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Catalyzed Precipitation in Aluminum

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Ph.D. Thesis

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Catalyzed Precipitation in Aluminum

by

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Catalyzed Precipitation in Aluminum

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by

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Abstract

Catalyzed Precipitation in Aluminum

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Doctor of Philosophy in Materials Science and Mineral Engineering

University of California, Berkeley

Professor John William Morris, Jr., Chair

The work reported in Chapter 1 concerned the influence of Si on the precipitation of θ' (metastable Al₂Cu) during the isothermal aging of Al-2Cu-1Si (wt. %). The binary alloys Al-2Cu and Al-1Si were studied for comparison. Only two precipitate phases were detected: pure Si in Al-Si and Al-Cu-Si, and θ' (metastable Al₂Cu) in Al-Cu and Al-Cu-Si. On aging the ternary, Si precipitates first, and provides heterogeneous sites to nucleate θ'. As a consequence, the density of θ' precipitates in Al-Cu-Si is much higher than in the binary Al-Cu. Also, the θ' precipitates in the ternary alloy have lower aspect ratio (at given particle size) and lose coherence on their broad faces at a slower rate. The principal focus of Chapter 2 is to explain precipitation in Al-1at.%%Si-1at%Ge. The microstructure is characterized using conventional and high resolution transmission electron microscopy, as well as energy dispersive X-ray
spectroscopy. The first precipitates to come out of solid solution have a cube-cube orientation relationship with the matrix. High resolution TEM demonstrated that all the precipitates start out, and remain multiply twinned throughout the aging treatment. There is a variation in the stoichiometry of the precipitates, with the mean composition being Si-44.5at.\%Ge. It is also shown that in Al-Si-Ge it is not possible to achieve satisfactory hardness through a conventional heat treatment. This result is explained in terms of sluggish precipitation of the diamond-cubic Si-Ge phase coupled with particle coarsening. The purpose of Chapters 3 and 4 is to explain these properties in terms of the role that the Si-Ge additions have on modifying the conventional Al-Cu aging sequence. In both AlCu and AlCuSiGe the room temperature microstructure consists of both GP zones and θ'' precipitates. Upon aging at 190°C Al-Cu displays the well known precipitation sequence; the slow dissolution of GP zones and θ'' and the gradual formation of θ'. In the quaternary alloy, Si-Ge particles quickly nucleate and grow during elevated temperature aging (they are detected after as little as 30 min. at 190 °C). The Si-Ge particles then act as nucleation sites for θ' precipitates, resulting in a peak aged microstructure consisting of a dense distribution of θ' attached to Si-Ge.
This thesis is dedicated to BettyLou Blumberg, Terry Deck and Bruce Zundell.
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Background: The Precipitation Hardening Problem

In order to achieve high strength, a precipitation hardened alloy must contain a microstructure that impedes dislocation motion. To achieve this effect, an "ideal" microstructure consists of a dense distribution of fine unshearable precipitates. This statement can be explained by considering a dislocation gliding in a slip plane interacting with a distribution of pinning points (Figure b.1). These pinning points can be other dislocations, externally added particles, solute atmospheres or precipitates (as is the case this study). By applying an idealized force balance, one can approximate the stress necessary to bow a dislocation between two of these pinning points (Figure b.2) [b.1]. Original work on this subject was done by Orowan [b.2], Nabarro [b.3], Mott and Nabarro [b.4, b5], Mott [b.6], Friedel [b.7] and Williams [b.8]. The driving force moving the dislocation is the applied shear stress $\tau$ times the area over which it acts. Assuming that the dislocation bows into a semi-circle, the area over which it acts is the circumference of the circle, $2\pi r$, (the pinning points are a distance $2r$ apart) times its burgers vector $b$.

The force preventing dislocation motion is its line tension, approximated as $\alpha Gb^2$, where $\alpha$ is a constant between 0.5 and 1 (depending on the character of the dislocation) and $G$ is the shear modulus of the matrix. Each pinning point interacts with two arms of the dislocation, the angle between the arms being defined as $\phi$. At the
pinning point the arms are immobile, while on each side they are free to move as a result of the applied stress. As a dislocation bends in a semicircle, the two arms bend around the point decreasing the angle \( \phi \). The force resolved in the direction opposite the dislocation motion is then \( \alpha Gb^2(\cos \phi/2) \). Since there are two such pinning points the net force is \( 2\alpha Gb^2(\cos \phi/2) \). If the dislocation self interaction (which result in an attraction between the two line segments around a pinning point due to the opposite sign of their burgers vector) is neglected, the break away angle depends on whether the particles are strong or weak [b.1, b.9]. Strong particles are difficult to shear. Consequently, the dislocation becomes free of the particle only once the two dislocation arms become anti-parallel (\( \phi/2 \) is 90°) and cancel each other out. If the particle is weak, as the dislocation bows around the stress on the precipitate increases and at a critical stress the particle is sheared. In this situation a dislocation is able to glide past at an angle \( \phi/2 \) less that 90°.

Thus, the stress necessary to bow a dislocation between two pinning points is proportional to \( Gb(\cos \phi/2)/2r \), where \( 2r \) is the interparticle spacing. The requirement that the particles are ultra fine comes from the usual condition that there is only a limited high temperature solubility of the precipitate phase and consequently a limited volume fraction of the particles at the aging temperatures.
The resistance of a precipitate to shearing depends on how dissimilar it is with the matrix (in terms of crystallography, bonding, ordering, and common slip planes). In general, the more dissimilar the particle is to the matrix, the harder it is to pass a dislocation through it. There are several mechanisms that impede dislocation motion through a precipitate. An approaching dislocation is repelled by the elastic strain field around a precipitate (either from a coherency strain or a mismatch strain). Thus precipitates that strain the matrix are more effective in repelling dislocations than ones that don’t. The energy of a dislocation scales as $G \beta^2$. As a dislocation enters a precipitate, its energy will scale with the burgers vector and the shear modulus of the precipitate rather than the matrix. Thus hard particles, with complex slip systems impede dislocation passage better than precipitates with its modulus and crystal structure similar to the ductile matrix. Of the precipitate is ordered an additional antiphase boundary energy term has to be also included. In this case, precipitate geometry also becomes important since the total antiphase boundary energy scales with the cross-section of the slipped particle. Short stubby precipitates will be more difficult to shear than short thin ones.

Unfortunately, this “ideal” microstructure is difficult to achieve. This can be explained by thermodynamics of solid state nucleation [b.10]. The free energy change associated with solid state nucleation of a precipitate is $\Delta G$. It is the sum of the
reduction of the system's volume free energy due to the transformation \(-\Delta G_v\), the increase in the volume free energy due to any strain set up around the precipitate (either coherency or misfit), \(\gamma_e\), the increase in the system energy due to the additional surface area created by the precipitate \(\gamma_{sa}\), and the reduction in the system energy due to an annihilation of a defect \(-\Delta G_{defect}\) (this is for the case of heterogeneous nucleation). 

The net free energy change associated with nucleation of a spherical particle from solid solution is then expressed as

\[
\Delta G = \frac{4}{3} \pi r^3 (-\Delta G_v + \gamma_e) + 4\pi r^2 (\gamma_{sa}) - \Delta G_{defect}
\]

where the precipitate is assumed to be a sphere with a radius \(r\). The defect free energy can be associated with the elimination of a volume defect (for example the reduction of pre-existing strain in the matrix) of the elimination of a two dimensional defect (nucleation on a grain boundary) or the elimination of a certain portion of a dislocation line. The critical radius at which the precipitated is stable is then expressed as

\[
r_{\text{crit}} = 2 \left( \frac{2\gamma_{sa} - \Delta G_{def}}{\Delta G_{vol} - \gamma_e} \right)
\]
The above equation shows the intrinsic problem in achieving an "ideal" microstructure consisting of a dense distribution of fine unshearable precipitates. Particles that resist dislocation shearing have large critical nuclei. Often such particles are so hard to form that they nucleate only heterogeneously.

An additional limitation on forming ultra small precipitates is that their solubility scales inversely with the precipitate radius. When two phases are in contact the equilibrium composition of these phases is dictated by their chemical potential which is the Gibbs free energy per mole. In a two phase field a common tangent to the two chemical potential curves dictates the equilibrium composition. If one of the phases has a finite volume (as is the case for precipitates in a matrix), its chemical potential is defined as

\[ \mu/\text{vol} = (-G_v + \gamma_e) + 3\gamma_{sa}/r \]  

This is in fact the well known Gibbs-Thomson effect [i.11] which indicates that the equilibrium solute content of the matrix phase will be higher adjacent to a small precipitates than adjacent to a larger one. What this means in terms of obtaining an "ideal" microstructure is that when the precipitates are fine, much more solute may be
remained in the matrix than would be expected from the equilibrium phase diagram. It is only once the particles have coarsened may it be possible to achieve the expected volume fraction of the strengthening phase.

Figure b.3 shows the type of precipitates explored in this study. The two equilibrium phases are Si and $\theta$ (Al$_2$Cu). The phases $\theta''$ (Al$_3$Cu) and $\theta'$ (Al$_2$Cu) are metastable and form at lower temperatures than $\theta$ [b.11]. Not shown are GP zones which do not have a unique crystal structure but instead consist of monolayers of Cu situated on {100} Al planes. They are also a non-equilibrium phase. The fcc aluminum matrix is also shown for reference. From the precipitate crystal structure one can predict how resistant each phase will be to dislocation shearing and how easily it will nucleate. Diamond cubic Si particles have a lattice parameter of 5.4309 Å (compared to 4.0497 Å for Al) [b.12] and a shear modulus of 66 GPa (compared to 26 GPa for Al) [b.13]. The crystal is covalently bonded. All these factors make the precipitate very resistant to shearing but somewhat difficult to nucleate.

Both GP zones and $\theta''$ form easily at low temperatures and are very densely distributed [b.11, b.14, b.15] However, they can be sheared easily due to the similarity of their structure to that of the matrix [b.15]. Both $\theta$ and $\theta'$ are difficult to shear (since $\theta$ is non-coherent while $\theta'$ is semi-coherent, $\theta$ is more difficult to shear) [b.15]. However, both nucleate only heterogeneously due to the dissimilarity of their crystal structures.
and lattice parameters with the Al matrix [b.16, b.17]. Because there is a low density of such sites in binary Al-Cu (if it has not been cold worked prior to aging) a microstructure composted of only \( \theta \) and/or \( \theta' \) precipitates does not normally display peak strength [b.14, b.15].

The primary focus of this thesis is to explore novel ways in which an "ideal" microstructure can be achieved. As it turns out, such a microstructure consists of composite particles containing more than one precipitate where each precipitate reduces the energy of the other.

Chapter 1 explores the ability of Si to refine \( \theta' \) precipitate distribution in Al-Cu. In ternary Al-Cu-Si alloy, Si precipitates provide a distribution of heterogeneous nucleation sites that is much more dense than that available in the binary. The primary mechanism responsible for this effect is strain compensation. Since the transformation strain of Si is strongly positive, while that of \( \theta' \) is negative the strain energy of a \( \theta' \) precipitate is significantly lowered if it nucleates in the vicinity of a pre-existing Si precipitate.

Chapter 2 examines the possibility of using the ternary Al-Si-Ge as a structural alloy. It is shown that in Al-Si-Ge it is not possible to achieve satisfactory hardness through a conventional heat treatment. This result is explained in terms of an unfortunate combination of a limited solubility (leading to a low volume fraction of the
precipitate phase) and a high precipitate energy (resulting to a relatively coarse microstructure). This provides an example of a system where one is essentially stuck with an insufficiently dense array of strengthening particles due to the energy and solubility considerations.

Chapters 3 and 4 detail how such approaches for energy compensation can be used in practice to design alloys with improved mechanical properties. The systems investigated are Al-Cu-Si-Ge and binary Al-Cu (which is used for comparison). In the binary aged at 190 °C only \( \theta'' \) are formed. In the quaternary alloy a double catalyzation process achieves an ultra-dense distribution of composite \( \theta'-(\text{Si-Ge}) \) particles. GP zones and \( \theta'' \) precipitates formed during room temperature storage are used as a template to refine the Si-Ge (same structure as Si but a composition of Ge-45at.%Si) precipitate distribution. Strain cancellation becomes important since the GP zones and \( \theta'' \) precipitates are known to place the Al matrix in tension along the \( \{100\}_\text{Al} \) directions. The Si-Ge precipitates then catalyze the formation of \( \theta' \) by the same mechanism as observed in Al-Cu-Si.
References, Background


Figure i.1. A dislocation gliding in a slip plane interacting with a distribution of pinning points. In this work, the pinning points are diamond cubic Si, $\theta'$ and $\theta''$ precipitates.
Dislocation bows into a semi-circle

Resistance:
\[ 2 \text{(line tension)} \cos(\phi/2) \]
\[ \text{line tension} = \alpha G b^2 \]
\[ \alpha = 0.5 - 1 \]
Break away angle, \( \phi/2, = 90^\circ \)

- Force balance + assume a random array is weaker than an ordered array
- \( \Delta \sigma_{\text{yield}} = 1.5Gb/(\text{particle spacing}) \)
- If particles are shearable: \( \phi/2 < 90^\circ \)

Figure i.2. By applying an idealized force balance, one can approximate the stress necessary to bow a dislocation between two of these pinning points.
Figure i.3. Precipitate structures explored in this study: (a) Aluminum, (b) Silicon, (c) θ'' (Al₃Cu), (d) θ' (Al₂Cu), and (e) θ (equilibrium Al₂Cu).
Figure i.3. Precipitate structures explored in this study: (a) Aluminum, (b) Silicon, (c) $\theta''$ ($\text{Al}_3\text{Cu}$), (d) $\theta'$ ($\text{Al}_2\text{Cu}$), and (e) $\theta$ (equilibrium $\text{Al}_2\text{Cu}$).
Figure 1.3. Precipitate structures explored in this study: (a) Aluminum, (b) Silicon, (c) \(\theta'^{\prime\prime}\) (\(\text{Al}_3\text{Cu}\)), (d) \(\theta'\) (\(\text{Al}_2\text{Cu}\)), and (e) \(\theta\) (equilibrium \(\text{Al}_2\text{Cu}\)).
Figure i.3. Precipitate structures explored in this study: (a) Aluminum, (b) Silicon, (c) θ'' (Al₃Cu),
(d) θ' (Al₂Cu), and (e) θ (equilibrium Al₂Cu).
Chapter 1: Si Catalyzed Precipitation of $\theta'$ in Al-Cu-Si

1.1 Introduction

Al-Cu and Al-Cu-Si alloys containing 0.5-2Cu and 0.5-1Si (weight percent) are the most common alloys used for thin film metallization in microelectronics. Electromigration voiding and failure in these alloy films is affected by the precipitation of Al$_2$Cu intermetallics in the form of either $\theta$ (the equilibrium phase) or $\theta'$ (the metastable phase). Recent data suggest that aging treatments that enhance the lifetime of Al-Cu-Si [1.1-1.2] thin films are much less effective for binary Al-Cu [1.3-1.4]. An obvious hypothesis is that Si affects the precipitation process in some favorable way [1.5].

However, while precipitation in binary Al-Cu has been studied so extensively that it is used as the "textbook example" of precipitation in the solid state [1.6], there is very little published work on the influence of small additions of Si. The author knows of only two pieces of published work dealing with the effect of Si on the precipitation in binary Al-Cu [1.7-1.8]. Both are by Starink and Van Mourik, and concern alloys that are relatively rich in Si. There is a similar lack of work on the influence of Cu on precipitation in Al-(0.5-1)Si. The only published study known to the author is by Steward and Martin [1.9] who found that additions of 0.45wt.% Cu to Al-0.5wt.%Si
caused the Si precipitates to spheroidize and inhibited coarsening. They suggest that Cu segregates to the Al-Si interface, reducing the interfacial energy.

Given this background, the present work was undertaken to explore the influence of Si on precipitation from Al-Cu alloys. To do this the author compared precipitation in a bulk alloy of Al2Cu1Si (wt. %) to that in the binary alloys Al2Cu and Al1Si. As discussed below, the author found that Si precipitates preferentially from Al2Cu1Si in conventional aging treatments and provides heterogeneous nucleation sites for the direct precipitation of θ' (Al2Cu). Si also influences the morphology of the θ'. It inhibits the growth of θ', promoting a dense distribution of precipitates which, though plate-like, are somewhat less so (lower aspect ratio) than those in binary Al2Cu. The shape, state and density of Si precipitates are also different in the ternary Al2Cu1Si than in the binary Al1Si.

The possibility that third-component additions can produce heterogeneous nucleation sites in Al-Cu alloys is well-documented. For example, Ringer et al. [1.10] found that Ag forms co-clusters with Mg that act as heterogeneous sites for nucleation of the Ω-phase (a distorted form of the equilibrium Al2Cu phase) in Al-Cu-Mg lightly alloyed with Ag. Wilson [1.11] found that small additions of Si lead to a finer and more homogeneous distribution of S-phase (Al2CuMg) precipitates in an Al2.5Cu1.2Mg alloy. He attributed this effect to the stabilization of "GPB" zones that serve as
heterogeneous nucleation sites for the S-phase. Radmilovic, et al. [1.12] subsequently imaged these zones using high-resolution transmission electron microscopy. Das, Thomas and Rowcliffe found that trace additions of Cd, In and Sn promoted a dense and homogeneous distribution of \( \theta' \) precipitates in Al-Cu [1.13]. Later, Ringer, et al. [1.14] showed that the Sn precipitated first, and provided heterogeneous sites to nucleate \( \theta' \). Inclusions like \( \text{Al}_2\text{O}_3 \) particles [1.15] and SiC [1.16-1.17] also change the precipitation kinetics, since they, or the misfit dislocations they introduce into the matrix, provide heterogeneous nucleation sites. Still another heterogeneous nucleation mechanism was proposed by Thomas and Whelan [1.18], who observed the collapse of retained vacancies in binary Al-Cu to form vacancy loops and helices which provide sites for the \( \theta' \) nucleation.

While there are prior reports of third-component additions affecting the geometry of \( \theta' \) (\( \text{Al}_2\text{Cu} \)) precipitates, the main focus of prior work has been on the thin-plate morphology of the precipitates themselves. It is well known that there are two mechanisms that promote thin-plate shapes for coherent precipitates. The first is thermodynamic [1.19]. In the usual case, the elastic energy of a coherent precipitate is minimized if it takes the form of an arbitrarily thin plate on a definite habit plane. The second is kinetic. Coherent precipitates tend to grow by the nucleation and growth of "ledges" on well-matched surfaces [1.20]. If the nucleation of growth ledges is
difficult, the precipitate may simply spread out into a large-diameter plate. Other kinetic mechanisms have also been proposed.

All prior work on the growth of θ' (Al2Cu) that is known to the author (refs. [1.20-1.27] and references contained therein) assumes that the shape of the particle is kinetically controlled. Insofar as the author has been able to discover, no modern thermoelastic analysis of the precipitate shape has been done. The thermoelastic analysis is straightforward, and is given below. The results show that, while kinetic considerations are clearly important, the shapes of θ' precipitates in both Al2Cu and Al2Cu1Si tend to follow the predictions of the elastic theory. The favorable elastic interaction between the Si and θ' precipitates helps to explain the catalytic effect of pre-existing Si precipitates and the lower aspect ratio and slower growth of θ' precipitates in the ternary.

1.2 Experimental Procedure

Alloys of composition Al2Cu, Al1Si and Al2Cu1Si (wt.%) were made by arc melting 99.999 (wt.%) Cu, 99.999 (wt.%) Si and 99.99 (wt.%) Al. The cast samples were cold swaged to 10 to 15% plastic deformation. They were then encapsulated in sealed quartz glass tubes that were back-filled with argon, annealed for 48 hrs. at 525 °C
and quenched in ice water. The samples were roughly cylindrical, about 20 mm in length and 10 mm in diameter. Analysis by vacuum emission spectroscopy (at FTI Anameț Laboratories) gave a composition of Al-2.02 wt.%Cu for the binary Al-Cu alloy and Al-2.01 wt.%Cu-0.96 wt.%Si for the ternary Al-Cu-Si alloy. No other elements were present in concentrations greater than the detection limit of about 0.01 wt.%.

The cylindrical ingots were sliced normal to the cylinder axis into discs 1 mm in thickness, using a diamond saw operated at a low cutting speed with ample coolant to minimize sample heating. The discs were then core drilled into 3 mm diameter discs. These were isothermally aged for 10 minutes, 6, 24, and 48 hours at 225 °C, then air cooled. The temperature was monitored with an external thermocouple, and varied no more than 1 °C.

The samples were ground down to a thickness between 125 and 150 μm, using 500, 800, 1200 and 2400 grit silicon-carbide polishing paper. They were then electrochemically polished in a Struers Tenupol-3 jet polisher at a temperature of -25 °C with a polishing voltage of 15 V. The polishing solution was 75 methanol - 25 HNO₃ by volume.

Transmission electron microscopic (TEM) studies were done in a JEOL model JEM 200 CX equipped with a double tilt holder, operated at 200 kV. Diffraction
pattern simulation was done with the commercial software, "Desktop Microscopist", in the [001] zone axis of Al, using the well-known space groups of Al and Si, and the lattice parameters 4.0497 Å (Al) and 5.4309 Å (Si) [1.28]. θ' (metastable Al₄Cu) has space group I₄/mmm (tetragonal), with two Cu atoms per unit cell in the 2a special positions and four Al atoms in the 4d special positions. Its lattice parameters are a = 4.04 Å and c = 5.8 Å [1.29]. For Si in Al, the most common orientation relationship (by a wide margin) was the cube-cube, and this is used in the simulation. While the author did not attempt to determine orientation relationships for those Si precipitates that were not cube-on-cube, several alternates are well documented in the literature [1.30-1.33]. The behavior of Si resembles that of Ge in Al; recent work has shown that, while there are many possible orientation relationships, the cube-cube relation dominates in frequency [1.34-1.37]. Double diffraction from the Al Bragg beams was very extensive for the silicon precipitates due to their small size and geometry, and was consequently incorporated into the simulation. The θ' precipitates grow as plates on the {100} planes of Al [1.29], with three distinct variants: [100]ₙ∥[100]ₐ₁ and [010]ₙ∥[010]ₐ₁; [100]ₙ∥[100]ₐ₁ and [001]ₙ∥[010]ₐ₁; and [001]ₙ∥[100]ₐ₁ and [010]ₙ∥[010]ₐ₁.

The lengths and thicknesses of the θ' precipitates were measured from dark-field TEM micrographs of the precipitates viewed edge-on in the [001]ₐ₁ zone axis. The
measurements were made on 3x blow-ups of the photographic negatives taken in the microscope. As documented in the dark-field micrographs presented below, the precipitates are plates that lie on \( \{100\}_{\text{Al}} \) planes, and are sufficiently uniform in thickness that the thicknesses, while small, could be measured with consistent results. In every case, the measured thickness was very close to an integral multiple of a unit height, 5.43 Å. While this result is consistent with prior work [1.22] that shows 0° growth by successive propagation of growth ledges on the broad, (001) faces, the step heights should be nearly integral multiples of the unit cell height, with is 5.8 Å [1.29].

The author has not been able to identify the source of this discrepancy (which does not affect the results in any significant way), but it may be due to a small, consistent error in the instrument magnification or the magnification used in photographic processing. The thicknesses are therefore reported as multiples of the fundamental height.

The measured lengths of the precipitates are the projected lengths in the [010]_Al direction. In fact, the precipitate plates have somewhat irregular shapes. The measured lengths are indications of the plate diameters, and are used for that purpose in computing precipitate volumes and aspect ratios, but are not necessarily equal to the average diameter of the plates [1.22].
1.3 Results

1.3.1. Selected Area Diffraction Patterns

Fig. 1.1 shows representative selected-area diffraction (SAD) patterns of Al2Cu, Al1Si and Al2Cu1Si, after aging at 225 °C for 48 hours. Simulated diffraction patterns are displayed next to the experimental patterns. An 80 μm SAD aperture was used in obtaining these patterns. Only θ' (Al2Cu) and pure Si precipitates were detected in samples aged at 225 °C. In Fig. 1.1a a typical diffraction pattern of θ' in binary Al2Cu is compared to a simulated pattern that incorporates the orientation relationships listed in the experimental procedure. Double diffraction was negligible. Fig. 1.1b compares experimental and simulated diffraction patterns of Si precipitates in binary Al1Si. Fig. 1.1c includes experimental and simulated diffraction patterns from the aged ternary Al2Cu1Si. The Al matrix is decorated by Si and θ' precipitates, which have the same orientation relationships as in the binary alloys. Additionally, \([111]_\text{Si}\) reflections appear in the diffraction patterns adjacent to the \([002]_\theta'\) reflections (parallel to the \([200]_\text{Al}\) reflections). No attempt was made to deduce any orientation relationship from these spots.
1.3.2 Si Precipitation

The shape and distribution of the Si precipitates are illustrated in Figs. 1.2 and 1.3. The dark field images of Si were obtained using a $220_{\text{Si}}$ reflection taken close to the $[001]_{\text{Al}}$ zone axis, and are representative of the overall microstructure. The prevalence of the cube-cube orientation makes it possible to image most of the Si precipitates in either alloy with a single $220_{\text{Si}}$ reflection.

Fig. 1.2 shows Si precipitates in Al1Si. Figs. 1.2a and 1.2b show the microstructure after the alloy was aged for 10 minutes, Figs. 1.2c and d show the microstructure after aging for 6 hours and 48 hours, respectively. The precipitation of Si is rapid, uniform and extensive. The precipitates display the shapes that have been extensively studied in Al-Ge alloys: triangular plates, 100 rods and laths, 110 rods and laths, tetrahedra, octahedra and hexagonal plates [1.35-1.38]. In Fig. 1.2b, a two beam image of the microstructure reveals that there is significant Ashby-Brown type strain [1.38] in the matrix around many of the Si particles. The particles showing the most pronounced matrix strain are arrowed. The strain is expected since the volume mismatch associated with the transformation of two Al unit cells into one Si unit cell, $\Delta V/V_o$, is 20.6%, resulting in a transformation strain of 6.85%.
In the ternary alloy, the precipitation of Si initiates the precipitation sequence. Figs. 1.3a-c show the ternary after 10 min. aging. While Si precipitates are common, no Cu-rich precipitates were detected. Si precipitates initially form in clusters and on defects such as dislocations. A dense distribution appears on aging for longer times. Figs. 1.3d and 1.3e show the distribution of Si precipitates after aging for 6 and 24 hours, respectively.

Compared to the binary, the Si precipitates in the ternary alloy are coarser, less densely distributed, more equiaxed in shape and more extensively twinned. The degree of twinning is demonstrated in Figs. 1.3d and e, where, because of the extensive twinning, only part of each precipitate is imaged with a single 220$_{\text{Si}}$ reflection. This partial illumination accounts for the irregular appearance of the Si precipitates that are lit in the dark-field. Twinning is so common in Si precipitates in the ternary that after 48 hrs. aging spotty ring patterns from the (111) and (220) planes of silicon were visible in the diffraction patterns obtained using larger SAD apertures.
1.3.3 \( \theta' \) (Al\(_2\)Cu) precipitation

*The shape and distribution of \( \theta' \)*

The binary Al\(_2\)Cu alloy develops a distribution of thin plate-like \( \theta' \) precipitates after 6 hours aging at 225 °C. Fig. 1.4a is a bright-field image taken near the [110]\(_{\theta'}\) zone axis (10° from the [110]\(_{Al}\) zone axis, tilted along a 200 Kikuchi line). Fig. 1.4b is a dark-field image taken using a 1–12\(_{\theta'}\) reflection. The \( \theta' \) precipitates shown in Figs. 1.4a and b have growth ledges. Many of the precipitates are so large that they intersect one or both of the foil surfaces. This effect produces a misleading geometry in the micrographs; the true edges of the plate-like \( \theta' \) precipitates tend to run along <110> and <100> directions.

The development of the \( \theta' \) precipitates in ternary Al\(_2\)Cu1Si is illustrated in Figs. 1.5 and 1.6. Fig. 5 presents transmission electron micrographs of precipitates in Al\(_2\)Cu1Si after aging for 6 hours. Fig. 1.5a is a bright-field image taken near the [110]\(_{\theta'}\) zone axis. The precipitates appear to be composites, with thin plates growing out from compact cores. Fig. 1.5b is a dark-field image taken using a 1–12\(_{\theta'}\) reflection showing that the thin plates are \( \theta' \). Fig. 1.5c is dark field image taken using a 1–11\(_{Si}\) reflection, showing that the compact cores are Si precipitates. A survey of these and numerous
other micrographs shows that virtually every θ’ precipitate contains at least one Si particle.

The θ’ precipitates are smaller and appear to be much more densely distributed in ternary Al-2Cu-1Si than in binary Al-2Cu. While the author did not determine the exact foil thicknesses, the diffraction pattern from the regions examined contained both visible matrix and precipitate spots, and Kikuchi lines, suggesting that the foils were of similar thickness. Hence the relative densities can be roughly inferred from the figures.

While the θ’ precipitates are plates with high aspect ratios in both alloys, the precipitates in the binary are larger and more plate-like for all aging conditions. Fig. 1.6 compares the θ’ precipitates in Al-2Cu and Al-2Cu-1Si after prolonged aging. The plates in the binary after 24 hr. aging (Fig. 1.6a) are significantly larger than those in the ternary after aging for 48 hr. (Fig. 1.6b). Moreover, some of the larger precipitates in the binary have begun to develop interfacial dislocations, while none are detected in the ternary. It is well known that θ’ precipitates lose coherency after prolonged aging by developing arrays of interface dislocations of a/2<110>Al and a/2<100> character on their broad faces [1.22].

Figs. 1.7 and 1.8 are dark-field images showing θ’ precipitates edge-on in the binary (Fig. 1.7) and ternary (Fig. 1.8) after aging at 225 °C for 6 hrs. (1.7a, 1.8a) and 48 hours (1.7b, 1.8b). In Fig. 1.7a and 1.7b, some Si particles are bright because
diffraction spots that result from extensive twinning were included in the 20 μm objective aperture. However, the morphology of the Si particles in dark field is very irregular and quite distinct from that of θ'. Tilting experiments were done along 200 Kikuchi lines to confirm the identification of the θ' precipitates.

The average thickness (d), diameter (L), and aspect ratio (κ = L/d) of the θ' precipitates in the two alloys are compared quantitatively in Fig. 1.9. The data are mean values obtained from several regions, while the error bars are for the standard deviation associated with the measurements. The measurements were made on foils tilted similarly to those in Figs. 1.7 and 1.8. The θ' precipitates in the ternary are consistently shorter and thicker than those in the ternary, and coarsen very little, if at all, over the 48 hr. aging time. The aspect ratio of θ' in the ternary also remains constant, at about 9. The precipitates in the binary do coarsen slightly during aging. The mean value of the aspect ratio increases from about 40 at 6 hours to about 50 at 48 hours.
Both the thermoelastic [1.19] and kinetic [1.20] models of precipitate shape predict that the aspect ratio of the θ' plates increases monotonically with precipitate size. The kinetic "ledge growth" model suggests a linear increase in $\kappa$ with $L$ as the "ledge-nucleation-limited" precipitates spread out at constant $d$. The thermoelastic model [1.19,1.39,1.40] predicts a more complex dependence (discussed below) which simplifies to $\kappa \approx \sqrt{L}$ when the precipitates are large. We have, therefore, plotted $\kappa$ vs. $L$ for the full sample of θ' precipitates in Al2Cu (Fig. 1.10). The distributions of values from the three aging times are very similar, and are superimposed. Precipitates of the same thickness ($d$) are connected by straight lines, and are labeled with the value of $d$ in multiples of the unit thickness, $d_0 = 4.53 \, \text{Å}$.

Both the kinetic and thermoelastic interpretations of precipitate shape are supported by the data in Fig. 1.10, suggesting that both play an important role. If we focus on precipitates of given thickness, $d$, these exhibit a broad range of diameters, $L$. The spread is particularly broad for the thinnest precipitates. This result is consistent with the kinetic model which proposes that ledge nucleation is difficult and precipitates spread at constant $d$. On the other hand, the best fit to the overall data gives

$$\kappa = AL^{0.52}$$  \hspace{1cm} (1.1)
which is almost exactly the relation \((k \approx \sqrt{L})\) predicted by the thermoelastic theory.

The data suggest that ledge nucleation is difficult, and often limiting. Nonetheless, the precipitate shape does evolve, and does so as predicted by the elastic theory.

To explore this behavior further, the author tested a more complete form of the elastic theory to determine whether it yields plausible predictions for the precipitate shape, the surface energy of the \(\theta'\)-Al interface, and the relative shapes of the \(\theta'\) precipitates in \(\text{Al}_2\text{Cu}_1\text{Si}\). The basic theory of the shapes of coherent tetragonal precipitates in cubic media was developed by Khachaturyan and Hairapetyan [1.19,1.39,1.40]. For the \(\{001\}\) habit, they found a minimum in the total energy of a disc-shaped precipitate of diameter, \(L\), and thickness, \(d\), when the aspect ratio, \(\kappa = L/d\), satisfies the equation

\[
f(\kappa) = \frac{\kappa^{5/3}}{(\ln(\kappa) + 1)} = \frac{3}{4\pi} \left(\frac{4}{\pi}\right)^{1/3} \frac{v^{1/3}}{r_0}
\]

(1.2)

where \(v = \pi L^2 d/4\) is the volume of the disc, and

\[
r_0 = \frac{\gamma}{\beta}
\]

(1.3)
is a critical radius for transition from interface to elastic control. In this equation $\gamma$ is the interfacial tension of the broad \{001\} face, and the elastic factor, $(\beta)$ is

$$
\beta = -\frac{1}{c_{11}} \left( 2c_{12} \varepsilon_{11}^0 + c_{11} \varepsilon_{33}^0 \right)^2 \left( \frac{c_{11}(1 + \alpha^2) - 2c_{12} \alpha - 2(\alpha + 1)c_{44} - \left(\xi \left(\frac{c_{11} + c_{12}}{c_{11}}\right)\right)}{c_{44}} \right)
$$

where the $c_{ij}$ are elastic moduli, $\varepsilon_{11}^0$ and $\varepsilon_{33}^0$ are the transformation strains along the basal and tetragonal axes of the precipitate, $\alpha$ is the elastic function,

$$
\alpha = \frac{(c_{11} + c_{12}) \varepsilon_{11}^0 + c_{12} \varepsilon_{33}^0}{2c_{12} \varepsilon_{11}^0 + c_{12} \varepsilon_{33}^0}
$$

and $\xi$ is the dimensionless elastic anisotropy factor,

$$
\xi = \frac{c_{11} - c_{12} - 2c_{44}}{c_{44}}
$$

The theory is developed under an approximation of uniform elastic constants, and is most accurate when the elastic constants of the thin-plate precipitate are used.

If we substitute the relation, $v = \pi L^3/4\kappa$, into Eq. (1.2) then $\kappa$ can be written as a function of $L$:
\[ \frac{\kappa^2}{(\ln(k) + 1)} = KL \]  

(1.7)

where \( K \) is a constant. When \( \kappa \) is large, \( \ln(\kappa) \) varies slowly compared to \( \kappa^2 \) and \( \kappa \) becomes proportional to \( \sqrt{L} \), as noted above.

To investigate the applicability of Eq. (1.2) we plot \( f(\kappa) \) against \( r = \sqrt[3]{L} \) and test for a linear dependence. If all the data is included, the fit is marginal. But if we restrict the investigation to the thicker precipitates, whose shapes are less likely to be limited by ledge nucleation [20], a linear fit gives a good representation of the data. This is shown in Fig. 1.11, where precipitates with thickness \( d \leq 12 \) (about 65 Å) are separated from those (the substantial majority) that have \( d > 12 \). The best-fit power-law relation for the thicker precipitates gives \( f(\kappa) \propto r^{0.96} \), in very good agreement with the KH model.

The best linear fit to the shape data is shown in Fig. 1.12, and is

\[ f(\kappa) = 575r + 8 \]  

(1.8)

where \( r \) is measured in microns. From Eq. 1.2, the corresponding value of the critical radius is

\[ r_0 = 4.2 \times 10^{-3} \, (\mu m) \]  

(1.9)
In the elastic theory of precipitate shapes, high aspect-ratio plates are predicted when \( r >> r_0 \), a condition that is satisfied for all of the \( \theta' \) precipitates found in this research.

To compute the interfacial tension, the elastic factor is needed which requires the elastic constants of \( \theta' \). Since these are currently unknown, the author has used both the elastic constants of aluminum and a "law of mixtures" estimate for the elastic constants of \( \text{Al}_2\text{Cu} \). (The elastic constants for the equilibrium \( \theta \)-phase are known [1.41], but the structure is sufficiently different from \( \theta' \) that they are not expected to apply). The transformation strains for a \( \theta' \) precipitate with its tetragonal axis oriented along (001) are: \( \varepsilon_{11}^0 = -0.0024, \varepsilon_{33}^0 = -0.0452 \). Using the moduli of aluminum [1.42], \( c_{11} = 108 \text{ GPa}, c_{12} = 61.3 \text{ GPa}, c_{44} = 28.5 \text{ GPa} \), we obtain \( \beta = 0.0209 \) and

\[
\gamma = 87 \text{ mJ/m}^2 \tag{1.10}
\]

The "law of mixtures" moduli, \( c_{ij} = [2c_{ij}(\text{Al})+c_{ij}(\text{Cu})]/3 \), are: \( c_{11} = 128 \text{ GPa}, c_{12} = 81, c_{44} = 44 \). With these moduli we obtain \( \beta = 0.0231 \) and

\[
\gamma = 96 \text{ mJ/m}^2 \tag{1.11}
\]
These numbers are higher than the value, 30 mJ/m², that Aaronson, et al. [1.43] estimated, but are in the same range, and are comparable to typical internal surface energies in Al and its alloys. For example, the energy of an intrinsic stacking fault in Al is about 200 mJ/m² [1.44], the energy of a twin boundary is about 120 mJ/m² [1.44], and the estimated energy of an antiphase boundary in δ' Al₃Li is near 70 mJ/m² [1.45].
Application of the theory of precipitate shape to Al2Cu1Si alloys

The aspect ratio of the θ' precipitates in the Al2Cu1Si alloy is plotted as a function of L in Fig. 1.13. Data taken after 6, 24 and 48 hrs. aging are commingled since there is no apparent difference between the data sets. The binary Al2Cu data are re-plotted in the same figure. The smaller average size of the precipitates in the ternary is apparent from the data. However, there is a significant range of sizes, L, over which the data sets overlap. Almost all of the ternary-alloy precipitates with sizes in this range have lower aspect ratios than the corresponding binary-alloy precipitates.

A simple explanation for the lower aspect ratio of the θ' precipitates in the ternary is the compensation of the coherent strain field of the θ' by the strain field of the Si precipitate on which it nucleates. While the coherency strain of θ' is negative (ε_{11}^0 = -0.0024, ε_{33}^0 = -0.0452), the Si strain is large and positive (ε_{11}^0 = ε_{33}^0 = ε^0 = 0.0685), and is available to lower the elastic energy of θ' that forms in its neighborhood. Fig. 1.14 is a plot of f(κ) against \( n^{1/3} \) for θ' in Al2Cu1Si. Assuming \( γ = 96 \) mJ/m², as calculated above, the best fit to the data yields a value of \( r_0 \) of about 0.012 μm, which is, in fact, the experimental value of \( r \) at which the aspect ratio approaches 1. This value of \( r_0 \) is consistent with Eqs. 1.3 and 1.4 if it is assumed that, on average, about 40% of the
elastic strain of the $\theta'$ precipitate is relaxed by the strain field of the Si precipitate on which it nucleates. Since the transformation strain of Si is about four times the average transformation strain of $\theta'$, this degree of relaxation does not seem unreasonable.

1.4 Discussion

The principal observation made in this work is the strong interaction between Si and Cu in the precipitation behavior of Al$_2$CuSi. Copper retards the nucleation and growth of Si, leading to a Si precipitate distribution that is more coarse, less dense and more heterogeneous than that in the Al-Si binary. Si then catalyzes the heterogeneous nucleation of $\theta'$ (Al$_2$Cu), producing a distribution of $\theta'$ precipitates that are smaller and less plate-like than those that form when binary Al$_2$Cu is given a similar treatment. Si also seems to retard the coarsening of $\theta'$.

The probable reason that Cu retards the precipitation of Si from Al-Cu-Si is that it increases the solubility of Si, lowering the supersaturation at the aging temperature. Fig. 1.15a shows a plot of the solubility of Cu in Al (at.%) for binary Al-Cu [1.46] and pseudo-binary Al-Cu-1wt.%Si [1.47]. Fig. 1.15b shows a plot of solubility of Si in Al (at.%), replotted from the binary and pseudo-binary Al-Si-4wt.%Cu phase diagrams. At least at high temperature, the solubility of Si in Al and of Cu in Al is significantly
enhanced in the ternary alloy. While there is, unfortunately, no data available for the 225 °C aging temperature used in this study, it seems reasonable to infer enhanced solubility at a lower temperature as well. Increased solubility means less undercooling at given temperature and, hence, a lower driving force for precipitation. With a reduced driving force, heterogeneous nucleation sites such as dislocations or the strain fields of other precipitates become increasingly important, so the more heterogeneous nucleation of Si in the ternary alloy is expected.

The heavy twinning of Si precipitates in Al-Cu-Si is probably due to adsorption of Cu at the Si/Al interface [1.9] and its influence on the pattern of growth. Since Si precipitates have a higher specific volume than Al, and are known to be incoherent with the matrix, they effectively act as misfitting inclusions that place the surrounding matrix in compression. Cu atoms (r_Cu = 1.57 Å, r_Al = 1.82 Å) and vacancies should segregate to the precipitate-matrix interface to reduce this misfit strain. Adsorbed impurities can promote twinning by the "step poisoning" effect [1.48,1.49], which is believed to operate on addition of species such as Na, Ba, Ca or rare earths to Al-Si. These atoms adsorb onto the steps on the Si growth interface, creating a "traffic problem" [1.48] that induces twinning [1.49] to provide new growth directions. Step poisoning is particularly likely when the adsorbed atoms are significantly larger than the atoms constituting the growth steps, or when they form chemical bonds at the steps [1.49]. While Cu atoms
seem too close in size to Si atoms (r_{Si} = 1.46 \, \text{Å}) to effectively retard step growth by the size effect alone, they may react to form silicides that would.

While Cu retards the nucleation of Si, once the Si precipitates are formed they catalyze the nucleation of $\theta'$. In the ternary alloy Si precipitates provide a distribution of heterogeneous nucleation sites that is much more dense than that available in the binary (at 225 °C the dominant heterogeneous nucleation sites in Al-Cu are dislocations, impurities, and strain fields from other $\theta'$ precipitates). The higher density of $\theta'$ precipitates in the ternary is responsible for their smaller size at the aging times studied here, which are long enough to essentially eliminate the supersaturation, but not long enough for significant Ostwald ripening.

Two mechanisms apparently contribute to the catalytic action of the Si precipitates. The first is strain compensation. The transformation strain of Si is strongly positive ($\varepsilon^0 = 0.0685$), while that of $\theta'$ (Al$_2$Cu) is negative ($\varepsilon^{0}_{11} = -0.0024$, $\varepsilon^{0}_{33} = -0.0452$). It follows that the strain energy of a $\theta'$ precipitate is significantly lowered if it nucleates in the vicinity of a pre-existing Si precipitate. The second mechanism is the apparent segregation of Cu to the Si-Al interface, as evidenced by the extensive twinning of the Si precipitates. It follows that the Cu supersaturation is greatest at the Si interface.
So long as the precipitates are coherent, their aspect ratio increases with their size. This tendency is followed whether the aspect ratio is controlled by thermodynamic equilibrium [1.19] or by kinetic considerations [1.20]. From the thermodynamic perspective, the strain energy of a coherent particle is minimized if the particle takes the form of an extended thin plate, while the interfacial energy is minimized if it is equiaxed. As the particle grows, the strain energy (which varies with volume) increases more rapidly than the surface energy (which varies with surface area) so the particle tends to spread out, increasing its aspect ratio. From the kinetic perspective, the fact that the particles have \{100\} habit planes suggests that they grow by the stepwise nucleation and propagation of ledges, as we observed. If ledge nucleation is difficult, the precipitates increase in size by extending existing ledges, providing an alternate mechanism to increase the aspect ratio.

Both thermodynamic and kinetic effects affect the aspect ratio of \(\theta'\) in binary Al2Cu (Fig. 1.10). The kinetic constraint explains the broad spread in aspect ratio at given precipitate thickness, \(d\), particularly at smaller values of \(d\) [1.20]. The trend toward thermodynamic equilibrium explains the overall variation of \(\kappa\) with precipitate size [1.19] (Figs. 1.10-1.12), and leads to a plausible estimate of the interfacial tension of the broad face of the \(\theta'\) plate. The calculated value of the interfacial tension, 85-96 mJ/m\(^2\) (depending on the elastic constants chosen for \(\theta'\)) is somewhat larger than earlier
estimates (= 30 mJ/m² [1.43]) but is of the same order, and is encouragingly close to the tensions of other low-energy internal surfaces in Al, including the twin boundary energy (100 mJ/m² [1.44]) and the antiphase boundary energy of δ' Al₃Li (70 mJ/m² [1.45]).

Thermoelastic effects also provide straightforward explanations for the more equiaxed shapes of the θ' precipitates in the ternary and their resistance to coarsening. The variation of κ with ν in the ternary is consistent with that in the binary if we assume that the compressive strain of the pre-existing Si precipitates compensates for about 40% of the tensile transformation strain of θ'. Since the transformation strain of Si is about 4 times that of θ' (Δν/ν = (1/3)Tr(εii) = 0.0685 (Si) = - 0.0166 (θ')), and the volume fraction of Si is about 40% of that of θ' when all of the Si and Cu have precipitated, this number does not seem unreasonable. The resistance to coarsening is a characteristic feature of coherent precipitates, since these tend to adopt mesoscopic configurations that minimize elastic energy and resist change [1.50,1.51]. Composite precipitates with compensating strains (the so-called "compact morphology" [1.40]) are particularly resistant to coarsening since the elastic energy opposes coarsening unless the two phases can evolve together.

The influence of Si on the coarsening resistance of Al₂Cu may be particularly important to the relative electromigration resistance of thin-film conducting lines in microelectronic devices [1.2]. Si additions increase the time-to-failure of Al₂Cu
conducting lines. Studies of the mechanism of electromigration failure in Al-Cu thin-film conducting lines show that it is a two step process in which a portion of the line is swept clean of Cu by current-induced diffusion before voiding occurs. If Si precipitates stabilize θ' (Al₂Cu) against diffusional coarsening, they should inhibit the out-diffusion of Cu and retard failure, as is observed.
1.5 Conclusions

The precipitation of $\theta'$ from ternary Al$_2$Cu$_1$Si aged at 225 °C is a two-step process. Si precipitates first and catalyzes $\theta'$. The precipitates in the ternary are smaller, are more densely distributed, have lower aspect ratios and coarsen more slowly than those in the binary Al$_2$Cu aged at the same temperature.

While the shapes of individual $\theta'$ precipitates in binary Al$_2$Cu are strongly affected by the kinetic problem of nucleating growth ledges, which produces a significant scatter in aspect ratio for samples of given thickness, the overall evolution of particle shape with size follows the predictions of the Khachaturyan-Hairapetyan thermoelastic theory, which reduces to $\kappa = L/d \propto \sqrt{L}$ at large sizes. From the KH theory we can extract an estimate of the interfacial tension of the broad Al-$\theta'$ interface. The result is 85-96 mJ/m$^2$, depending on the elastic constants assumed for $\theta'$. This number is near the values of other low-energy coherent interfaces in Al, such as the twin boundary energy (100 mJ/m$^2$) and the antiphase boundary energy in $\delta'$ Al$_3$Li (70 mJ/m$^2$).

The Si and $\theta'$ precipitates in Al$_2$Cu$_1$Si have a strong elastic interaction because of their compensating strain fields: the transformation strain of Si is positive while that of $\theta'$ is negative. This elastic interaction promotes the nucleation of $\theta'$ on Si, decreases
the expected aspect ratio of $\theta'$, and inhibits coarsening.

Si precipitation in ternary Al$_2$Cu$_1$Si differs from that in binary Al$_1$Si in that the Si precipitates are coarser, more equiaxed, and more extensively twinned. These changes appear to be effects of Cu, which increases the solubility of Si in Al, decreasing the driving force for precipitation, and adsorbs on the Si-Al interface after the precipitates have formed, promoting twinning by the "step poisoning" effect at the interface.
References, Chapter 1


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Figure 1.1a. Experimental (taken from Al-2Cu aged for 48 hours at 225 °C) and simulated selected area diffraction pattern (SAD) of θ' precipitates in Al, showing the three unique variants of the cube-cube orientation relationship (Al = filled circles, θ' = open circles).
Figure 1.1b. Experimental (taken from Al-1Si aged for 48 hours at 225 °C) and simulated selected area diffraction pattern (SAD) of Si precipitates in Al, showing the cube-cube orientation relationship and double diffraction (Si = open squares, Si double diffraction = crosses).
Figure 1.1c. Experimental (taken from Al-2Cu-1Si aged for 48 hours at 225 °C) and simulated selected area diffraction pattern (SAD) of Si and $\theta'$ precipitates in Al.
Figure 1.2. Transmission electron micrographs of Si precipitates in Al-1Si taken near the [001]_Al zone axis: (a) Dark-field image taken using 220$_{\text{Si}}$ reflection, after aging for 10 minutes at 225 °C; (b) Bright-field image taken in a two beam condition with 200$_{\text{Al}}$ reflection being strongly excited, after aging for 10 minutes; (c) Dark-field image taken using 220$_{\text{Si}}$ reflection, after aging for 6 hours; (d) Dark-field image taken using 220$_{\text{Si}}$ reflection, after aging for 48 hours.
Figure 1.2. Transmission electron micrographs of Si precipitates in Al-1Si taken near the [001]_Al zone axis: (a) Dark-field image taken using 220_{Si} reflection, after aging for 10 minutes at 225 °C; (b) Bright-field image taken in a two beam condition with 200_{Al} reflection being strongly excited, after aging for 10 minutes; (c) Dark-field image taken using 220_{Si} reflection, after aging for 6 hours; (d) Dark-field image taken using 220_{Si} reflection, after aging for 48 hours.
Figure 1.2. Transmission electron micrographs of Si precipitates in Al-1Si taken near the [001]_{Al} zone axis: (a) Dark-field image taken using 220_{Si} reflection, after aging for 10 minutes at 225 °C; (b) Bright-field image taken in a two beam condition with 200_{Al} reflection being strongly excited, after aging for 10 minutes; (c) Dark-field image taken using 220_{Si} reflection, after aging for 6 hours; (d) Dark-field image taken using 220_{Si} reflection, after aging for 48 hours.
Figure 1.2. Transmission electron micrographs of Si precipitates in Al-1Si taken near the [001]$_{\text{Al}}$ zone axis: (a) Dark-field image taken using 220$_{\text{Si}}$ reflection, after aging for 10 minutes at 225 °C; (b) Bright-field image taken in a two beam condition with 200$_{\text{Al}}$ reflection being strongly excited, after aging for 10 minutes; (c) Dark-field image taken using 220$_{\text{Si}}$ reflection, after aging for 6 hours; (d) Dark-field image taken using 220$_{\text{Si}}$ reflection, after aging for 48 hours.
Figure 1.3. Transmission electron micrographs of Si precipitates in Al-2Cu-1Si taken near the [001]_Al zone axis: (a) and (b) Conventional bright-field images after aging for 10 minutes at 225 °C; (c) Dark-field image taken using 220_{Si} reflection, after aging for 10 minutes; (d) Dark-field image taken using 220_{Si} reflection, after aging for 6 hours; (e) Dark-field image taken using 220_{Si} reflection, after aging for 24 hours.
Figure 1.3. Transmission electron micrographs of Si precipitates in Al-2Cu-1Si taken near the [001]$_{Al}$ zone axis: (a) and (b) Conventional bright-field images after aging for 10 minutes at 225 °C; (c) Dark-field image taken using 220$_{Si}$ reflection, after aging for 10 minutes; (d) Dark-field image taken using 220$_{Si}$ reflection, after aging for 6 hours; (e) Dark-field image taken using 220$_{Si}$ reflection, after aging for 24 hours.
Figure 1.3. Transmission electron micrographs of Si precipitates in Al-2Cu-1Si taken near the [001]_Al zone axis: (a) and (b) Conventional bright-field images after aging for 10 minutes at 225 °C; (c) Dark-field image taken using 220_{Si} reflection, after aging for 10 minutes; (d) Dark-field image taken using 220_{Si} reflection, after aging for 6 hours; (e) Dark-field image taken using 220_{Si} reflection, after aging for 24 hours.
Figure 1.3. Transmission electron micrographs of Si precipitates in Al-2Cu-1Si taken near the [001]$_{Al}$ zone axis: (a) and (b) Conventional bright-field images after aging for 10 minutes at 225 °C; (c) Dark-field image taken using 220$_{Si}$ reflection, after aging for 10 minutes; (d) Dark-field image taken using 220$_{Si}$ reflection, after aging for 6 hours; (e) Dark-field image taken using 220$_{Si}$ reflection, after aging for 24 hours.
Figure 1.3. Transmission electron micrographs of Si precipitates in Al-2Cu-1Si taken near the [001]_Al zone axis: (a) and (b) Conventional bright-field images after aging for 1C minutes at 225 °C; (c) Dark-field image taken using 220_{Si} reflection, after aging for 1C minutes; (d) Dark-field image taken using 220_{Si} reflection, after aging for 6 hours; (e) Dark-field image taken using 220_{Si} reflection, after aging for 24 hours.
Figure 1.4. TEM micrographs of $\theta'$ precipitates in Al-2Cu taken near [110]$_{\theta'}$ zone axis, after aging for 6 hours at 225 °C: (a) Conventional bright-field image; (b) Dark-field image using a $1\overline{1}2_{\theta'}$ reflection.
Figure 1.4. TEM micrographs of θ' precipitates in Al-2Cu taken near [110]_\psi zone axis, after aging for 6 hours at 225 °C: (a) Conventional bright-field image; (b) Dark-field image using a 1\overline{2}_\psi reflection.
Figure 1.5. Transmission electron micrographs of precipitates in Al-2Cu-1Si after aging for 6 hours at 225 °C: (a) Bright-field image taken near [110]_γ zone axis (10° from the [110]_Al zone axis, tilted along 220 Kikuchi lines); (b) Dark-field image taken using a 1T2_γ reflection; (c) Dark field image taken using a 111_Si reflection.
Figure 1.5. Transmission electron micrographs of precipitates in Al-2Cu-1Si after aging for 6 hours at 225 °C: (a) Bright-field image taken near [110]_α zone axis (10° from the [110]_Al zone axis, tilted along 220 Kikuchi lines); (b) Dark-field image taken using a 1\bar{1}2_α reflection; (c) Dark field image taken using a 1\bar{1}1_{si} reflection.
Figure 1.5. Transmission electron micrographs of precipitates in Al-2Cu-1Si after aging for 6 hours at 225 °C: (a) Bright-field image taken near [110]_α' zone axis (10° from the [110]_Al zone axis, tilted along 220 Kikuchi lines); (b) Dark-field image taken using a 1 2 2_α' reflection; (c) Dark field image taken using a 1 1 1_α_Si reflection.
Figure 1.6. TEM dark-field images of θ' precipitates, taken near [110]₀ zone axis, using a $\bar{1}12_0$ reflection: (a) Al-Cu after aging for 24 hours at 225 °C; (b) Al-Cu-Si after aging for 48 hours at 225 °C.
Figure 1.6. TEM dark-field images of θ' precipitates, taken near [110]₀ zone axis, using a $\bar{1}\bar{1}0$ reflection: (a) Al-Cu after aging for 24 hours at 225 °C; (b) Al-Cu-Si after aging for 48 hours at 225 °C.
Figure 1.7. TEM dark-field images of one of the variants of the edge-on $\theta'$ precipitates in Al-2Cu, taken near the [001]$_{\text{Al}}$ zone axis: (a) after aging at 6 hours at 225 °C, imaged using a $10\overline{1}\theta'$ reflection; (b) after aging at 48 hours at 225 °C, imaged using a $101\theta'$ reflection.
Figure 1.7. TEM dark-field images of one of the variants of the edge-on $\theta'$ precipitates in Al-2Cu, taken near the [001]$_{Al}$ zone axis: (a) after aging at 6 hours at 225 °C, imaged using a $\{10\bar{1}\}_{\theta'}$ reflection; (b) after aging at 48 hours at 225 °C, imaged using a $\{101\}_{\theta'}$ reflection.
Figure 1.8. TEM dark-field images of one of the variants of the edge-on θ' precipitates in Al-2Cu-1Si taken near the [001]_Al zone axis: (a) after aging at 6 hours at 225 °C, imaged using a 101_θ reflection; (b) after aging at 48 hours at 225 °C, imaged using a 101_θ reflection.
Figure 1.8. TEM dark-field images of one of the variants of the edge-on θ' precipitates in Al-2Cu-1Si taken near the [001]_A1 zone axis: (a) after aging at 6 hours at 225 °C, imaged using a 101₀ reflection; (b) after aging at 48 hours at 225 °C, imaged using a $\overline{1}01₀$ reflection.
Fig. 1.9. Mean θ' precipitate dimensions, as a function of aging time for Al2Cu and Al2Cu1Si: (a) precipitate thickness, d; (b) precipitate length, L; (c) aspect ratio, L/d.
Fig. 1.9. Mean $\theta'$ precipitate dimensions, as a function of aging time for Al$_2$Cu and Al$_2$Cu$_1$Si: (a) precipitate thickness, $d$; (b) precipitate length, $L$; (c) aspect ratio, $L/d$. 
Fig. 1.9. Mean θ’ precipitate dimensions, as a function of aging time for Al2Cu and Al2Cu1Si: (a) precipitate thickness, d; (b) precipitate length, L; (c) aspect ratio, L/d.
Figure 1.10. The aspect ratio $\kappa (=L/d)$ for the full sample of $\theta'$ precipitates in Al2Cu. The distribution of values from the three aging times are superimposed. Precipitates of the same thickness (d) are connected by straight lines, and are labeled with the value of d in multiples of unit thickness, $d_0 = 4.53 \text{ Å}$. 

$k = 58(L)^{0.52}$
Figure 1.11. A plot of the KH elastic function, \( f(\kappa) \) against \( r = \nu^{1/3} \) for \( \theta' \) in Al2Cu. We have separated precipitates with thickness \( d \leq 12 \) (about 65 Å) from those that have \( d > 12 \). The best-fit power-law relation for the thicker precipitates gives \( f(\kappa) \propto r^{0.96} \), in very good agreement with the KH model.
Figure 1.12. Repeat of Figure 1.11, showing the best straight-line fit to the precipitates with \( d > 12 \) (about 65 Å). The interfacial tension on the broad face of the \( \theta' \) precipitate can be inferred from the slope, as discussed in the text.
Figure 1.13. Plot of $\kappa (=L/d)$ vs. $L$ for $\theta'$ in Al2Cu and Al2Cu1Si, showing that the precipitates in the ternary tend to have lower aspect ratios at the same size.
Figure 1.14. Plot of KH elastic function, $f(\kappa)$, against $r = \sqrt[13]{\kappa}$ for $\theta'$ precipitates in Al2Cu1Si. The extent of elastic relaxation is inferred from the slope as discussed in the text.
Fig. 1.15. (a) Solubility of Cu in Al (at.%) versus temperature (°C), replotted from binary Al-Cu [1.46] and pseudo-binary Al-Cu-1wt.%Si phase diagrams [1.47]. (b) Solubility of Si in Al (in at.%) versus temperature (°C), replotted from the binary Al-Si [1.46] and pseudo-binary Al-Si-4wt.%Cu phase diagrams [1.47].
Fig. 1.15. (a) Solubility of Cu in Al (at.% versus temperature (°C), replotted from binary Al-Cu [1.46] and pseudo-binary Al-Cu-1wt.%Si phase diagrams [1.47]. (b) Solubility of Si in Al (in at.%) versus temperature (°C), replotted from the binary Al-Si [1.46] and pseudo-binary Al-Si-4wt.%Cu phase diagrams [1.47].
Chapter 2: Precipitation and Hardening in Al-Si-Ge

2.1 Introduction

The essential factor that controls the properties of precipitation hardened structural alloys is the type, size and distribution of the strengthening precipitates in the metal matrix. To meet a sufficient level of strength it is important to achieve an adequate volume fraction and number density of strengthening precipitates which are resistant to dislocation shearing. A recent series of papers detailing precipitation and mechanical properties of Al-Si-Ge alloys [2.1-2.6] demonstrated that the precipitate dispersion in Al-Si-Ge is almost an order of magnitude finer than that in binary Al-Si and Al-Ge alloys. It was proposed that by obtaining a dense distribution of such fine precipitates sufficient dispersion hardening was achieved to make these alloys candidates for medium strength structural applications. The authors reported that in the ternary alloy, the precipitates were not only finer but also much more equiaxed than in the binary Al-Si or Al-Ge. It was assumed that the composition of these precipitates was 50 at.% Si and 50 at.% Ge. However, there was no detailed investigation of the reason for the spherical morphology, nor was the composition accurately determined.

In our group there has been an ongoing effort to investigate the crystallographic aspects of precipitation of Ge in Al [2.7-2.9]. One of the most important conclusions to have come out of this work is that twinning determines the precipitate morphology. The author is also in the process of researching the effect of ternary additions on the precipitation of Si in Al [2.10]. It was demonstrated that by adding Cu to Al-Si, the Si precipitates became equiaxed and multiply twinned early in the precipitation process. This was attributed to the Cu atoms segregating to the ledges of the growing Si particles, resulting in the well known “ledge-poisoning” mechanism [2.11-2.12].
The aim of this work is to characterize the Al-Si-Ge microstructure in detail. Additionally, the author seeks to determine the extent to which Si-Ge precipitates can be used as a strengthening phase for aluminum.

2.2 Experimental Procedure

Bulk alloy of composition Al-1 at.%Si-1 at.%Ge, was made by arc melting, 99.999 (wt.%) Si, 99.9999 (wt.%) Ge, and 99.99 (wt.%) Al. The samples then were cold swaged to achieve 10 to 15% plastic deformation. They were then encapsulated in a sealed quartz glass tube that was back-filled with argon and annealed for 24 hours at 500 °C and quenched into ice water. The final shape of the bulk alloy was roughly cylindrical, approximately 20 mm in length and 10 mm in diameter. The cylindrical ingots were sliced into discs 0.5 mm in thickness, cut normal to the cylinder axis.

TEM samples were electrochemically polished in 75% methanol–25% HNO₃ solution at a temperature of -25 °C with a polishing voltage of around 20 V.

Conventional TEM was performed using a JEOL 200 CX at 200 kV. Energy dispersive X-ray spectroscopy (EDXS) was done using a JEOL 200CX and Philips CM200-FEG Analytical Transmission Electron Microscopes, equipped with light element detectors and operated at 200 kV. High Resolution TEM was performed on a Philips CM300-FEG operated at 300kV.

Al-Si-Ge samples were aged for varying times at 160 °C. This aging temperature corresponds to the temperature at which peak hardness was previously reported [2.1]. After aging the Al-Si-Ge samples were indented using the Superficial Hardness 15-T (1/16th inch steel ball and a 15 kg load).

Stereological analysis consisted of precipitate diameter measurements, and foil thickness measurements done to calculate the number of precipitates per unit volume. For each precipitate, the diameter was taken as the average of the maximum and the minimum
projected dimensions. Several regions of the microstructure were analyzed, with a total of approximately 100 precipitates being counted per heat treatment condition. All measurements were performed near the [110] zone axis of aluminum. However, tilting to the [001] zone axis showed that the precipitates project a similar size and aspect ratio in either orientation.

To obtain the number of precipitates per unit volume, the foil was tilted into an exact two-beam condition, near the [110] zone axis of aluminum. In all cases one of the \{111\} aluminum reflections was excited. The exact Bragg condition was achieved with the use of Kikuchi lines. With a deviation parameter of zero and the extinction distance known (\(\xi_{111} = 705 \text{ Å}\)) the foil thickness was calculated from the well known relationship described by Hirsch et al. [2.13]. For bright field micrographs, the white fringes correspond to \((t/\xi_{111}) = 0, 1, 2, \text{ etc.}\), and the dark fringes correspond to \((t/\xi_{111}) = 1/2, 3/2, 5/2, \text{ etc.}\), where \(t\) is the foil thickness and \(\xi_g\) is the true extinction distance. The reverse is true for dark field micrographs. Complementary bright and dark field micrographs were taken of every region to ensure exact Bragg conditions were obeyed there. Figures 2.1a and 2.1b show representative bright field and dark field images of thickness contours in a sample aged for 9 hours. At least three such bright field - dark field pairs were analyzed per aging condition. A volume was then calculated as the length of the thickness contour, times its width, times its thickness (approximated by \(t\)). To obtain the number of precipitates per unit volume, all the precipitates contained in that contour were counted.

Diffraction pattern simulation was done with the commercial software, "Desktop Microscopist", in the [001] zone axis of Al, using the well-known space groups of Al and Si, and the lattice parameters 4.0497 Å (Al) and 5.4309 Å (Si) [2.14].
2.3 Results and Discussion

2.3.1 Microstructural Evolution

Figures 2.2a-e show bright field images of Al-Si-Ge near the [110]_Al zone axis. The samples were aged for 30 minutes, 2 hours, 9 hours, 48 hours and 180 hours, respectively. Precipitates were not detected after aging for 30 minutes; instead the microstructure consisted of dislocation loops and extended dislocations threading all the way through the foil. After 2 hours, the microstructure consisted of a sparse distribution of fine Si-Ge precipitates with matrix strain contrast around them [2.13]. After 9 hours, the precipitates were still small in size, however there were many more of them detectable in the foil. While samples aged for 48 and 180 hours showed a progressively coarser microstructure, the precipitate morphology was relatively constant throughout the aging sequence. At all aging times, the matrix around many of the particles exhibited substantial strain contrast. This was especially true for particles that were plate-like.

2.3.2 Initial Stage of Precipitation

Figure 2.3 shows a selected area diffraction pattern of Al-Si-Ge after aging at 160 °C for 2 hours and an insert simulated diffraction pattern simulation for Al and Si in the cube-cube orientation relationship. Double diffraction due to the fine size of the particles is also included in the simulation.

Figures 2.4a and 2.4b show a bright field and a dark field image of the precipitates after 2 hours. The images were recorded near the [110]_Al zone axis. The bright field image was taken in a two beam condition using a (\overline{1}11)_Al reflection, while the dark field image was obtained using a (\overline{1}11)_Si reflection. Whereas every precipitate
visible in a bright field image shows up in dark field as well, it is often not the entire precipitate but a specific crystallographic section of it that appears bright. From Figures 2.3 and 2.4 it can be concluded that early in the aging process the Si-Ge precipitates adopt a cube-cube orientation relationship. In the next section, high resolution images will demonstrate that the reason only sections, rather than the entire precipitates, are imaged in dark field is because the precipitates are multiply twinned.

2.3.3 High Resolution Microscopy

Figures 2.5a and 2.5b show high resolution micrographs of Si-Ge precipitates, taken near the [110]Al zone axis. Figure 2.5a shows a multiply twinned Si-Ge precipitate for a sample that was aged for 2 hours at 190 °C. Because the precipitate did not span the entire thickness of the foil, the resultant image consists of a moiré pattern, due to overlapping with Al-matrix, rather than a lattice image of Si-Ge precipitate. Figure 2.5b shows a section of a multiply twinned Si-Ge precipitate after aging for 180 hours at 160 °C. In this case a fraction of the particle intersected the foil on both sides so a lattice image is visible. For both of these aging conditions all the precipitates that were examined were twinned. The spherical morphology of many precipitates can now be understood in terms of the twinning action eliminating the high symmetry cube-cube interface between the precipitates and the matrix. To reduce surface energy, the interface becomes rounded.

Figure 2.6 shows a plot of the measured composition of precipitates as a function of their diameter, for samples aged for 48 hours at 160 °C. Only the Si content is shown, the balance being Ge. No other elements were detected in the alloy. A total of 30 precipitates was analyzed. A statistical analysis from the 30 particles gave a mean of Si-44.5at.%Ge and a standard deviation of 7.6at.%. Several large (on the scale of μm) Si inclusions were also detected in the microstructure. The composition of one of these
inclusions was identified to be Si-16.1 at.% Ge. This inclusion was surrounded by coarse crystallographic precipitates that were slightly Si rich (see the large particles in Figure 2.6).

2.3.4 Hardness

Figure 2.7 shows a plot of Superficial Hardness 15-T versus aging time. The error bars in Figure 2.7 represent the standard error associated with the mean. Maximum hardness is obtained after 21 hours (Superficial Hardness = 55), with the 9 hour samples being only slightly softer (Superficial Hardness = 54). All the measured hardness values were too low to make this alloy useful in medium strength structural applications. 15-T Superficial Hardness of 59 corresponds to a 500 kgf Brinell Hardness of 40, and is too low for the H_{RB} scale. The shape of the hardness versus aging curve agrees well with the results reported by other workers [2.1]. (Note, however, the typographical error [2.15] in Hornbogen et al. [2.1], where 15-T hardness values are reported as H_{RB}).

The contribution of unshearable particles to the yield strength of an alloy, \( \Delta \sigma \), may be approximated by the well-known Orowan relation [2.16, 2.17]:

\[
\Delta \sigma = \alpha G b / L.
\]

Where \( G \) is the shear modulus of the matrix, \( b \) is the Burgers vector, \( L \) is the spacing of the particle centers and \( K \) is a constant. For a given volume fraction of precipitates, \( L \) is proportional to the precipitate diameter. Table 2.1 gives the measured Si-Ge particle size and the number of particles per unit volume. Also shown are the calculated and the equilibrium volume fraction of Si-Ge particles. The calculated volume fraction was obtained from the particle diameter and the number of particles per unit volume values, assuming spherical particles. The equilibrium volume fraction was calculated by assuming that at 160 °C negligible Si and Ge remain in solid solution. It can be seen from the table that early in the precipitation process, when the strengthening particles are fine, most of
the Si and/or Ge is still in solid solution. Since the interparticle spacing scales as the inverse of the cube root of the number of particles per unit volume, even though the particles are fine their overall contribution to the strength of the alloy is low. At longer aging times, when both the Si and the Ge have fully precipitated, the particles are too coarse to cause appreciable hardening.

Table 2.1. Stereological parameters of the Al-Si-Ge microstructure.

<table>
<thead>
<tr>
<th>time (hrs.)</th>
<th>mean diameter (nm)</th>
<th>standard error</th>
<th>number/unit vol.</th>
<th>standard error</th>
<th>calculated volume fraction</th>
<th>equilibrium vol. fraction</th>
</tr>
</thead>
<tbody>
<tr>
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<td>260</td>
<td>37</td>
<td>0.00034</td>
<td>0.025</td>
</tr>
<tr>
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<td>0.48</td>
<td>1041</td>
<td>137</td>
<td>0.0035</td>
<td>0.025</td>
</tr>
<tr>
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<td>0.22</td>
<td>2069</td>
<td>497</td>
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<td>0.025</td>
</tr>
<tr>
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<td>1.11</td>
<td>853</td>
<td>27</td>
<td>0.023</td>
<td>0.025</td>
</tr>
</tbody>
</table>

2.4 Conclusions

Conventional microscopy demonstrated that Si-Ge precipitates nucleate with a cube-cube orientation relationship with the matrix. EDXS analysis indicates that there is a variation in the stoichiometry of the precipitates, with the mean composition being Si-44.5at.%Ge.

High resolution TEM showed that the Si-Ge precipitates are all multiply twinned. Since upon twinning the cube-cube orientation relationship between the matrix and the precipitate is lost, the twinned sections assume a rounded interface with the matrix.

In Al-1at.%Si-1at.%Ge the obtained hardness was too low to make this ternary alloy useful for structural applications. This result agrees well with theory. It was shown
that when the precipitates are fine, much of the Si and Ge is still in solid solution resulting in a larger precipitate spacing than predicted from the equilibrium volume fraction.
References, Chapter 2


2.10. D. Mitlin, V. Radmilovic, and J. W. Morris, Jr., Submitted to Mat. Trans. A.


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Figure 2.1(a,b). Representative bright field (a), and dark field (b) micrographs of thickness contours in Al-1Si-1Ge aged for 9 hours.
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Chapter 3: Precipitation and Aging in Al-Cu-Si-Ge

3.1 Introduction

In commercial, Al-Cu based alloys the elements Si, Mn, Be, Ge, Sn, Ag and Cd have all been used to modify the dominant precipitation reaction [3.1-3.11]. One mechanism by which the precipitation reaction is altered is the preferential precipitation of alloy modifiers, producing heterogeneous sites that nucleate Al-Cu or Al-Cu-Mg precipitates [3.3-3.5]. It has been found [3.5-3.6] that trace additions of Sn, Cd or In promote a dense and homogeneous distribution of fine $\theta'$ precipitates (a metastable form of the equilibrium $\theta$ phase, Al$_2$Cu). In the case of Sn, TEM studies showed that the Sn precipitates first, providing heterogeneous sites for nucleation of $\theta'$. We have recently shown that Si behaves in a similar way [3.11]. Inclusions such as Al$_2$O$_3$ [3.12] or SiC particles [3.13] also change the precipitation kinetics, since they, or the misfit dislocations they introduce into the matrix, also serve as heterogeneous nucleation sites.

Recent studies of Al-Si-Ge alloys [3.14-3.19] have shown that the precipitates formed in Al-Si-Ge can be almost an order of magnitude smaller than those commonly found in binary Al-Si or Al-Ge. This is attributed to the fact that Si and Ge atoms have compensating volumetric strains in Al solid solution; Ge is larger than Al, while Si is smaller. The strain compensation promotes a dense distribution of Si-Ge solute clusters that transform to diamond cubic Si-Ge precipitates upon elevated temperature aging. The precipitates found in the ternary alloy are not only finer, but also more equiaxed than those in binary Al-Si or Al-Ge alloys.
Unfortunately, the Si-Ge precipitates do not form a sufficiently dense distribution to accomplish dramatic hardening [3.15]. The reason appears to be the high interfacial tension of the Si-Ge precipitates, which has the consequence that the solubility of Si and Ge in equilibrium with the precipitates remains relatively high, and the volume fraction of precipitates correspondingly low, until they have coarsened [3.20].

While Si-Ge precipitates may not harden effectively in their own right, their dense distribution, compared to that of Si, Ge or Sn, and their large lattice mismatch once they have transformed into the diamond structure [3.11] suggests that they would offer an excellent template of heterogeneous sites for the nucleation of θ' in a quaternary Al-Si-Ge-Cu alloy. The present work was done to explore that possibility. The results show that Al-Si-Ge-Cu alloys combine rapid precipitation hardening with high peak hardness and exceptional thermal stability.

3.2 Experimental Procedure

Bulk alloys of Al-0.5at.%Si-0.5at.%Ge, Al-1at.%Si-1at.%Ge-2at.%Cu and Al-0.5at.%Si-0.5at.%Ge-2.5at.%Cu, were made by arc melting, 99.999 (wt.%) Si, 99.9999 (wt.%) Ge, 99.999 (wt.%) Cu and 99.99 (wt.%) Al. The cast samples were cold swaged to achieve 10 to 15% plastic deformation. They were then encapsulated in a sealed quartz glass tube that was back-filled with argon and annealed for 24 hours at 500 °C. From that temperature they were quenched into an ice water bath. The final shape of the bulk alloy was roughly cylindrical, approximately 20 mm in length and 10 mm in diameter. The cylindrical ingots were sliced into discs 0.5 cm in thickness cut normal to the cylinder axis. The samples were aged at 190 °C. The temperature was monitored with an external thermocouple, and varied no more than 1 °C. Hardness tests were done with a Rockwell hardness tester using the “B” scale (1/16th inch steel ball, 100
kg load). Rockwell “B” values were converted to Brinell hardness using the appropriate ASTM standard [3.21].

Analysis by vacuum emission spectroscopy on Al-0.5at.%Si-0.5at.%Ge-2.5at.%Cu and Al-0.5at.%Si-0.5at.%Ge (at FTI Anamet Laboratories) produced a composition of Al-0.48at.%Si-0.49at.%Ge-2.48at.%Cu and Al-0.55at.%Si-0.5at.%Ge with no other elements present in quantities greater than 0.005%.

TEM samples were made from 200 µm thick slices cut from the tested specimens. The cuts were made with a diamond saw using a low cutting speed and ample cooling fluid to minimize sample heating. The slices were ground down to a thickness between 125 to 150 µm using a 2400 grit silicon carbide polishing paper. They were then electrochemically polished in a Struers Tenupol-3 jet polisher at a temperature of −25 °C with a polishing voltage of 12.5 V. The polishing solution was 75% methanol – 25% HNO₃ by volume.

Conventional transmission electron microscopy (TEM) was performed using a JEOL 200 CX at 200 kV. High Resolution TEM was performed on a Philips CM300-FEG operated at 300kV.

3.3 Experimental Results and Discussion

Figure 3.1 shows the hardening curves for the two alloys, Al-2Cu-1Si-1Ge and Al-2.5Cu-0.5Si-0.5Ge. The hardening curves show the rapid hardening, high peak strength and thermal stability of the Al-Si-Ge-Cu alloys. Note that the alloy with the higher Cu content exhibits higher peak hardness than the alloy with the higher (Si,Ge) content. This is expected because the hardening of these alloys is due almost entirely to the precipitation of $\theta'$ ($\text{Al}_2\text{Cu}$).
Hardening curves for alloy 2219 (Al-2.8at.%Cu-0.15Mn-0.05Zr-0.055V-0.035Ti) [3.22] and for alloy 2014 (Al-1.94at.%Cu-0.8Si-0.4Mn-0.6Mg) [3.23] are included in the plot for comparison. Alloys 2219 and 2014 are used for comparison since they represent two Al-Cu based alloys known to exhibit high strength in their T-6 (solutionized, quenched and artificially aged) condition.

At 190 °C alloy 2014, which is not known to display high temperature stability, quickly deteriorates. It should be noted that by aging 2014 at 160 °C for 13 hours it is possible to obtain a Brinell Hardness of 122. However, the alloy overages relatively quickly.

The alloy that is known for its high temperature stability is 2219 [3.22]. The microstructure of 2219 consists of various dispersoids used to control grain size and θ' precipitates. Compared to 2219, both Al-Cu-Si-Ge alloys possess higher peak hardness. Also, they reach maximum hardness after only 3 hours, instead of the 8 hours required for 2219 to obtain optimum hardness. On prolonged aging, Al-Cu-Si-Ge alloys overage at a rate similar to 2219, and after approximately 400 hours at elevated temperature the hardness of all three alloys decreases asymptotically to approximately 86 HB.

Figure 3.2 shows the microstructure of Al-2Cu-1Si-1Ge, after aging for 3 hours at 190 °C. Figure 3.2a is a bright field image of the microstructure near the [110]_Al zone axis. Visible are both plates, identified in dark field (Figure 3.2b.) as edge-on θ' and spherical Si-Ge particles. From Figures 3.2a and 3.2b it can be observed that both phases are densely distributed, and are relatively fine and uniform in size. Figure 3.2c shows a dark field image of the θ' precipitates oriented approximately 35° to the foil normal. They are imaged in the [110]_θ' zone axis which is oriented 10° away from the [110]_Al zone axis tilted along the 200 Kikuchi lines. The θ' precipitates are growing around the Si-Ge
particles, giving the appearance in dark field of the θ' containing holes. The most
dramatic examples of this are arrowed in the figure.

The juxtaposition of θ' and Si-Ge is illustrated in Fig. 3.3, which is a high
resolution image of two edge-on θ' precipitates (or a single one that was thinned from
both sides) in contact with a multiply twinned Si-Ge particle. The sample was aged for 1
hour, and the image was taken in the [001]_Al zone axis.

The twin segments B and D of Si-Ge particle in Fig. 3.3 have the Baker-Nutting
orientation relationship with aluminum matrix: (100)_{Al} // (100)_{Si-Ge} and [001]_{Al} // [011]_{Si-Ge}.
The heavy twinning of the Si-Ge precipitates may be due to the adsorption of different
solute atoms at the diamond cubic/Al interface and their influence on the pattern of
growth. Other adsorbed impurities, such as Na, Ba, Ca or rare earth elements have
previously been observed to promote twinning in Al-Si [3.24,3.25]. But whatever the
specific mechanism that causes the fine-scale multiple twinning, it seems clear that it is
largely responsible for the small-diameter, equiaxed shapes of the Si-Ge particles.

In Fig. 3.4, a two beam image of Al-0.5at.%Si-0.5at.%Ge aged for 3 hours
reveals that there is significant strain contrast in the matrix [3.26] around many of the Si-
Ge particles. The particles showing the most pronounced matrix strain are arrowed. The
strain is expected since the volume mismatch associated with the transformation of two Al
unit cells into one Si or one Ge unit cell, ΔV/V_o, is 20.6% and 36.4% respectively (a_{Si} =
5.43 Å, a_{Ge} = 5.66 Å, a_{Al} = 4.05 Å [3.27]). This results in a compressive transformation
strain in the matrix of 6.85%, and 12.1%. On the other hand, the nucleation of θ' results
in a tensile coherency strain along its broad plate faces [3.28]. Thus, upon heterogeneous
nucleation strain compensation should result, lowering the overall energy.
3.4 Conclusions

Al-Cu-Si-Ge alloys display a uniquely fast aging response, a high peak hardness and a good stability during prolonged aging. The high hardness of the Cu containing alloy is due to the dense and uniform distribution of fine θ' precipitates (metastable Al₃Cu) which are heterogeneously nucleated on the Si-Ge particles. High resolution TEM demonstrated that in both alloys all the Si-Ge precipitates are multiply twinned throughout the aging treatment. Since the twinned section of the precipitate does not maintain a low index interface with the matrix, the Si-Ge precipitates are equiaxed in morphology.
References, Chapter 3


Figure 3.1. Precipitation hardening in Al-Cu based alloys isothermally aged near 190 °C.
Figure 3.2. Al-2Cu-1at.%Si-1at.%Ge alloy aged for 3 hours at 190 °C; Bright field image near [110]$_{Al}$ zone axis (a); Dark field images of θ' precipitates obtained using -11-2$_{θ'}$ (b) and 1-12$_{θ'}$ (c); Si-Ge nucleation sites for θ' are indicated by arrows.
Figure 3.2. Al-2Cu-1at.%Si-1at.%Ge alloy aged for 3 hours at 190 °C; Bright field image near [110]_Al zone axis (a); Dark field images of θ' precipitates obtained using -11-2_g. (b) and 1-12_g. (c); Si-Ge nucleation sites for θ' are indicated by arrows.
Figure 3.3. HREM image of two θ'-precipitates connected to a Si-Ge particle in Al-2Cu-1Si-1Ge alloy; Note that twin segments of Si-Ge, B and D, have a Baker-Nutting orientation relationship to Al matrix: $(100)_\text{Al} // (110)_{\text{Si-Ge}}$ & $[001]_\text{Al} // [001]_{\text{Si-Ge}}$. 
Figure 3.4. Al-0.5 at.% Si-0.5 at.% Ge microstructure aged for 3 hours. Image taken in [110]$_{\text{Al}}$ zone axis using a $1\bar{1}1_{\text{Al}}$ reflection.
Chapter 4: On the Influence of Si-Ge Additions on the Aging Response of Al-Cu

4.1 Introduction

In the previous chapter it was demonstrated that by adding Cu to the ternary Al-Si-Ge a dramatic hardening result can be achieved. Alloys of composition Al-5.7wt.%Cu-0.5wt.%Si-1.3wt.%Ge (which is Al-2.5at.%Cu-0.5at.%Si-0.5at.%Ge) and Al-5.4wt.%Cu-1wt.%Si-2.63wt.%Ge (which is Al-2at.%Cu-1at.%Si-1at.%Ge) were aged at 190 °C. The hardening response of the Al-Cu-Si-Ge alloys was compared to two commercial Al-Cu based alloys (2219 and 2014) and was shown to be superior in terms of achieving a substantially higher peak hardness at a shorter aging time while displaying equal if not better microstructural stability after prolonged aging. It was shown that at peak hardness the microstructure consisted of a dense distribution of θ' precipitates heterogeneously nucleated on Si-Ge precipitates. However, a detailed examination of the microstructure during the entire aging regime was not done. The present study seeks to further explain the unique hardening response of the ternary Al-Cu-Si-Ge alloy by examining its microstructure in the post quench, room temperature aged condition, during initial stages of precipitation, at peak hardness, and in the
overaged condition. To further understand the role of Si-Ge additions binary Al-5.5wt.%Cu, (which is Al-2.4at.%Cu) is examined for comparison.

4.2 Experimental Procedure

Bulk alloys of composition Al-5.7wt.%Cu-0.5wt.%Si-1.3wt.%Ge, (Al-2.5at.%Cu-0.5at.%Si-0.5at.%Ge) and Al-5.5wt.%Cu, (Al-2.4at.%Cu) were made by arc melting, 99.999 (wt.%) Si, 99.9999 (wt.%) Ge, 99.999 (wt.%) Cu and 99.99 (wt.%) Al.

The cast samples were cold swaged to achieve 10 to 15% plastic deformation in order to break up the dendritic as-cast microstructure and promote homogenization during the high temperature anneal. They were then encapsulated in a sealed quartz glass tube that was back-filled with argon and annealed for 24 hours at 500 °C. From that temperature they were quenched into an ice water bath. The final shape of the bulk alloy was roughly cylindrical, approximately 20 mm in length and 10 mm in diameter. The cylindrical ingots were sliced into discs 0.5 cm in thickness cut normal to the cylinder axis. The samples were aged at 190 °C. The temperature was monitored with an external thermocouple, and varied no more than 1 °C. Hardness tests were done with a Rockwell hardness tester using the “B” scale (1/16th inch steel ball, 100 kg load).
Rockwell "B" values were converted to Brinell hardness using the appropriate ASTM standard [4.1].

Analysis by vacuum emission spectroscopy on Al-Cu-Si-Ge and Al-Cu (at FTI Anamet Laboratories) produced compositions of Al-5.62wt.%Cu-0.48wt.%Si-1.26wt.%Ge and Al-5.31wt.%Cu, with no other elements present in quantities greater than 0.01%.

TEM samples were made from 200 μm thick slices cut from the tested specimens. The cuts were made with a diamond saw using a low cutting speed and ample cooling fluid to minimize sample heating. The slices were ground down to a thickness between 125 to 150 μm using a 2400 grit silicon carbide polishing paper. They were then electrochemically polished in a Struers Tenupol-3 jet polisher at a temperature of −25 °C with a polishing voltage of 12.5 V. The polishing solution was 75% methanol – 25% HNO₃ by volume.

Conventional TEM was performed using a JEOL 200 CX at 200 kV. Energy dispersive X-ray spectroscopy (EDX) was done using a JEOL 200CX and Philips CM200-FEG Analytical Transmission Electron Microscopes, equipped with light element detectors and operated at 200 kV. High Resolution TEM was performed on a Philips CM300-FEG operated at 300kV.
Diffraction pattern simulation was done with the commercial software, "Desktop Microscopist", in the [001] zone axis of Al, using the well-known space groups of Al and Si, and the lattice parameters 4.0497 Å (Al) and 5.4309 Å (Si) \([4.2]\). \(\theta^\prime\) (metastable Al\(_2\)Cu) has space group I4/mmm (tetragonal), with two Cu atoms per unit cell in the 2a special positions and four Al atoms in the 4d special positions. Its lattice parameters are \(a = 4.04\ \text{Å}\) and \(c = 5.8\ \text{Å}\) \([4.3]\). \(\theta^\prime\) (metastable Al\(_3\)Cu) has a space group P4/mbm, with 2 Cu atoms in the 2a special positions, four Al atoms in 4f special positions and 2 Al atoms in 2b special positions. Its lattice parameters are \(a = 4.04\ \text{Å}\) and \(c = 7.68\ \text{Å}\) \([4.3,4.4]\). Both \(\theta^\prime\) and \(\theta^\prime\) precipitates grow as plates on the \(\{100\}\) planes of Al \([4.3]\), with three distinct variants \([4.3-4.4]\): \([100]_{\theta^\prime}\ \text{or} \ [001]_{\theta^\prime}\ \parallel [100]_{\text{Al}}\) and \([010]_{\theta^\prime}\ \text{or} \ [001]_{\theta^\prime}\ \parallel [010]_{\text{Al}}\); \([100]_{\theta^\prime}\ \text{or} \ [001]_{\theta^\prime}\ \parallel [100]_{\text{Al}}\) and \([010]_{\theta^\prime}\ \text{or} \ [001]_{\theta^\prime}\ \parallel [010]_{\text{Al}}\).

In Al-Cu-Si-Ge, the Si-Ge precipitates have various morphologies and orientation relationships (ORs). Many are multiply twinned, spheroidized particles having no obvious orientation relationship with the matrix. Some are plates having a cube-cube OR with the matrix. However, the majority of the Si-Ge precipitates are rods lying along \(<001>_{\text{Al}}\) planes that adopt an orientation relationship \([001]_{\text{Al}}\parallel[-112]_{\text{Si-Ge}}\), \([100]_{\text{Al}}\parallel[-11-1]_{\text{Si-Ge}}\), and \([010]_{\text{Al}}\parallel[-1-10]_{\text{Si-Ge}}\). This OR had been previously reported by
several authors [4.5-4.7] for the case of pure Ge and pure Si precipitates in Al. This OR is incorporated into the simulation along with double diffraction (which was extensive).

Figures 4.1a and 4.1b show the simulated diffraction patterns of $\theta''$ in Al. without and with double diffraction. Figures 4.1c and 4.1d show this for $\theta'$ in Al. while Figures 4.1e and 4.1f display the simulated diffraction patterns for Si-Ge precipitates in Al.

4.3 Results

4.3.1 Hardening Response of Al-Cu-Si-Ge and of Al-Cu.

The T-4 hardness (solutionized, quenched and room temperature aged to a stable condition) of both alloys was found to be very similar. Al-Cu-Si-Ge displayed a very fast room temperature hardening response. After the sample was stored for 8 hours after the quench the hardness was 54 HRB. After 8 months aging there was no increase in the hardness of the samples (the samples were tested after 8 hours, 1 day, 12 days, 3 months and 8 months) with a final hardness also of 54 HRB. The binary Al-Cu samples were tested only after 8 months of storage at room temperature, resulting in a HRB of 57.

Figure 4.2 shows the artificial aging response of both alloys. Both samples were aged at 191 °C. Two hardening curves are displayed for AlCuSiGe. One curve is for the
alloy after it was stored at room temperature for 8 hrs. prior to aging at 191 °C. The same aging treatment was applied to the remaining ingot after it was kept at room temperature for twelve more days. The results show that prolonged room temperature aging does promote a slightly better hardening response. Initially, the binary alloy displays a higher hardness. However, the Si-Ge containing alloy quickly catches up (1 hour) and surpasses the binary. The quaternary alloy displays a peak hardness of 117 HRB after 3 hours aging, whereas the binary alloy peaks at 104 HRB after 14 hours of aging. Interestingly, the two alloys overage nearly at the same rate, and reach an identical hardness of 87 HRB after 144 hours of aging.

4.3.2 Precipitation in Al-Cu

Figure 4.3 shows representative symmetric [001]_A1 zone axis selected area diffraction patterns for Al-Cu samples. Figure 4.3a shows a diffraction pattern after the alloy was aged at room temperature. The diffraction pattern exhibits streaking along the <100>_{A1} directions along with 110_{α''} spots from the face-on α'' precipitates. The streaking is most likely a result of both α'' that are edge on and of GP zones that are well known to exist in Al-Cu at room temperature. After 30 minutes (Fig. 4.3b) and 3 hours (Fig 4.3c.) the microstructure consist of predominantly α''. While some α' may
also be present at those aging times, they are not present in sufficient volume fraction to have their reflections appear in the diffraction pattern. After 14 hours (peak hardness) the microstructure consists of mostly θ'' (Fig. 4.3d). However, very weak and elongated \{110\} spots from the two variants of the edge on θ' can be discerned in the pattern. This result agrees with Silcock et al. [4.3], who reported that the peak aged microstructure of binary Al-4.5wt.%Cu consists of a mix of θ'' and θ' precipitates. In the overaged condition (144 hours) the microstructure consists of θ' precipitates (Fig 4.3e), again agreeing with previous results [4.3].

Figures 4.4a and 4.4b show the AlCu microstructure after aging for 14 hours (peak hardness) and 144 hours. Both images were taken near the [001]Al zone axis. Figure 4.4a shows a dense distribution of θ'' precipitates imaged using the edge-on 002_{θ''} reflection. Figure 4.4b shows a coarse distribution of edge-on θ' precipitates imaged using an -101_{θ} reflection.

4.3.2 Precipitation in Al-Cu-Si-Ge

The quaternary alloy displays a similar room temperature microstructure. Figure 4.5a shows a symmetric [001]_{Al} zone axis pattern after the sample was aged for 8
months at room temperature. Again, streaks and $110_\theta^*$ spots are observed. In general, the intensity of the streaks and spots was less than in the binary alloy. After 30 minutes at $190$ °C (Fig. 4.5b), the microstructure still consists of streaks and $110_\theta^*$ spots. After 1 hour aging (Fig. 4.5c), besides the $\theta''$ spots and streaks, Si-Ge reflections are present. These spots were simulated in Figure 4.1. Additionally, very faint $\theta'$ reflections were detected in SAD's exposed for prolonged time (not shown), indicating the early onset of $\theta'$ precipitation in the quaternary. After 3 hours (peak hardness) the microstructure consists of $\theta'$ and Si-Ge precipitates (Fig. 4.5d). This microstructure persists in the overaged condition as well (144 hours) (Fig. 4.5e). However, after prolonged aging, the twinning of the Si-Ge particles is so extensive that spotty $\{111\}_{\text{Si-Ge}}$ and $\{220\}_{\text{Si-Ge}}$ ring patterns appear in the microstructure.

Figure 4.6 shows a high resolution image of the microstructure in the quenched and then room temperature aged condition. As expected, the microstructure contains $\theta''$ and GP zones. In binary Al-Cu, the $\theta''$ precipitates are three layers of aluminum between two layers of Cu, while the GP zones are monolayers of Cu. No attempt was made to deduce the chemical composition of these precipitates or the zones in the quaternary alloy. It may be quite plausible that Si and/or Ge atoms are also incorporated into the structure.
Figure 4.7 shows a dark-field image of the AlCuSiGe microstructure after the sample was aged for 30 minutes at 190 °C. The particles appearing bright are Si-Ge rods, imaged using a 1\( \text{11}_{\text{Si-Ge}} \) reflection. These rods were identified to run along the \(<100>_{\text{Al}}\). Other morphologies and orientation relationships were present as well, including heavily twinned, spheroidized particles. However, the rod morphology was the one most frequently observed by a wide margin. Also, many of the seemingly spherical precipitates may actually be the end-on variant of the observed rods.

Figure 4.8 shows a two beam image of the AlCuSiGe microstructure after the sample was aged for 30 minutes. There is significant strain present in the matrix. This is most likely the result of both the strain due to the undissolved GP zones and \(0''\) as well as due to the Si-Ge rods.

Figure 4.9 shows EDXS maps of the microstructure after 30 minutes. It can be seen that even this early in the precipitation sequence, the Cu is already associated with the Si-Ge particles.

Figure 4.10 shows a high resolution image of a \(\theta'\) precipitate growing from a Si-Ge particle, imaged in the symmetric [001]\(_{\text{Al}}\) zone axis. The sample was aged for 1 hour at 190 °C. The Si-Ge particle is multiply twinned. As expected, the aluminum around the particle is strained. It is unclear whether the Si-Ge particle is actually a sphere or an
edge-on rod. The θ' precipitate has a low aspect ratio (length/thickness), agreeing well with both elastic [4.9] and ledge nucleation [4.10] considerations.

Figures 4.11a and 4.11b show a dark field image of the AlCuSiGe microstructure in the peak aged (3 hours) and averaged (144 hours) condition, respectively. In both cases, the θ' precipitates were imaged using a 10-1α reflection. The magnification and foil orientation Figures 4.10a and 4.10b are the same as in Figures 4.4a and 4.4b. One intriguing observation is that in the overaged samples the hardness of both alloys is nearly the same, whereas the θ' distribution in the binary appears to be much coarser.

4.4 Discussion

4.4.1 Precipitation of Si-Ge

Table I gives the lattice mismatch between pure Si or pure Ge planes and the Al matrix for the orientation relationship [001]A||[-112]Si-Ge, [100]A||[-11-1]Si-Ge, and [010]A||[-1-10]Si-Ge.
Table 5.1 Lattice mismatch along special directions.

<table>
<thead>
<tr>
<th>OR</th>
<th>Al-Ge, %mismatch</th>
<th>Al-Si, %mismatch</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001]Al</td>
<td></td>
<td>[-112]</td>
</tr>
<tr>
<td>[100]Al</td>
<td></td>
<td>[-11-1]</td>
</tr>
<tr>
<td>[010]Al</td>
<td></td>
<td>[-1-10]</td>
</tr>
</tbody>
</table>

It can be seen right away that in this orientation relationship, one out of the three $<001>_\text{Al}$ has a small mismatch with the Si-Ge particles while the other two have a large mismatch. The actual lattice parameter of the Si-Ge precipitates has not been measured. However, work discussed in Chapter 2 on Al-Si-Ge showed the particles to have a varying composition, with a mean of Si-44.5at.%Ge. Thus, it is reasonable to assume that the lattice mismatch should be intermediate between the two. It has been experimentally [4.11] and theoretically [4.12] demonstrated that precipitates tend to adopt dimensions that are the inverse of directional matching. For needles, the prediction being that their long axis would lie along the invariant line directions (an invariant line can be visualized as a row of atoms common to both structures) [4.12]. Hence, for the case of Si-Ge precipitates in the above orientation relationship the directional mismatch criteria would correctly predict $<100>$ needles.

The existing G.P. zones and $\theta^\prime\prime$ may promote precipitation of the Si-Ge particles. Strain compensation arguments similar to those applied for nucleation of $\theta^\prime$ on
Si-Ge – θ' can be made in reverse for nucleation of Si-Ge on θ''' or on GP zones. GP zones and θ''' precipitates are known to compress the Al matrix along the 100_{Al} direction that is normal to the plate [4.13-4.16]. In the case of GP zones (assumed to be monolayers of Cu), the two well known models are by Gerold [4.13] and Toman [4.14]. According to Gerold’s model the relative displacement (Δa/a) of the Al planes around a zone varies from -10% at the adjacent 100_{Al} plane to -2% at the tenth 100_{Al} plane. According to Toman’s model, the displacement varies from -3.9% at the adjacent plane to -0.3% at third plane. From this observation, it seems reasonable that the room temperature formation of GP zones and θ''' should promote precipitation of Si-Ge in the observed orientation relationship by reducing lattice mismatch along the [100_{Al}][{-1-10}]_{Si-Ge}.

4.4.2 Precipitation of θ'

In AlCuSiGe the precipitation of θ' is catalyzed by the strain cancellation effect that results when θ' forms heterogeneously on Si-Ge. The strain for transformation of Si and/or Ge in solid solution to a diamond cubic unit cell can be calculated by assuming that before precipitation, Si and Ge atoms form FCC clusters that have the lattice
parameter of Al \( (a_{Al} = 4.0497 \text{ Å} [4.2]) \). Since a diamond cubic unit cell has twice as many atoms in it than a FCC unit cell, it takes the volume of two FCC cells to transform into one diamond cubic cell. The volume of two FCC lattices is 0.13283 nm\(^3\), while the volume of one diamond cubic cell is 0.16018 nm\(^3\) for Si \( (a_{Si} = 0.54309 \text{ nm} [4.2]) \) and 0.1811 nm\(^3\) for Ge \( (a_{Ge} = 0.56577 \text{ nm} [4.2]) \). The volume mismatch associated with this transformation, \( \Delta V/V_0 \), is 20.6\% for Si and 36.4\% for Ge. The strain can be related to the volume mismatch by the following expression:

\[
\frac{\Delta L}{L_0} = \frac{1}{3} \frac{\Delta V}{V_0}
\]

(4.1)

This results in \( \varepsilon_0 = 6.85\% \) for Si and \( \varepsilon_0 = 12.1\% \) for Ge. The Si-Ge precipitates effectively act as misfitting inclusions that place the surrounding matrix in compression. Cu atoms \( (r_{Cu} = 1.57 \text{ Å}, r_{Al} = 1.82 \text{ Å}) \) and vacancies should segregate to the precipitate-matrix interface to reduce this misfit strain. The (Si-Ge)-Al interface is also the logical place for the \( \theta' \) to form. The transformation strain of Si is strongly positive \( (\varepsilon^0 = 0.0685) \), while that of \( \theta' \) (Al\(_2\)Cu) is negative \( (\varepsilon_{11}^0 = -0.0024, \varepsilon_{33}^0 = -0.0452) \). It follows that the strain energy of a \( \theta' \) precipitate is significantly lowered if it nucleates in the vicinity of
a pre-existing Si precipitate. By acting to compensate some of the transformation strain, the Si-Ge particle makes it thermodynamically easier for θ' to nucleate.

4.4.3 Improved Hardness

The significantly higher peak hardness of the Si-Ge containing alloy is probably due to both the better effectiveness of θ' compared to θ'' as a hardening phase and the additional contribution of the Si-Ge particles. The θ' precipitates are more resistant to dislocation motion compared to θ'' and are less likely to be sheared [4.16-4.17]. This can be rationalized as a result of both the morphology of the precipitate and its structure. The θ' tends to be thicker than θ'', requiring a greater force to shear the particle. Additionally, the structure of θ'' is very similar to Al making for easy dislocation passage from the matrix into the precipitate (θ'' can be visualized as two fcc cells slightly compressed along the c direction, with the Cu occupying the top and bottom 100 planes). Alternatively, the structure of θ' is sufficiently dissimilar to Al making for a tortuous dislocation path from one to the other. In binary Al-Cu, by the time the microstructure has transformed to mostly θ', the precipitate spacing is too large to be effective in preventing dislocation passage. However, this problem is avoided in
the quaternary AlCuSiGe since the $\theta'$ distribution scales with the Si-Ge distribution (which is very dense).

Additionally, Si-Ge particles may also provide some contribution to the strength of the quaternary alloy. In the ternary Al-Si-Ge, their contribution is small but not negligible [70] (peak hardness of Al-1wt.%Si-2.65wt.%Ge was 40 HB, whereas 99.9 pure Al has a hardness of 10 HB [4.18]). However, a direct comparison between the two systems is difficult because of the different volume fraction of the Si-Ge phase in the quaternary alloy compared to the ternary.

4.5 Conclusions

The room temperature microstructure of both AlCu and AlCuSiGe consists of GP zones and $\theta''$ precipitates. In the quaternary alloy a stable hardness is achieved after 8 hours of room temperature aging.

Upon aging at 190$^\circ$C, Al-Cu displays the well known precipitation sequence consisting of the slow dissolution of GP zones and $\theta''$ and a gradual formation of $\theta'$. In the binary alloy, peak hardness is achieved after 14 hours of aging, with the microstructure consisting of predominantly $\theta''$ precipitates.
In the quaternary alloy, Si-Ge particles quickly nucleate and grow during elevated
temperature aging (they are detected as early as 30 min. at 190 °C). Many of these
precipitates adopt the morphology of needles lying along the $<001>_{A1}$ with an
orientation relationship of $001]_{A1} \| [-112]_{Si-Ge}$, $[100]_{A1} \| [-1-11]_{Si-Ge}$, and $[010]_{A1} \| [-1-10]_{Si-Ge}$.
Other particles grow as multiply twinned spheroids.

The pre-existence of GP zones and $\theta''$ may enhance the precipitation of the Si-
Ge particles by reducing the nucleation strain. The Si-Ge particles then act as nucleation
sites for $\theta'$ precipitates, resulting in a peak aged microstructure consisting of a dense
distribution of $\theta'$ attached to Si-Ge. This occurs relatively fast (3 hours at 190°C) and
may also be attributed to strain cancellation.

Prolonged room temperature aging prior to elevated temperature aging enhanced
the hardening response. This is presumably due to the role of pre existing GP zones and
$\theta''$ in catalyzing the elevated temperature precipitation sequence.
References


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Figures 4.1a and 4.1b: Simulated selected area diffraction pattern (SAD) of $\theta''$ ($\text{Al}_3\text{Cu}$) precipitates in Al, showing the three unique variants of the cube-cube orientation relationship (a) and double diffraction (b) ($\text{Al} =$ filled circles, $\theta'' =$ open circles, double diffraction = crosses).
Figures 4.1c and 4.1d: Simulated selected area diffraction pattern (SAD) of $\theta'$ (Al$_2$Cu) precipitates in Al, showing the three unique variants of the cube-cube orientation relationship (a) and double diffraction (b) (Al = filled circles, $\theta'$ = open squares, double diffraction = crosses).
Figures 4.1e and 4.1f: Simulated selected area diffraction pattern (SAD) of Si-Ge precipitates in Al, showing the orientation relationship (111)$_\text{Al}$$\parallel$(-112)$_\text{Si-Ge}$ and [-100]$_\text{Al}$$\parallel$[1-10]$_\text{Si-Ge}$. (a) and double diffraction (b) (Al = filled circles, Si-Ge = open diamonds, double diffraction = crosses).
Figure 4.2. Hardening response of AlCuSiGe and of AlCu aged at 191 °C.
Figures 4.3a-4.3c. Representative selected area diffraction patterns of Al-Cu, taken in the [001]_A1 zone axis. (4.3a) sample was aged at room temperature for 8 months. (4.3b) 30 minutes at 190 °C. (4.3c) 3 hours at 190 °C. (4.3d) 14 hours at 190 °C. (4.3e) 144 hours at 190 °C.
Figures 4.3a-4.3c. Representative selected area diffraction patterns of Al-Cu, taken in the [001]_{Al} zone axis. (4.3a) sample was aged at room temperature for 8 months. (4.3b) 30 minutes at 190 °C. (4.3c) 3 hours at 190 °C. (4.3d) 14 hours at 190 °C. (4.3e) 144 hours at 190 °C.
Figures 4.4a-4.4b. AlCu microstructure after aging for 14 hrs at 190 °C (4a) and 144 hours at 190 °C (4b), taken in the [001]_x zone axis. Figure 4.4a shows edge-one θ' precipitates, imaged using 002_φ reflection. Figure 4.4b shows edge on θ' precipitates, imaged using an edge-on -101_φ reflection.
Figures 4.5a-4.5f. Representative selected area diffraction patterns of AlCuSiGe, taken in the [001]_Al zone axis. (4.5a) sample was aged at room temperature for 8 months. (4.5b) 30 minutes at 190 °C. (4.5c) 1 hour at 190 °C. (4.5d) 3 hours at 190 °C. (4.5e) 144 hours at 190 °C.
Figures 4.5a-4.5f. Representative selected area diffraction patterns of AlCuSiGe, taken in the [001]_Al zone axis. (4.5a) sample was aged at room temperature for 8 months. (4.5b) 30 minutes at 190 °C. (4.5c) 1 hour at 190 °C. (4.5d) 3 hours at 190 °C. (4.5e) 144 hours at 190 °C.
Figure 4.6. High resolution image of AlCuSiGe microstructure in the room temperature aged condition, taken in [001]$_A$ zone axis.
Figure 4.7. Dark-field image of AlCuSiGe microstructure after the sample was aged for 30 minutes at 190 °C. Si-Ge precipitates were imaged using a 1-11_{Si-Ge} reflection.
Figure 4.8. Two-beam image of AlCuSiGe microstructure after 30 minutes at 190 °C. The Al matrix displays significant strain contrast.
Figure 4.9. Energy dispersive x-ray spectroscopy map of the AlCuSiGe microstructure after 30 minutes of aging.
Figure 4.10. High resolution of a $\theta'$ precipitate heterogeneously nucleated on a Si-Ge particle, imaged in [001]$_{Al}$ zone axis. The sample was aged for 30 minutes at 190°C.
Figures 4.11a and 4.11b. Dark field image of AlCuSiGe microstructure in the peak aged (4.11a) and overaged (4.11b) conditions. The edge-on $\theta'$ precipitates were imaged using 10-1\text{$_{\beta}$}.
Summary

The ideal microstructure for a precipitation hardened alloy consists of a dense distribution of ultra-fine unshearable precipitates. Unfortunately, this microstructure is difficult to obtain because the same factors that make precipitates resistant to dislocation shearing result in a large energy barrier to precipitation. This thesis explored methods to overcome this problem through alloy design.

It was demonstrated that it is possible to significantly refine the precipitate distribution by providing templates for heterogeneous nucleation (θ' on Si, and Si-Ge on GP zones and θ''). In Al-Cu-Si-Ge alloys, such an approach made it possible to obtain an ultra dense distribution of relatively unshearable precipitates leading to excellent mechanical properties. It was also shown that in the ternary Al-Si-Ge it is practically impossible to obtain good mechanical properties due to an insufficient volume fraction of the strengthening phase combined with sluggish precipitation kinetics.

It is concluded that the “ideal” microstructure is actually a composite of several precipitate phases clustered together, thereby reducing each other’s nucleation energy. This microstructure also leads to enhanced aging stability due to the lower net energy of the precipitates.
Appendix 1: The Role of Vacancies in the Precipitation Process

Wrought Aluminum alloys are produced by homogenizing the ingot at temperatures slightly below the liquidus (usually around 500°C), followed by quenching and aging at a lower temperature (room temp. – 200 °C). If the quench is severe enough much of the vacancies that exist at the solutionizing temperature (~ 10⁴) are temporarily retained after the quench. What effect this has on the subsequent microstructural evolution critically depends on how long this non-equilibrium vacancy concentration is retained. For a given alloy, the processing factors that most critically determine the non-equilibrium vacancy concentration are the quenching temperature, the quenching rate, the solute-vacancy binding energy, and the subsequent aging temperature [a1.1]. For TEM samples foil thickness also becomes a critical parameter.

After the quench, the vacancy concentration is excess of the equilibrium. To reach equilibrium, excess vacancies may diffuse to sinks such as grain boundaries and inclusions [a1.2, a1.3]. This may lead to very serious problems stemming from the vacancy depleted regions not containing precipitates (as will be discussed subsequently). These precipitate free zones (“PFZs” as coined by [a1.3]) exist near grain boundaries and inclusions and can cause catastrophic failure of otherwise strong alloys (typically by nucleating cracks in the soft precipitate free matrix).
If these sinks are not in the immediate proximity, the vacancies will collect as small voids and subsequently collapse to form dislocation loops [a1.4] or interact with existing dislocations (e.g. vacancies interacting with screw dislocations in Al-Cu resulting in helices [a1.5]. These loops are typically non-uniformly distributed [a1.4], and increase in density with the solutionizing temperature [a1.6]. However, before being annihilated these non-equilibrium vacancies significantly increase substitutional self diffusion by providing excess atomic jump sites.

In alloys the role of vacancies is complex. Vacancies can behave either independently of impurities, or form point defect – impurity atom(s) complexes [a1.1]. The impurity-vacancy binding energy is thought to be the sum of energy due to the electronic misfit and elastic misfit between the solute atoms and the vacancies [a1.7]. The electronic contribution arises from the interaction between the outer-electron orbitals of the impurity and matrix atoms, while the elastic energy contribution comes from any strain relaxation or increase due to placing a solute atom next to a vacancy in a perfect matrix.

There have been numerous approaches to determining the impurity-vacancy binding energies. A popular indirect method is to measure the change in electrical resistivity after quenching [a1.8]. A direct approach used by Peck and Westmacott compares the rates of dislocation loop shrinkage in alloys (Al-Si) and pure materials.
(Al) during elevated temperature annealing [a1.9]. The differences in the activation energies for loop shrinkage are related to the vacancy/solute binding energy during the flux of the vacancies from the loops to the TEM foil surface.

If the vacancies did not interact with the solute, the system would behave as a pure material. Initially there would be an increase in diffusivity due to quenched in vacancies, followed by a decay to an equilibrium value. In Aluminum alloys, however, vacancies do profoundly interact with the solute atoms. This has been verified experimentally in terms of the differences in the post-quench dislocation arrays formed in Al-Cu, Al-Zn, Al-Ag and Al-Mg atoms [a1.6]. For example, in Al-Mg$_2$Si and Al-Mg alloys very few loops were observed, indicating that most of the vacancies were trapped in the matrix [a1.6]. A strong vacancy-solute interaction is also known from consideration of Ag, Cu, Mg, Zn, Si, Zr, Ag, Ge and Sb – vacancy binding energies in Aluminum [a1.10].

Once bound to a solute, vacancies influence both the rate of zone formation and the rate of precipitation [a1.11]. In both cases, diffusivity is greatly enhanced since the high temperature vacancy concentration is preserved throughout aging. Additionally, since the vacancy is now intimately bound to the solute, the activation energy for solute migration is drastically lowered.
The fate of a vacancy upon reaching a precipitate or a zone can also vary. When a solute-vacancy pair reaches a zone, the vacancy can be freed and diffuse back into the matrix to pick up another solute atom. This is the well known “vacancy pump mechanism” [a1.12] believed to occur during the formation of GP zones in Al-Cu. Alternatively, the vacancies can become incorporated in the zone or in its proximity, consequently removing themselves from the circuit. This should result in a rapid decay in the rate of zone formation with aging time, leading to a final microstructure composed of a dense distribution of fine zones [a1.13]. Which of these two effects occurs for a particular alloy system depends on the vacancy-zone binding energy, which should again depend on both elastic and electronic considerations.

Vacancies play several roles in the nucleation and growth of precipitates. The first case to be considered is when vacancies become incorporated into the precipitate. This may occur during nucleation of diamond cubic Ge from an Aluminum matrix [a1.14, a1.15] since the Ge structure is much more open than Aluminum (relative density of 1 atom/22.6Å³ versus 1 atom/16.6Å³). The incorporation of vacancies into the structure of the precipitate has also been postulated to be a way for $\theta^\prime$ precipitates to directly transform to $\theta^\prime$ [a1.16]. The process is thought to occur through the replacement of one of the Al planes by a plane of vacancies, followed by a redistribution of two of the Cu atoms and a contraction of the unit cell along the c-axis.
Another role that vacancies play in solute precipitation is in the reduction of compressive strain in the matrix during the nucleation and/or growth of misfitting precipitates. Al-Si-Ge [a1.17] serves as an excellent examples of a system where this is expected to occur. When N atoms of Al are replaced by a diamond cubic Si and/or Ge precipitate containing the same number of atoms, a compressive stress is developed in the matrix (this is the alternative view of the role of vacancies in the formation of Si and/or Ge precipitates). This stress may then be relieved either via slip or by a positive vacancy flux into the region.

Finally, vacancies play a role in nucleating misfit dislocations either in the matrix or in the precipitates. For example, Nicholson [a1.18] postulated that the loss of coherency of θ' precipitates in Al-Cu occurs by condensation of vacancies on the \{100\}_θ planes and their subsequent expansion to become a\langle100\rangle_α dislocation loops. Sankaran and Laird latter confirmed this mechanism, but showed that the burgers vector of the dislocations was actually a/2\langle100\rangle_α [a1.19].

From these considerations it is obvious that any serious attempt at design of a new alloy will always include the consideration of the possible vacancy-solute interactions. For binary Al-Cu, Al-Si and Al-Ge alloys, Ge has the highest binding energy with vacancies (0.33 eV), followed by Si (0.3 eV), followed by Cu (0.14 eV) [a1.10]. In the ternary and quaternary alloys explored in this study complexes may form
(vacancy-solutes, divacancy-solutes). Unfortunately, these binding energies in the Al-Cu-Si, Al-Si-Ge and Al-Cu-Si-Ge are not known, and finding them is beyond the scope of this thesis. However, future work should include a series of dislocation loop shrinkage experiments intended to determine the binding energies in these very interesting systems.
References


a1.4. G. Thomas and M. J. Whelan; *Phil. Mag.*, vol. 4, 1959, pp. 511-27.


Appendix 2: Precipitate Morphology Analysis:

Using the approach outlined by Thomas and Goringe [a2.1] it is possible to determine the shape of small particles by examining the symmetry of their strain field in the surrounding matrix. If the particles do not strain the matrix it is also possible to obtain some information about their geometry by simply examining the same particles at different tilt conditions. In Figures A2.1-A2.9 the geometry of several Si-Ge precipitates was analyzed by examining both the symmetry of their strain field and their morphology at different tilt conditions. The general conclusions that can be drawn from this analysis is that the geometry of the precipitates ranges from that of multiply-twinned irregular plates to that of multiply-twinned spheres. The larger the particle, the more the tendency for it to be plate-like. However, this distinction is somewhat arbitrary since all these particles have ill defined geometry due to the heavy twinning.

In general, the matrix strain around the precipitates is non-uniform, as demonstrated in Figure A2.5. While imaging in bright field with the [020]_Al and [200]_Al reflections strongly excited does reveal strain in the matrix, practically no strain is observed if [2-20]_Al reflection is strongly excited. The imaged particle is most likely a sphere rather than an edge on rod since very few rods were observed in either the [001]_Al or the [110]_Al zone axis (see Chapter 2 for more precipitate analysis).
Figure A2.4 shows three Si-Ge precipitates in contact with each other. The two large ones appear to be plates. This can be seen both from their morphology and from the strain contrast in the surrounding matrix which tends to surround the particles almost uniformly. The small spherical particle does not exhibit strain contrast. This precipitate may actually be a particle that was etched out of the matrix and is consequently laying on the surface of the foil.

Figure A2.5 shows bright field images of a spherical Si-Ge precipitate. Strain contrast is the strongest when the \([020]_{Al}\) reflection is strongly excited, followed by \([2-20]_{Al}\). Very little strain is visible when \([200]_{Al}\) reflection is strongly excited. It can again be concluded that the matrix strain around this precipitate is non-uniform.

Figure A2.6–A2.9 all show either plates (A2.6, A2.8, A2.9) or spheres (2.7). Since the matrix strain around these particles tends to be non-uniform (due to the particles' ill defined geometry) it is difficult to conclusively perform the strain contrast analysis outlined in [a2.1].

Reference

Figure A2.1. Al-lat.%Si-lat.%Ge aged at 160°C for 9 hours. Images taken in [001]_Al zone axis. (a) Two beam bright field using 020 Al (b) 200 Al (c) 220 Al.
Figure A2.2. Unrotated selected area diffraction patterns (SADs). SADs need to be rotated 53° CW with respect to image.
Figure A2.3. Bright field images of individual precipitates obtained by enlarging sections of Figure A2.1.
Figure A2.4. Bright field images of individual precipitates obtained by enlarging sections of Figure A2.1.
Figure A2.5. Bright field images of individual precipitates obtained by enlarging sections of Figure A2.1.
Figure A2.6. Bright field images of individual precipitates obtained by enlarging sections of Figure A2.1.
Figure A2.7. Bright field images of individual precipitates obtained by
enlarging sections of Figure A2.1.
Figure A2.8. Bright field images of individual precipitates obtained by enlarging sections of Figure A2.1.
Figure A2.9. Bright field images of individual precipitates obtained by enlarging sections of Figure A2.1.