



Corrosion resistance of Al and Al–Mn thin films



Hesham Mraied^a, Wenjun Cai^{a,*}, Alberto A. Sagüés^b

^a Department of Mechanical Engineering, University of South Florida, 4202 E Fowler Avenue, Tampa, FL 33620, USA

^b Department of Civil and Environmental Engineering, University of South Florida, 4202 E Fowler Avenue, Tampa, FL 33620, USA

ARTICLE INFO

Article history:

Received 26 February 2016

Received in revised form 11 July 2016

Accepted 25 July 2016

Available online 26 July 2016

Keywords:

Alloy
Aluminum
Microstructure
Polarization
Passivity
Pitting corrosion

ABSTRACT

Magnetron-sputtered aluminum (Al) and aluminum–manganese (Al–Mn) films with structures ranging from nanocrystalline to amorphous were obtained by tuning the Mn% up to 20.5 at.%. Corrosion behavior of the films was investigated in 0.6 M and 0.01 M NaCl aqueous solutions by potentiodynamic polarization and electrochemical impedance spectroscopy. Pitting corrosion was found to be strongly affected by alloy composition. The amorphous Al–20.5 at.% Mn exhibited the best pitting resistance during short term exposure. However, over longer immersion in 0.01 M NaCl up to 108 h, nanocrystalline Al–5.2 at.% Mn showed the highest corrosion resistance. The dual-phase Al–11.5 at.% Mn alloy was found to have higher nominal corrosion rate compared to its nanocrystalline or amorphous counterparts.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Aluminum (Al) films are frequently applied as a corrosion protection coating for steel [1,2], magnesium alloys [3,4], and NdFeB magnets [5] etc., replacing the toxic cadmium coatings [6]. Al coatings can be deposited using various methods including electroplating [1], physical and chemical vapor deposition [3,7], and hot-dipping [2]. An amorphous semiconducting passive film forms on the surface of Al in neutral (pH 4–9) solutions to protect the metal underneath from corrosion [8,9]. However, this passive film is still vulnerable to local attack from different halide ions in saline environments, which eventually leads to pitting and crevice corrosion of Al. In addition to its pitting susceptibility, the low mechanical strength of Al coating also leads to poor wear resistance, which greatly limits its potential usage in industrial applications where mechanical contact and corrosive environment coexist [10].

Alloying has been found to be a highly effective method to strengthen Al by forming precipitates or secondary particles [11]. However, the presence of precipitation and secondary particles enhances corrosion by catalyzing oxygen reduction, increasing the alloy corrosion potential, and localizing the electrochemical activity due to chemical inhomogeneity from the Al matrix [10]. Recent studies show that alloying can increase the pitting potential (E_{pit}) of Al provided that the alloying elements are retained in solid solution [12–15]. For example, age-hardened 2000 series Al alloys (with Cu as the major alloying element) exhibit poor corrosion resistance [10], but Kim et al. observed an ennoblement of E_{pit} with

increasing Cu content in Al–Cu solid solutions [12,13]. Alloying Al with appropriate transition metals (TMs) such as Mo, Mn, W, Nb, Cr, Ta, V, and Zr in metastable solid solutions offers the possibility to significantly enhance its pitting resistance in chloride solutions [16]. These TMs improve corrosion resistance and decrease pitting susceptibility of Al by increasing the overpotential for anodic dissolution and decreasing metastable pit initiation and growth rates [12]. In addition, alloying is an effective way to minimize grain size and produce nanocrystalline microstructure. These refined microstructures are likely to promote passive film growth due to the high density of point defect sinks and sources at the intersection between grain boundaries and the film/metal interface [9,17].

Al–Mn is chosen in the present work as a model system to investigate the effects of alloy concentration and microstructure on the corrosion resistance of Al–TM solid solution thin films. This binary system exhibits a wide range of equilibrium phases from solid solution to more than nine intermetallics [18]. Such rich variety of phases indicates the possibility of forming tunable nanostructures by adjusting the alloying concentration [19,20]. Unlike Mo, Ta, Cr, etc. which improve the pitting resistance of Al by increasing the solute concentration in the passive layer that impede the ingress of chloride ions, Mn is found to be absent from the passive film of Al–Mn in chloride solutions [21,22]. Instead, it was suggested that Mn solute atoms improve the pitting resistance by hindering the pit growth kinetics of Al [21,23]. Despite these past studies, findings on how alloying concentration affects the corrosion resistance of Al–Mn are not fully consistent. Moffat et al. [21] investigated the corrosion resistance of Al–Mn alloys with 0–26 at.% Mn electrodeposited at 150 °C. They found that E_{pit} is greatly increased for crystalline (0–5 at.% Mn) and amorphous (22–26 at.% Mn) Al–Mn but decreased at the intermediate

* Corresponding author.

E-mail address: caiw@usf.edu (W. Cai).

composition (5–22 at.% Mn) where crystalline and amorphous phases coexist. On the other hand, Frankel et al. [23] found alloying with Mn enhanced pitting resistance of Al but both the pitting and repassivation potentials of Al-Mn alloys were not strong functions of Mn concentration. In addition, their work did not include characterization of the alloy microstructure or pit morphology. Recently, Reffass et al. [24] showed that the E_{pit} increases monotonically with alloying concentration up to 32 at.% Mn while the corrosion current density remain insensitive to alloy composition. Given the variability and limitations of prior findings noted above, the present work aims at evaluating the composition-corrosion resistance relationship by investigating the role of Mn on the microstructure and corrosion resistance of Al-Mn solid solutions. Attention is given to the microstructure and surface morphology of as-deposited and corroded samples towards better understanding the roles of composition as well as microstructure on corrosion resistance.

2. Experimental procedure

The equilibrium solubility of Mn in Al at room temperature is low, ~0.62 at.% [25], so nonequilibrium processing techniques are needed to achieve extended solubility. Physical vapor deposition (PVD) with its associated high quench rates was chosen here to produce supersaturated Al-Mn alloys with crystalline, dual phase, and amorphous microstructure. Pure Al and Al-Mn alloys with 5.2, 11.5, and 20.5 at.% Mn were sputtered on Si wafer using a CRC sputter coater at 80 W radio frequency power under Ar (99.99%, 5 mTorr) atmosphere. To produce Al-Mn alloys, an Al (99.99%) sheet with uniformly spaced holes was placed over a Mn (99.999%) disc and used as the target, 6 cm away from the specimen. The number and size of the holes on the Al sheet was varied to achieve different alloy compositions. Post deposition chemical analysis confirmed the formation of compositionally homogenous films over the entire sample size of $1.2 \times 2 \text{ cm}^2$. Prior to deposition, the Si wafers were etched with 1:50 hydrofluoric acid water solution to remove the native oxide layer to improve coating adhesion. Both Al and Al-Mn were deposited with a nominal film thickness of ~1 μm , confirmed using a Detak 3030 ST profilometer. All experiments were performed on as-deposited samples without any pretreatment.

The as-deposited samples were characterized using scanning electron microscopy (SEM, Hitachi SU-70), energy-dispersive X-ray spectroscopy (EDS, EDAX-Phoenix attached to SEM, Hitachi S-800), and grazing incidence X-ray diffraction (XRD, PANalytical X'Pert). Transmission electron microscopy (TEM) analysis including bright-field (BF), dark-field (DF) imaging, and selected area diffraction (SAD) was performed using Tecani F20 TEM. TEM samples were prepared by directly sputtering Al and Al-Mn alloys on continuous carbon film TEM grids for 15 min, which resulted in a sample thickness of ~150 nm.

Electrochemical behavior was characterized at regimes of mild and severe environmental exposure, consisting respectively of naturally aerated 0.01 and 0.6 M NaCl aqueous solutions, both pH \approx 6.4 and at ambient temperature. The evaluations were conducted in 3-electrode cells where the deposited samples, a mixed metal oxide coated titanium mesh, and a commercial silver-silver chloride electrode (1 M KCl internal solution) were used as the working, counter, and reference electrode respectively. Prior to the corrosion tests, the sample surfaces were covered with stop-off lacquer except to expose a square region with an effective surface area of 1 cm^2 to the electrolyte, and another region allowing for an electrical contact using an alligator clip. Optical microscopy was performed after each test and results from samples that showed any indication of crevice corrosion under the stop-off lacquer were discarded. The results reported here for each test condition correspond to at least three separate tests without crevice corrosion. All tests were conducted with a Gamry Reference 600® potentiostat.

In the severe 0.6 M NaCl regime, in addition to open circuit potential (E_{oc}) determinations only short-term solution potentiodynamic polarization (PD) measurements were conducted, after allowing 1 h of immersion for E_{oc} to approach a stable regime. The PD scans were conducted in the

anodic direction at a rate of 0.167 mV/s, starting from a potential ~150 mV more negative than E_{oc} . The scans were terminated when a rapid increase in the anodic current density took place and reached 10 $\mu\text{A} \cdot \text{cm}^{-2}$. Given the low current densities and solution resistivity involved, no correction was made for solution resistance effects in these tests. The potential at which that rapid increase took place was named E_{pit} . A nominal value of the cathodic polarization slope (β_c) was assigned by fitting a straight line to the portion of the polarization curve that corresponded to potentials >50 mV lower than E_{oc} . A nominal value of the anodic polarization slope (β_a), was likewise assigned, using the portion of the curve that started at potentials >50 mV higher than E_{oc} and ended at E_{pit} . Extrapolation of both of those trends to E_{oc} and suitable averaging of both was used to obtain a nominal corrosion current density (i_{corr}). The i_{corr} was converted to a nominal corrosion rate in ($\mu\text{m}/\text{y}$) by Faradaic conversion ($1 \mu\text{A} \cdot \text{cm}^{-2} \approx 10.9 \mu\text{m}/\text{y}$) treating the corrosion as if it were uniform with formation of Al^{+3} . It is noted that unless indicated otherwise current densities and associated corrosion rates are reported as a value averaged over the nominal area of the specimen, recognizing that corrosion rates at localized features may be much larger. Hence, the reported values of corrosion rates in $\mu\text{m}/\text{year}$ are considered as a rough estimation and are used only for comparing the corrosion resistance of Al-Mn with various Mn%. The unit of corrosion rate ($\mu\text{m}/\text{year}$) is chosen here to be consistent with that commonly adopted in the literature. However it should be noted that the corrosion experiments performed here were over a much shorter period of time than one year. The reported polarization slopes may reflect passive film properties and ohmic components due to current localization, and are not viewed as representing simple Tafel behavior. Likewise, the potential E_{pit} has been named so by analogy to the behavior observed upon pitting in bulk specimens, but the morphology of localized corrosion in these thin films may differ from that of conventional pits, as discussed later on.

In the milder, 0.01 M NaCl regime E_{oc} and PD measurements were conducted in selected specimens following the same methodology as for the 0.6 M NaCl exposures. The milder conditions enabled longer term evaluations, so with another set of specimens, E_{oc} measurements were conducted regularly over periods of up to 108 h, supplemented by non-destructive electrochemical impedance spectroscopy (EIS) tests via 10 mV *rms* sinusoidal potential excitation around E_{oc} in the frequency range of 10 mHz to 100 kHz, 5 points per decade. Analysis of the EIS results, described further below, was conducted to obtain a nominal value of i_{corr} as function of exposure time. Finally, corrosion tests results plotted in the all figures here are averages of at least three data points with error bars representing the range of the data. SEM examination was conducted on one of the exposed specimens of each alloy after extraction from the test solution for the longer duration tests. Post-corrosion cross-sectional samples were prepared from areas exposed to the corrosive environment using focused ion beam microscope (FIB, Quanta 200 3D Dual Beam).

3. Results and discussion

3.1. Materials characterization

EDS chemical analysis with spatial resolution of ~200 nm, confirmed the formation of compositionally homogeneous Al-Mn alloy films with 5.2, 11.5, and 20.5 at.% Mn, hereafter noted as alloy A5, A11, and A20, as listed in Table 1. The average oxygen concentration measured for all alloys was 0.62 ± 0.17 at.%. SEM images of as-deposited Al (A0) and Al-Mn alloys are shown in Fig. 1. From alloy A0 to alloy A20, the surface morphology became smoother, indicating the formation of finer microstructures (e.g. smaller grain size and/or greater content of amorphous phase) at higher alloying concentration. The faceted angular structures of alloy A0 and alloy A5 indicate the formation of crystalline phases where each angular structure often corresponds to an individual grain [26]. Surfaces of alloy A11 and alloy A20 exhibited compact round

Download English Version:

<https://daneshyari.com/en/article/1663855>

Download Persian Version:

<https://daneshyari.com/article/1663855>

[Daneshyari.com](https://daneshyari.com)