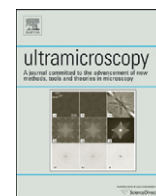




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Gallium-enhanced phase contrast in atom probe tomography of nanocrystalline and amorphous Al–Mn alloys

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ABSTRACT

Over a narrow range of composition, electrodeposited Al–Mn alloys transition from a nanocrystalline structure to an amorphous one, passing through an intermediate dual-phase nanocrystal/amorphous structure. Although the structural change is significant, the chemical difference between the phases is subtle. In this study, the solute distribution in these alloys is revealed by developing a method to enhance phase contrast in atom probe tomography (APT). Standard APT data analysis techniques show that Mn distributes uniformly in single phase (nanocrystalline or amorphous) specimens, and despite some slight deviations from randomness, standard methods reveal no convincing evidence of Mn segregation in dual-phase samples either. However, implanted Ga ions deposited during sample preparation by focused ion-beam milling are found to act as chemical markers that preferentially occupy the amorphous phase. This additional information permits more robust identification of the phases and measurement of their compositions. As a result, a weak partitioning tendency of Mn into the amorphous phase (about 2 at%) is discerned in these alloys.

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1. Introduction

The properties of nanostructured and amorphous alloys rely on details of the solute content and its distribution at the finest scales. For example, in nanocrystalline alloys, chemical ordering and solute enrichment at grain boundaries affect such properties as strength and thermal stability [1–7]. In amorphous alloys, subtle changes in chemical composition influence crystallization behavior and glass forming ability [8–25]. In dual-phase nanocrystal/amorphous composites, the phase composition, phase fraction and phase distribution impact, for instance, their magnetic [2,10,11,26–29] and mechanical properties [30–32]. Thus, a sound understanding of solute distribution at scales from the nanometer down to the sub-nanometer regime is central to tailoring the properties of nanostructured and amorphous alloys. Unfortunately, many traditional chemical mapping methods like the Auger microscopy and energy dispersive X-ray spectroscopy in the transmission electron microscope (TEM) lack the resolution necessary for these advanced problems. On the other hand, three-dimensional atom probe tomography (APT) has very high spatial and chemical resolution, as well as equal sensitivity for all elements [33–35]; as a result, APT has been increasingly used to

probe the spatial distribution of atoms in nanostructured and amorphous alloys.

There have been several APT studies on nanocrystalline alloys. Among these, the most common issue addressed is local chemistry at grain boundaries [1–5,10,36–43]; nanostructure formation in many such alloy systems is attributed either to the thermodynamic effect of solutes in decreasing grain boundary energy [3–5], or to the kinetic effect of solutes in inhibiting grain growth [39,43]. Additionally, APT studies on some Ni–P [1,2] and Co–P [5] alloys help account for their high thermal stabilities; in such systems, as the alloys are heated to higher temperatures, the extent of solute segregation to grain boundaries increases, thus decreasing the driving force for grain growth. APT has also been employed to elucidate the phase transformation sequence and mechanisms in nanocrystalline alloys [1,2,5,37,42,44]: as temperature increases, solute enrichment occurs at the grain boundaries until a new solute-rich phase precipitates there.

Valuable knowledge about amorphous alloys, such as their crystallization mechanism during heat treatment, has also been acquired from APT studies [8–25]. In these studies, clusters of atoms are identified by considering the local density around each atom [9–15,17,20,22–25,28,45,46]. The chemical identity of atoms in these pre-nuclei, in turn, helps rationalize the effects of subtle chemical composition changes on the nucleation behavior of the alloys. Dual-phase nanocrystalline/amorphous composites formed by such partial devitrification processes have also

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been the subject of many APT studies, where the segregation tendencies of solute atoms to the different co-existing phases are established [2,10,19,21,26–32,47–55]. In some of these works, the volume fraction of each phase, together with its composition, is quantified, and the microstructures that optimize the magnetic properties [2,10,11,26–29] and malleability [30–32] are identified.

The above studies contribute significantly to our fundamental understanding of nanostructured and amorphous alloys. However, most of these studies are restricted to alloy systems that exhibit strong tendencies for solute segregation to interfaces [1–5] or among different phases [2,10,11,26–32], and to alloys that experience long thermal exposures [2,8,10,19,21,26–32,47–55], which aids redistribution of solute atoms. In such cases the extent of solute segregation often exceeds a factor of two, so compositional differences are easily visualized via atom dot maps, and quantified by standard atom probe data analysis techniques, such as ladder diagrams and one-dimensional composition profiles. Very few APT studies have been carried out on weakly-segregating systems, or on multi-phase alloys that are formed by driven or out-of-equilibrium processes without post-annealing, because in such cases, it is challenging to distinguish the different phases and features [3,4,50].

In this work, we investigate the solute distribution in electro-deposited Al–Mn alloys with nanocrystalline and amorphous structures. Using single phase alloys as baselines for comparison, we specifically aim to understand the solute distribution in a two-phase nanocrystal/amorphous alloy, where the solute is only weakly partitioned between the two phases, which are themselves homogeneously distributed spatially. We show that although the compositional difference between the two phases is far too small to provide contrast for imaging and analysis of the phases, we can identify the phases using implanted Ga ions as markers, because they preferentially decorate the amorphous phase. The use of such chemical markers can enhance the capability of APT as an avenue for probing the structures of nanostructured and amorphous alloys with subtle composition inhomogeneities.

2. Experimental procedures

Room temperature electrodeposition of Al–Mn alloys was carried out in a chloroaluminate ionic liquid that was synthesized and purified by techniques described in Ref. [56]. Electropolished copper (99%) was used as the cathode and pure aluminum (99.9%) as the anode. The applied deposition current waveform comprised

repeated units of a cathodic pulse of 20 ms, followed by an anodic pulse of 20 ms. The magnitudes of the cathodic and anodic current densities were 6 and 3 mA/cm², respectively. Electrodeposition of alloy sheets was carried out in a glove box under a nitrogen atmosphere, with H₂O and O₂ contents below 1 ppm, to a thickness of approximately 10 μm. Four samples were prepared, with compositions measured by calibrated energy-dispersive spectroscopy (X-ray Optics/AAT #31102 in a Leo 438VP scanning electron microscope) and confirmed by Rutherford backscatter measurements as: ~8.0, 9.2, 10.2, and 15.0 at% Mn (see Table 1). In what follows we will refer to these samples by their compositions.

The copper substrates were dissolved in concentrated nitric acid to obtain free-standing alloy sheets. A PANalytical X'Pert Pro diffractometer operating at 45 kV and 40 mA with a Cu-Kα radiation source and Bragg–Brentano para-focusing geometry was used to obtain X-ray diffraction (XRD) patterns, which were analyzed using a software package MDI Jade 8. After subtracting a linear background profile, a regular Pearson VII function was fit to each diffraction peak, so as to calculate the full-width-at-half-maximum. A modified Williamson–Hall method, as detailed in Ref. [56], was employed to estimate the crystallite size from the full-width-at-half-maximum values. TEM specimens were prepared by twin-jet electropolishing at 10 V in a 20% solution of perchloric acid in methanol at –60 °C. The TEM specimens were examined using a JEOL 200CX TEM, and a probe diameter of 1 μm was used to obtain the electron diffraction patterns. High resolution imaging was carried out with a JEOL 2010 TEM.

Sharp atom probe tips with radii of curvature between 50 and 100 nm were prepared from the alloy sheets by annular focused ion beam (FIB) milling. The *in situ* lift-out technique described by Thompson et al. [57] was used to shape the tips into the appropriate geometry. The lift-out procedure was conducted using a FEI Quanta 3D dual-beam FIB. Initial milling was performed at 30 keV and final milling at 5 keV. The atom probe tips were analyzed using an Imago Scientific Instruments Local Electrode Atom Probe (LEAP[®]) 3000XSi. All analyses were performed at 10^{–9} Pa, with a temperature setting of 60 K, a pulse fraction of 25%, and a pulse repetition rate of 200 kHz. Multiple atom probe tips were prepared and analyzed to ensure data reproducibility, and that the resulting bulk atom compositions measured by APT were consistent with the other composition measurement methods described above for each respective specimen. Table 1 lists the total number of atoms collected for each APT tip; the typical sample size was between 5 and 15 million atoms. Data analysis was conducted with custom software programs written by the authors.

Table 1

Summary of the total number of atoms collected for each APT specimen, along with its APT and SEM/EDX alloy composition. Also shown are the grain sizes determined from XRD and TEM analysis.

Deposition number	APT sample	Total number of atoms collected	Composition			Grain size (nm)	
			APT		SEM/EDX	XRD	TEM
			Ga (at%)	Mn (at%)	Mn (at%)		
1	A	5,977,410	0.02	8.25	7.8 ± 0.2	–	159
	B	8,765,416	0.17	8.39			
2	C	14,197,531	0.34	9.12	9.5 ± 0.3	25 ± 4	19
	D	9,604,795	0.25	9.03			
3	E	13,401,688	0.24	10.07	10.5 ± 0.3	–	5
	F	10,153,271	0.23	10.21			
	G	7,342,614	0.22	10.13			
4	H	2,202,166	0.12	16.15	14.0 ± 0.3	–	–

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