Materials Characterization 146 (2018) 47–54

Contents lists available at ScienceDirect

Materials Characterization

journal homepage: www.elsevier.com/locate/matchar

The effect of grain boundary character evolution on the intergranular corrosion behavior of advanced Al-Mg-3wt%Zn alloy with Mg variation

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ARTICLE INFO

Keywords:
Aluminum alloy
Intergranular corrosion
EBSD
TEM

ABSTRACT

The characteristics of grain boundary and grain boundary precipitates of Al-Mg-3wt%Zn alloy with different Mg contents were systematically investigated. Observation by optical microscopy, transmission electron microscopy, scanning transmission electron microscopy and energy-dispersive X-ray spectroscopy show that the morphology and composition of the grain boundary precipitates change little with the variation in the Mg content. Based on the statistical analysis of the spacings between two adjacent grain boundary precipitates, we find that the decrease in the Mg content reduces the continuity of the grain boundary precipitates. Comparing this result with the electron backscattered diffraction analysis, it can be concluded that the continuity of grain boundary precipitates is affected by the proportion of low angle grain boundaries. The observations of grain boundary precipitates at both low angle grain boundaries and high angle grain boundaries using transmission electron microscopy indicate that low angle grain boundaries have more discontinuous grain boundary precipitates. Combining these results with the results of the intergranular corrosion test, the microscopic features of this corrosion behavior and corrosion mechanism are revealed.

1. Introduction

Al-Mg alloys are widely applied in the marine industry due to their excellent properties such as high strength, fine formability, favorable weldability and corrosion resistance [1–4]. The corrosion behavior of 5× × × alloy during prolonged exposure to certain environments includes pitting, exfoliation corrosion, stress corrosion cracking and intergranular corrosion (IGC) [5,6]. IGC is an important grain boundary (GB) degradation phenomenon in aluminum alloys that arises due to the effect of the continuous or nearly continuous grain boundary precipitates (GBPs) in aluminum alloys [7]. IGC usually leads to “grain-dropping” with a significant loss of material and a simultaneous reduction in ductility, strength and, ultimately, structural integrity [8]. Many studies [9–13] have been performed on the relationship between IGC behavior and GBPs. The results showed that the alloys with continuous GBPs exhibited worse IGC behavior than those with discontinuous GBPs. Another factor that affects the IGC behavior of aluminum alloys is the precipitate free zone (PFZ) in the vicinity of GBs. Liu et al. [14] studied the IGC behavior under various aging treatments in an Al-Cu-Mg-Ag alloy and proposed that IGC resistance decreased due to the increase in the PFZ width, which was also observed in other studies [10–13]. In Al-Mg alloys, GBPs (actually the β-Al_3Mg_2 phase) act as the anodic phase relative to the matrix and form galvanic coupling upon exposure to a conductive medium such as sea water, leading to the dissolution of the β-Al_3Mg_2 phase [15,16].

Grain boundary character distribution (GBCD) is a parameter used to quantitatively describe the type and frequency of the GBs present in a microstructure [8], such as the misorientation angle and the coincidence site lattice (CSL) boundaries. Many researchers have studied the relationship between the GBCD and GBPs of Al-Mg alloys that affect the IGC property. Davenport et al. [17] studied the IGC behavior of 5182 alloy, and the results showed that low angle grain boundaries (LAGBs) had better immunity to precipitation and GB acid attack, which was supported by Yan et al. [4], and they also proposed that low Σ ($\Sigma \le 29$) CSL grain boundaries have thinner β precipitates in an Al-5.3wt%Mg alloy. However, Scotto D'Antuono et al. [18] suggested that initial β formation occurred more readily at LAGBs than at high angle grain boundaries (HAGBs), and this conclusion was also reached by Zhao et al. [19]. This disagreement may result from the differences between the samples under study, such as the differences in the chemical composition and processing state. Thus, this current controversy indicates that more systematic work on different aluminum alloys is required to further establish the relationship between GBCD and GBPs.

Zn has been added to improve the corrosion performance of Al-Mg

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https://doi.org/10.1016/j.matchar.2018.09.044
Received 18 April 2018; Received in revised form 25 September 2018; Accepted 28 September 2018
Available online 30 September 2018
1044-5803/

alloys in many studies. Carroll et al. [20] found that when Zn is added into 5083 alloy, a new kind of GBP (T-Mg_{32} (Al, Zn)$_{49}$) is substituted for the conventional β phase in the GBs of this alloy, leading to better corrosion resistance than that of the conventional 5083 alloy. Meng et al. [2,21] added Zn in Al-Mg alloys with higher Mg content as well and obtained similar results. They proposed that with the formation of T-Mg_{32} (Al, Zn)$_{49}$, the potential difference between the GBPs and the vicinity of the matrix decreases, thus enhancing the IGC resistance. This enhancement improves with increased Zn content due to the increase in the LAGB proportion. The precipitation sequence of the Al-Mg and Al-Mg-Zn alloys can be summarized as follows [22–24]:

supersaturated solid solution → intermediate phase β′ → equilibrium phase β (Al_3Mg_2)
supersaturated solid solution → metastable phase T′ → equilibrium phase T (Mg_{32}(Al, Zn)$_{49}$).

In previous studies, the added Zn content has always been below 1.0 wt% and has had little impact on the strength of Al-Mg alloys. Based on the precipitation sequence of Al-Mg-Zn alloys, an age-hardenable Al-Mg alloy with 3.0 wt% Zn was studied in our previous work, and it was found that its strength was significantly improved (> 100 MPa) [25]. Since the added Zn content was rather high, the precipitation characteristics were certainly changed, implying that the ICG behavior should also be different. In this work, for the Al-Mg-3.0wt%Zn alloy, we aim to reveal the characteristics of the GBPs, the GBP and GBCD evolution with Mg content variation, and their relationships to IGC behavior. Moreover, to optimize the IGC property of Al-Mg-Zn alloys for future use, the IGC mechanism was elucidated.

2. Experimental Procedure

2.1. Material

The alloys in this study were melted and cast to the dimensions of 125 × 100 × 225 mm, and were then homogenized, scalped, hot-rolled, fully recrystallized, cold-rolled, solid-solution-treated and T6 aged at 90 °C/24 h + 140 °C/25 h. The authentic chemical compositions of these alloys are shown in Table 1.

2.2. IGC Tests

The IGC tests were carried out in an atmosphere of a 35 °C mixed solution with 3% (wt%) sodium hydroxide and 1% hydrochloric acid solution (vol%) for 24 h. The specimens were (20 mm × 12.5 mm × thickness in size, testing area/solution volume < 20 mm^2/mL) ground and mechanically polished. To remove any grease, the samples were washed with ethanol, alkali washed with a 10% (wt%) sodium hydroxide solution, treated by acid pickling with a 30% (vol%) nitric acid solution and rinsed with deionized water prior to testing.

2.3. Microstructure Observations

The IGC depth of the longitudinal-transverse (L-T) cross-sections was observed by optical microscopy (OM, Zeiss MC80DX) and 2 samples (4 faces) were tested for each alloy. To study the metallographic structure of the GBPs, the samples were etched with a 40% (vol%) phosphoric acid (H_3PO_4) solution at 40 °C for 2 min, and then observed by OM.

Table 1
Chemical compositions of the Al-Mg-Zn alloys studied in this work (wt%).

Alloy	Mg	Zn	Mn	Cu	Cr	Ti	Zr	Fe	Si	Al
0#	5.58	3.10	0.4	0.15	0.03	0.07	0.15	0.2	0.1	Balance
1#	5.25	3.10	0.4	0.15	0.03	0.07	0.15	0.2	0.1	Balance
2#	4.63	3.10	0.4	0.15	0.03	0.07	0.15	0.2	0.1	Balance
3#	3.98	3.07	0.4	0.15	0.03	0.07	0.15	0.2	0.1	Balance
4#	3.48	3.15	0.4	0.15	0.03	0.07	0.15	0.2	0.1	Balance

The data sets for determining the GBCDs of these T6 treated sheet samples were obtained from the electron backscattered diffraction (EBSD) analysis using a Zeiss Ultra 55 SEM instrument and the software channel 5. LAGBs with the misorientation θ between 2° and 15° and HAGBs with misorientation θ > 15° were observed in the EBSD maps as gray and black lines, respectively. CSL grain boundaries with various Σ values were shown as colored lines. The EBSD samples sectioned in the longitudinal-short transverse (L-ST) plane were electro-polished with a solution of 70% methanol and 30% nitric acid (vol%) at −35 °C and a voltage of 30 V after mechanical polishing.

To reveal the types, morphologies and distribution of the GBPs, transmission electron microscopy (TEM, FEI Tecnai F20 microscope) was used. Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) were used to determine the distribution of Al, Mg and Zn at the grain boundaries. To observe the difference of the GBP continuity between LAGB and HAGB, TEM (JEM2010F), selected area diffraction (SEAD) and map scanning EDS were used. Thin foils of 3 mm discs were ground to ~80 μm and then were thinned by double jet electro-polishing in a 25% nitric acid + 75% methanol solution (vol%) at −35 °C with an applied current of ~60 mA.

3. Results

3.1. IGC Behavior

The metallographic structure of different samples after IGC is shown in Fig. 1(a–e). It is significant that IGC is clearly observed in Alloys 0 and 1, while Alloys 2–4 show less IGC. Fig. 1(f) shows the maximum IGC depth of different alloys. The results show that the IGC depth decreases with decreasing Mg content in the range of 4.6%–5.6%, but that the variation in the Mg content has little effect on the IGC depth when the Mg content is below 4.6%. Fig. 2 shows the metallographic structure of different alloy samples etched by the phosphoric acid solution. Significant GBPs are observed, and it appears that more broken GBs are observed as the Mg content decreases.

3.2. GBCD Analysis

The EBSD analysis was applied to reveal the GBCDs of different samples; the analysis results are shown in Fig. 3. The distributions of HAGB (black boundaries), LAGB (gray boundaries) and CSL GBs (colored boundaries) in different alloy samples are shown in Fig. 3(a–e). Fig. 3(f) shows the metallographic structure etched by the phosphoric acid solution corresponding to Fig. 3(b). Comparison of Fig. 3(b) and (f) shows that all kinds of GBs have been etched which means that none of the GBs are immune to the precipitation of GBPs. Fig. 3(g) shows the average grain size of the five alloys, and a coarsening phenomenon is observed with the reduction in the Mg content. To reveal the effect of Mg on the generation of LAGB and CSL GBs, the proportions of different kinds of GBs with various Mg content were counted and are shown in Fig. 3(h). The proportion of LAGBs increases when the Mg content decreases from 5.6% to 4.6%. The LAGB proportion of the 4.6%Mg sample is more than two times higher than that of the 5.2–5.6%Mg sample, but the LAGB proportions of the 3.5–4.6%Mg samples do not change much. The proportions of Σ ≤ 29 CSL GBs, Σ = 3^n CSL GBs and Σ = 3 CSL GBs are small and change little in different alloy samples. Taken together with the results shown in Fig. 1, these results mean that greater IGC resistance is obtained for an alloy with a higher LAGB proportion.