Review
Aluminium–lithium alloys

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A review is presented on the development of aluminium–lithium alloys spanning several decades including both ingot metallurgy and rapid solidification. Initial interest in aluminium–lithium alloys derived from the benefits associated with lithium, both in the presence of solid solution and as the coherent Al_3Li phase which result in a density reduction of about 3% for each weight per cent addition of lithium and an increase in Young's modulus of about 6%. In principle weight savings in aircraft structural parts could reach 15%. The less than optimum deformation and fracture behaviour of aluminium–lithium alloys has been attributed in part to the strain localization that results from the planar slip of shearable Al_3Li precipitates. The physical metallurgy of aluminium–lithium alloys is reviewed together with various approaches that investigators have carried out, to various degrees of success, to improve the deformation behaviour inherent to these alloys. Many of the problems associated with ingot processed Al–Li alloys were alleviated to a certain extent by rapid solidification-powder metallurgy (RS-PM) processes. Although considerable progress was indeed achieved by RS-PM processing technology, the RS-PM approach introduced another problem, namely that of oxide contamination. Recently it has been demonstrated that "spray atomization and collection" processes, properly managed, are able to produce rapidly solidified, wrought, fully dense alloys which overcome the faults of RS-PM alloys. The developments of such processes are also reviewed.

1. Introduction

The development of new aerospace structures which demand improved damage tolerance and weight efficiency led to the development of a number of interesting alloys. It is currently believed that aircraft redesign alone, with currently available commercial materials, will not meet the demands for a significant improvement in structural efficiency (weight/density) for the new generation of fighter aircrafts. In the race for the development of new structural materials meeting the requirements of increased specific strength at lower density, epoxy based composites and aluminium have remained the two favourite contenders. While research in the field of composite materials has yielded very exciting results, aluminium has remained at the centre of attention due to its attractive manufacturing costs, its extensive previous use in aircraft structures, and the availability of aluminium manufacturing facilities [1].

The density of aluminium is reduced by about 3% for each weight per cent addition of lithium, while Young's modulus is increased by about 6% [2, 3]: see Figs 1 and 2. In principle, weight savings in aircraft structural parts could reach up to 15% [1, 4–6] or possibly 18% [7]. While the addition of beryllium has a similar effect as lithium on the properties of aluminium, beryllium's cost and toxicity make it an unlikely immediate candidate.

In 1957 the first Al–Li alloy (X2020) was used in the structure of an experimental Navy RA-SC Vigilante aircraft [6]. This alloy, however, was withdrawn from production shortly afterwards because of segregation effects, lowered toughness and ductility, and problems during melting which were caused by the high reactivity of lithium. A very interesting and thorough historical review on the development of Al–Li alloys is presented by Balmuth and Schmidt [7]. With the advent of rapid solidification technology, RS-PM was proposed as a potential solution to the low toughness and ductility evidenced by the cast IM X2020. Although significant improvements in the alloy's mechanical behaviour have indeed been achieved by RS-PM processing, the principal problems, namely low toughness and high crack growth rates, remain far from being solved.

As part of the growing family of high strength Al–Li alloys discussed at the First International Conference on Aluminium–Lithium Alloys (May 1980), significant interest was evident in the Al–Cu–Li and Al–Mg–Li types of alloys. The high specific strength and elastic modulus values of X2020 sustained great interest in such an alloy, in spite of a lower than desired ductility, poor fatigue crack growth rates and notch weakening in tensile tests.

2. Lithium additions

The effect of lithium additions on the elastic properties of aluminium alloys will depend on whether lithium is in solution or present as a second phase. In the former case, the elastic constants will depend on the atomic
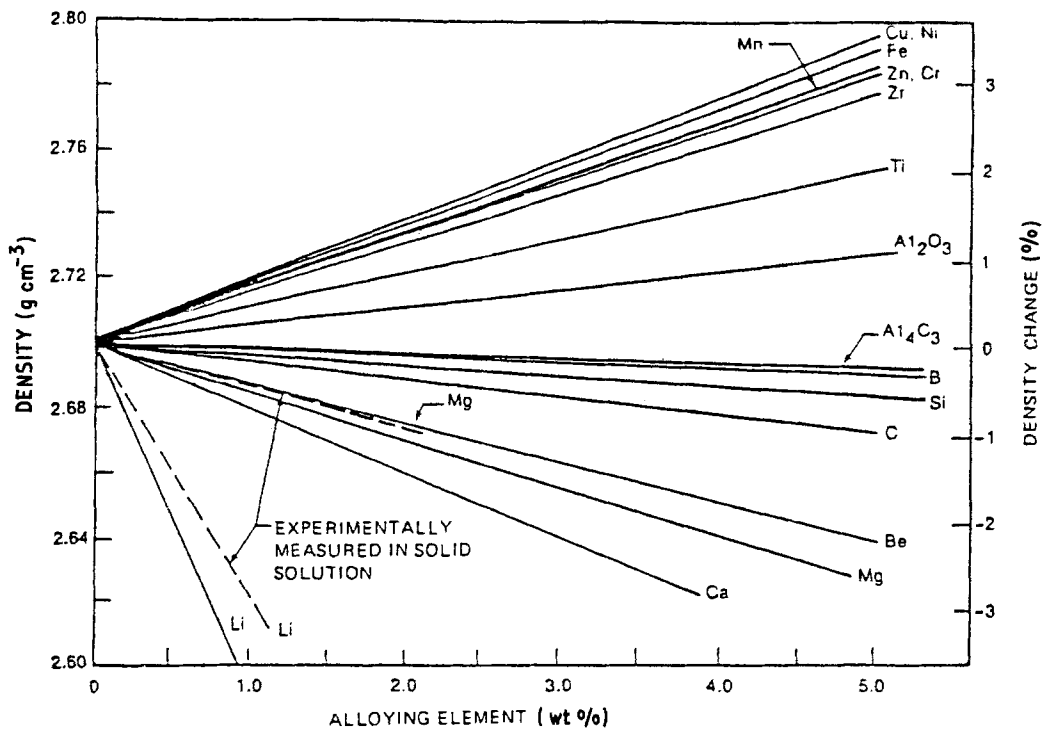
Figure 1 Influence of alloying additions on the density of aluminium (calculated) [2].

interactions and interatomic potentials and, in the latter case, on the volume fraction and intrinsic modulus of the second phase [8]. The measured elastic constants of Al-solid solutions (excluding magnesium and lithium) agree well with the calculated values of the weighted sum of the elastic constants of the respective solute [9]. The effect of lithium is unexpected in that it substantially increases the values of the elastic constants of Al–Li solid solutions although the values of its own constants are lower than those of aluminium [8].

3. Physical metallurgy of Al–Li alloys
The precipitation hardening of lithium containing

alloys involves the formation of a large volume fraction of a metastable, ordered and coherent $\delta'(Al_3Li)$ phase having a Ll_2 type superlattice structure [10–12]. The δ' phase has been observed in Al–Li, Al–Mg–Li, and Al–Cu–Li alloys [13]. In Al–Cu–Li alloys additional strengthening is achieved by the co-precipitation of copper-rich phases independent of the δ' precipitation [10]. In high copper, low lithium alloys (3 to 4.5 % Cu, 1 to 2 % Li), the decomposition of the supersaturated solid solution (α_{ss}) occurs by the reactions [10, 12, 14]:

$$\alpha_{ss} \begin{cases} \delta'(Al_3Li) \to \delta(AlLi) \\ GP\ Z's \to \theta'' \to \theta' \to \theta\ (Al_2Cu) \end{cases} \quad (1)$$

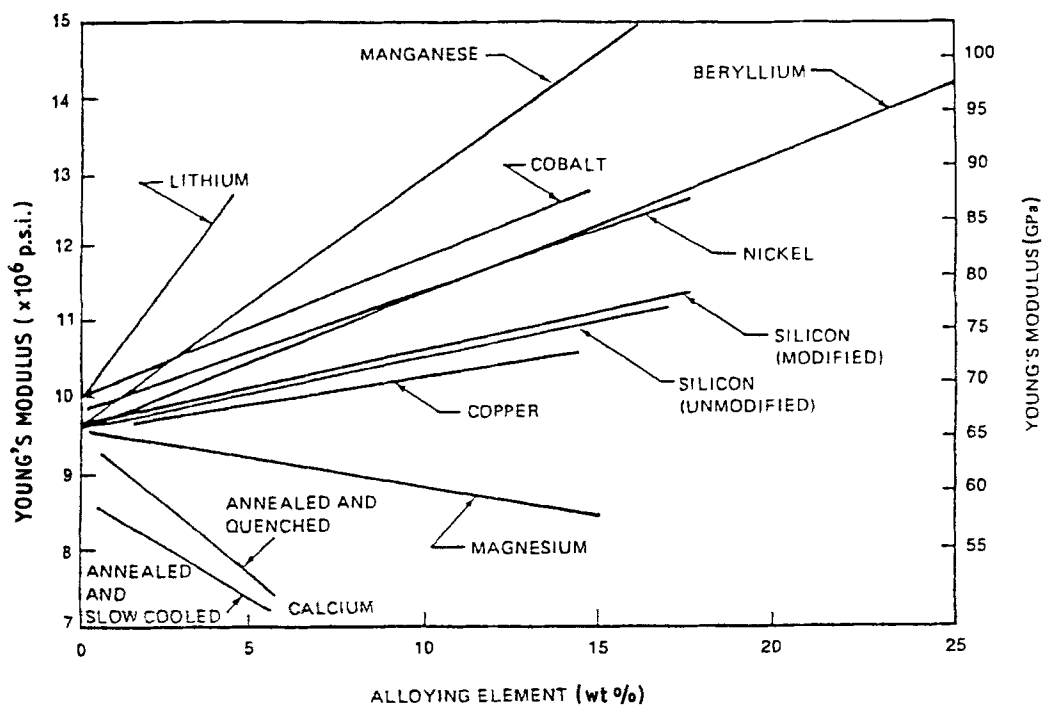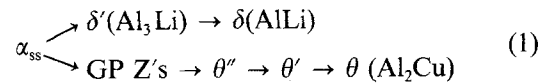*Figure 2* Influence of alloy additions on Young's modulus of aluminium [2].
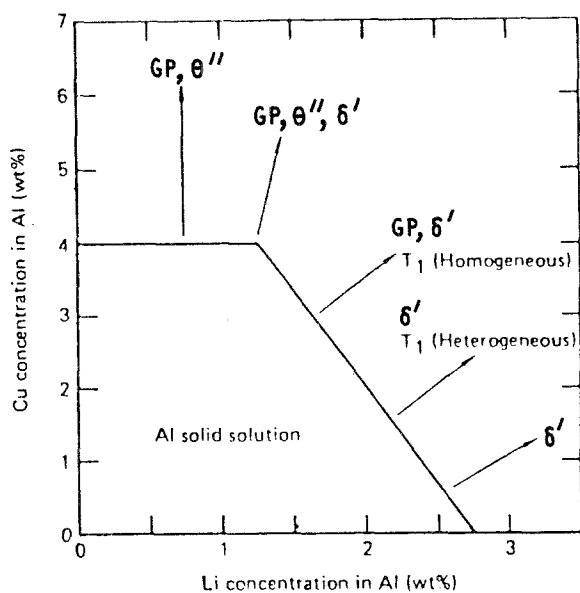
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Figure 3 The solvus line at 500°C at the Al-rich end of the Al–Cu–Li system. The strengthening phases at various copper and lithium levels are indicated [15].

TABLE I Compositions and structures of equilibrium and non-equilibrium phases in the Al–Cu–Li system

Phase	Composition	Structure	Lattice parameter (nm)
T_B	$Al_{7.5}Cu_4Li$	Cubic (CaF_2) Cl	$a = 0.583$
T_1	Al_2CuLi	Hexagonal	$a = 0.497$ $c = 0.935$
T_2	Al_6CuLi_3	?	?
δ	AlLi	Cubic (NaTl) B32	$a = 0.637$
θ	Al_2Cu	Tetragonal C16	$a = 0.6066$ $c = 0.4874$
δ'	Al_3Li	Cubic (Au_3Cu) $L1_2$	$a = 0.401$
θ''	Al_2Cu	Tetragonal	$a = 0.404$ $c = 0.78$
θ'	Al_2Cu	Tetragonal	$a = 0.404$ $c = 0.580$

For the high lithium, low copper alloys (2 % Cu, > 2 % Li) the reaction sequence leading to the formation of Al_2Cu is suppressed and the precipitation of the T_1 (Al_2Cu Li) phase occurs by:

$$\alpha_{ss} \nearrow \delta' \ (Al_3Li) \rightarrow \delta \ (AlLi) \atop \searrow T_1(Al_2CuLi) \qquad (2)$$
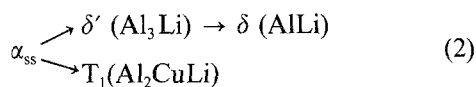
In the Al–Cu–Li system the types of strengthening phases that precipitate from the supersaturated Al-solid solution strongly depend on the Cu : Li ratios [15–18]. The concentration dependence of the precipitation sequence on the Cu : Li ratios was discussed in the work of Pao et al. [15], and a summary plot is shown in Fig. 3. A listing of the compositions and structures of the equilibrium and non-equilibrium phases in the Al–Cu–Li system was compiled by Kang et al. [19].

There is, however, some disagreement with respect to the sequence of the δ'–δ precipitation reaction shown in Equations 1 and 2. While Field et al. [20] and several investigators [16–18] proposed that in the grain boundary region the δ' precipitates preferentially coarsened and ultimately transformed to δ, other investigators disagreed. Williams [21] suggested that the small amount of lattice strain generated by the coherent δ' phase is not sufficient to justify its possible use as a heterogeneous nucleation site for δ. Because of the relatively large α:δ phase misfit, the large change in lithium concentrations, and a different crystal structure, heterogeneous nucleation of δ will require the aid of large heterogeneities such as dislocations and grain boundaries. Williams [21] hence proposed that δ nucleates independently of δ' and grows by dissolution of metastable δ'.

In general the precipitation of T type phases in high copper Al–Cu–Li alloys has been shown to be detrimental to the strength-toughness relationship in those alloys [13, 15, 18, 22, 23] (see Table I). In Al–Li alloys containing 4 to 4.5 wt % Cu, the copper available for strengthening can be reduced by precipitation of

the T phase. Thus, the strength of the higher lithium Al–Cu–Li alloys would be lower because of the reduction in copper that otherwise would be available for precipitation of the θ' (Al_2Cu) strengthening phase [22, 24]

The precipitation of the equilibrium phase, T_1 (Al_2CuLi), and the simultaneous coarsening and dissolution of δ' in an overaged, inert gas atomized Al–Cu–Li–Mn alloy resulted in significantly reduced strength and toughness [15].

Several investigators, however, have associated improvements in the mechanical properties of rapidly solidified (RS) Al–Li alloys with the presence of T type phases, in particular with the T_1 (Al_2CuLi) phase. Sankaran and O'Neil [23] reported an increase in the strength and ductility of a PM Al–4Cu–2Li–0.2Zr when compared to those of a PM Al–2.5Cu–2.5Li–0.2Zr alloy and associated the improvements in mechanical behaviour with the type of strengthening phases involved. The higher strength and ductility of the higher copper alloy was associated with the presence of the T_1 and δ' phases. The strength and ductility of the high lithium alloy, strengthened solely by δ', were lower than those of the high copper alloy. The heterogeneous precipitation of T_1 (Al_2CuLi) in the high lithium alloy was associated with a reduction in the strength and ductility values. The Al–2.5Cu–2.5Li–0.2Zr strengthened solely by homogeneous precipitation of T_1, possessed the lowest strength but the highest ductility. Kang and Grant [19] attributed the improvements in mechanical behaviour associated with a high copper (> 4 wt %), low lithium (< 2 wt %) RS-PM alloy to the presence of the θ' (Al_2Cu) and T_1 (Al_2CuLi) phases, whereas in a high lithium (> 2 wt %), low copper (< 3 wt %) RS-PM alloy the δ' phase was found to be responsible for only limited property improvements. A listing of the compositions and structures of equilibrium and non-equilibrium phases in the Al–Cu–Li system studied by Kang and Grant [19] are shown in Table I.

The δ' phase has been found to coarsen according to Lifshitz–Wagner Kinetics, following an increase in average radius r with $(time)^{1/3}$ [11, 13, 20, 21, 25]. The coarsening rate varies directly with the energy of the Al–δ' interface, the diffusion coefficient of lithium, and the equilibrium solubility of lithium in aluminium (8, 11). The Ostwald ripening process has been reported
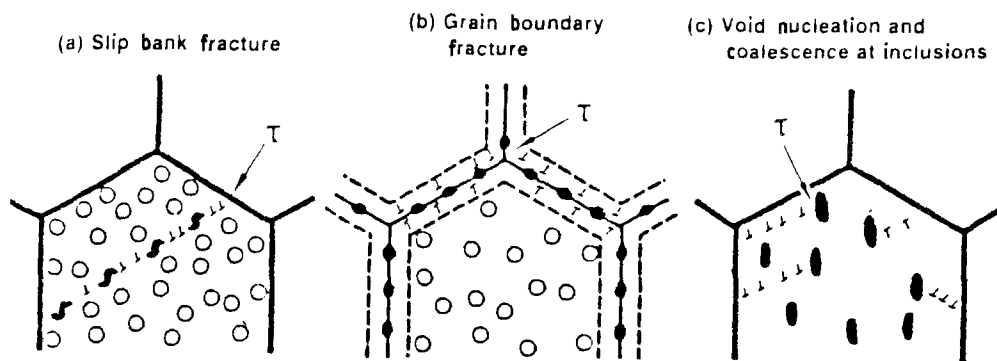
Figure 4 Tensile deformation and crack nucleation mechanisms in δ'-strengthened Al–Li alloys [27].

to begin immediately upon ageing [26]. Also, along with the δ' coarsening within the grains, preferential coarsening of the precipitates at the grain boundaries and growth of precipiate free zones (PFZ) has been observed; the latter was also approximated by a $(time)^{1/3}$ behaviour. The development and growth of precipitate free zones has been interpreted as being the result of preferential coarsening of δ' on the grain boundaries by enhanced diffusion, thereby depleting the grain boundaries of solute [20, 25]. The PFZs have been found along grain and subgrain boundaries for all ageing conditions for ingot alloys as well as RS-PM materials and also along interfaces between Al_6Mn particles [27]. The occurrence of PFZs at subgrain boundaries has been reported to depend on the crystallographic orientation difference between the neighbouring subgrains [27].

4. Deformation and fracture of Al–Li alloys

The less than optimum deformation and fracture behaviour of Al–Li types of alloys have been attributed to one or several of the following: (a) strain localization that results from planar slip of shearable precipitates; (b) formation of coarse intermetallics during slow solidification; (c) high levels of hydrogen present in Al–Li alloys; and (d) grain boundary segregation of tramp elements such as sodium, potassium and sulphur.

During plastic deformation of Al–Li alloys, the coherent δ' precipitates are sheared by dislocations. The planar slip associated with δ' shearing leads to heavy, localized dislocation pile-ups at grain boundaries, which in turn generate stress concentration across the boundaries. Hence, cracks can nucleate at the slip and grain-boundary intersections and can then propagate readily along the PFZs. Gysler et al. [27] have proposed several crack nucleation mechanisms for Al–Li alloys strengthened by the δ' phase (see Fig. 4). Regardless of which strengthening mechanism dominates, the implication of precipitate shearing is that once deformation has occurred on a particular glide plane, continued deformation on that plane is favoured.

Aluminium–lithium alloys have been reported to contain over ten times the amount of hydrogen normally found in high strength, non-lithium aluminum alloys. Such disproportionately high concentrations of H_2 have been attributed to a large increase in the solid

solubility of H_2 in the lithium alloyed matrix, and to the formation of a hydrogen-rich phase during solidification of aluminium–lithium alloys [13, 29–31]. Several investigators have suggested that the poor ductility of aluminium–lithium alloys might be caused by the formation of a stable hydride of either lithium or of aluminium and lithium, such as LiH or Li_3AlH_6 [29].

An investigation conducted by Hill and Williams [29] reported that a significant increase in ductility and toughness was achieved by reducing the hydrogen content of Al–Mg–Li alloys from 43 to 14 p.p.m. Palmer et al. [30], however, found no difference between the mechanical properties of a PM Al–3Li–1.5Cu–0.5Co–0.2Zr alloy with 1 to 46 p.p.m. hydrogen and those reported for a similar PM alloy, Al–3Li–1.5Cu–1Mg–0.2Zr, which had 1 to 3 p.p.m. hydrogen. Clearly, there is still no agreement on the role of H_2 on the deformation behaviour of Al–Li alloys.

White [32] presents a general discussion on the harmful effects that trace elements and impurity segregation on grain boundaries have on the ductility of metals and alloys. The precise effect that trace elements have on the fracture and deformation of Al–Li alloys, however, is not clear, and has been reported to depend on other factors. Vasudevan et al. [33] reported that sodium segregation on grain boundaries in an Al–11.4 at % Li IM alloy resulted in a decrease in fracture toughness. Slow bend Charpy toughness properties were found to be significantly affected by bulk (as opposed to fracture surface) sodium concentrations. The loss in toughness was significant in the as-quenched and underaged alloys where the planarity of slip was less intense. In the peak aged condition, toughness was found to be insensitive to both bulk and fracture surface sodium concentrations. This was attributed to the planar slip in the peak aged condition which in fact dominates the brittle fracture behaviour of the alloys. Webster [28], however, reported that neither the levels of sodium nor potassium correlated with the observed toughness or ductility regardless of whether the alloys contained lithium.

5. Past approaches to improving deformation behaviour

Over the past decade considerable research efforts have been directed to improving the poor ductility and

fracture behaviour of RS-PM and IM Al–Li alloys. Some of the approaches taken for improving toughness in Al–Li–X alloys involve: (1) encouraging dislocation cross-slip or precipitate bypassing in the alloy by modifications of the lattice parameters to increase mismatch in the Al–Al_3Li system; (2) introducing secondary precipitation systems; and (3) using a dispersion hardening system in addition to the precipitation hardening system. Other approaches taken include grain refinement via additions of manganese, zirconium, chromium and cobalt and minimization of tramp elements (potassium, sodium, sulphur) through alloy control. Structure control and increased solid solubility that became possible with the advent of rapid solidification technology allowed many investigators to take the aforementioned approaches with various degrees of success.

During plastic deformation of Al–Li alloys containing non-shearable dispersoids, dislocations accumulate at the particles hardening the active slip planes and causing transfer of slip to adjacent plances by the Orowan bypass or the Hirsch cross slip mechanisms [34]. These mechanisms tend to increase the density of localized dislocation channels during deformation and cause widening of the slip bands. These wider slip bands, hence, result in decreased tip stress concentration. The presence of a dispersion of nondeforming particles has also been shown to increase the strain hardening exponent leading to an improvement in fracture toughness [4, 35, 36].

Coyne et al. [37] reported that the large volume fraction of incoherent Al_6Mn intermetallic particles formed in an IM Al–Mn–Li alloy homogenized the slip and promoted cyclic hardening; however, strain localization was present in large PFZs which were formed during aging to peak strength. Sastry and O'Neil [38] used rapid solidification by the twin roller quenching technique to process Al–3Li, Al–3Li–0.6Co and Al–3Li–0.3Zr alloys. The cobalt additions resulted in a uniform distribution of fine incoherent Co_2Al_9 dispersoids which were found effective in decreasing the planarity of slip and increasing high temperature strength. The additions of zirconium were reported to increase the strength and ductility by the preservation of dynamically recovered or partly recrystallized structures. Phillips [39] made additions of 2.82 wt % Mn to a PM Al–Li alloy in an attempt to disperse the strain localization caused by the coherent Al_3Li phase. The alloy was prepared from RS centrifugally atomized fine powders with the purpose of obtaining a fine distribution of $MnAl_6$ particles. The presence, however, or relatively coarse manganese-rich particles at interdendritic boundaries and elsewhere, provided an easy fracture path and led to extremely low ductilities ($\sim 3\%$).

Chanani et al. [14] reported an improvement in ductility with underaged Al–3Li–1.7Cu–0.23Mn and Al–2.5Li–4.8Mg–0.1Zr PM alloys due to a reduction in strain localization effects caused by the presence of narrower precipitate free zones at grain boundaries.

Pao et al. [15] added 0.5 Mn to a PM Al–2.5Li–1.5Cu to achieve grain refinement and to minimize strain localization, succeeding in the former but

not in the latter aim. The failure to achieve a slip-homogenizing effect was attributed to a low volume fraction of the manganese containing phase. The rapid coarsening of δ' and the presence of the equilibrium T_1 phase, however, were successful in dispersing slip in the overaged alloy.

Sankaran et al. [40] processed a high purity Al–3Li alloy, a commercial purity Al–3Li alloy with iron as an impurity, and Al–3Li alloys containing additions of cobalt, titanium, zirconium and yttrium, by rapid solidification using the twin roller quenching technique. The objective of the work was to enhance the ductility of Al–Li alloys by the slip homogenization that is enhanced by grain refinement and the presence of incoherent dispersoids. The microstructures of the Al–3Li–0.16Ti and the Al–3Li–0.23Co alloys were found to consist of 40 nm diameter δ' precipitates and 50 to 100 nm Al_3Ti and Co_2Al_9 phases, respectively. The total elongations exhibited by these two alloys (9.7% and 9.1% respectively) are good indications of the effectiveness of Al_3Ti, and Co_2Al_9 in dispersing slip and hence enhancing the ductility of the alloys.

Completely unrecrystallized alloys have shown elongation values of 10 to 13%, which are superior to those of the corresponding recrystallized states at 4 to 8% in both longitudinal and transverse directions. The higher ductility of the unrecrystallized material has been associated with a sharp texture and a transgranular fracture mode [4, 41–43]. Additions of about 0.5 wt % Zr have been shown to be effective in suppressing recrystallization through the precipitation of coherent Al_3Zr dispersoids [40, 42].

Feng et al. [42] had limited success at improving the properties of IM 2020 type alloys although they had lowered the iron and silicon contents in order to remove coarse constituent particles. They found that by eliminating cadmium and by replacing manganese with zirconium, they obtained a highly textured unrecrystallized structure. Cadmium was found to be more effective in promoting the nucleation of δ' than was a 2% cold stretch prior to ageing, but the difference in strength between the two materials in the peak aged conditions was only 12%.

Cadmium has been shown to increase the nucleation frequency of θ' in IM Al–Cu alloys [24, 42, 44]. The exact nucleation mechanism is subject to discussion, but several concepts have been proposed: (a) cadmium may lower the interfacial energy between the precipitate and the matrix; (b) the large cadmium atoms may produce quenching strains that eventually aid the nucleation of θ'; and (c) the increased number of vacancies associated with cadmium atoms may help decrease the activation energy for θ' nucleation.

The substitution of another element for aluminum or lithium in δ' may significantly change the lattice parameter and the αAl–δ' interfacial energy. This, in principle, should encourage dislocation cross-slip or precipitate bypassing rather than precipitate cutting, therefore reducing the amount of planar slip.

Gayle [31] had limited success with additions of Cu, Mg, Si, Mn, Fe, Sc, Ga and Ag to cast and rolled, and to cast and hot extruded IM Al–Li alloys. The additions were made in an attempt to improve ductility,

toughness and fracture behaviour by increasing the matrix–precipitate lattice misfit and/or by encouraging cross-slip by modifying the shear resistance of δ' or by formation of other second phases. The copper containing alloys showed the best fracture behaviour with moderate strength. Brittle fracture behaviour was attributed to grain-boundary failure. High hydrogen levels, inherent planar slip, and boundary precipitate free zones which grow with ageing all appeared to be important factors in the grain boundary weakness.

Bauman and Williams [45] tried to modify δ' precipitation with additions of Mg, Cu, Ag, Zn, Mn, Cr, Si and Zr by altering the δ'/α misfit in IM Al–Li alloys. Though silver and zinc show potential for increasing the δ'/α misfit they have the undesirable characteristics of being relatively heavy elements and of significantly decreasing the solubility of lithium within the matrix. Bauman and Williams [45], however, concluded that large increases in the misfit strain between δ' and the matrix phase in Al–Li based alloys does not seem to be achievable. Both Gayle [31] and Bauman and Williams [45], however, were severely limited by the slow solidification rates and poor structure control inherent to IM technology.

Very encouraging results involving the coprecipitation of δ' and other phases through additions of magnesium have been reported by several investigators [11, 41, 43, 46–50]. In Al–Mg–Li alloys, magnesium contributes to the strength in two ways. It acts as a solid solution strengthener [47], and it decreases the solubility of lithium in aluminium, resulting in an increase in the volume fraction of δ'.

Noble and Thompson (11) have found the ageing sequence for Al–Mg–Li alloys to be:

$$\alpha \text{ (supersaturated)} \rightarrow \delta'(Al_3Li) \rightarrow Al_2MgLi$$
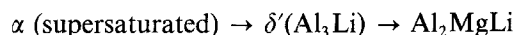
According to Noble and Thompson [11], the subsequent formation of Al_2MgLi consumes nearby δ' particles; therefore, the reaction $\delta' \rightarrow \delta$ is suppressed. Under equilibrium conditions, Al–Mg–Li alloys with a Mg/Li ratio in the range of 2.5 to 1.5 form the phase (Al_2MgLi) [47].

Other investigators argue, however, that strengthening in this system is due to the δ' precipitate and that the magnesium contributes primarily to solid solution strengthening [13]. In the work of Palmer et al. [41] the superior combination of strength and ductility obtained in an Al–Cu–Li–Mg–Zr RS–PM alloy when compared to its equivalent Al–Li–Cu–Zr alloy was attributed to the precipitation of S' (Al_2CuMg) phase and to the contribution to solid solution strengthening of the magnesium, which decreased the tendency for slip localization to occur. The S' phase in the Al–Li–Cu–Mg alloys appeared to be finer and more uniform than the θ' or T_1 phases in the Al–Cu–Li alloys. This has also been confirmed by the works of Miller et al. [49], Peel et al [43] and Balmuth and Schmidt [7]. The unrecrystallized alloys had much higher strengths than the recrystallized or partially recrystallized alloys. Zirconium was found to be the most effective element for inhibiting recrystallization in these alloys

and about 0.2 wt % zirconium was sufficient to completely prevent recrystallization.

Dinsdale et al. [48] found that in zirconium free IM Al–Li–Mg alloys the fracture surfaces were intergranular. Magnesium additions to the Al–Li–X alloys increased grain-boundary deformation substantially. Increased magnesium content, however, was found to lead to grain-boundary embrittlement, probably due to the presence of the Al_2LiMg phase.

Magnesium additions to RS–PM alloys have produced encouraging results. Wang and Grant [46], for example, used the USGA RS–PM technique to process an Al–4.16Cu–1.8Mg–0.96Li–0.50Mn–0.18Cd alloy. The alloy exhibited an excellent combination of mechanical properties: for example, the yield strength and tensile strength values were 58.4 k.s.i. (403 MPa) and 81.4 k.s.i. (516 MPa), respectively, with an elongation of 11.9%. The alloy was also notch tough and had a fracture toughness (K_Q) value of 33.9 k.s.i. inch$^{1/2}$ (37.3 MPa m$^{1/2}$)

6. Mechanical alloying

One way to improve strain localization problems and to avoid precipitate free zones is to add a fine homogeneously distributed dispersoid that would interact directly with dislocations, dispersing slip and inhibiting the formation of intense slip concentrations. Gilman [52] successfully incorporated 5 vol % of aluminium oxide and carbide dispersoids into Al–2.5Li–2Cu and Al–2.5Li–1Mg alloy powders by mechanical alloying. The mechanical properties of the mechanically alloyed (MA) Al–Li–Cu alloy were superior to those of the equivalent (but oxide free) IM alloy. The MA alloy, for example, showed an elongation of 7% (compared to 2% for the IM alloy) at higher strength levels. Donachie [53] significantly improved the toughness of a MA Al–Mg–Li alloy by variations of powder processing parameters and vacuum consolidation temperatures. The K_Q value was increased from 21.8 MPa m$^{1/2}$ to 29.6 MPa m$^{1/2}$ at the 483 MPa yield strength (YS) level. Narayanan et al. [2], however, report extremely low ductilities (3.5%) associated with a high strength MA Al–Li alloy. The fracture characteristics of the MA alloys in this study were dominated by crack nucleation at foreign particle inclusions and failure along prior particle boundaries. The poor interparticle bonding was attributed to an inadequate redistribution of the powder surface oxides during processing and fabrication.

7. Oxide contamination

Until recently Al–Li alloy had been developed and processed by the conventional ingot casting methods with various degrees of success [5, 27, 49, 54, 55]. The severe segregation of lithium at high lithium levels, particularly in coarse grained structures, are some of the inherent limitations of the IM approach.

Many of the problems associated with the ingot processed Al–Li alloys were alleviated to a certain extent by powder metallurgy (PM) or rapid solidification processing (RSP). The high solidification rates associated with RSP helped minimize the segregation of lithium, extensively reduced the grain size

and resulted in overall microstructural refinement. Although considerable success was indeed achieved, the PM–RSP approach introduced another problem, namely that of oxide contamination. The large surface areas generated by powder production techniques, together with the stability of the aluminium oxides (i.e. Al_2O_3, etc.) made it impossible to eliminate oxides from the final PM products; instead it was a matter of the amount of oxide one could tolerate.

The properties of RS–PM 2XXX alloys are strongly affected by the presence of oxides in the final product. In particular, the fracture characteristics of RS-PM X2020 alloys are enormously degraded due to the presence of oxide stringers in the fully densified, hot worked and heat treated alloys [4, 56–61].

Gysler et al. [27] observed early crack nucleation at almost continuous oxide films along prior flake boundaries in splat cooled flakes of Al–Li–Cu alloys. The large oxide particles were thought to dominate the crack nucleation process and, therefore, the ductility of the RST materials.

The oxide stringers in the X2020 alloys are shown to strongly influence the mechanical properties of the alloy. Kang and Grant [19] studies an RS-PM X2020 alloy which achieved significant improvements in room temperature tensile properties and an 11 to 15% increase in the specific modulus (E/ϱ) when compared to the IM material. The fracture toughness values, however, fell, in some cases, to less than 50% of those for ingot based 7075 (56–58). Comparison between RS-PM X2020–T6 and IM X2020–T6 shows that RS–PM alloys are superior in the low ΔK region, but fatigue crack growth rates (FCGR) of PM alloys are higher than those of IM alloys in the intermediate and high ΔK regions [19, 56–58, 60]. This behaviour was associated in all cases with a high volume fraction of oxide stringers [56–61].

8. New processing alternatives

Recently efforts to improve the quality of rapidly solidified crystalline materials, while simplifying the overall processing patterns have centred around a different consolidation technology. The process is basically a spray atomization and collection process for which the processing steps can be varied as needed. Similar processes are the Osprey process [62–66], CSD (controlled spray deposition) [67, 68], and more recently LDC (liquid dynamic compaction) [69–78].

Lavernia et al. [72] used the LDC technique to produce two X2020 Al–Cu–Li alloys. Improvements in the room temperature tensile ductilities and fatigue crack growth rates at the same strength levels were reported for the LDC alloys when compared to those of the equivalent RS-PM material. Meschter et al. [76, 77], also reported a significant improvement in the notched tensile behaviour of an LDC Al–4Li–1Cu–0.2Zr alloy over that shown by the same material in RS-PM form. Finally the addition of 1 wt % Li to an experimental 2024 alloy processed by the LDC technique, resulted in an excellent combination of strength, tensile ductility and notched strengthening (UTS = 74.4 k.s.i., YS = 52.6 k.s.i., elongation of

16.4%, notched tensile strength/yield strength ratio $N_{UTS}/YS = 1.44$) [78].

Noteworthy in all three cases was the absence of oxides in stringer form commonly found in the RS-PM material of equivalent composition.

9. Summary

The significant reductions in density and enhancement of the elastic modulus that are achievable through lithium additions to aluminium alloys have helped to generate and maintain a large interest in the Al–Li family of alloys. The large amount of research that continues to be done today clearly demonstrates that the aircraft manufacturing industry continues to believe in the great potential for near-term commercialization of Al–Li alloys.

Unfortunately, there are some problems associated with the physical metallurgy of Al–Li alloys that have resulted in a less than optimum deformation and fracture behaviour. There is ample experimental evidence that this behaviour can be traced to one or several of the following: (a) strain localization that results from planar slip of shearable precipitates together with precipitate free zones; (b) high levels of hydrogen in Al–Li alloys; (c) formation of coarse intermetallics during slow solidification; and (d) grain-boundary segregation of tramp elements such as sodium, potassium and sulphur.

Some of the approaches that have been taken for improving the less than optimum ductility and fracture behaviour of Al–Li alloys are: (a) encouraging dislocation cross-slip or precipitate bypassing in the alloy by modifications of the lattice parameters to increase mismatch in the $Al–Al_3Li$ system; (b) introducing secondary precipitation systems; and (c) using a dispersion hardening system in addition to the precipitation hardening system. Other approaches include grain refinement via additions of manganese, zirconium, chromium and cobalt and minimization of tramp elements potassium, sodium, sulphur through alloy control.

The structure control and increased solid solubility that became possible with the advent of rapid solidification technology allowed many investigators to take the aforementioned approaches with various degrees of success. The high solidification rates associated with RSP helped minimize the segregation of lithium, extensively reduced the grain size, and resulted in overall structural refinement. In spite of this considerable success, however, the PM-P⁅⁆ approach introduced a problem, that is, oxide c. tamination. In particular, the fracture characteristics of RS-PM Al–Li alloys are enormously degraded due to the presence of oxide stringers in the fully densified, hot worked and heat treated alloy.

Recent efforts to improve the quality of rapidly solidified crystalline materials have centred around the consolidation technologies that are available. In particular, the spray atomization and collection processes, Osprey, CSD (controlled spray deposition), and more recently LDC (liquid dynamic compaction), have begun to yield very exciting results in the Al–Li field. So far, the results available for spray deposition

processing of Al–Li alloys suggest that this may be the most promising route toward near term commercialization of Al–Li alloys.

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