Cu/Li Ratio on the Microstructure Evolution and Corrosion Behaviors of Al–xCu–yLi–Mg Alloys

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Abstract

The microstructure evolution and the corrosion feature of Al–xCu–yLi–Mg alloys ($x:y=0.44, 1.65$ and 4.2) were systematically investigated under the same artificial aging conditions. The relationships between types of precipitates and mechanical performance, as well as electrochemical behaviors, were discussed. Our results show that different types of precipitates can be obtained in alloys with different Cu/Li mass ratios, which significantly influences the mechanical performance of the alloys and substantial corrosion behaviors. Specifically, the analogous corrosion evolution in the aging Al–xCu–yLi–Mg alloys was first ascertained to be derived from the growth mechanism of the precipitates at the grain boundary (GB). Moreover, a small number of GB precipitates can be obtained in the aged alloy with the lowest Cu/Li mass ratio, thereby resulting in the largest intergranular corrosion resistance. A higher proportion of the GB T_1 phase in the continuous precipitates induces higher corrosion sensitivity in alloy with a high Cu/Li mass ratio.

Keywords Al–Cu–Li–Mg alloy · Cu/Li mass ratio · Microstructure evolution · Corrosion behaviors

1 Introduction

Al–Cu–Li alloys are regarded as one of the most promising structural materials in meeting the demands of the aerospace field due to their excellent features (rigidity, plasticity, malleability, and machinability) [1–3]. The third generations of Al–Cu–Li-based alloys with above-mentioned merits, such as 2195, 2099, and 2050, have been rapidly developed in

the last 30 years [4–6]. Recently, the influences of chemical composition and heat treatments on the microstructure evaluation and corrosion behaviors of such alloys have been widely studied [7–10].

The microstructures of Al–Cu–Li alloy have been comprehensively studied. Generally, the main precipitates in such alloys are a T_1 phase (Al_2CuLi), θ' phase (Al_2Cu), δ' phase (Al_3Li), and S' phase (Al_2CuMg); there are also other phases, like the T_2 phase (Al_6CuLi_3), T_B phase ($\text{Al}_{15}\text{Cu}_8\text{Li}_2$), δ phase (AlLi), or undetermined coarse phase existing or coexisting at the grain boundary (GB) [11]. The nucleation and growth mechanisms of the aforementioned precipitates were verified to associate with a mass ratio of Cu and Li in the alloys. For example, multiple δ' phases were precipitated within the grains of the studied Al–Cu–Li alloys with high Li concentrations (> 2.5 wt%) and low Cu concentrations (< 1.5 wt%) [12]. On the other hand, a great number of T_1 phases and θ' phases were present with a high Cu concentration (> 3.5 wt%) and a low Li concentration (< 1.2 wt%) within the grain of the aged alloy [13]. On the other hand, the Cu/Li atomic ratio also plays a significant role in controlling the nucleation and growth of the precipitate. For instance, when the Cu and Li atomic ratio was adjusted (the Cu concentration ranged from 1.5 to 3.5 wt% and the Li

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concentration from 1.2 to 2.5 wt%) in the Al–Cu–Li alloy, the δ' phase, the T_1 phase, and the θ' phase were shown to coexist in the grain or the grain boundary (GB) [14]. Additionally, micro-alloyed element additions and artificial aging heat treatments were other important factors in the microstructure evolution of aging Al–Cu–Li alloys, which would substantially influence the mechanical performance, corrosion features, and electrochemical behavior in the studied aging alloys [15].

Mechanical performance is a vital property for Al– x Cu– y Li alloys [5, 16, 17]. The differences in the mechanical performance of Al– x Cu– y Li alloys resulted from the different types of precipitates (locations, morphology, etc.) in aged alloys. The yield strength and tensile strength of the casted Al–2Li–2Cu–0.2Zr alloy after exposure aging at 100 °C were investigated. The critical increase in the aforementioned mechanical properties owes largely to the precipitation of the disk shape of θ' phase in $\{100\}_\alpha$ and coarsening of the spherical δ' phase [18]. In a welded joint section, the fusion zone possessed the best toughness performance, with a large number of needle-like intergranular T_1 phases, which verified that the T_1 phase played a significant role in improving the strength of the studied alloy [19]. Moreover, in a commercial AA2198-based alloy, the strength improvement via artificial aging (T8) was believed to be related to the θ' phase, δ' phase, and T_1 phase, and the aging temperature was also shown to have a critical influence on the morphology of the precipitates of the aging alloy [20]. As commonly believed, the precipitation sequence of the Al–Cu–Li alloy with a low Li concentration was different from that of the Al–Cu–Li alloy with a high concentration under room temperature aging [20–22]. For example, the precipitation sequence in the two Al–Cu–Li alloys with similar Cu concentrations and different Li concentrations revealed that Cu-rich clusters were precipitated before the T_1 phase in the low Li-containing alloy, while the T_1 phases were precipitated after the δ' phase in the high Li-containing alloy [23]. Besides, microstructural characteristics including chemical composition of the precipitates and structural aspects consisting of grain-stored energy and grain boundary misorientation were also confirmed to affect the corrosion behaviors of Al–Cu–Li alloy [24–27].

Further, many studies were performed on the corrosion behaviors of the Al–Cu–Li alloy with different Cu contents or Li contents. It has been confirmed that the corrosion features of the studied Al–Cu–Li of such alloys are predominately governed by the type and quantity of the precipitates in the grain and at the grain boundary, which is also related to the electrochemical behaviors of the aged sample. The effects of aging treatment on the microstructure evaluation, mechanical properties, and corrosion feature of the Al–3.5Cu–1.5Li–0.22 (Sc + Zr) alloy were investigated [28]. The main strengthening precipitate of the T_1 phase in the

alloy was ascertained, and the anodic dissolution of the T_1 phase and the precipitate-free zone (PFZ) was determined by intergranular corrosion (IGC) occurring and extending. In the 2195 alloy, the corrosion mechanism of the T_1 phase was studied through phase simulation casting. The alternate anodic dissolution of the T_1 phase and PFZ triggers the IGC or inter-subgranular corrosion (ISGC) [29, 30]. Additionally, the selective dissolution of lithium elements was possibly the primary cause of the initial corrosion of the Al–Cu–Li alloy [31]. Other factors, such as the difference between the pitting initiation potential and the passivation potential, were also a vital cause of corrosion [32].

Considering the balance of strength characteristics and corrosion behaviors to meet new lightweight structural material requirements, the aged Al– x Cu– y Li–Mg alloys were again particularly examined. In this paper, the microstructure evaluation, corrosion features, and the electrochemical behaviors of the aged Al– x Cu– y Li–Mg alloys with different Cu/Li mass ratios were systematically studied under the same artificial aging process, which is particularly designed to investigate the corrosion behaviors linked to microstructures under the same thermodynamic conditions. The different characteristics of the mechanical performance and the corrosion behaviors were linked to the different microstructure evolution of the studied aged alloy. Based on these studies, the mechanical performance, microstructure characteristics, and corrosion features, as well as the correlated corrosion mechanisms, among the Al– x Cu– y Li–Mg alloys were summarized. Our results provide an efficient reference for the research of Al–Cu–Li-based alloys with excellent comprehensive performance.

2 Experimental

The Al– x Cu– y Li–Mg alloy ingots were prepared by casting in a melting furnace under Ar gas protection. Three alloys with Cu/Li atomic ratio equal to 0.44, 1.65, and 4.20 were prepared; they were labelled as Alloy A, Alloy B, and Alloy C, with an atomic ratio of Cu/Li = 0.44, 1.65, and 4.20, respectively. The actual chemical composition of the above three devised alloys (Table 1) was measured with an inductively coupled plasma optical emission spectrometer (ICP-OES).

Different homogenization procedures were selected for the different Cu/Li ratio alloys to eliminate dendrite segregation of these ingots, due to the Cu concentration increasing in the studied alloy, leading to an increase in the quantity of the non-equilibrium Cu-bearing phase at the grain boundary [33–35]. The homogenized ingots were then hot rolled into sheets with a thickness of 5 mm, followed by cold rolling to 2 mm. These sheets were then subjected to a solution heat treatment after quenching in water at room

Table 1 Actual chemical composition of the prepared Al-*x*Cu-*y*Li-Mg alloys (wt%)

Alloy	Cu/Li ratio	Cu	Li	Mg	Mn	Zr	Al
Alloy A	0.44	1.08	2.43	0.42	0.35	0.12	Bal.
Alloy B	1.65	2.78	1.68	0.43	0.32	0.12	Bal.
Alloy C	4.20	3.82	0.91	0.42	0.32	0.12	Bal.

Fig. 1 A schematic diagram of the aged specimens used in the tensile measurement

temperature. The temperature/time of the solution heat treatments was 530 °C/1 h for Alloy A, 540 °C/1 h for Alloy B, and 510 °C/1 h for Alloy C. Artificial aging was conducted on the samples with different aging times after the solution treatment. The mechanical performance and corrosion depth of the samples aged at 175 °C for different times were recorded to comprehensively analyze the performance discrepancy between the three Al-*x*Cu-*y*Li-Mg alloys.

The aged samples with different aging times were fabricated in the standard way, as shown in Fig. 1. For every group of samples, three tensile samples were tested with one aging time. The mechanic performance measurement was carried out in the MTS—810 tester with a strain rate of approximately 2 mm/min. The average values of the yield strength and tensile strength at different aging times were calculated, and the error bars were given for each test. The yield strength curves and the tensile strength curves as a function of aging time were plotted.

The corrosion immersion test was conducted using a thermostatic bath with a constant temperature, according to the IGC corrosion standard of ASTM. Before the corrosion test, the aged samples were ground and polished for the prescribed test sample with a surface roughness less than Ra 0.05. 57 g/L NaCl + 10 mL/L H₂O₂ and were used as a corrosion solution (i.e., exposure electrolyte). The samples were soaked in the corrosion solution at 35 ± 2 °C. After immersion for 6 h, the corroded samples were rinsed, and the cross section of each sample was observed by a Leica metallographic microscope.

The open-circuit potential (OCP) and the Tafel plots were measured in a CHI 660D Electrochemical Workstation with a scan rate of 1 mV/s using a three-electrode cell setup. The aged sheets were used as a working electrode, the platinum

sheet was used as the counter electrode, and the saturated calomel electrode (SCE) was used as the reference electrode [36]. The samples for the transmission electron microscopy (TEM) test were prepared using the electrochemical dissolution method via a twin-jet electro-polishing appliance. The corrosion electrolyte for electro-polishing comprises 75% CH₃OH and 25% HNO₃. The preceding electrochemical dissolution temperature ranged from −25 to −30 °C. The microscopic characteristic of the studied alloys was observed using an FEI Tenai G² TEM and an FEI F20 TEM, with an operational voltage at 200 kV.

3 Results

3.1 Characterization of Mechanical Properties

In the paper, the mechanistic performance test including the yield strength curves and the tensile strength curves was executed on the three Al-*x*Cu-*y*Li-Mg alloys aged at 175 °C. The artificial aging temperatures of Alloy A, Alloy B, and Alloy C all selected under same heat treatment condition at 175 °C were used to compare the different aspects of performance among the three studied alloys under the same thermodynamic conditions. The thermodynamic factors are important influential conditions for precipitate formation in the aging process, which are linked to the mechanistic performance of the different Cu/Li mass ratios of the Al-Cu-Li Alloys [37].

The yield strength of the three aging Al-*x*Cu-*y*Li-Mg alloys as a function of aging time is shown in Fig. 2a. Here, the strength curves of these alloys exhibit diverse strength variation tendencies and maximum peak strength values. The yield strength of Alloy C (with high Cu/Li mass ratio) rapidly increased through aging from 2 to 18 h and then kept stable at a strength value of approximately 465–480 MPa at an aging time of 18 h to 56 h and subsequently declined gradually, with a strength value of 35 MPa and an aging time of 56 h. While the strength variation tendency of Alloy B (with medium Cu/Li mass ratio) agreed with that of Alloy C but with a peak strength value of 435 MPa from 18 to 72 h, the starting strength value declined at an aging time of 72 h. Moreover, the yield strength of Alloy A (with a low Cu/Li mass ratio) gradually rose and slowly increased with an aging time of 18 h, possessing its peak aging strength value of 330 MPa until an aging time of 100 h.

Fig. 2 Tensile properties of the Al-Cu-Li-Mg alloys with different Cu/Li ratios artificial aged at 175 °C: **a** yield strength; **b** tensile strength

The tensile strength variety of the studied Al- x Cu- y Li-Mg alloys conformed to the tendency of the yield strength curves, as shown in Fig. 2b. The differences between the tensile strength and the yield strength were as follows: Alloy C had a peak strength of 530 MPa with an aging time of 42 h, Alloy B had a peak strength value of 490 MPa at an aging time of 18 h or 72 h, and Alloy A had a peak strength value of 460 MPa at an aging time of 18 h or 100 h. In these figures, the tensile strength difference value between Alloy C and Alloy B of nearly 40 MPa is slightly more than that between Alloy B and Alloy A (approaching 30 MPa). On the contrary, the yield strength difference between Alloy B and Alloy A (about 110 MPa) is much greater than that between Alloy C and Alloy B (around 50 MPa). Furthermore, it can be observed in both the yield strength curve and the tensile strength curve that the aging response rate of Alloy C conformed to that of Alloy B, which was quicker than that of Alloy A. The different mechanical characteristics of the Al-Cu-Li-Mg alloys were attributed to the different microstructure characteristics

in the studied alloys with different Cu/Li mass ratios [38]. At the same time, many types of precipitates are present in the Al-Cu-Li-Mg alloy, and the different combined modes of these precipitates lead to different mechanical characteristics. The microstructure characteristics of Alloy A, Alloy B, and Alloy C during the whole aging process will be seriously examined in the following section.

3.2 Corrosion Characteristics

We observed the cross-sectional corrosion morphology of the studied Al- x Cu- y Li-Mg alloys during the whole aging process to investigate the corrosion behaviors of the alloys, including corrosion type evolution and corrosion depth transformation. The corrosion type and detailed data of the corrosion depth at more than ten aging time points are listed in Table 2. Figure 3 shows the representative cross-sectional corrosion morphology of the corroded samples with different Cu/Li mass ratios during the four typical aging stages. The four typical aging stages are of IA (initiate-aging stage

Table 2 Statistical table of corrosion type and intergranular corrosion depth in Al- x Cu- y Li-Mg alloys with different Cu/Li ratios aged at 175 °C

AT (h)	Cu/Li = 0.44 (low Cu/Li ratio)			AT (h)	Cu/Li = 1.65 (medium Cu/Li ratio)			AT (h)	Cu/Li = 4.20 (high Cu/Li ratio)		
	DCM	MID (μ m)	AID (μ m)		DCM	MID (μ m)	AID (μ m)		DCM	MID (μ m)	AID (μ m)
0.25	Pitting	–	–	0.25	LIGC	168.8	80.7	0.25	LIGC	261.3	166.3
0.5	LIGC	34.3	21.6	0.5	GIGC	206.3	140.3	0.5	LIGC	314.2	238.5
2	LIGC	53.2	44.5	2	GIGC	335.3	141.4	2	GIGC	358.1	276.1
4	LIGC	66.5	50.0	4	GIGC	356.4	215.7	4	GIGC	380.9	233.1
6	LIGC	110.8	70.5	6	GIGC	208.6	135.7	6	GIGC	301.5	223.9
8	LIGC	181.7	133.8	8	GIGC	284.2	203.1	8	LIGC	309.5	262.6
18	LIGC	106.1	72.3	12	LIGC	106.1	80.5	12	LIGC&P	< 10	< 5
32	LIGC	59.7	45.8	18	LIGC	90.2	52.9	26	Pitting	–	–
72	LIGC&P	52.7	45.3	26	Pitting	–	–	66	Pitting	–	–
100	LIGC&P	58.6	33.4	42	Pitting	–	–	80	LIGC&P	< 10	< 5
168	LIGC&P	80.3	64.5	54	Pitting	–	–	100	LIGC&P	< 10	< 5
198	Pitting	–	–	76	Pitting	–	–

Fig. 3 Typical morphology of corrosion in Al-Cu-Li-Mg alloys with different Cu/Li ratios: **a** Alloy A, low Cu/Li ratio, IA (2 h), LIGC; **b** Alloy B, medium Cu/Li ratio, IA (2 h), GIGC; **c** Alloy C, high Cu/Li ratio, IA (2 h), GIGC; **d** Alloy A, low Cu/Li ratio, UA (6 h), LIGC; **e** Alloy B, medium Cu/Li ratio, UA (6 h), GIGC; **f** Alloy C, high Cu/Li ratio, UA (6 h), GIGC; **g** Alloy A, low Cu/Li ratio, PA (24 h), LIGC; **h** Alloy B, medium Cu/Li ratio, PA (24 h), pitting; **i** Alloy C, high Cu/Li ratio, PA (24 h), pitting; **j** Alloy A, low Cu/Li ratio, OA (100 h), pitting; **k** Alloy B, medium Cu/Li ratio, OA (100 h), pitting; **l** Alloy C, high Cu/Li ratio, OA (100 h), pitting

with an aging time of 2 h), UA (under-aging stage at 6 h), PA (peak aging stage after 24 h aging), and OA (over-aging stage at an aging time of 100 h).

In previous studies [39, 40] on the corrosion features of Al-Cu-Li alloys, four typical corrosion types were found to be present in the extended aging process; these are LIGC (local intergranular corrosion), GIGC (general intergranular

corrosion), pitting, and LIGC&P (local intergranular corrosion and pitting), as shown in Fig. 4. These corrosion types were defined by their corrosion probability and corrosion depth in a study by Li et al. [41]. In the present study, the above four corrosion types appeared in different Cu/Li ratio Al-Cu-Li alloys in different combined modes, with corrosion evolution as a function of aging time. The corrosion

Fig. 4 Corrosion morphology of the cross section of the Al- x Cu- y Li-Mg alloys with different Cu/Li ratios aged at 175 °C: **a** LIGC; **b** GIGC; **c** Pitting; **d** LIGC&P

evolution of Alloy A with a low Cu/Li mass ratio in the aging process was as follows: pitting, LIGC, LIGC&P, and pitting. The corrosion type sequence of Alloy B was: pitting, LIGC, GIGC, LIGC&P, and pitting. Furthermore, the corrosion type evolution of Alloy C corresponded to that of Alloy B. In the aging of Alloy A, pitting happened at an aging time before 0.25 h and after 168 h, with LIGC occurring in a range from 0.5 to 32 h, and LIGC&P presence was found at aging time from 72 to 168 h. In Alloy B, pitting was found during aging after 36 h, while LIGC occurred during aging before 0.25 h and from 12 to 18 h; GIGC occurred during aging from 0.5 to 8 h. In alloy C, LIGC was found before 0.5 h, GIGC emerged at an aging time of 2 h to 6 h, LIGC&P happened at an aging time of 8 h to 12 h, and pitting occurred after 18 h. Overall, the corrosion type evolution of the Al- x Cu- y Li-Mg alloys with extended aging time can be summarized in the following order: pitting, IGC, and pitting.

The IGC depth variation in the three studied Al- x Cu- y Li-Mg alloys as a function of aging time is displayed in Fig. 5. The corrosion depth curves containing the average corrosion depth and the maximum corrosion depth were made from the plentiful corrosion data listed in Table 2. From Fig. 5, it can be found that the Al- x Cu- y Li-Mg alloys have different IGC corrosion depth variation traits and features in the aging interval of the corrosion happening during the aging process. The corrosion depth variation trait included the variation tendency of the average corrosion depth and the maximum corrosion depth. The corrosion depth trait of Alloy C was the same as that of Alloy B. However, the corrosion depth of Alloy A was significantly lower than that of the above two alloys, along with a much wider corrosion aging interval with a significant amount of slight IGC in the aging process. Alloy C possessed a maximum corrosion depth of approximately 380.9 μ m at an aging time of 4 h and an average corrosion depth of 276.1 μ m aged at

Fig. 5 IGC corrosion depth of Al-Cu-Li-Mg alloys with different Cu/Li ratios aged at 175 °C on different ageing time points: **a** maximum IGC corrosion depth (MID); **b** average IGC corrosion depth (AID)

2 h. Alloy B has a maximum corrosion depth of 356.4 μm aged at 4 h and an average corrosion depth of 215.7 μm aged at 4 h. The maximum corrosion depth and average corrosion depth of Alloy A were 181 μm and 133.8 μm , both at an ageing time of 8 h. Based on the corrosion aging interval, the aging interval of corrosion in Alloy B and Alloy C with an aging range from 0.25 to 12 h was much shorter than that of Alloy A at an aging time from 2 to 100 h.

Apart from IGC corrosion behaviors, different pitting features also emerged in the different Cu/Li alloys during the whole aging process [42]. The probability of pitting corrosion occurring and the pitting corrosion depth value in Alloy C was in agreement with that in the Alloy B, which was much greater than that in Alloy A. Moreover, the probability of pitting corrosion and the pitting corrosion depth value obviously increased with an increase in the Cu/Li mass ratio. It can be speculated that corrosion sensibility increased with an increase in the Cu/Li mass ratio, and corrosion resistance consequently increased as the Cu/Li mass ratio reduced in these studied Al-xCu-yLi-Mg alloys. The electrochemical behaviors of the studied alloys should also be used to analyze the reasons for the different corrosion behaviors in the studied Al-xCu-yLi-Mg alloys, as demonstrated by the open-circuit potential at different aging time points and Tafel curves during the whole aging process in the next section.

3.3 Electrochemical Behaviors

The potentiodynamic polarization curves (i.e., Tafel curves) of the three studied Al-xCu-yLi-Mg alloys at various aging time points (more than six aging time points) are shown in Fig. 6a-c. The OCP curves of the studied Al-xCu-yLi-Mg alloys as a function of aging time are displayed in Fig. 6d. In general, the corrosion potential of the three studied alloys gradually became more negative by extending aging time. The corrosion potential of Alloy A aged at 1 h was $-0.62 V_{\text{SCE}}$, the corrosion potential of Alloy A aged at 32 h was

$-0.70 V_{\text{SCE}}$, and the corrosion potential of Alloy A aged at 100 h was $-0.72 V_{\text{SCE}}$. While Alloy B was aged for 1 h with a corrosion potential of $-0.62 V_{\text{SCE}}$, that aged for 32 h had a value of $-0.72 V_{\text{SCE}}$, and that aged for 100 h had a value of $-0.78 V_{\text{SCE}}$. While the 1 h aged sample of Alloy C possessed a corrosion potential of $-0.52 V_{\text{SCE}}$, that aged for 32 h had a value of $-0.64 V_{\text{SCE}}$, and that aged for 138 h had a value of $-0.68 V_{\text{SCE}}$. Based on the variation tendency of the electrochemical characterization of the studied alloys with different Cu/Li mass ratios [43, 44], with an increase in aging time, the value of the open-circuit potential notably decreased and then remained stable during the over-peak stage. The overall OCP value of Alloy C during the aging process was the lowest among the three studied alloys, and the OCP value of Alloy B was the highest of the three alloys. Different precipitates exhibited the different electrochemical features in the aging process. The negative shift of the corrosion potential and decreases in the OCP values are related to the variation tendency of microstructural characteristics under similar aging heat treatment systems [45].

3.4 Microstructure Characteristics

The TEM images of the studied Al-xCu-yLi-Mg alloys under the under-aging conditions (aging for 6 h) are shown in Fig. 7. In Fig. 7a, a great number of spherical precipitates with particle sizes of 3–7 nm are formed within the grain of the alloy matrix. This spherical precipitate was determined to be δ' phase, with nucleation and growth at a lower aging temperature, as reported by previous studies [46–48]. In Fig. 7b, no visible precipitates were observed at the grain boundary of the Alloy A aged for 6 h, except for a small amount of fine spherical precipitates. In the microstructure photograph (Fig. 7c, d) of the Alloy B aged for 6 h, apart from a great quantity of the spherical δ' phase, some lamella-shaped precipitates and a few needle-shaped precipitates were present in the under-aged samples. These

Fig. 6 TF curves and the OCP curves of Al-Cu-Li-Mg alloys with different Cu/Li ratios aged at 175 °C under different aging time points: **a** low Cu/Li ratio, Alloy A; **b** medium Cu/Li ratio, Alloy B; **c** high Cu/Li ratio, Alloy C; **d** OCP curves of these different Cu/Li ratios alloys

lamella-shaped and needle-shaped precipitates were the θ' phase and T_1 phase, respectively, according to some related research literature [49]. In the TEM images of the Alloy C samples under an under-aging condition (UA) (Fig. 7e, f), a large number of lamella-shaped precipitates and needle-shaped precipitates coexisted in the Al alloy matrix. These precipitates were also ascertained to be θ' phase and T_1 phase in the previous studies on the high Cu/Li mass ratio Al-Cu-Li alloys [50, 51], such as the 2195 alloy, according to the results of our analysis.

Figure 8 shows the microstructural characteristics of the Al- x Cu- y Li-Mg alloys under a peak aging condition (PA), aged for 18 h. As displayed in Fig. 8a, a great number of spherical δ' precipitates with a diameter of 8–16 nm appeared, indicating that the size of δ' gradually increased by extending the aging time. A small number of precipitates also appeared at the grain boundary, which fundamentally agrees with the results under the UA condition of Alloy A. Comparing Fig. 7b with Fig. 8b, it can be seen that the microstructural features of Alloy A remain basically unchanged at aging time from 2 to 18 h. Figure 8c, d shows a large amount of the δ' phase and a moderate amount of the θ' phase and T_1 phase under the peak aging condition (aged for 18 h). Moreover, a number of precipitates with lath-like shapes were observed at the grain boundary. Most

of the GB precipitates were of the T_1 phase and coarse T_1 phase, confirmed by reports [22, 29, 33]. In addition, a considerable amount of the T_1 phase and a moderate amount of the θ' phase occurred under the peak aging condition of Alloy C. The needle-shaped T_1 phase has an average length of 160–220 nm, and the lamella-shaped θ' phase has a mean length of 80–120 nm. In the grain boundary of Alloy C aged for 18 h, the θ' phase, the T_1 phase, and the coarse phase are shown in Fig. 8e, f.

The TEM images of these Al- x Cu- y Li-Mg alloys aged at 175 °C for 66 h are shown in Fig. 9. As the aging time increased to 66 h, the size of the spherical δ' phase increased to 20–32 nm, which is relatively larger than that for the aging time of 26 h. Under the over-peak conditions of the aged Alloy A, some coarsen precipitates appeared at the grain boundary, as shown in Fig. 9b. The coarse δ' phase with a size of 10–20 nm and a wide θ' phase with a length of 90–120 nm coexisted with a greater quantity of the T_1 phase with a long size of 80–160 nm, as illustrated in Fig. 9c, d. At the grain boundary of the alloy aged for 66 h, a much coarser phase with a phase width of approximately 40–60 nm appeared, compared to the Alloy B aged for 26 h. A large number of coarse θ' phases and T_1 phases are shown in Fig. 9e, f. Moreover, according to aging time, the sizes of the precipitates at the grain boundary gradually grew and the

Fig. 7 TEM images of Al-Cu-Li-Mg alloys with different Cu/Li ratios aged at 175 °C on under-aging condition (6 h): **a** low Cu/Li ratio, Alloy A, DF, $\langle 100 \rangle_{\text{Al}}$; **b** low Cu/Li ratio, Alloy A, DF, $\langle 100 \rangle_{\text{Al}}$; **c** medium Cu/Li ratio, Alloy B, DF, $\langle 100 \rangle_{\text{Al}}$; **d** medium Cu/Li ratio, Alloy B, DF, $\langle 112 \rangle_{\text{Al}}$; **e** high Cu/Li ratio, Alloy C, BF, $\langle 100 \rangle_{\text{Al}}$; **f** high Cu/Li ratio, Alloy C, DF, $\langle 112 \rangle_{\text{Al}}$

Fig. 8 TEM images of Al–Cu–Li–Mg alloys with different Cu/Li ratios aged at 175 °C on peak aging condition (18 h): **a** low Cu/Li ratio, Alloy A, DF, $\langle 100 \rangle_{\text{Al}}$; **b** low Cu/Li ratio, Alloy A, DF, $\langle 100 \rangle_{\text{Al}}$; **c** medium Cu/Li ratio, Alloy B, DF, $\langle 100 \rangle_{\text{Al}}$; **d** medium Cu/Li ratio, Alloy B, DF, $\langle 112 \rangle_{\text{Al}}$; **e** high Cu/Li ratio, Alloy C, DF, $\langle 100 \rangle_{\text{Al}}$; **f** high Cu/Li ratio, Alloy C, DF, $\langle 112 \rangle_{\text{Al}}$

Fig. 9 TEM images of Al-Cu-Li-Mg alloys with different Cu/Li ratios aged at 175 °C on over-aging condition (66 h): **a** low Cu/Li ratio, Alloy A, DF, $\langle 100 \rangle_{\text{Al}}$; **b** low Cu/Li ratio, Alloy A, DF, $\langle 100 \rangle_{\text{Al}}$; **c** medium Cu/Li ratio, Alloy B, DF, $\langle 100 \rangle_{\text{Al}}$; **d** medium Cu/Li ratio, Alloy B, DF, $\langle 112 \rangle_{\text{Al}}$; **e** high Cu/Li ratio, Alloy C, DF, $\langle 100 \rangle_{\text{Al}}$; **f** high Cu/Li ratio, Alloy C, DF, $\langle 112 \rangle_{\text{Al}}$

interval of the precipitates at the grain boundary obviously shrunk. It can be found that the coarse phases were not determined to be a T_1 phase, as they had different crystal structures than the T_1 phase. When the Cu/Li mass ratio increased in the aged Al- x Cu- y Li-Mg alloys, the proportion of the coarse phase at the grain boundary significantly increased.

Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDXS) mapping are usually used to demonstrate the microstructure characteristics at the grain boundary and the distribution of elements in the GB precipitates of the studied three alloys at peak

aging conditions as provided in Figs. 10, 11, and 12. In this study, STEM, selected area electron diffraction (SEAD), and EDXS were carried out on the GB zone to comprehensively distinguish the phases at the GB. From all these images, we can discover that no visible S' phases containing Mg elements were present at the grain boundary of the studied aged alloys with different Cu/Li mass ratios, while Cu-bearing phases are presented in Figs. 10, 11, and 12, corresponding to the T_1 phase and coarse T_1 phase at the GB, which could be confirmed by the SEAD of these images with distinct streaks located at $1/3 \{220\}$ and $2/3 \{220\}$ from the

Fig. 10 STEM image and the EDXS maps of Al-Cu-Li-Mg alloys with low Cu/Li ratio aged at 175 °C under peak aging condition (24 h)

Fig. 11 STEM image and he EDXS maps of Al-Cu-Li-Mg alloys with medium Cu/Li ratio aged at 175 °C under peak aging condition (24 h)

Fig. 12 STEM image and the EDXS maps of Al-Cu-Li-Mg alloys with high Cu/Li ratio aged at 175 °C under peak aging condition (24 h)

[112]_{Al} zone axis (Fig. 11) or at {200} from the [110]_{Al} zone axis (Fig. 12). Moreover, the quantity of the GB precipitates obviously increased by increasing the Cu/Li mass ratio value. In addition, the T_1 phase was determined in the Al-Cu-Li-Mg alloy with a low Cu/Li ratio by the EDXS analysis in the coarse phase, resulting in only Cu elements. Furthermore, the proportion of the T_1 phases and the T_1 coarse phases in the aged alloy with a high Cu/Li mass ratio was higher than that in the aged alloy with a medium Cu/Li mass ratio.

4 Discussion

4.1 The Effect of the Cu/Li Mass Ratio on Mechanical Properties

In this paper, the same aging temperature (at 175 °C) selected for the artificial aging process of three Al-*x*Cu-*y*Li-Mg alloys with different Cu/Li ratios was used to study the transformation of the proportion and chemical composition of the precipitates under similar thermodynamic conditions, linked to corrosion behaviors. Also, the mechanical properties and

the corrosion behaviors of the three alloys were investigated and compared under the same artificial aging temperature offer dates for selecting an optimized chemical composition of the Al-*x*Cu-*y*Li-Mg alloy with the required combination of mechanical and corrosion properties.

Firstly, the alloys with different Cu/Li mass ratios possessed different mechanical properties, as shown in Fig. 2. The obvious distinctions in the yield strength and the tensile strength of the Al-*x*Cu-*y*Li-Mg alloy were attributed to the differences of the microstructural characteristics in different Cu/Li mass ratio alloys, as depicted in Table 3. As previous studies on precipitates acting on strength have improved [52], the phase with the largest effect on strength enhancement has been principally shown to be the T_1 phase. The better mechanical strengthening effect of the T_1 phase is derived from its non-coherent crystal structure and higher aspect ratio of about 50:1–70:1 [53]. Also, the addition of Mg elements to the Al-Cu-Li alloy could prompt the precipitation of the T_1 phase [54]. The θ' phase is also a critical precipitate for improving the mechanical properties and affecting the corrosion behaviors of the Al-*x*Cu-*y*Li alloys with different Cu/Li mass ratios. The tendency of the prompting effect on precipitation and strengthening mechanical properties was

Table 3 Microstructure characteristics of the Al-*x*Cu-*y*Li-Mg alloys with different Cu/Li ratios under peak aging condition

Precipitates type	Alloy C High Cu/Li ratio	Alloy B Medium Cu/Li ratio	Alloy A Low Cu/Li ratio
Major precipitates	T_1 phase, θ' phase	δ' phase, T_1 phase, θ' phase	δ' phase
Minor precipitates	S' phase	S' phase	T_1 phase, S' phase
Precipitates at GB	A few T_1 phase	Some T_1 phase and coarse phase	A great many of T_1 phase and coarse phase

magnified by the increase in the Cu/Li mass ratio in the aged Al- x Cu- y Li alloy. Hence, Alloy C has the best mechanical properties, resulting in the higher proportion of the T_1 phase in the Al matrix. With a decrease in the Cu/Li mass ratio, the tensile properties of the alloys gradually declined, which was related to the quantity decreasing of the T_1 phase.

4.2 The Effect of the Aging Process on Corrosion Behaviors

By comprehensively analyzing the corrosion features in Fig. 3 and Table 2, it can be found that the Al- x Cu- y Li-Mg alloys have similar corrosion type evolutions during the artificial aging process. When the aging time extended, the corrosion sequence was as follows: pitting, IGC, and pitting. Thus, the main corrosion types in the corrosion immersion test of the aged Al-Cu-Li alloy samples are IGC and pitting [55, 56]. The formation and growth of the IGC were related to the precipitate's distribution characteristic at the grain boundary, the width of the solution element depletion zone near the grain boundary, and the precipitate characteristics within the grain [57]. Similarly, the three-pole micro-battery system containing the above-mentioned three microscopic areas with different electrochemical characteristics was produced to simulate above the structural features. In this simulation system, the prior anodic dissolution of the areas with greater negative potential leads to the appearance of IGC [58]. On the other hand, pitting was confirmed to be associated with the preformation of the Al-Cu-Li alloy matrix and the types of elements added into the alloy [59, 60]. Using the Al-Cu-Li alloy in this paper as an example, the more positive the pitting potential, the stronger the pitting resistance.

The IGC corrosion evolution feature is mainly related to the grain boundary structural evolution characteristics of the studied Al-Cu-Li alloy [61]. In the under-aging stage, some phases at the GB began to precipitate, as shown in Fig. 7. In the peak aging stage, continuous precipitates at the GB were present (Fig. 8). Finally, in the over-aging stage, as displayed in Fig. 9, the precipitates at the GB became coarse and discontinuous. Hence, the coarsening and continuity of the precipitates at the GB were important factors to the depth value and the corrosion aging time interval of the IGC (Figs. 3 and 5). In addition, the OCP variation tendency (Fig. 6) of the studied alloy was related to the microstructural characteristics in the grain of the studied aged alloy. As the aging time extended, the quantity of the precipitates gradually increased in the aged alloy matrix, which has a different potential and possesses a negative potential in the alloy matrix. Hence, the potential of the aged alloy gradually decreases according to the declining tendency of the OCP curve as a function of aging time (Fig. 6d), determined by the change in the increase in microstructural characteristics with precipitates, as we surmised.

4.3 The Effect of the Cu/Li Mass Ratio on Corrosion Behaviors

The corrosion behavior of the Al- x Cu- y Li-Mg alloys depends on the microstructural characteristics in the aged sample, such as the precipitate's features in the grain, the precipitate's performance at the grain boundary, and the PFZ distinction close to grain boundary [62]. Different types of the precipitates coexisted in the grain or at the grain boundary under the aging condition of the studied Al- x Cu- y Li-Mg alloys, which are shown in Figs. 7, 8, and 9. Different precipitates showed various corrosion mechanisms in the same corroded solution according to the corresponding reports [63]. The corrosion mechanism of the T_1 phase, along with those of the T_2 phase and S' phase, showed this phenomenon after the dissolution of active elements in the phase [64]. The potential discrepancy between the dissolved phase with positive potential and the prior dissolution of the adjacent area without precipitation and a relatively negative potential caused the IGC. However, the δ' phase always dissolved first due to its lower potential than the adjacent area [65].

Overall, the better IGC corrosion resistance in Alloy A is speculated to produce the uniform size δ' phase in the grain and the fewer precipitates nearly the grain boundary [66]. Moreover, the IGC corrosion sensibility of the alloys with medium Cu/Li mass ratio and high Cu/Li mass ratio is similarly ascribed to the T_1 phase and the coarse phases at the grain boundary. The continuous precipitates were speculated to produce the continuous corrosion channel reported by the IGC corrosion mechanism of the Cu-bearing phase [67], which resulted in an increase in the IGC corrosion sensibility in these studied alloys. Notably, by comparing the aged Alloy B and Alloy C, when the Cu/Li mass ratio increased, the IGC corrosion sensibility significantly improved. The reason for this phenomenon was assumed to be the uniformity and continuity of the grain boundary phase. As shown in Figs. 8, 9, 11, and 12, the proportion of the T_1 phase at the grain boundary increased, alongside the continuous enhancement of the precipitates at the grain boundary, with an increase in the Cu/Li mass ratio. The microscopic characteristics at the grain boundary linked to the different IGC corrosion sensibilities were consistent with the above assumptions. Moreover, the higher Cu/Li ratio Al- x Cu- y Li alloy with more T_1 phase in grain was linked to the greater negative potential shown in Fig. 6 and possessed greater IGC corrosion sensibility, resulting in greater potential difference between the zone near the GB and the grain zone. Furthermore, the influence of the grain characteristics of the Al-Cu-Li alloy with different Cu/Li ratios acting on IGC corrosion sensibility must also be considered from the perspective of stored energy of grain and the misorientation of grain boundary [68, 69]. The above inferences will

be precisely confirmed and discussed in future experiments using more advanced representations.

Based on our study, the reason for the different corrosion behaviors in the Al-*x*Cu-*y*Li-Mg alloys is the various microstructure characteristics in the grain and at the grain boundary. This paper summarized the reasons for the different corrosion performances in different kinds of Al-*x*Cu-*y*Li-Mg alloys artificially aged at the same temperature with different microscopic structural characteristics. This could be an effective technical approach to improve the corrosion resistance of the Al-Cu-Li alloy through the accurate control of inhomogeneous microscopic characteristics.

5 Conclusions

In this study, the mechanical properties, corrosion behaviors, and microstructural characteristic evolution of Al-*x*Cu-*y*Li-Mg alloys were systematically summarized and analyzed. The main conclusions are as follows:

1. As the Cu/Li mass ratio increased in the Al-*x*Cu-*y*Li-Mg alloys, the mechanical properties including the yield strength and the tensile strength of the studied alloys increased. The Al-*x*Cu-*y*Li alloy with a high Cu/Li ratio possessed good mechanical properties, which were ascribed to the greater quantity of the T_1 phase in the alloy with a higher Cu/Li ratio.
2. A combination of the precipitates under the aging conditions transformed the changing values for the Cu/Li mass ratio. The main precipitate in the alloy with a low Cu/Li mass ratio was the δ' phase, the main precipitates in the alloy with the medium Cu/Li mass ratio were the δ' phase, θ' phase, and T_1 phase, and the main precipitates in the alloy with a high Cu/Li mass ratio were the θ' phase and T_1 phase.
3. The superior IGC corrosion resistance of the alloy with a low Cu/Li mass ratio among the three studied Al-*x*Cu-*y*Li-Mg alloys was confirmed. This resistance exists because there are fewer precipitates at the grain boundary. Additionally, the alloys with medium and high Cu/Li mass ratios had higher IGC corrosion sensitivity because of their greater anodic dissolution of the continuous precipitates at the grain boundary, which resulted in the accelerated formation and growth of the IGC.
4. Comparing the IGC corrosion sensitivity of the high Cu/Li mass ratio alloy with that of the medium Cu/Li alloy, the higher IGC corrosion sensitivity that presented in the alloy with a high Cu/Li mass ratio was attributed to its higher proportion of T_1 phases or coarse T_1 phases at the grain boundary.

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