Journal of Materials Science & Technology 33 (2017) 991–1003

Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org

Characterizing and modeling the precipitation of Mg-rich phases in Al 5xxx alloys aged at low temperatures

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ARTICLE INFO

Article history:
Received 1 December 2016
Received in revised form 24 January 2017
Accepted 25 January 2017
Available online 20 February 2017

Keywords:
Al 5xxx alloys
Precipitation
Scanning transmission electron microscopy
Atom probe tomography
Long-term aging

ABSTRACT

Al 5083 alloys (5.25 at.% Mg) of different tempers (H131 and H116) were aged at low temperatures (50 and 70 °C) for 41 months. Scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDS), and atom probe tomography (APT) were applied to characterize precipitates formed in the sensitized samples. Experimental results revealed that the size of Mg-rich precipitates increased with aging time at 70 °C for both alloys. APT results showed that Mg-rich precipitates of different Mg concentrations and morphologies formed in Al matrix and on the interface of Al matrix/pre-existing particles. In addition, a model based on local equilibrium of chemical potential and multi-class precipitates number evolution was adopted to predict the multiphase precipitation process in the Al-Mg binary system. The overall trend of precipitate radius and number density predicted by the model matched well with the experimental results. Moreover, modeling results revealed that nucleation and coarsening occurred faster in Al 5083 H131 than in Al 5083 H116 when aged at same temperature. The high density of dislocations and the pipe diffusion mechanism of dislocations can be used to explain such behavior.

1. Introduction

Al-Mg 5xxx alloys are widely used in marine, offshore structures, and military applications for their excellent balance of high strength, low density, and good corrosion resistance [1]. Intergranular precipitates, β phase (Al_3Mg_2), will form at grain boundaries of Al 5xxx alloys when exposed to elevated temperature for a long time [2–4]. The selective dissolution of the anodic β phase will cause intergranular corrosion (IGC) and stress corrosion cracking (SCC), which subsequently leads to the failure of the bulk material [5,6]. Extensive characterization and modeling have been conducted on the precipitation behavior of intergranular β phases [7–11].

The aging behavior of Al-Mg binary alloys has been broadly investigated. Nozato and Ishihara [12] examined the precipitation process of Al-Mg (7.6–12.5 at.%) alloys through calorimetric study, and their results revealed that a four-stage precipitation process occurred in Al-Mg alloys below 50 °C. Transmission electron microscopy (TEM) work of Sato et al.[13] showed that an $L1_2$ structure formed after a modulated structure when Al-Mg (10 wt.%) alloys were aged at room temperature. Based on the results of electrical resistivity measurements [14,15], calorimetric study [12,16,17], and high resolution transmission electron microscopy [13,18], the precipitation sequence [13,16] of Al-Mg binary alloys was proposed as:

Supersaturated solid solution → GP zone → β'' phase (Al_3Mg, $L1_2$) → β' phase (Al_3Mg_2, hcp) → β phase (Al_3Mg_2, fcc)

GP zones form at relatively low temperature and have the same structure as the Al matrix (but enriched in Mg atoms) [13,16]. Based on TEM analyses and diffraction studies, β'' phase (Al_3Mg) has been shown to have an $L1_2$ crystal structure [13,14], and it is coherent with the Al matrix [13]. β' phase is a metastable phase with a stoichiometry of Al_3Mg_2 (hcp), and it is semi-coherent with the Al matrix [16]. The equilibrium β phase is reported to have a complex fcc structure with $a = 2.824$ nm and approximate composition Al_3Mg_2 [7,19]. However, the precipitation sequence can be altered if Mg concentration or aging temperature are different. For exam-

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http://dx.doi.org/10.1016/j.jmst.2017.02.001
1005-0302/

ple, Sato and Kamio [13] reported that β'' phase formed directly in the Al-Mg alloys of high Mg concentration (>20 at.%).

Atom probe tomography (APT) has been used to characterize nanoscale precipitates for several decades, and its use has been expanded significantly with the invention of the local electrode atom probe (LEAP) [20]. Zandbergen et al. [21] examined the early stage precipitation behavior of Al-Mg-Si alloy using APT, and their results revealed that the formation of low Mg/Si ratio clusters at 25 °C lowered the solute concentration in the matrix. Moreover, these clusters were not effective precursors for elongated precipitates, which acted as a precipitation hardening phase. Aboulfadl et al. [22] investigated cold rolled (90% reduction in thickness direction) and stabilized Al-4.8 at.% Mg alloy aged at 120 °C for 20 h, and Mg-rich precipitates of 23 nm in length were found along ⟨110⟩ aligned dislocations. Mg concentration in the precipitate was 12 at.% based on APT data. In addition, they also observed the asymmetrical distribution of Mg above and below the slip plane of dislocations.

The measurement and calculation of phase diagrams for Al-Mg binary alloys have been performed by many researchers. Zuo and Chang [23] calculated the phase diagram by treating different phases as ordered ($Al_{12}Mg_{17}$), disordered (liquid, Al (fcc), and, Mg (hcp)), and stoichiometric (Al_8Mg_5, $Al_{0.56}Mg_{0.44}$, and $Al_{0.525}Mg_{0.475}$), and the calculated results agreed with their experimental results. In order to improve the accuracy of energetics of solid phases, Zhong et al. [24] obtained the enthalpy of formation at 0 K for the phases such as $Al_{30}Mg_{23}$, $Al_{12}Mg_{17}$, and Al_2Mg, using first-principles calculations. The binary Al-Mg phase diagram calculated through the CALPHAD/first-principles approach aligns more consistently with the experimental results than that was shown in the previous modeling study. Karadeniz et al. [25] calculated the thermodynamic properties for metastable phase in Al-Mg-Si alloys using CALPHAD method, and the calculated molar entropy of Al_3Mg at 300 K was higher than that obtained from first-principles calculations. The precipitation behavior of intragranular precipitates in Al alloys has been simulated using the classical nucleation and growth theories [26], phase field model (PFM) [27], and kinetic Monte Carlo (KMC) methods [28]. Myhr and Grong [29] developed a multi-class approach based on the classical growth theory and a control volume method to simulate the precipitation behavior in Al-Mg-Si alloy. Perez et al. [30] compared the mean radius method with the multi-class methods (including Euler-like and Lagrange-like methods) and found that the multi-class method was essential in modeling some complex multi-step heat treatment processes. A KMC method based on the first-principles density-functional theory was applied to study the early-stage precipitation behavior in Al-Mg alloys, and temperature was found to affect the cluster process [31]. In order to simulate the evolution of multiple precipitates in a multiphase multicomponent system, a model [7] was developed based on the thermodynamic extremum principle [32,33], and it has been successfully applied to complex precipitation processes in Al [34] and Fe alloys [35]. Chen et al. [36] developed a precipitate growth rate equation for precipitation in multicomponent systems by considering the cross-diffusion and high supersaturation. This method was further improved by Rettig and Singer [37] to describe the precipitation process for multicomponent, multiphase, and multi-particle scenarios. A similar method was adopted by Rougier et al. [38] to simulate γ' phase precipitation in Ni-based alloys.

Al alloys 5083 H131 and H116 were widely used to build ships by US Navy [4,39]. However, cracks caused by IGC/SCC were identified on the deck of these ships when exposed to ocean environment for a few years [39]. Therefore, it is of great interest for US Navy to understand the precipitation behavior of the Mg-rich phases associated with IGC/SCC in Al alloys 5083 H131 and H116. In the present study, Al alloys 5083 H131 and H116 were aged at 50 and 70 °C for 41 months, and scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (EDS), and APT were used to characterize the Mg-rich precipitates formed in the sensitized alloys (aged at 50 and 70 °C for different time durations). In addition, a model based on the equilibrium of Mg chemical potential and the multi-class approach was developed to predict the precipitation of Mg-rich precipitates.

Table 1
Composition (at.%) of Al 5083 alloys.

Al	Mg	Mn	Fe	Cr	Si
Bal.	5.25	0.34	0.37	0.03	0.04

2. Experimental procedures

Commercial Al alloys 5083 H131 and Al 5083 H116 received from Alcoa Inc. were used in this research. For Al 5xxx alloys, H1xx is a strain hardened only temper, and the second digit of the temper represents the strain hardening extent [40]. For example, Hx8 is the fully hardened temper (approximately 75% cold reduction after full annealing), and Hx1 and Hx3 stand for 1/8 and 3/8 hard of the Hx8 temper respectively. The third digit "1" of H131 means that the strain hardened degree is less than the controlled H13 temper, and H116 is a special corrosion-resistant temper [40]. The dimensions of the samples used for the aging experiments were 1 cm × 1 cm × 1 cm. Al alloy 5083 H131 samples were put into an oven and aged at 70 °C for 1.5, 9, 18, and 30 months. Al alloy 5083 H116 samples were aged at 70 °C for 3, 9, 18, and 30 months and at 50 °C for 9, 24, and 41 months. The temperatures were selected to mimic the measured deck sample temperatures of a navy ship traveling to different regions of the world [41]. Temperature of the ovens was monitored using thermometer. The chemical composition of Al 5083 H131 and Al 5083 H116 is presented in Table 1. The micro hardness of Al 5083 H131 is 107.1 ± 4.2 HRC, which is larger than that of Al 5083 H116 (89.8 ± 2.5 HRC).

A JEOL 2800 STEM/TEM (operated at 200 kV) equipped with an ultrafast EDS system (dual high counts SDD-EDS detectors) was used to characterize the microstructure of Al 5083 H131 and H116 alloy samples. TEM foils were prepared by mechanically polishing the samples (3 mm in diameter) to a thickness of 10 μm using a Gatan dimple grinder, followed by ion milling using a Fischione 1010 Ar ion mill. The ion mill was operated at 4 kV with an incident angle of 9°, and final cleaning was performed at 3 kV with an incident angle of 4°.

APT needle-shaped samples were prepared by the top-down and cross-sectional FIB lift-out method [42] using an FEI Nova 200 dual beam SEM/focused ion beam (FIB). The lift-out section was subsequently mounted on a microtip array post that was annularly milled (30 kV) and cleaned with 5 kV ion beam to make needle-shaped specimens suitable for field evaporation [43]. APT analyses were performed using CAMECA Instruments LEAP 4000 XHR. The LEAP was operated in laser-pulse mode with a specimen temperature of 30 K, a pulse repetition rate of 200 kHz, a 100 pJ laser energy, and a 0.5% to 1% detection rate. The resulting data were reconstructed and analyzed using commercial CAMECA IVAS software.

3. Results

Fig. 1(a) is the dark field (DF) STEM image of Al 5083 H131 aged at 70 °C for 1.5 months. EDS maps (Fig. 1(b)) reveal that the bright particles are Al_6(Mn-Cr-Fe) type pre-existing particles as reported by Goswami et al. [7] and Zhu et al. [8]. In addition, a lamellar precipitate (highlighted by an arrow), formed on top of an Al_6(Mn-Cr-Fe) type pre-existing particle, is rich in Mg and Si, which could be an Mg_2Si-type precipitate [44,45]. Whereas a Mg-rich precipitate (21.4 at.% Mg) (identified by a circle) is found at the bottom of the