

Review

Strength, deformation, fracture behaviour and ductility of aluminium–lithium alloys

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The ever increasing need for high strength, improved performance, lightweight and cost-effective materials has resulted in significant improvements and development of new aluminium alloys for structural applications. Lithium additions to aluminium have the potential for providing a class of high strength alloys with exceptional properties suitable for weight-critical applications. In this paper, published studies of composition–processing–microstructure relationships are discussed. Contributions to strength of the solid solution are discussed with reference to the presence of lithium in solid solution, the presence of coherent, ordered precipitates in the matrix and the co-precipitation of binary, ternary and more complex strengthening phases. Microstructural influences on strength are discussed with reference to metallurgical variables. These variables include the intrinsic microstructural features; the presence of dispersoids, the nature and type of matrix strengthening precipitates and the presence of denuded zones adjacent to grain boundaries. The extrinsic and intrinsic micromechanisms governing the deformation characteristics and fracture behaviour are critically examined with specific reference to ageing condition of the alloy, the matrix slip characteristics, and the nature, volume fraction and distribution of strengthening precipitates. The deleterious effects of strain localization and the exacerbating effect of precipitate-free zones are also highlighted. The micromechanics governing the fracture processes are examined and the sequence of events in the fracture process is reviewed in light of the specific role of several concurrent factors involving nature and volume fraction of second-phase particles, deformation mode, and dislocation–microstructure interactions. Past attempts made to improve the tensile ductility and mechanical response of these alloys are also examined so as to provide a better basis for understanding processing–microstructure–deformation interactions.

1. Introduction

The successful development of new generation transport vehicles which can travel at higher speeds, for longer ranges, withstand greater payload capacity, provide better fuel economy and have improved landing capabilities, requires reliance on the use of more efficient engines such as the supersonic breathing engine, improved airframe design, and use of high performance materials. While improvements in engine performance and aircraft design have been realized, it is currently believed that design with available commercial materials alone will not meet the demands for a significant improvement in structural efficiency for the newer generation aerospace vehicles such as advanced tactical fighter and the national aerospace plane. In a typical commercial airliner every pound of material saved translates into savings of about 250 dollars in fuel costs over the projected life of the aircraft, at present day fuel prices [1]. Savings in fuel result in savings in weight which translate into substantial increase in payload capabilities. A 10% saving in aircraft structural weight increases the available reserve payload by 4% [2–4].

Selection of materials for commercial, military and space-related applications often involves a compromise between performance and cost. The material that will provide the least expensive component while delivering the specified performance is usually preferred and used. The need for a certain level of performance is often dictated by the mission and this justifies the use of a certain type or class of material. The new structural materials on the horizon that offer the promise of attractive weight savings encompass a variety of new metallic materials to include the aluminium alloys, the titanium alloys, ordered intermetallics, matrix–matrix composites (MMC), and resin–matrix composites. Aluminium alloys for example, have for long been used for airframe structures. These alloys, both conventional and advanced, were developed for improved mechanical properties so that improvements in aircraft performance could be obtained by efficiently reducing structural weight. This can be achieved through reduction in density and improvements in strength, stiffness, durability and damage tolerance [5].

Organic matrix composites emerged to threaten the

traditional use of aluminium alloys in the aerospace and transportation industry. The principal advantage of these composites is that they offer a density (0.05 lb in^{-3}) approximately half that of conventional aluminium alloys (0.10 lb in^{-3}). While lower density favours strongly the use of composite materials for weight-critical applications, the significantly higher costs relative to aluminium alloys changes the picture dramatically in the selection of a cost effective material. For example, costs of graphite-epoxy composite structures are high on account of the extensive and expensive handwork required coupled with material costs. Furthermore, the weight savings achieved are out-weighed when comparing the intrinsic properties of graphite fibres with those of metals. This is attributed in part to fibre anisotropy and the low strain to fracture. In addition, the properties of a composite material are susceptible to environmental degradation, and inspection of composite structures is difficult, time consuming, and expensive. Other contending materials for aircraft structures are titanium alloys. However, at present the prohibitively high cost and associated manufacturing and fabrication difficulties involved in the use of titanium for large pieces of aircraft structure limit its use to areas where superior properties at elevated temperature in corrosive environments are required [6]. On account of these drawbacks, materials scientists and engineers are examining alternative materials to provide savings in weight in a cost-effective manner. A NASA-funded study by Lockheed Corporation [2] revealed that reducing the density of aluminium alloys by only 7 to 10% could provide more cost-effective structural weight reductions than composite materials, based on the high production costs for the latter. Thus, the stage was set for the development of low density aluminium alloys.

The critical need for structural materials to be both cost-effective and provide an optimum level of performance coupled with an increased emphasis on efficiency and reliability have engendered considerable widespread interest in the development of new aluminium alloys. These alloys could potentially provide excellent combinations of reduced density, high strength, good fracture toughness, resistance to exfoliation corrosion, resistance to stress corrosion cracking, improved thermal stability and better stiffness. The family of lithium-containing aluminium alloys has in recent years received much attention for use in weight-critical and stiffness-critical structures for military, space and commercial applications because they offer the promise of low density, improved specific strength and high stiffness-to-weight ratio over the other commercial 2XXX and 7XXX series aluminium alloys and carbon-fibre composites [7-9].

The critical need for lightweight structures resurrected interest in the aluminium-lithium alloy system during the late 1970s. Unfortunately, the beneficial effects associated with lithium additions to aluminium is accompanied by a reduction in monotonic ductility and fracture toughness in alloys which are solution heat treated, quenched and aged to peak strength [10-19], making these alloys unsuitable for many structural applications. With the advent of rapid

solidification technology (RST), rapid quenching was sought as the solution to improving the low fracture toughness and inferior monotonic ductility of the lithium-containing aluminium alloys. Although significant progress was achieved towards improving the mechanical behaviour of these alloys using RST, problems, namely, poor deformation and fracture behaviour continued to persist and remained far from being solved, and an obstacle to the development of these alloys. In contrast, techniques such as refinement in melting practices, various modifications in alloy chemistry and novel processing procedures have been successfully used in an attempt to improve the monotonic or tensile ductility and fracture toughness to acceptable levels while maintaining the benefit of high strength.

Rapid solidification technology offers several advantages over the ingot metallurgy methods when used for the manufacture of lightweight aluminium-lithium alloys [20-22]. These include:

1. incorporating lithium contents in excess of the practical maximum of 2.7 wt % for the ingot alloys;
2. utilization of strengthening mechanisms such as dispersion hardening and substructure hardening;
3. increased amount of alloying additions; and
4. refinement of secondary phases [20-22].

Although significant improvements in tensile ductility, fracture toughness and other mechanical properties including corrosion behaviour have been achieved through: (i) refinements in conventional ingot casting practices, (ii) use of novel thermomechanical processing treatments, (iii) rapid solidification methods, and (iv) mechanical alloying, there still exist a few inherent drawbacks. The commercially available aluminium-lithium ingot alloy continues to remain expensive in comparison with conventional aluminium alloys of comparable strength and ageing condition. It has been estimated that in order to achieve a 10% reduction in structural weight the current cost of these materials would be as high as 320 dollars per kilogram [2, 3]. To this effect, superplastic forming is being actively studied as an alternative manufacturing route which would help offset the higher costs associated with processing and lithium additions [23-25].

The objective of this paper is to examine the various approaches that have been used to improve the strength, deformation, fracture behaviour and tensile ductility of lightweight aluminium-lithium alloys. In particular, the relevant metallurgical issues which influence the extrinsic and intrinsic micromechanisms governing the deformation and fracture processes are examined in an attempt to clarify the key failure mechanisms. Recent research results are emphasized, although some significant work from earlier years is also included to provide continuity. We begin with a brief discussion of the influence of lithium additions to aluminium.

2. Effects of lithium additions to aluminium

Lithium additions to aluminium give the greatest reduction in density (Fig. 1) and increase in elastic modulus (stiffness) (Fig. 2) per wt % of any known

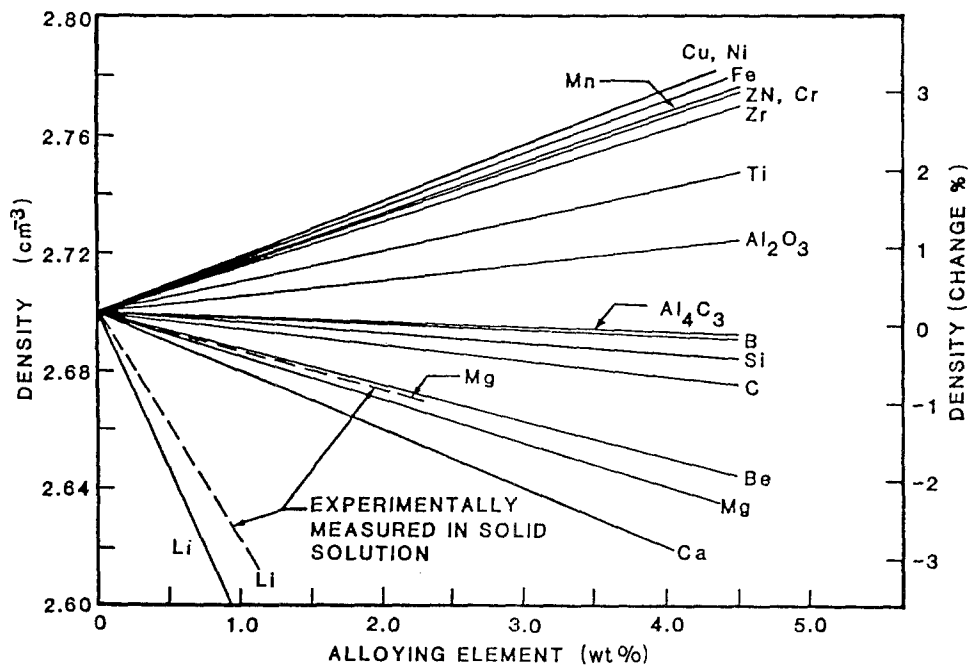


Figure 1 Effect of solute additions on the density of aluminium alloys (from [107]).

alloying element. Lithium is one of the few elements with substantial solubility in solid aluminium (4.2 wt % in a binary aluminium-lithium alloy). The potential for aluminium alloy density reduction through lithium additions is evident by comparing its atomic weight (6.94) with that of aluminium (26.98). Each 1% increment of lithium addition to an aluminium alloy up to 4 wt % lithium decreases the density by about 3% and increases the elastic modulus (stiffness) by 6% [26, 27]. In principle, weight savings in aircraft structural parts could reach 15% or possibly as high as 19%. Secondly, compared to fibre-reinforced composite materials, the lithium-containing aluminium alloys can be easily fabricated and assembled using existing facilities and consequently, they possess lower manufacturing costs. Besides, the lightweight

aluminium-lithium alloys would be available in various product forms and sizes commensurate with currently available commercial aluminium alloys, thereby, allowing manufacturers of aircraft and aerospace structures to make use of standard manufacturing methods. Lastly, their potential long term use in large quantities has resulted in an emphasis on the development of extremely high standards of both equality and reproducibility. These are important factors that would help avoid the large expenditures of money required by other technologies associated with the manufacture of fibre-reinforced composite materials and rapidly solidified materials.

The potential benefit of lithium additions to aluminium in terms of reduced density, improved stiffness, combined with high strength (yield strength >

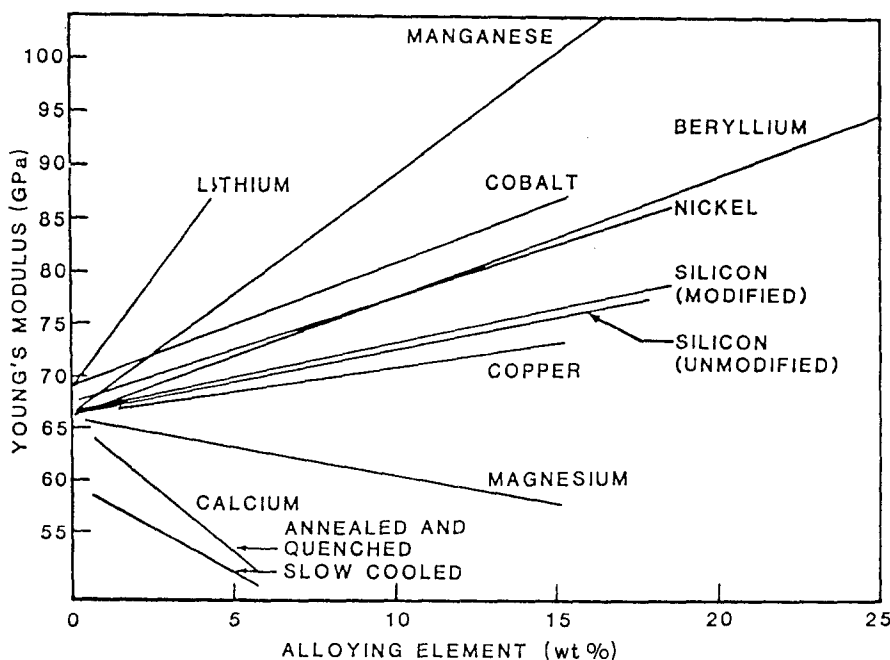


Figure 2 The effect of solute additions on the elastic modulus of aluminium alloys (from [107]).

500 MPa) was first recognized by LeBaron [28] and resulted in the development of the Al-4.45Cu-1.21Li-0.51Mn-0.20Cd alloy, designated as 2020 by the Aluminium Association. Besides possessing high monotonic tensile and yield strengths, low density and an increased elastic modulus, aluminium alloy 2020 offered freedom from exfoliation corrosion and stress corrosion cracking, thus making it potentially superior to other commercially available aluminium alloys for use in high performance military structures. Alloy 2020 was used in the wing skins of the US Navy RA-5C Vigilante Aircraft [1, 11]. Around the same time design studies in the United Kingdom suggested significant mass savings as a result of using aluminium alloy 2020 on a large scale in relatively thin sections. Savings of 400 kg were predicted, with around 90 kg resulting as a consequence of the lower density of the alloy. The high elastic modulus and strength of the alloy offered advantages in areas where elastic stability was highly critical. Interest in the use of aluminium alloy 2020, however, was not pursued further because of:

1. segregation effects,
2. the associated low ductility,
3. inadequate fracture toughness for many potential applications, which made its efficient use at high stresses inadvisable, and
4. problems during melting which were caused by the high reactivity of lithium.

These limitations resulted in the early withdrawal of 2020 as a commercial alloy [10, 11]. A thorough historical review on the development of lithium-containing aluminium alloys is presented elsewhere [11].

The effect of lithium additions on the elastic properties of aluminium alloys will depend on whether the lithium is in solution or is present as a second phase. The solubility of lithium in the parent fcc matrix phase is limited to approximately 13 at % [26]. When the lithium is in solid solution the elastic constants depend on atomic interactions and interatomic potential. However, when the lithium is present as precipitated second phase, the elastic constants depend on both the volume fraction and intrinsic modulus of the second phase [26, 27]. The solution of lithium atoms in aluminium produces only a small degree of solid solution strengthening. In comparison with copper-containing aluminium alloys, the solid solution strengthening is caused principally by the differences in size and/or differences in elastic modulus between the solute and the solvent atoms. The general strength in these alloys is derived from the presence of a large volume fraction of the coherent δ' (Al_3Li) phase (Fig. 3). The δ' phase has a high intrinsic modulus due to its ordered nature, and this contributes to the high values of elastic modulus observed in these alloys [13, 14, 27]. The effect of lithium additions to aluminium is unexpected since it substantially increases the values of elastic constants of aluminium-lithium solid solutions although the values of its own constants are lower than those of aluminium [26, 27]. Moreover, it has been shown that the elastic constants of aluminium-lithium alloys increase with lithium content [29, 30],

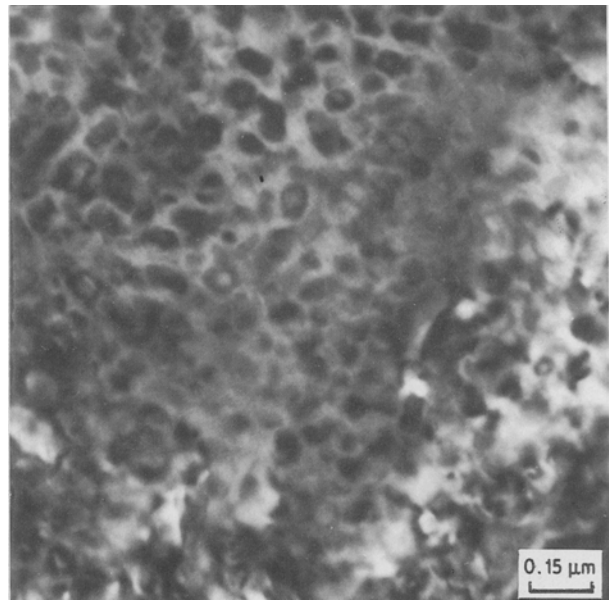


Figure 3 Bright field transmission electron micrograph showing the Al_3Li precipitates in a peak aged Al-3Li-1.25Mn alloy.

and are independent of both the size and distribution of the precipitates [31].

When an aluminium alloy containing sufficient lithium is quenched from the single phase field (solid solution region) and subsequently aged in the two-phase field, it has been proposed that decomposition of the supersaturated solid solution occurs by a three step mechanism [32]. At first, the quenched solid solution undergoes an ordering reaction. This reaction is energetically favoured under rapid quenching conditions, since it requires only short range diffusion, and is kinetically preferred over nucleation growth of an equilibrium phase [13, 32, 33]. Secondly, the solid solution breaks down by a spinoidal mechanism into ordered regions having differing lithium contents [34, 35]. During the third and final stage, the lithium precipitates as the metastable δ' (Al_3Li) phase in a disordered aluminium matrix.

In precipitation hardenable aluminium-lithium alloys the Al_3Li phase is the principle strengthening precipitate that has an ordered $\text{L}_2(\text{Cu}_3\text{Au})$ superlattice structure equivalent to a preferred positioning of lithium atoms on one of the four sublattices in a face centred cubic (fcc) structure (Fig. 4) [33, 36, 37]. The Al_3Li precipitate is spherical in shape, possessing a cube-cube orientation and is coherent with the aluminium matrix [36, 37]. These precipitates have a crystallographic structure similar to that of the aluminium matrix and a small lattice misfit, reported to vary from 0.025 to 0.33% depending on stoichiometry and temperature [35-38]. The metastable Al_3Li precipitate maintains a spherical shape and remains coherent upto a size of about $0.3 \mu\text{m}$ [39].

During ageing at higher temperatures (artificial ageing) the δ' (Al_3Li) precipitate particles coarsen. The coarsening rate with time follows the Lifshitz-Wagner kinetics, with an increase in average particle radius (r) with time (t)^{1/3} [39-43]. The activation energy for coarsening varies from 100 to 140 kJ mol^{-1}

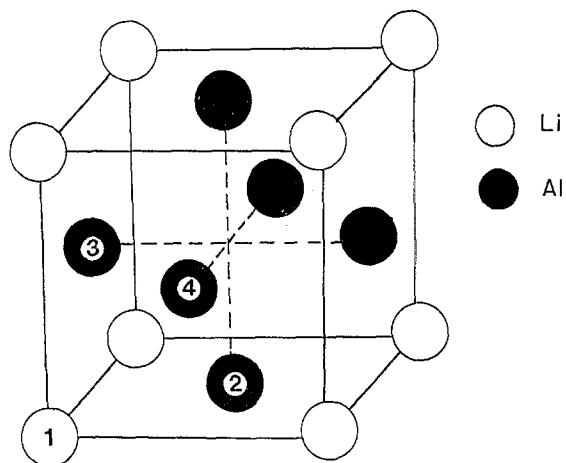


Figure 4 The $L1_2$ unit cell, the structure of Al_3Li . Precipitation of δ' is effectively a clustering and ordering of lithium atoms within the fcc aluminium solid solution.

in binary aluminium–lithium alloys, and from 112 to 127 kJ mol⁻¹ in the ternary aluminium–lithium–copper alloys. These values are consistent with the activation energy for diffusion of lithium in aluminium–lithium and the aluminium–lithium–copper alloys. The coarsening rate of the particles has been reported to be affected by [41–43]:

1. the energy of the aluminium matrix–precipitate interface,
2. the diffusion coefficient of lithium,
3. the concentration of lithium and zirconium in the matrix, and
4. the equilibrium solubility of lithium in aluminium.

Moreover, the Ostwald ripening process has been reported to begin immediately upon artificial ageing [32, 40, 45], thus providing support for the hypothesis that precipitation of δ' involves a spinoidal decomposition step [32]. Mahalingam and co-workers [42, 43] in their study found that increasing the amount of lithium served to accelerate the coarsening rate of the precipitates, and that an increasing volume fraction of δ' was accompanied by an increase in the proportion of precipitates having an aspect ratio significantly different than one. However, Mahalingam and co-workers [42, 43] also observed that increasing the ageing time at the ageing temperature resulted in the particles having a more spherical morphology [43]. In a parallel study, Glazer and co-workers [41] calculated the critical resolved shear stress for the glide of dislocations through a random array of δ' (Al_3Li) precipitates. These researchers concluded that the more sharply peaked the distribution of the Al_3Li precipitates, the more effective is its strengthening effect. It is interesting to note that a comparison of the experimentally observed particle size distributions (PSDs) of the Al_3Li precipitates are not consistent with those predicted by classical coarsening theories [42, 43]. While the classical coarsening theories are based on the hypothesis that coarsening is a diffusion controlled process, and hence the PSDs should be negatively skewed. However, the experimentally determined PSDs were found to be symmetrical. This behaviour was attributed to a coalescence of the Al_3Li

particles at high volume fractions [42, 43]. Based on a comprehensive study of the precipitation characteristics in Al–Li–Cu alloys Huang and Ardell [44] proposed that the energy of an antiphase boundary (APB) dictates that only those particles with perfectly matching sub-lattices will coalesce. This implied that only a small percentage of the δ' particles would coalesce and consequently, it was not clear as to whether it provided a plausible explanation for the experimentally determined PSDs.

3. Strengthening mechanism in aluminium–lithium alloys

The intrinsic strengthening mechanism in age-hardenable lithium-containing aluminium alloys are derived from the presence of lithium in solid solution, and by the presence of coherent, ordered precipitates in the matrix. Although it is widely accepted that the principal strengthening mechanism is due to precipitation [36, 39, 40, 45, 46], there exists some disagreement as to the exact mechanism. In precipitation strengthening, several factors affect the dislocation/precipitate particle interaction. The principle factors can be classified as being [46–50]:

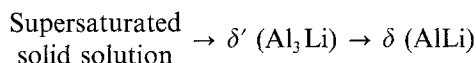
1. friction stress of the matrix solid solution
2. stress arising from coherency strains,
3. stress due to modulus hardening effects,
4. energy of the Al_3Li precipitate–matrix interface,
5. energy of the antiphase boundary, and
6. friction stress of the precipitate particles.

Sainford and Guyot [51], and Jensrud [52], based on the results of their study, proposed that the principle strengthening mechanism in these alloys is associated with order hardening as a result of the creation of APBs. However, Noble and co-workers [45, 47] attributed the strength in these alloys to combinations of order hardening and modulus hardening. Coherency strains around the Al_3Li precipitates and an increased area of the sheared precipitate contribute very little to the observed strength. More recently, Miura and co-workers [53] proposed that the relative importance of various factors influencing dislocation–precipitate interaction depended on alloy composition and ageing condition. Results of their study revealed that contributions from coherency strain hardening, modulus hardening and hardening due to interfacial energy are relatively important during the early stages of the ageing process, but amount to only 15% of the total hardening in alloys aged to peak strength [53]. Subsequently, as the Al_3Li precipitates coarsen during artificial ageing, the contributions from antiphase boundary energy and friction stress to the total hardening increase, each being responsible for about 30% of the total stress. Based on the morphology of the dislocation loops surrounding the coherent Al_3Li particles in the overaged condition of an aluminium–lithium alloy, they concluded that contributions from modulus hardening to the total hardening of the alloy are not very important [53].

Recent studies have reported that Orowan looping is preferred to particle shearing when the δ' particle radius reaches 30 nm, which corresponds to the critical particle diameter in alloys aged to peak strength [43].

These results revealed that when a transition from an underaged (UA) condition to an overaged (OA) condition occurs, then the dislocations are forced to loop or bow around the precipitates, rather than cut or shear through them.

In addition to the δ' (Al_3Li) phase, precipitation of the equilibrium δ (AlLi) phase occurs both within the matrix and at grain boundaries during overaging. Precipitation in a binary alloy system during the course of artificial ageing follows the sequence [33, 37, 54]



Various techniques such as thermal analysis [55], transmission electron microscopy [33, 37] and small angle X-ray scattering [56] have confirmed the above reaction. The equilibrium δ phase has a B_{32} structure of the NaTl prototype with a lattice parameter of 0.637 nm [37]. There is, however, some disagreement with respect to the sequence of precipitation reaction as given by the above equation. The exact mechanism governing the formation of the equilibrium δ phase has been the subject of several independent studies [57–60]. Early studies by Niskanen and co-workers [60] led to the conclusion that formation of the equilibrium phase on grain boundaries was a direct consequence of preferential coarsening of the metastable δ' precipitate. The grain boundaries provided the additional energy required for the metastable precipitate to transform to the equilibrium phase. Subsequently, Williams [39] found δ' precipitates of size larger than $0.3\ \mu\text{m}$ still maintaining a spherical shape and no reasonable cause for the δ' to transform to δ at and along the grain boundaries, when a size of $0.3\ \mu\text{m}$ was attained. Williams [39, 54] proposed that the equilibrium precipitate nucleated heterogeneously within the matrix and on the grain boundaries, independent of δ' . Williams [39] also suggested that the small amount of lattice strain generated by the coherent phase is not sufficient to justify it as a heterogeneous nucleation site for the equilibrium δ phase. In general, on account of the relatively large $\alpha:\delta$ misfit, the change in lithium concentrations, and a different crystal structure (a NaTl type cubic structure), heterogeneous nucleation of the precipitate occurs at grain boundaries. Schegoleva and Rybalko [59] proposed an independent model for transformation from fcc structure to a NaTl -type bcc structure.

In high purity binary alloys, a discontinuous precipitation of the equilibrium δ phase was observed at grain boundaries in the temperature range $120\text{--}150^\circ\text{C}$ [54]. Williams [39, 54] proposed that the equilibrium AlLi phase nucleated independently of Al_3Li and grows by: (a) the migration and/or localized coarsening of particles at the grain boundary, and (b) dissolution of the metastable Al_3Li phase. In general, precipitation of the equilibrium phase occurs on high angle grain boundaries, resulting in detrimental influence on the deformation and fracture behaviour [46, 61–65]. In addition to preferential growth and coarsening of precipitates on the grain boundary, the formation of precipitate-free zones (PFZs) has been

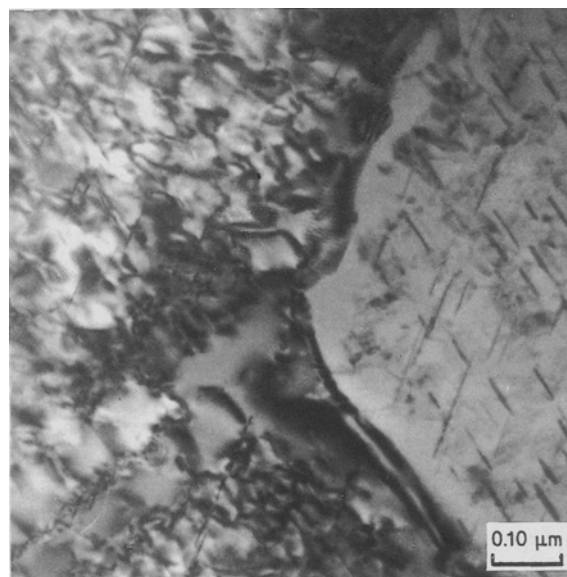


Figure 5 Bright field transmission electron micrograph showing PFZ along the high angle grain boundary in an Al-4.5Cu-1.2Li alloy.

shown to occur during overaging. The formation and growth of precipitate free zones have been interpreted as being the result of higher diffusivity of lithium at grain boundaries. The solute necessary for the continued growth of the AlLi precipitates is provided by the dissolution of the Al_3Li particles in the immediate vicinity of grain boundaries [13, 60]. The PFZs were found to grow with ageing time [60, 61, 66, 67]. In these studies, the width of the PFZ was observed to be proportional to t^n , t being the ageing time and the exponent, n , a constant. Sanders and co-workers [66] reported a value of $1/3$ for the exponent n based on limited experimental data. In a subsequent and more exhaustive recent study, Jensrud and Ryum [68] found that in aluminium–lithium alloys growth of the PFZ is a diffusion controlled process and is parabolic with ageing time. The growth rate of the PFZ was observed to increase with an increase in lithium content. An acceleration in PFZ growth with time was attributed to possible variations in the interdiffusion coefficient as a function of lithium content in the alloy [69]. Precipitation-free zones have been found both along the high-angle grain boundaries (Fig. 5) and subgrain boundaries for all ageing conditions of ingot metallurgy (I/M) and rapidly solidified-powder metallurgy (RS-PM) alloys [70–74]. PFZs were also observed along the interfaces between Al_6Mn particles and the aluminium matrix (Fig. 6). The occurrence of PFZ along the subgrain boundaries has been reported to depend on the crystallographic orientation differences between the neighbouring subgrains since not all the boundaries exhibited PFZs [73, 74].

4. Ternary and quaternary additions to aluminium–lithium alloys

Since the challenge of strengthening aluminium–lithium alloys with coherent lithium-rich phases, such as Al_3Li , which do not increase the density has been met with limited success [41], additional

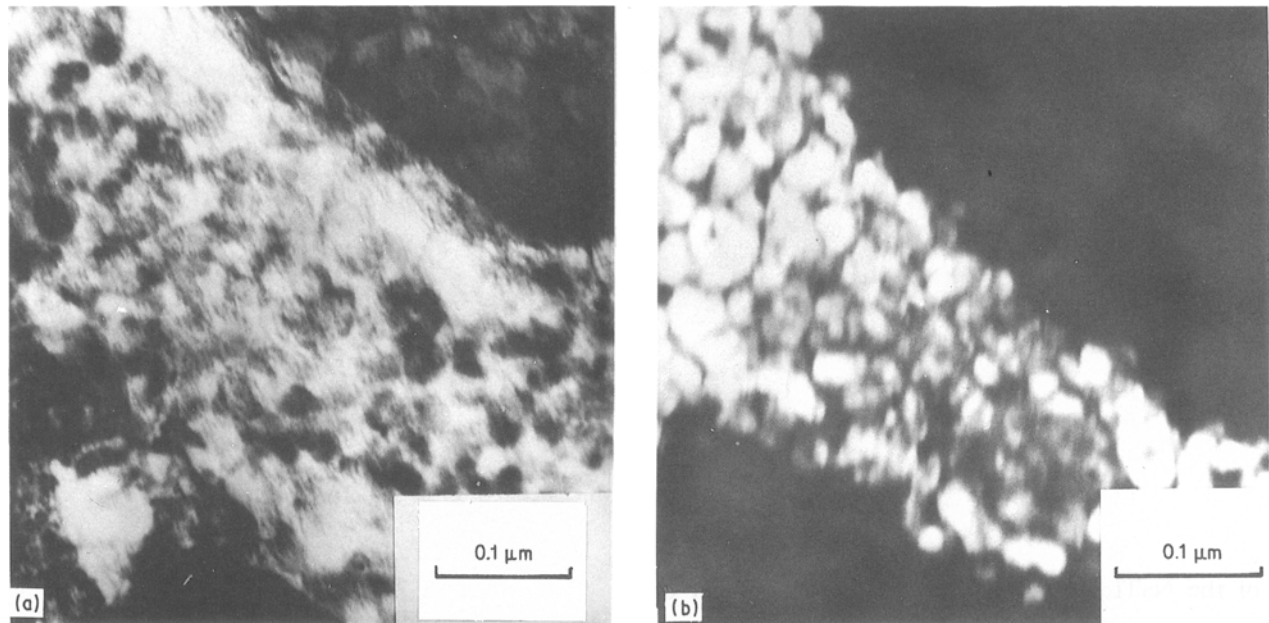
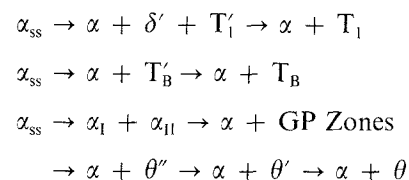
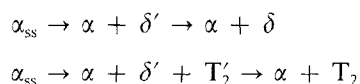


Figure 6 Transmission electron micrograph showing PFZ at the Al_6Mn particles in an $Al_3Li-1.25Mn$ alloy: (a) bright field, (b) dark field.

strengthening has been achieved by the co-precipitation of other binary and ternary phases. The addition of various amounts of copper and magnesium to lithium-containing aluminium alloys has been shown to be effective in strengthening. These elements modify the precipitation sequence either by altering the solubility of the principal alloying elements, or by forming copper-rich and magnesium-rich phases, and co-precipitating with the δ' (Al_3Li). The elements also combine with lithium and precipitate as phases that exist in the ternary and quaternary systems.

In ternary Al–Li–Cu alloys additional strengthening is achieved by the co-precipitation of copper-rich phases independent of δ' precipitation [37, 75]. Hardy and Silcock [75] have identified six ternary compounds in aluminium-rich alloys, the most important being $T_1(Al_2CuLi)$, $T_2(Al_6CuLi_3)$ and $T_B(Al_{15}Cu_8Li_2)$. In leaner aluminium alloys, three other intermetallic compounds designated P, Q, and R (Al_5CuLi_3) are present. A systematic study of the compositions and structures of the equilibrium and non-equilibrium phases present in the Al–Li–Cu system was made by Kang and Grant [76, 77] and their results summarized in Table I. Rioja and Ludwiczak [48, 78] have suggested the following precipitation sequence for the binary and pseudo-binary systems:



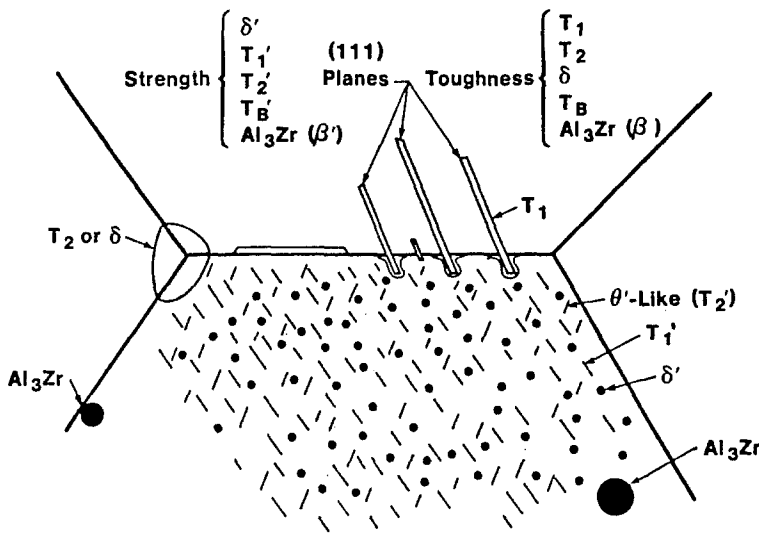
There exists some disagreement regarding the presence of the metastable T_1' and T_2' phases. Although the structures of the T_1' , T_2' and T_B' phases have yet to be established, Rioja and Ludwiczak [48] proposed, based on minimum misfit arguments, that the metastable T_1' and T_2' phases are precursors to the equilibrium T_1 and T_2 phases. They also suggested that lithium is incorporated into the θ' (Al_2Cu) lattice and have termed the phase as being either T_B' or T_2' depending on alloy composition. Huang and Ardell [44] based on their study on precipitation behaviour in Al–Li–Cu alloys using microdiffraction analysis proposed that the existence of the metastable T_1' is unlikely.

The $T_1(Al_2CuLi)$ phase forms as thin hexagonal platelets on the $\{111\}$ matrix planes [58]. This phase forms either by the dissociation of $a/2 \langle 110 \rangle$ dislocations into $a/6 \langle 112 \rangle$ Shockley partials followed by a copper and lithium enrichment, or by nucleation at the matrix/Guinier–Preston (GP) zone interface [57, 58, 79]. In a ternary Al–2Li–3Cu alloy, the T_1 precipitate was observed to grow at the expense of the δ' precipitate in the underaged (UA) condition and at the

TABLE I Phases encountered in Al–Li–Cu–Mg alloy systems

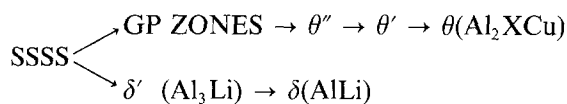
Phase	Composition	Crystal structure	Orientation relationship
δ'	Al_3Li	Ll_2	cube–cube
δ	$AlLi$	B_{32} (cubic)	$(001)_\delta \parallel (111)_\alpha$; $(100)_\delta \parallel (110)_\alpha$
θ'	Al_2Cu	tetragonal	$(001)_{\theta'} \parallel (001)_\alpha$; $[100]_{\theta'} \parallel [100]_\alpha$
T_1	Al_2CuLi	hexagonal	$(0001)_{T_1} \parallel (111)_\alpha$; $[10\bar{1}0]_{T_1} \parallel [1\bar{1}0]_\alpha$
T_B	$Al_{15}Cu_8Li_2$	cubic	$(001)_{T_B} \parallel (001)_\alpha$; $[110]_{T_B} \parallel [100]_\alpha$
T_2	Al_6CuLi_3	icosahedral	unknown
β'	Al_3Zr	Ll_2	cube–cube
S'	Al_2CuMg	orthorhombic	$[100]_{S'} \parallel [100]_\alpha$; $[010]_{S'} \parallel [021]_\alpha$

Figure 7 Schematic showing morphology of precipitates present in Al-Li-Cu alloys. The T_1' and T_2' precipitates are plate-like along the (111) and (100) matrix planes respectively (from [78]).

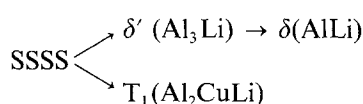


expense of the δ and θ precipitates in the overaged (OA) condition. A number of interactions occur between the T_1 and the δ' precipitates, with T_1 either cutting or growing through the spherical δ' and the δ' on the θ' (Al_2Cu) [79, 80]. In zirconium containing alloys, the θ' and T_1 were found to nucleate on the Al_3Zr interface in addition to heterogeneous nucleation on matrix dislocations. The nucleation of the T_1 precipitates occurred to a lesser degree than the θ' . Galbraith and co-workers [81] rationalized the occurrence of Al_3Zr as a nucleation substrate on the basis of solid-solid nucleation theory. The T_1 phase was found to have a beneficial influence on modulus of elasticity [82]. In addition, the diameters of the T_1 platelets were found to increase linearly with the cube root of ageing time during the early stages of ageing [44]. Although the $T_1(Al_2CuLi)$ precipitates grow at the expense of Al_3Li precipitates, their presence is beneficial to mechanical behaviour primarily because they act as unsharable obstacles which must be bypassed by the dislocations during deformation [44, 79].

In the Al-Cu-Li system the types of strengthening phases that precipitate from the supersaturated solid solution (SSSS) strongly depends on the Cu:Li ratios [33, 57, 58, 83]. The dependence of the precipitation sequence on the Cu:Li ratio has been discussed by Pao and co-workers [83]. In high copper, low lithium containing alloys (3–4.5 wt% copper, 1–2 wt% lithium), the decomposition of the SSSS occurs by the reactions [37, 58, 83, 84].



For high lithium, low copper-containing alloys (2 wt% copper, > 2 wt% lithium), the reaction sequence leading to the formation of Al_2Cu is suppressed and precipitation of the $T_1(Al_2CuLi)$ phase occurs. The morphology of precipitates likely to be present in Al-Li-Cu alloys is shown schematically in Fig. 7.



The effect of T-type ($Al_xCu_yLi_z$) phases on the mechanical behaviour of Al-Li-Cu alloys depends on their size, distribution, and synergism with the other phases present in a particular alloy. In some instances the presence of a T-type phase ($Al_xCu_yLi_z$) in high copper-containing aluminium-lithium alloys has been shown to be detrimental to the strength-toughness relationship [48, 58, 83, 85]. In binary alloys containing 4 to 4.5 wt% copper, the copper available for strengthening is reduced by the precipitation of a T-type phase. Thus, the strength of a higher-lithium containing Al-Cu-Li alloy would be lower on account of the reduction in the amount of copper that would otherwise be available for precipitation of the θ' (Al_2Cu) phase [84–86]. Pao and co-workers [83] observed that precipitation of the ternary phase, $T_1(Al_2CuLi)$, coupled with simultaneous coarsening and dissolution of the δ' (Al_3Li) in an OA, inert gas atomized powder metallurgy Al-Cu-Li alloy containing manganese as the grain refining element, resulted in marked reductions in both tensile strength and toughness.

Other investigators have associated the improvements in mechanical properties of rapidly solidified aluminium-lithium alloys to the presence of the T-type phases, in particular, the $T_1(Al_2CuLi)$. Sankaran and O'Neil [87] reported marked improvements in both strength and ductility of a powder metallurgy (PM) processed Al-4Cu-2Li-0.2Zr alloy when compared to a PM processed Al-2.5Cu-2.5Li-0.2Zr alloy. Then improvement in mechanical behaviour was associated with the type of strengthening phases present in the microstructure. The higher strength and improved ductility of the high copper-containing alloy was attributed to the presence of the T_1 and δ' phases. However, the strength and ductility of the high lithium-containing alloy, strengthened largely by the presence of coherent δ' , were lower than those of the copper-containing alloy. Heterogeneous precipitation of the $T_1(Al_2CuLi)$ phase in the high lithium-containing alloy was associated with degradation in strength and reduction in tensile ductility.

Kang and Grant [76, 77] studied the influence of alloy composition on the mechanical properties of rapidly solidified PM alloys of the 2020 type. They

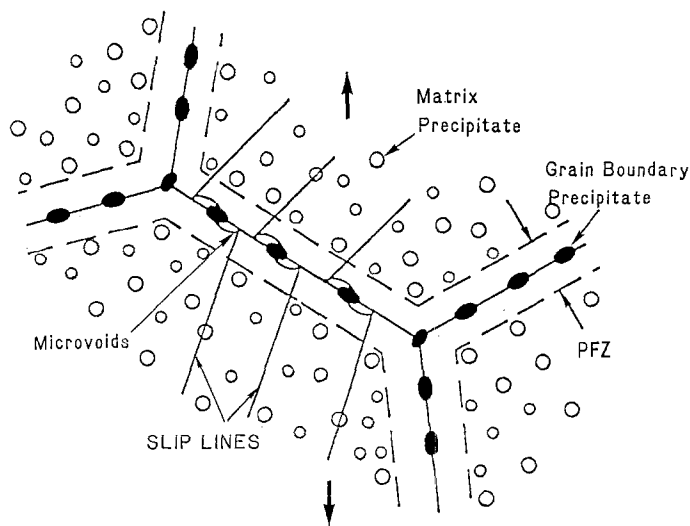


Figure 8 Schematic representation of the deformation process when PFZ is present, showing void nucleation at grain boundary particles [111].

attributed the improvements in mechanical behaviour associated with high copper (greater than 4 wt %) and low lithium (less than 2 wt %) alloys to the presence of the θ' (Al_2Cu) and T_1 (Al_2CuLi) phases, whereas, for a high lithium (> 2 wt %), low copper (< 3 wt %) alloy the Al_3Li phase was responsible for only limited property improvements. The RS-PM 2020 alloys had much higher strength when compared to the ingot metallurgy (I/M) counterparts. Furthermore, the presence of up to 2 wt % lithium combined with rapid solidification technology provided the RS alloys better ductility than the I/M X2020 alloy.

Sainford and Guyot [51] proposed that copper additions to binary aluminium-lithium alloys have two opposing effects on mechanical behaviour. The presence of copper in lithium-containing aluminium alloy results in an increase in stacking fault energy of the δ' precipitate, thereby, leading to a more favorable dislocation bypassing mechanism (transition from dislocation shearing of the precipitate to dislocation bypassing of the precipitate particle occurs at 18 nm), and also promotes precipitation of the T_1 phase. The T_1 phase contributes to an increase in the yield strength and tensile strength of the alloy.

The effects of magnesium additions to binary aluminium-lithium alloys have been the subject of several investigations [88–95]. The addition of magnesium reduces the solubility of lithium during the early stages of ageing and increases the volume fraction of the coherent δ' strengthening precipitate. Each wt % of magnesium addition increases the hardening rate of these alloys by 50 MPa [88]. The precipitation sequence in ternary Al-Li-Mg alloys is:



The ternary Al_2MgLi precipitate is the equilibrium phase [93]. The Al_2MgLi is rod shaped, incoherent with the aluminium matrix and forms either as a result of overageing or due to heterogeneous nucleation on grain and subgrain boundaries during quenching and subsequent artificial ageing. Magnesium additions to aluminium-lithium alloys are usually made in the presence of copper, in order to promote the formation of metastable, needle-like phases S'' and S' (Al_2CuMg). The S' phase has been shown to promote homogeneous deformation by dispersing slip [90, 96–100]. A

homogeneous distribution of fine S' phase in the aluminium matrix has been documented in stretched samples [92, 101]. In addition to producing a fine and more homogeneous distribution of S' in the microstructure, the stretch prior to artificial ageing was also observed to reduce the size and number density of grain boundary precipitates [99]. The S' (Al_2CuMg) precipitates are very effective in dispersing slip when it nucleates heterogeneously on dislocations and grain boundaries; this behaviour is similar to the precipitation of the T_1 phase and is the result of large coherency strains [35]. On account of this advantage, aluminium-lithium alloys containing both copper and magnesium are stretched prior to ageing.

Magnesium and copper improve the overall strength of a binary alloy by co-precipitating with δ' (Al_3Li) and/or incorporating lithium to form coherent and partially coherent ternary and more complex matrix strengthening precipitates. Co-precipitation of partially coherent phases is beneficial because in addition to improving the strength of the alloy it also promotes homogeneous deformation. Furthermore, magnesium by the precipitation of S'' and S' phases near grain boundaries minimizes or eliminates the formation of precipitate-free zones [100–102]. In a recent study, Ashton and co-workers [96] showed that with the absence of a cold working step, the quaternary Al-Li-Cu-Mg alloys develop grain boundary precipitation and precipitate-free zones (PFZs), leading to stress concentration when the localized slip bands impinge upon grain boundaries with concomitant void nucleation at coarse grain boundary precipitates (Fig. 8). Results of their study also revealed that an optimum mechanical behaviour is achieved only when the material is given a stretch prior to ageing. Around the same time, Ahmad and Ericson [97] reported a 15% improvement in yield strength (495 MPa against 431 MPa) by stretching the quaternary Al-Li-Cu-Mg alloys prior to ageing. The improvement in strength was attributed to an increase in both number and density of the S' (Al_2CuMg) and T_1 (Al_2CuLi) phases.

5. Deformation and fracture behaviour of aluminium-lithium alloys

The intrinsic micromechanism governing the

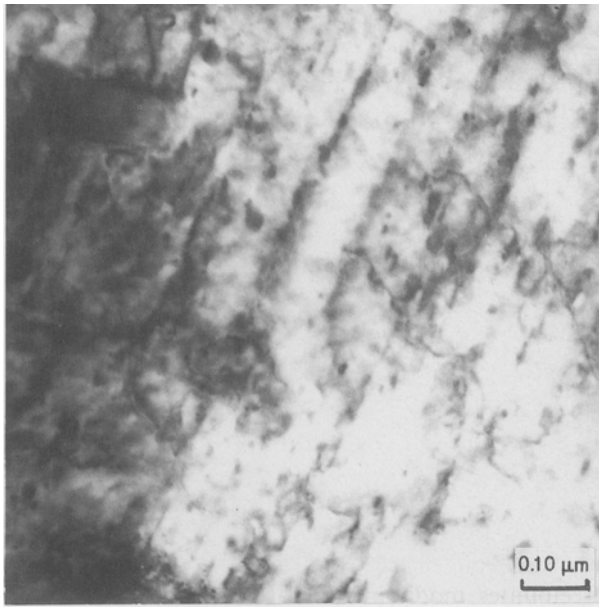


Figure 9 Bright field transmission electron micrograph showing inhomogeneous planar deformation in peak aged Al-3Li-1.25Mn alloy.

deformation and fracture behaviour of these alloys depend on the ageing condition and involve the combined effects of: (a) slip characteristics, and (b) the volume fraction and distribution of the matrix and grain boundary precipitates [103–107]. The effects of ageing condition can best be described in alloys containing low impurity levels since intrinsic effects associated with void nucleation at the coarse constituents and intermetallic particles are minimized. In underaged microstructures of such alloys fine slip bands form along closely packed crystallographic planes [66, 108–112], resulting in stress concentration at the ends of matrix slip bands which are adequate to crack open the grain boundaries. However, in alloys aged to peak strength the deformation is concentrated in widely spaced coarse slip bands (Fig. 9). The slip bands influence the fracture process through strain localization

effects. For, example, localized slip could initiate fracture by cracking open the grain boundary [111] or can shear the grain boundary without causing decohesion [66]. The fracture process is generally dictated by several synergistic and mutually-competitive processes involving:

1. presence of coarse constituents from ingot casting [113],
2. segregation of tramp elements such as sodium, potassium and sulphur to the grain boundaries [113, 114],
3. the presence of a high density of coarse grain boundary precipitates, often a more stable phase than the matrix strengthening phase [115],
4. strain localization in coarse planar bands due to heterogeneity of slip [116],
5. the exacerbating effect of precipitate-free zones adjacent to grain boundary regions which aids in enhancing the stress concentration at grain boundaries and grain boundary triple junctions [110, 117–120].
6. the existence of a low energy interface between the equilibrium AlLi phase and the matrix.

The localization of strain results in the build-up of high stresses at the grain boundary regions. The high stress concentration at the grain boundaries and at grain boundary triple junctions promotes easy separation resulting in low energy intergranular fracture (Fig. 10), and is a major cause for the low tensile ductility and fracture toughness of these alloys when compared to conventional aluminium alloys of comparable strength and ageing condition.

Several mechanisms and semi-quantitative models have been proposed to account for the influence of intrinsic microstructural features on the response of these alloys to deformation [104, 105, 115–122]. These models have identified and focused on the following processes:

1. cracking of the iron- and silicon-rich constituent particles with concomitant growth of microvoids at the cracked constituents [104, 105],

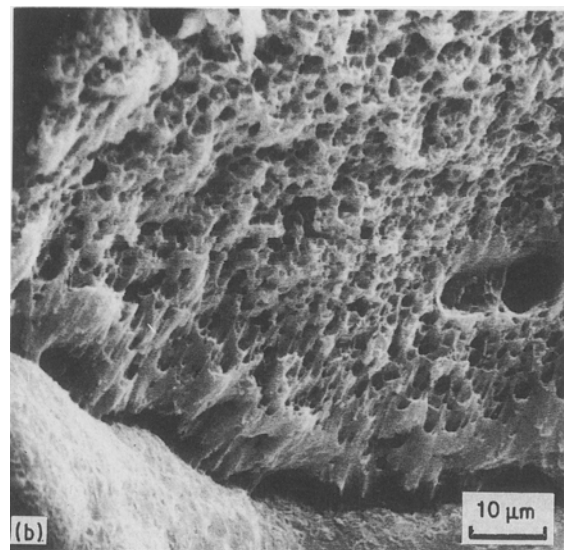
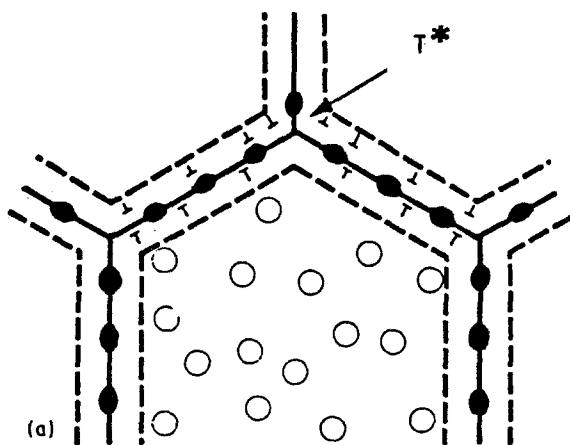


Figure 10 (a) Schematic showing PFZ at grain boundary and build-up of high stress concentration at grain boundary triple junction. (b) Scanning electron micrograph showing intergranular fracture in a peak aged Al-4.5Cu-1.21Li alloy as a result of crack initiation at the grain boundary trip junction.

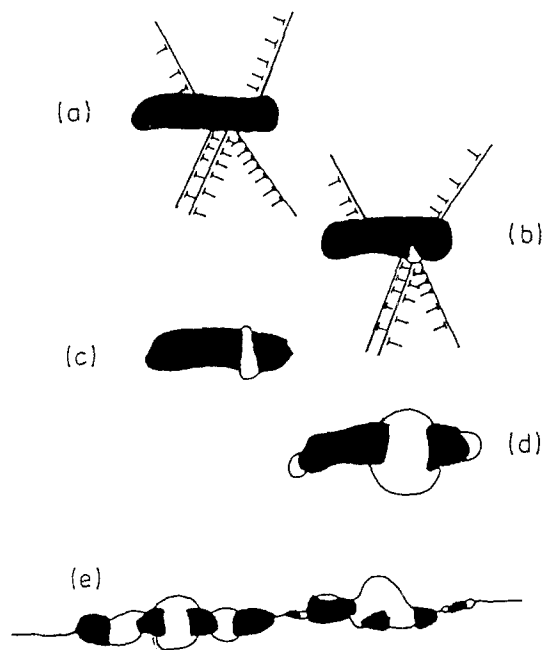


Figure 11 Mechanism of fracture initiation in Al-Li-Cu-Mg alloys: (a) slip bands impinge on particle, (b) impinging slip bands fracture the second phase particle, (c) void grows under the action of hydrostatic stress, (d) decohesion occurs at the end of cracked particles, (e) voids coalesce and propagate down grain boundaries [106].

2. formation of void sheets by coalescence of microvoids initiated at dispersoids which aid in linking the failure sites at cracked constituents [105],

3. formation of intense shear bands, or large slip offsets with concomitant strain localization effects resulting in progressive loss in strain hardening capacity [13, 104],

4. intergranular fracture resulting from the presence of coarse grain boundary precipitates [114, 115],

5. intergranular fracture caused by differences in strength between the age-hardened matrix and the soft precipitate free zone ($\sigma_{\text{matrix}} > \sigma_{\text{PFZ}}$) [123],

6. the extent of heavily strained region ahead of the advancing crack tip, which is directly related to the modulus, to the flow stress, the strain hardening exponent, and the influence of this region on critical strain or critical stress to fracture [123, 124].

In alloys containing a large volume fraction of second-phase particles, the sequence of events leading to fracture is shown schematically in Fig. 11 and is summarized as follows:

1. dislocation pile-up at the second-phase particle interface as a consequence of coarse planar slip,

2. stress at the second-phase particle interface due to dislocation pile-up exceeds the fracture strength of the particle causing it to fracture, and thereby, initiating a void,

3. the voids grow under the influence of applied stress,

4. as deformation continues, decohesion of the particle-matrix occurs particularly at the ends of the large second-phase particles,

5. coalescence of voids initiated at the cracked particles and subsequent crack propagation along grain boundaries.

In precipitation hardenable aluminium-lithium alloys strain localization results from planar slip

deformation, that is, the dislocation shearing the coherent and partially coherent precipitates dispersed in the matrix. The deleterious effects of strain localization can be minimized by:

1. overageing to produce incoherent precipitates,
2. refining the grain structure, and

3. alloying additions to improve the overall homogeneity of deformation.

Overageing results in the precipitation of equilibrium phases at grain boundaries with concomitant formation of wide PFZs which are detrimental to ductility. A refinement in grain structure through reductions in grain size decreases the slip length and reduces the stress concentration at grain boundaries. Furthermore, the small grains enhance multiple slip and assist in promoting homogeneous deformation. Since the deformation behaviour of these alloys is governed by the interaction of dislocations with the precipitates, modifying the nature, size, coherency and distribution of the precipitates present through alloying is an attractive method of eliminating strain localization effects.

Consideration of the basic strengthening mechanism in these alloys is important since it markedly affects the deformation process. The increase in yield strength of an aluminium-lithium alloy containing coherent precipitates is dependent upon the interaction between these matrix strengthening precipitates and the moving dislocations. The obstacle strength resisting dislocation motion can be associated with the following factors:

1. hardening due to coherency strains has been observed to be small for the particles in aluminium-lithium alloys [36, 52, 125],

2. chemical hardening which has only a minor strengthening effect on binary aluminium-lithium alloys [35],

3. modulus hardening is totally inadequate to account for the observed hardening in these alloys [52],

4. order hardening due to the creation of an anti-phase boundary (APB) within the ordered Al_3Li particles as a result of particle shearing, is a major source of strengthening [13, 110, 121, 126] in these alloys. Jensrud [52] predicted a theoretical yield strength increase of 87% for a binary Al-3 wt % Li alloy which accorded well with an experimental value of 67 MPa.

Plastic deformation in precipitation strengthened aluminium-lithium alloys occurs through the motion of dislocations on close-packed (111) planes and in the close-packed directions [13, 66]. The deformation behaviour is strongly influenced by the presence of coherent and partially coherent, ordered strengthening precipitates. The motion of unit dislocations through an ordered lattice of the precipitate creates disorder in the form of an antiphase boundary (APB), as shown in Fig. 12. To eliminate the extra energy required to create the APB, deformation occurs by the motion of identical pairs of unit dislocations (or super-dislocations) [66, 127]. The separation of two unit dislocations is determined by a balance between the force improved by the structure to maintain its

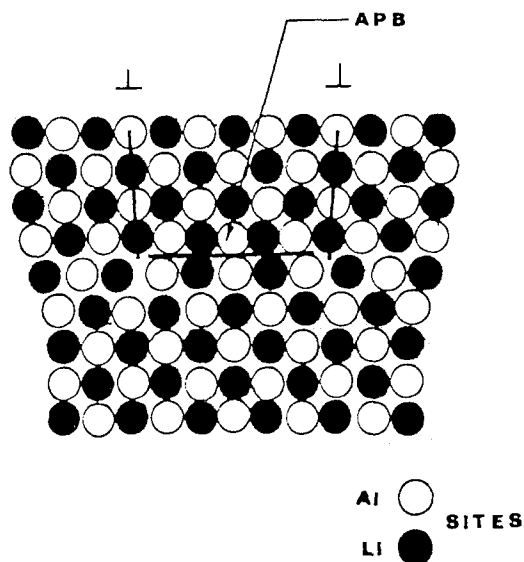


Figure 12 A section through a region of an ordered alloy illustrating the formation of an anti-phase boundary.

order and the repulsive force between two dislocations of the same sign. When plastic flow occurs through the motion of super-dislocations, deformation is planar (Fig. 13) and is restricted to a few active slip planes.

Jensrud [52] rationalized the deformation behaviour of aluminium–lithium alloys using a model for fracture at critical strain in the PFZ. He found that the strain in the PFZ, ϵ_{PFZ} , is related to the total plastic deformation, ϵ_{F} , by the relationship

$$\epsilon_{\text{F}} = K \left(\frac{W}{D} \right) \epsilon_{\text{PFZ}}$$

where W is the width of the PFZ, D is the grain diameter and K is a numerical constant. His calculations revealed that for a grain size (D) of $150 \mu\text{m}$ and a PFZ width of $0.4 \mu\text{m}$, the strain in the precipitate free zone (ϵ_{PFZ}) is as high as 135%.

During the process of casting these alloys, coarse insoluble constituent phases rich in the impurity

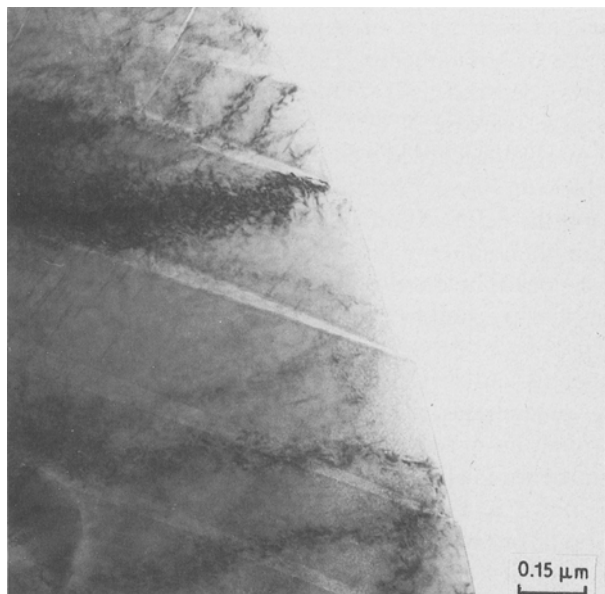


Figure 13 Bright field transmission electron micrograph showing planar deformation in peak aged Al-4.5Cu-1.2Li alloy.

elements iron and silicon form, and alkali impurities such as sodium, potassium and sulphur segregate to the grain boundaries [13, 113, 128]. The harmful effects of sodium segregation on mechanical properties of aluminium–lithium alloys have been studied [113, 128–132]. The segregation of tramp elements results in increasing the grain boundary alkali content with a consequent loss in fracture toughness due to grain boundary embrittlement. Starke and co-workers [128] observed that a sodium content of less than 6 p.p.m. is the limit above which embrittlement can occur. Webster observed the detrimental effect of sodium and potassium on toughness and tensile ductility to exist only in alloys containing substantial amounts of lithium or magnesium [129, 132].

In a study on the influence of impurity content on the mechanical behaviour of aluminium–lithium alloys, Reynolds and co-workers [133] showed that the iron content from 0.09 to 0.27 wt % in a quaternary Al–Li–Cu–Mg alloy resulted in a 25% reduction in toughness. Owen and co-workers [106] studied the formation of intermetallic phases in as-cast and rolled Al–Li–Cu–Mg alloys using quantitative X-ray microanalysis and back scattered electron imaging. Their results revealed that the iron-rich constituent phases lie in the form of stringers along the high-angle grain boundaries. During deformation void nucleation was observed to occur at these elongated particles either as a result of particle cracking of particle–matrix decohesion. Following particle cracking and decohesion, the voids coalesced and propagated down grain boundaries to form isolated ligaments which failed by shear.

White [134], based on the results of his study, discussed the deleterious effects of trace elements and impurity segregation to grain boundaries on the ductility of metals and alloys. The precise influence of trace elements on the deformation and fracture behaviour of these alloys, however, is not clear. Vasudevan and co-workers [115] reported that sodium segregation to grain boundaries in Al-11.4 at % Li ingot metallurgy alloys resulted in degradation in toughness. The segregation occurred during the solution heat treatment or after quenching the alloys from the solution heat treatment temperature. The amount of segregation depended on the bulk sodium concentration up to a level of 176 p.p.m. The 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 found to be more significant in the as-quenched and underaged (UA) alloys where inhomogeneous planar slip deformation was less intense (Fig. 14). In the peak-aged alloy, toughness was found to be insensitive to both bulk and fracture surface sodium concentrations. This was attributed to the intense planar deformation in the peak-aged condition which dominated the brittle fracture behaviour in the Al-11.4 Li (at %) alloys. Webster [129] observed that the levels of sodium or potassium failed to correlate with the observed toughness and ductility regardless of whether the alloy contained lithium. The results of some of his later work revealed that in the underaged and peak-aged conditions the impurity particles exist in liquid

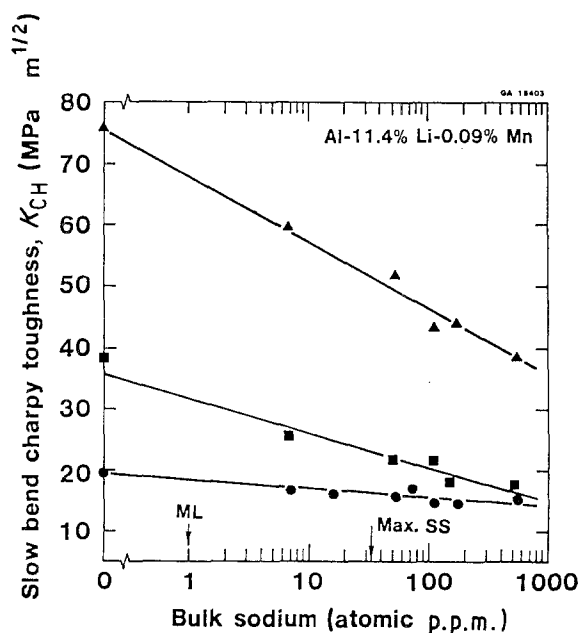


Figure 14 Dependency of slow bend Charpy toughness on bulk sodium concentration for as-quenched, underaged and peak aged alloys [113]. ML: calculated one monolayer of sodium coverage at 1 atomic p.p.m. bulk sodium. Max SS: maximum sodium solubility in aluminium. (▲) As-quenched, $\sigma_y \approx 59$ MPa; (■) aged 204°C for 4h, $\sigma_y \approx 231$ MPa; (●) aged 204°C for 48h, $\sigma_y \approx 265$ MPa.

phase and the toughness and ductility of the alloys in this condition were found to improve at temperatures below the freezing point of the impurity [132]. However, Webster also observed the low melting point impurities to have little influence in toughness or ductility of high purity aluminium.

The aluminium–lithium alloys have been reported to contain larger amounts of hydrogen than is normally in other high strength, non-lithium containing aluminium alloys. Such disproportionately high concentrations of hydrogen have been attributed to:

1. a large increase in the solid solubility of hydrogen in the lithium alloyed matrix, and
2. the formation of the hydrogen-rich phase during solidification of these alloys [135].

Hill and Williams [135] proposed that a possible factor contributing to the poor ductility of these alloys might be the result of the formation of a stable hydride of either lithium (LiH) or of aluminium and lithium (Li_3AlH_6). A detailed investigation conducted by these researchers on the relationship between hydrogen content, toughness, ductility and yield strength in Al–Li–Mg alloys revealed that a significant improvement in both ductility (tensile elongation) and toughness (notched tensile strength/yield strength), and a small decrease in yield strength could be achieved by reducing the hydrogen content from 43 to 14 p.p.m. The presence of hydrogen resulted from the processing treatment and the hydrogen of alloys in sheet form were twice as high as those in the ingots from which the sheets were produced. The control of hydrogen content in the Al–Mg–Li alloys was found to be more difficult than in conventional aluminium alloys, and refinement in melting and casting procedures were considered to be the only methods to reduce the high

hydrogen contents. Around the same time, Palmer and co-workers [136] found no difference between the mechanical properties of a powder metallurgy processed Al–3Li–1.5Cu–0.5Co–0.2Zr alloy containing up to 46 p.p.m. hydrogen and those reported for a similar PM alloy, Al–3Li–1.5Cu–1Mg–0.2Zr, having 1 to 3 p.p.m. hydrogen. The powder metallurgy extrusions had high hydrogen contents and even solution heat treatment in vacuum was found to be ineffective in decreasing the hydrogen levels. Based on the limited information available there is no conclusive evidence as to the precise effect of hydrogen on the deformation behaviour of aluminium–lithium alloys.

Recent investigations by Starke and co-workers [137, 138], Peters and co-workers [139] and Gregson and Flower [112] suggest that the presence of a strong crystallographic texture should be considered as a key factor responsible for governing an improvement in both tensile ductility and fracture toughness of these alloys. As the misorientation between neighbouring grains decreases, the effectiveness of grain boundaries as barriers to dislocation motion is decreased. Consequently, this results in an increase in slip length which effectively reduces ductility. Starke and Lin [10] and subsequently Feng and co-workers [140–142] and Srivatsan and co-workers [143] have reported significant improvement in strain to failure (about 120%) for completely unrecrystallized microstructures of an Al–4.45Cu–1.21Li–0.51Mn–0.2Cd alloy. The improvement in tensile elongation was rationalized as being due to:

1. sharp texture which relieves stress concentrations at grain boundaries, resulting from planar deformation, as a consequence of shear in neighbouring grains, and
2. a change in fracture mode from predominantly low energy intergranular rupture for recrystallized and partially recrystallized microstructures of the Al–4.45Cu–1.21Li–0.5Mn–0.2Cd alloy, to higher energy absorbing transgranular dimpled rupture for unrecrystallized microstructure.

In random-textured materials, such as recrystallized and partially recrystallized microstructures, the stress concentration effects due to planar deformation are not relieved by the transfer of plasticity to adjacent grains. For such a situation, initiating microvoids at the coarse second-phase constituents and dispersoid particles lying along the grain boundary is easier than initiating slip in the neighbouring grain. Nucleation of a crack localizes the plastic zone in the soft PFZ with concomitant crack propagation along the grain boundary aided by the coalescence of microvoids initiated at the grain boundary precipitates. The influence of other factors besides crystallographic texture on the deformation, fracture behaviour and tensile ductility of these alloys were examined. These include:

1. the nature of precipitates present at and along the grain boundaries,
2. the nature of matrix strengthening precipitates, and
3. the orientation of the slip directions relative to the loading axis.

6. Past approaches to improve the deformation behaviour of aluminium–lithium alloys

During the last few years considerable research efforts have been directed at improving the inferior tensile ductility and fracture behaviour of rapidly solidified-powder metallurgy processed and ingot metallurgy aluminium–lithium alloys while continuing to maintain the benefit of high strength. A few of the approaches made in an attempt to improve the inferior ductility of these alloys include:

1. promoting homogeneous deformation through dislocation cross-slip or precipitate bypassing by modification of lattice parameters to increase mismatch in the matrix–AlLi system.
2. introducing secondary precipitation systems,
3. encouraging dispersion hardening in addition to precipitation hardening,
4. refinement of grain structure through addition of grain refining elements such as manganese, zirconium, chromium and cobalt,
5. minimization of tramp elements such as sodium, potassium and sulphur through alloy control, and
6. novel thermochemical processing procedures which combine mechanical deformation and thermal treatment for the purpose of refining the grain structure, optimizing the grain size and degree of recrystallization.

Furthermore, with the advent of rapid solidification technology, structure control and increased solid solubility were made possible and this permitted investigators to take the aforementioned approaches with various degrees of success.

The poor fracture resistance, inferior ductility, and low toughness of these alloys is largely a result of strain localization effects both in the matrix and at grain boundaries. During deformation, the coherent and partially coherent strengthening precipitates are sheared by moving dislocations resulting in localization of slip along closely-packed crystallographic planes [13, 110, 112, 144]. In addition, the presence of PFZs along both high angle grain boundaries and subgrain boundaries localizes the plastic deformation in these regions, causing thereby, cracks to nucleate either at the grain boundary triple junctions or at grain boundary precipitates (Fig. 10b). Stress concentration occurs once the crack is nucleated. The crack grows either transgranularly along the intense slip bands or intergranularly along the soft PFZ adjacent to the grain boundaries. Sanders and Starke [110] and subsequently other researchers have suggested that a major cause responsible for the inferior ductility and toughness of these alloys as compared to conventional aluminium alloys of comparable strength and ageing was planar slip deformation [110, 112, 121]. This deformation process was believed to be responsible for degrading the strain-hardening capacity, tensile ductility and fracture toughness with progressive ageing to peak strength in the case of precipitation hardenable aluminium–lithium alloys. The detrimental effect of localization of strain due to planar slip deformation is that it causes stress concentration to occur at grain boundaries resulting in low energy intergranular rup-

ture. Changing the deformation mode from one of dislocation shearing of precipitates to that of dislocation looping or bypassing of precipitates resulted in improved homogeneity of deformation with concomitant improvement in ductility. In age-hardenable alloys this was accomplished through overageing. However, the loss in strength due to overageing made this method of improving ductility by minimizing strain localization effects not very attractive.

Grain structure refinement through addition of elements that form dispersoids during solidification and/or high temperature homogenization treatment was found to be an attractive method to improve ductility [66, 145]. In addition to controlling the grain size, grain shape and degree of recrystallization, the dispersoids aid in dispersing slip and inhibit the formation of intense slip bands. The dispersoids promote homogeneous plastic deformation and early crack nucleation due to strain localization effects caused by the intense planar slip bands is avoided. Rapid solidification processing of these alloys aided in refining both the dispersoid particle size and their distribution, thereby, eliminating the possibility of these particles being potential crack initiation sites.

Changing the misfit strain of the Al_3Li precipitate [10, 146, 147], changes in alloy chemistry coupled with precipitation of other phases such as the S-phase in magnesium-containing alloys [112], and thermomechanical processing [141, 148] have also been successfully used to minimize the deleterious effects of localized planar slip deformation in these alloys. A reduction in grain size achieved through thermomechanical processing treatments promotes homogeneous deformation and is an effective method of preventing early crack nucleation and premature failure due to strain localization effects [149–152]. A reduction in grain size decreases the dislocation pile-up length and consequently, lowers the high stress concentrations at grain boundaries and grain boundary triple junctions. Furthermore, a reduction in grain size helps in alleviating the deleterious effects arising from the presence of shearable matrix strengthening precipitates, coarse grain boundary precipitates and soft PFZs [152–154] and a fracture mode change from low energy intergranular to high energy absorbing transgranular dimpled rupture occurs. Grain size refinements in these alloys have been accomplished through:

1. powder metallurgical processing [155],
2. thermomechanical processing treatments [10, 148, 156], and
3. addition of grain refining elements [66, 157, 158].

The tensile ductility of Al–Li alloys can be improved by slip homogenization effected both by grain refinement and the introduction of incoherent, nonshearable dispersoids [128]. Manganese (Mn), chromium (Cr) and zirconium (Zr) are grain refining additions. These alloying elements have limited solubility (up to about 1.8% Mn, 0.75% Cr and 0.28% Zr) in the aluminium matrix and precipitate as intermetallic phases during elevated-temperature processing [159]. The fine, hard, intermetallic phases present in the microstructure of these alloys are referred to as

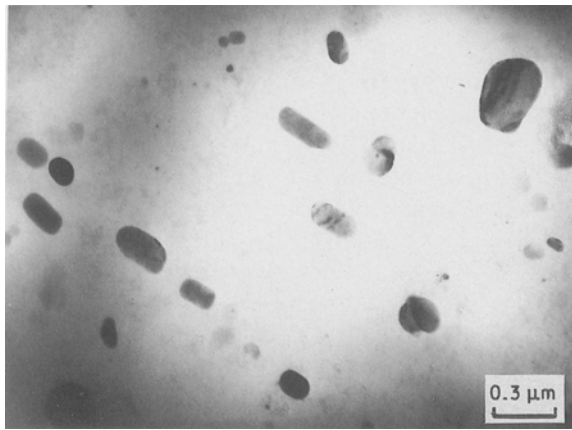


Figure 15 Bright field transmission electron micrograph showing the distribution of manganese dispersoids in an Al-4.5Cu-1.21Li alloy.

dispersoids. Figure 15 presents the microstructure of an Al-Cu-Li alloy following solution treatment and shows the manganese dispersoids. The manganese and chromium dispersoids are larger (about 0.02–1 μm in the longest dimension) and develop an incoherent interface with the aluminium matrix. In contrast, the zirconium dispersoid is smaller (less than 0.02 μm in the longest dimension) and coherent with the aluminium matrix [160]. The dispersoid particles are generally non-deformable. As such, the barrier they represent to dislocation motion is inversely proportional to the spacing as predicted by the Orowan equation:

$$\tau \propto \frac{Gb}{\lambda}$$

where τ is the shear stress, G is the matrix shear modulus, b is the Burgers vector, and λ is the inter-particle spacing.

During deformation, dislocation interaction with the non-shearable dispersoids results in the generation of new dislocations necessary to accommodate the strain. In this way, the dispersoids increase at least initially, the work hardening rate of an alloy [104, 161, 162]. The extent of work hardening, however, depends upon the nature of: (a) dislocation-particle interaction, (b) the dispersion parameters, and (c) the recovery processes occurring. The dispersoids control the grain structure of the wrought, high strength, lightweight lithium-containing aluminium alloys. In addition to influencing grain structure, the fine dispersoid particles influence the mechanical properties by dispersing slip [128, 163].

Manganese was added to the first commercial lithium-containing aluminium alloy 2020 (Al-4.45 wt % Cu-1.21 wt % Li) for the primary purpose of grain structure control. The manganese combined with aluminium to form Al_6Mn and $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$ dispersoid particles. These dispersoids are incoherent with the aluminium matrix and act as nucleating sites for recrystallization. Pao and co-workers [164] added 0.5 wt % manganese to a (PM) Al-2.5 wt % Li-1.5 wt % Cu alloy for the dual purpose of refining the grain structure, and minimizing strain localization effects. While grain refinement was achieved, the failure to minimize the detrimental effects of strain

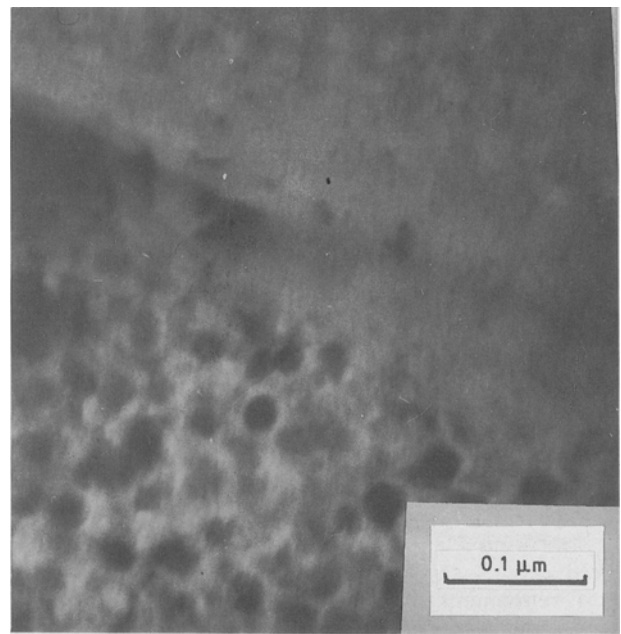


Figure 16 Bright field transmission electron micrograph showing pfz at grain boundary in a peak aged Al-3Li-1.25Mn alloy.

localization and homogenize slip was attributed to the low fraction of the incoherent manganese-rich particles. The manganese-rich dispersoids were reported to be detrimental to ductility by facilitating the initiation of voids during plastic deformation [10]. On the other hand, Coyne and co-workers [12] observed that a large volume fraction of incoherent Al_6Mn intermetallic particles in an IM Al-3.0 wt % Li-1.25 wt % Mn alloy homogenized the slip and promoted hardening during cyclic straining. However, strain localization was present in the large PFZs which were formed during ageing to peak strength (Fig. 16).

Zirconium additions to aluminium-lithium alloys result in the alloy having a finer as-cast microstructure and the formation of the metastable cubic Al_3Zr phase which are: (a) spherical in morphology, (b) fully or partially coherent with the aluminium matrix, depending on the processing history, and (c) can effectively pin the grain and subgrain boundaries. Rioja and Ludwiczak [48] and Galbraith and co-workers [81] termed the Al_3Zr as β' . The β' has an Ll_2 crystal structure and a cube-cube orientation to the matrix [81]. The smaller, coherent precipitates are effective in retarding subgrain boundary migration and coalescence, and this stabilizes the subgrain structure and inhibits recrystallization [165]. The β' (Al_3Zr) nucleates heterogeneously on dislocations and grain boundaries with an average misfit of 0.3–0.6% [165, 166]. Zirconium additions are particularly attractive since they inhibit recrystallization without the deleterious effects on corrosion resistance that accompanies manganese additions [166].

Sastry and O'Neil [167] demonstrated the use of rapid solidification by the twin roller quenching technique to process Al-3Li, Al-3Li-0.6Co, and Al-3Li-0.3Zr. The addition of small amounts of cobalt resulted in a uniform distribution of fine incoherent Co_2Al_9 dispersoids which were found to be very effective in decreasing the planarity of slip and improved the high temperature strength. Sankaran

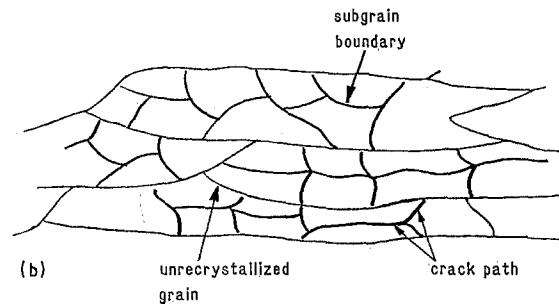
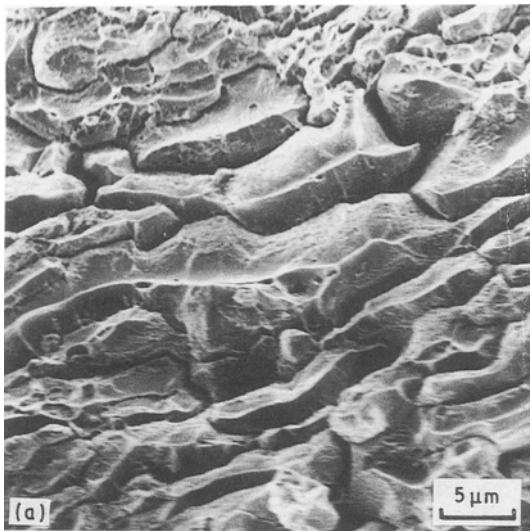


Figure 17 (a) Scanning electron micrograph showing intersubgranular fracture in an Al-2.8Li-1.3Cu-0.7Mg-0.12Zr alloy. (b) Schematic showing intergranular cracking along the subgrains with an unrecrystallized grain.

and co-workers [168] processed a high purity Al-3Li alloy, and commercial purity Al-3Li alloys containing additions of cobalt, titanium, zirconium and yttrium by rapid solidification using the twin roller quenching technique. The objective of their study was to enhance the ductility of these alloys by homogenizing slip through grain refinement and promoting microstructural homogeneity through incoherent dispersoids. The microstructures of the Al-3Li-0.16Ti and the Al-3Li-0.23Co alloys were found to consist of a bimodal distribution of 40 nm diameter Al_3Li precipitates and 50–100 nm slip dispersing Al_3Ti and Co_2Al_9 dispersoids. The total elongation to failure exhibited by these two alloys (9.7% and 9.12%) were observed to be indications of the effectiveness of the dispersoid particles and the fine grain structure on dispersing slip, promoting homogeneous deformation and, thereby, enhancing the ductility of the alloys.

Dispersoid type, spacing and volume fraction influences both toughness and tensile ductility. The energy required to propagate a crack increases as the volume fraction of dispersoids decreases, and the dispersoid spacing increases. In a recent study, toughness of the manganese containing alloy (Al-2.7Cu-2.1Li-0.62Mn-0.16Cr) was observed to be slightly superior to that of the zirconium-containing alloy (Al-2.7Cu-2.23Li-0.11Zr) [169]. While the exact micromechanism responsible for this improvement was not obvious, it was attributed to the fact that the strength of the random textured, manganese-chromium containing alloy was comparable to that of the strongly textured, zirconium-containing alloy. The dispersoids decrease the energy required to propagate monotonically loaded cracks by initiating microvoids which coalesce in void sheets. The void sheets help link the incipient cracks initiated at large constituent particles [170]. Alloys containing the coherent zirconium dispersoids develop improved resistance to stable propagation of a crack under monotonic loading. However, alloys containing the larger, incoherent manganese-rich particles ($Al_{20}Cu_2Mn_3$) have inferior resistance.

Fracture mode and morphology are significantly influenced by the type of dispersoid particle. Zirconium-containing alloys with unrecrystallized grain structure tend to fail by transgranular and intersubgranular fracture along the subgrain boundaries (Fig. 17). While the manganese-containing alloys with recrystallized grain structure failed predominantly by intergranular rupture with fracture along the large recrystallized grain boundaries (Fig. 18). The improved strength-ductility relationships in unrecrystallized zirconium-containing alloys have been associated with a sharp texture and a higher energy absorbing transgranular energy absorbing transgranular fracture mode [10, 171–174].

Feng and co-workers [140, 141] in their intensive study on the effect of minor alloying elements on the mechanical properties of Al-Cu-Li alloys achieved limited success at improving the properties of the ingot alloys by lowering the impurity levels, namely,

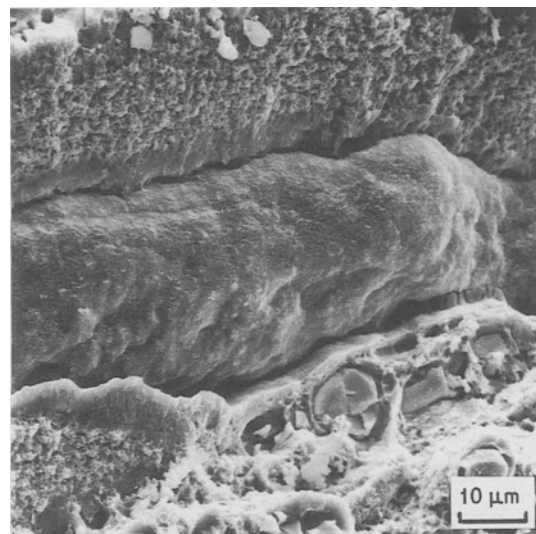


Figure 18 Scanning electron micrograph showing intergranular fracture along the large recrystallized grain boundaries in an Al-4.5Cu-1.21Li-0.51Mn alloy.

iron and silicon. The improvement in fracture toughness was attributed primarily to the lower volume fraction of intermetallic particles. They also found that by replacing the grain refining element manganese with zirconium, a highly textured unrecrystallized structure could be obtained resulting in an improvement in fracture toughness. The influence of cadmium additions on intrinsic deformation and fracture response was also evaluated. Cadmium was found to be more effective in promoting the nucleation of the θ' precipitate than a 2% stretch given prior to ageing. However, the observed difference in strength between two materials (one containing cadmium addition and the other no cadmium) in the peak aged condition, was only 12%. Lowering the levels of impurity elements had an influence through improvements in tensile ductility, fracture toughness and fatigue crack initiation as a consequence of a lower volume fraction of coarse constituents and intermetallic particles. The improvement in tensile ductility was however, not commensurate with improvement in fracture toughness. This was rationalized as being due to coarse planar slip and the lack of necking that occurs in the tensile tests which minimizes stress concentrations at the coarse constituent and intermetallic particles.

Substitution of another element for aluminium, or lithium in the Al_3Li precipitate may significantly change the lattice parameter, and the matrix- Al_3Li precipitate interface energy. This in principle, encourages the dislocation to cross-slip or by-pass the precipitate rather than dislocation cutting the precipitate particle, thereby minimizing coarse planar slip. Gayle [175] has limited success in his study on the influence of copper, magnesium, silicon, manganese, iron, gallium and silver additions to:

1. cast and rolled ingot aluminium-lithium alloys, and

2. cast and hot extruded ingot metallurgy alloys.

Additions of these elements were made in an attempt to improve the tensile ductility, fracture toughness and fracture resistance through: (1) an increase in the matrix- δ' precipitate lattice misfit, (2) encouraging dislocation cross slip through modifications in the shear resistance of the δ' (Al_3Li) precipitate particles, and (3) formation of other second-phase particles. The copper containing aluminium-lithium alloys showed the best fracture behaviour with moderate strength. Brittle fracture behaviour was rationalized as being due to grain boundary failure. Presence of high hydrogen levels coupled with coarse planar slip and grain boundary PFZ appeared to be the key factors responsible for intrinsic grain boundary weakness.

Baumann and Williams [176] attempted to modify the precipitation of the δ' (Al_3Li) precipitate by altering the δ'/α misfit in Ingot metallurgy aluminium-lithium alloys. They achieved this through additions of magnesium, copper, silver, zinc, manganese, chromium, silicon and zirconium. While silver and zinc showed the potential for increasing the δ'/α misfit, they have the undesirable characteristics of being relatively heavy elements besides decreasing the solubility of lithium in the aluminium matrix. Baumann and Williams [176] concluded that a large increase in

misfit strain between the δ' and the matrix phase in aluminium-lithium alloys is not achievable. In their studies, Gayle [177] and Baumann and Williams [176] were severely limited by the slow solidification rates and poor structure control inherent to the ingot metallurgy technique.

Palmer and co-workers [178] observed superior combinations of strength and ductility in rapidly solidified, PM processed Al-Li-Cu-Mg alloys containing zirconium. In addition to an unrecrystallized microstructure the improvement in both strength and tensile ductility were attributed to precipitation of the S' (Al_2CuMg) phase, and to the contribution of magnesium to solid solution strengthening. Both these factors decreased the tendency for localized planar slip and concomitant strain localization effects. The S' (Al_2CuMg) phase in the quaternary alloys appeared to be finer and more uniformly distributed than the θ' (Al_2Cu) or T_1 (Al_2CuLi) phases in Al-Li-Cu alloys. A similar observation was made by other researchers in their studies [179, 180].

Starke and Lin [10] studied the influence of a spectrum of grain structures produced by novel thermochemical processing treatments on the ductility of a ternary Al-4.45Cu-1.21Li-0.51Mn alloy. Alloys having completely unrecrystallized microstructures were shown to have ductility values (10 to 14%) superior to those of the recrystallized and partially recrystallized counterparts (4 to 8%) in both the longitudinal and transverse direction and strength-ductility relationship comparable with aluminium alloy 7075-T651. The improved ductility of the unrecrystallized microstructures was associated with a sharp texture and a transgranular dimpled fracture. The improvement in tensile ductility for the alloy having an unrecrystallized microstructure was as high as 120%. Subsequent studies by Feng and co-workers [140-142] and Srivatsan and co-workers [143] reported similar improvement in ductility for alloys having an unrecrystallized microstructure.

In an attempt to find an alloying element that markedly improved both tensile ductility and toughness, Cassada and co-workers [181] investigated the effect of germanium addition (0.2 wt %) to Al-2 wt % lithium alloys. The alloys were processed as ingots, solutionized at 823 K for 30 min, water quenched and aged at 473 K for various time periods. The presence of germanium was observed not to affect grain size after processing. The germanium particles are partially coherent with the matrix, an important factor in determining the shearability of the precipitate. In comparing the elongation to failure of two alloys, one with germanium addition and the other not containing any germanium, it was observed that the alloy containing germanium has approximately twice the elongation over the non-germanium containing alloy, despite the fact that the non-germanium containing alloy had more lithium and consequently a larger volume fraction of the coherent Al_3Li phase. Transmission electron microscopy observations revealed different fracture modes for each alloy. The germanium-containing alloy revealed a higher degree of ductile transgranular feature, consistent with a greater tensile ductility. A

uniform distribution of dislocations was observed with the dislocations pinned at the germanium particle sites. In the binary alloy, fracture was found to be predominantly intergranular with intense planar slip deformation limiting the ductility. Germanium has limited solubility in the Al-2 wt % lithium alloy at 473 K; its covalent nature results in little chemical interaction with the lithium atoms. The germanium addition was found to have no effect on the Al₃Li-matrix mismatch, and hence, Cassada and co-workers concluded that the non-shearable nature of the germanium precipitates which effectively dispersed slip and homogenized deformation.

7. Concluding remarks

The large body of literature reviewed in this paper presents the cross section of views and experimental results that have been obtained over the years by several investigators in the field of lithium-containing aluminium alloys. The increasing need for materials for use in weight-critical and stiffness-critical applications has in recent times resurrected interest and stimulated studies on understanding the physical metallurgy, metallurgical characteristics and mechanical properties of aluminium-lithium alloys. The potential use of these alloys in aerospace structures looks promising. Not only do these low density alloys offer the benefit of substantial weight savings of themselves, but they also will help maintain the preeminence of aluminium alloys as the primary structural material for airframes. The general strengthening contributions to these alloys are summarized. Results obtained by several researchers in their studies on composition-processing-microstructure relationships are discussed. Rationalizations for observed enhancement in strength of the solid solution are made with reference to the presence of lithium in solid solution, and to the presence of coherent, ordered precipitates in the matrix. The contributions from coherency strain hardening, modulus hardening and order hardening to the total hardening in binary alloys aged to peak strength is examined.

Several examples drawn from the literature suggest that additional strengthening in these alloys is achieved by the co-precipitation of other binary and ternary phases. The addition of various amounts of copper and magnesium to these alloys modifies the precipitation sequence by altering the solubility of the principle alloying elements and by also co-precipitating with the lithium-rich ordered matrix precipitates. Co-precipitation of ternary and more complex matrix strengthening phases is found to be beneficial because in addition to improving the strength of the material, it promotes homogeneous deformation. The dependence of the overall strength of these alloys is made with reference to metallurgical variables. Such variables include the alloy chemistry and intrinsic microstructural features, such as, the nature and type of matrix strengthening precipitates, the presence of dispersoids, presence of denuded zones adjacent to grain boundaries, and the synergistic interactions between the dislocations generated during deformation and the intrinsic microstructural features.

The intrinsic micromechanics governing the deformation characteristics and fracture behaviour are discussed with specific reference to ageing condition, the slip characteristics, and the nature, volume fraction and distribution of matrix and grain boundary precipitates. The fracture process is dictated by several synergistic and mutually-competitive processes ranging from the presence of coarse second-phase constituents to the existence of a low energy interface between the equilibrium precipitates and the matrix, and including strain localization effects due to heterogeneous deformation and the exacerbating effect of PFZ. The detrimental effect of grain boundary precipitates and stress incompatibility at the grain boundary are also highlighted. Contributions from microstructure to fracture behaviour is the conjoint action of several competing effects ranging from stress history, to dislocation-microstructure interactions and the deformation mode. The sequence of events leading to premature fracture on alloys containing a large volume of second-phase particles is highlighted and the methods to minimize the deleterious effects of strain localization in these alloys are discussed. The work done and techniques used by several researchers to improve the deformation, fracture behaviour and tensile ductility if these alloys are examined. Past attempts to improve the ductility and mechanical response of these alloys are critically examined so as to provide a basis for understanding processing-microstructure-deformation interactions.

The broad observations made in this paper lead the authors to the conclusion that there are several mechanisms which control the strength, deformation characteristics, fracture behaviour and mechanical response of these alloys. For a particular ageing condition, the micromechanisms governing the deformation characteristics and fracture processes appear to be influenced more by the alloy chemistry and intrinsic microstructural effects with minimal influence from the stress history. The development of several processing techniques has definitely stimulated the possibility of tailoring the properties of an alloy for a particular application. It is hoped that cross-pollenization of ideas among researchers combined with additional experimental efforts aimed at resolving a few anomalies that exist should aid in a better understanding of mechanical response of these alloys for different compositions and microstructural conditions.

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