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On the corrosion, electrochemistry and microstructure of Al-Cu-Li alloy AA2050 as a function of ageing

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ABSTRACT

The corrosion and microstructure of the Al-Cu-Li alloy AA2050 were investigated as a function of artificial ageing. The work herein seeks to provide a consolidated overview of the corrosion of AA2050, in particular the influence of T_1 (Al_2CuLi) precipitates on the observed behaviour. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were performed to characterise the microstructural evolution of AA2050 during ageing. Accelerated immersion testing revealed that ageing was accompanied by the evolution of three unique stages of resultant corrosion morphologies – which were not correlated with the fine T_1 precipitate evolution. Electrochemical testing also revealed that AA2050 showed no discernible metastable pitting from potentiostatic testing. This phenomenon suggests that T_1 precipitates may remain too fine to induce localised corrosion in the matrix, and that T_1 precipitates in AA2050 are unlikely the controlling factor leading to the evolution of corrosion morphologies observed in AA2050. An elaboration of factors influencing the intergranular corrosion evolution and the role of grain boundary chemistry is also presented.

1. Introduction

Metallic materials with a high strength to weight ratio remain desirable in aerospace applications. As such, the pursuit of aluminium (Al) alloys which contain lithium (Li) has remained topical on the basis that Li additions can significantly reduce alloy density, whilst increasing Young's modulus [1]. There has been a well-documented evolution of Li-containing Al-alloys from compositions that are rich in Li (8xxx series alloys) [2], to contemporary compositions that contain more copper (Cu) than Li by mass, which are 2xxx series Al-alloys. After several decades of Li-containing Al-alloy development, a group of Al-Cu-Li(-Mg-Ag) alloys have emerged with mechanical properties superior to what were incumbent aerospace alloys. Such alloys are often termed third-generation Al-Li alloys, and they derive their mechanical properties from age-hardening, which stimulates the precipitation of hardening phases such as T_1 (Al_2CuLi) [3,4]. By tuning the alloy composition such as a Li:Cu ratio and appropriate heat treatment conditions, it is possible to obtain desired precipitate densities, and a good combination of damage tolerance, stiffness, density and strength [5]. Unlike the relatively well-studied mechanical properties of Al-Cu-Li alloys, there is comparatively little information in the open literature regarding the corrosion behaviour of third-generation Al-Cu-Li alloys, particularly in regard to the evolution of intergranular corrosion (IGC) and *intra*granular corrosion as a function of artificial ageing.

It is common to observe a transition in the principal corrosion mode in response to thermal treatment for high strength Al-alloys, or Al-alloys that form precipitates more generally. A so-called "sensitisation" window corresponds to ageing (or thermal exposure) conditions, where the major corrosion mode evolves from pitting to intergranular corrosion (IGC) [2,6–12]. The IGC susceptible condition is usually ascribed to the formation of so-called anodic grain boundary precipitates (GBPs) in systems such as 5xxx (Al-Mg) and some 7xxx (Al-Zn-Mg) series Al-alloys [13–15]. Conversely, in other Al-alloy systems, it is the development of so-called cathodic (noble) GBPs that result in solute-depleted (and subsequently anodic) precipitate free zones (PFZs), causing dissolution and IGC in the region immediately adjacent to the grain boundary [16]. In some cases, the compositional complexity of certain 6xxx and 7xxx series Al-alloys (that contain appreciable concentrations of Cu) results in IGC caused by either anodic GBPs or anodic PFZs, dependent on specific grain boundary chemistry and microstructure [15,17–19]. More specifically, in Al-Cu and Al-Li alloys, sensitisation phenomena are usually attributed to the formation of noble θ (Al_2Cu) and active δ (Al_3Li) precipitates at grain boundaries [20,21]. However, in contemporary Al-Cu-Li alloys, the precipitate entity and evolution is dependent on the addition of minor alloying elements, thermomechanical history and the Li:Cu ratio [22,23]. For high strength third generation Al-Cu-Li alloys such as AA2050, AA2090 and AA2099, T_1 phase (Al_2CuLi) is the major strengthening phase and widely distributed throughout the alloy.

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Herein, we study the alloy AA2050, where it has been noted that two distinct stages of corrosion morphology are observed accompanying the precipitation of T_1 phase [24–26]. Specifically, the alloy experiences a high susceptibility to IGC in the under-aged condition; whilst AA2050 becomes prone to *intra*granular attack after ageing to the peak-aged condition. In addition, the research performed by Henon and Rouault [27] indicated an additional sensitisation window for AA2050, whereby the alloy once again reveals susceptibility to IGC upon prolonged ageing to the over-aged condition (termed the "re-sensitised" state). Given that T_1 phase contains Li, several authors have attributed the IGC susceptibility observed in Al-Cu-Li alloys to the anodic dissolution of grain boundary T_1 precipitates [28–34]. The electrochemical potential of T_1 phase was determined by Buchheit et al. [35] and also reported by Padgett [36] and Li et al. [37]; using bulk produced T_1 analogues. The results reveal that T_1 is less noble than the potential of any alloy it may occupy, and then may be susceptible to anodic dissolution when in the Al-matrix. However, the dissolution kinetics of T_1 phase were shown by Padgett [36] via the electrochemical microcell to be sluggish compared to the typical dissolution rates of so-called anodic precipitates [38–40]. In a study by Li et al. [37], it was suggested that the corrosion of AA2195 Al-Cu-Li was a result of T_1 dissolution, however, there is a paucity of associated work to validate this assertion. Whilst the literature to date has focused on ascribing localised corrosion in Al-Cu-Li alloys to T_1 phase – it is neither possible nor rational to explain all three stages of "sensitisation" phenomena in Al-Cu-Li on T_1 precipitates. In a recent study, Luo et al. [41] suggested T_1 may also act as a cathode after some critical dissolution whereby Li has been selectively dissolved. This notion would be akin to the dynamic evolution of the electrochemical properties of S phase (Al_2CuMg) which is associated with selective dissolution of Mg leaving behind a Cu rich precipitate (i.e. nanoscale dealloying), as first reported by Buchheit et al. [42,43]; however, a focused study on apparent dealloying of T_1 does not exist. In some studies, T_1 precipitates were claimed to cause IGC solely due to their presence [28]; however, In the specific case of AA2050, Proton et al. [25] reported the heat-treatment with high density of grain boundary T_1 can still possess high IGC resistance. Such recent research contributes towards the notion that the IGC of Al-Cu-Li alloys is unique, and that its understanding does not rely on the same classical concepts reported in the literature for other series of Al-alloys [2,11]–which are principally based on first order GBP and PFZ dissolution models.

To date, only limited works have been conducted upon AA2050 in the over-aged condition and a phenomenological mechanism for the 3-stage evolution of corrosion behaviour (i.e. sensitised-desensitised-sensitised) in such an alloy remains unclear. Adopting previous research of stress corrosion cracking (SCC) and IGC in Al-Cu-Li alloys, the 3-stage evolution of corrosion behaviour in T_1-strengthened Al-Cu-Li alloys may be controlled by multiple mechanisms which still need to be studied [44–46]. The "sensitisation" to IGC upon over ageing is not desirable from an engineering point of view for applications of warm service, as it may lead to time dependant evolution of properties [3]. It is however noted, that the specimens nominally studied by researchers (including herein) are over-aged at elevated temperatures (i.e. > 150 °C) – whilst the sensitization behaviour of specimens at operating temperatures (which nominally may be up to 85 °C for aircraft) have not been reported to date. It is, however, critical to understand the mechanisms that control the IGC susceptibility in AA2050 in response to over ageing; as AA2050 is a candidature to replace 7xxx series alloys on aircraft where periodic service temperature alternations may be expected.

In the present work, we studied the microstructure-corrosion relationships in AA2050. By controlled ageing at 155 °C and 200 °C, different T_1 morphologies were developed and the related corrosion behaviours determined. In addition, an over-aged sample was aged up to 600 h at 155 °C, which serves as a unique specimen, as most prior studies have reported ageing times of less than 250 h at similar temperatures [23–26,47–50]. The precipitate microstructure was characterised by transmission electron microscopy (TEM), whilst in parallel, corrosion morphologies were obtained following immersion corrosion testing and assessment by optical microscopy. The electrochemical behaviour of specimens was assessed by potentiodynamic and potentiostatic polarisation tests.

2. Experimental procedures

2.1. Materials

All testing was carried out on AA2050 supplied in the form of 50 mm thick rolled plate. The composition of AA2050 as determined by inductively coupled plasma - atomic emission spectroscopy (ICP-AES) is shown in Table 1.

The initial alloy condition was the T351 temper, in what is commonly referred to as the naturally-aged (NA) condition; which implies a history of solution treatment, quenching, plastic deformation and room temperature (natural) ageing. To study the evolution of corrosion behaviour and precipitate microstructure, small cuboids with a size of $1 \times 0.6 \times 1.5\ cm^3$ were cut from the centreline of the thick plate. All specimen exposures and surfaces studied correspond to being taken from in-plane of the centreline of the plate (often termed the T/2 or mid-thickness plane). Specimens were artificially aged in an oil bath with no heating ramp at 155 °C for 1, 5, 15, 72, 312, 432 and 600 h, or at 200 °C for 1, 5 and 15 h. Samples aged at 155 °C for 1 and 5 h are referred to as UA (under-aged) samples, while samples aged over 15 h are referred to as OA (over-aged) samples. The samples aged at 155 °C for 15 h are referred to as PA (peak-aged).

The Vickers hardness of samples were measured using a Struers® Duramin A-300 Hardness tester with the load of 1 kg.

2.2. Microstructural characterisation

The distribution and morphology of constituent particles and dispersoids were characterised using a JEOL® 7001F scanning electron microscope (SEM) coupled with energy-dispersive X-ray spectroscopy (EDXS). Specimens for SEM were ground using silicon carbide (SiC) paper to a 4000-grit finish, cleaned in ethanol, and polished using non-aqueous diamond suspensions of 3 μm, 1 μm and 0.25 μm. Final polishing was done by using 0.05 μm colloidal silica.

Precipitate microstructure was characterised by transmission electron microscopy (TEM) using an FEI® Tecnai T20. Bright field (BF) images were taken to measure the average length and width of T_1 precipitates. Imaging was carried out in the $<110>_\alpha$ direction to obtain edge-on conditions for T_1 precipitates. Selected area diffraction (SAD) was also performed. In cases where EDXS was carried out, an FEI® Tecnai F20 was used in the high angle annular dark filed (HAADF)-Scanning TEM mode. Specimens for TEM analysis were prepared by slicing 400 μm thin discs from the plate centreline (TD-RD surface). Thin discs were first hand ground to a thickness of ~100 μm, then thinned by electropolishing using a Struers® Tenupol 5 twin-jet polishing system. Electropolishing employed an electrolyte of 33% nitric acid–67% methanol at −25 °C and an applied voltage of 12.7 V.

2.3. Electrochemical testing

Two unique electrochemical tests were performed in this work, which included potentiodynamic polarisation and potentiostatic polarisation, the latter conducted to ascertain current transients for the purposes of metastable pit analysis. Testing was carried out in all cases using a Princeton Applied Research 3-electrode flat cell with a Pt mesh counter electrode and saturated calomel electrode (SCE) reference electrode. A Bio-logic® VMP3 potentiostat was used. Alloy samples of AA2050 were cold mounted in epoxy to expose 1 mm^2 of the TD-RD T/2 surface. The electrolyte for all electrochemical tests was argon (Ar) deaerated 0.1 M NaCl, with the electrolyte deaerated for ~45 min before use. Test specimens were introduced to deaerated electrolyte for the measurement of