

Regular Article

Auger electron spectroscopy analysis of grain boundary microchemistry in an Al–Cu–Li alloy

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ABSTRACT

In situ impact fracture combined with Auger electron spectroscopy (AES) was employed to determine grain boundary (GB) microchemistry, namely lithium (Li) concentration, for an Al–Cu–Li alloy. The Li/Al ratio of GBs in the naturally aged condition was revealed to be significantly higher than in the overaged condition (or in the bulk alloy). GB fracture surfaces for the naturally aged alloy were depleted in Cu, whereas in the overaged condition the GB fracture surfaces were depleted in Li and enriched in Cu relative to the bulk composition. These findings are discussed in the context of intergranular corrosion and the precipitation sequence in Al–Cu–Li alloys.

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In recent years, Al–Cu–Li alloys have received increasing attention, driven primarily by the need of reducing weight in aircraft without compromising structural performance [1,2]. Due to the low density of Li and its ability to dramatically reduce alloy density, there have been a number of Li-containing Al-alloys studied over the past several decades. However such Al–Li alloys revealed a number of issues that range from poor fracture toughness to poor corrosion resistance [3]. More recently however, the so-called third generation of Li-containing alloys, which actually have more copper (Cu) than Li (by mass) has emerged as possessing advantageous property portfolios that are superior to Al-alloys richer in Li. The AA205X and AA209X series, in particular, exhibit a combination of low density, high stiffness and high strength [1,2,4], in addition to low rates of corrosion.

However, despite the favourable specific mechanical properties and general corrosion resistance, the present generation of Al–Cu–Li alloys remains incompletely characterised, particularly with regard to the origin of their unique intergranular corrosion (IGC) and intergranular stress corrosion cracking (IGSCC) response. Conventional aerospace Al-alloys to date (such as the 7XXX series Al–Zn–Mg alloys) display the maximum resistance to intergranular corrosion in the underaged (*i.e.* grain boundary precipitate deficient) or the overaged condition (*i.e.* following grain boundary precipitate coarsened and increased inter-precipitate separation). As a result, 7XXX series alloys are nominally not deployed in the peak aged condition where IGC/IGSCC is

most rapid. Contrary to the response of 7XXX series alloys, the Al–Cu–Li alloys display the maximum resistance to IGC/IGSCC in the peak-aged condition, with enhanced susceptibility in underaged and overaged conditions [5–9].

The transition from IGC sensitivity in the underaged condition to so-called ‘desensitisation’ in the peak aged condition has been generally attributed to the distribution of the strengthening Al_2CuLi (T_1) precipitates on the alloy surfaces [5,6,8–13]. Using conventional wisdom adopted from what is known regarding Li-free age-hardenable Al-alloys, some hypotheses have been put forth to date. For example in underaged alloys (which can include the solution heat treated, quenched and naturally aged condition), T_1 precipitates may nucleate at grain boundaries, leading to the formation of Cu depleted zones. Such Cu depleted zones may provide a preferential path for dissolution [13–17]. It was proposed that upon further ageing, near the peak aged condition, T_1 precipitates also forming throughout the grains result in lowering the matrix potential, subsequently reducing the selective dissolution of grain boundary precipitates and propagation of cracks [6,9,12,13,16,18,19]. Meletis et al. [7] described the transition from desensitisation back to sensitisation with a similar rationale, which attributed the IGSCC susceptibility in overaged conditions to the formation of large T_1 precipitates at the grain boundaries associated with the development of strain. Connolly et al. [5,20] on the other hand indicated that the T_1 precipitation sequence is not the key factor in resensitisation but that it results more likely from a combination of different microstructural factors, such as precipitate free zones, grain boundary precipitates, planar slip and solute segregation. Undoubtedly however, the intrinsic mechanisms driving resensitisation remain

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inadequately understood. Based on the above introduction, two key factors remain in need of further work to better understand IGC/IGSCC in Al–Cu–Li alloys. These include (i) the detection and rationalisation of the role of Li in the sensitisation/resensitisation behaviour, and (ii) the microchemistry and microstructure at grain boundaries [21–26].

To date, it has been shown that the fracture behaviour of AA2198 and AA2050 was related to solute segregation at grain boundaries, whereby during (over)ageing, Cu controls the growth rate of T_1 [27]. This points towards a need for determination of Cu and Li concentrations in the vicinity of, and including, grain boundaries. Direct microanalysis of Li segregation is however challenging. Therefore, to accurately quantify grain boundary segregation, the use of unique methods is required, each with their own limitations. Known techniques capable of detecting Li include: electron energy loss spectroscopy (EELS) [28,29], secondary ion mass spectrometry (SIMS) [30], *in situ* Auger electron spectroscopy (AES) [31,32] or atom probe tomography [29,33].

In this study, conventional transmission electron microscopy (TEM) for structural characterisation was coupled with *in situ* Auger electron spectroscopy (AES) to investigate the grain boundary microchemistry and microstructure of AA2050. The latter method was unique on the basis that grain boundaries could be analysed following *in-situ* fracture at cryogenic temperatures. The chemical composition of the studied AA2050 as determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) was Al–1.40 Cu–3.00 Li–0.19 Mn–0.36 Mg–0.04 Ag–0.10 Si–0.02 Zr–0.03 Fe–0.02 Ti–0.008 Zn (in at. %). Two different alloy conditions were studied, namely the naturally aged (T351) condition and the overaged (600 h at 155 °C) condition, in an attempt to characterise the compositional changes at the grain boundaries, and subsequently to contribute towards the mechanisms governing sensitisation. It is understood that the work herein represents a finite contribution to a complex system, and indeed the methodologies required for quantification of Li concentration need to be considered in light of experimental limitations, but nonetheless the present work addresses a unique and timely knowledge gap.

Fig. 1 reveals the general microstructure of the specimens tested, via both scanning and transmission electron microscopy. SEM was carried out using a Jeol 7001F, while TEM was carried out using an FEI Tecnai G2 F20 S-TWIN FEG and X-Flash X-ray detector (Bruker). Thin foils for transmission electron microscopy (TEM) were prepared from 3 mm

discs using twin jet electropolishing (TenuPol-5, Struers) at 12.7 V in a solution of 33% nitric acid–67% methanol maintained at –20 °C.

On the micrometre length scale, the backscattered SEM images (Fig. 1a, c) reveal a typical population of coarse constituent particles (X-ray analysis indicating such particles being rich in Cu, Fe and Mn) that do not contribute to strength or IGC, and are present in the naturally aged alloy and remain unaltered during over ageing. On the nanoscale, Fig. 1b reveals an essentially homogeneous feature free microstructure for the T351 condition, where the grain boundary does not appear to have any structural variations (indicative of precipitates) at the conventional length scale. Within grains, there is an absence of discernible lattice reflections for T_1 precipitates using selected area diffraction (SAD) patterns (inset Fig. 1b). However, after 600 h ageing at 155 °C, the overaged AA2050 presents strong characteristic reflections of T_1 in the $[110]_{Al}$ direction (inset Fig. 1d), with T_1 precipitates visibly evident. Fig. 1d also reveals that T_1 is homogeneously distributed in the matrix. However, because grain boundary precipitates (GBPs) do not have a strict orientation relationship with the matrix in projected images, elemental mapping using scanning-TEM was carried out, revealing a strong presence of Cu (and Mg) at the grain boundaries, associated with GBPs. The precise composition of such grain boundary precipitates is not unambiguous from the literature, with reports indicating that GBPs in Al–Cu–Li alloys being coarsened T_1 , whilst also there exists the possibility of being Cu-rich GBPs, including θ' - (Al_2Cu) and S' -phase (Al_2CuMg), which may form due to local solute saturation and local GB composition – although not necessarily predicted as equilibrium phases from the bulk alloy composition [34,35].

In order to analyse the GB composition uniquely, an *in-situ* impact fracture was realised within a PHI 660 scanning Auger microprobe (Physical Electronics). To achieve this, the samples were cooled down to liquid nitrogen temperature and then impact fractured with an in-chamber hammer and a fracture arm. For such experiments, specimens were prepared to conform to the PHI model 192 fracture specimen holder, which required carefully prepared samples of 15 mm length and 3.14 mm diameter. A 0.7 mm notch was machined 10 mm from the end of the specimen, to facilitate fast fracture. The fracture surfaces are shown in Fig. 2. It is noted that specimens were successfully fractured (Fig. 2a, c), and the fracture surfaces present what is predominately brittle fracture. To this end, a small proportion of the surface revealed some ductility in the fracture surface; however the subsequent AES

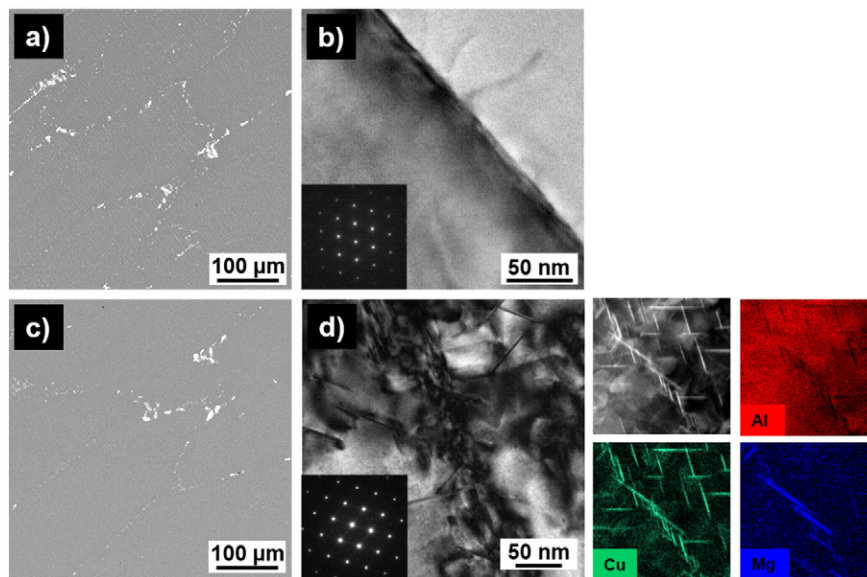


Fig. 1. a) BSE-SEM image of AA2050 in the naturally aged (T351) condition, b) BF-TEM image of AA2050 in the T351 condition (inset: corresponding selected area diffraction pattern along $[110]_{Al}$ zone axis), c) BSE-SEM image of AA2050 aged for 600 h at 155 °C (overaged), and d) BF-TEM image of AA2050 aged for 600 h at 155 °C presented with DF-TEM image and elemental mapping for Al, Cu and Mg collected in STEM mode (inset: corresponding selected area diffraction pattern along $[110]_{Al}$ zone axis showing presence on intragranular T_1 phase).

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