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Solubility of beryllium in pseudobinary aluminum-magnesium(2)silicide.

Ali. Hatab
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SOLUBILITY OF BERYLLIUM IN PSEUDOBINARY
Al-Mg₂Si

by
Ali Hatab

A Thesis
Submitted to the Faculty of Graduate Studies and Research
Through the Department of Mechanical Engineering
Materials Science Group
in Partial Fulfilment
of the Requirements for the Degree of
Master of Applied Science
at the University of Windsor

Windsor, Ontario, Canada
1992
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ABSTRACT

The Al-Mg-Si system is the basis of a major class of heat treatable alloys used for both wrought and cast products. Several heat treatable alloys exhibit age hardening at room temperature after a solution treatment (natural aging), and this property is exploited to develop the mechanical properties of the alloy. The active precipitate in the natural age hardening Al-Mg-Si alloys is Mg₂Si, but the precipitation is sluggish and its acceleration would be beneficial.

In a previous investigation, it was shown that Be microadditions to an Al-0.75%Mg-0.50%Si alloy significantly enhances the age hardening response of the alloy, which is associated with a refinement of the Mg₂Si precipitate. A study of the precipitation kinetics showed this is due to a Be-enhanced nucleation rate. It can be shown that the nucleation rate increases with the nucleation entropy of the precipitating compound (Mg₂Si), which can be effected by the concentration of the Be in the precipitate compound, or by restricting solubilities of the precipitate's components in the Al solid solution.

This study was undertaken to determine the extent to which Be can be incorporated into Mg₂Si, and its effects on the solubility of Mg and Si in Al(α). Direct spectroscopic analysis of Be using EDS is not possible due to the low atomic number of Be, and consequently the Be content must be inferred from the combined results using several techniques. In this study, the solubility determination was made using energy dispersive spectroscopy (for Al, Mg, Si), wavelength dispersive spectroscopy (for Be).
ray diffraction, and optical microscopy coupled with microhardness. From the X-ray diffraction results, it is estimated that Be decreases the solubility of Mg$_2$Si in Al(α) up to about 0.3 at.% at 550°C, and up to about 4.8 at.% Be may be incorporated into Mg$_2$Si compound.
To my blessed children, Isra and Ahmed
ACKNOWLEDGEMENTS

The author would like to take this opportunity to express his sincere gratitude to his advisor Dr. W.V. Youdelis for his advice, guidance, supervision, and encouragement throughout this investigation.

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Chapter 1

INTRODUCTION

The heat treatable Al-Mg-Si alloys, such as 6061, find a wide range of application in heavy duty structures where corrosion resistance is needed; e.g., for truck and marine structures, rolling stock, bridge railing, and hydraulic tubing. Most of heat treatable alloys exhibit age hardening at room temperature after quenching to develop the mechanical properties of the heat treated alloys. Age hardening in Al-Mg-Si alloys is due to GP zone formation and subsequent $\beta'$ (metastable Mg$_2$Si) precipitation. Although the GP zones are coherent with the matrix, coherency strains are low. The hardening effect appears to be due primarily to the higher modulus of $\beta$(Mg$_2$Si) phase relative to that of the Al matrix, which increases the resistance to dislocation motion and the alloy’s shear strength. The rate and extent of hardening resulting from natural aging varies from one alloy to another, and over a wide range, so that to reach a stable condition may require extended periods of time. Precipitation can be accelerated in these alloys, and their strengths further increased by using higher aging temperatures, i.e., artificial aging, or by microalloying with specific alloying elements.

In a previous investigation, it was shown that small additions of Be to Al-0.75%Mg-0.50%Si alloy enhances the age hardening response of the alloy, which is associated with a refinement of the Mg$_2$Si precipitate. A study of the precipitation kinetics showed this is due to a Be-enhanced nucleation rate. The nucleation rate determines the density of the particles following solution and aging treatments, which
strongly affects the hardening rate and maximum hardness obtained for the alloy. The nucleation rate increases with the nucleation entropy of the precipitating compound (Mg₂Si), which can be effected by concentration of the Be in the precipitate compound, or by restricting solubilities of the precipitate's components in the Al(α).

The object of this study is to determine the effect of Be on the solubility of Mg and Si in Al solid solution, and the solubility of Be in Mg₂Si compound. The solubility data obtained is then used to determine the relative nucleation rates for comparison with previous age hardening and transformation rate studies.

The solubility determinations are made using the following analytical techniques: energy dispersive spectroscopy (EDS), coupled with SEM for Al, Mg, Si, and wavelength dispersive spectroscopy (WDS) for Be, are used to measure the approximate elemental compositions. X-ray diffraction (XRD) is used to determine the lattice parameter changes for phases resulting from microalloying. Optical microscopy, coupled with microhardness, and also XRD are used for phase identification.
Chapter 2

LITERATURE REVIEW

2.1 Aluminum Alloy Systems

2.1.1 Aluminum-Beryllium System

The binary Al-Be phase diagram shown in Fig. 1, is a simple eutectic system with two solid solution phases, fcc Al(α) with a maximum solubility of Be in Al of about 0.3 at.% at the eutectic temperature of 644°C, and hcp Be with negligible solid solubility of Al. The eutectic reaction \( L \leftrightarrow Al + Be \) occurs at 2.5 at.% Be [1]. The incorporation of Be in Al(α) results in a contraction in the lattice parameter, e.g., for 0.06% Be the lattice parameter is 0.40411 nm at room temperature compared to 0.40494 nm for pure Al [2].

2.1.2 Aluminum-Magnesium System

The equilibrium solid phases of the Al-Mg system (Fig. 2) are: (1) fcc Al(α), with a maximum solubility of Mg in Al of 18.9 at.% at eutectic temperature of 450°C; (2) hcp Mg(δ) solid solution, with a maximum solubility of Al in Mg of 11.8 at.% at eutectic temperature of 437°C; (3) β compound with the approximate stoichiometry \( Al_3Mg_2 \), which has a complex fcc structure (at low temperature, β-phase transforms martensitically to another structure that may be a distortion of the β structure); (4) the line compound R (often designated e), of composition 42 at.% Mg; and (5) the compound \( \gamma \), with \( \alpha-Mn \)

All concentrations are in wt% unless otherwise indicated.
Fig. 1 Aluminum-Beryllium phase diagram (after Murray and Kahan [1]).
Fig. 2 Aluminum-Magnesium phase diagram (after Murray [3]).
structure, which has composition range of approximately 45 to 60 at.%Mg at 450°C, but
the ideal crystal structure has the stoichiometry Al₁₂Mg₁₇ at 58.6 at.%Mg [3]. Solid
solutions of Al-Mg alloys show an expansion in the Al(α) lattice parameter, e.g., for 2.75
at.%Mg, the lattice parameter is 0.40521 nm at room temperature [4].

2.1.3 Aluminum-Magnesium-Beryllium System

The partial ternary phase diagram for the Al-Mg-Be system as determined by
Nagorskaya et al [5] is shown in Fig.3. A ternary eutectic, L ↔ Al + Be + β(AlₓMgᵧ,Be),
occurs at ~35%Mg and ~0.6%Be, at 445±3°C. Fig.3 shows that the solubility of Mg in
Al(α) decreases as Be content increases, and that no ternary compounds are formed.
Also, Nagorskaya et al.[5] and Fridlyander et al.[6] report some dissolution of Be in the
binary β phase. The lattice parameter of the Al solid solution quenched from 440°C is
0.41032 nm vs. 0.40494 nm for pure Al [7], which suggests that Be incorporation in
Al(α) is not substitutional but interstitial.

2.1.4 Aluminum-Silicon System

The binary Al-Si phase diagram shown in Fig.4, is a simple eutectic system with
one solid solution phases, fcc Al(α) with a maximum solubility of Si in Al of about 1.5
at.% at the eutectic temperature of 577°C, and diamond cubic Si with negligible solid
solubility of Al[8]. The eutectic reaction L ↔ Al + Si occurs at approximately 12.2 at.%Si.
Silicon in solid solution decreases the lattice parameter of Al(α), e.g., for 0.74 at.%Si
Al(α) has a lattice parameter of 0.40400 nm compared to 0.40494 nm for pure Al [9].
Fig. 3 Partial Aluminum-Magnesium-Beryllium phase diagram (after Nagorskaya et al. [5]).
Fig. 4 Aluminum-Silicon phase diagram (after Murray and McAlister [8]).
2.1.5 Aluminum-Silicon-Beryllium System

According to Nowotny [10], the system is a simple eutectic one in which neither binary nor ternary compounds are formed. The ternary Al-Si-Be phase diagram (Fig.5) in the Al corner is comprised of two binary Al-Si and Al-Be eutectics, and a ternary eutectic, \( L \leftrightarrow Al + Be + Si \), at approximately 12-13 %Si and 1-1.5 %Be at 845\(^\circ\)K.

2.1.6 Aluminum-Magnesium Silicide System

The quasibinary Al-Mg\(_2\)Si equilibrium diagram [11] shown in Fig.6, is relatively simple and well established. The compound Mg\(_2\)Si is in equilibrium with Al, and the quasibinary line Al-Mg\(_2\)Si in the ternary diagram occurs at the Mg/Si ratio of 1.73 (Fig.7). The binary and ternary invariant reactions at the Al end are shown in Table 1 [12].

Table 1 Invariant reactions at the Al end of the Al-Mg-Si diagram (after Mondolfo[12]).

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Temperature,(^\circ)C</th>
<th>Liquid</th>
<th>Al((\alpha))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>%Si</td>
<td>%Mg</td>
</tr>
<tr>
<td>(A) ( L \leftrightarrow Al + Al(_3)Mg(_2) )</td>
<td>450</td>
<td>---</td>
<td>34.0</td>
</tr>
<tr>
<td>(B) ( L \leftrightarrow Al + Mg(_2)Si + Al(_3)Mg(_2) )</td>
<td>449</td>
<td>0.37</td>
<td>32.2</td>
</tr>
<tr>
<td>(C) ( L \leftrightarrow Al + Mg(_2)Si )</td>
<td>595</td>
<td>4.75</td>
<td>8.15</td>
</tr>
<tr>
<td>(D) ( L \leftrightarrow Al + Mg(_2)Si + Si )</td>
<td>555</td>
<td>12.95</td>
<td>4.96</td>
</tr>
<tr>
<td>(E) ( L \leftrightarrow Al + Si )</td>
<td>577</td>
<td>12.5</td>
<td>---</td>
</tr>
</tbody>
</table>
Fig. 5 Aluminum-Silicon-Beryllium phase diagram (after Nowotny [10]).
Fig.6  Aluminum-Magnesium Silicide quasibinary phase diagram (after Anderson [11]).
Fig. 7 Partial Aluminum-Magnesium-Silicon ternary phase diagram (after Mondolfo [12]).
The Si, Al$_3$Mg$_2$ (β-phase) and Mg$_2$Si phases in the reactions do not differ substantially from stoichiometric compositions. The solid solubility of Mg$_2$Si in Al(α) is reduced only slightly with Si above the Mg/Si ratio of 1.73, but an excess of Mg greatly reduces Mg$_2$Si solubility [12]. As Mg expands and Si contracts the lattice parameter of Al(α) solid solution, the lattice of the ternary Al(α) solid solution may increase or decrease depending on the ratio of Mg/Si [13].

The compound Mg$_2$Si (63.2% Mg, 36.8% Si) is cubic, space group Fm3m, 12 atoms in the unit cell and a lattice parameter $a_0 = 0.635$-0.640 nm. The melting point, Vickers hardness and density for Mg$_2$Si are 1085°C, 459 kg/mm$^2$, and 1.88 gm/cm$^3$ [12] respectively.

2.2 Trace Element Effects

It is well known that minor or trace amounts of elements can significantly alter the binary phase diagrams, and precipitate highly insoluble binary compound precipitates. For example, Youdelis [14] has shown that small amounts of Si significantly reduces the Ti concentration for the peritectic reaction to occur in Al-Ti alloy, and also results in Si incorporation into the TiAl$_3$ compound. Both effects have the net result of increasing the nucleation rate of TiAl$_3$, and ultimately enhancing grain refinement. Youdelis and Fang [15] have calculated the Al corner of the ternary Al-Ti-Be phase diagram using thermodynamic data calculated from the binary diagrams, known thermochemical data for compounds, and free energies of formation for binary compounds. It has shown that small additions of Be transform the isothermal peritectic reaction for the Al-Ti binary to
a monovariant reaction in which secondary Al crystals are formed over a temperature range, and that Be and Ti severely restrict their mutual solubilities in solid Al, precipitating as TiBe₁₂. The effects of Be on the Al-Ti system has been investigated by Youdelis and Yang [16], who show that the addition of small amounts of Be markedly enhances the grain refinement of Al by Ti. It was shown that Be is incorporated into the peritectic compound TiAl₃, and that the ternary compound Ti(Al,Be)₃ has a higher nucleation entropy and a corresponding significantly higher nucleation rate.

It is evident that small amounts of trace elements may modify the nucleation of precipitates and thus exert large effects upon the structure and properties of age hardening alloys. Several mechanisms have been recognised by which trace additions may modify precipitate nucleation, and these have been reviewed by Polmear [17]:

(a) trace elements may interact with vacancies, leading to a reduction in the rate of lattice diffusion of substitutional elements. Thus the marked effects of small amounts of Cd, In and Sn in reducing the rate of GP zone formation in Al-Cu alloys may be attributed to this type of interaction; (b) trace elements may modify the interfacial energy (γ) between a precipitate and the matrix, thereby changing the nucleation rate of that phase through the change in the value of γ; (c) trace elements may change the free energy relationships in an alloy system, so that precipitation of a different phase is favoured. It has been shown that the addition of 0.1 at.%Ag to Al-Cu-Mg alloys induces homogeneous nucleation of a ternary T-phase instead of the normal GP zones, and the S'-phase (Al₂CuMg) is nucleated on dislocations [18].
2.3 Beryllium Effect on Aluminum-Magnesium Silicide System

The effect of Be microadditions on Mg$_2$Si precipitation in age hardenable Al-0.75%Mg-0.50%Si alloy has been investigated by Youdelis and Xiao [19,20]. A study of the precipitation kinetics (using resistivity) showed that in both alloys (Be-free and Be-containing), the Mg$_2$Si precipitation obeys the Avrami equation [21], given by

$$ Y = 1 - \exp(-kt^n) $$

where $Y$ is the fraction of excess solute precipitated at time $t$, and $k$ and $n$ are parameters dependent on nuclei density and growth mechanism, respectively. The results of their work for the kinetic and precipitate particle density are shown in Table 2 and Figs.8,9. Youdelis and Xiao showed that an addition of 0.10%Be to the alloy significantly increases the transformation rate as reflected in higher ($k$) value of the alloy following solution and aging treatments. The enhanced age hardening rate and hardness for the Be containing alloy is associated with a significant increase in the density of precipitate particles. The higher $k$ value and precipitate density for the Be-containing alloy is thus attributed to Be-enhanced nucleation rate. It was proposed that the increased nucleation rate may be

Table 2: Comparison of kinetic data and precipitate particle count for alloys aged at 250°C (after Xiao and Youdelis [20]).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Growth dependent parameter $n$</th>
<th>Nucleation dependent parameter $k$</th>
<th>Activation energy KJ/mol. $Q$</th>
<th>Precipitate particle count, cm$^{-2}$ (aged 100h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-0.75%Mg-0.5%Si</td>
<td>0.83±0.06</td>
<td>0.038±0.009</td>
<td>61.0±5.3</td>
<td>2.5 x 10$^7$</td>
</tr>
<tr>
<td>Al-0.75%Mg-0.5%Si-0.1%Be</td>
<td>0.74±0.04</td>
<td>0.081±0.013</td>
<td>70.6±6.1</td>
<td>8.0 x 10$^7$</td>
</tr>
</tbody>
</table>
Fig. 8  SEM micrograph for Al-0.75%Mg-0.50%Si over-aged alloy (100 hr. at 250°C); (after Xiao and Youdelis [20]).
Fig. 9 SEM micrograph for Al-0.75%Mg-0.50%Si-0.10%Be over-aged alloy (100 hr at 250°C); (after Xiao and Youdelis [20]).
attributed to an increase in the nucleation entropy associated with Be concentrating in the precipitating Mg₂Si compound, and the decreased solubility of Mg and Si in Al(α) [22].

The effect of small additions of Be to Al-7.0%Si-0.5%Mg-0.1%Fe (A357) alloy has been investigated by Granger et al [23]. They found by microprobe analysis, that in addition to Si and Mg₂Si phases, the Be-free alloy contains three Fe-rich phases (Al₁₅Si₇Fe or Al₁₅Si₂Fe₂, Al₁₃(MnFe)₂Si₂ or Al₁₂(MnFe)₃Si, and Al₁₆Si₅Mg₄Fe or Al₁₆Si₅Mg₃Fe), while the Be containing alloy has only one Fe-rich phase (Al₁₃(MnFe)₂Si₂ or Al₁₆Fe₃Si). They also report 12% of the particle area is Fe-bearing in the Be-free alloy, compared to 3% in the Be-containing alloy. Using D.S.C.(Differential Scanning Calorimetry) analysis, Granger et al show that the addition of Be lowers the ternary eutectic melting point by 6°C, and that the second (higher) temperature peak, which is an Fe reaction, is affected by the Be addition. These observations lend further support to the microprobe results, e.g., that the presence of Be reduces the number of Fe-bearing constituents. The above results show that the phase types and distribution in Be-free and Be-containing A357 alloy are significantly different, and the presence of Al₁₆Mg₄Si₃Fe in the Be-free alloy is responsible for the decrease in strength of the alloy as it reduces the amount of Mg available to form Mg₂Si (the strengthening phase).

The effect of Be and Ti on mechanical properties of a cast Al-Si-Mg alloy has been investigated by Al’tman et al.[24]. Al’tman et al report that the effect of Be alone increases the grain size of the casting alloy, but the addition of Be and Ti significantly refines the grain size. The highest ultimate strength of the alloys (σₚ = 33.5 kg/mm²) is obtained for the composition of Al-7.50%Si-0.45%Mg-0.15-0.40%Be-0.15%Ti.
An interesting effect of Be is its modifying action on the Fe impurity. Fe is insoluble in Al-alloys and crystallizes out in the form of needles or platelet of Al<sub>3</sub>Fe, which under load initiate cracks that promotes brittle failure of the alloy. Be combines with Fe in a complex phase.

The effect of Be and Na on the aging phenomena of Al-Si-Mg alloys has been investigated by Nishi and Shinoda [25], who showed that the addition of 0.09% Be and 0.01% Na affected the formation of GP zones in Al-Si-Mg alloys, and the distribution density of the GP zones (composed of Si and Mg atoms) increased when Be was incorporated into the GP zones.
Chapter 3

EXPERIMENTAL

3.1 Alloy Preparation

Super pure aluminum and magnesium (99.99%), Al-50%Si and Al-5.23%Be master alloys were used in the preparation of the base eutectic alloy (Al-13%Mg, Si) and eutectic alloys containing up to 2%Be. The alloys were prepared in graphite crucibles, by induction melting in air, using a 15 KVA Ajax inductotherm unit at a frequency of 10 KHz. The melts were heated to well above the liquidus temperature (≈ 750°C), maintained for 10 minutes and stirred several times to ensure complete homogenization, and then poured into graphite molds 20 mm dia. by 70 mm length at room temperature. The melt temperature was monitored by a thermocouple embedded in the graphite crucible. The experimental work was carried out on the central parts of the ingots to ensure similar initial microstructures and compositions.

3.2 Solution Treatment

Specimens for solution treatment and analysis were cut from the central regions of the ingot (20 mm dia. x 5 mm). The solution treatments were carried out using an electric furnace with a temperature control of ± 3°C. Three different solution treatments were carried out. The first set of specimens were annealed at 550°C for 6 days, followed by a quench in water. The quench was performed to avoid the formation of β' phase (Al3Mg2), and to determine if excess Si phase was present in the alloy. The second and
third sets of specimens were annealed at 550°C (for 3 days) and 400°C (for 6 days) respectively, then furnace cooled (for 1 day). The furnace cool was to promote maximum transformation to the stable low temperature phases, and to determine in particular whether any β phase formed in the alloys.

3.3 Specimen Preparation

The specimens were then prepared for microscopical analyses by wet grinding on 240, 320, 400 and 600 grit papers, followed by polishing with 1.0 and 0.5 micron alumina media. Specimen etching was accomplished by using either a solution of 1.0 g of NaOH to 100 ml water, or 1.0 ml HF (48%) to 200 ml water (swab for 10 to 15 seconds). The specimens were then examined using optical microscopy, SEM, EDS, microhardness and XRD. A second set of specimens was also examined at Energy Conversion Devices, Inc. of Troy, Michigan using optical and SEM microscopy (backscattering image), EDS, WDS (wavelength dispersive spectrometer) and XRD.

3.4 EDS and WDS Techniques

The first and third sets of specimens were examined by EDS, using a Kevex 5100 coupled to the SEM. The analysis was performed using standards of pure Al, Mg, Si and Fe, and at least three or more determinations were made from different areas of each phase. The composition was calculated using Magic IV computer program. EDS can not detect elements with low atomic number (less than 11) and so Be incorporation into Mg,Si compound can be only estimated by comparing Mg/Si atomic ratios obtained for
the base and Be containing alloys. The second set of specimens was examined by EDS and WDS at ECD Troy, Michigan. Both EDS and WDS were used to measure the elemental compositions, EDS for the higher atomic number elements (Al, Mg, Si) using pure elements as standards, and WDS for O and Be. SiO₂ was used as the standard for O, and pure Be metal for Be.

3.5 X-Ray Diffraction Technique

X-ray diffraction scans were obtained for the solid alloys using a Phillips PW 1078 X-ray generator, with copper radiation (Cu Kα, λ = 1.54186 Å) filtered by Ni, and a scanning rate of 2°/min. The operating voltage and current were set at 40 KV and 20 mA respectively. A chart recorder was utilized to record the diffracted beams, and at least four runs were taken from each specimen. A set of powder alloy specimens were analyzed by XRD at ECD. Silicon powder was added into the powder specimens as an internal calibration reference.

The XRD technique was used to determine changes in the lattice parameters of Al and Mg₂Si resulting from Be additions to the alloy. Phases were identified by comparing against ASTM standard diffraction data (JCPDS file).

3.6 Optical and SEM Techniques

Specimens were examined using optical and SEM microscopes. The optical microscope used in this study is a Leitz Labor Lux 12 model, with a maximum objective lens magnification of 1000. The scanning electron microscope used is a Nanolab 7.
model, with a resolution of 700 nm, and maximum useful magnification of x10000. A second set of specimens was examined optically and by SEM microscopes at ECD. Backscattered electron image (BEI) photomicrographs were obtained, and provided the imaging phase contrasts associated with the elemental compositions. Photomicrographs were obtained from both optical and SEM analyses for study of the effect of Be additions on the morphology and distribution of the alloy phases.

3.7 Microhardness Technique

The microhardness technique was used to measure the hardness of individual microconstituents (phases), and to relate the change of hardness in Mg₂Si phase to the Be incorporated into the compound. The microhardness measurements were carried out on Micromet II with Digmet microhardness tester readout system, with a diamond pyramid indenter, using a 10 gram load, and a total load time of 20 seconds. For most hardness determinations, at least eight readings were taken randomly on each phase to obtain mean hardness value.
Chapter 4

RESULTS AND DISCUSSION

Direct spectroscopic analysis of Be using EDS is not possible due to the low atomic number of Be. Be can be detected using the more sensitive WDS technique; however, 2-3 at.%Be is the limit of sensitivity for the WDS technique used in this study, and consequently the Be content must be inferred from the combined results using several techniques. Only in the ternary compound Al-Fe-Be is the Be level sufficiently high for WDS detection.

4.1 EDS and WDS Analyses

Figures 10 and 11 show the phase morphologies and distributions in the base alloy and base alloy containing 2 %Be. Table 3 gives the compositions of the phases as determined at ECD, and compared against known compounds. The Be-free alloy contains small amounts of the ternary compound Al$_{3.25}$FeSi$_{1.33}$ (white), identified with the known Al$_3$FeSi (β phase) compound [26-28]. The Fe source in the preparation of the present alloy is the Al-Si master alloy, which is produced from commercial purity Al and contains 0.2-0.5%Fe. In the Be-containing alloy, Be is found in the Al$_{2.3}$FeBe$_{0.72}$ (white) compound, and can be identified with the known Al$_3$FeBe$_{2.3}$ compound [29]. It is interesting to note that the ternary Al$_3$FeSi phase was not found in the Be-containing alloy, suggesting a strong attraction of Fe to Be, and Be replacing Si in the ternary compound as a result.
A comparison of the compositions of the Al(α) phases shows that Be has reduced the Si amount from 3.0 at.% to 2.3 at.%, and increased the amount of Mg from 0.6 at.% to 0.7 at.% . The increase in Mg is not considered significant as it is within the estimated error limits of the analysis. The ternary phase diagram shows that the solid solubility limits along the locus for the Al-rich apex of the Al+Mg₃Si+Si phase field for Mg and Si are 0.67 at.% and 1.15 at.% at 559°C respectively. It is evident that the results for Mg

Table 3  Quantitative EDS and WDS results for Al alloy phases. Specimens annealed at 550°C and furnace cooled. α = Al, β = Mg₃Si.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Phases</th>
<th>Measured Compositions</th>
<th>Phase Diagram Compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-13%Mg₃Si</td>
<td>1(α)</td>
<td>Al₉₆.₄Mg₀.₆Si₁₃.₀</td>
<td>Al₀₈.₁₈Mg₀.₆₇Si₁.₁₅</td>
</tr>
<tr>
<td></td>
<td>2(β)</td>
<td>Mg₁.₉₂Si</td>
<td>Mg₃Si</td>
</tr>
<tr>
<td></td>
<td>3ᵇ</td>
<td>Al₁₅.₃₃FeSi₁.₃₃</td>
<td>Al₅FeSi</td>
</tr>
<tr>
<td>Al-13%Mg₂Si-2%Be</td>
<td>1(α)</td>
<td>Al₉₇.₀Mg₀.₇Si₂.₃</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>2(β)</td>
<td>Mg₁.₉₅Si</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>3ᵇ</td>
<td>Al₂₃FeBe₀.₇₂</td>
<td>Al₂FeBe₂.₃</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Be</td>
<td>-----</td>
</tr>
</tbody>
</table>

a-Low wt% in the phase might be due to the Be standard used in this work which did not take matrix effect into account and/or contain other light elements, such as C and N.

b- Mn, V, Cr and O were also detected.
Fig. 10 Photomicrograph of backscattered electron image, for Al-13%Mg₂Si, (1) Al-matrix, (2) Mg₁.₉₂Si, (3) Al₅.₂₃FeS₁.₃₃.
Fig.11 Photomicrograph of backscattered electron image, for Al-13%Mg$_2$Si-2%Be, (1) Al-matrix, (2) Mg$_{1.95}$Si, (3) Al$_{2.5}$FeBe$_{0.72}$, (4) Be.
is in agreement with the phase diagram compositions, but the Si shows a higher value than the phase diagram compositions, and this probably is due to the overlap of the Al and Si peaks (EDS analysis), so that the analysis cannot separate them. In a recent investigation of the Al-Cu-Mg alloy system by Fang [30], it was shown the Mg solubility is significantly reduced by the addition of Be to the ternary alloy. Also, a computer calculation of the Al rich corner of the Al-Ti-Be system by Youdelis and Fang [31] shows that as little as 0.13 at.%Be in Al reduces the Ti content from about 0.52 to 0.01 at.% . Thus the decrease in Si solubility in Al(α) by the Be additions in the present investigation is consistent with Be reducing the solubility of other elements in Al, and indicates Be incorporation into Al(α), is consistent with the higher Mg/Si ratio obtained for the alloy containing Be.

A comparison of the compositions of the Mg₅Si phases shows that the atomic ratio Mg/Si (from 1.92 to 1.95) is relatively constant for the Be-free and the Be-containing alloys. This suggests that Be is not replacing either Mg or Si in the Mg₅Si phase, but is accommodated as an interstitial atom in the Mg₅Si phase.

4.2 X-ray Diffraction Analysis

The XRD analysis was performed on the alloys in two conditions: fully annealed (6 days, at 400°C, furnace cooled) and quenched (from 550°C). The XRD analysis of the alloys in the fully annealed and quenched conditions aid in identifying Al₃Mg₂ (β phase) and Si phases. The equilibrated β phase, with a complex fcc structure (a₀ = 2.8239 nm, 1168 atoms in the unit cell [32]) and Si phase, with a diamond cubic structure (a₀ =
0.54301 nm, 8 atoms in the unit cell [33]), have several diffraction peaks that are difficult to distinguish from several Al and Mg$_2$Si peaks. It has been reported that $\beta$ phase has a low temperature martensitic structure [34] that develops on severe quenching. The martensitic form of $\beta$ phase, would be more readily distinguished from the other phases by microstructure. The results of the XRD analyses of the Al-Si, Mg-Si (an attempt was made), Al-Mg, and Al-Be alloys were studied and compared against the diffraction patterns obtained for the base alloy and base alloy containing 2%Be. A comparison of peaks shows that only Al and Mg$_2$Si peaks occur in the diffraction patterns for both alloys in both conditions, fully annealed (Fig.12 and 13) and quenched (Fig.14 and 15), showing no presence of either $\beta$ phase or Si phase, indicating that the alloy composition is essentially on the quasibinary line (cf. Fig.7). Only an excess Mg or Si over the atomic ratio of Mg/Si = 2 (or the presence of other alloying elements in sufficient quantity), will shift the composition coordinate off the quasibinary line, up into the area of Al + Mg$_2$Si + Al$_3$Mg$_2$, or down into the area of Al + Mg$_2$Si + Si of the ternary phase diagram. It should be noted that a minimum of about 3% by volume of a phase is required for detection by XRD analysis, and the presence of a small amount of $\beta$ phase or Si phase cannot be excluded. The diffraction patterns for the base alloy containing 2%Be are shown in Fig.13 and 15. Be peaks at Bragg angles of 52.90 and 52.85 degree are present, but detectable only when cps (counts per second) is set at low scale (100-400 cps full chart scale).

The results of the XRD analysis for the powder alloys (Table 4) for Al($\alpha$) show that the lattice planes have shifted to higher values for the Be-containing alloy, giving
Fig. 12  X-ray diffraction pattern for Al-13%MgSi. Specimen annealed 400°C, furnace cooled.
Fig. 13 X-ray diffraction pattern for Al-13%Mg$_2$Si-2%Be. Specimen annealed 400°C, furnace cooled.
Fig. 14 X-ray diffraction pattern for Al-13%MgSi. Specimen annealed 550°C, quenched.
Fig. 15  X-ray diffraction pattern for Al-13%Mg$_2$Si-2%Be. Specimen annealed 550°C, quenched.
Table 4  XRD data for Al. Specimens annealed 550°C, furnace cooled.

<table>
<thead>
<tr>
<th></th>
<th>Al-13%Mg₂Si</th>
<th>Al-13%Mg₂Si-2%Bc</th>
<th>Δ(I/I₁)</th>
<th>Δ(θ)</th>
<th>ASTM data, Al(fcc)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2θ</td>
<td>I/I₁</td>
<td>d,Å</td>
<td>2θ</td>
<td>I/I₁</td>
</tr>
<tr>
<td></td>
<td>38.42</td>
<td>100</td>
<td>2.3411</td>
<td>38.25</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>44.65</td>
<td>43</td>
<td>2.0279</td>
<td>44.47</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>65.05</td>
<td>23</td>
<td>1.4326</td>
<td>64.86</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>78.20</td>
<td>23</td>
<td>1.2214</td>
<td>78.00</td>
<td>18</td>
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<tr>
<td></td>
<td>82.39</td>
<td>5</td>
<td>1.1696</td>
<td>82.21</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>99.01</td>
<td>1.4</td>
<td>1.0130</td>
<td>98.85</td>
<td>2.2</td>
</tr>
</tbody>
</table>
Table 5  Unit cell data for Al. Specimens annealed 550°C, furnace cooled.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$a_0$, nm</th>
<th>$\Delta a_0$ (%)</th>
<th>$\Delta V/V$ (%)</th>
<th>$\rho$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-13%Mg$_2$Si</td>
<td>0.40520 ± 0.0005</td>
<td>-----</td>
<td>-----</td>
<td>2.6947</td>
</tr>
<tr>
<td>Al-13%Mg$_2$Si-2%Be</td>
<td>0.40585 ± 0.0012</td>
<td>+0.16</td>
<td>+0.48</td>
<td>2.6852</td>
</tr>
</tbody>
</table>

an increase of 0.16% in lattice parameter "$a_0\)", and a 0.48% increase in unit cell volume (Table 5). The increase in "$a_0\)" and unit cell volume suggests the possibility that Be atoms are associated with GP zones, causing lattice strain (Be atoms are smaller than Al, Mg, and Si atoms) and so increasing scattering; the solute is also said to be a more effective scatterer inside a zone than when occupying a normal lattice position [35]. The presence of Be atoms in solid solution may cause the efficient trapping of vacancies [36]. The size and the magnitude of the solute-vacancy binding energy depends basically on two factors: electronic effects arising from differences in valence, and from differences in the volume of the solute and solvent atoms. Vacancies may be considered to possess negative charge. The doubly charged positive Be ion cores, and the negative charged vacancy interact by the electrostatic screened coulomb attraction. The reported binding energy values for Mg-vacancy, Si-vacancy, and Be-vacancy in Al are 0.17-0.19 eV [37-39], 0.20 and 0.23 eV [40,41], and 0.26 and 0.28 eV [42,43] respectively. The high Be-vacancy binding energy will result in a higher retained vacancy concentration in the matrix to increase the critical scattering size of the GP zones, which may influence the rate of precipitation [44]. Based on the significant increase in "$a_0\)" and unit cell volume
Table 6  XRD data for Mg$_2$Si. Specimens annealed 550°C, furnace cooled.

<table>
<thead>
<tr>
<th>Al-13%Mg$_2$Si</th>
<th>Al-13%Mg$_2$Si-2%Be</th>
<th>$\Delta(I/I_1)$</th>
<th>$\Delta(2\theta)$</th>
<th>ASTM data, Mg$_2$Si(fcc)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\theta$</td>
<td>$I/I_1$</td>
<td>$d, \text{Å}$</td>
</tr>
<tr>
<td>24.18</td>
<td>51</td>
<td>3.6778</td>
<td>24.01</td>
<td>31</td>
</tr>
<tr>
<td>40.05</td>
<td>100</td>
<td>2.2495</td>
<td>39.89</td>
<td>100</td>
</tr>
<tr>
<td>57.95</td>
<td>12</td>
<td>1.5901</td>
<td>57.81</td>
<td>12</td>
</tr>
<tr>
<td>72.85</td>
<td>28</td>
<td>1.2973</td>
<td>72.64</td>
<td>24</td>
</tr>
</tbody>
</table>
calculated from the XRD results for Al(α), it is estimated that Be decreases the solubility of Mg₂Si in Al(α) from 1.6 at.% to 1.3 at.% at 550°C, and that Be atoms may occupy the interstitial positions in the Al unit cell (cf. Appendix B).

The results of XRD analysis for the powder alloys in Table 6 for Mg₂Si show that the lattice planes have shifted to higher values for the Be-containing alloy, giving an increase of 0.16% (Table 7) in lattice parameter "a₀". The increase in "a₀" and unit cell volume suggest that Be incorporation in Mg₂Si is not substitutional but interstitial. A calculation of the interstitial dimensions for Mg₂Si lattice, using atomic diameters based on the closest distance of approach in the crystals of the elements, shows Be can be accommodated as an interstitial atom into Mg₂Si unit cell (cf. Appendix A). The increase in "a₀" and unit cell volume, suggest that up to 4.8 at.% Be can be incorporated interstitially in the Mg₂Si unit cell (cf. Appendix C). Thus a ternary compound having the approximate formula of Mg₂SiBe₀.₁₅ is possible compared to the calculated of Mg₂SiBe₀.₂₃.

Table 7 Unit cell data for Mg₂Si. Specimens annealed 550°C, furnace cooled.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>a₀, nm</th>
<th>Δa₀(%)</th>
<th>ΔV/V (%)</th>
<th>ρ (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-13%Mg₂Si</td>
<td>0.63570 ± 0.0016</td>
<td>-----</td>
<td>-----</td>
<td>1.9790</td>
</tr>
<tr>
<td>Al-13%Mg₂Si-2%Be</td>
<td>0.63670 ± 0.0019</td>
<td>+0.16</td>
<td>+0.47</td>
<td>1.9729</td>
</tr>
</tbody>
</table>
4.3 Optical and Microhardness Analyses

Metallography combined with microhardness techniques were used to identify the phases shown in Figs. 16-22. Fig. 16 shows a cellular grain structure typical of eutectic composition alloys, with the Al solid solution (light) and Mg₂Si (dark) phases combined in a fine lamellar structure. The addition of other alloying components to an eutectic composition alloy tends to break down the lamellar structure if the alloying components are in one or both of the eutectic constituents (Fig. 17). Karov and Youdelis [45] have shown that as little as 0.5% Be, which is soluble in the metalloid constituent (CuAl₂) up to 0.8%, severely disrupts lamellar growth during solidification, tending to form irregular two-phase microstructures. It is evident that the addition of 0.5% Be has a similar effect in the quasibinary Al-Mg₂Si eutectic, and suggests incorporation of Be into Mg₂Si has occurred. The excess Be has separated as essentially pure Be (phase No. 3 in Fig. 18). Xiao and Youdelis [46] have shown that the addition of 0.10% Be to the Al-0.75%Mg-0.50%Si alloy, significantly increases the density of the precipitate particles (cf. Figs. 8 and 9), indicating that the Be-enhanced the age hardening response of the alloy is associated with a refinement of the Mg₂Si precipitate. SEM photomicrographs (Figs. 19 and 20) show the morphologies and distributions of the phases, indicating the presence of Fe compounds resulted from Fe impurity contained in Al-Si master alloy. Figs. 21 and 22 show a comparison of the indentation sizes. A smaller indentation is observed for the Be-containing alloy, indicating an increase in hardness.

The results of the microhardness analysis (Table 8) show a significant increase in the hardness of Al(α) (from 31 to 41 HVN) for the Be-containing alloy. The increased
Fig.16 Photomicrograph showing as-cast structure for Al-13%Mg₃Si alloy.
Fig. 17 Photomicrograph showing as-cast structure for Al-13%Mg2Si-2%Be alloy.
Fig. 18 Photomicrograph showing the effect of 0.5% Be additions to an Al-13% Mg$_2$Si alloy, fully annealed. (1) Al-matrix, (2) Mg$_2$Si, (3) Be.
Fig. 19  SEM Photomicrograph showing the distribution of phases for Al-13% Mg$_2$Si alloy, fully annealed, (1) Al-matrix, (2) Mg$_2$Si.
Fig. 20  SEM Photomicrograph showing the distribution of phases for Al-13% Mg₃Si-2% Be alloy, fully annealed, (1) Al-matrix, (2) Mg₃Si, (3) Al-Fe-Be, (4) Be.
Fig. 21 Photomicrograph showing microhardness indentations for Al-13%Mg$_3$Si alloy, fully annealed, (1) Al-matrix, (2) Mg$_{1.95}$Si, (3) Al$_{5.25}$FeSi$_{1.33}$.
Fig. 22 Photomicrograph showing microhardness indentations for Al13%Mg2Si-2%Be alloy, fully annealed, (1) Al-matrix, (2) Mg1.91Si, (3) Al2.3FeBe0.72, (4) Be.
hardness suggests interstitial incorporation of Be in Al(α), which is consistent with the XRD results (an increase in lattice parameter of Al unit cell). The increase in hardness could be the result of the interaction between solute atoms and vacancies due to their high binding energy, leading to a higher retained vacancy concentration within the matrix. The present of excess vacancies may migrate into clusters, and clustering may interact and impede the movement of dislocations, causing lattice strain and an increase in hardness of the solid solution. Xiao and Youdelis [47] have shown that the addition of 0.10%Be to an Al-0.75%Mg-0.50%Si alloy significantly increases the hardening rate and the peak hardness level following solution and aging treatments. Youdelis and Karov [48] have shown that Al-3.0%Cu-0.1%Be alloy has a significantly higher hardening rate than the Al-3.0%Cu alloy at room temperature and 110°C. The higher hardening rate for the Al-3.0%Cu-0.1%Be alloy is attributed to the early and extensive formation of vacancy loops adjacent to network dislocations, the loops acting as barriers to the glide of network dislocations. The formation of Cu-Be-vacancy clusters may be the cause of the accelerated hardening rate.

The results for Mg₂Si show a significant increase in hardness (from 361 to 396 HVN) for the Be containing alloy. The observed change is in agreement with the XRD results (increase in a₀), suggesting that the Be is incorporated interstitially into Mg₂Si. It is noted that there is a difference between the measured and reported hardness values, however, the condition of the reported values is not stated, and thus a comparison can not be made.
Table 8  Hardness values for Al alloy phases. Specimens annealed at 550°C, furnace cooled.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Phases</th>
<th>Measured Hardness HVN</th>
<th>Reported Hardness HVN [49]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-13%Mg$_2$Si</td>
<td>1-Al($\alpha$)</td>
<td>31 ± 3</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>2-Mg$_{1.92}$Si</td>
<td>361 ± 13</td>
<td>457</td>
</tr>
<tr>
<td></td>
<td>3-Al$<em>{5.25}$FeSi$</em>{1.33}$</td>
<td>----</td>
<td>591</td>
</tr>
<tr>
<td>Al-13%Mg$_2$Si-2%Be</td>
<td>1-Al($\alpha$)</td>
<td>41 ± 5</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>2-Mg$_{1.93}$Si</td>
<td>396 ± 16</td>
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<tr>
<td></td>
<td>3-Al$<em>{2.3}$FeBe$</em>{0.72}$</td>
<td>1133 ± 82</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>4-Be</td>
<td>110 ± 13</td>
<td>170</td>
</tr>
</tbody>
</table>
Chapter 5
EFFECT OF BERYLLIUM ON NUCLEATION RATE OF Mg₂Si

5.1 Nucleation Entropy Concept

Youdelis [50] has derived an expression for the nucleation entropy ($\Delta S_n$) for transformations for the special case of regular solution behavior for binary alloy phases, assuming isothermal, isobaric, and constant phase composition conditions are maintained during nucleation. For the case of solidification, the molar entropy of nucleation can be separated into two parts: (a) the entropy change due to the freezing of the pure components, $\Delta S_F$, and (b) the change in the mixing entropy of the solid/liquid system resulting from the precipitation of the solid phase, $\Delta S_M$, given by

$$\Delta S = \Delta S_F + \Delta S_M \quad (2)$$

$$\Delta S_F = N_1^S (S_1^S - S_1^L) + N_2^S (S_2^S - S_2^L) \quad (3)$$

$$\Delta S_M = R \left( N_1^S \ln \left( \frac{N_1^L}{N_1^S} \right) + N_2^S \ln \left( \frac{N_2^L}{N_2^S} \right) \right) \quad (4)$$

where $N$ refers to the mole fraction, the $S$ to the molar entropy, the subscripts 1,2 to the components, and $S,L$ to the solid and liquid phases respectively.

For a multicomponent system, $\Delta S$ is obtained by including terms for all components(r) in the system,

$$\Delta S_F = \sum_r N_r^S (S_r^S - S_r^L) \quad (5)$$

$$\Delta S_M = R \sum_r N_r^S \ln \left( \frac{N_r^L}{N_r^S} \right) \quad (6)$$

Equation (6) shows that the mixing entropy change increases (in magnitude) with the
difference in composition between the solid and the liquid phases in equilibrium, and with the number of components present in dilute concentration in the liquid which concentrate in the nucleating phase.

5.2 Nucleation Entropy of Mg, Si

The mixing entropy contributions to the nucleation entropy given by equation (6) apply to regular solutions, but may also be used as reasonably good approximations for liquid and solid solutions having complete or wide solubility ranges [50]. The behavior of intermediate compounds or phases with limited solid solubility, however, may be far removed from regular solution behavior, and additional thermodynamic data will be required to calculate the nucleation entropy. The regular solution constraint can be removed by an appropriate combination and sequence of reactions for which entropy changes can be calculated or are given. The procedure used to calculate nucleation entropy for precipitation in solid alloys is similar to that for primary phase nucleation in liquid alloys, except that the solidification reaction must be replaced by the appropriate solid phase transformation, and the corresponding entropy change calculated or estimated.

The concentrations of Mg and Si in the solid solution alloy is determined from the solvus line in Al-Mg, Si phase diagram (cf. Fig.6) at the solution treatment temperature (550°C). Table 9 gives the reaction sequence used for calculating the molar nucleation entropy of Mg, Si in an Al-1.04 at.%Mg-0.52 at.%Si alloy at the aging temperature of 250°C used by Xiao and Youdelis [51].

The (reverse) formation of 1 mole (3g-atom) of a regular solid solution of Mg-
Table 9  Reaction sequence for calculating $\Delta S$ for precipitation of Mg$_2$Si at 250°C .  
(All concentrations in at.%) 

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Entropy change $\Delta S$ (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>$3(Mg-33.33%Si)_{ag}^{\text{mol}} \leftrightarrow 2Mg + Si$</td>
</tr>
<tr>
<td>2a</td>
<td>$2Mg + Si \leftrightarrow Mg_2Si$</td>
</tr>
<tr>
<td>3a</td>
<td>$3(Mg-33.33%Si)_{ag}^{\text{mol}} \leftrightarrow Mg_2Si$</td>
</tr>
<tr>
<td>4a</td>
<td>$\infty(Al-1.04%Mg-0.52%Si)<em>{ag}^{\text{mol}} \leftrightarrow 3(Mg-33.33%Si)</em>{ag}^{\text{mol}} + \infty(Al-1.04%Mg-0.52%Si)_{ag}^{\text{mol}}$</td>
</tr>
<tr>
<td>5a</td>
<td>$\infty(Al-1.04%Mg-0.52%Si)<em>{ag}^{\text{mol}} \leftrightarrow Mg_2Si + \infty(Al-1.04%Mg-0.52%Si)</em>{ag}^{\text{mol}}$</td>
</tr>
</tbody>
</table>

33.33 at.%Si alloy is given by reaction 1a, for which the mixing entropy is given by

$$\Delta S^{ag} = -R(N_{Mg}\ln N_{Mg} + N_{Si}\ln N_{Si})$$  \hspace{1cm} (7)$$

The formation of 1 mole of Mg$_2$Si is given in reaction 2a, for which the formation entropy is calculated using the thermodynamic data for Mg$_2$Si, Mg and Si [52-54].

Adding reaction 1a to 2a gives 3a, the reaction and corresponding entropy change for the formation of 1 mole of Mg$_2$Si from 1 mole of regular solid solution of Mg-33.33 at.%Si alloy. The reference of the regular solid solution in 3a to the stable state structures of Mg (hcp) and Si (diamond cubic) removes the transformation entropy to the Mg$_2$Si structure (fcc). Reaction 4a denotes the nucleation reaction by which 1 mole of regular solid solution of Mg-33.33 at.%Si alloy is formed or precipitated in an infinite amount of regular solid solution of Al-1.04 at.%Mg-0.52 at.%Si. The entropy change for this
reaction is calculated using equation (6), except that the liquid phase is now replaced by
the supersaturated solid solution. Adding reaction 3a to 4a gives 5a. Reaction 5a gives
the nucleation reaction and corresponding nucleation entropy for the formation of 1 mole
of Mg$_2$Si from a regular solid solution of Al-1.04 at.%Mg-0.52 at.%Si at the aging
temperature of 250°C (cf. Appendix D).

The determination of the nucleation entropy of Mg$_2$Si from the real solid solution
alloy requires appropriate thermodynamics 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 the real vs. regular solid
solution will likewise be small, and for the dilute solute concentrations of the present
alloy ($N_{Mg} = 0.0104$, $N_{Si} = 0.0052$) negligible.

5.3 Nucleation Entropy of Mg$_2$SiBe$_{0.15}$

The results of X-ray diffraction show that the Be decreases the solubility of Mg$_2$Si
in Al($\alpha$) from about 1.6 at.% to 1.3 at.% at 550°C and the amount of Be incorporated into
Mg$_2$Si compound is estimated to be about 4.8 at.%. The increase in lattice parameter
"a\\(_0\)" and unit cell volume suggest that Be incorporation in Mg$_2$Si is not substitutional but
interstitial. Table 10 gives the appropriate reactions by which the nucleation entropy for
Mg$_2$SiBe$_{0.15}$ in an Al-0.88 at.%Mg-0.44 at.%Si-0.06 at.%Be, is obtained. Note that the
Be concentration in Al($\alpha$) alloy is determined from the solvus line in Al-Be phase
diagram (cf. Fig. 1), and the Mg and Si concentrations in Al($\alpha$) are obtained from the
XRD results at the solution treatment temperature (550°C). The procedure is similar to that performed for Mg₃Si except for one approximation which is needed because of the absence of the thermodynamic data for Mg₂SiBe₉₅. It is assumed that the entropy change for reaction 2b does not differ appreciably from the entropy of formation of Mg₃Si as given in reaction 2a. The basis for this assumption is the common crystal structure (fcc,C1 type) and lattice parameters (from XRD analysis) for both Mg₃Si and Mg₂SiBe₉₅ phases. The principal factors determining the entropy of a phase are structure and bond energy. Because the structures of the two compounds are essentially identical, and because the Be atoms in the ternary compound occupy the existing vacant site in the centre of unit cell, the bond energies, and hence the entropies of the two compounds

Table 10 Reaction sequence for calculating ΔS for precipitation of Mg₂SiBe₉₅ at 250°C.

<table>
<thead>
<tr>
<th>reaction</th>
<th>entropy change ΔS (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b 3.15(Mg-31.75%Si-4.76%Be)⁰sol ↔ 2Mg + Si + 0.15Be +</td>
<td>-20.80</td>
</tr>
<tr>
<td>2b 2Mg + Si + 0.15Be ↔ Mg₂SiBe₉₅</td>
<td>~-21.22</td>
</tr>
<tr>
<td>3b 3.15(Mg-31.75%Si-4.76%Be)⁰sol ↔ Mg₂SiBe₉₅</td>
<td>-42.02</td>
</tr>
<tr>
<td>4b (Al-0.88%Mg-0.44%Si-0.06%Be)⁰sol ↔ 3.15(Mg-31.75%Si-4.76%Be)⁰sol + (Al-0.88%Mg-0.44%Si-0.06%Be)⁰sol</td>
<td>-111.78</td>
</tr>
<tr>
<td>5b (Al-0.88%Mg-0.44%Si-0.06%Be)⁰sol ↔ Mg₂SiBe₉₅ + (Al-0.88%Mg-0.44%Si-0.06%Be)⁰sol</td>
<td>-153.80</td>
</tr>
</tbody>
</table>
should not differ appreciably (except for the additional mixing entropy for the ternary compound). The molar nucleation entropy (absolute) value of Mg₂SiBe₀.₁₅ is about 13.48 J/mol.K (3.19 cal/mol.K) above that of Mg₂Si. In the above calculations, only the entropy change for reaction 2b introduces a possibly significant degree of uncertainty; however, the assumption of approximately equal entropy changes for reactions 2a and 2b is not an unreasonable one, based on the structural similarity of the constituents involved. The higher nucleation entropy for Mg₂SiBe₀.₁₅ is largely due to the increase in mixing entropy when Be is incorporated into Mg₂Si, and illustrates the sensitivity of the nucleation entropy to the presence of small concentrations of solutes in the solid alloy when the solutes concentrate in the nucleating phase.

5.4 Comparison of Nucleation Rates

According to classical nucleation theory [55], the homogeneous nucleation rate for a spherical, strain free nucleus is given by,

\[ \dot{N} \propto \exp(-\Delta G^*/kT) \]  \hspace{1cm} (8)

where the Gibbs free energy (\(\Delta G^*\)) of formation of a spherical, strain free, critical-sized nucleus is given by,

\[ \Delta G^* = \frac{16\pi\gamma^2}{3(\Delta G_v)^2} \]  \hspace{1cm} (9)

where \(\gamma\) is the interfacial energy and \(\Delta G_v\) the volume Gibbs free energy of transformation. For small to moderate undercooling (\(\Delta T\)), \(\Delta G_v = -\Delta S_v \Delta T\), where \(\Delta S_v\) is the volume entropy change, i.e., \(\Delta S_v = \Delta S / V_m\), where \(V_m\) is the molar volume of the precipitate [50]. The sensitivity of nucleation rate to changes in \(\Delta S_v\) is evident in equation
(9), increasing exponentially with the square of nucleation entropy. Equation (9) is applicable to phase changes in which strain energy is negligible (e.g. liq → solid transformation). In the solid state, transformations are generally accompanied by elastic strain due to volume changes, and this elastic strain energy must be included in the calculation of \( \Delta G^* \). Two general cases must be considered: (1) incoherent nucleation where there is no lattice continuity between the matrix and precipitate and the strain is hydrostatic (being either positive or negative), and (2) coherent nucleation in which the lattices of the precipitate and the matrix are constrained to match, and strain is determined by the degree of lattice mis-match. The spherical form of the embryo is not the lowest energy configuration when strain becomes significant, and nucleus will take on a disk-like shape (e.g. oblate spheroid) to minimize the total energy [56].

For incoherent nucleation, assuming an elastically isotropic system and strain residing in the matrix, \( \Delta G^* \) is given by [57],

\[
\Delta G^* = 8\pi^2 \gamma^2 \mu_m^2 (\Delta V/V)^{4/3} (\Delta G_v)^4
\]  

and the nucleation rate becomes,

\[
\dot{N} \propto \exp(8\pi^2 \gamma^2 \mu_m^2 (\Delta V/V)^{4/3} (\Delta G_v)^4 kT)
\]  

where \( \mu_m \) is the matrix shear modulus given by \( \mu_m = E/2(1+\nu) \), where \( \nu \) is the Poisson's ratio for the matrix, and \( \Delta V/V \) the fractional volume change in the matrix accompanying the transformation.

For coherent nucleation, \( \Delta G^* \) is given by [58,59],

\[
\Delta G^* = \pi \gamma^2 [2+f(c/r)]^2/12(c/r)^2(\Delta G_v + W)^3
\]  

where the strain energy per unit volume of precipitate (W) is given by [56].
\[ W = 2\mu_m(\Delta V/V)^2(1+\nu/1-\nu) \]  
\[ (13) \]

The nucleation rate then becomes,
\[ \dot{N} \propto \exp(\pi \gamma/12(c/r)^2(\Delta G_v+W)^3kT) \]
\[ (14) \]

where \((c/r)\) is the aspect ratio of the nucleus (minor to major axis) and \(f(c/r)\) the shape factor. \(f(c/r)\) defines an oblate spheroid, sphere or prolate spheroid when \((c/r) < 1, 1, > 1\) respectively. The strain energy \((W)\) is a function of the aspect ratio, and for the anisotropic case varies markedly with orientation relationships between precipitate and matrix. Lee et al.\[59\] have treated the special case of Cu and Ag precipitates in an Al matrix, i.e., the classic GP zone, and show that as the ratio \((-W/\Delta G_v)\) increases the particle shape changes from a spherical to a disk-like shape to minimize the total energy of the system.

A comparison of nucleation rates for the two intermetallic compounds is obtained using equations (12) to (14) for coherent nucleation, and is given by in Table 11. The fractional volume change \((\Delta V/V)\) is calculated from the difference in gram atomic volumes,
\[ \Delta V/V = (V^B - V^2)/V^B \]
\[ (15) \]

The calculations are based on X-ray diffraction results, a spherical precipitate with shape factor \([f(c/r)]\) is equal to 2, and the calculated \(\Delta S_v\) values given in Tables 9 and 10. The interfacial energy \(\gamma\) used is \(\sim 110\text{mJ/m}^2\), which is assumed reasonable based on results of Ostwald ripening (particle coarsening) studies for coherent interface \[60\]. \(\Delta T\) is 300 K based on solution treatment temperature and aging temperature. \(\mu_{Al}\) at 250°C is assumed to be 10\% of its room temperature value of 2.71x10^{16} \text{J/m}^2 \[61\], since relaxation
processes will be operative at the aging temperature of 250°C [62], and $v_{Al}$ is taken as 0.33 [63]. The difference in $\Delta G^*$ for the alloys derives primarily from two sources: (1) difference in nucleation entropy ($\Delta S_\nu$) and; (2) difference in interfacial energy ($\gamma$). It can be assumed that $\gamma$ will not differ appreciably, since the precipitate structures and alloy compositions essentially the same, so the difference in $\Delta G^*$ arises from the change in $\Delta S_\nu$. The corresponding relative nucleation rates are given in Table 11 (cf. Appendix E), which show that the incorporation of Be into Mg$_2$Si increases the strain energy ($W$) by $\sim$0.19%, the nucleation entropy ($\Delta S_\nu$) by $\sim$9.1%, to give a net decrease of $\sim$28% in free energy of formation of the critical-sized ($\Delta G^*$). The decrease in $\Delta G^*$ causes the nucleation rate to increase by $\sim$17 times for the Be-containing alloy than the Be-free alloy.

In a previous study, Xiao and Youdelis [64,65] have shown that small additions of Be markedly enhance the refinement and precipitation of Mg$_2$Si in Al-0.75%Mg-0.50%Si alloy. An analysis of kinetic data showed the refinement of the precipitate particles, and increased precipitation rate, is the result of a Be-enhanced nucleation rate. The previous study is consistent with the present results, which show that some Be is incorporated into Mg$_2$Si compound, and also significantly decreases the solubility of Si in Al solid solution. Both factors contribute to an increase in the nucleation entropy and nucleation rate, to which the refinement of Mg$_2$Si may be attributed.
Table 11  Comparison of nucleation rates for Mg$_2$Si and Mg$_2$SiBe$_{0.15}$ at 250°C.

<table>
<thead>
<tr>
<th>Phase</th>
<th>V  cm$^3$/g.ato.</th>
<th>$\Delta V / V$</th>
<th>W  J/m$^3$</th>
<th>$\Delta S_v$ J/m$^3$ K</th>
<th>$\gamma$ mJ/m$^2$</th>
<th>$\Delta G^*$ $\Delta T= 300$ K J</th>
<th>$\dot{N}<em>{Mg_2SiBe</em>{0.15}}$ $\dot{N}_{Mg_2Si}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Mg$_2$Si</td>
<td>12.90</td>
<td>0.2232</td>
<td>5.36 x 10$^8$</td>
<td>-3.63 x 10$^6$</td>
<td>110</td>
<td>7.29 x 10$^{-20}$</td>
<td>-----</td>
</tr>
<tr>
<td>(2) Mg$<em>2$SiBe$</em>{0.15}$</td>
<td>12.94</td>
<td>0.2233</td>
<td>5.37 x 10$^8$</td>
<td>-3.96 x 10$^6$</td>
<td>110</td>
<td>5.25 x 10$^{-20}$</td>
<td>~17</td>
</tr>
</tbody>
</table>
Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The combined results of the EDS, WDS, XRD, metallography and microhardness techniques used in this investigation indicate that some of Si is dissolved by Mg$_2$Si and Be reduces the solubility of Mg$_2$Si in Al solid solution. The EDS analysis indicates that Be decreases the amount of Si in Al(α), and the WDS shows a constant Mg/Si ratio for Mg$_2$Si, suggesting that Be incorporation has occurred. The XRD analysis shows an expansion in unit cell volume for both Al and Mg$_2$Si, when Be is contained in the alloy, indicating that Be incorporation in Al(α) and Mg$_2$Si is not substitutional but interstitial. It is estimated that Be decreases the solubility of Mg$_2$Si in Al(α) from about 1.6 at.% to 1.3 at.% at 550°C, and up to 4.8 at.% Be is incorporated in Mg$_2$Si to give a ternary compound of the approximate composition Mg$_2$SiBe$_{0.15}$. The results of optical microscopy coupled with microhardness show an increase in hardness, indicating interstitial incorporation of Be in Mg$_2$Si and Al(α).

The XRD and previous study results are in agreement with the increased nucleation rates in the solid state as predicted by the nucleation entropy theory. Calculations based on the Mg$_2$SiBe$_{0.15}$ compound show that although strain energy is increased, the increase in the nucleation entropy exceeds that necessary to decrease the free energy of formation of the critical-sized nucleus. The decrease in the free energy of formation of the critical-sized nucleus gives a nucleation rate increase of ~17 times faster.
for Mg$_2$SiBc$_{0.15}$ than for Mg$_2$Si, based on an assumed γ of ~110 mJ/m$^2$. The increased nucleation rate is in agreement with the observed refinement of Mg$_2$Si precipitate in Al-Mg-Si alloy reported in earlier investigations.

6.2 Recommendations

In a previous study, it was recommended that Transmission Electron Microscopy (TEM) techniques be employed to directly observe and compare the GP zone and metastable phase formation in the alloys with and without Be.

Due to insufficient sensitivity of the WDS technique used in this study to detect the Be content in Mg$_2$Si phase, accurate determinations are essential for nucleation entropy calculations; thus more sophisticated analytical techniques such as Auger Electron Spectroscopy should be tried.

A determination of the Al/Mg$_2$Si interfacial energy (γ), and the effect of Be is required for accurate calculations of the relative nucleation rates. Studies of particle coarsening (Ostwald ripening) can be effectively used to obtain a reasonably accurate value for γ.

The heat treatable Al-Mg-Si alloys are commercially important, due to their natural aging properties. The active precipitate in the natural age hardening alloys is Mg$_2$Si, but the precipitation is sluggish and its acceleration would be beneficial. The results of the present and previous study show considerable potential for improving the aging response of the commercially important alloys by Be microalloying, and such an investigation is recommended.
REFERENCES


APPENDIX A
Calculation of Interstitial Site

The crystal structure of Mg$_2$Si (fcc,C1 type) is the same as CaF$_2$ structure (Fig. 23) with Mg occupying the F atoms and Si occupying the Ca atoms. The CaF$_2$ structure has cations, Ca$^{2+}$ at fcc locations: 0,0,0; 1/2,1/2,0; 1/2,0,1/2; and 0,1/2,1/2. The anions, F$^-$, are in 4-f interstitial positions among the cations 1/4,1/4,1/4; 3/4,3/4,1/4; 3/4; 1/4,3/4; 1/4,3/4,3/4 3/4,3/4,3/4 1/4,1/4,3/4; 1/4,3/4,1/4; and 3/4,1/4,1/4, note that there is no atom at the centre of the unit cell.

This 4-to-8 ratio of Si to Mg accommodates the 1-to-2 of m-to-p in A$_m$X$_p$. The vacant site in the centre of the unit cell can provide the required space for accommodating a Be atom.

Fig.23  AX$_2$ structure (CaF$_2$ type). There is an fcc lattice of A atoms, with X atoms occupying all of the interstitial sites among 4 atoms [unit cell and (110) plane].
The interstice (D) is calculated from Fig. 23 as follows:

\[ D_{Si} + 2D_{Mg} + D = \sqrt{3} a_o \]

where \( D_{Si} \) and \( D_{Mg} \) are the atomic diameters of Si and Mg, and \( a_o \) is the lattice parameter of the unit cell. The values for D used are 0.235, 0.322, and 0.228 nm for Si, Mg, Be respectively [66]. Table 12 gives the values of D calculated using different values for \( a_o \).

Table 12 - Comparison of interstice (D) values.

<table>
<thead>
<tr>
<th>( a^{(1)} ), nm</th>
<th>( D^{(1)} ), nm</th>
<th>( a^{(2)} ), nm</th>
<th>( D^{(2)} ), nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6390</td>
<td>0.2318</td>
<td>0.6357</td>
<td>0.2261</td>
</tr>
<tr>
<td>0.6351</td>
<td>0.2251</td>
<td>0.6367</td>
<td>0.2278</td>
</tr>
</tbody>
</table>

1- obtained from ref.[67 and 68]
2- obtained from Table 7

The results of Table 12 show that Be atom can fit in the interstice which exists in the centre of the unit cell, to give a ternary compound with ratio of 4 Si: 8 Mg: 1 Be or 1:2:0.25. This corresponds to a stoichiometric formula of \( Mg_2SiBe_{0.25}\), and an atomic percent of 61.54 Mg, 30.77 Si and 7.69 Be.
APPENDIX B
Solubility of Mg₃Si in Al(α) Containing Be

X-Ray Diffraction Results

The X-ray density (ρ) is given by,

$$\rho = \frac{[Z][M.W.]}{[N_A][V]}$$

where Z is the number of atoms per unit cell, M.W molecular weight, N_A Avogadro number, and V volume of unit cell (a³).

Al-13% Mg₃Si alloy

$$a_{Al} = 0.4052\pm0.0005 \text{ nm}$$

$$\rho_{Al} = \frac{[4][27]/[6.02\times10^{23}][4.0525\times10^{-8}]}{3}$$

$$\rho_{Al} = 2.6947 \text{ g/cm}^3$$

$$a_{Mg_3Si} = 0.6357\pm0.0016 \text{ nm}$$

$$\rho_{Mg_3Si} = \frac{[4][76.6]/[6.02\times10^{23}][6.3586\times10^{-8}]}{3}$$

$$\rho_{Mg_3Si} = 1.979 \text{ g/cm}^3$$

Al-13% Mg₃Si-2% Be alloy

$$a_{Al} = 0.40585\pm0.0012 \text{ nm}$$

$$\rho_{Al} = \frac{[4][27]/[6.02\times10^{23}][4.0573\times10^{-8}]}{3}$$

$$\rho_{Al} = 2.6852 \text{ g/cm}^3$$

Assuming that Al(α) obeys the law of mixtures, and therefore the volume fraction, V%, or atomic fraction can be calculated using the above density relationship, gives

$$\rho_{AlBe} = [V\%_{Mg_3Si}][\rho_{Mg_3Si}] + [V\%_{Al}][\rho_{Al}]$$

$$2.6852 = [V\%_{Mg_3Si}][1.979] + [V\%_{Al}][2.6947]$$

or

V\%_{Mg_3Si} = 1.32 \sim 1.3, \text{ and } V\%_{Al} = 98.68 \sim 98.7
APPENDIX C
Solubility of Be in Mg\textsubscript{2}Si Compound

\textbf{Al-13\% Mg\textsubscript{2}Si alloy}

\[ a_{\text{Mg}_{2}\text{Si}} = 0.6357 \pm 0.0016 \text{ nm} \]
\[ \rho_{\text{Mg}_{2}\text{Si}} = [4][76.6]/[6.02 \times 10^{23}]/[6.3586 \times 10^{-3}]^3 \]
\[ \rho_{\text{Mg}_{2}\text{Si}} = 1.979 \text{ g/cm}^3 \]

\textbf{Al-13\% Mg\textsubscript{2}Si-2\% Be alloy}

\[ a_{\text{Mg}_{2}\text{Si}} = 0.6367 \pm 0.0019 \text{ nm} \]
\[ \rho_{\text{Mg}_{2}\text{Si}} = [4][76.6]/[6.02 \times 10^{23}]/[6.3651 \times 10^{-3}]^3 \]
\[ \rho_{\text{Mg}_{2}\text{Si}} = 1.9729 \text{ g/cm}^3 \]

Assuming that the compound of Mg\textsubscript{2}SiBe obeys the law of mixtures, and therefore the volume fraction, V\%, or atomic fraction can be calculated using the density relationship, gives,

\[ \rho_{\text{Mg}_{2}\text{SiBe}} = [V\%_{\text{Mg}_{2}\text{Si}}][\rho_{\text{Mg}_{2}\text{Si}}] + [V\%_{\text{Be}}][\rho_{\text{Be}}] \]
\[ 1.9729 = [V\%_{\text{Mg}_{2}\text{Si}}][1.979] + [V\%_{\text{Be}}][1.85] \]

or

\[ V\%_{\text{Mg}_{2}\text{Si}} = 95.24 \sim 95.2, \text{ and } V\%_{\text{Be}} = 4.76 \sim 4.8 \]
APPENDIX D
Nucleation Entropy Calculation

Nucleation entropy of Mg₃Si

Reaction 1a

\[ \Delta S^{wa} = R(N_{Mg} \ln N_{Mg} + N_{Si} \ln N_{Si}) \]

\[ = (3)(1.98)(0.6667 \ln 0.6667 + 0.3333 \ln 0.3333) \]

\[ = -3.78 \text{ cal/mol.K} = -15.80 \text{ J/mol.K} \]

Reaction 2a

\[ \Delta S = \Delta S^o_{298} + \int_{298}^T \Delta C_p \ d\ln T \]

\[ \Delta S^o_{298} = S^o_{Mg_{2}Si} - 2S^o_{Mg} - S^o_{Si} \]

\[ \Delta S^o_{298} = 15.25 - 2(7.81) - 4.5 \]

\[ \Delta S^o_{298} = -4.87 \text{ cal/mol.K} = -20.38 \text{ J/mol.K} \]

\[ \Delta C_p = C_{P,Mg_{2}Si} - 2C_{P,Mg} - C_{P,si} \]

\[ C_{P,Mg_{2}Si} = 17.52 + 3.58 \times 10^{-3} T - 2.11 \times 10^5 T^2 \ (\text{cal/mol.K}) \]

\[ C_{P,Mg} = 5.33 + 2.45 \times 10^{-3} T - 0.103 \times 10^5 T^2 \ (\text{cal/mol.K}) \]

\[ C_{P,si} = 5.70 + 1.02 \times 10^{-3} T - 1.06 \times 10^5 T^2 \ (\text{cal/mol.K}) \]

\[ \Delta C_p = 1.16 - 2.34 \times 10^{-3} T - 0.844 \times 10^5 T^2 \]

\[ \Delta S = -4.87 + \int_{298}^T \left[ (1.16/T) - (2.34 \times 10^{-3}) - (0.844 \times 10^5/T^3) \right]dT \]

\[ \Delta S = -5.07 \text{ cal/mol.K} = -21.22 \text{ J/mol.K} \]

Reaction 3a

\[ \Delta S = \Delta S(1a) + \Delta S(2a) \]

\[ \Delta S = -3.78 - 5.07 = -8.85 \text{ cal/mol.K} = -37.02 \text{ J/mol.K} \]
Reaction 4a

\[ \Delta S_M = R \left( N_{Mg}^\alpha \ln \left( \frac{N_{Mg}^\alpha}{N_{Mg}^\beta} \right) + N_{Si}^\beta \ln \left( \frac{N_{Si}^\alpha}{N_{Si}^\beta} \right) \right) \]

\[ \Delta S_M = (3)(1.98)(0.6667 \ln[0.0104/0.6667]+0.33333\ln[0.0052/0.3333]) \]

\[ \Delta S_M = -24.71 \text{ cal/mol.K} = -103.30 \text{ J/mol.K} \]

Reaction 5a

\[ \Delta S = \Delta S(3a) + \Delta S(4a) \]

\[ \Delta S = -8.85 - 24.71 = -33.56 \text{ cal/mol.K} = -140.32 \text{ J/mol.K} \]

Molar Volume

\[ V_m = \frac{[V][N_A]}{Z} \]

where \( V_m \) is the molar volume, \( V \) volume of unit cell (\( a^3 \)), \( N_A \) Avogadro number, and \( Z \) number of atoms per unit cell, the values were obtained from x-ray diffraction results, thus,

\[ V_m = \left[6.3586 \times 10^4\right]\left[6.02 \times 10^{23}\right]/4 \]

\[ V_m = 38.70 \text{ cm}^3/\text{mol.} \]

Volume Nucleation Entropy Change

\[ \Delta S_v = \Delta S(5a) / V_m = -140.32/38.70 = -3.63 \text{ J/cm}^3 \text{ K} \]
APPENDIX E
Nucleation Rate Calculation

$\Delta G^*$ for MgSi

$\Delta V/V = V^\beta - V^\alpha / V^\beta = 12.90 - 10.02 / 12.90 = 0.2232$

$\mu_m = E / 2(1+\nu) = 72 \times 10^6 / 2(1+0.33) = 2.71 \times 10^{10} \text{ J/m}^3$

$\mu_m,350 = (10\%) \phi,71 \times 10^{10} = 2.71 \times 10^9 \text{ J/m}^3$

$W = 2\mu_m (\Delta V/V)^2(1+\nu/1-\nu) = 2(2.71 \times 10^9)(0.2232)^2\{(1+0.33)/(1-0.33)\}$

$W = 5.36 \times 10^6 \text{ J/m}^3$

$\gamma = 110 \text{ mJ/m}^2$

$\Delta G^* = \pi \gamma\{(2+f(c/r))\}^2/12(c/r)(-\Delta S_v \Delta T+W)^2$

$\Delta G^* = \pi(0.11)^3\{(2+2)\}^2/12(1)(-3.63 \times 10^6 \times 300 + 5.36 \times 10^6)^2$

$\Delta G^* = 7.29 \times 10^{20} \text{ J}$

$\dot{N}_{bon} \propto \exp(-\Delta G^*/kT)$

$\dot{N}_{bon} \propto \exp(-7.29 \times 10^{20} / 1.38 \times 10^{23} \times 523)$

$\dot{N}_{bon} \propto \exp(-10.1)$

$\Delta G^*$ for MgSiBe$_{0.15}$

$\Delta G^* = \pi(0.11)^3(2+2)^3/12(1)(-3.96 \times 10^6 \times 300 + 5.37 \times 10^6)^2$

$\Delta G^* = 5.25 \times 10^{20} \text{ J}$

$\dot{N}_{bon} \propto \exp(-5.25 \times 10^{20} / 1.38 \times 10^{23} \times 523)$

$\dot{N}_{bon} \propto \exp(-7.27)$

Relative Nucleation Rate:

$\dot{N}_{Mg2SiBe_{0.15}} / \dot{N}_{Mg2Si} = \exp(-7.27)/\exp(-10.1)$

$\dot{N}_{Mg2SiBe_{0.15}} / \dot{N}_{Mg2Si} = 17$
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