Spreading of intergranular corrosion on the surface of sensitized Al-4.4Mg alloys: A general finding

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ABSTRACT

Intergranular corrosion (IGC) of sensitized AA5083 was investigated in 0.6 M NaCl solution. Corrosion of a finite fraction of the anodically active β-phase (Al_3Mg_2) precipitates triggers the spreading of IGC to other precipitates, resulting in formation of large clusters of corroded grain boundaries. Such IGC spreading is observed only for highly sensitized AA5083 at potentials above a critical spreading potential. The total length of corroded β-phase clusters is less than the total length of β-phase available. The breakdown potential in short-term upward potential scans, often attributed to the isolated attack of less noble phases [1–4], is linked to IGC spreading.

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1. Introduction

AA5000 series alloys (Al–Mg alloys) are attractive due to their light weight, high strength, and corrosion resistance. Magnesium (Mg) is added to these alloys to achieve high strength via solid solution strengthening [5]. However, Mg segregates to the grain boundaries after exposure to elevated temperatures (50–200 °C) in Al–Mg alloys with high concentrations of Mg [6,7]. Consequently, the electrochemically active β-phase (Al_3Mg_2) precipitates form at grain boundaries from a supersaturated Al–Mg solid solution [6] rendering these grain boundaries susceptible to intergranular corrosion (IGC).

The continuity of the β-phase precipitates along the grain boundaries is an important factor influencing the IGC susceptibility of sensitized alloys. The β-phase distribution and morphology are dictated by sensitization conditions such as temperature and time of exposure to heat [7–10]. Studies of sensitized AA5083 [Al-4.4 Mg-0.7Mn-0.22Fe-0.1Si; wt.%] alloys indicate that discrete β-phase precipitates form along the grain boundaries and near Al_6Mn intermetallics after short exposure times. The β-phase precipitates formed along the grain boundaries coarsen and are more closely spaced after longer exposure times [7,9–11]. The size of the β-phase precipitates ranges from 50 to 190 nm in width and 100–1000 nm in length. Sensitized AA5XXX with very high NAMLT (nitric acid mass loss test) mass losses per unit area [12], often contain 50% or more grain boundaries that are nearly continuously

covered with β-phase precipitates. In contrast, sensitization levels with very low NAMLT values contain few β-phase precipitates [8]. Metallurgical factors such as grain boundary type and their misorientation also influence β-phase precipitation. Low angle boundaries (<20°) do not develop β-phase precipitates, while high angle boundaries may contain varying proportions of discontinuous β-phase precipitates after sensitization [8].

The earliest developed electrochemical frameworks for IGC of precipitation hardened aluminum alloys hypothesized that the difference in the breakdown potentials of the β-phase-rich grain boundaries and the matrix determines the IGC susceptibility of these alloys. The breakdown potential[1] of the β-phase in 0.6 M NaCl solution is at least 200 mV lower than the open circuit potential (OCP) of sensitized AA5XXX alloys [7,9,13]. Applied potentials in the range between these two breakdown potentials trigger IGC via attack of β-phase precipitates at the grain boundaries.

The same type of electrochemical framework has been proposed for heat treated Al-4% Cu [1,3], Al–Cu–Mg [4,14], AA7075 [2], Al–Zn–Mg alloys [2,15], Al–Cu–Li [16–19], Al–Mg [7,20], Al–Cu–Mg–Ag [14], and Al–Si–Mg [10,21] alloys. These alloys contain either anodically active phases or solute depleted zones along grain boundaries after aging that are argued to have lower breakdown potentials than the intragranular material. The difference in the breakdown potentials was crucial in determining the IGC susceptibility of these alloys [2]. An alloy was regarded to be very susceptible to IGC if a large difference existed. IGC was especially

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[1] Breakdown potential is the potential associated with abrupt increase in current above the passive current density with a small change in potential.

possible when the OCP was in the range between the two breakdown potentials such that the matrix remained passive while the boundaries corroded. If the difference in potential was small, such as the condition of uniform Cu depletion from the Al solid solution after long heat treatment, no IGC was observed at OCP [3,14].

In the case of Al–Mg alloys, the low breakdown potential of the β-phase relative to the Al–Mg solid solution is preserved in a variety of electrolytes. The breakdown potentials observed for sensitized Al–Mg alloys lie between that of the β-phase and the Al–Mg solid solution of the matrix [13]. Moreover, this potential decreases with aging and increasing β-phase precipitation in 5XXX alloys. While the pre-existing electrochemical framework involving β-phases suggests why the aged samples might have lower breakdown potentials, existing theories are not sufficient to explain the meaning of intermediate breakdown potentials that are much higher than the breakdown potentials of the isolated β-phase. Also, another point of confusion is that the potential that triggers IGC is not as low as the breakdown potential of synthesized β-phase. One explanation is that the critical breakdown potential is a function of β-phase size and orientation with respect to the surface, as observed for stainless steels pitting at MnS inclusions [22]. The increase in sizes of MnS inclusions above a certain threshold leads to a decrease in the breakdown potentials [22]. However, this explanation suggested that dominant pits were formed at the largest and/or deepest inclusions [23]. This behavior is not seen in the case of Al–Mg alloys. Another theory is that the attack of a deformed surface layer, produces a susceptible microstructural zone in AA7075 alloys that pits at intermediate potentials [24–26].

An alternative explanation developed in this paper is that the critical breakdown potential is associated not with formation and stabilization of pits at individual β-phase precipitates but instead with the spreading of corrosion to proximate β-phase precipitates across the surface triggered by pH drop and Cl⁻ ion accumulation at initially corroding sites [27–29]. Such a spreading potential would be intermediate even though β-phase precipitates would be likely sites for this type of spreading attack.

A cooperative interaction model has shown that random pits at a MnS inclusions in stainless steels could promote the nucleation of many more new pits within an interaction radius of 100 μm from the initial pit sites [30,31]. Subsequent pit nucleation around the preexisting pits led to an explosion of the pitting events and spreading of corrosion across the surface [28,29,31,32]. The nearest neighbor distances between inclusions/defects affected the critical potentials associated with such spreading. Lower potential thresholds were seen for high inclusion density or small nearest neighbor distances. Clustering of pits occurred if the surface potential was greater than the critical spreading potential. Random pitting was observed at lower potentials. The cooperative interaction model was also used to explain the surface spreading of IGC on the surface of stainless steels albeit with different electrochemical details [28,33]. In that case, chromium depletion at the grain boundaries was responsible for spreading. Localized changes in potential and concentration occurring due to the corrosion of some highly prone grain boundaries triggered the corrosion of other chromium depleted boundaries and resulted in formation of a well-connected path of corroded grain boundaries if the mean proportion of the chromium depleted grain boundaries was above a certain threshold.

The objective of this work is to develop an electrochemical framework to predict the important parameters governing the IGC surface spreading on sensitized AA5083-H131 alloys. We hypothesize that, similar to previous examples [28,32], the localized pitting of β-phase along the grain boundaries can induce pitting of the other sensitized grain boundaries, the matrix, and of other defects/inclusions on the surface. The spreading of corrosion would then be dictated by the spatial proximity and continuity of the β-phase precipitates along the grain boundaries, linked to the degree of sensitization (DoS). Metallurgical, physical, and chemical factors are shown to influence this critical spreading potential.

2. Materials and methods

2.1. Materials

The AA5083-H131 (composition in Table 1) material was supplied by Alcoa as 5.18 cm thick plates. These plates were solutionized at 275 °C for 10 h and then cut into slabs of dimensions 5.08 cm × 0.635 cm × 1.27 cm (L × T × S) and heat treated for various times at 100 °C [34]. These plates were then tested according to the ASTM G-67 procedure to determine the NAMLT values[2] [12].

The particular sensitization conditions and the corresponding NAMLT values are listed in Table 2. LT surfaces were exposed in corrosion studies. The average grain size (determined by ASTM E112 method) was 72.3 μm in L-direction and is 65.2 μm in T-

Table 1
Nominal composition in wt.% of the AA5083 alloy. Compositions provided by Alcoa Technical Center.

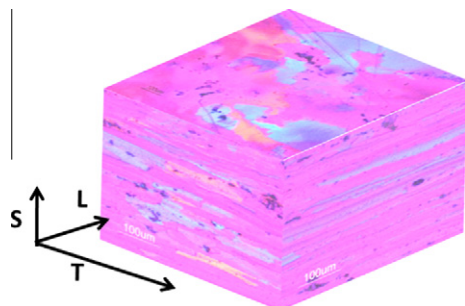|	Mg	Mn	Fe	Si	Cr	Zn	Ti	Ga	V	Ni
wt.%	4.4	0.7	0.22	0.10	0.08	0.02	0.02	0.01	0.009	0.004

Fig. 1. Microstructure of the AA5083-H131 plate. The grain structure was revealed after growing an oxide film and using polarized light to view the sample [35]. Grain length in L direction = 72.27 μm and in T direction = 65.15 μm.

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[2] The NAMLT value (nitric acid mass loss test value) is the mass loss in ASTM G-67 solution [12]. The alloys are exposed to a solution of nitric acid and the mass loss is recorded. Nitric acid preferentially attacks the β-phase precipitates; therefore, the NAMLT value can be considered a measure of the degree of sensitization.