Precipitation In Al-Mg-Si Alloys with Cu Additions and the Role of the Q' and Related Phases

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Keywords: Al-Mg-Si, Al-Mg-Si-Cu, Balanced alloy, Excess-Si, Precipitation, Q, Metastable phase, Q', β", Strengthening phase

Abstract. Application prospects in the automotive industry have led to extensive studies of Al-Mg-Si and Al-Mg-Si-Cu alloys. Ternary Al-Mg-Si alloys have been reported to go through the sequence of precipitation stages, GP→β"→β'→β, during artificial aging. Recent results indicate that the precipitation sequence is considerably more complex, and the precipitates more numerous and varied depending upon the relative amounts of the different solutes present, including Cu. Conflicting reports of the metastable phases and their sequences are compared and critically analyzed. All of these alloys have been reported to be strengthened primarily by the β'' phase. The source of such strengthening in quaternary alloys is critically analyzed in light of conflicting reports on the ubiquity of β'' and our studies on the role of the Q' phase.

Introduction

The precipitation events in 6xxx alloys as represented by the Al-Mg-Si ternary system have been reported to be: solid solution → GP → β" → β' → β [1,2]. Several additional clustering phases [2] and, in the presence of Cu, a quaternary Q phase with its metastable versions have been reported [3-7]. Application prospects of these alloys in the automotive industry have led to the report of many alloy compositions of both ternary alloys, and quaternary alloys at different Cu levels, and with a shift in preference to excess Si compositions (over the Mg_2Si stoichiometry). In addition, high resolution electron microscopy has exposed a plethora of new metastable phases and their varied precipitation sequences. Confusion is arising from the use of different nomenclatures by different researchers for the same phases. A logical framework which encompasses the metastable phase precipitation details in the 6xxx alloys is needed.

The prevailing viewpoint ascribes strengthening in all these families of alloys to the β" phase which occurs at peak age [2, 8]. Yet other phases have been reported present together with β" at peak age, in particular in Cu-containing quaternary alloys, while the relative β" population is reported to vary depending upon the alloy composition [7, 9]. Thus the sources of strengthening in these families of alloys need to be critically analyzed.

Precipitation Phases

As discussed above, the phases and their sequence during precipitation are quite complex. An attempt is made here to systematize the findings, paying attention to only those metastable phases that occur near the peak age and overage conditions, and the subsequent stable phases. This is displayed in Table 1. The table lists in separate columns the precipitating phases at peak age, and at three arbitrary, progressively overaged conditions (OA1, OA2, OA3) as well as the stable, equilibrium phases. The alloys under the "composition" are listed in terms of ternary versus quaternary, balanced (Mg_2Si stoichiometry) versus excess-Si (wt.% Mg < 1.732*wt.% Si), high versus low excess-Si levels, and high versus low Cu levels in the quaternary composition - each one of which noticeably modifies the precipitation processes. Also added in Table 1 are crystal structure and lattice parameter information for the different phases according to the sequence in which they occur under the specific columns. Some of the phases shown within parentheses were added for completeness, but were not specifically mentioned in the quoted works.

Table 1. Precipitation Sequence and Precipitate Structure for Different 6xxx Alloy Compositions

Composition	Peak Age	OA 1	OA 2	OA 3	Equilibrium	Ref.
Ternary, Excess Si	$\beta'' + \beta_d''$			**M**	β	7
Ternary, Excess-Si (low)	β''	β' + **Type B**		**Type C**	β + **Si**	5, 6
Ternary, Excess-Si (high)	β''	β' + **Type A**		**Type A**	**Si** + β	5, 6
Ternary, Balanced	β''	$\beta' + \beta''$	β'	β'	β	1, 2
Balanced + low Cu	β'' + **L**	**L** + $\beta' + \beta''$	**L** + β'	β' + **L**	$\beta + \lambda$ **(Q)** + **(θ)**	7
Balanced + high Cu	β'' + **L**	**L** + β''		**L**	λ **(Q)** + β + **(θ)**	7
Excess Si + low Cu	β''	β''	β''	**Q'**	**(Si)** + **Q** + **(θ)**	9
Excess Si + high Cu	β'' + **Q'**	β'' + **Q'**	β'' + **Q'**		**Q** + **(β)** + **(θ)**	9
Al-Mg-Si-Cu	β'' + **QP**	**QC+QP+**β'		**Q'**	**Q+(Si** or β**)+(θ)**	12, 13

β''
Monoclinic
a=0.65nm, b=0.76nm
c=0.405nm, γ=70°

β'
Hexagonal
(a=0.705, c=0.405)nm

β
Cubic
a=0.642 nm

L

(a=0.8, c=0.7)nm

Q'
Hexagonal
(a=1.03, c=0.405)nm

Q, λ
Hexagonal
(a=1.04, c=0.405)nm

λ_d''

M
(a=1.03, c=0.405)nm

QP
Hexagonal
(a=0.393, c=0.405)nm

QC
Hexagonal
(a=0.67, c=0.405)nm

B'
Hexagonal
(a=1.03, c=0.405)nm

Type B
Hexagonal
(a=0.67, c=0.405)nm

Type C
Hexagonal
(a=1.04, c=0.401)nm

Type A
Hexagonal
(a=0.405, c=0.67)nm

A representative of the ternary alloy precipitation is the “Ternary Balanced” case. Here the precipitates are the needle shaped β” phase with a monoclinic structure at peak age, a mixture of β” and hexagonal β’ progressively approaching β’ with overaging, and the equilibrium cubic β phase (Mg_2Si) [1,2]. The “Excess-Si + low Cu” case represents the quaternary alloy [9]. Here the precipitate at peak age is still cited as β”, while a new phase originally designated as B’ by Dumolt et al. [4], which is identical to the hexagonal Q’ phase, precursor to Q, appears at over age and leads to the equilibrium Q phase. (To clear some confusion, Dumolt et al. studied the commercial 6061 alloy that contains 0.18-0.3% Cu - hence a quaternary alloy - and the B’ phase for which they provided detailed precipitate structure referred to the metastable precursor phase of Q, which is better termed Q’ [10].) For “Excess-Si + high Cu” alloy, Q’ occurred together with β” at peak age [9]. For the “Balanced + low Cu” alloy (0.65Si, 1Mg, 0.25Cu), a new lath-shaped phase L is cited to occur at peak age along with β”, for which only the lattice parameter but no crystal structure data are available [7]. Apparently the L phase is different from Q’ and occurs as a precursor to Q’ and is present at peak age through over age, while Q’ more often occurs at over age. The same L phase also occurs in “Balanced + high Cu” alloy (0.65Si, 0.87Mg, 1Cu), but as the Cu additions increase the relative proportion of L to β” phase at peak age increases [7]. The L phase also becomes more prominent with overaging.

Precipitation in ternary excess-Si alloys provides a notable contrast to that in ternary balanced alloy. Segalowicz et al. [7] observed β” present at peak age together with a lath shaped metastable phase, designated β_d”, that preferentially precipitated on dislocations. This phase was replaced on over aging by a phase termed M. M, which has similar lattice parameters, crystal structure (hexagonal) and morphology (lath) as the quaternary metastable phase Q’, was the only phase present on prolonged over aging (OA3). However, it was replaced later by β the stable equilibrium phase. Matsuda et al. [5,6] reported the occurrence of a lath-shaped, hexagonal metastable phase, denoted as Type B, on over aging which was replaced on prolonged over aging by another metastable phase, termed Type C, in a “Ternary, Excess-Si (low)” alloy. Type C which shares similar precipitate characteristics as M and Q’ (see Table 1) was replaced, as was M, by β the stable equilibrium phase. A metastable hexagonal phase Type A, different from Type B, was observed by the same authors in “Ternary, Excess-Si (high)” alloys, which was replaced at equilibrium directly by the stable (Si) phase. The above studies clearly indicate that metstable phase(s) sharing the precipitate characteristics of the quaternary metastable Q’ phase can be formed in over aged ternary alloys with excess Si content. This is noteworthy, since Q is stable only as a quaternary phase, while a metastable version of it can be formed even in ternary alloys in the presence of excess Si.

The existence of a metastable ternary phase (termed M by [7] and Type C by [5]) that has a similar structure as the Q' phase is an interesting finding. The Q phase has a structure similar to that of Th_7S_{12} in which Si atoms take the place of the Th atoms and Al and Mg atoms are randomly placed on the sites occupied by S in the prototype structure. In addition, Cu atoms are thought to be placed at other sites that are not occupied in the Th_7S_{12} structure [11]. One explanation of the ternary Q' like phase (M or Type C) is that these sites are not occupied in the ternary structure. The structure has the same space group designation as the Q phase and similar lattice parameters and would be practically indistinguishable from the Q phase by normal diffraction techniques.

Detailed systematic studies including high resolution TEM by Cayron et al. [12,13] on Al-Mg-Si-Cu alloys, derived from reactions in metal matrix composites, also revealed several metastable phases to Q, namely the hexagonal QP at peak age and the hexagonal QC similar to Type B on over age. It has been shown by Cayron that the sequence of precipitation:

$$QP \rightarrow QC \rightarrow Q$$

can be understood as an atomic ordering process within the basal plane of the hexagonal lattice. The c lattice parameter is the same for each of the phases (see Table 1) while the a lattice parameter varies from that of QP to $\sqrt{3}$ times that of QP (QC phase) to $\sqrt{7}$ times that of QP (Q phase). These different phases have the same stacking sequence of the basal planes (ABAB…) but different arrangements of atoms within the basal planes. This proposal of Cayron nicely ties together several of the structures shown in Table 1.

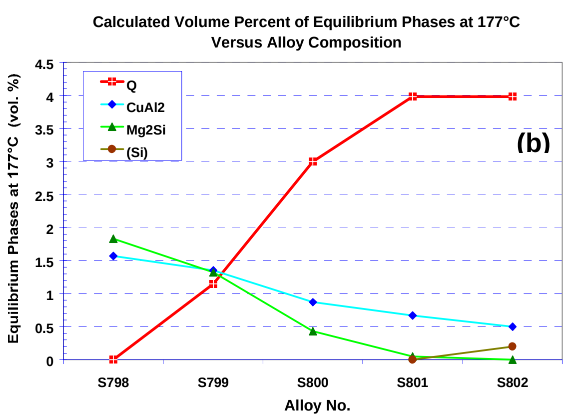
Strengthening Phases

Numerous studies indicate that the strengthening phase involved in the Al-Mg-Si ternary alloys is the metastable β” phase [2, 8]. This phase is a precursor to the metastable β’ phase which in turn is a precursor to the equilibrium β phase. Thus, the increased strengthening in excess-Si alloys has been ascribed to a greater volume fraction of β” formation. In quaternary Al-Mg-Si-Cu alloys, the strength was observed to increase progressively with increasing Cu additions. Here again some ascribed this to the formation of more β” and in finer sizes. In what follows, these interpretations will be analyzed with reference to some of our experimental results and some recent literature data.

We conducted experiments in which Al-Mg-Si-Cu samples were studied for hardness variation with artificial aging times. The variations were compared against the systematic changes in equilibrium phases and their calculated relative amounts in samples of selected composition levels. Several such groups of samples were studied, the results from one of which is presented Figure 1. The five compositions were selected in a way such that the calculated volume fraction of Q phase at 177°C progressively increased reaching a plateau, while those of β (Mg_2Si) and θ ($CuAl_2$) correspondingly decreased. Figure 1 shows several inserts, one for the composition of the five alloys studied (a), another for the volume fraction of different equilibrium phases present at the artificial aging temperature 177°C calculated from the equilibrium phase diagram (b), and a plot for the hardness (Rockwell-B) variations with aging times at 177°C (c). Prior to the artificial aging, the book mold cast ingots were subjected to the standard processing steps of homogenization, hot rolling, solution treatment, quenching and natural aging. The hardness results show a systematic increase mirroring the increase in Q phase amount, even though the amounts of β and θ phases, both well known for the strengthening capability of their precursor phases, decreased. Assuming that the relative amounts of the precursor phases are proportional to the relative amounts of the stable phases, this then offers the interesting possibility that a precursor phase of Q has a significant strengthening capability.

(a)

Specimen Number	Composition (wt.%)		
	Mg	Si	Cu
S798	1.18	0.61	0.90
S799	1.17	0.81	0.93
S800	1.19	1.03	0.94
S801	1.20	1.13	0.95
S802	1.22	1.36	0.88



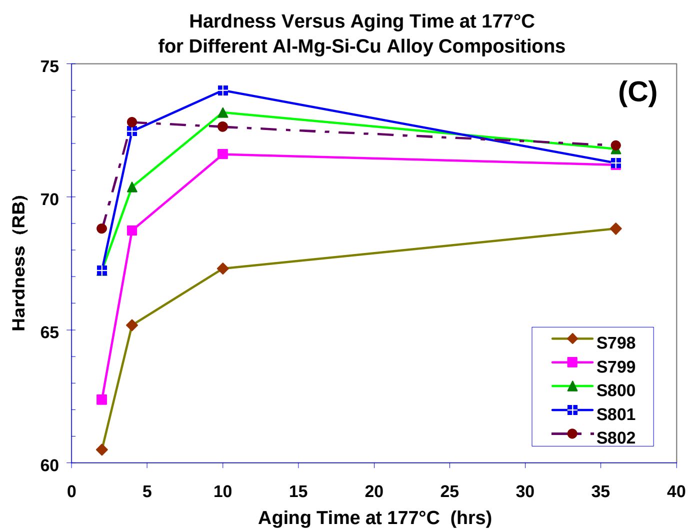


Figure 1. Alloy Compositions (a), Calculated Equilibrium Phases (b) and Hardness with Aging Time (c) Results

Literature reports, however, indicate that the phase present at peak age in Al-Mg-Si-Cu alloys is primarily β", while Q' is generally present during overaging and would be thus associated with decreases in strength [2,8]. Thus, the Q' precursor phase of Q does not appear to be a strengthening phase capable of explaining the results of Figure 1. In contrast, in one study the strength of an Al-Mg-Si balanced alloy was reported to increase progressively with increased additions of Cu. A concomitant increase in the population of a phase having rectangular cross section and containing Cu was observed in the TEM [14]. In the earlier mentioned work of Segalowicz et al. [7], the proportion of L increased with increased Cu additions. On overaging the L phase eventually led to another lath shaped phase which they termed λ or Q. In excess-Si ternary alloys lath shaped phases λ_d" [7] and Type B, which is precursor to Type C as described earlier [5], also were reported. Our high resolution TEM studies on a quaternary alloy (sample no. S802 in Fig. 1) that has a large amount of Q phase as an equilibrium phase in near peak age conditions show both the β" precursor phase to β' and another phase with a lath shape that is most likely the L phase identified by Sagalowicz et al. [7]. See Figure 2. In Figure 2(a) three precursor precipitates are shown edge on, only one of which is β" as can be seen from Figure 2 (b) and (c) and comparing with Figure 4 of Andersen et al. [15] Thus, at peak age along with the normal needle-shaped β" phase, a lath-shaped phase also is present. This lath shaped precursor phase to Q (different from Q') therefore plays a strong role on the strengthening process in quaternary alloys. Thus, composition changes that show increases in the equilibrium Q phase can be indicative of corresponding increases in the lath shaped precursor phase with its significant strengthening capability, confirming the inference from the results in Figure 1. According to the above results and interpretation, though neither Q or Q' has recognizable strengthening potential, the lath-shaped precursor phases to Q' does play a significant role in the strengthening of Al-Mg-Si-Cu alloys. Further work is in progress.

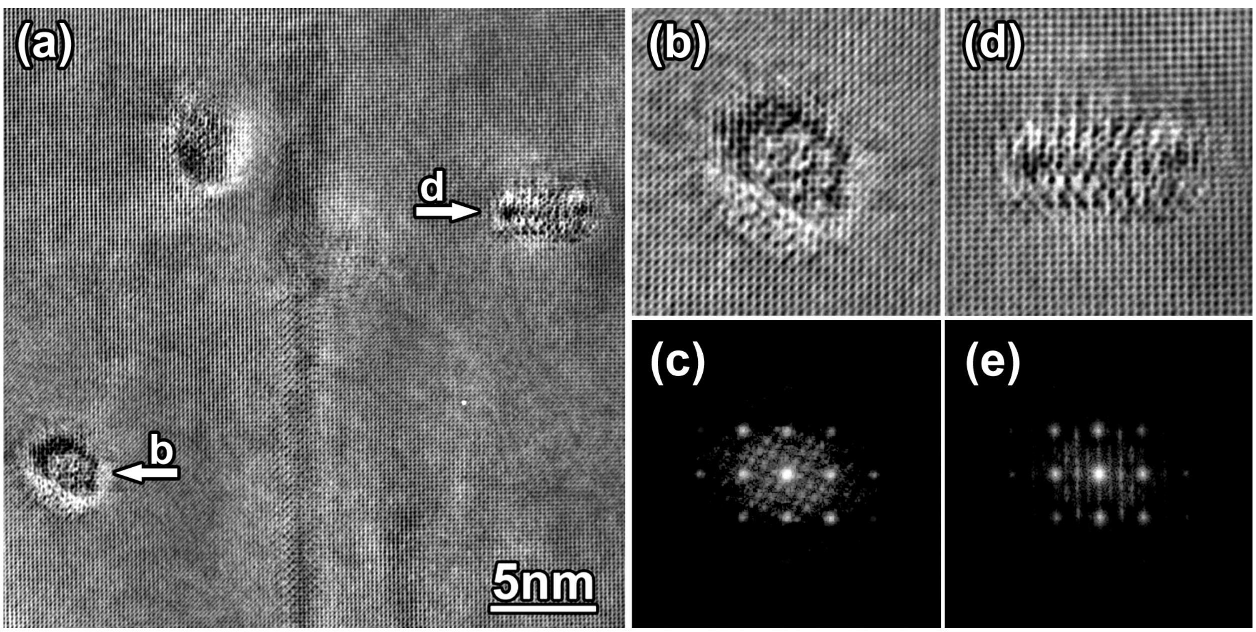


Figure 2. High resolution TEM image of alloy S802 showing several metastable phases (a). The phase enlarged in (b) is β" and that enlarged in (d) is a lath shaped phase similar to L. Fourier transforms of images (b) and (d) are those in (c) and (e), respectively.

Summary and Conclusions

- Complex combinations of precursor phases, as revealed by high resolution TEM, are observed in Al-Mg-Si-(Cu) alloys as influenced by Mg to Si ratio (balanced versus excess), level of excess Si, presence of Cu or Cu level.
- The quaternary metastable phase, Q', is isostructural with Q (hexagonal) with similar lattice parameters, but is smaller in size, and is coherent along its c-axis with the Al matrix. It has been also called B' in the literature.
- The precipitate types and forming sequences listed in Table 1 for the three composition groups (ternary excess Si, balanced and quaternary alloys) suggest the following:
  - A phase similar to Q', with the same crystal system and lattice parameter as Q (termed variously as M and Type C), can be formed in excess Si alloys without Cu, but is

metastable. On overaging, it is replaced by β and/or (Si) instead of forming an equilibrium Q like phase.
    - In quaternary alloys with Cu, both metastable Q' and equilibrium Q phases are formed.
    - Similar to β' having the precursor phase β", precursor phases with the lath morphology exist for the Q' phase, for example "L" for quaternary and "β_d" for ternary excess Si compositions.
- In Al-Mg-Si-Cu quaternary alloys, significant strengthening effects arise from the lath shaped, hexagonal precursor phase(s) to Q' in addition to the generally recognized β" phase.

Acknowledgments

DJC wishes to thank the Alcoa management for their support of this study and approval of its publication.

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