



## A unified constitutive model for multiphase precipitation and multi-stage creep ageing behavior of Al–Li–S4 alloy

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**Abstract:** A unified constitutive model is presented to predict the recently observed “multi-stage” creep behavior of Al–Li–S4 alloy. The corresponding microstructural variables related to the yield strength and creep deformation of the alloy during the creep ageing process, including dislocations and multiple precipitates, have been characterized in detail by X-ray diffraction (XRD) and transmission electron microscopy (TEM). For the yield strength, the model considers the multiphase strengthening behavior of the alloy based on strengthening mechanisms, which includes shearable  $T_1$  precipitate strengthening, non-shearable  $T_1$  precipitate strengthening and  $\theta'$  precipitate strengthening. Based on creep deformation mechanism, the “multi-stage” creep behavior of the alloy is predicted by introducing the effects of interacting microstructural variables, including the radius of multiple precipitates, dislocation density and solute concentration, into the creep stress–strain model. It is concluded that the results calculated by the model are in a good agreement with the experimental data, which validates the proposed model.

**Key words:** constitutive modelling; Al–Li–S4 alloy; creep age forming; microstructures; numerical algorithms

### 1 Introduction

Creep age forming is an advanced metal forming technique originally developed to manufacture large aluminum components in aircraft and aerospace industry [1]. This method utilizes the heating and pressurizing capabilities of an autoclave in combination with special tools to exploit the basic creep phenomenon that occurs during the artificial ageing of metals [2]. In order to significantly improve the forming accuracy and mechanical performance of large complex components, the creep age forming (CAF) process

has been widely studied in recent years [3–6]. During the CAF process, stress-induced deformation and artificial ageing occur simultaneously and interact with each other. This process determines the springback and mechanical properties of the formed components. Recent experiments revealed the “multi-stage” creep behavior of Al–Li–S4 alloys. Therefore, it is important to establish a constitutive model to predict the creep ageing behavior affected by various types of precipitates.

Precipitation hardened Al–Cu–Li alloys have excellent properties such as low density, high specific rigidity, high elastic modulus, high specific

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strength, good fatigue, good corrosion resistance and sound weldability [7,8]. Therefore, they have been widely used to manufacture structural components in the aerospace industry [7,9]. Al–Li–S4 alloy, the newest third generation Al–Li alloy launched by Alcoa Inc. in 2011, has been used in thin-walled components such as fuselage and lower wings [10]. The Al–Cu–Li alloys with the major solute elements of Cu and Li and minor solute additions of Mg and Ag show a complicated precipitation sequence [11]. The binary Al–Cu system involves Guinier–Preston (GP) zones,  $\theta''$  and  $\theta'$ . The Al–Li system forms the  $\delta'$  precipitate with the nominal composition of  $\text{Al}_3\text{Li}$ . The tertiary system generates the main strengthening  $T_1$  precipitate with the nominal composition of  $\text{Al}_2\text{CuLi}$ , which forms thin platelets on  $\{111\}$  planes of the Al matrix. The  $T_1$  precipitate was initially thought to be hardly shearable. However, recent experiments revealed that the  $T_1$  precipitate can be sheared by dislocation [12]. Therefore, the contribution of  $T_1$  precipitate to the strength of the alloy should be divided into shearable and non-shearable parts.

In recent decades, the constitutive modelling of the CAF process involving creep deformation and strengthening mechanisms has attracted extensive attentions. Many age hardening and creep damage variables were introduced to precisely predict the creep behavior during CAF process. KOWALEWSKI et al [13] developed a creep constitutive model by introducing two variables for the damage caused by creep cavitation and overaging. They showed that the developed equations can accurately describe the strain rate and fracture behavior in a narrow stress range. HO et al [14] established a unified creep ageing constitutive model, which could simultaneously demonstrate creep deformation and age-hardening behavior of Al alloys. With the increasing understanding of the microstructural evolution of Al alloys during the CAF process, some of the newly established creep constitutive models have made remarkable improvements in modeling the evolution of microstructures and yield strength of Al alloys. LI et al [15] developed a unified creep-ageing constitutive model for the 7B04 Al alloy, which investigated the effects of the relative volume fraction and the mean radius of precipitates on the creep rate and yield strength. ZHAN et al [16]

recently proposed a unified creep ageing constitutive equation, which can simulate the evolution of precipitates, dislocation hardening, solid solution hardening and precipitation hardening and yield strength of Al alloys during the CAF process. The obtained simulation results were in good agreement with the experimental data. LI et al [17] introduced the interactions among precipitates, solutes and dislocations. Moreover, they presented the concepts of the threshold stress to construct a unified constitutive model for asymmetric tensile and compressive creep ageing behavior of the Al–Cu–Li alloy (AA2050). They also accurately described the evolutions of the average diameter of  $T_1$  precipitates, yield strength and creep rate. Moreover, some of the models were successfully implemented into the finite element software to model the forming behavior and springback of components during the CAF process [18–20].

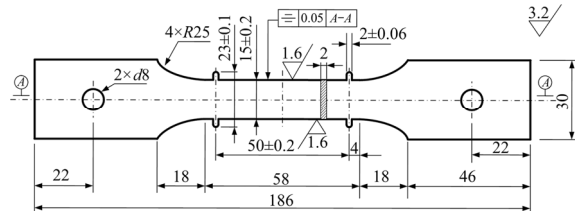
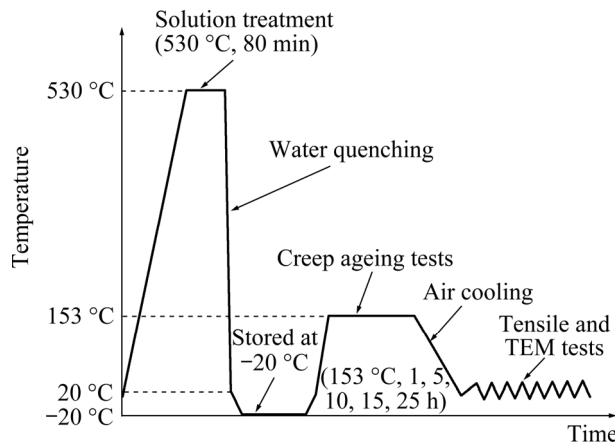
The existing models mainly consider the total effect of the precipitation strengthening on yield strength. However, there are few reports on the constitutive model that can describe the creep rate, strength and microstructure evolution of Al–Cu–Li alloys with multiphase under different stress levels. In the present study, a unified creep ageing constitutive model for Al–Li–S4 alloy under different stress levels is developed, which can demonstrate the morphological evolution of  $T_1$  and  $\theta'$  phases.

## 2 Experimental

Table 1 presents the chemical compositions of the 2 mm-thick commercial Al–Li–S4 plate used in this study. Dog-bone-shaped tensile specimens were cut from the plate using an electrical discharge machine with the loading direction parallel to the rolling direction. Figure 1 shows the geometric dimensions of the specimen. The process diagram of the whole heat treatment and test conditions is shown in Fig. 2. Specifically, the samples were initially solution-treated in a resistance furnace at 530 °C for 80 min, and immediately water quenched. The temperature deviation of the furnace was less than 2 °C during solution treatment, and it took less than 20 s to carry samples from the furnace to the water tank. In order to reduce the effects of natural ageing, these samples were stored at –20 °C before creep tests.

**Table 1** Chemical compositions of Al–Li–S4 aluminum alloy (wt.%)

Cu	Mg	Mn	Fe	Si
3.64	0.71	0.29	0.028	0.014
Zn	Zr	Li	Ti	Al
0.36	0.12	0.69	0.026	Bal.

**Fig. 1** Geometry of creep specimen (Unit: mm)**Fig. 2** Schematic diagram showing heat treatment and test conditions

Uniaxial tensile creep tests were carried out on an RDL50 creep machine equipped with a furnace, and the tests were carried out at 153 °C under constant stresses of 200, 220 and 240 MPa for 1, 5, 15, 20 and 25 h, respectively. The specimen was first heated to 153 °C at a heating rate of 4 °C/min, and kept for 10 min in resistance heating furnace. Then, the exterior stress was smoothly loaded at a rate of 15 N/s using computer-aided controlling system. When the experiment was finished, all specimens were cooled to room temperature in the air. Tensile tests were carried out using a DDL100 electronic testing machine at a strain rate of 2 mm/min at room temperature. Three tensile tests were performed to obtain an average value.

The microstructural evolution of Al–Li–S4 alloys was characterized by scanning transmission electron microscopy (STEM) and XRD. STEM samples were first mechanically thinned to 60–80  $\mu\text{m}$  using metallographic sandpapers. Then,

the samples were cut into 3 mm-diameter discs and finally thinned by the twin-jet electropolishing using a solution of 80% methanol and 20% nitric acid at approximately  $-25$  °C, with a potential of 14 V. Aberration corrected high angle annular dark field (HAADF) TEM observations were carried out on a Tecnai-F20 operated at 200 kV. The XRD samples are cut from the middle part of the creep-aged samples by an electrical discharge machine and mechanically polished and thinned to the size of 5 mm  $\times$  5 mm  $\times$  1 mm. The XRD tests are conducted on an advance D8 X-ray diffractometer with a scan range ( $2\theta$ ) from 20° to 90° and a speed of 0.02° for each step. Three XRD tests are performed to obtain an average value of the peak full width at half maximum (FWHM).

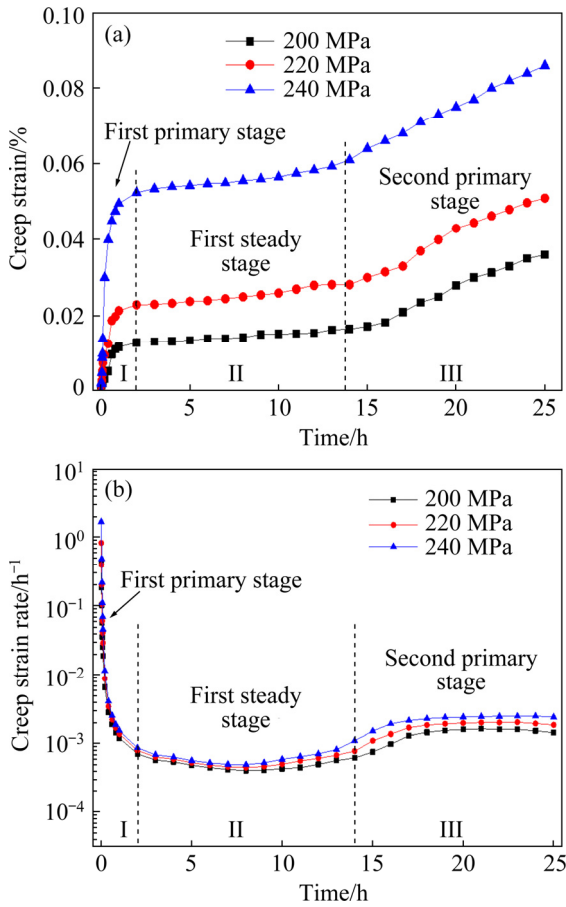
### 3 Results

#### 3.1 Creep behavior

Figure 3(a) shows the creep strain curves of Al–Li–S4 alloys at 153 °C under applied stresses of 200, 220 and 240 MPa for 25 h. The corresponding creep strain rate curves of the alloy are shown in Fig. 3(b). It is observed that all creep strain curves exhibit “multi-stage” behavior during the creep ageing (CA) process. According to the trend of creep strain rate during CA process [21], the creep strain curves demonstrate a special three-stage (I, II and III) phenomenon, including the first primary CA stage (Stage I), the first steady CA stage (Stage II), and the second primary CA stage (Stage III). It is worth noting that the creep rate of the alloy in Stage III tends to be constant, which is different from the traditional tertiary creep stage where the creep rate increases rapidly. More details of the experimental setup and results can be found in the study of MA et al [22]. The “multi-stage” creep feature is reported to be mainly controlled by the microstructural evolution, including dislocations, solutes and precipitates [21,22].

#### 3.2 Dislocations density evolution during CA process

During the CA process, it is difficult to quantitatively analyze the dislocation density by TEM. In addition, some dislocations are easily interfered and covered by the precipitates [23]. According to the study of RODGERS and PRANGNELL [23] and UNGÁR et al [24], the



**Fig. 3** Creep strain curves (a) and creep strain rate curves (b) of Al-Li-S4 alloy under different applied stresses at 153 °C for 25 h

dislocation density can be calculated by the modified Williamson-Hall plot, which is mathematically described as Eq. (1):

$$\Delta K \approx 0.9/D_a + (\pi M^2 b^2 / 2)^{1/2} \rho^{1/2} K \bar{C}^{1/2} \quad (1)$$

$$K = 2 \sin \theta / \lambda \quad (2)$$

$$\Delta K = 2 \cos \theta \cdot \Delta \theta / \lambda \quad (3)$$

where  $D_a$  is the average grain size,  $M$  is a constant depending on the effective outer cut-off radius of dislocations,  $b$  is the magnitude of Burgers vector (0.286 nm for aluminium),  $\rho$  is the dislocation density,  $\theta$  is the diffraction angle,  $\lambda$  is the wavelength of X-rays,  $\Delta \theta$  is the full width at half maximum (FWHM),  $K$  is the diffraction constant,  $\Delta K$  is the strain broadened FWHM in the reciprocal space, and  $\bar{C}$  is the average contrast factor for each particular plane ( $hkl$ ) given by

$$\bar{C} = \bar{C}_{h00} (1 - qH^2) \quad (4)$$

where  $H^2$  and  $\bar{C}_{h00}$  denote the fourth-order ratio

and the average contrast factor corresponding to the ( $h00$ ) reflection, respectively. Moreover,  $q$  represents different broadening anisotropies, and its value depends on whether dislocations are edge or screw in the character [24,25]. It is worth noting that the value of  $\bar{C}_{h00}$  can vary significantly between the edge and screw dislocations. In order to simplify the algorithm, it is assumed that the distribution of both edge dislocations and screw dislocations is uniform. According to the study of UNGÁR et al [24], the average values of  $\bar{C}_{h00}$  and  $q$  are 0.40 and 2.3369, respectively.

According to the study of WILLIAMSON and HALL [26], the quadratic form of the modified Williamson-Hall plot was written as

$$(\Delta K)^2 \approx (0.9/D_a)^2 + (\pi M^2 b^2 / 2) \rho K^2 \bar{C} \pm O(K^4 C^2) \quad (5)$$

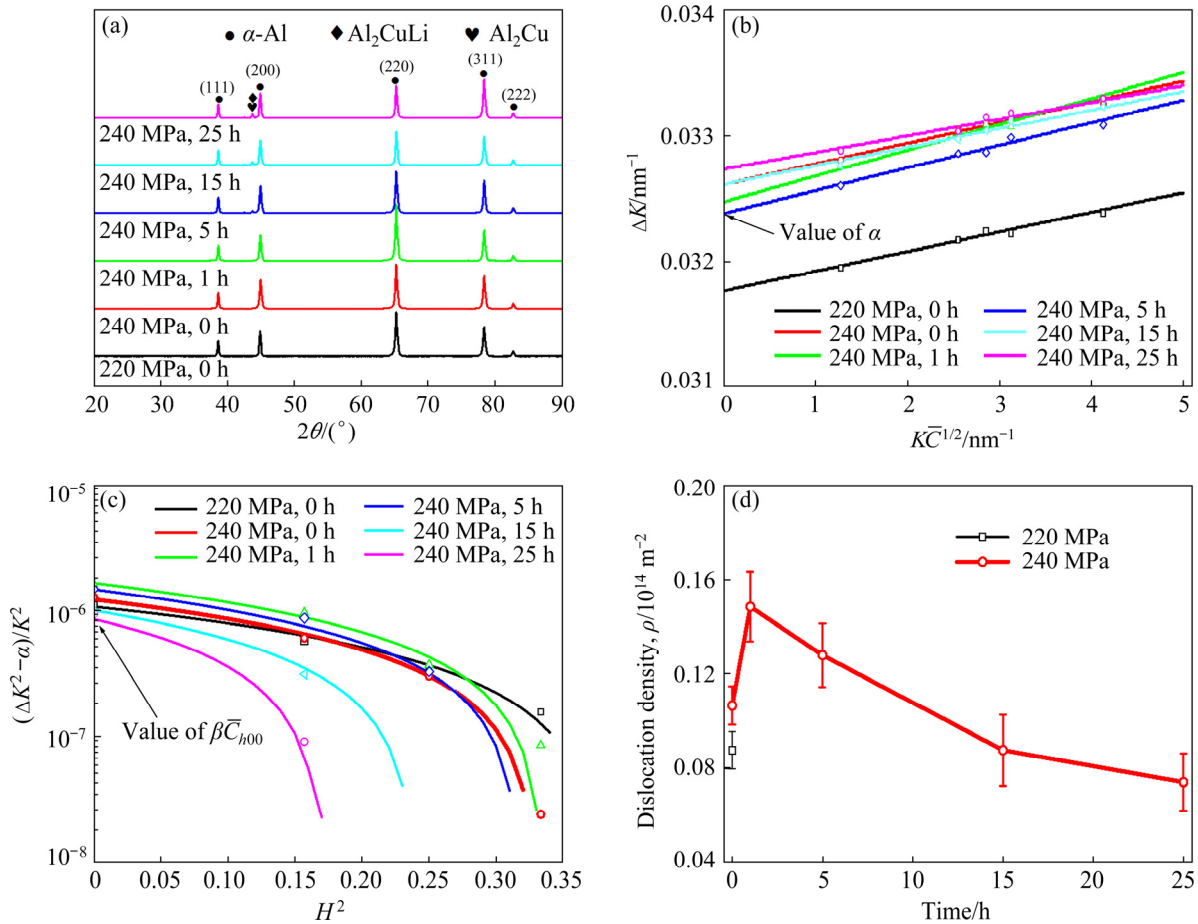
where  $O(K^4 C^2)$  denotes non-interpreted higher-order term. Substituting Eq. (4) into Eq. (5) yields

$$\frac{\Delta K^2 - \alpha}{K^2} \approx \beta \bar{C}_{h00} (1 - qH^2) \quad (6)$$

$$\rho = \frac{2\beta}{\pi M^2 b^2} \quad (7)$$

where  $\alpha = (0.9/D_a)^2$  and  $\beta = \pi M^2 b^2 \rho / 2$ . The value of  $\beta \bar{C}_{h00}$  can be determined by the linear regression of  $(\Delta K^2 - \alpha)/K^2$  versus  $H^2$ .

Figure 4(a) presents the X-ray diffraction curves of the selected samples under 220 MPa for 0 h and under 240 MPa for 0, 1, 5, 15 and 25 h, respectively. Moreover, it is found that the diffraction peaks of  $T_1$  and  $\theta'$  phases increase gradually during the CA process, which indicates that  $T_1$  and  $\theta'$  precipitates nucleate and grow gradually. The XRD spectra of Al-Li-S4 alloy are analyzed with the JADE software to obtain the value of FWHM and the diffraction angle  $\theta$ . The parameters of  $\alpha$  and  $\beta \bar{C}_{h00}$  corresponding to the five diffraction peaks of each X-ray diffraction curve are fitted by the least square method. Furthermore, the value of the dislocation density  $\rho$  is calculated by Eq. (7). Figures 4(b-d) show the values of  $\alpha$ ,  $\beta \bar{C}_{h00}$  and  $\rho$ , respectively. Three XRD tests are performed to obtain an average value. As shown in Fig. 4(d), dislocation density of the selected samples under 240 MPa increases rapidly at 1 h and decreases significantly from 5 to 15 h. Then, the dislocation density decreases slightly until the end of the CA process. Besides, when the



**Fig. 4** X-ray diffraction patterns of Al–Li–S4 alloy under different stresses for different time (a), value of  $\alpha$  from Eq. (1) (b), value of  $\beta\bar{C}_{h00}$  from Eq. (6) (c), and dislocation density  $\rho$  according to Eq. (7) (d)

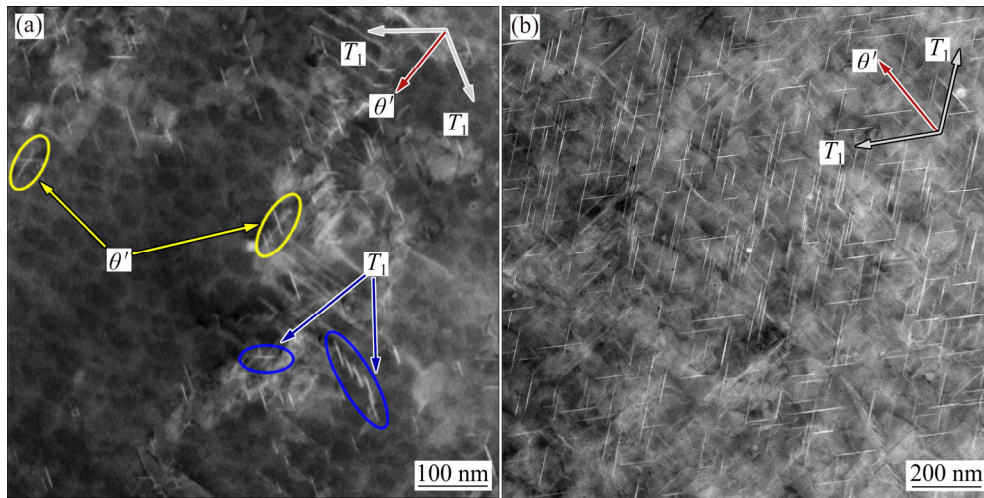
applied stress is 240 MPa, 0.65% plastic deformation is generated in the sample, which increases the dislocation density of the sample. Therefore, the initial dislocation density of the specimen under 220 MPa is lower than that under 240 MPa.

### 3.3 Precipitates evolution

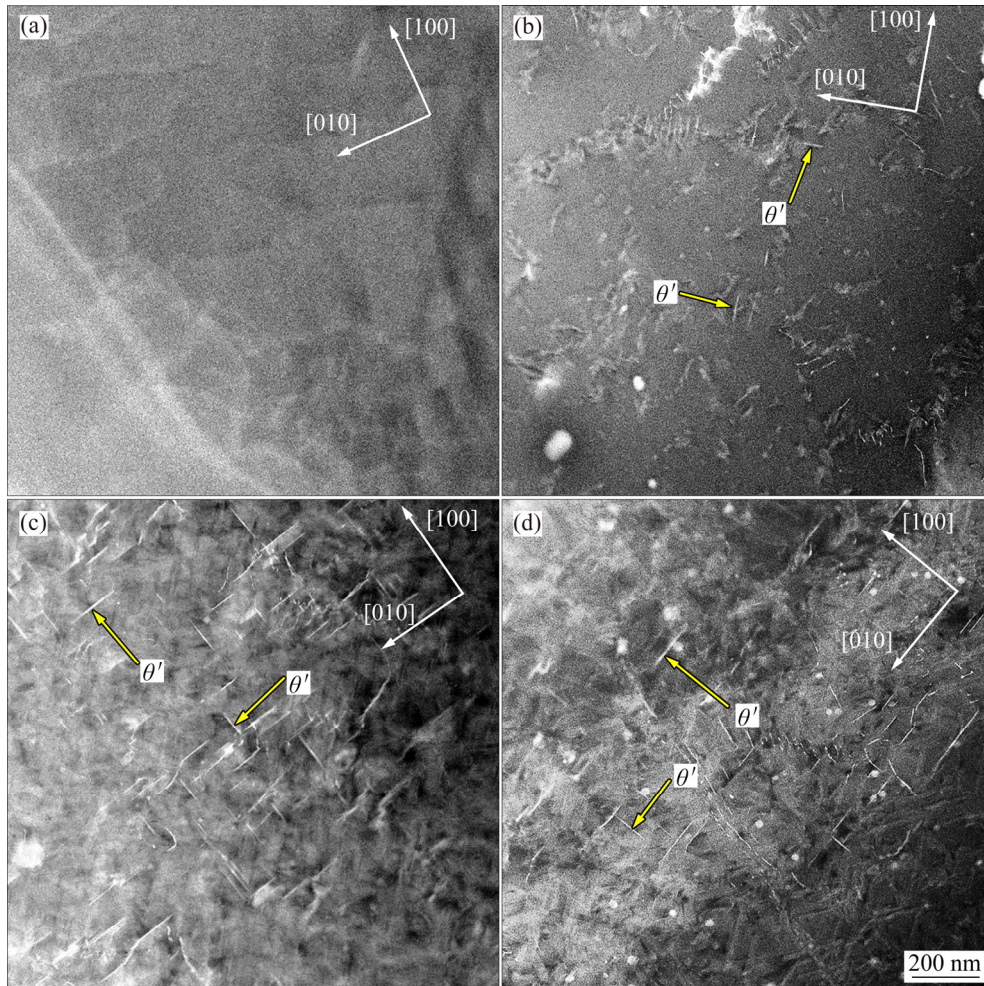
Figures 5(a, b) show TEM images of the distributions of  $T_1$  and  $\theta'$  precipitates of the selected samples under 240 MPa at 153 °C for 5 and 25 h, respectively. It should be indicated that all images were taken along  $\langle 110 \rangle$  matrix zone axis. There are four variants of  $T_1$  precipitate lying on the  $\{111\}_{\text{Matrix}}$  planes and three variants of  $\theta'$  precipitate lying on the  $\{100\}_{\text{Matrix}}$  planes. Under the TEM observation along the  $\langle 110 \rangle$  matrix zone axis of Al matrix, two variants of the  $T_1$  precipitate and one variant of  $\theta'$  precipitate are in the edge-on configuration. The angle between the two variants of  $T_1$  precipitate is 109.4° and the variant of the  $\theta'$  precipitate is on the angle bisector of the two

variants of  $T_1$  precipitate. Furthermore, the crystallographic orientations are indicated at the upper right of each graph, which was also demonstrated in an earlier study [22]. It can be seen from Fig. 5 that  $T_1$  and  $\theta'$  precipitates play an important role in the strengthening behavior of the alloy during the CA process.

Figure 6 presents the HAADF-STEM images of Al–Li–S4 alloys taken along  $\langle 100 \rangle$  matrix zone axis. All samples in Figs. 6(a–d) are aged at 153 °C under 240 MPa for 1, 5, 15 and 25 h, respectively. Figure 6(a) shows that the matrices are very pure without any precipitates. Moreover, it is found that a large number of dislocations caused by the plastic deformation during the creep loading stage distribute uniformly in the matrices. In Fig. 6(b), a small quantity of  $\theta'$  precipitates appear in the crystal. In Fig. 6(c), a large number of  $\theta'$  precipitates are generated along with a close-packed  $\{001\}_{\text{Matrix}}$  habit plane and distribute uniformly. In Fig. 6(d), the size and number of  $\theta'$  phases are reduced compared with those of the alloy aged for 15 h,



**Fig. 5** HAADF-STEM images of Al-Li-S4 alloy during CA process under stress of 240 MPa for 5 h (a) and 25 h (b) (All images were taken along  $(110)$  matrix zone axis)



**Fig. 6** TEM images of selected specimens under stress of 240 MPa at 153 °C for 1 h (a), 5 h (b), 15 h (c) and 25 h (d) (All images were taken along  $(100)$  matrix zone axis)

which is also consistent with the results reported about Al-Cu-Li alloys [27]. According to RODGERS and PRANGNELL [23], the higher the

dislocation density is, the more homogeneously the  $T_1$  precipitates distribute, and the higher the volume fraction of  $T_1$  precipitate is. When  $T_1$  precipitates

nucleate and grow up, the formation of  $T_1$  precipitates consumes much Li and Cu atoms, thereby reducing  $\theta'$  precipitates.

### 4 Constitutive modelling

In the present study, a unified creep ageing constitutive model is developed for the analysis and simulation of the correlation between material properties and corresponding microstructural variables of the aluminum alloy. There are many kinds of precipitates in Al–Li–S4 alloy, including  $T_1$ ,  $\theta'$  and  $\delta'$  phases. Compared with the single kind of precipitate of 2219 aluminum alloy [28], the evolution of microstructures of Al–Li–S4 alloy during the CA process is more complicated. In order to accurately describe the creep deformation and ageing strengthening behavior of the alloy, the effects of the dislocation density  $\rho$  and two kinds of the main precipitates ( $T_1$  and  $\theta'$ ) on the creep ageing behavior are comprehensively considered in this study. For the purpose of simplification, the profiles of  $T_1$  and  $\theta'$  precipitates are in the same plate shape [17,28]. Figure 7 shows the corresponding geometrical model. In order to describe the variation law of the plate-shaped precipitates in the aluminum alloy, the necessary parameters are average diameter  $D$ , average thickness  $T$  and relative volume fraction  $f_v$  of the precipitate.

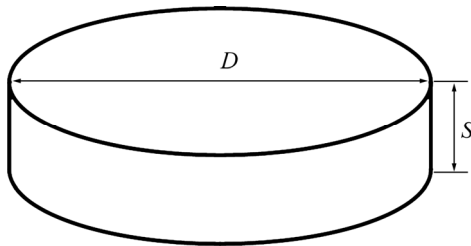


Fig. 7 Geometrical model for plate-shaped  $T_1$  and  $\theta'$  precipitates

#### 4.1 Model for dislocation density evolution

It should be indicated that dislocation movement generally dominates the plastic deformation. Therefore, the evolution of dislocation density plays a key role in the creep behavior during the CA process. The evolution of the dislocation density  $\rho$  during the CA process is determined by two parts, including the dislocation accumulated before the CA process  $\rho_i$  and the dislocation developed with the creep deformation  $\rho_c$ , which can be expressed with Eq. (8) [17]:

$$\rho = \rho_i + \rho_c \tag{8}$$

A number of dislocations can be initially produced during the loading stage when the applied stress is higher than the initial yield strength of the material. The dislocation density  $\rho_i$  generated before the CA process can be divided into two parts, including dislocations generated by quenching and the applied stress during the loading stage. The dislocation density can be expressed as [29]

$$\rho_i = \rho_0 + c_{17} \exp[c_{18}(1 + (\sigma - \sigma_{0.2})/\sigma_{0.2})] \tag{9}$$

$$\bar{\rho} = \rho_i / \rho_{total} \tag{10}$$

where  $c_{17}$  and  $c_{18}$  are the material-related constants.  $\sigma_{0.2}$  and  $\rho_0$  denote the initial yield strength of the material before the loading stage and the dislocation density caused by quenching, respectively. It should be indicated that  $\rho_0$  is assumed to be  $0.05 \times 10^{14} \text{ m}^{-2}$ . Dislocation density  $\bar{\rho}_i$  is normalized by dividing  $\rho_i$  by  $\rho_{total}$  in Eq. (10).  $\rho_{total}$  is the saturated dislocation density. According to the study of LI et al [21], there is a limit of the pre-stretch level. Above this limit, the age hardening progress would be hardly affected by further increasing pre-stretch levels. More specifically, for the Al–2.45Cu–2.45Li alloy, the limit is about 6%. For the sake of simplicity, its value is equal to the dislocation density generated by the 6% pre-deformation ( $0.43 \times 10^{14} \text{ m}^{-2}$ ).

The evolution of the dislocation density during the CA process is determined by two factors, including the dislocation multiplication caused by creep deformation and dynamic recovery during the CA stage at relatively high temperature [16]. The evolution of the dislocation density has been modelled in many previous publications [17,29]. Moreover, its rate can be described as

$$\dot{\bar{\rho}}_c = c_{19}(1 - \bar{\rho})|\dot{\epsilon}_c|^{m_{13}} - c_{20}\bar{\rho}^{n_{13}} \tag{11}$$

where  $c_{19}$ ,  $c_{20}$ ,  $m_{13}$  and  $n_{13}$  are the material-related constants, and  $\dot{\epsilon}_c$  is the creep rate. Equation (11) is composed of two parts. The first part of  $c_{19}(1 - \bar{\rho})|\dot{\epsilon}_c|^{m_{13}}$  means dislocation multiplication caused by the creep deformation, and  $\bar{\rho}_c$  is the normalized dislocation density in the CA process. The second part of  $-c_{20}\bar{\rho}^{n_{13}}$  denotes the dislocation dynamic recovery.

#### 4.2 Model for precipitate growth

For the multiple types of precipitate distribution of Al–Li–S4 alloys, the  $T_1/\theta'$

competition during the CA process should be considered at different applied stress levels. As discussed before, the growth of both  $\theta'$  and  $T_1$  phases consumes Cu atoms in the Al matrix, while  $T_1$  precipitation continues consuming  $\theta'$  during the CA process [27]. Moreover, there are two types of  $T_1$  precipitates, including shearable and non-shearable ones, which affect the mechanical properties and creep behavior of the alloy. For the purpose of simplification, three assumptions are made: (1) In the CA process,  $T_1$  precipitate with the thickness less than 3 nm is shearable, while it is non-shearable with the thickness greater than 3 nm [30]. (2) The volume fraction of plate-shaped  $T_1$  and  $\theta'$  precipitates under homogeneous nucleation satisfies the same evolution laws [17]. (3) The dissolved volume fraction of  $\theta'$  precipitate is all converted to  $T_1$  precipitate. Moreover, the non-shearable  $T_1$  precipitate evolves from the shearable  $T_1$  precipitate.

#### 4.2.1 Relative volume fraction of $T_1$ and $\theta'$ precipitates

During the CA process, the supersaturated solute atoms are gradually consumed to form precipitates from the Al matrix [28]. According to the study of LIU et al [31], the volume fraction of plate-shaped  $T_1$  and  $\theta'$  precipitates under the homogeneous nucleation conditions can be mathematically expressed as

$$f_v = \frac{\pi D^2 S}{4} R N_0 Z \beta^* \exp\left(\frac{-\Delta G}{kT}\right) t \quad (12)$$

where  $D$  and  $S$  are average length and thickness of precipitates, respectively.  $R$  is the Avogadro number,  $N_0$  is the number of mole by unit volume,  $Z$  is the Zeldovich's factor ( $\approx 0.05$ ),  $\beta^*$  is material parameter,  $k$  is the Boltzmann constant,  $T$  is the ageing temperature,  $\Delta G$  is the critical activation energy for precipitation, and  $t$  is the ageing time.

In order to simplify the modeling process, a more general parameter named the normalized volume fraction is introduced:

$$\begin{cases} \bar{f}_v = f_v / f_{v-\max} \\ \bar{f}_v = f_{v-\theta'} + f_{v-T} \\ \dot{\bar{f}}_v = \dot{f}_{v-\theta'} + \dot{f}_{v-T} \end{cases} \quad (13)$$

where  $f_v$  is the current absolute volume fraction of both  $T_1$  and  $\theta'$  precipitates.  $f_{v-\max}$  is the maximum sum of the volume fraction of  $T_1$  and  $\theta'$  precipitates.

$\dot{f}_v$ ,  $\dot{f}_{v-\theta'}$  and  $\dot{f}_{v-T}$  are corresponding current relative volume fraction rates of different precipitates, respectively. In the CA process, the parameter  $\beta^*$  and the activation energy  $\Delta G$  of  $T_1$  and  $\theta'$  precipitates are different, which depends on temperature, ageing time, and dislocation density. According to the abovementioned data and relevant research of ZHANG et al [32], the evolution of the relative volume fraction of  $\theta'$  precipitate can be expressed as

$$\dot{f}_{v-\theta'} = c_1 \dot{D}_{\theta'} D_{\theta'}^2 S_{\theta'} (1 + k_6 \bar{\rho}^{n_4}) (1 - \bar{f}_{v-\theta'})^{m_3} - c_2 \dot{f}_{v-\theta'}^{m_4} \quad (14)$$

where  $c_1$ ,  $c_2$ ,  $m_3$ ,  $m_4$ ,  $n_4$  and  $k_6$  are the material-related constants.  $\dot{D}_{\theta'}$ ,  $D_{\theta'}$  and  $S_{\theta'}$  denote the average diameter evolution rate, the average diameter and average thickness evolution of  $\theta'$  precipitate, respectively. The first term  $c_1 \dot{D}_{\theta'} D_{\theta'}^2 S_{\theta'} (1 + k_6 \bar{\rho}^{n_4}) (1 - \bar{f}_{v-\theta'})^{m_3}$  plays a dominant role in describing the increasing process of the relative volume fraction of the  $\theta'$  precipitate, which leads to a decreasing rate with time. Moreover, the second term  $-c_2 \dot{f}_{v-\theta'}^{m_4}$  controls the dissolution process of the  $\theta'$  precipitate, which can be transformed into the  $T_1$  precipitate. According to the previous study of MA et al [29], the relative volume fraction of the shearable and non-shearable  $T_1$  precipitates can be expressed as Eqs. (15) and (16), respectively:

$$\begin{aligned} \dot{f}_{v-T_s} = & c_3 \dot{D}_{T_s} D_{T_s}^2 S_{T_s} (1 + k_7 \bar{\rho}^{n_5}) (1 - \bar{f}_{v-T_s})^{m_5} + \\ & c_4 c_2 \dot{f}_{v-\theta'}^{m_4} - c_5 \dot{f}_{v-T_s}^{m_6} \end{aligned} \quad (15)$$

$$\begin{aligned} \dot{f}_{v-T_{ns}} = & [c_5 \dot{f}_{v-T_s}^{m_6} + (1 - c_4) c_2 \dot{f}_{v-\theta'}^{m_4}] \cdot \\ & [1 + c_6 (1 + k_8 \bar{\rho}^{n_6}) (1 - \bar{f}_{v-T_{ns}})^{m_7}] \end{aligned} \quad (16)$$

where  $c_{2-6}$ ,  $m_{4-7}$ ,  $n_5$ ,  $n_6$ ,  $k_7$  and  $k_8$  are the material-related constants.  $\dot{f}_{v-T_s}$  and  $\dot{f}_{v-T_{ns}}$  are the current relative volume fraction rates of the shearable and non-shearable  $T_1$  precipitates, respectively.  $\dot{D}_{T_s}$  and  $\dot{D}_{T_{ns}}$  are the average diameter evolution rates of the shearable and non-shearable  $T_1$  precipitates, respectively.  $D_{T_s}$  and  $D_{T_{ns}}$  are the average diameters of the shearable and non-shearable  $T_1$  precipitates, respectively.  $S_{T_s}$  and  $S_{T_{ns}}$  are the average thicknesses of the shearable and non-shearable  $T_1$  precipitates, respectively.  $c_4 c_2 \dot{f}_{v-\theta'}^{m_4}$  indicates the relative volume fraction rate of shearable  $T_1$  precipitate transformed from  $\theta'$  precipitate, and  $-c_5 \dot{f}_{v-T_s}^{m_6}$  represents the relative volume fraction rate of non-shearable  $T_1$  precipitate



transformed from the shearable  $T_1$  precipitate in Eq. (15).  $c_5\bar{f}_{v-Ts}^{m_6}$  is the relative evolution rate of the non-shearable  $T_1$  precipitate, and  $(1-c_4)c_2\bar{f}_{v-\theta'}^{m_4}$  is the relative evolution rate of the non-shearable  $T_1$  precipitate transformed from  $\theta'$  precipitate.

#### 4.2.2 Average length of $T_1$ and $\theta'$ precipitates

During the CAF process, the variation of the precipitate length depends mainly on the dislocation density, ageing temperature and time. As the temperature is constant during the CA process, the influence of temperature is not taken into account. However, the decrease of  $\theta'$  average size caused by Cu atom transformed from  $\theta'$  to  $T_1$  should be considered. According to the researches [28,29], the evolution equation of the length of  $\theta'$  precipitate can be expressed as

$$\dot{D}_{\theta'} = c_7(Q_1 - D_{\theta'})^{m_8} (1 + k_9 \bar{\rho}^{n_7}) - c_8[\bar{f}_{v-\theta'} / (1 - c_9 \bar{f}_v)]^{m_9} \quad (17)$$

where  $c_{7-9}$ ,  $m_8$ ,  $m_9$ ,  $n_7$ ,  $k_9$  and  $Q_1$  are the material-related constants. The first term  $c_7(Q_1 - D_{\theta'})^{m_8} (1 + k_9 \bar{\rho}^{n_7})$  denotes the growth rate of the average length of  $\theta'$  precipitate, and the second term  $-c_8[\bar{f}_{v-\theta'} / (1 - c_9 \bar{f}_v)]^{m_9}$  denotes the influence of the dissolution on the length evolution rate of  $\theta'$  precipitate. Similarly, According to the study of YANG et al [28], the average length of the shearable and non-shearable  $T_1$  precipitates can be expressed as Eqs. (18) and (19), respectively:

$$\dot{D}_{Ts} = c_{10}(Q_2 - D_{Ts})^{m_{10}} (1 + k_{10} \bar{\rho}^{n_8}) \quad (18)$$

$$\dot{D}_{Tns} = c_{11}(Q_3 - D_{Tns})^{m_{11}} (1 - k_{11} \bar{\rho}^{n_9}) \quad (19)$$

where  $c_{10}$ ,  $c_{11}$ ,  $m_{10}$ ,  $m_{11}$ ,  $n_8$ ,  $n_9$ ,  $k_{10}$ ,  $k_{11}$ ,  $Q_2$  and  $Q_3$  are the material-related constants. According to aforementioned data and relevant investigation of HU et al [33], during the CA process, the dislocation density in the material gradually increases as the creep stress increases, which gradually reduces the average length of the non-shearable  $T_1$  precipitate. The second item on the right side of Eq. (19)  $(1 - k_{11} \bar{\rho}^{n_9})$  represents the influence of the dislocation on the growth of the non-shearable  $T_1$  precipitate.

#### 4.2.3 Average thickness of $T_1$ and $\theta'$ precipitates

Precipitate thickness is also an important parameter for precipitation hardening potential [29]. It should be indicated that during the isothermal CA process, the precipitate grows mainly by the volume diffusion mechanism. According to Fick's second

law of diffusion, the growth rate of the precipitate thickness is proportional to the  $(-1/2)$  power of time. Considering the dissolution factor of  $\theta'$  precipitate and the effect of the dislocation, and according to the study of MA et al [29], the thickness evolution of  $\theta'$  precipitate can be expressed as

$$\dot{S}_{\theta'} = c_{12}t^{-1/2} (1 + k_{12} \bar{\rho}^{n_{10}}) - c_{13}[\bar{f}_{v-\theta'} / (1 - c_{14} \bar{f}_v)]^{m_{12}} \quad (20)$$

where  $c_{12-14}$ ,  $m_{12}$ ,  $n_{10}$  and  $k_{12}$  are the material-related constants.  $\dot{S}_{\theta'}$  is the average thickness rate evolution of  $\theta'$  precipitate. The first term  $c_{12}t^{-1/2} (1 + k_{12} \bar{\rho}^{n_{10}})$  and the second term  $-c_{13}[\bar{f}_{v-\theta'} / (1 - c_{14} \bar{f}_v)]^{m_{12}}$  denote the growth rate of the average thickness of  $\theta'$  precipitate and the influence of dissolution of  $\theta'$  precipitate on thickness evolution rate, respectively. Similarly, the average thickness of the sheared and non-sheared  $T_1$  precipitates can be expressed as Eqs. (21) and (22), respectively:

$$\dot{S}_{Ts} = c_{15}t^{-1/2} (1 + k_{13} \bar{\rho}^{n_{11}}) \quad (21)$$

$$\dot{S}_{Tns} = c_{16}t^{-1/2} (1 - k_{14} \bar{\rho}^{n_{12}}) \quad (22)$$

where  $c_{15}$ ,  $c_{16}$ ,  $n_{11}$ ,  $n_{12}$ ,  $k_{13}$  and  $k_{14}$  are the material-related constants.  $\dot{S}_{Ts}$  and  $\dot{S}_{Tns}$  are the average thickness evolution rates of the sheared and non-sheared  $T_1$  precipitates, respectively. According to abovementioned data and relevant research of HU et al [33], during the CA process, the dislocation density in the material gradually increases as the applied stress increases, which gradually reduces the average thickness of the non-shearable  $T_1$  precipitate. The second item  $(1 - k_{14} \bar{\rho}^{n_{12}})$  on the right side of Eq. (22) represents the influence of the dislocation on the average length of the non-shearable  $T_1$  precipitate.

### 4.3 Strengthening models

For heat-treatable strengthening aluminum alloys, the yield strength can be modelled according to a classic law of mixtures, including three strengthening components of precipitation hardening, dislocation hardening and solid solution hardening [17], which can be expressed as

$$\sigma_y = \sigma_{Al} + \sigma_{ss} + \sqrt{\sigma_{ppt}^2 + \sigma_{dis}^2} \quad (23)$$

where  $\sigma_{Al}$  is the aluminum matrix hardening (about 77 MPa), which is determined by the properties of

pure Al and the strengthening contribution originates from grain boundaries.  $\sigma_{ss}$ ,  $\sigma_{ppt}$  and  $\sigma_{dis}$  denote the solid solution hardening, the precipitation hardening and the dislocation hardening, respectively.

#### 4.3.1 Solid solution hardening

The solid solution hardening contributions can be represented as a function of the solid atom concentration in the aluminum matrix. Solid solution hardening can be decreased with the nucleation and growth of the precipitates. According to the existing literatures [28,32], it can be expressed

$$\sigma_{ss} = C_S (1 - \bar{f}_v)^{m_2} \quad (24)$$

where  $m_2$  and  $C_S$  are material constants.

#### 4.3.2 Precipitation hardening

The maximum strength and the hardness of Al–Cu–Li alloys are achieved through the precipitation hardening involving predominantly plate-shaped  $T_1$  and  $\theta'$  precipitates formed on rational habit planes  $\{111\}_\alpha$  and  $\{100\}_\alpha$  in  $\alpha(\text{Al})$  matrix, respectively [23,34].  $\theta'$  precipitate is non-shearable by dislocations with deformation [29]. However, the interaction mechanism of  $T_1$  precipitate and dislocation depends on the thickness of the  $T_1$  precipitate. When the thickness of the  $T_1$  precipitate is less than 3 nm, it can be sheared by dislocations, and it becomes non-shearable when the thickness is larger than 3 nm [35]. Moreover, the hardening contribution of the precipitates is determined by the absolute volume fraction that can be converted from the relative values multiplied by the maximum absolute volume fraction [29]. With the extension of ageing time,  $\theta'$  precipitate can gradually convert to  $T_1$  precipitate [27]. Moreover, the precipitate in the alloy is mainly  $T_1$  phase. In order to simplify the model, the maximum volume fraction of the precipitate is considered to be approximately equal to that of the  $T_1$  precipitate, and according to previous studies [23,33], the maximum volume fraction  $f_{\max}$  of  $T_1$  precipitate is approximately 0.27%. It is necessary to analyze the hardening contribution of  $T_1$  and  $\theta'$  precipitates, respectively. According to the literature [36], the overall precipitate hardening  $\sigma_{ppt}$  is calculated as

$$\sigma_{ppt} = M (\Delta\tau_{Ts}^{1.4} + \Delta\tau_{Tns}^{1.4} + \Delta\tau_{\theta'}^{1.4}) \quad (25)$$

where  $M$  is the Taylor factor and its value is 3.331,  $\Delta\tau_{\theta'}^{1.4}$  is the hardening contribution of  $\theta'$

precipitate,  $\Delta\tau_{Ts}^{1.4}$  is the hardening contribution of  $T_1$  precipitate which can be sheared by dislocations,  $\Delta\tau_{Tns}^{1.4}$  is the hardening contribution of the non-sheared  $T_1$  precipitate. The  $\theta'$  precipitate tends to be bypassed when interacting with the dislocation during the CA process, and its hardening contribution is calculated with Eq. (26) [34]:

$$\Delta\tau_{\theta'} = \frac{Gb}{2\pi\sqrt{1-\nu}} \ln(1.225S_{\theta'}/r_i) / [0.931\sqrt{(0.306\pi D_{\theta'} S_{\theta'}) / (\bar{f}_{v-\theta'} f_{\max})} - \pi D_{\theta'} / 8 - 1.061S_{\theta'}] \quad (26)$$

where  $G$  and  $b$  denote the shear modulus of the Al matrix and the magnitude of Burgers vector of the slip dislocations, respectively;  $\nu$  and  $r_i$  denote the Poisson ratio and the inner cut-off distance, respectively. It is worth noting that the hardening contribution of the shearable  $T_1$  precipitate is  $\Delta\tau_{Ts}$  which can be expressed as [34]

$$\Delta\tau_{Ts} = \frac{1.211D_{Ts}}{S_{Ts}^2} \left( \frac{b\bar{f}_{v-Ts} f_{\max}}{\Gamma} \right)^{1/2} \gamma_i^{3/2} \quad (27)$$

$$\Gamma = (Gb/2\pi) \ln(r_0/r_i) \quad (28)$$

$$r_0 = D_{Ts} / \sqrt{2\bar{f}_{v-Ts} f_{\max}} \quad (29)$$

where  $\gamma_i$  is the interfacial energy between  $T_1$  and the Al matrix,  $\Gamma$  is the dislocation line tension, and  $r_0$  represents the outer cut-off distance. The hardening contribution of non-sheared  $T_1$  phase is  $\Delta\tau_{Tns}$ , which can be expressed as [34]

$$\Delta\tau_{Tns} = \frac{Gb}{2\pi\sqrt{1-\nu}} \ln(1.061S_{Tns}/r_0) / [0.931\sqrt{(0.265\pi D_{Tns} S_{Tns}) / (\bar{f}_{Tns} f_{\max})} - \pi D_{Tns} / 8 - 0.91S_{Tns}] \quad (30)$$

#### 4.3.3 Dislocation hardening

Dislocation hardening is essentially caused by the plastic deformation, which increases with the dislocation density. Many investigations have been conducted to model this phenomenon based on the evolution of the dislocation density [37,38]. Dislocation hardening can be mathematically expressed as

$$\sigma_{dis} = C_{dis} \bar{\rho}^{n_3} \quad (31)$$

where  $C_{dis}$  and  $n_3$  are material constants.

#### 4.4 Creep strain–stress correlation

The creep behavior of Al–Li–S4 alloy during the CAF process, which has been studied previously [22,33], demonstrates a novel “multi-stage” creep feature with three creep stages. This new feature is introduced in Section 3.1 and discussed in detail in the study of LI et al [17]. The evolution of three micro-structural parameters, radius of multiple precipitates, dislocation density and solute concentration, contribute to the new “multi-stage” creep feature of the alloy. Therefore, the creep strain–stress correlation is established as

$$\dot{\varepsilon}_c = A \sinh[B(\sigma - \sigma_0)I] \quad (32)$$

$$I = (1 + k_1 \bar{\rho}^{n_1})(k_0 - k^* \bar{C}^{n_2}) / (1 + k_3 D_{Ts} + k_4 D_{Tns} + k_5 D_{\theta'})^{m_1} \quad (33)$$

where  $A$ ,  $B$ ,  $m_1$ ,  $n_1$ ,  $n_2$ ,  $k^*$ ,  $k_0$ ,  $k_1$ , and  $k_{3-5}$  are material constants,  $\sigma_0$  denotes the threshold stress of the alloy during the CA process, and  $I$  represents the influence of microstructure variables on creep rate of the alloy, which contains the three micro-structural parameters. The first part  $(1 + k_1 \bar{\rho}^{n_1})$  of  $I$  represents the positive effect of mobile dislocation caused by applied stress and creep deformation on creep strain rate. The second part  $(k_0 - k^* \bar{C}^{n_2})$  shows the influence of the solute concentration on the creep rate, and  $-k^* \bar{C}^{n_2}$  represents the negative effect on the creep strain rate. And the last part  $(1 + k_3 D_{Ts} + k_4 D_{Tns} + k_5 D_{\theta'})^{m_1}$  denotes the negative impact of the radius of different kinds of precipitates on the creep rate. During the CA process, microstructure variables influence each other and dominate the “multi-stage” creep feature of the alloy. In Stage I, different kinds of precipitates gradually nucleate and grow up. In addition, due to the applied stress and creep deformation, a large number of dislocations are generated and they reach the saturation level quickly [39], and dislocation strengthening plays a major role at this stage, which makes the creep rate decrease gradually. In Stage II,  $T_1$  and  $\theta'$  precipitates grow up gradually along the dislocations [21], solute elements in Al matrix continue to be consumed and the dislocation density of the alloy gradually decreases due to dynamic recovery effects of dislocations [17], which makes creep strain increase stably. At the beginning of Stage III, due to the accelerated growth of  $T_1$  and  $\theta'$

phases, the solute concentration in matrix decreases rapidly, which leads to the decrease of creep resistance [40], and the creep rate increases gradually. As ageing continues, the size and volume fraction of the  $T_1$  precipitate continue to increase, but the  $\theta'$  precipitate gradually decreases. Besides, the dislocation density and solute concentration tend to stabilize. Combined with the above factors, the creep rate gradually approaches a steady state in Stage III.

According to the previous studies [28,41], the correlation between the relative solute concentration  $\bar{C}$  and the relative volume fraction of the precipitate  $\bar{f}_v$  can be expressed as

$$\bar{C} = \alpha - \beta \bar{f}_v \quad (34)$$

where  $\alpha$  and  $\beta$  are material constants. Therefore,  $(k_0 - k^* \bar{C}^{n_2})$  can be expressed as

$$k_0 - k^* \bar{C}^{n_2} = k_0 - k^* (\alpha - \beta \bar{f}_v)^{n_2} \quad (35)$$

where  $k_0$  and  $k^*$  are material constants. In order to eliminate possible numerical difficulties near  $n_2 \approx 1$ , Eq. (35) is transformed to a new form, while keeping its main characteristics shown in Eq. (36):

$$k_0 - k^* (\alpha - \beta \bar{f}_v)^{n_2} = k_0 - k^* \alpha^{n_2} + k^* \beta \bar{f}_v^{n_2} = 1 + k_2 \bar{f}_v^{n_2} \quad (36)$$

where  $k_2$  and  $n_2$  are material constants. Equation (33) transforms to a new form as

$$I = (1 + k_1 \bar{\rho}^{n_1})(1 + k_2 \bar{f}_v^{n_2}) / (1 + k_3 D_{Ts} + k_4 D_{Tns} + k_5 D_{\theta'})^{m_1} \quad (37)$$

#### 4.5 Unified creep ageing constitutive model

A new set of unified creep ageing constitutive equations for Al–Li–S4 alloys is established, which is based on the correlation among microstructural variables, strengthening responses and creep strain–stress. The creep ageing constitutive equations can be expressed as follows:

$$\dot{\varepsilon}_c = A \sinh[B(\sigma - \sigma_0)I];$$

$$I = (1 + k_1 \bar{\rho}^{n_1})(1 + k_2 \bar{f}_v^{n_2}) / (1 + k_3 D_{Ts} + k_4 D_{Tns} + k_5 D_{\theta'})^{m_1};$$

$$\sigma_y = \sigma_{Al} + \sigma_{ss} + \sqrt{\sigma_{ppt}^2 + \sigma_{dis}^2};$$

$$\sigma_{ss} = C_s (1 - \bar{f}_v)^{m_2};$$

$$\sigma_{\text{dis}} = C_{\text{dis}} \bar{\rho}^{n_3};$$

$$\sigma_{\text{ppt}} = M(\Delta\tau_{\text{Ts}}^{1.4} + \Delta\tau_{\text{Tns}}^{1.4} + \Delta\tau_{\theta'}^{1.4});$$

$$\Delta\tau_{\text{Tns}} = \frac{Gb}{2\pi\sqrt{1-\nu}} \ln(1.061S_{\text{Tns}}/r_0) / [0.931\sqrt{(0.265\pi D_{\text{Tns}} S_{\text{Tns}}) / (\bar{f}_{\text{Tns}} f_{\text{max}})} - \pi D_{\text{Tns}} / 8 - 0.91S_{\text{Tns}}];$$

$$\Delta\tau_{\theta'} = \frac{Gb}{2\pi\sqrt{1-\nu}} [\ln(1.225S_{\theta'}/r_i)] / [0.931\sqrt{(0.306\pi D_{\theta'} S_{\theta'}) / (\bar{f}_{v-\theta'} f_{\text{max}})} - \pi D_{\theta'} / 8 - 1.061S_{\theta'}];$$

$$\Delta\tau_{\text{Ts}} = \frac{1.211D_{\text{Ts}}}{S_{\text{Ts}}^2} \left( \frac{b\bar{f}_{v-\text{Ts}} f_{\text{max}}}{\Gamma} \right)^{1/2} \gamma_i^{3/2};$$

$$\Gamma = (Gb/2\pi) \ln(r_0/r_i);$$

$$r_0 = D_{\text{Ts}} / \sqrt{2\bar{f}_{v-\text{Ts}} f_{\text{max}}};$$

$$\bar{f}_v = \bar{f}_{v-\theta'} + \bar{f}_{v-\text{T}};$$

$$\dot{\bar{f}}_{v-\theta'} = c_1 \dot{D}_{\theta'} D_{\theta'}^2 S_{\theta'} (1+k_6 \bar{\rho}^{n_4}) (1-\bar{f}_{v-\theta'})^{m_3} - c_2 \dot{\bar{f}}_{v-\theta'}^{m_4};$$

$$\dot{\bar{f}}_{v-\text{T}} = c_3 \dot{D}_{\text{Ts}} D_{\text{Ts}}^2 S_{\text{Ts}} (1+k_7 \bar{\rho}^{n_5}) (1-\bar{f}_{v-\text{T}})^{m_5} + c_4 c_2 \dot{\bar{f}}_{v-\theta'}^{m_4} - c_5 \dot{\bar{f}}_{v-\text{T}}^{m_6};$$

$$\dot{\bar{f}}_{v-\text{Tns}} = [c_5 \dot{\bar{f}}_{v-\text{T}}^{m_6} + (1-c_4) c_2 \dot{\bar{f}}_{v-\theta'}^{m_4}] \cdot [1+c_6(1+k_8 \bar{\rho}^{n_6}) (1-\bar{f}_{v-\text{Tns}})^{m_7}];$$

$$\dot{D}_{\theta'} = c_7 (Q_1 - D_{\theta'})^{m_8} (1+k_9 \bar{\rho}^{n_7}) - c_8 [\bar{f}_{v-\theta'} / (1-c_9 \bar{f}_v)]^{m_9};$$

$$\dot{D}_{\text{Ts}} = c_{10} (Q_2 - D_{\text{Ts}})^{m_{10}} (1+k_{10} \bar{\rho}^{n_8});$$

$$\dot{D}_{\text{Tns}} = c_{11} (Q_3 - D_{\text{Tns}})^{m_{11}} (1-k_{11} \bar{\rho}^{n_9});$$

$$\dot{S}_{\theta'} = c_{12} t^{-1/2} (1+k_{12} \bar{\rho}^{n_{10}}) - c_{13} [\bar{f}_{v-\theta'} / (1-c_{14} \bar{f}_v)]^{m_{12}};$$

$$\dot{S}_{\text{Ts}} = c_{15} t^{-1/2} (1+k_{13} \bar{\rho}^{n_{11}});$$

$$\dot{S}_{\text{Tns}} = c_{16} t^{-1/2} (1-k_{14} \bar{\rho}^{n_{12}});$$

$$\bar{\rho} = \bar{\rho}_i + \bar{\rho}_c;$$

$$\bar{\rho}_i = \{\rho_0 + c_{17} \exp[c_{18}(1+(\sigma-\sigma_{0.2})/\sigma_{0.2})]\} / \rho_{\text{total}};$$

$$\dot{\bar{\rho}}_c = c_{19} (1-\bar{\rho}) |\dot{\epsilon}_c|^{m_{13}} - c_{20} \bar{\rho}^{n_{13}}.$$

#### 4.6 Determination of material constants

The unified creep ageing constitutive equations presented above, containing many

unknown material constants, are non-linear ordinary differential equations. Therefore, they are difficult to be solved analytically. It is necessary to decouple the model and fit the parameters step by step. According to previous researches [29,32], particle swarm optimization (PSO), one of the optimization algorithms, has been used to determine the parameters of creep ageing constitutive equations by obtaining the minimum fitness values between experimental data and calculated data. The fitness value is evaluated as

$$f(u) = \sum_{i=1}^{n'} \sum_{j=1}^{m'} w_c (u_{ij}^c - u_{ij}^e)^2 \quad (38)$$

where  $u$  represents the variables to be fitted in the constitutive equation.  $n'$  and  $m'$  are the numbers of fitted curves and data points on the relevant curves, respectively.  $i$  and  $j$  represent current fitted curve and current fitted data point on corresponding curve, respectively.  $w_c$  is a weighting function and  $(u_{ij}^c - u_{ij}^e)^2$  is the difference between the points on the calculated curve and the experimental curve.

It should be indicated that the parameters in the constitutive equation are solved step by step using the optimization algorithm of PSO, and the fitting procedure is as follows. First, the creep strain curves are fitted with polynomials to acquire a function of the creep strain rate. Second, Fig. 8 shows that the material constants correlated to the normalized dislocation density  $\bar{\rho}$  ( $c_{17-20}$ ,  $m_{13}$  and  $n_{13}$ ) are determined using experimental results of the normalized dislocation density evolution with time. Third, based on the fitting parameters of the

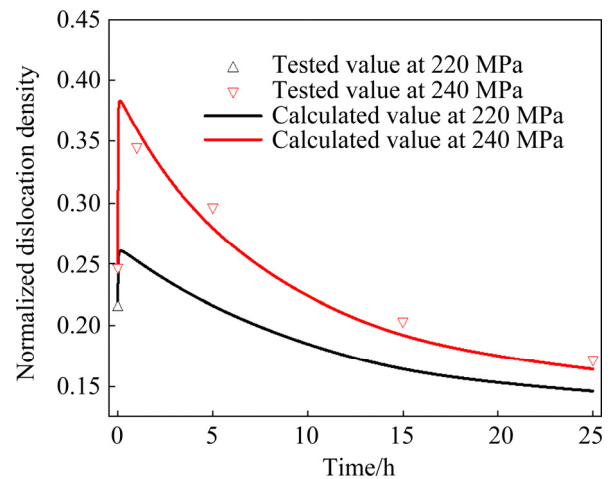
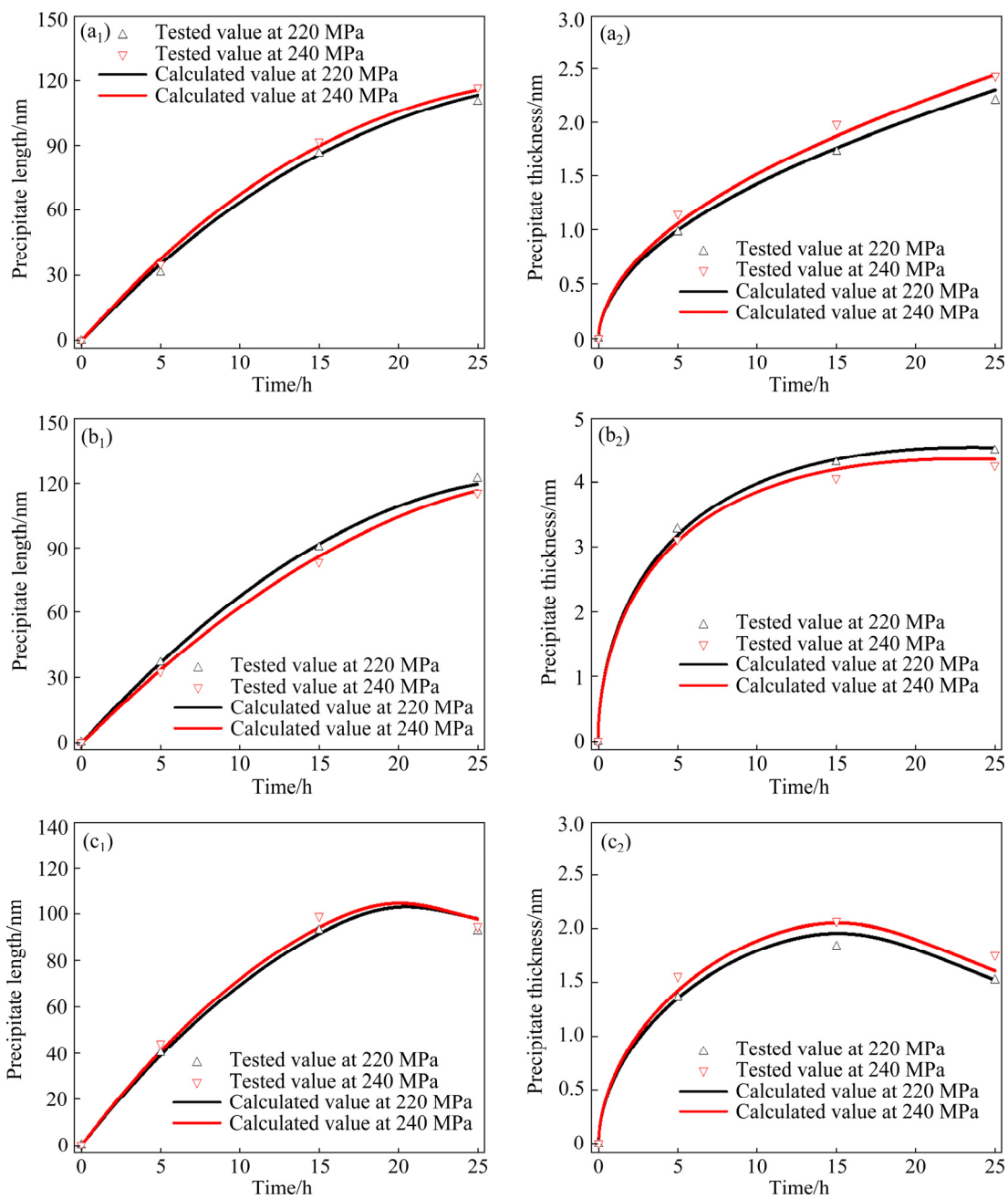


Fig. 8 Predicted evolution of normalized dislocation density during CA process

first and second steps and the experimental results of precipitate size, the material constants correlated to the length and thickness of the  $T_1$  precipitate ( $c_{10,11,15,16}$ ,  $k_{10,11,13,14}$ ,  $n_{8,9,11,12}$  and  $m_{10,11}$ ) are determined, as shown in Figs. 9(a<sub>1</sub>, a<sub>2</sub>, b<sub>1</sub>, b<sub>2</sub>). Moreover, Figs. 9(c<sub>1</sub>, c<sub>2</sub>) show that material constants correlated to the length and thickness of  $\theta'$  precipitate ( $c_{7-9,12-14}$ ,  $k_{9,12}$ ,  $n_{7,10}$  and  $m_{8,9,12}$ ) are determined in the same way. Fourth, based on the fitting parameters of the previous three steps and the experimental results of the relative volume fraction of precipitates, the material constants

correlated to the relative volume fraction of different precipitates ( $c_{1-6}$ ,  $k_{6-8}$ ,  $n_{4-6}$  and  $m_{3-7}$ ) can be obtained, as shown in Fig. 10. Fifth, based on the fitting parameters of the previous four steps and the experimental results of the yield strength during CA process, the remaining constants correlated to yield strength ( $C_S$ ,  $C_{dis}$ ,  $m_2$  and  $n_3$ ) are determined, as shown in Fig. 11. Finally, the rest of constants can be determined, as shown in Fig. 12. Some initial values of variables in the constitutive model are listed in Table 2, and the parameters of the constitutive model are listed in Table 3.



**Fig. 9** Comparisons of predicted and experimental average length (a<sub>1</sub>, b<sub>1</sub>, c<sub>1</sub>) and average thickness (a<sub>2</sub>, b<sub>2</sub>, c<sub>2</sub>) of shearable  $T_1$  phase (a<sub>1</sub>, b<sub>1</sub>) non-shearable  $T_1$  phase (a<sub>2</sub>, b<sub>2</sub>) and  $\theta'$  phase (a<sub>3</sub>, b<sub>3</sub>)



**Table 3** Material constants in uniform constitutive equation for creep-ageing of Al–Li–S4 at 153 °C

$A$	$B$	$C_s/\text{MPa}$	$C_{\text{dis}}/\text{MPa}$	$\sigma_0/\text{MPa}$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$
$1.05 \times 10^{-3}$	0.021	105.6	115.2	14.56	$5.06 \times 10^{-7}$	0.0152	$7.1 \times 10^{-7}$	0.83	0.10
$c_6$	$c_7$	$c_8$	$c_9$	$c_{10}$	$c_{11}$	$c_{12}/\text{h}^{-1}$	$c_{13}$	$c_{14}$	$c_{15}/\text{h}^{-1}$
0.12	0.49	0.25	0.98	0.39	1.38	$3.1 \times 10^{-4}$	$1 \times 10^{-4}$	0.9	$2.1 \times 10^{-4}$
$c_{16}/\text{h}^{-1}$	$c_{17}$	$c_{18}$	$c_{19}/\text{h}^{-1}$	$c_{20}$	$n_1$	$n_2$	$n_3$	$n_4$	$n_5$
$6.9 \times 10^{-4}$	$5.5 \times 10^{-4}$	5.616	1.83	0.15	0.409	1.15	0.50	0.36	0.18
$n_6$	$n_7$	$n_8$	$n_9$	$n_{10}$	$n_{11}$	$n_{12}$	$n_{13}$	$m_1$	$m_2$
1.12	1.31	1.42	0.32	0.97	1.58	0.52	2.49	0.673	0.66
$m_3$	$m_4$	$m_5$	$m_6$	$m_7$	$m_8$	$m_9$	$m_{10}$	$m_{11}$	$m_{12}$
3.32	1.27	1.93	1.82	1.53	0.59	1.25	0.59	0.71	0.40
$m_{13}$	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$	$k_6$	$k_7$	$k_8$	$k_9$
1.26	1.403	6.89	0.516	0.76	0.422	0.59	1.20	0.2	1.31
$k_{10}$	$k_{11}$	$k_{12}$	$k_{13}$	$k_{14}$	$Q_1/\text{nm}$	$Q_2/\text{nm}$	$Q_3/\text{nm}$		
1.80	1.01	0.80	1.89	0.53	104.62	115.78	119.51		

## 5 Model validation and discussion

### 5.1 Microstructural evolution

During the CAF process, the evolution of microstructure variables plays a dominant role in the creep rate and mechanical properties of Al–Li–S4 alloys. Figures 8, 9 and 10 show the normalized dislocation density, the average lengths and thicknesses of  $T_1$  and  $\theta'$  precipitates, and the relative volume fractions of  $T_1$  and  $\theta'$  precipitates, respectively. In Figs. 9 and 10, the average size and relative volume fraction of shearable  $T_1$  and  $\theta'$  precipitates increase with the applied stress during the CA process, while the average size of non-shearable  $T_1$  precipitate decreases as the applied stress increases. This is due to a large number of dislocations and vacancies generated under the applied stress above the initial yield strength of the alloy, which can promote the nucleation of  $T_1$  precipitate and make  $T_1$  precipitate more dispersive and finer. Moreover, the average size and relative volume fraction of the  $\theta'$  precipitate decrease in the later stages of the CA process due to the competitive correlation between  $\theta'$  precipitate and  $T_1$  precipitate. Furthermore, Figs. 8, 9 and 10 show that the experimental data are consistent with the simulated data by the proposed model. This confirms that the established constitutive model is feasible to characterize creep

ageing behavior for Al–Li–S4 alloy.

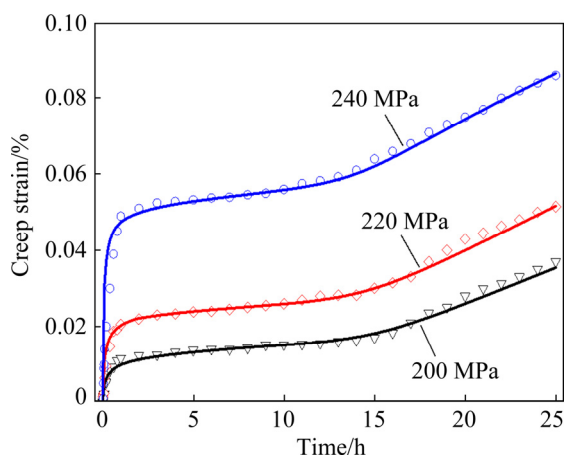
### 5.2 Yield strength evolution during CA process

Figure 11 shows the comparisons of the experimental data and calculated results for the evolution of the yield strength and various strengthening contributions, including the dislocation hardening, the precipitation hardening and the solid solution hardening during the CA process. The calculated yield strength curves are consistent with the experimental data in both cases, which verifies the effectiveness of the established model and relevant material parameters in this study. Precipitation strengthening includes sheared  $T_1$  precipitation strengthening, non-sheared  $T_1$  precipitation strengthening and  $\theta'$  precipitation strengthening. It should be indicated that the strengthening contribution of  $T_1$  precipitate is greater than that of  $\theta'$  precipitate. Moreover, the strengthening contribution of the sheared  $T_1$  precipitate is greater than that of the non-sheared  $T_1$  precipitate. Furthermore, the evolution law of the strengthening contribution of  $\theta'$  precipitate is similar to that of its volume fraction, which increases gradually in the early stage of the CA process and decreases gradually in the later stage of CA process. In the early stage of the CA process, dislocation strengthening is the main source of the increase of yield strength, which is the main reason for the different yield strengths under different

applied stresses. The solid solution hardening gradually decreases as the solute atomic concentration decreases during the CA process. The aluminum matrix hardening remains constant during the CA process.

### 5.3 Creep behavior under different stress levels

Figure 12 shows the comparison of the experimental data and calculated results for the evolution of the creep strains under stress levels from 200 to 240 MPa. It is observed that all predicted creep strain curves are in good agreement with the experimental results during the CA process. The established model and correlated material parameters can not only predict the “multi-stage” creep characteristics of the alloy, but also accurately predict the creep behavior of the alloy under the applied stresses greater or less than the initial yield strength. Therefore, the proposed model can successfully predict the creep strain behavior of Al–Li–S4 alloy.



**Fig. 12** Comparison of predicted (solid lines) and experimental (symbols) creep-aging curves of Al–Li–S4 alloy under different stress levels at 153 °C

## 6 Conclusions

(1) The equations that correlate the yield strength and various strengthening contributions to the microstructural variables of Al–Li–S4 are established according to the basic age hardening model of the Al alloy. The model considers not only the strengthening contributions of sheared and non-sheared  $T_1$  precipitates, but also the strengthening contributions of the  $\theta'$  precipitate, as well as the strengthening caused by dislocations and solutes. It is observed that the predicted yield

strength values are consistent with the experimental data.

(2) The “multi-stage” creep behavior of the Al–Li–S4 alloy changes slightly under different applied stresses. However, the creep deformation of the alloy in the first stage of the CA process varies significantly. The “multi-stage” creep behavior of Al–Li alloys is mainly determined by the dislocation movement, interaction between dislocation and precipitate, and interaction between solute clusters and dislocations. In this study, a new set of the unified creep ageing constitutive model relating the creep rate to the microstructural variables, including the normalized dislocation density, solute concentration and the average precipitate radius is established under different applied stresses. The model successfully describes the “multi-stage” creep characteristics of Al–Li–S4 alloy, which is in good agreement with the experimental results.

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## Al–Li–S4 合金多相析出和多阶段蠕变时效行为的统一本构模型

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**摘要:** 提出统一的本构模型, 以预测最近观察到的 Al–Li–S4 合金的“多阶段”蠕变行为。通过 X 射线衍射(XRD)和透射电子显微镜(TEM), 详细表征蠕变时效过程中与合金的屈服强度和蠕变变形相关的微观结构变量, 包括位错和多种析出相。对于合金的屈服强度, 该模型基于强化机制考虑多相强化行为, 包括可剪切的  $T_1$  析出相强化, 不可剪切的  $T_1$  析出相强化和  $\theta'$  析出相强化。基于蠕变变形机理, 通过将相互作用的微观结构变量(包括多种析出相的半径, 位错密度和溶质浓度)引入蠕变应力应变模型, 可以预测合金的“多阶段”蠕变行为。结果表明, 模型的计算结果与实验数据吻合良好, 验证该模型的有效性。

**关键词:** 本构模型; Al–Li–S4 合金; 蠕变时效成形; 微观结构; 数值算法

(Edited by Bing YANG)