



Localized dissolution initiated at single and clustered intermetallic particles during immersion of Al–Cu–Mg alloy in sodium chloride solution



Chen LUO¹, Xiaorong ZHOU², George E. THOMPSON²

1. Aviation Key Laboratory of Science and Technology on Advanced Corrosion and Protection for Aviation Materials, AVIC Beijing Institute of Aeronautical Materials, Beijing 100095, China;
2. School of Materials, The University of Manchester, Manchester M13 9PL, UK

Received 16 August 2015; accepted 18 September 2016

Abstract: Aiming at understanding how intermetallic phases response when AA2024-T3 aluminium alloy is exposed to chloride-containing aqueous medium, scanning electron microscopy was employed to provide morphological information on alloy surface before and after corrosion testing. Energy dispersive X-ray spectroscopy was carried out to determine compositional change in intermetallic particles. Atomic force microscopy was used to examine topographical variation introduced by the reactions of intermetallic phases. Transmission electron microscopy combined with ultramicrotomy was carried out on dealloyed Al₂CuMg particles and their periphery region. It is found that dealloyed Al₂CuMg particles exhibited porous, polycrystalline structure comprised of body-centred cubic copper particles with sizes of 5 to 20 nm. Aluminium matrix started to trench in the periphery of Al₂CuMg particles at the early stage of dealloying. Development of trenching in Al–Cu–Fe–Mn–(Si) particle's periphery was not uniform and took longer time to initiate than Al₂CuMg dealloying. Localized corrosion at a cluster of Al₂CuMg and Al₂Cu particles was mainly associated with Al₂CuMg particles.

Key words: aluminium alloy; intermetallic particle; localized dissolution; dealloying; trenching

1 Introduction

High-strength aluminium alloys such as AA2024-T3 have been widely used for aerospace applications because of their light mass, high strength and damage tolerance [1,2]. Good mechanical properties of these alloys are obtained mainly through nano-sized hardening precipitates, and to a less extent submicron sized dispersoids and coarse intermetallic particles, formed by alloying additions [3,4]. Research has shown that their great corrosion susceptibility is due to the heterogeneous distribution of copper in the alloys, specifically, in the form of copper-rich intermetallic particles [5–7]. Local microgalvanic coupling is established between the inhomogeneities and aluminium matrix and essentially causes localized attack [8–13].

Coarse intermetallic particles interdendritically solidify as lacy networks surrounding the cast grains by the eutectic decomposition. Subsequent ingot

homogenization dissolves soluble constituents [14–16]. The remaining particles fracture and become aligned in the direction of metal flow during fabrication of the cast ingots [17]. Copper and other elements, such as iron, manganese and silicon, form intermetallic phases, most of which are cathodic with respect to aluminium. The formation of trenching next to cathodic intermetallic particles in AA2024-T3 aluminium alloy has been well documented [10–13]. LEBLANC and FRANKEL [10] investigated the electrochemical interactions between intermetallic particles and aluminium matrix. The alloy surface was covered by ink before corrosion testing and then scratched using a tip on atomic force microscopy (AFM) cantilever during immersion. No attack was seen in a small exposed area that contained only aluminium matrix or only α -phase (Al–Cu–Fe–Mn–(Si)) particle. Matrix dissolution took place in an area containing a large area fraction of Al–Cu–Fe–Mn particles. Further, Al–Cu–Fe–Mn particles promote oxygen reduction and OH[−] generation which consequently results in the

Foundation item: Project (51201157) supported by the National Natural Science Foundation of China; Project (H052013A003) supported by the National Defense Technology Foundation, China; Project supported by the UK-ESPRC LATEST2 Program

Corresponding author: Chen LUO; Tel: +86-13611077600; E-mail: chen.luo.23@qq.com

DOI: 10.1016/S1003-6326(16)64408-4

alkalization of local environment. The electrochemical response of intermetallic phase is heavily dependent on pH. According to BIRBILIS and BUCHHEIT [11], cathodic efficiency of Fe-rich intermetallic phase increased as the pH increased. Thus, it can be predicted that Al–Cu–Fe–Mn particles become more cathodic after corrosion has taken place around them. BUCHLER et al [12] monitored the initiation of those localized corrosion sites that are related to cathodic intermetallic particles using fluorescence microscopy. It was found that oxygen reduction on the cathodic phases mainly supports active dissolution of nearby anodic intermetallic particles (e.g., *S*-phase (Al₂CuMg) particles). However, the reduction reaction also causes certain anodic dissolution in the adjacent matrix of cathodic phases as a side effect. The net current at the cathodic sites (the particle region and its trenched periphery) is cathodic.

The propensity to promote trenching in matrix is not the same for Al–Cu particles and Al–Cu–Fe–Mn particles although they are both cathodic to aluminium matrix [13]. Al–Cu particles are more susceptible to trenching than Al–Cu–Fe–Mn particles, especially in solutions of low chloride content [18]. OSORIO et al [19–21] reported the surface corrosion behavior of hypoeutectic Al–Cu cast alloys which are constituted by Al–Cu–Fe–Mn and θ -phase (Al₂Cu) particles. Reduction rate is about 4.5 times higher for the θ -phase region which exhibits a cathodic behavior with respect to the Al–Cu–Fe–Mn region. The alloy damage is achieved by θ -phase induced corrosion. A higher susceptibility to corrosion in NaCl solution is detected as the θ -phase fraction increases.

S-phase particle actively undergoes severe magnesium dealloying, which leads to the formation of high potential copper-rich remnant. Some of the remnant particles remained largely intact and others decomposed into clusters of 10–100 nm copper particles. Then, the clusters became detached from the alloy surface and were dispersed by mechanical action of growing corrosion product or solution movement. This observation suggests that nonfaradaic liberation of copper from corroding alloy surface is possible [22]. Copper enrichment of Al₂Cu and Al–Cu–Fe–Mn such as Al₇Cu₂Fe has also been highlighted by some authors [23,24]. When exposed to NaCl solution, these particles transform into a nanometric sponge of pure copper due to a selective dissolution, covered with amorphous aluminium hydroxide. The dealloying mechanism for various intermetallic phases depends both on copper content in the phase and crystallographic structure. Generally, aluminium dissolution is activated in the presence of magnesium and inhibited in the presence of iron.

ZHU and OOIJ [25] reported that *S*-phase particles

were dealloyed of both magnesium and aluminium and the phenomenon was the most severe during the first 3.5 h of immersion in a neutral 0.6 mol/L NaCl solution, whereas the very interesting work of BOAG et al [26] demonstrated that the dealloying process was quickly completed within 5 min. Thus, even the same kind of intermetallic particles can be completely different in terms of kinetics. LACROIX et al [27,28] have performed statistical studies on the corrosion behavior of *S*-phase particles which show huge differences in their corrosion activity. When a particle dissolves it enriches with copper, which causes the increase in potential. In the case of non-corroded *S*-phase particles, almost no potential difference with the matrix was observed, suggesting the initial presence of a thick aluminium-rich oxide layer on the whole alloy. Most likely differences in the thickness of the aluminium-rich oxide layer will determine the corrosion performance. Difference in the electrochemical activity of the θ -phase particles was also detected and it was verified that these differences in activity determined the propagation of filiform corrosion underneath coatings [29].

S-phase particles play an important role in the corrosion of AA2024-T3 aluminium alloy [10,22,25, 26,30]. According to BLANC et al [30], the electrochemical behaviour of the alloy is similar to that of *S*-phase in the anodic range during electrochemical polarization in the presence of chloride ions. LEBLANC and FRANKEL [10] found that pitting of AA2024-T3 aluminium alloy originated at *S*-phase particles during corrosion testing in NaCl solutions under open-circuit condition. *S*-phase particles corroded even in the absence of local cathodic intermetallic particles such as Al–Cu–Fe–Mn particles.

BOAG et al [26] reported the end result of the dealloying process that trenching is developed around the copper-rich remnant of *S*-phase particles, indicating that these sites act as active cathodes. In fact, at a more advanced stage of degradation, *S*-phase particles were completely enveloped by a dark layer of reacted matrix adjacent to them [31]. However, attack around the isolated *S*-phase particles remains localized without spreading deeply into the matrix [26].

The aim of the current study is to advance the understanding of localized dissolution phenomenon related to intermetallic particles, including dealloying of *S*-phase particles and trenching in the periphery of *S*-phase particles and Al–Cu–Fe–Mn–(Si) particles. Corrosion behaviours of clustered *S*-phase and θ -phase particles were also investigated using a combination of electron microscopy and ultramicrotomy. Experimental proof of microgalvanic coupling on metallurgical scale and the relationship between the metallurgy and the electrochemical properties were characterized in order to

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