Tuning nanoscale grain size distribution in multilayered Al–Mn alloys

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Al–Mnx/Al–Mny multilayers with a wide range of structures ranging from microcrystalline to nanocrystalline and amorphous were electrodeposited using a single-bath method under galvanostatic control from room temperature ionic liquid. By varying the Mn composition by \( \approx 1–3 \) at.% between layers, the grain sizes in one material can be systematically modulated between two values. Control over both the layer structure and the structure within individual layers together offers unique opportunities to optimize multiple properties simultaneously.

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Nanostructured materials have been shown to exhibit high strength, strong strain rate sensitivity, and in some cases work-hardening ability, ductility and damage tolerance [1–5]. These properties, if they could be delivered together, would constitute an ideal target for structural and engineering applications. Unfortunately, there is not generally a single grain size that simultaneously optimizes all of these properties. For example, nanostructured materials with a uniform grain size of about 10 nm are known to optimize strength and rate sensitivity, but do not necessarily optimize strain hardening capacity or toughness [3,4]. Similarly, nanocrystalline grains are beneficial for slowing fatigue crack initiation under cyclic loading, but detrimental in terms of fatigue crack propagation [5]. In order to take full advantage of the tremendous potential of nanostuctured materials, a higher order of microstructure design, combining the various optimum grain sizes for each property, may be needed. Examples of prior work using this strategy include bimodal grain size nanocrystalline materials [6,7], nanotwinned structures that have a characteristic twin spacing considerably different than the grain size [8–10], functionally graded nanocrystalline materials [11,12] and recently, modulated or multilayer nanocrystalline materials [13–15].

Multilayered nanocrystalline materials offer a straightforward means of producing a hierarchy of structures and structural length scales, and in a geometry that is conducive to the deposition technologies that are most pertinent to commercialization of nanocrystalline materials. Additionally, new material properties may also be introduced from the presence of an additional length-scale (layer thickness), the interactions of the constituent materials, as well as the interface properties between nanocrystalline layers. In this paper, we employ a single-bath electrodeposition process, which is a versatile, economical and scalable route to produce complex shapes. During electrodeposition in a properly designed system, composition modulation can be obtained using galvanostatic or potentiostatic control, and the layer thickness can be controlled by monitoring the transferred charge [16]. The recent introduction of room temperature ionic liquids has made it possible to produce high quality dense films from an even wider array of materials (such as Al, Ti and Mg and their alloys, which cannot be electrodeposited from aqueous solutions) with tunable nanostructures [17]. In the Al–Mn system in particular, recent work from our group has shown that alloys with structures ranging from microcrystalline, to nanocrystalline (grain sizes from 100 to as fine as \( \approx 5 \) nm) and to apparently amorphous by X-ray diffraction can all be formed through electrodeposition [18]. In the present work, we leverage the
tunability of this system by using galvanostatic control to create multilayered nanostructured alloys with individual layers of each of these unique structures.

We electrodeposit multilayered Al–Mn$_x$/Al–Mn$_y$ (hereafter referred to as Al–Mn for simplicity) by alternating the deposition between two levels of direct current, 4 and 10 mA cm$^{-2}$, for durations of 144 and 60 s respectively, accumulating to a total deposition time of 4 h. The room temperature ionic liquid electrolyte solution, which contains 1-ethyl-3-methylimidazolium chloride and anhydrous AlCl$_3$ in a molar ratio of 2:1, was prepared as reported in Ref. [18]. Anhydrous MnCl$_2$, incorporated at 0.06, 0.09 and 0.12 mol l$^{-1}$, was then added to the electrolyte to prepare three different baths, used to synthesize three different samples. Pure polycrystalline Cu (99.9%) and Al (99.99%) sheets were used as the cathode (substrate) and anode, respectively, at a separation distance of 2 cm. All experiments were performed in a nitrogen-filled glove box with O$_2$ and H$_2$O concentrations maintained below 1 ppm through combined use of a molecular sieve and a copper catalyst.

Material characterization was performed using scanning electron microscopy (SEM; Helios Nanolab 600 microscope operated at 5 kV), calibrated energy-dispersive X-ray spectroscopy (EDS; Oxford Instruments), and transmission electron microscopy (TEM; JEOL 2010F operated at 200 kV), including selected area diffraction (SAD) and high angle annular dark-field (HAADF) imaging. Cross-sections for SEM observation were prepared by cutting a trench from the sample surface using focused ion beam (FIB; Helios Nanolab 600 dual beam milling system). Cross-section TEM samples were prepared by either a standard lift-out technique in FIB or conventional mechanical preparation followed by ion milling. X-ray diffractometry (XRD; X’Pert PANalytical) of free-standing Al–Mn multilayers was carried out using Cu K$_\alpha$ radiation at 45 kV and 40 mA. Nanoindentation tests were performed on polished cross-sections using a Berkovich tip at 10 mN maximum load with a 1 mN s$^{-1}$ loading rate, using a Hysitron TriboIndenter.

Figure 1 shows SEM images of the surface and cross-sections of the three multilayered Al–Mn samples.

Samples 2 and 3 (prepared at [MnCl$_2$] = 0.09 and 0.12 mol l$^{-1}$ respectively) exhibit very different surface morphologies, comprising rounded nodular “colonies” with average characteristic sizes of 17 and 5 μm, respectively. These features are typical for electrodeposited materials with nanocrystalline structures [19]; their presence is in fact a sign that a much finer nanostructure is likely present. SEM images of cross-sections (Fig. 1b, d and f) clearly indicate the presence of composition modulations in the three samples, where the dark and light contrast correspond respectively to Mn-lean and -rich layers (noted as layers A and B hereafter) grown using 4 and 10 mA cm$^{-2}$ current density respectively; during alloy electrodeposition under galvanostatic control, an increase in current density favors the deposition of the less noble Mn [20]. For all three samples, the typical composition variation between layers A and B is ~1–3 at.% Mn (Table 1).

Cross-sectional TEM images and the corresponding SAD patterns of the three samples are shown in Figure 2. In sample 1, each grain comprises multiple layers of both types A and B with the same crystallographic orientation. XRD analysis of sample 1 confirms the formation of a single face-centered cubic (fcc) phase, indicating the formation of a solid solution of manganese in aluminum far beyond the equilibrium solubility [18,21]. In sample 2, layer A contains fcc nanocrystalline grains of average diameter 52 nm, while layer B comprises a duplex of fcc (with grain size of 21 nm) and amorphous phase, indicated by the presence of a broad halo between (111) and (200) reflections in the SAD pattern (Fig. 2d). In sample 3, fcc nanocrystalline grains...
of average size ~5 nm coexist with an amorphous phase in layer A, while layer B is almost completely amorphous. XRD analysis indicates average fcc phase fractions of 47 and 17% in samples 2 and 3 respectively.

It has been noted that in the Al–Mn system the introduction of the secondary alloying element promotes finer structure, likely through a combination of effects, both thermodynamic and kinetic [18]. The present work confirms that, by increasing local Mn concentration up to 15.9 at.%, grain sizes are tunable over orders of magnitude. What is more, in this work we see that, when the additional length scale of layer thickness is introduced extrinsically through the processing conditions, a noteworthy array of new structures can be produced. Figure 3 summarizes the breadth of the materials produced in this work, focusing on the interplay of the two length scales – grain size and layer wavelength.

We have been able to produce materials in which either of these two scales is larger than the other, and in fact the intersection of the two curves in Figure 3 marks the transition between two classes of materials:

1. When the grain size is larger than the layer wavelength, composition modulations occur within individual crystals, leading to a conventional multilayer structure with an epitaxial relationship between the layers. In the present case these multilayers are polycrystalline, with the layer structure appearing in each individual grain, such as in sample 1.

2. When the grain sizes are smaller than the layer wavelength, composition modulations lead to nanostructure modulation, which is directly controlled by the applied current waveform in the present work, such as in samples 2 and 3. Whereas multilayers with two alternating grain sizes are one class of materials produced here, we also see that it is possible to prepare multilayers combining amorphous and nanocrystalline layers.
Taken together, all of the above results show that an extremely diverse array of new materials can be formed comprising microcrystalline, nanocrystalline and even amorphous Al–Mn. Other systems or processes used to produce multiscale nanostructured materials have not been able to produce such a diversity of multiscale composite nanostructures. Each layer can be tuned to deliver an optimum for one or more desirable properties, and multiple layers can be used to provide balance among these optima. While void formation is often observed in electrodeposited materials from aqueous solution due to hydrogen evolution and dissolution [17], we note here that the Al–Mn multilayers deposited from ionic liquid (where there is no hydrogen production) generally appear to be fully dense, with no obvious voids observed by optical or electron microscopy. Nanoindentation tests performed on sample cross-sections revealed a significant increase in hardness with Mn concentration (Table 1), as expected from the increasing prevalence of nanostructure across these samples. Note that the high hardness values of samples 2 and 3 correspond to specific strengths of more than 400 kN m kg\(^{-1}\) (assuming a factor of three proportionality between hardness and strength), well in excess of most commercial engineering alloys (e.g. steel at 130 kN m kg\(^{-1}\), Al-6061 at 110 kN m kg\(^{-1}\) and Ti–6Al–4 V at 240 kN m kg\(^{-1}\)) [22] and many nanostructured alloys (e.g. nanotwinned Cu with an average nanotwin spacing of 7 nm at 130 kN m kg\(^{-1}\) [9] and nanocrystalline Ni–W alloy with an average grain size of 3 nm at 270 kN m kg\(^{-1}\) [23]). The additional possibility of balancing other important properties (toughness, work hardening, rate sensitivity, etc.) using the multilayering approach demonstrated here presents an interesting direction for future work in design and optimization of multiscale nanocrystalline materials.

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