Chapter 3
Aluminium–Lithium Alloys

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Abstract This chapter summarises the development and limitations of the first and second generation Al–Li alloys, and then discusses the recent developments leading to the third generation alloys. Emphasis is placed on the physical metallurgy of Al–Li alloys, progressive development of the three generations of these alloys, and finally the strategies for obtaining improved property combinations via various microstructural modifications closely linked to multistage processing. The way forward for Indian development of Al–Li alloys is also briefly discussed.

Keywords Aluminium–Lithium alloys · Mechanical properties · Fatigue · Fracture · Corrosion · Applications

3.1 History of Alloy Development

Interest in aluminium–lithium (Al–Li) alloys arises from the important consideration that as the lightest metal, lithium additions to Al reduce its density (~3 % decrease per every wt%) and increase the elastic modulus (~6 % increase per every wt%). The increases in *specific* strength (strength/density) and *specific* stiffness (E/density) combine with good fatigue and cryogenic properties to offer possibilities for the use of Al–Li alloys in aerospace structural applications, including fuel tanks in launch vehicles, like the external tank of the US Space Shuttle [1–3].

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Developmental activities started from the 1920s, but the first commercial alloy AA2020 (Al–1.1Li–4.5Cu–0.5Mn–0.2Cd) was introduced only in 1958. This alloy was successfully used for the wing skins and tails of the Northrop RA-5C Vigilante aircraft, but concerns about its fracture toughness led to its withdrawal in the 1960s. In the same time period, research work in the former Soviet Union led to the development of VAD-23 with the nominal composition Al–1.1Li–5.3Cu–0.6Mn–0.17Cd and 1420 (Al–2.0Li–5.3 Mg–0.5Mn). All three alloys are customarily referred to as first generation alloys.

In the 1970s the potential threat of replacement of aluminium alloys by carbon fibre composites resulted in extensive research work on a new, second generation of Al–Li alloys. Development of these alloys has been largely unsuccessful owing to unacceptable degrees of property anisotropy, low short transverse properties and thermal instability. Work began in the late 1980s and early 1990s on a third generation of Al–Li alloys, and developments are ongoing. These newer alloys are candidates for widespread replacement of conventional aluminium alloys in aerospace structures. Table 3.1 lists typical compositions of some Al–Li alloys from all three generations [1].

3.2 Aircraft Structural Property Requirements

Figure 3.1 illustrates the engineering property requirements for several of the main structural areas in a transport aircraft, namely (i) Fuselage and Pressure Cabins, (ii) Wings and (iii) Empennage. The engineering properties required for these aircraft structures are strength (TS, CYS), stiffness (E), damage tolerance (DT: fatigue, fatigue crack growth, fracture toughness), and corrosion (general and stress corrosion). Also very important is the material density (ρ), reflected in weight savings per se and the specific strength and stiffness.

Figure 3.2 summarises calculations of aircraft structural weight savings due to property improvements [2], showing that a lower density is the most effective way of reducing the overall weight of an aircraft structure. Next are enhancements in strength and stiffness, which combine with reduced density to give improvements in specific strength and stiffness. Finally, improvements in damage tolerance (DT) properties have the least potential for saving weight, though even small amounts of weight savings can be important.

Additions of lithium to aluminium alloys decrease the density and increase the stiffness, thereby having a synergistic effect on the specific stiffness (E/ρ). Thus Al–Li alloy development may already be successful from an engineering property viewpoint—certainly with respect to equivalent conventional alloy products—if other properties are simply maintained. This is attractive to commercial alloy producers, since there is the possibility of obtaining families of Al–Li alloys to replace conventional alloys for a variety of applications.

Table 3.1 Compositions and densities of commercial Al–Li alloys [1]

Alloy	Composition (all elements in wt%)									Density, ρ (g/cm^3)	Introduction /Reference(s)
	Li	Cu	Mg	Ag	Zr	Sc	Mn	Zn	Other elements		
First generation											
2020	1.2	4.5					0.5			2.71	Alcoa (1958)
1420	2.1		5.2		0.11					2.47	Soviet (1965)
1421	2.1		5.2		0.11	0.17				2.47	Soviet (1965)
Second generation (Li ≥ 2 %)											
2090	2.1	2.7			0.11					2.59	Alcoa (1984)
2091	2.0	2.0	1.3		0.11					2.58	Pechiney (1985)
8090	2.4	1.2	0.8		0.11					2.54	EAA (1984)
1440	2.4	1.5	0.8		0.11					2.55	Soviet 1980s
1441	1.95	1.65	0.9		0.11					2.59	Soviet 1980s
1450	2.1	2.9			0.11					2.60	Soviet 1980s
1460	2.25	2.9			0.11	0.09				2.60	Soviet 1980s
Third generation (Li < 2 %)											
2195	1.0	4.0	0.4	0.4	0.11					2.71	LM/Reynolds (1992)
2196	1.75	2.9	0.5	0.4	0.11		0.35 max	0.35 max		2.63	LM/Reynolds/McCook Metals (2000)
2297	1.4	2.8	0.25 max		0.11		0.3	0.5 max		2.65	LM/Reynolds (1997)
2397	1.4	2.8	0.25 max		0.11		0.3	0.10		2.65	Alcoa (1993)
2098	1.05	3.5	0.53	0.43	0.11		0.35 max	0.35		2.70	McCook Metals (2000)
2198	1.0	3.2	0.5	0.4	0.11		0.5 max	0.35 max		2.69	Reynolds/McCook Metals/Alcan (2005)
2099	1.8	2.7	0.3		0.09		0.3	0.7		2.63	Alcoa (2003)

(continued)

Table 3.1 (continued)

Alloy	Composition (all elements in wt%)									Density, ρ (g/cm^3)	Introduction /Reference(s)
	Li	Cu	Mg	Ag	Zr	Sc	Mn	Zn	Other elements		
2199	1.6	2.6	0.2		0.09		0.3	0.6		2.64	Alcoa (2005)
2050	1.0	3.6	0.4	0.4	0.11		0.35	0.25 max		2.70	Pechiney/Alcan (2004)
2296	1.6	2.45	0.6	0.43	0.11		0.28	0.25 max		2.63	Constellium Alcan (2010)
2060	0.75	3.95	0.85	0.25	0.11		0.3	0.4		2.72	Alcoa (2011)
2055	1.15	3.7	0.4	0.4	0.11		0.3	0.5		2.70	Alcoa (2011)
2065	1.2	4.2	0.50	0.30	0.11		0.40	0.2		2.70	Constellium (2012)
2076	1.5	2.35	0.5	0.28	0.11		0.33	0.30 max		2.64	Constellium (2012)

Fig. 3.1 Engineering property requirements for a transport aircraft. See the text for the abbreviations [1]

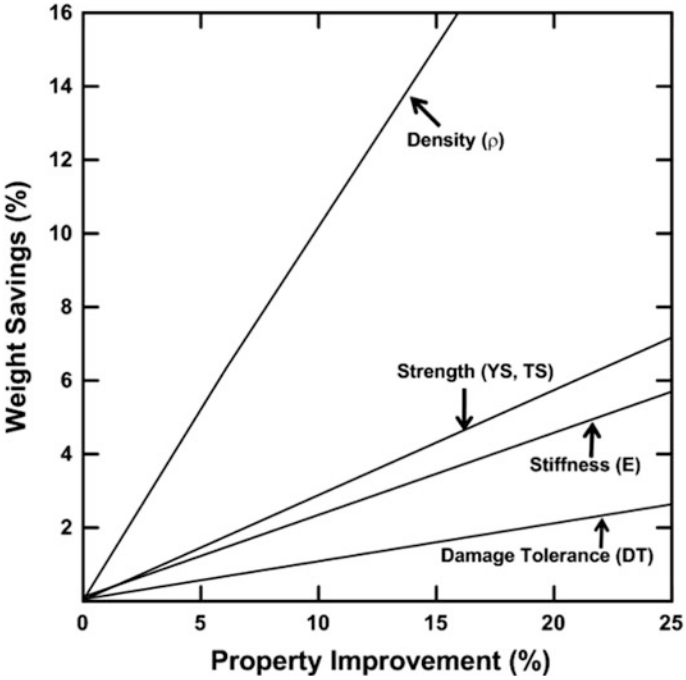

Fig. 3.2 Potential weight savings for aircraft structures owing to various property improvements [2]

3.3 Physical Metallurgy of Al–Li Alloys

The presence of lithium atoms in an aluminium matrix gives only a small degree of solid solution strengthening, owing principally to atomic size differences. However, lithium substantially increases the elastic constants of the aluminium–lithium solid solution even though the values of its own constants are noticeably lower than those of aluminium [4, 5].

The general strength in Al–Li alloys is derived from the presence of large volume fractions of the coherent δ′ (Al_3Li) phase. The δ′ phase has a high intrinsic modulus due to its ordered nature, and this contributes to the high values of elastic modulus in these alloys. It should be noted that when lithium is in solid solution the elastic constants depend on both atomic interactions and interatomic potential. However, when lithium is present in a precipitated second phase the elastic constants depend on both the volume fraction and intrinsic modulus of the second phase [4]. Strength increases owing to the presence of δ′ precipitates are obtained via several mechanisms. Figure 3.3 summarises the contributions of various mechanisms to the overall strength in terms of the shear stress for slip to occur. The net shear stress (reflected in the variation of observed strength in Fig. 3.3) is the weighted average of all the contributing strengthening mechanisms.

Order hardening and modulus hardening contribute the most, while coherency and surface hardening contribute relatively less. Order hardening makes a major contribution to strength owing to the creation of antiphase boundaries (APBs) [6, 7]. In order to eliminate the extra energy required to create the antiphase boundary (APB), the dislocations in Al–Li alloys move in pairs connected by a region of antiphase boundary such that passage of the second dislocation restores the disorder

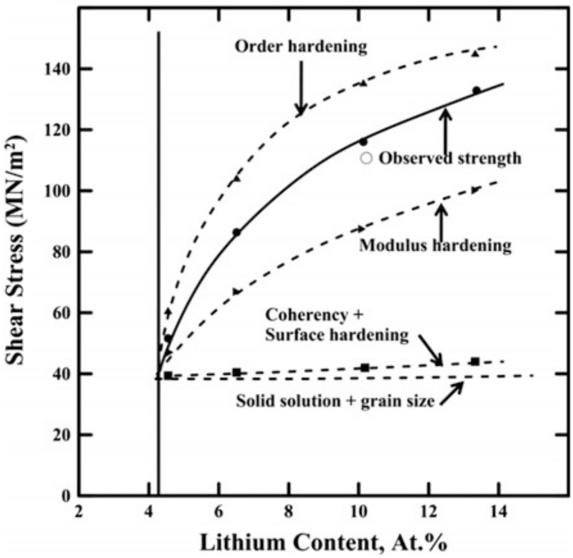

Fig. 3.3 Contributions of various mechanisms to strengthening by δ′ precipitates in Al–Li alloys [6, 7]

caused by the first [6, 7]. The critical resolved shear stress ($\boldsymbol{\tau}_{\mathrm{CRSS}}$) for such a process was found to be [8]:

$$\tau_{\mathrm{CRSS}} \propto \quad (\gamma_{\mathbf{APB}})^{3/2} \;.\; \mathbf{r}^{1/2} \;.\; \mathbf{f}^{1/2}. \tag{3.1}$$

In this expression γ_{APB} is the antiphase boundary energy of the δ' (Al_3Li) particles, **r** is the mean radius, and **f** is the volume fraction of the precipitate particles. Once sheared, the ordered precipitate particles would result in reduced contributions from order strengthening. This is essentially due to a reduction in cross-sectional area of the precipitate particles upon initial shearing. If $\mathbf{n_d}$ dislocations, each having a Burger's vector $\mathbf{b_v}$, shear a given particle and we assume shearing to take place across the diameter of the precipitate particle, then $\boldsymbol{\tau}_{\mathrm{CRSS}}$ for continued shearing becomes

$$\tau_{\mathrm{CRSS}} \propto \quad (\gamma_{\mathbf{APB}})^{3/2} \;.\; \mathbf{f}^{1/2}\left[(\mathbf{r} - \mathbf{n_d b_v})^{1/2}\right]. \tag{3.2}$$

Thus a reduction in the critical resolved shear stress ($\boldsymbol{\tau}_{\mathbf{CRSS}}$) becomes significant, making further slip on that particular plane conducive. Hence slip is favoured to become planar and the particular plane on which repeated slip occurs gradually becomes work-softened. Al–Li alloys that are artificially aged to the peak strength condition tend to exhibit such planar slip deformation behaviour [9–11], which is detrimental to some engineering properties, notably ductility and fracture toughness.

Besides order/APB strengthening, the contributions to modulus hardening were also found to be significant for Al–Li alloys [7] and can be estimated as [12]

$$\Delta\sigma = \frac{\Delta G}{2\pi^2}\left[\frac{3\mathrm{I}\Delta G\mathrm{I}}{G_m b v}\right]^{\frac{1}{2}}\left[0.8 - 0.143\ln\left[\frac{r}{bv}\right]\right]^{\frac{3}{2}} r^{\frac{1}{2}} f^{\frac{1}{2}} \tag{3.3}$$

where ΔG is the difference in the shear modulus values of the matrix (G_m) and the precipitate particles.

Apart from δ' (the major strengthening phase in second generation Al–Li alloys), other co-precipitates contribute to and control the strength, deformation and fracture of Al–Li alloys. They include θ′ (Al_2Cu, the major strengthening phase in first generation Al–Li alloys); T_1 (Al_2CuLi), the major strengthening phase in third generation Al–Li alloys; and S/S′ (Al_2CuMg), whose presence leads to significant slip homogenisation. There is also the β′ (Al_3Zr) phase, which is the primary phase that pins the high angle grain boundaries and is therefore important in controlling and restricting recrystallisation and subsequent grain growth.

All other equilibrium phases are undesirable as they have been found to promote low energy intergranular fracture and result in low ductilities and inferior damage tolerant properties. Hence the following phases are kept to a minimum—δ (AlLi), T_2(Al_6CuLi_3), T_B ($Al_{15}Cu_8Li_2$) and Ω (hexagonal thin plates in high Cu:Mg alloys).

For a summary of the various phases present in different Al–Li alloys see Figs. 3.4 and 3.5. It is evident that the microstructural situations can be complex for Al–Li–Cu–Mg–Zr alloys, including the Al–Li-low-Cu-high-Mg–Zr third generation alloys that are of most commercial interest. Thus it is no easy task for commercial processing to optimise the microstructures with respect to obtaining a good balance of engineering properties for these alloys.

3.4 Processing Technologies

Commercial and semi-commercial Al–Li alloys in different temper conditions are produced using the following process technologies:

1. Melting in fuel-fired reverberatory furnaces in air atmosphere (adding fluxes to the melt to reduce atmospheric oxidation), followed by melt degassing and filtration and Direct Chill (DC) casting into slabs and billets. These processes are much more challenging to carry out owing to high reactivity of lithium in the molten alloys [1, 13–19].
2. Thermomechanical working of the DC cast ingots and slabs by hot and cold working (mainly by rolling, forging and extrusion), employing workability/processing

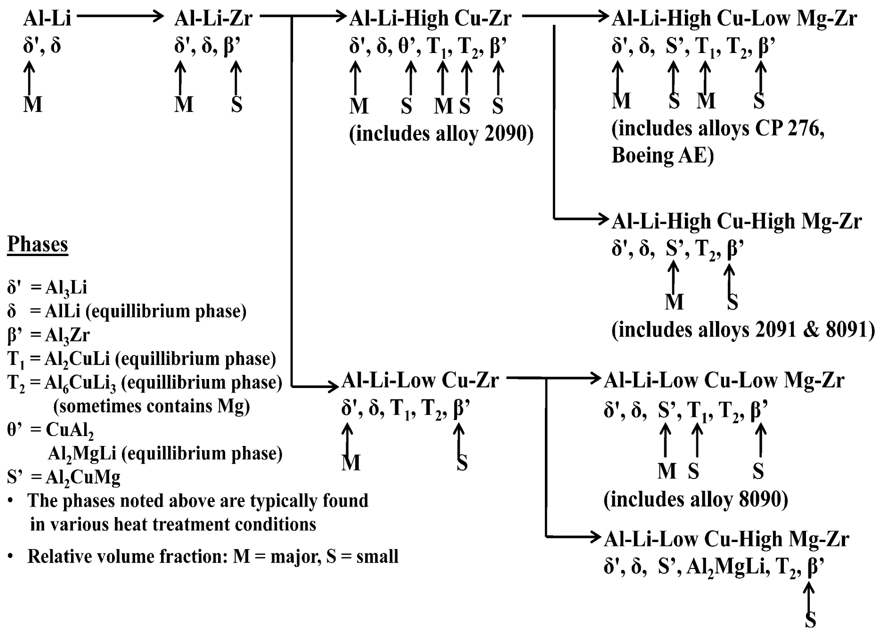

Fig. 3.4 Various precipitate phases that form in different Al–Li alloys depending on the concentrations of alloying elements [1]

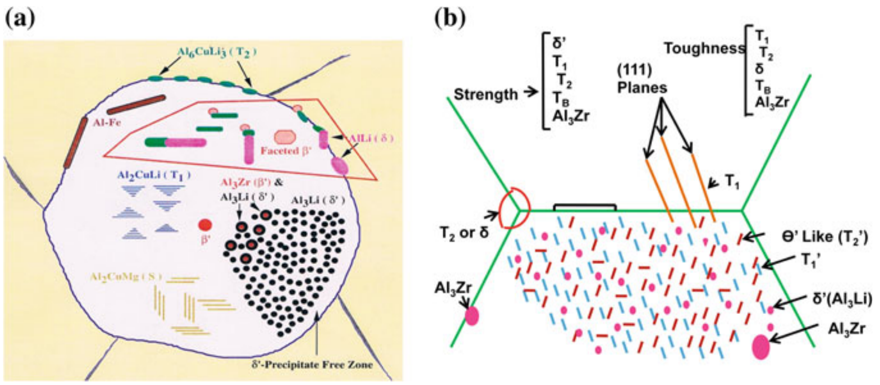

Fig. 3.5 Schematics of typical microstructural features in **a** second and **b** third generation Al–Li alloys [1]

maps [1, 20–26]. The thermomechanical processing consists of well-defined multiple steps [1] since, as mentioned in Sect. 3.3, it is no easy task to optimise the microstructures for a good balance of engineering properties.

3. Al–Li alloy products in near net shapes can be produced by superplastic forming [1, 27–30].
4. Various metal joining techniques can be used, including conventional gas tungsten arc (GTA) welding for the specially developed Weldalite™ family of Al–Li alloys and the third generation low-Li alloy 2195; laser beam welding (LBW), friction stir welding (FSW), and friction welding [1, 31–36].

3.5 Mechanical Properties

The mechanical properties of Al–Li alloys (overall strength, deformation (quasi-static, dynamic and cyclic) and fracture (in corrosive and noncorrosive environments)) are governed by metallurgical variables, including chemical composition; microstructure (strengthening precipitates, precipitate free zones (PFZs)) and grain boundary characteristics; the processing conditions, including thermal (ageing) and thermomechanical (ageing with cold work/stretch) treatments; and finally the shape, size and orientation of the product(s) [1, 37, 38]. Some of the salient features of the mechanical properties of Al–Li alloys are briefly discussed in the following sections.

3.5.1 Tensile Properties

The first generation Al–Li alloys suffered from low ductilities and the second generation from large degrees of anisotropy in yield and ultimate tensile strengths, especially very low yield strengths in the direction 45° from the rolling direction and severe delamination (low ductilities and work hardening exponents) in the through-thickness directions [37–40]. The development of third generation Al–Li alloys with lower lithium contents and novel processing techniques have made it possible for these alloys to possess tensile properties in both in-plane and through-thickness directions that are comparable to or even better than those of the traditionally used aluminium alloys [22].

3.5.2 Fatigue Properties

Low cycle fatigue (LCF)
The low cycle fatigue (LCF) behaviour of Al–Li alloys is primarily influenced by microstructural characteristics and to a lesser extent by crystallographic texture. Microstructural influences are the lithium content; volume fraction, size and distribution of the major strengthening precipitates; the degrees of ageing and recrystallisation; and incorporation of tensile stretching with or without natural ageing. The only available LCF data are for first and second generation alloys, see Table 3.2 and Fig. 3.6. These data indicate that the LCF properties of Al–Li alloys are generally inferior to those of conventional aluminium alloys [46, 47, 51].
High cycle fatigue (HCF)
The HCF resistance of Al–Li alloys is enhanced by solid solution strengthening and coarsening of δ' precipitates. Additional contributions come from thermomechanical treatments involving artificial ageing and tensile pre-straining, or cold work prior to artificial ageing. The available data for all three generations of Al–Li alloys show that their HCF properties are generally equivalent to, but not significantly better than those of conventional alloys. This is notably the case for notched fatigue behaviour, e.g. Fig. 3.7, and is of major importance for aerospace structures [48–51].
Fatigue crack growth (FCG)
Most of the available data for Al–Li FCG have been obtained for second generation alloys. These data showed that the Al–Li FCG rates were often lower than those of equivalent conventional alloys [52]. The main reason for this is 'crack tip shielding', i.e. the development of rough fracture surfaces causing high levels of crack closure in the wakes of the fatigue cracks and concomitant reductions in crack driving force. Unfortunately, this behaviour was associated with unacceptably high anisotropic mechanical properties.

Table 3.2 Some mechanical properties of Al–Li alloys

Alloy		Tensile properties at room temperature			Low cycle fatigue life power—law constants				Fracture toughness	Ref(s).
		0.2 % YS (MPa)	UTS (MPa)	El. (%)	σ_f' (MPa)	ε_f'	−b	−c	K_{Ic} (MPa $m^{1/2}$)	
Al (99.98 %)		–	–	–		0.87		0.62		[41]
Al–0.7 Li		45	65	26		0.42		0.6		[41]
Al–2.5Li	Underaged	67	157	33		$>10^{3}$[a] 2.1[b]		2.38[a] 0.8[b]		[41]
	Peak aged	185	220	2.6		0.032		0.71		[41]
Al–3Li+Mn	Underaged	314	351	2.3		0.059		0.76		[42]
	Peak aged	342	373	1.4		0.146		0.96		[42]
First generation										
2020 plate	Underaged	333–500	–	15–17					27–19	[43]
	Peak aged	530	–	3–6					14	
	Overaged	460–420	–	6–9					16	
2020-T651	TMP (PR)	530	567	5		97[a] 0.038[a]		1.6[a] 0.451[b]		[44]
	TMP (UR)	462	509	12		250[a] 0.058[b]	–	1.56[a] 0.448[b]		

(continued)

Table 3.2 (continued)

Alloy		Tensile properties at room temperature			Low cycle fatigue life power—law constants				Fracture toughness	Ref(s).
		0.2 % YS (MPa)	UTS (MPa)	El. (%)	σ_f' (MPa)	ε_f'	−b	−c	K_{Ic} (MPa $m^{1/2}$)	
Second generation (Li ≥ 2 %)										
2091		300–350								[45]
8090-T81 plate		300–340							25–30 (L-T, T-L); 12–16 (S-L, S-T)	[45]
8090-T8E51 plate (12.5 mm)	L	485	555	5.4	887[a] 575[b]	5.5[a] 0.06[b]	0.093 0.035[b]	1.15[a] 0.46[b]	26–29	[37,46, 47]
	L+45	393	478	11.5	662[a] 501[b]	2.7[a] 0.012[b]	0.67[a] 0.037[b]	1.02[a] 0.56[b]	19	
	LT	467	534	7	832[a] 562[b]	1.77[a] 0.096[b]	0.8[a] 0.042[b]	0.95[a] 0.52[b]	17	
8090 sheet	Underaged T3	350–360								[37]
	Peak aged T6	450–500								
	Damage tolerant T8	360–380								

(continued)

Table 3.2 (continued)

Alloy		Tensile properties at room temperature			Low cycle fatigue life power—law constants				Fracture toughness	Ref(s).
		0.2 % YS (MPa)	UTS (MPa)	El. (%)	σ_f' (MPa)	ε_f'	−b	−c	K_{Ic} (MPa $m^{1/2}$)	
Third generation (Li < 2 %)										
2198 sheet	L	324	442	13						[49]
	L+45	266	363	21						
	LT	300	416	15.4						
2050-T84 plate (51–76 mm)		420–460							28-30 (L-T, T-L) 22-24 (S-L, S-T)	[51, 54]
2060-T8E33 plate (51–76 mm)		450–500							29–30 (L-T, T-L) 24 (S-L)	[22, 54]

[a] Low strain amplitudes (Hypo-transition region)
[b] High strain amplitudes (Hyper-transition region)

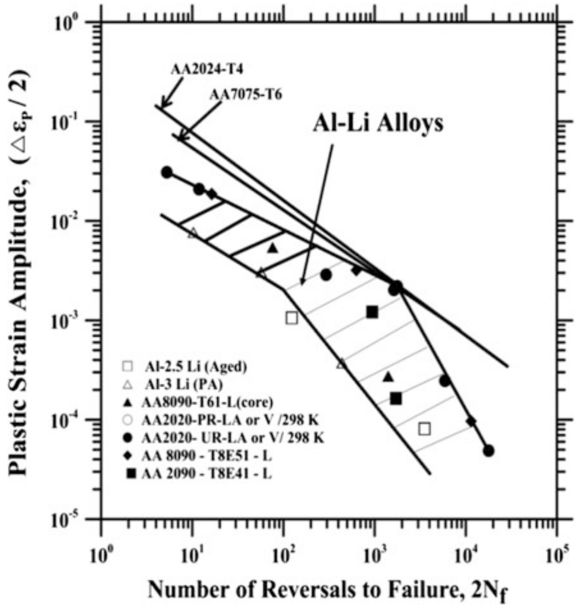

Fig. 3.6 Low cycle fatigue life as a function of plastic strain amplitude (Coffin-Manson Power law) for various Al–Li alloys. These data are compared with those of the conventional alloys AA2024-T4 and AA7075-T6 [46, 47, 51]

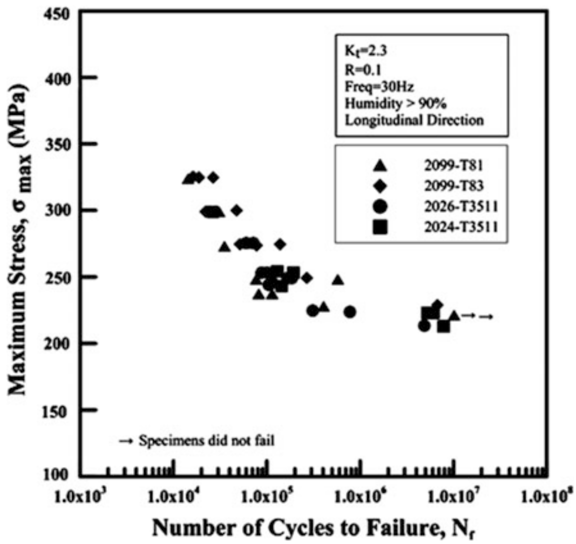

Fig. 3.7 High cycle fatigue life data as a function of maximum applied stress for various third generation Al–Li alloys compared with data for the conventional alloys AA2024-T3511 and AA2026-T3511 [50]

FCG data for third generation Al–Li alloys are becoming more available [52]. The anisotropy problems associated with second generation alloys have been eliminated or greatly alleviated in third generation alloys, resulting in much less rough FCG fracture surfaces. Nevertheless, third generation Al–Li alloys appear to have generally better FCG properties compared to those of the conventional Al alloys they are intended to replace, e.g. Fig. 3.8.

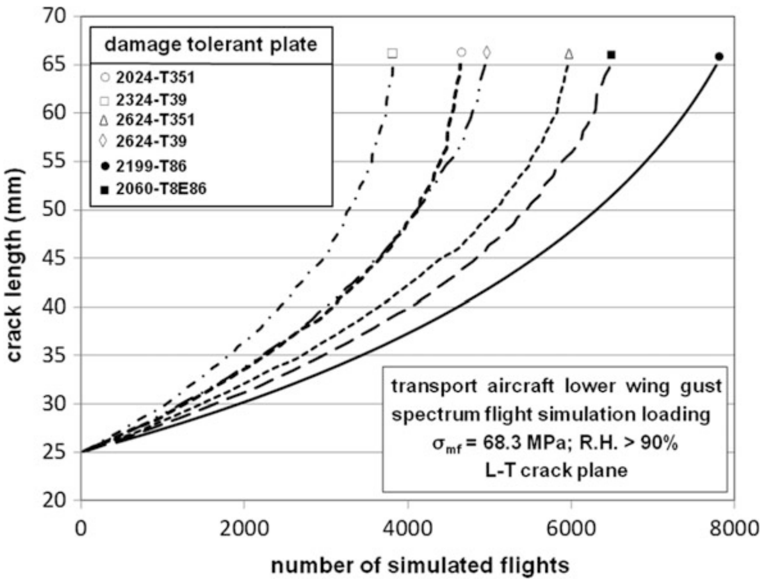

Fig. 3.8 Flight simulation FCG curves comparing the third generation damage tolerant AA2199 and AA2060 Al–Li alloys with equivalent conventional alloys: plate thickness 12 mm [52]

3.5.3 Fracture Toughness and R-curves

Fracture toughness is a critical property when selecting materials for aerospace applications, and has been a major limitation for the first and second generation Al–Li alloys. In particular, the short transverse (S-L and S-T) plane strain fracture toughness were too low, e.g. the values for AA 8090-T81 plate in Table 3.2. This problem has been solved for third generation plate alloys (see the data for AA2050 and AA2060 in Table 3.2).

Plane stress fracture toughness and R-curve data for third generation sheet and plate materials consistently show similar or better properties than those of equivalent conventional alloys at similar strength levels [53]. R-curve examples are given in Fig. 3.9: the third generation alloys AA2060 and AA2199 are superior to the conventional AA2X24 alloys. Also shown is the much inferior performance of the second generation Al–Li alloy AA 8090-T86, which was also in a damage tolerant temper.

3.6 Corrosion and Stress Corrosion Cracking

Corrosion

The first generation Al–Li alloys had adequate corrosion resistance, with no service problems. However, this changed for the second generation alloys, which were

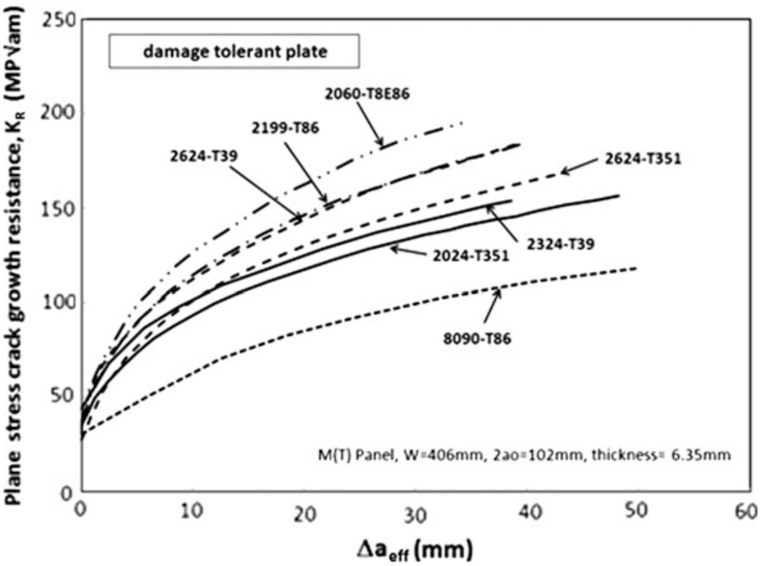

Fig. 3.9 Comparisons of R-curves for third generation AA2060 and AA2199 Al–Li damage tolerant plate alloys, conventional damage tolerant AA2X24 alloys and the second generation AA8090 Al–Li plate alloy [53]

found to be susceptible to intergranular corrosion (IGC), especially at higher Cu and Mg contents and with increased ageing: increasing susceptibility in the order: Underaged (UA) < Peak Aged (PA) < Overaged (OA) [54].

Available data on the third generation Al–Li alloys indicate that their IGC susceptibility can be significantly less than for the second generation alloys, particularly when ageing is done at lower temperatures [54]. The addition of Zn to these third generation Al–Li alloys, see Table 3.1, also improves the corrosion resistance [22]. Currently, it appears that optimum corrosion resistance, notably against exfoliation corrosion, is obtained from an intermediate regime of ageing, including peak aged tempers [54].

Stress corrosion cracking

Stress corrosion cracking (SCC) has also been a problem for the second generation Al–Li alloys, and unlike the IGC susceptibility the SCC resistance decreased with increased ageing: UA > PA > OA [54].

A similar trend has been found for third generation alloys, but these alloys benefit from a lower Li content and additions of Zn and Ag (see Table 3.1) such that in PA tempers they are capable of providing SCC resistances better than those of equivalent conventional Al alloys [54]. There is a caveat here: this conclusion is limited to product thicknesses up to about 30 mm. For thicker products it will likely be more difficult to apply the required thermomechanical processing and multistage ageing practices needed to optimise the grain boundary microstructures and hence the SCC resistances [54].

3.7 Current Indian Scenario

The Indian efforts in development of Al–Li products and components are summarised here

(i) Extensive R&D at the Defence Metallurgical Research Laboratory, Hyderabad, during 1985–2000, establishing (a) Melting and casting technologies at 50 kg capacity, (b) Processing using process maps, (c) Microstructure /texture—processing—property relationships and (d) production of extrusions, forgings and clad sheets—all for the alloy 1440, equivalent to AA 8090. There has also been limited industrial level production of 1440 components for the Indian Light Combat Aircraft, using the large scale melting, casting and processing facilities of VIAM, Moscow.

(ii) Concurrent R&D by IISc. and HAL (Foundry/Forge), Bangalore, with emphasis on optimization of thermal and thermomechanical treatments for improved corrosion and stress corrosion cracking resistances—again on alloys equivalent to AA 8090 and its products.

(iii) Establishing welding technologies for Al–Li products.

(iv) Detailed microstructural analyses, mechanical properties anisotropy, fatigue power law relationships, fracture toughness (including under mixed-mode loading) and fatigue crack growth (including Constant Amplitude, Random and Flight Spectrum Loading).

(v) Most recently, there are initiatives to melt, cast and process third generation Al–Li alloy flat products at MIDHANI, Hyderabad, for the Indian Space Programme.

3.8 Conclusions

The third generation Al–Li alloys are actual and potential candidate materials for replacing the traditionally used Al alloys and competing with carbon fibre composites for applications in aerospace structures. Intense international scientific research, development and commercial production efforts have addressed the most outstanding problems associated with Al–Li alloy deployment in various aerostructural applications. This has meant establishing (i) production technologies for large-scale melting and casting Al–Li alloys with optimised chemistry, (ii) advanced processing based on process modelling, (iii) thermal and thermomechanical treatments to achieve the desired microstructures for optimum property combinations, and (iv) fabrication and joining technologies, including superplastic forming and innovative welding techniques.

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