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Precipitation during creep in magnesium–aluminum alloys

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Abstract We employ a free energy density for Mg–Al alloys that is dependent on concentration, strain, and temperature, and derived from quantum mechanical calculations by Ghosh & Bhattacharya (Acta Mater 193:28–39, 2020), to model the dynamic precipitation of the Mg$_{17}$Al$_{12}$ phase during creep experiments in Mg–Al alloys. Our calculations show that the overall volume fraction of the dynamically formed precipitates is influenced by stress, and furthermore, this influence is anisotropic and asymmetric. Specifically, when the stress is volumetric or along the c-axis direction, the volume fraction of the precipitate phase is greater in compression and lower in tension. Surprisingly, stress along the a- or b-axis directions does not alter the volume fraction of the precipitates. The resistance to creep is improved by the presence of finely dispersed precipitates with a small aspect ratio, closer to spherical or ellipsoidal in shape and high number density. A greater volume fraction of these fine particles are produced during compressive creep tests than tensile creep experiments and thereby explaining the higher creep rate observed in tension than in compression in these alloys. Overall, our calculations explain the tension–compression asymmetry of the creep rate observed in creep experiments in Mg–Al alloys (Agnew et al. in Magn Technol 2000:285–290, 2000; Agnew et al. in Magn. Alloys Appl. 685–692, 2000).

Keywords Magnesium alloys · Creep · Anisotropy · Precipitation · First-principles · Free-energy

1 Introduction

Magnesium is a technologically relevant structural material. It has the potential to be integrated into a wide range of applications such as aerospace, aeronautics, automotive, and consumer electronics due to its several appealing features such as abundant availability in high purity, low melting temperature, and high specific heat. Furthermore, it is lightweight and has the highest strength to weight ratio among all commonly used structural metals. Though there has been significant research over the last few years, the integration of magnesium and its alloys into practical engineering applications have been restricted by several shortcomings, primarily low ductility and fracture toughness [1–3], corrosion, and poor creep resistance [4,5].

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Pure Magnesium has a hexagonal closed-packed (HCP) crystal structure and is highly anisotropic. Aluminum is a commonly used alloying element for developing lightweight magnesium alloys, which include the commonly used AM and AZ class of Mg–Al alloys. Aluminum has several desirable properties, including availability in high purity, low density, corrosion resistance, and suitable mechanical properties. The maximum solubility of aluminum in magnesium is 11.8 at. percent [6]. When Mg–Al alloys are aged, they precipitate out into an intermetallic compound with a composition of Mg$_{17}$Al$_{12}$ and a body-centered cubic structure (space group $I\bar{4}3m$). This secondary phase is termed as the $\beta$ phase and the HCP Mg phase is termed as the $\alpha$ phase. The existence of these precipitates is critical for strengthening Magnesium alloys, as they resist the motion of basal dislocations thereby effectively imparting strength [1–3,7]. The number density and orientation of these precipitates can critically influence the amount of hardening [8]. Furthermore, large sizes of precipitates contribute to the lack of ductility, fracture and fatigue, reduced spall strength and creep [9–11].

Precipitation can occur primarily by two processes. First is during ageing, and second by application of stress. The size, shape, aspect ratio, and number density of precipitates formed during the ageing process are critically influenced by the different heat treatment conditions [12–15]. The second process of precipitation—by the application of mechanical loads—is termed as dynamic precipitation and is influenced by the different conditions of applied stress and temperature [9,16–18]. Defects also play an important role in dynamic precipitation. Dislocations generate local stress fields which attract solute atoms. These solute atoms cluster to nucleate precipitates near the dislocation core. Further, solutes can bind to vacancies, which due to their high mobility can accelerate solute clustering and precipitation in metallic alloys. Thus, dynamic precipitation can be tuned by strategically controlling defects [19]. A critical difference between the morphology of the precipitates formed by the two different processes is that dynamically formed precipitates are typically continuous, nanosized, closer to spherical or ellipsoidal in shape, with high number density and low aspect ratio [9,18], unlike the typical large sized, highly elongated precipitates formed during ageing of Mg–Al alloys. Figure 1 shows the transmission electron microscopy images of the microstructures of Mg–9wt% Al alloy that is subject to conventional ageing and dynamic precipitation.

The AZ and AM class of alloys have good castability. At elevated temperatures of above 100–130 C, they undergo excessive creep deformation even at low stress levels. The creep resistance of Mg–Al alloys is associated with the formation of the Mg$_{17}$Al$_{12}$ precipitates at elevated temperatures [21,22]. Experiments conducted by Agnew et al. [4] showed that the creep-behavior of Mg alloys can be very different under tension and compression. In their follow-up work [5], they attributed this asymmetric creep behavior to the dynamic precipitation of Mg$_{17}$Al$_{12}$. However, there is a lack of clear understanding of the anisotropic creep behavior of Mg–Al alloys.

In a recent work by Ghosh & Bhattacharya [23], the authors derived a strain- and temperature-dependent free-energy density for Mg–Al alloys based on first principles Density Functional Theory (DFT) calculations. This energy density was used to investigate the influence of strains and temperature on the solubility limits and equilibrium chemical potential in Mg–Al alloys, and also to probe the influence of thermal and mechanical loads that arise during thermomechanical processing on the growth of precipitates. In this work, we use the free
energy density to investigate the influence of thermal and mechanical loads on the creep behavior of Mg–Al alloys.

The remainder of this manuscript is arranged as follows. In Sect. 2 we discuss the temperature- and strain-dependent free energy density. Next, in Sect. 3 we discuss the asymmetric and anisotropic influence of strain on the precipitation process, and in Sect. 4, we discuss the anisotropic creep behavior of Mg–Al alloys. Finally, in Sect. 5, we provide concluding remarks.

2 Quantum mechanically informed free-energy density

First principles calculations based on Density Functional Theory [24,25] have been very successful for high-fidelity predictions of material properties [26–29]. Significant advances towards the development of efficient computational methods to solve the DFT problem [30–37], has lead to the adoption of first-principles techniques in multiscale analysis of materials. Specifically, inputs from first-principles calculations at lower length scales have been used to develop quantum mechanically informed multiscale models, which can successfully predict or help understand mesoscale or macroscale phenomena such as hydrogen embrittlement [38], nanovoid nucleation under extreme deformation [39], vacancy formation under macroscopic deformation [40–42], and microstructure evolution during thermomechanical processing [23].

In this section, we introduce the reader to a temperature- and strain-dependent quantum mechanically informed free-energy density derived using first-principles calculations from Ref. [23].

The Helmholtz free energy density of the solid solutions as a function of magnesium concentration \( c \), strain \( \epsilon \) and temperature \( T \) is

\[
\mathcal{F}^{\alpha,\beta}[c, \epsilon, T] = \mathcal{E}^{\alpha,\beta}[c, \epsilon] - T S^{\alpha,\beta}[c],
\]

where the superscript \( \alpha \) corresponds to the \( \alpha \) phase and the superscript \( \beta \) corresponds to the precipitate, i.e., \( \text{Mg}_{17}\text{Al}_{12} \) phase, \( \mathcal{E}^{\alpha,\beta}[c, \epsilon] \) is the internal energy of the phases, and \( S^{\alpha,\beta}[c] \) the entropy of the phases is independent of strain, and is given by

\[
S^{\alpha,\beta}[c] = S[c] = -k_B(c \log c + (1 - c) \log(1 - c)),
\]

where \( k_B \) is the Boltzmann constant.

In Eq. 1, the internal energy per atom \( \mathcal{E}^{\alpha,\beta}[c, \epsilon] \) as a function of concentration and strain is

\[
\mathcal{E}^{\alpha,\beta}[c, \epsilon] = \mathcal{E}_0^{\alpha,\beta}[c] + C_{ij}^{\alpha,\beta}[c](\epsilon_{ij} - \epsilon_{ij}^{\alpha,\beta}[c]) (\epsilon_{kl} - \epsilon_{kl}^{\alpha,\beta}[c]) + M_{ijkl}^{\alpha,\beta}[c](\epsilon_{ij} - \epsilon_{ij}^{\alpha,\beta}[c]) (\epsilon_{kl} - \epsilon_{kl}^{\alpha,\beta}[c])(\epsilon_{mn} - \epsilon_{mn}^{\alpha,\beta}[c]).
\]

In the above expression, \( \mathcal{E}_0^{\alpha,\beta} \) is the phase- and concentration-dependent ground state (strain-free) energy, \( C^{\alpha,\beta} \) and \( M^{\alpha,\beta} \) are the phase- and concentration-dependent second-order and third-order moduli, respectively, and the strain \( \epsilon_{ij}^{\alpha,\beta}[c] \) is the eigenstrain due to the expansion of the lattice with the increase in magnesium concentration, and is measured with respect to the pure Mg or \( \text{Mg}_{17}\text{Al}_{12} \), respectively. This can be calculated from the expression of the equilibrium volume \( V^{\alpha,\beta} \) given as a function of concentration.

\[
V^{\alpha,\beta}[c] = V_1^{\alpha,\beta}(c - c_{\alpha}^{\alpha,\beta}) + V_0^{\alpha,\beta}
\]

where \( V_0^{\alpha,\beta} = \{22.02, 18.85\} \text{ Angstrom}^3/\text{atom} \) and \( V_1^{\alpha,\beta} = \{3.904, 6.029\} \text{ Angstrom}^3/\text{atom} \) are constants calculated from first-principles calculations, and \( c_{\alpha}^{\alpha,\beta} \) are concentrations of the pure \( \alpha \) and \( \beta \) phases \( (c_{\alpha}^{\alpha} = 1, c_{\beta}^{\beta} = 0.586) \). Density Functional Theory calculations show that the equilibrium volume increases with an increase in concentration of magnesium, and in the \( \alpha \) phase with Hexagonal Closed-packed crystal structure, both the lattice parameters \( c_{\text{hcp}} \) and \( a_{\text{hcp}} \) decrease with increasing aluminum concentration, which is in excellent agreement with experimental observations [43]. In Ref. [23], the \( c_{\text{hcp}} / a_{\text{hcp}} \) ratio of 1.624 increases slightly to 1.628 when the aluminum concentration is increased from 0 to 10 at. percent. This is in very good agreement with the experimentally observed ratio of 1.6275 [43].
Table 1 Constants of energy surface (3) from Ref. [23]. All constants are in eV/atom

Zero strain coefficients

| Phase | $E_0$ | $E_1$ | $E_2$ | $E_3$ |
|-------|-------|-------|-------|-------|
| $\beta$ | $-38.0461$ | $32.5114$ | $12.1023$ | $-69.9654$ |
| $\alpha$ | $-24.5554$ | $32.8235$ | $6.1759$ | $34.5826$ |

Elastic constants

| Phase | Strain | $C_{ijkl}^0$ | $C_{ijkl}^1$ | $C_{ijkl}^2$ |
|-------|-------|--------------|--------------|--------------|
| $\beta$ | Volumetric | $2.914$ | $39.49$ | $-255.2$ |
| {1111,2222,3333} | $5.482$ | $3.624$ | $-503.7$ |
| {1122,1133,2233} | $1.630$ | $57.423$ | $-130.950$ |
| $\alpha$ | Volumetric | $2.596$ | $-7.676$ | $-66.41$ |
| {1111} | $5.017$ | $-13.61$ | $-92.49$ |
| {2222} | $4.473$ | $-12.39$ | $-184.1$ |
| {3333} | $4.847$ | $-5.27$ | $36.86$ |

Third-order Elastic constants

| Phase | Strain | $M_{ijklmn}^0$ | $M_{ijklmn}^1$ |
|-------|-------|---------------|---------------|
| $\beta$ | Volumetric | $0$ | $0$ |
| {111111,222222,333333} | $0$ | $0$ |
| $\alpha$ | Volumetric | $-3.951$ | $10.460$ |
| {111111} | $-9.612$ | $71.74$ |
| {222222} | $-11.95$ | $6.326$ |
| {333333} | $-9.961$ | $0.018$ |

In Eq. 3, the phase- and concentration-dependent ground state (strain-free) energy $E_{0,\beta}^\alpha$ as well as the phase- and concentration-dependent second-order and third-order moduli $C_{ijkl}^{\alpha,\beta}$ and $M_{ijklmn}^{\alpha,\beta}$ are

$$E_{0,\beta}^\alpha[c] = \sum_{p=0}^{3} E_{p}^{\alpha,\beta} (c - c_{\alpha,\beta})^p,$$  \hspace{1cm} (5)

$$C_{ijkl}^{\alpha,\beta}[c] = \sum_{p=0}^{2} (C_p)_{ijkl}^{\alpha,\beta} (c - c_{\alpha,\beta})^p,$$  \hspace{1cm} (6)

$$M_{ijklmn}^{\alpha,\beta}[c] = \sum_{p=0}^{1} (M_p)_{ijklmn}^{\alpha,\beta} (c - c_{\alpha,\beta})^p.$$  \hspace{1cm} (7)

The fitted coefficients of $E_{0,\beta}^\alpha$, $C_{ijkl}^{\alpha,\beta}$ and $M_{ijklmn}^{\alpha,\beta}$ are calculated from first-principles simulation data and is shown in Table 1. The second-order moduli capture linear elastic behavior, while the third-order moduli can accurately describe the nonlinear response of materials such as anharmonicity of the crystal lattice.

3 Asymmetric and anisotropic influence of strain on precipitation

The free energy expression (Eq. 1) can be used to analyze the influence of temperature and applied strain on the growth of precipitates. The growth of precipitates in Mg–Al alloys is not only influenced by temperature but also depends on the nature (i.e., tensile or compressive) and directionality of strain [23]. For the sake of completeness, we concisely present this analysis in the ensuing discussion.

In Mg–Al alloys, the orientation relationship between the $\beta$ and $\alpha$ phase is $(0001)_\alpha = (110)_\beta$, $[1\bar{2}10]_\alpha \parallel [111]_\beta$, and the interface is assumed to be coherent [2,46]. The associated transformation strain for this HCP to BCC transformation is given by [46].

1 Alternatively, a neural network can be used to define the mapping from strain tensor to the energy [44].

2 We refer the reader to Ref. [45] for an exposition on third-order elastic moduli for modeling the nonlinear response of crystalline solids.
the orientation relationship can be used to solve for the stresses and strains in the $\beta$ phase. We plot the contours of the difference in grand potential specified at the interface of the $\alpha$ and $\beta$ phases to analyze the energetics of precipitate growth. When zero. Additionally, within each phase, the transformation strains are assumed to be independent of the change in concentration.

For illustrative purposes, let us consider an alloy with 92 at. percent Mg and 8 at. percent Al. In Figure 2a–d, we plot the contours of the difference in grand potential of the each phase is

$$
\left[\frac{|\phi_{\alpha,\beta}|}{\Phi_{\alpha,\beta}}\right], \dot{\mathbf{n}} = 0, \left[\frac{|\epsilon_{\alpha,\beta}|}{\Phi_{\alpha,\beta}}\right], \dot{\mathbf{i}} = 0,
$$

where the notation $[|\phi_{\alpha,\beta}|] = \phi_{\beta} - \phi_{\alpha}$ is the jump of the quantity $\phi$ across the phase boundary. In our analysis, the normal direction $\mathbf{n}$ is along the c-axis of the $\alpha$ phase, and the tangential directions $\mathbf{i}$ are along a- and b-axis. If the strain in the $\alpha$ phase is known, the jump conditions, the expression of transformation strain in (8), and the orientation relationship can be used to solve for the stresses and strains in the $\beta$ phase ($\epsilon^\beta$).

The grand potential $\Phi^\alpha_{\alpha,\beta}$ of the each phase is

$$
\Phi^\alpha_{\alpha,\beta} = F^\alpha_{\alpha,\beta} - \mu c^\alpha_{\alpha,\beta} - \langle \sigma \rangle \epsilon^\alpha_{\alpha,\beta},
$$

where the chemical potential $\mu$ and average stress $\langle \sigma \rangle$ are calculated from the derivative of the free-energy density of each phase

$$
\mu[\epsilon^\alpha_{\alpha,\beta}, T] = \frac{\partial F^\beta_{\alpha,\beta}}{\partial c}[c = c^\alpha_{\alpha,\beta} ; \epsilon^\alpha_{\alpha,\beta}, T] = \frac{\partial F^\alpha_{\alpha,\beta}}{\partial c}[c = c^\alpha_{\alpha,\beta} ; \epsilon^\alpha_{\alpha,\beta}, T],
$$

$$
\langle \sigma \rangle[c^\beta_{\alpha,\beta}, c^\alpha_{\alpha,\beta}, T] = \frac{\partial F^\beta_{\alpha,\beta}}{\partial \epsilon}[c = c^\beta_{\alpha,\beta} ; \epsilon^\beta_{\alpha,\beta}, T] = \frac{\partial F^\alpha_{\alpha,\beta}}{\partial \epsilon}[c = c^\alpha_{\alpha,\beta} ; \epsilon = \epsilon^\alpha_{\alpha,\beta}, T].
$$

The difference in grand potential $[|\Phi^\alpha_{\alpha,\beta}|] = \Phi^\beta_{\alpha,\beta} - \Phi^\alpha_{\alpha,\beta}$ across the interface of the two phases can be used to analyze the energetics of precipitate growth. When $[|\Phi^\alpha_{\alpha,\beta}|] = 0$, the system is in equilibrium, the grand potential in the individual phases is minimum with respect to the concentration, and the precipitate will neither grow nor shrink. When $[|\Phi^\alpha_{\alpha,\beta}|] < 0$, the precipitate will grow, and when $[|\Phi^\alpha_{\alpha,\beta}|] > 0$, the precipitate will shrink in size. Therefore, each phase grows or shrinks such that the chemical potential in each phase is equal to the equilibrium chemical potential $\mu_{eq}$. This can be computed from the slope of the common tangent between the $\beta$ phase and $\alpha$ phase

$$
\mu_{eq}[^\beta_{\alpha,\beta}, c^\alpha_{\alpha,\beta}, T] = \left[\frac{|F^\beta_{\alpha,\beta} - \langle \sigma \rangle \epsilon^\beta_{\alpha,\beta}|}{\Phi_{\alpha,\beta}}\right] = \frac{\partial F^\beta_{\alpha,\beta}}{\partial c}[c = c^\beta_{\alpha,\beta} ; \epsilon^\beta_{\alpha,\beta}, T] = \frac{\partial F^\alpha_{\alpha,\beta}}{\partial c}[c = c^\alpha_{\alpha,\beta} ; \epsilon = \epsilon^\alpha_{\alpha,\beta}, T],
$$

where $c^\alpha_{\alpha}$ and $c^\beta_{\alpha}$ are the equilibrium concentrations of magnesium in the $\alpha$ and $\beta$ phases, respectively. These can also be interpreted as equilibrium solubility limits influenced by strain and temperature. We first solve Eq. 13 for $c^\alpha_{\alpha}$ and $c^\beta_{\alpha}$, and then calculate $\mu_{eq}$.

For illustrative purposes, let us consider an alloy with 92 at. percent Mg and 8 at. percent Al. In Figure 2a–d, we plot the contours of the difference in grand potential $[|\Phi^\alpha_{\alpha,\beta}|]$ as a function of temperature and various cases of applied strains. We observe the following from these plots. First, even when the strain is zero, the grand potential of the $\beta$ phase is lower than the grand potential of the $\alpha$ phase ($\Phi^\beta_{\alpha,\beta} < \Phi^\alpha_{\alpha,\beta}$) at all temperatures between 200 and 600 K, thereby providing the thermodynamic driving force for the development of precipitates. This is because the concentration of Al is above the equilibrium solubility limits of Al in Mg. Next, the role of applied strain on the grand potential can be determined from these plots. We consider four cases, where compressive and tensile strains are applied as volumetric deformations, and along the c-, a- and b-axes, respectively. From
Figure 2a and d, we observe that compressive volumetric and c-axis strains decrease the potential jump $|\Phi^{\alpha,\beta}|$, thereby increasing the energetic favorability of $\beta$ phase over $\alpha$ phase, promoting the growth of precipitates. When tensile strains are applied volumetric or along the c-axis, they increase the jump in grand potential, $|\Phi^{\alpha,\beta}|$, decreasing the energetic favorability of $\beta$ phase over $\alpha$ phase, thereby impeding the growth of precipitates. Surprisingly, Fig. 2a and d show us that when strains are along a and b directions, the influence of these deformations on the difference in grand potential is negligible. Therefore, strains along a and b directions do not influence the energetics of growth of precipitates.

As evident from Eq. 13, the equilibrium solubility limits, and therefore the equilibrium volume fraction of the precipitates are also influenced by strain and temperature. The equilibrium volume fraction of the $\beta$ phase is given by

$$V_{eq}^\beta[\epsilon, T] = \frac{w_\beta[\epsilon, T] \rho_\alpha}{w_\beta[\epsilon, T] \rho_\alpha + w_\alpha[\epsilon, T] \rho_\beta}$$

(14)

where $\rho_\alpha = 1.1037$ amu/Angstrom$^3$, $\rho_\beta = 1.3481$ amu/Angstrom$^3$ and the mass fractions $w_\beta$ and $w_\alpha$ of the $\beta$ and $\alpha$ phases are:

$$w_\beta[\epsilon, T] = \frac{\tilde{c}_\beta[\epsilon, T] - \tilde{c}}{\tilde{c}_\alpha - \tilde{c}_\beta[\epsilon, T]}$$
$$w_\alpha[\epsilon, T] = \frac{\tilde{c} - \tilde{c}_\alpha[\epsilon, T]}{\tilde{c}_\alpha - \tilde{c}_\beta[\epsilon, T]}.$$
where the bar ($\bar{\cdot}$) denotes the concentration in expressed terms of weight percent.

In Fig. 3a–d, we show the equilibrium volume fraction of the $\beta$ phase in the strain–temperature space for different cases of applied strains. We immediately observe that volumetric strains and strains applied along the c-axis directions influence the volume fraction of the $\beta$-phase, whereas strains applied along the a- and b-axis directions have negligible influence on the volume fraction. Furthermore, compressive strains increase the volume fraction, whereas tensile strains decrease it. Finally, the $\beta$ phase dissolves with increase in temperature, which leads to the overall reduction in the equilibrium volume fraction of precipitates. It is also worthwhile to note the influence of temperature on the kinetics of diffusional phase transformations. The mobility of solutes and vacancies increases with the increase in temperature, which lead to rapid increase in the volume fraction of precipitates. However, under long time scales, the precipitate volume fraction in an alloy will approach the equilibrium volume fraction of precipitates. Experimental investigations for Mg–Al alloys by Payzant and co-workers [47] have shown that the long term precipitate volume fraction is lower at a higher temperature. In Sect. 4, we discuss the influence of creep loadings and temperature on the long term volume fraction of the $\beta$ phase.

4 Application to creep in Mg–Al alloys

Creep is the time-dependent permanent deformation of materials subject to a constant load. Unlike the strain in elastic–plastic deformation, which is a function of stress, the creep strain also depends on temperature ($T$), time ($t$), in addition to stress ($\sigma$). A typical creep strain vs time curve for a metal can be divided into three regions. First, the primary (transient) creep, where after an initial instantaneous restructuring of the metal, the
Fig. 4  A log–log plot of the minimum creep rate versus applied tensile and compressive stress for AM60B Mg–Al alloy at $T = 150 \, ^\circ C$, adapted from Ref. [5]. The stress exponent for compressive stresses and low tensile stress range is $n \approx 4$. At high tensile stresses, the stress exponent is $n \approx 10$.

creep rate decreases with time. In this regime, the material experiences an increase in creep resistance or strain hardening. Next, is the secondary or steady state creep, where the creep rate is constant due to the balance between the competing strain hardening and recovery processes. Finally, in the tertiary creep region, the creep rate is accelerated which leads to fracture due to changes such as grain boundary separation, formation of internal cracks, necking, cavities and voids. The strain rate in the steady-state creep region is the minimum strain rate experienced by the material.

In the steady-state creep regime, the creep rate is minimum and is given by

$$\dot{\epsilon} = A\sigma^n \exp \left( -\frac{Q_c}{RT} \right),$$

where $A$ is a constant, $Q_c$ is activation energy of creep, $R$ is the gas constant, and $T$ is the temperature. The mechanism of creep in Mg–Al alloys depends on stress and temperature. At low to moderate temperatures, stress activated recovery due to grain substructures such as precipitates and twins influence creep. In the creep experiments performed by Dargusch et. al. [22], the development of the Mg$_{17}$Al$_{12}$ phase in the evolved microstructure after creep was observed. Furthermore, by comparing the activation energy of creep $Q_c$ in Eq. 16 with the activation energy of precipitation, the precipitate phase was attributed for the creep in Mg–Al alloys. Agnew and co-workers [4,5] performed creep experiments on Mg–Al alloys under uniaxial tensile and compressive stresses, and observed significant tension compression asymmetry, with the creep rate in tension being much higher than the creep rate in compression. Figure 4 shows the plot of minimum strain rate (strain rate during steady-state creep) versus applied tensile and compressive stresses calculated using experiments [5]. Clearly from the plot, the rate is about an order of magnitude lower in compression than in tension. There is a lack of complete understanding of this behavior. This motivates us to analyze the influence of stress and temperature on the time evolution of the volume fraction $\beta$ phase precipitates.

The time evolution of the volume fraction of the $\beta$ phase can be expressed by the Johnson–Mehl–Avrami–Kolmogorov Eqs. [48–50]

$$V^\beta [t; \sigma, T] = (V^\beta_{eq}[\sigma, T] - V^\beta_0)(1 - \exp (-\kappa t^p)) + V^\beta_0,$$

where $V^\beta_0$ and $V^\beta_{eq}$ are the initial and equilibrium volume fractions of the $\beta$ phase, respectively, $t$ is time, $\kappa$ is the rate, and $p$ is the time exponent.

Previous experimental studies on the phase precipitation kinetics of Mg–Al alloys have reported the values of $\kappa$ and $p$ at different temperatures [47]. For illustrative purposes in our study, we consider two cases. First, at a temperature $T = 175 \, ^\circ C$, where the values of the rate and time exponent are $\kappa = 0.20$, $p = 0.28$, and second, we consider $T = 250 \, ^\circ C$, for which $\kappa = 0.52$, $p = 0.42$ [47]. We assume the initial volume fraction

3 This data corresponds to a die cast polycrystalline AM60B alloy, where the sub-grain microstructure consists of as cast eutectic Mg$_{17}$Al$_{12}$ phase which is large sized and is surrounded by Mg solid solution. Small particles of the Mg$_{17}$Al$_{12}$ were observed during service at elevated temperatures.
Fig. 5 Volume fraction of $\beta$ phases versus time for creep stresses of $-80$, $-40$, $0$, $40$ and $80$ MPa and temperature of $175$ C. The four different loading conditions correspond to stress applied a volumetric, b along c-axis, c along a-axis and d along b-axis.

Figures 5 and 6 show the time evolution of $\beta$ phase under the four different loading conditions, and at temperatures $T = 175$ C and $T = 250$ C, respectively. Comparing Figures 5 and 6, we observe that the time taken to reach the equilibrium volume fraction decreases when temperature increases from $175$ C to $250$ C. Specifically, time taken to reach the equilibrium volume fraction at $T = 175$ C is $\sim 200$ hours. When the temperature is increased to $T = 250$ C, the time taken to reach the equilibrium volume fraction decreases to $5$ hours. This 40-fold decrease in time is due to the increase in the rate $\kappa$ and the exponent $p$ with increase in temperature from $175$ C to $250$ C, which is due to the increased mobility of solutes and vacancies with the increase in temperature. Further, in Mg–Al alloys, the solutes can favorable bind to vacancies which aid to diffusion; solutes and also bind to other solute atoms which aid to solute clustering [51]. The role of temperature on kinetics can be understood in terms of a Time–Temperature–Transformation (TTT) diagram. These diagrams have a point of inflection below which the time of transformation increases with temperature. At even higher temperatures, approaching the eutectoid temperature, the chemical driving force for the transformation is reduced and the rate of precipitation slows down even though diffusion at higher temperatures is faster. It is also interesting to note the strong influence of applied stress on the time evolution of the volume fraction of the $\beta$ phase. It is evident from Figure 5a–d and Figure 6a–d that the time evolution of the volume fraction of the $\beta$ phase depends on the direction and the nature of applied stress. At a fixed temperature, the volumetric stress and the stress applied along the c-axis influences the time evolution of the $\beta$ phase, whereas it is unaffected by applied stress along the a- and b-axis directions. Furthermore, at any instant of time, compressive stresses...
applied volumetric and along the c-axis will increase the volume fraction of $\beta$ phase, whereas tensile stresses applied volumetric and along the c-axis is shown to decrease the volume fraction of $\beta$ phase.

The aforediscussed anisotropic and asymmetric influence of stress on the creep induced dynamic precipitation in Mg–Al alloys can be used to explain the asymmetric creep rate in these alloys. The resistance to creep is improved by the presence of finely dispersed precipitates with small aspect ratio and high number density, which are stable at high temperature. Unlike the precipitates developed by conventional ageing, which are large sized, highly elongated, and with low number density; the precipitates formed during dynamic precipitation are continuous, nanosized, closer to spherical or ellipsoidal in shape, and with high number density and low aspect ratio [9, 10, 18], as shown in Figure 1. Therefore, a microstructure with higher volume fraction of the dynamically formed precipitates will have lower creep rate. Our calculations show that the overall volume fraction of the dynamically formed precipitates, and thus the creep rate is strongly influenced by directionality and the type of stress. Specifically, when the stress is volumetric or along the c-axis direction, the volume fraction of the $\beta$ phase particles will be greater in compression than in tension, and thereby a higher creep rate will be observed in tensile creep experiments than in compressive creep, as observed in [4, 5]. However, there is no significant influence of stress along the a and b directions on the creep rate.

5 Concluding remarks

Summarizing, we have used a first principles derived temperature-, strain- and concentration-dependent free energy density to model dynamic precipitation of the $\text{Mg}_{17}\text{Al}_{12}$ phase during creep in Mg–Al alloys. Our
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calculations have showed that the overall volume fraction of the dynamically formed precipitates is influenced by stress, and furthermore, this influence is anisotropic and asymmetric. Specifically, when the stress is along the volumetric or along the c-axis direction, the volume fraction of the precipitate phase is greater in compression and lower in tension, whereas stress along the a- or b-axis directions do not alter the volume fraction of the precipitates. Overall, our results explain the tension compression asymmetry of the creep rate observed in creep experiments of Mg–Al alloys [4,5]. The resistance to creep is improved by the presence of finely dispersed precipitates with small aspect ratio and high number density. A greater volume fraction of these particles are produced during compressive creep tests than tensile creep experiments, and thereby explaining the higher creep rate observed in tension than in compression in these alloys. Finally, we have considered a single crystal Mg–Al alloy sample in this work. In most cases, dynamic precipitation experiments are performed in polycrystalline samples where the stress is not homogeneously distributed across the grains. Our future direction of research includes extending the scope of the current work to polycrystalline samples.

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