

PRECIPITATION IN Al-Mg-Si-Cu ALLOYS AND
THE ROLE OF THE Q PHASE AND ITS PRECURSORS

D. J. Chakrabarti, Alcoa Technical Center, Alcoa Center, PA 15069, USA
Byung-ki Cheong, Korea Institute of Science and Technology, Seoul, Korea
David E. Laughlin, Carnegie Mellon University, Pittsburgh, PA 15213, USA

Abstract

Several 6000 series Aluminum alloys are being used as automotive body panels, because of their ability to be strengthened by artificial aging after forming. These alloys often contain Cu to varying amounts. This leads to the formation of the quaternary Al-Mg-Si-Cu family of alloys with distinctive properties. Unlike in Al-Mg-Si alloys where the hardening phases are β'' and β' , additional hardening phases appear in these quaternary alloys, thus making the aging response for these alloys quite complex. One of the important phases present in these alloys is a quaternary phase, denoted as Q, which forms as an equilibrium phase. In this paper we will discuss the occurrence of the Q phase in commercial 6000 and 2000 series (for example when Si is added to Al-Cu-Mg alloys) alloys in some detail. The thermodynamic stability of the phase will be discussed against the other coexisting phases. A metastable version of this phase has been reported to exist in the peak age temper which may be important in understanding the overall precipitation hardening mechanism in these alloys. The existence of this phase will be documented by TEM micrographs and diffraction patterns and the crystallographic features which distinguish it from the β' phase will be presented.

Introduction

The properties of 6XXX Al-Mg-Si alloys have been known to be influenced by the precursor phases to the equilibrium Mg_2Si (β). In many commercial 6XXX alloys, which often contain Cu in varying amounts (e.g. 6061) forming the Al-Mg-Si-Cu alloys, several other equilibrium phases coexist with β . The aging response in such alloys often appears to be quite complex owing to the occurrence of many intermediate phases. This is an important issue now because of the large amount of activity in auto body sheet (ABS) alloys, particularly, to tailor the aging response to paint bake conditions.

One of the least known phases contributing to this complexity is a unique one in that it occurs as a quaternary intermediate phase in commercial aluminum (Al) alloys. This quaternary phase has been designated variously, including more commonly as the Q phase. From all accounts it appears now that Q plays a pivotal role in controlling the properties in Al-Mg-Si-Cu alloys because of its ubiquitous and often dominant presence. Yet, historically Q did not receive the kind of systematic studies for its precipitation behavior or for its influence on properties as did some of the other phases, like β in 6XXX or θ (Al_2Cu) and S (Al_2CuMg) in 2XXX or η [$Mg(Zn,Al,Cu)_2$] and S in 7XXX alloys. In recent years, however, several studies have been reported in the literature with interesting results, particularly in the area of precipitation. We intend to gather together this information and include results from our studies to gain further clarity and perspective in this complex area by providing the following information:

- (1) Given an alloy composition in the Al-Mg-Si-Cu system, what are the coexisting stable equilibrium (equilibrium) phases present at the aging temperatures? This would help indicate the corresponding metastable equilibrium (metastable) phases expected during aging.
- (2) For a given composition change, how do the relative amounts of the coexisting equilibrium phases change? This would suggest a corresponding trend for the metastable phases, and the resultant influence on properties.
- (3) The relative importance of the different metastable phases in the selected alloys of interest,
- (4) In the context of (1) to (3), delineating the role and relative importance of Q and its precursor phase(s) in the Al-Mg-Si-Cu alloys.

We will present this information through the following topics:

- (a) a description of the phase fields occurring in the Al-Mg-Si system with the addition of Cu,
- (b) the ubiquitous presence of the quaternary phase Q in combination with other phases in the three broad composition regions in this system,
- (c) the morphology and crystallography data of Q,
- (d) the intermediate phases occurring in these composition regions and their relationship with the equilibrium phases,
- (e) the examination of a precursor phase of Q, its morphology and crystallography data,
- (f) identification of this Q phase precursor from another more familiar intermediate phase,
- (g) rationale for the formation of the metastable Q phase,
- (h) strengthening response of the different metastable phases.

Phase Fields of Al-Mg-Si-Cu Alloys

When Cu is added to the 6XXX series Al-Mg-Si alloys or Si is added to the 2XXX series Al-Cu-Mg alloys, the Al-Mg-Si-Cu family of alloys is formed with varied properties and applications. They straddle both the 2XXX and 6XXX alloy compositions and are not given a separate designation in the Aluminum Association's scheme. One important underlying common feature in all these alloys is the occurrence of a quaternary phase first experimentally observed in the Alcoa Laboratories by Dix et al. (1), which has been variously designated as Q (2-5), W (6), h-AlCuMgSi (7) and λ (8).

Most commercial compositions in the ternary Al-Mg-Si alloys, at normal aging temperatures, occur in a ternary phase field consisting of the equilibrium phases: primary aluminum, (Al), β and (Si). When Cu is added, the coexisting phase fields expand into three tetrahedron composition spaces. Inside each of these there exists a four phase equilibrium consisting of the two common phases, namely (Al), and the quaternary intermediate phase, designated here as Q, and two of the other three phases, namely θ , β and (Si). This is schematically shown in the skeletal phase diagram representation in Figure 1, modified from an earlier one by Collins (4).

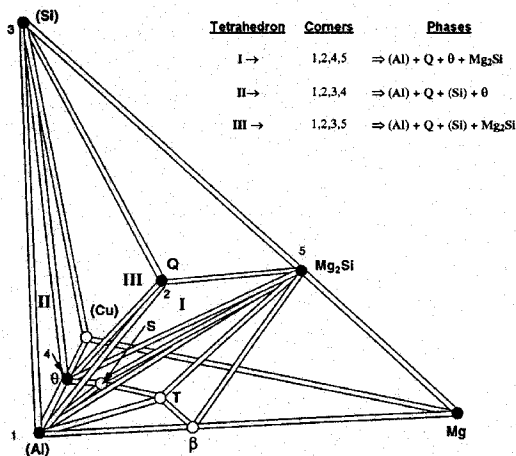


Figure 1 - Line diagram of stable equilibrium phase fields in Al-Mg-Si-Cu system at normal aging temperatures

It is noteworthy that, when Si is added to the Al-Cu-Mg alloys, the three-phase field consisting of (Al), θ and S, likewise, expands into the tetrahedron consisting of (Al), θ , S and β phases at low Si. At higher Si, a switch over occurs to the tetrahedron in which Q replaces S, and the tetrahedron consists of the phases (Al), θ , β and Q, similar to those present when Cu is added to 6XXX alloys. This switch over of the tetrahedron phase fields containing S to the tetrahedron containing Q accounts for the abrupt change in phase combinations that have been

observed in the past above certain Si levels in Al-Cu-Mg alloys (9). Hereafter, only the instances of Cu additions to Al-Mg-Si will be discussed, although equivalent phase relations and property results will also ensue with Si additions to Al-Cu-Mg.

When the Mg/Si ratio (all compositions in the paper are expressed in weight percentage) is greater than about 1, the compositions have been observed to lie, at normal aging temperatures, in Tetrahedron I having the coexisting phases, (Al), Q, θ and β (10). When Mg/Si < 1, the compositions correspondingly occupy Tetrahedron II having the coexisting phases, (Al), Q, θ and (Si). Tetrahedron III composition field is occupied when the Cu level is low. This level of Cu varies with the Mg and Si and is generally less than 0.2-0.5%. A clearer view of the tetrahedral phase fields is shown in a schematic projection of the (Al) corner of the tetrahedron onto the Q corner of the tetrahedron whereby the tetrahedrons are projected in two dimensions as triangular fields, as shown in Figure 2.

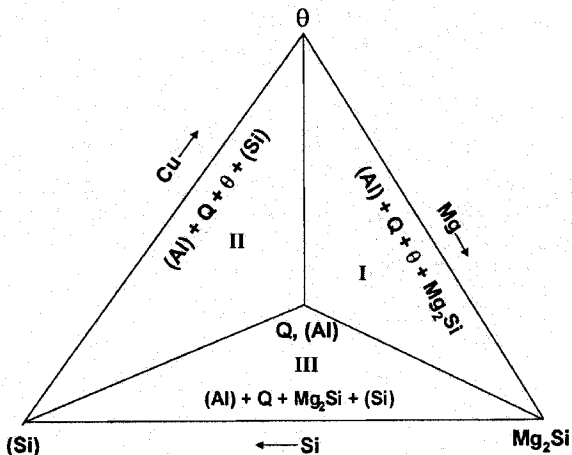


Figure 2 - Al-Mg-Si-Cu alloys grouped by phase field occupancy on a pseudo-projection of four-phase-field tetrahedron (projection of (Al) corner of the tetrahedron on to Q corner of the tetrahedron)

One striking aspect of the composition-phase field relationship is immediately apparent. In the Al-Mg-Si alloys, a Mg/Si ratio of 1.73 (corresponding to the 2:1 stoichiometry for Mg_2Si) is assumed for the formation of β and for the calculation of "excess Si" required to form the (Si) phase. Recent studies by Edwards et al. (11), however, showed that for the metastable precursor phases, the appropriate composition ratio should be more like 1:1. In the Al-Mg-Si-Cu system, the Mg/Si ratio defining the tetrahedron phase boundary appears to be also close to 1:1 (10). Thus of all the "excess Si" compositions of ABS only those having Mg/Si < 1, belong to the Tetrahedron II phase field. Put another way, the stabilization of (Si) in preference to Mg_2Si requires higher Si in the quaternary alloy than assumed in the ternary alloy. The coincidence of the same Mg/Si ratio of about 1:1 for delineating the stable phase field boundary in the quaternary system and for preference by the β'' and β' metastable phases of Mg_2Si is noteworthy.

Regarding the composition effect on the relative phase stability, our equilibrium diagram calculations (10) indicate certain definite trends. In both Tetrahedron I and II, Cu has the strongest (positive) effect on the amount of θ and much less on the amount of the other coexisting phases. Increasing Si strongly increases Q in Tetrahedron I, and (Si) in Tetrahedron II. Increasing Mg increases Mg_2Si in Tetrahedron I and Q in Tetrahedron II. It is important to note that although the addition of Cu to Al-Mg-Si alloys introduces the Q phase, it also introduces θ , and modifies the amounts of (Si) and Mg_2Si , due to a change in phase stability. Its relative impact, however, is still much stronger on θ than on Q.

The Ubiquity of Q and the Coexisting Equilibrium Phases

The Q phase exists as a quaternary phase. More importantly, Q is ubiquitous as an equilibrium phase at most of the compositions in the Al-Mg-Si-Cu alloys. It is also obvious from Figure 1 that the Q phase cannot coexist with the S or T phases commonly observed in the Al-Cu-Mg system, or with the Al_8Mg_5 (β) phase in the Al-Mg system.

Each tetrahedron being associated with specific phase combinations also shares the particular engineering properties identified with different alloys. The distribution of some of the common commercial alloys in the three tetrahedron phase fields is listed in Table I.

Table I - Examples of Common Al-Mg-Si-Cu Alloys and Their Four-Phase Equilibrium Fields around Normal Aging Temperatures

I	Tetrahedron		Composition			Application
	II	III	Mg	Si	Cu	
2017			0.40-0.8	0.2-0.8	3.50-4.5	(a)
2036			0.30-0.6	0.5**	2.20-3.0	(c1)
6061		6061*	0.80-1.2	0.4-0.8	0.15-0.4	(a,c3)
6013			0.80-1.2	0.6-1.0	0.60-1.1	(a, b)
	2014		0.20-0.8	0.5-1.2	3.90-5.0	(a, b)
	2008		0.25-0.5	0.5-0.8	0.70-1.1	(c1)
	6111		0.50-1.0	0.7-1.1	0.50-0.9	(c1)
	6009	6009*	0.40-0.8	0.6-1.0	0.15-0.6	(c1,c2)
		6016	0.25-0.6	0.9-1.3	0.20**	(c1,c2)
		6022	0.45-0.7	0.8-1.5	0.01-0.11	(c1)

Stable phases: I: (Al)+Q+ Mg_2Si + θ ; II: (Al)+Q+(Si)+ θ ; III: (Al)+Q+ Mg_2Si +(Si)

(a): general; (b): aerospace; (c1): auto exterior, (c2): auto inner, (c3): auto extrusion

* indicates occupancy at low Cu end of the composition

** indicates maximum; no lower limits

Figure 3 shows how specific composition alterations, often in terms of Mg/Si ratio, can change alloy types. The composition alterations changes the alloy type from one tetrahedron phase field to another, or even to a three phase or two phase field paralleling a shift to a ternary composition. It may be noted that the switch from tetrahedron I to II occurs with a decrease of Mg or an increase of Si or their combinations. The reverse composition relations hold for a switch from tetrahedron II to I. Also, chronological ordering of the alloys under each column shows that the Si content in the ABS alloys (under tetrahedron II) has progressively increased.

Phase Fields at Aging Temperatures(Alloy System)

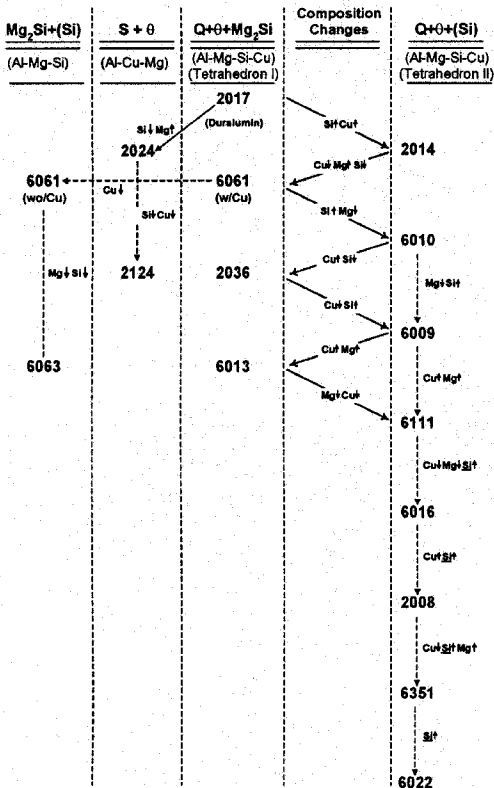


Figure 3 - Commercial Al-Mg-Si-Cu alloys grouped in different phase fields. The shift of the phase fields with composition changes from one alloy to another is shown by the arrow heads. The alloys are arranged vertically down in each column in the chronological order of their development, but no particular significance is implied otherwise.

Crystallography and Microstructure of the Q Phase

As stated earlier, the Q phase has been cited in the literature with various designations; so care must be taken to be sure of the identity of the phase in question (2-8).

The equilibrium Q phase is based on the hexagonal system (7) and has the space group $P\bar{6}$. It has lattice parameters $c = 0.405$ nm and $a = 1.04$ nm, has 21 atoms in a unit cell and its Pearson symbol is hP21 (12). A schematic of the structure is shown in Figure 4. Its exact composition is unknown but has been stated as $Al_4Cu_2Mg_8Si_7$ (13), $Al_5Cu_2Mg_8Si_6$ (7) and $Al_4CuMg_5Si_4$ (14).

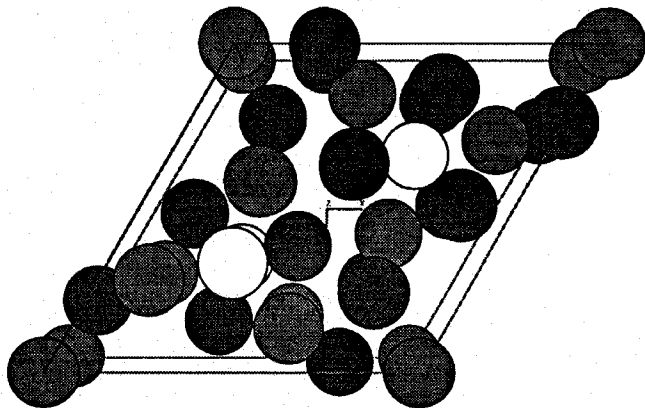


Figure 4 - Schematic projection of the Q phase looking down the c axis. The atoms at the corner of the cell are Si and the open atoms are Cu. The other atomic positions are randomly filled with Al and Mg

When Q forms from the liquid it appears in a complex honeycomb type morphology of micron size, as shown in the SEM secondary electron image for a 2014 sample in Figure 5. Optically, the structure appears as heavily networked as shown in Figure 6a. Sometimes, Q has the Mg_2Si phase interspersed within its interstices, as shown by the black dots in the 2017 sample in Figure 6b. The as-cast Q phase morphology changes with long thermal exposure during homogenization, and the Q phase may also precipitate in the solid state during high temperature anneals. In these cases, it often forms as round or oval particles at the grain boundaries (15).

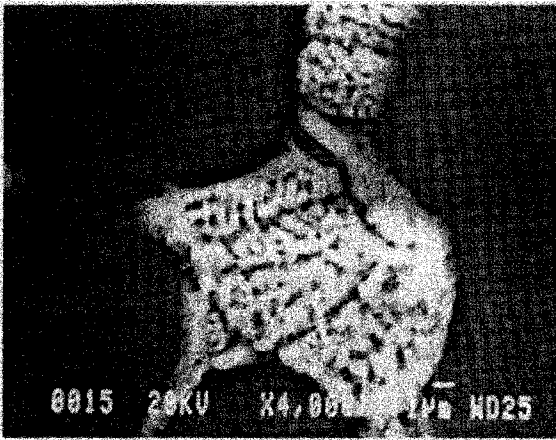


Figure 5 - SEM back-scattered electron image of 2014 ingot sample showing the honeycomb type structure of the Q phase

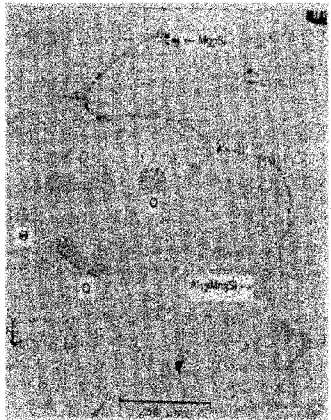


Figure 6b - Optical micrograph of 2017 ingot sample showing dark Mg_2Si particles interspersed inside the Q phase

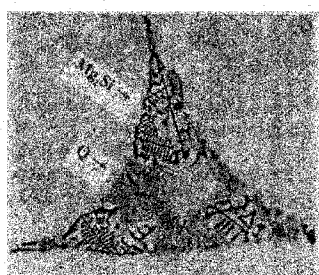


Figure 6a - Optical micrograph of an ingot sample with $Mg/Si > 1$ (Mg:1.15, Si:0.92, Cu:1.99) showing the Q phase with an intertwined structure

Metastable Phases in Al-Mg-Si-Cu Alloys

The tetrahedron phase fields discussed above refer to the equilibrium phases. They do not predict all the metastable phases that may occur during artificial aging. However, the equilibrium phase field information is still very useful, as it predicts the precipitation of at least those metastable phases that are natural precursors to the equilibrium phases, even though their relative amounts may differ due to kinetic reasons.

Additional metastable phases may also form which cannot be predicted from the equilibrium phases, but certain generalizations may apply. For example, a metastable phase that has a crystal structure distinctly different from its equilibrium counterpart, could also form even when the equilibrium phase is absent. Conversely, a metastable phase which has similar crystal structure and lattice parameters as the equilibrium phase cannot be expected to form if the equilibrium phase does not exist (in that phase field), since the metastable phase has an even higher free energy than the non equilibrium phase. This argument can be used against the simultaneous occurrence of the metastable S' phase and the Q phase precursor. As stated earlier, S does not occur in any tetrahedron containing Q, and hence is not an equilibrium phase in many of the commercial Al-Mg-Si-Cu alloys. Since its precursor, S', has the same orthorhombic crystal structure, space group Cmc₂m and lattice parameters (16), its occurrence in metastable phase fields along with Q phase precursor is highly unlikely. Therefore, any report of S' in the Al-Mg-Si-Cu alloys needs to be carefully checked in this context. Table II lists the two categories of metastable phases discussed above for the current alloy systems of interest.

Table II - Crystallographic and Morphological Data of Selected Phases in Aluminum Alloys

Alloy System	Equilibrium Phase (Bravais Lattice)	Metastable Phase		Metastable Phase		
		Isostructural (with equilibrium phase)	Non-Isostruct.	Bravais Lattice (Shape)	Habit Plane	Orientation Relation
Al-Cu	θ (body cent. tetragonal)		θ'	body cent. tetragonal (plate)	{100}	[001] _{Al} //[001]θ' (100) _{Al} //(100)θ'
Al-Mg-Si	β (face cent. cubic)		β'	hexagonal (rod)	---	[001] _{Al} //[0001]β' (110) _{Al} //(10 $\bar{1}$ 0)β'
Al-Cu-Mg	S (side cent. orthorhombic)	S'		side centered orthorhombic (lath)	{210}	[001] _{Al} //[001]S' (210) _{Al} //(010)S'
Al-Mg-Si-Cu	Q (hexagonal)	Q'		hexagonal (lath)	{510}	[001] _{Al} //[0001]Q' (020) _{Al} //(2130)Q'

Experimental studies are key to metastable phase information. We, therefore, summarize the literature, particularly since several precipitation studies in recent years have brought in some needed clarity in this area. Observations show that irrespective of the composition fields, the metastable β'' is the dominant intermediate phase present in both the Al-Mg-Si and the Al-Mg-Si-Cu alloys in the early stages of aging. The β'' phase is needle shaped with the long axis along $\langle 100 \rangle$ of the matrix Aluminum and is based on the monoclinic crystal system (11). After peak aging of the Al-Mg-Si-Cu alloys, some of the needle shaped β'' precipitates are replaced by rod shaped phase β' and others are replaced by lath shaped precipitates. The lath shaped phase was originally observed in 6061 alloy by Dumult et al., (17) who called it B', and its habit plane and orientation relations were determined. Both Sagalowicz et al.(18) and Edwards et al. (11) confirmed the distinct lath morphology associated with this precursor of the Q phase. Sagalowicz et al. named it L. They observed it to appear with Cu additions to Al-Mg-Si and to increase in amount with increasing Cu. The same phase was named λ' by (19). Matsuda et al. (23) have found a precipitate in the ternary Al-Mg-Si alloy with similar characteristics.

Thus the lath shaped phase is a precursor of the equilibrium Q phase. Unlike the β' to β transition which involves a transition to a crystallographically new phase, i.e. from hexagonal to one based on the CaF_2 structure, the lath shaped precursor phase of Q maintained the same crystal structure and even morphology from peak age through the overaged condition. Only its size increased, according to Sagalowicz et al. (18). Dumult et al. (17) also observed the same phase characteristics. Our TEM studies also confirmed the above conclusions. Based on the above data, this is one of those instances in which a precursor phase is crystallographically identical with the stable equilibrium phase. Table III provides a brief review of the literature in terms of the phases identified during the artificial aging of Al-Mg-Si-Cu alloys, and the compositions of the alloys studied.

Table III - Observed Metastable Phases and the Equilibrium Phase Fields for Different Al-Mg-Si-Cu Alloy Compositions

Mg	Si	Cu	Metastable Phase(s)	Stable Phase Tetrahedron	Reference
1.0	0.6	0.3	B', β'	I	(17)
0.9	0.25	2.0	β' , S', X'	I	(9)
0.9	0.48	2.0	Q', θ' , X'	I	(9)
0.8	0.79	0.18	B', β'	III	(11)
0.87	0.65	1.0	L, β'	I	(18)
1.0	0.58	0.52	β' ; "Rectangular"	I	(20)
0.6	0.8	0.3, 0.6	β' ; θ'	II	(21)
0.53	0.87	4.3	λ' ; θ'	II	(19)
1.2	0.25	2.5	β' ; "Cuboid"	I	(22)
0.63	0.77	?	β' ; "Elongated"	?	(23)

Several authors observed large increases in strength on adding Cu to Al-Mg-Si alloys that was accompanied by considerable refinement in the precipitate structure. Sakurai et al. (21) ascribed the strength increase to finer and more numerous β' precipitates, but we believe they are most likely the Q phase precursors (see below). Their claim of observing Θ' , though questioned by (11), appears consistent, since with Cu additions both Q and Θ are stabilized, and their alloy belongs to the tetrahedron that contains Θ . Tamizifar et al. (20) identified the fine precipitates due to Cu addition to the ones with "rectangular" cross section, that also contained Cu, thus clearly showing these to be the metastable precursors of Q. High resolution imaging of precipitates by (11) showed two types of metastable phases, one with equiaxed cross section due to β' , and the other with rectangular cross sections which they ascribed to B' , i.e. metastable Q. The authors claimed B' to be the dominant phase, which is noteworthy, indicating that even though the alloy contained only 0.18% Cu, once the composition moved into Tetrahedron I, Q is stabilized in large amounts due to the relatively high Si content in their alloy. The low Cu resulted in less Θ phase, and the metastable phases merely reflected the relative proportions of the stable phases.

Both (11) and (18) observed more rod shaped β' in peak aged materials, while on overaging more lath shaped Q phase precursor formed in preference to β' . This appears consistent since with progressive aging the equilibrium distribution is approached, where the volume fraction of Q is higher than β for their alloy compositions.

The higher strength observed in 2214 alloys with high Si/Mg ratios was ascribed by (19) to the λ' phase, apparently the same as the metastable Q, but they reported it to be needle shaped. They ascribed the lower strength obtained with lower Si/Mg ratios to the formation of S' . As argued earlier, this is unlikely unless the S phase is in stable equilibrium at this composition, and no Q phase precursor was coexisting. The metastable phase diagram for Al-Mg-Si-Cu alloys presented by (24) is apparently faulty, as in none of its phase fields the metastable precursor of Q was shown while S' , an unlikely possibility, was shown in many of them.

In summary, the metastable phase field studies indicated that the lath morphology and habit plane of $\{150\}$ of Al uniquely differentiates the Q phase precursor from β' , S' or Θ' .

Crystallography of the Precursor Phase of Q

Dumult et al. (17) characterized a phase they called B' as follows:

1. hexagonal with $a=1.04$ nm and $c=0.404$ nm
2. lath shaped with long directions parallel to $\langle 100 \rangle_{Al}$
3. habit planes $\{150\}$ of the Al matrix

We claim that this phase is really a coherent version of the equilibrium Q phase. In analogy with the well known designation of the coherent γ phase as γ' in superalloys (or the S and S' of Al-Cu-Mg alloys) we will call the phase Q' when it forms in the solid state with the above morphology and habit relations. In all the above instances, the two corresponding phases have the same crystal structure but differ in that the metastable phase is coherent with the matrix, while the other phase is not.

Figure 7 shows a bright field TEM micrograph of an overaged Al-Mg-Si-Cu alloy. The long dimensions of the precipitate phase can be seen to lie along the $\langle 100 \rangle$ matrix directions. The variants along the normal direction are rectangular in shape and have $\{150\}$ habits with the Al matrix. This is similar to what Dumult et al. reported (17).

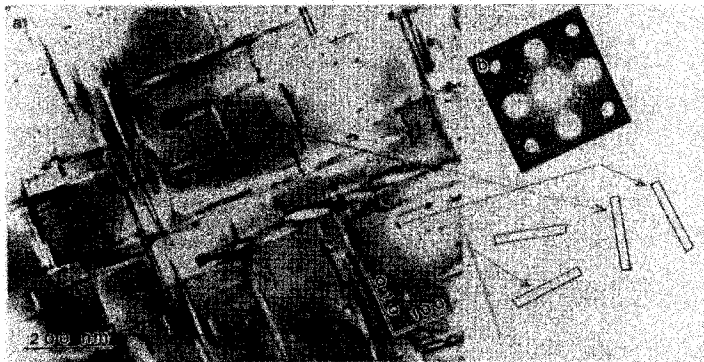


Figure 7 - TEM micrograph of an Al-Mg-Si-Cu sheet sample (overaged) at the [001] foil orientation. (a) BF (bright field), (b) SADP (selected area diffraction pattern), (c) schematic of the four end-on variants of the Q phase. Arrows indicate some of the variants in the BF image in (a).

Figure 8a is a diffraction pattern taken along [001] zone axis of Aluminum. Faint rings can be seen in the pattern (see schematic of rings in Figure 8b). The ratio of the radii of the rings is 1: 1.16: 1.52: 1.73: 2.06: 2.63 which fits perfectly to a primitive hexagonal lattice. These rings come from Q' precipitates where the c axis is parallel to [001] of aluminum. The precipitates with their c axes along [100] or [010], give rise to the extra reflections near the {110} positions in Figure 8a. An indexed pattern for Q'//(200)_{Al} is shown in Figure 9. From this it can be seen that the $(2\bar{1}30)_{Q'}$ is parallel to the $(020)_{Al}$.

The orientation relationship of $(2\bar{1}30)_{Q'} // (020)_{Al}$ is within 2° of that reported by (17). Their relationship was derived from the habit planes of the precipitate. Their orientation relationships can be rationalized on the basis of a good fit of lattice spacing. The perfect match in one direction (viz, the c axis of Q' along the $\langle 100 \rangle_{Al}$) is what gives rise to the long dimension of the lath parallel to one of the $\langle 100 \rangle_{Al}$ directions (25). The repeat distance along the $\langle 150 \rangle$ directions of the aluminum matrix is $0.404 * \sqrt{26} / 2 = 1.03$ nm. This is nearly the same as the "a" lattice parameter of the Q' phase, see Figure 10. Hence during the solid state precipitation Q' minimizes its surface energy by maximizing its area on the {150} planes. Overall then, the Q' phase is lath shaped.

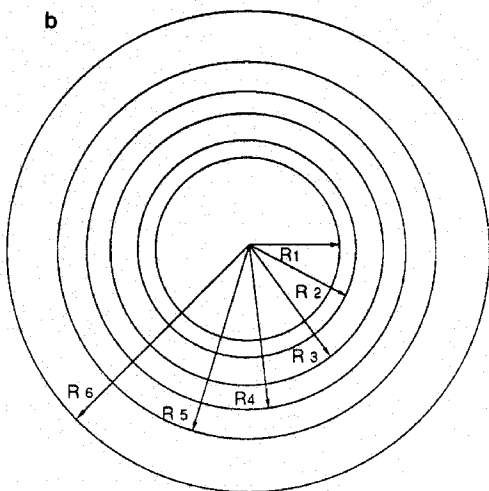
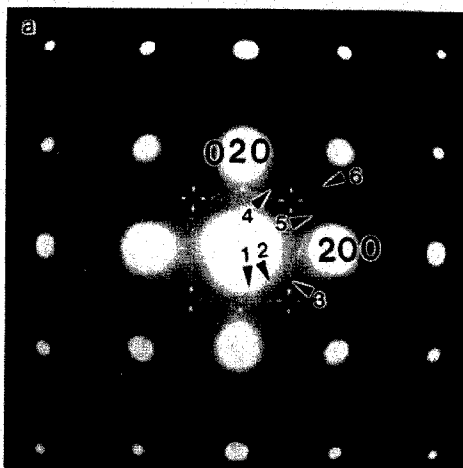


Figure 8 - Enlarged view of the SADP of Figure 7(b) showing the ring structure (a) and a schematic view of the same in (b)

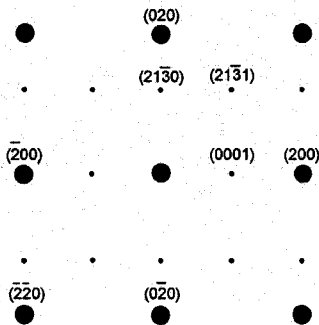


Figure 9 - Indexed schematic of a [001] Al diffraction pattern, showing reflections from a Q' variant whose long axis is parallel to [010] direction of Al

Identification of the Q' Phase

When examining electron micrographs of aged 6000 series Al alloys Q' can easily be mistaken for β' . Both β' and Q' have their long dimensions parallel to the $\langle 100 \rangle$ directions of the Aluminum matrix. This occurs because both β' and Q' have their c lattice parameters approximately equal to that of the Al lattice parameter which is what favors extension along the cube directions. The two phases, however, can usually be distinguished in cross section. The β' precipitate has a more or less equiaxed, almost circular shape. This occurs because there is no low index matching of $\{hki0\}$ planes of β' with $\{hk0\}$ planes of the Al matrix. Q' , however, does have a good match (see above under crystallography and Figure 10). This is what gives rise to the nearly rectangular cross section of the Q' phase.

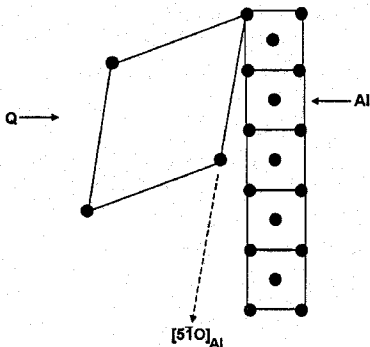


Figure 10 - Schematic of the Q' phase unit cell and its orientation with the Al matrix. Note that the lattice parameter of the Q' phase fits well along the [510] direction of the Al matrix.

Another way to distinguish the two phases is by electron diffraction. As mentioned above, the a lattice parameter of Q' can be determined from the ring patterns (see Figures 8). This parameter is very different from the a lattice parameter of the β' phase (1.04 nm vs. 0.705 nm). Also, the reflections that occur near the {110} positions can be used to differentiate β' from Q'. As can be seen from the electron diffraction pattern of Figure 8a, these reflections are streaked. For a [001] matrix zone axis, the streaks are in the [010] and [100] directions. These streaks along with double diffraction is what gives rise to the characteristic crosses near the {110} positions of reciprocal space. The streaks arise from the shape transform of the elongated precipitates. The streaks are perpendicular to the long dimension of the precipitates. This makes it difficult to measure the d spacing exactly. However, the interplaner spacing of the Q' planes which diffract near that position (i.e. the (2131) planes) is 0.260 nm, while the reflection for the β' which occurs there is the (2021) with the d spacing of 0.244 nm, assuming that the a lattice parameter of β' is 0.705 nm. It is therefore within the experimental accuracy of electron diffraction to distinguish these two phases.

Thus, Q' can be distinguished from β' by its morphology as well as from its electron diffraction pattern.

Kinetics of Formation of the Q' Phase

One of the reasons that a metastable phase forms prior to the equilibrium phase during precipitation is the fact that its surface energy is lower than that of the equilibrium phase. The barrier to nucleation can be written as:

$$\Delta G^* = \frac{(G.F.)(\sigma)^3}{(\Delta g_v + w)}$$

where G.F. is a geometric factor which depends on the shape of the critical nucleus, σ is the specific surface energy of the new phase, Δg_v is the change in free energy per unit volume of the new phase and w is the strain energy per unit volume of the new phase. Although equilibrium phases have the largest values of Δg_v (by definition!) their surface energy term is usually larger than metastable phases because in general, they cannot form in low surface energy configurations with the matrix. Since this term is cubed and since the entire expression for ΔG^* is part of the argument of an exponential, the rate of formation of the equilibrium phase is usually very much slower than that of competing metastable phases. However, the Q' phase is an exception to this because it is an equilibrium phase and therefore has a large value of Δg_v and it also can form in a low surface energy configuration as explained above in the crystallography section. Hence, its surface energy term is low and the entire expression for the barrier to formation of the phase is low giving rise to a relatively larger value of the rate of nucleation of this phase compared to competing phases.

Relative Strengthening Response of Different Metastable Phases

Because of the shape and habit plane of the Q' precipitate, it has a total of 12 variants within the Aluminum matrix. A moving dislocation, therefore, sees a different configuration of strain fields and precipitate morphologies in front of it. We suspect that this may be one of the causes of the increase in strength of the Al-Mg-Si alloys with Cu additions.

Also, for many commercial alloy compositions, the relative amount of Q' phase is expected to be higher than the other strengthening phases. This follows from the fact that equilibrium phase calculations show Q as the dominant phase present at all these compositions, and experimental studies indicated that the lath phase (i.e. Q') increased in amount with aging compared to other phases (11, 18). Thus, for example in ABS alloys, the overall volume fraction of Q' may be much higher than either β' or θ' . Also, the Q' precipitates have very fine size, most likely even finer than β' . Thus, the combinations of high volume fraction, fine size and morphological advantage puts Q' as a likely dominant strengthening phase in the ABS and many other low Cu versions of the Al-Mg-Si-Cu alloys.

Summary and Conclusions

General:

- (1) The Al-Mg-Si-Cu alloy family incorporates many 6XXX and 2XXX alloys to which belong also many commercial and auto-body sheet (ABS) alloys.
- (2) These alloys all contain the common quaternary phase Q. This phase is stable at normal aging temperatures, and often has the largest calculated volume fraction of all the precipitate phases. This has not been well recognized.
- (3) A metastable version of Q has been identified to exist. It has an extremely fine precipitate structure and it often occurs in high volume fractions. Thus, it is expected to strongly influence strength and other properties in ABS and other alloys.
- (4) Careful analysis of the literature indicates that many instances of strengthening ascribed to the more familiar metastable phases, namely β' , θ' or S' could in part or mostly be due to this Q phase precursor.
- (5) The complex aging response in many Al-Mg-Si-Cu alloys arises because of the simultaneous occurrence of two to three precipitating phases. This is further exacerbated due to inadequate knowledge about one of the major participants in them, namely the precursor of the Q phase. Systematic and discriminating studies are needed in this area.

Particular:

- (1) The bulk of Al-Mg-Si-Cu alloys often occupy one of the three tetrahedron composition spaces having a four-phase equilibrium at normal aging temperatures. The phases consist of aluminum matrix, (Al), and Q as the common ones and two out of the three phases, namely Mg_2Si , (Si) and θ .
- (2) When the Mg/Si ratio is less than about 1, the (Si) phase is stabilized, while Mg_2Si is stabilized when Mg/Si is greater than about 1. Increasing Cu stabilizes the Q and θ phases and also increases the amount of θ .
- (3) The metastable version of Q has the same crystal structure as the equilibrium Q, but unlike Q it also shares lattice coherency with the matrix. We propose the designation Q' for the metastable version of Q.
- (4) Q' has a lath morphology and a hexagonal structure, and the orientation relationship has the long axis parallel to $\langle 100 \rangle_{Al}$ and {150} habit planes of the matrix.
- (5) The lath morphology distinguishes Q' from the needle shaped β' , the precursor of Mg_2Si , which often precipitates together in early stages of aging and has a different hexagonal structure.
- (7) The diffraction pattern of Q', though in some respects similar to that of β' ; can be distinguished from that of β' .

- (8) The combinations of relatively high volume fraction, fine size and morphological advantage suggest that Q' may be a dominant strengthening phase in ABS and other low-Cu versions of the Al-Mg-Si-Cu alloys.

References

1. E. H. Dix, G. F. Sager and B. P. Sager, "Equilibrium Relations in Aluminum-Copper-Magnesium and Aluminum-Copper-Magnesium Silicide Alloys of High Purity," *Trans. Amer. Inst. Min. Met. Eng.*, 99 (1932), 119-131.
2. J. Crowther, "Overheating Phenomena in Aluminium-Magnesium-Silicon Alloys of the Duralumin Type," *J. Inst. Metals*, 76 (1949-50), 201-236.
3. H. J. Axon, "Equilibrium Relations at 460°C in Aluminium-Rich Alloys Containing 0-7% Copper, 0-7% Magnesium and 1.2% Silicon," *J. Inst. Metals*, 81 (1952-53), 209-213.
4. D. L. W. Collins, "Constitutional Factors Affecting the Tensile Properties of Wrought Aluminium-Magnesium-Silicon-Copper Alloys," *J. Inst. Met.*, 86 (1957-58), 325-336.
5. D. P. Smith, "The Constitution of Quaternary Aluminium-Copper-Magnesium-Silicon Alloys at 500°C," *Metallurgia*, 63 (1961), 223-231.
6. D. A. Petrov, "On the Composition of the Quaternary Phase in the System Al-Mg-Si-Cu," *Acta PhysicoChimica U.R.S.S.*, VI(4) (1937), 505-512; D. A. Petrov and N. D. Nagorskaya, *Zhur Obschey Khimi*, (1949), 1994-2037.
7. G. Phragmen, "On the Phases Occupying in Alloys of Aluminium with Copper, Magnesium, Manganese, Iron, and Silicon," *J. Inst. Metals*, 77 (1950), 489-552.
8. H. W. L. Philips, Equilibrium Diagrams of Aluminium Alloy Systems (London, The Aluminium Development Assoc., 1961), 128-133.
9. H. Suzuki, I. Araki, M. Kanno and K. Ito, "Effect of Si Addition on the Aging Behavior of an Al-2%Cu-0.9%Mg Alloy," *J. Japn. Inst. Metals*, 27(5) (1977), 239-245. (Japanese)
10. H. C. Stumpf, Alcoa proprietary internal data.
11. G. A. Edwards, G. L. Dunlop and M. J. Couper, "Fine Scale Precipitation in Al Alloy 6061," *The Fourth International Conference on Aluminum Alloys* (1994), 620-627.
12. P. Villars and L. D. Calvert, ed. Pearson's Handbook of Crystallographic Data for Intermetallic Phases, 2nd Ed., vol. 1 (Metals Park, OH: ASM, 1991), 769.
13. L. Arnberg and B. Aurivillius, "The Crystal Structure of $Al_xCu_2Mg_{12-x}Si_7$ (h-AlCuMgSi)," *Acta Chemica Scandinavica*, Series A, 34A (1980), 1-5.
14. L. F. Mondolfo, Aluminum Alloys: Structure and Properties (Boston, Butterworths, 1979), 644-651.

15. A. K. Gupta, A. K. Jena and M. C. Chaturvedi, "Insoluble Phases in Al-1.52Cu-0.75Mg Alloys Containing Silicon," *Mater. Sci. Tech.*, 3 (1987), 1012-1018.
16. A. K. Gupta, P. Gaunt and M. C. Chaturvedi, "The Crystallography and Morphology of the S'-Phase Precipitate in an Al(CuMg) Alloy," *Phil. Mag.*, 55 (1987), 375-387.
17. S. D. Dumolt, D. E. Laughlin and J. C. Williams, "Formation of a Modified β' Phase in Aluminum Alloy 6061," *Scripta Met.*, 18 (1984), 1347-1350.
18. L. Sagalowicz, G. Hug, D. Bechet, P. Sainfort and G. Lapasset, "A Study of the Structural Precipitation in the Al-Mg-Si-Cu System," *The Fourth International Conference on Aluminum Alloys (1994)*, 636-643.
19. B. Dubost, J. Bouvaist and M. Reboul, "Prevention of Intercrystalline Corrosion and Stress Corrosion on Alloy 2214 Through 'High-Low' Precipitation Aging," *The First International Conference on Aluminum Alloys, Vol. II (1986)*, 1109-1123.
20. M. Tamizifar and G. W. Lorimer, "The Effect of Copper on the Aging Response of an Aluminum-Magnesium-Silicon Alloy," *The Third International Conference on Aluminum Alloys, Vol. I (1992)*, 220-225.
21. T. Sakurai and T. Eto, "Effect of Cu Addition on the Mechanical Properties of Al-Mg-Si Alloys," *The Third International Conference on Aluminum Alloys, Vol. I (1992)*, 208-213.
22. R. N. Wilson, D. M. Moore and P. J. E. Forsyth, "Effects of 0.25% Silicon on Precipitation Processes in an Aluminium-2.0% Copper-1.2% Magnesium Alloy," *J. Inst. Metals*, 95 (1967), 177-183.
23. K. Matsuda, Y. Uetani, H. Anada, S. Tada and S. Ikeno, "HRTEM Observation of Precipitates in Al-Mg-Si Alloys," *The Third International Conference on Aluminum Alloys, Vol. I (1992)*, 272-277.
24. D. G. Eskin, "Investigation of the Optimization of Phase and Alloy Compositions of Al-Cu-Si-Mg Alloys," *Z. Metallkd.*, 83 (1992), 762-765.
25. Armen Khachaturyan, Theory of Structural Transformation in Solids (Wiley Interscience, 1983).

Acknowledgments

DJC wishes to thank Alcoa management for supporting a part of the work reported and for the permission to publish the paper. DEL acknowledges support from Alcoa Technical Center during a sabbatical as well as a grant from the Ford Motor Company. We also thank Dr. J. T. Staley for encouraging this study and for critical discussions on the content of this paper.