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δ' precipitation in Al–Li–Mg–Cu–Zr alloys

P. J. GREGSON
Engineering Materials, Southampton University, Southampton, UK

H. M. FLOWER
Department of Metallurgy and Materials Science, Imperial College of Science and Technology, London, SW7 2BP, UK

Aluminium alloys containing lithium as a major alloying element rely upon heat-treatment to develop their high-strength potential [1]. Noble and Thompson [2] have summarized the precipitation sequence as a two-stage process:

$$\alpha\text{-supersaturated solid solution} \rightarrow \alpha + \delta'(Al_3Li)$$
$$\rightarrow \alpha + \delta(AlLi)$$

Maximum strengthening was found to be associated with precipitation of the metastable ordered Li_2 δ' phase, which grow as coherent spherical particles. Later work [3, 4] redefined the δ' solvus but confirmed that the transition phase forms during ageing treatments below 200° C.

Jones and Das [1] showed that the strength of Al–Li alloys could be enhanced by additions of magnesium or copper; more recently both these additions have been included in the development of a quaternary Al–Li–Mg–Cu alloy [5]. Within such an alloy further precipitate phase can form during age-hardening [6, 7]. Furthermore, the presence of such additional alloying elements might be expected to influence precipitation of δ' itself. The purpose of this note is to report the results of an investigation [6] into δ' precipitation in the presence of magnesium, copper, and zirconium in aluminium alloys containing lithium.

Ternary and quaternary Al–Li alloys containing magnesium and/or copper were prepared at the Royal Aircraft Establishment, Farnborough via conventional casting techniques; their compositions are given in Table I. The cold-worked sheet product was solution-treated at 520° C for 15 min and cold-water quenched; subsequent age-hardening was carried out at either 170 or 190° C. Transmission electron microscopy (TEM) revealed the presence of two precipitate phases in the as-quenched microstructure of both ternary and quaternary alloys. Dispersions of small (20 to 30 nm diameter) $ZrAl_3$ particles were observed in clusters which were unevenly distributed in the matrix grains. In addition electron diffraction indicated the highly uniform formation of $\delta'(Al_3Li)$ via the presence of weak superlattice reflections; a period of natural ageing, however, was required before the δ' particles were of sufficient size and adequate contrast to be imaged in TEM. Artificial ageing at 170 and 190° C increased the rate of growth of this metastable precipitate, and the spherical δ' particles were easily identified (Fig. 1). δ' Precipitation was accompanied by the formation of additional ternary precipitate phases in the copper containing alloys [6, 7]; however the existence of these phases was found not to influence the nucleation of the δ' which in all cases precedes the formation of the other phases. The influence of copper and magnesium on the growth of δ' particles was determined via measurement of average particle size during ageing and via X-ray diffractometry to monitor lattice parameter changes (Table II). The particle size measurements are summarized in Fig. 2. Within the experimental error of average size measurement copper and magnesium exhibit no effect on growth: neither does the small variation in lithium content. All the data points lie on a single curve at either 170 or 190° C and follow $\bar{r}^3\alpha$ time relationship with the volume fraction of δ' increasing during growth.

TABLE I Alloy compositions

Code	Alloy composition (wt %)			
	Li	Mg	Cu	Zr
A	3.0	2.0	–	0.12
B	3.0	–	1.50	0.12
C	3.0	2.0	1.50	0.12
D	2.3	0.5	1.22	0.12

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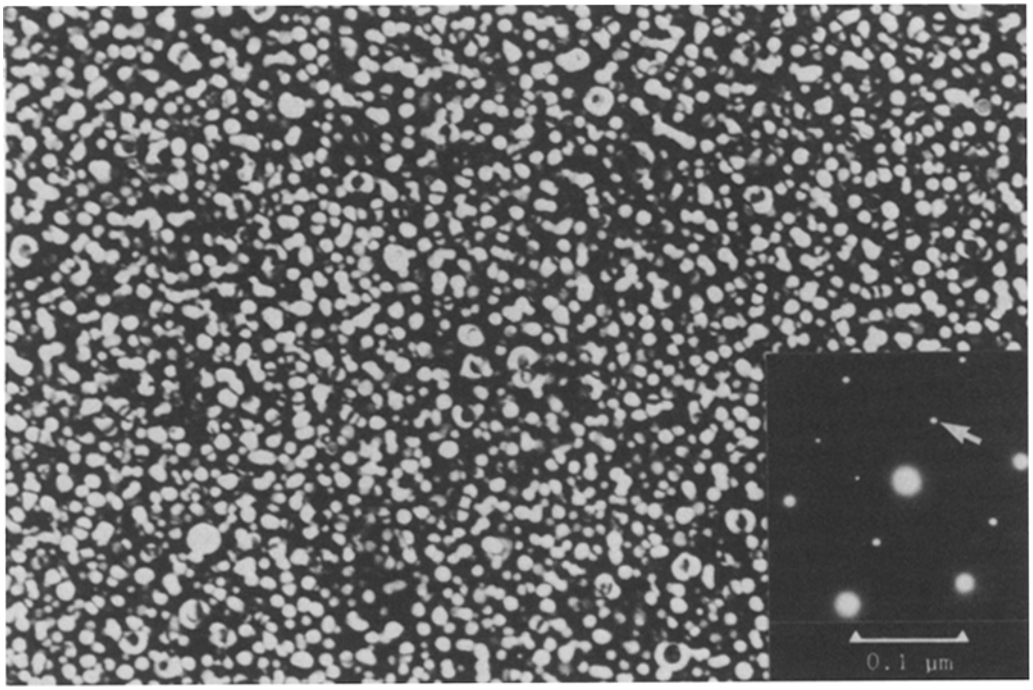

Figure 1 δ′ Precipitation in alloy A aged for 9 h at 190° C. ⟨110⟩ Al orientation. Dark field image. $g = (001)\delta'$.

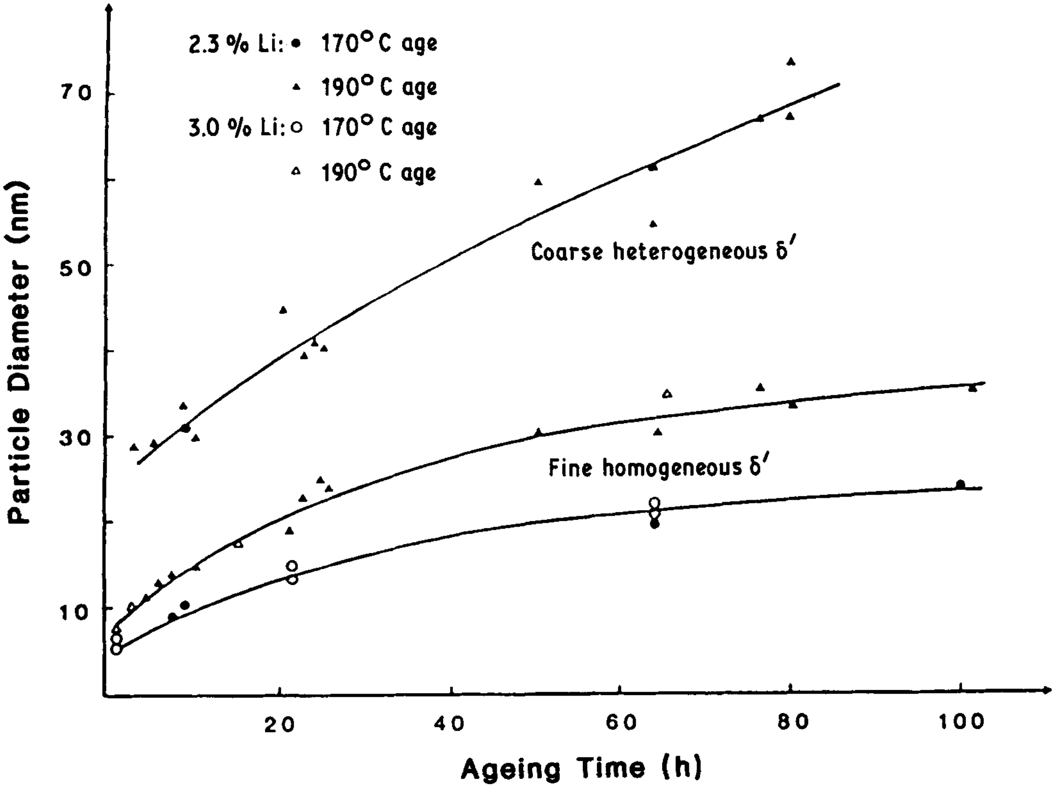

Figure 2 δ′ Precipitate growth (all alloys) at 170 and 190° C.

TABLE II Lattice parameter measurements. (Measurements by courtesy of C. J. Peel, RAE, Farnborough)

Alloy	Phase	Lattice parameter (nm) after age-hardening	
		15 h at 170° C	24 h at 250° C
Al–Li–Mg (A)	Matrix	0.4055	0.4058
	$\delta'(Al_3Li)$	0.4051	–
	$\delta(AlLi)$	–	0.636
Al–Li–Cu (B)	Matrix	0.4045	0.4048
	$\delta'(Al_3Li)$	0.4043	–
	$\delta(AlLi)$	–	0.636

In all the alloys some grains consistently exhibited a heterogeneously distributed dispersion of δ' particles which were much larger than the average particles in size and clearly formed a quite separate population with an apparent size at zero ageing time in the range 20 to 30 nm. These particles followed a distinct growth curve although it still approximated to an $\bar{r}^3 \alpha t$ relationship. The nature of the duplex δ' distribution in such grains is shown in the dark field image of Fig. 3. The large particles of uniform size are randomly distributed amongst the fine δ' particles. There is no evidence of any precipitate denuded zone around the enlarged particles which might be expected if they were the result of preferential coarsening. The large particles consistently contained a dark central core, regardless of the imaging conditions used. Such behaviour cannot be rationalized in terms of any elastic scattering contrast mechanism and is suggestive of inelastic scattering associated with a core of much greater average atomic number than the remainder of the particle. The results of X-ray energy dispersive microanalysis, carried out in the TEM mode, using an electron beam less than 5 nm in diameter are summarized in Fig. 4. The dark-field image clearly shows a "cored" particle. The X-ray spectrum from the central core of the particle reveals the zirconium "L" peak in addition to the aluminium "K" peak in that part of the spectrum displayed in Fig. 4a. The remaining spectra show the same part of the spectrum for analyses carried out on the periphery of the cored particle, the matrix, and a "normal" δ' particle, respectively; in each the spectrum is compared with that from the core, after normalizing with respect to the aluminium peak. It is obvious that the anomalously large particles have zirconium rich cores whereas the normal δ' particles do not. It is the zirconium which gives rise to the characteristic contrast observed in the TEM work.

The present results are in good agreement with previous studies employing electron microscopy to study the formation of δ' within binary Al–Li alloys [2, 3]. The existence of superlattice reflec-

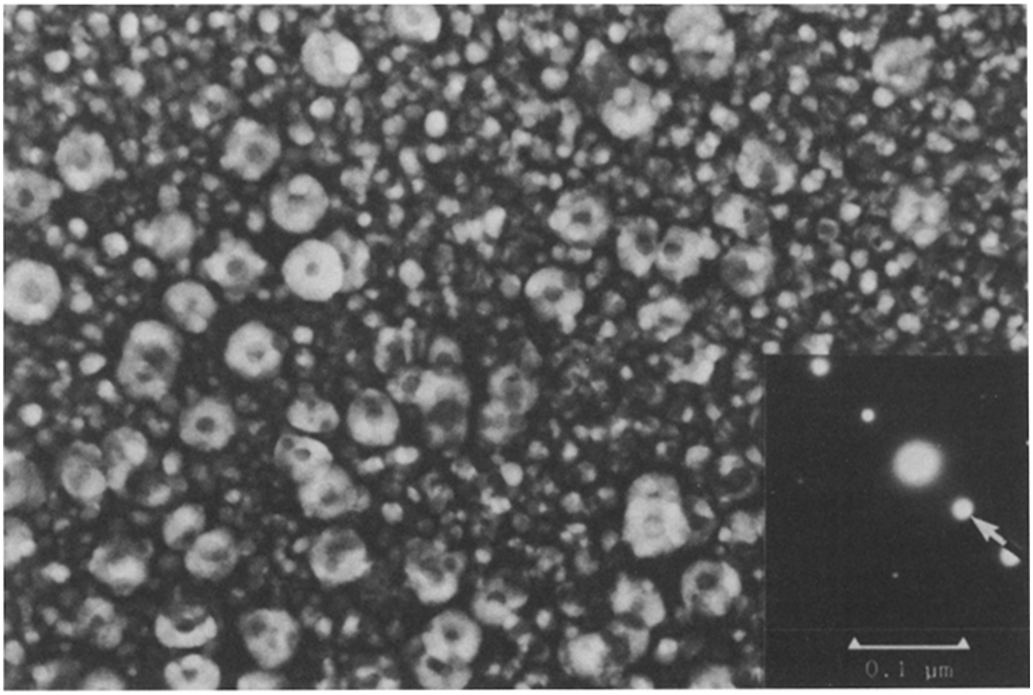

Figure 3 δ' Precipitation in alloy C aged for 64 h at 170° C ⟨1 1 0⟩ Al orientation. Dark field image $g = (001)\delta'$.

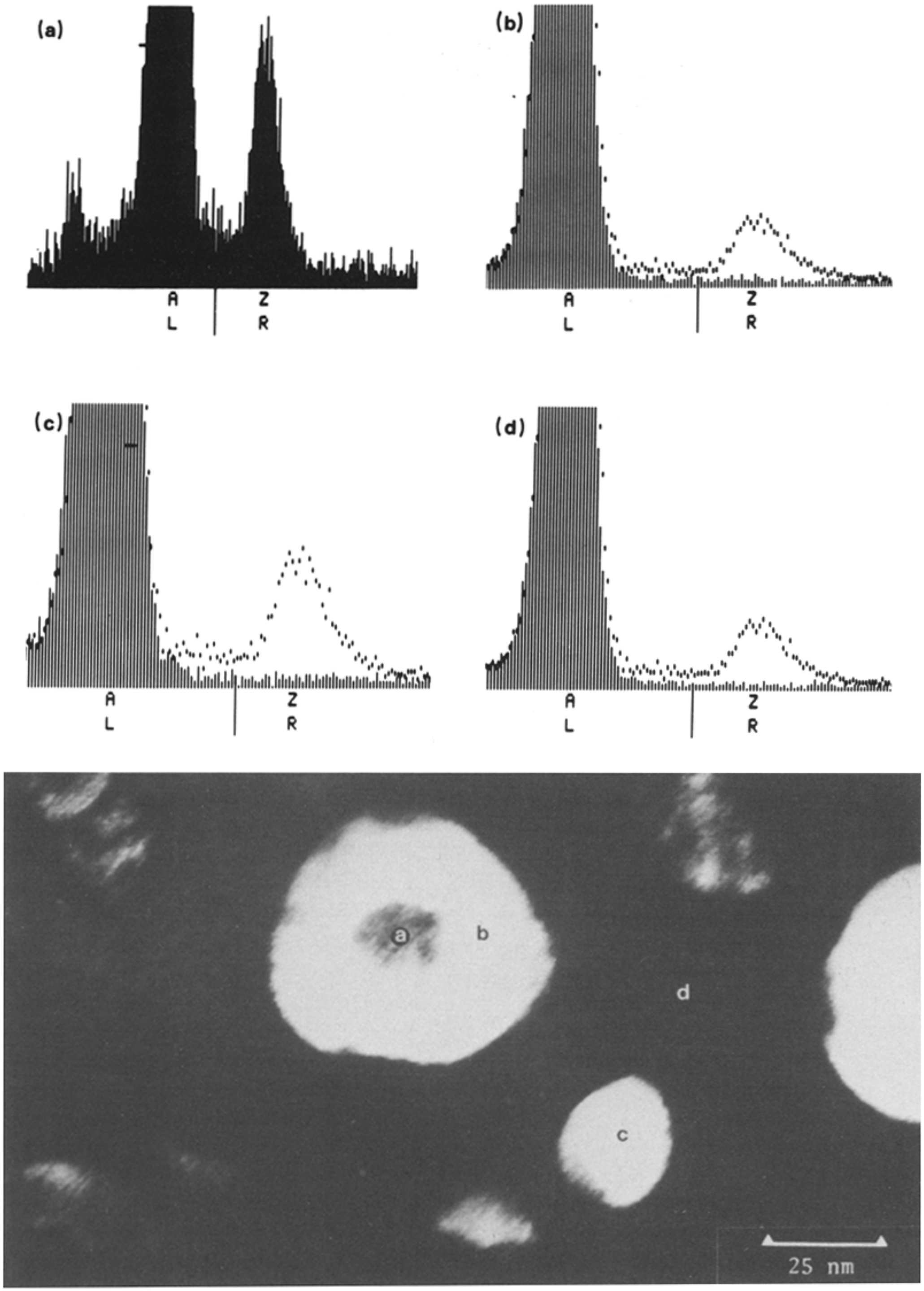

Figure 4 Dark field image of δ′ particles in alloy D and X-ray spectra of (a) central core of the large particle (b) periphery of the same particle (c) a typical δ′ particle and (d) the matrix.

tions in the as-quenched condition demonstrates that water quenching is inadequate to prevent nucleation of the ordered δ′ phase. The growth of δ′ in the present alloys has been shown to obey a relationship of the form $\bar{r}^3 \alpha t$; in agreement with previous work which suggested that δ′ invariably coarsens according to Lifshitz–Wagner kinetics [2]. However, observation in this work, of a concurrent increase in volume fraction of δ' implies that growth of the δ' particles does not conform to the boundary conditions of the Lifshitz–Wagner theory. It has previously been observed that the stiffness decreases as ageing progresses [8]; such observations, taken in conjunction with the findings of Noble and his co-workers [9] in which the major contribution to modulus was shown to be associated with lithium in solid solution, further indicates that δ' particle growth involves continued precipitation of Al_3Li from solid solution.

In the age-hardened condition, the lithium present in binary Al–Li alloys is partitioned between the δ' precipitates and solid solution; in the range 170 to 200° C about 5 at% lithium would be expected to remain in solid solution [2–4]. Kellington *et al.* [10] determined the lattice parameter of a similar binary solid solution (4.5 at% Li) and obtained a value of 0.4046 nm; lattice parameters of the ordered δ' phase are similar, the reported mismatch in binary alloys being $< 0.2\%$ [2]. Lattice parameters determined for matrix (0.4045 nm) and δ' (0.4043 nm) in the present Al–Li–Cu alloy are in close agreement with the 0.4046 nm of the binary alloys. There is no indication from the lattice parameter measurements that significant amounts of copper enter the δ' phase.

The presence of magnesium in the Al–Li–Mg alloy however has given rise to an increase in the lattice parameters of both matrix and δ'. The dilation of the matrix is consistent with the 0.0005 nm expansion of aluminium for each 1% magnesium addition quoted by Mondolfo [11]. The lattice expansion exhibited by the δ' particles indicates that the magnesium must also be incorporated into the δ'. This view is strengthened by consideration of the additional lattice parameter changes induced by overageing at 250° C. The observed lattice parameter of the equilibrium δ phase (0.636 nm) is the same in both magnesium and copper containing alloys and is in agreement with Mondolfo's value for the binary aluminium lithium system [11]. This indicates that magnesium is not incorporated into δ. Thus as δ' transforms to δ the magnesium present in the δ' must be rejected into the matrix phase. This is entirely consistent with the observed further increase in matrix lattice parameter (Table II). The observation that magnesium is incorporated into δ' as well as the matrix has important implications with respect to the properties of Al–Li–Mg alloys. It has been suggested that magnesium might increase the mismatch and hence inhibit particle cutting and coplanar slip. The parallel increases in lattice parameters of the δ' and the matrix results in no significant increase in misfit between them and hence coherency criteria remain unchanged. Therefore, apart from an increment of strength afforded by solid-solution strengthening, magnesium additions would not be expected to alter significantly the deformation characteristics of Al–Li alloys. This is observed in practice [6].

The presence of zirconium in the 20 to 30 nm central core of the enlarged δ' particles, together with the inhomogeneous distribution of these particles, indicates that they arise as a result of heterogeneous precipitation of δ' upon pre-existing $ZrAl_3$ particles. This is a most unusual phenomenon involving complete wetting of $ZrAl_3$ by the δ'. Such precipitation can be understood by reference to the free energy change associated with heterogeneous nucleation:

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

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 of the present alloys have shown that the small mismatch which exists between δ' and the matrix is negative in nature. The strain between $ZrAl_3$ particles and the matrix in a binary Al–Zr alloy on the other hand is reported to be positive [12], hence heterogeneous precipitation of δ' upon $ZrAl_3$ will relieve the misfit strain thereby reducing the activation barrier for nucleation. More importantly the interfacial free energy will also be modified for the case of heterogeneous nucleation:

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

The observed complete "wetting" of the $ZrAl_3$ by the δ' implies that $\gamma_{\delta'/\text{ZrAl}_3}$ is negligible: the expression is thus reduced to

$$\gamma_{\text{het}} \approx \gamma_{\delta'/\alpha} - \gamma_{\text{ZrAl}_3/\alpha}$$

which implies a further reduction in the activation barrier to nucleation, which presumably occurs competitively with the homogeneous nucleation during the quench from the solution treatment temperature. The existence of the duplex δ' precipitation within Al–Li alloys employing zirconium in concentrations typically employed to induce grain refinement would not be expected to influence directly the mechanical properties of the age-hardened alloys; such properties are dominated by the much higher volume fraction of homogeneously nucleated δ' particles.

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