MICROSTRUCTURAL CHARACTERIZATION OF CREPT Mg-Gd(-Zn-Y)-Zr ALLOYS

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THE DEGREE OF DOCTOR OF PHILOSOPHY
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ABSTRACT

Mg alloys containing rare-earth elements are promising for applications in the automobile and aerospace industries due to their low densities and high specific strengths. However, most Mg alloys do not exhibit desirable high temperature performance, which limits applications of Mg alloys at elevated temperatures. The development of Mg alloys with attractive creep strength has been one of the Mg alloy research focuses, and then WE (Mg-Y-Nd based) series alloys were developed for the application at elevated temperatures. Recently, it was reported that Mg-Gd binary alloys and Mg-Gd(-Y)-Zn based alloys exhibited better creep resistance than the WE series alloys. Furthermore, it was found that the desirable high-temperature properties were attributed to the precipitation of the lenticular $\beta'$ (Mg$_7$Gd) and plate-shaped $\beta_1$ (Mg$_3$Gd) phases on the prismatic planes in the Mg-Gd binary alloys, and the $\gamma''$ (Mg$_{70}$Gd$_{15}$Zn$_{15}$), $\gamma'$ (MgGdZn) particles and long period stacking ordered structures (LPSO) on the basal planes in the Mg-Gd(-Y)-Zn based alloys. However, a systematic investigation of effects of the Gd, Y and Zn elements on the creep properties of Mg-Gd alloys and the evolution of precipitates during creep tests are still lacking.

Therefore, the principle aims of this project are to investigate creep properties of Mg-Gd based alloys and find out roles of Gd, Y and Zn additions in determining the creep properties. Four alloy compositions were designed, namely Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr (at.%). Zr is used as a grain refiner to keep the grain size similar in these alloys prior to the creep tests. The creep tests were performed at 250 °C under 80, 100, 120 MPa and 300 °C under 40, 60, 80 MPa. The microstructures of the samples before and after the creep tests were also investigated using scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and computer simulation.

The results of the creep tests show that the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy exhibits the best creep resistance, for instance, the minimum creep rates obtained at 250 °C under 80, 100 and 120 MPa are $1.7 \times 10^{-9}$, $4.5 \times 10^{-9}$, $1.3 \times 10^{-8}$ s$^{-1}$, respectively. In contrast, the Mg-2.5Gd-1.0Zn-0.1Zr
alloy shows the worst creep resistance. It is also found that dislocation creep predominates in the steady-state creep stages for all alloys, except the Mg-2.5Gd-0.1Zr alloy which exhibits a combination of dislocation creep and grain boundary sliding at 300 °C. Comparing the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Zn-0.1Zr alloys, it is found that the addition of 1.0 at.% Zn decreases the creep resistance due to a reduction in the number density of the β′ precipitates. Comparing the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys, it is found that the substitution of 1.0 at.% Gd with Y improves the creep resistance due to the low diffusion rate of Y in Mg matrix. Comparing the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys, it is found that increasing the Gd concentration can improve the creep resistance due to the increase in the number density of the β′ precipitates. Comparing the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys, it is found that the 1.0 at.% addition of Y leads to much better creep performance because of a higher density of the β′ precipitates.

The creep resistance is strengthened by the β′ precipitates that hinder dislocation movement in the Mg-2.5Gd-0.1Zr alloy. Before the creep tests, the separated lenticular shaped β′ precipitates are uniformly distributed. After the creep tests at 250 °C, it is found that the distribution of the β′ precipitates is linear precipitate chains extending along the direction that is approximately normal to the direction of the applied stress. The linear precipitate chains consist of alternate β′ and β′ F particles. The β′ F phase is previously unreported in Mg-Gd based alloys, and it has a base-centred orthorhombic (bco) structure (a = 0.6811 nm, b = 1.0883 nm, c = 0.5169 nm). Furthermore, distribution of alternate β′ and β′ F particles is not only found in the crept samples, but also observed in over aged samples (aged for 512 h at 250 °C). There are four types of transitional zones between the adjoining β′ F and β′ particles: continuous zigzag zones, consisting of a zigzag array with a fixed interplanar distance of ~1.11 nm to the nearest β′ F and β′ particles; discontinuous hexagonal zones, consisting of a hexagonal array with a wider gap on one side; continuous hexagonal zones, consisting of a hexagonal array with a wider gap on both sides; discontinuous zigzag zones, consisting of zigzag arrays with a wider gap on one side, and the width of the wide gap is about 1.66 nm.

Creep fracture is likely to start from the cavities on grain boundaries, and the denuded zones observed in the Mg-2.5Gd-0.1Zr alloy after creep tests at 250 and 300 °C can weaken the creep resistance. The denuded zones are found in matrix regions adjacent to grain boundaries lying
approximately perpendicular to the applied stress direction, and mainly widen in the tertiary creep stage. The majority of the denuded zones are characterized by the distribution of an array of grain boundary particles on one side and a misorientation between the denuded zone and the grain interior. The misorientation is caused by the formation of a dislocation wall between the denuded zone and the grain interior, and it leads to a loss of coherent matching between the otherwise coherent precipitates and the surrounding matrix in this region, which in turn results in the dissolution of the precipitates in this region and hence the formation of a denuded zone.
DECLARATION

This thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

WENFAN XU
Nov. 2015

This thesis is a part of a co-badged project between Monash University and Shanghai Jiao Tong University, which requires two versions of theses, a Chinese version for Shanghai Jiao Tong University and a English version for Monash University.
PUBLICATIONS DURING ENROLMENT


Wen-Fan Xu, Yu Zhang, Li-Ming Peng, Wen-Jiang Ding, and Jian-Feng Nie: Linear precipitate chains in Mg-2.5Gd-0.1Zr alloy after creep, Materials Letters, 137 (2014) 417-420.

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CHAPTER 1.

INTRODUCTION
Mg alloys are promising in applications and research for their low densities, high specific strength, high resistant ability to electro-magnetic interference et al. For example, they can be used in the automobile industry to replace many components made of steel, resulting in decreasing the vehicle weight and reducing the energy consumption. Current applications of commercial Mg alloys include the shells of electronic products, car dashboards, seat supports, steering wheels etc. In future, Mg alloys aim to be used in the engine and power transmission systems such as gearbox, engine block and piston, which require excellent high-temperatures properties. These potential applications require heat-resistant Mg alloys, while normal Mg alloys show poor strength at elevated temperatures. The commercially available Mg alloys used at elevated temperatures are Mg-Y-Nd based alloys (WE54 and WE43), and the useful working temperature of WE series alloys is below 200 °C. However, the engine parts require the material working at 300 °C. Therefore, it is urgent to develop a new heat-resistant Mg alloy.

Recently, Mg-Gd based alloys have been the focus of developing heat-resistant Mg alloys, because they were reported to have superior strength (tensile strength and creep resistance) than the WE series alloys (WE54 and WE43) at elevated temperatures [1]. Moreover, it has been reported that the addition of Y or/and Zn (forming Mg-Gd-Y, Mg-Gd-Zn, Mg-Gd-Y-Zn) will further improve the creep resistance [2, 3]. However, the effects of the additions of Gd, Y, Zn elements on the creep properties and microstructure during creep tests of Mg-Gd(-Y-Zn)-Zr alloys are not clear. So this project will investigate the creep properties obtained at 250 °C and 300 °C, and the microstructures before and after creep tests of four alloys with a fixed total concentration of Gd and Y elements: Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr (at.%) using scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and computer simulation, and reveal the effects of Zn, Y, Gd addition on creep properties, which can provide the theoretical guidance for the future development of heat-resistant Mg alloys.

The microstructures of Mg-Gd(-Y)-Zn alloys after heat treatments have been studied, and the precipitation sequence: SSSS → ordered G.P. zones → $\beta''$ (Mg$_3$Gd) → $\beta'$ (Mg$_7$Gd) → $\beta_1$ (Mg$_3$Gd) → $\beta$ (Mg$_5$Gd) is widely reported to exist in Mg-Gd(Y) alloys during the heat treatments [4]. However, only a few papers concerning the microstructures of Mg-Gd(-Y)-Zn alloys after
creep tests have been reported. These papers revealed a high dislocation density and coarse
equilibrium $\beta$ particles found in the crept WE43 and WE54 alloys [5, 6]. Thus in the current
project, the microstructures of the Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-
1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys before and after creep tests will be
characterized. Especially, the precipitate evolution in the Mg-2.5Gd-0.1Zr alloy during creep tests
will be studied in detail. Additionally, dislocation creep has been reported as the dominant creep
mechanism operating in the Mg-RE alloys in the temperature range 250~300 °C and the stress
regime 50~100 MPa based on the corresponding stress exponent values being in the range of
3.7~5.7 [7]. So a good understanding of precipitate evolution in the Mg-Gd based alloys is critical
for the development of Mg-RE alloys with better creep resistance in the future.

Besides the precipitates and dislocations, denuded zones that are free of precipitates have
been reported in crept Mg-10Gd-3Y-0.5Zr (wt.%) and WE54 alloys [3, 6]. The denuded zones
were observed adjacent to grain boundaries that were approximately perpendicular to the applied
stress in the tensile creep tests, and creep cracks always occurred in the denuded zones. The
formation mechanism of denuded zones formed during creep tests has been reported as directional
diffusion [8] and grain boundary migration [9]. However, both mechanisms cannot explain the
denuded zones convincingly. The directional diffusion conflicts with the dislocation creep
mechanism; and grain boundary migration cannot lead to denuded zones on both sides of the grain
boundary. Thus the denuded zones formed in the Mg-2.5Gd-0.1Zr alloy crept under 250 and 300
°C will be examined and the corresponding formation mechanism will be discussed.

In this thesis, the creep properties and microstructures of Mg-RE alloys reported in
previous papers are reviewed in Chapter 2, and the basic knowledge of creep process and creep
mechanisms are also introduced in this chapter. The experimental procedures are introduced in
Chapter 3. The creep properties of the Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-
1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys obtained at 250 °C under 80/100/120 MPa
and 300 °C under 40/60/80 MPa are present in Chapter 4, and the microstructures of these alloys
before and after the creep tests are also characterized in this chapter. The effects of Gd, Y and Zn
elements on creep properties of Mg-Gd-Zr based alloys are derived at the end of this chapter. In
Chapter 5, the precipitate chains observed in the crept Mg-2.5Gd-0.1Zr alloys are studied using
HAADF-STEM technology and computer simulation, and the corresponding formation
mechanism of the precipitate chains is discussed. In Chapter 6, the denuded zones formed in the
crept samples of the Mg-2.5Gd-0.1Zr alloy at 250 and 300 °C are characterized using EBSD and TEM technologies. The formation mechanism of the denuded zones is also discussed in this chapter. The most important conclusions arising from the work are presented in Chapter 7.
CHAPTER 2.

LITERATURE REVIEW
2.1. Introduction

Mg alloys are promising materials for use in the automobile and aerospace industries, due to their low densities and high specific strength [10-13]. Among Mg alloys, Mg-RE alloys are developed for higher temperature applications, e.g., WE54 alloy (Mg-5Y-4RE, wt.%) can be used up to ~250 °C. In contrast, AZ91 (Mg-9Al-1Zn, wt.%) alloy can only be used up to ~120 °C [1, 12, 14]. Creep tests are widely used to characterise the mechanical properties of alloys at high temperatures. The creep resistance of commercial alloys WE54 and WE43 (Mg-4Y-3RE, wt.%) is better than that of AZ (Mg-Al-Zn) series alloys at 200 °C [1]. Recently, Mg-Gd binary alloys were reported to show better creep resistance than the WE series alloys, and the additions of Zn or Y element can further improve the creep resistance of the Mg-Gd alloys [1, 15, 16]. Although the Mg-Gd(-Y-Zn) alloy system lacks a systematic study on creep properties and effects of elemental additions of Y/Zn on the creep performance, the previous work related to the creep properties of Mg-Gd(-Y-Zn) alloys will be reviewed in this chapter.

Firstly, basic physical properties and crystallography of pure magnesium, and the applications of Mg alloys are illustrated. Secondly, the background knowledge of tensile creep deformation is introduced, including creep processes and mechanisms. Thirdly, the creep properties and microstructures of Mg-Gd, Mg-Gd-Zn, Mg-Gd-Y-Zn alloys are reviewed, respectively. Finally, influences of the second-phase and grain boundary configuration on the creep strength of alloys are summarised.

2.2. Magnesium and Its Alloys

2.2.1. Properties of pure magnesium

Magnesium is an energy-efficient material due to its low density (1.74 g/cm³) which is much lower than that of steel (7.2 g/cm³). The automotive vehicles made of magnesium alloys are much lighter than those made of steels, and therefore they have less gasoline consumption. Additionally, magnesium is the sixth most abundant element in the earth’s crust, representing 2.7% of the earth’s crust [17]. These characteristics give magnesium wide potential applications in future, and the atomic and physical properties of magnesium are listed in Table 2.1.
Table 2.1 Atomic and physical properties of magnesium [17, 18].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>12</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>24.3050</td>
</tr>
<tr>
<td>Atomic volume</td>
<td>14.0 cm³/mol</td>
</tr>
<tr>
<td>Atomic radius</td>
<td>0.160 nm</td>
</tr>
<tr>
<td>Ionic radius</td>
<td>0.072 nm</td>
</tr>
<tr>
<td>Orbital electron states in free atoms</td>
<td>1s², 2s², 2p⁶, 3s²</td>
</tr>
<tr>
<td>Density (at 20 °C)</td>
<td>1.738 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>(650 ± 1) °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>1090 °C</td>
</tr>
<tr>
<td>Thermal conductivity (at 27 °C)</td>
<td>156 W·m⁻¹·K⁻¹</td>
</tr>
<tr>
<td>Specific heat capacity (at 20 °C)</td>
<td>1.025 kJ·kg⁻¹·K⁻¹</td>
</tr>
<tr>
<td>Elastic modulus: C₁₁</td>
<td>59.3 GPa</td>
</tr>
<tr>
<td></td>
<td>C₃₃</td>
</tr>
<tr>
<td></td>
<td>C₄₄</td>
</tr>
<tr>
<td></td>
<td>C₁₂</td>
</tr>
<tr>
<td></td>
<td>C₁₃</td>
</tr>
<tr>
<td>Young’s modulus (at 20 °C)</td>
<td>45 GPa</td>
</tr>
<tr>
<td>Poisson’s ratio (at 20 °C)</td>
<td>0.35</td>
</tr>
<tr>
<td>Shear modulus</td>
<td>17 GPa</td>
</tr>
</tbody>
</table>

The lattice structure of magnesium is close packed hexagonal (h.c.p.) with lattice parameters of $a = 0.321$ nm in the $\langle 11\bar{2}0 \rangle_\alpha$ direction, and $c = 0.521$ nm in the $\langle 0001 \rangle_\alpha$ direction [19, 20]. The principle planes and directions in a h.c.p. lattice are illustrated in Fig. 2.1. The $\langle 0001 \rangle$, $\langle 10\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$ directions are the main directions in magnesium.
There are two modes of deformation in magnesium: slip and twinning [22]. Slip is accomplished by dislocation motion and the Burgers vectors of possible perfect and imperfect dislocations can be described using a convenient notation defined in Fig. 2.2 [23, 24]. Table 2.2 gives the details of the perfect and imperfect dislocations, including the number of crystallographically equivalent variants of the dislocations and their Burgers vectors. Among the dislocations, the perfect dislocation with the shortest Burgers vector of \(1/3 \langle 11\bar{2}0\rangle\) (\(a\) type dislocation) lying in the close-packed directions on the basal planes is the most commonly observed, due to its low critical resolved shear stress (0.5 MPa) at room temperature [25-27]. Besides \(a\) type dislocations, the perfect dislocations with Burgers vectors of \(\langle 0001\rangle\) (\(c\) type dislocation) and \(1/3 \langle 11\bar{2}3\rangle\) (\(a+c\) type dislocation) are also widely observed, and these dislocations accommodate the deformation in the \(\langle 0001\rangle_a\) direction. A slip system is a particular combination of a slip direction and a slip plane that gives an equivalent of a simple shear, and five independent slip systems are required for a crystal to generate a homogenous strain by slip [28]. However, in magnesium (h.c.p.) crystal the independent slip systems are less than five. Therefore, twinning works as an additional deformation mode in magnesium. The most common twinning plane is \(\{10\bar{1}2\}_a\) and the corresponding shear direction is along the \(\langle 10\bar{1}1\rangle_a\) direction [24, 29].
Fig. 2.2 – Burgers vectors in an h.c.p. structure [24].

Table 2.2 Burgers vectors of dislocations in an h.c.p. structure [22].

<table>
<thead>
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<th>Type of dislocation (Fig. 2.2)</th>
<th>Total number of dislocations</th>
<th>Direction vector</th>
</tr>
</thead>
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<tr>
<td>Perfect dislocations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td>6</td>
<td>$\frac{1}{3}(11\overline{2}0)$</td>
</tr>
<tr>
<td>ST, TS</td>
<td>2</td>
<td>(0001)</td>
</tr>
<tr>
<td>ST + AB</td>
<td>12</td>
<td>$\frac{1}{3}(11\overline{2}3)$</td>
</tr>
<tr>
<td>Imperfect dislocations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aσ</td>
<td>6</td>
<td>$\frac{1}{3}(10\overline{1}0)$</td>
</tr>
<tr>
<td>σS, σT</td>
<td>4</td>
<td>$\frac{1}{2}(0001)$</td>
</tr>
<tr>
<td>AS, BS</td>
<td>12</td>
<td>$\frac{1}{6}(20\overline{2}3)$</td>
</tr>
</tbody>
</table>

2.2.2. Applications of Mg alloys

Applications of Mg alloys mainly focus on the automobile and aerospace fields. In these fields, weight reduction is one of the most critical objectives due to the increasing need for emission reduction and fuel efficiency. For instance, Mg alloys are used in the automobile industry to make the gearbox housing of VW Passat and Audi A4 [30], the steering wheels of Toyota Lexus/Carina/Celica/Corolla, the fuel tank cover of Mercedes-Benz SLK, the interior parts such as the seat frame, steering column housing, driver’s air bag housing, steering wheel, and lock body
of Hyundai Azera and Kia Amanti, as shown in Fig. 2.3 [17, 31]. In both civil and military aircrafts, magnesium-based materials are extensively used, such as the thrust reverser of Boeing 737/747/757/767, gearbox of Rolls-Royce, and helicopter transmission casings, etc [10, 17].

![Magnesium automotive components](image)

Fig. 2.3 – Magnesium automotive components: (a) steering wheel core, (b) seat support, (c) rear transfer case, (d) cam cover [17].

Recently, Mg alloys are also used in the medical, sports and electronic areas. In the orthopaedic field, lightweight and compatibility of magnesium with natural bones make magnesium-based materials promising implant materials [17, 32-34]. In the sporting industry, the lightweight and excellent damping characteristics of magnesium-based materials are popular for making bicycle frames and the chassis of in-line skates [17, 35]. In the electronic equipment industry, besides the lightweight characteristic, magnesium-based materials are also welcome attributed to their good behaviour at strength, heat transfer, and shielding electromagnetic interference and radio frequency interference. All these characteristics meet the necessary requirements of electronic components, and thus magnesium-based material are used in shells of cell phones, laptops, and portable media players [35].
2.3. Creep Deformation and Its Mechanisms

2.3.1. Creep processes

Creep tests are defined as subjecting a specimen to a constant applied tensile/compression stress at a constant temperature and recording the progress of deformation strain as a function of creep time, which builds a creep curve. A typical creep curve is shown in Fig. 2.4, which consists of three stages and the slope of the curve at any point represents the corresponding creep rate at that time. The primary stage occurs almost immediately when the stress is applied. The creep strain increases significantly at beginning, and then the slope of the strain gradually reduces as creep time increases \[36\]. This phenomenon can be explained by two theories. One is the strain hardening theory that the thermal activation energy required for creep increases with strain, which results in the reduction of the flow rate \[37, 38\]. The other is the exhaustion theory, which describes the creep strain as the result of the deformation of “soft spots” in the specimen, as creep time goes on, the “soft spots” exhaust and the creep rate decreases \[36, 39-41\].

In this stage, the creep strain can be described using the logarithmic creep law \[42\],

\[
\varepsilon = \alpha \log t, \quad (t > 1)
\]  \hspace{1cm} (2.1)

or Andrade’s transient creep law \[43\],

\[
\varepsilon = \beta t^{1/3},
\]  \hspace{1cm} (2.2)

where \(\varepsilon\) is the strain, \(\alpha, \beta\) are constants and \(t\) the creep time.

![Fig. 2.4 - A typical creep curve consisting of three stages [7].](image)
The secondary creep stage (or the steady state creep stage) is a focus of creep research, because it usually takes the major part of the creep curve and a great deal of strain can be accumulated in this stage, as stage II shown in Fig. 2.4. In this stage, the relationship between the creep strain and creep time can be described by the following equation:

$$\varepsilon = \kappa t,$$

where $\kappa$ represents the steady state creep rate ($\dot{\varepsilon}_s$) is nearly constant, which is due to the balance between strain hardening and the rate of thermal recovery [7]. The steady state creep rate is also called the minimum creep rate, because it is the minimum value of creep rate during the whole creep curve.

The steady state creep rate is a function of the applied stress and temperature in the secondary creep stage. Based on experimental results, the equation can be expressed as:

$$\dot{\varepsilon}_s = A \left(\frac{\sigma}{E}\right)^n \exp\left(-\frac{Q_c}{kT}\right) \text{ or } \dot{\varepsilon}_s = B \left(\frac{\sigma}{E}\right)^n \exp\left(-\frac{Q_c}{RT}\right),$$

(2.4)

where $\dot{\varepsilon}_s$ is the steady state creep rate, $\sigma$ is the applied stress, $A$ is a constant, $E$ is elastic modulus, $Q_c$ is the activation energy for steady state creep, $T$ is absolute temperature, $k$ is Boltzmann’s constant, $n$ is the stress exponent and $R$ is universal gas constant [7, 44]. The parameters of $n$ and $Q_c$ are related to the mechanism which operates in the secondary creep stage, which commonly is called creep mechanism in most papers. There are three creep mechanisms: dislocation creep, diffusional creep and grain boundary sliding. The details of these creep mechanisms will be summarised in the following section.

The tertiary creep stage has the characteristic that the creep rate accelerates rapidly and leads to final fracture, as stage III shown in Fig. 2.4. During this period, cavities are formed in the grain boundary and a quantity of slip bands occur [45].

2.3.2. Dislocation creep

The model of dislocation creep describes the creep strain accumulated in the secondary creep stage by virtue of the movement of dislocations. This mechanism usually operates at moderate temperatures under intermediate stress levels, as illustrated in Fig. 2.5.
Wu and Sherby investigated the steady state creep behaviours of coarse grained polycrystalline aluminium over a wide range of stresses and found an exponential dependence of creep rate on stress when the applied stress is intermediate, as shown in Fig. 2.6 that the exponent is approximately equal to 5 [48]. The existence of an exponential relationship between the steady state creep rate and the applied stress was also reported in other papers in various metals over a relatively wide range of creep stresses and temperatures [48-54]. These results lead to the existence of a power law, and Dorn suggested the following equation [55]:

\[ \dot{\epsilon}_s = C \sigma^\alpha exp \left( -\frac{Q_c}{kT} \right), \]  

(2.5)

where $C$ and $\alpha$ are constants, $Q_c$ is the activation energy of creep.
For pure metals, a number of theories have been developed to support a power law with the exponent in the range 3-5. Weertman raised the first creep model of edge dislocations generated from one source gliding on one plane, until they were blocked by dislocations spreading from other sources, forming edge dislocation dipoles, and the creep rate was controlled by the annihilation of edge dislocation dipoles by bulk self-diffusion [45, 56, 57]. This model is illustrated in Fig. 2.7,
which shows edge dislocations gliding on planes, and annihilating with dislocations of opposite Burgers vectors on neighbouring planes during creep. The equation derived from this model is as follows [45]:

$$
\dot{\varepsilon}_s = \frac{\pi^{1/2} \gamma \beta^{4.5}}{\gamma^*} \left( \frac{d}{b} \right) \frac{\Omega}{b^2 M^{1/2} b^{3/2} \mu^{7/2} k T},
$$

(2.6)

where $\gamma$, $\beta^*$, $\gamma^*$ are constants, $b$ is Burgers vector, $d$ is the spacing between neighbouring slip planes, $\Omega$ is the atomic volume, $D_b$ is the bulk self-diffusion coefficient, $M$ is the density of dislocations. This equation indicates the stress exponent is equal to 4.5 in dislocation creep.

Fig. 2.7 – The creep model developed by Weertman [45, 56, 57].

Spingarn and Nix proposed another dislocation creep model that dislocations moved inside grains and piled up at grain boundaries. The rate-controlling process is the smoothing of the steps caused by dislocation pile-ups by diffusion along the grain boundary [45, 58]. This model leads to a power-law exponent of 5, and suggests the creep rate is affected by the grain size. Argon and Takeuchi suggested a dislocation creep model considering internal stresses [59]. Brehm and Daehn developed a model based on the dislocation network, and yielded a fifth-power law [60].

For alloys, the dislocation models include dislocation-obstacle interaction model, dislocation network model and viscous glide model [7]. The dislocation-obstacle interaction model is based on climb of dislocations pinned by obstacles and the stress exponent is in the range of 3-8 [61, 62]. The corresponding creep rate equation is as follows:

$$
\dot{\varepsilon}_s = D \sigma^\alpha exp \left( \frac{-Q_{SD}}{kT} \right),
$$

(2.7)

where $D$ is constant, $\alpha$ is equal to 4 and $Q_{SD}$ is the activation energy for lattice self-diffusion [63]. The dislocation network model developed by Gittus describes a three-dimensional dislocation
network, and the stress exponent yielded from this model is equal to 3 [64, 65]. Viscous glide creep is based on the proposition that the movement of dislocations is impeded and controlled by the interaction with solute atoms, and the corresponding stress exponent is equal to 3 [66-68]. Viscous glide creep can be described by the following equation:

$$\dot{\varepsilon}_s = \frac{0.35}{F} G \left( \frac{\sigma}{\sigma_G} \right)^3,$$

(2.8)

where $F$ is an interaction parameter which characterises the particular viscous drag process controlling dislocation glide, $G$ is shear modulus [69, 70]. Additionally, the creep rate based on the combination of dislocation-precipitates and dislocation-solute atoms interactions can be expressed as [71, 72]:

$$\dot{\varepsilon} = \frac{AGbD_{el}}{kT} \left( \frac{\sigma}{\sigma_G} - \frac{\sigma_T}{\sigma_G} \right)^m$$

(2.9)

where $A$ and $n$ are constants, $G$ the shear modulus of the matrix phase, $b$ the magnitude of Burgers vector of the slip/climb dislocations, $D_{el}$ the effective lattice diffusion coefficient, $k$ Boltzmann’s constant, $T$ absolute temperature, $\sigma$ the applied stress and $\sigma_T$ the threshold stress. $\sigma_T$ is the stress required for a pinned dislocation to escape from the pinning particles, and it is affected by the size, shape and distribution of precipitates in alloys. $D_{el}$ is affected by solute atoms according to the following equation [73]:

$$D_{el} = \frac{D_s D_M}{(1-C_s)D_s + C_s D_M}$$

(2.10)

where $D_s$ is the diffusion coefficient of solute atoms in the matrix phase, $D_M$ is the self-diffusion coefficient of the matrix phase, and $C_s$ is the concentration of solute atoms. In this equation, it is the identity of solute atoms and their concentration that determine $D_{el}$. A higher diffusion coefficient suggests a higher diffusion rate, which in turn results in a higher creep rate. For example, it has been reported [74] that Y might have a lower diffusivity than Al in solid magnesium and that it was the lower diffusivity of Y that was responsible for the lower steady-state creep rate of the Mg-1.1 at.%Y alloy than that of the Mg-1.0 at.%Al alloy.

As above, there are two common key parameters in the creep equations: stress exponent and activation energy. For dislocation creep, the stress exponent is in the range of 3~8, and the activation energy is frequently observed to be essentially equal to the activation energy for lattice self-diffusion, as illustrated in Fig. 2.8, which covers over 20 (various crystal structures) metals.
Fig. 2.8 – The activation energy for lattice self-diffusion ($Q_{sd}$) versus the activation energy for creep ($Q_c$) [75].

Many investigations prove that the power-law creep can be affected by other parameters, such as the grain size, impurity, stacking-fault energy, etc. Spingarn and Nix predicted that the creep rate was proportional to the grain size, and Wilshire and Palmer observed that the creep rate of copper decreased with increasing grain size up to about 100 µm, and increased for grain sizes greater than 100 µm [58, 76]. Perdrix et al. reported that 0.5% impurity would strengthen the creep resistance of aluminium [77]. Creep rate would also be reduced with a lower stacking-fault energy, because lower stacking-fault energy led to more partial dislocations with slower climbing speed [45].

Vagarali and Langdon investigated the sscreep behaviour of polycrystalline magnesium over the temperature range from 200 to 547 °C [78]. There are two distinct regimes of dislocation creep. One occurs at lower temperatures (up to 327-477 °C), which has a stress exponent of ~5.2 and an activation energy of ~135 kJ·mol$^{-1}$. Under this condition, extensive basal slip is observed. The other regime of dislocation creep is at higher temperatures (above 327-477 °C), which has a
stress exponent of ~6.0 and an activation energy depending on the applied stress. In this regime, extensive non-basal slip is observed.

Vagarali and Langdon also investigated the creep behaviour of a Mg-0.8 wt% Al solid solution alloy over the temperature range from 200 to 537 °C [79]. There are three distinct regimes of dislocation creep. In the lower temperature range (up to 327-477 °C), the creep mechanism is dislocation viscous glide when the applied stresses are low and dislocation climb when the applied stresses are high. The stress exponents are in the range of 3.0~6.0, and the activation energy for creep is equal to ~140 kJ·mol$^{-1}$. In the higher temperature range (above 327-477 °C), the creep mechanism is cross-slip of dislocations from the basal to the prismatic planes. The activation energy is ~230 kJ·mol$^{-1}$ and decreases with increasing stresses, the stress exponent is equal to ~4.0 and there is extensive non-basal slip.

2.3.3. Diffusional creep

Diffusional creep describes the process of creep deformation accumulated by the diffusion of vacancies and atoms under applied stresses. Diffusional creep usually occurs at high temperatures under low applied stresses. If the diffusion occurs through the crystal lattice, it is called Nabarro-Herring creep, and this process is displayed in Fig. 2.9 as bulk-crystal diffusion [80, 81]. If the diffusion occurs mainly along grain boundaries, it is called Coble creep, and this process is displayed in Fig. 2.9 as grain-boundary diffusion [7, 82]. Figure 2.5 depicts the domains of the two diffusional creep mechanisms: Coble creep dominates when the creep temperature is relatively low ($T < 0.7T_m$) and Nabarro-Herring creep operates when the creep temperature is relatively high [68].
Steady state creep rates of diffusional creep suggested by Nabarro-Herring and Coble are given in Eq. 2.11 and 2.12, respectively [7, 61, 63].

\[
\dot{\varepsilon}_s = \frac{K_1 D_{SD} \Omega \sigma}{d^2 kT}, \tag{2.11}
\]

\[
\dot{\varepsilon}_s = \frac{K_2 D_{GB} \delta \Omega \sigma}{d^3 kT}, \tag{2.12}
\]

where \(K_1\) and \(K_2\) are constants, \(D_{SD}\) is self-diffusion coefficient, \(D_{GB}\) is grain boundary self-diffusion coefficient, \(d\) is the average grain diameter, \(\delta\) is the width of the narrow zone of vacancy transfer adjacent to the grain boundary and \(\Omega\) is the volume of a vacancy/atom. According to Eq. 2.11 and 2.12, the characteristic of diffusional creep is that the stress exponent is unity.

In Mg alloys, denuded zones were observed in crept Mg-0.5 wt% Zr samples reported by Squires et al. as the evidence of diffusional creep [83]. As the horizontal white bands shown in Fig. 2.10, the denuded zones were adjacent to the grain boundaries normal to the tensile axis when the creep test were under tensile stresses, and the formation mechanism of the denuded zones were deduced as the results of Mg atoms directional diffusion. However, the existence of denuded zones as the evidence of diffusional creep is questioned by investigators because the corresponding stress exponents obtained in these creep experiments are not unity [9, 84-86]. The debate on the formation mechanism of the denuded zones during creep is still undergoing.
2.3.4. Grain boundary sliding

Grain boundary sliding refers to the creep process in which grains exhibit no significant elongation during creep, but they become displaced with respect to each other so that there is a net increase in their number lying along the tensile axis, which is generally termed Rachinger sliding [88-91]. Grain boundary sliding is generally accepted as the dominant creep mechanism when the grain size is reasonably large and in superplasticity when the grain size is very small (< 10 µm) at high temperatures [92].

The stress exponent of the mechanism of grain boundary sliding is typically equal to 2. Grain boundary sliding is accommodated by dislocation slip, and the process is illustrated in Fig. 2.11, in which dislocations pile up at grain boundaries leading to the deformation [92, 93].

A study on the creep behaviour of a Mg-0.7 wt.% Al alloy shows that the grain boundary sliding occurs when the applied stresses are low. As the applied stress increases, dislocation creep accounts for more deformation [94].
2.4. Creep Properties and Microstructures of Mg Alloys

2.4.1. Mg-Al based alloys

The conventional magnesium alloys such as Mg-Al-Mn (AM alloys) and Mg-Al-Zn systems (AZ alloys) are widely used in the automotive industry, however, their poor creep resistance at temperature exceeding 125 °C limits the applications in the powertrain system, where engine pistons can operate up to 300 °C, engine blocks up to 200 °C and automatic transmission cases up to 175 °C [17, 95]. The poor creep performance of these alloys is attributed to the precipitation of Mg17Al12 phase during creep process. The Mg17Al12 phase is found to assist grain boundary sliding and migration, and these precipitates coarsen during creep at elevated temperatures [96, 97].

In the past decade, much improvement has been put into the development of creep-resistant Mg-Al based alloys such as Mg-Al-Si, Mg-Al-RE, Mg-Al-Ca, and Mg-Al-Sr alloys [7, 17].

Mg-Al-Si alloys have been used by VW for the powertrain components of the Beatle in 1970 [7]. The two main compositions of the Mg-Al-Si alloys are Mg-4Al-1Si (AS41) and Mg-2Al-1Si (AS21), which have the main precipitate phase of Mg2Si. The Mg2Si phase has high hardness and high melting point (1085 °C), and it prohibits dislocation moving and grain boundary sliding. However, Si addition does not prevent the formation of the Mg17Al12 phase. The Mg2Si phase is present in Mg-Al-Si system alloys [96, 98, 99].
exhibits better creep performance than AZ91 under the compression creep tests at 70-150 °C below 130 MPa because of lower amount of Mg\textsubscript{17}Al\textsubscript{12} precipitate present and pinning effects of Mg\textsubscript{2}Si precipitate [100].

Mg-Al-RE alloys such as AE41, AE42, AE44 alloys are made up of at least one, and in general a mixture of RE elements [12, 46]. The AE42 alloy exhibits superior creep performance over AZ91 alloy at high temperatures, because the suppression of the formation of the Mg\textsubscript{17}Al\textsubscript{12} phase and the presence of Al-RE containing intermetallics (Al\textsubscript{11}RE and Al\textsubscript{2}RE) in the AE series alloys [12, 101, 102]. However, the creep performance of these alloys is limited by the decomposition of Al\textsubscript{11}RE into Al\textsubscript{2}RE and Al to form Mg\textsubscript{17}Al\textsubscript{12} during creep tests above 150 °C, and the Mg\textsubscript{17}Al\textsubscript{12} phase is detrimental to the creep performance [103, 104].

Ca was considered to be a lighter and cheaper substitute to RE elements, so Mg-Al-Ca (AX) alloys were developed for the application at high temperatures[12, 46]. Moreover, the creep performance of the Mg-Al-Ca alloys was enhanced with the incorporation of ~0.1% Sr addition. The comparison of secondary creep rate of AE42 (Mg-Al-RE), AX (Mg-Al-Ca), and AXJ (Mg-Al-Ca-Sr) alloys tested under different conditions is illustrated in Fig. 2.12, and it was observed that the AX and AXJ alloys yielded lower secondary creep rate (better creep resistance) over the AE42 alloy [105]. The improved creep resistance of the AX and AXJ alloys is attributed to the existence of intermetallic compounds of Al\textsubscript{2}Ca and Mg\textsubscript{2}Ca along grain boundaries, which inhibit grain boundary sliding efficiently [106]. The stress exponent in AX53 was investigated to be 8.5 in the 70-100 MPa range at 175 °C, and the activation energy was 120 kJ/mol at 150-200 °C [107]. These results indicate dislocation creep operating in the secondary creep stage.
Fig. 2.12 – A comparison of secondary creep rates of AE42 (Mg-Al-RE), AX (Mg-Al-Ca), and AXJ (Mg-Al-Ca-Sr) alloys tested at (a) 150 °C and (b) 175 °C [105].

Sr addition to Mg-Al system leads to precipitation of Al₄Sr phase in Mg-Al-Sr alloys (AJ51, AJ52, AJ62), inhibits the formation of Mg₁₇Al₁₂ and results in high creep resistance, which is due to the high thermal stability of the Al₄Sr precipitate which coarsens after 1500 h heat treatment at 175 °C [46, 108-113]. The distribution of the Al₄Sr precipitates at grain boundaries in the Mg-Al-Sr alloys in as cast condition is shown in Fig. 2.13, and morphology of the Al₄Sr phase is lamellar. It was observed that a ternary phase Al₃Mg₁₃Sr existed in the Mg-5Al-2Sr (AJ52x) alloy, and the Mg₁₇Al₁₂ phase was found in the Mg-6Al-2Sr (AJ62Lx) alloy which has a low level of strontium.
The Mg-6Al-2.4Sr (AJ62x) and Mg-5Al-2Sr (AJ52x) alloys showed less creep elongation (superior creep performance) than the AE42 alloy at the same creep conditions as 175 ºC with stressed 50 MPa as listed in Table 2.3 [110]. It was reported that the Al₄Sr phase strengthened grain boundaries, which resulted in preventing creep as a result of grain boundary diffusion at 175 ºC under 35-70 MPa in the AJ51 alloy [114].

Fig. 2.13 – SEM images showing the microstructures of Mg-Al-Sr alloys in as cast condition (a) AJ51x (Mg-5Al-1Sr, wt.%), (b) AJ52x (Mg-5Al-2Sr, wt.%), (c) AJ62x (Mg-6Al-2.4Sr, wt.%), (d) AJ62Lx (Mg-6Al-2Sr, wt.%) [110].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>% Creep at 50 MPa for 200 h</th>
<th>% Creep at 50 MPa for 500 h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150 ºC</td>
<td>175 ºC</td>
</tr>
<tr>
<td>AJ52x</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>AJ62x</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>AE42</td>
<td>0.06</td>
<td>0.33</td>
</tr>
</tbody>
</table>

In summary, Fig. 2.14 graphically illustrate a comparison of the creep strength of magnesium alloys with the aluminium (A380) alloy. It can be seen that the AX (Mg-Al-Ca) and
AXJ ((Mg-Al-Ca-Sr) alloys have better creep performance than other magnesium alloys, but marginally inferior to Al (A380) alloy which is the leading material used in powertrain systems [17]. The applications of the Mg-Al-Si, Mg-Al-RE, Mg-Al-Ca, and Mg-Al-Sr alloys are up to 200 °C, because the creep is often overlapped with long range plastic deformation and dislocation glide at higher temperatures [7]. Therefore, it is meaningful to explore other alloy systems that have precipitates efficiently preventing dislocation glide.

Fig. 2.14 – Creep strength to produce 0.1% creep strain in 100 h at 175 °C of magnesium and aluminum die casting alloys [17, 102, 105].

2.4.2. WE series alloys

In order to extend applications of magnesium alloys above 200 °C, Mg-RE based alloys were developed, such as WE series alloys. WE series alloys refer to the commercial alloys WE54 (Mg-5.0Y-4.0RE, wt.%) and WE43 (Mg-4.0Y-3.0RE, wt.%). These alloys have a good combination of creep resistance, tensile strength, corrosion resistance and castability. The two commercial series alloys are developed for the applications up to 300 °C, such as helicopter transmissions, missiles, racing cars, and power systems [115]. The comparison of compressive 0.2% proof stress at ambient and elevated temperatures up to 300 °C among widely used commercial Mg alloys is displayed in Fig. 2.15 [116]. It is clear that the 0.2% proof stresses of the
WE54 and WE43 alloys are superior than those of other commercial Mg alloys, including the widely used AZ91 and AX alloys, when the temperature is above 100 °C.

![Graph showing compressive 0.2% proof stress varies as a function of temperatures for the rapidly solidified Mg alloys.](image)

Fig. 2.15 – Compressive 0.2% proof stress varies as a function of temperatures for the rapidly solidified Mg alloys (AZ91: Mg-9.0Al-1.0Zn, AZ151: Mg-15.0Al-1.0Zn, ACa54: Mg-5.0Al-4.0Ca, ZE41: Mg-4.0Zn-1.0RE, wt.%) [116].

Additionally, the ultimate tensile strength (UTS) of the heat treated WE54 and WE43 alloys is compared with other heat treated commercial Mg alloys, such as QE22 (Mg-2.0Ag-2.0RE, wt.%), ZE41 (Mg-4.0Zn-1.0RE, wt.%), ZC63 (Mg-6.0Zn-3.0Cu, wt.%), in Fig. 2.16(a). It is showed that the WE54 alloy has the highest UTS at all tested temperatures. In Fig. 2.16(b), the creep strength of these alloys are compared, and it shows that the WE54 alloy needs the highest stress to yield a plastic strain of 0.2% in 100 h at 200 °C, which means that the WE54 alloy has the best creep resistance among these alloys [1]. So it can be seen that the WE series alloys, especially the WE54 alloy, have the best high-temperature strength and creep resistance among the commercial Mg alloys.

The creep behaviour of a heat treated WE43 alloy under 35-220 MPa in the temperature range of 200-250 °C was investigated by Wang et al. [5]. The stress exponent and creep activation energy were measured to be 4.0-5.7 and 232.9 kJ·mol⁻¹, respectively. The results indicate that dislocation creep is the dominant creep mechanism under these creep test conditions. Additionally, the creep behaviour of a WE54 alloy in the temperature range of 200-300 °C under 32-150 MPa
was investigated by Mordike and Lukac [117, 118]. The stress exponents were found in the range of 3.3-5, and the creep activation energy in the range of 175-230 kJ·mol\(^{-1}\). The results also imply that the dominant creep mechanism operating in the WE54 alloy is dislocation creep.

The creep rate of dislocation creep is controlled by the velocity of dislocation motion, and dislocations can be pinned by precipitates. So it is worthy to investigate the precipitate distribution in the alloys. The WE series alloys are precipitation hardening alloys [119, 120], and Fig 2.17 gives the age-hardening response of a WE43 alloy heat treated at 150 and 210 °C, which shows that the hardness of the sample significantly increases from ~70 to ~100 at 210 °C for 7 days. As the ageing temperature decreased to 150 °C, the hardness reaches the highest value of ~87 after 1 day.

Fig. 2.16 – (a) UTS (ultimate tensile strength) varies as a function of temperatures. (b) Stress required to produce the plastic strain of 0.2% in 100 h at 200 °C for Mg alloys [1].
Fig. 2.17 – Age-hardening response (Vickers hardness) of a WE43 alloy heat treated at 150 and 210 °C [120].

The precipitation sequence in the WE series alloys during heat treatments is: SSSS → ordered G.P. zones → $\beta^*$ (Mg$_2$Nd) → $\beta'$ (Mg$_{12}$YNd) → $\beta_1$ (Mg$_3$(Nd, Y)) → $\beta$ (Mg$_{14}$Nd$_2$Y), and the $\beta$ phase is the equilibrium phase [4]. In the peak-aged WE samples, $\beta'$ and $\beta_1$ precipitates are widely distributed [4], and Fig. 2.18(a) displays the distribution and morphology of $\beta'$ and $\beta_1$ precipitates in an aged WE54 sample [121, 122]. The $\beta'$ precipitate is irregular globular shaped, and has an orthorhombic cell structure with the lattice parameters of $a = 0.64 \, nm$, $b = 2.24 \, nm$, $c = 0.52 \, nm$. The HAADF-STEM image of the $\beta'$ precipitates in Fig 2.18(b) shows characteristic white strips along $\langle 11\bar{2}0 \rangle_\alpha$ directions, and the bright areas represent the higher concentration of Gd atoms. The $\beta'$ precipitate has three types of variants and their mid-rib planes are parallel to $[0\bar{1}10]_\alpha$, $[\bar{1}100]_\alpha$ and $[10\bar{1}0]_\alpha$ respectively. The orientation relationship between the $\beta'$ phase and the Mg matrix phase is that of $(100)_{\beta'} \parallel (1\bar{2}10)_\alpha$, $[001]_{\beta'} \parallel [0001]_\alpha$. The $\beta_1$ precipitate has a f.c.c. (face-centred cubic) structure with the lattice parameters of $a = 0.74 \, nm$, and forms as plates with habit plane parallel to $\{1\bar{1}00\}_\alpha$. The orientation relationship between the $\beta_1$ phase and the Mg matrix phase is that of $(\bar{1}12)_{\beta_1} \parallel (1\bar{1}00)_\alpha$, $[110]_{\beta_1} \parallel [0001]_\alpha$ [4].
2.4.3. Mg-Gd alloys

Mg-Gd alloys were developed due to their better creep resistance than the commercial WE series alloys, and Fig. 2.19 shows that the aged Mg-Gd binary alloys (MgGd9: Mg-9.0%Gd, MgGd15: Mg-15.0%Gd, wt.%) had much lower secondary creep rates than the aged WE43 alloy, when the creep test was conducted at 200 °C under 60 MPa [1].

Fig. 2.19 – A comparison of the secondary creep rate obtained at 200 °C under 60 MPa [1].
The Mg-Gd binary alloys are precipitation hardening, similar to the WE series alloys. As shown in the Mg-Gd phase diagram of Fig. 2.20, the solubility of Gd in Mg is 23.5 wt.% at 548 °C, but drops to less than 3.82 wt.% at 200 °C. This solubility trend offers the possibility of precipitate formation after heat treatments, which is confirmed by the age-hardening curve of Mg–15Gd–0.5Zr (wt.%) alloy obtained at 250 °C in Fig. 2.21 [123]. In this instance, Zr was added to refine the grain size, and almost did not contribute to the precipitation process [21]. The precipitation sequence of Mg-Gd alloys is similar to the WE series alloys: SSSS → ordered G.P. zones → $\beta''$ (Mg₃Gd) → $\beta'$ (Mg₇Gd) → $\beta_1$ (Mg₃Gd) → $\beta$ (Mg₅Gd) [4]. Figure 2.21 shows that the hardness of the Mg-15Gd-0.5Zr alloy increased from ~72 when it was as-quenched to ~105 when it was aged for 8 h, and the $\beta'$ precipitates were the main hardening phase at the peak-aged stage.

![Fig. 2.20 – The Mg-Gd phase diagram of Mg-rich portion [11, 124].](image-url)
Fig. 2.21 – The age-hardening curve of a Mg-15Gd-0.5Zr (wt.%) alloy obtained at 250 °C and the distribution of precipitates along the curve [123].

The distribution of the $\beta'$ precipitates in an aged Mg-5.0 at.%Gd sample is shown in Fig. 2.22 [125]. It is clear in Fig. 2.22(a) that the truncated lenticular shaped $\beta'$ precipitates link together, and no $\beta_1$ particles are observed. At higher magnification, Fig. 2.22 (b), it can be seen that the $\beta'$ precipitates in the Mg-Gd alloy have a similar strip pattern with the $\beta'$ precipitates in the WE series alloys (Fig. 2.18(b)).

Fig. 2.22 – HAADF-STEM images of a Mg-5.0 at.%Gd alloy aged at 200 °C for 10 h viewed along [0001]$_\alpha$ [125].
The $\beta'$ precipitates have three types of variants, which are related by a 120° rotation with respect to each other around $[0001]_{\alpha}$. The three variants are not only distinguished by the extending direction of white strips observed along $[0001]_{\alpha}$ in Fig. 2.22(b), but also can be found in the microdiffraction patterns obtained from $[0001]_{\alpha}$. The microdiffraction patterns of the three variants are schematically shown in Figs. 2.23(a-c), respectively, and Fig. 2.23(d) gives the overlapping result of Figs. 2.23(a-c) [123].

Fig. 2.23 – Schematic patterns for the superimposed $\beta'$ phase and Mg matrix viewed from $[0001]_{\alpha}$. (a-c) Microdiffraction patterns for three different variants of the $\beta'$ phase with an angle of 120° each other, (d) SAED pattern composed of microdiffraction patterns (a-c) by overlapping [123].

The $\beta'$ precipitates have an orthorhombic crystal structure with the lattice parameters of $a = 0.65 \text{ nm}, b = 2.27 \text{ nm}, c = 0.52 \text{ nm}$ in Mg-Gd alloys. An atomic-scaled HAADF-STEM image of the $\beta'$ phase in a Mg-5.0 at.%Gd alloy (Fig. 2.24(a)) shows the projection of Gd atoms on $(0001)_{\alpha}$ plane, which appears to be zigzag along $[11\overline{2}0]_{\alpha}$ direction. Based on the HAADF-STEM result (Fig. 2.24(a)) and the SAED pattern (selected area diffraction pattern) of the $\beta'$ phase, the atomic model of the $\beta'$ phase is given in Fig. 2.24(b) [126, 127].
Fig. 2.24 – (a) An atomic-scaled HAADF-STEM image of the $\beta''$ phase in a Mg-5.0 at.%Gd alloy, the incident beam parallel to [0001]$_{\alpha}$, (b) the atomic model of the $\beta''$ phase [126, 127].

2.4.4. Mg-Gd-Zn alloys

Nie et al. reported that the creep resistance of Mg-Gd binary alloys could be improved by the addition of Zn [2]. For example, the addition of 1-2 wt.% Zn to the Mg-6Gd-0.6Zr (wt.%) alloy significantly enhanced the creep resistance at 175 and 200 °C under the creep stresses of 40-90 MPa (Fig. 2.25) [2].
The effect of Zn addition on creep resistance could be attributed to the age-hardening strengthening. Figure 2.26 shows that the ageing hardness response of a Mg-6Gd-0.6Zr alloy was raised by the Zn addition of 1-2 wt.%, such that the peak-aged hardness of the Mg-6Gd-0.6Zr alloy was increased from 45 to 70 when 1 wt.% Zn was added [2]. It is worth noting that the Zn addition also enhances the hardness of as-quenched samples. The as-quenched hardness of the Mg-6Gd-0.6Zr alloy was increased from 43 to 60 when 1 wt.% Zn was added, as shown in Fig. 2.26.

Fig. 2.26 – Age-hardening response at 250 °C of the Mg-6Gd-0.6Zr (wt.%) alloys with and without Zn additions [2].

Compared with Mg-Gd alloys, the addition of Zn brings an additional precipitation sequence in Mg-Gd-Zn alloys: SSSS → γ'' (Mg_{70}Gd_{15}Zn_{15}) → γ' (MgGdZn) → γ (Mg_{12}GdZn), and the key strengthening precipitate phase is γ'' [4]. Figure 2.27 displays the TEM images of γ'' and γ' precipitates formed during heat treatments of the Mg-1.0Gd-0.4Zn-0.2Zr (at.%) samples at 200 and 250 °C. The precipitates with a relative small aspect ratio are γ'' particles, and those with an extraordinarily large aspect ratio are γ' particles [128]. The Fourier-filtered HAADF-STEM images in Figs. 2.28(a, b) show the atomic projection of γ'' phase on \{1\overline{1}0\}α and \{10\overline{1}0\}α planes, which indicates that the γ'' phase has three atomic layers; the top and bottom layers are the brightest, while the middle layer has a brightness between the brightest layers and that of Mg atoms.
in the matrix. The brightness of HAADF-STEM images is proportional to the square of atomic number. Thus Figs. 2.28(a, b) imply that the brightest spots correspond to atomic column of a higher Gd concentration and that the bright spots in the middle layer are columns of atoms containing a higher Zn content. Figure 2.28(c) gives the schematic drawing of a unit cell of the \( \gamma'' \) phase, and it can be seen that the \( \gamma'' \) phase has an ordered hexagonal structure with the lattice parameters of \( a = 0.56 \, \text{nm}, c = 0.444 \, \text{nm} \), and it forms as \((0001)_\alpha\) plates, with a thickness of a single unit cell height and an aspect ratio typically of 60:1, as shown in Fig. 2.27(a, b, e, f). The orientation relationship between the \( \gamma'' \) and Mg matrix phase is such that \((0001)_{\gamma''} \parallel (0001)_\alpha\), \([10\overline{1}0]_{\gamma''} \parallel [2\overline{1}0]_\alpha\) [128].

![TEM images showing the distributions of precipitates](image)

**Fig. 2.27** – TEM images showing the distributions of precipitates in the Mg-1.0Gd-0.4Zn-0.2Zr (at.%) samples aged for (a) 1 h, (b) 5 h, (c) 500 h and (d) 1000 h at 250 °C. (e, f) Precipitates formed in the Mg-1.0Gd-0.4Zn-0.2Zr samples aged for 20 and 200 h at 200 °C, respectively [128].
The γ'' phase is gradually replaced by the γ' precipitates during prolonged ageing at 250 °C, as shown in Figs. 2.27(c, d). Figures 2.29(a, b) show that the closely packed planes of γ' precipitates have an ABCA stacking sequence, with Gd and Zn atoms distributed in the B and C planes viewed along ⟨11̅20⟩_α. The schematic drawings of a unit cell and the structure of the γ' phase are given in Figs 2.29(d, e). It can be seen that the γ' phase has a disordered hexagonal structure with the lattice parameters of \( a = 0.321 \) nm, \( c = 0.781 \) nm, and it forms as (0001)_α plates with a thickness of a single unit cell height and an extraordinarily large aspect ratio (Figs. 2.27(c, d)). The orientation relationship between the γ'' phase and the Mg matrix is such that (0001)_γ' \parallel (0001)_α, [21̅10]γ' \parallel [21̅10]_α [128].
Precipitates of the $\gamma$ phase were not observed in the Mg-1.0Gd-0.4Zn-0.2Zr (at.%) sample aged up to 1000 h at 250 °C. However, Yamasaki et al. reported the $\gamma$ phase in the Mg$_{97}$Zn$_1$Gd$_2$ (at.%) alloy annealed at 500 °C for 10 h, as shown in Fig. 2.30 as the black bands [129]. The $\gamma$ phase is also denoted as the 14H long-period stacking-ordered (LPSO) structure in Mg-Gd-Zn based alloys, and the 14H LPSO structure has a unit cell of 14 atomic layers along [0001]$_{\alpha}$ direction, which can be proved by the selected-area electron diffraction (SAED) pattern of the 14H LPSO structure in Fig. 2.30 that 13 extra diffraction spots are presented at positions of $n/14$ (where $n$ is an integer) of the (0002)$_{\alpha}$ diffraction [129]. The LPSO structure is found widely in Mg-Zn-RE (RE: Y, Dy, Ho, Er, Gd, Tb) alloys, and these alloys have a typical elemental composition ratio of Zn : RE equalling to 1 : 2 [130, 131]. The LPSO structure varies in these alloys, and contains 6H, 10H, 14H, 18R and 24R structures. The LPSO phase of 14H is widely found in Mg$_{97}$Zn$_1$RE$_2$ alloys with RE = Gd, Y, Dy, Ho, Er and Tm. The LPSO phase of 18R is generally observed in Mg$_{97}$Zn$_1$RE$_2$ alloys with RE = Y, Dy, Ho, Er, Tm [130].
The LPSO structures are long-period stacking derivatives of the h.c.p. structure, and the Zn/RE distributions are restricted at the four close-packed atomic layers forming local f.c.c. stacking [131]. Solution-treated Mg-Y-Zn alloys were widely studied due to the co-existence of the 10H, 14H and 18R LPSO structures [131-135]. The Fourier-filtered HAADF-STEM images in Fig. 2.31 showing the local four layer of f.c.c. stacking of Zn/RE atoms in the 14H and 18R LPSO structures of a Mg-8Y-2Zn-0.6Zr (wt.%) alloy heat treated at 500 °C for 16 h [136].

Recently, the crystallographic details of the 10H, 14H and 18R LPSO structures in Mg-Y-Zn alloys were revealed, and the concept of the order-disordered (OD) structure was applied to describe the crystal structures [131, 133, 135]. The stacking sequences of the 14H and 18R LPSO structures can be described as ABAB/CACACAC/BAB and ABA/CBCBCB/ACACAC/BAB, respectively, where A, B, C represent the stacking of close-packed atomic layers in the LPSO structures and the slash marks imply the positions of the stacking faults.
Fig. 2.31 – HAADF-STEM images in the Mg-8Y-2Zn-0.6Zr (wt.%) samples heat-treated at 500 °C for 16 h showing the (a) 18R and (b) 14H LPSO structures viewed in (11\bar{2}0)_{\alpha} [136].

The atomic resolution HAADF-STEM images of the 14H and 10H LPSO structures observed in the Mg-11.4Zn-12.8Y and Mg-9.2Zn-11.2Y (at. %) alloys heat-treated at 500 °C for 72 h are presented in Figs. 2.32(a, b) and (c), respectively. It can be seen that the stacking sequence is ordered in the 14H LPSO structures that the relative shifts of +1/3 and -1/3 occur alternately in the (1\bar{1}00)_{\alpha} direction (Fig. 2.32(a)), while the relative shift of 0 in the (11\bar{2}0)_{\alpha} direction (Fig. 2.32(b)) [135]. The stable 14H LPSO structure was deduced to have a space group of \textit{P6_3}22, and the ideal chemical composition was estimated to be Mg-7.1 Zn-9.5 Y (at.%) [135]. Figure 2.32(c) shows the 10H LPSO structures with relative shifts of 0 and 1/2 in the Mg-11.4Zn-12.8Y alloy viewed along the (1\bar{1}00)_{\alpha} direction. The space group of the stable 10H LPSO structure was determined to be \textit{Cmce}, and the average chemical composition was estimated to be Mg-10.0 Zn-13.3 Y (at.%) [135].
Fig. 2.32 – HAADF-STEM images showing the 14H (a, b) and 10H (c) LPSO structures in the Mg-11.4Zn-12.8Y and Mg-9.2Zn-11.2Y (at. %) alloys heat-treated at 500 °C for 72 h viewed along (a, c) \( \langle 1\overline{1}00\rangle_\alpha \) and (b) \( \langle 11\overline{2}0\rangle_\alpha \) directions. Numbers indicate the relative shifts between adjacent structural blocks in the unit of the projected spacing between adjacent Y-enriched atomic columns in the outer layers of the Y, Zn-enriched four consecutive atomic layers [135].

The 18R LPSO structure observed in the Mg-11.4Zn-12.8Y (at. %) alloy heat-treated at 500 °C for 72 h is shown in atomic resolution HAADF-STEM images in Fig. 2.33 that relative shifts between the adjoining Y/Zn-enriched structural four blocks, and the sequence of the relative shift is irregular, which indicates one dimensional stacking disorder [135]. It is also reported that as the heat-treated time was prolonged to 300 h at 500 °C, the one-dimensional stacking disorder in the 18R LPSO structures tended to transform into a fully-ordered one with the space group of \( C2/c \), which was similar to the 18R LPSO structures observed in the Mg-Al-Gd alloys [135, 137].
Fig. 2.33 – HAADF-STEM images showing the 18R LPSO structures in the Mg-11.4Zn-12.8Y (at. %) alloy heat-treated at 500 °C for 72 h viewed along (a) \(\{1\overline{1}00\}_\alpha\) and (b) \(\{1\overline{1}20\}_\alpha\) directions. Numbers indicate the relative shifts between adjacent structural blocks in the unit of the projected spacing between adjacent Y-enriched atomic columns in the outer layers of the Y, Zn-enriched four consecutive atomic layers [135].

2.4.5. Mg-Gd-Y-Zn alloys

The addition of Y and Gd elements is commonly used in Mg alloys for precipitation strengthening. Recently, Mg-Gd-Y-Zn alloys were studied due to their good creep resistance than the commercial WE series alloys, for instance, a heat treated Mg-11Y-5Gd-2Zn-0.5Zr (wt.%) alloy shows ten times lower minimum creep rate than the WE54 alloy at 300 °C under 50 MPa, and the creep fracture life of the Mg-11Y-5Gd-2Zn-0.5Zr alloy is about 700 h compared with less than 100 h for the WE54 alloy, as shown in Fig. 2.34 [3].
Fig. 2.34 – Minimum creep rate and creep fracture life of WGZ1152 (Mg-11Y-5Gd-2Zn-0.5Zr, wt.%) and WE54 alloys crept at 300 °C under 50 MPa [3].

The morphology of precipitates in Mg-Gd-Y-Zn alloys during the ageing treatment, such as the Mg-2.0Gd-1.2Y-1.0Zn-0.2Zr alloy aged at 225 °C, is displayed in Fig. 2.35 [138]. It can be seen that two series of precipitates exist: one is the series of $\beta''$, $\beta'$ and $\beta_1$ precipitates inside grains, the other is the 14H LPSO (lamella precipitates) extending from the grain boundary into the grains [138]. Additionally, the 14H LPSO structure does not change much as the ageing time proceeds, which indicates that the 14H LPSO structure is relatively stable at 225 °C.

Fig. 2.35 – Schematic diagrams of observed microstructures in the Mg-2.0Gd-1.2Y-1.0Zn-0.2Zr alloy aged at 225 °C for 2, 32, and 288 h [138].
2.5. Methods of Improving Creep Resistance in Alloys

2.5.1. Second-phase strengthening

Creep resistance of metallic alloys can be improved by dispersed second-phase particles in the matrix. The second-phase includes coherent particles such as precipitates, and incoherent particles such as dispersed oxides. For the second-phase strengthened alloys, their creep rate in the secondary creep stage is controlled by dislocation movement. The \( n \) (stress exponent) value in Eq. 2.4 reflects the creep mechanism in this stage. As mentioned in Section 2.3.2, the creep mechanisms is inferred to be dislocation creep when the \( n \) value is in the range 3-8. However, in alloys such as Fe-Al-Ni-Cr, Al-Zr-Sc-Si, oxide dispersion strengthened (ODS), AE44 alloys, the \( n \) values are often larger than 8 [139]. These unusually high \( n \) values indicate strong interactions between strengthening particles and mobile dislocations, which can be described by threshold stresses [72]. Below the threshold stress, creep is not measurable within the normal laboratory used timeframe. The presence of threshold stresses is possibly due to: dislocation detachment from particles, particle shearing, particle bypass by Orowan dislocation looping, or dislocations climbing over particles [140-142].

With the modification of threshold stresses, the power-law creep equation can be re-written as Eq. 2.9, where \( \sigma_T \) is the threshold stress. The threshold stress can be obtained from a linear least-squares regression of \( \dot{\varepsilon}^{1/n} \) vs. \( \sigma \), with a weight of \( 1/(\sigma^2 \dot{\varepsilon}^{1/n}) \), where \( \sigma^2 \dot{\varepsilon}^{1/n} \) is the uncertainty in the \( n \)th root of the strain rate [71, 72, 143]. The modified \( n \) value can be derived from the plot of the steady-state creep rate vs. the effective applied stress \( (\sigma - \sigma_T) \). The modified \( n \) value is usually in the range of 3-8.

Mg-RE alloys are the focus of this study, and they are precipitation strengthening alloys. The creep mechanism of Mg-RE alloys is mostly reported as dislocation creep, which indicates that precipitates can efficiently hinder the dislocation movement [7]. The precipitate type affects the creep resistance of Mg-RE alloys because precipitates on prismatic planes being efficiently obstacles to the motion of dislocations on basal planes of Mg-RE alloys, such as \( \beta' \), \( \beta_1 \) and \( \beta \) precipitates in the WE series alloys [144]. Figures 2.36 and 2.37 give the evidence of dislocations interacting with \( \beta \) precipitates in the WE43 and WE54 alloys during creep tests. The dislocations
are limited to areas between the adjacent $\beta$ precipitates as white curved lines marked by arrows in Fig. 2.36 and dark curved lines in Fig. 2.37.

![Image](image.png)

**Fig. 2.36** – Weak-beam dark-field TEM image showing the interaction between matrix dislocations and $\beta$ precipitates in the crept sample of a heat treated WE43 alloy [5].

![Image](image.png)

**Fig. 2.37** – TEM images showing the distribution of dislocations in the crept samples of a heat treated WE54 alloy crept at 250 °C under 61 MPa, (a) viewed along [0001]$_{\alpha}$, (b) viewed along [2110]$_{\alpha}$ [6].

The size and distribution of precipitates also effect the creep resistance. Dispersed precipitates of a fine size work better than the precipitates of a large size. During creep tests, precipitates are prone to coarsening, which softens the material. Figure 2.38 presents the microstructures of a WE43 alloy before and after a creep test at 200 °C under 220 MPa [5]. Before the creep test, the dominant precipitates were $\beta'$ and $\beta$ particles of a fine size. After the creep test,
the $\beta$ precipitates of much larger size were observed. As the total amount of solute atoms is fixed in the alloy, the coarse $\beta$ precipitates indicate that the number density of precipitates is decreasing, which deteriorates the creep performance.

![Fig. 2.38 – Dark-field TEM images of a heat treated WE43 alloy: (a) fine $\beta$ precipitates and (b) coarse $\beta$ precipitates in a sample crept at 200 °C under 220 MPa [5].](image)

According to the above experimental results, precipitates that are stable at high temperatures will benefit the creep resistance. The LPSO structures are reported to be stable up to 500 °C and they have higher elastic modulus compared with Mg matrix [129, 145, 146]. The effect of the addition of LPSO structures on creep resistance was demonstrated by the study of the creep behaviour of Mg-Y and Mg-Y-Zn alloys, in which the Zn addition introduces LPSO structures into the Mg-Y alloy [147]. It is found that the Mg-Y-Zn alloys (with LPSO structures) have better creep resistance compared with the Mg-Y alloy (without LPSO structures), as shown in Fig. 2.39(a). Figure 2.39(b) gives the applies stresses dependence of the minimum creep rates of Mg-Y(-Zn) alloys, and the slopes of fitting lines reveal that the stress exponents of the Mg-Y(-Zn) alloys at 377 °C under 10-60 MPa are equal to 5-6, indicating that the operative creep mechanism is dislocation creep. Thus the better creep resistance of Mg-Y-Zn alloys is related to the more efficient blocking of dislocation motion contributed by the LPSO structures.
F. 2.39 – (a) Creep curves of Mg-Y and Mg-Y-Zn alloys containing about 1 at.% Y at 377 °C under 30 MPa, and minimum creep rates as a function of applied stresses [147].

Figure 2.40 shows the distribution of dislocations in the Mg-Y and Mg-Y-Zn alloys crept at 375 °C under 30 MPa [147], where as non-basal dislocations are the dominant feature in the Mg-Y alloy (Fig. 2.40(a)), the bulk of dislocations are confined to the basal planes in the Mg-Y-Zn alloys (Figs. 2.40(b, c)). Thus these micrographs provide evidence of the Zn addition (LPSO structures) suppressing the non-basal slip, which leads to improving creep strength of Mg-Y based alloys.

F. 2.40 – Distributions of dislocations in the samples crept to the minimum creep rate (375 °C under 30 MPa) of (a) Mg-1.1 Y, (b) Mg-1.6Y-0.02Zn and (c) Mg-0.9Y-0.04Zn (at.%) alloys. The direction of the incident beam is [21̅10]. [147] Grain boundary strengthening
Creep fracture frequently occurs at grain boundaries at the tertiary creep stage. It starts from voids on grain boundaries that lie normal to the tensile stress direction [47, 148]. The mechanisms of the cavity nucleation are schematically illustrated in Fig. 2.41. Figure 2.41(a) explains that grain boundary sliding could lead to a wedge crack at the triple junctions. Figure 2.41(b) reveals that the diffusion of atoms at grain boundaries could form voids. Figure 2.41(c) illustrates that dislocation pile-ups against grain boundaries or hard second-phase particles could result in the vacancy accumulation. Figure 2.41(d) demonstrates that second-phase particles at grain boundaries are the common locations for cavities when grain boundary sliding occurs [68]. The voids cannot support load, and the stress increases on the remaining intact parts of the grain boundary, which makes the voids grow quickly and link together, until finally fracture takes place.

The strength of a grain boundary can also be deteriorated by the formation during the creep tests of denuded zones next to the grain boundary, which are free of precipitates as the white horizontal bands shown in Fig. 2.42. These zones are relatively weaker compared with the interior precipitate containing area, and thus the stress level that the precipitate free zones can bear is lower.

![Fig. 2.41 – Cavity nucleation mechanisms: (a) grain boundary sliding, (b) diffusion, (c) dislocation pile up, (d) particle-obstacle in conjunction [47, 68].](image-url)
than the precipitate area, which leads to the formation of cavities in the denuded zones during creep tests.

Fig. 2.42 – Optical micrograph showing the denuded zones along grain boundaries approximately perpendicular to the stress axis in the crept sample of alloy WE54 in the T6 condition at 250 °C under 61 MPa [6].

The denuded zones were firstly reported in a Mg-0.5 wt.% Zr alloy crept under 1.4 MPa at 450 °C [83]. The formation mechanism of the denuded zones is in debate between two mechanisms: directional diffusion and grain boundary migration. The model of directional diffusion is illustrated in Fig. 2.43 that during the tensile creep along vertical direction, the atoms of matrix near the vertical grain boundaries diffuse to the areas adjoining the horizontal grain boundaries and forming the denuded zones, as shown in Fig. 2.43(b) [8]. As for the grain boundary migration model shown in Fig. 2.44, it demonstrates that the grain boundaries approximately normal to the applied stress direction are driven by the applied stress to sweep precipitate areas, and the precipitates dissolve and the solute atoms diffuse along the grain boundaries to precipitate on the section of grain boundaries that are nearly parallel to the applied stress direction. The denuded zones are left behind the migrating grain boundaries [9].
Fig. 2.43 – A schematic diagram showing the redistribution of precipitates in the grain boundaries and denuded zones during tensile creep tests according to the mechanism of directional diffusion, and the applied stress is vertical [8].

Fig. 2.44 – A schematic diagram showing the redistribution of precipitates in the grain boundaries and denuded zones during tensile creep tests according to the mechanism of grain boundary migration, and the applied stress is vertical [9].

The existence of denuded zones has been reported in crept WE54 alloy (Fig. 2.42) and Mg-11Y-5Gd-2Zn-0.5Zr (wt.%) alloy, and these zones were treated as the evidence of diffusional creep [3, 6]. However, the stress exponents of these alloys under the reported creep test conditions indicate that dislocation creep dominates. There is still no clear explanation of the contradiction
between diffusional creep and dislocation creep mechanisms, and there is no sufficient experimental results to support the directional diffusion process in these Mg-RE alloys. Additionally, the reported directional diffusion occurred in Mg-Zr alloys at high temperatures such as 450 °C, but the denuded zones observed in the WE54 alloy were formed during creep tests at 250 °C. Thus, a thorough study of the denuded zones in Mg-RE alloys is needed.

2.6. Research Aims and Approaches

The extension of applications of Mg alloys at elevated temperatures is one of the main focuses of Mg alloy development. In this chapter, the creep performance of Mg alloys has been reviewed. It is found that the WE series, Mg-Gd, Mg-Gd-Zn and Mg-Gd-Y-Zn alloys exhibit desirable creep resistance in the temperature range of 200-300 °C, especially the Mg-Gd binary alloys and Mg-Gd-Y-Zn alloys show much better creep resistance than the WE series alloys. However, reasons of the superior creep performance of Mg-Gd(-Y-Zn) based alloys lack of adequate investigation. So far, reported research has found that the creep mechanism of the Mg-Gd(-Y-Zn) based alloys are dislocation creep in the temperature range of 200-300 °C, and therefore precipitates in the alloys are the mainly rate-controlling factors [1, 7]. These alloys are precipitation hardening and the strengthening precipitates are mainly \(\beta'\) and \(\beta_1\) particles on prismatic planes, and LPSO structures on basal planes for the alloys containing Zn [4]. However, the comparison of effects of the different types of precipitates on creep performance of alloys are unclear. Furthermore, the microstructure evolution of the Mg-Gd(-Y-Zn) based alloys during creep tests lacks of a systematic study.

Therefore, the principle research aim of this thesis is to investigate the creep properties of the Mg-Gd(-Y-Zn)-Zr alloys (Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys (at.%) ), especially the microstructure evolution during creep tests. The addition of Zr is to refine the grain size, and Zr almost does not involve in the precipitation process. The research aims of each chapter are presented as follows:

In Chapter 4, the aim is to investigate effects of alloying elements such as Zn, Gd, and Y on creep properties of the Mg-Gd(-Y-Zn)-Zr alloys. The creep tests were conducted at 250 and 300 °C. The minimum creep rate and creep life of the alloys were compared, and the creep mechanism of the alloys based on stress exponents were deduced. Additionally, the microstructure
of the alloys before and after creep tests were examined. The creep performance was associated with the microstructure, and then the different alloys were discussed based on their different compositions and creep performances. The effects of Zn additions can be deduced through the comparison between the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Zn-0.1Zr alloys. The effects of Y additions can be deduced through the comparison between the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys. The effects of changing the Gd concentration can be deduced through the comparison between Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys.

In Chapter 5, the aim is to investigate the precipitate evolution in the Mg-2.5Gd-0.1Zr alloy during creep tests at 250 °C. According to results obtained in Chapter 4, the creep mechanism of the Mg-Gd(-Y-Zn)-Zr alloys is dislocation creep, and the $\beta'$ precipitates efficiently hinder the dislocation movement. It was also observed that the distribution of $\beta'$ precipitates changed during creep tests at 250 °C. Therefore, the distribution of the $\beta'$ precipitates in the Mg-2.5Gd-0.1Zr alloy was characterized at different stages during creep tests, and the first principles and phase-field methods were applied to simulate the precipitate evolution process.

In Chapter 6, the aim is to investigate the denuded zones formed in the Mg-2.5Gd-0.1Zr alloy during creep tests. According to the observation in Chapter 4, denuded zones were found in the Mg-2.5Gd-0.1Zr alloy after creep tests. Since creep fracture is likely to start from the cavities on grain boundaries, and the denuded zones formed during creep tests lying adjacent to grain boundaries weaken the creep resistance, so it is meaningful to investigate the formation process and mechanism of denuded zones in the alloys. The grain boundaries of the Mg-2.5Gd-0.1Zr alloy were examined at different creep stages during the tests. Additionally, there are two types of the formation mechanisms of the denuded zones: directional diffusion and grain boundary migration. The feasibility of the two mechanisms in the Mg-2.5Gd-0.1Zr alloy were discussed in this chapter.
CHAPTER 3.

EXPERIMENTAL PROCEDURES
3.1. Alloy Compositions and Casting Procedures

Four alloys were designed in this study for the research, and Table 3.1 gives the chemical compositions of the four alloys measured by inductively coupled plasma (ICP) analyser. These alloys are notated as Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr in the later context. The purpose of Zr additions is to refine the grain size, which will ensure all alloys have a similar grain size of approximately 40 μm.

The four alloys can be divided into three groups for investigating the effects of Zn and Y additions on the creep behaviour of Mg-2.5Gd-0.1Zr alloy. First, the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Zn-0.1Zr alloys were designed with the difference in Zn concentration. Secondly, the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys were designed with partial substitution of Y for Gd. Finally, the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys were designed with a difference in Gd concentration.

Table 3.1. Chemical compositions of the designed alloys.

<table>
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<tr>
<th></th>
<th>Gd</th>
<th>Y</th>
<th>Zn</th>
<th>Zr</th>
<th>Mg</th>
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<tr>
<td>Mg-2.5Gd-0.1Zr</td>
<td>at.%</td>
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<td>–</td>
<td>0.1 Bal.</td>
</tr>
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<td>–</td>
<td>–</td>
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<td></td>
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<td>–</td>
<td>2.32</td>
<td>0.39 Bal.</td>
</tr>
<tr>
<td>Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr</td>
<td>at.%</td>
<td>1.6</td>
<td>1</td>
<td>1</td>
<td>0.12 Bal.</td>
</tr>
<tr>
<td></td>
<td>wt.%</td>
<td>9.4</td>
<td>3</td>
<td>2</td>
<td>0.45 Bal.</td>
</tr>
<tr>
<td>Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr</td>
<td>at.%</td>
<td>2.5</td>
<td>0.9</td>
<td>1</td>
<td>0.12 Bal.</td>
</tr>
<tr>
<td></td>
<td>wt.%</td>
<td>13.5</td>
<td>2.7</td>
<td>2</td>
<td>0.4 Bal.</td>
</tr>
</tbody>
</table>

These alloys were prepared from high purity Mg (99.9%), Zn, Mg-25Gd (wt.%), Mg-25Y (wt.%) and Mg-30Zr (wt.%) by induction melting in a mild steel crucible at approximately 750 °C under a mixed atmosphere of CO₂ and SF₆, and then casting into a steel mold pre-heated to ~200 °C.

3.2. Heat Treatment and Hardness Tests

Alloy ingots were firstly solution treated using the parameters listed in Table 3.2. The solution treated samples were quenched into cold water, and then subsequently aged in an oil bath furnace at 250 °C.

In order to determine the peak-aged condition, hardness tests were conducted using a Vickers indenter with the load of 5 kg and a hold time of 15 s.
Table 3.2. Heat treatment parameters.

<table>
<thead>
<tr>
<th></th>
<th>Solid Solution</th>
<th>Ageing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-2.5Gd-0.1Zr</td>
<td>490 °C × 3 h</td>
<td>250 °C × 4 h</td>
</tr>
<tr>
<td>Mg-2.5Gd-1.0Zn-0.1Zr</td>
<td>500 °C × 35 h</td>
<td>250 °C × 32 h</td>
</tr>
<tr>
<td>Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr</td>
<td>520 °C × 10 h</td>
<td>250 °C × 16 h</td>
</tr>
<tr>
<td>Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr</td>
<td>520 °C × 10 h</td>
<td>250 °C × 16 h</td>
</tr>
</tbody>
</table>

3.3. Tensile and Creep Test

The specimens for tensile tests were cut from the ingots using wire cutting, with dimensions of 3.5 mm in width, 2 mm in thickness and 15 mm in gauge length. The tensile tests were carried out on a Shimadzu machine in the range of 25-350 °C. The specimens were kept in the furnace for 15 mins to ensure a homogeneous temperature environment before the start of testing.

The creep tests were performed at 250 °C and 300 °C under constant load within a furnace. The creep specimens had dimensions of 6 mm in width, 2 mm in thickness and 25 mm in gauge length, and were prepared by linear cutting from the ingots. Before starting the creep tests, specimens were mounted in the creep apparatus for half an hour to homogenize the temperature. If the specimen did not fracture in two weeks (~336 h), the experiment was stopped manually. After either fracture or manual stopping, the specimen was demounted as soon as possible, then quenched into cold water.

3.4. Microstructural Characterization

3.4.1. Scanning electron microscopy

The grain size and intermetallics on grain boundaries before and after creep tests were examined using scanning electron microscopy (SEM), using a JEOL 7001F FEG equipped with an energy dispersive x-ray spectrometer.

The orientation of grains was examined using the Oxford Instruments Aztec EBSD system equipped on the JEOL 7001F FEG. The step size for the EBSD scanning was 0.1 µm. The test samples were prepared by punching into disks 3 mm in diameter, ground to 0.15 mm thickness, then twin-jet electro-polished in a solution of 5.3 g lithium chloride, 11.2 g magnesium perchlorate, 500 ml methanol and 100 ml 2-butoxy-ethanol at -55 °C and 0.1 A.
3.4.2. Conventional transmission electron microscopy

The crystal structure of precipitates and the type and distribution of dislocations were studied by conventional transmission electron microscopy (TEM) using an FEI Tecnai G2 F20 S-TWIN FEGTEM equipped with EDXS. The dislocations in this project were almost observed using the weak beam dark field technique.

The crystal structure of precipitates could be studied using selected area electron diffraction (SAED) patterns. The dislocations were observed using weak-beam dark-field (WBDF) microscopy, because dislocations are shown as narrow lines (~ 1.5 nm wide) in WBDF images. The difference between bright-field (BF) and dark-field (DF) imaging systems is illustrated in Fig. 3.1, with BF images being formed using the direct beam and DF images using scattered beams. Contrast in BF and DF TEM images is usually diffraction contrast, and the WBDF images are formed under certain special diffraction conditions that a particular reflection \( \mathbf{g} \) is activated. This \( \mathbf{g} \) vector gives a clue to determine the Burgers vector of dislocations. If \( \mathbf{g} \cdot \mathbf{b} = 0 \), then dislocations cannot be observed due to no contrast. So the Burgers vector of dislocations can be determined by observing the disappearance of dislocations under certain \( \mathbf{g} \) vectors [149]. The samples used for TEM were prepared the same as the ones used for EBSD tests.

![Fig. 3.1 – Comparison of the use of an objective aperture in TEM to select (A) the direct or (B) the scattered electrons forming bright-field (BF) and dark-field (DF) images, respectively [149].](image)

3.4.3. High-angle annular dark-field scanning transmission electron microscopy
In this study, the distribution and morphology of precipitates were also observed using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), which is performed using a HAADF-STEM detector on the FEI Tecnai G2 F20 S-TWIN FEGTEM.

Generally, STEM BF images are noisier than TEM BF images, but STEM DF images are widely used, which are formed by collecting most of the scattered electrons on the annular dark-field (ADF). The locations of STEM BF and DF detectors are schematically illustrated in Fig. 3.2. To collect the scattering electrons, there are two types of detectors: ADF detector and high-angle ADF detector (HAADF). In this study, the HAADF detector was selected to make images, because it collects the very high angle, incoherently scattered electrons (the semiangle > 50 mrad as shown in Fig. 3.3) and forms Z (atomic number) contrast images, which are high-resolution (atomic) images showing the atoms of higher Z brighter. The alloys being studied in the present work are Mg-Gd(-Zn-Y)-Zr alloys, and the atomic numbers of Mg, Gd, Zn, Y are 12, 64, 30, 39, respectively. The alloying elements (Gd, Zn, Y) have much higher atomic numbers than Mg matrix, which could give a clear contrast between the precipitate containing alloying elements (bright) and the Mg matrix (dark) in the HAADF-STEM images. The samples for HAADF-STEM were prepared the same as the ones used for EBSD tests.

Fig. 3.2 – Comparison of the use of detectors in STEM to select (A) the direct or (B) the scattered electrons forming BF and ADF images, respectively [149].
3.5. Computer Simulation

3.5.1. First-principles calculations

The first principles method was adopted to calculate the lattice parameters of precipitates and the total energy of precipitates based on the atomic models using the Viena Ab-initial Simulation Package (VASP) [150, 151], the projected-augmented-wave (PAW) method [152, 153] and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [154, 155]. The cut-off energy of the plane wave basis set was 400eV. The geometry optimization was concluded when the total energy change was less than $10^{-3}$ eV/atom. Spin polarized calculations were used for all calculations.

3.5.2. Phase-field method

The phase-field method is a powerful computational approach to model the microstructure evolution, such as phase transformation in alloys. It is widely used to explain and predict the distribution and type of precipitates during the heat treatment [156]. In Al-Cu alloys, the tetragonal coherent $\theta'$ precipitates have six variants with their habit planes parallel to $\{100\}$ planes of the
matrix, and the distribution of the $\theta'$ precipitates is strongly affected by the externally applied stresses during ageing. A parallel alignment distribution of the $\theta'$ variants was observed when the external stress was applied [157-159]. The stress effect on $\theta'$ precipitation was studied and modelled using the phase-field method [160]. The simulation results are shown in Fig. 3.4. The variants lying vertically and horizontally were uniformly distributed when no external stress is applied (Fig. 3.4(a)). But only a single variant was observed under the influence of the external stress, lying vertically when a tensile stress was applied vertically (Fig. 3.4(b)) or lying horizontally when a compressive stress was applied vertically (Fig. 3.4(c)). These simulation results were verified experimentally [157-159].

![Fig. 3.4 – Microstructures formed without external stresses (a), under external stresses applied vertically: (b) $\sigma = 67$ MPa, (c) $\sigma = -67$ MPa [160].](image)

In the present work, the phase field method was adopted to simulate the morphology of precipitates formed under the effect of uniform stress field or pre-existing dislocations. The input parameters of the phase field model are the variation of chemical free energy as a function of composition, elastic strain energy and interfacial energy. The chemical free energy of the $\alpha$-Mg matrix and $\beta'$ precipitates are calculated from the existing thermodynamic databases obtained from CALPHAD database [161], and the elastic strain energy is calculated based on Khachaturyan and Shatalov’s microelasticity (KS) theory. The system size used for this thesis is $1024l_0 \times 1024l_0$ (i.e. $184.32\ nm \times 184.32\ nm$), and the Langevin noise terms are used to generate microstructures consisting of multi-particles in the simulation [162].

The interaction energy between a nucleating $\beta'$ particle and a pre-existing dislocation is calculated by using the following equation [163, 164]:

\[
E_{\text{int}} = \frac{1}{2} k_B T \ln \left( \frac{\lambda}{\lambda_0} \right)
\]
\[ E^{\text{int}} = -\sigma_{ij}^{\text{dis}}(r)\varepsilon_{ij}^0(r). \] (3.1)

A negative value of \( E^{\text{int}} \) indicates that the formation of the \( \beta' \) precipitate under the influence of stress field of the pre-existing dislocation is energetically favoured. In this equation, \( \sigma_{ij}^{\text{dis}}(r) \) is the stress field of the pre-existing dislocation.
CHAPTER 4.

EFFECTS OF ALLOYING ELEMENTS ON CREEP PROPERTIES OF THE Mg-Gd-Zr ALLOYS
4.1. Introduction

The binary Mg-Gd alloys have attracted much attention because of their outstanding tensile and creep properties which are better than commercial WE (Mg-Y-RE) series alloys [1, 130, 165-167]. Moreover, it has been reported that the additions of Y and Zn elements to the Mg-Gd alloys could further improve the creep resistance, and the improved creep resistance is associated with precipitation hardening [2, 148, 166, 168-174]. This is because the dominant creep mechanism operating in the Mg-Gd(-Y-Zn) alloys in the temperature range 250~300 °C and the stress regime 50~100 MPa has been attributed to dislocation creep, on the basis of the stress exponent values being in the range of 3.7~5.7 [44, 140, 168, 175-177]. The precipitates contribute to the the creep resistance by blocking the dislocation motion in the Mg-Gd(-Y-Zn) alloys.

The microstructures of the Mg-Gd(-Y) and Mg-Gd(-Y)-Zn alloys in the aged conditions have been investigated [4, 123, 126, 128, 129, 131, 138]. In the Mg-Gd and Mg-Gd-Y alloys, the predominant precipitates are β′ (body-centered orthorhombic) and β1 (face-centered cubic) particles that are lenticular or plate-shaped on prismatic planes of the magnesium matrix. In the Mg-Gd(-Y)-Zn alloys with relatively low Gd:Zn atomic ratios, besides the β′ and β1 phases, the precipitates also include γ″, γ′ and long-period stacking-ordered phase (14H), all of them form as plates on the basal plane [4, 128]. Although the microstructures of these alloys prior to creep tests have been relatively well studied, there are few studies on the microstructures of creep Mg-Gd based alloys. Thus far, only the microstructures of crept samples of WE alloys [5, 6, 148, 178] and Mg-Gd-Y-Zn alloys [132, 133, 179] have been examined separately. These studies reported that a high dislocation density and coarsened equilibrium β phase (face-centered cubic) were observed in the samples experiencing creep tests at 230-300 °C under 32-93 MPa and 30-140 MPa. However, the roles of Gd, Y and Zn elements in improving the creep resistance of magnesium alloys are still unclear.

Therefore, this chapter will focus on a systematic study of microstructures and creep properties of Mg-Gd(-Y-Zn)-Zr alloys to find out the effects of Gd, Y and Zn additions on creep resistance of Mg-Gd alloys. Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr (at.%) alloys are studied (Zr is used as a grain refiner to keep the magnesium grain sizes similar in the four alloys prior to the creep tests [11]). Firstly, the peak-aged conditions of the alloys are determined by hardness tests, and the microstructure under
peak-aged conditions is investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Then the results of tensile tests at room and elevated temperatures, and constant-load tensile creep tests performed at 250/300 °C and under 80-120/40-80 MPa are presented. Next, the microstructures of the crept samples of the four alloys are studied using SEM, TEM and HAADF-STEM. In the last, the roles of Gd, Y and Zn elements in influencing the creep resistance of the Mg-Gd alloys are discussed.

4.2. Microstructures of the Mg-Gd(-Y-Zn)-Zr Alloys before Creep Tests

The Mg-Gd(-Y-Zn)-Zr samples were heat treated before the creep tests to obtain the maximum age-hardening response. All the samples experienced solution treatments at higher temperatures (490-520 °C), followed with ageing treatments at 250 °C (the details of heat treatment parameters are listed in Table 3.2). The solution treatments are designed to increase the concentration of solute elements within grains and keep the grain size at a similar level for all four alloys (the statistical results of the grain size obtained from the solution treated alloys are: 44 μm for Mg-2.5Gd-0.1Zr, 36 μm for Mg-2.5Gd-1.0Zn-0.1Zr, 45 μm for Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and 44 μm for Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr).

The ageing treatments for the alloys were performed at 250 °C, and the hardening response curves are present in Fig. 4.1. It shows that the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys have an obvious increase in hardness during the ageing processes, while little increase is observed for the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys. The ageing conditions for the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys obtaining the maximum hardness (4 and 16 h, respectively), as shown in Fig. 4.1, were chosen as peak-aged conditions. As for the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys, certain ageing treatments (32 and 16 h, respectively), notated as the peak-aged conditions, were adopted for the homogenisation of solute atoms inside grains. The peak-aged conditions for the four alloys are indicated by orange arrows in Fig. 4.1. It is insufficient to explain the difference in ageing responses among the alloys only based on Fig. 4.1 of the age-hardening response. Microstructures of the aged alloys, especially the distribution of precipitates, were examined in the following to investigate the age-hardening difference.
Fig. 4.1- Age-hardening response during isothermal ageing at 250 °C, the selected peak-aged conditions are indicated by orange arrows.

The microstructures of these peak-aged samples under SEM are displayed in Fig. 4.2. The bright areas in these backscattered electron images indicate high concentrations of solute atoms with larger atomic numbers in these areas. In present work, all solute atoms (Zn, Y, Gd) have larger atomic numbers than the magnesium matrix, and thus the bright areas in Figs. 4.2 (b-d) indicate the presence of intermetallic particles. By contrast, Fig. 4.2 (a) has no obvious contrast, which implies no intermetallic particles observed under this magnification. The slightly bright areas of approximately 40 µm wide in Fig. 4.2(a) correspond to grains with particular orientations, and the contrast is due to the difference in orientations of various grains. The intermetallics along grain boundaries in the Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys after heat treatments (Fig. 4.2b-d) were found to be 14H long-period stacking-ordered (LPSO) phase, which was observed in Mg-Gd(-Y)-Zn based alloys after heat treatments above 350 °C [129, 138]. The 14H phase was not found in the Mg-2.5Gd-0.1Zr alloy, and Zn additions resulted in the formation of LPSO structures in the Mg-2.5Gd-1.0Zn-0.1Zr, Mg-
1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys during heat treatments. However, the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy had obvious age-hardening response, while the Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys had little ageing response in Fig. 4.1, implying that the intermetallics along grain boundaries were not the main reason causing the difference in age hardening.

Fig. 4.2 - Backscattered electron images showing the distributions of primary intermetallic particles in aged samples of (a) Mg-2.5Gd-0.1Zr, (b) Mg-2.5Gd-1.0Zn-0.1Zr, (c) Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr, and (d) Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys. The corresponding ageing conditions are indicated by orange arrows in Fig. 4.1.

The distributions of precipitates in the peak-aged samples were examined using TEM and HAADF-STEM. In the HAADF-STEM images, the contrast is relative to the variations in the atomic number of atoms in the sample, and the brighter areas indicate the higher concentrations of RE/Zn atoms in these areas, corresponding to the precipitates in the alloys.

The distribution of precipitates viewed along the [0001]_α direction is given in Fig. 4.3. Under this condition, the precipitates lying on non-basal planes can be observed. Figure 4.3(a)
shows that the Mg-2.5Gd-0.1Zr alloy has a great number of lenticular $\beta'$ ($\text{Mg}_7\text{Gd}$) precipitates. The $\beta'$ phase has three variants that are uniformly distributed in the $[0\bar{1}10]_\alpha$, $[\bar{1}100]_\alpha$ and $[10\bar{1}0]_\alpha$ directions. The corresponding selected area electron diffraction (SAED) pattern in Fig. 4.3(f) shows the evidence of the presence of the three variants of $\beta'$ phase, which has three sets of diffraction spots from the $\beta'$ phase, as schematically shown in Fig. 2.23. The Mg-2.5Gd-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys have the same types of precipitate phases of the $\beta'$ and $\beta_1$ ($\text{Mg}_3\text{Gd}$) as shown in Figs. 4.3 (b, d), respectively. The $\beta_1$ particles are plate-shaped and have attaching $\beta'$ particles at each end. The precipitate density is higher in the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy than that in the Mg-2.5Gd-1.0Zn-0.1Zr alloy. However, no precipitate is observed in the aged Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy, as shown in Fig. 4.3(c), which is verified by the corresponding SAED pattern image of the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy in Fig. 4.3(e) shows no diffraction spots from precipitate, only the diffraction spots of the magnesium matrix.

The $\beta'$ and $\beta_1$ phases are hardening precipitates in Mg-Gd based alloys. The higher precipitate density of the $\beta'$ and $\beta_1$ phases in the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys corresponds to the higher age-hardening response in Fig. 4.1. Apart from the $\beta'$ and $\beta_1$ phases formed on the prismatic planes of the matrix, $\gamma'$ precipitates and 14H long-period stacking-ordered (LPSO) structures were also observed in Zn-containing alloys (Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys) shown in Fig. 4.4.
Fig. 4.3 - HAADF-STEM images showing the distributions of precipitates in aged samples of (a) Mg-2.5Gd-0.1Zr, (b) Mg-2.5Gd-1.0Zn-0.1Zr, (c) Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and (d) Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys, (e, f) are the corresponding SAED patterns of Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-0.1Zr alloys. Electron beam is parallel to the [0001]_α direction.
Figure 4.4 presents the distribution of precipitates viewed along the [11\overline{2}0]_\alpha direction. Under this condition, the \(\gamma'\) precipitates and 14H long-period stacking-ordered (LPSO) structures lying on basal planes can be observed: Mg-2.5Gd-1.0Zn-0.1Zr (Figs. 4.4(a, b)), Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr (Figs. 4.4(c, d)) and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr (Figs. 4.4(e, f)) alloys. The \(\gamma'\) particles are thin plates on basal planes having a large aspect ratio shown in Figs. 4.4(a, c, e) as the white horizontal lines. The enlarged HAADF-STEM image of a \(\gamma'\) particle in Fig. 4.4(g) indicates that the solute atoms (Zn/RE) are mainly concentrated in the centre two layers. The 14H LPSO structures have an atomic periodicity of 14 layers along c-axis direction, shown as white bands in Figs. 4.4(b, d, f). An enlarged section of the 14H LPSO structure is shown in Fig. 4.4(h), which displays that the Zn/RE atoms are distributed extending across the local four close-packed layers. From the perspective of precipitate density, the Mg-2.5Gd-1.0Zn-0.1Zr alloy has a higher density of \(\gamma'\) precipitates than the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys, and no big difference is found in the density of the 14H LPSO structures among these alloys. It can be seen from Figs. 4.1 and 4.4 that the \(\gamma'\) precipitates and 14H LPSO structures are not primary hardening precipitates in the Mg-Gd(-Y)-Zn-Zr alloys because the density of \(\gamma'\) precipitates and 14H LPSO structures in the aged Mg-2.5Gd-1.0Zn-0.1Zr (Figs. 4.4(a, b)) and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr (Figs. 4.4(e, f)) alloys are similar while the age-hardening responses are significantly different.
Fig. 4.4 - HAADF-STEM images showing the distributions of precipitates in aged Zn-containing samples of (a, b) Mg-2.5Gd-1.0Zn-0.1Zr, (c, d, g, h) Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr, and (e, f) Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys. Electron beam is parallel to the [11\(\bar{2}0\)]\(\alpha\) direction.
Based on the observation of Figs. 4.1-4.4, the effects of the alloy element type and concentration on precipitation distribution in the peak-aged alloys can be made. Comparing the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Zn-0.1Zr alloys, it can be found that 1.0 at.% addition of Zn significantly reduces the density of the $\beta'$ particles and brings the presence of the $\gamma'$ particles and 14H LPSO structure, as shown in Figs. 4.3(a, b) and 4.4(a, b), which reduces the age-hardening response as shown in Fig. 4.1.

Comparing the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys, it can be seen that 1.0 at.% addition of Y can considerably increase the density of the $\beta'$ particles and slightly reduce the density of the $\gamma'$ particles, which increases the age-hardening response as shown in Fig. 4.1.

Comparing the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys, it is found that partial substitution of Gd with Y leads to the disappearance of the $\beta'$ particles and a small reduction of the $\gamma'$ particle density, which does not affect the age-hardening response as shown in Fig. 4.1.

Comparing the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys, it is observed that the increase in Gd concentration would result in the presence of the $\beta'$ particles on prismatic planes of the magnesium matrix, which significantly increases the age-hardening response as shown in Fig. 4.1.

### 4.3. Tensile Properties of the Mg-Gd(-Y-Zn)-Zr Alloys

Tensile tests were performed at room and elevated temperatures, in order to obtain the 0.2% proof strength used as the maximum stress applied in the following creep tests.

The 0.2% proof strengths of the aged alloys are shown in Fig. 4.5(a). The strength gradually reduces as the temperature raises, except the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy exhibiting a lower 0.2% proof strength at room temperature compared with higher strengths at 200 ºC. When the test temperature is same (up to 300 ºC), the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys show higher 0.2% proof strengths than the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys.
The ultimate tensile strengths of the aged alloys are shown in Fig. 4.5(b). The ultimate tensile strength decreases slowly as the temperature increases up to 300 °C, and starts to descend dramatically above 300 °C. When the test temperature is same (up to 300 °C), the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys show higher ultimate tensile strengths than the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys.

The elongations of the aged alloys are shown in Fig. 4.5(c). The elongation curves of the Mg-2.5Gd-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys share a similar ascending tendency up to 200 °C, followed with a gradually descending from 200 to 300 °C, then rise significantly at 325 °C and end with a sharp drop at 350 °C. For the Mg-2.5Gd-1.0Zn-0.1Zr alloy, the elongation curve keeps ascending until the temperature reaches 325 °C and then followed by a drop at 350 °C.

The tensile test properties including 0.2% proof strength, ultimate tensile strength and elongation are closely related to the microstructure, such as grain size and precipitate distribution. Combined with the observation of microstructures of the alloys shown in Figs. 4.2-4.4, it can be seen that the grain sizes of the aged alloys are similar, but the precipitate distributions are much different. Therefore, it is deduced that the alloys having higher density of the $\beta'$ and $\beta_1$ precipitates exhibit higher 0.2% proof and ultimate tensile strengths, lower elongations, such as the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys. In contrast, the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys show lower 0.2% proof and ultimate tensile strengths due to the lower densities of the $\beta'$ and $\beta_1$ precipitates.

Creep tests were performed at 250 and 300 °C. At the two temperatures, the Mg-2.5Gd-0.1Zr alloy showed the highest 0.2% proof strength at 250 °C and the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy showed the best at 300 °C. In contrast, the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys exhibited much lower 0.2% proof strength. The values of 0.2% proof strength of the alloys obtained from the tensile tests are listed in Table 4.1, and it is obvious that the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy exhibits the highest 0.2% proof strength: 230 MPa at 200 °C, 216 MPa at 250 °C and 203 MPa at 300 °C. In contrast, the Mg-2.5Gd-1.0Zn-0.1Zr alloy shows lowest 0.2% proof strength of 142 MPa at 200 °C, 126 MPa at 300 °C, and the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy exhibits the lowest 0.2% proof strength of 145 MPa at 250 °C.
Fig. 4.5 - Tensile properties of the alloys: (a) 0.2% proof strength, (b) ultimate tensile strength, (c) elongation at ambient and elevated temperatures.
Table 4.1. 0.2% proof strength of alloys.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>200 °C</th>
<th>250 °C</th>
<th>300 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-2.5Gd-0.1Zr</td>
<td>204 MPa</td>
<td>220 MPa</td>
<td>189 MPa</td>
</tr>
<tr>
<td>Mg-2.5Gd-1.0Zn-0.1Zr</td>
<td>142 MPa</td>
<td>151 MPa</td>
<td>126 MPa</td>
</tr>
<tr>
<td>Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr</td>
<td>147 MPa</td>
<td>145 MPa</td>
<td>132 MPa</td>
</tr>
<tr>
<td>Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr</td>
<td>230 MPa</td>
<td>216 MPa</td>
<td>203 MPa</td>
</tr>
</tbody>
</table>

4.4. Creep Deformation Behaviour of the Mg-Gd(-Y-Zn)-Zr Alloys

4.4.1. Creep tests conducted at 250 °C

Creep deformation occurs in the scope of elastic deformation, so the stress applied in creep tests should below the 0.2% proof strength at the same temperature. According to the values of 0.2% proof strength of the Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys given in Table 4.1, the stresses applied in creep tests at 250 °C were chosen to be 80, 100, 120 MPa. The creep curves obtained from the creep tests are shown in Figs. 4.6(a, c, e), and the corresponding creep rates as a function of creep time are illustrated in Figs. 4.6(b, d, f).

When the applied stress was 80 MPa, the Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys did not fail within the creep time of 336 h, and the corresponding creep strain curves are shown in Fig. 4.6(a), which indicate that these alloys were still in the secondary creep stage when the creep tests were manually ended. The creep rate curves in Fig. 4.6(b) imply that in the secondary creep stage, the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys have lower creep rates, which represent better creep resistance. In contrast, the Mg-2.5Gd-1.0Zn-0.1Zr alloy has the highest creep rate, which means the worst creep resistance among the alloys.

When the applied stress was 100 MPa, the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys did not fail within the creep time of 336 h, while the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Zn-0.1Zr alloys ruptured within 300 h, and the corresponding creep curves are shown in Fig. 4.6(c). According to the creep rate curves shown in Fig. 4.6(d), the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy has the best creep resistance (the lowest creep rate in the secondary creep stage). By contrast, the Mg-2.5Gd-1.0Zn-0.1Zr alloy shows the worst creep resistance (the highest creep rate in the secondary creep stage).
When the applied stress was 120 MPa, all the four alloys ruptured within the creep time, and the corresponding creep curves are shown in Fig. 4.6(c). Based on the creep rate curves shown in Fig. 4.6(f), the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy has the best creep resistance and the Mg-2.5Gd-1.0Zn-0.1Zr alloy has the worst. The performances of the Mg-2.5Gd-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys are in the middle.

Fig. 4.6 - Creep curves and the corresponding creep rates as a function of creep time at 250 °C: (a, b) 80 MPa, (c, d) 100 MPa and (e, f) 120 MPa.
The creep rate of the secondary creep stage (steady creep rate) is an important parameter used in the creep analysis, and the steady-state creep rate is usually taken as the minimum creep rate, which can be obtained from the creep rate curves shown in Figs. 4.6(b, d, f). Although Figs. 4.6(a, b) do not show an apparent tertiary creep stage, all these samples experienced the secondary creep stage for at least 200 h. It is reasonable to treat the minimum creep rates obtained from these curves as the steady creep rate. The minimum creep rates obtained from Fig. 4.6 are listed in Table 4.2, and it shows that the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy has the lowest minimum creep rates below 1.5×10⁻⁸ s⁻¹ under all the creep test conditions. In contrast, the Mg-2.5Gd-1.0Zn-0.1Zr alloy shows the highest minimum creep rates above 1.5×10⁻⁸ s⁻¹ under all test conditions.

Table 4.2. Minimum creep rates obtained at 250 ℃

<table>
<thead>
<tr>
<th>Alloys</th>
<th>80 MPa</th>
<th>100 MPa</th>
<th>120 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-2.5Gd-0.1Zr</td>
<td>1.0×10⁻⁸ s⁻¹</td>
<td>1.9×10⁻⁸ s⁻¹</td>
<td>3.8×10⁻⁸ s⁻¹</td>
</tr>
<tr>
<td>Mg-2.5Gd-1.0Zn-0.1Zr</td>
<td>1.8×10⁻⁸ s⁻¹</td>
<td>7.2×10⁻⁹ s⁻¹</td>
<td>1.7×10⁻⁷ s⁻¹</td>
</tr>
<tr>
<td>Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr</td>
<td>2.0×10⁻⁹ s⁻¹</td>
<td>1.1×10⁻⁸ s⁻¹</td>
<td>5.0×10⁻⁸ s⁻¹</td>
</tr>
<tr>
<td>Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr</td>
<td>1.7×10⁻⁹ s⁻¹</td>
<td>4.5×10⁻⁹ s⁻¹</td>
<td>1.3×10⁻⁸ s⁻¹</td>
</tr>
</tbody>
</table>

The minimum creep rate can be plotted in a graph of the minimum creep rate versus the applied stress, as shown in Fig. 4.7. The best linear fitting lines were found for each alloy in Fig. 4.7, and the corresponding slopes of the fitting lines are equal to the values of the stress exponent (n) used in the power-law. The n value indicates the operative dominant creep mechanism during the secondary creep stage. When n value is above 3, the creep mechanism is usually predicted as dislocation creep. The n values for these alloys under the creep conditions of 80 - 120 MPa at 250 ℃ are all above 3, which indicates the dominant creep mechanism for these alloys is dislocation creep at the secondary creep stage.
4.4.2. Creep tests conducted at 300 °C

Based on the 0.2% proof strength of the Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys obtained at 300 °C (Table 4.1), the stresses applied in the creep tests performed at 300 °C were chosen to be 40, 60, 80 MPa. The creep curves obtained from the creep tests are shown in Figs. 4.8(a, c, e), and the corresponding creep rates as a function of creep time are illustrated in Figs. 4.8(b, d, f).

When the applied stress was 40 MPa, the Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys did not fracture within the creep time of 336 h, while the Mg-2.5Gd-0.1Zr alloy failed within 300 h, and the corresponding creep strain curves are shown in Fig. 4.8(a). Based on the creep rate curves in Fig. 4.8(b), the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy has the lowest creep rates in the secondary creep stage, which means the alloy having the best creep resistance. The Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy shows a similar creep curve as that of the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy, but has a little higher creep rate in the secondary creep stage indicating the inferior creep resistance. The Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys exhibit similar creep curves before the creep time of 125 h, and after 125
h, the creep curve of the Mg-2.5Gd-1.0Zn-0.1Zr alloy ascends significantly till fracture while that of the Mg-2.5Gd-1.0Zn-0.1Zr alloy arises gradually.

When the applied stress was 60 MPa, except the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy did not fail within 336 h, the Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys fracture within 336 h, and the corresponding creep strain curves are shown in Fig. 4.8(c). The Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy shows the best creep resistance. The Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy exhibits an inferior creep resistance to the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy, but has better creep resistance than the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Zn-0.1Zr alloys. The creep strains of the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Zn-0.1Zr alloys increase relatively quickly as creep time proceeds, and both fracture within 150 h.

When the applied stress was 80 MPa, all the alloys failed within the creep time of 150 h, and the corresponding creep strain curves are shown in Fig. 4.8(e). Among these alloys, the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy still shows the best creep resistance. The Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy exhibits an inferior creep resistance to the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy. The Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Zn-0.1Zr alloys have much worse creep resistance compared with the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys.

The minimum creep rates obtained from Fig. 4.8 are listed in Table 4.3, and it shows that the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy has the lowest minimum creep rates under all the creep test conditions. In contrast, the Mg-2.5Gd-1.0Zn-0.1Zr alloy shows the highest minimum creep rates under all test conditions. It is worthy to note that the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy exhibited better creep resistance than the Mg-2.5Gd-0.1Zr alloy at 250 and 300 °C, while the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy has worse 0.2% proof strength and ultimate tensile strength than the Mg-2.5Gd-0.1Zr alloy at 250 and 300 °C. Microstructures are needed to be investigated to reveal the uncommon phenomena.
Fig. 4.8 - Creep curves and the corresponding creep rates as a function of the creep testing time at 300 °C: (a, b) 40 MPa, (c, d) 60 MPa and (e, f) 80 MPa.

Table 4.3. Minimum creep rates obtained at 300 °C

<table>
<thead>
<tr>
<th>Alloys</th>
<th>40 MPa</th>
<th>60 MPa</th>
<th>80 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-2.5Gd-0.1Zr</td>
<td>2.4×10^{-8} s^{-1}</td>
<td>7.3×10^{-8} s^{-1}</td>
<td>1.5×10^{-7} s^{-1}</td>
</tr>
<tr>
<td>Mg-2.5Gd-1.0Zn-0.1Zr</td>
<td>4.3×10^{-8} s^{-1}</td>
<td>2.1×10^{-7} s^{-1}</td>
<td>7.0×10^{-7} s^{-1}</td>
</tr>
<tr>
<td>Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr</td>
<td>1.0×10^{-8} s^{-1}</td>
<td>4.3×10^{-8} s^{-1}</td>
<td>1.8×10^{-7} s^{-1}</td>
</tr>
<tr>
<td>Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr</td>
<td>3.4×10^{-9} s^{-1}</td>
<td>6.0×10^{-9} s^{-1}</td>
<td>7.3×10^{-8} s^{-1}</td>
</tr>
</tbody>
</table>
The minimum creep rates obtained from the creep tests are plotted in a graph of the minimum creep rate versus the applied stress, as shown in Fig. 4.9. The slopes of the best fitting lines are equal to the values of the stress exponent ($n$) used in power-law. It is found that $n$ values of the Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys are about 4.0, which indicates that the operative dominant creep mechanism in the secondary creep stage is dislocation creep. For the Mg-2.5Gd-0.1Zr alloy, $n$ value equals to 2.6, which is between the value of 2 representing the grain boundary sliding mechanism and the value of 3 signifying the dislocation creep mechanism. This $n$ value of the Mg-2.5Gd-0.1Zr alloy implies that the two mechanisms maybe co-exist, and which one is dominant needs further research.

Fig. 4.9 - Minimum creep rate versus the applied stress for creep tests at 300 °C. The stress exponent (slope of the fitting line) is provided for the alloys.

4.5. Microstructural Characterization of the Mg-Gd(-Y-Zn)-Zr Alloys after Creep Tests

4.5.1. Microstructures of the alloys crept at 250 °C

The samples after the creep tests at 250 °C were firstly examined using SEM BSE mode, and the results are shown in Fig. 4.10. Compared with the BSE images obtained from the samples before the creep tests (Fig. 4.2), the crept samples have obvious grain boundaries indicated by the white lines in Fig. 4.10, while the grain boundaries are difficult to identify in the samples before
the creep tests in Fig. 4.2. As for the intermetallic particles distributed along grain boundaries in the Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys, no apparent changes were observed between Figs. 4.2 and 4.10.

As the applied stress was 80 MPa and the creep tests lasted for 336 h, no crack is observed in the microstructures of the crept samples in Figs. 4.10(a, d, g, j). It is worthy to note that the four samples in Figs. 4.10(a, d, g, j) did not fracture during the creep tests. As the applied stress increased to 100 MPa, cracks (indicated by the yellow arrows) are observed along the grain boundaries in the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Zn-0.1Zr samples (Figs. 4.10(b, e)), and the two samples failed during the creep tests. In contrast, as shown in Figs. 4.10(h, k), no cracks are observed in the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr samples that did not fracture during the creep tests. When the applied stress increased to 120 MPa, cracks are observed in all the samples and these samples failed during the creep tests. So it is inferred that the cracks occur in the tertiary creep stage.

The applied stresses in Fig. 4.10 is along the vertical direction, thus it is worthy to note that the cracks are likely to occur at the grain boundaries that are approximately normal to the applied stress direction.
Fig. 4.10 - BSE images showing the microstructures of (a-c) Mg-2.5Gd-0.1Zr, (d-f) Mg-2.5Gd-1.0Zn-0.1Zr, (g-i) Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr, (j-l) Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr samples crept at 250 °C: (a, d, g, j) under 80 MPa, (b, e, h, k) 100 MPa, (c, f, i, l) 120 MPa. The applied stress is along vertical direction. The corresponding creep time and creep strain are (a) 336 h, 0.019, (b) 297 h, 0.063, (c) 155 h, 0.050, (d) 336 h, 0.030, (e) 235 h, 0.107, (f) 90 h, 0.130, (g) 336 h, 0.006, (h) 336 h, 0.019, (i) 172 h, 0.084, (j) 336 h, 0.006, (k) 336 h, 0.009, (l) 333 h, 0.037, respectively.

The precipitates of the samples after the creep tests of 80 MPa for 336 h were examined under HAADF-STEM mode with the electron beam parallel to the [0001]_α direction, and the results are shown in Fig. 4.11. In the Mg-2.5Gd-0.1Zr sample (Fig. 4.11(a)), linear precipitate chains are observed, and the corresponding SAED pattern at the top right corner of Fig. 4.11(a) indicates that the precipitate chains are made of the $\beta'$ particles, and only one set of diffraction spots of the $\beta'$ phase is found. By contrast, individual $\beta'$ particles of three variants were observed uniformly distributed in the Mg-2.5Gd-0.1Zr sample before the creep test shown in Fig. 4.3(a). In the Mg-2.5Gd-1.0Zn-0.1Zr sample (Fig. 4.11(b)), coarsened equilibrium $\beta$ particles are observed.
By contrast, uniform distributed $\beta'$ and $\beta_1$ particles are found in the Mg-2.5Gd-1.0Zn-0.1Zr sample before the creep test (Fig. 4.3(b)). In the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr sample (Fig. 4.11(c)), a number of $\beta'$ and $\beta_1$ precipitates are observed. By contrast, no precipitates on prismatic planes are observed in the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr sample before the creep test (Fig. 4.3(c)). In the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr sample (Fig. 4.11(d)), a great number of $\beta'$ and $\beta_1$ particles are observed, while no $\beta_1$ particles are found in the sample before the creep test.

Fig. 4.11 - HAADF-STEM images showing the distributions of precipitates in the samples crept under 80 MPa at 250 °C for 336 h. (a) Mg-2.5Gd-0.1Zr alloy with a creep strain of 0.019, (b) Mg-2.5Gd-1.0Zn-0.1Zr alloy with a creep strain of 0.030, (c) Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy with a creep strain of 0.006, and (d) Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy with a creep strain of 0.006. Electron beam is parallel to the [0001]$\alpha$ direction.
When the applied stress was 120 MPa, the microstructure of the crept Mg-2.5Gd-0.1Zr sample shown in Fig. 4.12(f) is similar to the one crept under 80 MPa (Fig. 4.11(a)), that the precipitate chains are observed. In the Mg-2.5Gd-1.0Zn-0.1Zr crept sample, a few of \( \beta' \) and \( \beta_1 \) precipitates are found, as shown in Fig. 4.12(g). For the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr crept sample, a number of \( \beta' \) particles are observed in Fig. 4.12(a). For the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr crept sample, a great number of \( \beta' \) and \( \beta_1 \) particles are found in Fig. 4.12(b). However, an additional dispersion of finer-scale \( \beta' \) precipitates was detected in the Y-containing alloys, i.e. the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys, as shown in Figs. 4.12(a, b). In order to find out the reasons triggering the formation of finer-scale \( \beta' \) precipitates during the creep tests, a comparison was made between the microstructures of the crept sample of the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy and that of the specimen aged for an identical time at the creep testing temperature without any stresses (i.e. subjected to the heat treatment for the same period of time as the creep test at 250 °C). The finer-scale dispersion of \( \beta' \) precipitates, which was detected in the crept sample, was not found in the aged sample, Fig. 4.12(e). Furthermore, the number density of the coarse \( \beta' \) precipitates in the crept sample was higher than that in the aged sample. These observations imply that the finely dispersed \( \beta' \) precipitates were caused by the applied stresses.
Fig. 4.12 - HAADF-STEM images showing the distribution of precipitates in the samples crept under 120 MPa at 250 °C to rupture of (a) the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy crept for 172 h, with a rupture strain of 0.084, (b) the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy crept for 333 h, with a rupture strain of 0.037. (c, d) enlarged images of β′ precipitates indicated by arrows in (a) and (b) respectively. HAADF-STEM images (e) showing precipitates in a Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy subjected to an ageing treatment at 250 °C for 172 h. (f) the Mg-2.5Gd-0.1Zr alloy crept for 155 h, with a rupture strain of 0.05, (g) the Mg-2.5Gd-1.0Zn-0.1Zr alloy crept for 90 h, with a rupture strain of 0.13. Electron beam is parallel to the [0001]_α direction.
The distributions of dislocations in the samples of the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys crept at 250 °C under 120 MPa for 70 h are shown in Figs. 4.13(b-d). The Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy was in the secondary creep stage, while the Mg-2.5Gd-1.0Zn-0.1Zr sample was in the tertiary stage, as indicated in the creep curves shown in Fig. 4.13(a). Viewed along the [0001]_α direction, it can be seen that the dislocation density in the Mg-2.5Gd-1.0Zn-0.1Zr sample (Fig. 4.13(b)) is higher than that in the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr sample (Fig. 4.13(d)). It is worthy to note that not all the dislocations shown in Fig. 4.13(d) generated during the creep test — the observation of a portion of dislocations accords with the characteristics of the partial dislocations bounding the basal plates of the γ’ and 14H precipitates reported in previous paper [132]. Figure 4.13(d) reveals that the dislocations tangled severely around the β’ precipitates in the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr sample. The dark-field image of Fig. 4.13(c) viewed along the [1\overline{1}00]_α direction indicates that non-basal dislocations were also activated during the secondary creep stage.
4.5.2. Microstructures of the alloys crept at 300 °C

As the creep temperature was 300 °C, the BSE images of the microstructures of the crept alloys are shown in Fig. 4.14. Similar as the samples crept at 250 °C shown in Fig. 4.10, the samples experiencing the creep tests at 300 °C fractured during the creep tests (Figs. 4.14(a, b, c, e, f, h, i, l)) have cracks (indicated by the yellow arrows) along the grain boundaries approximately normal to the applied stress direction. Additionally, a few cracks were also observed inside grains,
such as the ones indicated by red arrows in Fig. 4.14(c, e), and these cracks extended along the direction nearly perpendicular to the applied stress direction.

![Fig. 4.14 - BSE images showing the microstructures of (a-c) Mg-2.5Gd-0.1Zr, (d-f) Mg-2.5Gd-1.0Zn-0.1Zr, (g-i) Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr, (j-l) Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys crept at 300 °C: (a, d, g, j) under 40 MPa, (b, e, h, k) 60 MPa, (c, f, i, l) 80 MPa. The applied stress is along vertical direction. The corresponding creep time and creep strain are (a) 263 h, 0.154, (b) 66 h, 0.196, (c) 27 h, 0.154, (d) 336 h, 0.070, (e) 129 h, 0.213, (f) 36 h, 0.172, (g) 336 h, 0.016, (h) 316 h, 0.100, (i) 71 h, 0.143, (j) 336 h, 0.012, (k) 316 h, 0.028, (l) 120 h, 0.061, respectively.]

The distributions of precipitates in the samples after the creep tests held under 60 MPa at 300 °C, are shown in Fig. 4.15 with the incident beam parallel to the [0001]_α direction. Equilibrium β phase precipitates were observed in all the samples, but the size and density differ. The Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr sample has the highest density, and the smallest size of β precipitates. In contrast, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr sample shows the lowest density, and the biggest size of β precipitates.
4.6. Discussion

Based on the apparent stress exponents obtained from the creep tests at 250 °C under 80-
120 MPa, the operative dominant creep mechanism in the secondary creep stage for the alloys,
namely Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-
1.0Y-1.0Zn-0.1Zr, is inferred to be dislocation creep. The deduced mechanism of dislocation creep
is further supported by the presence of dislocations in crept samples, as shown in Fig. 4.13, and it
is consistent with some early and recent studies of sand or permanent mold cast magnesium alloys.
and high pressure die-cast magnesium alloys [5, 6, 148, 179-184]. As for the creep tests conducted at 300 °C, dislocation creep is also determined to be the operative predominant creep mechanism in the secondary creep stage for the Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys. If the notion that dislocation creep is the dominant mechanism of the creep deformation is accepted as correct, then the size, shape and distribution of precipitates and the identity of solute atoms in the solid solution magnesium matrix phase become important factors because they can affect the motion of dislocations, irrespective of dislocation climb or dislocation gliding. Different alloying elements may cause different changes to the characteristic features of the strengthening precipitates and solutes in the magnesium matrix. It is therefore important to discuss the qualitative effects of individual alloying elements on creep properties based on their influence on precipitation and solutes in the magnesium matrix.

The influence of precipitates and solute atoms on the minimum creep rate of dislocation creep can be expressed by Eq. 4.1 [71]:

\[
\dot{\varepsilon} = \frac{AGbD_{el}}{kT} \left( \frac{\sigma}{G} - \frac{\sigma_T}{G} \right)^m
\]  

(4.1)

where \( A \) and \( n \) are constants, \( G \) the shear modulus of the magnesium matrix phase, \( b \) the magnitude of Burgers vector of the slip/climb dislocations, \( D_{el} \) the effective lattice diffusion coefficient, \( k \) Boltzmann’s constant, \( T \) absolute temperature, \( \sigma \) the applied stress and \( \sigma_T \) the threshold stress. According to this equation, for a given creep testing temperature and an applied stress, \( \sigma_T \) and \( D_{el} \) are the variables for the minimum creep rate of the Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloys. \( \sigma_T \) is the stress required for a pinned dislocation to escape from the pinning particles, and it is affected by the size, shape and distribution of precipitates. \( D_{el} \) is affected by solute atoms according to the following equation [73]:

\[
D_{el} = \frac{D_s D_{Mg}}{(1-C_s)D_s+C_s D_{Mg}}
\]

(4.2)

where \( D_s \) is the diffusion coefficient of solute atoms in the \( \alpha \)-Mg lattice, \( D_{Mg} \) is the self-diffusion coefficient, and \( C_s \) is the concentration of solute atoms. In this equation, it is the identity of solute atoms and their concentration that determine \( D_{el} \). A higher diffusion coefficient suggests a higher diffusion rate, which in turn results in a higher creep rate.
Fig. 4.16 - Comparison of the 0.2% proof strength and minimum creep rate obtained at 250 °C between (a) Mg-2.5Gd-0.1Zr (G) and Mg-2.5Gd-1.0Zn-0.1Zr (GZ) alloys, (b) Mg-2.5Gd-1.0Zn-0.1Zr (GZ) and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr (GWZ1) alloys, (c) Mg-2.5Gd-1.0Zn-0.1Zr (GZ) and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr (GWZ2) alloys, (d) Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr (GWZ1) and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr (GWZ2) alloys.

4.6.1. Effects of the Zn addition

The effect of the Zn addition on the effective lattice diffusivity remains unclear in the present study. The diffusion coefficient of Zn in magnesium is approximately $2.8 \times 10^{-17}$ m$^2$·s$^{-1}$ at 250 °C, and the self-diffusion coefficients of magnesium parallel and normal to c axis are about $9.8 \times 10^{-18}$ and $1.5 \times 10^{-17}$ m$^2$·s$^{-1}$, respectively [185]. Since the diffusivity of Zn atoms is higher than the self-diffusion of Mg atoms, the addition of Zn atoms to the Mg-2.5Gd-0.1Zr alloy is not expected to reduce the effective diffusivity $D_{el}$ according to Eq. 4.2.

Examination of the microstructures of the Mg-2.5Gd-0.1Zr and Mg-2.5Gd-1.0Zn-0.1Zr alloys indicates that the Zn addition changes the identities of the major strengthening precipitate phases. The predominant precipitates in the Mg-2.5Gd-0.1Zr alloy are $\beta'$ precipitates of a lenticular shape on prismatic planes of the magnesium matrix phase. The addition of Zn to the Mg-2.5Gd-0.1Zr alloy leads to the formation of basal plates of $\gamma'$ precipitates at the expense of $\beta'$
precipitates. The number density of $\beta'$ precipitates in the Zn-containing alloy is significantly lower than that in the counterpart Zn-free alloy, Figs. 4.3(a, b). While the Zn-containing alloy also has many basal plates of $\gamma'$ and 14H precipitates, such basal precipitate plates are however much less effective in strengthening than the lenticular-shaped $\beta'$ precipitates [144]. Therefore, the Mg-2.5Gd-1.0Zn-0.1Zr alloy is expected to have much lower 0.2% proof strength than the Mg-2.5Gd-0.1Zr alloy, as experimentally observed, Fig. 4.5(a). The tensile and creep test results obtained at 250 °C for the Mg-2.5Gd-1.0Zn-0.1Zr and Mg-2.5Gd-0.1Zr alloys shown in Figs. 4.5 and 4.6 are extracted and re-plotted in Fig. 4.16(a). It is apparent that the 0.2% proof strength drops, and the minimum creep rate increases when Zn is added to the Mg-2.5Gd-0.1Zr alloy. It is therefore reasonable to infer that the Zn addition leads to the formation of precipitates which are much less effective in impeding dislocation gliding or climb, which in turn leads to an increased value of the minimum creep rate by reducing $\sigma_T$.

4.6.2. Effects of the Y addition

The partial replacement of Gd by Y in the Mg-Gd-Zn-Zr alloy, for example from Mg-2.5Gd-1.0Zn-0.1Zr to Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr, leads to a further reduction in the number density of $\beta'$ precipitates, Figs. 4.3(b, c). The aged microstructure of the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy contains essentially an exclusive dispersion of the $\gamma'$ and 14H precipitates. This further reduction in the number density of $\beta'$ precipitates leads to a small decrease in the 0.2% proof strength at room temperature, but is not associated with any apparent change in the 0.2% proof strength at 250 °C, Figs. 4.5(a) and 4.16(b). Despite the little change in strength, the minimum creep rate is reduced by 5-10 times for the 1.0 at.% replacement of Gd by Y, Figs. 4.7 and 4.16(b). The combined examination of tensile and creep properties and microstructures of the two alloys indicates that the substantial variation in the minimum creep rate is not caused by the threshold stress $\sigma_T$. It is therefore reasonable to focus on the examination of the effect of the Gd replacement by Y on the effective diffusivity $D_{el}$.

The precise effect of Y atoms on the effective diffusivity is difficult to assess due to the lack of the data of the diffusivities of Y and Gd in the solid magnesium at 250 °C. Nevertheless, a qualitative comparison of their diffusivities could be made by comparing precipitate sizes in the two alloys (Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr) aged under similar
conditions, Fig. 4.17. A coarse distribution of the equilibrium $\beta$ phase has already formed in the Mg-2.5Gd-1.0Zn-0.1Zr alloy, but the precipitates in the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy are still the metastable $\beta'$ phase and have a much smaller size. Calculations made by using the CompuTherm Pandat 8.2 software with the PanMg2012.pdb database indicate that the total solute contents (Gd and Y) in the magnesium solid solution matrix of the solution treated Mg-2.5Gd-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys are 1.69 at.% and 1.76 at.%, respectively, and that it drops to 0.54 at.% and 0.60 at.%, respectively, when the temperature decreases to 250 °C. So the solute supersaturation levels in the two alloys are similar, and if we assume that the driving force for precipitation is similar for the two alloys, then it is plausible that the smaller precipitate size in the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy is due to a lower growth rate of precipitates which is in turn from a lower diffusivity of solutes in the magnesium matrix. If the notion that Y atoms have a much lower diffusion rate than Gd atoms in the solid magnesium is accepted as true, then the partial replacement of Gd atoms by Y atoms, or by adding more Y atoms into the magnesium solid solution, will lead to a remarkable reduction in the effective diffusivity $D_{el}$, which in turn leads to a significant reduction in the minimum creep rate, Eqs. 4.1 and 4.2.

![Fig. 4.17 - HAADF-STEM images showing the microstructures of (a) Mg-2.5Gd-1.0Zn-0.1Zr, and (b) Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys aged for 512 h at 250 °C. Electron beam is parallel to the [0001]$_{\alpha}$ direction.](image)

The difference between the minimum creep rates of the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Zn-0.1Zr alloys decreases when the applied stress is increased from 80 MPa to 120
MPa, Fig. 4.7. A change in the creep mechanism could perhaps account for this difference in behaviour. The rate of dislocation creep is controlled predominately by recovery, consisting of climb and annihilation of edge dislocations, at low stresses, and by dislocation glide at high stresses [186, 187]. This suggests that at lower stresses, the creep rate will be most affected by the diffusion rate since dislocation climb is diffusion dependent. Thus, the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy, with its slower diffusion rate, is expected to have lower minimum creep rates (i.e. superior creep performance) at lower applied stresses. At higher applied stresses where glide is expected to predominate, creep behaviour depends less on the diffusion rate (since glide is independent of diffusion) and more on the threshold stress. The $\beta'$ precipitates have a greater effect blocking dislocation glide, and thus become more important as the applied stress increases. Therefore, the creep resistance of the Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloy should decrease compared to the Mg-2.5Gd-1.0Zn-0.1Zr at high stresses, due to its lower volume fraction of precipitates. However, to confirm that the operative creep mechanism does indeed change with stress, the dislocation substructures will need to be examined in more detail. Alternatively, additional stresses could be tested to see if the stress exponent changes between 80 and 120 MPa.

While the significant improvement in the creep resistance caused by the partial replacement of Gd by Y is attributable to the Y influence on the effective diffusivity $D_{el}$, it is to be noted that the addition of 1.0 at.% Y to the Mg-2.5Gd-1.0Zn-0.1Zr alloys can lead to a stronger effect on the minimum creep rate and that this enhancement in the creep resistance is attributable to a reduced value of the effective diffusivity $D_{el}$ and an increased value of $\sigma_T$. The increment in $\sigma_T$, which is supported by an increased number density of $\beta'$ precipitates, Figs. 4.3(b, d), and an increased 0.2% proof strength, Figs. 4.5(a) and 4.16(c), will yield a further reduction in the minimum creep rate.

4.6.3. Effects of the Gd addition

The effect of the Gd addition on the minimum creep rate can be deduced by the comparison of the Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr alloys. The former alloy has a significantly higher volume fraction of precipitates than the latter alloy, and therefore the former alloy is expected to have a higher 0.2% proof strength and a lower minimum creep rate. While the 0.2% proof strength of the former alloy is much higher than that of the latter alloy, its minimum creep rate is only slightly higher than that of the latter alloy at lower applied stresses such as 80
MPa, but much higher at higher applied stresses such as 120 MPa, Figs. 4.7 and 4.16(d). Since both alloys contain an equal concentration of Y and thus the $D_{el}$ values of the two alloys are expected to be similar, such result seems to suggest that the threshold stress plays a less important role than the diffusion rate in the alloy system when the applied stress is relatively low.

4.7. Summary

In this chapter, creep properties of the Mg-Gd(-Y-Zn)-Zr alloys, namely Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr (at.%), have been examined under the conditions of 250 °C with the applied stresses of 80 MPa, 100 MPa and 120 MPa, 300 °C with applied stresses of 40 MPa, 60 MPa and 80 MPa:

1. The Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy has the lowest minimum creep rate (the best creep resistance), by contrast, the Mg-2.5Gd-1.0Zn-0.1Zr alloy has the highest (the worst creep resistance) under the experimental conditions.

2. For the creep conditions applied in the present work, dislocation creep is the predominant operative mechanism in the secondary creep stage of these four alloys, except the creep mechanism of the Mg-2.5Gd-0.1Zr crept at 300 °C is attributed to the combination of dislocation creep and grain boundary sliding.

3. The addition of 1.0 at.% Zn to the Mg-2.5Gd-0.1Zr alloy leads to the formation of basal plates of $\gamma'$ precipitates at the expense of $\beta'$ precipitates. The number density of $\beta'$ precipitates in the resultant alloy is significantly lower than that in the Zn-free alloy. The $\gamma'$ plates are much less effective in impeding dislocation gliding or climbing, leading to reduced values of the threshold stress and thus increased values of the minimum creep rate.

4. The replacement of 1.0 at.% Gd by Y in the Mg-2.5Gd-1.0Zn-0.1Zr alloy results in a further reduction in the number density of $\beta'$ precipitates. While there is little change in the 0.2% proof strength, the minimum creep rate is reduced by 10 times at 80 MPa. The substantial reduction in the minimum creep rate is not caused by the threshold stress. It is suspected that Y atoms have a much lower diffusion rate than Gd atoms in the solid magnesium matrix, and that the partial replacement of Gd by Y reduces the effective lattice diffusivity which in turn leads to a reduction in the minimum creep rate.
(5) Keeping the concentrations of the other alloying elements in the Mg-Gd-Y-Zn-Zr alloys unchanged, an increase in the Gd content reduces the minimum creep rate and this effect becomes more pronounced at higher applied stresses. The increased concentration of Gd also leads to a higher volume fraction of precipitates and a higher 0.2% proof strength, which may contribute to the reduction of the minimum creep rate by increasing the threshold stress.
CHAPTER 5.

CHARACTERIZATION OF PRECIPITATE CHAINS OBSERVED IN THE Mg-2.5Gd-0.1Zr ALLOY
5.1. Introduction

In Chapter 4, precipitate chains of $\beta'$ particles were observed in the Mg-2.5Gd-0.1Zr alloy crept under 80 and 120 MPa at 250 °C (Figs. 4.11(a) and 4.12(f)), and the corresponding SAED pattern (Fig. 4.11(a)) indicated that there was only one $\beta'$ variant in the precipitate chains. In contrast, all three $\beta'$ variants were found in the aged sample before creep tests (Fig. 4.3(a)). The experimental results imply that two $\beta'$ variants gradually disappeared during the creep tests, and the third variant formed precipitate chains extending in a particular direction.

In order to reveal the configuration and formation mechanism of the $\beta'$ precipitate chains during the creep tests, the precipitate chains formed in the Mg-2.5Gd-0.1Zr samples crept at 250 °C are characterized using HAADF-STEM and TEM, and two precipitate phases, the $\beta'$ and unreported $\beta'_F$, are found. The atomic model of the $\beta'_F$ phase is deduced based on the HAADF-STEM images and the lattice parameters are calculated using first-principles. Next, the interfaces between the adjoining $\beta'$ and $\beta'_F$ precipitates are studied. Finally, the discussion includes: the influences of the stress field and the pre-existing dislocations on the formation of the precipitate chains; the occurrence of the $\beta'$ or/and $\beta'_F$ phases in Mg-RE alloys; and the types of transitional zones between the adjoining $\beta'$ and $\beta'_F$ precipitates.

5.2. Morphology of Precipitate Chains in Crept and Aged Samples

Before the creep tests, the $\beta'$ precipitates in the peak-aged Mg-2.5Gd-0.1Zr sample are distributed as shown in Fig. 5.1(a) viewed along $[0001]_\alpha$: the separated lenticular shaped $\beta'$ precipitates are uniformly distributed. The $\beta'$ precipitates of three types of variants are distinguished by their mid-rib planes (the mid-rib planes of variants ①, ②, ③ are parallel to $[0\overline{1}10]_\alpha$, $[\overline{1}100]_\alpha$ and $[10\overline{1}0]_\alpha$ respectively). A typical $\beta'$ precipitate is enlarged in Fig. 5.1(b), and it has a few of protrusions (indicated by the yellow arrows) connected to the lenticular main body of the $\beta'$ precipitate. The protrusions are rod-shaped consisting of hexagonal structures and zigzag arrays of Gd atoms. The main body of the $\beta'$ precipitate contains inverted zigzag arrays of Gd atoms (white dots shown in HAADF-STEM images) along the $[11\overline{2}0]_\alpha$ direction, as illustrated in Fig. 5.1(c).
Fig. 5.1 - Dark-field HAADF-STEM images showing (a) the distribution of \( \beta' \) precipitates in three directions ([1\( \bar{1} \)0]\( \alpha \), [\( \bar{1} \)100]\( \alpha \), [0\( \bar{1} \)10]\( \alpha \)) in a peak-aged sample, (b) the morphology of an individual \( \beta' \) precipitate, (c) the structure of a typical protrusion. The incident beam is along [0001]\( \alpha \).

The distribution of precipitates in the samples after the creep tests conducted at 250 °C under 80/100/120 MPa are shown in Fig. 5.2(a, b, c), respectively. It can be seen that the lenticular shaped \( \beta' \) particles were arranged in chains extending along the \( \{\bar{1}100\}\)\( \alpha \) direction. In contrast to the presence of three \( \beta' \) variants observed in the sample before creep tests (Fig. 5.1(a)), only one \( \beta' \) variant was found in the samples after creep tests, which was indicated by the SAED pattern given in Fig. 5.2(d) that only one variant of the \( \beta' \) diffraction pattern was found. All three sets of the diffraction patterns of the \( \beta' \) variants are illustrated in Fig. 2.23.

The relationship between the extending direction of precipitate chains and the direction of the applied stresses was also investigated. When the sample was examined under TEM, the direction of the applied stress was kept along the direction of the TEM sample holder, and the [0001] zone of the magnesium matrix was found when the beta tilting angle of the TEM was less than 10°. Under this observing condition, the projected direction of the applied stresses on (0001)\( \alpha \) was nearly parallel to [1\( \bar{1} \)20]\( \alpha \), which was approximately normal to the direction of the precipitate chains, as indicated in Fig. 5.2(b). The maximum angle between the applied stress and (0001)\( \alpha \) was around 10°. The length of precipitate chains changed when the magnitude of applied stresses and creep time changed. As shown in Fig. 5.2, the sample crept under 80 MPa for 336 h has the longest precipitate chains (Fig. 5.2(a)), while the sample crept under 120 MPa for 155 h has the shortest precipitate chains (Fig. 5.2(c)).
Chapter 5  Characterization of Precipitate Chains Observed in the Mg-2.5Gd-0.1Zr Alloy after Creep Tests

Fig. 5.2 - Dark-field HAADF-STEM images showing the distribution of precipitates in the samples crept at 250 °C: (a) under 80 MPa for 336 h, (b) under 100 MPa for 297 h and (c) under 120 MPa for 155 h. (d) SAED patterns obtained from (c). The applied stress is approximately along horizontal direction and the incident beam is along [0001]$_\alpha$.

In contrast, the precipitate distribution of the sample pure aged at 250 °C for 512 h is presented in Fig. 5.3(a) that the $\beta'$ precipitates were arranged as chains extending along the $[\bar{1}100]_\alpha$, $[10\bar{1}0]_\alpha$ and $[0\bar{1}10]_\alpha$ directions forming precipitate networks. The corresponding SAED pattern in Fig. 5.3(b) indicates that all the three $\beta'$ variants coexisted in the aged sample.

Therefore, it is clear that the single variant of precipitate chains observed in the crept samples are a result of the applied stress. If there is no external stress, three $\beta'$ variants would develop evenly and form precipitate networks.
Chapter 5  Characterization of Precipitate Chains Observed in the Mg-2.5Gd-0.1Zr Alloy after Creep Tests

Fig. 5.3 – (a) Dark-field HAADF-STEM images showing the distribution of precipitates in the samples aged at 250 °C for 336 h, and the corresponding SAED pattern in (b). The incident beam is along [0001]_α.

To reveal the effects of the magnitude of applied stresses on the morphology of precipitate chains formed during the creep tests, the precipitate distributions in the samples crept at 250 °C for 70 h under 80/100/120 MPa were investigated. The results are shown in Fig. 5.4, and the applied stresses are along the horizontal direction. When the applied stress was 80 MPa, Fig. 5.4(a), the precipitate chains of the β’ precipitates extended along three directions ([1̅100]_α, [10̅1̅0]_α and [0̅1̅10]_α), but the chains extending vertically were longer, and the size of the β’ precipitates in the vertical chains was bigger than the chains of other two directions. As the applied stress increased (100 or 120 MPa), Figs. 5.4(b, c), the vertical precipitate chains grew longer, and the precipitate chains extending in other two directions were much shorter or even disappeared. It is noted that the precipitate chains are developed during creep tests when their extending direction is approximately normal to the external stress direction.
The formation process of $\beta'$ precipitate chains during the creep test at 250 °C under 80 MPa was investigated by observing the distributions of precipitates in the samples crept for 5, 10, 20, 40 and 70 h, as shown in Fig. 5.5 where the applied stresses were along horizontal direction. When the sample crept for 5 h (Figs. 5.5(a, b)), short precipitate chains were developed almost evenly along three directions ([1100]$_{\alpha}$, [10$\overline{1}$0]$_{\alpha}$ and [0$\overline{1}$10]$_{\alpha}$). As the creep time extended to 10–20 h (Figs. 5.5(c–f)), the number density of the precipitates decreased. The precipitate chains along three directions extended and the average size of the $\beta'$ precipitates was larger. In the sample crept for 40 h (Figs. 5.5(g, h)), the vertical precipitate chains (normal to the applied stress direction) became relatively longer (~ 100 nm) comparing to the precipitate chains in the other two directions (~ 70 nm), and the average size along the [11$\overline{2}$0]$_{\alpha}$ direction of the $\beta'$ precipitates in the vertical precipitate chains was almost twice of the size of the $\beta'$ precipitates in the other directions. When the sample was crept for 70 h (Figs. 5.5(i, j)), the vertical precipitate chains grew further longer and larger, in contrast, the precipitate chains extending in other two directions were further narrower and even disappeared. According to the observation shown in Fig. 5.5, it is noted that the $\beta'$ precipitate evolution during creep tests is as following: the three $\beta'$ variants gradually rearrange into chains, and these chains extend in three directions evenly ([1100]$_{\alpha}$, [10$\overline{1}$0]$_{\alpha}$ and [0$\overline{1}$10]$_{\alpha}$); as the creep time prolongs, although the number density of precipitates gradually decreases, the precipitate chains normal to the external stress direction develop longer and larger while the chains extending in the other two directions become narrower or disappear.
Fig. 5.5 - HAADF-STEM images showing the distribution of precipitates in the Mg-2.5Gd-0.1Zr sample crept at 250 °C under 80 MPa for 5 h (a, b), 10 h (c, d), 20 h (e, f), 40 h (g, h), 70 h (i, j). The applied stress is approximately horizontal and the incident beam is parallel to [0001]_α.
5.3. Components of Precipitate Chains

It is worthy to note that the precipitate chain consists of alternate wide and narrow sections, as shown in Fig. 5.5(j), and the components of the precipitate chains are still unclear. In order to study the components of the precipitate chains observed in the crept samples, a section of a precipitate chain in the sample crept under 80 MPa at 250 °C for 336 h is enlarged in Fig. 5.6. The morphology of the precipitate chain observed from the $[0001]_\alpha$ direction, Fig. 5.6(a), reveals alternate wide and narrow sections. The wide and narrow sections are enlarged in Figs. 5.6(b, c), respectively, where the bright dots represent Gd atoms. It can be seen that Gd atoms are arranged in inverted zigzag arrays in the $[11\bar{2}0]_\alpha$ direction in the wide sections, Fig. 5.6(b), and in parallel zigzag arrays in the narrow sections, Fig. 5.6(c), as highlighted by the yellow waves. Additionally, the unit cells of the wide and narrow sections are different as indicated by the red rectangles in Figs. 5.6(b, c), where the length of the unit cell of the wide section in $[\bar{1}100]_\alpha$ direction is twice that of the narrow section. The microdiffraction patterns corresponding to Figs. 5.6(b, c) are presented in Figs. 5.6(d, e), respectively. The observations in Figs. 5.6(b, d) of the wide section are consistent with the $\beta'$ phase ($a = 0.65 \text{ nm}, b = 2.27 \text{ nm}, c = 0.52 \text{ nm}$) that reported in Mg-Gd based alloys in the literature [4]. However, the observations in Figs. 5.6(c, e) of the narrow section indicate that it is an unreported precipitate phase in Mg-Gd based alloys, and it is designated $\beta'_F$ phase for clarity. The $\beta'_F$ phase has an irregular morphology, and the HAADF-STEM image projected on $[0001]_\alpha$ planes and the microdiffraction patterns of the $\beta'_F$ phase in this study are identical with the $\beta'$ phase observed in Mg-Nd based alloys, which has an orthorhombic structure of $a = 0.64 \text{ nm}, b = 1.11 \text{ nm and } c = 0.52 \text{ nm}$, a composition of Mg:Nd, the space group of $Cmcm$, and a lenticular morphology [188]. The atomic models of the $\beta'$ and $\beta'_F$ phases are schematically illustrated in Fig. 5.7. It shows the difference between the two phases: the length of the unit cell of the $\beta'$ phase in the $[\bar{1}100]_\alpha$ direction is twice that of the $\beta'_F$ phase; the adjoining Gd zigzag arrays in the $\beta'$ phase are inverted, while the zigzag arrays in the $\beta'_F$ phase are parallel.

Further, Figs. 5.6 (d, e) imply the orientation relationship among the $\beta'_F$, $\beta'$ and $\alpha$-Mg phases: $(100)_{\beta'_F} / ((100)_{\beta'}/(11\bar{2}0)_\alpha$, $[001]_{\beta'_F} / [001]_{\beta'}/[0001]_\alpha$. As the precipitate chains were also observed in the over-aged sample (aged at 250 °C for 336 h in Fig. 5.3(a)) that developed in the $[10\bar{1}0]_\alpha$, $[\bar{1}100]_\alpha$, and $[0\bar{1}10]_\alpha$ directions, which indicates that the $\beta'_F$ phase has three variants distributed in the $[10\bar{1}0]_\alpha$, $[\bar{1}100]_\alpha$, and $[0\bar{1}10]_\alpha$ directions, like the $\beta'$ phase.
Nevertheless, an individual precipitate chain almost consists of the $\beta'$ and $\beta_F'$ particles of one variant, and Fig. 5.6(a) shows that the majority of white strips (Gd atomic arrays) in the $\beta'$ and $\beta_F'$ particles are parallel. Occasionally, the other variants were observed, like the centre $\beta'$ precipitate in Fig. 5.6(a). Moreover, the $\beta_F'$ phase does not only exist in the crept sample, it is also observed in the over-aged sample (Fig. 5.3(a)), which indicates that the precipitation sequence of Mg-Gd binary alloys probably needs to be modified, such as that SSSS $\rightarrow$ ordered G.P. zones $\rightarrow$ $\beta^\ast$ $\rightarrow$ $\beta'$ $\rightarrow$ $\beta_F' \rightarrow \beta_1 \rightarrow \beta$.

![Fig. 5.6 - Dark-field HAADF-STEM images showing (a) the distribution of $\beta'$ and $\beta_F'$ precipitates in a precipitate chain observed in the sample aged under 80 MPa at 250 °C for 336 h, (b, c) the configuration of Gd atoms in the $\beta'$ and $\beta_F'$ precipitates, respectively, and the corresponding microdiffraction pattern is given in (d, e), respectively. The incident beam is along $[0001]_\alpha$.](image)

Based on the atomic model of the $\beta_F'$ phase shown in Fig. 5.7(b), the lattice parameters of the $\beta_F'$ cell were calculated and structurally optimized using first-principles and the results are listed in Table 5.1. For the comparison, lattice parameters of the $\beta'$ and Mg phases were also calculated using the same first-principles conditions and the results are also listed in Table 5.1. The lattice parameters of $a$, $b$, $c$ are obtained along $[11\bar{2}0]_\alpha$, $[\bar{1}100]_\alpha$ and $[0001]_\alpha$ directions. The unit cells of the $\beta_F'$ and $\beta'$ phases used in the calculation are shown in the left part of Fig. 5.7, and the unit cell of Mg is shown in Fig. 2.2 as a hexagon structure. In the direction of $[11\bar{2}0]_\alpha$ (a
direction), the first-principle calculated lattice parameter of $\beta'_F$ phase is slightly larger than that of $\beta'$ phase although the two parameters should be same based on the models shown in Fig. 5.7. In the direction of $[\bar{1}100]_\alpha$ ($b$ direction), the lattice parameter of $\beta'_F$ phase is half of the parameter of $\beta'$ phase according to the unit cell models in Fig. 5.7, but the calculated results in Table 5.1 show that the parameter of $\beta'_F$ is less than half of the $\beta'$ phase. In the direction of $[0001]_\alpha$ ($c$ direction), the lattice parameters of $\beta'_F$ and $\beta'$ phases are similar. The calculated results in Table 5.1 imply that compared to the $\beta'$ phase, the $\beta'_F$ phase dilates in the $[11\bar{2}0]_\alpha$ direction ($a$ direction), and compresses in the $[\bar{1}100]_\alpha$ direction ($b$ direction). Compared with Mg matrix model, the lattice parameters of the $\beta'_F$ and $\beta'$ phase models along the $[11\bar{2}0]_\alpha$ direction ($a$ direction) should be twice of that of Mg matrix, however, the first-principle results demonstrate that the $\beta'_F$ and $\beta'$ phases dilate in the $[11\bar{2}0]_\alpha$ direction ($a$ direction).

Fig. 5.7 - Atomic models of the $\beta'$ and $\beta'_F$ phases.

<table>
<thead>
<tr>
<th>Lattice Parameters (nm)</th>
<th>$\beta'_F$</th>
<th>$\beta'$</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ $[11\bar{2}0]_\alpha$</td>
<td>0.6811</td>
<td>0.6618</td>
<td>0.3198</td>
</tr>
<tr>
<td>$b$ $[\bar{1}100]_\alpha$</td>
<td>1.0883</td>
<td>2.2573</td>
<td>–</td>
</tr>
<tr>
<td>$c$ $[0001]_\alpha$</td>
<td>0.5169</td>
<td>0.5172</td>
<td>0.5180</td>
</tr>
</tbody>
</table>
5.4. Interfaces/Transitional Zones between the $\beta'_F$ and $\beta'$ Phases

The interfaces/transitional zones between the adjoining $\beta'_F$ and $\beta'$ precipitates in the precipitate chains in the sample crept under 80 MPa at 250 °C for 336 h and the sample aged for 512 h were examined. It is found that the interfaces in the two samples were similar, and five types of interfaces (transitional zones) were observed.

Figure 5.8 presents the five types of interfaces/transitional zones in the sample crept under 80 MPa at 250 °C for 336 h. One type is an interface having an angle of $\sim 40^\circ$ with the [11\overline{2}0]$_\alpha$ direction, as marked by white lines in Figs. 5.8(a, b) no matter what kind of variants of the $\beta'$ phase next to the interface. The $\beta'_F$ precipitate next to this kind of interfaces has a habit plane with Mg matrix, and the habit plane has an angle of $\sim 65^\circ$ with the [11\overline{2}0]$_\alpha$ direction, as illustrated in Figs. 5.8(a, b). Additionally, the [100]$_{\beta'_F}$ direction is not exactly parallel with the [100]$_{\beta'}$ direction, the angle between the two directions was measured to be about 2.4 °.

The other four types of interfaces/transitional zones are all parallel with the [11\overline{2}0]$_\alpha$ direction, as illustrated in Figs. 5.8(c - e). It is hard to distinguish the exact interfaces in these cases, thus the transitional areas are designated as the transitional zones. There are four types of transitional zones. Type 1, continuous zigzag zones, as shown in Figs. 5.8(c, d, e), consist of zigzag arrays with a fixed interplanar distance of $\sim 1.11$ nm between the adjoining Gd arrays of the $\beta'_F$ and $\beta'$ particles. This type of transitional zones is the most commonly observed. Type 2, discontinuous hexagonal zones, as shown in Fig. 5.8(c), consist of a hexagonal array with a wider gap on one side. Type 3, continuous hexagonal zones, as shown in Fig. 5.8(d), consist of a hexagonal array with fixed interplanar distance on both sides. Type 4, discontinuous zigzag zones, as shown in Fig. 5.8(e), consist of zigzag arrays with a wider gap on one side, and the width of the gap is about 1.66 nm.
Chapter 5  Characterization of Precipitate Chains Observed in the Mg-2.5Gd-0.1Zr Alloy after Creep Tests

Fig. 5.8 - Dark-field HAADF-STEM images showing the interfaces/transitional zones between the $\beta'$ and $\beta'_F$ precipitates in the sample crept under 80 MPa at 250°C for 336 h. (a, b) the interface is not parallel to $[1\bar{1}20]_\alpha$, (c - e) the interfaces are parallel to $[1\bar{1}20]_\alpha$. The incident beam is along $[0001]_\alpha$.

5.5.  Discussion

5.5.1.  Effect of uniform stress field on the formation of precipitate chains

The formation of the linear chain distribution of $\beta'$ precipitates is influenced by the external stress, and the effects of the external stress on the distribution of precipitates have been
reported in Al-Cu and other alloys [189-191]. The applied stress can be considered to generate a uniformly distributed stress field \( \sigma_{ij}^{\text{app}} \) on the sample during the creep test. The effect of this uniformly distributed stress field on the distribution of \( \beta' \) particles was examined initially via interaction energy calculations. The interaction energy between the stress field of the applied tensile stress \( \sigma_{ij}^{\text{app}} \) and the stress free transformation strain tensor (SFTS) of the \( p \)-th orientation variant of \( \beta' \) \( (\epsilon_{ij}^p, p = \{1, 2 \text{ and } 3\}) \) precipitates is \( E_{\text{int}}^p = -\sigma_{ij}^{\text{app}}\epsilon_{ij}^p \). The SFTS in the principle axes can be calculated via setting \( x \) axis to \([100]_\beta//[11\overline{2}_0]_\alpha\), \( y \) axis to \([010]_\beta//[\overline{1}100]_\alpha\) and \( z \) axis to \([001]_\beta//[0001]_\alpha\) [192]:

\[
\epsilon_{ij} = \begin{pmatrix}
\frac{a-2a_0}{2a_0} & 0 & 0 \\
0 & \frac{b-4\sqrt{3}a_0}{4\sqrt{3}a_0} & 0 \\
0 & 0 & \frac{c-c_0}{c_0}
\end{pmatrix}
\]  

(5.1)

where \( a, b, c \) refers to the lattice parameters of the \( \beta' \) phase in the \([100]_\beta\), \([010]_\beta\) and \([001]_\beta\) directions, which equals to 0.6618 nm, 2.2574 nm and 0.5172 nm respectively, obtained via the first-principles calculations. \( a_0 \) and \( c_0 \) refer to the lattice parameters of the Mg matrix in the \([11\overline{2}_0]_\alpha\) and \([0001]_\alpha\) directions, which equals to 0.3199 nm and 0.5186 nm respectively.

The distribution of the three variants \( (p = \{1, 2 \text{ and } 3\}) \) is shown in Fig. 5.10(b), and the corresponding calculated SFTS tensors are [192]:

\[
\epsilon^1 = \begin{pmatrix}
0.0345 & 0 & 0 \\
0 & 0.0185 & 0 \\
0 & 0 & -0.00270
\end{pmatrix},
\]

\[
\epsilon^2 = \begin{pmatrix}
0.0225 & -0.0069 & 0 \\
-0.0069 & 0.0305 & 0 \\
0 & 0 & -0.00270
\end{pmatrix},
\]

\[
\epsilon^3 = \begin{pmatrix}
0.0225 & 0.0069 & 0 \\
0.0069 & 0.0305 & 0 \\
0 & 0 & -0.00270
\end{pmatrix}.
\]

A negative value of interaction energy means that the formation of \( \beta' \) particles is more favourable in terms of elastic strain energy. If the applied tensile stress is 120 MPa, then the interaction energy between \( \sigma_{ij}^{\text{app}} \) and \( \epsilon_{ij}^p \) for the variants \( 1, 2 \) and \( 3 \) of \( \beta' \) precipitates are -0.0378, -0.0579 and -0.0378 kJ/mol respectively. Thus variant 2 is easier to nucleation and
growth under the effect of applied stress, which is consistent with the variant selection in the creep tests.

In order to visualize the effects of interaction energy on the distribution of different variants of the $\beta'$ particles, the phase field method was adopted. The phase field method was advised by Hong Liu, and the details of phase field method used in this thesis are presented in Appendix.

Figure 5.9(a) shows the phase field simulation result of the distribution of homogeneously formed $\beta'$ precipitates at $t^* = 300$, where $t^*$ is the time step in reduced unit. The $\beta'$ precipitates of three orientation variants are clearly observed. If a 120 MPa tensile stress is applied after $t^* = 300$, at $t^* = 10000$ (Fig. 5.9(b)), the volume fraction of variant $\overline{2}$ is significantly larger than that of variants $\overline{1}$ and $\overline{3}$.

These results reveal that under the influence of the applied stress that nearly parallels to $[11\overline{2}0]_\alpha$, variant $\overline{2}$ is more favoured to grow than the other two variants. The result in Fig. 5.9 agrees with the $E_{\text{int}}^p$ calculation results. However, we cannot see linear chain distribution of $\beta'$ precipitates in the simulation. This is possibly because the nucleation of $\beta'$ precipitates is a stochastic process and the particles will not arrange themselves into a linear chain distribution without external guidance, such as dislocations. The creep mechanism of this alloy at 250 °C under 80-120 MPa has been inferred to be dislocation creep in Chapter 4 based on the obtained stress exponent value of 3.3 (Fig. 4.7), which means that plenty of dislocations are activated during creep tests. These dislocations could be pinned and act as heterogeneous nucleation sites [193]. Thus the precipitation of $\beta'$ particles on pre-existing dislocations will be investigated.
5.5.2. Effect of dislocations on the formation of precipitate chains

If the linear chains of $\beta'$ particles are formed on pre-existing dislocations, then a proper dislocation type is required, which not only can lower the activation energy barrier for $\beta'$ nucleation, but also can select a proper $\beta'$ variant along the dislocation line. According to Fig. 5.2, the $\beta'$ precipitate chains are nearly parallel to $[1\bar{1}00]_\alpha$. If these precipitates grow along a certain type of pre-existing dislocations, the projections of the dislocation lines on $(0001)_\alpha$ should parallel to the precipitate chains, i.e., to $[1\bar{1}00]_\alpha$. Figure 5.10(a) shows three different types of slip planes which are often observed in Mg matrix [194] – $(0001)_\alpha$ (the basal plane), $\{10\bar{1}0\}_\alpha$ (the prismatic plane) and $\{10\bar{1}1\}_\alpha$ (the pyramidal plane). It is easily found that for a prismatic dislocation, the projection of the dislocation line on $(0001)_\alpha$ cannot be parallel to $[1\bar{1}00]_\alpha$ no matter what the dislocation type (edge, screw or mixed) is. The projections of most pyramidal dislocations on $(0001)_\alpha$ are not parallel to $[1\bar{1}00]_\alpha$ except the dislocation line parallel to AB in Fig. 5.10(a). If the linear chain distributed $\beta'$ precipitates are formed on a dislocation parallel to AB, then the maximum chain length should approximately equal to $m/tan \alpha$, where $m$ is the sample thickness, $\alpha$ is the angle between AB and $[1\bar{1}00]_\alpha$ and $tan \alpha = c/\sqrt{3}a$ ($c$ and $a$ are lattice parameters of $\alpha$-Mg). Since the thickness of the TEM sample is around $100 – 200$ nm, the maximum chain length is around 213 nm. However, this length is far less than the length of precipitate chains observed in experiments (Fig. 5.2). Therefore, neither the prismatic nor the pyramidal dislocations would lead the $\beta'$ precipitates to form the observed linear chain distribution. Thus only the basal type dislocation is geometrically preferred.

Figure 5.10(b) shows all possible Burgers vectors of basal dislocations. The Burgers vectors of perfect and partial dislocations are $a/3\langle 1\bar{1}20\rangle_\alpha$ and $a/3\langle 10\bar{1}0\rangle_\alpha$ respectively. The interaction energy between the stress field of a pre-existing dislocation and SFTS of the $p$-th variant of to-be-nucleated $\beta'$ particles, $E_{\text{int}}^{\text{dis}}$, is expressed as $e_{ij}^p \cdot (b \otimes n + n \otimes b)/2d$ [195, 196], where $b$ and $n$ are Burgers vector and slip plane normal, and $d$ is the inter-planar spacing of the slip plane. According to this expression, compared with partial dislocations, perfect dislocations have a larger magnitude of Burgers vector, thus they may interact more strongly with $\beta'$ precipitates. If the sense vector of an $a$-type basal perfect dislocation is parallel to $[1\bar{1}00]_\alpha$, then this dislocation may belong to one of three types: an edge dislocation with a Burgers vector of $a/3\langle 1\bar{1}20\rangle_\alpha$, a mixed dislocation with a Burgers vector of $a/3\langle 2110\rangle_\alpha$ and a mixed dislocation
with a Burgers vector of $a/3[\bar{1}210]_\alpha$. Figures. 5.10c(i, iv, vii; ii, v, viii and iii, vi, ix) show the interaction energy calculation results of $E_{\text{int}}^{\text{dis}}$ when $p = \{1\}, \{2\}, \text{ and } \{3\}$ respectively. The Burgers vectors of pre-existing dislocations in Figs. 5.10c(i-iii, iv-vi and vii-ix) are $a/3[11\bar{2}0]_\alpha$, $a/3[2110]_\alpha$ and $a/3[1210]_\alpha$ respectively. The pre-existing dislocations in Figs. 5.10c(i-iii) have an edge character and the extra-half plane is located above the slip plane. In this case, the interaction energy calculation results indicate that all $\beta'$ variants prefer to nucleate on the opposite of the extra-half plane of the edge dislocation because the tensile stress field on the opposite of the extra-half plane can well compensate the compression stress field around $\beta'$ particles. For the plane lying one Burgers vector (a typical cut-off radius for a dislocation core) below the pre-existing edge dislocation with $\mathbf{b} = a/3[11\bar{2}0]_\alpha$, when $p = \{1\}, \{2\}, \text{ and } \{3\}$, the $E_{\text{int}}^{\text{dis}}$ of $\{1\}, \{2\} \text{ and } \{3\}$ are -0.168, -0.195 and -0.168 kJ/mol, respectively. These values are more negative than $E_{\text{int}}^{\text{p}}$. This calculation result is consistent with previous one that was calculated in Mg-Nd alloys [168].

It indicates that compared with $\sigma_{ij}^{\text{app}}$, the $\beta'$ particles have a stronger interaction with pre-existing edge dislocations. Also, compared with variants $\{1\}$ and $\{3\}$, variant $\{2\}$ is energetically more favourable to nucleate on pre-existing edge dislocations, and then form a precipitate chain. This is consistent with the experimental observations in Fig. 5.2. The pre-existing dislocations set in Figs. 5.10c(iv-ix) are mixed type. The interaction calculation results indicate that $\beta'$ particles prefer to form above these dislocations. These results also indicate that the formation of variant $\{1\}$ or $\{3\}$ is energetically more favoured if the Burgers vector of the pre-existing dislocation is $a/3[2110]_\alpha$ or $a/3[1210]_\alpha$ (Fig. 5.10c). If $\beta'$ particles form on these two types of dislocations, the habit planes of $\beta'$ particles in the precipitate chains have a $120^\circ$ angle to the dislocation line, which has not been often observed in experiments.

It is worth noting that the projection of the applied stress on (0001)$_\alpha$ is nearly parallel to $[11\bar{2}0]_\alpha$. The Schmid factor of the $[11\bar{2}0]_\alpha(0001)_\alpha$ slip system is larger than the other two basal slip systems ($[1\bar{2}10]_\alpha(0001)_\alpha$ and $[\bar{2}110]_\alpha(0001)_\alpha$). If the angle between the applied stress and (0001)$_\alpha$ is assumed to 10°, the Schmid factors of $[11\bar{2}0]_\alpha(0001)_\alpha$, $[1\bar{2}10]_\alpha(0001)_\alpha$ and $[\bar{2}110]_\alpha(0001)_\alpha$ slip systems are 0.1736, 0.0868 and 0.0868 respectively. Additionally, only the edge dislocation will climb during creep.

Thus slip system is more easily activated. The variations of the interaction energy between the stress fields of all types of dislocations in $[11\bar{2}0]_\alpha(0001)_\alpha$ slip system and SFTS of the three
orientation variants of $\beta'$ particles at the point lying one Burgers vector below the dislocation line are plotted in Fig. 5.10(d). The type of dislocation is distinguished by the angle $\theta$ between the Burgers vector $b$ and the sense vector $\xi$ of the dislocation. In this figure, compared with other types of dislocations, the interaction energy between the edge dislocation ($\theta = 90^\circ$) and variant $\hat{2}$ is more negative. Thus the edge dislocation is energetically more favoured to interact with $\beta'$ particles in this slip system.
Fig. 5.10 - Schematic diagrams showing (a) the basal, prism, and pyramidal slip planes, (b) the directions of Burgers vectors of perfect basal dislocations (b1, b2, b3), partial basal dislocations (bp1, bp2, bp3), three orientation variants of \( \beta' \) particles and the direction of pre-existing dislocations, (c i-ix) interaction energy calculation results between the stress fields of three different orientation variants of \( \beta' \) and three types of basal dislocations. The Burgers vectors of pre-existing dislocations and the minimum interaction energy calculation results are shown in right and left bottom of each figure. (d) Variations of interaction energy between a pre-existing \( a \)-type basal dislocation and different variants of \( \beta' \) particles as a function of the angle \( \theta \) between the Burgers vector and sense vector of the dislocation.
5.5.3. The coexistence of the $\beta'_F$ and $\beta'$ phases

The $\beta'_F$ and $\beta'$ phases were observed to be coexistent in the crept and aged Mg-2.5Gd-0.1Zr samples (Figs. 5.2 and 5.3). However, only the $\beta'$ phase with inverted Gd zigzag arrays was reported in Mg-Y and Mg-Dy binary aged samples [197, 198]. In Mg-Nd binary aged samples, only the $\beta'_F$ phase with parallel Gd zigzag arrays was observed [188]. Therefore, it is inferred that the formation of the $\beta'_F$ and $\beta'$ phases is affected by the particular RE element involved determining the formation energy of the $\beta'_F$ and $\beta'$ phases.

The formation energy per atom of these structures was calculated according to the following equation:

$$E_f = (E_{tot} - n\text{Mg}E_{\text{Mg}} - n\text{RE}E_{\text{RE}})/(n\text{Mg} + n\text{RE}) ,$$  

(5.2)

where $E_{tot}$ is the total energy of the Mg-RE supercell and calculated using density functional theory, $E_{\text{Mg}}$ and $E_{\text{RE}}$ are the energy per Mg and RE atom, and $n\text{Mg}$ and $n\text{RE}$ are the number of Mg and RE atoms in each supercell, respectively. The supercells of the $\beta'_F$ and $\beta'$ phases are illustrated in Fig. 5.7. The calculated formation energy per atom of the $\beta'_F$ and $\beta'$ phases of various Mg-RE alloys is given in Table 5.2, and the lower formation energy, the easier to precipitate. It can be seen from Table 5.2 that the Mg-Y, Mg-Tb, Mg-Dy, Mg-Ho, Mg-Er, Mg-Tm binary alloys have lower values of the formation energy per atom for the $\beta'$ phase, which indicates that these alloys prefer to precipitate the $\beta'$ phase. In contrast, the Mg-La, Mg-Pr, Mg-Nd, Mg-Pm, Mg-Sm, Mg-Eu alloys have lower values of the formation energy per atom for the $\beta'_F$ phase, which indicates that these alloys prefer to precipitate the $\beta'_F$ phase during the ageing process. It is worthy to note that the Mg-Gd alloy has almost identical values of the formation energy per atom for the $\beta'_F$ and $\beta'$ phases, which implies that the $\beta'$ and $\beta'_F$ phases have equal possibility to precipitate in the Mg-Gd alloy during the ageing process.

These results explain the experimental observation of both $\beta'$ and $\beta'_F$ phases in the Mg-2.5Gd-0.1Zr alloy shown in Fig. 5.6, and why the coexistence of the $\beta'$ and $\beta'_F$ phases is not observed in other Mg-RE alloy systems. Note that it is difficult to distinguish $\beta'$ and $\beta'_F$ phases under conventional TEM observations. Only the $\beta'_F$ phase is observed to form in Mg-Nd alloys under HAADF-STEM imaging [188].
Chapter 5  Characterization of Precipitate Chains Observed in the Mg-2.5Gd-0.1Zr Alloy after Creep Tests

Table 5.2 The formation energy per atom of the $\beta'$ and $\beta_F'$ phases of various Mg-RE binary alloys.

<table>
<thead>
<tr>
<th>RE</th>
<th>Y</th>
<th>La</th>
<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Eu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta'$</td>
<td>-2.1692</td>
<td>-1.9778</td>
<td>-1.9634</td>
<td>-1.96</td>
<td>-1.9536</td>
<td>-1.9463</td>
<td>-1.9382</td>
</tr>
<tr>
<td>$\beta_F'$</td>
<td>-2.1672</td>
<td>-1.9843</td>
<td>-1.9683</td>
<td>-1.9636</td>
<td>-1.9562</td>
<td>-1.95</td>
<td>-1.9388</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>RE</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta'$</td>
<td>-1.9338</td>
<td>-1.9271</td>
<td>-1.9201</td>
<td>-1.9132</td>
<td>-1.9069</td>
<td>-1.9001</td>
</tr>
<tr>
<td>$\beta_F'$</td>
<td>-1.9338</td>
<td>-1.9263</td>
<td>-1.9188</td>
<td>-1.9112</td>
<td>-1.9051</td>
<td>-1.8983</td>
</tr>
</tbody>
</table>

5.5.4. Transitional zones between the $\beta_F'$ and $\beta'$ phases

In the crept samples (crept at 250 °C under 80 – 120 MPa for 155 h or longer) and over-aged samples (aged at 250 °C for 512 h), the $\beta_F'$ and $\beta'$ particles have a linear chain distribution or form networks. The transitional zones between the $\beta_F'$ and $\beta'$ phases have been investigated, and it is found to be similar in the crept and aged samples. There are four types of transitional zones between the $\beta_F'$ and $\beta'$ phases, and they are shown in the HAADF-STEM images obtained from [0001]$_\alpha$ direction in Fig. 5.8.

Taking the sample crept at 250 °C under 80 MPa as the example, $\beta'$ particles are distributed individually before the creep test, but the $\beta_F'$ and $\beta'$ particles form chains after the creep test. It implies that the distance between the adjoining $\beta_F'$ and $\beta'$ particles would determine the morphology of the transitional zone between them.

The four types of the transition zones are listed as follows:

Type 1: continuous zigzag zone. This type of transition zones could be formed when the distance between the nearest zigzag Gd arrays of the adjoining $\beta_F'$ and $\beta'$ particles equals to $4d_{\{\bar{1}100\} \alpha} + b_{\beta_F'}$, as shown in Figs. 5.11(a, b), where $d_{\{\bar{1}100\} \alpha}$ is the interplanar distance of $\{\bar{1}100\} \alpha$ planes and $b_{\beta_F'}$ is the width of the unit cell of the $\beta_F'$ phase along $\{\bar{1}100\} \alpha$ direction and equals to $4d_{\{\bar{1}100\} \alpha}$. Under this condition, there are two cases: the adjoining Gd zigzag arrays are parallel in case 1 (Fig. 5.11(a)) and inverted in case 2 (Fig. 5.11(b)). As the creep test proceeds, Gd atoms will deposit as a zigzag array in the centre layers of the transitional zones, as shown in Figs. 5.11(c - e). There are two outcomes: one is the deposited Gd zigzag array parallel with the zigzag arrays in the $\beta_F'$ particles, as shown in Figs. 5.11(c, d); the other is the deposited Gd zigzag array is
opposite with the adjoining zigzag arrays in the \( \beta' \) particles, as shown in Fig. 5.11(e). Figure 5.11(f) gives an example of a type 1 transitional zone observed under HAADF-STEM condition, which has the deposited Gd zigzag array parallel with the zigzag arrays in the \( \beta'_F \) particle.

![Atomic Models Showing Two Kinds of Formation Processes of Type 1 Transitional Zones](image)

Type 2: discontinuous hexagonal zone. These transition zones could be formed when the distance between the nearest zigzag Gd arrays of the adjoining \( \beta'_F \) and \( \beta' \) particles equals \( 3d_{\{1\over 100\}_\alpha} + b_{\beta'_F}, \) as shown in Figs. 5.12(a, b). Similar to the situations in Figs. 5.11(a, b), there are two cases different in the parallel or inverted relationship between the adjoining Gd zigzag arrays as shown in Figs. 5.12(a, b). As the creep test proceeds, Gd atoms will deposit in the transitional zone next to the Gd zigzag array in the \( \beta'_F \) particle, and form hexagons along the \( [1\over 1120]_\alpha \) direction, as shown in Figs. 5.12(c, d). The distances between the hexagons and \( \beta'/\beta'_F \) particles are
different in that the distance between the hexagons and the Gd zigzag array of the $\beta'$ particle is bigger than the one between the hexagons and the Gd zigzag array of the $\beta'_F$ particle. For the two cases, the hexagons formed in the transitional zones are identical viewed along the $[0001]_\alpha$ direction, as shown in the HAADF-STEM images in Figs. 5.12(e, f).

![Diagram showing two kinds of formation processes of type 2 transitional zones between the $\beta'_F$ and $\beta'$ phases: case 1 (a, c) and case 2 (b, d). (e, f) The HAADF-STEM images showing type 2 transitional zones between the $\beta'_F$ and $\beta'$ phases obtained from $[0001]_\alpha$.](image)

**Fig. 5.12** - The atomic models showing two kinds of formation processes of type 2 transitional zones between the $\beta'_F$ and $\beta'$ phases: case 1 (a, c) and case 2 (b, d). (e, f) The HAADF-STEM images showing type 2 transitional zones between the $\beta'_F$ and $\beta'$ phases obtained from $[0001]_\alpha$.

**Type 3: continuous hexagonal zone.** This type of transition zones could be formed when the distance between the nearest zigzag Gd arrays of the adjoining $\beta'_F$ and $\beta'$ particles equals to $2d_{(\overline{1}100)\alpha} + b_{\beta'_F}$, as shown in Figs. 5.13(a, b). Similar to the situations in Figs. 5.11(a, b), there are two cases different in the parallel or inverted relationship between the adjoining Gd zigzag arrays as shown in Figs. 5.13(a, b). As the creep test proceeds, for the case 1, Gd atoms will deposit as a zigzag array opposite to the nearest zigzag array of the $\beta'_F$ particle, and form a hexagonal array, as shown in Fig. 5.13(c). For the case 2, Gd atoms will deposit as a zigzag array parallel to the nearest
zigzag array of the $\beta_F'$ particle, which is possibly unstable, and the Gd atoms will possibly then rearrange to a hexagonal array, as shown in Fig. 5.13(f). In both cases, the hexagonal array has the same distance to the nearest zigzag arrays of the $\beta_F'$ and $\beta'$ particles, which is significantly different from type 2 transitional zones. Figure 5.13(e) gives a HAADF-STEM image showing a type 3 transitional zone observed along the $[0001]_\alpha$ direction.

![Atomic models showing two kinds of formation processes of type 3 transitional zones between the $\beta_F'$ and $\beta'$ phases: case 1 (a, c) and case 2 (b, d, f). (e) The HAADF-STEM image showing a type 3 transitional zone between the $\beta_F'$ and $\beta'$ phases obtained from $[0001]_\alpha$.](image)

**Fig. 5.13** - The atomic models showing two kinds of formation processes of type 3 transitional zones between the $\beta_F'$ and $\beta'$ phases: case 1 (a, c) and case 2 (b, d, f). (e) The HAADF-STEM image showing a type 3 transitional zone between the $\beta_F'$ and $\beta'$ phases obtained from $[0001]_\alpha$.

**Type 4**: discontinuous zigzag zone. This type of transition zones could be formed when the distance between the nearest zigzag Gd arrays of the adjoining $\beta_F'$ and $\beta'$ particles equals to $d_{[1100]} + b_{\beta_F'}$, as shown in Figs. 5.14(a, b). Similar to Figs. 5.12(a, b), there are two cases, as shown in Figs. 5.14(a, b). However, no Gd atoms in type 4 transitional zones will be deposited. Figure 5.14(c) gives a HAADF-STEM image showing a type 4 transitional zone observed along the $[0001]_\alpha$ direction. Different from the type 1 transitional zone (continuous zigzag zone, Fig.
5.11), the type 4 transitional zone has an obvious gap between the $\beta_F'$ and $\beta'$ particles (Fig. 5.14(c)). The gap is $d_{\{1100\}_\alpha}$ wider than the regular distance between the adjoining Gd arrays in the $\beta_F'$ and $\beta'$ particles, and was measured to be 1.66 nm.

Fig. 5.14 - The atomic models showing two kinds of formation processes of type 4 transitional zones between the $\beta_F'$ and $\beta'$ phases: case 1 (a) and case 2 (b). (c) The HAADF-STEM image showing a type 4 transitional zone between the $\beta_F'$ and $\beta'$ phases obtained from $[0001]_\alpha$.

### 5.6. Summary

In this chapter, the linear precipitate chains observed in the Mg-2.5Gd-0.1Zr samples crept under 80-120 MPa at 250 $^\circ$C have been characterized and the formation mechanism has been discussed:

1. The observed linear precipitate chains approximately extend normal to the direction of the applied stress, and they consist of alternative $\beta_F'$ and $\beta'$ particles.
(2) The $\beta'_F$ phase is unreported in the Mg-Gd based alloys, but it was reported in Mg-Nd based alloys that had a base-centred orthorhombic structure ($a = 0.6811$ nm, $b = 1.0883$ nm, $c = 0.5169$ nm). The coexistence of the $\beta'_F$ and $\beta'$ phases in the aged and crept Mg-2.5Gd-0.1Zr alloy is probably due to the approximately equal formation energy per atom of the $\beta'_F$ and $\beta'$ phases.

(3) The linear chain distribution of $\beta'$ particles likely form on pre-existing $a$-type basal edge dislocations under the external tensile stress condition. During creep tests, compared with other variants of $\beta'$ particles, the variant with Gd zigzag arrays approximately normal to the direction of dislocations is energetically more favourable to nucleate and growth on the dislocations and forms a linear chain distribution.

(4) There are four types of transitional zones between the adjoining $\beta'_F$ and $\beta'$ particles in the precipitate chains. Type 1 is the continuous zigzag zone consisting of a zigzag array with a fixed distance of $\sim 1.11$ nm with the nearest Gd arrays of the $\beta'_F$ and $\beta'$ particles. Type 2 is the discontinuous hexagonal zone consisting of a hexagonal array with a wider gap on one side. Type 3 is the continuous hexagonal zone consisting of a hexagonal array with fixed distance to the nearest Gd arrays of the $\beta'_F$ and $\beta'$ particles. Type 4 is the discontinuous zigzag zone consisting of zigzag arrays with a wider gap on one side, and the width of the wide gap is about 1.66 nm.

(5) The four types of transitional zones between the $\beta'_F$ and $\beta'$ particles are probably determined by the distance between them. If the distance equals to $4d_{(1100)\alpha} + b_{\beta'_F}$, type 1 of transitional zones will be formed. If the distance is $3d_{(1100)\alpha} + b_{\beta'_F}$, type 2 will be observed. If the distance equals to $2d_{(1100)\alpha} + b_{\beta'_F}$, type 3 will be found. If the distance is $d_{(1100)\alpha} + b_{\beta'_F}$, type 4 will be formed.
CHAPTER 6.

FORMATION OF DENUDED ZONES IN THE CREPT Mg-2.5Gd-0.1Zr ALLOY
Chapter 6

Formation of Denuded Zones in the Crept Mg-2.5Gd-0.1Zr Alloy

6.1. Introduction

Precipitation hardening is a predominant strengthening mechanism in Mg-Gd(Y) based alloys, and major strengthening precipitates contains $\beta'$ and $\beta_1$ phases [4, 121, 123, 125, 199]. However, the precipitates in the regions adjacent to grain boundaries that are approximately perpendicular to the applied stress direction are prone to dissolution during tensile creep tests at 250 and 300 °C and under 50~120 MPa, leading to the formation of denuded zones [3, 6, 148, 200, 201]. The denuded zones act as weaker regions and ultimately lead to cavitation and fracture. In Chapter 4, cracks were observed at grain boundaries in the crept samples (Figs. 4.10 and 4.14), which implies that the denuded zones near grain boundaries are possibly detrimental to the creep strength. The formation mechanism of the denuded zones has been reported as directional diffusion and grain boundary migration in Mg-Gd(Y) based alloys [6, 201].

The mechanism of directional diffusion was adopted by Wang et al. [201] to account for the denuded zones formed in Mg-10Gd-3Y-0.5Zr (wt.%) samples crept to rupture under 50 MPa at 300 °C and under 80 MPa at 250 °C. This adoption is based on their energy dispersive X-ray spectrometer (EDXS) measurements in scanning electron microscopy (SEM) that the concentrations of Gd and Y in the denuded zone (Gd: 0.62 at.%, Y: 0.45 at.%) were much lower than those in the core of the grain (Gd: 1.8 at.%, Y: 1.36 at.%) [201]. However, the validity of their measurements is questionable because the measured concentrations of solute atoms in the denuded zone are below the detectability of EDXS which is typically about 1 at.%, and the measured solute concentrations in the grain core might be affected by the precipitates there. Furthermore, the derived values of the apparent stress exponent were several times higher than unity, which is not consistent with that (unity) expected for diffusional creep. Directional diffusion was raised in studying of Mg-Zr alloys crept at much higher temperatures (above 450 °C) and much lower stresses (below 1.5 MPa) [83], which are far different from the creep conditions for Mg-RE alloys found with denuded zones.

The mechanism of grain boundary migration was adopted by Khosrhoshahi et al. [6] to explain the denuded zones found in WE54 (Mg-5.1Y-1.9Nd-0.9HRE-0.5Zr (wt. %)) samples crept to rupture under 61 MPa at 250 °C. The adoption is based on the measured value of the stress exponent, between 4 and 5, and optical observations of excessive particles accumulated on grain boundaries perpendicular to the applied stress direction. Their stress exponent values are consistent
with that obtained by Wang et al. [5] from WE43 (Mg-4.0Y-3.0RE (wt.%)) alloy creep tested under 30-300 MPa at 150-250 °C. However, it is difficult to confirm whether there are excessive particles on the grain boundaries from optical micrographs. More importantly, the mechanism of grain boundary migration cannot explain the formation of denuded zones on both sides of grain boundaries [6].

To reveal and establish the characteristic features of denuded zones, the work presented in this chapter involves the use of backscattered electron (BSE) imaging mode of SEM, electron backscattered diffraction (EBSD) and transmission electron microscopy (TEM) to allow studies at much higher spatial resolution. A Mg-2.5Gd-0.1Zr (at.%) alloy was selected for research because of no obvious intermetallics along grain boundaries in the aged samples. The observations of BSE, EBSD and TEM reveal the presence of denuded zones in matrix regions that are adjacent to grain boundaries lying approximately perpendicular to the applied stress direction. It is found that the majority of the denuded zones have misorientations with the grain cores and that it is the misorientation, rather than directional diffusion or grain boundary migration, that leads to the dissolution of precipitates.

6.2. Configuration of Grain Boundaries before Creep Tests

The grain shape and size of the peak-aged sample, aged at 250 °C for 4 h, are shown in Fig. 6.1. In the BSE image shown in Fig. 6.1(a), grain boundaries are barely visible and no apparent particles are observed inside grains or along grain boundaries. However, the grain shape and size are displayed clearly in the corresponding EBSD map, Fig. 6.1(b). Few of grain boundaries are curved, as indicated by arrows in Fig. 6.1(b), and these grain boundaries are likely distributed in random directions. The grains are approximately equiaxed in shape and were randomly orientated, without any detectable misorientations inside individual magnesium grains. The grain size is ~40 μm.
6.3. Denuded Zones Formed in the Crept Mg-2.5Gd-0.1Zr Samples

6.3.1. Configuration of denuded zones formed under different creep conditions

Creep tests of the peak-aged samples were conducted under 80, 100 and 120 MPa at 250 °C, under 40, 60 and 80 MPa at 300 °C, respectively. The corresponding creep curves are shown in Fig. 6.2. The creep curves obtained under 250 °C in Fig. 6.2(a) showed that the samples fractured within 300 h under 100 and 120 MPa had entire secondary and tertiary creep stages, and the sample crept under 80 MPa was still at the secondary creep stage until it was dismounted manually at 336 h. The value of the apparent stress exponent measured from the creep tests is shown in Fig. 6.2(a). This value was approximately equal to 3.3, which indicated dislocation creep [7].

The creep curves obtained under 300 °C in Fig. 6.2(b) showed that the samples fractured within 100 h under 60 and 80 MPa had a very short secondary creep stage followed by a tertiary creep stage, and that the sample crept for 263 h under 40 MPa had a distinct secondary creep stage and a tertiary creep stage. The value of the apparent stress exponent measured from the creep tests is also shown in Fig. 6.2(b). This value was approximately equal to 2.6, which was between the values for grain boundary sliding (~2) and dislocation creep (3~7) [7].
Fig. 6.2 - Creep curves obtained at (a) 250 °C under 80, 100 and 120 MPa, (b) 300 °C under 40, 60 and 80 MPa. Minimum creep rates versus applied stresses are given in both graphs, and the stress exponents (the slope of the fitting line) are provided.

The microstructures of the samples crept to fracture at 250 °C under 100, 120 MPa, at 300 °C under 40, 60 and 80 MPa are displayed in Figs. 6.3(c, e, b, d, f), respectively. The sample crept for 336 h under 80 MPa at 250 °C is also shown in Fig. 6.3(a). The grain boundaries appearing as white lines in the BSE images which were caused by the presence of accumulated particles rich in Gd. The microstructures also show the development of dark bands adjacent to the grain boundaries transverse to the applied stress direction, indicated by the white arrows in Fig. 6.3. These bands are precipitate denuded zones (denuded zones). It was noted that the denuded zones were found in all crept samples, especially, the samples crept at 300 °C had much wider denuded zones (Fig. 6.3(b, d, f)), and that the widest denuded zones were formed in the sample crept under 40 MPa at 300 °C for 263 h, Fig. 6.3(a). In contrast, grain boundaries that were approximately parallel to the applied stress direction do not appear to be associated with any obvious denuded zones.
Denuded zones were also found in over-aged samples subjected to an ageing at 300 °C for 263 h, as shown in Fig. 6.4. The formation of the denuded zones during the ageing process was due to the depletion of vacancies and/or solute atoms in these regions [202]. These denuded zones were formed uniformly in regions next to all grain boundaries and were much narrower than those observed in the sample crept under 40 MPa at 300 °C for 263 h, Fig. 6.3(b). This phenomenon indicated that the wider denuded zones formed in crept samples were mainly due to the applied stresses at 300 °C.
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Formation of Denuded Zones in the Crept Mg-2.5Gd-0.1Zr Alloy

Fig. 6.4 - BSE images of the microstructures of a sample aged for 263 h at 300 °C (i.e., ageing without any stress) (a) at low magnification and (b) at high magnification, showing narrow and uniform denuded zones on both sides of grain boundaries.

6.3.2. Configuration of denuded zones in different creep stages

The main developing period of the denuded zones during creep tests was investigated through studying the evolution of denuded zones in samples crept under 40 MPa at 300 °C, because this creep condition produced the widest denuded zones and distinct secondary and tertiary creep stages. The creep rate variation as a function of the creep time of the sample crept under 40 MPa at 300 °C is shown in Fig. 6.5(a). The primary creep stage with a decreasing creep rate was very short. The secondary creep stage with a roughly constant creep rate approximately lasted for 72 h. The creep rate increased slowly from 72 h to 192 h in the tertiary creep stage. After that the creep rate ascended rapidly until fracture at 263 h. Figures 6.5(b-d) display the microstructures of the samples crept for 72 h, 192 h and 263 h, respectively. Narrow denuded zones were distributed approximately uniformly adjacent to every grain boundary in the sample crept for 72 h, Fig. 6.5(b), which was similar to the distribution of denuded zones in the over-aged sample shown in Fig. 6.4. This observation implied that the denuded zones were combined products of the ageing and creep processes. As the creep time was extended to 192 h, the denuded zones that were adjacent to grain boundaries lying roughly normal to the applied stress direction became wider, Fig. 6.5(c), and at the same time the denuded zones adjacent to grain boundaries that are approximately parallel to the applied stress direction were narrower. Finally, when the sample crept for 263 h to fracture, the denuded zones that were adjacent to the transverse grain boundaries became obviously wider and the denuded zones that were next to the longitudinal grain boundaries got even narrower or disappeared. Figure 6.5 indicated that denuded zones were formed next to every grain boundary at
the end of the secondary creep stage, and those adjacent to the transverse grain boundaries apparently widened and those adjacent to the longitudinal grain boundaries changed little in the tertiary creep stage.

Fig. 6.5 - (a) Variation of the creep rate as a function of creep testing time under 40 MPa at 300 °C, and the distribution and configuration of denuded zones in the samples crept for 72 h (b), 192 h (c) and 263 h (d). The direction of applied stress is horizontal.

This fact was confirmed in Fig. 6.6, which shows the measured width of paired denuded zones formed in different creep stages under 40 MPa at 300 °C and different ageing periods at 300 °C. The paired denuded zones referred to the two denuded zones formed next to the same grain boundary that is approximately normal to the applied stress direction. The width of paired denuded zones was measured in the way displayed in Fig. 6.6(a). Each width was an average value of 30 pairs of denuded zones observed in BSE images obtained under a magnification of 800 times, and these paired denuded zones were selected from regions adjacent to the grain boundaries that were lying 60~90° with respect to the direction of the applied stress. Figure 6.6(b) shows that the width of the paired denuded zones in the aged samples roughly remained at 2.4 μm until 263 h of ageing. And the widths of the paired denuded zones in the samples crept for 72 h, 192 h and 263 h under
40 MPa at 300 °C were approximately 2.7, 4.5 and 6.7 μm, respectively. If the width of the paired denuded zones in the aged samples was used as a benchmark, then the width of the paired denuded zones caused by the applied stress in creep tests for 72 h, 192 h and 263 h under 40 MPa at 300 °C became 0.3, 2.1 and 4.3 μm, respectively. These measurements suggested that the width of the paired denuded zones increased by 0.3 μm during the secondary creep stage of 72 h while the width increased by 2.2 μm during the last 71 h in the tertiary creep stage. The result indicated the denuded zones widened mainly in the tertiary creep stage. If the creep strain mainly occurred in the denuded zones, then the fracture strain would be approximately equal to 0.15, which was calculated by dividing the width of the denuded zones by the average diameter of grains. The strain value of 0.15 was close to the experimental result of 0.16 (Fig. 4.8(a)), which means that the denuded zones possibly account for the major part of the creep strain.

Fig. 6.6 - (a) Schematic diagram showing the measuring method of the width of paired denuded zones, (b) measured widths of paired denuded zones in samples aged at 300 °C for different time, and crept at 300 °C under 40 MPa for different time.
6.3.3. Characterization of denuded zones

A detailed examination was made on the sample crept to rupture under 40 MPa at 300 °C, as its denuded zones were the widest. Two types of grain boundary regions, decorated by the denuded zones, were observed and they could be distinguished by the distribution of particles in the grain boundary regions, Figs. 6.7(a, b). The majority of grain boundary regions consisted of one array of particles, together with a wide denuded zone, designated type A, on one side of the particles, and a much narrower denuded zone was on the other side of the particles, Fig. 6.7(a). The type A denuded zones approximately account for 90% of the observed denuded zones. Occasionally, the type A denuded zones contained some precipitates that were originally in the grain interior, as shown in Fig. 6.7(a) by a red arrow. The second type of grain boundary regions had a wide denuded zone, designated type B, between two arrays of particles in the grain boundary region, together with a significant narrower denuded zone on either side of the wider denuded zone, Fig. 6.7(b). Occasionally, cavitation had formed within the denuded zones and some of these cavities propagated along the zones, as shown in Figs. 6.7(c, d).
Fig. 6.7 - BSE images of a sample crept to rupture at 300 °C and 40 MPa showing: (a) a grain boundary in the center of the image with a wide type A denuded zone on left side and a narrow denuded zone on right side of the grain boundary, (b) two arrays of particles in the grain boundary region with a wide type B denuded zone between them, (c) a small crack formed in a denude zone, and (d) a large crack propagated along denuded zones. The direction of the applied stress is horizontal.

Type A denuded zones

Three representative type A denuded zones are shown in Fig. 6.8. Judged from the BSE images, these denuded zones appear to have the same orientation as the grain interior. However, EBSD maps obtained from these regions indicated that most of them had misorientations with respect to the grain interior. As shown in Fig. 6.8, the degree of misorientations are quite variable. The type A denuded zone in Fig. 6.8(a) appears to have no apparent misorientation with respect to the grain interior, as there is a uniform colour (beige) spreading from the denuded zone to the grain interior in the EBSD map in Fig. 6.8(b). It is to be noted that the reliable EBSD resolution in this study is ~2.0° and that any misorientation lower than 2° could not be detected by the EBSD mapping. The type A denuded zone shown in Fig. 6.8(c) has an obvious misorientation with the grain interior. The denuded zone is indicated by a light beige colour and the grain interior is represented by a light grey colour in the EBSD map in Fig. 6.8(d). The misorientation was measured to be approximately 3.7°, Fig. 6.8(e), which displays the point-to-origin misorientation...
along the black arrow in Fig. 6.8(d). A third example of the type A denuded zone is shown in Figs. 6.8(f, g), which has a low-angle boundary (marked by an orange arrow) with the interior of the grain. The misorientation across the cell boundary was measured to be approximately 15.0°. It is noted that some precipitates are isolated in the denuded zone near the cell boundary, Fig. 6.8(f), which is similar to the observation in Fig. 6.7(a).

Fig. 6.8 - (a, c, f) BSE images and (b, d, g) the corresponding EBSD maps showing three type A denuded zones. (e) Diagram showing the misorientation along the black arrow in (d). The direction of the applied stress is horizontal. The difference in grain orientation is reflected by the color variation.

This misorientation was further confirmed under TEM by observing a type A denuded zone in Fig. 6.9. There are two grains oriented differently. No misorientation was observed in the lower grain. The type A denude zone was in the upper grain above the grain boundary, and a distinct interface existed between the denuded zone and the grain interior marked by an orange dash line, which indicated a misorientation between them. This misorientation was confirmed by the Kikuchi patterns obtained from the grain interior, Fig. 6.9(b), and the denuded zone, Fig. 6.9(c), when the c axis of the denuded zone was parallel to the incident electron beam direction. Additionally, some isolated yet-to-be-dissolved precipitates were found in this denuded zone, as shown in Fig. 6.9(a).
The morphology of these precipitates was similar to those in the grain interior, which implied that these precipitates nucleated and grew inside the grain.

Fig. 6.9 - (a) TEM image showing a wider type A denuded zone above and a narrower denuded zone below a grain boundary lying horizontal. The Kikuchi patterns in (b, c) obtained from the areas labeled B and C respectively in (a) after a small tilting from the orientation in (a).

More details of a type A denuded zone are revealed in Fig. 6.10. The type A denuded zone was on the left side of the grain boundary, and almost no denuded zone was on the right. Figure 6.10(a) reveals that a dislocation wall comprising a high density of dislocations existed between the type A denuded zone and the grain interior, which caused a misorientation between them. Some dislocations were also visible inside the denuded zone. Figures 6.10(b, c) show enlarged images that corresponded to the areas labeled as “B” and “C” in Fig. 6.10(a), but were slightly tilted with respect to the incident electron beam. While the dislocations inside the region of the denuded zone in Fig. 6.10(c) were sparsely distributed, those in regions such as that shown in Fig. 6.10(b) were dense enough to form a dislocation wall. It was noteworthy that no precipitates were found in the denuded zone, which was different from the case presented in Fig. 6.9. This observation implied that the misorientation caused by the dislocation wall led to the dissolution of precipitates isolated in the denuded zones.
Fig. 6.10 - TEM images showing a type A denuded zone on the left of the grain boundary: (a) dislocation walls separating and inside the type A denuded zone as noted by arrows, (b) enlargement of the B area in (a) showing a dislocation wall between the type A denuded zone and grain interior, (c) enlargement of the C area in (a) showing an array of dislocations inside the type A denuded zone. The incident beam is near $[11\overline{2}0]_\alpha$ in the left grain and near $[0001]_\alpha$ in the right grain.

The dislocation walls observed in Fig. 6.10, as a signature of the type A denuded zones, were examined in Figs. 6.11 and 6.12 for determining the configuration and Burgers vector. Figure 6.11 displays the projections of the dislocation walls under different incident beam directions (the directions were near $[22\overline{4}3]_\alpha$, $[11\overline{2}3]_\alpha$, $[01\overline{1}0]_\alpha$, respectively): Figs. 6.11(a-c) correspond to the dislocation wall shown in Fig. 6.10(b), and Figs. 6.11(d-f) correspond to the dislocation wall shown in Fig. 6.10(c). In each beam direction, most of the projections of the dislocations in these dislocation walls were straight and the line directions of them appeared parallel in Fig. 6.11. This indicated that most of these dislocations were parallel and straight in three dimensions. Their directions were the same and were found to be $\sim 80^\circ$ with the $\langle 1\overline{2}10 \rangle_\alpha$ direction on the basal plane of matrix by analyzing the directions of dislocation projections, incident beam directions and $g$ vectors in Fig. 6.11 [203].
Fig. 6.11 - Centered dark field TEM images shows the configuration of dislocations: (a-c) separating the Type A denuded zone and grain interior in Fig. 6.10(b), and (d-f) in the Type A denuded zone in Fig. 6.10(c). The incident electron beam is near \([22\bar{3}]_\alpha\) in (a, d), near \([11\bar{2}\bar{3}]_\alpha\) in (b, e) and near \([01\bar{1}0]_\alpha\) in (c, f).
The Burgers vectors of the dislocations in the dislocation walls were identified through checking their visibility under different incident beam directions (different $g$ vectors), as shown in Fig. 6.12. The dislocation wall within the type A denuded zone in Figs. 6.12(a-d), which corresponds to the dislocation wall shown in Fig. 6.10(c), consists of straight dislocations with a Burgers vector of $1/3 \langle \overline{1}210 \rangle_\alpha$ (visible in Figs. 6.12(b, d), invisible in Figs. 6.12(a, c)), as illustrated by the orange lines in the schematic diagram of Fig. 6.13. A few curved dislocations with a Burgers vector of $1/3 \langle \overline{2}10 \rangle_\alpha$ in the vicinity of the dislocation wall were also identified (visible in Figs. 6.12(c, d), invisible in Fig. 6.12(a)), as illustrated by the green lines in Fig. 6.13. The dislocation wall separated the type A denuded zone and the grain interior contained $a$ type dislocations with the Burgers vectors of $1/3 \langle \overline{1}210 \rangle_\alpha$ (visible in Fig. 6.12(f), invisible in Fig. 6.12(e)), as illustrated by the orange lines in Fig. 6.13, and $a+c$ type dislocations with the Burgers vectors of $1/3 \langle \overline{2}13 \rangle_\alpha$ (visible in Figs. 6.12(e, f)), as illustrated by the blue lines in Fig. 6.13. Most of the dislocations displayed in Fig. 6.13 shared a similar Burgers vector, which implied that they possibly originated from a similar source.

Taking the line direction and Burgers vector of these straight dislocations into consideration, it was found that these dislocations were mixed dislocations. Most of the dislocations (in orange colour in Fig. 6.13) had an angle of $\sim 80^\circ$ between the line direction and Burgers vector, i.e., they were close to edge orientations.
Fig. 6.12 - (a, b) Bright field and (c-f) centered dark field TEM images showing the visibility of dislocations using different $g$ vectors: (a-d) dislocations in the denuded zone in Fig. 6.10(c), and (e, f) dislocations separating the denuded zone and grain interior in Fig. 6.10(b). The incident electron beam is near $[\bar{1}1\bar{2}0]_\alpha$ in (a, b, f), near $[01\bar{1}0]_\alpha$ in (e), and near $[01\bar{1}1]_\alpha$ in (c, d).
Type B denuded zones

Three representative examples of the type B denuded zones, as highlighted in the centre of Figs. 6.14(a, c, f), were characterized using EBSD, as shown in Figs. 6.14(b, d, g), respectively. The EBSD maps showed the presence of the bulged grain boundaries, and some particles possibly originally in grain boundaries were found inside the grains, as marked by the yellow arrows in Figs. 6.14(c, d). In each case no misorientation was found between the denuded zone and the grain interior, as indicated by the absence of colour variation between the denuded zone and the core of the grains in the EBSD maps of Figs. 6.14(b, d, g). This observation was confirmed by the point-to-origin misorientation diagram in Fig. 6.14(e), which shows the misorientation along the black arrow in Fig. 6.14(d) across the grain boundary. This diagram indicated that there was only one obvious change in the orientation due to the grain boundary, and that no distinct misorientation existed within the denuded zones or between the denuded zone and the grain interior, which is different from the type A denuded zones.

Fig. 6.14 - (a, c, f) BSE images and (b, d, g) the corresponding EBSD maps showing three type B denuded zones. (e) Diagram showing no misorientation along the black arrow in (d) except the grain boundary. The direction of the applied stress is horizontal.

A type B denuded zone was examined under TEM for further characterization in Fig. 6.15. Two nearly parallel arrays of particles were found lying in the grain boundary region, and the bulges of the grain boundary were visible by a slight tilting of the incident electron beam direction, as shown in Figs. 6.15(a, b). These two figures suggested that certain particles indicated by yellow arrows, having a different shape to the precipitates inside the grains, were probably originally nucleated in grain boundaries. These particles are not along the grain boundary now, because the contrast of the area around the particles is the same as the grain interior, which is due to the same orientation. If these particles were on the grain boundary, the contrast of the area around these particles would not be even. After the creep test, these particles might have been left within the grain. Figures 6.15(c, d), which corresponded to the areas marked as “C” and “D” in Fig. 6.15(a), revealed the existence of a great number of dislocations in the denuded zone and the two grains.
Chapter 6

Formation of Denuded Zones in the Crept Mg-2.5Gd-0.1Zr Alloy

Fig. 6.15 - TEM images of a type B denuded zone showing: (a) two arrays of particles in the grain boundary region, (b) a bulged grain boundary and some particles (marked by yellow arrows) that are originally in the grain boundary but now left inside the grain, (c, d) many dislocations in these two adjoining grains and denuded zones.

The dislocation configuration around the particles that were now left inside the denuded zone of another type B denuded zone was revealed in Figs. 6.16(a-c). A net of dislocations was found around the particle labeled as “B” in Fig. 6.16(a), as shown in Fig. 6.16(b). Another particle labeled as “C” in Fig. 6.16(a) was surrounded by a set of dislocation loops, as shown in Fig. 6.16(c). These dislocations were possibly misfit dislocations that were associated with the rational orientation relationship shown in Fig. 6.16(c), as they were similar to the set of misfit dislocations that were commonly observed around intragranular precipitates in the sample aged at 300 °C for 263 h, Fig. 6.16(d).
6.4. Discussion

The denuded zones of the Mg-2.5Gd-0.1Zr alloy mainly studied in this work are formed under 40-80 MPa at 300 °C, which is roughly consistent with the conditions reported in the literatures for the formation of denuded zones in Mg-Gd(Y) based alloys (under 50-120 MPa at 300 °C) [3, 201]. However, the temperature (300 °C, ~0.6 Tm, where Tm is the melting temperature
of the alloy in Kelvin) is much lower than those reported for crept Mg-Zr alloy samples in which the denuded zones were formed (400–500 °C, ~0.8 $T_m$) [8, 9, 83, 204-206]. Also the stresses used in this study (40–80 MPa) are higher than those for the Mg-Zr samples (below 10 MPa).

The main period of the development of denuded zones has not been reported in previous studies. The denuded zones in Mg-Gd(Y) based alloys were found in ruptured samples, which had experienced the tertiary creep stage. As for the Mg-Zr alloys, samples crept during the secondary creep stage and samples crept to rupture were both reported with denuded zones formed next to the grain boundaries that are normal to the applied stress direction [8, 204]. It is possible that the denuded zones are mainly formed in the secondary creep stage in the Mg-Zr alloys because of their higher creep temperatures and lower applied stresses, which may involve a different formation mechanism of denuded zones during creep tests. The experimental results obtained in the present study, Figs. 6.5 and 6.6, indicate that denuded zones in the Mg-2.5Gd-0.1Zr alloy are mainly formed in the tertiary creep stage. The tertiary creep stage is different from the secondary creep stage. Diffusional creep is inferred as one of dominant creep mechanisms during the secondary creep stage, but in the tertiary creep stage, the dislocation movement is more evident.

Two mechanisms, namely directional diffusion and grain boundary migration, have been adopted to account for denuded zones formed in crept Mg-Gd(Y) based alloys [6, 201]. The mechanism of directional diffusion depicts a process of vacancy generation at grain boundaries that are transverse to the applied stress direction and directional flow to grain boundaries that are parallel to the applied stress direction, resulting in atoms flowing in the reverse direction to deposit on the transverse grain boundaries to form denuded zones there, as illustrated in Fig. 6.17 [207]. This mechanism has also been adopted to account for the denuded zones formed in a Mg-0.5wt%Zr alloy crept under 1.4 MPa at 450 °C and under 0.77 MPa at 500 °C [83]. This mechanism was subsequently endorsed by Harris et al. who reported that it was the widening of the denuded zones that contributed to the majority of creep strain [208]. Later, the mechanism of directional diffusion was further developed by Bilde-Sørensen, Greenwood, Burton, Kloc, Nabarro et al. who proposed that the diffusion process could be affected by the ability of grain boundary to act as sources and sinks for vacancies [209-214]. This mechanism is further supported by experimental results obtained by McNee et al. [8]. Based on observations made from optical microscopy, SEM and EDXS, McNee and coworkers showed that denuded zones were formed only in the Mg-0.5wt%Zr
alloy samples crept under stresses below 5.1 MPa at 450~490 °C and that these denuded zones were free of Zr atoms.

![Schematic diagram showing the flow direction of vacancies and atoms under the applied stress.](image)

**Fig. 6.17** - Schematic diagram showing the flow direction of vacancies and atoms under the applied stress.

In general, the characteristic features of the directional diffusion thus include: (1) denuded zones are formed on one side or both sides of grain boundaries that are approximately normal to the applied stress direction, (2) the density of particles on the grain boundaries that are parallel to the applied stress direction is higher than that on the grain boundaries that are perpendicular to the applied stress direction, and (3) the creep rate of the secondary creep stage is approximately directly proportional to the applied stress, i.e., the apparent stress exponent value is equal to unity.

The mechanism of grain boundary migration was initially proposed by Vickers et al. to account for denuded zones formed in the Mg-0.5wt%Zr alloy samples crept at 400 °C and 450 °C under stresses of 0.6~3.4 MPa, which yielded an apparent stress exponent value of 4 [204]. This mechanism depicts a process of grain boundaries, lying perpendicular to the applied stress direction, moving along this direction. This process is associated with dissolving and dragging precipitates in regions that the grain boundaries have passed by—the solute atoms diffuse along these moving grain boundaries to those grain boundaries that are roughly parallel to the applied stress direction and precipitate on particles that have already formed there. This process is characterized by an apparent stress exponent value in the range of 4~6, which is a signature of dislocation creep. This mechanism of grain boundary migration was supported by the analysis made by Wolfenstine et al.—that the value of the apparent stress exponent derived from creep test data of Mg-0.5wt%Zr samples at 500 °C under 0.25~1 MPa was equal to 6 [86]. It was endorsed by Wadsworth et al. who analyzed the creep data of the Mg-Zr alloys in the literature and found a value of 4 for the apparent stress exponent [9].
Therefore, the denuded zones that originate from the grain boundary migration mechanism have the following characteristic features: (1) denuded zones are formed on only one side of the grain boundary lying perpendicular to the applied stress direction, (2) the particles on the grain boundaries that are parallel to the applied stress direction are larger than those on the grain boundaries that are normal to the applied stress direction, and (3) the apparent stress exponent values are in the range of 4~6, which indicates dislocation creep.

The characteristic features of the denuded zones in the present study are not fully consistent with those expected for directional diffusion or grain boundary migration. The formation of denuded zones on both sides of the grain boundaries that are normal to the applied stress direction, Fig. 6.3, is not consistent with the mechanism of grain boundary migration. The uniform distribution and size of second phase particles in grain boundaries that lie in different directions, Fig. 6.3, cannot be explained by the mechanism of directional diffusion or grain boundary migration. The apparent stress exponent derived from the creep tests performed at 250 °C done in this study is equal to 3.3, as shown in Fig. 6.2(a), which implies dislocation creep, and the apparent stress exponent derived from the creep tests performed at 300 °C is equal to 2.6, as shown in Fig. 6.2(b), which is between those corresponding to grain boundary sliding (~2) and dislocation creep (3~5). Grain boundary sliding is unlikely to be the dominant mechanism in the present case because of the presence of second phase particles in grain boundaries, as shown in Figs. 6.5(b-d). These particles can efficiently obstruct grain boundary sliding. Hence the predominant creep mechanism in the secondary creep stage is speculated to be associated with dislocations instead of grain boundary sliding. It is to be noted that mechanisms of directional diffusion and grain boundary migration are often deduced from stress exponent values obtained from the data from the secondary creep stage. The observations made in the present study, Figs. 6.5 and 6.6, unambiguously reveal that denuded zones widen mainly in the tertiary creep stage. In this creep stage, the increasing creep rate suggests that more dislocations are generated and move rapidly, leading to a larger strain per second and the ultimate formation of cavities in grain boundaries [176, 215].

It is demonstrated in the present study that approximately 90% of the denuded zones are type A that are separated from the grain interior by dislocation walls, Fig. 6.10, and these denuded zones have misorientations with their grain interiors, Fig. 6.8. Since precipitates inside each grain are originally fully coherent with the α-Mg matrix, any change in the matrix orientation will cause
a loss of coherent matching between the precipitates and the surrounding matrix, which in turn leads to an increased interfacial energy of the precipitates and elastic strain energy of the surrounding matrix phase and the precipitates. This increase in the interfacial energy and elastic strain energy is expected to result in precipitate dissolution and thus the formation of denuded zones.

It is noteworthy that the dislocation densities in the two adjoining grains are significantly different, Fig. 6.10. The dislocation density is related with the shear stress resolved within the operative slip plane and direction. The resolved shear stress depends on the orientation of the grain with respect to the applied stress direction. Therefore, the orientations of the two adjoining grains will influence the dislocation density. Figures 6.8(c, d) demonstrate that the orientations of the two adjoining grains, with a type A denuded zone between them, are significantly different, as indicated by the hexagonal unit cell in each of the two grains in Fig. 6.8(d). The angles between the applied stress direction and the [0001] axis (c-axis) for the left and right grains are ~45° and ~90°, respectively. This observation implies that resolved shear stress on the basal plane of the right grain is almost zero and therefore significantly lower than that in the left grain. Hence the dislocation density in the right grain is expected to be substantially lower than that in the left grain. During the creep process, multiple dislocations might be generated in the left grain and they would accumulate in the grain boundary region while few dislocations are in the right grain, leading to the formation of a type A denuded zone in the left grain.

While the formation of most denuded zones can be explained by the mechanism mentioned above, it is currently difficult to reconcile this mechanism and the formation of type B denuded zones. A type B denuded zone is located between two arrays of grain boundary particles, contains bulged grain boundaries, and has no obvious misorientation with the grain interior, Fig. 6.14. Among the mechanisms commonly accepted for the formation of denuded zones, namely directional diffusion and grain boundary migration, neither of them seems to be fully responsible for the type B denuded zone. The presence of many dislocations in grain boundary regions, Fig. 6.15, might absorb vacancies diffusing from grain boundaries, if any, and thus interrupt the flow of vacancies and atoms, making the directional diffusion difficult to operate. While it is possible that localized grain boundary migration might have occurred, as shown in Figs. 6.14 and 6.16, it remains unclear how this localized grain boundary migration could result in the dissolution of particles in the whole denuded zone. It is also difficult for this localized grain boundary migration
to account for the formation of two nearly parallel arrays of second phase particles in the whole denuded zone. The presence of many dislocations in the grain boundary regions, together with an apparent stress exponent value close to 2, might imply the occurrence of grain boundary sliding to some extent, in which dislocations are generated in grain boundary regions to accommodate the strain associated with the boundary sliding. However, it is difficult to reconcile the mechanism of grain boundary sliding and the formation of type B denuded zone. This aspect requires more experimental observations to be made in the future study.

6.5. Summary

The denuded zones formed in the crept samples of the Mg-2.5Gd-0.1Zr alloy (under 80, 100, 120 MPa at 250 °C and under 40, 60 and 80 MPa at 300 °C) have been characterized using BSE, EBSD and TEM:

(1) Although the creep testing temperatures (250/300 °C) are much lower and applied stresses (40~120 MPa) are much higher than those that lead to denuded zone formation in Mg alloys that have been reported in the literature, denuded zones are still observed in matrix regions adjacent to grain boundaries lying approximately normal to the applied stress. The width of the denuded zones increases very slowly during the primary and secondary creep stages, but increases significantly in the tertiary stage of the creep process.

(2) Approximately 90% of the denuded zones are type A, which are characterized by the distribution of an array of grain boundary particles on its one side. This type of denuded zones has misorientations (3°~15°) with their grain interiors. The rest of the denuded zones are type B, which are characterized by two arrays of grain boundary particles and a bulged grain boundary. This type of denuded zones exhibits no obvious misorientation with the grain interior.

(3) For a denuded zone that has a misorientation with its grain interior, the misorientation is caused by the formation of a dislocation wall between the denuded zone and the grain interior. This misorientation leads to a loss of coherent matching between the otherwise coherent precipitates and the surrounding matrix in this region, which in turn results in the dissolution of the precipitates in this region and hence the formation of a denuded zone.
CHAPTER 7.

CONCLUSIONS
This project has involved the investigation of creep properties and microstructural characterization of the Mg-2.5Gd-0.1Zr, Mg-2.5Gd-1.0Zn-0.1Zr, Mg-1.5Gd-1.0Y-1.0Zn-0.1Zr and Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr (at.%) alloys. The creep tests were performed at 250 °C under 80, 100, 120 MPa, and at 300 °C under 40, 60, 80 MPa. The microstructures have been characterized using scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and the analysis of the precipitate chains formation involves the usage of first-principles theory and phase field simulation method. The main conclusions obtained in this investigation are summarized as follows:

1) The Mg-2.5Gd-1.0Y-1.0Zn-0.1Zr alloy has the lowest minimum creep rate (the best creep resistance), by contrast, the Mg-2.5Gd-1.0Zn-0.1Zr alloy has the highest (the worst creep resistance) under the experimental conditions.

2) For the creep conditions applied in this work, dislocation creep is the predominant operative mechanism in the secondary creep stage of the four alloys based on the secondary creep rates, except the creep mechanism of the Mg-2.5Gd-0.1Zr crept at 300 °C is attributed to the combination of dislocation creep and grain boundary sliding.

3) The addition of 1.0 at.% Zn to the Mg-2.5Gd-0.1Zr alloy leads to the formation of basal plates of $\gamma'$ precipitates at the expense of $\beta'$ precipitates. The number density of $\beta'$ precipitates in the resultant alloy is significantly lower than that in the Zn-free alloy. The $\gamma'$ plates are much less effective in impeding dislocation gliding or climbing, leading to reduced values of the threshold stress and thus increased values of the minimum creep rate.

4) The replacement of 1.0 at.% Gd by Y in the Mg-2.5Gd-1.0Zn-0.1Zr alloy results in a further reduction in the number density of $\beta'$ precipitates. While there is little change in the 0.2% proof strength, the minimum creep rate is reduced by 10 times at 80 MPa. The substantial reduction in the minimum creep rate is not caused by the threshold stress. It is suspected that Y atoms have a much lower diffusion rate than Gd atoms in the solid magnesium matrix, and that the partial replacement of Gd by Y reduces the effective lattice diffusivity which in turn leads to a reduction in the minimum creep rate.

5) Keeping the concentrations of the other alloying elements in the Mg-Gd-Y-Zn-Zr alloys unchanged, an increase in the Gd content reduces the minimum creep rate and this effect
becomes more pronounced at higher applied stresses. The increased concentration of Gd also
leads to a higher volume fraction of precipitates and a higher 0.2% proof strength, which may
counter to the reduction of the minimum creep rate by increasing the threshold stress.

(6) When the Mg-2.5Gd-0.1Zr alloy crept under 80-120 MPa at 250 °C, linear precipitate
chains were observed approximately extending normal to the direction of the applied stress,
and the precipitate chains consist of alternative $\beta'_F$ and $\beta'$ particles.

(7) The $\beta'_F$ phase is unreported in the Mg-Gd based alloys, and it was previously reported in
Mg-Nd alloys. The coexistence of the $\beta'_F$ and $\beta'$ phases in the aged and crept Mg-2.5Gd-0.1Zr
alloy is probably due to the approximately equal formation energy per atom of the $\beta'_F$ and $\beta'$
phases.

(8) The linear chain distribution of $\beta'$ particles likely form on pre-existing $\alpha$-type basal edge
dislocations under the external tensile stress condition. During creep tests, compared with other
variants of $\beta'$ particles, the variant with Gd zigzag arrays approximately normal to the
direction of dislocations is energetically more favourable to nucleate and growth on the
dislocations and forms a linear chain distribution.

(9) There are four types of transitional zones between the adjoining $\beta'_F$ and $\beta'$ particles in the
precipitate chains. Type 1 is continuous zigzag zones consisting of a zigzag array with a fixed
distance of $\sim 1.11$ nm with the nearest Gd arrays of the $\beta'_F$ and $\beta'$ particles. Type 2 is
discontinuous hexagonal zones consisting of a hexagonal array with a wider gap on one side.
Type 3 is continuous hexagonal zones consisting of a hexagonal array with fixed distance to
the nearest Gd arrays of the $\beta'_F$ and $\beta'$ particles. Type 4 is discontinuous zigzag zones
consisting of zigzag arrays with a wider gap on one side, and the width of the wide gap is about
1.66 nm.

(10) The four types of transitional zones between the $\beta'_F$ and $\beta'$ particles are probably
determined by the distance between them. If the distance equals to $4d_{(1100)} + b_{\beta'_F}$, type 1 of
transitional zones will be formed. If the distance is $3d_{(1100)} + b_{\beta'_F}$, type 2 will be observed. If
the distance equals to $2d_{(1100)} + b_{\beta'_F}$, type 3 will be found. If the distance is $d_{(1100)} + b_{\beta'_F}$,
type 4 will be formed.
(11) Although the creep testing temperatures (250/300 °C) are much lower and applied stresses (40–120 MPa) are much higher than those that lead to denuded zone (free of precipitates) formation in Mg alloys that have been reported in the literature, denuded zones are still observed in matrix regions adjacent to grain boundaries lying approximately normal to the applied stress. The width of the denuded zones increases very slowly during the primary and secondary creep stages, but increases significantly in the tertiary stage of the creep process.

(12) The approximately 90% of the denuded zones are type A, which are characterized by the distribution of an array of grain boundary particles on its one side. This type of denuded zones has misorientations (3°~15°) with their grain interiors. The rest of the denuded zones, designated type B, are characterized by two arrays of grain boundary particles and a bulged grain boundary. These denuded zones exhibit no obvious misorientation with the grain interior.

(13) For a denuded zone that has a misorientation with its grain interior, the misorientation is caused by the formation of a dislocation wall between the denuded zone and the grain interior. This misorientation leads to a loss of coherent matching between the otherwise coherent precipitates and the surrounding matrix in this region, which in turn results in the dissolution of the precipitates in this region and hence the formation of a denuded zone.
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APPENDIX

The phase field method used in this thesis involves the application of elastic strain energy, chemical free energy and kinetics equations.

1. Elastic strain energy

According to the Landau’s theory of phase transformations [216, 217], a set of three structural order parameters, \{\eta_1, \eta_2, \eta_3\}, were introduced to distinguish the Mg matrix and the three different orientation variants of \(\beta'\) phase. In the present study, \(\eta_1 = \eta_2 = \eta_3 = 0\) represents the Mg matrix and \{\eta_i = 1, \eta_{j\neq i} = 0\} (i = 1, 2, 3; j = 1, 2, 3) represents the three different orientation variants of the \(\beta'\) phase. The stress-free transformation strain tensors (SFTS) of the three orientation variants of \(\beta'\) are presented as \(\varepsilon^0(1)\), \(\varepsilon^0(2)\) and \(\varepsilon^0(3)\) respectively. An interpolation function \(H(\eta_i) = \eta_i^2(10-15\eta_i+6\eta_i^2)\) was used to connect the equilibrium free energy of the Mg matrix and the \(\beta'\) phase through the structural order parameters, \(\eta_i\), which satisfies the constraints that \(H(0) = 0\), \(H(1)=1\) and \(dH/d\eta_i = 0\) at \(\eta_i = 0\) and 1. The lattice misfit between the two co-existing phases (\(\alpha\)-Mg and \(\beta'\)) was assumed to be associated only with the structural non-uniformities, and the SFTS field was formulated as a function of the structural order parameters:

\[
\varepsilon^0_i(r) = \sum_{p=1}^{3} \varepsilon^0_{i}(p)H[\eta_i(r)],
\]

where \(\varepsilon^0_i(p)\) is the SFTS tensor of the \(p^{th}\) orientation variant of the \(\beta'\) precipitates. When \(p = 1, 2\) and 3, \(\varepsilon^0_i(p)\) refers to \(\varepsilon^0(1), \varepsilon^0(2)\) and \(\varepsilon^0(3)\), respectively.

The elastic strain energy was formulated by using Khachatryan and Shatalov’s micro-elasticiy theory (KS theory) [218]. The modulus of the Mg matrix was selected as the reference state, and the following values \(C_{11} = 63.5\) GPa, \(C_{12} = 24.85\) GPa, \(C_{13} = 20.0\) GPa, \(C_{33} = 66\) GPa and \(C_{44} = 19.3\) GPa [219] were used in the simulations, which were calculated via the first-principles approach. The final equilibrium shape could be influenced by this choice. A clamped boundary condition (i.e., no macroscopic strain) was applied in the calculation, which corresponded to a grain embedded in a polycrystalline aggregate. Thus the elastic strain energy was given by:

\[
E^{el} = \frac{1}{2} \sum_{p,q=1}^{3} \int \frac{d^3g}{(2\pi)^3} B_{pq}(n)[\tilde{\eta}_i]_g [\tilde{\eta}_i]_g^*,
\]

and

\[
B_{pq}(n) = \begin{cases} 
C_{ijkl}\varepsilon^0_{ij}(p)\varepsilon^0_{kl}(q) - n_i\sigma^0_{ij}(p)\Omega_{ij}(n)\sigma^0_{kl}(q)n_l & n \neq 0 \\
C_{ijkl}\varepsilon^0_{ij}(p)\varepsilon^0_{kl}(q) & n = 0
\end{cases},
\]

where \(p\) and \(q\) represent the \(p^{th}\) and \(q^{th}\) orientation variants, \(g\) is a vector in the reciprocal space, \(\Omega_{jk} = (n_iC_{ijkl}n_j)^{-1}\) where \(n\) is a unit vector in the reciprocal space, i.e. \(n = g/|g|\). The integral \(\int'\) means that the point \(g = 0\) is excluded from the integration. \(\sigma^0_{ij}(p) = C_{ijkl}\varepsilon^0_{ij}(p)\) where \(C_{ijkl}\) is the elastic constant. The superscript asterisk denotes complex conjugate. \([\tilde{\eta}_i]_g\) is the Fourier transform of \(\eta_i\).
which is a function of space.

2. Chemical free energy

The chemical free energies of the Mg matrix in Mg-Gd alloys are available from the CALPHAD database, and they could be described by the following expression [220, 221]:

$$F_{\text{Mg}} = \sum_{i=Mg,RE} x_i G_i + RT \sum_{i=Mg,RE} x_i \ln x_i + G_E,$$  

(4)

where $x_i$ are the mole concentrations of Mg and RE when $i$ equals to Mg and RE. In this thesis, RE represents Gd. The $G_i$ is the molar Gibbs free energies of pure elements (Mg and Gd) and $G_E$ is the excess Gibbs energy, which is expressed by the Redlich-Kister polynomial [222]:

$$G_E = x_{\text{Mg}} x_{\text{RE}} \sum_{j=0,1,...} L_j \text{MgRE} (x_{\text{Mg}} - x_{\text{RE}})^j,$$  

(5)

The thermodynamic parameters in Equations 4 and 5 are listed as follows [219]:

$$G_{\text{Mg}}^{\text{hcp}} = -8367.34 + 143.675547 \times T - 26.1849782 \times T \times \log(T) + 4.85 \times 10^{-4} \times T^2 - 1.393669 \times 10^{-6} \times T^3 + 78950 \times T^{-1} \quad (298 < T(\text{K}) < 923)$$

$$G_{\text{Gd}}^{\text{hcp}} = -11600.525 + 151.111948 \times T - 32.5013 \times T \times \log(T) + 0.00281265 \times T^2 - 1.081237 \times 10^{-6} \times T^3 + 421363 \times T^{-1} \quad (298 < T(\text{K}) < 1300)$$

$$L_{0\text{MgGd}} = -33346.6 + 19.3451 \times T \quad (298 < T(\text{K}) < 3000)$$

$$L_{1\text{MgGd}} = 13854 \quad (298 < T(\text{K}) < 3000)$$

The chemical free energy of the Mg matrix as a function of Gd concentration in Mg-Gd alloy could be simplified by a fourth order polynomial:

$$F_{\text{Mg}}(x_{\text{Gd}}) = -1.6704 - 4.776 x_{\text{Gd}} + 5.1622 x_{\text{Gd}}^2 - 2.7375 x_{\text{Gd}}^3 + 1.3687 x_{\text{Gd}}^4.$$  

(6)

Since $\beta'$ is a metastable phase, its chemical free energy function is not available in the current thermodynamic database. In the present study, the free energy of $\beta'$ was approximated by a parabolic function of solute concentration. Then, a tangent line could be drawn from $F_{\text{Mg}}$ curve at the equilibrium concentration point of the Mg matrix to the equilibrium concentration point of $\beta'$, as shown in Fig. 1 [223, 224]. The equilibrium composition of the Mg matrix was estimated as 0.5 at.% Gd in the Mg-Gd alloys, based on the Mg-Gd phase diagram [225]. The equilibrium composition of $\beta'$ was considered to be Mg$_7$RE. The only degree of freedom of the parabolic curve is its curvature. Considering the effect of the curvature on the $\beta'$/Mg interfacial energy, the following parabolic functions were obtained (in a unit of $10^4$ J/mol):

$$F_{\beta'}(x_{\text{Gd}}) = -1.6704 - 4.776 x_{\text{Gd}} + 5.1622 x_{\text{Gd}}^2 - 2.7375 x_{\text{Gd}}^3 + 1.3687 x_{\text{Gd}}^4.$$  

(6)
The complete form of the bulk chemical free energy density was expressed as a function of four field variables, i.e., three structural order parameters \( \{ \eta_1, \eta_2, \eta_3 \} \) and one concentration \( x_{\text{RE}} \).

\[
f(x_{\text{RE}}, \{ \eta_1, \eta_2, \eta_3 \}) = V_m^{-1} \left[ F_{\text{Mg}} \cdot \left( 1 - \sum_{i=1}^{3} H(\eta_i) \right) + F_{\beta'} \cdot \sum_{i=1}^{3} H(\eta_i) \right].
\]  

where \( V_m \) is a constant molar value and equals to \( 10^{-4} \) m\(^3\)/mol.

Combined with gradient energy terms [226-228], the total free energy of the system could be expressed as:

\[
E_{\text{tot}} = \int_V \left( f(x_{\text{RE}}, \{ \eta_1, \eta_2, \eta_3 \}) + \frac{\kappa_{\text{RE}}}{2}(\nabla x_{\text{RE}})^2 + \frac{1}{2} \sum_{p=1}^{3} \alpha_{ij}(p)\nabla_i \eta_p \nabla_j \eta_p \right) dV + E^{el},
\]

where \( \kappa_{\text{RE}} \) and \( \alpha_{ij}(p) \) are the gradient energy coefficients for concentration and order parameter fields respectively, and \( \alpha_{ij}(p) \) is a second-rank tensor used to describe the anisotropy in interfacial energy. The \( \kappa_{\text{RE}} \) and \( \alpha_{ij}(p) \) of the Mg-Gd alloy are shown as follows:

\[ \kappa_{\text{Gd}} = 4.5 \]

Fig. 1. Chemical free energy curves of \( \beta' \) and Mg phases as a function of RE (Y or Gd) concentration (at.%) in Mg-Gd alloys. The purple line is the common tangent line between the chemical free energy curves of \( \beta' \) and Mg phases.
\[ \alpha_{ij}(1) = \begin{pmatrix} 17.00 \\ 0.244 \end{pmatrix}, \]
\[ \alpha_{ij}(2) = \begin{pmatrix} 4.4330 \\ -7.2556 \\ 12.8110 \end{pmatrix}, \]
\[ \alpha_{ij}(3) = \begin{pmatrix} 4.4330 \\ 7.2556 \\ 12.8110 \end{pmatrix}. \] (10)

3. Kinetics equations

The Cahn-Hilliard [226] and Allen-Cahn [227] equations were used to describe the time evolution of the concentration and structural order parameter fields:

\[ \frac{1}{V_m} \frac{\partial x_{RE}}{\partial t} = \nabla \cdot \left\{ M \cdot \nabla \left( \frac{\delta E_{tot}}{\delta x_{RE}} \right) \right\} + \xi(r,t), \] (11)

\[ \frac{\partial \eta_i(r,t)}{\partial t} = -L \cdot \left\{ \frac{\delta E_{tot}}{\delta \eta_i} \right\} + \xi(r,t). \] (12)

Since the diffusion coefficient of Gd in Mg matrix is unknown, the time used in this thesis was expressed in a reduced unit, which could be converted easily to real time unit when the diffusivities become available. The growth of \( \beta' \) was assumed to be isotropic.