Challenges in Developing High Performance Al-Li Alloys

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The goal of replacing 'conventional' Al alloys with Al-Li alloys to reduce weight of aerospace structures has had only limited success to date, despite one of the largest alloy-development programs ever undertaken. One of the reasons being, for some product forms and crack-plane orientations, fracture toughness is lower compared with conventional Al alloys due to a greater propensity for low-energy intergranular fracture. Proposed explanations for brittle intergranular fracture include: (i) planar slip resulting in high stresses where slip bands impinge on grain-boundaries, (ii) embrittlement due to alkali-metal-impurity phases, and (iii) grain-boundary structural changes associated with segregation of lithium. The present paper reviews evidence for and against these proposed mechanisms based on (i) studies of 8090 and 2090 alloys, and the more recently developed 2297 alloy, and (ii) comparisons of fracture of these alloys with other materials that exhibit grain-boundary weakness. It appears that lithium segregation to grain boundaries is the prime cause of low-energy intergranular fracture in Al-Li alloys. Embrittlement by alkali-metal impurities is not important providing that impurity levels are less than about 5 ppm (as is the case for most commercially produced alloys). Planar slip and other factors probably play only a minor role.

Key Words: Al-Li alloys, grain boundaries, embrittlement, segregation, slip mode

1 INTRODUCTION

Al-Li alloys have a fairly long and chequered history, with their first significant use in the late 1950's when an Al 4.5Cu-1.1Li-0.5Mn-0.2Cd (wt.%) alloy (2020) was successfully used for the wing skins and tails of the RA-5C Vigilante aircraft [1,2]. In the mid 1960's, a relatively low strength, but much lighter, Al 5Mg-2Li-0.1Zr (wt.%) alloy (1420) was used in Russia for the welded fuel tank and cockpit areas of the MiG 25 and 29 supersonic aircraft [1,2]. In the 1970's and early 80's, extensive Al-Li development programs were carried out with the aim of replacing 'conventional' Al alloys in aircraft structures with Al-Li alloys that had equivalent high strength and other requisite properties, but were 8-10% lighter (and stiffer) due to the presence of about 2.0 wt.% (~8 at.%) lithium. Alloys 8090 (Al 2.3Li-1.2Cu-0.7Mg-0.12Zr) and 2090 (Al 2.8Cu-2Li-0.1Zr) proved to be the most promising, and have been used in a number of 'niche' applications [1-3]. However, they have not seen the anticipated widespread use due to some property shortcomings and, to some extent, their greater cost compared with conventional Al alloys. The continued improvement in the properties of conventional Al alloys in the 1980's and 90's has also contributed to the continued preference for such alloys [1].

Further developments in the late 80's and 90's, aimed at overcoming some of the property deficiencies of earlier alloys, led to alloys such as 2297 (Al 3Cu-1.2Li-0.33Mn-0.1Zr) which has been used for bulkheads and other parts in military aircraft [4-6]. Other

significant developments include the weldable high-strength 2195 alloy (Al 4.0Cu-1.0Li-0.3Ag-0.3Mg-0.14Zr) which has excellent combinations of strength and fracture toughness at ambient and cryogenic temperatures and is now the main structural alloy for the external tank of the space shuttle (Figure 1), and is used for other applications [7]. However, it has not seen significant use in commercial aircraft.

Figure 1 External fuel tank of space shuttle made of 2195 Al-Li alloy.

The main property shortcomings that have prevented more widespread use of Al-Li alloys such as 8090 and 2090 include (i) lower thermal stability, and (ii) more marked anisotropy, than conventional alloys [1,2]. The poor thermal stability is associated with the high lithium content (>8 at.%) of these alloys such that, after ageing to near peak-aged conditions (at high temperatures), further ageing occurs at low temperatures. This additional ageing (which could occur in service) increases strength but decreases toughness below desirable levels. Alloys with lower lithium contents such as 2297 (~5 at.%Li) do not suffer from this problem [4-6].

The greater anisotropy of Al-Li alloys compared with conventional alloys results from a more marked crystallographic texture or, in product forms with elongated grains, a greater tendency for low-energy ('brittle') intergranular fracture. A problem associated with sharp crystallographic textures, besides variations in strength with testing orientation, is the tendency for cracks to deviate from a plane normal to the applied stress to one that is steeply External tank inclined to the stress direction. Such behaviour has been observed in a number of alloys including 8090 [8] and 2297 [9], and is a problem because it makes damage-tolerance assessments difficult.

The susceptibility to brittle intergranular fracture (BIF) leads, in particular, to low short-transverse (S-L, S-T) fracture toughness of plate and extrusions. Delaminations (due to low toughness) during hole drilling and rivet installation have prevented the use of some Al-Li alloys [1]. Alloys with higher lithium contents appear to be more prone to BIF but, as shown in the present work, it still occurs to some extent in lower-lithium alloys such as 2297. A review of the reasons for the propensity of Al-Li alloys to exhibit BIF is therefore in order, and is the focus of the present paper. Further, more-detailed property comparisons between Al-Li and conventional Al alloys, including relative strength, toughness, fatigue, and corrosion behaviour, can be found in refs [8,10,11].

2 PROPOSED MECHANISMS FOR BRITTLE INTERGRANULAR FRACTURE

2.1 Planar Slip

Planar slip impinging on grain boundaries is the most commonly cited cause of BIF of Al-Li alloys [12]. Alloys such as 8090 that are strengthened primarily by coherent δ' (Al₃Li) precipitates are particularly prone to planar slip (Figure 2) since these precipitates are easily sheared by dislocations. There does not, however, appear to be a good correlation between the propen-

Figure 2 TEM of planar slip bands in 8090-T8771 alloy strained 7% at 20°C.

sity for BIF and the degree of slip planarity. For example, BIF in 8090-T8771 plate (aged 32 h at 170°C) can largely be eliminated (and S-L fracture toughness doubled) without a significant change in the observed slip mode by re-ageing for very short times (10 min) at 200°C (Figure 3) [13,14]. Little change in slip mode would be expected as the second ageing step produces little change in microstructure - just a small degree of reversion of smaller δ' precipitates.

For *very underaged* 8090 alloys, there is a remarkably sharp transition from ductile transgranular fracture (DTF) to BIF over about 30-50°C as the temperature is decreased (Figure 4), but no detectable change in slip mode (and little change in strength) occurs over this temperature range. Moreover, slip is fairly homogeneous at low temperatures [13-15]. For the 2297-T87 alloy, strengthening precipitates are primarily T_1 and θ' , which are not as easily sheared by dislocations as δ' , and there are numerous Mn-based dispersoids within grains, which should promote homogeneous slip [4-6]. However, BIF occurs in 2297, especially

Figure 3 Plot of S-L fracture toughness (K_{IC}) for an 8090-T8771 plate (32 h at 170°C) re-aged at 200°C and 230°C showing large increase in K_{IC} after short re-ageing times, (b, c) SEM of fracture surfaces showing predominantly BIF in the T8771 condition and ductile intergranular fracture (DIF) in the toughened condition, and (d) optical micrograph of slip around hardness impressions in the same grain before and after toughening (re-ageing) showing no significant change [13,14].

Figure 4 (a) Diagram showing chevron notched specimen from a 67.5 mm thick plate. (b and c) Plot showing abrupt change from 100% DTF to 100% BIF with decreasing temperature for a very underaged 8090 plate: (b) for two different through-thickness positions corresponding to a strong texture (T/2 - mid thickness) and a weak texture (T/6), and (c) for different ageing times [14-16].

at low temperatures (Figure 5). Thus, planar slip is probably not an important cause of BIF, and other explanations must be sought.

2.2 Grain-Boundary Precipitates and Precipitate-Free Zones

Preferential precipitation at grain boundaries during quenching (especially in thicker plates where cooling rates are slower) and during ageing leads to solute-depleted precipitate-free zones (PFZ) in most Al alloys. Strain localisation in PFZ and around grain-boundary precipitates (GBP) can result in void nucleation and growth, thereby resulting in dimpled intergranular fractures. The depth and spacing of the dimples depends, *inter alia*, on the GBP spacing and PFZ width, and in alloys with fairly well separated GBP and quite wide PFZ, such as 8090-T8771 plate (Figure 6 (a)), well defined dimples would be expected on fracture surfaces. Such 'ductile' intergranular fractures (DIF) are observed in some areas but BIF predominates in the T8771 condition (Figure 3 (b)) [13]. The double-ageing treatment, mentioned in the previous section, which promotes DIF and largely eliminates BIF, does not change the PFZ width or GBP [13,14]. Furthermore, BIF occurs in very underaged 8090, 2090, and 2297 alloys where GBP and PFZ have not developed (Figure 6 (b)) [15], further demonstrating that such factors are not the *primary* cause of BIF. However, GBP and PFZ in near peak-aged alloys undoubtedly contribute to BIF by localising strains at grain boundaries.

2.3 Grain-Boundary Impurities

Segregation of impurity atoms to grain boundaries promotes

Figure 5 SEM showing fracture surfaces for a 2297 alloy plate: (a) peak-aged (T87) condition (VH~152) tested at 20°C showing area of BIF (with numerous GBP on facets) and adjacent area of DTF, and (b) very underaged condition (64 h at 100°C) (VH~75) tested at -196°C showing BIF (with very few GBP on facets) and isolated dimples.

Figure 6 TEM of an 8090 alloy in (a) near peak-aged condition showing PFZ and GBP, and (b) very underaged condition (2 h at 60°C) with no PFZ or GBP at grain boundary (arrowed).

BIF in many materials - the best known example being the temper embrittlement of steels due to monolayer segregation of metalloid impurities (P, S, As, Sb). For Al-Li alloys, analysis of grain-boundary fractures by sensitive techniques such as Auger Electron Spectroscopy (AES) has not shown any evidence of elemental impurity segregation [17]. However, alkali-metal impurity (AMI) phases have been detected at grain boundaries by transmission-electron microscopy [18], and thin Na-K rich films have been observed on intergranular fractures for alloys with high Na-K contents [18, 19]. The mechanism of AMI embrittlement involves transport of AMI atoms to crack tips during crack growth, and adsorption-induced weakening of interatomic bonds at crack tips [19]. Transport occurs by capillary flow when the Na-K phases are liquid (the Na-K eutectic melting point is about -12°C) or by surface diffusion. Transitions from BIF to DIF occur when the supply of embrittling atoms is exhausted, so that 'brittle islands' surrounded by dimples are observed on fracture surfaces (Figure 7).

For Al-Li alloys with less than about 5 ppm (wt.%) Na+K, there is no evidence of significant embrittlement due to impurity phases, presumably because they are not present in sufficient numbers or sizes [19]. For Al-Li alloys with high Na+K contents tested at low temperatures (down to -196°C), there is also no evidence of AMI-phase embrittlement, and none would be expected since the phases would be solid and impurity atoms would be unable to migrate to crack tips at sufficient rates [19]. BIF does, however, still occur in Al-Li alloys with low Na+K contents, and occurs particularly at low temperatures. Thus, another mechanism of embrittlement must be operating in such circumstances.

The presence of high levels of hydrogen has been suggested as a cause of embrittlement [20], but studies of 2090 alloys with high and low hydrogen levels suggest that there is little or no effect, possibly because hydrogen combines with lithium to produce small, innocuous lithiumhydride particles [21]. As mentioned above, there is no evidence of other impurity segregation at grain boundaries which could be responsible for embrittlement. There are, however, close similarities between embrittlement of Al-Li alloys and embrittlement of other materials by segregation, and it appears that segregation of lithium itself may be involved, as discussed in the following section.

2.4 Lithium Segregation

Segregation of lithium at grain boundaries cannot be detected by techniques such as AES commonly used to detect segregation of other (heavier) elements. Attempts to detect lithium segregation

Figure 7 SEM of intergranular fracture at 20°C in near peakaged 8090 alloy containing 10ppm Na impurity, showing brittle islands surrounded by dimpled areas.

by other techniques have been limited, but one study of an 8090 alloy using TEM and parallel electron-energy-loss spectroscopy (PEELS) has shown that lithium segregation develops during ageing, as does the occurrence of BIF [14]. Theoretical calculations and a number of experimental observations also support a lithium segregation embrittlement hypothesis.

Firstly, thermodynamic (pair-bonding) calculations indicate that lithium segregation should produce embrittlement of aluminium [22]. Secondly, the activation energy for embrittlement of very underaged 8090 alloys (tested at -196°C), and for re-embrittlement of near-peak aged 8090 alloys given the re-ageing toughening treatment, is about the same as that for lithium diffusion to grain boundaries [13-16]. Thirdly, the effects of temperature, ageing treatments, texture, and lithium content on BIF can be explained in terms of lithium segregation to grain boundaries.

Effects of Testing Temperature: Sharp ductile to brittle transitions with decreasing temperature, observed for very underaged 8090 alloys (Figure 4), have also been observed in other alloys, such as Cu-Sb (Figure 8 (a)) and Steel-P [23, 24], where it is well established that grain-boundary segregation is involved. In these other systems, the ductile-to-brittle transition temperature (DBTT) increases with increasing impurity content (and grain boundary segregation levels). For 8090 alloys, the DBTT increases with ageing time (at a given temperature) (Figure 4 (b)), consistent with increased lithium segregation at grain boundaries.

The ductile-to-brittle transitions can be explained in terms of 'two-dimensional' (2-D) grain-boundary phase transitions (i.e. changes in atomic structure) below a critical temperature that is dependant on the level of grain-boundary segregation [15, 16]. There are several indications [15, 16, 25, 26] that such grain-boundary phase transitions might occur, e.g. (i) analogous 2-D phase changes on surfaces with adsorbates, (ii) transitions from planar to faceted boundaries and re-arrangements of intrinsic grain-boundary dislocations with changes of temperature, and (iii) molecular-dynamics studies. However, no specific observations related to ductile-to-brittle transitions have been reported, and TEM observations of very underaged 8090 alloys did not reveal any

changes at grain boundaries during *in-situ* cooling through the DBTT [27]. However, this is not surprising as structures at the atomic scale were not resolved, and it is subtle changes in the atomic arrangements which are probably involved in controlling fracture behaviour.

A change in grain-boundary structure and composition could facilitate BIF by (i) decreasing cohesion across grain boundaries so that 'decohesion' occurs in preference to slip, (ii) hindering slip transmission across grain boundaries so that higher stresses are developed across them, and (iii) affecting dislocation emission from intergranular crack tips [22]. Detailed fractographic observations of intergranular facets indicate that BIF occurs by a localised microvoid coalescence process, as for DIF but on a much more localised scale, suggesting that grain-boundary structural changes facilitate dislocation emission from crack tips [16].

Effects of Ageing Treatment: The decreasing propensity for BIF and increase in fracture toughness for 8090-T8771 alloys after very short re-ageing treatments at higher ageing temperatures (Figure 3) is analogous to the behaviour of steels embrittled by phosphorus re-tempered for very short times at higher temperatures (Figure 8 (b)) [28]. These effects are not completely understood, but there is no doubt that segregation is involved for steels and, hence, it is likely that segregation is also involved for Al-Li alloys. For Al-Li alloys and steels, it has been suggested that re-ageing/re-tempering for short times produces transient decreases in the level of grain boundary segregation, with segregants initially diffusing to, for example, grain-boundary precipitates at faster rates than they can be replenished by diffusion from the matrix [13, 14, 28].

Effects of Texture: Studies of 8090-T8771 alloys have shown that BIF occurs to lesser extents when crystallographic textures are stronger (corresponding to a greater proportion of low-angle boundaries), e.g. near the mid-thickness position of plates. The DBTT for very underaged 8090 alloys are also lower when textures are stronger (Figure 4 (a)) [15]. Analogous effects have been observed for tungsten bi-crystals embrittled by oxygen segregation, where the DBTT is lower for lower angle grain boundaries (Figure 8 (c)) [29]. Such effects can be explained on the basis that levels of segregation are lower for low-angle grain boundaries compared with high-angle boundaries, due to the 'more-compact' structures of low angle boundaries.

Effects of Lithium Content: An increasing tendency for BIF and lower fracture toughness for alloys with higher lithium contents (other factors being equal) would be expected if lithium segregation is responsible for facilitating fracture. Comparisons of the behaviour of alloys with different lithium contents is, however, difficult due to differences in the amounts of other elements and, consequently, different microstructures and strengths. Nevertheless, there does appear to be a general trend of decreasing toughness with increasing lithium content. For example, alloy 2297 (1.2 Li) has a higher (minimum) S-L fracture toughness than alloy 8090 (2.2 Li) which, in turn, has a higher S-L toughness than alloy 8091 (2.5 Li). Moreover, for very underaged alloys, where matrix and grain-boundary precipitation have not developed to any extent, more ageing is required to produce BIF in alloys with lower lithium contents. Thus, for tests at -196°C , an Al 2.7 Li 0.1 Zr alloy exhibited BIF in the as-quenched condition, alloy 8090 required ageing for about 2 h at 60°C , and alloy 2297 required ageing for 64 h at 100°C .

Figure 8 (a) Plot showing decrease in fracture energy with decreasing temperature (corresponding to the development of BIF) in Cu-Sb alloys [23], (b) Plot of fracture energy versus re-tempering time at 525°C (following initial tempering at 425°C for 24 h) showing peak after short times for a high-strength steel containing phosphorus [28], and (c) Plot of fracture energy versus temperature for tungsten bicrystals containing oxygen impurities with low- and high-angle grain boundaries [29].

3 IMPLICATIONS FOR ALLOY DEVELOPMENT

If one accepts the view that segregation of lithium to grain boundaries is the main cause of BIF and low fracture toughness in Al-Li alloys, then it is doubtful whether there are any remedial measures besides those that have been tried. Reducing lithium content much below the 1.2 wt.% present in the 2297 alloy would, of course, largely defeat the purpose of Al-Li alloy development. In any case, the S-L fracture toughness of 2297-T87 (18MPa $\sqrt{m}$ minimum) may be sufficient to preclude problems during assembly or in service. For higher lithium-containing alloys such as 8090, re-ageing treatments (Figure 3) could be applied to increase toughness (so that delamination during assembly processes would probably be prevented), and decreasing toughness during service would probably be tolerable. "Grain-boundary engineering", e.g. increasing the proportion of low angle/low Σ boundaries, would be beneficial, but may not be practical. Previous alloy-design efforts that have been aimed at reducing the degree of planar slip in order to increase intergranular fracture toughness have, arguably, been misguided since there appears to be little correlation between slip planarity and BIF.

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