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Electrodeposited Al-Mn Alloys with Microcrystalline, Nanocrystalline, Amorphous and Nano-quasicrystalline Structures

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Al-Mn alloys with Mn content ranging from 0 to 15.8 at.% are prepared by electrodeposition from an ionic liquid at room temperature, and exhibit a remarkably broad range of structures. The alloys are characterized through a combination of techniques, including x-ray diffraction, electron microscopy, and calorimetry. For alloys with Mn content up to 7.5 at.%, increasing Mn additions lead to a decrease in grain size of single-phase microcrystalline FCC Al(Mn). Between 8.2 and 12.3 at.% Mn, an amorphous phase appears, accompanied by a dramatic reduction in the size of the coexisting FCC crystallites to the ~2-50 nm level. At higher Mn contents, the structure nominally appears entirely amorphous, but is shown to contain order in the form of pre-existing nuclei of the icosahedral quasicrystalline phase. Additionally, nanoindentation tests reveal that the nanostructured and amorphous specimens have very high hardnesses that exhibit complex trends with Mn content.

Keywords: Electrodeposition, Aluminum alloys, Nanocrystalline, Quasicrystals, Hardness

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1. Introduction

The binary aluminum-manganese (Al-Mn) system has stimulated much curiosity in the scientific community because of the rich variety of equilibrium and metastable phases it exhibits, which include solid solutions, at least nine intermetallic phases, icosahedral and decagonal quasicrystalline phases, as well as amorphous structures. Interestingly, a great many of these phases can be produced by a single technique, i.e., electrodeposition from acidic chloroaluminate salts [1-13]. While phases predicted by the equilibrium phase diagram have been electrodeposited in the temperature range of 250 to 425°C [6, 8], non-equilibrium phases, such as the quasicrystalline phases, amorphous phase, and supersaturated FCC phase, have been deposited at lower temperatures from 150 to 325°C [3, 4, 6, 7, 9-11].

Despite the significant number of works conducted on electrodeposited Al-Mn alloys [2-14], only a few studies have provided detailed characterization of the deposited structure. In 1966, Read and Shores presented transmission electron diffraction patterns of Al-Mn alloys electrodeposited from a chloroaluminate molten salt electrolyte (AlCl₃-KCl-NaCl-MnCl₂) presumably at 200°C [10]. Their data suggested that for alloys with low Mn content below about 6 at.%, a single FCC phase was deposited, with higher Mn content promoting apparently finer grains. At somewhat higher Mn contents up to about 12 at.%, a second phase coexisted with the FCC phase, as evidenced by an additional diffuse reflection between the first and second rings in the electron diffraction patterns. The authors identified the second phase as the intermetallic compound Al₆Mn. However, because no transmission electron microscope (TEM) images were provided, the grain size and structure, as well as phase distribution of these Al-Mn alloys were not discussed.

Later, Grushko and Stafford carried out structural studies on Al-Mn alloys electrodeposited from AlCl₃-NaCl-MnCl₂ molten salt at 150 °C [2, 4]. Their x-ray diffraction (XRD) results suggested that, similar to the results of Read and Shores, intermediate Mn levels between 6 and 15 at.% led to a second phase coexisting with the FCC Al(Mn) solid solution. However, unlike Read and Shores, Grushko and Stafford identified the second phase as amorphous, due to the broad diffraction halo it exhibited. In these two-phase alloys, increasing the Mn content also caused some broadening of the
dominant XRD peaks for the FCC phase, which might suggest a gradual size reduction of the FCC crystals (although no quantitative grain size measurements were made). Some bright-field TEM images of the duplex structures were presented, but without local area diffraction or dark-field images to identify the phases present.

Takayama and co-workers investigated the local structure and concentration of the two-phase Al-Mn alloys electrodeposited from eutectic molten salts of AlCl$_3$-NaCl-KCl-MnCl$_2$ at 200 °C [11]. Micro-area elemental analysis on deposits containing 5.8, 8.8 and 14.9 at.% Mn provided direct evidence that the amorphous phase was enriched with Mn relative to the crystalline phase. Using high resolution TEM (HRTEM) and electron microbeam diffraction, the authors implied that there was actually one crystalline phase with two distinct morphologies coexisting with the amorphous phase, but the micrographs presented did not clarify the two proposed morphologies. Furthermore, while the micro-area images showed that the local structures of the 5.8, 8.8 and 14.9 at.% Mn alloys were somewhat different, the trends were unclear and only qualitative because of the limited fields of view.

Although the above studies provide some hints about the structural changes that occur as the Mn content rises in Al-Mn electrodeposits, many details are clearly missing for a complete understanding of the duplex structures; the crystal morphology and size remains unclear, as does the spatial distribution of the crystalline and amorphous phases. What is more, the nature of the amorphous phase remains ambiguous as well, especially in light of other studies that hint of possible relationships between the amorphous and quasicrystalline phases: First, Grushko and Stafford found that the amorphous phase deposited at 150 °C transformed into the quasicrystalline phase upon annealing [6]. In a separate study, Grushko and Stafford directly electrodeposited the quasicrystalline phase, instead of the amorphous phase, at a higher deposition temperature of 325 °C [3].

Thus, although Grushko et al. [2, 4] and Takayama et al. [11] have identified an “amorphous” second phase in Al-Mn deposits owing to its broad diffraction halo, this could also correspond to an extremely fine ensemble of quasicrystalline domains [15]. Such “micro-quasicrystalline” (or, more aptly, “nano-quasicrystalline”) structures have been observed in Al-Mn alloys produced by techniques other than electrodeposition, and are indeed characterized by a broad, amorphous-like diffraction halo at the primary...
reflection. For example, Bendersky and Ridder used HRTEM and diffraction to suggest that rapidly-quenched Al-14 at.% Mn “amorphous” droplets might in fact contain nano-quasicrystalline domains smaller than 2-3 nm [16]. Chen and co-workers used a combination of HRTEM and differential scanning calorimetry (DSC) to establish that “amorphous” Al-17 at.% Mn produced by sputtering had a nano-quasicrystalline structure [17-19]. These findings are decidedly relevant for interpretation of the structures formed in electrodeposited Al-Mn alloys where an “amorphous” phase has been frequently observed, and call for renewed study of such electrodeposits.

Our purpose in this paper is to systematically investigate the structure of electrodeposited Al-Mn alloys across a broad range of compositions (from 0 to 16 at.% Mn), through the transition from a microcrystalline to an amorphous structure. We prepare these alloys using a different electrodeposition solution than used in the studies reviewed above, and at a lower temperature (ambient). We present a detailed analysis of structure and composition, using combined analysis by XRD, DSC, TEM, HRTEM and scanning transmission electron microscopy (STEM), and show that the “amorphous” phase in these electrodeposits indeed comprises nanoscale quasicrystalline grains. In addition, we present preliminary studies of the mechanical properties of these electrodeposits, and identify structures with maximum hardness across the range of Mn content studied.

2. Experimental Procedures

Our Al-Mn alloys were prepared through a process of electrodeposition from a non-aqueous ionic liquid. All chemicals were handled in a glove box under a nitrogen atmosphere, with H₂O and O₂ contents below 1 ppm. The organic salt, 1-ethyl-3-methylimidazolium chloride, [EMIm]Cl (>98% pure, from IoLiTec), was dried under vacuum at 60 °C for several days prior to use. Anhydrous AlCl₃ powder (>99.99% pure, from Aldrich) was mixed with [EMIm]Cl in a 2:1 molar ratio to prepare the deposition bath. Prior to deposition, pure Al foil (99.9%) was added to the ionic liquid, and the solution was agitated for several days, in order to remove oxide impurities and residual hydrogen chloride [20, 21]. After filtering through a 1.0 μm pore size syringe filter, a faint yellowish liquid was obtained. The nominal manganese chloride (MnCl₂) concentrations
were varied between 0 and 0.20 mol/L by controlled addition of anhydrous MnCl₂ (>98% pure, from Aldrich) to the ionic liquid; Table 1 lists the various MnCl₂ contents used in this study.

Electropolished copper (99%) was used as the cathode and pure aluminum (99.9%) as the anode. Electrodeposition was carried out at room temperature under galvanostatic conditions at a current density of 6 mA/cm². Alloy sheets of approximately 20 μm thickness were obtained after 4 hours.

Scanning electron microscope (SEM) images of the as-deposited surfaces were obtained using a Leo 438VP SEM, and chemical composition was quantified via energy dispersive x-ray analysis (EDX, X-ray Optics/AAT #31102). Prior to XRD measurements, the copper substrates were removed by dissolution in concentrated nitric acid. X-ray patterns of the free-standing Al-Mn films were obtained using a PANalytical X’Pert Pro diffractometer operating at 45 kV and 40 mA with a Cu-Kα radiation source and Bragg-Brentano parafocusing geometry. Diffraction data was collected over a range of 5 to 130 °2θ with a 0.0167 °θ step size and 60 s count time per step. Data analysis was carried out using the software package MDI Jade 8. After accounting for a linear background profile, each diffraction peak was fitted with a regular Pearson VII function, yielding the position of the peak center and the full width at half maximum. The peak positions were used to refine the unit cell lattice parameters, while the full width at half maximum values were used to estimate the crystallite size via a modified Williamson-Hall method: A Cauchy-Gaussian relationship was used to separate instrumental from intrinsic (i.e., strain plus size) broadening. Strain broadening was approximated by a Gaussian function, while effects of crystallite size were captured with a Cauchy profile [22].

TEM specimens were prepared from the free-standing Al-Mn films by twin-jet electropolishing at 10 V in a 20% solution of perchloric acid in methanol at -60 °C. Selected alloy films were also ion-milled at -80 °C with an ion accelerating voltage of 4 kV and source current of 4 mA (Fischione Model 1010). The TEM specimens were examined using two TEM instruments: a JEOL 200CX and a JEOL 2010F, both of which were operated at 200 kV. The probe area used to obtain the selected area diffraction patterns was 1 μm in diameter. Chemical composition of the different nanostructures
was studied quantitatively by EDX using the JEOL 2010F in STEM mode. A probe size of 1 nm was used and typical acquisition times were 200 s. Inca software was used to process the STEM/EDX data.

Calorimetric measurements of films with 15.8 at.% Mn were carried out in a Perkin-Elmer Diamond DSC under a nitrogen atmosphere. For each measurement, 4.0 mg of free-standing film pieces were sealed in an aluminum pan. Scanning measurements were made at 10 °C/min up to 520 °C. The sample was cooled to room temperature, and then re-heated to 520 °C at the same rate to obtain the baseline heat flow. Isothermal experiments were performed by heating the sample at 10 °C/min to 310 °C and then maintained at 310 °C for 55 minutes before cooling to room temperature. The baseline heat flow was obtained by repeating the isothermal experiment a second time on the same sample. X-ray diffractograms of the alloys subjected to both scanning and isothermal experiments were obtained using the PANalytical X’Pert Pro diffractometer following similar procedures as described earlier. Samples from the isothermal experiment were also observed using TEM (JEOL 2010F).

To evaluate the hardness of the alloys, nanoindentation tests were carried out using a Ubi1 nanoindenter from Hysitron Inc. (Minneapolis, MN) using a diamond Berkovich indenter. Samples were prepared for indentation through a standard regimen of mechanical polishing, to a surface roughness of less than 1 nm. The indentation depth was in all cases significantly less than 1/10th the film thickness, ensuring a clean bulk measurement. Each indentation was carried out with a loading rate of 4 mN/s and the maximum applied load was 10 mN. The instantaneous contact area was determined using the calibrated area function of the Berkovich tip, and hardness was determined using the Oliver-Pharr method [23]. Each reported data point represents an average of at least 36 indentations.

3. Results

In this section we present detailed characterization results on all of the alloys prepared in this study. Rather than refer to the composition of the deposition bath, it is more convenient to label samples with their alloy composition, which is presented in Table 1 based on EDX analysis. Table 1 also assembles quantitative results from our
SEM, XRD, TEM and STEM investigations, along with uncertainty ranges on all of our measured values.

3.1 SEM—Surface Morphology

A series of representative surface morphologies of the deposited alloys are shown in Figure 1. Broadly, two distinct classes of surface morphologies are observed. Alloys with global Mn content below about 7.5 at.% exhibit angular or polyhedral-like structures (Figure 1(a)-(d)), while alloys with higher Mn content exhibit a smoother morphology comprising rounded nodules (Figure 1(e)-(h)). The characteristic lengths of the surface structures are determined using a linear intercept method and the results are shown in Table 1. As the Mn content increases from 0 to 7.5 at.%, the characteristic length of the angular surface structures decreases continually from 14 to 7 µm. For alloys with compositions between 8.2 and 12.3 at.% Mn, the average diameters of the nodules are about 5 µm. For the 15.8 at.% Mn alloy, the nodules are only about 3 µm in diameter.

The faceted and angular structures seen in Figure 1(a)-(d) are characteristic of conventional microcrystalline films, where each angular feature corresponds to a single grain [24]. The rounded nodule structures seen in Figure 1(e)-(h) are commonly observed in nanocrystalline electrodeposits when no organic leveling agents are used in the deposition; in such cases each nodule is a “colony” of many smaller grains [25-27]. The present data thus indirectly suggest that a structural transition from coarse- to fine-grained structures occurs in the vicinity of ~8 at.% Mn; more detailed structural analysis will clarify this point in what follows.

3.2 XRD—phase identification and characteristics

X-ray diffractograms of the as-deposited alloys are shown in Figure 2. For alloys with global Mn content between 0 and 7.5 at.%, we observe peaks that are all consistent with the FCC Al(Mn) solid solution reflections. A broad and low-intensity amorphous-like halo starts to appear at $2\theta \approx 42^\circ$ for the 8.2 at.% Mn alloy, and for alloys with global Mn content between 8.2 and 12.3 at.%, the patterns suggest that the Al-rich FCC phase coexists with an amorphous phase. The percent contribution of the FCC peaks to the total integrated intensities observed in each diffractogram is calculated and tabulated in
Table 1. As the alloy composition increases from 8.2 to 12.3 at.% Mn, the FCC peak contribution decreases from 73 to 21%. For alloys with Mn content between 13.6 and 15.8 at.%, no FCC peaks are observed.

Also evident in Figure 2 is the shift in FCC peak positions as the alloy composition changes. We employ the Jade software to solve for the lattice parameter of each XRD profile; the software explicitly solves and corrects for systematic errors, such as in specimen positioning, and then uses the refined peak positions to obtain a least-squares fit for the lattice parameter. Figure 3 shows the lattice parameter of the FCC phase as a function of global Mn content of the alloys. As the Mn content increases from 0 to 7.5 at.%, the lattice parameter decreases from 4.049 to 4.005 Å. Beyond this point, for the two-phase alloys, the opposite trend is observed: increasing the global Mn content from 8.2 to 12.3 at.% causes the lattice parameter to increase from 3.996 to 4.044 Å.

As shown in Figure 2, for alloys with Mn content between 0 and 7.5 at.%, the FCC peaks are narrow. Thus, instrumental broadening effects dominate and the modified Williamson-Hall method is insufficiently resolved to determine the grain sizes of these alloys, which are greater than about 100 nm. On the other hand, the two-phase alloys with Mn content between 8.2 and 12.3 at.% exhibit significant FCC peak broadening, which increases with Mn content. Over this compositional range, the XRD grain sizes of these alloys, as tabulated in Table 1, decrease from 19 to 3 nm.

3.3 TEM—phase distribution and structure

TEM samples that were jet-polished exhibited similar features to the ion-milled ones, and we conclude that sample preparation did not significantly alter the microstructure of the alloys. Bright field images and electron diffraction patterns of alloys with compositions ranging from 7.5 to 15.8 at.% Mn are shown in Figure 4.

The bright field image of an alloy with 7.5 at.% Mn (Figure 4(a)) shows that the grains have characteristic sizes between 3 and 10 µm, in line with the ~7 µm surface features seen in the SEM in Figure 1(a). The electron diffraction pattern exhibits discrete spots consistent with a single phase FCC crystal structure. The zone axis of the electron diffraction pattern in Figure 4(a) is [111].
As shown in the bright field image in Figure 4(b), an 8.2 at.% Mn alloy consists primarily of grains that are approximately 40 nm in diameter. The rings in the electron diffraction pattern, as shown in Figure 5(a) for better clarity, are indexed consistently with an FCC crystal structure. The spottiness of the rings confirms that the FCC phase consists of small grains. However, unlike a conventional grain structure, these grains are apparently embedded in a matrix; rather than being separated by grain boundaries, they are separated by a network of matrix ligaments about 10 nm thick. At first glance, it might appear that what we term the “matrix” or “network” region in this system is amorphous, as suggested by the diffuse ring between the (111) and (200) reflections in the diffraction pattern (see Figure 5(a)). However, HRTEM reveals that the matrix region is more complex than this: a typical high resolution image is shown in Figure 6, revealing that the ~10 nm thick matrix region between large FCC grains (which are labeled ‘A’ in Figure 6) comprises small (~3 nm) crystallites (labeled ‘B’) in a featureless amorphous-like field (labeled ‘C’). We conclude that the 8.2 at.% Mn alloys consists of two phases- an amorphous-like phase and a FCC phase that has bimodal grain size distribution with peaks at ~40 nm and ~3 nm; the larger grains are surrounded by a network of the amorphous-like phase containing the smaller grains.

The bright-field image of a 9.2 at.% Mn alloy is shown in Figure 4(c). We observe domains that are between 20 and 40 nm in diameter, again surrounded by a network region that is about 10 nm thick. However, unlike the 8.2 at.% Mn sample, in this sample the domains do not appear to be crystalline, and we can more clearly see a population of small crystallites located in the network structure, with sizes in the range of 5 – 10 nm. HRTEM image of the domains and their surrounding network structure is shown in Figure 7(a). Here the domains are outlined in bold and labeled ‘D’, and seem featureless. A higher magnification image of the network region, taken from the region denoted by dotted lines in Figure 7(a), is shown in Figure 7(b). Figure 7(b) provides compelling evidence that the network comprises mainly small crystallites (labeled ‘E’). The spots that constitute the FCC rings in the electron diffraction pattern of the 9.2 at.% Mn alloy (Figure 5(b)) are finer than in the 8.2 at.% Mn alloy (Figure 5(a)), which is consistent with the smaller grain sizes observed in the bright field images. In addition, the electron diffraction pattern in Figure 5(b) also shows that the intensity of the diffuse
ring relative to the FCC rings is higher than that shown in Figure 5(a), suggesting a higher amorphous phase fraction in line with the XRD results in Table 1. In short, the 9.2 at.% Mn alloy apparently also has two phases, comprising an amorphous-like phase that exists as large convex domains, embedded in a network of small FCC crystals of about 5 to 10 nm diameter.

Bright field images of the 10.8 and 12.3 at.% Mn alloys are shown in Figures 4(d) and (e). The features observed in these images are very similar to those seen in Figure 4(c): amorphous domains are surrounded by a network structure comprised mainly of crystallites. As the alloy composition increases from 10.8 to 12.3 at.% Mn, the average crystallite diameter decreases to just a few nm. The electron diffraction patterns of both alloys (Figure 5(c) and (d)) consist of continuous FCC rings and the diffuse halo, consistent with a duplex structure of fine grains and an amorphous-like phase. As the Mn content increases from 10.8 to 12.3 at.%, the relative intensity of the diffuse ring increases, thus suggesting an increasing amount of amorphous-like phase, which agrees with the XRD results in Table 1.

For alloys with compositions above 13.6 at.% Mn, the TEM images appear featureless. Figure 4(f) shows a HRTEM image of an as-deposited 15.8 at.% Mn alloy. No lattice fringes are observed, indicating that the alloy lacks long-range order, thus resulting in the halo observed in the electron diffraction pattern.

### 3.4 STEM—phase composition

As noted above, for a range of Mn contents between about 8.2 and 12.3 at.%, we observe two-phase structures that comprise larger grains or domains embedded in a matrix or network. For these alloys, the local chemical compositions of the domains and the network regions are analyzed using STEM/EDX and the results are shown in Figure 8.

For an 8.2 at.% Mn alloy, recall that the ~40 nm diameter “domains” were in fact FCC solid solution crystals (see Figure 4(b) and the regions labeled ‘A’ in Figure 6). In Figure 8 we now see that these larger grains are depleted of Mn, whereas the featureless regions on the network (labeled ‘C’ in Figure 6) are enriched with Mn. Their compositions are 7.9 and 9.0 (±0.2) at.%, respectively. For alloys with higher global Mn
content, the partitioning tendency of Mn is reversed: the domains, which are apparently amorphous (see Figure 4(c) and regions ‘D’ in Figure 7(b)) are enriched with Mn, while the surrounding network of crystallites is depleted of Mn. As the global Mn content increases from 9.2 to 12.3 at.%, the Mn content of the larger domains increases from 10.1 to 13.4 at.% and the composition of the network increases from 7.5 to 9.2 at.%. In all of the data collected in Figure 8, there is thus one common feature: the microstructures are duplex, and the amorphous-like regions are always found to have an enrichment of Mn, while the crystalline regions are depleted of Mn. The specific arrangement of these phases is different from lower to higher Mn content, but the tendency of Mn to preferentially populate the amorphous regions is consistent.

3.5 DSC—structure of the amorphous phase

The scanning calorimetry signal from a 15.8 at.% Mn sample at a heating rate of 10 °C/min is shown in Figure 9(a), exhibiting a first exothermic peak at 341 °C and a second at 463 °C. The enthalpy of the first transformation is 900 J/mol, much smaller than that of the second transformation at 2770 J/mol. Qualitatively, we note that both peaks are asymmetric, and whereas the rising edge of the first peak is steeper, the converse is observed for the second peak. Figure 9(b) shows the calorimetric signal from another 15.8 at.% Mn sample that is subject to isothermal heat treatment at 310 °C—just at the onset of the first transformation—where a monotonically decaying signal is observed. The total heat evolved is 840 J/mol, which is close to that of the first crystallization event observed in the scanning experiment.

X-ray diffractograms of samples subjected to these thermal cycles in the DSC are shown in the bottom panel of Figure 10 along with data for an as-deposited specimen. Along the top of this figure the expected peak positions and relative intensities of the icosahedral and orthorhombic Al₆Mn phases are shown, as obtained from the x-ray powder diffraction files (PDF#00-044-1195 and 00-041-1285 respectively) [28]. The diffractogram of the as-deposited alloy, labeled (a), exhibits a broad halo at 2θ ≈ 42°, and another lower intensity hump at 2θ ≈ 80°. After isothermal annealing at 310 °C, however, a series of additional broadened peaks appear at positions that correspond well to the icosahedral Al₆Mn produced by rapid quenching [29]. The diffractogram (labeled (c)) of
the sample that was heated to 520 °C during the scanning experiment (i.e., across both exothermic reactions) exhibits sharp peaks that are consistent with orthorhombic Al₆Mn [30].

Figure 11 shows a HRTEM image of a 15.8 at.% Mn sample that was subject to isothermal annealing at 310 °C. Lattice fringes are clearly evident and the grain size is approximately 2 nm. This value agrees well with the results of a Williamson-Hall analysis of the XRD data in Figure 10 (curve b), which yields a grain size for the icosahedral phase of ~2 nm. The electron diffraction pattern, as shown in Figure 11 exhibits continuous rings. The diffraction peak positions are similar to those of icosahedral Al-Mn particles studied by Bendersky and Ridder [16]. Figure 12(a) and (b) show the electron diffraction patterns of the as-deposited and annealed samples respectively. We note that the diffraction pattern of the annealed sample consists of rings that are sharper and more discernible than that of the as-deposited sample, and which are consistent with the reflections expected for the icosahedral phase.

3.6 Nanoindentation—hardness

Figure 13 shows the measured hardness values of the various deposits, in comparison to their structural length scales. The hardness of pure microcrystalline electrodeposited Al is about 1 GPa. For the single FCC phase alloys, increasing the Mn content from 0 to 7.5 at.% Mn causes the hardness to increase from 1 to 2.8 GPa. At 8.2 at.% Mn, hardness reaches a local maximum value of 5.2 GPa. Further increase in Mn content causes the hardness to decrease to a local minimum of 4.3 GPa near 10.8 at.% Mn, followed by an increase to 5.4 GPa for our sample with highest Mn content.

4. Discussion

The above results show the following general trend as Mn increases in our deposits. First, at low Mn levels below about 7.5 at.%, the deposits are FCC and have micron-scale grains that decrease in size with Mn content. Second, at intermediate Mn levels (between 8.2 and 12.3 at.%) we see complex dual-phase structures involving nano-scale FCC crystallites and domains of amorphous-like material. Finally, at sufficiently high Mn levels (above 13.6 at.%) we see only the amorphous-like phase, which
transforms first to a quasicrystalline phase and then intermetallic Al₆Mn upon heating. In the following sections, we discuss in more detail the phases and microstructures in these alloys.

4.1 Phase composition

Even though the maximum equilibrium solubility of Mn in Al is 0.62 at.% [31], Figure 2 shows that our electrodeposited alloys exhibit a single FCC phase up to about 7.5 at.% Mn. Such extended solubility is frequently found in electrodeposited alloys because of the non-equilibrium processing conditions [1]. For our single FCC phase alloys, the decrease in lattice parameter with increasing Mn content, as shown in Figure 3, is indicative of Mn (which has a smaller Goldschmidt radius than Al by about 11%) being substitutionally incorporated into the Al lattice. Figure 3 also shows that our results are in very good quantitative agreement with those obtained for melt-spun alloys [32] and alloys electrodeposited from AlCl₃-NaCl electrolyte at 150 °C [4]. The following equation relates the lattice parameter, $a$ (Å), of our single phase alloys to the global atomic fraction of Mn, $X_{Mn}$:

$$a = a_0 - bX_{Mn},$$

(1)

where $a_0$ is the lattice parameter of pure Al (4.049 Å) and $b = 0.640$ Å.

At the first appearance of the amorphous phase at 8.2 at.% Mn, the FCC lattice parameter is the lowest at 3.996 Å. While this result may suggest that the FCC phase is the most super-saturated at this composition, we note that the microstructure of an 8.2 at.% Mn alloy exhibits two types of crystallites, which differ not only in their grain size, but also in their local environment (Figure 4(b) and 6). Thus, these two types of crystalline grains may have different lattice parameters. Additionally, the bimodal grain size distribution may have implications on the XRD peak locations, which may thus affect the accuracy of our lattice parameter calculations.

For even higher Mn contents ($\geq 9.2$ at.%), Figure 3 reflects an increasing lattice parameter of the FCC phase. We suggest that this increase is a result of Mn partitioning into the amorphous-like phase (cf. Figure 8), depleting from the FCC crystallites and thus reducing their lattice parameter according to Equation (1). Using our STEM data, we
compare the extent of Mn enrichment in the amorphous phase by introducing a normalized enrichment parameter, \( \eta \), as:

\[
\eta = \left( \frac{X_{\text{amorphous}}^{\text{Mn}} - X_{\text{FCC}}^{\text{Mn}}}{X_{\text{Mn}}} \right),
\]

where \( X_{\text{amorphous}}^{\text{Mn}} \) and \( X_{\text{FCC}}^{\text{Mn}} \) correspond to the atomic fraction of Mn in the regions that consist primarily of the amorphous and FCC phases respectively. The results are shown in Table 1. As the global Mn content increases from 8.2 to 12.3 at.%, the Mn enrichment in the amorphous phase increases from 0.13 to 0.34.

Our results above are broadly in line with those for alloys electrodeposited at 150 °C by Grushko and Stafford [2, 4]. They observed a single FCC phase up to 5.9 at.% Mn, and at 8.7 and 11.9 at.% Mn found an amorphous phase co-existing with an FCC phase depleted in Mn [1, 4]. Whereas these authors only inferred the composition of the FCC crystals from the inflection in lattice parameter measurements (cf. Figure 3), here we have more direct confirmation of Mn partitioning from our STEM data and the values of \( \eta \) in Table 1. Because Grushko and Stafford did not examine alloys of composition between 5.9 and 8.7 at.% Mn, we are not able to precisely compare the composition at which the alloys transition from a single crystalline phase to a duplex structure, although it is clearly in the general vicinity of the transition that we observe in our deposits.

4.2 “Amorphous” phase character

The shapes of the peaks in the DSC signal obtained from heating the 15.8 at.% Mn alloy (Figure 9(a)) give an indication that the first and second exotherms correspond to different types of transformation events. Greer [33] and Chen et al. [17-19] modeled the nucleation-and-growth process during such a linear heating profile using a modified Johnson-Mehl-Avrami equation. They showed that for a transformation involving nucleation and growth of a new phase, the trailing edge of the exothermic peak should be steeper than the leading edge. On the other hand, for the case of phase growth from pre-existing nuclei, the leading edge should be steeper than the trailing edge. With these results in mind, examination of Figure 9(a) suggests that the first exotherm corresponds to a transformation that proceeds by growth from pre-existing nuclei, whereas the second
corresponds to a nucleation-and-growth process. Additionally, the enthalpy of the first transformation event (900 J/mol) is unusually small compared to that of crystallization from a truly amorphous metal (usually a few kilojoules per mole), which is consistent with the first event being one of growth from pre-existing nuclei [18, 34].

While scanning calorimetric experiments provide qualitative hints on the nature of a transformation event, isothermal experiments such as those in Figure 9(b) allow unambiguous determination of the transformation type. Again, the work of Chen et al. [17-19] provides some guidance in the interpretation: for nucleation and growth a peak should be observed in the heat flow at non-zero time due to the formation of nuclei, whereas during a growth process from pre-existing nuclei, a monotonically decreasing signal should be observed. Thus, the monotonically decreasing signal obtained upon annealing our 15.8 at.% Mn alloy (Figure 9(b)) provides compelling evidence that our as-deposited alloy, nominally called “amorphous” based on diffraction data, in fact contained pre-existing nuclei.

Our microscopic and XRD evidence also conform to the above interpretation. In the as-deposited state, HRTEM reveals an amorphous-like structure, whereas after isothermal annealing at 310 °C pre-existing nuclei grew to a clearly discernible size in the range of 1-3 nm (see Figure 11). What is more, these grains exhibit diffraction patterns consistent with the icosahedral phase (Figure 10(b), 11 and 12(b)). Thus, these HRTEM and DSC results together establish that our as-deposited 15.8 at.% Mn is seeded with pre-existing quasicrystalline nuclei that grow into nano-quasicrystalline domains upon annealing at low temperatures (~310 °C). Annealing at higher temperatures leads to the nucleation-and-growth transformation to orthorhombic Al$_6$Mn crystalline grains.

Our results present a clear parallel to those of Chen and co-workers, who carried out a calorimetric study on magnetron sputtered Al-17 at.% Mn films [17-19]. In their scanning experiments, two exotherms qualitatively similar to ours were observed. The first exotherm obtained in both that study and ours have similar peak temperatures (341 °C and 337 °C) and heats of transformation (900 J/mol and 1046 J/mol, respectively). Monotonically decreasing signals were obtained upon isothermal annealing of their samples in the vicinity of the first exothermic peak, and their annealed samples exhibited diffraction patterns consistent with the icosahedral phase. The structure of the
“amorphous” phase in the sputtered films of Chen et al. is thus believed to be essentially similar to that seen in our electrodeposited films.

We note that when Grushko and Stafford thermally annealed their “amorphous” 16 at.% Mn alloy that was electrodeposited at 150 °C, they also observed the formation of very small icosahedral grains, which transformed to intermetallics with further annealing [6]. However, to our knowledge, our results here represent the first time that the apparently “amorphous” structure of Al-Mn electrodeposits has been established as containing pre-existing nanoquasicrystalline nuclei. Additionally, our observation that these pre-existing nuclei grow into clearly discernible quasi-crystals at about 300° C helps to unify prior reports in the literature, where deposition at 325° C directly yielded the quasicrystalline phase [3], while deposition at lower temperatures led to an apparently amorphous phase [1, 2, 4]. In combination with these literature results, our analysis suggests that quasicrystalline order is in fact preferred at all deposition temperatures; below about 300° C, the quasicrystalline nuclei are sufficiently small that the structure appears amorphous, while above this temperature they grow to the ~2-3 nm size required to discern them in diffraction data and HRTEM images.

4.3 Structure-composition relationship

The structures produced in this study span an impressive range of length scales, ranging from supermicron FCC grains (e.g., Figure 1(a)) to extremely fine nanocrystals of dimension ~3 nm (e.g., Figure 6). No single characterization technique can be used to assess grain/domain sizes across this entire range, so in this section we compile our measurements from various techniques, to develop a picture of how the characteristic structural length scales change with composition.

Across the entire range of composition examined, the size of the FCC solid solution phase, including grains and embedded crystallites, decreases as the global Mn content increases, as shown in Figure 13(a). For the single phase alloys, as the Mn content increases from 0 to 7.5 at.%, the average crystallite size decreases from 15 to 7 μm. At around 8 at.%, the grain size decreases drastically from several microns to nanometer-scale dimensions, and it is also at this composition that we observe a bimodal distribution of crystallites (~40 and 3 nm). At higher Mn content, from 9.2 to 12.3 at.%,
the average crystallite size decreases further to about 4 nm. Beyond this point, the apparently amorphous structure contains nano-quasicrystalline nuclei, which must be of ~1 nm or finer scale.

The monotonic relationship between grain size and solute content of our single phase alloys (i.e., 0 to 7.5 at.%) has also been observed in other alloy systems, such as Ni-W and Ni-P [35, 36], where the observed trend has been attributed to grain boundary segregation effects (i.e. because solute segregation to the grain boundaries reduces the grain boundary energy, increasing the solute content allows promotes finer grains [37, 38]). In light of this possibility, we carried out STEM analysis of the grain boundaries and grain interior regions for some of our single phase alloys. We also used Auger electron spectroscopy to compare the Mn content at the intergranular and transgranular regions using standard procedures [39]. Both techniques yielded similar results: there was insignificant variation in composition between the bulk and grain boundaries. We conclude that the progressive refinement of structure as summarized in Fig. 14 is not principally driven by segregation of solute to intergranular regions.

On the other hand, the structure-composition relationship may be related to nucleation kinetics at the electrode. Stafford carried out linear sweep voltammetry in a 2:1 mole ratio AlCl₃:NaCl electrolyte and found that as the content of MnCl₂ in the electrolyte increases, the cathodic overpotential becomes more negative [7]. A similar trend was also observed in the AlCl₃-NaCl-KCl electrolyte by Hayashi [40]. Assuming that our ionic liquid electrolyte behaves similarly, an increase in MnCl₂ content in the electrolyte would drive the cathodic overpotential more negative, which in turn favors the nucleation of new grains, and thus a finer grain size, during electrodeposition [41-43].

Upon the appearance of a second phase at higher Mn content (> 8 at.%), the FCC grain size decreases drastically from microns to nanometers. Recall that the structures of all the two-phase alloys exhibit one similarity: they all contain domains that are between 10 and 25 nm in radius, and surrounded by a network or matrix structure. We speculate that this recurring characteristic length scale may be associated with the characteristic diffusion distance, L, for atoms on the surface of the growing film. Given a deposition rate of 5 µm/hr, we take \( \tau \approx 0.2 \) s as a characteristic time to deposit one monolayer, and for Al surface self-diffusion, a typical diffusivity \( D \approx 4 \times 10^{-12} \) cm²/s at ambient
temperature [44]. With these values we approximate a diffusion length of \( L \approx 2\sqrt{D\tau} = 18 \text{ nm} \), very close to the characteristic radius (10-25 nm) of the domains in our deposits. Interestingly, in Grushko and Stafford’s studies, similar domains were also observed in a 12 at.% alloy, but with a larger characteristic domain size ranging from 125 to 250 nm in radius [1, 2, 4]. Because Grushko and Stafford used higher current densities (as much as ten times higher), we approximate \( \tau \approx 0.02 \text{ s} \), and given their higher deposition temperature of 150 °C, \( D \approx 3\times10^{-9} \text{ cm}^2/\text{s} \). The approximate surface diffusion length in this case is about 150 nm, again in good agreement with the experimental scale of the structural domains. These considerations offer some support for the notion that phase separation in these alloys is a surface phenomenon that occurs during electrodeposition, and that the surface diffusion length governs the domain size of two-phase electrodeposits (cf. Figure 4(b)-(e)).

4.4 Hardness of the deposits

It is beyond our scope to provide a detailed mechanistic interpretation of the hardness trends seen in Figure 13(b), especially in light of the fact that many of our deposits have extremely complex duplex structures, the hardness of which is not simply predicted. However, since these measurements are, to our knowledge, the first mechanical property data presented for Al-Mn alloys electrodeposited from ionic liquid, we offer a few observations about our results.

First, the initial increase in hardness from 0 to 7.5 at.% Mn covers the range of compositions where the alloys remain single-phase FCC solid solutions and the grain size decreases; the strength increase can likely be attributed to the combined effects of solution strengthening and the Hall-Petch effect. Second, within the composition range of 13.6 to 15.8 at.% Mn, the alloys are “amorphous” (containing nanoquasicrystalline nuclei), and hardness increases with Mn content. The role of solute content on the strength of amorphous phases is neither simple nor well understood, but the negative heat of mixing of our system indicates that Mn additions increase the average bond strength in the alloy, which, all other things being equal, would promote higher hardness. Other amorphous Al alloys are hardened by increases in solute content in a similar way [45-47]. Changes in the degree of chemical order (the density of nano-quasicrystalline nuclei)
with Mn content are also plausible, and could lead to strengthening in the manner well-known for amorphous metals containing nanocrystals [48-50]. A similar argument could explain the decrease in hardness from 8.2 to 10.8 at.% Mn, over which range the structure is essentially an amorphous/nanocrystal composite, but with a decreasing volume fraction of reinforcing nanocrystalline particles at higher Mn levels. In any event, it is interesting to observe that the complex changes in structure we observe with Mn content in these alloys are mirrored by unusual trends in hardness; the suggestion that there may be local optimums in the composition space (e.g., at ~8 at.% Mn) is also of practical interest.

5. Conclusions

We have presented a detailed microstructural study of Al-Mn alloys electrodeposited from an ionic liquid at room temperature. Additionally, we have provided the first measurements of hardness in Al-Mn electrodeposits across a broad range of structural conditions. Using a combination of characterization techniques, we have broadly identified three structural regimes, defined by the alloy Mn content:

(a) 0 to 7.5 at.% Mn: These alloys are microcrystalline FCC solid solutions exhibiting rough angular surface morphologies. As the Mn content increases over this range, the grain size decreases from 15 to 7 µm due to kinetic effects on deposition, and the hardness increases from about 1.0 to 2.8 GPa.

(b) 8.2 to 12.3 at.% Mn: These deposits have a smooth, nodular surface structure, and comprise nanometer-scale crystals of the FCC solid solution phase coexisting with an amorphous phase. The amorphous phase is Mn-enriched, and its volume fraction increases with the global Mn content. The phases are arranged as domains of one phase embedded in a network or matrix of the other; the characteristic radius of the domains is about 10-25 nm, which is consistent with the surface diffusion length during electrodeposition. These alloys exhibit a local peak in hardness of 5.2 GPa at 8.2 at.%, where the FCC phase is the majority phase.

(c) 13.6 to 15.8 at.% Mn: These alloys exhibit a single amorphous phase, whose hardness increases from 4.8 to 5.5 GPa as Mn content rises. For the first time, we confirm that this apparently amorphous phase contains pre-existing nano-quasicrystalline nuclei in the as-deposited state; these nuclei grow into nano-quasicrystals at about 300
°C. This observation unifies prior reports in the literature, where deposition at temperatures above 300° C directly yields the quasicrystalline phase, while deposition at lower temperatures leads to an amorphous phase.

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References

Captions

Table 1 Summary of the various electrolytic compositions used in this study, and the deposits produced with them. The global Mn content is measured by EDX; the size of surface features is measured from SEM images; the area % of FCC peaks is calculated from the X-ray diffractograms; average grain size is reported from both XRD and TEM measurements; the extent of Mn enrichment in the amorphous phase, as determined by STEM, is reported according to the formula of Eq. (2).

Figure 1 SEM images of as-deposited Al-Mn alloys with global Mn content as shown in the lower-left corner of each panel. Note the transition from facetted features in images (a)-(d) to rounded nodules in images (e)-(h).

Figure 2 X-ray diffractograms of as-deposited Al-Mn alloys, the compositions of which are shown at the right. Locations of the FCC Al(Mn) reflections are shown at the top. Note also the emergence of a broad amorphous halo at ~42 °2θ for compositions above 8.2 at%.

Figure 3 Lattice parameter of the FCC phase, as calculated from peak positions in the X-ray diffractograms of Figure 2. Also shown for comparison are data obtained for Al-Mn alloys electrodeposited at 150 °C by Grushko and Stafford [4], and for melt-spun alloys by Schaefer et al [32].

Figure 4 Bright-field TEM images and electron diffraction patterns of as-deposited alloys with global Mn content as shown in the lower-left corner of each panel. Note the transition from micron-size grains in image (a) to nanocrystalline grains in images (b)-(e). Note also that images (b)-(e) show ~20-50 nm convex domains surrounded by a matrix or network structure.

Figure 5 Electron diffraction patterns of two-phase alloys with global Mn content labeled in each panel. Peak positions of the sharp reflections are indexed to be consistent with FCC Al(Mn), as shown in panel (a). Note that the relative intensity of the broad halo, whose peak position is located between the (111) and (200) reflections, increases as the global Mn content increases.

Figure 6 HRTEM image of an 8.2 at.% Mn alloy, showing the “matrix” or “network” region between two large grains that are labeled ‘A’. This region comprises small ~3 nm crystallites (some of which are circled and labeled ‘B’) embedded in an amorphous-like field (labeled ‘C’).

Figure 7 HRTEM images of a 9.2 at.% Mn alloy, showing domains and the surrounding network structure in (a), where the domains are outlined in bold and labeled ‘D’, and appear featureless. A higher magnification image of the surrounding network region, taken from the region denoted by dotted lines in (a), is shown in (b). The network region comprises mainly small crystallites (labeled ‘E’).
Figure 8 STEM results comparing local compositions of domain and network regions of the two-phase alloys, along with a dashed line showing the expected composition for a homogeneous alloy. The amorphous phase is located in the network regions for the 8.2 at.% Mn alloy, but in the domain regions for alloys with higher Mn contents. Thus, Mn preferentially partitions to the amorphous phase for all these alloys.

Figure 9 (a) A Scanning-mode DSC trace showing the two exothermic peaks observed when a 15.8 at.% Mn alloy was heated from 30 °C to 520 °C at 10 °C/min. Using the dotted lines as baselines, the enthalpies of the two transformation events were 900 J/mol and 2770 J/mol respectively. (b) The isothermal DSC output for a 15.8 at.% Mn alloy annealed at 310 °C for 55 minutes; the total heat evolved was 840 J/mol.

Figure 10 X-ray diffractograms of 15.8 at.% Mn samples (a) in the as-deposited state, (b) after isothermal treatment at 310°C for 55 minutes and (c) after being heated from 30 °C to 520°C at 10 °C/min. For comparison, the top panel shows peak positions and relative intensities of icosahedral Al₆Mn produced by rapid quenching [29], while the second panel shows those for orthorhombic Al₆Mn [30].

Figure 11 HRTEM image and electron diffraction pattern of a 15.8 at.% Mn alloy after isothermal annealing at 310°C for 55 minutes. As compared to the as-deposited condition, which exhibited an amorphous-like field under the similar imaging conditions (Fig. 4(f)), this specimen exhibits small regions with clear lattice fringes. Some of the crystallites are outlined in bold; the average grain size is about 2 nm.

Figure 12 Electron diffraction patterns of 15.8 at.% Mn alloys (a) in the as-deposited state and (b) after isothermal annealing at 310 °C for 55 minutes. Note the appearance of additional reflections in (b), which are indexed as consistent with the icosahedral phase. The arrows indicate the positions of the rings in each panel.

Figure 13 (a) Plot summarizing the grain/crystal size measurements of the FCC solid solution phase as determined by various techniques. Phase compositions of the alloys are labeled at the top of the panel. (b) Plot of hardness vs. alloy composition; notice that the dramatic decrease in grain size at ~8.2 at.% Mn is accompanied by an increase in hardness by about a factor of 2.