

Atom probe microscopy investigation of Mg site occupancy within δ' precipitates in an Al–Mg–Li alloy

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The composition and site occupancy of Mg within ordered δ' precipitates in a model Al–Mg–Li alloy have been characterized by atom probe microscopy and first-principles simulations. The concentration in the precipitates is found to be almost the same as that of the matrix; however, we show evidence that Mg partitions to the sites normally occupied by Li in the $L1_2$ structure. Density functional calculations demonstrate that this partitioning is energetically favorable, in agreement with experimental results.

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In recent years there has been a renaissance in the research and development of Al–Li-based alloys, driven by their great potential for weight reduction in structural aerospace applications. In this context, Al–Li–Mg alloys (1420 alloy series) are of fundamental interest because they are lightweight, weldable, corrosion resistant and exhibit moderate strength [1,2]. It has previously been shown that, after solution treatment, a fast quench to room temperature and thermal ageing at intermediate temperatures (100–170 °C), these Al–Li–Mg alloys exhibit a microstructure dominated by the metastable δ' phase [1,3]. This phase, sometimes referred to as a GP zone [4], has an expected stoichiometry of $Al_3(Li, Mg)$, is fully coherent with the face-centred cubic (fcc) Al matrix, possesses an ordered $L1_2$ structure and appears to be very similar to the spherical Al_3Li precipitates found in the Al–Li binary system [5,6].

The precipitation of the δ' phase in Al–Mg–Li alloys has been the focus of many investigations over a number of years, yet much remains unknown about this phase

transformation [3,4,7,8]. Of particular interest is the exact role of Mg, which seems to greatly enhance the precipitation of δ' in comparison to that observed in the Al–Li binary system. Indeed, Mg has a high solubility in Al and precipitation of Al_3Mg is not expected in the compositional range commonly used in these alloys (1–5.5 at.%). A more detailed understanding of the atomic scale mechanisms that control the precipitation process requires the precise measurement of the Mg concentration within the precipitates. More specifically, the challenge is to explore whether there occurs a partitioning of Mg atoms within the δ' $L1_2$ lattice structure on to either the Li or Al sublattices, or otherwise. The experimental observation that Al alloys that contain high levels of Mg (>10 at.%) can precipitate a metastable $L1_2$ Al_3Mg phase (β'') would suggest that a preferential partitioning of Mg occurs on the Li sublattice [9,10]. However, the large volume fraction of precipitates, the low atomic number of Li and the small difference in atomic number between Al and Mg, conspire to make observations of this partitioning extremely challenging and not obviously amenable to conventional scattering techniques.

Here, we have applied atom probe tomography (APT) to characterize the distribution of Mg within a laboratory alloy of composition Al–5.18Mg – 6.79Li (at.%)

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(Al–5Mg–1.8Li (wt.)) aged for 8 h at 150 °C and also for 24 h at 120 °C. APT has the unique capacity for simultaneous chemical identification and precise three-dimensional location of the individual atoms in a material [11]. In particular, it has been demonstrated that extremely high spatial resolution can be achieved in the analysis of Al and its alloys [12]. APT is based upon the effect of an intense electric field to induce the ionization and desorption of individual atoms from the surface of a needle-shaped specimen subjected to the superposition of a DC high voltage (HV) and fast HV pulses [13]. This process is known as field evaporation. The field emitted ions are collected by a position-sensitive detector. Their time-of-flight is recorded and translated into a mass-to-charge-state ratio and the positional information is sequentially analyzed to build a tomographic reconstruction of the field-evaporated volume [14].

It is well documented that crystallographic information is partially retained within atom probe reconstructions, and this is exemplified by the capacity of the technique to directly image atomic planes [15]. Several methods have previously been developed to interrogate the atomic-scale crystallographic information within these tomograms, including Fourier transform (FT) approaches [16,17], three-dimensional autocorrelation functions, termed spatial distribution maps (SDMs), which are usually plotted in the form of a one-dimensional histogram along a specific crystallographic direction [18,19], and the three-dimensional Hough transformation [20]. These techniques enable the precise determination of interplanar spacings and angles between crystallographic features with varying degrees of success. For the work reported here, we have developed an extension of the advanced SDM technique introduced in Ref. [19] to enable investigation of the distribution of element-specific inter-atomic separations (e.g. partial pair correlation functions) along particular crystallographic directions. Similar approaches have previously been implemented in the atom vicinity algorithm [21] or conventional spatial distribution maps [18], and exploited, for example, to examine site occupancy in different materials [22–26]. However, such a method has never been applied to ordered precipitates in a ternary alloy to determine the specific localization of a specific species.

After casting, the experimental alloy was homogenized for 8 h at 500 °C, hot rolled, solution treated for 15 min at 500 °C and cold water quenched. The material was subsequently heat treated for 8 h at 150 °C or 24 h at 120 °C. To prepare atom probe specimens, the raw material was first cut into $0.4 \times 0.4 \times 30$ mm blanks with a low-speed diamond saw. Needle-shaped specimens were then fabricated by electropolishing in a solution of 25% perchloric acid in glacial acetic acid with a 10–12 V DC, followed by a second stage of fine polishing under a binocular microscope with 2% perchloric in 2-butoxyethanol with a 20–25 V DC [27]. Specimens were analyzed in a Cameca (formerly Imago) LEAP 3000X Si microscope under a pulse fraction of 20%. The specimens were maintained at cryogenic temperatures (~ 40 K) under ultrahigh vacuum conditions of approximately 4.5×10^{-9} Pa. A detection rate of $0.5\text{--}2 \times 10^{-2}$ ions per pulse was maintained through the experiment. Datasets containing 12–100 million ions were acquired. Our tomographic reconstructions were generated by using the protocol de-

scribed in Ref. [14], and the reconstruction parameters (i.e. the image compression factor ξ and the field factor k_f) were calibrated using the partial crystallographic information retained within the atom probe data following the protocols introduced in Refs. [28,29]. Data reconstruction and visualization were performed with commercial software (Cameca IVAS).

Typical atom probe tomograms for the respective heat treatments are presented in Figure 1(a and b). In each of these datasets, major crystallographic planes were observable, notably (111) and (022) in the specimen treated for 8 h at 150 °C and (002) in the specimen treated for 24 h at 120 °C. Figure 1(c and d) provides close-ups of thin slices through the reconstructions presented in Figure 1(a and b), where atomic planes are imaged to illustrate the atomic resolution available. Isoconcentration surfaces, which delineate regions containing more than 8 at.% Li, are included to aid visualization of the δ' precipitates, which are known to adopt an $L1_2$ structure (see Fig. 1(f)).

As reported in Table 1, the overall composition measured in the experiment is affected by the preferential field evaporation of Li and, to a lesser extent, of Mg. These elements require a lower electric field to be field evaporated than Al [30] and hence may field evaporate under the standing voltage in between the HV pulses. This prevents the time-of-flight measurement and precludes their identification, which induces an element-specific loss of these atoms. In these studies, preferential field evaporation caused the loss of 15–30% of the Li, with analyzes of the material treated for 24 h at 120 °C being the most affected. The matrix composition for each element and in each dataset was derived from the first nearest-neighbor distribution with the DIAM method described in Ref. [31], and values are reported in Table 1. By using the Li 8 at.% isoconcentration surface as a reference, proximity histograms were computed [32]. These composition profiles, shown in Figure 2, enable measurement of the composition of the precipitates. The composition of the δ' precipitates was taken as the average value of the plateau visible in the proximity histograms calculated for more than 100 precipitates. These results are displayed in

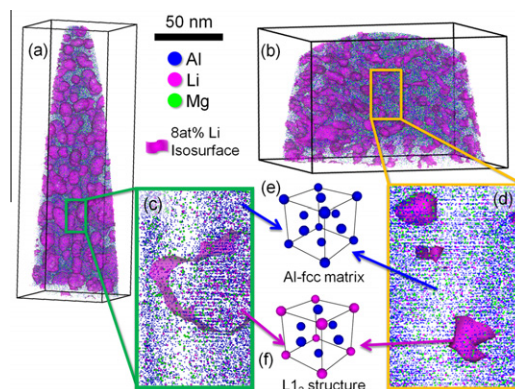


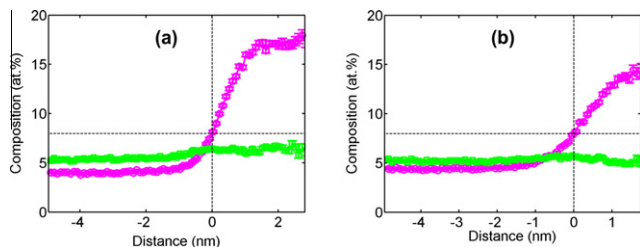
Figure 1. Typical three-dimensional reconstruction from atom probe tomography of the alloy after (a) 8 h at 150 °C and (b) 24 h at 120 °C shown at the same scale. (c) A close-up showing the (022) atomic planes imaged in the data set displayed in (a). (d) A close-up showing the (002) atomic planes imaged in the data set displayed in (b). (e, f) Model view of the fcc Al matrix and of the $L1_2$ structure. Note that the same colour code is used throughout the article. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1. Overall composition, composition and size of the δ' precipitates, and matrix composition obtained from the DIAM method [30] for the two heat treatments.

		8 h at 150 °C			24 h at 120 °C		
	Element	Overall	δ' Precipitates	Matrix	Overall	δ' Precipitates	Matrix
at. %	Li	5.72	17.15 ± 0.54	4.67	4.67	13.97 ± 0.59	4.88
	Mg	5.53	6.43 ± 0.35	5.26	5.26	5.17 ± 0.38	5.81
	Al	88.75	76.15 ± 0.61	90.07	90.07	80.86 ± 0.67	89.31
	Radius (nm)		3.85 ± 1.37		Radius (nm)	2.24 ± 0.86	

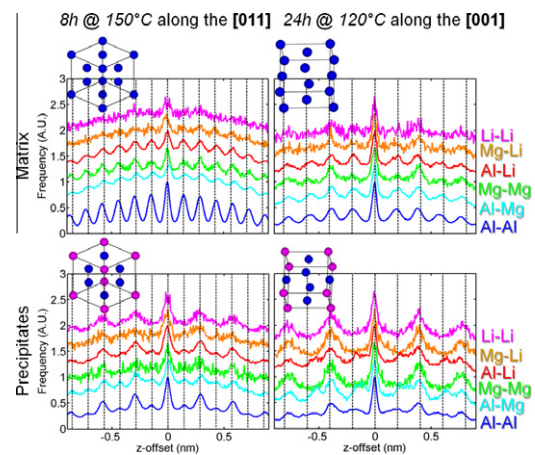
Figure 2, and the values are reported in Table 1. The size of the precipitates was estimated from the volume embedded by each individual isoconcentration surface, under the assumption that they were approximately spherical, as seems to be the case from previous transmission electron microscopy experiments [1,33]. The average size of the precipitates was found to be larger in the material treated for 8 h at 150 °C than when treated 24 h at 120 °C, as reported in Table 1. Interestingly, in both cases there is almost no change in the Mg concentration in the matrix and in the δ' precipitates. Preferential evaporation of Li and Mg could explain the difference in the measurement of the precipitate composition between the two samples, and also the gap with the expected $\text{Al}_3(\text{Li}, \text{Mg})$ stoichiometry.

To investigate the Mg site occupancy within the δ' precipitates, the tomogram for the specimen aged for 8 h at 150 °C was cropped to retain only the volume encompassing the {022} planes. Likewise, the tomogram from the sample aged for 24 h at 120 °C was cropped to include the region containing the {002} planes. Subsequently, the 8 at.% Li isoconcentration surfaces were used to generate two subsets of the data: (i) the atoms from the precipitates that were embedded within these surfaces; and (ii) the atoms from the surrounding matrix. Species-specific SDMs were then computed in both subvolumes and the resulting histograms are plotted in Figure 3. The peak-to-peak distance of Mg–Li distributions, for example, indicates the likely positions of Li atoms relative to an Mg atom along specific crystallographic directions. All peak-to-peak distances in the matrix data of Figure 3 correspond to a single interplanar spacing of the Al matrix. Significantly, this experimental self-consistency held for the samples analyzed in both heat treatment conditions and in all matrix SDMs, and indicates that the species Mg and Li occupy all the sites of the fcc Al matrix with equal probability. In comparison, close analysis of the SDMs corresponding to the δ' precipitate phase revealed a clear change in the periodicity of the Li–Li and Mg–Mg distances. Moreover, the magnitude of the change in periodicity

**Figure 2.** Proxigrams computed from the 8 at.% Li isoconcentration surface for the material aged (a) 8 h at 150 °C and (b) 24 h at 120 °C. Composition profiles of Li and Mg are respectively plotted in pink and green. The dashed lines show the position of the interface at 8 at.% Li. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

confirms that ordering has taken place, and the structure is consistent with the L_{12} structure shown in the inset of Figure 3. Finally, the peaks associated with Mg appear at the same location as the Li in the L_{12} structure, which indicates that most of the Mg atoms partition to the Li sublattice within the δ' precipitates. The exact amount of Li and Mg on the different sites of the L_{12} structures cannot be determined precisely using the method introduced here due to the filtering of the data based on the isoconcentration surface: this cannot ensure that atoms from the matrix are not also included, which could dramatically affect composition measurements. It is envisaged that other methods for data filtering could be developed in the future to try to reveal the exact composition of each sublattice.

To investigate the theoretical stability associated with the ordering reaction observed experimentally within δ' precipitates, we performed all-electron density functional theory (DFT) calculations by using the generalized gradient approximation [34] with the DMol³ program package [35]. The wave functions were expanded in terms of a double-numerical quality basis set, with a set of large values of real-space cutoff (Li: 13.76 Bohr; Mg: 12.09 Bohr; and Al: 12.75 Bohr). A reciprocal space of $3 \times 3 \times 3$ K-point meshes was employed in the calculations of the 32-atom Al_3Li -based supercells. We allowed full atomic relaxation, until the forces on the atoms were less than $0.005 \text{ eV \AA}^{-1}$. The fully optimized lattice constants for bulk Mg, Al and Li, as well as Al_3Li , were in good agreement with experimental values (errors below 1.85%). To evaluate the relative stability of various sublattice configurations, the energy required for substitution of Mg on either the Al (Mg_{Al}) or Li (Mg_{Li}) sublattice of the L_{12} structure is expressed as $E^f = E_{\text{Mg:Al}_3\text{Li}} - E_{\text{Al}_3\text{Li}} - E_{\text{Mg}} +$

**Figure 3.** Normalized species-specific spatial distribution maps for the two heat treatments in the matrix (top row) and the precipitates (bottom row). Note the change in the periodicity between the precipitates and the matrix in both cases. The corresponding structure is shown in the inset for each case.

$\mu_{\text{Al or Li}}$, where E_{Mg} , $E_{\text{Mg:Al}_3\text{Li}}$ and $E_{\text{Al}_3\text{Li}}$ are, respectively, the total energies of the bulk Mg, the Mg-doped Al_3Li and the pure Al_3Li reference structure as calculated with the same size supercell. The $\mu_{\text{Al or Li}}$ is the chemical potentials of Al or Li. The chemical potentials $\mu_{\text{Al or Li}}$ depend on the actual environment surrounding the supercell (reservoir). Here, surrounding the precipitate is an Al-rich (above 85 at.%) matrix, hence we used $\mu_{\text{Al}} = \mu_{\text{Al(bulk)}} = E_{\text{Al(bulk)}}$, and $\mu_{\text{Li}} = \mu_{\text{Al}_3\text{Li}} - 3\mu_{\text{Al(bulk)}} = E_{\text{Al}_3\text{Li(bulk)}} - 3E_{\text{Al(bulk)}}$, and we invoke the relationship $3\mu_{\text{Al}} + \mu_{\text{Li}} = \mu_{\text{Al}_3\text{Li}}$, assuming both species are in thermal equilibrium with Al_3Li [36]. The formation energies obtained were $\text{Mg}_{\text{Al}} = 0.43 \text{ eV}$ and $\text{Mg}_{\text{Li}} = 0.28 \text{ eV}$. Similar methods were used to calculate the formation energy of Mg substituting in the pure Al matrix. The value obtained was 0.35 eV , which is intermediate between the energies for Mg substitution within the precipitates.

These DFT calculations provide direct insights into the energetic origins of our atomic resolution microscopy observations. First, it is clear that there is a favorable energetic situation when Mg partitions to the Li sites within the δ' precipitates, as was observed. Secondly, the small difference in the amount of Mg between the matrix and the precipitates can be explained by the relatively small difference in total energy between the insertion of an Mg atom in the Al matrix and the most favorable energy state of Mg when substituted for Li in the Li_2 structure of the δ' precipitates.

In summary, we have proposed an original atom probe microscopy approach to identify and characterize ordering within the structure of nanoscale precipitates. Our atomic resolution microscopy experiments, in conjunction with first-principles DFT calculations, demonstrate that partitioning of Mg to the Li sublattice occurs in Li_2 -structured δ' precipitates in an $\text{Al}-5.18 \text{ Mg}-6.79 \text{ Li}$ (at.%) alloy aged for 8 h at 150°C , and for 24 h at 120°C . The composition of the Li-rich δ' precipitates was shown to be very close to the expected $\text{Al}_3(\text{Li}, \text{Mg})$ stoichiometry in both sets of samples, with Li and Mg both more concentrated in the 8 h/ 150°C aged alloy. The composition of Mg is almost the same in both the precipitate and matrix phases, and we have demonstrated unequivocally that Mg partitions to the Li sites of the Li_2 structure within the δ' phase precipitates. These observations correspond to the most energetically favorable scenarios, as confirmed by DFT calculations.

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