Microstructure and Precipitation in Al-Li-Cu-Mg-(Mn, Zr) alloys

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Abstract

Hot rolled Al-6Li-1Cu-1Mg-0.2Mn (at.%) (Al-1.6Li-2.2Cu-0.9Mg-0.4Mn, wt.%) and Al-6Li-1Cu-1Mg-0.03Zr (at.%) (Al-1.6Li-2.3Cu-1Mg-0.1Zr, wt.%) alloys developed for age forming were studied by tensile testing, electron backscatter diffraction (EBSD), three-dimensional atom probe (3DAP), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). For both alloys, DSC analysis shows that ageing at 150°C leads initially to formation of zones/clusters, which are later gradually replaced by S phase. On ageing at 190°C, S phase formation is completed within 12 h. The precipitates identified by 3D atom probe and TEM can be classified into (a) Li-rich clusters containing Cu and Mg, (b) a plate-shaped metastable precipitate (similar to GPB2 zones/S"), (c) S phase and (d) δ' spherical particles rich in Li. The Zr containing alloy also contains β' (Al_3Zr) precipitates and composite β'/δ' particles. The β' precipitates reduces recrystallisation and grain growth leading to fine grains and subgrains.

Keywords: Al-Li-Cu-Mg alloy, 3DAP, TEM, DSC, age forming

I. Introduction

Age-forming is a key innovation in the fabrication of curved structural components for aerospace applications, e.g. wing skin. This process offers considerable design and manufacturing benefits, such as reduced operator skill requirements, high potential of automation, increased component accuracy and reduced residual stress level. The process is directly applicable to artificially-aged high-strength 7xxx (Al-Zn-Mg-Cu) alloy components. However, standard 2xxx (Al-Cu-Mg) alloys, which are used for instance for lower wing skins, are generally naturally aged, and are ill-suited for age forming, as artificial ageing will compromise damage tolerance. This new method of forming curved components therefore requires the design of new damage tolerant alloys which have an enhanced formability but still retain good strength and damage tolerance after extended exposure at temperatures used for age forming (typically 140-200°C). Recently, it was shown that lithium-containing 2xxx alloys with Li content around 6 at.% aged at 150-190°C maintain good fatigue crack growth resistance,¹ comparable with the incumbent 2024-T351. Thus these Li-containing alloys appear to be potential candidates for age forming. In this work the ageing characteristics, microstructures (and nanostructures) and their contributions to tensile properties of these Li containing alloys have been investigated. The detailed microstructural investigation has been performed using electron backscatter diffraction (EBSD), three-dimensional atom probe (3DAP), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC).

Substantial work on Li-containing alloys has been performed especially in the 1980s and 90s. Lithium is the lightest metallic element, which reduces the density and

increases the modulus of Al-based alloys.² In addition, Li can allow the precipitation strengthening of aluminium by a homogeneous distribution of coherent, spherical δ' (Al_3Li) precipitates. Research showed that the strength of Al-Li alloys could be enhanced by additions of magnesium or copper; and both these additions have been included in the development of quaternary Al-Li-Mg-Cu alloys.³ The combined density-reducing and precipitation-strengthening characteristics of lithium were the main reasons for its choice as the alloying element for development of low-density Al-base alloys. The microstructures and precipitation of commercial Al-Li alloys (which normally contain about 8-12 at% of Li) have been intensively studied. In Al-Cu-Mg-Li-(Mn, Zr) alloys, two major precipitation sequences have been reported:⁴

where δ' is an L_{12} ordered phase (Al_3Li), fully coherent with the Al matrix, and δ is the equilibrium Al-Li phase (AlLi , BCC structure), which forms mainly at grain boundaries.⁵ GPB zones are Cu and Mg containing Guinier-Preston zones.^{6,7} It is suggested that the S' is a slightly strained semi-coherent version of the (incoherent) orthorhombic S phase and need not be distinguished from it,^{8,9} as both have composition Al_2CuMg . The T_2 (Al_6CuLi_3) particles, which can be identified by its quasicrystalline nature and 5-fold symmetry on selected area diffraction (SAD) patterns,¹⁰ are relatively large and located at sub-grain boundaries or within grains. Hence, they are not expected to have much influence on the yield strength of the

alloys. In Zr containing alloys, β' (Al_3Zr) particles are found, which, like δ' , have an Ll_2 structure and a spherical morphology.⁵

II. Experimental Procedures

Two Al-Li-Cu-Mg-(Mn, Zr) alloys have been manufactured by conventional casting and hot rolling (Table 1). Details on production of the alloys were given previously.¹ After solution treatment, water quenching and stretching by 2.5%, the alloys have been left at room temperature for a few months (named as SQSRT condition) before further ageing for 12-72 h at 150°C and for 6-48 h at 190°C. Tensile tests were carried out on an Instron machine with a cross head speed of 1 mm/min at room temperature. EBSD analysis was conducted on a Jeol JSM-6500 multi-purpose high performance field emission gun scanning electron microscope (FEG-SEM). Data was analysed with the aid of HKL Channel 5 software.

The DSC experiments were conducted using a Perkin-Elmer Pyris 1 within the temperature range 5-540°C at a constant heating rate of 10°C/min. Disc-shaped samples were made with a thickness about 0.9 mm and diameter 5 mm. Baseline correction was performed in two stages. First a DSC run with empty pans was subtracted from the experiment. Secondly, the data was corrected by assuming the combined effect of heat capacity differences and baseline fluctuations results in a heat flow which is a second order polynomial.¹¹ The coefficients were fitted by assuming that the heat effects due to reactions are zero at three temperatures: 40, 120 and 498°C.

Thin foils for transmission electron microscopy were prepared using a standard procedure: samples of 400 μm thickness were punched, ground to 250 μm and electro-polished using a 1/3 nitric acid, 2/3 methanol solution held at -20°C to -30°C , with a voltage of 25V. TEM observation was performed at 200kV using a Jeol JEM-2000FX.

The 3DAP analyses were conducted in the ECoPoSAP (Energy compensated position sensitive atom probe).¹² The specimens (in the shape of sharp needles with an end radius less than 100 nm) were prepared by a two-stage electro polishing method using a solution of 25% perchloric acid in 75% of acetic acid and a solution of 2% perchloric acid in 98% butoxyethanol. Analyses were carried out at a specimen temperature of 27K with a pulse fraction of 20% and a pulse repetition rate of 1500 Hz. The voltage varied between 4.5 and 9.5kV depending on the analysis.

III. Experimental Results

3.1 TENSILE TESTING

For both alloys yield strengths gradually increase during ageing at 150°C (Fig. 1), and they quickly improve during ageing at 190°C providing a yield strength well above the 2024 T351 standard (325MPa). The strength curves also show the influence of Zr addition, as the Al-6Li-1Cu-1Mg-0.03Zr alloy has higher strength than the Al-6Li-1Cu-1Mg-0.2Mn alloy, which is attributed to the smaller grain size¹³ and some

limited contribution of precipitation hardening by the coherent β' (Al_3Zr) particles.¹⁴ The yield stress reaches the 2024-T351 standard for the Al-6Li-1Cu-1Mg-0.03Zr alloy aged over 48h at 150°C and 6h at 190°C. However, this strength level can only be achieved by ageing longer than 12h at 190°C for the Al-6Li-1Cu-1Mg-0.2Mn alloy. Another difference between the Al-6Li-1Cu-1Mg-0.03Zr alloy and the Al-6Li-1Cu-1Mg-0.2Mn alloy is that the yield strength of the former remains high even until 48 hrs at 190°C, which means that it is still not significantly overaged at this stage.

Serrated flow has been found on the strain-stress curves of both alloys (Fig. 2). There are obvious serrated features for alloys aged 12-72 h at 150°C and 6 h at 190°C. However, serrated flow disappears gradually when alloys are aged for 12 to 48 h at 190°C. For 150°C ageing, the serrated flow occurs at almost the entire strain range (whole strain-stress curves), but the serrated flow only appears up to 6% strain when ageing at 190°C.

3.2 METALLOGRAPHY AND EBSD ANALYSIS

Optical micrographs of the grain structures of the two alloys are presented in Fig. 3. The Al-6Li-1Cu-1Mg-0.03Zr alloy possesses an apparently finer, more complex grain structure than the Al-6Li-1Cu-1Mg-0.2Mn alloy. Both alloys have similar Cu, Mg and Li contents and the only difference is the additional Zr (0.03 at.%) in the Al-6Li-1Cu-1Mg-0.03Zr alloy, which has a substantial effect in terms of restraining grain growth. EBSD analysis has been carried out for both alloys on both S-T and L-S planes. Table 2 shows the results of average grain area, grain diameter, aspect ratio and number of neighbour grains, which clearly demonstrate the smaller grain size in the Al-6Li-1Cu-

1Mg-0.03Zr alloy. The average of grain size on S-T planes is 8.2 μm in the Al-6Li-1Cu-1Mg-0.03Zr alloy and 51 μm in the Al-6Li-1Cu-1Mg-0.2Mn alloy. Fig. 4 shows the grain boundary maps of both alloys, in which the higher angle grain boundaries (misorientations $> 12^\circ$) are displayed by dark lines and low angle grain boundaries (misorientations 2 to 12°) by grey lines. These figures reveal that the Al-6Li-1Cu-1Mg-0.03Zr alloy has more limited recrystallisation and finer average grain size as compared to the Al-6Li-1Cu-1Mg-0.2Mn alloy.

3.3 3DAP ANALYSIS

3DAP analysis has been performed for both alloys aged at 150°C for 6 h to 24 h and the data was analysed using the maximum separation method to identify solute clusters present in the analysis.¹⁵⁻¹⁷ The parameters used are $d=0.4$, $L=0.45$ and $N_{min}=12$ and the erosion parameter used to remove the matrix shell is $e=0.45$. Between 6 h and 12 h at 150°C , the cluster density seems to be stable within error but after 24h, the density increases sharply (Table 3). The size of the clusters, as estimated from the radii of gyration, is similar for the three ageing conditions. The average composition of the clusters does not vary greatly with time and in particular the Li content stays close to 50%.

In addition to the clusters, Cu/Mg-rich precipitates were observed. In the early stages these precipitates have a clear platelet shape and are only composed of a few atomic layers (Fig. 5). After 24h at 150°C , the Cu/Mg-rich precipitates have also a platelet shape but one of the precipitates found in alloy Al-6Li-1Cu-1Mg-0.2Mn aged for 12h seems to be formed by the merging of two rod-like precipitates (Fig. 6a and 6b). All

these precipitates are similar in morphology and size to the precipitates observed in a Cu-rich Al-Cu-Mg-Mn alloy.¹⁸ The composition of these metastable precipitates is 61-66%Al, 6-8%Li, 14-16%Cu, 12-16%Mg. The variation in Cu and Mg contents is related to the ageing time with the higher Cu and Mg contents observed for the less extensive ageing (6 h at 150°C). The Li content is stable with ageing time. From comparison of observed precipitates the size of the precipitates is seen to increase with ageing (e.g. compare see Fig. 5 with Fig. 6).

In the Al-6Li-1Cu-1Mg-0.2Mn alloy, δ' precipitates have been observed after 6, 12 and 24h at 150°C (Fig. 7). Two methods to measure the evolution of the volume fraction have been used: the lever rule based on Li content in precipitates and matrix and the ratio of the precipitates volume over the total volume of analysis (Table 4). Although the two results calculated are significantly different, in particular for 24h heat treatment, they both show an increase in the volume fraction of the Li-rich precipitates with time. The numerous precipitates found after 12h are spherical with an average diameter of 4.5 nm. The lithium content within the precipitates is on average 32.5%, which is similar to the results from Sigli and Sanchez.¹⁹ After 24 h at 150°C, their size increases to 6 nm in diameter and the interfaces become more abrupt. In the 3DAP work on the Al-6Li-1Cu-1Mg-0.03Zr alloy, the Li containing precipitates always occurred in conjunction with Zr containing precipitates. Such a composite particle was found in the Al-6Li-1Cu-1Mg-0.03Zr alloy aged for 12 h at 150°C (Fig. 8a). Its core is enriched in Zr and Li, surrounded by a discontinuous shell rich in Li (Fig. 8b). The stoichiometry of both core and shell is close to $\text{Al}_3(\text{Li},\text{Zr})$.

3.4 TEM ANALYSIS

At SQRST condition and 150°C/12h, TEM revealed many dislocation lines and loops, arising mainly from the stretching after solution treatment, and the condensation of quenched-in vacancies, respectively. The zones/clusters detected by DSC and atom probe at this stage could not be detected due to their sizes being below the detection limit of the conventional TEM. TEM analysis also revealed composite Ll_2 ordered particles in the solution treated alloy and after 72h ageing at 150°C, similar to that seen in the 3DAP after 12h. These particles appear to be β' (Al_3Zr) covered by surrounding δ' (Al_3Li) (Fig. 9a), as observed by 3DAP analysis in Fig. 8. The precipitates have an average of diameter of 8.4 nm. Fig. 9b shows the corresponding [112] SAD pattern and schematic diagram; diffraction simulation confirmed that all diffraction spots and streaks can be identified as due to S, β'/δ' or Al. At 190°C/12 hrs, a high density of S precipitates in the form of needles or laths in the matrix was observed, whereas some of δ' shells of the composite β'/δ' are dissolved (Fig. 10a). The reflections on superlattices are weak and originate mainly from β' phase (Fig. 10b).

3.5 DSC ANALYSIS

Fig. 11 displays the DSC curves of the alloys aged at 150°C for different times. The cluster, zone and δ' (Al_3Li) dissolution occurs in the range 180-230°C,²⁰ and S formation occurs at 230-300°C.⁴ At about 390°C, an additional peak appears, which is thought to be due to T2 formation^{21,22} (In some publications the T2 phase has been

termed the I phase). The endothermic T2 and S dissolution effects appear in the range of 400-500°C. On ageing at 150°C the endothermic effect (180-230°C) due to cluster, zone and δ' (Al_3Li) dissolution increases for both alloys. There is very little change in the S formation effect for the Al-6Li-1Cu-1Mg-0.03Zr alloy within 24 h ageing at 150°C. Any changes in the S phase formation peak would be due to formation of S phase during prior ageing, or to the formation of a metastable phase that is stable at least up to the temperature of S formation in the DSC run. (The GPB2/S" phase suggested before^{23,24,25} could be such a relatively stable precursor phase.) Thus the limited change in this exothermic effect indicates that very little S precipitation had occurred during this isothermal treatment. The S phase formation peak reduces on further ageing at 150°C, indicating S precipitation occurs between 48 to 72 h ageing at 150°C. However, the Al-6Li-1Cu-1Mg-0.2Mn alloy shows some changes in the S phase formation effect even from 12 hours. This corresponds to the strength curves, which show a strengthening of the Al-6Li-1Cu-1Mg-0.2Mn alloy on 12h ageing at 150°C, whereas the Al-6Li-1Cu-1Mg-0.03Zr alloy shows no change for this ageing period (Fig. 1). DSC data for both alloys aged at 190°C reveal a very limited dissolution effect after ageing for 6 h, but after 12 h ageing no zones, clusters or δ' (Al_3Li) are present, whilst S formation occurs during ageing (Fig. 12). At 12 h ageing there is still a small S formation peak and with further ageing, the S precipitation peak disappears. This indicates that on isothermal ageing at 190°C most of the S formation is completed within about 12 h for both alloys. There is not much difference between the DSC curves of samples aged for 24 and 48 h at 190°C, indicating precipitation is completed.

IV Discussion

4.1 GRAIN STRUCTURE

It is well known that recrystallisation behaviour is altered by the presence of second phase particles. Nucleation of recrystallisation is associated with subgrain coalescence by slide and climb of dislocations which form low angle boundaries adjacent to neighbouring high angle boundaries. Fine particles may inhibit this rearrangement of dislocations and also prevent migration of high angle boundaries, thus retarding the start of recrystallization. From comparison of grain structures of the Al-6Li-1Cu-1Mg-0.03Zr alloy and the Al-6Li-1Cu-1Mg-0.2Mn alloy, it can be seen that Zr has a substantial effect in terms of restraining grain growth (Figs. 3 and 4). The reason for this is that small additions of zirconium form fine coherent β' (Al_3Zr) dispersoids (Ll_2 ordered small coherent particles), with the loss of coherency required by boundary motion particularly increasing their boundary pinning effect over that of Mn containing dispersoids.²⁶ Fine particles ($<1 \mu\text{m}$) inhibit primary recrystallization and grain growth as described by Nes.²⁷ The model developed by Zener²⁸ produces a simple relationship between the grain radius R , the volume fraction of the second phase particles f and the average radius of the particles r :

$$R = \frac{4r}{3f} \quad (1)$$

Considering that the Zr solubility in Al is about 0.015 at%,²⁹ and that the Zr content of the β' particles is about 15 at% (see Fig. 8b) we can see that about 0.1 at% β' forms in

the Al-6Li-1Cu-1Mg-0.03Zr alloy. Because the atomic density of β' is almost the same as that of aluminium, the atomic fraction of β' is the same as its volume fraction. TEM measurement gives an average Al_3Zr particle radius: $r = 4.2 \text{ nm}$. The above Zener equation would then predict $D = 2R = 11 \mu\text{m}$. This is very similar to the grain size ($8.2 \mu\text{m}$) obtained from EBSD results (see Table 2), confirming that the β' particles dominate the grain structure development.

4.2 PRECIPITATION AND STRENGTHENING

Serrated flow is thought to be related to the presence of alloying elements in solution, especially Li³⁰ and Cu and Mg.³¹ The serrated yielding also is attributed to the rapid release of dislocations previously pinned by an atmosphere of lithium atoms (and their associated vacancies).³² Wert and Wycliffe³³ have shown that serrated flow vanishes concurrently with precipitation of S phase in an Al-10Li-0.5Cu-0.8Mg-0.02Zr alloy. Also for the present alloys, serrated yielding is eliminated once substantial S phase formation has taken place, indicating that dispersing of slip by S phase is effective in counteracting serrated yielding.

With δ' being observed after ageing at 150°C by 3DAP and the low temperature dissolution effects in DSC curves disappearing after ageing at 190°C, the present results indicate that the solvus of δ' is between these two temperatures. This is in line with data for the α/δ' (Al_3Li) solvus reported in the literature³⁴⁻³⁶ which indicates that for our alloys with Li content of 6 at%, the δ' metastable solvus is at about 150-160°C.

On the basis of this, the pronounced and distinct endothermic dissolution effect within 80-170°C that was present in DSC curves of SQRST alloys, but not present for alloys aged at 150/190°C (Figs. 11-12), is likely to be due to the dissolution of the fine homogeneously precipitated δ' ^{20,22,37,38}, that formed during the room temperature ageing. Also the dissolution of Li bearing zones has been considered,^{39,40} but little evidence for their existence exists, and the present results are consistent with Li precipitating to form $L1_2$ ordered δ' phase with a Li content that is slightly lower than the stoichiometric one (Al_3Li).

The atom probe results show that the Al content of Cu/Mg rich precipitates is high, and well in excess of the equilibrium composition of S phase (Al_2CuMg). The results given by atom probe are probably affected by local magnification effects, due to the difference of evaporation field between the matrix and the small precipitates. This may lead to trajectories aberrations which cause atoms from the matrix to be detected within the imaged area of the precipitate. Therefore the measured Al concentration should be seen as an upper limit. The Cu/Mg-rich precipitates stoichiometry may be compared to the $Al_{10}Cu_3Mg_3$ composition for the fully coherent, orthorhombic GPB2/S" phase which was proposed for Al-Cu-Mg alloys.^{23,24} Surprisingly, the Li content inside the metastable precipitates remains at the bulk level (Figs. 5b and 6b), and varies little with ageing time at 150°C. The presence of Li in S phase has already been observed in Al-2.1Cu-4.7Li-0.6Mg alloys, where it was suggested to substitute for Mg.⁴¹ In view of the changes observed in the DSC curves (Fig. 11), the strengthening of the alloys on ageing for several days at 150°C is ascribed to the formation of these zones, with possible additional contributions from limited S phase precipitation, which was evidenced by SAD patterns for the Al-6Li-1Cu-1Mg-0.03Zr

alloy aged 72 h at 150°C (Fig. 9). Also the δ' phase, when present, will cause some strengthening. However, due to the relatively low Li content in the present alloys, the volume fraction of δ' phase will always be much lower than alloys such as 809x alloys, and models for strengthening¹⁴ indicate contribution of δ' phase will be much less than the other precipitates. In terms of strength development on ageing the alloys should be considered as Al-Cu-Mg based, with Li providing some solution strengthening.

It is known that the Zr-rich phase β' (Al_3Zr) is a preferential nucleation site for the Li-rich phase, the shell being δ' .⁴² However the Zr content, with an average of 15% (Fig. 8b), is well below the stoichiometric level of 25%. It is possible that the low measured Zr content is due to preferential evaporation. Nevertheless, since the specimen is not representative of the bulk, we cannot use the overall composition to test this and correct the composition. In fact, taking the Li and Zr composition together, it is close to a $\text{Al}_3(\text{Zr, Li})$ composition. Such substitution of Zr by Li has already been observed by Gayle and Vander Sande.⁴³ The presence of a β' central core of the enlarged δ' particles indicates that it involves complete wetting of Al_3Zr by the δ' . Such precipitation can be understood by reference to the free energy change associated with heterogeneous nucleation:³

$$\Delta G = -V(\Delta G_v - \Delta G_s) + A\gamma \quad (2)$$

The driving force for nucleation is given by the bulk free energy change per unit volume ΔG_v . The two terms representing the barrier to nucleation are the misfit strain energy (ΔG_s) per unit volume (V) and the interfacial free energy (γ) per unit area

(A). X-ray measurements have shown that the small mismatch which exists between δ' and the matrix is negative (In the Al-Li-Cu alloy, the lattice parameter for the matrix is 0.4045 nm and 0.4043 nm for δ' ²). The strain between Al_3Zr particles and the matrix is reported to be positive (that is, the measurements of the Al_3Zr lattice parameter indicate a slight expansion of 1% relative to the matrix lattice),⁴⁴ hence heterogeneous precipitation of δ' upon Al_3Zr possibly combined with some intermixing of δ' with β' to form a $\text{Al}_3(\text{Li,Zr})$ phase will relieve misfit strains thereby reducing the activation barrier for nucleation. More importantly, the interfacial free energy will also be modified for the case of heterogeneous nucleation:

$$\gamma_{het} = \gamma_{\alpha/\delta'} + \gamma_{\delta'/\text{ZrAl}_3} - \gamma_{\text{ZrAl}_3/\alpha} \quad (3)$$

The observed complete “wetting” of the Al_3Zr by the δ' suggests that $\gamma_{\delta'/\text{ZrAl}_3}$ is negligible: the expression is thus reduced to

$$\gamma_{het} \approx \gamma_{\alpha/\delta'} - \gamma_{\text{ZrAl}_3/\alpha} \quad (4)$$

This implies a further reduction in the activation barrier to nucleation, which presumably occurs competitively with the homogeneous nucleation.

4.3 APPLICATION TO AGE FORMING

As mentioned in the introduction, the present alloys are considered to be candidate alloys for age forming of damage tolerant structural elements in aircrafts, especially

lower wing skins. The present results show that the precipitation and precipitation hardening is very sensitive to ageing temperature, with precipitation at 150°C being very different from precipitation at 190°C. Thus for application of age forming to these alloys, selection and control of ageing temperature will be critical. Achieving the right strength levels to make the present type of alloys competitive with incumbent damage tolerant alloys (such as 2024) is relatively straightforward, as tuning of ageing temperature and alloying element level will allow yield strengths between 320 and 400MPa to be engineered.

The choice of grain structure controlling element (Zr/Mn) has a limited influence on the precipitation in the alloys, with the main influence being on the grain structure. The grain structure of the alloys influences the strength to some extent, but its main relevance lies in the influence it exerts on the fatigue crack growth through influencing roughness induced crack closure. In general, a finer grain structure will reduce crack closure effects, which is detrimental for the fatigue resistance.⁴⁵ With the present alloys being envisaged for use as age-formed damage tolerant structural elements, the detrimental influence of grain refinement on fatigue resistance will need to be analysed. The grain structure will also influence creep rates during age forming, and will thus influence the process temperatures needed to obtain sufficient creep. These issues are currently under investigation.

V Conclusions

The microstructure and precipitation hardening of hot rolled Al-6Li-1Cu-1Mg-0.2Mn and Al-6Li-1Cu-1Mg-0.03Zr (at.%) alloys which are candidates for age forming of

damage tolerant structures have been studied by tensile testing, EBSD, 3DAP, TEM and DSC. The following main conclusions can be drawn:

1. The Zr containing alloy contains precipitates of the $L1_2$ ordered β' (Al_3Zr), which reduce recrystallisation and grain growth leading to fine grains and subgrains.
2. The particles identified by 3D atom probe and TEM in alloys aged at 150°C and 190°C are (a) Li-rich clusters containing Cu and Mg, (b) a plate-shaped metastable precipitate (similar to GPB2 zones/S''), (c) S phase and (d) δ' spherical particles rich in Li. The Zr containing alloy contains composite β'/δ' particles.
3. DSC analysis shows that ageing at 150°C leads initially to formation of zones and clusters, with some S phase formation occurring for ageing times in excess of about one day. On ageing at 190°C, S phase formation is rapid and is completed within 12 h. There is good agreement between DSC data on zone/cluster and S phase formation and strength change.

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Table 1: The chemical composition of the alloys (at.%)

Alloy	Li	Cu	Mg	Mn	Zr	Al
Al-6Li-1Cu-1Mg-0.2Mn	5.98	0.93	1.02	0.2	-	remainder
Al-6Li-1Cu-1Mg-0.03Zr	5.8	0.94	1.12	0.005	0.03	remainder

Table 2: Average of microstructural parameters for both alloys measured by EBSD

Alloy	Plane	Ave. Grain area (μm^2)	Ave. Grain diameter (μm)	Ave. Grain aspect ratio	Ave. No. neighbour grain
Al-6Li-1Cu-1Mg-0.2Mn	S-T	5669	51	1.8	3.5
Al-6Li-1Cu-1Mg-0.2Mn	L-S	11294	103	3.8	3.5
Al-6Li-1Cu-1Mg-0.03Zr	S-T	358	8.2	2.4	4.1
Al-6Li-1Cu-1Mg-0.03Zr	L-S	380	8.4	3.5	4.2

Table 3: Density, average radius of gyration and average composition of clusters in the Al-6Li-1Cu-1Mg-0.2Mn alloy after variable ageing time

		6h	12h	24h
Cluster density per m^3		$1.4(\pm 0.7) \times 10^{23}$	$2(\pm 1) \times 10^{23}$	$4.6(\pm 1.3) \times 10^{23}$
Radius of gyration in nm		0.51 ± 0.07	0.53 ± 0.10	0.56 ± 0.09
Average composition (at%)	Al	35 ± 5.7	38.9 ± 2.6	35.5 ± 3.6
	Li	52.3 ± 6.7	48.6 ± 2.8	46.5 ± 4.1
	Mg	7.3 ± 2.6	7.9 ± 1.2	9.3 ± 1.8
	Cu	5.3 ± 2.2	4.6 ± 0.9	8.7 ± 1.8

* Errors in composition are calculated on the total number of atoms within the clusters found for each ageing time

Table 4: Volume fraction of the δ' precipitates calculated by mean of the lever rule and by direct measurement of the total precipitate volumes (V_p) and the total analysed volume (V_a)

	6h		12h		24h	
Lever rule (%)	0.10	± 0.01	2.00	± 0.02	2.18	± 0.01
V_p/V_a (%)	0.37	± 0.02	1.32	± 0.07	9.89	± 0.49

Fig. 1 Yield stress after ageing at 150°C and 190°C for both alloys. Ageing at 150°C (open symbols) and 190°C (closed symbols) for the Al-6Li-1Cu-1Mg-0.2Mn alloy (squares) and the Al-6Li-1Cu-1Mg-0.03Zr alloy (triangles).

Fig. 2 Stress-strain curves of the Al-6Li-1Cu-1Mg-0.03Zr alloy.

Fig 3. Three dimensional microstructures obtained from optical microscopy: *a* the Al-6Li-1Cu-1Mg-0.2Mn alloy; *b* the Al-6Li-1Cu-1Mg-0.03Zr alloy.

Fig. 4 Grain boundary map from EBSD: *a* the Al-6Li-1Cu-1Mg-0.2Mn alloy; *b* the Al-6Li-1Cu-1Mg-0.03Zr alloy - showing higher angle grain boundaries (>12°) by dark lines and lower angle grain boundaries (2~12°) by grey lines.

Fig. 5 *a* 3DAP elemental mapping of Cu and Mg in the Al-6Li-1Cu-1Mg-0.2Mn alloy aged at 150°C for 6h showing a plate-shaped metastable precipitate; *b* corresponding composition profile perpendicular to the zone/matrix broad interface.

Fig. 6 3DAP elemental mapping of Cu and Mg in the Al-6Li-1Cu-1Mg-0.2Mn alloy aged at 150°C for 12h showing a precipitate: *a* side view; *b* top view with the two white lines showing the two directions of growth of the supposed merging precipitate; *c* corresponding composition profile perpendicular to the precipitate/matrix broad interface.

Fig. 7 *a* 3DAP elemental mapping of Li in the Al-6Li-1Cu-1Mg-0.2Mn alloy aged at 150°C for 12h exhibiting several δ' particles; *b* composition profile through one of the δ' particles.

Fig. 8 *a* 3DAP elemental mapping of Li (black) and Zr (grey) in the Al-6Li-1Cu-1Mg-0.03Zr alloy aged at 150°C for 12h showing a plate-like shape δ'/β' duplex; *b* composition profile perpendicular to the interface β'/matrix .

Fig. 9 TEM dark field micrograph of the Al-6Li-1Cu-1Mg-0.03Zr alloy aged 72 h at 150°C showing that many of the spherical precipitates are formed by β' (Al₃Zr) covered by shell of δ' (Al₃Li) (dark field, B=[112]).

Fig. 10 TEM micrograph and SADP of the Al-6Li-1Cu-1Mg-0.03Zr alloy aged at 190°C/12 h (dark field, B=[100]).

Fig. 11 DSC curves: *a* the Al-6Li-1Cu-1Mg-0.2Mn alloy; *b* the Al-6Li-1Cu-1Mg-0.03Zr alloy aged for various times at 150°C.

Fig. 12 DSC curves: *a* the Al-6Li-1Cu-1Mg-0.2Mn alloy; *b* the Al-6Li-1Cu-1Mg-0.03Zr alloy aged for various times at 190°C.