

PRECIPITATE NUCLEATION IN ALLOYS BASED ON THE Al-Cu SYSTEM

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Abstract

The combined use of APFIM and TEM has provided an improved understanding of the precise mechanisms involved in precipitate nucleation in selected alloys based on the Al-Cu system. Nucleation of the phases θ' , Ω and T_1 has been studied and it is shown that certain trace elements may stimulate these processes by providing a sequence of clustering events during quenching and/or at the early stages of ageing.

Introduction

Although a generalised thermodynamic description of precipitate nucleation in alloys has been available for many years, comparatively little is known about the actual atomic processes involved. Moreover, uncertainty also exists concerning the role of trace elements that can cause marked changes in the response of some Al alloys to age hardening by modifying the nucleation and growth of certain precipitates. This situation is changing, however, through the combined use of transmission electron microscopy (TEM) and atom probe field ion microscopy (APFIM).

This paper describes the application of these techniques to investigate the mechanisms by which single or combined additions of Sn, Mg, Ag and Li stimulate nucleation of precipitates during the early stages of ageing of alloys based on the Al-Cu system. Special attention has been paid to the nucleation of fine, uniform dispersions of the phases θ' (Al_2Cu), Ω (Al_2Cu), and T_1 (Al_2CuLi) in the following three alloy systems: (1) Al-Cu-Sn, (2) Al-Cu-Mg-Ag and (3) Al-Cu-Li-Mg-Ag-Li-Zr.

Experimental Details

Small chill castings of alloy 1 and 2 were prepared from high purity materials which were then homogenized and fabricated to plate by hot rolling. The nominal composition of alloy 1 was Al-4wt%(1.7at%)Cu-0.06wt%(0.01at%)Sn. To improve the probability of detecting Ag in the atom probe, an Al-4.5wt%(1.9at%)Cu-0.3wt%(0.3at%)Mg-0.7wt%(0.2at%)Ag alloy, having a somewhat higher Ag content, was used for APFIM, whereas the well characterised [1-3] Al-4wt%(1.7at%)Cu-0.3wt%(0.3at%)Mg-0.4wt%(0.1at%)Ag alloy was used in TEM experiments. Alloy 3, known commercially as Weldalite™ 049, was kindly supplied in plate form by J.R. Pickens of Martin Marietta Ltd. Rods of 5 mm diameter were machined and drawn to 0.5 mm diameter in order to prepare specimens for APFIM. Other material was used for rolling to sheet to make thin foils for TEM. Specimens were solution treated under an argon atmosphere for 30 minutes at 525°C. They were then examined after cold water quenching and after quenching and immediately ageing at elevated temperatures in oil baths. Tips for APFIM were electropolished in two stages in a solution of concentrated HNO_3 , to which was added a few drops of water. First, a direct current (dc) of ~4V was applied to produce a sharp, needle-like shape after which final polishing was performed using alternating current at the same voltage. An energy compensated time-of-flight APFIM with low temperature cooling capacity was used which has been described elsewhere [4]. Field ion images were observed with He as the imaging gas at 20K and the atom probe analyses were conducted at 25-30K in an ultra-high vacuum of 10^{-10} Torr, although some analyses were performed under $\sim 10^{-9}$ He. The pulse fraction (ratio of pulse fraction to dc standing voltage) was 15% and a pulse frequency of 100Hz was used. The evaporation rate was controlled to be approximately 5×10^{-3} ions per pulse. Samples for TEM were prepared by twin jet electropolishing at ~12V in a solution of 33% HNO_3 in methanol cooled to $\sim -30^\circ C$ and examined in a Philips CM12 instrument operating at 120 kV.

Alloy 1: Al-Cu-Sn

Previous Work

Trace additions of Cd, In and Sn are well known for their effects in modifying ageing in Al-Cu alloys [5]. These elements reduce or inhibit natural ageing by retarding GP-zone formation. This behavior has been attributed to a preferential interaction between the trace element and quenched-in vacancies that would normally be available to assist diffusion of the solute Cu atoms [6]. This conclusion is supported by calculations that suggest the binding energy between a vacancy and a Sn atom is 0.2 eV greater than that existing between a vacancy and a Cu atom [7], and by TEM observations which show that these trace elements increase both the rate and extent of hardening in Al-Cu alloys aged at temperatures in the range 100 to 200°C [5, 10]. Comparisons between binary and ternary alloys have shown that, whereas these elements suppress the formation of the phase θ' [11], they stimulate a finer and more uniform dispersion of the semi-coherent phase θ' [12]. This change occurs without altering the crystal structure of θ' [11, 12], but opinions differ concerning the mechanisms involved. One hypothesis is that the trace elements are absorbed at the θ' /matrix interfaces resulting in a lowering of the interfacial energy required to nucleate θ' . This explanation was first proposed by Silcock et al. [11] to account for weak X-ray reflections (designated "p-diffractions") that were observed during the early stages of ageing. This proposal [13] received indirect experimental support from calorimetric measurements by Boyd and Nicholson [13] and TEM observations by Sankaren and Laird [14] who claimed to detect what they referred to as Sn (Cd or In) segregates and precipitates in association with the θ' particle/matrix interface. An alternative explanation is that the trace elements facilitate heterogeneous nucleation of θ' either directly at Sn (Cd or In) particles [15], or indirectly at the dislocation loops mentioned above [8, 9].

Results and Discussion

Figure 1(a) shows an integrated concentration depth profile, or ladder plot, obtained from the quenched samples of alloy 1. The diagram shows the number of solute atoms plotted against the total number of atoms collected in the APFIM. The slope of each plot corresponds to the local solute concentration in the sample and it is immediately obvious that the Sn atoms are not homogeneously distributed in the Al matrix. Rather they appear as discrete clusters such as at A in Fig. 1(a). Moreover, the result suggests that these clusters are composed of Sn atoms and there is no evidence of enrichment of Cu at their locations. Occasional clusters of Cu atoms were also observed but these appeared to be fewer in number and not spatially correlated with the Sn clusters.

Ageing at 190°C for 1 h. results in rapid precipitation of fine (~5 nm diameter), approximately spherical particles which APFIM analysis also indicated to be pure Sn. As shown in Fig. 1(b), θ' precipitates were often found associated with these particles suggesting that they had provided sites at which heterogeneous nucleation of θ' could occur. The Sn particles appeared to be incoherent with the Al matrix since they were visible only through diffraction and structure factor contrast and no contrast effects suggestive of coherence strains were observed in tilting experiments. It is apparent that the Sn-particles are in contact with the narrow, incoherent planes of θ' . This is similar to the observation made in an Al-Cu-Zr-alloy by Kanno and Ou [16] in which θ' nucleated at incoherent particles of the compound Al_3Zr . APFIM was also used to determine whether or not Sn atoms were segregated at the θ' /matrix interfaces and separate selected area analyses were performed across both the coherent broad face of the θ' plates and across the rim or edge. Results for the latter analysis are shown in Fig. 1(c) for the alloy aged 1h. at 190°C, which is approaching peak hardness (~3h.). It is clear that no Sn has segregated to this interface and the same result was obtained across the broad face of the platelets.

These results appear to give strong support to the proposal by Kanno et al. [15] that Sn (Cd or In) facilitates precipitation of θ' at elevated temperatures by providing heterogeneous sites at which nucleation occurs. For alloy 1, the actual nucleation process would seem to involve:

- (i) Rapid vacancy assisted formation of clusters of Sn atoms during, or immediately after quenching. Evidence for the preferential interaction between trace elements and vacancies

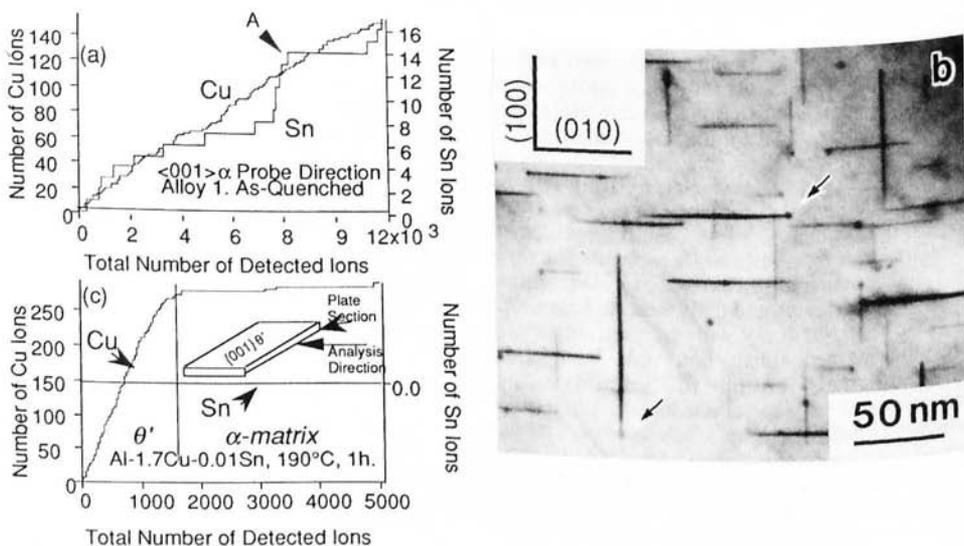


Figure 1. (a) APFIM ladder plot from alloy 1 in as-quenched condition, showing Sn cluster (A). (b) BF TEM micrograph of the alloy aged 1h. at 190°C showing the θ' phase, which appears to be nucleated at the sites of small Sn-particles (arrowed). (c) Ladder plot from atom probe analysis of the rim of a θ' precipitate. Sn appears to be absent from the particle/matrix interface.

has already been mentioned and it is also relevant to note that the diffusion rate of Sn in Al may exceed that of Cu by at least two orders of magnitude [17].

(ii) Precipitation of Sn particles.

(iii) Heterogeneous nucleation of θ' at the Sn particles. Here it is suggested that it is the incoherent rim or edge of the θ' plates which nucleate, and that this occurs at those surfaces of the incoherent Sn particles which will allow growth of θ' along $\{001\}_\alpha$ planes.

Alloy 2. Al-Cu-Mg-Ag

Ω Phase

The Ω precipitate phase was first observed in artificially aged Al-Cu-Mg alloys with high Cu:Mg ratios (i.e. low Mg contents) to which small amounts of Ag had been added [18, 19]. The Ω phase forms as a uniform dispersion of thin, hexagonal-shaped plates that precipitate on $\{111\}_\alpha$ planes. The crystal structure of Ω has been described as monoclinic [20], hexagonal [21], orthorhombic [3], for which there is now strong experimental support [2], and tetragonal [22]. There is general agreement, however, that Ω is a distorted form of the equilibrium precipitate θ that precipitates in Al-Cu alloys and has the same composition (Al_2Cu) as this phase [23]. The Ω phase is coherent direct transformation of a supersaturated solid solution (SSSS) to a semi-coherent precipitate is normally difficult, and usually occurs heterogeneously, nucleation of the Ω phase appears to be an energetically easy process. It is therefore of special interest to understand the actual mechanism that is involved. Accordingly, Al-Cu-Mg-Ag alloys were examined by APFIM and TEM immediately after quenching, and after ageing for very short times at 180°C.

Results and Discussion

TEM examination of quenched foils showed that the presence of Ag effectively eliminated dislocation loops [24] that are normally present in ternary Al-Cu-Mg alloys [25, 26]. This implies a high binding energy with vacancies which prevents the latter from aggregating and condensing

from the SSSS. A second observation was that APFIM detected the presence of individual clusters of Cu, Mg and Ag atoms although no evidence of co-clustering was observed [23, 24].

After ageing samples of the Al-4.5Cu-0.3Mg-0.7Ag alloy (wt%) for 15 sec. at 180°C, both Mg and Ag were found to be highly concentrated in the same region. This is shown in Fig. 2(a), which contains a small segment of an integral concentration depth profile. The ratio of these two elements was approximately 1:1 although the count of atoms was insufficient to draw a definite conclusion on this matter. It seems clear that the rapid co-clustering of Ag and Mg atoms has occurred during ageing for this short time and diffusion may have been facilitated through the proposed interaction between Ag atoms and vacancies. It is also clear that, after ageing for 15 sec., no localised concentration of Cu has occurred at the sites of these Ag-Mg co-clusters.

After ageing this alloy for 30 sec. at 180°C, the concentration depth profile now reveals that Cu atoms have also aggregated at the sites of the Ag-Mg co-clusters (Fig. 2(b)). Furthermore, the contrast in BF TEM images suggested the presence of very fine precipitates (Fig. 2(c)). Consideration was initially given to the notion that these were images of a proposed Al-Cu-Mg phase, Ω' , suggested recently by Abis et al. [27] and reported to be the precursor to the Ω phase. However, a detailed analysis of the proposed Ω' structure suggests that this was not the case and other results, which are believed to disprove the existence of Ω' , are to be published elsewhere [28]. In Fig. 2(c), the inset SAED pattern shows diffuse reflections at the $1/3$ and $2/3$ $g(220)_\alpha$ positions, consistent with those normally associated with the presence of the Ω phase [19, 20]. Furthermore, close examination of BF TEM micrographs revealed the presence of very fine (<5 nm diameter) plate-like images, parallel to $\{111\}_\alpha$. Thus it appears that the Ω phase is directly nucleated from the SSSS following ageing for as little as 30 sec. at 180°C. Based on the combined experimental evidence derived from APFIM and TEM, it seems likely that this nucleation takes place at the sites of the Ag-Mg co-clusters.

It is also interesting to observe the location of Mg and Ag at a later stage when the Ω plates are well developed. In this regard, Fig. 2(d) shows an integrated concentration depth profile in the $\langle 111 \rangle_\alpha$ direction of the alloy after ageing for 2 h at 190°C. It may be noted that these elements have now segregated to both sides of the coherent interfaces between Ω and the matrix. It seems reasonable to presume that the Mg and Ag atoms serve to modify the $\{111\}_\alpha$ particle/matrix interface so as to allow the formation of a modified Vaughan II θ -phase precipitate [29]. In effect, the Mg and Ag modification produces a fully coherent $\{111\}_\alpha$ particle/matrix interface which obeys a rational orientation relationship, as distinct from Vaughan II θ -phase, which has a distorted $\{111\}_\alpha$ particle/matrix interface and for which there is some experimental evidence of a slight deviation from the rational relationship [1]. This modification is effected by the slight elongation of the "c" axis of the tetragonal unit cell of the θ phase and results in the Ω structure [2, 3]. This elongation may be readily accomplished if some of the larger Mg atoms substitute for Al, and some Ag atoms substitute for Cu in the precipitate lattice near the particle/matrix interface [23].

Alloy 3: Al-Cu-Li-Mg-Ag-Zr

Precipitation of the T_1 phase

Al-Cu-Li alloys, such as the commercial material 2090, are hardened predominantly by the presence of the phase T_1 which also forms as thin, hexagonal-shaped platelets on the $\{111\}_\alpha$ planes. However, nucleation of T_1 is difficult in this system and it is necessary to apply cold work (e.g. 5%) to the alloy prior to ageing (T8 temper) in order to obtain a maximum response to hardening. Such a treatment increases the dislocation density and provides heterogeneous nucleation sites so that a more uniform dispersion of T_1 is obtained.

If small amounts of Ag and Mg are added to certain of these Al-Cu-Li alloys, an abnormally high response to age hardening may be obtained [30] and a range of so-called Weldalite Al-Cu-Li-Mg-Ag-Zr alloys have been developed (X2094 and X2095) which may achieve yield strengths exceeding 700 MPa [31]. These high properties have been attributed to the simultaneous precipitation of three semi-coherent precipitates, each of which forms on a different set of

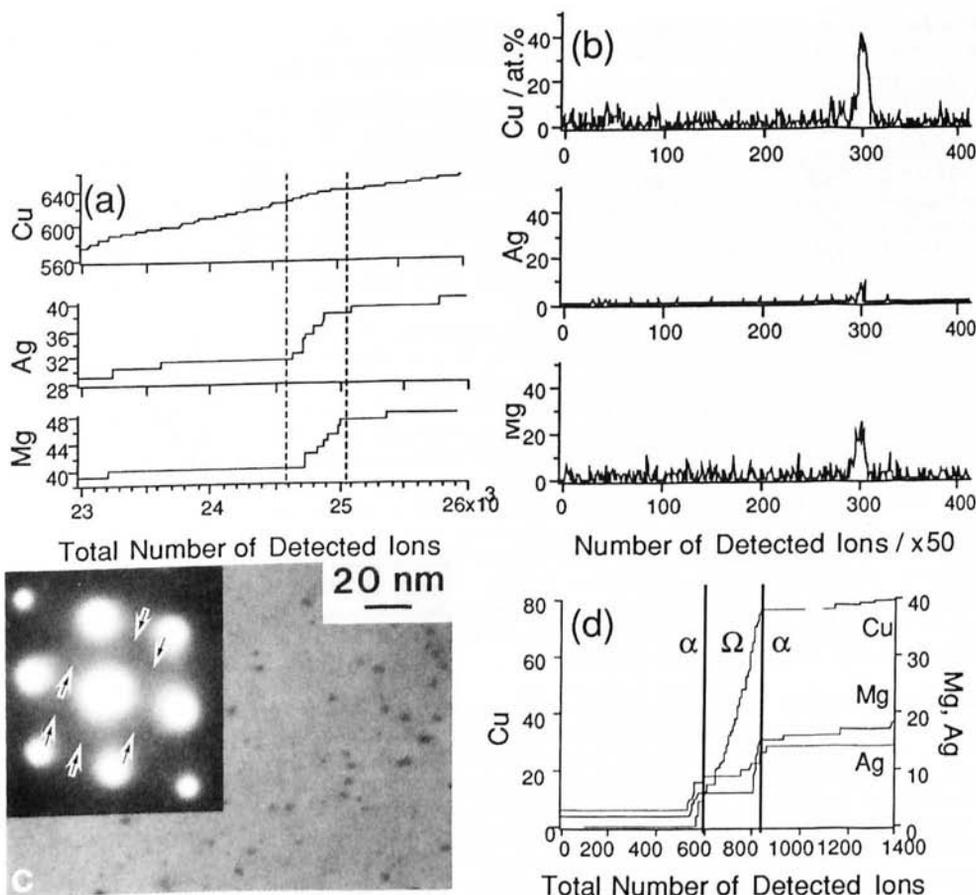


Figure 2. (a) Ladder plot from alloy 2, aged 15 sec. at 180°C showing co-clustering of Ag and Mg. (b) Concentration depth profile following ageing for 30 sec. at 180°C showing that Cu is now associated with the Ag and Mg co-clusters. (c) BF TEM micrograph and inset SAED pattern from alloy 2 aged 30 sec. at 180°C showing early stages of Ω precipitation. (d) Ladder plot of alloy 2 after ageing 2 h. at 190°C showing Mg and Ag at both sides of the Ω platelet. The probe direction in (a), (b) and (d) was $\langle 111 \rangle_{\alpha}$.

crystallographic planes [30]. Again the T_1 is predominant but, in this case, a more uniform dispersion is obtained without recourse to cold work prior to ageing [32]. It now remains to account for the mechanism by which Ag and Mg facilitate nucleation of T_1 in Al-Cu-Li-Mg-Ag-Zr alloys aged at elevated temperatures.

Results and Discussion

Figure 3(a) shows the microstructure of alloy 3 in the underaged condition (10 h at 160°C). A high density of fine plates on the $\{001\}_{\alpha}$ planes, which appear to be θ'' , is visible together with occasional T_1 precipitates on $\{111\}_{\alpha}$ planes. An APFIM integrated concentration/depth profile taken in the $\langle 001 \rangle_{\alpha}$ direction (Fig. 3(b)) shows Li to be associated with the θ'' and it is suggested that a shell of the δ' (Al_3Li) is attached to the θ'' plates in the manner proposed in Fig. 3(c). The presence of δ' was confirmed after careful inspection of $\langle 001 \rangle_{\alpha}$ SAED patterns such as Fig. 3(d). Here, reflections in the $L1_2$ positions are visible, together with continuous streaking in the $\langle 001 \rangle_{\alpha}$

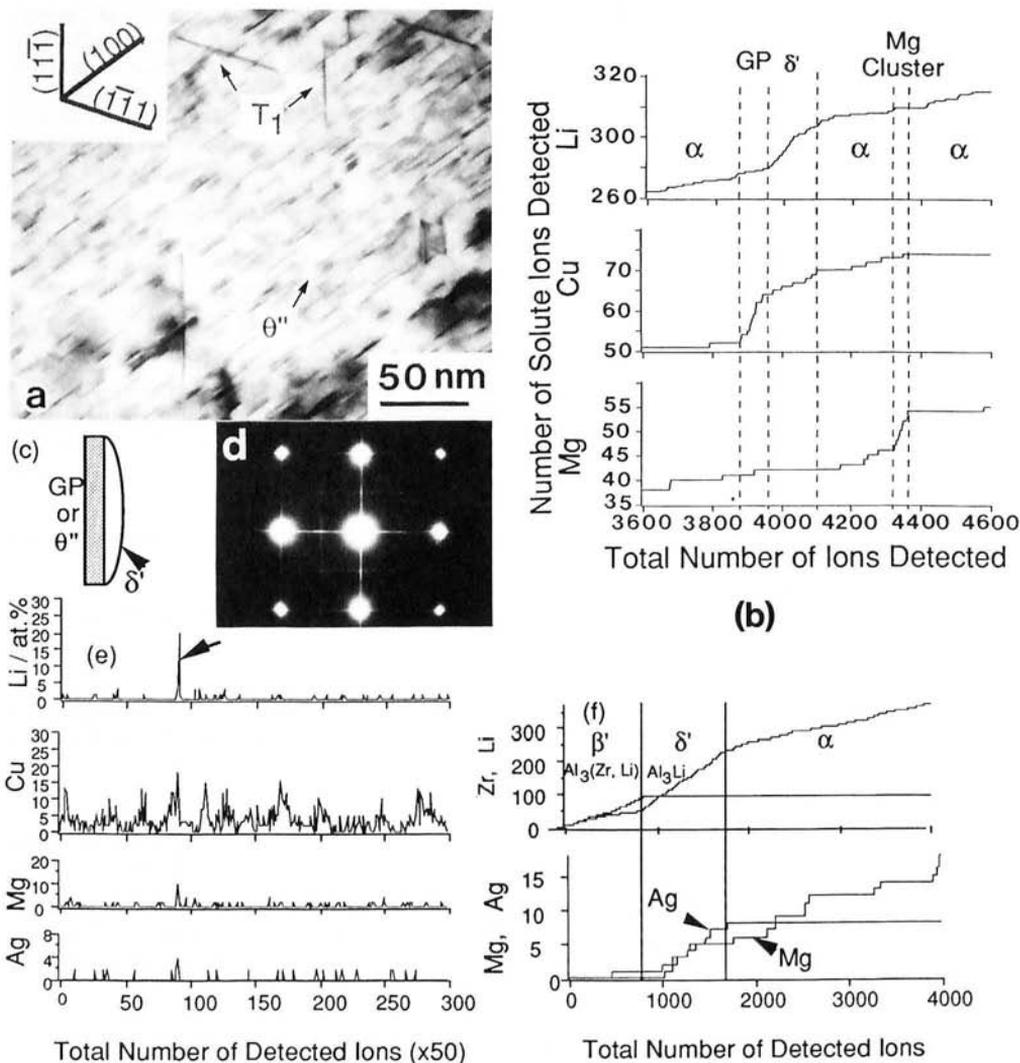


Figure 3(a) TEM micrograph of alloy 3 aged 10 h. at 160°C showing θ'' on $\{001\}_\alpha$ together with occasional T_1 precipitates on $\{111\}_\alpha$. (b) Ladder plot from selected area probing of a θ'' precipitate in the $\langle 001 \rangle_\alpha$ direction. Sample aged 10 h. at 160°C. (c) Suggested association of θ'' and δ' . (d) $\langle 001 \rangle_\alpha$ SAED pattern showing diffraction effects from θ'' and δ' . (e) Concentration depth profile from selected area probing of a T_1 precipitate in the $\langle 111 \rangle_\alpha$ direction. Note the association of Ag and Mg. Sample aged 10 h. at 160°C. (f) Ladder plot from selected area probing of a β'/δ' agglomerate along a direction near $\langle 001 \rangle_\alpha$. Note the association of Ag (and possibly Mg) in the δ' . Sample aged 10 h. at 130°C.

directions through the $\{100\}_\alpha$ positions and this may be attributed to shape effects from the δ' phase which, from atom probe analysis, appears to be distributed as a thin shell-like coating around the θ'' platelets. Moreover, it may be noted that Gayle et al. [32] have proposed the concept of

coupled growth of GP-zones and δ' to explain the high response of alloy 3 to natural ageing. Another concentration depth profile taken from probing a T_1 precipitate in the $\langle 111 \rangle_\alpha$ direction, normal to the habit plane, is provided in Fig. 3(e). Again, the sample was from alloy 3 following ageing 10 h. at 160°C and this data clearly associates Ag and Mg with the T_1 precipitate particles. Finally, Fig. 3(f) shows a ladder plot from selected area analysis taken after the alloy was aged 10 h. at the lower temperature of 130°C. Ag and, to a lesser extent, Mg are segregated throughout δ' (which in this case has itself nucleated at a β' (Al_3Zr) particle, as commonly occurs in Al-Li alloys).

This aspect of the research is at an early stage and any conclusions that are drawn must be regarded as speculative. One possible sequence of events leading to nucleation of the T_1 phase in alloy 3 could be as follows:

- (i) Segregation of Ag (and possibly Mg) occurs in some or all δ' precipitates, which themselves are known to form as a fine dispersion during quenching, and at an early stage of ageing of many Al-Li alloys.
- (ii) The presence of these elements in δ' bestows upon this phase the ability to assist nucleation of T_1 precipitates so that they form as a uniform dispersion. Here, some similarity may be noted with the way Ag and Mg clusters lead to nucleation of Ω phase in Al-Cu-Mg-Ag alloys. However, the sequence of events at the very early stages of ageing has not yet been examined.

Conclusions

1. The technique of APFIM is enabling an understanding of the precise atomic events associated with precipitate nucleation in aged Al alloys.
2. The trace elements studied all show a preferred interaction with vacancies during or immediately after quenching from the solution treatment temperature.
3. Trace amounts of Sn (Cd or In) stimulate precipitation of uniform dispersions of the phase θ' in Al-Cu alloys by providing sites, i.e. particles of Sn, Cd or In, at which heterogeneous nucleation can occur. Contrary to earlier suggestions, these elements do not segregate to the θ' /matrix interfaces during growth of this precipitate.
4. Small amounts of Ag promote precipitation of the Ω phase in certain Al-Cu-Mg alloys by forming Ag-Mg atom clusters at which nucleation occurs during elevated temperature ageing. These elements then segregate to the coherent $\{111\}_\alpha$ interfaces facilitating growth along $\{111\}_\alpha$ planes.
5. Ag and Mg are associated with the T_1 phase in an aged Al-Cu-Li-Mg-Ag-Zr alloy. Segregation of Ag (and possibly Mg) has been observed in the δ' phase that forms earlier in the precipitation process. It is speculated that this may be a significant factor in the nucleation of T_1 in this alloy.

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