PRECIPITATE STABILITY IN ALLOYS BASED ON THE Al-Cu SYSTEM

Y.-S. Lee, S.P. Ringer, B.C. Muddle and I.J. Polmear
Department of Materials Engineering, Monash University, Clayton, Victoria, 3168, Australia

Abstract

A series of microalloyed Al-Cu based alloys have been exposed to long term ageing at high temperatures (150-300°C), and the identity and relative thermal stability of the resulting precipitate structures characterised using transmission electron microscopy. The results are presented in the context of a brief review of the effects of individual or combined additions of Mg, Ag, Li, Si and Ge on the precipitate phases formed in age-hardened Al-Cu alloys. In Al-Cu-Mg alloys of high Cu:Mg ratio (>3:1-4:1 by weight), trace additions of Ag promote formation of metastable Ω phase as thin plates on matrix $\{111\}_\alpha$ planes. With the further addition of Li in concentrations up to 0.5 wt%, the Ω phase is retained, but for Li additions of ~1 wt%, the $\{111\}_\alpha$ precipitates are observed to be the T_1 phase common in Al-Cu-Li alloys. The Mg and Ag in trace-modified Al-Cu-Li alloys are partitioned to the T_1 plates and appear to facilitate the development of a fine and uniform dispersion of the T_1 phase in ultra-high strength Al-Cu-Li-Mg-Ag alloys at maximum hardness. Both the Ω and T_1 phases exhibit good thermal stability at temperatures up to 200°C, with the T_1 phase more resistant to coarsening than Ω phase for equivalent thermal treatments. With longer term ageing at temperatures above 200°C, both Ω and T_1 are unstable and replaced by the θ' and/or θ phases. Trace concentrations of Si and Ge in Al-Cu-Mg-Ag alloys with high Cu:Mg ratio suppress the formation of the Ω phase and sustain a mix of rod-like (Cu,Mg) zones and θ' phase.

Introduction

The elevated temperature properties of age-hardened aluminium alloys are controlled primarily by the identity and relative stability of the dispersed precipitate phases. Of current commercial alloys, best performance in service is provided by the alloy 2219 (Al-6.3%Cu), in which the principal hardening phase is θ' (Al_2Cu). However, the yield and tensile strengths of 2219 in the T6 condition at room temperature are relatively low at typically 300 MPa and 420 MPa respectively.

Alloy 2219 has served as the basis for several new alloy developments in which the addition of particular elements, individually or in combination, has stimulated changes to the precipitation processes which, in turn, have resulted in improved performance at both room and elevated temperatures. In ternary Al-Cu-Mg alloys with high Cu:Mg ratios (e.g. 20:1 by weight), for example, the presence of small concentrations of Mg (e.g. 0.3 wt%) promotes formation of GP(Cu,Mg) zones and S' or S phase (Al_2CuMg), in addition to θ', and is the basis for the commercial alloy 2519 [1]. Further minor additions of Si and/or Ge to alloys of this type have been shown to improve creep resistance at moderately elevated temperatures (e.g. 150°C) by increasing the stability of the θ' phase [2].

In contrast, trace additions of Ag (e.g. 0.4 wt%) to these Al-Cu-Mg alloys promote precipitation of the phase designated Ω (Al_2Cu), which forms as a fine dispersion of thin plates on the $\{111\}_\alpha$ planes [3-5]. Alloys based on the quaternary Al-Cu-Mg-Ag system may have yield strengths

Table 1 Experimental Alloy Compositions

	Elemental Concentrations (wt%)						
Alloy	**Cu**	**Mg**	**Ag**	**Li**	**Si**	**Ge**	**Al**
1	4.0	0.3	0.4	-	-	-	Balance
2	4.0	0.3	0.4	0.5	-	-	Balance
3	4.0	0.3	0.4	1.0	-	-	Balance
4	5.5	0.3	-	-	0.1	0.1	Balance
5	5.5	0.3	0.4	-	0.1	0.1	Balance

exceeding 500 MPa [6]. The presence of the Ω phase also enhances creep resistance at temperatures up to 180-200°C [7], but recent work has shown that Ω is unstable at higher temperatures (e.g. 250°C) and is replaced by the equilibrium θ phase after prolonged ageing [8].

In still more complex alloys with high Cu:Mg ratios, based on the Al-Cu-Mg-Ag system, the addition of Li may lead to the replacement of the Ω phase by the phase T_1 (Al_2CuLi), which has similar form and habit plane to Ω, but a different crystal structure [9]. The resulting Al-Cu-Li-Mg-Ag alloys now form the basis for the so-called Weldalite 049™ series of ultra-high strength alloys (X2094 and X2095), which have yield strengths that may exceed 700 MPa [10].

Currently, there is much interest in the long term creep properties of these high strength alloys for potential aerospace applications at temperatures in the range 120-180°C. Their behaviour under these conditions is controlled primarily by the relative thermal stabilities of the various precipitating phases. It is the purpose of this paper to summarize results of recent work on the effects of individual or combined additions of Mg, Ag, Si, Ge and Li on the identity and thermal stability of the phases that form in the various alloys based on the Al-Cu system.

Experimental Procedures

The nominal compositions of the alloys examined experimentally are provided in Table 1. Alloys were chill cast, homogenized and hot rolled to produce specimens for hardness testing and transmission electron microscopy. Strips of each alloy 0.5-1.0 mm thick were solution treated in a salt bath at 525°C for 1h, cold water quenched and aged in oil baths at temperatures in the range 150-300°C for times up to 2400h.

Specimens for TEM were punched mechanically from the strips, ground to a thickness of 0.1 mm and twin-jet electrolytically polished in a solution of 33 vol.% nitric acid and 67 vol.% methanol at -25°C. Microscopy was carried out in Philips EM420 and CM20 instruments operating at 120 and 200 kV respectively. Electron microdiffraction patterns were recorded in conventional TEM mode using condenser apertures within the range 50 to 150 μm and an electron beam nominally 40-100 nm in diameter. Energy dispersive x-ray spectroscopy (EDXS) with high spatial resolution (~2-3 nm) was carried out in a Philips CM20FEG instrument operating in scanning TEM (STEM) mode.

Results and Discussion

Al-Cu-Mg-Ag

Small concentrations of Ag are known to enhance age hardening in all aluminium alloys containing Mg [12], and Figure 1 illustrates the acceleration in the hardening response and increase in maximum hardness associated with the addition of 0.4 wt% Ag to an Al-Cu-Mg alloy with high Cu:Mg ratio. It is well-established that Ag stimulates precipitation of a fine and uniform dispersion of the Ω phase, which forms as thin, hexagonal plates on $\{111\}_\alpha$ planes, Fig. 2, and that it is the Ω phase which generates the substantial increment in hardness in the quaternary alloys of high Cu:Mg ratio, Fig. 1 [3].

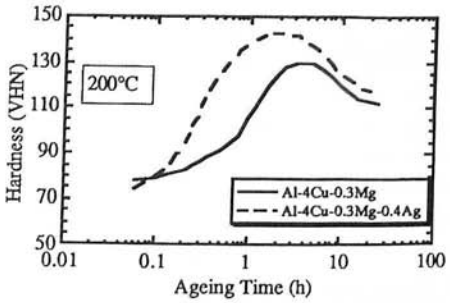

Figure 1. Isothermal age hardening response for Al-4Cu-0.3Mg alloy, with and without the addition of 0.4 wt% Ag, at 200°C [11].

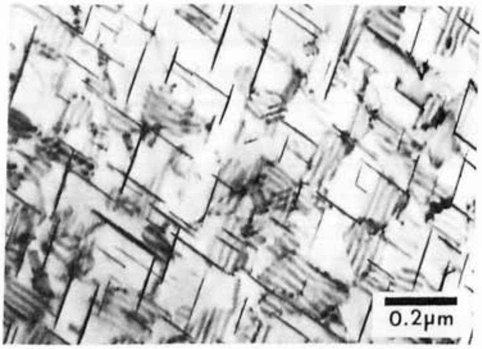

Figure 2. TEM micrograph showing the Ω phase in an Al-4Cu-0.3Mg-0.4Ag alloy aged 100h at 190°C. The electron beam is parallel to $\langle 110 \rangle_{\alpha}$.

Events associated with the nucleation of Ω phase in the alloy Al-4Cu-0.3Mg-0.4Ag have recently been examined using atom probe field ion microscopy [13]. This phase is believed to nucleate directly at the sites of co-clusters of Mg and Ag atoms that form very early in the ageing process (e.g. 30s at 180°C). However, the precise role of Ag (and Mg) in stimulating Ω phase in preference to θ' remains unclear.

Alloys based on the Al-Cu-Mg-Ag system have shown promising creep properties at temperatures up to 200°C, because of the relatively high thermal stability of Ω in this temperature range [6]. However, recent studies of the thermal stability of the Al-4Cu-0.3Mg-0.4Ag alloy exposed to long term ageing (2400h) at the higher temperature of 250°C have shown that the Ω phase is replaced by coarse particles of the equilibrium θ phase (Al_2Cu) that forms in binary Al-Cu alloys [8].

Al-Cu-Li-Mg-Ag

The age-hardening response of Al-Cu-Mg-Ag alloys with high Cu:Mg ratios can be enhanced significantly by the addition of Li. The hardness curves in Figure 3 represent Al-4Cu-0.3Mg-0.4Ag alloys containing systematic Li additions of between 0 and 2.5 wt%, aged at 200°C [14]. They show an increase in maximum hardness with increasing Li content up to ~1 wt%, but at 2.5 wt% Li, the peak hardness is reduced. While the Al-4Cu-0.3Mg-0.4Ag alloy is hardened by a fine and uniform dispersion of Ω plates on $\{111\}_{\alpha}$, and a minor fraction of θ' phase, the addition of Li has been reported to reduce the density of $\{111\}_{\alpha}$ precipitates, promote a finer dispersion of θ' and

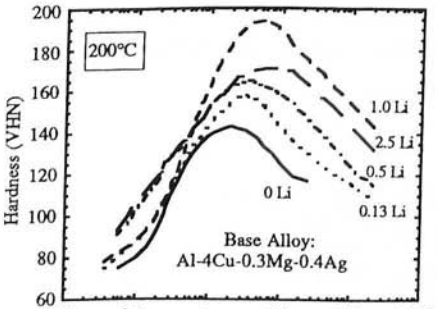

Figure 3. Variation in hardness with ageing time at 200°C for an Al-4Cu-0.3Mg-0.4Ag alloy containing systematic additions of Li. [14].

introduce laths of the S' (or S) phase [14]. It has been suggested [14] that, while the $\{111\}_\alpha$ precipitates remain the primary strengthening constituent, the exceptional hardness of the 1 wt% Li alloy may be attributable to the coexistence of these three effective strengthening precipitates, each

of which has a different crystal structure and forms on different crystal planes. The $\{111\}_\alpha$ precipitates were initially thought to be Ω phase [14], but recent high resolution electron microscopy [15] has indicated that they have a structure similar to that of the T_1 phase, which is the primary intermediate strengthening phase in Al-Cu-Li alloys such as 2090 [16,17].

In the present work, electron microscopy has been carried out on a series of Al-Cu-Mg-Ag alloys containing systematic additions of Li subjected to extended (24h) ageing treatments at high temperatures (250-300°C) to promote relatively coarse precipitate plates. In those alloys containing up to ~0.5 wt% Li, the $\{111\}_\alpha$ precipitates remain exclusively Ω phase, while in those alloys with $\geq$1 wt% Li, the $\{111\}_\alpha$ plates are uniformly T_1. Figure 4 compares micrographs from samples of (a) 0.5 wt% Li alloy, aged 4h at 300°C, and (b) 1.0 wt % Li alloy, aged 24h at 300°C. In each case the electron beam is parallel to $<110>_\alpha$ and there are two variants of $\{111\}_\alpha$ precipitate plates parallel to the electron beam. The electron microdiffraction patterns recorded from such plates in the 0.5 wt% Li alloy, Figs. 4(c) and (d), are consistent with those expected from the orthorhombic Ω phase [5], while those obtained from plates in the 1.0 wt % Li alloy parallel to $<110>_\alpha$ and $<\bar{1}12>_\alpha$ zone axes are distinguishably different and consistent with T_1 phase. The precipitate patterns in Figs. 4(e) and (f) may be indexed as consistent with $<10\bar{1}0>$ and $<11\bar{2}0>$ zone axis patterns respectively from hexagonal T_1.

The T_1 phase forms with some difficulty in ternary Al-Cu-Li alloys during conventional isothermal

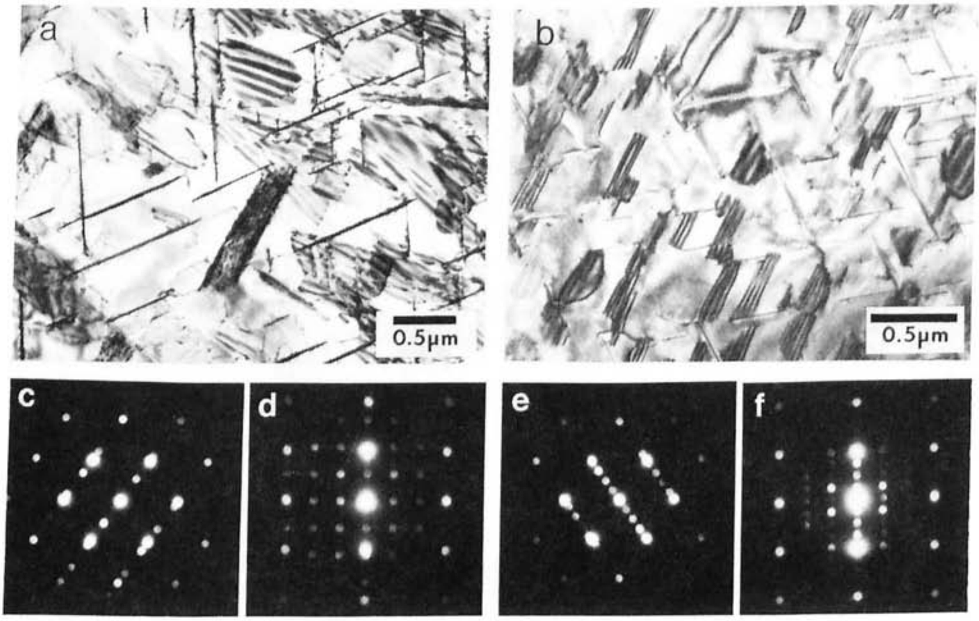

Figure 4. Transmission electron micrographs from Al-Cu-Mg-Ag alloys with additions of (a) 0.5 wt% Li, aged 4h at 300°C, and (b) 1.0 wt% Li, aged 24h at 300°C. Electron beam is parallel to $<110>_\alpha$. Corresponding electron microdiffraction patterns shown in (c) and (d) are from Ω phase precipitates observed in 0.5% Li alloy parallel to $<110>_\alpha$ and $<112>_\alpha$ zone axes respectively, while those in (e) and (f) are from T_1 plates in 1.0% Li again parallel to $<110>_\alpha$ and $<112>_\alpha$ zone axes respectively.

ageing treatments and it is common practice for such alloys to be deformed plastically prior to ageing (T8 treatment) to increase the density of dislocations on which T_1 can nucleate heterogeneously and promote a more uniform precipitate distribution [16,17]. In the present Al-Cu-Li alloys containing microalloying additions of Mg and Ag, these elements have been detected in association with the T_1 plates using energy dispersive x-ray spectroscopy with high spatial resolution. Figure 5 shows the x-ray spectrum recorded from a single T_1 plate in a sample of alloy 3 (1 wt% Li) that had been heated continuously to 350°C at a rate of 10°Cmin.$^{-1}$ to produce relatively coarse T_1 precipitates. The spectrum was recorded with the electron beam parallel to the habit plane of the precipitate plate and, despite some overlap of the electron beam to the adjacent matrix phase, clearly indicates the partitioning of both Mg and Ag to the precipitate phase. The Mg and Ag were not detectable in the matrix phase surrounding such plates. This association of these trace elements with the T_1 precipitates has recently been confirmed in atom probe field ion microscopy of an alloy of the Weldalite 049™ series [18].

A fine and uniform distribution of T_1 precipitates is a feature of the trace-modified Al-Cu-Li alloys aged to peak hardness [14] and it appears likely that it is the distribution of T_1 phase that emerges in the presence of the Mg and Ag that is the main factor in promoting the exceptional strength and hardness of the Al-Cu-Li-Mg-Ag alloys that have emerged as the Weldalite series. The role of the trace elements remains to be understood in detail, but their association with the T_1 plates suggests that combined additions of Mg and Ag appear to facilitate the nucleation of the T_1 phase in the absence of prior plastic deformation.

The T_1 plates observed in Li-containing alloys subjected to extended high temperature ageing, Fig. 4(b), remain noticeably finer in scale than the Ω plates in lower Li alloys given shorter term treatments, Fig. 4(a). After 24h at 300°C, the Ω phase in the 0.5 wt% Li alloy had disappeared, to be replaced by θ' phase, Figure 6(a). This suggests that the T_1 phase may well prove more

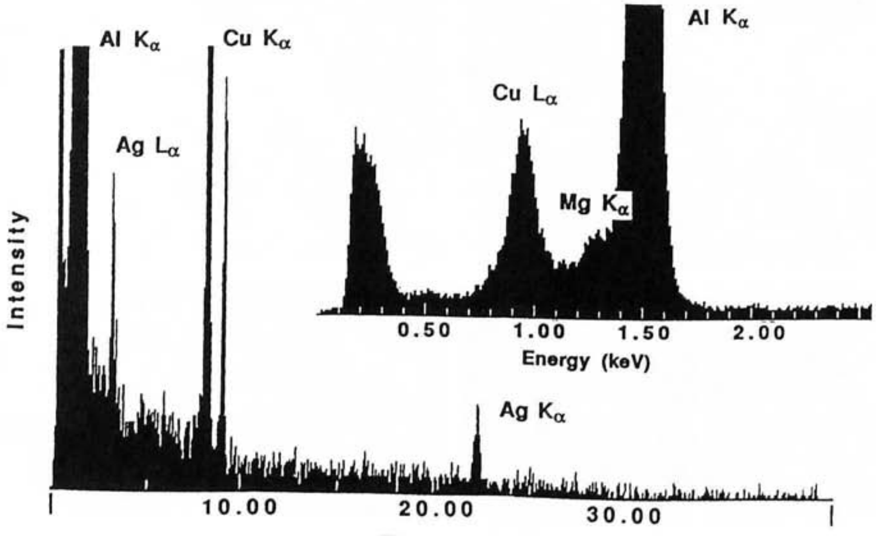

Figure 5. Energy dispersive x-ray spectrum recorded from a single T_1 plate in a sample of Al-Cu-Li-Mg-Ag alloy (1 wt% Li) heated continuously to 350°C at a rate of 10°Cmin.$^{-1}$. The spectrum was recorded with the electron beam parallel to the habit plane of the precipitate plate.

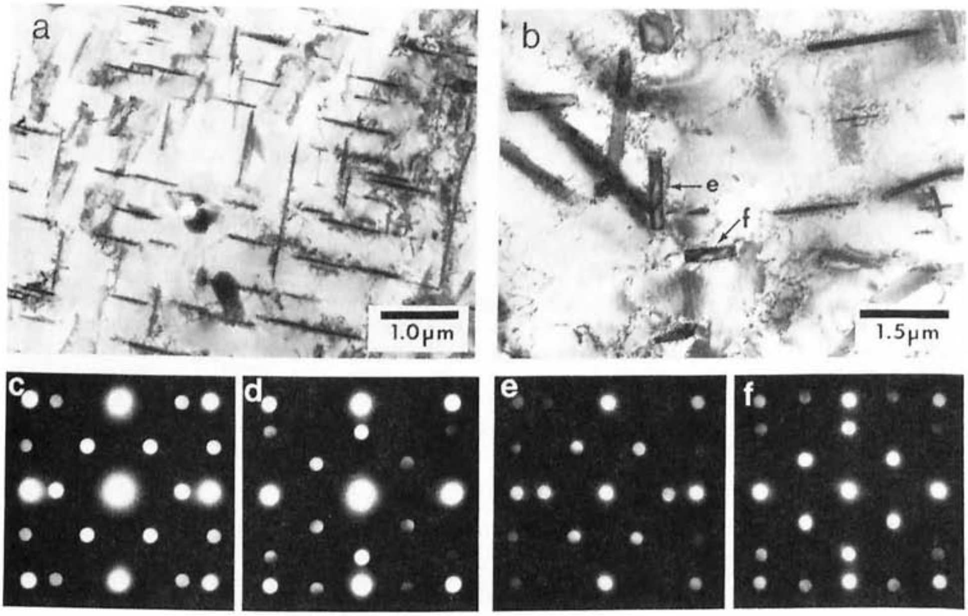

Figure 6. Transmission electron micrographs of Al-Cu-Li-Mg-Ag with (a) 0.5 wt% Li, aged 24h at 300°C, and (b) 1.0 wt% Li, aged 725h at 300°C. Electron microdiffraction patterns from (c), (d) 0.5Li alloy, and (e),(f) arrowed precipitates in 1.0Li alloy confirm that , in both alloys, the dominant precipitate is θ'.

thermally stable than Ω. However, whereas it has been established that the Ω phase is replaced by equilibrium θ phase after extended ageing at temperatures above 200°C [8], there have yet to be any systematic studies of the longer term thermal stability of T_1.

To assess the stability of T_1 at higher ageing temperatures, samples of the 1 wt% Li alloy (alloy 3) have been exposed for extended periods at temperatures of 250 and 300°C. As with the Ω phase, it has been observed that the T_1 is unstable at these temperatures and is replaced initially by θ' and eventually by θ phase. Figure 6(b) shows a transmission electron micrograph of the microstructure of a sample of alloy 3, aged 725h at 300°C, and corresponding electron microdiffraction patterns from the orthogonal precipitate variants (e) and (f) (arrowed). These patterns are consistent with those expected from θ' phase [5], as were patterns from most of the dispersed particles following this heat treatment.

Al-Cu-Mg-Ag-Ge-Si

It is well known that trace additions of Cd, In or Sn increase both the rate and extent of hardening in binary Al-Cu alloys aged in the medium temperature range of 120-200°C [19]. Comparisons of binary and ternary alloys have shown that these trace elements suppress formation of the coherent θ" phase [20], while stimulating finer and more uniform dispersions of θ' [21]. In an interesting further development, it has been shown that small concentrations of Mg, Ge and Si interact together to also modify precipitation precipitation in Al-Cu alloys [22]. For example, quaternary Al-Cu-Mg-Ge alloys exhibit a much stronger response to age hardening than the equivalent Al-Cu-Mg alloy. A smaller, but still significant, increase in age hardening is also observed in Al-Cu-Mg-Si alloys. In each case, maximum hardness is also associated with fine and uniform dispersions of the θ' phase. These observations suggest that the stronger the interaction between trace elements, either individually or in combination, and vacancies after quenching, the more rapid is θ' nucleation at elevated temperatures, and the finer and more uniform is the dispersion. It has been proposed [22] that the efficiency of nucleation of θ' increases with trace element additions in the order (Mg+Si), Sn (In or Cd), and (Mg+Ge). At the same time, the stability of the resultant θ' dispersion would decrease in the above order. It has been suggested [22] that the increase in θ' stability may be attributable to the segregation of the trace elements, individually or collectively, to the θ'/α interface in such a manner that they retard growth. These results led to the development of an experimental alloy called Almagem (Al-5.5Cu-0.3Mg-0.1Si-0.1Ge) which showed promising creep strength at 150°C [2].

In a further interesting example of the effects of multiple trace element additions, recent characterisation of an Al-Cu-Mg-Ag alloys containing microalloying additions of Si, Ge (and Zr) (alloys 5 and 6) has revealed that, in the presence of small concentrations of Si and/or Ge, Ag has a less significant effect on the age hardening response. Figure 7 shows a comparison of the hardness curves obtained for an Al-Cu-Mg-Si-Ge alloy with and without Ag additions and indicates that, while there is a systematic increase in the hardness of the Ag-containing alloy, the difference between the Ag-free and Ag-containing alloys is modest. While a quaternary Al-Cu-Mg-Ag alloy contains predominantly Ω phase at maximum hardness, the alloy with Si and/or Ge additions is strengthened by a combination of rod-like (Cu,Mg) zones and θ' phase, Figure 8, up to maximum hardness, irrespective of whether the alloy contains Ag or not.

Figure 8 is an electron micrograph recorded from a sample of alloy 5 aged to peak hardness at 150°C (8h) and the microstructure comprises a mixture of rod-like (Cu,Mg) zones [23] parallel to $<100>_\alpha$ and fine θ' plates on $\{100\}_\alpha$ planes. The presence of Si and Ge appears to favour the formation of the rod-like zones during the early stages of ageing, exhausting the supply of Mg and thus preventing the formation of the Ω phase that is characteristic of the quaternary alloy.

Summary

In Al-Cu-Mg alloys of high Cu:Mg ratio (>3:1-4:1 by weight), trace additions of Ag promote the formation of a uniform dispersion of the metastable Ω phase on matrix $\{111\}_\alpha$ planes. With the addition of Li to these quaternary alloys in concentrations up to 0.5 wt%, the Ω phase is retained, with increased minor fractions of θ' and S phases. However, for Li additions of ~1 wt%, the primary strengthening $\{111\}_\alpha$ precipitates are observed to be the T_1 phase common in Al-Cu-Li alloys. The Mg and Ag in these trace-modified Al-Cu-Li alloys partition to the T_1 plates and appear to facilitate the development of a fine and uniform dispersion of the T_1 phase.

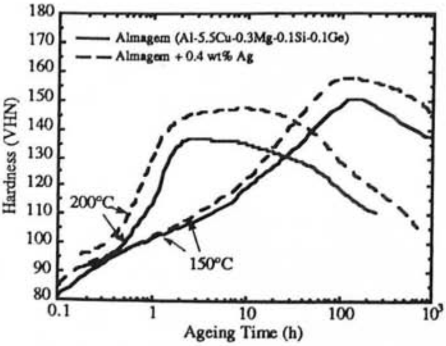

Figure 7. Variation in hardness (VHN) with ageing time at 150°C and 200°C for an Al-Cu-Mg-Si-Ge alloy with and without an addition of 0.4 wt% Ag.

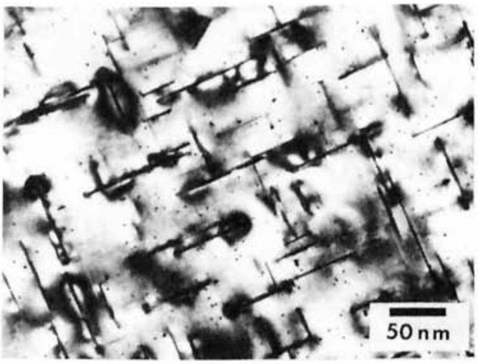

Figure 8. Microstructure of Ag-modified Almagem (alloy 5) aged 18h to maximum hardness at 170°C.

Both Ω and T_1 exhibit good thermal stability at temperatures up to 200°C, with T_1 showing a greater resistance to coarsening than Ω phase for equivalent thermal treatments. However, with longer term ageing at temperatures >200°C, both Ω and T_1 prove to be unstable and are replaced by θ' (and θ) phase in the case of T_1 and the equilibrium θ phase (Al_2Cu) in the case of Ω phase.

The addition of trace concentrations of Si and Ge to Al-Cu-Mg-Ag alloys with high Cu:Mg ratio suppresses the formation of the Ω phase. At maximum hardness those complex alloys containing Si and Ge are strengthened by a mix of rod-like (Cu,Mg) zones and θ' phase.

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