

CONTROL OF PRECIPITATION PROCESSES AND PROPERTIES IN AGED ALUMINIUM ALLOYS BY TRACE ELEMENT ADDITIONS

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ABSTRACT Minor or trace amounts (~0.1 at.%) of certain elements can cause marked changes to the microstructure and properties of aged aluminium alloys. These effects generally arise because the trace elements can promote or suppress existing precipitation processes, or stimulate formation of new precipitates. A review of the behaviour of the trace elements in various aluminium alloys has revealed three features which appear common. The first two are that these elements are only sparingly soluble in the alloys concerned and they interact preferentially with vacancies retained on quenching. The third is that they facilitate nucleation of existing or new metastable, intermediate precipitates. Examples are also given of the ability of the trace elements to enhance mechanical properties in several alloy systems.

Keywords: *precipitation, trace element effects, nucleation, aluminium alloys*

1. INTRODUCTION

It is well known that minor or trace element additions may exert a disproportionate influence on the microstructure and properties of metals and alloys. Most of these effects arise because these additions modify the nucleation and/or growth of new phases forming during solid state transformations. Precipitation in alloys undergoing age hardening constitute an important group of such reactions and changes that may occur when trace additions are made to certain aluminium alloys have been reviewed on several occasions during the period 1956 to 1994 [1-5]. The aim of the present paper is to examine these effects in the light of recent experimental observations. Attention is given to possible mechanisms by which precipitation processes may be modified, as well as to the possible practical significance of these changes. In this regard, a trace element addition is generally taken to be an amount up to 0.1at.%, although compositions and alloying additions mentioned in the paper are expressed in wt.%

2. TRACE ADDITIONS OF Cd, In AND Sn

2.1 Al-Cu Alloys

Interest in the addition of trace elements to age hardenable aluminium alloys appears to originate largely from observations by Hardy [6] of the effects of Cd, In and Sn on ageing in the binary Al-Cu system. This work showed that, whereas these elements reduced the response to hardening at low temperatures (Fig. (1a)), ageing was both accelerated and enhanced at elevated temperatures (Fig. (1b)). Such behaviour has subsequently been shown to be characteristic of trace element additions to several other aluminium alloy systems [7].

The reduction in the rate of age hardening in Al-Cu alloys at low temperatures has been attributed to a preferential interaction between Cd, In or Sn atoms and vacancies retained on quenching which reduces their availability to assist diffusion of the copper atoms to form GP zones [e.g. 8,9]. The implication is that the trace element atoms have larger binding energies with vacancies than is the case with the solute atoms. With Al-Cu-Sn alloys, for example, Kimura and Hasiguti [9] have calculated that the binding energy between a vacancy and a Sn atom is 0.2eV greater than that existing between a vacancy and a Cu atom. It is also interesting to note, from Fig.

1(a), that the rate of hardening of the Al-Cu-Sn (and Al-Cu-Ag) alloys undergoes a sudden increase after relatively long ageing times, perhaps suggesting that a stage is reached when the vacancies are eventually released so that they are free to assist diffusion of the Cu atoms.

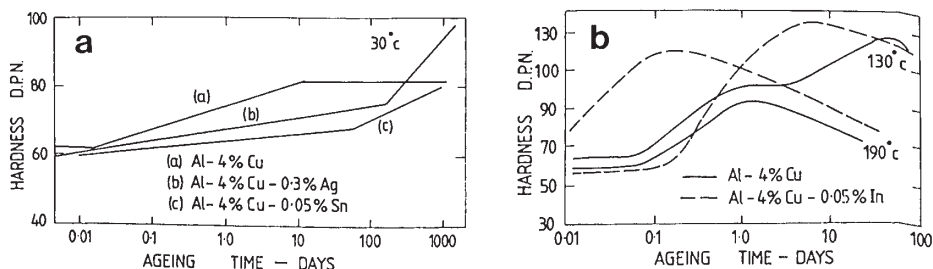


Fig. 1 Hardness-time curves at (a) 30°C and (b) 130 and 190°C [6,7].

Enhanced elevated temperature ageing in Al-Cu-(Cd, In, Sn) alloys is attributed to the effects of the trace additions in stimulating precipitation of a finer and more uniform dispersion of the semi-coherent, intermediate precipitate θ' in preference to the zone-like phase θ'' [10,11]. Normally, nucleation of θ' is energetically difficult and this phase tends to precipitate heterogeneously on dislocation lines. Since the trace elements do not alter the crystal structure of θ' , its morphology, or the $\{100\}_\alpha$ habit planes on which it forms [11], their role in the Al-Cu system is clearly to modify an existing precipitation process.

Several mechanisms have been proposed to account for the effects of Cd, In and Sn. One which was widely accepted is that the trace elements are absorbed at the θ' /matrix interfaces thereby lowering the interfacial energy associated with nucleation of θ' [2]. However, more recent work on an Al-Cu-In alloy involving transmission electron microscopy (TEM) has revealed that θ' appears to nucleate and grow at the sites small particles which x-ray microanalysis has shown to be In [12]. A similar observation has since been made using an Al-Cu-Sn alloy and atom probe field ion microscopy (APFIM) has confirmed both the presence of small particles of Sn and the fact that Sn is absent at the θ' /matrix interfaces (Fig. 2) [13]. It therefore seems probable that precipitation of the sparingly soluble Cd, In or Sn elements occurs during quenching, or at an early stage of elevated temperature ageing, and that these particles serve as sites for the heterogeneous nucleation of θ' .

Whereas Cd, In and Sn each have similar effects on ageing in binary Al-Cu alloys, a difference arises if Mg is also present because this element removes In and Sn into the stable compounds Mg_2In and Mg_2Sn . On the other hand, Cd remains unaffected and continues to promote nucleation of θ' , at least in those ternary Al-Cu-Mg alloys having high Cu:Mg ratios [6].

A practical outcome of these results was the development of a wrought Al-Cu-Cd alloy (Al-5%Cu-0.12%Cd-0.5%Mn) in the early 1950's that had mechanical properties comparable to the Al-Cu-Mg alloys of the 2xxx series [15]. Advantages were improved hot working characteristics due to absence of Mg, and the fact that the Al-Cu-Cd remained soft at ambient temperatures in the solution treated and quenched condition, whereas the 2xxx series alloys harden quite rapidly because of GP zone formation. However, the Al-Cu-Cd alloy had the disadvantage that cold working (eg. by stretching) after quenching and before elevated temperature ageing (T8 temper) caused a reduced response to hardening. This is contrary to the normal behaviour of the 2xxx series alloys and has

been attributed to the trapping of the rather large Cd atoms by dislocations introduced by cold working so that they are not free to facilitate nucleation of θ' [14]. Another disadvantage was the toxicity of Cd which required that casting operations be carefully controlled. Nevertheless, limited use was made later of a commercial alloy 2021 (Al-6.3%Cu-0.15%Cd-0.05%Sn), in the form of rolled plate, which has tensile properties in the T6 condition some 10-15% higher than the well known alloy 2219 (Al-6.3%Cu) on which it was based.

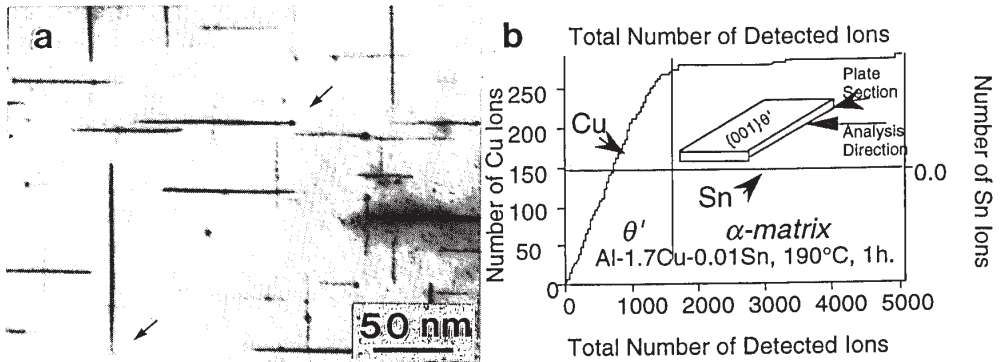


Fig. 2 Al-4%Cu-0.05%Sn alloy (Al-1.7at.%Cu-0.01At.%Sn) aged 1h at 190°C. (a) Bright field TEM micrograph showing plates of θ' phase which appears to have nucleated at the sites of Sn particles (arrowed). (b) APFIM ladder plot of the rim of a θ' precipitate showing that Sn appears is absent at the θ' /matrix interface [13]. (Courtesy S.P. Ringer.)

2.2 Al-Cu-Li Alloys

Le Baron showed that the response of Al-Cu alloys to age hardening was increased when Li was added in combination with several trace elements including Cd [16]. This observation, together with studies of trace element additions to Al-Cu-Li alloys by Hardy [1], contributed to the development of the first commercial, Li-containing aluminium alloy 2020 (Al-4.5%Cu-1.1%Li-0.5%Mn-0.2%Cd). The role of Cd was again shown to stimulate precipitation of the θ' phase.

Al-Cu-Li alloys developed more recently have lower Cu contents and higher Li:Cu ratios, one example being 2090 (Al-2.7%Cu-2.2%Li-0.12%Zr). Elevated temperature ageing of 2090 normally leads to precipitation of the coherent phase δ' (Al₃Li) together with the hexagonal, semi-coherent phase T₁(Al₂CuLi) which forms as thin plates on the {111}_α planes. Plates of θ' on the {100}_α planes may also be present. Nucleation of T₁ is also difficult and normally occurs heterogeneously on dislocation lines, so that 2090 is usually cold-worked before artificial ageing (T8 temper) to promote a more uniform dispersion of each precipitate.

Earlier work by Silcock [17] suggested that Cd additions have relatively little effect on the Al-Cu-Li alloys with higher Li contents. More recently, Blackburn & Starke [18] confirmed this general result, but showed that In additions did improve the response to ageing by increasing the density and uniformity of both the T₁ and θ' precipitates. Careful examination of the microstructure revealed that many of the T₁ plates were associated with small particles which were In-rich [18]. This suggests that the mechanism for assisting heterogeneous nucleation of T₁ by In in Al-Cu-Li alloys may be similar to that described for Al-Cu alloys containing Sn (Cd or In).

3. TRACE ADDITIONS OF Ag

The addition of Ag to Al-4%Cu also reduces age hardening at low temperatures and the ageing curve at 30°C (Fig. 1a) is similar in form to that obtained for the Al-Cu-Sn alloy [7]. A sudden increase in the rate of hardening is again observed after prolonged ageing which may be due to the release of a flux of vacancies. For alloys aged at elevated temperatures, it has been shown that Ag may stimulate enhanced hardening in all aluminium alloys in which Mg is present [7]. These effects are considered to have their origin in a preferred interaction between Ag atoms, Mg atoms and vacancies during, or immediately following quenching from the solution treatment temperature. However, the mechanisms involved have been found to vary with different alloy systems.

3.1 Al-Zn-Mg-(Cu) Alloys

Alloys based on the Al-Zn-Mg system (7xxx series) show the greatest response of the commonly used aluminium alloys to age hardening. The ageing sequence in a wide range of ternary compositions is: GP (Zn,Mg) zones (spheres) \rightarrow η' (MgZn_2) (plates) \rightarrow η' (MgZn_2) (plates or rods). Maximum hardening occurs at relatively low ageing temperatures, eg. 125°C (Fig. 3) when the microstructure comprises a mixture of finely dispersed GP zones together with some plates of the hexagonal, intermediate phase η' that form on the $\{111\}_\alpha$ planes [19]. The phase η' is generally believed to nucleate from, or at the sites of GP zones [19].

Investigations by Polmear [20-23] revealed that small additions of Ag stimulated an enhanced response of a wide range of ternary Al-Zn-Mg alloys to age hardening in the temperature range of 120 to 220°C. These effects were also observed in the more complex commercial compositions such as 7075 (Al-5.6%Zn-2.5%Mg-1.6%Cu-0.23%Cr) indicating that neither of the solute additional elements Cu or Cr, or the impurities such as Fe and Si interfered with Ag (Fig. 3) [23]. The addition of Ag to Al-Zn-Mg alloys again appears to modify and stimulates an existing ageing process. However, contrary to results shown for the addition of Cd, In or Sn to Al-Cu alloys (Fig. 1(b)), the presence of Ag in alloys based on the Al-Zn-Mg system does not increase the maximum level of hardening. Rather, Ag enables a high level of hardening to be retained at significantly higher ageing temperatures (Fig. 3). Another difference between the two alloy systems is that the effects of Ag on Al-Zn-Mg-(Cu) alloys are not destroyed by cold work prior to artificial ageing [23].

TEM has revealed that Ag promotes precipitation of finer dispersions of the η' phase at the higher ageing temperatures which suggested that Ag stimulates nucleation of η' [22]. However, Baba [24] proposed that the role of Ag was to modify the dispersion GP zones and Parker [25] showed that the GP zones solvus of a range of Al-Zn-Mg alloys was raised from 120-140°C to 200°C. As a consequence, it was proposed that the finer dispersion of η' in the Ag-containing alloys may be attributed to the in-situ formation of this phase from GP zones which retain their stability at the higher ageing temperatures. The precise mechanism by which their stability may be increased remains uncertain. One suggestion is that Ag may promote internal ordering within the zones due to a preferred interaction between Ag and Mg atoms [3] and a new three-dimensional atom probe (3DAP) study by Ringer [26] has confirmed that Ag atoms are, in fact, dispersed through the GP(Zn,Mg) zones. Another suggestion is that Ag may increase the stability of η' by modifying the electron:atom ratio of this phase [4].

Alloys based on the Al-Zn-Mg system may be susceptible to stress-corrosion cracking and microstructural changes induced by trace additions of Ag were shown to increase resistance to this phenomenon [23,27]. Independent work by Rosenkranz in Germany [28] led to the development of a commercial, Ag-containing alloy known as AZ74 (7009) which later found limited application in aircraft forgings.

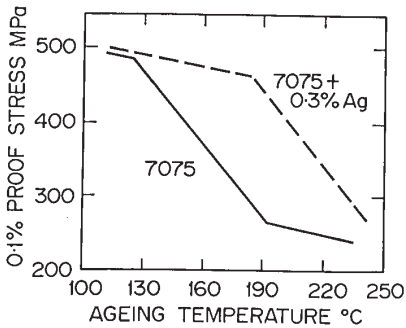


Fig. 3 Maximum values of 0.2% proof stress of 7075 and 7075+0.3%Ag aged to peak strength at different temperatures [23].

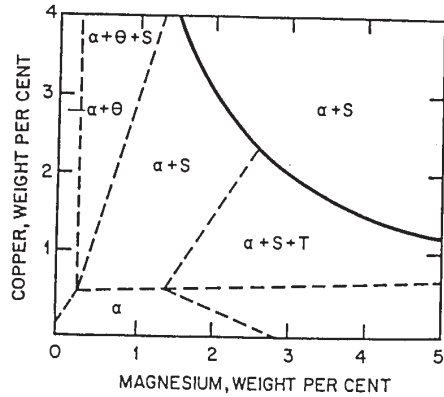


Fig. 4 Phases present in the Al-Cu-Mg system after long term ageing at 190°C [29]
 — phase boundary at 500°C
 phase boundary at 190°C

3.2 Al-Cu-Mg Alloys

For ternary alloys with high Cu:Mg ratios that lie in the $\alpha+\theta$ and $\alpha+\theta+S$ regions of the ternary phase diagram (Fig. 4), artificial ageing leads to precipitation of a mixture of phases that normally form in the Al-Cu and Al-Cu-Mg systems [30]. The addition of 0.1 at.%Ag causes an increased response to hardening due to precipitation of a metastable phase, designated Ω , which forms on the $\{111\}_{\alpha}$ planes as thin plates that are coherent along the flat faces [e.g. 31-34].

APFIM studies have shown that these quenched Al-Cu-Mg-Ag alloys contain separate clusters of Cu, Mg and Ag atoms [35,36]. Rapid co-clustering of Mg and Ag atoms occurs immediately after commencing ageing at elevated temperatures to which Cu atoms diffuse leading to the nucleation of Ω . It is suggested that the diffusion of Cu atoms may be assisted by the release of a flux of vacancies from the Mg-Ag co-clusters. Furthermore it has been proposed by Suh and Park [37] that elastic strain energy is minimized when the Mg-containing clusters form as disks on the $\{111\}_{\alpha}$ planes and that this is the reason why Ω nucleated on these planes rather than on the $\{100\}_{\alpha}$ planes.

The Ω phase is closely related to the tetragonal equilibrium phase $\theta(\text{Al}_2\text{Cu})$ that forms in Al-Cu alloys although it is now generally accepted that Ω has an orthorhombic structure [33,34]. During the growth of Ω , all the Ag and Mg atoms partition to the Ω /matrix interfaces [34,38,39] which is presumed to promote coherency along the $\{111\}_{\alpha}$ planes. Ω is relatively stable at temperatures up to 200°C and experimental Al-Cu-Mg-Ag alloys hardened by this phase show high strength (e.g. 0.2%P.S. 480MPa) combined with promising creep properties which appear to be superior to existing commercial 2xxx series alloys (e.g. Fig. 5) [40-42]. At ageing temperatures above 200°C, Ω is replaced by the equilibrium phase θ [43].

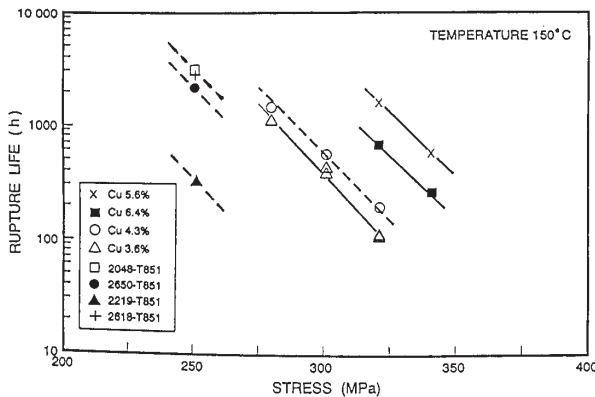


Fig. 5 Rupture life-stress curves at 150°C for Al-3.5-6.3%Cu-0.45%Mg-0.4%Ag-0.3%Mn-0.18%Zr (T6 temper) compared with several commercial 2xxx series alloys. (Courtesy H. Octor.)

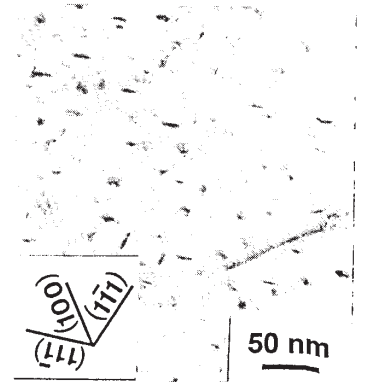


Fig. 6 Plates of hexagonal X' phase on $\{111\}_\alpha$ phases of alloy Al-2.5%Cu-1.5%Mg-0.5%Ag aged at 1h at 200°C. (Courtesy S.P. Ringer.)

Silver also promotes enhanced age hardening in other Al-Cu-Mg alloys with higher Mg:Cu ratios that lie in the α +S and α +S+T regions of the ternary phase diagram (Fig. 4) [42]. Initially it was proposed that Ag promoted formation of a finely dispersed T phase, $\text{Al}_6(\text{Cu,Ag})\text{Mg}_4$, rather than S'(S) in alloys aged at elevated temperatures [44,45]. However, recent work using convergent beam electron diffraction has revealed that two quite different precipitates are present at peak hardness depending on the Mg:Cu ratio. For alloys with Cu and Mg ratios that would place them in the α +S region, a metastable, intermediate precipitate termed X' is formed which has an hexagonal structure ($a=0.496$ nm and $c=1.375$ nm) and lies on the $\{111\}_\alpha$ planes [46] (Fig. 6). For higher Mg:Cu ratios corresponding to the α +S+T region of the phase diagram, maximum hardening is associated with another precipitate which has a f.c.c. structure ($a=1.999$ nm), and has been designated Z [47] (Fig. 7). The phase Z has two variants that form on the $\{110\}_\alpha$ and $\{111\}_\alpha$ planes, with the latter becoming dominant as ageing is continued [47].

The X'(S) phases have been investigated by APFIM [48,49]. Each has compositions within the ranges 50-65 at.%Al, 20-25 at.%Cu, and 15-25 at.%Mg implying a possible Al:Cu:Mg ratio of 2:1:1. This is similar to the S'(S) phase (Al_2CuMg) to which they may possibly transform on prolonged ageing [44]. However, in contrast to Ω , Ag does not partition to the precipitate/matrix interfaces and up to 5 at.% of this element is contained within each of these two precipitates. This difference in location of Ag in the various precipitates can be explained in terms of their respective compositions. Because of the strong interaction postulated between Mg and Ag atoms [7], it is to be expected that Ag will accompany Mg into the X' and Z phases, particularly as Ag may substitute for the atoms due to their similar atomic sizes [50].

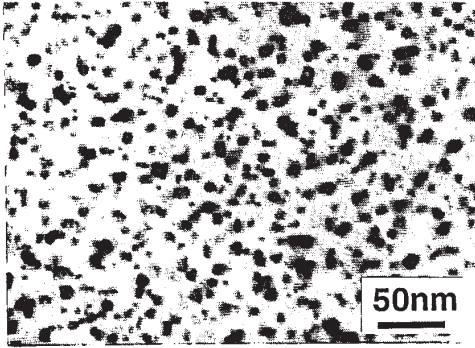


Fig. 7 Precipitates of cubic Z phase in alloy Al-1.5%Cu-4%Mg-0.5%Ag aged 9 h at 200°C. (Courtesy G.C. Quan.)

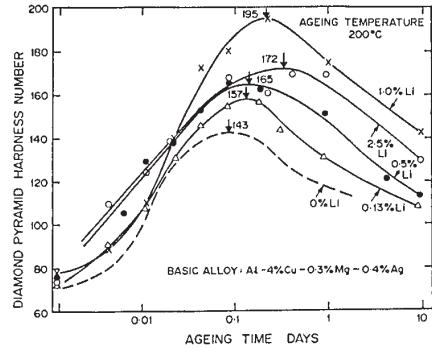


Fig. 8 Hardness-time curves at 200°C for Al-4%Cu-0.3%Mg-0.4%Ag containing Li additions from 0 to 2.5% [51].

3.3 Al-Cu-Li

Although small amounts of Ag do not change the ageing behaviour of Al-Cu-Li alloys, the addition of Ag and Mg together can stimulate an exceptional hardening response [51]. This effect is illustrated in Fig. 8 in which increasing amounts of Li have been added to the alloy Al-4%Cu-0.3%Ag-0.4%Mg. Peak hardening occurs with approximately 1%Li and Pickens and his colleagues [52] have developed a series of commercial Al-Cu-Li-Ag-Mg alloys (X2194, X2195) which may have tensile properties exceeding 700MPa. On a strength:weight basis, an equivalent steel would need to have tensile properties exceeding 2100 MPa, which suggests that these new compositions are the first ultra-high strength aluminium alloys to be produced from conventionally cast ingots. In this regard, alloy X2194 has been specified for the “super light weight” main fuel tanks for future launches of the US Space Shuttle [53].

The alloy Al-4%Cu-0.3%Ag-0.4%Mg is hardened mainly by Ω phase together with small amounts of θ' [30]. Progressive additions of Li above 0.5% lead to the replacement of Ω by T_1 , [50,51] although this change is not readily apparent in the microstructure because Ω and T_1 , both form on the $\{111\}_\alpha$ planes as thin plates having high aspect ratios. What is particularly interesting is the mechanism by which the Al-Cu-Li-Ag-Mg alloys develop such high strength. Observations of the microstructure of alloys containing around 1%Li aged to peak hardness reveal the presence of three intermediate precipitates T_1 , θ' and S'(S) [56]. Since each of these phases forms on a different crystallographic plane, and all are thought to be relatively resistant to shearing by dislocations, it may be that the high level of age hardening is due to their presence together. However, there may also be some intrinsic differences in the ability of the primary strengthening phases, T_1 and Ω , to resist shearing of dislocations which contributes to the superiority in strength of the Li-containing Al-Cu-Ag-Mg alloy over the Li-free alloy. Here, one possibility is the fact that the T_1 plates tend to have higher aspect ratios than Ω plates since recent work has shown that the critical resolved shear stress in dispersion hardened alloys increases with an increase in plate aspect ratio [58].

Nucleation of the T_1 phase in aged Al-Cu-Li alloys is difficult and this phase normally forms heterogeneously on dislocations [59]. For this reason, it is normal for a T8 temper to be used. The presence of Ag and Mg stimulates nucleation of a finer and more uniform dispersion of T_1 and eliminates the need for this deformation step in the processing of the Al-Cu-Li-Ag-Mg alloys. Recent 3DAP studies [60] have shown that these elements segregate to the interfaces of the T_1

plates and the matrix. Since this behaviour is similar to that observed for the Ω phase, it may be that the mechanism by which Ag and Mg facilitate nucleation T_1 is also similar. However, an alternative explanation has been proposed by Itoh *et al.* [61] who claim that T_1 is nucleated at the sites of pre-existing GP zones and that the role of Ag and Mg is to increase the density of these zones.

3.4 Al-Mg Alloys

Although the solid solubility of Mg in Al is as high as 15% at 450°C and decreases to around 1% at 20°C, the binary alloys show an abnormally small response to age hardening. The Mg content must exceed about 6% before any hardening occurs and, even then the response is small. This behaviour has been attributed to the GP zones solvus being below room temperature for a wide range of compositions [62].

Small additions of Ag cause a marked increase in supersaturation in the Al-Mg alloys [63] and can induce hardening in Al-Mg alloys with Mg levels as low as 0.5%, aged at 100 to 240°C [7,64,65]. Ito *et al.* [65] have proposed that GP zones can be stable up to 200°C in Al-Mg-Ag alloys and X-ray diffraction studies by Auld [66] have shown that an intermediate precipitate, which is a b.c.c. T phase $Mg_{32}(Al,Ag)_{49}$ is present at peak hardness. Prolonged ageing at this temperature leads to precipitation of a much coarser dispersion of what may be the equilibrium, f.c.c., β phase Al_8Mg_5 [67].

4. SUNDRY TRACE ELEMENT ADDITIONS

4.1 Ge and Si in Al-Cu-Mg Alloys

Brook and Hatt [68] showed that the combination of small additions of Mg and Ge also inhibit GP zone formation in Al-4%Cu aged at ambient temperatures, whereas hardening was both accelerated and increased at 165°C due to nucleation of a fine dispersion of θ' . These effects were attributed to a particularly strong interaction between Mg-Ge complexes and vacancies. The addition of Mg and Si had similar, but weaker effects although the presence of Si was considered to have a stabilizing effect on the θ' phase. These observations led to the development of an experimental, creep-resistant alloy known as Almagem (Al-5.3%Cu-0.3%Mg-0.2%Ge-0.1%Si) which showed a desirable combination of high strength at ambient temperatures (e.g. 0.2%P.S. of 445MPa) and a total plastic strain of <0.05% in 1000h at 150°C, and a stress of 185 MPa [69].

The evolution of the microstructure of Almagem during elevated temperature ageing at 170°C was recently characterized by Ringer *et al.* [70] and shown to be a complex process. APFIM revealed that the as-quenched alloy contained independent clusters of Cu, Mg, Ge and Si atoms. Co-clusters of Mg and Ge were detected within minutes of ageing at 170°C, together with GP zones which quickly reverted in favour of precipitation of the θ' phase. Two other phases were also observed. The more significant was a rod-shaped phase which was elongated in the $\langle 001 \rangle_\alpha$ directions. These rods appeared to contain equi-atomic amounts of Cu and Mg, together with Si and smaller levels of Ge. They have characteristics similar to GP(Cu,Mg) zones that form in Al-Cu-Mg alloys [71,72]. Also present is a fine scale precipitate with a Mg:(Ge+Si) ratio of approximately 2:1.

It may also be noted that the addition of 0.1 at.%Ag to Almagem does not stimulate precipitation of the Ω phase that normally occurs in ternary Al-Cu-Mg alloys with high Cu:Mg ratios [5]. This suggests that the supply of Mg atoms needed to form the Mg-Ag clusters which serve to nucleate Ω has been exhausted through the preferential interaction of Ge and Si.

4.2 Zr, Ge and Sc in Al-Li Alloys

Alloys based on the Al-Li system are frequently age hardened at least in part, due to precipitation of the coherent phase δ' (Al_3Li) throughout the matrix. In the presence of Zr, which forms stable Al_3Zr particles, and is commonly added to aluminium alloys to control grain structure, δ' may nucleate heterogeneously which accelerates the precipitation process [73,74].

A different effect is observed if small amounts of Ge are added to an Al-Li alloy because Ge precipitates as small elemental particles which are independent of δ' [75]. Normally, deformation of Al-Li alloys hardened by that the δ' phase leads to the undesirable localisation of strain in intense slip bands due to the fact δ' particles are readily sheared by moving dislocations. If the Ge particles are present, they can serve to pin the dislocations so that the strain is distributed more uniformly. A similar effect is observed with the addition of small amounts of Sc which forms fine, stable particles of Al_3Sc during solidification and thermomechanical processing [71]. As with Al_3Zr these particles also provide heterogeneous sites at which δ' can nucleate.

4.3 Be in Al-Cu, Al-Cu-Mg and Al-Mg-Si Alloys

Somewhat larger amounts of Be (0.3-0.45 at.%) have been shown to accelerate and increase hardening in the alloys Al-3%Cu [77], Al-2.5%Cu-1.2%Mg [78] and Al-0.75%Mg-0.5%Si [79] in both the naturally and artificially aged conditions. With the Al-Cu-Mg alloy, Be was found to inhibit vacancy condensation on quenching, while encouraging formation of small dislocation loops during subsequent natural ageing. Upon artificial ageing, these loops and small, spherical precipitates containing Be, serve as sites for the heterogeneous nucleation of a finer dispersion of the S'(S) phase (Al_2CuMg) [78]. In the Al-Cu-Be alloy, it has been proposed that Cu-Be-vacancy clusters accelerate natural ageing whereas, at higher ageing temperatures, Be dissolves in the precipitates θ' and $\theta(\text{Al}_2\text{Cu})$ accelerating their nucleation rates by increasing their nucleation entropies [77].

5. DISCUSSION AND CONCLUSIONS

The examples which have been described show that specific trace elements can modify age hardening in various aluminium alloys by:

- (i) stimulating or suppressing existing precipitation processes (e.g. Cd, In, Sn and Be in Al-Cu alloys; Ag in Al-Zn-Mg-(Cu) alloys; Ag+Mg in Al-Cu-Li alloys)
- (ii) promoting precipitation of new phases that form in addition to an existing precipitation process (Ge, Zr and Sc in Al-Cu-Li alloys)
- (iii) changing the precipitation process (Ag in Al-Cu-Mg alloys) with various Cu:Mg ratios
- (iv) increasing supersaturation (Ag in Al-Mg alloys)

So far as the actual roles of trace elements are concerned, two features seem common to most of the aluminium alloys. One is the indirect, but strong evidence that trace elements interact with, and change the distribution of vacancies retained during the quenching operation. Such interactions may have a profound influence on the nucleation events that precede precipitation. The other common feature is that, on ageing at elevated temperatures, the trace elements seem invariably to facilitate nucleation of fine dispersion of semi-coherent, intermediate precipitates. Such precipitates normally resist shearing of dislocations and may now be too closely spaced to be bypassed by them. Significant increases in strength may result which have important practical implications.

The usual mechanism by which trace elements influence precipitation of intermediate precipitates is to provide sites at which they can form by heterogeneous nucleation. Examples appear to be Cd, In and Sn in Al-Cu alloys, Zr and Sc in Al-Li based alloys and Be in Al-Cu-Mg alloys. In each case, the trace element is sparingly soluble in aluminium and precipitates as small elemental particles or compounds during processing, quenching or immediately after ageing commences. When such a mechanism is operative, it is an existing precipitate that is nucleated.

The addition of Ag to Al-Zn-Mg-(Cu) alloys also facilitates nucleation of finer dispersions of an existing intermediate precipitate. In this case, the phase η' is generally considered to nucleate at, or from pre-existing GP zones to which Ag segregates at an earlier stage in the ageing process, apparently increasing their stability. The role of Be in Al-Cu alloys may have a similar origin, as may the combined effects of Ag+Mg on nucleation of the T_1 phase in Al-Cu-Li-(Mg) alloys.

The effects of Ag additions to Al-Cu-Mg are of special interest because the usual ageing processes are changed and one of three new precipitates, Ω , X' and Z, form depending on the Cu:Mg ratio. Recent APFIM studies have suggested that the stimulus for these changes comes from clustering events that precede precipitation, notably a preferred interaction which occurs between Ag and Mg atoms. These Ag-Mg clusters then appear to provide sites at which the direct nucleation of Ω , and probably all three precipitates may take place. Furthermore, since strain energy considerations dictate that clusters containing Mg will form preferentially on the $\{111\}_\alpha$ planes, this may be the reason why all three phases precipitate on these particular planes.

Attention should also be directed at possible rules that may govern trace element behaviour since this may allow the prediction of minor additions that will stimulate desired changes to the structure and properties of alloys undergoing precipitation. From the results described above, two features seem common. One is that the trace element should have only sparing solid solubility in the alloy. The other is that the trace element should interact preferentially with vacancies during, or immediately following quenching since early clustering events may dictate the course of subsequent precipitation. In some aluminium alloys, evidence for such an interaction may be available from a study of ageing behaviour at ambient temperatures at which the response to hardening is reduced.

Three other features can be identified which have more restricted applicability. One is the suggestion that in some alloys, the trace element should have a relatively high heat of formation with one of the solute atoms and prospects for this can be identified from trace element-solute atom phase diagrams. The preferred interaction of Mg and Ag in aluminium alloys is a striking example since this may influence early clustering reactions, alter the stability of existing zones or precipitates, or stimulate the nucleation of new phases. At the same time, it is necessary to require that such an interaction does not remove the trace element into a stable intermetallic compound as may happen in the case of Sn and In if they are added to an Al-Cu alloy containing Mg. On the other hand, if the trace element does form such a stable compound with the solvent element Al, and this compound is finely dispersed, then heterogeneous nucleation of an existing precipitate may be facilitated (Zr in Al-Cu-Li alloys) and/or the compound may provide supplementary hardening (e.g. Zr and Sc in Al-Cu-Li alloys). The third feature is the possibility that the trace element increases the stability of a particular precipitate by partitioning to it and altering the electron:atom ratio.

Finally, it is important to note that certain trace elements may segregate to the surfaces of growing precipitates, thereby promoting coherency with the matrix planes. Such an effect can enhance the stability of the precipitate and improve the performance of an alloy at elevated temperatures.

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