Beryllium-enhanced precipitation in Al-Mg-Si alloy role of nucleation entropy and interfacial energy.

Xiao. Tian

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BERYLLIUM-ENHANCED PRECIPITATION IN AL-MG-SI ALLOY: ROLE OF NUCLEATION ENTROPY AND INTERFACIAL ENERGY

BY

XIAO TIAN

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES THROUGH THE DEPARTMENT OF ENGINEERING MATERIALS IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF APPLIED SCIENCE
AT THE UNIVERSITY OF WINDSOR

WINDSOR, ONTARIO
1988
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To My Dear Parents
ABSTRACT

The effect of Be microadditions on β (Mg2Si) precipitation in age-hardenable Al-0.75%Mg-0.5%Si* alloy has been investigated. By monitoring microhardness and resistivity changes, coupled with optical and SEM microscopical observations, it is shown that the Be addition greatly accelerates the precipitation kinetics, and significantly increases the hardness level of the alloy following solution and aging treatment between 22°C to 300°C.

The precipitation of β phase, monitored by resistivity measurements, is found to obey the Avrami equation:

\[ Y = 1 - \exp(-kt^n) \]

where \( Y \) is the fraction of excess solute precipitated at time \( t \), and \( k \) and \( n \) are parameters dependent on nucleation rate and growth mechanism, respectively. It is found that the addition of Be to the Al-Mg-Si alloy significantly increased the transformation rate as reflected in the higher "k" values, while the growth constant (n) and activation energy remain relatively constant. The much higher precipitate count (observed both by optical and SEM microscope) and "k" value obtained for Al-Mg-Si alloy containing Be is attributed to a beryllium-enhanced nucleation rate. Using classical nucleation theory, it is shown that the increased nucleation rate may be attributed to an increase in the nucleation entropy associated with Be concentrating in the precipitating.

* Concentrations are all in wt.%, if not otherwise indicated
phase. And analysis of the precipitate growth kinetics indicates a decrease in the precipitate-matrix interfacial energy, which could likewise contribute to the increased nucleation rate for precipitation of the \( \beta \) phase containing Be.

Microhardness results show that at aging temperatures between 22°C - 300°C, the Al-Mg-Si-0.1%Be alloy age hardens much faster and reaches a higher maximum hardness level than the Al-Mg-Si alloy, which is in agreement with the accelerated transformation rates and higher "k" values for Al-Mg-Si alloy containing Be, monitored by resistivity measurements.

To support the argument that the drastic change of nucleation rate does depend, to a large extent, on the small change in nucleation entropy, another element, Ca, which decreases the nucleation entropy, is added to the Al-Mg-Si alloy. It has been found that the significantly depressed age-hardening in Al-Mg-Si-0.2%Ca, compared with Al-Mg-Si alloy, is again in agreement with its significantly lower nucleation rate.
ACKNOWLEDGEMENTS

The author wishes to take this opportunity to express his sincere gratitude to Dr. W.V. Youdelis for his invaluable guidance, supervision and encouragement throughout this investigation.

He would also like to thank Mr. J. Robinson for his assistance in electron microscopy, and Mr. H. L. Ge for his helpful discussion concerning this investigation.

Finally, he would like to acknowledge the Aluminum Company of Canada for the supply of superpurity aluminum, and the Natural Sciences and Engineering Research Council of Canada (NSERC) for the financial support in the form of a research grant.
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CHAPTER I  INTRODUCTION

Commercial Al-Mg-Si alloys are noted for their excellent resistance to corrosion, good welding properties and relatively high strength that are realized by thermal processing.

The heat-treatable Al-Mg-Si alloy products find wide applications ranging from purely decorative to structural because of good mechanical properties, formability and resistance to corrosion. For example, commercial 61S alloy is widely used in bus, truck, railway construction, marine applications, welded structures and rivets. However, the heat treatment process applied for strengthening purposes is costly. Therefore, it is practically meaningful to find ways to accelerate the age-hardening stage of the heat treatment process as well as increase the strength of the alloy in its optimally aged condition.

The addition of trace elements to Al-alloys affects strongly their aging response by changing the thermodynamic properties of the precipitate phase. Incorporation of trace elements into the precipitate phase can significantly change the free energy of formation of a critical-sized nucleus (ΔG*) through change in the interfacial energy, strain energy, and nucleation entropy.

This research was undertaken to determine if the precipitation process in the natural-aging and commercially important Al-Mg-Si (Duralumin type) alloy can be accelerated.
through the nucleation stage. Earlier studies [1-4] have shown that small Be additions enhanced grain refinement and precipitation processes in Al-Ti and Al-Cu alloys respectively. The above beneficial effects were attributed to Be-enhanced nucleation processes associated with the increase in nucleation entropy of the peritectic and precipitating compound phases containing Be. Therefore, the possibility for similarly enhancing the age-hardening response of the Al-Mg-Si alloy through Be incorporation in the Mg2Si precipitate naturally presented itself.

CHAPTER II LITERATURE REVIEW

1. General Concept of Precipitation

A necessary condition for precipitation is that a multi-component phase becomes thermodynamically unstable and tends to decompose into phases of differing compositions. This requirement is usually accomplished by quenching the alloy from high temperature to obtain a supersaturated solid solution, and then heat it at higher temperatures to induce the precipitation. The desirable result is the generation of an additional crystalline phase distributed uniformly throughout the matrix. Common types of phase diagrams in which precipitation can occur are shown in Fig.1. A feature common to all of these is a phase boundary which slopes with lowering temperature toward decreasing concentration of one component. The precipitating phase may be a solute-rich phase whose crystal structure bears no similarity to the matrix.
Fig. 1: Common Types of Phase Diagrams and Corresponding Free Energy-Composition Relationships in Which Precipitation Can Occur.

(After Hardy and Heal [5])
Possibly two terminal solid solutions separated by a miscibility gap will precipitate or perhaps a eutectoid reaction will occur. The precipitate itself may be an intermediate compound or more probably a metastable transition phase which ultimately redissolves or transforms into another more stable phase.

The aluminum-magnesium-silicon system, which is the focus of the present work, includes a quasibinary eutectic between the aluminum solid solution and the intermediate compound Mg$_2$Si. As shown in Fig. 2, the solubility of Mg$_2$Si in aluminum decreases from 1.85wt.% at the eutectic temperature to only about 0.1wt.% at the room temperature. Generally, alloys containing 0.6wt.% or more of Mg$_2$Si show marked precipitation hardening [7]. In this work, therefore, a composition of about 1.2wt% Mg$_2$Si is chosen to study the precipitation.

2. Driving Forces for Precipitation

All structural transformations are driven, at constant temperature and pressure, by the possible reduction in the Gibbs free energy, ΔG, from the original to the final structure.

Consider a super-saturated single-phase alloy α, whose composition lies inside the two-phase region, α+β, at a certain temperature. At the start of the precipitation, the driving force for the formation of a small amount of β from a large amount of α is obtained from the tangent representing the super-saturated α matrix. This construction is shown in
Fig. 2: Aluminum - Magnesium Silicide Quasi-Binary Phase Diagram. (After Mehl et al. [6])
the free energy-composition diagram of Fig.3. The magnitude of this driving force ($\Delta G_m$), for low supersaturations, is obtained as follows:

$$\Delta G_m = (X^*_o - X^p_o) \, d^2 G_m / dX^2_o \Delta X^o_0$$  \hspace{1cm} (1)

where $\Delta X^o_0 = X^*_o - X^p_o$ is the amount of supersaturation. From eqn. (1), it is seen that the driving force for precipitation is proportional to the difference in composition between matrix and precipitating phase. Therefore, at the start of precipitation, a new phase may thus be favored if it differs much in composition, even though it can not be in stable equilibrium with the matrix phase. Fig.4 illustrates the larger driving force (represented by the length of the arrow) for metastable transition phase ($\beta$) compared with equilibrium $\beta$ phase at the start of precipitation. It is thus conceivable that the nucleation of a stable equilibrium precipitate directly from solid solution may be difficult if its composition is close to that of the matrix, whereas a metastable phase, whose composition differs greatly from that of the matrix can form and assist in nucleating the stable phase.

3. Precipitation Sequence

The precipitation from supersaturated solid solution is generally a process expressed as a series of sequential stages, the basis of which was described above.

Mishra and Oswalt [9] and Lutts [10] studied Al-Mg-Si alloys and reported that the previous phase nucleates each
Fig. 3: Demonstration of the Driving Force at the Start of a Precipitation Reaction.
(After Aaronson [8])

Fig. 4: Demonstration of the Effect of Phase Composition on the Driving Force at the Start of Precipitation.
(After Aaronson [8])
successive phase according to the following reaction:

\[ \text{GP zones} - \beta'(\text{metastable } \text{Mg}_2\text{Si}) \rightarrow \beta(\text{stable } \text{Mg}_2\text{Si}) \quad (2) \]

Noble [11] reports that the \( \theta' \) phase in Al-Cu alloys is a direct result of Cu-rich clusters which have grown to a critical size. Lorimer and Nicholson [12] and March et al [13] also support the belief of sequential nucleation of more stable precipitates on or through less stable ones. On the other hand, it has been proposed [14] that nucleation of the equilibrium phase directly from the matrix is also possible. Laird and Aaronson [15] found that only a small fraction of \( \theta' \) serve as nucleation sites for \( \theta \) in Al-Cu alloy. Karov [16] recently proposed that the sequence of \( \theta \) formation involves dissolution of \( \theta' \), transport of Cu to dislocations and diffusion of Cu atoms along dislocation pipes to the growing \( \theta \) precipitate. Buttler [17] also observed a dislocation net linking \( \theta' \) to \( \theta \) during \( \theta' \) to \( \theta \) transition, and proposed that the \( \theta \) dissolution occurs by an atomic detachment followed by a pipe diffusion.

In general, the sequence of precipitation and the corresponding mechanism for each stage of transition depends largely on aging temperature and on the particular alloy system involved.

The metastable-phase diagram, with the solvus line for each metastable phase as shown in Fig.5 can help us determine what metastable phase can form and exist at different temperatures. For instance, aging above the GP zone solvus line will lead to resolution of all GP zones, and ageing
Fig. 5: Al-Cu Phase Diagram Showing the Solvus Lines of the Metastable Phases

(After Porter et al. [18])
above the q" solvus line will lead to resolution of all 0"
precipitates.

4. Nucleation of Precipitation

(1) Development of Classical Nucleation Theory

The basis of the theory of nucleation is that when a new
phase nucleates within a parent phase, an interface is formed
between the two phases. This interface exerts a local
increase of free energy when the first few atoms assemble in
the new structure. The theory of this process, which
describes the interfacial energy barrier to nucleation, was
originally developed for vapor to liquid condensation by
Volmer and Flood [19] and Becker and Doring [20]. The method
was applied by Turnbull to solidification of metals and
subsequently to solid-solid metallic phase transformations in
the late 1940s [21], and since then has been fundamental to
the qualitative and quantitative understanding of structural
changes in physical metallurgy and is therefore termed
"classical theory of nucleation". The theory appears to be,
qualitatively at least, highly successful both for
solidification and in describing the nucleation step in solid
state nucleation and growth transformations.

Solid state nucleation has received much attention in the
past two decades, and has been reviewed on many occasions.
For example, Kelly and Nicholson [22], Russell [23],
Nicholson [24], Christian [25] and Russell [26], in
developing the general theories for solid state nucleation,
arrived at basically similar conclusions and showed
good agreements between theories and experiments.

(2) Nucleation Rate for Solidification

According to the classical theory of nucleation [27], a
steady state distribution of embryos with \( i \) atoms is given
by:

\[
N_i = N_* \exp[-\Delta G_i / kT]
\]

(3)

where \( N_* \), \( N_i \) and \( \Delta G_i \) are the total number of atoms in the
system, the number of embryos with \( i \) atoms and free energy of
formation of such embryo, respectively. For a spherical
embryo, in the absence of strain energy, the free energy of
formation is:

\[
\Delta G = 4/3 \pi r^3 \Delta G_v + 4 \pi r^2 \gamma
\]

(4)

where \( r \), \( \Delta G_v \) and \( \gamma \) are the radius of embryo, the free
energy change per unit volume of embryo and the interfacial
energy respectively. Minimizing eqn.(4) with respect to "\( r \)"
gives the free energy of formation of critical-sized embryo:

\[
\Delta G^* = 16 \pi \gamma^3 / 3(\Delta G_v)^2
\]

(5)

Substituting eqn.(5) for \( \Delta G_v \) in eqn.(3) gives the number
of critical-sized embryos \( (N_i^*) \) as:

\[
N_i^* = N_* \exp[-16 \pi \gamma^3 / 3(\Delta G_v)^2 kT]
\]

or \( N_i^* / N_* = \exp[-16 \pi \gamma^3 / 3(\Delta G_v)^2 kT] \)

(6)

The resulting homogeneous nucleation rate, which is
proportional to the density of critical-sized embryos \( (N_i^* / N_*) \)
and the diffusion rate across the embryo’s boundary may be
expressed as:
\[
N_{hv} = K \exp[-16 \pi \gamma^3 / 3(\Delta G_v)^2] kT
\]  

(7)

where the parameter \( K \) includes the embryo surface concentration of atoms and the jump frequency for the atom which has an exponential dependence on the activation energy for diffusion.

For heterogeneous nucleation, substrates reduce the surface energy needed to form a nucleus, and thereby decrease the free energy of formation of the critical-sized nucleus by a factor that is a function of contact angle \( \theta \) at the nucleus/substrate interface. That is:

\[
\Delta G_{hr} = f(\theta) \frac{16 \pi \gamma^3}{3(\Delta G_v)^2}
\]  

(8)

where \( f(\theta) = (2 - 3 \cos \theta + \cos^3 \theta) / 4 \)  

(9)

Therefore, the heterogeneous nucleation rate, quite similar to the homogeneous case, can be expressed as:

\[
N_{hv} = K \exp[-16 \pi \gamma^3 f(\theta) / 3(\Delta G_v)^2]
\]  

(10)

(3) Nucleation Rate for Solid-State Precipitation

Eqn. (11) is applicable to liquid-solid transformation (solidification) or other phase changes in which strain energy is negligible. Transformations in solid state (e.g., precipitation), however, are usually accompanied by volume changes that create elastic strain, which must be taken into account in calculating the free energy of formation of critical-sized nucleus (\( \Delta G^* \)). Two general cases must be considered: (a) Incoherent nucleation where there is no lattice continuity between the precipitate and matrix, and the strain is hydrostatic in character, and (b) Coherent
nucleation where the lattices of the precipitate and the surrounding matrix are constrained to match, and the strain is determined by the degree of mismatch of the lattices. The spherical form of embryo is not the lowest energy configuration when strain becomes significant, and the general form of the free energy of formation of an embryo now includes the strain energy per unit volume of precipitate, $W$, i.e.,

$$\Delta G = (\Delta G_v + W) V + \gamma A$$

(11)

Since $W$ is always positive, it is evident that strain energy increases the critical size for the nucleus, and correspondingly decreases the nucleation rate.

(a) Incoherent Nucleation

The problem of strain energy (hydrostatic) arising from incoherent precipitation has been treated by Nabarro [28]. Assuming that all strains are stored in the matrix and that the matrix is elastically isotropic, the strain energy per unit volume of oblate and prolate spheroidal particles (with semi axes $r$ and $c$) formed is given by:

$$W = \frac{2}{3} \mu \kappa (\Delta V/V)^2 f(c/r)$$

(12)

where $\Delta V/V$ is the fractional volume change in the matrix accompanying the transformation and $\mu \kappa$ is the shear modulus of the matrix. $f(c/r)$ is a particle shape factor function that has the following values: 1 for a sphere ($c/r=1$), 0.75 for a rod ($c/r>>1$), and $3c/4r$ for a disk ($c/r<<1$). Thus the strain energy is minimum when the precipitate is in the form of a disc or thin plate and becomes zero as $c/r$ approaches
zero. For the oblate spheroid \((c/r<1)\), \(V=4/3 \pi r^2 c\), \(A=2\pi r^2\),
\(f(c/r)=3 c/4r\), which on substituting into eqn. (12) and
minimizing \(\Delta G\) with respect to \(r\) and \(c\) gives [29]:
\[
\Delta G = 8 \pi \mu \gamma^2 (\Delta V/V)^3 / 3 (\Delta G_V)^4
\]  
(13)
so that the homogeneous nucleation rate \(\dot{N}\) is expressed as:
\[
\dot{N} \propto \exp[-8 \pi \mu \gamma^2 (\Delta V/V)^3 / 3 (\Delta G_V)^4 kT]
\]  
(14)

(b) Coherent Nucleation (GP Zones)

Eshelby [30] has presented a detailed treatment of the
elastic strain energy associated with an ellipsoidal coherent
precipitate in an isotropic matrix. Lee et al [31] later
extended Eshelby’s treatment to the general anisotropic case,
and also incorporated the strain energy into the \(\Delta G^*\) calcula-
tion, which is now expressed as:
\[
\Delta G^* = \pi \gamma^2 [2+f(c/r)]^3 / 12(c/r)^3 [\Delta G_V+W]^2
\]  
(15)
where \((c/r)\) is the aspect ratio of the nucleus. \(f(c/r)\) is
a particle shape function which has the following values:
\[
f(c/r) = \begin{cases} 2(c/r)^2/(1-(c/r)^2)^{1/2} \tanh^{-1} [1-(c/r)^2]^{1/2} & \text{when } c/r<1 \\ 1 & \text{when } c/r=1 \\ 2(c/r)^2/(1-(c/r)^2)^{1/2} \sin^{-1} [1-(c/r)^2]^{1/2} & \text{when } c/r>1 \end{cases}
\]  
(16)
The nucleation rate is expressed as:
\[
\dot{N} = \exp[-\pi \gamma^2 [2+f(c/r)^3] / 12(c/r)^3 [\Delta G_V+W]^2]
\]  
(17)
the strain energy is a function of the aspect ratio, and
for the anisotropic case varies markedly with the orientation
relationships between precipitate and matrix. Lee et al [31]
have treated the special case of Cu and Ag coherent precipi-
tates in an Al matrix, i.e., the GP zone, and show that as the ratio $(-W/\Delta G_v)$ exceeds 0.8, the nucleus begins to deviate from a spherical shape and changes progressively towards an oblate spheroid (or disk-like shape), as the $(-W/\Delta G_v)$ ratio increases.

4) The Nucleation Entropy Theory

It has been shown that the nucleation rates for both solidification [eqn. (7) and (10)] and solid-state transformations [eqn. (14) and (17)] are closely related to the Gibbs free energy of transformation per unit volume ($\Delta G_v$). No estimation of nucleation rates can be made without this key information. Although $\Delta G_v$ can be formally related to the extensive and partial molar free energies of the solid and liquid solutions [32], this approach for calculating $\Delta G_v$ is not possible for most alloy systems since the free energy data for the solutions are not available. The volume free energy of transformation is more usefully, although approximately, related to the volume entropy change of transformation and the degree of supercooling.

It can be shown [33] that for small to moderate undercooling ($\Delta T$), $\Delta G = -\Delta S_v \Delta T$, assuming $\Delta S_v$ is relatively constant over $\Delta T$ interval. Here $\Delta S_v$ is the volume entropy change of transformation, or volume entropy of nucleation (entropy change for the system per unit volume of precipitating phase nucleated). Therefore, if we can calculate $\Delta S_v$ and estimate $\Delta T$, we are able to evaluate $\Delta G_v$, and thus the nucleation rate
for solidification [using eqn. (7) or (10)] or precipitation [using eqn. (14) or (17)]. In all cases, the nucleation rate is extremely sensitive to changes in $\Delta S_v$, increasing exponentially with the square or fourth power of $\Delta S_v$.

(a) Nucleation Entropy in Liquid-Solid Phase Transformation

Youdelis [29] has derived an expression for the molar nucleation entropy $\Delta S (= \Delta S_v V_m$, where $V_m$ is the molar volume of the solid nucleated) for the special case of regular solution behavior for binary alloy phases, assuming isothermal, isobaric, constant phase-composition conditions are maintained during nucleation. The molar entropy of nucleation ($\Delta S$) can be separated into two parts: (i) the entropy change due to the freezing of the pure components ($\Delta S_F$) and, (ii) the change in the mixing entropy for the solid/liquid system resulting from the precipitation of the solid phase ($\Delta S_m$), i.e.,

\[ \Delta S = \Delta S_F + \Delta S_m \]  

where,

\[ \Delta S_F = N_1^s (S_1^s - S_1^l) + N_2^s (S_2^s - S_2^l) \]  

\[ \Delta S_m = R [N_1^s \ln(N_1^s/N_1^l) + N_2^s \ln(N_2^s/N_2^l)] \]

In the above equations, the $N$'s refer to the mole fractions, the $S$'s to the molar entropies, the subscripts 1,2 to the components, the superscripts s,l to the solid and liquid phases respectively.

The extension of eqn. (19) and (20) to the multicomponent system is straightforward and is obtained by including terms for all components in the system in the equations for the binary system [34], thus,
\[ \Delta S_{f} = \sum_{r}^{N} \frac{R}{N_{r}} \left( S_{r}^{S} - S_{r}^{L} \right) \]  

\[ \Delta S_{A} = R \sum_{r}^{N} \frac{N_{r}^{S}}{N_{r}} \ln \left( \frac{N_{r}^{L}}{N_{r}^{S}} \right) \]  

where \( N_{r}^{S} \) and \( N_{r}^{L} \) refer to the mole fractions of the \( r \)-th component in the solid and liquid phases respectively, and \( S_{r}^{S} \) and \( S_{r}^{L} \) are the molar entropies of the \( r \)-th component in the pure solid and liquid states respectively at the nucleation temperature. Eqn. (22) shows that the mixing entropy change increases (in magnitude) with the difference in composition between the solid and liquid phases and with the number of components present in dilute concentration in the liquid which concentrate in the nucleating phase. The application of eqn. (22) to the special cases of simple binary eutectic[33] or peritectic [35] systems shows that in general \( |\Delta S_{A}| \) and therefore \( |\Delta S| \) increases with increasing separation of solidus and liquidus lines, and for the eutectic system is maximum at the eutectic composition. Thus, the generally observed decrease in grain size for castings with increase in alloying content might be attributed (in part) to the increase in nucleation entropy. The nucleation entropy effect is particularly significant in the precipitation of intermediate compounds or phases of limited solubility range, where only the principle component (solvent, 1) is more concentrated in liquid phase than in solid phase \( (N_{1}^{L} > N_{1}^{S}) \), while all remaining minor components (solutes 2, 3, ..., \( n \)) are much more concentrated in solid phase than in liquid phase \( (N_{r}^{S} \ll N_{r}^{L}, r = 2, 3, ..., n) \), so that only the first term in eqn. (22) is positive (decreasing \( |\Delta S_{A}| \)), while the remaining terms are negative. In
general, since the nucleation of the intermediate compound necessarily involves a high degree of concentration of solute components into solid phase, it follows that the nucleation entropy and the corresponding nucleation rate increase with the number of solute components comprising the nucleating intermediate compound and results in an increased refinement of the solidification structure.

(i) Role of Nucleation Entropy in Grain Refinement of Aluminum Alloys

The effect of third element additions on the grain refinement of Al by Ti has been investigated by Youdelis and coworkers [1-3]. The enhancement of grain refinement of Al-Ti alloys by the addition of Si or Be as third element is attributed largely to the precipitation of the ternary peritectic compound Ti(Al,Si)₃ or Ti(Al,Be)₃ which has substantially higher nucleation entropy than the binary TiAl₃ compound. The higher nucleation entropies of ternary compounds compared with binary TiAl₃ result in a tremendous increase in their nucleation rates, as a result of the exponential dependence of nucleation rate on the square of the nucleation entropy. That explains successfully the significant enhancement of grain refinement of Al-Ti alloys by small amount of Si or Be additions. It is also important to note [36] that the addition of Al-insoluble elements Bi, Co, In, Pb, Sb and Sn to Al-Ti alloys only results in a relatively small enhancement of grain refinement (which is
attributed to the constitutional supercooling effect). This is because these Al-insoluble elements can not significantly affect the nucleation entropy and therefore the nucleation rate.

(ii) Role of Nucleation Entropy in the Refinement of Carbides

Youdelis and Kwon [37,38] also investigated the carbide refinement in superalloys and showed that the addition of Ta and Nb significantly refined the primary carbides in the Co-base alloy (HS21) [37], but had almost no effect on the primary carbides in the Ni-base alloy (713C) [38]. The results for both alloys are consistent with the proposed nucleation entropy theory for structure refinement.

For the Co-base superalloy, the primary carbides were determined to be $M_{23}C_6$ type having the approximate stoichiometric formula $(Cr_{17}Co_{15}Mo_{13})_3C_6$ [37]. Increasing the Ta or Nb content in the alloy progressively transformed the carbides to MC type, and for Ta or Nb contents exceeding ~1%, the transformation to fine and numerous TaC or NbC carbides was essentially complete. The considerably finer and more numerous carbide particles in the HS-alloys containing Ta and Nb is in agreement with the higher calculated nucleation entropies and rates for MC vs. $M_{23}C_6$ type carbides.

For the Ni-base superalloy (713), the primary carbides were determined to be MC type having the approximate composition $(Nb_{37}Ti_{13})C$ [38]. The addition of Ta or Nb resulted in the incorporation of Ta or Nb into the carbides mostly at
the expense of Ti, but the carbide type was not changed. No significant refinement of carbides occurred on Ta or Nb additions to 713C alloy, which is in agreement with the absence of any significant difference in the nucleation entropies.

(b) Nucleation Entropy in Solid-State Precipitations

Precipitations in various binary Al alloys and the effects of additional alloying elements on precipitation has been the subject of numerous investigations. The introduction of nucleation entropy theory to account for enhanced precipitation in some Al alloys due to small additions of Be has proved to be quite successful [4,39].

For the precipitation in Al-3%Cu alloy, it has been found that [4]: (i) the addition of 0.1%Be to the alloy increases significantly the hardening rate when ageing at room temperature and at 110 C, (ii) the rate of \( \Theta \) formation in Al-3%Cu alloy is significantly increased by the addition of Be, manifested in the earlier \( \Theta' \rightarrow \Theta \) transition and in the faster overall transformation rate, (iii) for Al-3%Cu-0.1%Be alloy, although the incorporation of Be into the precipitate compound to form Cu(Al,Be)\(_2\) increases the strain energy by an estimated 16%, the increase in nucleation entropy more than offsets the strain energy effect to give a net decrease of 39% in the free energy of formation of the critical-sized nucleus (\( \Delta G^* \)), thus resulting in a much higher nucleation rate for Cu(Al,Be)\(_2\) compared with CuAl\(_2\), (iv) the higher
calculated nucleation rate for the Al-3%Cu-0.1%Be alloy is consistent with the higher "k" values (which include nuclei density) obtained for Cu(Al,Be)₂ precipitation compared with CuAl₂ precipitation, which is also consistent with the observed higher initial densities of θ particles in Al-3%Cu-0.1%Be alloy.

For the effect of Be on precipitation in Al-0.2%Ti alloy, it has been found [39] that: (i) Al-0.2%Ti-0.2%Be alloy shows significant age-hardening, whereas Al-0.2%Ti does not age harden at room temperature and 150°C, (ii) Al-0.2%Ti-0.2%Be alloy shows significant resistivity decreases (indicating massive precipitation), whereas Al-0.2%Ti alloy only shows resistivity increases (indicating vacancy clustering, etc.) at ageing temperatures 350°C - 410°C, (iii) Despite the increase in strain energy for Ti(Al,Be)₂, the significant increase in nucleation entropy again overrides the strain energy effect to give a net decrease of free energy of formation of a critical-sized nucleus (ΔG*), thus giving an increased nucleation rate for Al-0.2%Ti-0.2%Be alloy, (iv) the higher calculated nucleation rate for Al-0.2%Ti-0.2%Be is consistent with the observed high density of precipitates, and explains the accelerated precipitation in Al-0.2%Ti-0.2%Be vs. Al-0.2%Ti alloy.

5. Kinetics of Precipitation

(1) General

Many attempts have been made to measure and rationalize
precipitation kinetics [40,41,42,43]. However, the complex nature of the precipitation process makes it difficult for generalization of the overall kinetics when monitoring the change of only one property during precipitation. Customarily the hardness, electrical resistivity, heat capacity, or other property is plotted against isothermal ageing time. The changes of these different properties, which are associated with different mechanisms, reflect the precipitation process from different perspectives. A combined information of the changes of these properties, together with the microscopical observation of microstructural changes enables us to have a fuller understanding of what is really happening during precipitation. Sometimes, the time needed to reach an arbitrary value of a property is plotted against the reciprocal of the absolute ageing temperature, the slope of which provides a measure of the "activation energy", a highly ambiguous quantity since so many contributing processes are involved. However, within a limited temperature range, most of the sub-processes are diffusion controlled and therefore, in that range a plot of this type gives an activation energy for the diffusion process for the specific system. The observations of Cohen [44] show this effect clearly. Since diffusion usually controls the overall precipitation rate [45] the precipitation is certainly faster at higher temperatures.
(2) Property Changes During Precipitation

(a) Hardness

The hardness of a material is a combined measure of many processes, the most direct of which is the resistance of the material to slip or plastic flow. Since the free movements of dislocations depends upon a uniform and continuous crystal-line lattice, anything that interrupts the periodicity of the lattice and therefore interferes with the motion of dislocations will harden and strengthen the crystal by making it more resistant to slip or plastic flow. The hardening potency of coherent precipitates is very much higher than that of incoherent precipitates of the same size and distribution. The strains surrounding a coherent precipitate extend into an appreciable volume of the matrix and serve to be obstruct slip. The greater the misfit between the matrix and precipitate, the greater will be the coherency strains and therefore, the more potent will be the particles in affecting the hardness. Incoherent precipitates, on the other hand, influence only a relatively small volume of matrix so that a dislocation moving in a slip plane has a smaller chance of encountering one. It has been proposed that hardening in systems where little coherency strain occurs, may be due to a state of order in the precipitate lattice [46]. Fisher [47] has pointed out that slip in an ordered lattice generates an interface of higher energy than the one that existed before slip occurred. Therefore, more than normal work is required to accomplish slip and strengthening
is the result. An extension of this idea is the suggestion that when a dislocation moves through a precipitate, the particle experiences a shear in the direction of the dislocation motion, producing an offset step so that the surface area of the precipitate is increased, raising the total energy level.

In general, the strength of the precipitate itself is not important in overall hardening, what is important is the state of coherency and the influence of the precipitate on the motion of dislocations through the lattice. If considerable age-hardening occurs, a coherent precipitate is usually found. When coherency is gradually lost, through growth of metastable phase towards equilibrium phase, the hardness begins to decline, and the alloy is said to be over-aged.

(b) Electrical Resistivity

Electrical resistivity has been frequently used to follow the course of precipitation. This property depends primarily on the degree of freedom of motion of conduction electrons associated with a metallic crystal[48]. A perfectly periodic metallic lattice should offer no resistance to the flow of electricity and the material is termed superconducting, a state which is reached by only a few materials and only at low temperatures. Anything which perturbs the periodicity of the lattice introduces a resistance to electron flow and some of the energy of the moving electrons is converted into increased atomic vibrations, i.e., heat. The presence of a
foreign atom in an otherwise perfect lattice constitutes a lattice perturbation and therefore, increases the electrical resistivity. Therefore, the addition of small amounts of solute atoms invariably increases the electrical resistivity of a pure metal. Atoms, in a pure crystal, which are not located precisely at lattice sites also constitute perturbations. Therefore, lattice strains of any type raise the electrical resistivity. Grain boundaries, being highly disorganized regions, also increase the resistivity.

The simplest course for electrical resistivity change during precipitation would be the monotonic decrease as the original solid solution becomes purified due to the migration of solute atoms to precipitate particles. More typically, however, a slight increase in resistivity usually occurs during the first stage of aging in many alloys. This resistivity increase, which is clearly associated with the clustering and GP zone formation, was at one time thought to be associated with abnormally high resonant scattering of conduction electrons by particles of the size in the order of the wavelength of electrons - 10Å [49]. Rossiter and Wells [50] also concluded that the maximum in the resistivity occurs when the cluster size becomes comparable with the conduction electron mean free path length. However, in some alloys (e.g. in Al-Ag), it has been found that the resistivity increase occurs long after most of precipitation particles have grown many orders of magnitude larger than 10Å in diameter [51,52]. Therefore, a better explanation for the
resistivity increase during pre-precipitation is based upon the effect of matrix strains induced by the presence of coherent precipitate. Since a coherent precipitate with a high degree of disregistry imposes strains in the matrix far beyond its own dimensions, such particles can be potent sources of resistance increase. On the other hand, incoherent particles while introducing matrix discontinuity, are not influential much beyond their own dimensions and, therefore, are relatively ineffective.

In summary, the most influential factors determining the resistivity changes are (a) Depletion of the solid solution, (b) the straining effect of a coherent precipitate. During the initial stage of aging, (b) might be dominant factor, the net effect being a slight increase in electrical resistivity. With further aging, the precipitates gradually lose coherency and (a) becomes more important compared with (b), so that electrical resistivity decreases.

(3) Kinetic Law of Precipitation

(a) Avrami Equation

The Avrami equation [53], originally developed for constant growth recrystallization, and later modified to include diffusion-controlled transformation [54], is known as the most general form of the kinetic law of precipitation [55]. The volume fraction transformed \( (Y) \) is related to isothermal aging-time \( (t) \) by:

\[
Y = 1 - \exp(-kt^n)
\]

(23)
where \( n \) is growth constant dependent on growth mechanism, and parameter \( k \) is given by[53]:

\[
k = a(N_0 r_c D)^{\frac{3}{2}}
\]

(24)

where \( a \) is a constant, \( N_0 \) the nuclei density, \( r_c \) the final mean radius of the particle, and \( D \) the solute diffusivity. Since \( k \propto D^{\frac{3}{2}} \), \( k \) must have an exponential dependence on temperature \((T)\), and thus \( \ln k \) versus \( 1/T \) plot should be a straight line, which has been verified in this investigation.

(b) LSW Theory of Particle Coarsening

For diffusion-controlled particle coarsening, Lifshitz and Slyozov [56] and Wagner[57] have derived an expression (primarily by applying Gibbs-Thomson equation), relating the average solute content in matrix \((C)\) with the isothermal aging time \((t)\) by:

\[
C = C_e + (kt)^{\frac{1}{3}}
\]

(25)

where \( k \) is the rate constant given by:

\[
k = D(RT)^{\frac{2}{3}}/(9\gamma V_m^{\frac{2}{3}})
\]

(26)

where \( V_m \) is the molar volume of precipitate, \( C_e \) the solute concentration in the matrix in equilibrium with a particle of infinite size, \( D \) is the diffusion coefficient of solute in the matrix, and \( RT \) has its usual meaning.

Therefore, by monitoring the change of solute concentration in the matrix during coarsening, one can derive quantitative information about the particle-matrix interfacial energy, provided values of other parameters \((D, C_e, \text{ and } V_m, \text{ etc.})\) are known and remain constant.
CHAPTER III  EXPERIMENTAL

1. Preparation of Alloys

Superpure aluminum and magnesium (99.99%), Al-50%Si master alloy, Al-5.23%Be master alloy and Al-7%Ca master alloy were used in the preparation of Al-0.75%Mg-0.5%Si (approximately Al-1.2%Mg-Si), Al-0.75%Mg-0.5%Si-0.1%Be and Al-0.75%Mg-0.5%Si-0.2%Ca alloy castings. The alloys were prepared in graphite crucibles, by induction melting in air, using a 15KVA Ajax Inductotherm unit at a frequency of 10 kilohertz. The melts were heated to well above the liquidus temperature (~750°C) and maintained for about 10 minutes to ensure complete homogenization, and then stirred and poured into graphite molds 25mm(dia.) x 70mm(length) at room temperature. Before casting, the molds were dried by heating to 500°C, and then cleaned using compressed air to minimize impurity inclusions. The melt temperature was monitored by a thermocouple embedded in the graphite crucible. In the preparation of Al-0.75%Mg-0.5%Si-0.2%Ca alloy, a thin graphite cover was also used during melting to protect against excessive vaporization loss of calcium. The ingots were commercially analysed for chemical compositions (at Met. Chem Testing Laboratories, Inc., Dearborn, Michigan) and the results agreed approximately with the nominal compositions. All subsequent experimental work was carried out on the central parts of the ingots to ensure similar initial microstructures and compositions.

Eutectic alloys (Al-13%Mg Si) with 0, 0.2, 0.4, and 0.6
%Be were also prepared for metallographic and X-ray diffraction studies to determine the Be incorporation in the Mg₃Si phase.

2. Solution Treatment and Aging

For optical and SEM microscopical observations and microhardness measurements, cylindrical sections approximately 5mm thick were cut from the central regions of the ingot for solution and aging treatments. The solution treatments consisted of a 60hr anneal at 560°C, followed by a quench in iced brine solution. The samples were then aged at various temperatures in the range 22°C - 300°C. An electrical muffle furnace, with a temperature control of ±2°C, was used for solution and aging treatments. Evacuated capsules were not necessary for heat treating, because thin oxide layers which quickly develop on Al, protect the alloy from further internal oxidation at elevated temperatures.

For the resistivity measurements, sections (~5mm thick) of the ingots were first solution treated at 560°C for 60 hr and then cut into thin slices 1-2mm thick. The slices were cold rolled to a strip approximately 0.1mm thick, from which test samples (4mm x 72mm) were cut. Prior to each aging treatment, the strip samples were solution treated again at 560°C for two hours to ensure a homogeneous supersaturated solid solution, and also to relieve any residual stresses in the samples.
3. Analytical Procedures

(1) Microhardness Analysis

Microhardness measurements to monitor age hardening process were carried out on a Leitz Miniload microhardness tester with a diamond pyramid indenter, a 50 gram load, and a total test time of 25 - 30 seconds. Test samples (~5mm thick) were polished to a finish (1.0μm alumina) using the conventional polishing technique. To follow the hardness change during the aging process, the same sample was tested by constantly interrupting the aging treatment. For each hardness determination, at least five readings were taken randomly on the specimen to obtain a mean hardness value.

(2) Optical and SEM Microscopical Analysis

Specimens for optical and SEM microscopy (~5mm thick) were prepared in the conventional way until 0.05μm alumina polish, following which an additional polish, up to 30 minutes, using colloidal silica suspension (Buehler) as the polishing media, was performed. This procedure is recommended [58] for soft aluminum alloys. The etchants used were dilute hydrofluoric acid solution [0.5mlHCl(48%) + 99.5mlH₂O] and Keller's etch (2.5mlHNO₃, 1.5mlHCl, 1mlHF and 95mlH₂O). Etching was performed by submerging the sample into the etchant for 10 to 30 seconds and then washing the specimen surface with running water. A progressive etching was sometimes needed to create an optimum contrast under the microscope. For SEM analysis, longer etching time was necessary to create sufficient topo-
graphic contrast.

The optical microscope used in this study was a Leitz Laborlux 12 model, with binocular observation and phototube FSA, Mechanical Stage No.78 and UKL universal condenser. The maximum magnification possible was 1,000.

The scanning electron microscope used was a Nanolab 7 model, with a resolution of 700um and maximum useful magnification of 10,000.

(3) Resistivity Analysis

For the resistivity analysis, samples were made by cold rolling thin slices (~1-2mm) into 0.1mm thick sheet, from which strips approximately 72mmx4mmx0.1mm were prepared. Separate voltage and current leads were made at the specimen ends to eliminate contact resistance. The standard potentiometric method was employed with pure Al as the reference sample. The experimental set-up (Fig.6) consisted of a current-regulated power supply (Spectromagnetic Industries Model 6021, with an average current drift of 0.03%), a Leeds and Northrup potentiometric facility capable of resolving 10^-6 V, a Haake heat and circulating pump which maintained the temperature of the distilled water bath at ±0.01°C, and an Omega chart recorder (optional).

Since the test sample and the standard Al sample were in series connection, the same current (I) passed through both samples, thus

\[ V_{Al} = I R_{Al} \quad \text{and} \quad V_{S} = I R_{S} \]
Fig. 6: Experimental Set-up for Resistivity Measurements
\[ R_s = \left( \frac{V_s}{V_{AI}} \right) R_{AI} \]  

(27)

where subscripts Al and s refer to the Al standard sample and the test sample respectively. Knowing the cross-sectional area \( A \), and the length \( l \), the resistivity of the test sample is given by:

\[ \rho_s = \left( \frac{A}{l} \right) R_s = \left( \frac{A}{l} \right) \left( \frac{V_s}{V_{AI}} \right) R_{AI} \]  

(28)

Since the resistance of the Al standard is constant, and the determination of potential drop accurate to \( \pm 10^{-6} \) \( V \), the current in the resistance measuring circuit could be maintained constant to \( \pm 10^{-5} \) \( A \). By frequently monitoring the voltage drop across the Al standard for constancy, any slight shift in current was immediately detected and corrected by adjusting the current regulated power supply. This procedure enabled the resistivity change during precipitation to be measured to an accuracy of 0.5 to 1%.

(4) X-Ray Diffraction Analysis

X-ray diffraction analysis of the Mg\(_2\)Si precipitate on the bulk alloy was not possible, since the amount of precipitate was not sufficient to give observable diffractions. Therefore, eutectic alloys (Al-13% Mg\(_2\)Si), with and without Be, were prepared for X-ray diffraction analysis. Specimens approximately 10x8x3mm were cut from the eutectic alloy ingots for placing in the specimen holder. The X-ray generator used is a Philips PW 1078 model. The diffractometer technique was employed, with copper K\(_x\) radiation (\( \lambda = 1.542\)A) filtered by Ni (0.02mm thick) and a scanning rate of 2°/min. (29). The
operating voltage and current were set at 40KV and 20mA respectively.
CHAPTER IV RESULTS AND DISCUSSION

1. Age Hardening Behavior of Solution Treated Alloys

Al-0.75%Mg-0.5%Si alloy is age hardenable even at room temperature after solution treatment. Fig. 7 shows the age hardening curves for the Al-0.75%Mg-0.5%Si, Al-0.75%Mg-0.5%Si-0.1%Be and Al-0.75%Mg-0.5%Si-0.2%Ca alloys, when aged at room temperature after solution treatment. Each experimental point represents an average of five points with a typical uncertainty of about ±5%. For the Al-0.75%Mg-0.5%Si alloy, there is an incubation period of about five hours before the onset of rapid hardening. The maximum hardness (Hv67) is reached in about 100 hours after which the hardness remains relatively constant. For the Al-0.75%Mg-0.5%Si-0.1%Be alloy, rapid age hardening takes place almost immediately after solution treatment. The maximum hardness reached is Hv83, about 24% higher than that of Al-0.75%Mg-0.5%Si alloy. The alloy containing 0.2%Ca however, shows no sign of age hardening at room temperature.

Fig. 8 gives the age hardening curves for the three alloys aged at 175°C. For the Al-0.75%Mg-0.5%Si alloy, there is an incubation period of about 100 minutes before the rapid hardening begins. The addition of 0.1%Be to the alloy shortens the incubation period to about 20 minutes, whereas the addition of 0.2%Ca prolongs the incubation period to about 300 minutes.

Fig. 9 shows the aging response for the three alloys aged at 250°C. The curves show a two-stage hardening character.
Fig. 7: HARDINESS VS. LOG(t) AT ROOM TEMP.

- AL-MG-SI-0.1%BE
- AL-MG-SI
- AL-MG-SI-0.2%CA
Fig. 8: HARDNESS VS. LOG(t) AT 175°C

- AL-MG-SI-0.1%BE
- AL-MG-SI
- AL-MG-SI-0.2%CA
Fig. 9: HARDNESS VS. LOG(t) AT 250°C

- □ AL-MG-SI-0.1%BE
- ✫ AL-MG-SI
- ○ AL-MG-SI-0.2%CA
The initial, slow stage of hardening may be associated with the formation of GP zones, while the second, much faster stage of hardening, is presumably related to the precipitation of metastable $\beta'$ phase. Smith [59] has shown that the replacement of GP zones by metastable and partially coherent $\beta'$ increases the strength of the Al-Mg-Si alloy. In both stages the Al-0.75%Mg-0.5%Si-0.1%Be alloy age hardens much faster and reaches a higher maximum hardness level than the Al-0.75%Mg-0.5%Si alloy. The addition of Ca has the opposite effect of Be, i.e., both the rate of hardening and the maximum hardness level attainable is decreased.

When the aging temperature is raised to 300°C (Fig.10), it is again observed that Be-containing alloy age hardens the fastest and reaches a highest hardness level, while the Ca-containing alloy age hardens the slowest and exhibits the lowest maximum hardness level, leaving Al-0.75%Mg-0.5%Si approximately in the middle.

It is noticed that the initial hardness for the Be-containing alloy is higher than the base alloy in Fig.8 and 10, indicating additional solid solution hardening of Be. In Fig.7 and 9 however, due to a possible delay for the quenching of Be-containing alloy, the initial hardness for both alloys are rather close to each other.

In summary, the much faster hardening rate and higher maximum hardness level of Al-0.75%Mg-0.5%Si-0.1%Be alloy when aged between 22°C and 300°C is not due to the independent precipitation of Be from the supersaturated solid solution,
Fig. 10: HARDNESS VS. LOG(t) AT 300 C

VICKERS HARDNESS VALUE
as earlier studies \cite{60,61} pointed out that Al-0.2\%Be alloy hardly showed any hardening when aged at room temperature, 150\°C or 350\°C. Therefore, a more likely explanation seems to be associated with a higher nucleation rate for the precipitation of Be-containing \(\beta\) phase, as will be discussed in details in CHAPTER V. For the Ca-containing alloy, the age hardening is suppressed almost completely at room temperature and to a great extent at 175\°C, 250\°C and 300\°C, which may likewise be attributed to a decreased nucleation rate due to incorporation of Ca into \(\text{Mg}_2\text{Si}\), as will be shown in CHAPTER V as well.

2. Optical and SEM Microscopy

The optical and SEM microscopical analyses were carried out primarily to monitor the microstructural changes accompanying the aging process. The study involved observing and comparing the microstructural changes for the Al-0.75\%Mg-0.5\%Si and Al-0.75\%Mg-0.5\%Si-0.1\%Be alloys aged at 250\°C, following a solution treatment at 560\°C for 60 hours. The cast microstructures for both alloys were also studied and compared.

Fig.11 shows the optical micrographs of the as-cast alloys at low magnification (100x, Keller's etch). The dendrites in Al-0.75\%Mg-0.5\% Si-0.1\%Be alloy is readily seen in Fig.11(a). Due to coring during solidification, the interdendritic liquid becomes richer in solute, resulting in the formation of eutectic phase in the interdendritic regions. The dark
Fig. 11: As-cast microstructures, x100: (a) Al-0.75%Mg-0.5%Si
-0.1%Be alloy; (b) Al-0.75%Mg-0.5%Si alloy.
thread-like structure is primary (eutectic) \( \text{Mg}_2\text{Si} \). The corresponding eutectic Al-rich phase is not evident, having deposited onto the primary Al-rich dendrites. The lighter interdendritic structure is Be precipitate delineating the boundaries of the primary Al-rich dendrites or cells. The dendritic structure of the alloy containing no Be is not as apparent (Fig. 11b), even though the same etchant (Keller’s etch) was applied for a period twice as long. This further points to Be as the more potent core component. Fig. 12, which compares the both alloys at a higher magnification, shows the interdendritic eutectic \( \text{Mg}_2\text{Si} \) (thread-like black phase) in both alloys more clearly, and the interdendritic precipitation in the alloy containing beryllium is more readily visible. In Fig. 13, the microstructures are shown at 500x magnification. Now evident in the Be-containing alloy is a fine precipitate within the grains, which is not present in the alloy containing no Be. The black round spots observed here are probably gas porosities or inclusions. In a study of precipitation in binary Al-Be alloys [34], it was shown that very rapid quench rates are required to retain (excess) Be in solid solution, and in cast structures, where cooling rates are relatively slow, excess Be precipitates within the grain to give a precipitate structure similar to that of Fig. 13(a).

Fig. 14 to Fig. 17 is a series of micrographs showing the sequential progress of age hardening for both alloys when aged at 250\(^\circ\) C. To show the corresponding hardness change accompanying the microstructural change, an indentation is
Fig. 12: As-cast microstructures, x200: (a) Al-0.75%Mg-0.5%Si-0.1%Be alloy; (b) Al-0.75%Mg-0.5%Si alloy.
Fig. 13: As-cast microstructures, x500: (a) Al-0.75%Mg-0.5%Si-0.1%Be; (b) Al-0.75%Mg-0.5%Si.
shown in each micrograph. Fig.14 shows the microstructures after solution treatment at 560°C for 60 hours. Virtually all the Mg₃Si is dissolved in the solid solution. The smaller indentation for the alloy with Be results from Be solid solution hardening [34]. Fig.15 shows the microstructures at aging times corresponding to their respective maximum hardness level. The lack of optically observable precipitation and the smaller indentation size [Fig.15(a)] suggest the hardening in the Be-containing alloy is associated with the submicroscopic precipitates, probably metastable β phase or/and GP zones, whereas in the alloy containing no Be the relatively large precipitate particles indicate precipitation of more equilibrium phases. Fig.16 shows the microstructures when both alloys become over aged. The precipitates in both alloys are clearly visible in this stage. The higher hardness (smaller indentation) of the Be-containing alloy [Fig.16(a)] is associated with the finer precipitate distribution compared with the alloy containing no Be [Fig.16(b)]. The precipitates in both alloys are more readily distinguishable at higher magnification in Fig.17, where it is evident that the alloy containing Be has a significantly higher precipitate particle count. When both alloys are further aged for an additional 4000 minutes, their microstructures are shown in Fig.18. The hardness difference between the two alloys does not disappear as reflected in the significant difference in indentation sizes. A closer examination of the precipitates at 1000x magnification
Fig. 14: Microstructures after solution treatment, x500:

(a) Al-0.75%Mg-0.5%S-0.1%Be; (b) Al-0.75%Mg-0.5%Si.
Fig. 15: Microstructures corresponding to maximum hardness level when aged at 250°C, x500: (a) Al-0.75%Mg-0.5%Si-0.1%Be; (b) Al-0.75%Mg-0.5%Si.
Fig. 16: Microstructures for over-aged alloys (1960 minutes at 250 °C), x500: (a) Al-0.75%Mg-0.5%Si-0.1%Be; (b) Al-0.75%Mg-0.5%Si.
Fig. 17: Microstructures for over-aged alloys (1980 minutes at 250 °C), x1,000: (a) Al-0.75%Mg-0.5%Si-0.1%Be; (b) Al-0.75%Mg-0.5%Si.
Fig. 18: Microstructures for over-aged alloys (6000 minutes at 250°C), x500: (a) Al-0.75%Mg-0.5%Si-0.1%Be; (b) Al-0.75%Mg-0.5%Si.
Fig. 19: Microstructures for over-aged alloys (6000 minutes at 250°C), x1,000: (a) Al-0.75%Mg-0.5%Si-0.1%Be; (b) Al-0.75%Mg-0.5%Si.
[Fig.(19)] again shows definitely much finer and more numerous precipitate particles in the alloy containing Be.

To confirm the much higher density of precipitate particles observed under the optical microscope, the microstructures were further examined under a scanning electron microscope. Fig.20 shows SEM micrographs taken from the same specimens as in Fig.19. The much higher density of equilibrium precipitates in the alloy containing Be is clearly evident.

In summary, a comparative study of the optical and SEM microstructures of Al-0.75%Mg-0.5%Si and Al-0.75%Mg-0.5%Si-0.1%Be alloys in different heat-treated states shows that: (1) Be precipitation is present in the as-cast microstructure for the alloy containing Be; (2) the significantly higher hardness level attained on aging in the Be-containing alloy is associated with the much more numerous and finer precipitate particles; (3) the absence of observable precipitates in the Be-containing alloy when aged to maximum hardness suggests the precipitation of a much finer and therefore submicroscopic metastable phase.

3. Resistivity Measurements and Precipitation Kinetics

Resistivity measurements were carried out to monitor the aging process at room temperature, and five higher temperatures between 225 and 350°C. The fraction of precipitation completed (Y) at time t is given by eqn. (29) (see Jena et al [62]):
Fig. 20: SEM micrographs for over-aged alloys (6000 minutes at 250°C), x4,000: (a) Al-0.75%Mg-0.5%Si-0.1%Be; (b) Al-0.75%Mg-0.5%Si.
\[ Y = \frac{\rho_0 - \rho_t}{\rho_0 - \rho_\infty} \quad (29) \]

where \( \rho_0 \), \( \rho_t \) and \( \rho_\infty \) are the specific resistivities at \( t=0 \), \( t=t \) and \( t=\infty \) (when reaction is completed). The precipitation is assumed to obey Avrami equation,

\[ Y = 1 - \exp \left(-kt^n\right) \quad (23) \]

where \( k \) and \( n \) are parameters dependent on nucleation rate and growth mechanism, respectively. Rewriting eqn. (23), we have:

\[
\frac{1}{1-Y} = \exp(kt^n)
\]

or

\[
\ln(1/(1-Y)) = kt^n
\]

so that

\[ \log(\ln(1/(1-Y))) = \log k + n\log t \quad (30) \]

According to eqn. (30), if we plot \( \log(\ln(1/(1-Y))) \) against \( \log t \), we should get a straight line, whose slope is the parameter \( n \) and intercept at \( \log(\ln(1/(1-Y))) \) axis gives \( \log k \).

Fig. 21 shows the specific resistivity versus time plots for specimens aged at room temperature. The alloy containing Be shows a slight increase in resistivity within the first 100 hours, and remains constant thereafter. This slight increase in resistivity, which is characteristic of clustering and GP zone formation in the alloy [63], is in agreement with the considerable age hardening at room temperature (see Fig. 7) for the alloy. The resistivity for the alloy without Be addition, however, remains relatively constant, suggesting a much weaker tendency of clustering and
Fig. 21: RESISTIVITY VS. TIME (ROOM TEMP.)

SPECIFIC RESISTIVITY

TIME, hr.

AL-MG-SI

AL-MG-SI-0.1%BE
GP zone formation, which are responsible for natural age hardening in the alloy.

Aging at higher temperatures (225°C - 350°C) produce essentially similar resistivity/time curves: a monotonic decrease of resistivity with aging time. These plots are shown in Fig.22 to Fig.26. A common feature to these plots is the much faster resistivity decrease (during initial stage), and shorter time required to reach \( \rho_{\infty} \) for the alloy containing Be. These plots are then transformed to \( Y \) versus \( t \) plots, using equation (29). Fig.27 and Fig.28 are two typical plots, which show the much faster transformation rate (\( dY/dt \)) during the initial stage of the transformation for the alloy containing Be. Since the rate of transformation for precipitation is exponentially dependent on temperature, the Arrhenius plot of \( \ln(dY/dt)_{Y=1/2} \) versus \( 1/T \), or \( \ln(t)_{Y=1/2} \) versus \( 1/T \) should be a straight line, whose slope is \( (-Q/R) \) or \( Q/R \) respectively, where \( Q \) is the activation energy for the precipitation process. Fig.29 and Fig.30 show both ways of determining the activation energy for the alloys, and the values of activation energy so obtained are tabulated in Table 1.

It is seen from Table 1 that the values of activation energy obtained in both methods agree with each other reasonably well, and the difference between the two alloys is not significant, considering the experimental errors.
Fig. 22 - RESISTIVITY vs. TIME (T=225°C)
Fig. 24 - RESISTIVITY VS. TIME (T=275°C)

SPECIFIC RESISTIVITY
(μΩ mm)

TIME, min.

AL-MG-SI

AL-MG-SI-0.1%BE
Fig. 25 - RESISTIVITY VS. TIME (T=300 °C)

SPECIFIC RESISTIVITY ($\mu\Omega \text{mm}$)

TIME, min.

AL-MG-SI
AL-MG-SI-0.1%BE
Fig. 26 - RESISTIVITY VS. TIME (T=350 °C)

SPECIFIC RESISTIVITY (µΩ·mm)

TIME, min.

[Graph showing specific resistivity vs. time for AL-MG-SI and AL-MG-SI-0.1%BE]
Fig. 27 - Y vs. t Plot (T=275°C)

Y-FRACTION TRANSFORMED (%)

- AL-MG-SI
- AL-MG-SI-0.1%BE
Fig. 29: Ln(dy/dt) VS. 10000/T(K) PLOTS

\[\ln \left(\frac{dy}{dt}\right)_{T=0}\]

- AL-MG-SI
- AL-MG-SI-0.1%BE
<table>
<thead>
<tr>
<th>METHOD</th>
<th>Al-Mg-Si</th>
<th>Al-Mg-Si-0.1%Be</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ln(dY/dt)\text{\textsubscript{1/2}} vs. 1/T</td>
<td>61.0 ± 5.3 KJ</td>
<td>70.6 ± 6.1 KJ</td>
</tr>
<tr>
<td>Ln(t)\text{\textsubscript{1/2}} vs. 1/T</td>
<td>64.2 ± 6.3 KJ</td>
<td>66.0 ± 6.6 KJ</td>
</tr>
</tbody>
</table>

Table 1: Activation Energies Obtained from Arrhenius Plots

Fig. 31 to Fig. 33 show the typical Log(Ln[1/(1-Y)]) versus Log(t) plots. For T=250 °C (Fig. 31), the plots are distinctly composed of two straight-line segments, which presumably represent \( \beta' \) and \( \beta \) precipitation respectively. However, as the temperature rises, this feature gradually fades (Fig. 32), and at T=300 °C (Fig. 33), no such distinction is recognizable. This is because at higher temperatures, the formation and dissolution of metastable phases is too fast to be observed. Since not enough data points are available for the initial (\( \beta' \)) stage of transformation, the determination of Avrami parameters \( n \) and \( k \) are carried out only for the latter (\( \beta \)) stage of precipitation. Table 2 summarizes the values of \( n \) and \( k \) obtained from the slopes and intercepts of the plots (\( \beta \) stage) in Fig. 31 and Fig. 33.

From Table 2, we can see that growth constant \( n \) is not significantly different between the two alloys and is relatively independent of temperature, while \( k \) value for the alloy containing 0.1%Be is significantly higher (2 to 3 times) compared to the \( k \) value for the alloy without Be addition.
Fig. 32 - \( \log \left( \frac{1}{1-Y} \right) \) vs. \( \log(t) \), \( T=275^\circ C \)
Fig. 33 - LOG(\text{In}[1/(1-Y)]) VS. \text{LOG}(t), T=300^\circ C
and in both cases $k$ is extremely sensitive to temperature, due to its dependence on diffusion coefficient [see eqn. (24)].

<table>
<thead>
<tr>
<th>$T=250^\circ$C</th>
<th>$T=300^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>$n$</td>
</tr>
<tr>
<td>$0.83 \pm 0.06$</td>
<td>$0.78 \pm 0.05$</td>
</tr>
<tr>
<td>$k$</td>
<td>$k$</td>
</tr>
<tr>
<td>$0.038 \pm 0.009$</td>
<td>$0.122 \pm 0.013$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$n$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.74 \pm 0.04$</td>
<td>$0.081 \pm 0.013$</td>
</tr>
<tr>
<td>$0.67 \pm 0.04$</td>
<td>$0.332 \pm 0.029$</td>
</tr>
</tbody>
</table>

Table 2: Avrami Parameters ($n,k$) for $\beta$ Precipitation

Fig. 34 shows the straight-line Arrhenius plot for $\ln k$ vs. $1/T$. The $k$ parameter for the beryllium-containing alloy is consistently much higher than that for the alloy without Be. Since $k$ is related to the nuclei density by equation (24), the higher $k$ value for the Be-containing alloy suggests a higher nucleation rate for the precipitation in this alloy, which is consistent with a Be-enhanced nucleation entropy to be discussed in CHAPTER V.

4. X-Ray Diffraction Results

The X-ray diffraction results for Al-13%Mg$_2$Si (eutectic) are compared against the results obtained for Al-13%Mg$_2$Si-
Fig. 34 - $\ln(k)$ vs. $10000/T(K)$ Plot

- $\ln(k)$
- $10000/T(K)$
- AL-MG-SI
- AL-MG-SI-0.1%BE
0.6% Be alloy. In both alloys, two sets of diffraction peaks, corresponding to Al and Mg$_2$Si respectively, are identified.

In Table 3, the 2θ positions and intensities (arbitrary unit) of Al-13%Mg$_2$Si and Al-13%Mg$_2$Si are shown:

<table>
<thead>
<tr>
<th>Reflection</th>
<th>Al-13%Mg$_2$Si</th>
<th>Al-13%Mg$_2$Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ (°)</td>
<td>I (arbitrary unit)</td>
<td>2θ (°)</td>
</tr>
<tr>
<td>Al(100%)</td>
<td>38.45 : 7.62 : 38.48 : 7.63 : 1</td>
<td></td>
</tr>
<tr>
<td>Mg$_2$Si(100%)</td>
<td>39.95 : 4.90 : 39.98 : 3.49 : 1.40 : 0</td>
<td></td>
</tr>
<tr>
<td>Mg$_2$Si(40%)</td>
<td>72.70 : 1.27 : 72.75 : 0.86 : 1.48 : +0.02</td>
<td></td>
</tr>
<tr>
<td>Mg$_2$Si(20%)</td>
<td>57.85 : 0.75 : 57.90 : 0.58 : 1.29 : +0.02</td>
<td></td>
</tr>
<tr>
<td>Mg$_2$Si(9%)</td>
<td>99.98 : 0.44 : 100.00 : 0.28 : 1.57 : -0.01</td>
<td></td>
</tr>
<tr>
<td>Mg$_2$Si(8%)</td>
<td>86.40 : 0.34 : 86.40 : 0.20 : 1.70 : -0.03</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Comparison of Principal Reflections in Two Alloys

of several principal reflections for both alloys are compared with each other.

It is noticed that the intensities of Mg$_2$Si reflections in the alloy containing Be are significantly lower (ranging from about 30% to 70%) than those in the alloy without Be. The
same intensity of Al reflections in both alloys precludes the possibility of specimen size effects, etc. It is assumed that the lower diffraction peak for the Mg$_2$Si phase in the alloy containing Be is attributed to a higher scattering effect due to the incorporation of Be into the interstitial sites of Mg$_2$Si lattice (see appendix 1 for details).

2θ shifts of Mg$_2$Si peaks between the two alloys, measured relative to the respective strongest Al reflection peak to eliminate any possible changes of 2θ due to misalignment and the mounting procedure, are extremely small and uncertain and are therefore presumed to be experimental errors.
CHAPTER V COMPARISON OF NUCLEATION RATES

1. Calculation of Nucleation Entropy

(1) Al-0.75% Mg-0.5% Si Alloy

The procedure used to calculate the nucleation entropy for precipitation in solid alloys is similar to that for primary phase nucleation in liquid alloys, except that the solidification reaction is replaced by the appropriate solid state transformation, and the corresponding entropy change calculated or estimated. Table 4 shows the reaction sequence.

\[
\begin{align*}
\text{Reaction} & \quad \Delta S, \text{ JK mol}^{-1} \\
(1a) & \quad 3(\text{Mg-33.3\% Si})^{R_2}\text{(s)} = 2\text{Mg(s)} + \text{Si(s)} & -15.8 \\
(2a) & \quad 2\text{Mg(s)} + \text{Si(s)} = \text{Mg}_2\text{Si(s)} & -10.1 \\
(3a) & \quad \infty(\text{Al-83\% Mg-48\% Si})^{R_3}\text{(s)} = 3(\text{Mg-33.3\% Si})^{R_2}\text{(s)} + \\
& \quad \infty(\text{Al-83\% Mg-48\% Si})^{R_3}\text{(s)} & -108.1 \\
(4a) & \quad \infty(\text{Al-83\% Mg-48\% Si})^{R_3}\text{(s)} = \text{Mg}_2\text{Si(s)} + \\
& \quad \infty(\text{Al-83\% Mg-48\% Si})^{R_3}\text{(s)} & -134.0
\end{align*}
\]

Table 4: Reaction Sequence for Calculating Molar Nucleation Entropy for Mg2Si at 250°C

Table 4 is designed to calculate the molar entropy of nucleation of Mg2Si from Al-0.75% Mg-0.5% Si alloy at 250°C. Note that the concentrations in Table 4 are all in atomic percent.

The (reverse) formation of 1 mole (3 g-atom) of regular solid solution of Mg-33.3% Si alloy is given by reaction (1a) in Table 4, for which the entropy change (-15.8 JK mol\(^{-1}\)) is
calculated using equation (31):
\[ \Delta S = -R(N_{\text{g}}\text{LnN}_{\text{g}} + N_{\text{t}}\text{LnN}_{\text{t}}) \]  
(31)

Reaction (2a) is the formation of 1 mole of Mg$_2$Si, for which the formation entropy ($-10.1 \text{JK}^{-1} \text{mol}^{-1}$) is calculated using the available thermodynamic data (see appendix 2 for details).

Reaction (3a) is the nucleation reaction by which 1 mole of regular solid solution of Mg-33.3%Si is formed or precipitated from an infinite amount of regular solid solution of Al-0.83%Mg-0.48%Si. The entropy change ($-108.1 \text{JK}^{-1} \text{mol}^{-1}$) for this reaction is calculated using equations analogous to eqns. (18) to (20), except that the liquid phase is now replaced by the supersaturated solid solution.

Reaction (4a) is obtained by adding reactions (1a) to (3a) which gives the nucleation reaction and corresponding nucleation entropy ($-134.0 \text{JK}^{-1} \text{mol}^{-1}$) for the precipitation of one mole of real Mg$_2$Si from a regular behaving supersaturated solid solution of Al-0.83%Mg-0.48%Si at the aging temperature of 250°C.

The determination of the nucleation entropy of Mg$_2$Si from the real solid solution alloy requires appropriate thermodynamic information for the latter, which is not available. However, since the difference in molar entropies of mixing for regular and real solutions is small for dilute alloys (both converge and become zero at infinite dilution), the difference in the molar entropy for nucleation of Mg$_2$Si, in real vs. regular solid solution will be negligible for the
dilute solute concentrations in the present alloy \( N_{Mg} = 0.0083, \)
\( N_{Si} = 0.0048 \).

\[(2) Al^0.75Mg^0.5Si^0.1Be \text{ Alloy} \]

Since Be is not known to form any compound with Mg or Si, it is unlikely that Be would replace Mg or Si in Mg\(_2\)Si to form a \((Mg,Be)_{2}Si\) or \(Mg_{2}(Si,Be)\)-type compound. The energy dispersive analysis (performed on a Kevex 5100 spectrometer coupled to the SEM) shows that the atomic ratio Mg/Si is relatively constant (~2) for the Mg\(_2\)Si phase in the eutectic alloy with and without Be. This indicates that Be is not replacing either Mg or Si in the Mg\(_2\)Si phase. However, Be can be accommodated as an interstitial atom in the compound. It is shown in Appendix 1 that each unit cell of Mg\(_2\)Si (FCC, Cl type) is capable of accommodating one Be atom in its body center. Assuming this occurs, and since there are eight Mg atoms and four Si atoms in the unit cell, the atomic ratio for the Be-containing Mg\(_2\)Si phase becomes: Mg:Si:Be = 8:4:1 = 2:1:0.25. Thus a ternary compound having the plausible stoichiometric formula Mg\(_2\)SiBe\(_{0.25}\) is possible. Table 5 gives the appropriate reactions and sequence for calculating its molar nucleation entropy.

Note that the Be concentration in the solid solution alloy is determined from the solvus line in Al-Be phase diagram at the solution treatment temperature (560\(^{\circ}\)C). The procedure for calculating the nucleation entropy in Table 5 is essentially identical to that performed for the Mg\(_2\)Si compound, except
Reactions

\( \Delta S, \text{JK}^1 \text{mol}^{-1} \)

(1b) \( 3.25(\text{Mg}-30.77\%\text{Si}-7.69\%\text{Be}) \)\( ^s \) = \( 2\text{Mg} + \text{Si} + 0.25\text{Be} \) \( -23.2 \)

(2b) \( 2\text{Mg} + 0.25\text{Be} = 2.25(\text{Mg}-11.11\%\text{Be}) \)\( ^s \)

(3b) \( 2.25(\text{Mg}-11.11\%\text{Be}) \)\( ^s \) + \( \text{Si} = \text{Mg}_2\text{SiBe}_{1.5} \)

(4b) \( \infty(\text{Al}-0.83\%\text{Mg}-48\%\text{Si}-0.67\%\text{Be}) \)\( ^s \) = \( 3.25(\text{Mg}-30.77\%\text{Si}-7.69\%\text{Be}) \)\( ^s \) + \( \infty(\text{Al}-0.83\%\text{Mg}-48\%\text{Si}-0.67\%\text{Be}) \)\( ^s \)

\( \textbf{-116.0} \)

(5b) \( \infty(\text{Al}-0.83\%\text{Mg}-48\%\text{Si}-0.67\%\text{Be}) \)\( ^s \) = \( \text{Mg}_2\text{SiBe}_{1.5} \) + \( \infty(\text{Al}-0.83\%\text{Mg}-48\%\text{Si}-0.67\%\text{Be}) \)\( ^s \)

\( \textbf{-142.8} \)

Table 5: Reaction Sequence for Calculating Molar Nucleation Entropy for \( \text{Mg}_2\text{SiBe}_{1.5} \) at 250°C

The reaction sequence is used to calculate the molar nucleation entropy for the \( \text{Mg}_2\text{SiBe}_{1.5} \) phase. Each step in the sequence is assumed to have a negligible entropy change, allowing the calculation of the total entropy change.

Table 5 includes the following reactions:

(1) \( \text{Mg} + \text{Si} + 0.25\text{Be} \) \( \rightarrow \) \( \text{Mg}_2\text{SiBe}_{1.5} \)

(2) \( 2\text{Mg} + 0.25\text{Be} \) \( \rightarrow \) \( 2.25(\text{Mg}-11.11\%\text{Be}) \)

(3) \( 2.25(\text{Mg}-11.11\%\text{Be}) + \text{Si} \) \( \rightarrow \) \( \text{Mg}_2\text{SiBe}_{1.5} \)

(4) \( \infty(\text{Al}-0.83\%\text{Mg}-48\%\text{Si}-0.67\%\text{Be}) \) \( \rightarrow \) \( 3.25(\text{Mg}-30.77\%\text{Si}-7.69\%\text{Be}) \) + \( \infty(\text{Al}-0.83\%\text{Mg}-48\%\text{Si}-0.67\%\text{Be}) \)

(5) \( \infty(\text{Al}-0.83\%\text{Mg}-48\%\text{Si}-0.67\%\text{Be}) + \) \( \text{Mg}_2\text{SiBe}_{1.5} \) \( \rightarrow \) \( \infty(\text{Al}-0.83\%\text{Mg}-48\%\text{Si}-0.67\%\text{Be}) \)

The reaction sequence is used to calculate the molar nucleation entropy for the \( \text{Mg}_2\text{SiBe}_{1.5} \) phase. Each step in the sequence is assumed to have a negligible entropy change, allowing the calculation of the total entropy change.

It is noted that the approximately \( 8.8\text{JK}^1 \text{mol}^{-1} \) increase in the molar nucleation entropy derives mostly from the Be contribution to the mixing entropy [cf. reactions (3a) and (4b)], which is not altered by errors introduced in the above approximations.
(3) Al-0.75%Mg-0.5%Si-0.2%Ca Alloy

Ca is very similar to Mg in both chemical behavior and atomic size. Calcium combines with silicon to form a compound Ca₂Si, similar to Mg₂Si in crystal structure (both FCC). Therefore, it is natural to assume that Ca might replace a small fraction of Mg in Mg₂Si to form a (Mg,Ca)₂Si type compound in the alloy containing Ca. Table 6 gives the appropriate reactions and sequence for calculating the molar nucleation entropy of Mg₀.₆₃Ca₀.₃₇Si, assuming that up to 10% of the Mg is replaced by Ca.

Reaction

\[
\begin{align*}
(1c) & \quad 3(Mg_{33.33\%}Si_{66.66\%}Ca_{2}\%)(s) = 1.8Mg+0.2Ca+Si \\
(2c) & \quad 1.8Mg + 0.2Ca = 2(Mg_{10\%}Ca_{90\%})(s) \\
(3c) & \quad 2(Mg_{10\%}Ca_{90\%})(s) + Si = Mg_{0.5}Ca_{2.5}Si \\
(4c) & \quad \infty(Al_{-83\%}Mg_{-48\%}Si_{-296\%}Ca_{2\%})(s) = 3(Mg_{33.33\%}Si_{-66.66\%}Ca_{2\%})(s) + \infty(Al_{-83\%}Mg_{-48\%}Si_{-296\%}Ca_{2\%})(s) \\
\end{align*}
\]

\[\Delta S, \text{JK}^\text{mol}^{-1}\]

-21.3

+5.4

-10.1

-104.4

\[
(5c) \quad \infty(Al_{-83\%}Mg_{-48\%}Si_{-296\%}Ca_{2\%})(s) = Mg_{0.5}Ca_{2.5}Si + \\
\infty(Al_{-83\%}Mg_{-48\%}Si_{-296\%}Ca_{2\%})(s) \quad -130.4
\]

Table 6: Reaction Sequence for Calculating Molar Nucleation Entropy of Mg₀.₆₃Ca₀.₃₇Si at 250°C

It is seen from Table 6 that the approximately 3.6JK^\text{mol}^{-1} or 2.7% decrease (in magnitude) of molar nucleation entropy [comparing (5c) with (4a)] derives mostly from the loss of mixing entropy in (4c) [compared with 3(a)], due to the
replacement of Mg by Ca, which contributes less than the former to the mixing entropy.

2. Estimate of Interfacial Energy

According to the LSW theory of diffusion-controlled coarsening [56, 57], the average content of solute, C, in the matrix varies asymptotically with time (t) as

\[ C = C_e + \left(\frac{k}{\gamma C_0 V_n}\right)^{1/3} \]  

(25)

where \( k \) is the rate constant given by:

\[ k = \frac{D(RT)^2}{(9 \gamma C_0 V_n)} \]  

(26)

In equation (26), \( V_n \) is the molar volume of the precipitate, \( D \) the diffusion constant and \( \gamma \) the interfacial energy. The value of \( C_e \) corresponds to the solute content in the Al matrix in equilibrium with the precipitate of infinite size, which is determined by the phase diagram.

In the present investigation, the electrical resistivity of Al-1.2%Mg₂Si and Al-1.2%Mg₂Si-0.1%Be alloys was measured at isothermal aging times at 250°C. Since the resistivity of the dilute solid solution alloy is linearly proportional to the solute content [64, 65], the time variation of resistivity obtained was readily transformed into the time variation of the average solute content in the Al matrix, caused by the coarsening of precipitates. A linear relationship between \( C \) and \( t^{1/3} \) (Fig. 35) which occurred only after an initial period of 15 minutes, suggests that the coarsening of precipitates had happened very fast because of small interparticle spacing. The slopes of the plots in Fig. 35 yield values for \( k \), and
Fig. 35: \( C \left(10^4 \text{ mol/cm}^3\right) \) VS. \([t(\text{min.})]^{1/3}\)
therefore the interfacial energy can be obtained by inserting values of the other parameters in equation (26). The diffusion constant for Si in Al is given by [66]:

\[ D_{\text{Si}}^{\text{Al}}(\text{cm}^2/\text{sec.}) = 1.25 \times 10^{-7} \exp[-1.28 \times 10^4 J/\text{kT}] \]

At \( T = 250^\circ C \), \( D_{\text{Si}}^{\text{Al}} = 2.427 \times 10^{-15} \text{ cm}^2/\text{sec.} \).

The diffusion constant for Mg in Al is given by [67]:

\[ D_{\text{Mg}}^{\text{Al}}(\text{cm}^2/\text{sec.}) = 1.24 \exp[1.302 \times 10^5 J/\text{RT}] \]

At \( T = 250^\circ C \), \( D_{\text{Mg}}^{\text{Al}} = 1.19 \times 10^{-13} \text{ cm}^2/\text{sec.} \).

Since the diffusion of Si in Al is relatively slower and therefore rate-controlling, \( D_{\text{Si}}^{\text{Al}} = 2.427 \times 10^{-15} \text{ cm}^2/\text{sec.} \) is used for calculating the interfacial energy.

The value of \( C_c (=0.703 \times 10^4 \text{ mol cm}^{-3}) \) is determined from Al-Mg Si quasi-binary phase diagram (see Fig.2), and is assumed to be the same for both alloys. The molar volume (=39.29 cm\(^3\)) is calculated from the lattice parameter of Mg\(_2\)Si.

Rewriting (26) gives:

\[ \gamma = (RT/3C_c)[D/(kV_m)]^{1/2} \]  \hspace{1cm} (32)

For Al-1.2%Mg\(_2\)Si, the slope of the corresponding plot in Fig.34 gives:

\[ k^{1/3} = 8.11 \times 10^4 \text{ mol cm}^{-3} \text{ min}^{-1/3} \] or \( k = 1.875 \times 10^9 \text{ mol}^{-3} \text{ cm}^{-2} \text{ min}^{-1} \)

Substituting the values of \( k \), \( V_m \), \( D \) and \( C_c \) into eqn. (32) yields:

\[ \gamma = 2.90 \times 10^5 \text{ J/cm}^2 \]

For Al-1.2%Mg\(_2\)Si-0.1%Be alloy, the corresponding slope in Fig.34 gives:

\[ k^{1/3} = 6.77 \times 10^4 \text{ mol cm}^{-3} \text{ min}^{-1/3} \] or \( k = 3.223 \times 10^9 \text{ mol}^{-3} \text{ cm}^{-2} \text{ min}^{-1} \) and the values for the other parameters are the same, so that we
obtain:
\[ \gamma = 2.21 \times 10^5 \text{ J/cm}^2 \]

It should be pointed out that, although the studies of the change of concentration of solute in the matrix during coarsening can be used to derive quantitative information about the particle-matrix interfacial energy [65], this method involves uncertainties in the exact values of \( C_0 \) and \( D \), which makes the obtained values of interfacial energy only an approximate estimate.

3. Calculation of \( \Delta G^* \) and Comparison of Nucleation Rates

For precipitation of equilibrium \( \beta \), which is incoherent with the matrix [68], equation (13) [refer to CHAPTER II, 4-(3)-(a) for details] is used to calculate the free energy of formation of a critical-sized spherical nucleus (\( \Delta G^* \)):

\[
\Delta G^* = 8 \pi \mu^2 (\Delta V/V)^2 / [3(\Delta S_v)(\Delta T) \gamma] \quad (13)
\]

This equation has incorporated the strain energy associated with the transformation. The fractional volume change (\( \Delta V/V \)) is calculated from the difference in gram-atomic volume:

\[
\Delta V/V = [V_m(Mg_2Si)/3 - V_m(Al)]/V_m(Al)
= (39.29/3 - 9.99)/9.99 = 0.311
\]

The shear modulus of the Al matrix (\( \mu_m \)) at 250°C is assumed to be 10% of its room temperature value of 2.85x10^6 J/cm^2 [69], i.e., \( \mu_m(T=250°C) = 2.85 \times 10^6 \text{ J/cm}^2 \), since at \( T=250°C \), the relaxation processes will be operative[70] to drastically decrease the elastic constants. The difference in \( \Delta G^* \) for the
alloys derives primarily from two sources: (i) difference in nucleation entropy $\Delta S_V$ and, (ii) difference in interfacial energy $\gamma$. The difference in $\Delta G^*$ arising from both sources are estimated separately and the corresponding relative nucleation rates are given in Table 7 and 8.

Table 7 shows the effect of $\Delta S_V$ on the relative nucleation rates for the alloys aged at 523K, assuming the same interfacial energy in each case.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\gamma$ (J cm$^{-2}$)</th>
<th>$\Delta S_V$ (JK$^{-1}$ cm$^{-3}$)</th>
<th>$\Delta G^*$ (J)</th>
<th>N(Mg$_2$SiBe$_x$) / N(Mg$_2$Si)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$Si</td>
<td>2.9x10$^5$</td>
<td>-3.41</td>
<td>1.84x10$^{10}$</td>
<td>293</td>
</tr>
<tr>
<td>Mg$_2$SiBe$_x$</td>
<td>2.9x10$^5$</td>
<td>-3.63</td>
<td>1.43x10$^{10}$</td>
<td>N(Mg$_2$Ca$_x$Si) / N(Mg$_2$Si)</td>
</tr>
<tr>
<td>Mg$_2$Ca$_x$Si</td>
<td>2.9x10$^5$</td>
<td>-3.32</td>
<td>2.05x10$^{10}$</td>
<td>0.054</td>
</tr>
</tbody>
</table>

Table 7: Effect of $\Delta S_V$ on Relative Nucleation Rates

Table 8 shows the effect of $\gamma$ on the relative nucleation rate, assuming the same $\Delta S_V$ in each case.

The calculated relative nucleation rates in Table 7 appear to have more reasonable values than that in Table 8. Since the determination of $\gamma$ involves some uncertainties, the actual difference in $\gamma$ may not be as large as in Table 8, and the corresponding relative nucleation rate could be much smaller than that in Table 8. Therefore, it is still
Phase : $\gamma$ (J cm$^{-2}$) : $\Delta S_\gamma$ (JK$^{-1}$ cm$^{-3}$) : $\Delta G^\circ$ (J) : $\ln(\text{Mg}_2\text{SiBe}) / \ln(\text{Mg}_2\text{Si})$

\[
\begin{array}{cccc}
\text{Mg}_2\text{Si} & 2.9\times10^5 & -3.414 & 1.835\times10^5 \\
\text{Mg}_2\text{SiBe}_y & 2.2\times10^5 & -3.414 & 8.122\times10^4 \\
\end{array}
\]

Table 8: Effect of $\gamma$ on Relative Nucleation Rate

difficult to tell which factor, $\gamma$ or $\Delta S_\gamma$, is playing a dominant role in increasing or decreasing the nucleation rate. Possibly, it is the combined effect of both $\gamma$ and $\Delta S$ that is contributing to the significant change in the nucleation rate.

In the present determination of interfacial energy, the errors derive mostly from the uncertainties in $D$ and $C_e$, which can be avoided by studying the time variation of both solute content and average particle size concurrently. The latter method enables the determination of interfacial energy independent of either $D$ or $C_e$. 

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CHAPTER VI CONCLUSIONS AND RECOMMENDATIONS

1. Conclusions

The following conclusions are drawn from the results of this investigation:

(1) Addition of 0.1%Be to the Al-0.75%Mg-0.5%Si alloy significantly increases the hardening rate and the maximum hardness level of the alloy following solution and aging treatments.

(2) Addition of 0.1%Be to the Al-Mg-Si alloy greatly enhances the density of precipitates after aging, as evident in both optical and SEM microscopical observation.

(3) Addition of 0.1%Be to the Al-Mg-Si alloy significantly increases the transformation kinetics via the nucleation stage, as reflected in an considerable increase in the "k" parameter (in Avrami equation). The growth constant and activation energy remain relatively constant.

(4) The higher precipitate particle count and "k" value (related to nuclei density) for the alloy containing Be is consistent with a higher nucleation entropy (magnitude) for the Mg$_2$Si precipitate containing Be, and a possible decrease in interfacial energy (estimated from resistivity and diffusion data).

(5) The opposite role of Ca (decreasing hardening rate and maximum hardness level) is also consistent with a smaller nucleation entropy (magnitude) for the Mg$_2$Si precipitate containing Ca.
2. Recommendations for Future Research

(1) It is recommended that transmission electron microscopy techniques be employed to directly observe and compare the GP zone and metastable phase formation in the alloys with and without Be.

(2) Determination of the ternary compound composition by energy dispersive spectrometer is not possible because of the extremely low atomic number of Be. It is suggested that more sophisticated techniques, such as ion probe and Auger electron spectroscopy be employed to determine the Be content in the ternary compound.

(3) Although certain correlations do exist between the value of the growth constant (n) and the precipitate growth mode (spherical, disc-like or rod-like) [4] in some alloy systems, further research is needed to establish such correlation in the specific Al-Mg$_2$Si alloy system, in order to have a deeper understanding of the precipitation process in the system.
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APPENDIX I

The crystal structure of Mg₂Si (FCC, C1 type) is analogous to that of CaF₂, shown in Fig. 36, with Mg occupying the positions of the small shaded spheres and Si occupying the large open circles. Within the Mg₂Si unit cell, there are eight Mg atoms occupying the corners of an internal simple cubic of side a/2, having an interstice in its body center.

The diameter (D) of the interstice is calculated as follows:

\[ D + 2R_{Mg} = \sqrt[3]{a} \frac{a}{2} \]

or

\[ D = \sqrt[3]{a} \frac{a}{2} - 2R_{Mg} \]

where \( R_{Mg} \) is the atomic radius of Mg.

From reference [71]:

\[ a = 6.351 \ \text{Å} \]
\[ 2R_{Mg} = 3.197 \ \text{Å} \]

so that

\[ D = (\sqrt[3]{a}/2) \times 6.351 - 3.197 \]
\[ = 2.303 \ \text{Å} \]

Also from reference [71], the diameter of Be atom is
2.226 Å at room temperature (α-Be), and is 2.209 Å at higher temperatures (β-Be). In both cases, the atomic size of Be is small enough to fit in with the interstice existing in the body center of the Mg_Si unit cell.
APPENDIX II

The formation entropy of Mg Si at 250 °C (=523K) is calculated as follows:

\[ \Delta S(523K) = \Delta S(298K) + \int_{298K}^{523K} \Delta C_p d\ln T \]  

(33)

The value of \( \Delta S(298K) = -8.05 \text{ J/K/mol} \) is obtained from reference [72], which also agrees with reference [73].

P. Dorner et al [74] gives:

\[ C_p(\text{Mg}_2\text{Si}) = 23 + 0.007(T - 300) \]  

[J/g-atomK]

Reference [73] gives:

\[ C_p(\text{Mg}) = 5.33 + (2.45 \times 10^3) T - 0.403 \times 10^5 / T^2 \]  

[cal/g-atomK]

\[ C_p(\text{Si}) = 5.7 + (1.02 \times 10^3) T - 1.06 \times 10^5 / T^2 \]  

[cal/g-atomK]

so that \( \Delta C_p = 3C_p(\text{Mg}_2\text{Si}) - 2C_p(\text{Mg}) - C_p(\text{Si}) \)

\[ = 3[23 + 0.007(T - 300)] - 2[5.33 + (2.45 \times 10^3) T - 0.403 \times 10^5 / T^2] \times 4.184 - [5.7 + (1.02 \times 10^3) T - 1.06 \times 10^5 / T^2] \times 4.184 \]  

[J/Kmol]

\[ \Delta C_p = -5.75 - 3.77 \times 10^3 T + 5.3 \times 10^5 / T^2 \]  

[J/Kmol]  

(34)

Substituting eqn. (34) and value of \( \Delta S(298K) = -8.05 \text{ J/K/mol} \)

into eqn. (33) gives:

\[ S(523K) = -8.05 + \int_{298K}^{523K} (-5.75 / T - 3.77 \times 10^3 + 5.3 \times 10^5 / T^3) dT \]  

[J/Kmol]

\[ = -10.11 \]  

[J/Kmol]
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