efficient at creep resistance are consumed by the Al to form thermally unstable and non-interconnected Al-rich phases at the GBs, rather than solution into the Mg matrix for solution or precipitation strengthening, which results in a poor creep resistance of Mg-Al-based alloys above 175 °C [6,13]. The Al-free die-cast Mg alloys, especially the Mg-RE(La,Ce,Nd) alloys, have a good creep resistance up to 200 °C that is associated with the thermally stable $Mg_{12}RE(La,Ce,Nd)$ phase at the GBs [24,26]. Nonetheless, castability is a concern, and the resultant limited addition of RE restricts the strength of the alloys. Moreover, the Al-free and RE(Zn)-based precipitates formed in the Mg matrix of these alloys might not be as stable as

some of the Al-containing precipitates [36,37]. For a long time, Al was unfairly viewed as unbeneficial for the creep resistance of Mg alloys; it is also hard to imagine a die-cast Mg alloy with a super creep resistance, especially at the higher temperatures of 200–300 °C, via the addition of Al in a die-cast Gd-containing Mg alloy.

In this work, an exceptional creep resistance has been achieved in our newly developed die-cast Gd-containing Mg_{3.5}RE(La,Ce,Nd)_{1.5}GdMnAl alloy [25,38], at the critically high temperature of 300 °C, via the addition of Al. The characterisation and mechanisms of the improvements in creep resistance in the Mg_{3.5}RE(La,Ce,Nd)_{1.5}GdMnAl alloy were closely studied at an atomic level to provide a new approach for designing heat-resistant Mg alloys.

2. Experimental

2.1. Material preparation

Cylindrical creep samples designed with ISO 204:2018 were prepared by high pressure die casting (HPDC) on a 4500 kN cold chamber machine; the gauge diameter and length of the creep samples were 6.35 mm and 20 mm, respectively. The newly developed die-cast Mg_{1.6}La_{0.9}Ce_{1.0}Nd_{1.5}Gd_{0.3}Zn_{0.3}Mn_{0.5}Al (Mg_{3.5}RE_{1.5}GdMnAl) alloy was melted in a steel liner and held at 720 °C. The die and pour temperatures were controlled at 225 °C and 715 °C during HPDC. For comparison, the counterpart Al-free Mg_{1.6}La_{0.9}Ce_{1.0}Nd_{1.5}Gd_{0.3}Zn_{0.3}Mn (Mg_{3.5}RE_{1.5}GdMn) alloy and representative Mg-Al-based commercial die-cast alloys (MRI153M, AJ62, MRI230D and AE44) for elevated applications were also melted and cast to make identical creep samples using the same HPDC.

2.2. Creep and tensile tests

Tensile creep tests were conducted on a lever-type Instron machine following ISO 204:2018. Several creep temperatures (200–300 °C) and stress levels (40–80 MPa) were applied for the creep tests. The temperature of the creep samples was controlled by thermocouples with an accuracy of ±1 °C, and the loaded stresses were lower than the yield strength (YS) under different test temperatures. One extensometer was attached to the gauge section of the samples to measure the strains during a creep test. The tensile tests were performed using an Instron 5500 Testing System following ASTM E8 and E21 standards, and the ramp rates for room temperature (RT) and high temperature tensile tests were 1 mm/min and 0.0002/s, respectively.

2.3. Microstructure characterisation

Backscattered scanning electron microscopy (BSD-SEM) observation was performed on a Zeiss SUPRA 35VP microscope. Transmission electron microscopy (TEM) samples were prepared by mechanical polishing followed by final ion thinning. TEM analysis including nano-diffraction, bright-field (BF) imaging and high-resolution TEM (HRTEM) imaging were conducted using a FEI Tecnai G2 microscope. An in-depth TEM analysis was carried out on a Thermofisher Titan Themis 60-300 microscope operated at 300 kV. It was equipped with a highly efficient (4 quadrant) energy dispersive X-ray (EDX) system and a probe aberration corrector for atomic and nano-scale characterisation in the scanning TEM (STEM) mode. The collection angle of the high-angle annular dark field (HAADF) detector ranged from 80 to 150 mrad. The probe size was set to 0.1 nm with a convergent semi-angle of 22.5 mrad. Energy dispersive spectrometer (EDS) mapping was also applied under STEM. A 3D visualisation program for structural models, VESTA [39], was used to construct interfacial atomic structures.

3. Results

3.1. Tensile and creep properties

The representative tensile curves of the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy and the counterpart Al-free Mg_{3.5}RE_{1.5}GdMn alloy at RT and 300 °C are provided in the Supplementary Fig. S1. The yield strength and ductility of the Mg_{3.5}RE_{1.5}GdMnAl alloy and the counterpart Mg_{3.5}RE_{1.5}GdMn alloy at RT were 165.3±4.2 MPa and 2.45±0.21 %, 163.3±3.8 MPa and 0.93±0.24 %, respectively. The addition of 0.5wt.% Al led to a considerable improvement of 163 % in RT ductility, which made the Mg_{3.5}RE_{1.5}GdMnAl alloy die castable. This is because it is well accepted [4,5] in this industry that 2 % is the required ductility for die-cast alloys. The yield strength and ductility of the Mg_{3.5}RE_{1.5}GdMnAl alloy and the counterpart Mg_{3.5}RE_{1.5}GdMn alloy at 300 °C were 94.4±2.5 MPa and 32.5±5.2 %, 92.1±2.3 MPa and 28.7±5.0 %, respectively. Fig. 1 shows the creep properties of the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy, the comparison with the counterpart Al-free Mg_{3.5}RE_{1.5}GdMn alloy and the traditional representative Mg-Al-based commercial die-cast MRI153M, AJ62, MRI230D and AE44 alloys for elevated applications. As illustrated in Fig. 1a, under the creep temperature of 300 °C and the stress of 50 MPa, the Mg_{3.5}RE_{1.5}GdMnAl alloy went into the tertiary state after creep for 460 hours (h) and did not reach the rupture point after 620 h; the counterpart Mg_{3.5}RE_{1.5}GdMn alloy went into the tertiary state after creep for 350 h and

ruptured after 450 h, whereas the secondary steady-state creep strain of the Mg_{3.5}RE_{1.5}GdMnAl alloy was much lower than the counterpart Mg_{3.5}RE_{1.5}GdMn alloy and the four commercial alloys. As shown in Fig. 1b, the steady-state creep rate (SCR, s⁻¹) of the MRI153M, AJ62, MRI230D, AE44, Mg_{3.5}RE_{1.5}GdMn and Mg_{3.5}RE_{1.5}GdMnAl alloys at 300 °C/50 MPa were (4.58±1.19)×10⁻⁷, (3.39±0.88)×10⁻⁷, (3.15±0.82)×10⁻⁸, (5.69±1.41)×10⁻⁹, (4.68±1.23)×10⁻¹⁰ and (1.25±0.28)×10⁻¹⁰, respectively. The Mg_{3.5}RE_{1.5}GdMnAl alloy showed a 73 % reduction in the SCR compared with the counterpart Mg_{3.5}RE_{1.5}GdMn alloy; it further showed a much-improved creep resistance in contrast to the four typical Mg-Al-based commercial die-cast alloys. In addition, the SCR of the Mg_{3.5}RE_{1.5}GdMnAl alloy was lower than the heat-treated gravity cast Mg alloys (QE22, EQ21, AM-SC1, WE43, WE54, Mg15Gd, Mg8Gd4Y, Mg15Gd2Y, Mg10Gd3Y and Mg12Y5Gd) for applications at 200–300 °C [40–49]. Therefore, the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy has a super creep resistance that could promote the working temperatures of the die-cast Mg alloys from 120–200 °C [6,14] to 200–300 °C.

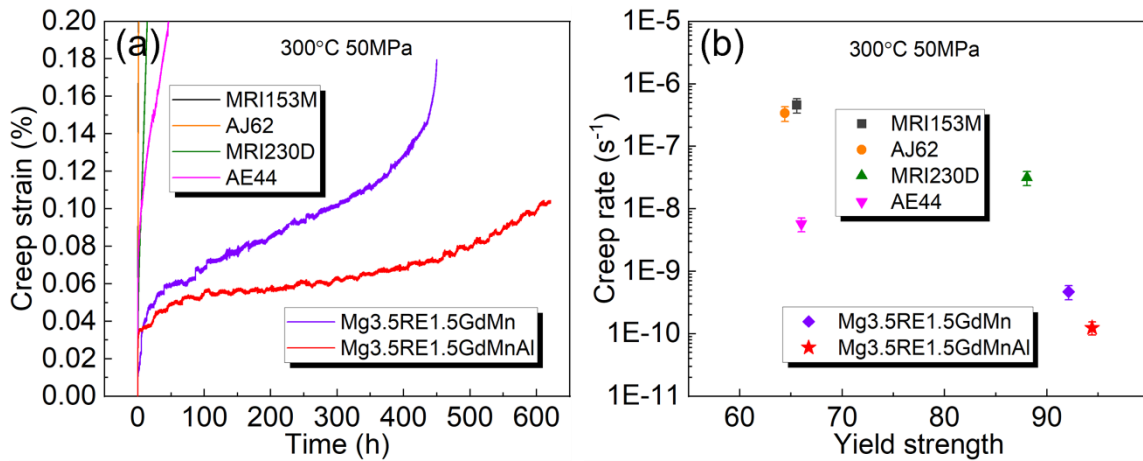


Fig. 1. Tensile creep properties of the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy under the as-cast condition, compared with the counterpart Al-free Mg_{3.5}RE_{1.5}GdMn alloy and the traditional representative Mg-Al-based commercial die-cast MRI153M, AJ62, MRI230D and AE44 alloys for elevated applications. (a) Representative creep curves; and (b) the steady-state creep rate of the alloys tested at 300 °C with a 50 MPa stress.

3.2. Microstructure evolution by creep

3.2.1. Overall morphology

Figs. 2a and 2b present the as-cast microstructure of the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy before creep. The microstructure comprised the primary α_1 -Mg matrix phase with a grain size of ~10–30 μ m, the secondary α_2 -Mg matrix phase with a grain size of ~2–10 μ m and the network of intermetallic phases at the GBs. Previous studies [14,25] have confirmed that the fine α_2 -Mg was

formed in die cavity with a higher cooling rate than the α_1 -Mg which was formed in a shot sleeve. The main body of the network at the GBs is the $Mg_{12}RE$ phase, while the blocky phase at the GBs is Al_2RE_3 (see Fig. 2b); moreover, the two intermetallic phases are determined by the composition and diffraction analysis in Sections 3.2.2 and 3.2.3. Figs. 2c and 2d present the microstructure of the $Mg_{3.5}RE_{1.5}GdMnAl$ alloy after creep at 300 °C/50 MPa for 400 h. The $Mg_{12}RE$ and Al_2RE_3 phases at the GBs showed no visible change in morphology in comparison to the phases before creep. A novel $AlMnGd$ ternary SRO/cluster was observed in the Mg matrix of the alloy both before and after creep, whereas Al_2Gd precipitate appeared in the Mg matrix of the alloy after creep (see Fig. 2d). The $AlMnGd$ SRO/cluster and Al_2Gd precipitate are further characterised in Sections 3.2.4 and 3.3. From Fig. 2d, a reported feature of denuded zones (DZ) of precipitates near the GBs of a crept Mg-Gd alloy [50] has also been observed.

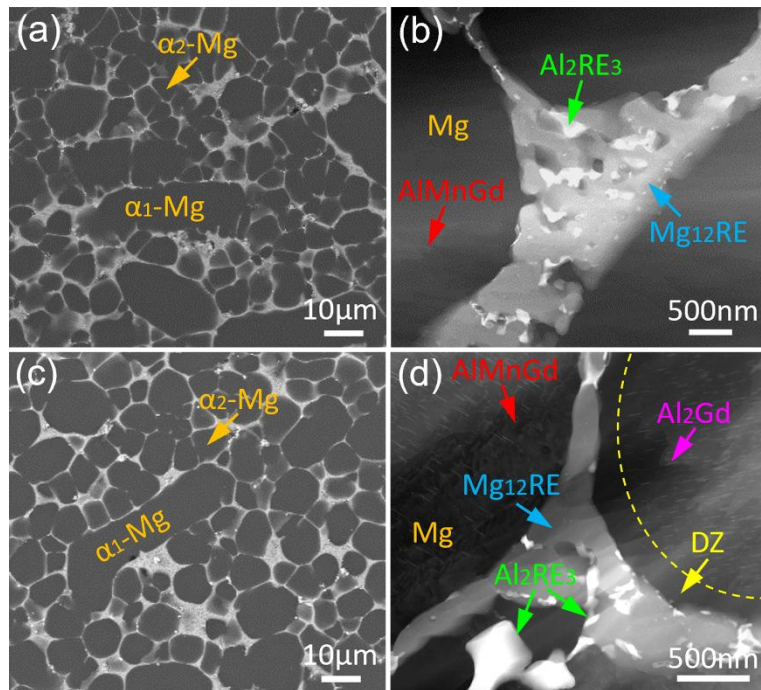


Fig. 2. Microstructure of the as-cast die-cast $Mg_{3.5}RE_{1.5}GdMnAl$ alloy (a,b) before creep and (c,d) after creep at 300 °C/50 MPa for 400 h. (a,c) BSD-SEM morphology; (b,d) STEM images showing the intermetallic phases at the GBs and the changes in the Mg matrix of the crept microstructure.

3.2.2. Mapping of the intermetallic phases at the GBs

Figs. 3a-i show the STEM/EDS mapping of elemental distributions at the GBs of the as-cast $Mg_{3.5}RE_{1.5}GdMnAl$ before creep. The $Mg_{12}RE$ phase was enriched by La, Ce, Nd, Zn and Mn, while the Al_2RE_3 phase was enriched by Gd, Nd, La, Ce, Al, Mn and Zn. At the GBs, Al and Gd

were preferred to precipitate in the Al_2RE_3 phase. The enrichment of Nd, Mn and Zn in the Al_2RE_3 phase was higher than that in the Mg_{12}RE phase, while the enrichment of the La and Ce in Al_2RE_3 and Mg_{12}RE phases were similar. Figs. 3j-r display the elemental distributions at the GBs of the die-cast $\text{Mg}_{3.5}\text{RE}_{1.5}\text{GdMnAl}$ alloy after creep at 300 °C/50 MPa for 400 h, which are similar to the distributions before creep. The measured compositions of the Mg_{12}RE and Al_2RE_3 intermetallic phases before and after creep are listed in Table 1; the atomic ratios of Mg:RE and Al:RE in the Mg_{12}RE and Al_2RE_3 intermetallic phases were approximately 12:1 and 2:3, respectively, while there was nearly no change in composition in the two intermetallic phases after creep.

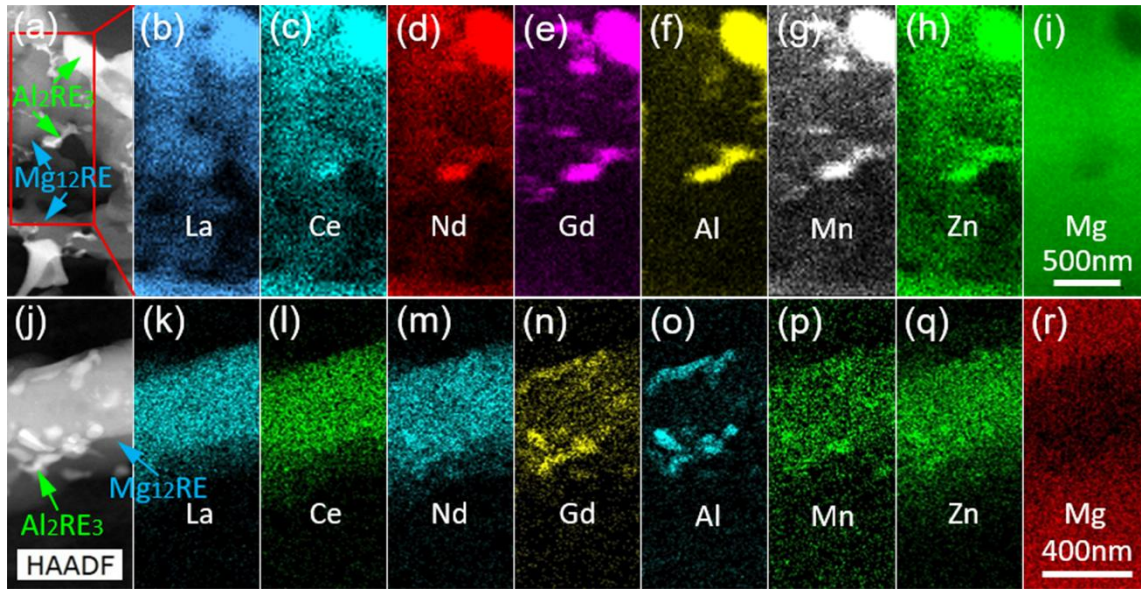


Fig. 3. STEM/EDS mapping of the elemental distributions at the GBs of the die-cast $\text{Mg}_{3.5}\text{RE}_{1.5}\text{GdMnAl}$ alloy (a-i) before creep and (j-r) after creep at 300 °C/50 MPa for 400 h. (a,j) STEM images of the Mg_{12}RE and Al_2RE_3 phases at the GBs; (b-i) maps of La, Ce, Nd, Gd, Al, Mn, Zn and Mg in the area marked by the box in (a); (k-r) maps of La, Ce, Nd, Gd, Al, Mn, Zn and Mg in (j).

Table 1 Measured compositions (in at.%) by STEM/EDS for the Mg_{12}RE and Al_2RE_3 intermetallic phases at the GBs of the die-cast $\text{Mg}_{3.5}\text{RE}_{1.5}\text{GdMnAl}$ alloy before and after creep at 300 °C/50 MPa for 400 h.

Intermetallic phases	La	Ce	Nd	Gd	Al	Mn	Zn	Mg
Mg_{12}RE (Before creep)	2.3	1.8	2.1	1.0	0.9	1.6	2.4	87.9
Mg_{12}RE (After creep)	2.5	1.8	1.9	1.2	0.8	1.6	2.5	87.7
Al_2RE_3 (Before creep)	2.7	2.3	7.9	15.1	18.9	9.2	8.3	35.6
Al_2RE_3 (After creep)	3.0	2.2	7.7	15.4	18.7	9.1	8.6	35.3

3.2.3. Diffraction of the intermetallic phases at the GBs

Figs. 4a-c and Figs. 4d-f present the diffraction patterns of the $Mg_{12}RE$ and Al_2RE_3 phases at the GBs of the die-cast $Mg_{3.5}RE_{1.5}GdMnAl$ alloy before and after creep at 300 °C/50 MPa for 400 h, respectively. $Mg_{12}RE$ has been well determined in Mg-RE-based alloys [10,26], so one diffraction pattern was given here for $Mg_{12}RE$ (see Figs. 4a, 4d), which fits with the diffraction pattern of $Mg_{12}Nd$ (Tetragonal, $a=b=10.31$ Å, $c=5.93$ Å, Space group: $I4/mmm$ [51]). Additionally, the $\{101\}$ twins can be observed in the $Mg_{12}RE$ phase. The existence of the domains of the $\{101\}$ twins in the $Mg_{12}RE$ phase has been well reported [52]. Two diffraction patterns were provided for Al_2RE_3 (see Figs. 4b, 4c, 4e and 4f), which agree with the diffraction pattern of Al_2Gd_3 (Tetragonal, $a=b=8.344$ Å, $c=7.656$ Å, Space group: $P4_2nm$ [53]). The composition and diffraction analysis demonstrated that the phases at the GBs were $Mg_{12}RE$ and Al_2RE_3 ; moreover, there were no phase transformations at the GBs after creep, indicating that $Mg_{12}RE$ and Al_2RE_3 were stable and did not degrade at the high creep temperature of 300 °C.

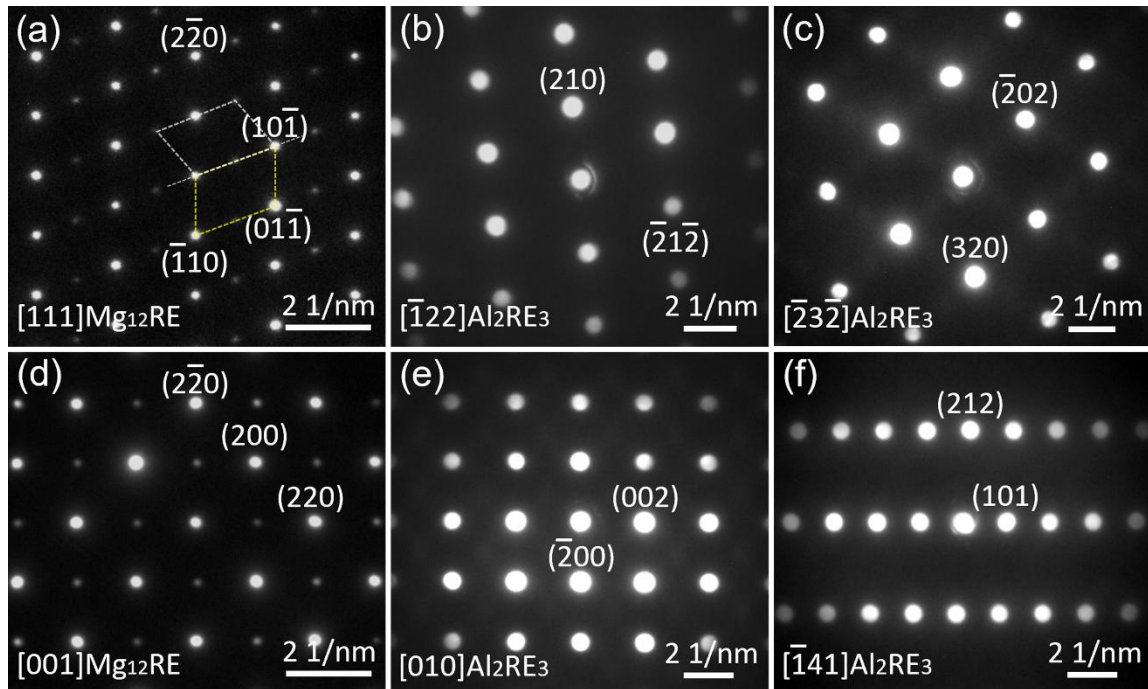


Fig. 4. Diffraction patterns of the intermetallic phases at the GBs of the die-cast $Mg_{3.5}RE_{1.5}GdMnAl$ alloy (a-c) before creep and (d-f) after creep at 300 °C/50 MPa for 400 h. (a) The diffraction pattern of a $Mg_{12}RE$ twin observed along the $[111]$ zone axis; (b, c) diffraction patterns of Al_2RE_3 observed along the $[\bar{1}22]$ and $[\bar{2}3\bar{2}]$ zone axes; (d) the diffraction pattern of a $Mg_{12}RE$ twin observed along the $[001]$ zone axis; (e, f) diffraction patterns of Al_2RE_3 observed along the $[010]$ and $[\bar{1}41]$ zone axes.

3.2.4. Microstructure evolution in the Mg matrix

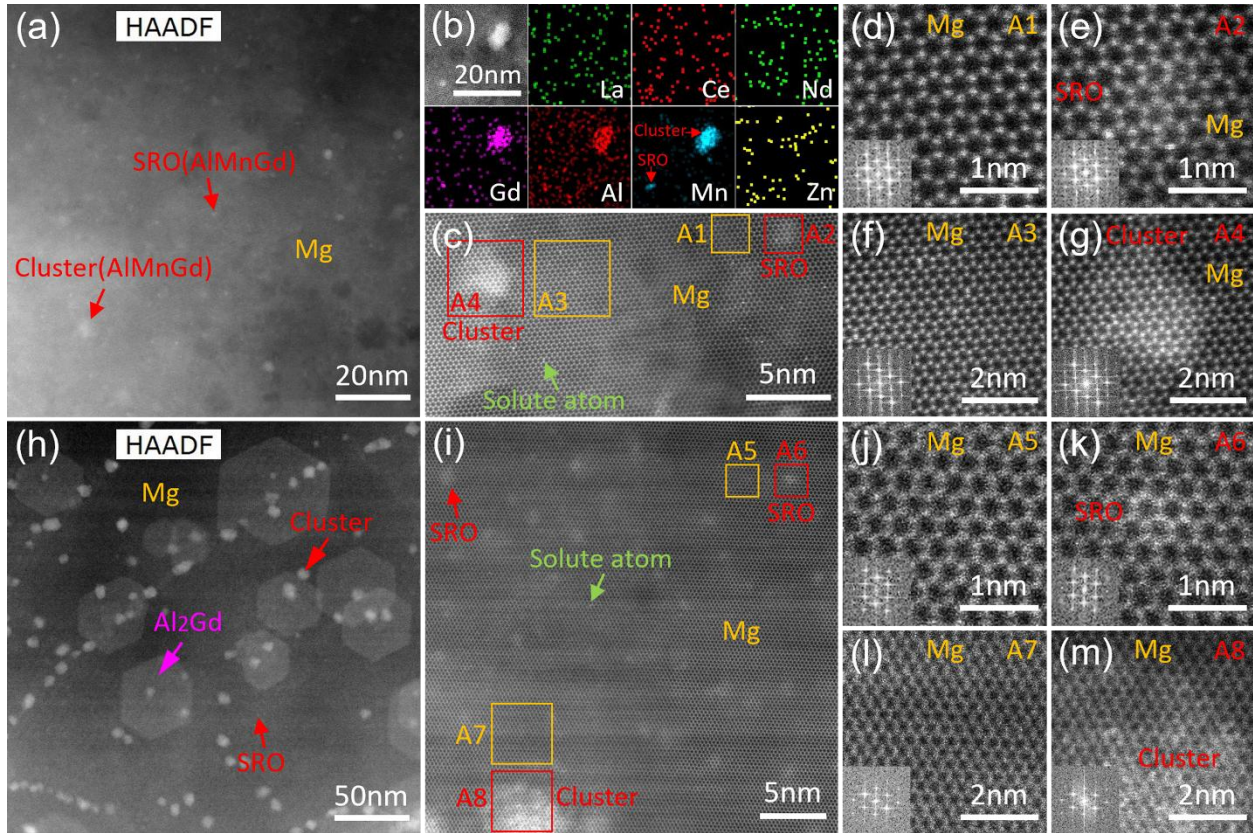


Fig. 5. STEM images showing the microstructure in the Mg matrix of the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy (a-g) before creep and (h-m) after creep at 300 °C/50 MPa for 400 h, under the projection direction of $\langle 0001 \rangle_{\text{Mg}}$. (a, c-g) The STEM-HAADF images and (b) STEM/EDS mapping of the solute atoms and AlMnGd SRO/clusters in the Mg matrix before creep; (h-m) the STEM-HAADF images showing the solute atoms, AlMnGd SRO/clusters and Al₂Gd precipitates in the Mg matrix after creep.

Figs. 5a-g and Figs. 5h-m show the microstructure in the Mg matrix of the Mg_{3.5}RE_{1.5}GdMnAl alloy before and after creep at 300 °C/50 MPa for 400 h, respectively. Solute atoms and a novel ternary AlMnGd SRO/cluster were observed in the Mg matrix of the alloy before creep. After creep at 300 °C/50 MPa for a duration of 400 h, solute atoms and the AlMnGd SRO/clusters still existed in the Mg matrix; the quantity of solute atoms decreased, while the size of some clusters slightly increased. However, the size of the clusters was under 10 nm. In this work, the AlMnGd microstructure with the size of 0–2 nm and 2–10 nm was called the SRO and cluster, respectively. In addition, the Al₂Gd precipitate with a size of ~27–75 nm appeared in the Mg matrix (see Fig. 5h). Further, the Al₂Gd precipitate exhibited a hexagonal-faceted morphology under the projection direction of $\langle 0001 \rangle_{\text{Mg}}$. The AlMnGd SRO/clusters

well occupied the positions of the Mg atoms and were coherent with the Mg matrix without a unit cell structure, both before and after creep (see Figs. 5d-g and Figs. 5j-m). SRO and clusters were also reported in some Mg alloys [29,30,54]. Therefore, the microstructure evolution mainly occurred in the Mg matrix after creep. Details of the composition and atomic-resolution structure of the Al_2Gd precipitate and AlMnGd clusters after creep are discussed in Section 3.3.

3.3. Microstructure in the crept Mg matrix

3.3.1. Elemental distribution in the Mg matrix

Fig. 6 displays the STEM/EDS mapping of the elemental distributions in the Mg matrix of the die-cast $\text{Mg}_{3.5}\text{RE}_{1.5}\text{GdMnAl}$ alloy after creep at 300 °C/50 MPa for 400 h. Fig. 6a shows the STEM-HAADF image of the Al_2Gd precipitate and AlMnGd SRO/cluster in the Mg matrix under a different projection direction of $\langle 10\bar{1}1 \rangle_{\text{Mg}}$, which was 46.8° from $\langle 0001 \rangle_{\text{Mg}}$. The observed morphology of the Al_2Gd precipitate accordingly changed a little from Fig. 5h. In addition, the AlMnGd cluster was still seen in granular morphology with a size less than 10 nm. Figs. 6b-i show the corresponding STEM/EDS maps of the elements La, Ce, Nd, Gd, Al, Mn, Zn and Mg in Fig. 6a, sequentially. The Al_2Gd precipitate was enriched in Al and Gd while the AlMnGd SRO/cluster was enriched in Al, Mn and Gd. The measured composition of the Al_2Gd precipitate by STEM/EDS is presented in Table 2. Note the compositions shown in Table 2 were relative values rather than absolute values as the effect of the Mg matrix could not be eliminated during the STEM/EDS measurement. Also, the compositions given by STEM/EDS were semi-quantitative, rather than 100 % accurate since the measurement was inevitably affected by the channeling of electrons along atomic columns in zone axis conditions [55]. However, a repeatable atomic ratio of $\text{Al}:\text{RE}(\text{Gd},\text{Nd},\text{Ce},\text{La})$ as $\sim 2:1$ could be clearly detected for a group of Al_2Gd precipitates by STEM/EDS (see Table 2); the Al_2Gd precipitate can be approximately written as $\text{Al}_2\text{Gd}_{0.5}\text{Nd}_{0.31}\text{Ce}_{0.13}\text{La}_{0.07}$. Further confirmation of the Al_2Gd precipitate was achieved by an atomic-resolution study, as discussed in Section 3.3.2. An obvious difference between the Al_2Gd precipitate and AlMnGd cluster was that the concentration of Mn in the AlMnGd cluster was much higher than in the Al_2Gd precipitate, as shown in Fig. 6g. Considering that the AlMnGd cluster was much smaller than the Al_2Gd precipitate in size, the semi-quantitative composition of the AlMnGd cluster was investigated by STEM/EDS under a higher resolution, as seen in Fig. 8.

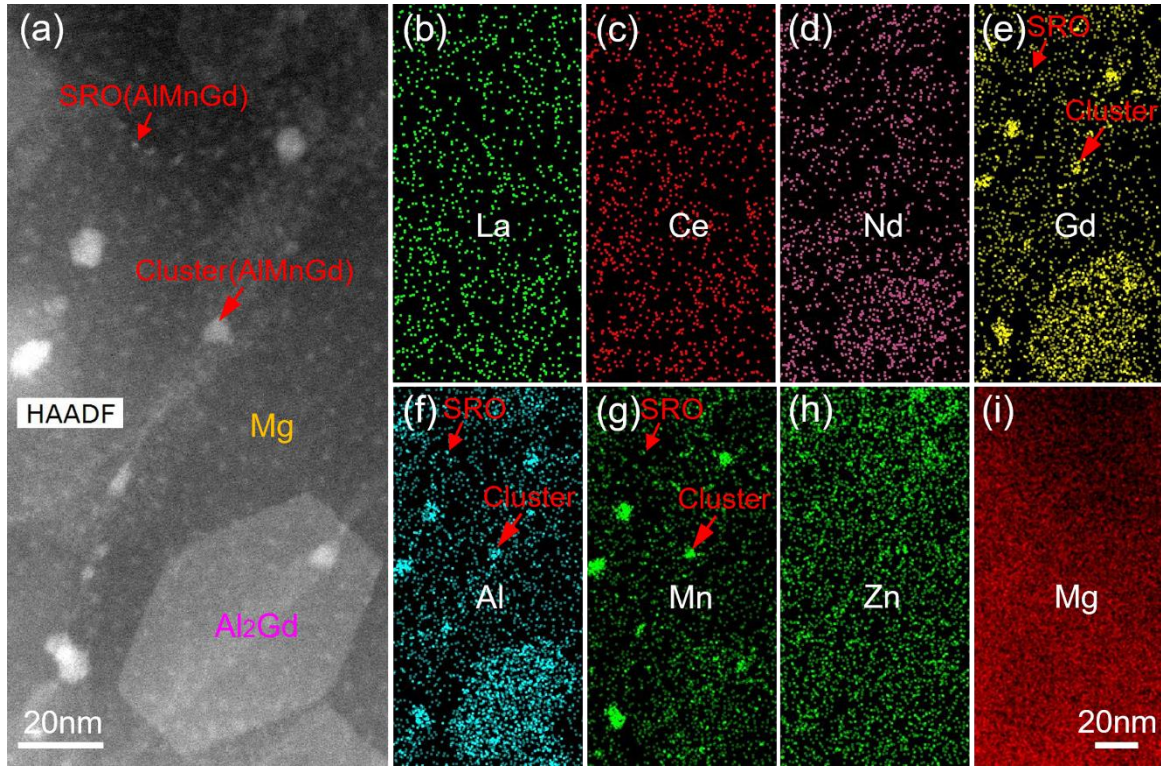


Fig. 6. STEM/EDS mapping of the elemental distributions in the Mg matrix of the die-cast $\text{Mg}_{3.5}\text{RE}_{1.5}\text{GdMnAl}$ alloy after creep at 300 °C/50 MPa for 400 h. (a) The STEM-HAADF image of the Al_2Gd precipitate and AlMnGd SRO/cluster in the Mg matrix under the projection direction of $\langle 10\bar{1}1 \rangle_{\text{Mg}}$; (b-i) STEM/EDS maps of the elements: (b) La, (c) Ce, (d) Nd, (e) Gd, (f) Al, (g) Mn, (h) Zn and (i) Mg in (a).

Table 2 Measured compositions (in at.%) by STEM/EDS for the Al_2Gd precipitates and AlMnGd clusters in the Mg matrix of the die-cast $\text{Mg}_{3.5}\text{RE}_{1.5}\text{GdMnAl}$ alloy after creep at 300 °C/50 MPa for 400 h.

Particle	La	Ce	Nd	Gd	Al	Mn	Zn	Mg
Al_2Gd	0.34	0.66	1.56	2.47	9.94	1.37	0.59	83.07
AlMnGd	0.17	0.28	0.31	1.58	9.22	7.86	0.42	80.16

3.3.2. Atomic structure of the Al_2Gd precipitate

Fig. 7 presents the typical atomic structure of the interface between the Al_2Gd precipitate and Mg matrix in the die-cast $\text{Mg}_{3.5}\text{RE}_{1.5}\text{GdMnAl}$ alloy after creep at 300 °C/50 MPa for 400 h, which was observed under the projection direction of $[111]_{\text{Al}_2\text{Gd}}/[0001]_{\text{Mg}}$. The atomic-resolution STEM-HAADF images in Figs. 7a and 7b show that the Al_2Gd precipitate has a hexagon-faceted morphology, with $\{11\bar{2}\}_{\text{Al}_2\text{RE}}/\{2\bar{1}\bar{1}0\}_{\text{Mg}}$ or $\langle 11\bar{2} \rangle_{\text{Al}_2\text{RE}}/\langle 2\bar{1}\bar{1}0 \rangle_{\text{Mg}}$. Fig. 7c shows the corresponding Fast Fourier Transform (FFT) pattern of the $\text{Al}_2\text{Gd}/\text{Mg}$ interface

illustrated in Fig. 7a. It can be seen that the FFT pattern of the Al_2Gd precipitate nearly coincided with that of the Mg matrix, indicating a very small misfit between the Al_2Gd precipitate and Mg matrix in the 2D hexagon plane that is perpendicular to $[111]\text{Al}_2\text{Gd}$ or $[0001]\text{Mg}$. Fig. 7d presents the simulated atomic structure model of the $\text{Al}_2\text{Gd}/\text{Mg}$ interface under the same projection direction of $[111]\text{Al}_2\text{Gd}/[0001]\text{Mg}$, based on the standard unit cells of Mg and Al_2Gd (face-centred cubic, $a=7.899 \text{ \AA}$, Space group: Fd-3m [56]), which agrees with the results shown in Fig. 7b. The theoretical in-plane ($\perp[0001]\text{Mg}$) misfit between the Al_2Gd precipitate and Mg matrix along the directions of $\langle 11\bar{2} \rangle\text{Al}_2\text{Gd}/\langle 2\bar{1}\bar{1}0 \rangle\text{Mg}$ is only 0.49 %.

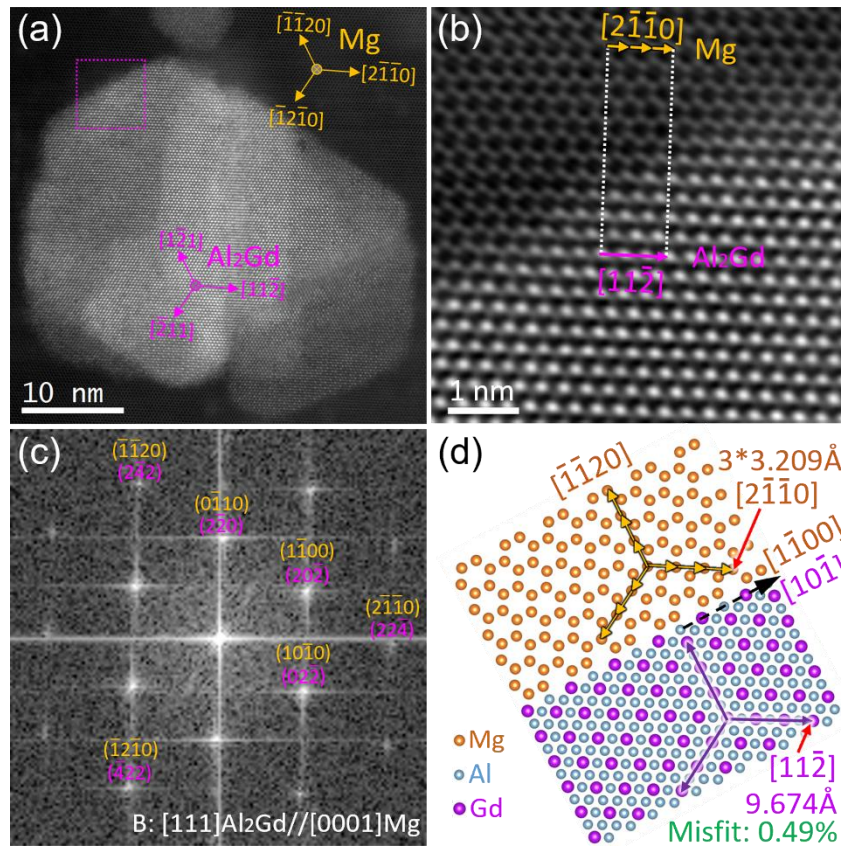


Fig. 7. (a) Atomic-resolution STEM-HAADF image showing the Al_2Gd precipitate in the Mg matrix of the die-cast $\text{Mg}_{3.5}\text{RE}_{1.5}\text{GdMnAl}$ alloy after creep at $300 \text{ }^\circ\text{C}/50 \text{ MPa}$ for 400 h, observed along the zone axis $[111]\text{Al}_2\text{Gd}/[0001]\text{Mg}$; (b) enlarged view of the $\text{Al}_2\text{Gd}/\text{Mg}$ interface marked by a dotted box in (a); (c) FFT pattern of the $\text{Al}_2\text{Gd}/\text{Mg}$ interface in (a); (d) simulated atomic structure model showing the $\text{Al}_2\text{Gd}/\text{Mg}$ interface ($\{11\bar{2}\}\text{Al}_2\text{Gd}/\{2\bar{1}\bar{1}0\}\text{Mg}$, $[10\bar{1}]\text{Al}_2\text{Gd}/[1\bar{1}00]\text{Mg}$) in (a, b). All projection directions are $[111]\text{Al}_2\text{Gd}/[0001]\text{Mg}$.

3.3.3. AlMnGd clusters in the Mg matrix

3.3.3.1. High-resolution mapping of the AlMnGd clusters

Fig. 8 displays a high-resolution STEM/EDS mapping of the **AlMnGd cluster** in the Mg matrix of the die-cast **Mg_{3.5}RE_{1.5}GdMnAl** alloy after creep at 300 °C/50 MPa for 400 h. The **AlMnGd cluster** was enriched by Al, Mn and Gd, and the concentrations of Al and Mn were higher than Gd in the cluster (see Figs. 8b-i). The measured composition of the **AlMnGd cluster** by STEM/EDS is listed in Table 2, that is 9.22at.%Al, 7.86at.%Mn, 1.58at.%Gd, 0.31at.%Nd, 0.28at.%Ce, 0.17at.%Ce and 0.42at.%Zn.

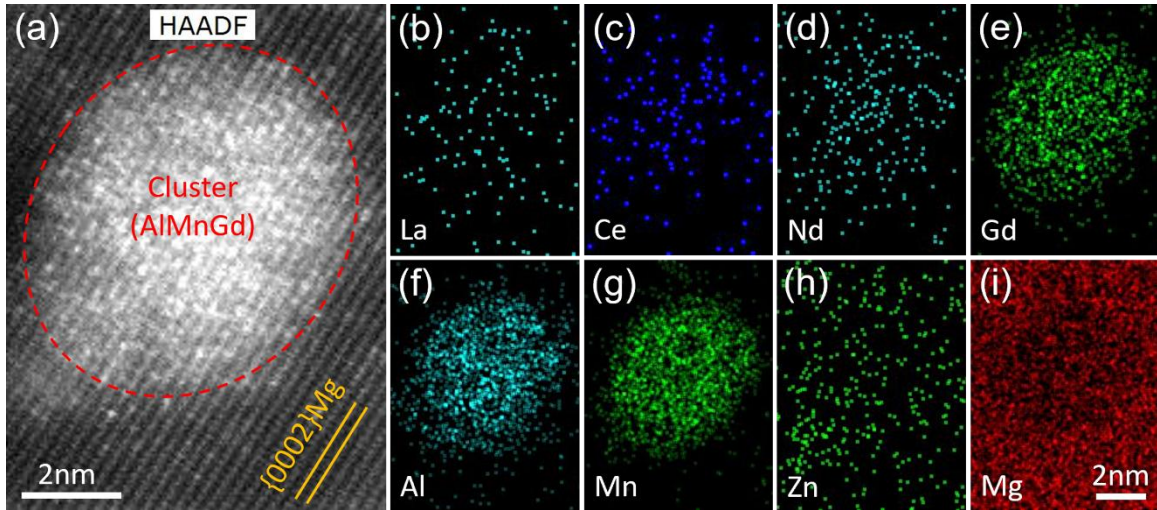


Fig. 8. STEM/EDS mapping of the **AlMnGd cluster** in the Mg matrix of the die-cast **Mg_{3.5}RE_{1.5}GdMnAl** alloy after creep at 300 °C/50 MPa for 400 h. (a) Atomic-resolution STEM-HAADF image showing the **AlMnGd cluster** in the Mg matrix, observed along the zone axis of $[10\bar{1}0]\text{Mg}$; (b-i) STEM/EDS maps of the elements: (b) La, (c) Ce, (d) Nd, (e) Gd, (f) Al, (g) Mn, (h) Zn and (i) Mg in (a).

3.3.3.2. Atomic structure of the **AlMnGd clusters**

Figs. 9a-c present the atomic-resolution STEM-HAADF images of the **AlMnGd clusters** in the Mg matrix of the die-cast **Mg_{3.5}RE_{1.5}GdMnAl** alloy after creep at 300 °C/50 MPa for 400 h, under three different projection directions of $[0001]\text{Mg}$, $[10\bar{1}0]\text{Mg}$ and $[10\bar{1}1]\text{Mg}$, respectively. $[10\bar{1}1]\text{Mg}$ and $[10\bar{1}0]\text{Mg}$ were 46.8° and 90° from $[0001]\text{Mg}$, respectively. The **AlMnGd clusters** were in granular shapes under all the three projection directions, demonstrating that **AlMnGd clusters** are in 3D spheroidal shapes. In addition, the **AlMnGd clusters** were observed as being coherent with the Mg matrix (see Figs. 9a-c), which was also verified by the corresponding FFT patterns in Figs. 9d-f. Furthermore, the **AlMnGd clusters** were still far from forming a clear unit cell structure with corresponding diffraction patterns (see Figs. 9d-f) after

creep at 300 °C/50 MPa for a duration of 400 h; they can also be considered as clusters that have well occupied the positions of the Mg atoms (see Figs. 9a-c).

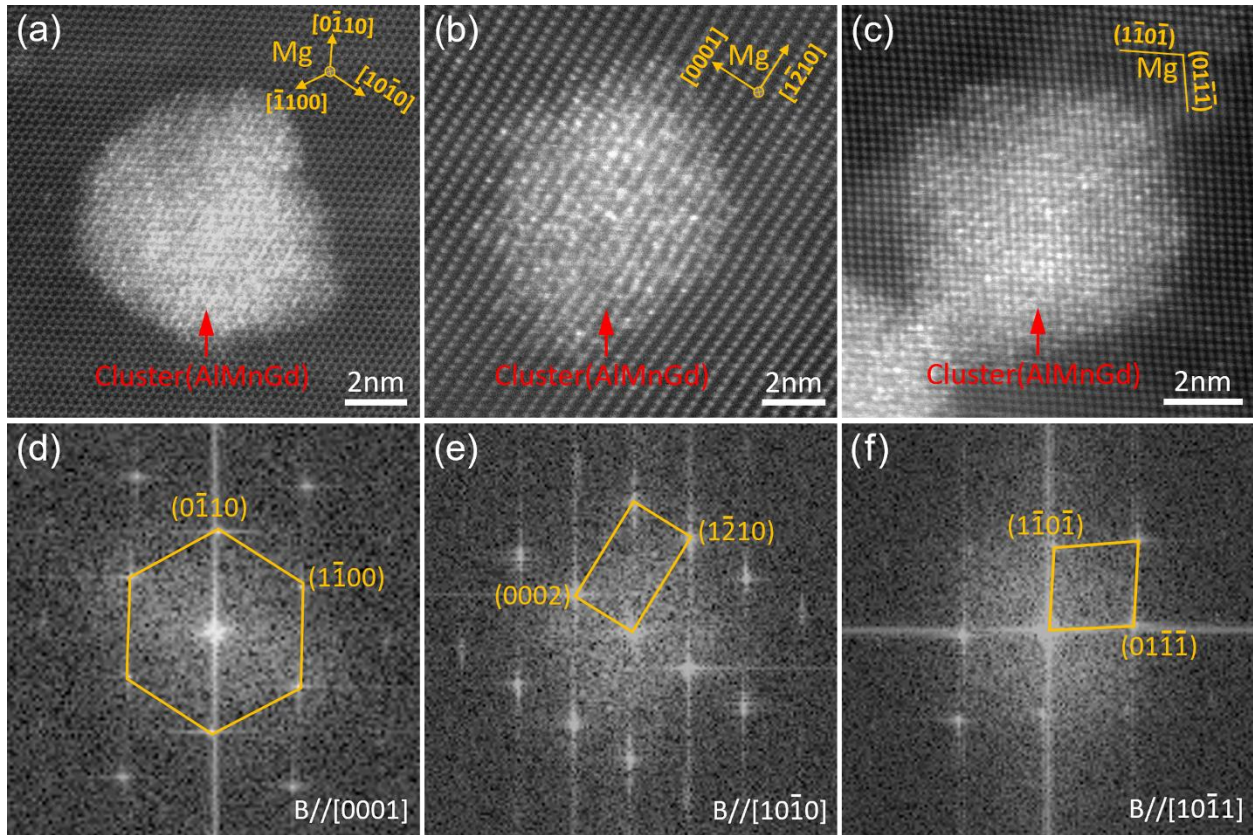


Fig. 9. Atomic-resolution STEM-HAADF imaging from three directions of the 3D morphology and coherence of the AlMnGd clusters in the Mg matrix of the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy after creep at 300 °C/50 MPa for 400 h. (a), (b) and (c) are atomic-resolution STEM-HAADF images of the AlMnGd clusters in the Mg matrix, observed along the zone axes of [0001]Mg, [1 0 $\bar{1}$ 0]Mg and [1 0 $\bar{1}$ 1]Mg, respectively; (d), (e) and (f) are FFT patterns corresponding to the AlMnGd cluster and Mg matrix in (a), (b) and (c), respectively.

4. Discussion

4.1. Stability of the precipitate and SRO/cluster in the Mg matrix

After creep at 300 °C/50 MPa for 400 h, Al₂Gd precipitates showed a limited growth to ~27–75 nm (see Fig. 5h); the size of the AlMnGd SRO/clusters did not exceed 10 nm (see Figs. 5h and 6a), indicating the excellent coarsening resistance and thermal stability of these two microstructures, especially the AlMnGd SRO/clusters. Al₂RE had the maximum thermal stability among the Al-RE serials compounds, due to its lowest negative formation energy of -0.46 eV/atom [57,58]. It also had a melting point of ~1200 °C [2]. As discussed in Section 3.3.1, the

Al_2Gd precipitates are enriched by the later lanthanides Gd that has a strong combination with Al [30,58]. The Al-Mn dynamic precipitates can improve the creep resistance of the die-cast Mg-Al-based alloys, such as Mg-4Al-4RE-0.3Mn [36]. Further, the Al_8Mn_5 precipitate was identified in these alloys [37]. From the Al-Mn-RE ternary phase diagram, $\text{Al}_8\text{Mn}_4\text{RE}$ is a possible constituent. It was reported [59] that the addition of Y resulted in the precipitation of $\text{Al}_8\text{Mn}_4\text{RE}$ in a heat-treated AZ31-0.5Ca-0.25Y alloy, instead of Al_8Mn_5 , demonstrating that $\text{Al}_8\text{Mn}_4\text{RE}$ is more stable than Al_8Mn_5 . The addition of Gd led to the formation of the AlMnGd clusters (see Fig. 8) with a semi-quantitative composition of $\text{Al}_{9.22}\text{Mn}_{7.86}\text{RE}_{2.34}(\text{Gd}_{1.58}\text{Nd}_{0.31}\text{Ce}_{0.28}\text{La}_{0.17})$ (see Table 2), which has been shown to be very close to the $\text{Al}_{10}\text{Mn}_7\text{RE}_2$ phase [60,61]. Note that the $\text{Al}_{10}\text{Mn}_7\text{RE}_2$ intermetallic phase was located at the GBs, rather than in the Mg matrix in these reports. The formation energy of the $\text{Al}_x\text{Mn}_y\text{RE}_z$ phases can be determined as follows:

$$\Delta H = (E_{\text{total}} - xE_{\text{Al}} - yE_{\text{Mn}} - zE_{\text{RE}})/(x + y + z) \quad (1)$$

Where E_{total} is the total energy, E_{Al} , E_{Mn} and E_{RE} are the ground state energies per atom of Al, Mn and RE, and x, y and z are the numbers of the Al, Mn and RE atoms, respectively.

As can be seen in Eq. (1), the formation energies of the $\text{Al}_{10}\text{Mn}_7\text{RE}_2$ and $\text{Al}_8\text{Mn}_4\text{RE}$ phases were calculated as -2.17 eV/atom and -1.90 eV/atom [62], respectively, indicating that $\text{Al}_{10}\text{Mn}_7\text{RE}_2$ can be more stable than $\text{Al}_8\text{Mn}_4\text{RE}$. Moreover, the thermal stability of these three Al-Mn(RE) precipitates is $\text{Al}_{10}\text{Mn}_7\text{RE}_2 > \text{Al}_8\text{Mn}_4\text{RE} > \text{Al}_8\text{Mn}_5$. Therefore, both the Al_2Gd precipitates and approximate $\text{Al}_{10}\text{Mn}_7\text{Gd}_2$ clusters formed here are very stable among the possible series of Al-Gd and Al-Mn-Gd precipitates. The approximate $\text{Al}_{10}\text{Mn}_7\text{Gd}_2$ clusters can be far more stable than the Al_2Gd precipitates, as the formation energy of $\text{Al}_{10}\text{Mn}_7\text{Gd}_2$ is considerably lower than that of Al_2Gd by -1.71 eV/atom [57,58,62]. As illustrated in Fig. 9, the approximate $\text{Al}_{10}\text{Mn}_7\text{Gd}_2$ clusters are still in the early stage of clustering without any clear unit cell structure or corresponding FFT pattern. However, the alloy has been crept under the critical conditions of 300 °C/50 MPa for a duration of 400 h, further demonstrating the high thermal stability of the AMnGd SRO/clusters.

4.2. Precipitates/GBs and dislocation interaction

Fig. 10 shows the interactions between dislocations and precipitates in the Mg matrix, and between the dislocations and intermetallic phases at the GBs during the steady-state creep of the die-cast Mg3.5RE1.5GdMnAl alloy at 300 °C/50 MPa. Following the Burgers vector analysis method and the invisibility criteria of dislocations in Mg alloys [23], the dislocations were

viewed with $\mathbf{g} = [10\bar{1}1]\text{Mg}$ (see Figs. 10a,b), $\mathbf{g} = [0002]\text{Mg}$ (see Fig. 10c) and $\mathbf{g} = [10\bar{1}0]\text{Mg}$ (see Fig. 10d), under the projection direction of $[1\bar{2}10]\text{Mg}$. The dislocations are aligned on both basal and non-basal planes of the Mg matrix when observed with $\mathbf{g} = [10\bar{1}1]\text{Mg}$ (see Fig. 10a). However, some of the dislocations become invisible when viewed with $\mathbf{g} = [0002]\text{Mg}$ (see Fig. 10c), indicating the presence of $\langle a \rangle$ Burgers vector. The dislocations that are visible under $\mathbf{g} = [0002]\text{Mg}$ should have a $\langle c \rangle$ component. A further observation under $\mathbf{g} = [10\bar{1}0]\text{Mg}$ (see Fig. 10d) indicates that the dislocations having a $\langle c \rangle$ component are in the forms of both the $\langle c \rangle$ and $\langle a+c \rangle$ dislocations.

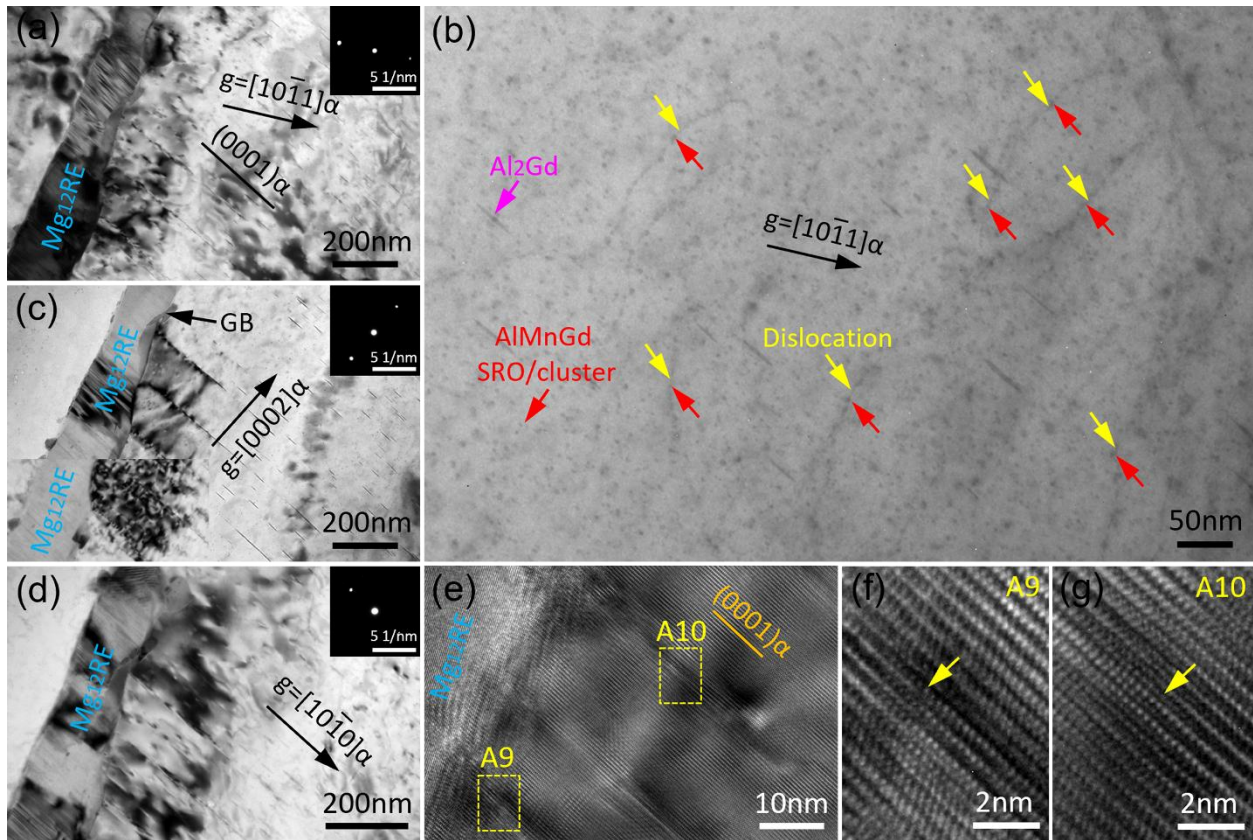


Fig. 10. (a-d) BF-TEM under two-beam conditions and (e-g) HRTEM images viewed along the $[1\bar{2}10]\text{Mg}$, showing the dislocations in the die-cast $\text{Mg}_{3.5}\text{RE}_{1.5}\text{GdMnAl}$ alloy after creep at $300^\circ\text{C}/50\text{ MPa}$ for 400 h. (a, b) The dislocations viewed with $\mathbf{g} = [10\bar{1}1]\text{Mg}$: (a) dislocations near the GBs; (b) dislocations far from the GBs, and dislocations massively pinning by the AlMnGd SRO and clusters; (c) dislocations at a similar area to (a) and viewed with $\mathbf{g} = [0002]\text{Mg}$, and the insert shows dislocation pile-up at the GBs; (d) dislocations at similar area to (a, c) and viewed with $\mathbf{g} = [10\bar{1}0]\text{Mg}$; (e) HRTEM image showing the dislocations very near the GBs; (f) and (g) enlarged views of the dislocation areas marked by A9 and A10 in (e), respectively.

Importantly, the AlMnGd SRO/clusters were massively observed for pinning dislocations in the Mg matrix (see Fig. 10b). Al_2Gd precipitates can also contribute to dislocation pinning (see

Fig. 10c); however, due to the lower number density and larger size, their contribution to the dislocation pinning may not be as significant as the AlMnGd SRO/clusters. Furthermore, a dislocation pile-up can be observed at the GBs (see Fig. 10c), which indicated that the Mg₁₂RE network at the GBs retarded any further motion of the dislocations. The HRTEM images in Figs. 10e-g show the impeding of the dislocations across the GBs by the Mg₁₂RE network.

4.3. Effects of the precipitates and SRO/clusters on creep

Dynamic precipitates were traditionally thought to contribute to the creep resistance of Mg alloys via dislocation pinning [28,35,36]. However, in some alloys such as Mg-0.45La-1.2Y (in at.%), SRO/clusters can play an important role for creep resistance [29]. There have been some intense debates about the effects of the dynamic precipitates and SRO/clusters on creep resistance [6]. Some researchers thought that SRO/clusters were thermally unstable and disappeared after ageing and/or creep for a while [31,32]. Clearly, massive amounts of the AlMnGd SRO/clusters still existed in the Mg matrix of the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy, after creep at 300 °C/50 MPa for a duration of 400 h, which can be attributed to the high thermal stability of the AlMnGd SRO/clusters, as discussed in Section 4.1. SRO/clusters could also hinder dislocation movement and contribute to creep resistance [30,54]. Here, both the Al₂Gd precipitates (see Fig. 10c) and the AlMnGd SRO/clusters (see Fig. 10b) were observed for dislocation pinning in the Mg matrix, which can contribute to creep resistance. However, the number density (see Figs. 5h, 6a and 10b) and thermal stability (see Section 4.1) of the AlMnGd SRO/clusters were much higher than the Al₂Gd precipitates, so the AlMnGd SRO/clusters should play an important role for the creep resistance of the Mg_{3.5}RE_{1.5}GdMnAl alloy. The microstructure and composition analysis (see Supplementary Fig. S2 and Fig. S3) demonstrated that the addition of Al hardly changed the Mg₁₂RE network at the GBs, and it also did not change the content of the other solute atoms in the Mg matrix, compared with the counterpart Al-free Mg_{3.5}RE(La,Ce,Nd)_{1.5}GdMn alloy. The combination of Al and Gd mainly resulted in two changes in the Mg_{3.5}RE(La,Ce,Nd)_{1.5}GdMnAl alloy: (1) forming the minority of the Al and Gd rich Al₂RE₃ phase at the GBs (see Figs. 2-4, Table 1 and Supplementary Fig. S2) that had a limited effect on creep; (2) forming a large number of thermally stable and creep-resistant AlMnGd SRO/clusters in the Mg matrix (see Figs. 5, 6, 8 and 10b, and Table 2). In addition, the singular addition of Al into traditional Gd-free Mg-RE(La,Ce,Nd) alloys has been extensively researched for deteriorating creep resistance [10,26]. Therefore, it is not the singular effect of Al

or Gd that provides the exceptional improvement of creep resistance; it is the synthetic effect of Al, Gd and Mn to form the novel thermally stable and creep-resistant ternary AlMnGd SRO/clusters in the Mg matrix that provides the exceptional improvement in the creep resistance in the Mg_{3.5}RE(La,Ce,Nd)_{1.5}GdMnAl alloy. This is in contrast to the counterpart Al-free Mg_{3.5}RE(La,Ce,Nd)_{1.5}GdMn alloy and the traditional Gd-free Mg-RE(La,Ce,Nd) alloys [10,26].

4.4. Effects of Mg₁₂RE/Al₂RE₃ at the GBs on creep

It was suggested that the formation of the Mg₁₂RE phase at the GBs became possible in Mg-Al-RE alloys when the RE/Al weight ratio was above 1.4 [60]. In differentiation to the divorced or lamellar Al-containing compounds in the die-cast Mg-Al-based alloys, Mg₁₂RE constitutes the major intermetallic phase at the GBs of the Al-free die-cast Mg-RE alloys [10,23]. More importantly, Mg₁₂RE can form a network. With the increase of the RE/Al weight ratio, there is a transition from the Al-rich Al₁₁RE₃ to the Al-free Mg₁₂RE at the GBs. In theory, the transition sequence is Al₁₁RE₃ → Al₂RE → AlRE → Al₂RE₃ → AlRE₂ → Mg₁₂RE [57]. As the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy has a RE/Al weight ratio of ~10:1, the Mg₁₂RE network can form at the GBs (see Fig. 2). However, Al is tied up by RE, especially Gd, to form the divorced Al₂RE₃ compound at the GBs (see Fig. 3). Mg₁₂RE was reported to be more stable than Al₁₁RE₃, which can degrade to Al₂RE via a releasing of Al [24,26]. The diffraction analysis after creep (see Fig. 4) also supported the stability of Mg₁₂RE. It was further reported [33] that the increasing interconnectivity of the intermetallic phase at the GBs was important for the enhancement of creep resistance as it can shield more load from the matrix. Regarding Al₂RE₃, it is highly rich in RE, rather than Al, and it has the only theoretical possibility of decomposition into AlRE₂. However, this decomposition would not occur (see Fig. 4) even at 300 °C/50 MPa as the later lanthanides including Gd had a strong combination with Al [58]. Moreover, Al₂RE₃ has a melting point of more than 1000 °C [57]. Thus, in terms of the intermetallic phases at the GBs, the addition of Al here did not deteriorate the creep properties as Al was tied up by Gd to form the thermally stable Al₂RE₃ compound. Considering that the major phase at the GBs was the thermally stable network of Mg₁₂RE, Mg₁₂RE should also play a significant part in the excellent creep resistance in the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy via impeding the movement of dislocations across the GBs (see Figs. 10c and 10e). This is in comparison to the traditional Mg-

Al-based commercial die-cast alloys (see Fig. 1) for elevated applications. However, for the counterpart Al-free Mg_{3.5}RE_{1.5}GdMn alloy, the addition of 0.5wt.% Al should have a very limited effect on the improvement of creep resistance at the GBs since it hardly changed the major Mg₁₂RE network at the GBs (see Supplementary Fig. S3 and Table S1). In addition, the grain size of the Mg_{3.5}RE_{1.5}GdMnAl alloy and the counterpart Al-free Mg_{3.5}RE_{1.5}GdMn alloy were measured as 13.2 μm and 13.7 μm (see Supplementary Fig. S4), respectively, so the effect of grain size on the improvement of creep resistance was very limited.

4.5. Creep mechanisms from n/Q values

In the secondary steady-state of creep, a near-constant creep rate is normally achieved, **that** is the steady-state creep rate (SCR, $\dot{\epsilon}$), which can be described by the **power law** equation as follows [9]:

$$\dot{\epsilon} = A\sigma^n \exp\left(-\frac{Q}{RT}\right) \quad (2)$$

Where A is a constant, σ is the applied stress, n is the stress exponent **and** Q is the activation energy for creep, T is the absolute **temperature** **and** R is the gas constant. For n , it is generally accepted that the dominant steady-state creep mechanisms of Mg alloys are diffusional creep ($n=1$), GBS ($n=2$) and dislocation creep ($n=3-7$); $n=3$ indicates solute atom or precipitate drag dislocation gliding, while $n=4-7$ demonstrates dislocation gliding and climbing [6]. For Q , the indicating main steady-state creep mechanisms of Mg alloys are GBS ($Q=40-60$ kJ/mol), **GB diffusion (GBD)** ($Q=60-80$ kJ/mol), pipe diffusion through dislocations ($Q=92$ kJ/mol), self-diffusion of Mg ($Q=135$ kJ/mol) and cross-slip ($Q=229-325$ kJ/mol) [9]. At higher creep temperatures and applied stresses, the breakdown of **the power law can** happen, which can be determined by Eqs. (3 and 4) [6]:

$$\dot{\epsilon}/D > 10^{13} \text{m}^{-2} \quad (3)$$

$$D = 10^{-4} \exp\left(-\frac{Q_L}{RT}\right) \text{ (m}^2\text{s}^{-1}\text{)} \quad (4)$$

Where Q_L is the activation energy of the self-diffusion of Mg (135 kJ/mol).

Fig. 11a shows the variation of $\text{Ln}\dot{\epsilon}$ versus $\text{Ln}\sigma$, and n **was** determined as 2.3, 2.5 and 3.1 at 200 °C, 250 °C and 300 °C, respectively. **Fig. 11b** presents the evolution of $\text{Ln}\dot{\epsilon}$ versus $1/T$ under different creep stresses. At the creep temperature range of 200–300 °C, Q are 62.1 kJ/mol and 85.4 kJ/mol at 50 MPa and 80 MPa, **respectively**. At 200–250 °C and 50–80 MPa, n is 2.3–2.5, and Q (62.1–85.4 kJ/mol) is close to the activation energy of GBD [9], indicating that the

dominant steady-state creep mechanisms are GBS and GBD. At 300 °C and 50–80 MPa, n increases to 3.1 while Q maintains at 62.1–85.4 kJ/mol, demonstrating that the dominant steady-state creep mechanisms are drag dislocation gliding and GBD, in which the dislocation gliding can be mainly dragged by the AlMnGd SRO/clusters (see Fig. 10b). At the critical creep conditions of 300 °C/50–80 MPa, $\dot{\epsilon}/D$ ($0.32\text{--}1.71\times 10^7\text{ m}^{-2}$) is less than 10^{13} m^{-2} , indicating that creep still satisfies the power-law.

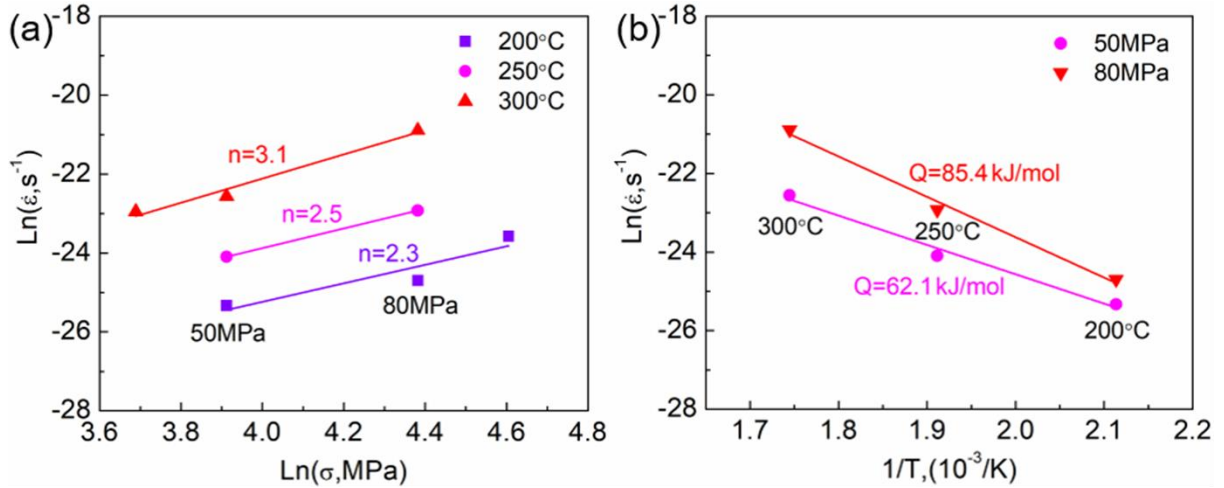


Fig. 11. (a) Steady-state creep rate plotted against applied stress and (b) temperature dependence of the steady-state creep rate for the determination of the n and Q values in the power-law equation for the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy during creep.

Overall, the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy offers a super low steady-state creep rate of $1.25\times 10^{-10}\text{ s}^{-1}$ under the critical condition of 300 °C/50 MPa, and it now enables the die-cast Mg alloys to work at the higher temperatures of 200–300 °C. Compared with the counterpart Al-free Mg_{3.5}RE_{1.5}GdMn alloy, the addition of 0.5wt.% Al led to a 73 % reduction in the steady-state creep rate. It is the synthetic effect of Al, Gd and Mn in forming the novel thermally stable and creep-resistant ternary AlMnGd SRO/clusters in the Mg matrix that provides the exceptional improvement of creep resistance in the Mg_{3.5}RE_{1.5}GdMnAl alloy. This is in contrast to the counterpart Al-free Mg_{3.5}RE_{1.5}GdMn alloy and the traditional Gd-free Mg-RE(La,Ce,Nd) alloys [10,26], which breaks the traditional understanding of the disadvantage of Al on the creep resistance of Mg alloys. The formation of a thermally stable network of the Mg₁₂RE(La,Ce,Nd) intermetallic phase at the GBs, which impeded dislocation mobility, also played an important role in achieving the super creep resistance in the Mg_{3.5}RE_{1.5}GdMnAl alloy. This compares starkly with the traditional Mg-Al-based commercial die-cast alloys for elevated applications. The hope is that this work can provide a novel approach for designing high performance Mg

alloys for higher elevated applications, with the positive effects of Al on both castability and elevated mechanical properties.

5. Conclusions

(1) The die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy offers a super-low steady-state creep rate of $1.25 \times 10^{-10} \text{ s}^{-1}$ under the critical condition of 300 °C/50 MPa, which is 73 % lower than the counterpart Al-free Mg_{3.5}RE_{1.5}GdMn alloy, and much lower than the traditional Mg-Al-based commercial die-cast alloys for elevated applications; this now enables die-cast Mg alloys to work at the higher temperatures of 200–300 °C.

(2) The addition of Al induces the formation of a novel thermally stable ternary AlMnGd SRO/cluster in the Mg matrix of the Gd-containing Mg_{3.5}RE_{1.5}GdMnAl alloy. The AlMnGd SRO/clusters still exist after creep at 300 °C/50 MPa for 400 hours. Moreover, the AlMnGd SRO/clusters can be massively observed for dislocation pinning during creep. It is the synthetic effect of Al, Gd and Mn to form the thermally stable and creep-resistant AlMnGd SRO/clusters that provides the exceptional improvement of creep resistance in the Mg_{3.5}RE_{1.5}GdMnAl alloy in comparison to the counterpart Al-free Mg_{3.5}RE_{1.5}GdMn alloy; this breaks the traditional understanding of the disadvantage of Al on the creep resistance of Mg alloys.

(3) A thermally stable network of the Mg₁₂RE(La,Ce,Nd) phase forms at the GBs of the Mg_{3.5}RE_{1.5}GdMnAl alloy; it also impedes the further motion of dislocations across the GBs, which plays a significant role in achieving the super creep resistance in the Mg_{3.5}RE_{1.5}GdMnAl alloy, in contrast to the traditional Mg-Al-based commercial die-cast alloys for elevated applications. In addition, at the GBs, Al is mainly tied up by Gd to form a minority of thermally stable RE-rich Al₂RE₃ compounds that do not degrade at the high creep temperature of 300 °C.

(4) The obtained n and Q values in the power law demonstrate that the dominant steady-state creep mechanisms of the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloys under different creep temperatures and applied stresses are: a) GBS and GBD at 200–250 °C/50–80 MPa ($n=2.3\text{--}2.5$, $Q=62.1\text{--}85.4 \text{ kJ/mol}$); and b) SRO/clusters drag dislocation gliding associated with GBD at 300 °C/50–80 MPa ($n=3.1$, $Q=62.1\text{--}85.4 \text{ kJ/mol}$). Under the critical creep conditions of 300 °C/50–80 MPa, $\dot{\epsilon}/D$ is $0.32\text{--}1.71 \times 10^7 \text{ m}^{-2}$, and the creep of the die-cast Mg_{3.5}RE_{1.5}GdMnAl alloy still satisfies the power law.

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