The role of silicon in the formation of the ($Al_5Cu_6Mg_2$) σ phase in Al-Cu-Mg alloys

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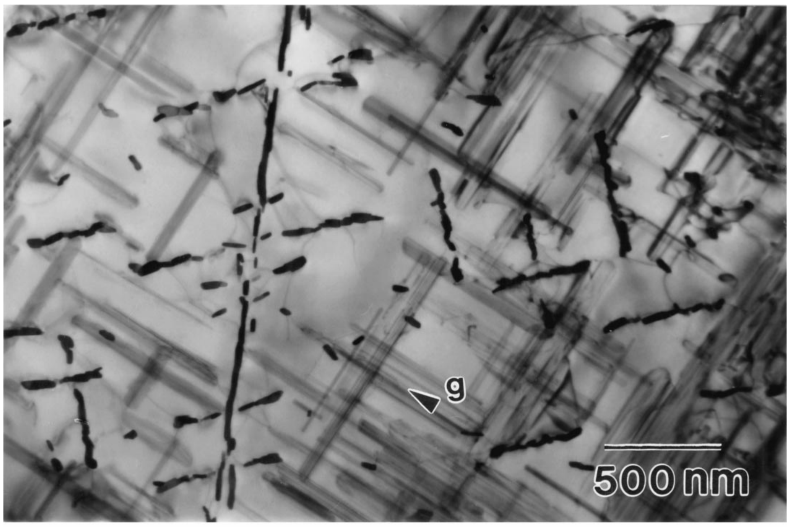
The role of silicon in the precipitation of the σ phase ($Al_5Cu_6Mg_2$) has been investigated through comparative studies on Al-3.63Cu-1.67Mg (wt%) and Al-3.63Cu-1.67Mg-0.5Si alloys. Both alloys were extensively examined after solution treating at 525°C for 2.5 h followed by ageing at 265°C for times up to 650 h. Limited studies were also undertaken on both alloys after ageing at 200 and 305°C. Precipitation of σ was observed in Al-3.62%Cu-1.66%Mg-0.5%Si for all ageing conditions studied but was absent in Si-free Al-3.62%Cu-1.66%Mg. In addition, S′ and θ' phases were observed in both alloys. The volume fraction of σ phase in the Si containing alloy was substantially reduced by a pre-age stretch followed by ageing for 24 h at 265°C with S′ being the dominant precipitate type. The volume fraction of σ phase in the Si containing alloy was lower after ageing 24 h at 200°C than after 24 h at 265 and 305°C. Peak hardness was higher for the Si free alloy on ageing at 200 and 265°C, but the Si free alloy softened more rapidly, reflecting the more rapid coarsening kinetics of S′ compared with σ. © *2000 Kluwer Academic Publishers*

1. Introduction

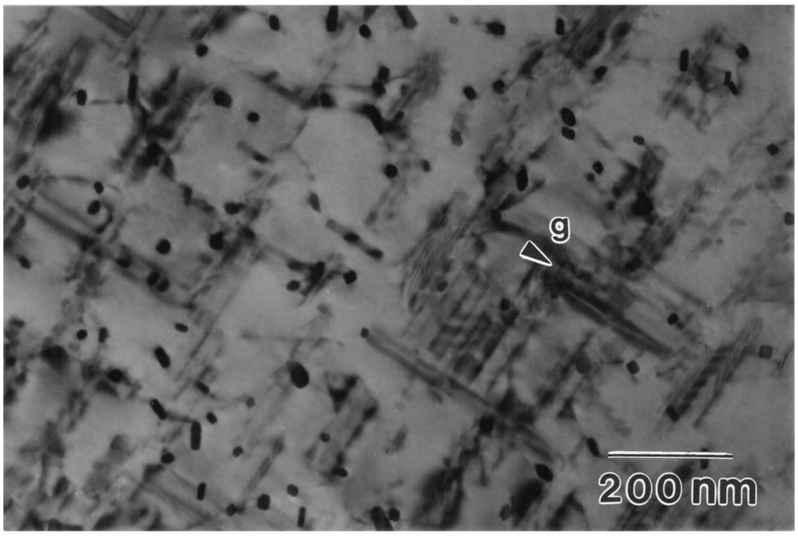
Phase formation in 2xxx series Al-Cu-Mg precipitation strengthened alloys is sensitive to the total solute content of the alloy and particularly to the Cu/Mg ratio [1]. The S′ (Al_2CuMg) precipitate exhibits good thermal stability [2] and increasingly displaces θ' as the Cu/Mg ratio is increased. A cubic 'σ' phase ($Al_5Cu_6Mg_2$), was first observed in this system by Weatherly [3] in an Al-2.7Cu-1.36Mg-0.2Si (wt%) alloy, and two further reports of its occurrence followed in the next decade [4, 5]. Schueller *et al.* [6–9] later observed σ in squeeze-cast Al-4.3Cu-2.0Mg/SiC composites and attributed its formation to the presence of Si in the matrix, dissolved from the SiC during processing. These authors demonstrated [7] that the coarsening kinetics of σ at 190°C were slower than for S′ and θ', and suggested that the σ phase could provide the basis of a superior precipitation hardened alloy. Li and Wawner [10] also obtained σ (in addition to Ω, S′ and θ') in Al-3.2/4.0Cu-0.45Mg-0.4Ag aged at 200°C at which its coarsening rate was found to be lower than for θ'. Barr *et al.* [11] obtained σ as the majority precipitate phase in a wrought Al-3.9%Cu-1.4%Mg-0.2%Si alloy, and found that σ phase formation was unaffected by quench rate from solution treatment (at 525°C) or by subsequent ageing temperature in the range 200–365°C. This work also showed that the coarsening rate of σ is lower than for S′ in treatments as long as 650 h at 265°C, although S′ was the more effective hardener. In contrast to these findings, Gao *et al.* [12] observed a quaternary Q phase ($Al_4Cu_2Mg_8Si_7$) in addition to S′ and θ' for Si additions (0.1–1.2 wt%) to a Al-4Cu-0.3Mg alloy, but no σ was present. Similarly, Gupta *et al.* [1] made a detailed examination of Al-1.75Cu-0.75Mg with 0.23–1.03Si and found no σ, but did observe Q phase for Si of 0.49% and above. It is evident from these various findings that the conditions under which σ phase forms and the role of Si in its formation are not yet well defined. In this paper, comparisons are made between two wrought alloys, Al-3.63%Cu-1.67%Mg (wt%)—AL1 and Al-3.62%Cu-1.66%Mg-0.5%Si—AL2 to elucidate the role of Si and its importance in the formation of the cubic σ ($Al_5Cu_6Mg_2$) phase. The effect of a pre-age stretch on the microstructure of the two alloys aged 24h at 265°C was also studied (samples designated AL1-S and AL2-S).

2. Experimental

A base alloy of composition Al-3.63%Cu-1.67%Mg (wt%) was vacuum melted from 99.99 wt% pure feedstock materials. One sample of this base alloy was cast directly while an addition of 0.5%Si was made to the remainder. The 3 kg cast ingots of 76 mm diameter were preheated to 300°C for 1 h prior to extrusion into rectangular cross-sectioned bar at an extrusion ratio of 10 : 1. The bar was then hot rolled to strip (thickness ∼1.3 mm) and subsequently cold rolled to ∼0.4 mm. Strip samples, 10 × 20 mm, were solution treated at 525°C for 2.5 h (with samples sandwiched between two massive aluminium blocks to minimise loss of alloy elements), and quenched into cold salt water (10°C). Samples were aged at temperatures of 200, 265 and 305°C for various times followed by an air cool. In addition, a pre-age stretch (5% strain) was applied to some samples of each alloy prior to ageing



(a)



(b)

Figure 1 (a) Bright field TEM micrograph of alloy AL1 aged at 265°C for 24 h without a pre-age stretch, showing S′ laths. (b) As (a), but with a pre-age stretch (AL1-S). Note the more homogeneous distribution and smaller size of the S′ phase in (b). $g = \langle 002 \rangle$ in both cases.

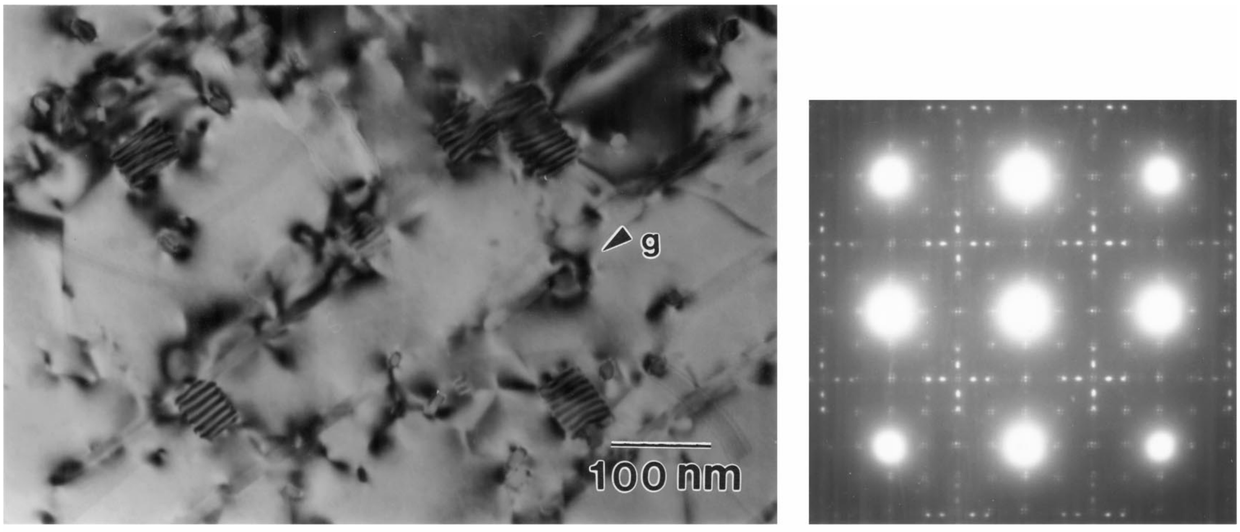
for 24 h at 265°C to examine the effect of prior dislocation density on ageing. TEM samples were prepared in the conventional manner and examined using a JEOL 200CX microscope. Average particle size and aspect ratio was obtained from 100 measurements made directly from TEM negatives. A LECO M-400 microhardness machine was used for hardness measurements using a Knoop indenter with a load of 25 g applied for 15 s and ten measurements were taken for each condition.

3. Results

S′ was the dominant precipitate in the Si-free alloy, AL1, aged at 265°C for 24 h, both with and without a pre-age stretch, Fig. 1a and b. Occasional θ'' plates were also present, but no σ phase was observed. The effect of the pre-age stretch was as expected, giving a reduction in precipitate size and increased homogeneity of the S′ distribution, Fig. 1a and b. Ageing the Si-free alloy, AL1, for longer periods at 265°C resulted in coarsening of the precipitate phases, in a manner consistent with the literature concerning the thermal size stability of S′ and θ'' [13]. Ageing this alloy at 200 or 305°C did not alter the phases present or their distribution.

The microstructure of the Si containing alloy, AL2, was completely different to the Si-free alloy. In the naturally aged condition, GP zones were present, but no precipitate phase could be uniquely identified. After 1 h at 265°C precipitation of σ phase was apparent in addition to S′ and a small fraction of θ'. The proportion of σ phase was greater after 24 h at 265°C, Figs 2a and 3. The addition of Si resulted in a homogeneous distribution of the S′, similar to the pre-age stretched AL1-S microstructure, (compare Figs 1b and 3). Although the distribution of both σ and S′ was generally homogeneous, the proportion of each phase varied appreciably from grain to grain and therefore no measurements of volume fraction were attempted.

Table I gives the σ phase dimensions, L1 and L2, in alloy AL2 as a function of ageing time at 265°C. Interestingly, the aspect ratio of the σ phase increased with time, resulting in a rectangular shape, but with truncated corners, Fig. 4. The relative proportions of the



(a) (b)

Figure 2 AL2 aged at 265°C for 24 h. (a) Bright field TEM micrograph showing σ phase, with the characteristic Moiré fringes, and finer S′ precipitates; $g = \langle 002 \rangle$. (b) [001] zone axis pattern of the σ phase.

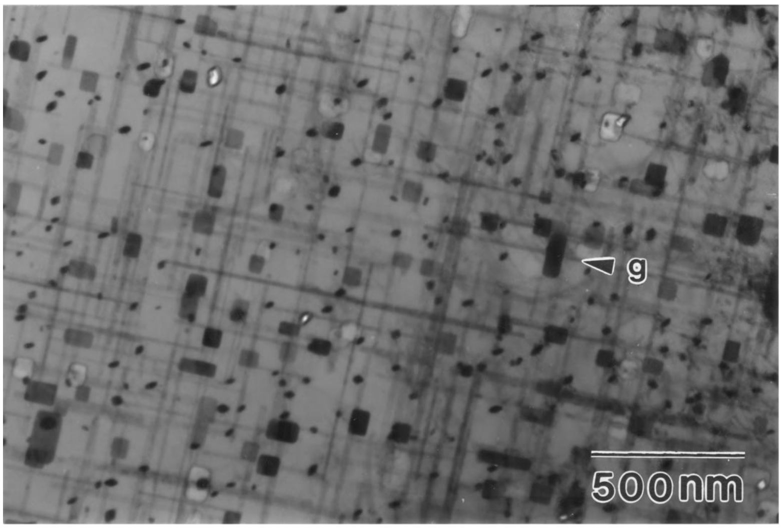


Figure 3 Bright field TEM micrograph of AL2-265°C-24 h, showing the distribution of σ phase and finer S′. $g = \langle 002 \rangle$.

TABLE I Summary of particle dimension measurements, $L1$ and $L2$, for the cubic phase in alloy AL2 as a function of ageing conditions

Ageing conditions	Ave. $L1$ (nm)	Ave. $L2$ (nm)	Average edge length (nm)	Aspect ratio
200°C-24 h	33 ± 6	41 ± 8	37	1.24
265°C-1 h	38 ± 6	46 ± 11	42	1.21
265°C-24 h	46 ± 12	64 ± 26	55	1.39
265°C-336 h	55 ± 10	80 ± 28	67.5	1.45
265°C-650 h	55 ± 11	85 ± 41	70	1.54
305°C-24 h	62 ± 32	103 ± 62	82.5	1.66

precipitate phases did not appear to change appreciably in the period 24–650 h at 265°C, Figs 3–5, although local variations in volume fraction of each phase made such a comparison subjective. However, after 650 h at this temperature, the truncation of the corners of the σ precipitates was more marked such that it was visible even at low magnification, Fig. 5.

Fig. 6 shows the microstructure of AL2 after the pre-age stretch followed by 24 h at 265°C (AL2-S). The

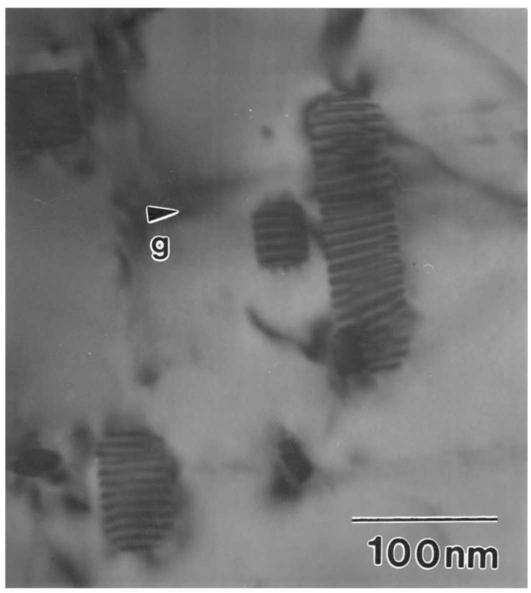


Figure 4 Bright field TEM micrograph of AL2-265°C-336 h showing the rectangular shape of the σ phase. $g = \langle 002 \rangle$.

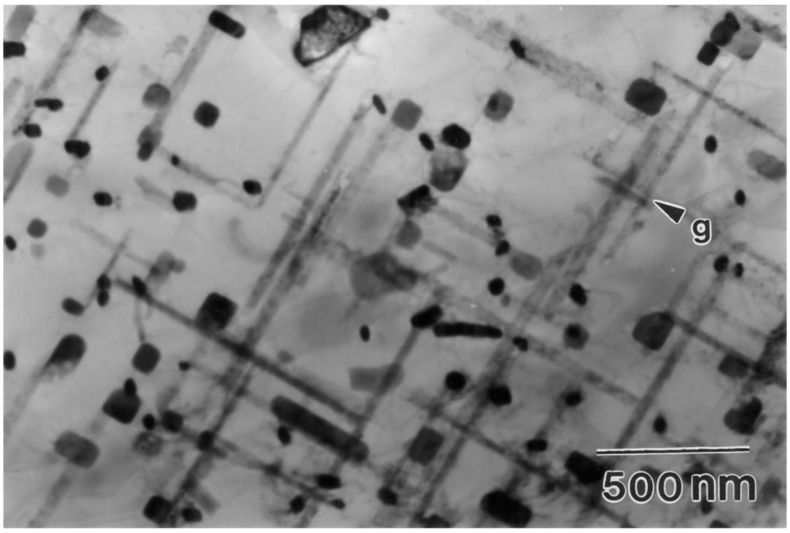
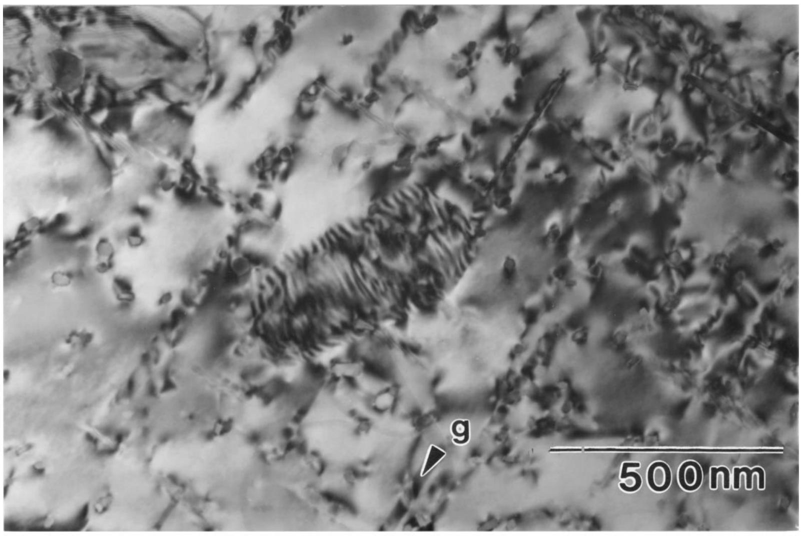
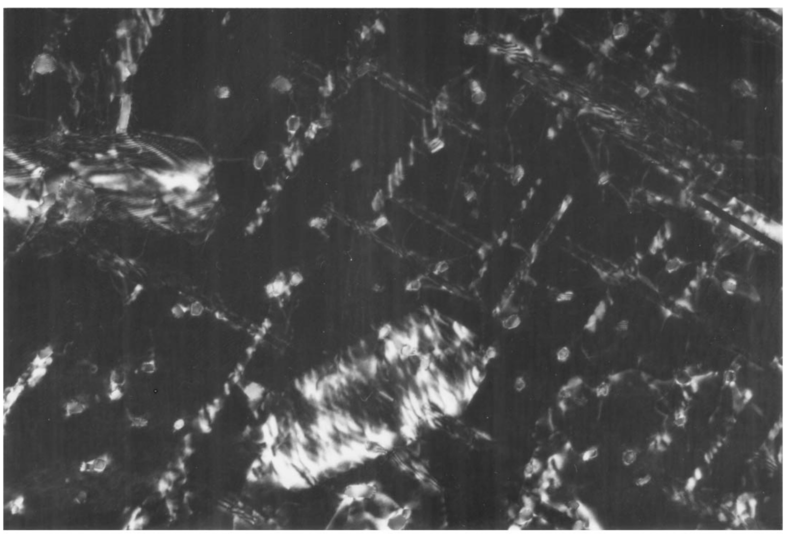


Figure 5 Bright field TEM micrograph of AL2-265°C-650 h, showing further rounding of corners of rectangular σ particles. $g = \langle 002 \rangle$.



(a)



(b)

Figure 6 (a) Bright field ($g = \langle 002 \rangle$) and (b) dark field TEM micrograph (using σ and S′ and reflections) of AL2-265°C-24 h with a pre-age stretch. The fraction of σ phase precipitates was generally lower than shown here.

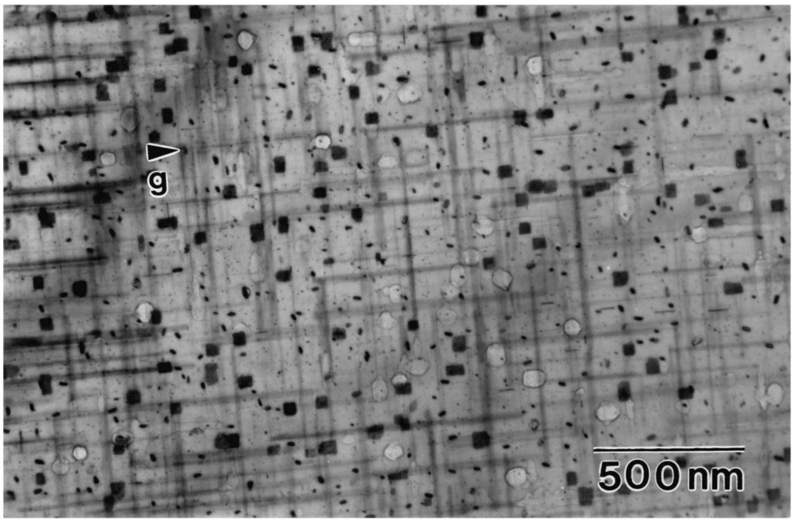


Figure 7 Bright field TEM micrograph of AL2-200°C-24 h, showing increased proportions of σ to S′ and finer precipitate size than Fig. 6. $g = \langle 002 \rangle$.

strain prior to ageing substantially reduced the volume fraction of σ (some areas were completely free of this phase) while the fraction of S′ was substantially increased. The distribution of S′ was similar to the Si free alloy (AL1-S).

Fig. 7 shows the microstructure of AL2 following ageing for 24 h at 200°C which resulted in an increase in the ratio of σ to S′ phase, and a finer precipitate size than in 24 h at 265°C, Table I. In addition, GPB zones were present. Ageing for 24 h at 305°C did not appear to alter appreciably the volume fraction of σ phase compared with 24 h at 265°C but resulted in the highest aspect ratio and precipitate size of any thermal treatment in this work, Table I

Fig. 8 provides the hardness of the two alloys as a function of ageing time at 265°C and 200°C. At 265°C, the Si free alloy showed more rapid softening up to 12 h, but there is little difference in hardness between the alloys heat treated for 12 to 650 h. For treatment at 200°C, the peak hardness of AL1 was greater than for AL2, but the hardness of the two alloys converged after 100 h at 200°C.

4. Discussion

In the current work, σ phase was not found in the Si free alloy, but was formed under all ageing conditions in the alloy containing 0.5%Si. Of the previous reports of σ occurrence [3–11] only those of Schueller *et al.* [6–9] and Barr *et al.* [11] consider the conditions for its formation in detail. In all but one case where σ phase has been found, Si was present in the alloy (at levels of 0.2–0.5%, although the exact level in the samples of Schueller *et al.* is not clear). The exception is the work of Li and Warner [10] who observed σ phase in a Al-Cu-Mg-Ag alloy (although the Si level or melting conditions were not specified by these authors). This suggests that Ag may play a similar role to that of Si. However, the presence of Si does not automatically lead to σ phase formation. For example, Gao *et al.* [12] did not observe σ phase in a detailed microstructural investigation of an Al-4Cu-0.3Mg alloy with Si levels of 0.1–1.1. Similarly, Gupta *et al.* [1] did not find σ phase in Al-1.75Cu-0.75Mg with Si in the range 0.23–1.03.

In both these cases, the processing route and thermal treatments used were similar to those that produced σ phase in the current work.

The Cu : Mg ratios in the Si containing alloys where σ phase has been observed were in the range 1.94–2.22 : 1, (2.17 : 1 in the current work). The ratio in Gao *et al.*'s [12] alloy, where σ phase was not observed, was 13.3 : 1, which suggests that sufficiently high Cu contents combined with low Mg contents suppress σ phase formation, as they do S′ formation. In their Ag containing alloy, Li and Warner observed σ phase for Cu : Mg ratios of 7 : 1 and 10 : 1, with more cubic phase found in the former, again suggesting that high volume fractions of σ phase can only be obtained with lower Cu : Mg ratios.

It is well established that Si additions to Al-Cu-Mg alloys reduce the number and size of dislocation helices formed on quenching from the solution temperature [eg4]. S′ nucleates preferentially on dislocations [4, 13] and therefore the reduction in dislocation density in Si containing alloys tends to promote a more uniform distribution of this phase (e.g. Fig. 3). The nucleation of σ phase appears to be homogenous, and its formation is competitive with S′. Therefore, the principal role of the Si may be simply to reduce the number of heterogeneous sites available for S′ nucleation. This view is supported by the observation that a pre-age stretch substantially increases the volume fraction of S′ at the expense of σ. It is proposed that this is the dominant effect, rather than the possible formation of Si clusters acting as nucleation sites, as proposed by Schueller *et al.* [6, 7].

The aspect ratio of the σ phase increased with both time at ageing temperature and temperature, believed to be associated with a decrease in coherency. There was no evidence that the crystal structure of the precipitate changed and therefore the shape change was believed to be a result of changes in interfacial and strain energies.

Peak hardness was higher for the Si free alloy on ageing at 200 and 265°C, Fig. 8. However, the Si free alloy

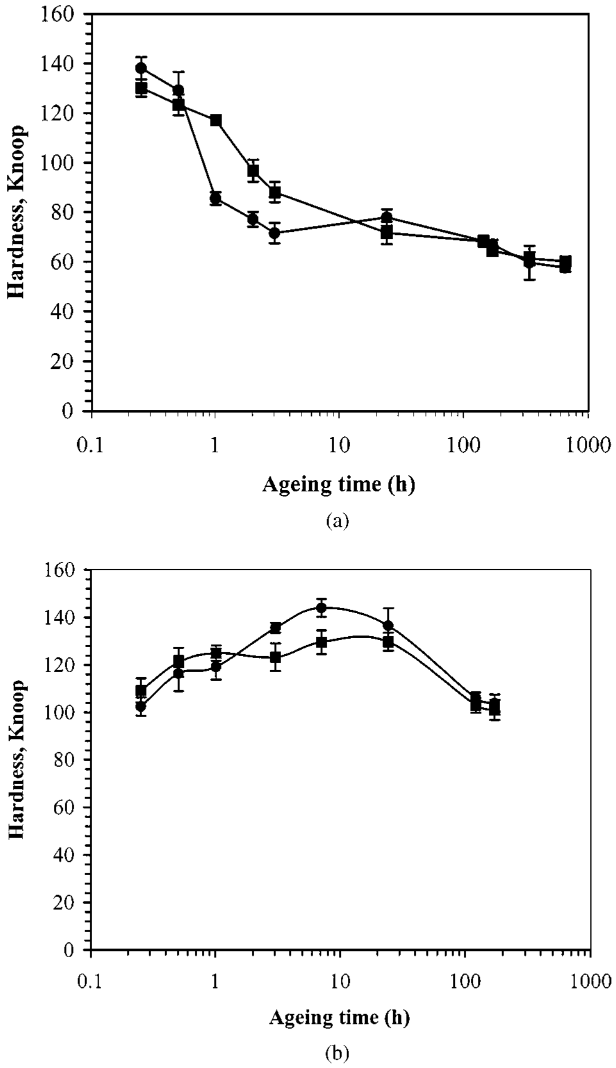


Figure 8 The hardness (Knoop, 25 g) of the two alloys as a function of ageing time at (a) 265°C and (b) 200°C. ●: Si free alloy, AL1. ■: Si containing alloy, AL2.

softened more rapidly, particularly at 265°C. This reflects the more rapid coarsening kinetics of the S′ compared with σ. The coarsening kinetics of the σ phase, as indicated by the size measurements in Table I, were similar to those reported by Schueller *et al.* [7] and Barr *et al.* [11]. The convergence of hardness after long ageing times presumably reflects the transition from cutting to dislocation bypassing of the precipitates.

5. Conclusions

1) Precipitation of σ ($Al_5Cu_6Mg_2$) was observed in Al-3.62%Cu-1.66%Mg-0.5%Si for all ageing conditions studied but was absent in Si-free Al-3.62%Cu-1.66%Mg. In addition, S′ and θ' phases were observed in both alloys.

2) The volume fraction of σ phase in the Si containing alloy was lower after ageing 24 h at 200°C than after 24 h at 265 and 305°C.

3) The volume fraction of σ phase in the Si containing alloy was substantially reduced by a pre-age stretch followed by ageing for 24 h at 265°C. Some regions of the sample were completely free of σ phase, with S′ being the dominant precipitate type. A high dislocation density promotes the formation of S′ in preference to σ phase.

4) Peak hardness was higher for the Si free alloy on ageing at 200 and 265°C, but the Si free alloy softened more rapidly, reflecting the more rapid coarsening kinetics of S′ compared with σ.

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