Corrosion resistance of Al and Al-Mn thin films

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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 hrs, 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.

Keywords: alloy; aluminum; microstructure; polarization; passivity; pitting corrosion

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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

1 metastable pit initiation and growth rates [12]. In addition, alloying is an effective way to
2 minimize grain size and produce nanocrystalline microstructure. These refined microstructures
3 are likely to promote passive film growth due to the high density of point defect sinks and
4 sources at the intersection between grain boundaries and the film/metal interface [9, 17].

5
6 Al-Mn is chosen in the present work as a model system to investigate the effects of alloy
7 concentration and microstructure on the corrosion resistance of Al-TM solid solution thin films.
8 This binary system exhibits a wide range of equilibrium phases from solid solution to more than
9 nine intermetallics [18]. Such rich variety of phases indicates the possibility of forming tunable
10 nanostructures by adjusting the alloying concentration [19, 20]. Unlike Mo, Ta, Cr, etc. which
11 improve the pitting resistance of Al by increasing the solute concentration in the passive layer
12 that impede the ingress of chloride ions, Mn is found to be absent from the passive film of Al-Mn
13 in chloride solutions [21, 22]. Instead, it was suggested that Mn solute atoms improve the pitting
14 resistance by hindering the pit growth kinetics of Al [21, 23]. Despite these past studies, findings
15 on how alloying concentration affects the corrosion resistance of Al-Mn are not fully consistent.
16 Moffat et al. [21] investigated the corrosion resistance of Al-Mn alloys with 0 – 26 at.% Mn
17 electrodeposited at 150 °C. They found that E_{pit} is greatly increased for crystalline (0 – 5 at.% Mn)
18 and amorphous (22 – 26 at.% Mn) Al-Mn but decreased at the intermediate composition (5 – 22
19 at.%Mn) where crystalline and amorphous phases coexist. On the other hand, Frankel et al.
20 [23]found alloying with Mn enhanced pitting resistance of Al but both the pitting and
21 repassivation potentials of Al-Mn alloys were not strong functions of Mn concentration. In
22 addition, their work did not include characterization of the alloy microstructure or pit
23 morphology. Recently, Reffass et al. [24] showed that the E_{pit} increases monotonically with
24 alloying concentration up to 32 at.% Mn while the corrosion current density remain insensitive to
25 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 toward 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 $\sim 1 \text{ }\mu\text{m}$, 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 $\text{pH} \approx 6.4$ 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 hr 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 more than 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 ($1 \mu\text{A}.\text{cm}^{-2} \approx 10.9 \mu\text{m}/\text{y}$) 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 hours, 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 nodules, similar to those observed in thin films with ultrafine grains and/or high amount of amorphous phase [27].

To establish the phase nature of the deposits, grazing-incidence angle XRD line scans were performed on a sample of each alloy. The results are shown in Fig. 2. The diffraction pattern of

alloy A5 was characteristic of a face-centered-cubic (fcc) crystalline structure, similar to that of pure Al (A0), indicating the formation of super-saturated solid solution well beyond the equilibrium solubility. For the alloy A11, broad fcc diffraction peaks and a hint of a diffuse peak at $2\theta \approx 42^\circ$ were observed, indicating that an amorphous phase coexisted with α -Al. At the highest alloying concentration, the alloy A20 was completely amorphous, where all crystalline diffractions were absent and only a broad hump around $2\theta \approx 42^\circ$ was observed. In addition to peak broadening, a right shift of the (111) diffraction peaks was observed from alloy A0 to alloy A11, indicating a decrease of lattice constant (as listed in Table 1) with increasing alloying concentration. This behavior is similar to that reported for electrodeposited Al-Mn [19], suggesting that Mn, which has a Goldschmidt radius $\sim 11\%$ smaller than Al, is substitutionally incorporated into the Al lattice.

Bright-field TEM **imaging** and selected-area diffraction (SAD) analysis were performed to reveal the detailed microstructure of the as-deposited samples, as shown in Fig. 3. The average **in-plane** grain size of alloy A0, A5, and A11 was 42, 15, and 12 nm respectively, measured using the line-intercept method from both bright-field and dark-field TEM images. The SAD patterns showed that both alloy A0 and alloy A5 exhibited discrete diffraction rings associated with single fcc phase (Fig. 3.a-b insets). A diffuse halo and sharp diffraction rings coexisted in the SAD pattern of alloy A11, confirming the presence of a dual-phase microstructure, in agreement with the XRD results. High-resolution TEM images (Fig. 3(d)) of alloy A20 indicated the absence of short-range-order, and the halo ring of the corresponding SAD pattern confirmed the amorphous nature of this alloy. In summary, by tuning the Mn content in the alloy from 5.2 to 20.5 at%, a microstructure transition from nanocrystalline, dual-phase, to complete amorphous phase was achieved.

3.2. 0.6 M NaCl - Short term exposures

Representative PD results in this more aggressive electrolyte are shown in Fig. 4. The crossover potentials for zero current ($E_{\text{zero current}}$) agreed reasonably well with the values of E_{oc} observed before initiating the scans. Pure Al (A0) showed highly active dissolution immediately on entering the anodic current regime, while all Al-Mn alloys showed regions of predominantly passive behavior (likely with some extent of localized activity), followed by a rapid increase in current density at E_{pit} . Additional tests which included a return scan confirmed that the increase in current was associated with permanent corrosion damage by showing a wide return loop and lateral propagation of a metal loss front revealing the silicon substrate. The E_{oc} values and the electrochemical parameters obtained from PD measurements are shown in Fig. 5 and Table 2. E_{pit} increased monotonically with Mn content. This observation is similar to that of Moffat et al.[21]. At the E_{oc} all Al-Mn alloys exhibited lower nominal corrosion rate compared to pure Al, consistent with the latter being in a distinct active dissolution pitting regime, while the others approached a passive condition. The amorphous Al-Mn (alloy A20) exhibited the smallest nominal corrosion rate, 0.9 $\mu\text{m}/\text{year}$. $E_{\text{zero current}}$ of nanocrystalline (alloy A5) and complete amorphous (alloy A20) Al-Mn were both anodic compared to that of pure Al (A0). However $E_{\text{zero current}}$ of the dual-phase (alloy A11) was more cathodic, $-750 \text{ mV}_{\text{Ag/AgCl}}$.

3.3. 0.01 M NaCl - Short and long term exposures

Representative PD results in this milder electrolyte are shown in Fig. 6. The IR drop in this electrolyte is estimated to be less than 2 mV thus is neglected here. As for the other electrolyte, the crossover potentials for zero current agreed reasonably well with the values of E_{oc} observed before initiating the scans. Despite the milder electrolyte, Alloy A0 showed highly active dissolution immediately on entering the anodic current regime as it did in the 0.6 M NaCl tests. The Al-Mn alloys, which had shown indications of an initially passive condition in 0.6 M NaCl

1 did as expected the same in 0.01 M NaCl. Unlike in the more severe environment however, none
2 of the Al-Mn alloys in 0.01 M NaCl showed clear indication of onset of pitting even when
3 anodically polarized up to +0.8 V as shown also in (Fig. 7. a). The E_{oc} values and the
4 electrochemical parameters obtained from PD measurements are shown in Fig. 7 and Table 3.
5 Compared to that of pure Al (A0), the $E_{zero\ current}$ of nanocrystalline (alloy A5) was more cathodic;
6 however it was more anodic for the dual-phase (alloy A11) and the complete amorphous (alloy
7 A20). The E_{oc} of the nanocrystalline (alloy A5) was more cathodic compared to that of pure Al.
8 Similar to the behavior in the more aggressive electrolyte, all Al-Mn alloys exposed to the milder
9 electrolyte exhibited lower nominal corrosion rate compared to pure Al. The amorphous Al-Mn
10 (alloy A20) exhibited the smallest nominal corrosion rate, 0.7 $\mu\text{m}/\text{year}$.

11
12 For the long term tests Fig. 8 shows that the E_{oc} of pure Al was always more negative than that of
13 all Al-Mn alloys, shifting towards more negative values as exposure time increased and reaching
14 $\sim -900\text{ mV}_{\text{Ag}/\text{AgCl}}$ at 24 hrs. This evolution was indicative of stable local passivity breakdown
15 even in this relatively mild environment, and was confirmed by direct observation as shown in
16 Fig. 9 where through thickness macroscopic pits are clearly seen. Given this early manifestation
17 of corrosion, the Al specimens were removed from the solution at 24 hrs.

18
19 In contrast to pure Al, the three Al-Mn alloys showed nobler E_{oc} values generally indicative of a
20 predominately passive regime [24]. E_{oc} values started at around -450 to -550 $\text{mV}_{\text{Ag}/\text{AgCl}}$. For
21 alloys A11 and A20, E_{oc} shifted towards more negative values around -750 to -800 $\text{mV}_{\text{Ag}/\text{AgCl}}$ for
22 up to 24 hrs but became increasingly nobler from then on, suggesting a period of some activity
23 but eventually the development of a more stable passive regime [24]. Alloy A5 showed a
24 consistently elevated value of E_{oc} , around -450 $\text{mV}_{\text{Ag}/\text{AgCl}}$ over the entire exposure period
25 suggesting stable passive behavior from the onset. After about 90 hrs of immersion, the E_{oc}

values for all three Al-Mn alloys tended to be comparably noble, similar to behavior observed by Refass et al indicative of predominantly passive conditions [24]. This interpretation was consistent with visual observation that showed no macroscopic pitting on any of the three Al-Mn alloys after 108 hrs of immersion, as exemplified in Fig. 9 for alloy A20.

EIS (Fig. 10) provided further insight on the relative corrosion resistance of the alloys evaluated. The Nyquist diagrams show a prominent high frequency semicircle followed by the onset of another at lower frequencies. This behavior was interpreted tentatively here with the treatment proposed by Akhoondan [28] by fitting the results to the impedance projected by the equivalent circuit and parameters shown in Fig. 11. There R_s represents the ohmic solution resistance, which was found, as expected, to be of a value consistent with the cell dimensions and electrolyte resistivity and independent of the material tested. The interfacial impedance is assumed to consist of a nearly ideal capacitive element (CPE_1 , with impedance represented by $Z_{CPE} = Y_o^{-1} (j\omega)^{-n}$ where Y_o is a constant, $j = (-1)^{1/2}$, ω is the angular frequency and n is a real number between 0 and 1), representative of the capacitance of the passive film, in parallel with components representing the impedance associated with the Faradaic reactions on the interface. Those processes consist of some form of anodic dissolution, either via slow ionic transport through the bulk film or at discrete film flaws, and a cathodic process that is likely to involve oxygen reduction given the aerated solution condition, and expected to take place preferentially at localized film imperfections. In the adopted interpretation [28] the impedance components of both reactions are assumed to be acting in parallel, but the one for the anodic reaction is taken as being large enough to be neglected given the high polarizability of that reaction in a predominantly passive metal. The remaining dominating impedance, that of the cathodic reaction, may be viewed as being responsible for the observed two-loop behavior by proposing that it reflects the presence of a two-step cathodic process [28]. In such treatment the impedance can be represented by a fast-

reacting term R_{ct} , and a slower reacting component corresponding to the parallel combination of R_2 and CPE_2 , with R_{ct} as a charge transfer resistance that is approximately related to the surface-averaged corrosion current density on the sample by Stern-Geary equation [29].

$$i_{corr} = B/R_{ct} \quad (1)$$

where B has a value of 52 mV, in the order of those commonly assumed for the Stern-Geary constant of predominantly passive metals [30]. The equivalent circuit produced simulations that closely matched the experimental behavior for much of the frequency range sampled, as shown by the solid lines in Fig. 10. The evolution of equivalent circuit parameters as a function of immersion time is shown in Fig. 12, which also indicates that reasonably similar trends were obtained with multiple replicate specimens.

As illustrated in Fig. 10, the high frequency semicircle was only moderately depressed, which on analysis yielded generally elevated values of the CPE parameter n as shown in Fig. 12(c). That was especially so at the beginning of the exposure with $n \sim 0.91$ for Alloy A5 and only somewhat smaller values for the other alloys. Under those conditions the CPE parameter Y_0 may be viewed as a rough estimate of the film capacitance C via

$$C \sim Y_0 \cdot \text{sec}^{n-1}, \quad (2)$$

recognizing that the expression becomes increasingly inaccurate as n decreases from unity [31]. From there, a nominal thickness of the passive film (d) may be obtained from the following equation [32]

$$d = \epsilon \epsilon_0 A / C, \quad (3)$$

where ϵ is the dielectric constant of the passive film (taking it to be ~ 10 for aluminum oxide [33]), ϵ_0 is the permittivity of vacuum ($8.85 \times 10^{-14} \text{ F} \cdot \text{cm}^{-1}$) and A is the exposed surface area ($\sim 1 \text{ cm}^2$). As shown in Fig. 12(d), the passive film thickness (d) for all alloys at early ages was in the range of ~ 1 – 1.5 nm. Those values are comparable to those reported in other investigations for

1 films resulting from natural air oxidation of Al alloys [28, 32], thus supportive of the
2 interpretation of the nature of the reactive term responsible for the high frequency semicircle. Per
3 Fig. 12 (b-c) the values of n and Y_o for Alloy A5 remained close to 0.9 and $8 \times 10^{-6} \text{ F sec}^{(1-n)}$
4 respectively during the entire exposure period, suggesting that the passive film thickness was not
5 changing much with exposure time. For the other alloys the values of n and Y_o experienced
6 moderate decreasing and increasing trends respectively. The corresponding values of d remained
7 not far from those experienced initially. Further interpretation of any apparent trends of changes
8 in d with time was not attempted, as they may merely reflect artifacts from data scatter and the
9 increasing uncertainty in the applicability of Eq. 2 associated with decreasing values of n .

10
11 As shown in Fig. 12(a) the values of nominal corrosion rate (estimated from EIS via Eq.(1) were
12 consistently the lowest (by about one order of magnitude over much of the exposure period) for
13 Alloy A5 than for the others. Alloy A20 had a brief initial period of low nominal corrosion rate
14 but rapidly approached the values for A0 and A11 afterwards. Alloy A0 had the highest nominal
15 corrosion rate, consistent with the early conspicuous surface deterioration illustrated in Fig. 9.

16 17 **3.4. Microstructure and electrochemical behavior**

18 Fig. 13(a) summarizes the average nominal corrosion rate estimates from PD and EIS tests of all
19 the alloys as a function of Mn% in both test environments and time frames investigated. While
20 the estimates were conducted using different techniques and working assumptions, both methods
21 still indicate as expected [34] corrosion severity that increased with increasing $[\text{Cl}^-]$. It is also
22 noted that despite the 60-fold change in $[\text{Cl}^-]$, the short term results show similar ranking in
23 nominal corrosion rate, with A5 and A20 exhibiting the slowest and A0 and A11 the highest
24 nominal corrosion rates by roughly the same proportions. In the long term 0.01 M NaCl solution

1 evaluation, alloy A5 showed the best indications of passive film stability of all alloys evaluated,
2 with consistently noble E_{oc} values (Fig. 8), lowest (although somewhat increasing with time)
3 nominal corrosion rate, well defined indications of retaining the initial passive film thickness
4 throughout the entire period of exposure, and as shown later visual absence of localized corrosion
5 after 108 hrs.

6
7 The behavior in 0.6 M $[Cl^-]$ allows comparison with work of others also performed in
8 comparably aggressive solutions. The relatively high nominal corrosion rate found here for the
9 dual phase alloy as compared to its nanocrystalline or amorphous Al-Mn counterparts is similar
10 to that reported by Refass et al. [24], Merl et al. [35] and Sanchette et al. [14]. It is likely
11 associated with local galvanic coupling between the crystalline and amorphous phases due to
12 their expected different electrochemical properties. Indeed, phase heterogeneity as a potentially
13 source of local galvanic coupling has already been reported in Al- [36] and Zr-based [37] metallic
14 glasses. For example, Li. et al. [37] found that partially crystallized $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ alloy
15 experienced accelerated dissolution compared to its crystalline or complete amorphous
16 counterparts, as a result of high chemical activity at the crystalline-amorphous interfaces and
17 grain boundaries.

18
19 To clarify the correlation between composition and microstructure and how their interplay affect
20 corrosion resistance in the more aggressive media, Fig. 13(b) summarizes the evolution of E_{pit} as
21 a function of Mn content and microstructure from the current work and previous reports [21-23].
22 Red, green, and blue symbols are used to represent crystalline, dual phase, and amorphous
23 microstructure respectively. It can be seen that the addition of Mn up to 10 at% was highly
24 effective in improving pitting resistance (as inferred from the value of E_{pit}) in 0.1–0.86 M

chloride solutions. This effect was less significant at higher compositions (beyond ~ 20 at. %) when Al-Mn becomes completely amorphous. This overall trend is consistent with observations by Frankel et al.[23], where pitting corrosion of Al-Mn was not much sensitive to alloy concentration in the range of $\sim 6 - 16$ at. Mn%. A deviation from this general trend is apparent in the dual phase region from the results by Moffat et al.[21]. However, this deviation is not surprising given the fact that Moffat et al. deposited Al-Mn at an elevated temperature of ~ 150 °C which promote large chemical inhomogeneity between the fcc and amorphous phase. They noted that the composition of the selectively dissolved fcc phase is ~ 1 at.% Mn, very close to the equilibrium solubility limit. All other data (including our results) in Fig. 13(b) were obtained from Al-Mn deposited at room temperature which favors the formation of the compositionally homogenous dual phase microstructure. This chemical homogeneity was also confirmed by Ruan et al. [38] using atom probe tomography (APT). They found that Mn solute atoms distributed homogeneously in the Al matrix with no significant clustering or ordering at the grain boundaries or in the amorphous phase, for either pure crystalline or dual phase Al-Mn. Taken together, in chemically homogenous Al-Mn solid solutions, pitting potential is seen to increase monotonically with alloying concentration regardless of the microstructure and phase of the alloy.

3.5. Exposed surface morphology

Fig. 14 shows SEM examination of the exposed alloys (one sample each) for any significant surface features after the 0.01 M NaCl immersion. Pure Al (A0) clearly showed through-thickness circular “pits” ~ 120 μm in diameter after 24 hrs of immersion; this observation is consistent with the direct visual observation of local corrosion (Figure 9) and the indication of an anodic current surge immediately after exceeding the freely corroding potential (Figure 6). Up to 108 hrs of exposure the surface of both alloys A5 and A11, while showing some alteration compared with the as-deposited state (Fig. 1) did not however reveal any marked localized attack.

1 In contrast, a network of conspicuous grooves developed on alloy A20, as shown in Fig. 14(d).
2 Al and Mn EDS maps of the corroded surface (Fig. 14(d) insets) were featureless, so the grooves
3 did not seem to be associated with any local compositional inhomogeneity. To reveal the depth of
4 the grooves, a cross-section of the sample was prepared by focused ion beam (FIB) milling (Fig
5 15). Edge rounding and overhanging milling debris introduce some uncertainty, but in general the
6 grooves appeared to be in the order of ~ 100 nm or less in depth (the depth of the grooves was
7 measured by tilting the sample by 40°).

8
9 Besides the grooves, a large population of circular pit-like features ~ 100 nm in diameter was
10 observed as well (white arrows, Fig. 15), resembling those observed in electrodeposited
11 amorphous Al-Mn (with 21 at.% and 26 at.% Mn). Closer examination indicated that these
12 features had a tendency to be connected with the groove network as illustrated by the red arrows
13 in box 2, Fig. 15. The features may be vestigial traces of metastable pits; Meng et al. [39]
14 demonstrated that the possibility of forming small metastable pits was higher for Al with smaller
15 grain sizes. This grain size dependency is generally consistent with our observation that
16 micrometer-scale stable pits are only observed in pure Al, while these apparent metastable pits
17 were observed on our amorphous Al-Mn alloy.

18
19 It is of interest to compare with the SEM evidence the amount of metal dissolution estimated
20 from the EIS apparent corrosion rate test results. From the nominal corrosion rates in Figure 12 (a)
21 alloys A11 and A12 would have had experienced after 108 hours, if the wastage was uniform, a
22 deposited layer thickness loss in the order of ~ 200 nm, or about 20% of the initial film thickness.
23 As indicated earlier, the interpretation of the EIS data is based only on working assumptions so
24 only a rough estimate of material loss can be expected. Nevertheless the estimated value is
25 consistent with the SEM indication of the initial film having been still present after 108 hours in

both alloys. The EIS estimate also suggests that if in the case of the A20 alloy the comparatively shallow grooves should be mostly irregularities in an advancing, relatively generalized front of metal wastage; otherwise the grooves would have needed to be much deeper to account for the metal loss estimate. Resolution of this issue merits consideration in subsequent investigations. For alloy A5 the metal loss estimate is about one order of magnitude less than for its two counterparts, fully consistent with the deposit still being in place and the absence of any other microscopic evidence of strong surface alteration. In all Al-Mn alloy cases the relatively sustained value of the passive film thickness indicated by the EIS data suggests that it was being globally regenerated while any metal wastage was taking place.

4. Summary of findings

Al and Al-Mn thin films with up to 20.5 at.% Mn were grown by PVD on Si substrates to evaluate the influence of Mn on microstructure formation as well as their short-term and long-term corrosion behavior. At low Mn concentration (5.2 at.%), Mn and Al form a supersaturated face-centered cubic solid solution with an average grain size of 15 nm. At an intermediate Mn concentration (11.5 at.%), a chemically homogenous dual-phase microstructure was formed consisting of fcc and amorphous Al-Mn. Further increasing alloy concentration to 20.5 at.% Mn leads to the formation of a complete amorphous Al-Mn with reduced surface roughness.

For the microstructures examined here Mn was found to be highly effective in improving the corrosion resistance of Al. The pitting potential increased monotonically with the alloying concentration and was insensitive to the microstructure as long as chemical homogeneity was attained. The alloys containing fully nanocrystalline (5.2 at.%Mn) and fully amorphous (20.5 at%Mn) microstructure exhibited better corrosion resistance than those containing dual phase (11.5 at%Mn). Finally, the amorphous Al-Mn was found to exhibit the highest corrosion

1 resistance at short exposure time in chloride solution while the nanocrystalline counterpart was
2 more stable over long exposure time up to 108 hrs. Post-corrosion surface characterization
3 revealed a network of surface grooves and circular pits formation on the amorphous Al-Mn after
4 108 hrs.

5
6 As a last note, the enhanced corrosion resistance and decreased pitting susceptibility of Al by
7 alloying with Mn is similar to that observed in other Al-TM (TM=Ta, Mo, Cu, W, etc.) systems.
8 A possible contribution to the enhanced pitting resistance by alloying with Mn is that Mn alters
9 the pit growth kinetics [23]. Since Mn^{2+} has a lower hydrolysis constant than Al^{3+} , thus a higher
10 dissolution rate is required for Al-Mn to maintain the pH necessary for pit growth than pure Al.
11 Finally, we note that while the current study focused on Al-Mn thin films deposited on Si
12 substrate by PVD, this material system can be easily electrodeposited in much thicker coatings (at
13 a deposition rate of $\sim 10 - 20 \mu\text{m/hr}$ [19, 40]) to protect various metal substrates such as Al alloys,
14 steel, and Mg alloys.

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References

- [1] S. Caporali, A. Fossati, A. Lavacchi, I. Perissi, A. Tolstogousov, U. Bardi, Aluminium electroplated from ionic liquids as protective coating against steel corrosion, *Corrosion Sci.*, 50 (2008) 534-539.
- [2] W.J. Cheng, C.J. Wang, Growth of intermetallic layer in the aluminide mild steel during hot-dipping, *Surf. Coat. Tech.*, 204 (2009) 824-828.
- [3] G. Wu, X. Zeng, G. Yuan, Growth and corrosion of aluminum PVD-coating on AZ31 magnesium alloy, *Mat. Lett.*, 62 (2008) 4325-4327.
- [4] A. Pardo, P. Casajus, M. Mohedano, A.E. Coy, F. Viejo, B. Torres, E. Matykina, Corrosion protection of Mg/Al alloys by thermal sprayed aluminium coatings, *Appl. Surf. Sci.*, 255 (2009) 6968-6977.
- [5] S. Mao, H. Yang, J. Li, F. Huang, Z. Song, Corrosion properties of aluminium coatings deposited on sintered NdFeB by ion-beam-assisted deposition, *Appl. Surf. Sci.*, 257 (2011) 5581-5585.
- [6] M. Bielawski, Development of unbalanced magnetron sputtered Al-Mo coatings for cadmium replacement, *Surf. Coat. Tech.*, 179 (2004) 10-17.
- [7] J.H. Yun, S.W. Rhee, Effect of carrier gas on metal-organic chemical vapour deposition of aluminium from dimethylethylamine alane, *J. Mater. Sci.- Mater. Electronics*, 9 (1998) 1-4.
- [8] J. Creus, H. Idrissi, H. Mazille, F. Sanchette, P. Jacquot, Corrosion behaviour of Al/Ti coating elaborated by cathodic arc PVD process onto mild steel substrate, *Thin Solid Films*, 346 (1999) 150-154.
- [9] D.D. Macdonald, Passivity - the key to our metals-based civilization, *Pure Appl. Chem.*, 71 (1999) 951-978.
- [10] C. Vargel, *Corrosion of Aluminium*, Elsevier, Oxford, 2004
- [11] K. Lepper, M. James, J. Chashechkina, D.A. Rigney, Sliding behavior of selected aluminum alloys, *Wear*, 203 (1997) 46-56.
- [12] Y. Kim, R.G. Buchheit, A characterization of the inhibiting effect of Cu on metastable pitting in dilute Al-Cu solid solution alloys, *Electrochim. Acta*, 52 (2007) 2437-2446.
- [13] Y. Kim, R.G. Buchheit, P.G. Kotula, Effect of alloyed Cu on localized corrosion susceptibility of Al-Cu solid solution alloys-Surface characterization by XPS and STEM, *Electrochim. Acta*, 55 (2010) 7367-7375.
- [14] F. Sanchette, C. Ducros, A. Billard, C. Rébéré, C. Berziou, M. Reffass, J. Creus, Nanostructured aluminium based coatings deposited by electron-beam evaporative PVD, *Thin Solid Films*, 518 (2009) 1575-1580.
- [15] D.K. Merl, P. Panjan, I. Milosev, Effect of tungsten content on properties of PVD sputtered Al-W-X alloys, *Surf. Eng.*, 29 (2013) 281-286.
- [16] Z. Szklarska-Smialowska, Pitting corrosion of aluminum, *Corrosion Sci.*, 41 (1999) 1743-1767.
- [17] A.C. Crossland, G.E. Thompson, C.J.E. Smith, H. Habazaki, K. Shimizu, P. Skeldon, Formation of manganese-rich layers during anodizing of Al-Mn alloys, *Corrosion Sci.*, 41 (1999) 2053-2069.
- [18] J.L. Murray, A.J. Mcalister, R.J. Schaefer, L.A. Bendersky, F.S. Biancaniello, D.L. Moffat, Stable and Metastable Phase-Equilibria in the Al-Mn System, *Metall Trans A*, 18 (1987) 385-392.
- [19] S. Ruan, C.A. Schuh, Electrodeposited Al-Mn alloys with microcrystalline, nanocrystalline, amorphous and nano-quasicrystalline structures, *Acta Mater.*, 57 (2009) 3810-3822.
- [20] B. Grushko, G. Stafford, Phase formation in electrodeposited and thermally annealed Al-Mn alloys, *Metall. Trans. A*, 21 (1990) 2869-2879.
- [21] T.P. Moffat, G.R. Stafford, D.E. Hall, Pitting Corrosion of Electrodeposited Aluminum - Manganese Alloys, *J. Electrochem. Soc.*, 140 (1993) 2779-2786.
- [22] J. Zhang, W. Zhang, C. Yan, K. Du, F. Wang, Corrosion behaviors of Zn/Al-Mn alloy composite coatings deposited on magnesium alloy AZ31B (Mg-Al-Zn), *Electrochim. Acta*, 55 (2009) 560-571.
- [23] G.S. Frankel, R.C. Newman, C.V. Jahnes, M.A. Russak, On the Pitting Resistance of Sputter - Deposited Aluminum Alloys, *J. Electrochem. Soc.*, 140 (1993) 2192-2197.
- [24] M. Reffass, C. Berziou, C. Rebere, A. Billard, J. Creus, Corrosion behaviour of magnetron-sputtered Al_{1-x}Mn_x coatings in neutral saline solution, *Corrosion Sci.*, 52 (2010) 3615-3623.
- [25] X.J. Liu, I. Ohnuma, R. Kainuma, K. Ishida, Thermodynamic assessment of the Aluminum-Manganese (Al-Mn) binary phase diagram, *J. Phase Equilib.*, 20 (1999) 45-56.

- [26] S. Ruan, C.A. Schuh, Mesoscale structure and segregation in electrodeposited nanocrystalline alloys, *Scripta Mater.*, 59 (2008) 1218-1221.
- [27] W. Cai, C.A. Schuh, Tuning nanoscale grain size distribution in multilayered Al-Mn alloys, *Scripta Mater.*, 66 (2012) 194-197.
- [28] M. Akhoondan, A.A. Sagues, Corrosion Mechanism of Aluminized Steel in Limestone Backfill, *Corrosion*, 69 (2013) 1147-1157.
- [29] M. Stern, A.L. Geary, Electrochemical Polarization: I. A Theoretical Analysis of the Shape of Polarization Curves, *J. Electrochem. Soc.*, 104 (1957) 56-63.
- [30] D.A. Jones, Principles and prevention of corrosion, New York : Macmillan Pub. Co. ; Toronto : Collier Macmillan Canada ; New York : Maxwell Macmillan International Pub. Group, c1992.1992.
- [31] A.A. Sagüés, S.C. Kranc, E.I. Moreno, The time-domain response of a corroding system with constant phase angle interfacial component: Application to steel in concrete, *Corrosion Sci.*, 37 (1995) 1097-1113.
- [32] J.R. Scully, D.C. Silverman, M.W. Kendig, Electrochemical impedance : analysis and interpretation, Philadelphia : ASTM, c1993.1993.
- [33] J.A. González, V. López, A. Bautista, E. Otero, X.R. Nóvoa, Characterization of porous aluminium oxide films from a.c. impedance measurements, *J. Appl. Electrochem.*, 29 (1999) 229-238.
- [34] E. McCafferty, The Electrode-Kinetics of Pit Initiation on Aluminum, *Corrosion Sci.*, 37 (1995) 481-492.
- [35] D. Kek Merl, P. Panjan, J. Kovač, Corrosion and surface study of sputtered Al-W coatings with a range of tungsten contents, *Corrosion Sci.*, 69 (2013) 359-368.
- [36] J.E. Sweitzer, G.J. Shiflet, J.R. Scully, Localized corrosion of Al₉₀Fe₅Gd₅ and Al₈₇Ni_{8.7}Y_{4.3} alloys in the amorphous, nanocrystalline and crystalline states: resistance to micrometer-scale pit formation, *Electrochim. Acta*, 48 (2003) 1223-1234.
- [37] W. Li, H.L. Su, J. Yue, Effects of crystallization on corrosion resistance and electron work function of Zr₆₅Al_{17.5}Cu_{17.5}Ni₁₀ amorphous alloys, *Philos. Mag. Lett.*, 93 (2013) 130-137.
- [38] S.Y. Ruan, K.L. Torres, G.B. Thompson, C.A. Schuh, Gallium-enhanced phase contrast in atom probe tomography of nanocrystalline and amorphous Al-Mn alloys, *Ultramicroscopy*, 111 (2011) 1062-1072.
- [39] G.Z. Meng, L.Y. Wei, T. Zhang, Y.W. Shao, F.H. Wang, C.F. Dong, X.G. Li, Effect of microcrystallization on pitting corrosion of pure aluminium, *Corrosion Sci.*, 51 (2009) 2151-2157.
- [40] I. Matsui, S. Ono, Y. Takigawa, T. Uesugi, K. Higashi, Fabrication of bulk nanocrystalline Al electrodeposited from a dimethylsulfone bath, *Mat. Sci. Eng.: A*, 550 (2012) 363-366.

Tables

Table 1. Summary of composition and microstructure results of as-deposited Al and Al-Mn alloys.

Alloy ID	Mn concentration (at.%)	Lattice constant (Å)	TEM grain size (nm)	Phase
A0	0	4.047	42	nanocrystalline
A5	5.2	4.036	15	nanocrystalline
A11	11.5	4.035	12	nanocrystalline + amorphous
A20	20.5	-	-	amorphous

Table 2. Electrochemical parameters from PD tests of Al and Al-Mn alloys in 0.6 M NaCl. Values shown as average (range).

Alloy ID	Nominal Corrosion					
	β_a (V/decade)	β_c (V/decade)	Nominal i_{corr} (A/cm ²) X10 ⁻⁷	E_{oc} (mV)	Rate (μm/year)	E_{pit} (mV)
A0	-	0.75 (0.17)	8.3 (3.0)	-730 (105)	9.1 (3.3)	-640 (12)
A5	0.23 (0.17)	0.23 (0.10)	0.9 (0.3)	-450 (64)	1.0 (0.4)	-276 (16)
A11	0.67 (0.16)	0.52 (0.25)	4.3 (3.2)	-810 (110)	4.7 (3.5)	-206 (15)
A20	0.35 (0.05)	0.31 (0.26)	0.8 (0.4)	-564 (62)	0.9 (0.5)	-110 (54)

Table 3. Electrochemical parameters from PD tests of Al and Al-Mn alloys in 0.01 M NaCl. Values shown as average (range).

Alloy ID	Nominal Corrosion					
	β_a (V/decade)	β_c (V/decade)	Nominal i_{corr} (A/cm ²) X10 ⁻⁷	E_{oc} (mV)	Rate (μm/year)	E_{pit} (mV)
A0	-	0.28 (0.29)	1.90 (0.50)	-487 (9)	2.1 (0.5)	-419 (38)
A5	0.28 (0.15)	0.21 (0.09)	1.05 (0.08)	-349 (93)	1.1 (0.2)	-
A11	0.49 (0.31)	0.30 (0.11)	1.18 (0.30)	-503 (106)	1.3 (0.3)	-
A20	0.39 (0.26)	0.24 (0.08)	0.66 (0.58)	-466 (172)	0.7 (0.6)	-

List of Figure Captions

Figure 1. Surface SEM images of as-deposited (a) Al, (b) Al-5.2at% Mn, (c) Al-11.5at% Mn, and (d) Al-20.5at% Mn.

Figure 2. XRD line scans of as-deposited Al and Al-Mn alloys.

Figure 3. Bright field TEM images and selected area diffraction (SAD) patterns (insets) of as-deposited (a) Al, (b) Al-5.2at% Mn, (c) Al-11.5at% Mn, and (d) Al-20.5at% Mn.

Figure 4. Typical potentiodynamic polarization curves of Al and Al-Mn alloys after 1 hour immersion in 0.6 M NaCl solution.

Figure 5. Electrochemical parameters (a) E_{pit} , (b) $E_{\text{zero current}}$, (c) E_{oc} , and (d) Nominal corrosion rate of Al and Al-Mn alloys obtained from potentiodynamic polarization tests after 1 hour immersion in 0.6 M NaCl solution.

Figure 6. Typical potentiodynamic polarization curves of Al and Al-Mn alloys after 1 hour immersion in 0.01 M NaCl solution.

Figure 7. Electrochemical parameters (a) E_{pit} , (b) $E_{\text{zero current}}$, (c) E_{oc} , and (d) nominal corrosion rate of Al and Al-Mn alloys obtained from potentiodynamic polarization tests after 1 hour immersion in 0.01 M NaCl solution. Arrows denote tests where current surges otherwise indicative of pitting were not observed during anodic polarization.

Figure 8. Long term evolution of E_{oc} of Al and Al-Mn alloys immersed in 0.01 M NaCl solution. Al was removed at 24 hrs; all other alloys were exposed up to 108 hrs. The error bars represent the range of data.

Figure 9. Photo of corrosion surfaces of Al (left) and Al-20.5 at.% Mn (right) after immersion in 0.01 M NaCl solution. A diffusive light source was used during photography to minimize surface reflection.

Figure 10. Typical Nyquist representation of EIS measurement (scattered data) and model fit (solid lines) of Al and Al-Mn alloys after 3 to 108 hrs immersion in 0.01 M NaCl solution at open circuit potential and 10 mHz minimum data collecting frequency.

Figure 11. Equivalent circuit model used to fit the EIS spectra in Fig.10.

Figure 12. The evolution of magnitudes derived from EIS tests (a) nominal corrosion rate, (b) Y_0 , (c) n_1 , and (d) nominal passive film thickness as a function of immersion time in 0.01 M NaCl solution. For plot clarity; 0.5, 1, 1.5 and 2 hrs data offset in the time axis was applied to A0, A5, A11 and A20 respectively. The error bars represent the range of data.

Figure 13. (a) Summary of nominal corrosion rate as a function of Mn concentration from PD and EIS tests in 0.01 and 0.6 M NaCl after 1–108 hr immersion. (b) Pitting potential as a function of Mn concentration from the current work and Moffat et al. [21], Refass et al. [26], and Zhang et al. [22]. *Solid diamond in (a) represent EIS taken after 108 hr of immersion for all alloys except for pure Al, which is measured at 24 hrs. Red, green, and blue symbols in (b) represent crystalline, dual phase, and amorphous microstructure respectively. The error bars represent the range of data.

1 Figure 14. SEM micrographs of (a) Al after immersion in 0.01 M NaCl solution for 24 hrs, (b)
2 Al-5.2 at.%Mn, (c) Al-11.5 at% Mn, and (d) Al-20.5at.%Mn after immersion in 0.01 M NaCl
3 solution for 108 hrs. Insets in (d) are the post-corrosion EDS maps of image (d).

4 Figure 15. Cross-section SEM micrographs of sample A20 after immersion in 0.01 M NaCl
5 solution for 108 hrs. Bottom left inset shows the enlarged area of box 1.

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