PHASE TRANSFORMATIONS AND DEFORMATION BEHAVIOR
IN THE ALUMINUM-LITHIUM-ZIRCONIUM SYSTEM

by

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ABSTRACT

Phase transformations, mechanical properties and deformation
behavior have been studied in the Al-Li-Zr alloy system. The aluminum-
lithium system has been extensively investigated in the past decade due
to the strong effectiveness of Li in increasing elastic modulus, lowering
density and providing high strength in aluminum alloys. The precipitate
of interest in the binary alloys is metastable Al3Li, or \( \delta' \), which
precipitates homogeneously as a spherical, simple cubic, \( \text{L1}_2 \)-ordered
(Cu3Au prototype) phase coherent with the fcc matrix. In the present
study it was proposed that the \( \text{L1}_2 \)-ordered Al3Zr and Al3Li phases might
show partial or total intersolubility, and that the production of an
Al3(Li,Zr) phase might prove valuable in improving the problems of low
ductility and fracture toughness of Al-Li alloys. For the purposes of
this work we have designated such an \( \text{L1}_2 \)-ordered Al3(Li,Zr) phase as \( \delta'' \).

The alloys analyzed in this study, Al-2.34Li-1.07Zr and Al-2.19Li-
0.12Zr (by wt. %), were produced by rapid solidification processing
(vacuum atomization) to produce the required Zr supersaturation. The
atomized powder was subsequently vacuum-hot-compacted and extruded.
Precipitation of the \( \delta'' \) or Al3(Li,Zr) phase initiates during the
extrusion process and continues during "solution"-heat-treatment (SHT) at
450-580°C. The \( \delta'' \) precipitates discontinuously as fine rods (typically 6
nm diameter) and as discrete spheres. Subsequent aging at 190°C results
in a preferred nucleation of \( \delta' \) at the \( \delta'' \)-matrix interface, producing
envelopes of \( \delta' \) completely surrounding the \( \delta'' \). The \( \delta' \) also precipitates
homogeneously as spheres in the usual manner in regions devoid of \( \delta'' \).

A method of quantitative compositional analysis has been developed
through which comparison of calculated electron micrograph images with
actual superlattice darkfield images yields a Li:Zr ratio in the \( \delta'' \)
phase. By this method it has been confirmed that the \( \delta'' \) phase has indeed
been produced, and that significant variations in the Li:Zr ratio in the
Al3(Li,Zr) occur which are dependent on heat treatment and precipitation
mechanism. The composition of Al3(Li_x,Zr_{1-x}) varies with "x" values from
0.2 to 0.6.

A thermodynamic model of free energy for the Al3(Li_x,Zr_{1-x}) phase as
a function of x, or composition, predicts a minimum chemical free energy
at \( x \geq 0.15 \) (at 450°C) to \( x \geq 0.2 \) (at 500-580°C). This compares with an experimentally determined value of \( x \geq 0.2 \) after the 580°C/15 h SHT, suggesting the \( \delta'' \) had reached its equilibrium composition. It is believed that the more Li-rich \( \delta'' \) produced under other SHT conditions did not attain an equilibrium composition due to very low Zr diffusivity.

The mechanical properties of the high-Zr alloy are significantly improved over the low-Zr alloy. At equivalent ductility, the high-Zr alloy has a 20 ksi (140 MPa) advantage in yield strength over the low-Zr alloy. At equivalent strength levels the high-Zr alloy has ~2 to 3 times the elongation. A comparison of deformation microstructures is presented. The improvement in properties has been determined to be due to a refined grain structure, slip dispersion by the \( \delta'' \) phase, and a strengthening of the \( \delta' \)-precipitate-free zones by \( \delta'' \).

Thesis Supervisor: Professor John B. VanderSande
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CHAPTER ONE

INTRODUCTION

Aluminum-lithium alloys have received much attention in the past decade due to an excellent combination of properties superior to those available in conventional aluminum alloys [1,2]. The addition of each weight percent Li to aluminum results in an increase in elastic modulus of approximately 6-8 percent [3-5] and a decrease in density of approximately 3 percent. In addition, the metastable precipitate Al₃Li, or δ', affords considerable strengthening, providing a combination of properties which is very attractive, especially for aerospace applications.

A major drawback to Li additions, however, is a reduction in toughness. This low toughness has been attributed primarily to soft precipitate-free zones at grain boundaries [6,7], high hydrogen levels [6-11], and slip localization and work-softening on active slip planes [4-7,12,13]. The first two factors can be minimized through process control and heat treatment [6-8,14]. The third, slip localization, is believed to result from shearing of δ' precipitates by dislocations during deformation [4,5,7,13]. Various investigators [6,7,15-17] have attempted to reduce the extent of shearing of the δ' precipitates by tying up lithium in complex precipitates, e.g. S-phase, effected through copper and magnesium additions.

The thesis of the present work is that a solution to the problem of slip localization in Al-Li alloys can be found by modifying the δ' precipitate so as to increase resistance to dislocation shear. Zirconium
additions were selected based on the similarity of the metastable Al3Zr phase to δ" (both are coherent, L12-ordered phases [18-22]), and the high resistance of Al3Zr to shear during deformation [21,23]. The goal is to ascertain if a modified δ', or Al3(Li,Zr), could be produced which has improved behavior during deformation. The successful employment of this approach would retain the benefits of lithium additions to aluminum, while increasing the toughness of the alloys.

Thus, in this study a new alloy containing high Li and Zr levels has been proposed and investigated. The primary objectives of this study are:

1. To determine if a ternary δ" phase, or Al3(Li,Zr), based on the δ' phase, can be produced, and to ascertain the kinetics associated with such a transformation.

2. To characterize the composition of the ternary phase.

3. To determine effects of such a phase on deformation behavior and mechanical properties of the alloy.

This study has been carried out primarily using Al-2.34Li-1.07Zr and Al-2.19Li-0.12Zr (wt.%) alloys. The alloys were produced using rapid solidification and controlled consolidation processing to produce the desired Zr supersaturation. Analysis of phase transformations and deformation microstructures was conducted primarily through electron microscopy, including image calculation as a tool for compositional analysis. Mechanical tests were used to provide tensile properties and data for structure-property relationships.
CHAPTER 2

BACKGROUND AND SURVEY OF RELEVANT LITERATURE

This chapter begins with a brief review of the past development of Al-Li alloys. The bulk of the chapter is then devoted to a collection of data from the literature relevant to this project. This includes characterizations of the Al-Li and Al-Zr binary systems with respect to thermodynamic and kinetic data (phase diagrams, diffusivities, etc.), precipitate characteristics (structure, lattice misfit and physical and mechanical properties), and deformation behavior. The limited literature on the Al-Li-Zr system is then reviewed, including the recent publications resulting from the present study and others. Finally, general studies on precipitate modification and inter solubility of intermetallic phases in aluminum systems are presented, along with implications regarding possible inter solubility of Al₃Zr and Al₃Li.

2.1 Historical Perspective

Lithium was actively pursued as an alloying addition for aluminum as long ago as the 1920's in Germany, where it was used as a minor element in the commercial Scleron alloys [24-27]. Lithium was successfully used at a nominal 1.1 wt.% level in Alcoa's commercial alloy 2020 for airframe applications near the end of the 1950's [28]. Though use of the alloy was discontinued due to concerns about fracture toughness, intensive development programs were undertaken in the 1970's and '80's in an effort to take advantage of the modulus and density benefits available through Li additions. These renewed efforts were spurred in part by reports in the Soviet literature suggesting that Fridlyander and coworkers [29] were close to achieving a commercial Al-Li-Mg alloy in the
mid 1960’s. By the late 1970’s, precipitation and deformation behavior in the Al-Li binary alloys were fairly well established, including the shearing of δ' during deformation and accompanying intense slip localization. (The reader is referred to the excellent review by Balmuth and Schmidt covering this developmental period up to 1980 [28].)

Alloy development efforts in the past few years have largely taken the approach of alloying with copper or copper and magnesium. These additions have the effect of tying up Li in complex ternary or quaternary precipitates, precluding δ' precipitation and its associated ductility loss. After much developmental work, this approach has been successful to the point of verging on the production of commercially viable alloys.

Zirconium is being used increasingly in commercial aluminum alloys as it very effectively inhibits recrystallization during hot-working and solution heat treatment [30]. It is used routinely at the 0.1 wt.% level in Al-Li alloys for this purpose. Zirconium is also used at higher levels, eg. 0.4 - 0.6 wt.%, to afford superplasticity in conventional Li-free aluminum alloys [31-35] and Al-Li alloys [36-38] Zirconium has also been proposed for use as a dispersoid in Al-Li to inhibit slip localization [15], though results were unpromising.

2.2. The Al-Li Binary System

Principal features of the aluminum-rich Al-Li binary system include the equilibrium AlLi phase (or δ) and the metastable strengthening precipitate Al₃Li (or δ'), the latter being of primary interest here.

2.2.1. The Equilibrium Al-Li phase diagram.

The equilibrium Al-Li binary phase diagram is well established [39-43], showing simple eutectic behavior between pure aluminum and the
equiatomic phase, AlLi (see Fig. 2.1). The AlLi phase (δ) is cubic with the B32 (NaTl) structure and a lattice parameter of 6.37 Å [44]. AlLi precipitates heterogeneously at grain boundaries with extended aging at normal aging temperatures (e.g. 150-200°C). This phase is fairly reactive and generally undesirable due to effects on mechanical properties (stress concentrations at grain boundaries) and corrosion resistance.

2.2.2 The α-δ' System.

Strengthening in aluminum-lithium alloys is provided by the metastable δ' (Al₃Li) precipitate. Al₃Li is an ordered, simple cubic crystal structure of the Cu₃Au (L1₂) type, derived by ordering the primitive face-centered cubic cell (see Fig. 2.2). The phase forms spherical, coherent precipitates with a cube-cube orientation relationship with the matrix and a small negative lattice misfit of approximately -0.08% [19,20]. It is generally believed that precipitation of δ' occurs homogeneously, although spinodal decomposition has been suggested as a mechanism [44].

The δ' solvus line is fairly well established for temperatures below 300°C [20,44-46] as shown in Fig. 2.1a. Baumann and Williams [47] have recently shown, however, that the solvus at the higher Li levels occurs at higher temperatures than indicated in Figures 2.1a and 2.1b (specifically, at 3.7 wt.% Li the solvus is higher by 35°C).

There remains some question as to the character of the α-δ' metastable system. Determination of the nature of the diagram through experimental means is not simple due to the fairly rapid precipitation of equilibrium AlLi at temperatures above approximately 300°C. The construction as generally accepted in the recent literature is the miscibility gap of Fig. 2.1b, as suggested by Cocco et al.[46]. However,
Figure 2.1. The Al-Li Phase Diagram. a) The Al-Alli equilibrium system and solvus data for the metastable α-δ' (or α') system. From [43]. b) The α-δ' system as generally used in the literature. After [44]. c) A proposed construction of the α-δ' system involving a monotectoid reaction. From [49].
Figure 2.2. Unit cells of the closely related Ll₂ (a), D₀₂₂ (b), and D₀₂₃ (c) phases. The metastable Al₃Li and Al₃Zr phases are Ll₂. Equilibrium Al₃Zr is D₀₂₃.
such a miscibility gap of two distinct crystal structures violates thermodynamic restrictions on phase diagram construction. Furthermore, a single phase δ' phase field is not readily fitted into the diagram.

Given that an L12 ordering reaction must be first order [48], the true metastable phase diagram must contain a single-phase δ' field and a two-phase (α + δ') field. The monotectoid system (Fig 2.1c) as proposed by Gayle and VanderSande [49] is thermodynamically acceptable and accounts for all data points of Fig. 2.1a. This diagram includes a critical ordering temperature of 537°C for Al3Li as calculated by Tasura et al.[50]. Such a configuration is appealing in that it allows for either homogeneous nucleation or spinodal decomposition, both of which have been proposed for the system. On the other hand, the more recent data point for the solvus at 3.7 wt.% Li mentioned above does not fit in well with this proposed phase diagram construction.

Present Analysis of the α - δ' System

Shown in Figure 2.3 is the α-δ' system as proposed in the present work. Data points along both sides of the α + δ' two-phase field below ~300°C are from Figure 2.1. The recent data point at 13 at.% Li from Baumann and Williams [47] is also included.

An additional reference point for construction of the phase diagram is obtained through calculation of the critical ordering temperature (Tc) for δ' based on a knowledge of antiphase boundary (APB) energy for the phase. Tasura et al. [50], have calculated the APB energy to be 195 ergs/cm² based on a measurement of spacing of superdislocation pairs. (Note there was very wide scatter in the data). Using,
Figure 2.3. The α-δ' system of the Al-Li system as proposed in the present study. Data points are from the literature (see Fig. 2.1). The critical ordering temperature for δ' has been calculated (see text).
\[
\delta_{\text{APB}} = \frac{4kT_C}{a^2 \sqrt{3} \ 0.82}
\]  

(2.1)

where \(k\) is the Boltzmann constant, \(a\) is the lattice parameter, and 0.82 is the value for a parameter which correlates to ordering energy for L1_2 structures (see (51,52)). Tamura has calculated \(T_C = 810\ K\) (537°C).

Noble et al. have calculated a maximum APB energy of 160 erg/cm^2 [AJ] by attributing all the strengthening in a \(\delta'\)-hardened binary alloy to order hardening. Using this value in Eqn. 2.1, one arrives at a \(T_C = 665\ K\) (392°C).

Averaging the above calculated values yields a \(T_C = (810+665)/2 = 738\ K = 465°C\). Using this value and the most reliable solvus data, the metastable phase diagram for \(\alpha-\delta'\) in Figure 2.3 has been constructed. This diagram is thermodynamically permissible, in contrast to the construction of Figure 2.1b. Figure 2.3 is preferred to the monotectoid system of Figure 2.1c since only a negative enthalpy of mixing in this region of the Al-Li system is implied rather than both a positive and negative enthalpy of mixing as discussed above.

2.2.3 AlLi-\(\delta'\)-Precipitate-Free Zone Interaction

Mention must be made regarding precipitate-free zone (PFZ) formation. After extended aging treatments, \(\delta'\) dissolves in regions near grain boundaries in the presence of grain-boundary AlLi. This PFZ has been observed to grow at normal aging temperatures with a (time)^{1/3} rate dependence [54]. A very high grain-boundary diffusivity (as indicated by a uniform PFZ width) allows the aluminum matrix at the boundary to be a "sink" whose composition is in equilibrium with AlLi once that phase has nucleated at the boundary. However, \(\delta'\) in the vicinity is in equilibrium with aluminum of higher Li content. Thus \(\delta'\) near the boundary will
dissolve with the resulting Li diffusing to the grain boundary to subsequently precipitate as Al\textsubscript{Li}.

The PFZ problem leads to intergranular weakness and can be a severe limitation to ductility. An underaged temper is often used to minimize PFZ width.

2.2.4 Other data regarding the Al-Li binary system.

The $\delta'$-aluminum interfacial energy has been reported to be from 180 to 240 erg/cm\textsuperscript{2},[50,55] and the antiphase boundary (APB) energy as 195 [50] and 160 erg/cm\textsuperscript{2} [53]. Noble and Thompson [55] suggested an interfacial energy of 25 ergs/cm\textsuperscript{2} would be more appropriate, based on a comparison with coherent, $\mathrm{Ll}_2$-ordered precipitates in other metal alloy systems. More recently, Baumann and Williams [56] have determined that the previous values for interfacial energy, as calculated from precipitate coarsening rates, failed to consider effects of the large volume fraction of $\delta'$. Including these effects, they obtained values of 8-25 erg/cm\textsuperscript{2}, and, by an independent method, 14 erg/cm\textsuperscript{2}.

The large increase in modulus in these alloys results from Li in solid solution or as $\delta'$. Al\textsubscript{13}Li has an elastic modulus of approximately 96 GPa [4], compared with 67 GPa for pure aluminum.[40] In solid solution, each wt.% Li affords an increase in modulus of approximately 8% [4,5].

Table 2.1 summarizes the above-described effects of Li in aluminum, as well as effects on lattice parameter, modulus, hardness and electrical resistivity. Notable is the fairly high diffusivity of Li in Al, given as $D = 4.5 \exp(-33,000/RT)$,[57] (D in cm\textsuperscript{2}/s, Q in cal/mol).

2.3. The Al-Zr Binary System.

The Al-rich side of the Al-Zr system features two intermetallic
Table 2.1 - Precipitate Characteristics in the Al-Li and Al-Zr Binary Systems and Effect of Li and Zr In Aluminum-Solid Solution.

<table>
<thead>
<tr>
<th>PRECIPITATE PHASES</th>
<th>$\text{Al}_3\text{Li}$</th>
<th>Ref</th>
<th>$\text{Al}_3\text{Zr}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Parameter (Å)</td>
<td>4.047</td>
<td>20</td>
<td>4.08</td>
<td>21,22</td>
</tr>
<tr>
<td>Lattice Misfit (Å%)</td>
<td>-0.08</td>
<td>20</td>
<td>+0.8-1.0</td>
<td>21,22</td>
</tr>
<tr>
<td>Interfacial Energy (erg/cm²)</td>
<td>8-25</td>
<td>56</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$\gamma_{\text{APB}(111)}$ (erg/cm²)</td>
<td>195</td>
<td>50</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Modulus (GPa)</td>
<td>96</td>
<td>4</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>IN SOLID SOLUTION</th>
<th>Li</th>
<th>Ref</th>
<th>Zr</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Parameter $\frac{1}{a} \text{da} \mid$ (per wt.fraction in SS)</td>
<td>-0.0200</td>
<td>40</td>
<td>+0.0576</td>
<td>76,100</td>
</tr>
<tr>
<td>Hardness $\frac{d \text{HV}}{d\text{C}}$ ((kg/mm²)/wt.% solute) (MPa/at.%))</td>
<td>+9.9</td>
<td>55</td>
<td>+27</td>
<td>100</td>
</tr>
<tr>
<td>Electrical Resistivity $\frac{d \mu \text{Ωcm}/\text{wt.}% \text{ solute}}{d\text{C}}$ ($\mu\text{Ωcm}/\text{wt.}% \text{ solute})</td>
<td>+0.92</td>
<td>55</td>
<td>+1.28</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>+0.4</td>
<td>40</td>
<td>+2.73</td>
<td>76</td>
</tr>
<tr>
<td>Elastic Modulus $\frac{d}{d\text{C}}$ (Å/ wt.% solute)</td>
<td>+13.29</td>
<td>94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusivity $D_0$ (cm²/sec)</td>
<td>4.5</td>
<td>57,101</td>
<td>728</td>
<td>40,101</td>
</tr>
<tr>
<td>$Q$ (cal/mole) (kJ/mole)</td>
<td>33,000</td>
<td>57,101</td>
<td>57,500</td>
<td>40,101</td>
</tr>
<tr>
<td>Dissolution of $\text{Al}_3\text{X}$ (DO23)</td>
<td>--</td>
<td>240</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(transfer of X into SS)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta H$ (J/mole)</td>
<td>--</td>
<td>-22,970</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>$\Delta S$ (J/moleK)</td>
<td>--</td>
<td>-15</td>
<td>94</td>
<td></td>
</tr>
</tbody>
</table>
phases, the equilibrium Al₃Zr (D₀₂₃ structure) and a metastable Al₃Zr (L₁₂ structure), the latter being of interest here. Zr was chosen for use as an alloying element in the present research in part because of this structural similarity to δ' and its comparable lattice parameter.

2.3.1 The Equilibrium Al-Zr phase diagram.

The equilibrium phase diagram features a peritectic system involving the equilibrium Al₃Zr phase (Fig. 2.4). Solubility of Zr in α-aluminum is very low at all temperatures (0.18 wt.% at the peritectic temperature). Solubility of Zr in liquid Al increases slowly with increasing temperature from 0.11 wt.% at the peritectic temperature (660.7°C) to -2.0 wt.% at 1000°C.

The equilibrium Al₃Zr phase is the tetragonal D₀₂₃ structure which is closely related to the L₁₂ structure (see Fig. 2.2). Lattice parameters are \( a = 4.013 \, \text{Å} \) and \( c = 17.321 \, \text{Å} \) [58].

2.3.2 The α-Al₃Zr (L₁₂) system and precipitation in the solid state.

Solid state precipitation in the Al-rich Al-Zr system occurs initially as the metastable (L₁₂) Al₃Zr phase. The phase typically precipitates as small spheres or rods coherent with the matrix with a small positive misfit (~ +0.8 %) [18,21,22,59]. Note that the misfit is about ten times that for δ' and of opposite sign. The phase is relatively stable and remains as the L₁₂ structure for long periods without transformation to (or dissolution because of growth of) the equilibrium D₀₂₃ phase (eg. stable longer than 700 hours at 460°C as the L₁₂ structure) [22]. With very extended, high temperature heat treatments, the equilibrium D₀₂₃ phase will precipitate heterogeneously, especially at grain boundaries [21,23].
Figure 2.4. The Al-Zr phase diagram. From [99].
The diffusivity of Zr in aluminum is very low, given as 
$D = 728 \exp(-57,500/RT)$ where the activation energy is in cal/mol and $D$ is in 
$\text{cm}^2/\text{sec}$ (40). This results in a $D_{Zr}$ of $4 \times 10^{-14}$ $\text{cm}^2/\text{sec}$ at 500°C, some 
five orders of magnitude lower than the lithium diffusivity at this 
temperature. Thus, precipitation requiring bulk diffusion is extremely 
sluggish, even in highly supersaturated conditions. As a consequence, 
precipitation often occurs by discontinuous precipitation at grain 
boundaries during recrystallization. The resulting distribution of $L_12$-
type $Al_2Zr$ is in a fan-like arrangement of rods of diameter typically 10 
$\text{nm}$ [21,23,31,60-62].

Additional data on the Al-Zr system are given in Table 2.1.

2.3.3 Extended Zr Solubility Through Rapid Solidification

The 1 wt.% solid solubility of Zr required for the proposed alloy is 
far in excess of equilibrium values. However, comparable extended 
solubilities are reported in the literature as obtained through rapid 
solidification processing. These values are given in Table 2.2.

2.4. Deformation Behavior of the Binary Alloys.

The present work was stimulated in part by the different deformation 
behavior observed in the Al-Li and Al-Zr binary systems. As described 
below, Li imparts high strength to the alloy but the $\delta'$ precipitates are 
sheared by dislocations and slip localization results. Zirconium, on the 
other hand, can afford some dispersion hardening (dependent upon a fine 
precipitate distribution) [40], and appears to have higher resistance to 
dislocation shearing.

2.4.1 Deformation in Alloys Containing Coherent, Ordered Precipitates.

As slip occurs in aluminum-based (and other fcc) alloys,
Table 2.2 - Studies of Extended Solid Solubility of Zirconium in Aluminum Obtained Through Rapid Solidification

<table>
<thead>
<tr>
<th>Solid Solubility(^1) wt.% (at.%)</th>
<th>Method, Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.4 (3.0)</td>
<td>Hammer and Anvil (est. (10^7) K/s)</td>
<td>82</td>
</tr>
<tr>
<td>8.6-9.4 (2.7-3.0)</td>
<td>but not 12.6 wt% (4.1%) Two piston, Cu plates (est. (8 \times 10^5) K/s)</td>
<td>81</td>
</tr>
<tr>
<td>3.4</td>
<td>splat (est (10^7-10^8) K/s)</td>
<td>79</td>
</tr>
<tr>
<td>2.2 (0.67)</td>
<td>&quot;granular,&quot; centri-fugal cast</td>
<td>76</td>
</tr>
<tr>
<td>2.0 (0.60)</td>
<td>&quot;granular,&quot; 1-4 mm</td>
<td>100</td>
</tr>
<tr>
<td>1.3</td>
<td>(but not 1.7 wt.%) Cu chill mold ((~3 \times 10^3) K/s) Fe chill mold</td>
<td>79</td>
</tr>
<tr>
<td>1.0 (0.30)</td>
<td>Cu-chill mold, from 1000 C, (10^3) K/sec</td>
<td>75</td>
</tr>
<tr>
<td>0.5 (0.15)</td>
<td>Cu-chill mold, from 1000 C.</td>
<td>21</td>
</tr>
<tr>
<td>0.63 (0.20)</td>
<td>Cu-chill mold, 25 mm diameter</td>
<td>23</td>
</tr>
</tbody>
</table>

\(^1\)These are solid solubilities obtained in the various studies, and are not to be construed as maxima obtainable by the quoted methods (except BZ).
dislocations with Burgers vectors of type 1/2 <110> glide along (111) slip planes. The presence of coherent precipitates on the slip plane impedes dislocation movement. This resistance is determined by modulus mismatch, precipitate-matrix interfacial energy, "frictional" (Peierls) stress mismatch, and coherency strains [63,64]. In addition, antiphase boundary (APB) energy in ordered precipitates can make a significant contribution to strengthening.

To move past a precipitate during plastic deformation, dislocations may loop around the precipitate or cut through the precipitate. Which mechanism operates is determined by the "Kelly-Nicholson criterion" for dislocation looping [65], i.e., whether the critical resolved shear stress is greater for shearing behavior than for looping behavior. The criterion is based on interparticle spacing and the resistance to shearing, which in turn is determined by the factors described in the preceding paragraph.

An approximate contribution of each factor in precipitate strength can be calculated when the required physical/mechanical parameters are known. Calculations relevant to the precipitate modifications proposed in the present study are discussed below and in the Results and Discussion sections.

2.4.2 Deformation in Al-Li Binary Alloys.

The primary factor controlling deformation behavior in Al-Li binary alloys is the S' precipitate. Although very high strengths are attainable, dislocations generally glide by cutting through the precipitates [5,13,53]. After passage of a dislocation the cross-sectional area of any precipitate on the slip plane is reduced by an amount proportional to the Burgers vector and the diameter of the circle.
of intersection with the slip plane. The precipitate size is then effectively reduced on that slip plane and subsequent slip on the plane can occur at a lower critical stress. Work softening results as additional dislocations pass on the slip plane.

Superdiabolations, indicative of shearing of ordered precipitates, and intense slip bands have been documented in Al-Li alloys. [5-7]. The intersection of slip bands with grain boundaries causes extreme stress concentration and leads to loss of ductility and toughness. The problem is further aggravated if the grain boundary regions have been weakened by the presence of PFZ's, as described earlier. This combination of slip localization and grain boundary PFZ's leads to the intergranular failure often characteristic of these alloys.

Noble et al. [53] have calculated the strength of the δ' precipitate to be due primarily to the energy of APB formation and, to a somewhat lesser extent, modulus mismatch. They concluded that coherency strains and interfacial energy were of minimal consequence. This is not unexpected considering the small lattice mismatch and interfacial energy for the phase.

2.4.3 Deformation in Al-Zr Binary Alloys.

The deformation behavior of binary Al-Zr alloys has not been extensively investigated. Zirconium is reported to afford only slight strengthening [40,66] whether in solid solution or precipitated as Al₃Zr. The strengthening observed is probably due largely to the Zr-stabilized fine or unrecrystallized grain structure, as described by the Hall-Petch relationship.

There is evidence in the literature, however, that Al₃Zr is resistant to dislocation shearing. As reported by Ryum [21] the Al₃Zr
metastable precipitate results in tangles of dislocations during deformation. Sundberg et al. [23] report that a high density of $\text{Al}_3\text{Zr}$ fan-type precipitates results in a high, homogeneous dislocation density. They also observed that isolated spherical precipitates very effectively pin dislocations. Superdislocations, which would indicate precipitate shearing, are not evident in their micrographs.

2.5. The Al-Li-Zr Ternary System.

Zirconium is used routinely at the 0.1 wt.% level in Al-Li alloys to inhibit recrystallization during processing. It has also been used at the 0.4 wt.% level to induce superplasticity in Al-Li alloys [36-38]. Considering this fairly extensive use of Zr in these alloys, investigations of phase transformations in the ternary system have been surprisingly lacking. (Note the very recent exceptions described below).

The implicit assumption in the literature has been that the precipitation sequences for $\text{Al}_3\text{Li}$ and $\text{Al}_3\text{Zr}$ occur independently.

For completeness, very recent work on the ternary system will be here described. This includes publications resulting from the present work as well as those of other investigators currently in press. Gayle and VanderSande [67,68], working with an Al-2.3Li-1.1Zr alloy have shown extensive substitution (~50%) of Li for Zr on the Zr-sublattice in $\text{Al}_3\text{Zr}$ at 500°C. The $\text{Al}_3(\text{Li},\text{Zr})$ phase precipitates discontinuously in a fan-like distribution and as discrete spherical precipitates in this alloy. This phase subsequently serves as a preferred nucleation site for $\text{Al}_3\text{Li}$ precipitation, with the $\delta'$ wetting the $\text{Al}_3(\text{Li},\text{Zr})$ precipitates, forming complete surrounding envelopes. This has led to the term "composite" precipitates.

Makin and Ralph [69], investigating lower Zr levels (0.1 wt.%), also
report the preferred nucleation behavior of \(\delta'\) observed by Gayle and VanderSande. Makin and Ralph report in their paper that the core of each precipitate is the binary phase Al\(_3\)Zr, and that the precipitation processes for Al\(_3\)Li and Al\(_3\)Zr occur "chemically independently."

Similarly, Gregson and Flower (70) report the \(\delta'\) envelopes surrounding cores of Al\(_3\)Zr in Al-Li-Mg-Cu-Zr alloys.

2.6. Precipitate Modification - Intersolubility of Intermetallic Phases.

The proposed modification of \(\delta'\) to form Al\(_3\)(Li,Zr) is basically a question of intersolubility of isostructural intermetallic phases. It is possible that Al\(_3\)Li and Al\(_3\)Zr have complete intersolubility across the ternary phase diagram since the phases are isostructural. Even partial solubility, however, may allow the proposed phase modification and concomitant property changes. General theoretical guidelines for such intersolubility and past investigations of precipitate modification in aluminum systems are presented below.

2.6.1. General Guidelines.

Guidelines for the solubility of one element in another are outlined by the Hume-Rothery rules and subsequent modifications (71), but are difficult to apply in systems involving transition metals (71,72). Additionally, these rules were developed for use with elemental substitutions into single component phases. Certain aspects of these rules (atomic size, electronegativity and electronic structure) will be discussed, however, as they may give some insight into the proposed substitution in \(\delta'\).

For the purpose of predicting the extent of solid solubility of various elements, electronegativity vs. atomic radius plots (Darken-Gurry
maps) have proven useful [71]. For example, using the atomic radius and electronegativity of the solute of interest as a center, the region inscribed by an ellipse of axes ±0.2 electronegativity units and ±8% radius indicates favorable conditions for significant solid solubility. A similar construction may be useful here. Figure 2.5 is a modified Darken-Gurry map for the elements constituting various L12 phases in aluminum. The atomic radii indicated are those assumed by the elements in the respective L12 structures, based on a hard sphere packing model and assuming $r_{\text{Al}} = 1.432$ Å.

This map indicates the narrow range of atomic radii between Al, Li, and Zr, well within the ±8% range which is favorable for elements to show some mutual solid solubility. In fact, for the present case, reduction of coherency strain energy is a driving force for solution of Zr (and Sc) in δ' due to the opposite sign of lattice misfit.

Li is seen to have a significantly lower electronegativity value than Zr, which may be indicative of somewhat different bonding with Al. On the other hand, the values for Li and Zr are each significantly lower than that for Al, possibly leading to similar bond types within their respective L12 phases.

A related factor is the electronic configuration of the elements involved. The electronic structure of Li, with one electron contributing to bonding, cannot be considered similar to that of a transition metal, with its d-shell and s-shell hybrid bonds. This may be considered unfavorable for the proposed substitution.

2.6.2 Intersolubility Within Al-based L12-type Intermetallics.

A survey of the literature has provided no information on the interaction of Al3Li with other intermetallics; however, there have been
Figure 2.5.
Modified Darken-Gurry map relating electronegativity and radii of atoms in Al$_3$X. Solid line is portion of ellipse about Li with axes of ±8% radius and ±0.2 electronegativity units (see text).
studies of other aluminum-based intermetallic systems with the L1₂ structure. For example, Zn is soluble in Al₃Zr (apparently on the Al sublattice) and actually stabilizes the phase as L1₂ [73]. Schubert and coworkers [73,74] have shown also that Al₃Ti (DO₂₂ structure at equilibrium) is stabilized as L1₂ by Zn, Cu, and Ni. Similarly, Al₃Nb and Al₃Hf will absorb significant amounts of Ni and Zn, respectively [74].

A proposed modification of the δ' precipitate through Sc, Ga and Ag additions has been investigated [6]. Results were not promising, although the Al-Li-Sc alloy, with large primary intermetallic phases (processed through ingot metallurgy), may hold promise if processed using rapid solidification techniques.
CHAPTER 3
OUTLINE AND PLAN OF WORK

There are two major goals of the present research: (1) the determination of the extent of inter.solubility of the Al₃Zr and Al₃Li phases and possible thermodynamic or elastic interaction of the two phases in the Al-Li-Zr ternary system; and (2) the characterization of deformation behavior in high and low-Zr Al-Li-based alloys and related mechanical properties in the ternary system. The overall approach, as discussed below, is diagrammed schematically in Figure 3.1.

The alloys chosen for this work are of the nominal compositions Al-2.4Li-1.0Zr and Al-2.4Li-0.12Zr (wt.%), and were processed under comparable conditions. The latter is a control alloy with a minimal Zr addition designed to inhibit recrystallization, thus providing comparable grain structures in the two alloys.

The high liquidus temperature of the high-Zr alloy and the low solubility of Zr in α-aluminum necessitated rapid-solidification-processing with a minimum pour temperature of approximately 1000°C. Inert gas atomization was employed, which normally provides cooling rates of 10³ to 10⁴ K/sec, sufficient to produce the desired Zr supersaturation. The atomization was followed by consolidation through vacuum hot compaction and extrusion. The steps of the consolidation process were carried out at the lowest possible temperatures to minimize the likelihood of depleting the zirconium supersaturation through the precipitation of Zr-rich phases. The preservation of the solid solution is made feasible by the very low diffusivity of Zr in aluminum.

Phase transformations and deformation microstructures in the alloys
Figure 3.1. Outline of approach taken in present investigation for characterization of phase transformations and deformation behavior in the Al-Li-Zr system.
were studied largely through various techniques of transmission and scanning transmission electron microscopy. A wide range of thermal treatments was investigated to characterize the phase transformations and compositional variations in the resulting phases as a function of thermal history. Standard methods of compositional analysis were not applicable, thus a method involving image calculations was developed.

The effect of selected thermo-mechanical treatments on phase transformations was also studied. Relationships between heat treatment, mechanical properties and deformation behavior were developed through analysis of tensile test results, hardneass-aging curves and deformation microstructures (as analyzed through electron microscopy). Study of the two alloys (high and low Zr) allowed the deformation structure of the "experimental" (high-Zr) alloy to be compared with that of an essentially binary Al-Li alloy. Tensile and yield strengths and elongation to failure were determined as a function of heat treatment and specimen orientation. In addition, samples were examined after 1% plastic strain in order to study dislocation behavior in the early stages of deformation.

Analysis of the fracture surfaces of the tensile samples was performed using optical and scanning electron microscopy to follow changes in fracture behavior as a function of composition and thermal treatments.
CHAPTER 4
EXPERIMENTAL PROCEDURE

There are two major sections to this description of the experimental procedure. The first involves the development and implementation of procedures for production of the proposed Al-2.4Li-1.0Zr and Al-2.4Li-0.1Zr alloys in a form with the desired supersaturation and structural integrity. The second grouping of procedures covers the mechanical and microstructural analysis of the alloys. This includes determination of aging and precipitation behavior and deformation characteristics, including mechanical properties. Extensive use was made of electron microscopical techniques for analysis, including transmission and scanning transmission microscopy, and electron energy loss spectroscopy.

4.1. Material Production.

The general approach in producing the material was to inert-gas-atomize the alloys at a pour temperature above the liquidus of the high-Zr alloy and subsequently process the alloys at temperatures low enough to retain the Zr largely in solid solution (preferably below 300-375°C [22,75,76]). The entire processing sequence is given schematically in Figure 4.1 and is described in detail below.

4.1.1. Powder Production.

The two alloys were prepared from high purity aluminum and 20 wt.% Li and 6 wt.% Zr master alloys. The alloys were inert-gas-atomized (IGA) by Homogeneous Metals, Inc. (Herkeimer, NY) at a nominal
Figure 4.1. Processing sequence for alloy production.
temperature of 960°C, equivalent to approximately 70°C superheat for the high-Zr alloy. Actual blow temperatures were 960°C and 980°C for the high and low-Zr alloys, respectively. The powder recovered was sieved and the -100 mesh fraction was used for further processing.

The two alloys were analyzed to be, in weight %, Al-2.34Li-1.07Zr (by Homogeneous Metals) and Al-2.19Li-0.12Zr (by Reynolds Metals Co., Richmond, Va.).

4.1.2. Vacuum Hot Compaction.

The powder (-100 mesh) of each alloy was subsequently consolidated through vacuum hot compaction (VHC) by ARCO Metals, Inc. (Greer, S.C.), using a single-acting press. The optimal procedure developed for compaction is as follows:

1. Load 1.1 kg of -100 mesh powder into the press (resulting billet dimensions: 2.5" diameter by 5.5-6.0" length).
2. De-gas on heating (under vacuum of ~2 μm).
3. Soak 15 min. at 300°C (340°C for high Zr).
4. Press 20 min. at a ram force of 50 tons (ie., 20,000 ksi or 138,000 kPa).
5. Reverse ends of billet in press.
6. Press from other end - repeating steps 3 and 4.

This procedure was found to result in sound billets of ~98% of ideal density. The actual conditions and resulting billet sizes and densities are given in Table 4.1.

4.1.3. Extrusion.

The VHC billets were extruded at Minalex, Inc. (White House
<table>
<thead>
<tr>
<th>ID</th>
<th>Temp.</th>
<th>Press</th>
<th>Billet Length</th>
<th>Mass</th>
<th>Density</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>380</td>
<td>48/36</td>
<td>168</td>
<td>1150</td>
<td>2.18</td>
<td>88 Billet crumbled on removal from press. &quot;Soft and powdery&quot;</td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>50/20</td>
<td></td>
<td></td>
<td></td>
<td>Billet broke in two (at 1/3 point).</td>
</tr>
<tr>
<td>27</td>
<td>340</td>
<td>50/60</td>
<td>147</td>
<td>1129</td>
<td>2.44</td>
<td>98 Sound billet.</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>50/20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>380</td>
<td>50/20</td>
<td>150</td>
<td>1147</td>
<td>2.44</td>
<td>98 Sound billet.</td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>50/20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>380</td>
<td>50/20</td>
<td>149</td>
<td>1150</td>
<td>2.45</td>
<td>98 Sound billet.</td>
</tr>
</tbody>
</table>

Common parameters
Billet diameter - 62.5 mm.
Degas under pressure of 2 μm.

1 All billets except #4 were pressed from both ends of the billet. The two sets of numbers quoted per billet are values for the two steps involved.
Station, NJ). Rod (0.500" diameter) and bar (1.630" x 0.260") shapes were produced at extrusion ratios (ER) of 29.2:1 and 13.5:1, respectively. Values for other pertinent parameters relating to the extrusion procedures are given in Table 4.2.

With the goal of retaining Zr in the supersaturated-solid-solution, it was desired to keep processing temperatures below 300-375°C. The billets were preheated by induction heating, and temperature profiles from front end to back end were taken prior to loading in the extrusion press (see Table 4.2 for values). Note that although the heating of the billets was non-uniform, the temperatures were relatively cold throughout each billet at this step (160 - 304°C). Additionally, as indicated in Table 4.2, the press cylinder was kept within the same temperature range.

A fast extrusion rate was found to give the best surface quality, with no breaks and tears as were seen using a slower rate. However, considerable heating during extrusion occurred with the faster extrusion rates due to the adiabatic heating associated with hot working. Some indication of the transient temperature peaks can be seen in Figure 4.1, which shows approximate cooling curves for the extrusions as they exited the press. Thus some extrusions experienced temperatures in excess of 400°C for periods of up to about one minute.

4.1.4. Thermal Treatments.

The extrusions were examined using various techniques (described in Section B below) in the as-extruded condition and after various combinations of heat treatments. "Solution-heat-treatments" (SHT) were carried out at 425-580°C for periods from 10 minutes to 500 hours. The
### Table 4.2

**Extrusion Processing Parameters**

<table>
<thead>
<tr>
<th>ID</th>
<th>%</th>
<th>Shape</th>
<th>ER</th>
<th>Billet Temp.</th>
<th>Cylinder Temp.</th>
<th>Hydr. Pressure</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fr</td>
<td>Mid</td>
<td>Bk</td>
<td>(°C)</td>
</tr>
<tr>
<td>Al-</td>
<td>4</td>
<td>—</td>
<td>rod</td>
<td>29:1</td>
<td>150</td>
<td>193</td>
<td>227</td>
</tr>
<tr>
<td>2.34Li-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.07Ir</td>
<td>8</td>
<td>88</td>
<td>bar</td>
<td>13:1</td>
<td>304</td>
<td>177</td>
<td>143</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>98</td>
<td>rod</td>
<td>29:1</td>
<td>250</td>
<td>249</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-</td>
<td>6</td>
<td>98</td>
<td>rod</td>
<td>29:1</td>
<td>250</td>
<td>238</td>
<td>238</td>
</tr>
<tr>
<td>2.19Li-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.12Ir</td>
<td>9</td>
<td>98</td>
<td>bar</td>
<td>13:1</td>
<td>304</td>
<td>250</td>
<td>252</td>
</tr>
</tbody>
</table>

**Dies** - rod 12.7 mm diameter
bar 41.4 x 6.6 mm.

**Press cylinder** - 68.6 mm diameter.
**Press capacity** - 5000 ton.

**Note:** No gas used on exit side for all but 09.
Figure 4.2. Temperature of extrusions upon exiting from the extrusion press. Time $= 0$ at approximately 10-20 seconds out of the die.
10 minute treatments were done in air. Heat treatments longer than 10 minutes were conducted with samples encapsulated in pyrex under an argon atmosphere.

Aging curves were determined after aging at 190°C using Rockwell B hardness measurements. All aging treatments were conducted at 190°C in air.

4.2. Analysis

4.2.1. Electron Microscopy.

Samples for TEM and STEM were prepared as 3 mm disks using standard techniques: twin-jet electropolishing using 30 vol.% HNO₃ in methanol, T = -30°C, V = 12.5 volts and J = 0.65 - 0.95 A/cm². Examination of the specimens was done on a JEOL 200CX TEM and a Vacuum Generators HB-5 STEM. The electron energy loss spectroscopy (EELS) work was carried out using a Philips 400T-FEG (field emission gun) at the Arizona State University Facility for High Resolution Microscopy (Tempe, Arizona).

4.2.2. Mechanical Testing.

The mechanical tests were performed at the Metallurgical Research Division of Reynolds Metals Co. (Richmond, Virginia). Longitudinal test specimens for the 0.5" rod were 0.350" diameter round tensile bars. Samples for 1% plastic strain were 0.160" rounds. Longitudinal and transverse tensile properties on the rectangular extrusion were measured using 0.113" rounds.
CHAPTER FIVE

PRECIPITATION BEHAVIOR AND AGING CHARACTERISTICS

5.1. INTRODUCTION

The following four chapters are devoted to the presentation and discussion of the results of this study. The first chapter presents the precipitation behavior and typical microstructures in the Al-Li-Zr system. Subsequent chapters will detail the compositional analysis of the Al₃(Li,Zr) phase (Chapter 6), deformation behavior of the alloys (Chapter 7), and thermodynamic and physical properties of the δ" phase (Chapter 8).

Precipitation behavior and microstructure of the alloy system are the focus of the present chapter. Various solution heat treatments have been analyzed, and hardness curves were used to characterize subsequent aging behavior. Microstructures were analyzed at different stages of thermal treatment. The microstructure prior to extrusion has been inferred. The influence of Zr on phase transformations, particularly precipitation behavior, in the Al-Li system is presented and discussed in detail.

Alloys 27 (high Zr) and 6 (low Zr) were used for this part of the study. hZ and LZ will be used to refer to the high zirconium and low zirconium alloys, respectively, in this chapter. For reference, the compositions are given in Table 5-1.
Table 5.1. Composition of Alloys Examined in Chapter 5 (wt.%).

<table>
<thead>
<tr>
<th>ID</th>
<th>Li</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2.19</td>
<td>0.12</td>
</tr>
<tr>
<td>27</td>
<td>2.34</td>
<td>1.07</td>
</tr>
</tbody>
</table>
5.2. RESULTS

5.2.1 Aging Curves

Rockwell B hardness values were used to characterize aging behavior. Aging curves at 190°C for the extrusions after various solution-heat-treatments are given in Figure 5.1. Included for comparison is the curve for an Al-2.87Li ingot metallurgy alloy [77].

From a comparison of the curves of Fig. 5.1 it is evident that alloy 27 (high Zr) responds to aging more quickly and to greater hardness values than alloy 6 (low Zr). The aging response of the high Zr alloy is very rapid compared with ingot metallurgy Al-Li alloys as well [77]. For the HZ alloy the shorter and lower temperature solution-heat-treatments are also associated with higher hardness and quicker response to aging.

5.2.2. Microstructures

High-Zr Alloy

The high-Zr alloy in the as-extruded condition has a fine-grained structure as shown in Fig. 5.2. Precipitation of a phase rich in zirconium (as determined by STEM-EDX analysis) has occurred discontinuously in some grains. This phase precipitates as fine filaments ~6 nm in diameter. The precipitation process is discussed below, but can be seen in the present figure to be driving the indicated grain boundary against its curvature.

Subsequent solution-heat-treatment had two primary effects: the solutionizing of lithium and the continued precipitation of the zirconium-rich phase. The precipitates generally took the morphology shown in Figure 5.3, where discontinuous precipitation during recovery,
Figure 5.1 Hardness-aging curves. Temperature = 190°C.
Figure 5.1, continued.
Figure 5.2. Alloy 27 (high Zr), as extruded. Note that the precipitation-induced grain boundary migration drives a grain boundary (arrows) against its curvature. TEM Bright-field.
Figure 5.3. Alloy 27 (high Zr), as-SHT 500 C/2h. 6" distribution as a product of a discontinuous precipitation reaction.
recrystallization, and/or precipitation-induced grain boundary migration (i.e., discontinuous precipitation where grain boundary migration is not assisted by the recovery or recrystallization process) has resulted in very fine aligned precipitates. Similar behavior in Al-Zr binary alloys has been characterized by Nes and coworkers [60,61] as the precipitation of the metastable cubic Al₃Zr phase (L1₂ structure). The shape of the grain boundary between precipitates (Figure 5.2 and 5.4) suggests that the growing precipitates push the grain boundary forward. This type of discontinuous precipitation is described by Purdy as "precipitate- traction"-assisted boundary migration [78].

As will be shown in the discussion later in this chapter and explored fully in Chapter 6, the precipitate phase is actually the modified δ' phase, or Al₃(Li,Zr), which we call δ". For the purposes of this discussion, the designation δ" will be used for any Zr-containing precipitate phase of the L1₂ structure which likely contains some Li.

The precipitates shown in Figures 5.2 to 5.4 consist of rods ~6 nm in diameter, which are aligned so as to show the pathlines of grain boundary or subgrain boundary motion. Regions where the discontinuous reaction does not occur remain supersaturated with Zr, enabling precipitation of Al₃Zr as discrete spherical particles during extended heat treatment (Fig. 5.5).

After solution-heat-treatment (SHT) for 2 hours at 500°C and water quenching, samples were aged at 190°C. The aging treatment results in the preferred precipitation of δ' at the δ"-α aluminum interface as well as the usual homogeneous nucleation of δ' in regions where no δ" is located. However, even before the aging treatment, δ' has nucleated and decorated the δ" filaments (Fig. 5.6). Numerous nucleation sites are
Figure 5.4. Reaction front (grain boundary) for discontinuous precipitation of δ". As extruded.

Figure 5.5. Precipitation of δ" as discrete spheres in area where discontinuous precipitation did not occur. SHT 500 C/24 h.
Figure 5.6. Superlattice dark-field image showing $\delta'$ outlining the $\delta''$ discontinuous reaction product. Note the $\delta''$ images strongly whereas $\delta'$ filaments do not. SHT 500 °C/2 h.
seen on each filament.

Figure 5.7 illustrates steps in the aging process which shows an increase in the thickness of the $\delta'$ "envelope" with aging time, both for the rod-shaped and spherical precipitates. After extended aging, $\delta'$ envelopes may enclose multiple $\delta''$ precipitates. EDX results indicate that no Zr is present in the $\delta'$ envelopes (Chapter 6).

Longer solution heat treatments (24 h. at 500°C) result in a coarsening of the $\delta''$ distribution (Figure 5.8a). The discontinuous reaction product now appears as larger precipitates with a lower aspect ratio for individual precipitates. The discrete spherical precipitates also coarsen by Ostwald ripening. Precipitation behavior of $\delta'$ is similar to those alloys with short 500°C heat treatments in that $\delta'$ precipitates at the $\delta''$-matrix interface (Figure 5.8b-d). It appears that more $\delta'$ precipitates independently of the Al$_3$(Li,Zr) for the longer SHT. Such behavior is understandable in view of the decreased availability of $\delta''$-matrix interfacial area as a preferred site.

Average grain size was measured as a function of SHT and is given in Figure 7.7. Both alloys retained a very fine grain size after SHT. The HZ grain size appears stable at 1.0 to 1.2 µm at 500°C for periods up to 24 hours.

Low-Zr Alloy.

The low-Zr alloy exhibits a precipitation sequence comparable to that reported in the literature for other binary Al-Li alloys (with or without small Zr additions). Solution heat treatment produced a single phase solid solution. During subsequent aging spherical, coherent $\delta'$ precipitates and grows. A few spherical Zr-containing $\delta''$ precipitates
Figure 5.7. Aging sequence showing growth of $\delta'$ envelopes surrounding $\delta''$. SHT 500 C/2 h + aged at 190 C for: (a) 0.25 h, (b) 4 h, and (c) 32 h. Superlattice dark-field images.
Figure 5.7. (continued).
Figure 5.8. Aging sequence showing growth of $\delta'$ envelopes surrounding $\delta''$. SHT 500 C/24 h + aged at 190 C for: (a) 0 h, (b) 0.25 h, (c) 4 h, and (d) 32 h. Bright field (a) and superlattice dark-field images.
Figure 5.8. (continued).
were observed dispersed within the matrix. As in the high-Zr alloy, these serve as preferred nucleation/growth sites for δ'. Average transverse grain widths after 500°C/1 h SHT are approximately 1.9 μm.

Primary Precipitates

Occasionally a micron-sized primary precipitate was observed which apparently precipitated during solidification. Examples are given in Fig. 5.9. A total of six or eight such precipitates were observed throughout the course of this study.

The primary precipitates of Fig. 5.9 may be Al₃Zr, or a ternary Al₃(Li,Zr). Whichever may be the case, diffraction patterns from these precipitates correspond to the L1₂ structure rather than the equilibrium (for Al₃Zr) D0₂₃.

The primary "precipitate" of Fig. 5.9c appears to be a coarsened two-phase fcc + L1₂ configuration, based on the superlattice dark field image. The ordered phase remains L1₂, even after extended 580°C SHT.

The "diffuse" DF image of Fig. 5.9c was produced with no diffracted beam within the aperture. Such imaging is generally due to inelastic scattering. In the present case the brighter image is apparently associated with either increased diffuse scattering or increased oxidation of the L1₂-ordered phase.

5.3. DISCUSSION

5.3.1. Structure Prior to Extrusion.

It is clear from the undistorted fan configurations that the precipitation of the fan arrangement of δ" has occurred after the deformation associated with the extrusion process. Thus it appears that
Figure 5.9. Primary precipitates as seen in extrusion 27 (high Zr).
a) After SHT 500°C + aged 190°C/4 h. Diffraction pattern shows intense superlattice reflections.
b) After SHT 580°C/15 hour. Bright field.
c) After SHT 580°C/15 h + aged 190°C/15 min. Bright-field, superlattice dark-field, and "diffuse" dark-field images. These images suggest that the "precipitate" is actually a two-phase, ordered + disordered structure after the 580°C heat treatment. The diffraction patterns indicate that the ordered phase is L12, rather than DO23.
Fig. 5.9 b) Bright-field image.

Fig. 5.9 c) Bright-field image.
Superlattice dark-field.

Diffuse dark-field image.

Fig. 5.9 c) continued.
a substantial fraction of the Zr was retained in solid solution through the atomization and hot compaction processing.

It is believed that, indeed, most of the Zr in the melt was put into solid solution and retained throughout the processing until extrusion, during which some fraction was precipitated. The atomization process obviously resulted in some precipitation from the melt as evidenced by the primary precipitates of Fig. 5.9. However, as primary precipitates were so rarely observed, it is concluded that there was little second phase precipitation during solidification and that a large Zr-supersaturation was preserved throughout the atomization and vacuum-hot-compaction steps.

Similar Zr solubilities have been achieved in previous studies in the Al-Zr system. In addition to the specific solidification methods and associated solubilities listed in Table 2-2, other studies suggest that 1.1 wt.% Zr should be retained in solid solution with cooling rates exceeding approximately 10^2 K/s [79] to 5 x 10^2 K/s [80]. Taking the cooling rate for IGA of aluminum to be 10^3 to 10^4 K/s, a complete solid solution could be expected in the atomized powder. A novelty in the present work is that the solid solution produced during atomization has been preserved throughout the vacuum-hot-compaction process.

**Primary precipitates.**

Detailed analysis of the primary precipitates of Fig. 5.9 is outside the scope of this thesis. However, some comment can be made regarding the morphology and coarsening behavior of the precipitates. The particles of Fig. 5-9a and 5-9b are similar in morphology to those reported in the Al-Zr system [61,79], but without the surrounding fringe
of dendritic structure seen by [61]. The lines subdividing the crystal into four parts have been suggested to be stacking faults, twin boundaries or APB's laying on (110) planes in the "L1_2 structure which has a slight tetragonality" [61]. (The proposed tetragonality suggests a DO_{22} or DO_{23} phase, however the diffraction patterns showed only superlattice reflections associated with the L1_2 structure.) The trace of the "faults" in the present case is consistent with the proposed (110) habit (see Fig. 5-9a).

After the extended 580°C/15 h SHT (Figure 5-9c) the primary precipitate appears to be composed of a coarsened disordered + ordered structure. Hori et al.[79] observed similar coarsening (in an Al-Zr alloy) at 450°C, though the L1_2 phase coarsened to plates or disks, rather than the irregular shapes in Fig. 5.9c.

Thus, the presence of Li appears to modify to some extent precipitation and coarsening of the primary phase.

5.3.2. Precipitation at Elevated Temperature - Extrusion and SHT.

The discontinuous precipitation of the Zr-rich δ" during high temperature deformation and heat treatment is similar to that reported in the Al-Zr system. In the Al-Zr system the phase precipitating is the L1_2-ordered metastable Al_3Zr [61]. Discontinuous precipitation occurs because of a large Zr-supersaturation and a low matrix Zr-diffusivity. Normal nucleation and growth processes are precluded by the very low D_{Zr}. Along grain or sub-grain boundaries, diffusivity is high enough to allow the Zr segregation required to produce a Zr-rich phase. The migration of boundaries is driven by the reduction in chemical energy associated with precipitation of Al_3Zr. A detailed description of
discontinuous precipitation in the Al-Zr system has been given in [61].

The Al-Li-Zr system can be considered to be analogous to the Al-Zr system, with the same driving forces for discontinuous precipitation and boundary migration. It appears indeed in Fig. 5.2 that precipitation serves as the force in pushing the grain boundary against its curvature. As mentioned earlier, this morphology is seen in the as-extruded condition. Driving forces for grain boundary migration during extrusion includes (1) the precipitation of Zr from the solid solution as $\delta''$ and (2) the removal of strain energy associated with boundary migration during dynamic recovery. The structure at this point appears to be rather well recovered, in that grains appear almost free of dislocations, especially where the discontinuous precipitation has occurred.

Precipitation appears to continue during subsequent high temperature heat treatment (e.g., 500°C) via boundary migration due to continued recovery, early stages of recrystallization and/or precipitation-induced grain boundary migration, though the last is believed to be the primary mechanism. The actual extent of discontinuous precipitation at the different stages of processing is difficult to establish since $\delta''$ is often extremely hard to image in bright field or dark field. (The difficulty in imaging will be shown below and in Chapter 6 to be associated with composition of the $\delta''$ being imaged.) However, after a 500°C/2 h SHT, discontinuously precipitated $\delta''$ can be observed in about half of the grains, and may be present in a significantly higher fraction.
δ" as the ternary Al₃(Li,Zr)

It has been suggested earlier in the chapter that the Zr-rich phase which precipitates during SHT is δ", or Al₃(Li,Zr), rather than Al₃Zr. Figure 5.6 gives evidence to support this proposal. The discontinuously precipitated phase in this figure does not image brightly in a superlattice DF image, and associated superlattice reflections in the diffraction patterns are very weak. The δ', of smaller diameter, appears very bright. In contrast to δ", the L1₂-ordered Al₃Zr does image strongly under superlattice DF conditions in Al-Zr systems [22,31,61,62,81-84] as well as in higher order systems [59,75], as would be expected for an ordered phase.

This anomalous imaging behavior of δ" can be explained through calculation of structure factors for the Al₃(Li,Zr) phase as a function of composition. The structure factor for such a phase with a Li:Zr ratio of 6:4 is approximately zero for the g = 100 superlattice reflection. Thus a g = 100 DF image would produce no image of δ" of such composition. Similarly, the structure factor for the fundamental reflections becomes very close to that of the Al-matrix at the 6:4 Li:Zr ratio. This leads to difficulty in imaging in bright field mode as in dark field, since diffraction contrast will be minimal. These calculations are discussed in detail in Chapter 6, where δ" composition is determined after various heat treatments.

5.3.3. Aging Behavior.

Upon aging at 190°C, δ' precipitates preferentially at the δ'-α aluminum interface as seen in Figures 5.7 and 5.8, resulting in a "composite" precipitate of δ" enveloped by δ'. This unusual condition,
perhaps unique in metals, occurs because of widely different solubilities and diffusivities of the two solute elements in aluminum at the SHT and aging temperatures (See Table 5-2). During 500°C SHT there is a large chemical driving energy for Zr to precipitate, whereas a binary Al-Li alloy at the same temperature would be a solid solution. At the 190°C aging temperature there is a driving force for both elements to precipitate. However, the low diffusivity of Zr, some 10 orders of magnitude lower than Li, precludes any Zr-rich phase formation, and prevents "homogenization" of the "monostructural" composite precipitate at 190°C.

5.3.4. The Epitaxial Precipitation of δ' on δ"

The configuration of δ' envelopes surrounding δ" can be considered as a single phase structure, i.e., all L12-ordered, with variations in composition. It might be expected that the nucleation of Al₃Li on Al₃(Li,Zr) would be barrierless, that δ' precipitation would be simply a continued growth of the δ" substrate. Figure 5.6 indicates, however, that discrete δ' nucleation sites exist on the δ". True barrierless nucleation should result in a continuous layer of δ', even at this early stage in the growth process. Thus it appears that certain thermodynamic effects are sufficient to preclude true barrierless nucleation. These effects may include lattice misfit (strain energy) or chemical gradient energy (due to δ'-δ" composition differences). The δ" should remain a potent nucleation site for δ' in any case. And clearly, in Fig. 5.6 it is apparent that heterogeneous precipitation has occurred more abundantly than homogeneous precipitation.

An additional driving force for the preferential growth of δ' is
Table 5.2. Solubility and Diffusivity of Li and Zr in Aluminum

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solubility (wt.%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500°C</td>
<td>3.1</td>
<td>0.08</td>
</tr>
<tr>
<td>190°C</td>
<td>1.61</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td><strong>Diffusivity (cm²/sec)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500°C</td>
<td>1.7 x 10⁻⁹</td>
<td>4.0 x 10⁻¹⁴</td>
</tr>
<tr>
<td>190°C</td>
<td>1.2 x 10⁻¹⁵</td>
<td>5.2 x 10⁻²⁵</td>
</tr>
</tbody>
</table>

---

1Solubility for Al₃Li
minimization of the elastic strain energy. Al₃Zr has a lattice mismatch with the matrix of approximately +0.8% [21,22], whereas δ' has a -0.08% mismatch [20]. An Al₃(Liₓ,Zr₁₋ₓ) phase (δ'') could then be expected to have a misfit which is a function of "x" (i.e., composition) as given in Figure 5.10. Any δ'' containing from 2.5 to 25 at% Zr would have a positive lattice misfit with the matrix, putting the surrounding matrix in compression. Subsequent precipitation of δ' with its negative misfit would then reduce the elastic strain energy of the system. Thus, reduction of elastic strain energy is a driving force for preferred precipitation of δ' at the δ''-matrix interface.

5.3.5. Aging Response

The rapid aging response of the HZ alloy (Fig.5.1) can be attributed to the presence of δ''. The availability of a large number of potent heterogeneous nucleation sites would be expected to allow rapid nucleation of δ'. In addition, the strain energy effects described above would stimulate rapid growth of any δ' in the vicinity of δ'', whether epitaxially or otherwise nucleated.

5.4. Summary

The processing sequence chosen for this study was successful in preserving a virtually complete solid solution in the Al-2.34Li-1.07Zr alloy through the powder atomization. The resulting Zr supersaturation apparently was maintained through the vacuum-hot-compaction step.

The precipitation sequence in this system has been characterized as follows. During extrusion and SHT, the δ'' or Al₃(Li,Zr) phase precipitates both discontinuously and continuously. During aging δ'
Figure 5.10  Lattice misfit of δ'' with matrix as a function of δ'' composition.
precipitates as the binary Al₃Li, or δ', with Zr immobilized due to its low diffusivity. The δ'' serves as a preferred nucleation site for δ' and envelopes of δ' completely surround each δ'' precipitate. In addition, δ' growth is stimulated by strain energy associated with the misfit of the precipitate phases with the aluminum matrix.

Further compositional analysis of the δ'' phase and analysis of the implications of the ternary phase on physical properties of the alloy are presented in Chapters 6 and 8, respectively. The effect of the δ'' and the unusual precipitate configuration on deformation behavior are discussed on Chapter 7.
CHAPTER SIX

THE COMPOSITION OF $\text{Al}_3(\text{Li,Zr})$, OR $\delta''$, IN THE Al-Li-Zr SYSTEM

6.1. INTRODUCTION

The research of this thesis is based on the proposal that the $\text{Al}_3\text{Li}$ and $\text{Al}_3\text{Zr}$ phases may show some intersolubility and that beneficial properties may result from the presence of such a ternary phase. Indeed, indications were given in the last chapter that the $\text{Al}_3(\text{Li,Zr})$ phase, or $\delta''$, was produced during extrusion and solution heat treatment. The Li:Zr ratio in the phase is expected to control properties and volume fraction of the phase. The purpose of this chapter is to investigate the composition of the $\delta''$ phase and ascertain if the Li:Zr ratio can be manipulated through thermal processing.

A variety of techniques are used to establish that $\delta''$ has indeed been produced, and to show how the phase composition may vary with processing. The most conclusive technique, and thus the emphasis of this chapter, involves a novel approach to compositional analysis through superlattice dark field image calculation.

6.2. ENERGY DISPERSIVE SPECTROSCOPY AND ELECTRON ENERGY LOSS SPECTROSCOPY

These standard methods of local compositional analysis have been applied in the present research, but have severe limitations due to characteristics of the light element lithium.

STEM-EDS

Energy dispersive spectroscopy (EDS) is effective for compositional
analysis on a microscale, especially in conjunction with scanning transmission electron microscopy (STEM). Unfortunately the technique is not suitable for Li analysis since the energy of Li K x-rays is below the detectability limit of present windowless detectors.

EDS was used to obtain a qualitative analysis for Zr distribution in a typical composite precipitate. As shown in Fig. 6.1, the core of the precipitate contains substantial Zr, whereas the envelope and surrounding matrix yield no Zr signal.

EELS

Electron energy loss spectroscopy (EELS) is valuable as a tool for analysis of the light elements. However, the detection of Li through electron energy loss spectroscopy also has limitations. The Li K-edge at 55 eV is relatively weak and is crowded by aluminum plasmon peaks (at 15, 30, and 45 eV), the Zr N4,5-edge at 38 eV, and the strong Al L-edge at 70 eV. At present the method has a minimum detectable mass fraction Li of ~10 at.% Li [85]. This severely limits the range of phase compositions wherein Li is even possible to detect, not to mention investigate on a quantitative basis.

Analysis was made of some as-SHT samples to determine if Li was present in the precipitate. Usable spectra were limited to those precipitates immediately adjacent to the foil perforation due to overwhelming plasmon signals. Three usable spectra (i.e., low plasmon signals) were obtained for δ" in alloy 27 (high Zr) heat treated 500°C for 24 hours. The spectra showed the presence of both Zr and Li in the δ". Using spectra from δ' (assumed to be 24 at.% Li) from an overaged low-Zr alloy as a standard, and the background stripping program at ASU, the Li content was estimated at approximately 10-20 at.% A Li K-
Figure 6.1. EDS spectra from composite precipitate. a) $\alpha$-Al matrix, b) $\delta'$ envelope, and c) $\delta''$ core indicating presence of Zr.
edge from a stripped spectrum is given in Fig. 6.2.

6.3. CALCULATION OF DARK-FIELD IMAGES OF COMPOSITE PRECIPITATES

The remainder of this chapter deals primarily with compositional analysis of δ" through image calculations. The phenomenon allowing these calculations to be an effective tool is that structure factors for superlattice reflections of an L12-ordered Al₃(Li,Zr) phase are a strong function of Li:Zr ratio. Application of the technique to δ", both with and without the δ' envelopes described in Chapter 5, allows a wide range of δ" compositions to be analyzed.

6.3.1 Structure Factor Calculations

The analyses involving image calculations are predicated upon the knowledge and use of structure factor values for various diffracted waves and phase compositions. The structure factor, Fₖ, of any unit cell for any reflection hkl is given for the general case as:

\[
F_{hkl} = \sum_i f_i \exp[-2\pi i(hu_i + kv_i + lw_i)] \quad (6.1)
\]

where \( f_i \) is the electron scattering factor for atom i, and \( u_i, v_i \) and \( w_i \) are the fractional cell coordinates of atom i [86]. For a superlattice reflection (i.e., mixed even and odd indices for hkl) of an Al₃X phase with a perfectly ordered L12 structure the structure factor reduces to [86]:

\[
F_{hkl} = f_X - f_{Al} \quad (6.2)
\]

For the reflection \( g = 100 \) (g being the reciprocal lattice vector
Figure 6.2. EELS spectrum of δ" after SHT 500°C/24 hours, showing presence of Li K-edge. Background has been stripped.
corresponding to the real-space plane hkl), scattering factors are available from the literature for Al (3.717 Å) [87], Li (1.545 Å) [87], and Zr (6.754 Å) [86] (taking \( f_i \) values for \( \sin \theta/\lambda = 1/(2d) = 0.1235 \) Å\(^{-1} \)). We thereby obtain \( F_{100} = 3.037 \) Å for Al\(_3\)Zr and 2.172 Å for Al\(_3\)Li. (Note that the calculated structure factors must be multiplied by \( (m_e/m_o) \) for the particular microscope accelerating voltage to account for relativistic effects).

*The calculations of Doyle and Turner [87] are used when available (i.e., for Li and Al). The values given in Hirsch et al. [86] are considered about as reliable (values given for Li and Al are very close to those given by Doyle and Turner) and are used where [87] data are not available, i.e., for Zr.

Calculation of structure factors for a ternary Al\(_3\)(Li\(_x\),Zr\(_{1-x}\)) phase, with Li and Zr randomly occupying the sublattice, requires a modification of Eqn. 6.2. Electron scattering from the minor sublattice will be equal to the sum of the scattering from the Li and the Zr occupying the sublattice. Thus, for a superlattice reflection,

\[
F_{hkl} = x f_{Li} + (1-x) f_{Zr} - f_{Al}
\]  

(6.3)

Substituting values for \( g = 100 \),

\[
F_{100} = 3.037 - 5.209 x
\]  

(6.4a)

for Al\(_3\)(Li\(_x\),Zr\(_{1-x}\)). Similarly, the structure factors for other reflections can be calculated as a function of composition of the Al\(_3\)(Li,Zr) phase:

\[
F_{110} = 2.899 - 4.656 x
\]  

(6.4b)

\[
F_{210} = 2.240 - 3.324 x
\]  

(6.4c)

\[
F_{211} = 2.070 - 3.029 x
\]  

(6.4d)
\[ F_{221} = F_{300} = 1.710 - 2.456x \]  
\[ F_{310} = 1.610 - 2.307x \]  
\[ F_{320} = 1.406 - 1.997x \]  
\[ F_{321} = 1.339 - 1.904x \]  

(6.4e)  
(6.4f)  
(6.4g)  
(6.4h)

Figure 6.3 gives a graphical representation of \( F_{hkl} \) for several superlattice reflections, showing changes with composition. Note that the signs for the ordinate axis (F) depend solely on the choice of origin within the unit cell and the corresponding substitutions into Eqn. (6.1).

6.3.2. Application of kinematical theory.

Extinction distances for 200 kV electrons associated with the various reflections and \( Al_3(Li, Zr) \) compositions run from 2000 Å (for \( Al_3Zr, g = 100 \)) to infinity (for cases where \( F_{hkl} = 0 \)). Extinction distances for the actual phase compositions seen in this investigation are a minimum of 2700 Å and in general are significantly higher. These large extinction distances are several times greater than the diameters of the precipitates being analyzed, enabling application of kinematical theory to image interpretation*.

* Other precautions must be observed, however, as discussed in section 6.3.4.

Using kinematical theory, the diffracted wave amplitude, \( \Phi g \), is proportional to the appropriate structure factor, \( F_g \). The diffracted intensity is proportional to \( \Phi g \cdot \Phi g^* \), and thus the square of \(|F|\). In Figure 6.4 the squares of the structure factors of Fig. 6.3 are plotted. From this plot the relative image intensities associated with various \( s^2 \)
Figure 6.3. Structure factors ($F$) for various superlattice reflections as a function of $\delta''$ composition.
Figure 6.4. Structure factors (straight lines) and their squares (curved lines) for the superlattice reflections $g = 100$ and 210 as a function of δ" composition.
compositions and imaging reflections can be predicted. For example, if a phase is of a composition which has a very low value of $F^2$ as given in Fig. 6.4, then a very low dark-field image intensity is to be expected.

6.3.3. Image Calculation

$\delta'$-$\delta''$ Epitaxy.

To calculate an image for any "composite" precipitate, the spatial relationship of the minor sublattice (i.e., Li-containing) of the $\delta'$ envelope to that of the $\delta''$ substrate must be known.

Within the fcc lattice, lattice sites can be arranged into four distinct sublattices. The preferential occupation of any one of the sublattices by solute atoms results in the Li$_{12}$-type order [51], reducing the symmetry to simple cubic. For Al$_3$Li four different variants correspond to the minor sublattice being situated on the four different atomic sites within the unit cell (see Fig. 6.5).

There are two possible scenarios to consider for nucleation of the embryonic $\delta'$ decorating the $\delta''$ filaments in Fig. 5.9. One is that perfect epitaxy is maintained across the interface, i.e., that the minor sublattice for $\delta'$ nuclei is of the same variant as that for the $\delta''$ substrate. In such a case all $\delta'$ nuclei on a given filament would be of the same variant and thus form a continuous, APB-free envelope of $\delta'$ surrounding the $\delta''$. This corresponds to actual micrograph images for aged specimens.

The second scenario to be considered, and shown not to be the case, is as follows. Here, $\delta''$ serves as a nucleation site for $\delta'$, but either no particular variant of $\delta'$ is preferred (leaving 4 variants of $\delta'$ to nucleate), or the variant matching that of the substrate is energetically
Figure 6.5. The Ll$_2$ unit cell. In Al$_3$X, four Ll$_2$ variants are obtained when "X" occupies site 1 (as shown) or sites 2, 3, or 4.
unfavorable\*\*\* (leaving 3 possible variants of $\delta'$). Figure 6.6
\*\*\*Such could be the case if, for instance, the opposite sign of atomic radius mismatch for Li and Zr lead to interfaces where Li and Zr prefer to
be nearest neighbors rather than second-nearest neighbors.

\*\*\*Schematically depicts the growth of two different variants in such a
situation. If such a condition existed, then the continuous envelopes
of $\delta'$ which eventually develop would have APB's running through them
(between sites of nucleation of differing variants).

Actual APB's formed in such a manner would occur in a variety of
orientations. Those of low-energy orientation, eg., (100), could be
expected to exist as APB's within the $\delta'$ envelope. As such they would
be readily visible in an appropriate superlattice DF image (such that
g\cdot R \neq 0$, where $R$ is the displacement vector associated with the APB).
APB's of high energy orientation, eg., lying close to (111), would
heavily groove. An example of the type of grooving to be expected at
the 190°C aging temperature is shown for a deformation APB (ie., lying
on (111)) in Figure 6.7.

In actual micrographs, neither grooving nor APB's are apparent for
the aged specimens which had been heat treated at 500-580°C. (The case
of the 450°C SHT will be discussed later). Thus for these conditions it
appears that the epitaxy across the $\delta''-\delta'$ interface is perfect, ie., the
identical minor sublattice is maintained across the interface.

**Calculated Image of a "Composite" Precipitate.**

Having established that $\delta'$ has perfect epitaxy with the $\delta''$
substrate, kinematical theory can be applied to calculate an image of a
composite precipitate. Images of a duplex precipitate of spherical
configuration will be calculated although other shapes may be handled
Figure 6.6. Schematic showing nucleation of different variants of $\delta'$ on $\delta''$.

a) nucleation of two variants of $\delta'$
b) growth
c) growth of continuous $\delta'$ layer. Requires APB in $\delta'$.
d) grooving of $\delta'$ layer due to high APB energy

The described nucleation of differing variants is not observed.
Figure 6.7. Low Zr tensile gage sample subsequently re-aged 190°C/4 h. Area of high-energy APB is reduced when grooves form in precipitate surface. Al-2.87Li ingot-metallurgy sheet.
with small modifications of the calculations.

Analysis is made for a spherical precipitate completely contained within the aluminum matrix between the foil surfaces. The so-called column approximation (Ch. 7 of ref. [86]) is used, and an arbitrary column is shown in Figure 6.8. Differential changes in the diffracted wave amplitude, \( \Phi_g \), are given by (Eqn. 7.1 in [86]):

\[
\frac{d\Phi_g}{d\cos\theta} = \frac{i \lambda}{V_c \cos\theta} \frac{F_g}{\exp(-2\pi i s z) dz} \quad (6.5)
\]

where \( \lambda \) is the electron wavelength, \( s \) is the deviation parameter, \( z \) is the position through the thickness of the foil, \( V_c \) is the volume of the unit cell, \( \theta \) is the angle of the diffracted beam with the incident beam, and \( i \) is the square root of \(-1\).

The amplitude of a diffracted wave exiting the foil at point P in Figure 6.8 can be calculated by integrating through the thickness of the foil (matrix, \( \delta' \) envelope and \( \delta'' \) core if present) the differential of Eqn. 6.5, giving a total amplitude of:

\[
\Phi_g = i \lambda \int_0^t \frac{F}{V_c \cos\theta} \exp(-2\pi i s z) dz \quad (6.6)
\]

Since \( \cos\theta \) is constant through the foil thickness, and \( V_c \) nearly so, they can be extracted from the integral. Setting the deviation parameter, \( s \), equal to zero (equivalent to being at the Bragg condition) we obtain:

\[
\Phi_g = \frac{i \lambda}{V_c \cos\theta} \int_0^t F \, dz \quad (6.7)
\]

Applying Eqn. (6.7) to the particular precipitate geometry and integrating, the diffracted wave amplitude for any reflection at any
Figure 6.8. Schematic of the column approximation.
location of the foil surface can be calculated:

\[
\Phi g = \frac{1}{V_C \cos \Theta} \left[ F_{\delta'} \, t_{\delta'} + F_{\delta''} \, t_{\delta''} \right]
\] (6.8)

where \( t_{\delta'} \) and \( t_{\delta''} \) equal the thicknesses of \( \delta' \) and \( \delta'' \) traversed by the wave. Here \( \Phi g \) is a function of location through its dependence on \( t_{\delta'} \) and \( t_{\delta''} \).

Structure factors for cores of various compositions can be obtained from Figure 6.3, or otherwise calculated from Eqn. 6.3 or 6.4 using appropriate electron scattering factors. Note that a change in sign of the structure factor in passing from the envelope to the core, or vice versa, corresponds to a 180° shift in phase of the diffracted wave and thus must be considered. (The effect of such a phase shift is that the wave amplitude which increases through the thickness of the envelope can be reduced during passage through the core.) Intensity of the diffracted beam can then be calculated as [86]:

\[
I_g = |\Phi g|^2
\] (6.9)

where \( |\Phi g|^2 \) is the complex conjugate of \( \Phi g \).

To calculate an image for a composite precipitate, \( I_g \) is determined using Eqns. 6.8 and 6.9 for each pixel of an 80 by 80 array containing the precipitate, thus a column approximation calculation is made for each pixel. (The array corresponds to the plane of the exit surface of the foil.) For the general case, the calculated intensities are then scaled to twelve levels. The calculated image is printed as a 20 x 20 cm image using a 12-level gray scale on a dot-matrix printer, and subsequently photographically reduced. The computer program used for
these calculations and sample output are given in Appendix A.

When the intensities are scaled to a gray scale, the actual values of $\lambda$, $V_C$ and $\cos\theta$ in Eqn. 7 become inconsequential. For a given geometry of composite precipitate, the actual scale (size) is also not important. For a spherical configuration of $\delta''$ with a concentric envelope of $\delta'$, the geometry can be characterized by a parameter $R$, the ratio of core diameter to total precipitate diameter.

Examples of calculated images are given in Figure 6.9 for various imaging reflections, $R$ values, and core compositions. Various imaging reflections are, of course, experimentally accessible on the microscope. A wide range of $R$ values are obtained by varying the aging treatment. Thus many different conditions can be analyzed through image matching to ascertain actual $\delta''$ compositions. (If the changes in the image are not sensitive to Li:Zr ratio under one $g$ and $R$ combination, then other combinations can be tested). It is generally possible to find a combination of $R$ and $g$ for which the image is sensitive to $\delta''$ Li:Zr ratio in the composition range of the actual precipitate.

Notable variations in an image are sharpness of $\delta' - \delta''$ interface image, relative intensities of core vs. envelope, and intensity of core near center vs. near the core-envelope interface. The power of this technique is that large qualitative changes in the image are associated with relatively small quantitative changes in Li:Zr ratio of the $\delta''$.

6.3.4. Precautions in image formation.

There are certain requirements in forming the dark field images in order to conform to the assumptions made in kinematical theory [86] and the simplification used in this paper that the deviation parameter, $s$,
Figure 6.9. "Composite" precipitate images as calculated for various g (imaging reflection), R values (d_{core}/d_{total}), and composition of core ("x" in Al\textsubscript{3}(Li\textsubscript{x},Zr\textsubscript{1-x}).

a) g = 110, and b) g = 100 and g = 210.
Figure 6.9 b.
be zero.

It is straightforward in practice to assure that \( a \) is near zero for the superlattice reflections used to form dark field images. Although Kikuchi bands are not visible for the superlattice reflections, \( a = 0 \) for a superlattice reflection, \( g \), is assured if the Kikuchi band for \( 2g \) lies halfway between the \( g \) and \( 2g \) reflections. The matrix first-order Kikuchi bands are rather diffuse, making a precise control of \( a \) often difficult, however, experiments have shown that small variations from the Bragg condition do not affect the important characteristics of the image. Generally, the effect is a lowering of contrast of the image. When \( a \) gets large, however, the contrast mechanism can change, and a "superlattice weakbeam" image may result. Such a condition images the strain field at the \( \delta' - \delta'' \) interface (where there is a relatively large lattice mismatch) and the \( \delta' \)-matrix interface (with a small mismatch). Figure 6.10 demonstrates the effects of these variations in deviation parameter.

Other limitations in the application of kinematical theory are described fully in [86]. Those limitations particularly relevant to the present work are included in the Discussion of section 6.5.1 of the present work.

6.4. RESULTS - APPLICATION TO COMPOSITIONAL ANALYSIS OF \( \delta'' \)

6.4.1. 580°C heat treatment

The \( \delta'' \) produced through a 580°C/15 hour SHT is of such a composition that dark-field images show high contrast for the various superlattice reflections (Fig.6.11). The respective structure factors are therefore not close to 0. Referring to Figure 6.4, it is seen,
Figure 6.10. "Composite" precipitate images as a function of deviation parameter, s. Dark-field images, $g = 110$ in each case. a) $s_{110} = 0$, b) $s_{220} = 0$, c) $s_{330} = 0$, resulting in weakbeam-type image.
Figure 6.11. Alloy 27 (high Zr). After the 580°C SHT, \(\delta''\) images strongly when little or no \(\delta'\) envelope is present. SHT 580°C/15 hours + aged 190°C/15 min.
then, that the δ" composition must lie in a region outside of approximately 12.5 - 17.5 at.% Li (x = 0.5 to 0.7). The technique of image calculation and matching is used as follows for determination of the composition.

Figure 6.12 is a micrograph from a specimen heat treated 15 hours at 580°C and aged at 190°C for 32 hours. The grain boundary shown exhibits a characteristic δ'-precipitate free zone (PFZ), however δ" remains stable in this area. Note that the δ" in the δ'-PFZ images brightly, whereas the core of the composite precipitate images weakly with respect to the matrix background. This establishes that the structure factors for δ' and δ" are of opposite sign, and thus, per Eqn. 6.8, the diffracted wave amplitude is reduced when the wave passes through both δ' and δ".

The composite precipitate of Figure 6.12 has been matched against a series of calculated images for the equivalent R value (0.65) and imaging reflection (g = 110). Such a matching identifies the core composition as approximately 5 to 10 at.% Li (x = 0.2 to 0.4 in f13(Liₓ[Zr1₋ₓ])).

Figure 6.13 demonstrates how various R values and imaging reflections can be used in combination to narrow the estimated range of composition for the δ" precipitate. The images of this figure were formed using two different superlattice reflections, g = 110 and 210. The upper marked precipitate (arrow) can be compared with the calculated images for R = 0.5 for both reflections to indicate a δ" position of 5 to 10 at.% Li (x = 0.2 to 0.4). The larger composite precipitate (lower arrow) corresponds to conditions (R = 0.75) for which a more
Figure 6.12. Comparison of calculated images with "composite" precipitate (arrow) indicates "x" of core is ~ 0.2-0.4. Note that $\delta^*$ is stable in $\delta'$-PFZ near grain boundary, and images brightly when no $\delta'$ envelope is present (i.e., when $R = 1$).
Figure 6.13. Use of various imaging conditions (g = 100 and g = 210), in order to narrow composition range of $\delta'$ core. Left image (g = 100) indicates $x \approx 0.2-0.4$. Right image (g = 210) indicates $x \approx 0.0-0.2$. 
narrow composition range can be specified. Here, core composition appears to be very close to 5 at.% Li and 20 at.% Zr.

6.4.2. 500°C Heat Treatment

The composition of δ" after the 500°C SHT is such that estimates of composition can be made in either the as-SHT condition or when aged to produce a δ' envelope.

SHT 500°C/2 hours.

The δ" present after a 500°C/2 hour SHT is very small, with diameters on the order of 6 to 8 nm (Fig. 5.9). The δ" of Fig. 5.9 gives rise to no image under superlattice dark-field imaging conditions. In comparison, the δ' which decorates the filaments is of smaller thickness yet images brightly. This suggests that the δ" is of such a composition that its structure factor is much less than that of δ'. The reader is referred to Fig. 6.4 for the δ'' composition range associated with a small g = 100 structure factor.

If it is assumed that the image intensity for δ" in Fig. 5.9 is less than 0.1 of the intensity of the brightly imaging δ', making the conservative assumption that the δ' and δ" are of equivalent thickness, then a quantitative estimate of δ" composition can be made. Using the F² curve for g = 100 in Fig. 6.4, the composition is identified as Al₃(LixZr1-x) where 0.45<x<0.71.

This corresponds to a Li concentration of the core in the range of 14.5 ± 3.25 at.%, and the Zr content to 10.5 ± 3.25 at.%. Furthermore, since the δ" appears to match the matrix background very closely, and the δ' which decorates the δ"-matrix interface images relatively brightly, this estimate of composition range could possibly be narrowed
down even further.

SHT 500°C/24 hours.

Figure 6.14 is from a sample SHT'ed 500/24 hours and aged 32 hours at 190°C. The region shown includes a grain-boundary δ'-PFZ where a δ" filament (marked "AB") is enveloped by little (B) or no δ' envelope (A). The δ" with no surrounding δ' (A) images weakly. The weak image is diminished further by the thin δ' envelope at "B". Thus the structure factors for the two phases must be of opposite sign. Referring to Fig. 6.3, this indicates that the δ" must contain less than ~15.5 at.% Li (x < 0.62).

A comparison of the precipitate marked "C" in Fig. 6.14 with the g = 110, R = 0.5 calculated image of Fig. 6.9 leads to conclusions consistent with the observation that Li < 15.5 at.%. The diffuse nature of the δ'-δ" interface and a center which is darker than the interface compares favorably with core compositions of approximately 5-10 % Li (x values from 0.2 to 0.4).

Similarly, in Fig. 6.15 (aged 190°C/32 h), the precipitates (R = 0.2 to 0.3) best correspond to Li percentages of approximately 5 to 10 %, though the matching is not clearly delimited and compositions of 5 to 15 % Li (x = 0.2 - 0.6) also correspond fairly well. Figure 6.16 contains precipitates of R = 0.65-0.70 (aged 190°C/4 h). These images correspond most closely to calculated images of x = 0.2 (5% Li). Figure 6.17 exemplifies a microstructure with a short aging treatment (190°C/15 min.). The precipitates, while not well defined, correspond to δ" compositions of about x = 0.3 - 0.6 (7.5-15 % Li). Figure 6.18 shows one precipitate (R = 0.37) suggesting a not very useful delimitation of
Figure 6.14. Alloy 27 (high Zr), SHT 500°C/24 h + aged 190°C/32 h. 
\( g = 110, s_{110} = 0. \)

Figure 6.15. Composite precipitates, SHT 500°C/24 h + aged 190°C/32 h. 
Various R values. \( g = 110, s_{110} = 0. \)
Figure 6.16. Composite precipitates, SHT 500°C/24 h + aged 190°C/4 h. Various R values. \( g = 110, a_{110} \neq 0 \).

Figure 6.17. Composite precipitates, SHT 500°C/24 h + aged 190°C/15 min. \( g = 110, a_{110} = 0.00019 \text{ Å}^{-1} \).

Figure 6.18. Composite precipitates, SHT 500°C/24 h + aged 190°C/32 h. Various R values. \( g = 110, a_{110} \neq 0 \).
x = 0 - 0.4, while matching the other precipitate (R = 0.75) suggests the δ" composition is close to 5 % Li (x = 0.2).

Thus the 500°C/24 hour SHT results in a δ" composition(s) which is not easy to define. However, a compilation of the above analysis indicates that the composition is in the approximate range of x = 0.2 - 0.3, or 5 - 7.5 at.% Li (20 - 17.5 at.% Zr), when the δ" is present as a spherical precipitate.

6.4.3. 450°C Heat Treatment

The δ" distribution proved to be very stable during the 450°C heat treatments (Fig. 6.19). Despite a 500 hour treatment, δ" diameters remained in general approximately 10 to 30 nm, occasionally larger, up to 50-75 nm.

After the 450°C/500 hour SHT the δ" produced little or no superlattice dark-field image. As in the other SHT'ed samples, aging of the sample resulted in precipitation of δ' envelopes around the δ". However, heavy grooving of the envelopes was apparent. Figure 6.20 shows a typical structure after aging.

The grooving in Fig. 6.20 produces gaps in the δ' envelope whereby the intensity of the δ" core image can be directly compared to adjacent matrix. As in the case of the 500°C SHT, the δ" image intensity matches very closely the fcc matrix. Again, this leads to the conclusion that the composition can be identified, using the parameter x, as 0.50 < x < 0.74, using the assumptions in Section 6.4.2.

Images of varying envelope thickness can be used to estimate the composition of the δ" present as discrete spheres. In Fig. 6.21, an
Figure 6.19. Alloy 27 (high Zr), SHT 450°C/500 h + aged 190°C/15 min. Note that δ' remains in a very fine distribution even after 500 h of heat treatment. g = 110, s_{110} ≈ 0.
Figure 6.20. SHT 450°C/500 h + aged 190°C/16 hours, showing gaps or grooves in δ' envelopes. δ'' at gaps matches matrix closely.
Figure 6.21. SHT 450°C/500 h + aged 190°C/16 h. $R = 0.61$. $g = 110$, $\delta_{110} = 0$. 
Figure 6.22. SHT 450°C/500 h + aged 190°C/15 min., various R-values. g = 110, a_{110} = 0.
image comparison indicates that the "x" parameter is very close to 0.4 (diffuse interface, dark core center). On the other hand, the four designated precipitates of Fig 6.22 suggest an "x" on the range of 0-0.5, 0.2-0.4, 0.3-0.5, and close to 0.3 for the indicated R values of 0.5, 0.72, 0.73 and 0.78, respectively.

The above results suggest that the δ" composition after a 450°C/500 hours SHT can be described by an x parameter of 0.3-0.4, corresponding to 7.5-10 at.% Li and 17.5-15 at.% Zr. The indications are that the δ" in a filament form (Fig. 6.20) contains somewhat greater Li, at x = 0.50 or greater (up to 0.75).

The results of the above compositional analyses are summarized in Table 6.1. The δ" composition appears to be a function of SHT and precipitate shape (spherical or filamentary), and is presented accordingly.

6.5 DISCUSSION.

A new technique has been used for compositional analysis of the δ" phase. The discussion will focus first on the methods used and secondly on the resulting data regarding phase transformations and δ' composition in the system.

6.5.1 Methods of compositional analysis.

Compositional analysis of very small precipitates (d < 100 nm) is difficult under the best of circumstances. In the present study there exist the complications that 1) the element Li is not readily detectable by standard analytical methods, and 2) the precipitates to be analyzed are extremely small (e.g., at 450°C the δ" is typically 10
Table 6.1. Summary of Compositional Analysis of the δ" Phase.

δ" described as Al$_3$(Li$_x$,Zr$_{1-x}$)

<table>
<thead>
<tr>
<th>Habit</th>
<th>SHT</th>
<th>&quot;x&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical</td>
<td>(&lt; 290°C)</td>
<td>(1.0)</td>
</tr>
<tr>
<td>450°C/500 h</td>
<td>0.2-0.5</td>
<td></td>
</tr>
<tr>
<td>500°C/24 h</td>
<td>0.1-0.4</td>
<td></td>
</tr>
<tr>
<td>580°C/15 h</td>
<td>0.1-0.3</td>
<td></td>
</tr>
<tr>
<td>Filamentary</td>
<td>450°C/500 h</td>
<td>0.5-0.75</td>
</tr>
<tr>
<td>500°C/2 h</td>
<td>0.45-0.70</td>
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</tr>
<tr>
<td>500°C/24 h</td>
<td>&lt; 0.6</td>
<td></td>
</tr>
</tbody>
</table>
to 30 nm in diameter even after 500 hours). EDS is particularly limited in that Li signals are not detectable to any extent.

EELS, on the other hand, can be used for Li analysis, but the sensitivity and accuracy is not good. Using state-of-the-art equipment, a recent study of the Al₃Li precipitate yielded a standard deviation of approximately ±3.1 at.% Most important, however, is that the minimum detectable fraction Li was determined to be approximately 1.3 at.% [85]. Considering that the present study indicates the δ" composition is in the range of 5-15 at.% Li, the implication is that EELS is not applicable to Li analysis in δ".

The EELS results in the present study were not sufficiently quantifiable to provide good data on δ" composition. The results do, however, support the existence of an Al₃(Li,Zr) phase by showing that Li and Zr are present in the δ".

Image Calculation as a Tool for Compositional Analysis

The unavailability of EDS and EELS for detection of low levels of Li predicates the need for other methods of compositional analysis. The image calculation and matching technique as developed and applies in this chapter provides a means of obtaining the desired analysis.

The best images in the TEM for comparison are formed of the larger precipitates, e.g., those with the 580°C SHT. The smaller precipitates create problems with regard to image intensity and resolution as well as access to useful R values through aging. (R values less than approximately 0.5 in general do not provide distinctive image characteristics as a function of δ" composition to the extent of larger values of R).
The composite precipitates after the 450°C SHT have total diameters on the order of 20-50 nm. The smaller precipitates (core radii less than approximately 30 nm) suffer from a lack of contrast and image intensity. This results in an effective lack of resolution. Additionally, the inherent resolution limit of the order of 1-2 nm [86] in the use of the column approximation may become significant with the smaller precipitates. The overall effect of these limitations is a widening of error bars resulting during analysis, especially when the smaller precipitates are studied.

Another concern in using the image calculation technique, variation in the deviation parameter ($a$), has proved to be of less significance. The effect of variation in $a$ has been shown experimentally to be small (Fig. 6.10). The deviation parameter could be included in the image calculation, although the shortening of the effective extinction distance associated with non-zero $a$ would become a concern, especially with the larger precipitates.

The sample thickness limitations on applicability of kinematical theory are related to the extinction distance ($\xi g$) for the various phases. The extinction distances associated with $\delta''$ compositions seen in this study are very large, as shown in Fig. 6.23. Precipitate diameters are much smaller than these $\xi g$, and multiple scattering is not considered to be a limitation to the application of kinematical theory in this case.

Another assumption in the present image calculations is that no other reflections are strongly excited. This criterion is often not met in that when a superlattice reflection, $g$, is at Bragg condition, the
Figure 6.23  Extinction distance for δ" for various superlattice reflections as a function of composition of δ".
fundamental reflection 2g is generally excited (For example, when s110 = 0, s220 = 0.0011 A⁻¹ for 100 kv electrons). Using 8-beam dynamical calculations, Allen has shown that effective extinction distances for superlattice reflections may be reduced by about one-third due to dynamical effects [88]. This effect is pronounced only near s = 0. (Note that his calculations were based on a B2-ordered Fe₃Al phase). Similar reductions in extinction distance in the present case, while significant, would still result in very large δg for the d" and d’ phases. These δg would be several times the diameters of the precipitates observed.

An additional precaution, as in all image comparison techniques, micrographs must be printed with the extremes of contrast within the range of contrast available considering the paper used.

6.5.2. Composition of δ"

The results of the δ" compositional analysis are assembled in Fig. 6.24. The discontinuously precipitated δ" has retained its characteristic morphology after the 500°C/2 hour and 450°C/500 hours SHT. Analysis of the discontinuously precipitated δ" indicates a composition range differing from the spherical δ", and so is indicated separately in Fig. 6.24. The trends appear as 1) a possible decrease in Li:Zr ratio with increasing SHT temperature, and 2) a lower Li:Zr ratio in the discrete spherical δ" than in the discontinuously-precipitated product.

The trends in composition described above appear to be controlled by the kinetics of Zr diffusion in the alloy. Discussing the second trend first, it is possible that δ" resulting from discontinuous
Figure 6.24. Composition of $\delta''$ as determined in the present study as a function of solution heat treatment and precipitate morphology. SHT for spherical $\delta''$ are $450^\circ$C/500 h, $500^\circ$C/24 h, and $580^\circ$C/15 h. SHT for the filamentary $\delta''$ are $450^\circ$C/500 h and $500^\circ$C/2 h. At $T < 300^\circ$C Zr diffusivity is so low that the $\text{Ll}_2$-ordered phase precipitates as the binary $\text{Al}_3\text{Li}$, or $\delta'$.
precipitation could be of a different composition than the $\delta''$ produced by normal nucleation and growth. Discontinuous precipitation occurs relatively rapidly and is dependent upon (sub-)grain boundary diffusion. Depending upon the relative grain-boundary diffusivities of Li and Zr, the resulting composition could be radically different from the normal nucleation-and-growth $\delta''$, since the latter is dependent on matrix diffusion. In other words, thermodynamics determine a composition range for $\delta''$ which results in a negative free energy change, but the difference in kinetics associated with the two precipitation modes may lead to variations in composition within that range.

The discontinuous precipitation reaction can be expected to result in a rather complete depletion of the Zr supersaturation of the matrix. Thus the $\delta''$ filaments cannot experience any further growth during heat-treatment. Size and shape changes can occur only through Ostwald ripening. The driving force for ripening (interfacial energy) is expected to be low since the precipitate is coherent with a small misfit (see Chapter 8). Of course the low Zr solubility and diffusivity also contribute to stability. The above argument can account for the stability of the $\delta''$ filaments at such small diameters after the 500°C/2 h ($d = 6-8 \text{ nm}$) and $450^\circ\text{C}/500$ h SHT ($d = 10-30 \text{ nm}$).

As discussed above, the discontinuous precipitation reaction results in extensive, rapid depletion of Zr in the matrix. In contrast, Zr depletion is considerably slower in precipitation by normal nucleation and growth, as the growth process occurs over a period of time. The slower nature of this precipitation process suggests that the associated $\delta''$ composition would be closer to equilibrium than the
discontinuously precipitated δ". This would account for the differences in the measured compositions of δ" from the two precipitation processes. Indeed, the thermodynamic analysis of Chapter 8 suggests that an equilibrium composition of δ" is ~5 at.% Li, which is the δ" composition determined experimentally after the 580°C/15 h SHT.

6.5.3 The 450°C/500 hours SHT - Implications of the Grooved δ' Envelopes.

The δ" filaments present after the 450°C/500 hour SHT are enveloped by non-continuous layers of δ' upon aging. As seen in Fig. 6.20, the δ' envelopes are not continuous on the δ" filaments but neck down at certain locations. Such heavy grooving is undoubtedly due to the sections of δ' being of different variants as described in Section 6.3.3. Such a configuration would require an APB if the envelope were to be continuous and smooth.

We have ruled out the possibility that a dislocation loop was left around the δ" core, during inadvertent deformation or otherwise, before aging. Such a configuration would result in the suggested change in δ' variant and the observed grooving, however an examination by the technique of weak-beam microscopy has not revealed any sign of such loops. In addition, there is no indication that the material has undergone any significant inadvertent deformation to produce such dislocation loops.

The observed grooving behavior could result if the δ'-δ" epitaxy were imperfect and various δ' variants could nucleate on a given δ" precipitate. This model, as described earlier in Section 6.3.3, predicts that numerous APB's would result. Domains of δ' might
subsequently coarsened during the 32 hours of aging to produce the structure of Fig 6.20. However, the structure was examined after 0.5 hours and 4 hours at 190°C and no such increased number of APB's or grooves was visible. Thus it is believed that perfect epitaxy is maintained during nucleation of δ' on δ''.

An alternative which is more likely is that during the extended SHT a transformation of the δ'' to the equilibrium (for Al₃Zr) D0₂₃ phase is initiated. This transformation has occurred in only a few locations and is complete at any location only to the extent of one or a few atomic planes. The L₁₂ and D0₂₃ structures are closely related such that the transformation is effected by a coordinated 1/2<110> shift of a (001) plane. As such the thin slice of D0₂₃, perhaps only a partial unit cell in thickness, is equivalent to an APB in the L₁₂ structure as shown in Fig. 6.25a. The "APB" in the substrate results in subsequently precipitated δ' being of different variants on either side of the D0₂₃ "slice" (Fig. 6.25b).

The suggested partial transformation of a metastable L₁₂ structure to an equilibrium tetragonal phase has been documented in the Al-Hf system during very extended heat treatment [89]. Within the Al₃Hf precipitates the transformation was from the L₁₂ structure to the D0₂₂ structure (also closely related by a 1/2<110> (001) translation). After 50 days at 450°C streaks in the diffraction patterns were seen. After 100 days at 450°C distinct D0₂₂ and L₁₂ diffraction patterns were observed from the same precipitates, which were described as a "laminate" of L₁₂ phase with thin sections of D0₂₂-ordered phase.

In the present case the diffraction patterns do not reflect such a transformation, but considering the small structure factors for the δ'
Figure 6.25. Schematic of possible mechanism for formation of grooved $\delta'$ envelopes as seen in Fig. 6.20.

a) normal filament of $Ll_2$-ordered $\delta''$.

b) $Ll_2$-ordered filament with "slice" of $DO_{22}$ or $DO_{23}$ structure of thickness ($n/2$) unit cells, $n$ is odd. (During very extended solution heat treatment, the transformation to a more stable structure is initiated.

c) $\delta'$ nucleates with perfect epitaxy, but adjacent nuclei are of different variants. Grooves will thus form as in Fig. 6.6d.
phase one would not expect to observe such effects. Associated with the small structure factor is the practical consideration that contrast from the δ'' phase is too low to observe any APB-type stacking faults in δ''. Despite this lack of direct evidence, the L12 to tetragonal transformation appears to be the best explanation for the observed δ' envelope grooving.

6.6 CONCLUSIONS

The analysis presented in this chapter leads to the following conclusions.

1. Dark-field image calculation has proved to be an effective tool in the analysis of Li content of the δ'' phase, or Al3(Li,2r). Standard analytical techniques are either not sensitive to Li (EDS), or have a minimum detectability level (10 at.% Li for EELS) which precludes their effective use in δ'' analysis.

2. The composition of the δ'' phase has been characterized as a function of heat treatment and precipitation mode. Estimated lithium content of the δ'' varies from 5 to 17.5 at.%.

3. It has been established that δ' nucleates on δ'' in the variant which allows perfect epitaxy with the substrate. In other words, the Li-containing sublattice is continuous across the δ'-δ'' phase boundary.

4. The δ'' phase is stable in the δ'-PFZ which grows at grain boundaries during aging. The presence of δ'' near grain boundaries is expected to strengthen the region, alleviating a problem of grain-boundary weakness in Al-Li alloys. (Implications are discussed in Chapter 7).
5. The grooving of \( \delta' \) envelopes in aged samples which had been solution-heat-treated for extended periods can be understood in terms of a partial transformation of \( \delta'' \) from the \( L1_2 \) to a more stable \( D0_{22} \) or \( D0_{23} \) structure.

6. The \( \delta'' \) phase maintains an extremely stable, fine distribution with little coarsening at 450°C. After 500 hours at 450°C the precipitate diameters are typically 10-30 nm.
CHAPTER SEVEN
MECHANICAL PROPERTIES / DEFORMATION BEHAVIOR

7.1. INTRODUCTION

A driving force behind the present research was the improvement of mechanical properties in the Al-Li system, especially with respect to ductility and toughness. The rationale behind Zr additions for this purpose has been described in detail. The high and low Zr alloys have been tested to measure tensile strength, yield strength and elongation for a variety of solution heat treatment (SHT) and aging conditions. This chapter reports these results and makes a comparison of yield strength/% elongation combinations to provide an assessment of relative toughnesses associated with the different alloys and heat treatments.

Mechanical property comparisons are quite useful in ranking the strength and toughness of various alloys. However, an analysis of the underlying fundamentals of deformation mechanisms is necessary to be able to make intelligent and creative recommendations to achieve further improvements within the class of alloys. Such fundamental analysis is even more essential if recommendations and new understanding are to be extended to a more general class of materials. Therefore the microstructures of the high and low zirconium alloys have been analyzed to ascertain the deformation behavior on a micro-scale. This analysis includes characterization of important microstructural characteristics in undeformed material and dislocation slip behavior in deformed alloys as a function of heat treatment and aging condition. Optical and SEM fractographic analyses were used as well, as an aid in identifying deformation mechanisms.
7.2. RESULTS

The mechanical test results will be presented first, followed by observations on the deformation microstructures.

7.2.1. Mechanical Properties

Complete tensile test results for the high and low Zr alloys are given in Tables 7.1 and 7.2 respectively. The 500°C SHT data are plotted as a function of aging time in Figures 7.1 and 7.2. The results for the extruded rod given in Fig. 7.1 illustrate the improved properties of the high Zr (HZ)* alloy, as compared to the low Zr alloy.

* HZ will be used as a general term including all high-zirconium alloys of this study, i.e., extrusions 27, 4, and 8. LZ likewise includes the low zirconium extrusions 6 and 9.

The improvement is evidenced by the large increase in strength while retaining comparable ductility (actually somewhat improved ductility in the underaged case).

Similar behavior is observed for the extruded bar as shown in Fig. 7.2. Tensile and yield strengths increase significantly with zirconium level, for both longitudinal (L) and long transverse (LT) test directions. Ductility is comparable for the two alloys, with perhaps some loss of ductility in the LT direction for the HZ alloy.

The effect of variation in solution heat treatment on peak-hardness properties was examined and is presented in Figure 7.3. The shorter, low temperature heat treatments lead to the best properties.

7.2.2. Microstructure and Deformation Behavior

The microstructure of each alloy was examined before and after
TABLE 7.1

Mechanical Properties of the High Zirconium Alloy

Al-2.34Li-1.07Zr

<table>
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<tr>
<th>ROD</th>
<th>SHT</th>
<th>AGE</th>
<th>UTS (kai)</th>
<th>YS (kai)</th>
<th>%el.</th>
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<td>Extrusion 27</td>
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<td>54.4</td>
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<td>48.2</td>
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<td>68.0</td>
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<td>73.7</td>
<td>71.9</td>
<td>5.71</td>
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<th>UTS (kai)</th>
<th>YS (kai)</th>
<th>%el.</th>
<th>LONG TRANSVERSE</th>
<th>UTS (kai)</th>
<th>YS (kai)</th>
<th>%el.</th>
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<td>55.5</td>
<td>-</td>
<td>56.0</td>
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<tr>
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<td>6.91</td>
<td>64.3</td>
<td>60.7</td>
<td>5.60</td>
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<tr>
<td></td>
<td>190°C/24 h</td>
<td></td>
<td>61.4</td>
<td>53.3</td>
<td>5.22</td>
<td>57.5</td>
<td>50.8</td>
<td>7.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*LT aged 180°C/0.25 h.
### TABLE 7.2

**Mechanical Properties of the Low Zirconium Alloy**

**Al-2.19Li-0.12Zr**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>UTS (ksi)</th>
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<th>%El.</th>
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<td>190°C/24 h</td>
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<td>190°C/2 h</td>
<td>57.1</td>
<td>52.4</td>
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</table>

<p>| | | | | | | | |</p>
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<td>YS (ksi)</td>
<td>%El.</td>
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<td>36.5</td>
<td>7.42</td>
<td>42.0</td>
<td>33.9</td>
<td>9.22</td>
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Figure 7.1. Tensile properties vs. aging treatment for the high and low-Zr extruded rod. SHT 500°C/1 hour.
Figure 7.2. Tensile properties vs. aging treatment for the high and low-Zr extruded bar. SHT 500°C/1 hour.
Figure 7.3. Peak strength of the high-Zr rod vs. solution heat treatment.
deformation. (Note - non-deformed structures have been presented in Chapter 5). Relevant observations regarding these structures are presented below.

The grain size was measured for the alloys in several SHT conditions, inasmuch as grain size can influence mechanical behavior. These measured grain sizes are given in Fig. 7.4. Grain size in general increases with increasing SHT temperature and time, though all conditions produced relatively fine microstructures. The HZ alloy grain size is extremely stable at 450°C; after 500 hours the grains remain at a very small size (1.0 μm). At 500°C the grain structure is also very stable at 1.0 to 1.2 μm in size for periods up to 24 hours. The high temperature SHT (580°C) HZ alloy and the 500°C SHT LZ alloy exhibit somewhat larger grains but still a very refined microstructure at grain sizes of 1.7 to 1.9 μm.

Observed grain aspect ratios were generally large, e.g. 2 to greater than 10, for both alloys. Subgrain aspect ratios were close to unity.

The low zirconium alloy exhibits deformation behavior characteristic of binary Al-Li alloys. Slip localization was observed in some grains as shown in Figure 7.5. Characteristic also were wide PFZ's along high angle grain boundaries (Figure 7.6). The δ' in the grain interiors helps impede dislocation motion, whereas the soft PFZ's contain no second phase and thus appear nearly dislocation-free.

The high Zr alloy in the SHT condition contains δ'' in an aluminum matrix with little or no δ' (Chapter 5). In this condition, after deformation of 1% the δ'' is able to produce a complex dislocation
Figure 7.4. Grain size as a function of alloy and solution heat treatment.
Figure 7.5. Slip localization as seen in alloy 6 (low Zr) after tensile deformation.
Figure 7.6. Precipitate-free zones as seen along high angle grain boundaries in Alloy 6 (low Zr). The soft PFZ’s remain relatively dislocation-free after deformation.
substructure, as shown in Figure 7.7. The \( \delta'' \) thus appears effective in impeding dislocation motion.

After deformation of the aged H2 alloy (Fig. 7.8), it appears that the \( \delta'' \) is still effective in resisting dislocation shear, more so than \( \delta' \). The spherical \( \delta' \) precipitates with no \( \delta'' \) core (e.g., those marked "A") have been sheared completely through, as evidenced by dark APB's which remain. In contrast, the large composite precipitates ("B") are not sheared through. The position of APB's within these precipitates indicate that dislocation cutting has occurred through the \( \delta' \) envelope but has not proceeded across the \( \delta'' \) core.

The inset in Fig. 7.8 is a superposition of a weak beam dark field image on the superlattice dark field image. Here the dislocation associated with an APB in the shell of a composite precipitate is pinned, presumably by the hard \( \delta'' \) core. (It should be noted that the superposition of images was effected within the microscope by changing imaging modes during plate exposure, and thus was not dependent upon any judgement in alignment.)

The high Zr alloy suffers from a \( \delta' \)-PFZ (Fig. 7.9) similar to that of the low Zr alloy. However, as Figure 7.9 clearly shows, \( \delta'' \) remains stable in this region, available for strengthening. Figure 7.10 gives an example of deformation structures which develop in a \( \delta' \)-PFZ containing \( \delta'' \). The grain on the left has a PFZ with no \( \delta'' \). The PFZ is totally lacking in second-phase particles for strengthening and thus is free of dislocations. On the other hand, the two grains on the right have \( \delta' \)-PFZ's which contain \( \delta'' \). This \( \delta'' \) is effective in tying up dislocations. Strengthening of the grain boundary region is implicit in this observation.
Figure 7.7. Alloy 27 (high Zr), as-SHT 500°C/1 h + stretched 1%. This unaged sample contains δ″ filaments (horizontal) which have resulted in this complex dislocation substructure. Weak-beam dark-field image.
Figure 7.8. Alloy 27 (high Zr), tensile gage section. Note spherical δ' precipitates have been sheared completely through. The composite precipitates exhibit a shearing of the δ' envelope but not completely across the δ'-δ" configuration. Superlattice dark-field image. The inset is a superimposed weak-beam and superlattice darkfield image. A dislocation which has cut the δ' envelopes appears pinned between two composite precipitates.
Figure 7.9. Alloy 27 (high Zr), SHT 450°C/500 h + aged 190°C/16 h. Note δ" is stable in the δ'-PFZ.
Figure 7.10. Alloy 27 (high Zr), tensile gage section. Both sides of grain boundary have a δ'-PFZ. Right side of grain boundary contain δ'' filaments in the δ'-PFZ which provide strengthening.
7.2.3. FRACTOGRAPHY

A survey was made of representative fracture surfaces after mechanical testing, using optical and scanning electron microscopy. This survey is not intended as a thorough analysis, but primarily to note major features.

Alloy 6 (LZ) exhibits characteristic 45 degree shear faces, or cup-and-cone type fracture surfaces throughout the aging sequence. Figure 7.11 gives a typical fracture surface and shows what appear to be dimples on the fracture surface. The dimples may be indicative of soft PFZ's along grain boundaries rather than a general ductility of the grain-interior matrix [6].

Alloy 27 (HZ) also exhibits 45 degree shear faces and cup-and-cone type surfaces for under and peak-aged conditions (Fig. 7.12), and about 40% flat, brittle-type fracture surface when overaged (Fig. 7.13). Again all areas and tempers showed dimpled surfaces.

Both alloys showed several small black inclusions on the surfaces, often appearing near a crack initiation site (e.g., at peak of cup or cone). A number of these inclusions were examined by EDS. One inclusion was the result of steel powder contamination (Fig.7.12a), but the others showed only Al peaks. These are most likely oxides of aluminum and lithium.

7.3. DISCUSSION.
7.3.1. Mechanical Properties Results.

The curves of Figures 7.1 and 7.2 illustrate clearly the improved strength of the high Zr alloy over the low Zr alloy for both of the
Figure 7.11. Alloy 6 (low Zr), SHT 500°C/1 h + aged 190°C/24 h (overaged). Fracture surface by SEM.
Figure 7.12. Alloy 27 (high Zr), SHT 500°C/1 h + aged 180°C/0.25 h (underaged). Fracture surface.
a) Fracture initiation site identified most likely as stainless-steel powder contamination by EDAX.
b) Typical higher magnification view of surface.
Figure 7.13. Alloy 27 (high Zr), SHT 500°C/1 h + aged 190°C/16 h (overaged). Fracture surface.
extruded shapes. Longitudinal and long transverse strengths are significantly improved, while ductility is comparable for the two alloys. The HZ alloy also responds to aging more rapidly than either the LZ alloy or ingot metallurgy Al-Li alloys [6]. The rapid aging response confirms the trend observed in the hardness-aging study of Chapter 5. As discussed in Chapter 5, the rapid aging response can be attributed to the abundant heterogeneous nucleation sites available for δ'.

The improvement in properties may be viewed as a 15 to 20 ksi (100 to 140 MPa) increase in tensile and yield strengths while maintaining comparable ductility. Conversely, if ductility improvement is of interest, Fig. 7.1 shows that for comparable strengths a 2 to 3-fold improvement in % elongation is realized (eg., underaged HZ vs. peak-hardness LZ).

The results of the mechanical property vs. SHT study (Fig. 7.3) suggest that in the HZ alloy short, low temperature SHT's provide the best properties. The better properties can be attributed to a retention of a more refined microstructure, with respect to both δ" distribution and grain size, and a modification of δ" composition as described in Chapter 6. The fine grain sizes associated with the short, lower temperature SHT (see Fig. 7.4) have a direct positive effect on strength as indicated through the Hall-Petch relationship. This is discussed in detail later in this chapter. The finer δ" distribution associated with the lower temperature SHT (see Chapter 6) also contributes to improved strength. The effect of δ" composition is somewhat complex. The greater the Li content of δ" the greater the volume fraction (f) of δ" (for a fixed Zr level. See Chapter 8). Since strength varies with the square
root of f [90], a strength increase might be expected. On the other hand, with increased Zr content the δ" may have increased resistance to dislocation shearing. These effects are discussed in detail later in this section.

Another possible effect of variation in SHT temperature on the HZ alloy is suggested by the work of Rystad and Ryum [83]. They found in the Al-Zr system that the kinetics of discontinuous precipitation were more rapid below approximately 500°C than for normal nucleation and growth, and vice versa above 500°C. In other words, increased discontinuous precipitation of δ" may be expected for the lower temperature SHT while more discrete spherical δ" may be expected at the higher temperatures. Such variations in δ" distribution would be expected to affect mechanical properties.

Since the 580°C heat treatment was very long (12-15 hours) in the present study, Ostwald ripening and reshaping of filaments to reduce surface area would be expected. Thus, there is insufficient data to confirm or reject the conclusions of Rystad and Ryum [83]. However, the rapid kinetics of decomposition at lower temperatures (<450°C) suggested by their C-curves for the two modes of precipitation must be questioned in light of the preservation of the Zr supersaturation through the vacuum hot compaction and extrusion pre- and at stages of the processing of the present extrusions.

It should be noted that alloys 4 and 27 (both HZ) have comparable properties. Alloy 4 was processed similarly to 27 (refer to Chapter 4) except the VHC resulted in a powdery, crumbling billet. Thus the alloy appears to afford some leeway in processing conditions.
Strength-Ductility Combinations.

Given the data of Tables 7.1 and 7.2, the best assessment of relative toughness is made by comparing yield strength-percent elongation combinations. The variation of strength-ductility combinations with aging time for the HZ rod is given in Fig. 7.14. The "aging curve" lies along a diagonal in the strength-% elongation plot in a pattern similar to those for commercial aluminum alloys. The minimum properties for commercial alloy 2024 in underaged and peak-hard conditions are given for comparison. Note that in similar tempers the properties of alloy 27 lie well above these minima.

Yield strength-elongation combinations for the rod and bar-shaped extrusions are plotted in Figures 7.15 and 7.16, respectively. In Figure 7.15 it is clear that the HZ alloy gives much better properties than the control LZ alloy. The LZ alloys (points EP, DU, EU, EO) do not meet the 2024 minima for any condition, whereas the HZ alloy (points AU, AP, BU, BP, BN, B'P, B'U) is well above these minima except in the extended SHT (CP) or overaged (BO) conditions.

Similar behavior is evident in Figure 7.16, where longitudinal and long transverse data are plotted. Again the HZ alloy (triangles) exhibits properties superior to those of low Zr content (circles), although properties for the HZ alloy are clustered near the minima for 2024 in this case.

7.3.2. Mechanical Properties and Microstructure.

The beneficial effects of zirconium on the mechanical behavior of these Al-Li extrusions is apparent. The microstructures observed before and after deformation give some indication as to the basis for this
Figure 7.14. Aging sequence for Alloy 27 (high Zr) shown as strength-ductility combinations. Commercial alloy 2024 extrusion property minima for two tempers shown for comparison.
Figure 7.15. Yield strength - elongation combinations for alloy 27 (high Zr) and alloy 6 (low Zr) extruded rod under various solution heat treatment and aging conditions. Commercial alloy 2024 minima in two tempers are given for comparison.

Key:  Alloy 27  Alloy 6  SHT  Aging treatment
   A    D    450°C/1 h  N  none
   B    E    500°C/1 h  U  underaged
   C    565°C/1 h  P  peak aged
          O  overaged
Figure 7.16. Yield strength-elongation combinations for the high and low-Zr extruded bar for various aging conditions (all SHT's 500°C/1 hour). Minima for commercial alloy 2024 in two tempers are shown for comparison.

Key:  T - Long Transverse  U - underaged
      L - Longitudinal  P - peak aged
      O - overaged
improvement in mechanical properties. Zirconium appears to be most effective through 1) preservation of extremely fine-grained microstructures, 2) ability of $\delta''$ to tie up dislocations, thereby dispersing slip, and 3) strengthening of grain boundary regions by the presence of $\delta''$ in $\delta'$-PFZ's. These factors are examined individually below.

**Grain Size**

The influence of grain size on yield strength is described by the Hall-Petch relationship [91]:

$$\sigma_y = \sigma_0 + kd^{-1/2}$$  \hspace{1cm} (7.1)

where $\sigma_0$ represents the inherent friction stress of the lattice, $d$ is the grain size and $k$ is an alloy-specific coefficient.

The very small grain size of these alloys (Fig. 7.4) suggests that there should be a contribution from grain size effects to yield strength, especially in the H2 alloys. It is difficult to estimate the actual importance of grain size in these alloys (i.e., value of $k$), however, since concomitant with any change in grain size is a significant shift in $\delta''$ distribution and/or composition (refer to Chapters 5 and 6).

An upper limit on the $k$ value may be estimated from a comparison of the 500°C and 565-580°C SHT data of Figures 7.3 and 7.4. A drop in yield strength of 6.4 ksi is associated with an increase in grain size from approximately 1.0 to 1.7 $\mu$m. Attributing the drop in yield strength entirely to grain size effects gives a value of $k$ of 27.5 ksi/$\mu m^{-1/2}$. At the same time, however, it should be recognized that the $\delta''$ distribution is much coarser and less favorable after the 565°C SHT,
thus grain size effects account for only a portion of the entire yield
strength difference. The actual k value should be significantly less
than 27.5 kai/µm\(^{-1/2}\). A more reasonable value of k is 18.5 kai/µm\(^{-1/2}\)
which was calculated for Al and Al-Si cast alloys by Armstrong [92].

Both alloys studied have a very well refined grain size with respect
to commercial alloys in general. Alloy 27 has a smaller grain size than
alloy 6, however, after a 500°C/1 h SHT (d = 1.0 and 1.9 µm,
respectively). Substitution of these values in Eqn. 7.1 leads to a
calculated improvement in yield strength of alloy 27 over alloy 6 due to
grain size of

\[
\Delta\sigma_S = k(d_1^{-1/2} - d_2^{-1/2}) = 0.276k \tag{7.2}
\]

where d\(_1\) and d\(_2\) are the grain diameters in alloys 27 and 6 respectively.

Using k = 18.5 kai/µm\(^{-1/2}\), the grain size advantage of alloy 27 is 5.1
kai (35.2 MPa). Note also that alloy 6 has an advantage of 0.723 k in
yield strength over a very coarse-grained alloy. Using the above k, this
amounts to 13.4 kai (92 MPa).

Thus, although the primary strengthening mechanism in these alloys
is undoubtedly precipitation hardening, the grain size effect likely
contributes significantly to yield strength of the alloys. The fine
grain size of the LZ alloy results in an improvement in yield strength of
approximately 13 kai (90 MPa) over coarse-grained alloys. Furthermore,
the HZ alloy enjoys an additional 5 kai (35 MPa) advantage over the LZ
alloy due to improved grain refinement. These benefits should be
especially realized when short, low-temperature SHT's are used, since the
finest grain sizes are retained under these conditions.
Dislocation Interaction with $\delta''$.

A major premise of this work was that the presence of Zr in $\delta''$ would provide increased resistance to dislocation shear relative to $\delta'$. The shearable $\delta'$ leads to work-softening and slip localization in binary Al-Li alloys, as was occasionally noted in the present LZ alloy (Figure 7.5), and it was proposed that a $\delta''$ phase could disperse this slip.

The resistance to shear of $\delta'$ in Al-Li alloys is due primarily to the energy of the antiphase boundary created when an fcc lattice dislocation cuts the particle [53]. The APB energy for $\delta'$ is reported to be from 160 [53] to 195 ergs/cm$^2$ [50]. The metastable Al$_3$Zr (L1$_2$), on the other hand, will be shown below to have a much larger APB energy, and thus should provide greater shear resistance.

The L1$_2$-ordered Al$_3$Zr phase has been observed to be stable at temperatures as high as 600°C [81,83]. The metastable L1$_2$ and equilibrium D0$_{23}$ structures are very similar. The two have identical first nearest neighbor configurations, which accounts for at least 90% of the ordering energy [51]. Thus it is expected that the metastable phase should have a critical ordering temperature ($T_C$) close to that of the equilibrium D0$_{23}$ phase. For the equilibrium phase, $T_C > T_m = 1582°C = 1855 K$. ($T_C$ is the critical ordering temperature with respect to the disordered $\alpha$-solid solution, and thus would be greater than the melting temperature.) Thus an estimate of $T_C = 1855 K$ for the metastable phase appears reasonable.

Another approach to estimating $T_C$ is to use the relationship for L1$_2$ structures relating $T_C$ to the enthalpy of disordering (dissolution) derived by Yang and Li [52,93]:

152
\[
\frac{\Delta H}{R \, T_C} = 1.072 \tag{7.3}
\]

where \(\Delta H\) is the enthalpy of the reaction per mole of \(A_3X^*\), and \(R\) is the gas constant. Using a value of \(\Delta H\) for dissolution of \(A_3Zr\) (implied \(\text{DO}_{23}\) structure) of 22,970 Joule/mole [94], a \(T_C = 2577\, \text{K} = 2304\, ^\circ\text{C}\) is calculated. Thus, for the \(L1_2\) structure, a \(T_C\) of 1582\,^\circ\text{C} = 1855\, \text{K} appears to be a conservative estimate.

"The dimensionless number given in [52] is 0.268 instead of 1.072, but was given per "Avogadro's number of atoms in \(A_3X^*\)," rather than per mole of \(A_3X\). An adjustment factor of 4\% was therefore applied."

The (111) APB energy can then be calculated using the relation [50]:

\[
\psi_{\text{APB}} = \frac{4 \, k \, T_C}{a^2 \, \sqrt{3} \, 0.82} \tag{7.4}
\]

where \(k\) is the Boltzmann constant, \(a\) is the lattice parameter, and 0.82 is the value for a parameter which relates to ordering energy calculations for \(L1_2\) structures [52]. Using for the metastable \(A_3Zr\) an estimated \(T_C = 1855\, \text{K}\), we arrive at an APB energy of 447 ergs/cm².

The APB energy for \(\delta''\) can be estimated by interpolation between values for \(\delta'\) and \(A_3Zr\). Values calculated for the \(\delta''\) compositions determined in Chapter 6 are found in Table 7.3. The influence of APB energy on the maximum shear stress required to shear the precipitates is described in the following:

\[
\tau_C = \left( \frac{2}{\pi A} \right)^{1/2} \frac{\psi^{3/2}}{b} \left( r f \right)^{1/2} \left( 1 - \frac{r}{R} \right)^{1/2} \tag{7.5}
\]

where \(b\) is the burgers vector, \(f\) the volume fraction precipitate, \(r\) the
precipitate radius, 2R the interparticle spacing, and A the dislocation line tension \([90]\). Since the critical stress is a strong function of \(\gamma\), and precipitate strengthening in the system is due primarily to ordering in the precipitate \([53]\), the ternary \(\delta''\) should provide significantly increased strength and resistance to shear. To gain a perspective on the degree of this effect, values of normalized \(\gamma^{3/2}\) are given in Table 7.3. The \(\delta''\) precipitate is then seen to afford 2 to 3.3 times the strengthening provided by the \(\delta'\) phase, depending on SHT. Thus, the presence of Zr in \(\delta''\) should result in a very large increase in resistance to cutting by dislocations.

<table>
<thead>
<tr>
<th>SHT</th>
<th>Li:Zr</th>
<th>Li(at.%)</th>
<th>APB Energy, (\gamma) (erg/cm(^2))</th>
<th>((\gamma/\gamma_{\delta'})^{3/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>((190^\circ C)) infinite</td>
<td>25</td>
<td>160-195</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>(500^\circ C/2\ h) 6:4</td>
<td>15</td>
<td>285</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>(580^\circ C/15\ h) 2:8</td>
<td>5</td>
<td>393</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>447</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

The presence of \(\delta''\) in the composite precipitates appears indeed to prevent cutting by dislocations. In Figure 7.8 the small spherical \(\delta'\) precipitates have been sheared completely through. The composite precipitates, on the other hand, exhibit a shearing through the \(\delta'\) envelope without a continuation across the entire particle. The incomplete shearing is attributed to the increased strength of the \(\delta''\) core. This behavior is further illustrated in the inset, where a
superposition of superlattice darkfield and weak beam images shows the pinning of a dislocation by $\delta''$ cores after cut-through of the $\delta'$ envelopes.

The $\delta''$ appears to be an effective strengthener even without the $\delta'$ envelopes. As Fig. 7.7 indicates, 1% deformation of a SHT'ed specimen containing $\delta''$ but no $\delta'$ results in a complex dislocation substructure. Thus it appears that $\delta''$ distributed as the fine, discontinuously-precipitated product is quite effective at dispersing slip.

Finally, the effect of $\delta''$ on strength of the HZ alloy can be estimated from mechanical properties and estimates of other strengthening mechanisms. In the unaged condition, alloy 6 (LZ) and 27 (HZ) have yield strengths of 21.0 and 46.1 ksi respectively. The difference in strength is largely maintained throughout aging, and can be attributed primarily to $\delta''$ and grain size effects. The grain size effect was previously calculated at approximately 5 ksi. Thus the $\delta''$ effect may be estimated as increasing yield strength by 10 to 20 ksi, depending on temper.

Precipitate Free Zones.

The aging behavior of Al-Li alloys results from $\delta'$ precipitation. During aging the equilibrium AlLi phase also nucleates, in general heterogeneously at grain boundaries. The grain boundaries, with a very high diffusivity, are in equilibrium with AlLi. The $\delta'$ in the vicinity of the grain boundary will then dissolve, since it is metastable and thus in equilibrium with a matrix of higher Li content.

The grain boundary precipitate free zones (PFZ) which grow throughout the aging process (e.g., Fig. 7.6) contribute to grain boundary weakness and low ductility in binary Al-Li alloys. Although the
HZ alloys also suffer a δ'-PFZ, δ'' remains stable within the PFZ. A dramatic example of δ'' stability in the "PFZ" is illustrated in Fig. 7.9. Various factors should contribute to this stability, including a lower free energy for δ'' (Chapter 6) and immobility of Zr at the aging temperature. This PFZ-δ'' can be expected to strengthen the grain boundary region in the same manner that δ'' strengthens grains in the as-SHT (non-aged) condition (Fig. 7.7).

The ability of δ'' to impede dislocation movement in the δ'-PFZ is demonstrated in Fig. 7.10. Here δ'' has discontinuously precipitated behind the grain boundary as it swept from right to center. The δ'' has remained in the δ'-PFZ and has tied up dislocations in the deformation process. The adjacent grain sharing the grain boundary exhibits a δ'-PFZ with no strengthening δ''. Those dislocations not pinned by δ' are then able to sweep into the grain boundary (or into the grain-side edge of the PFZ) with no impedance due to second-phase particles. The PFZ therefore remains free of dislocations. In contrast, the low Zr alloy of Fig. 7.6 suffers from PFZ's along both sides of the grain boundaries, and thus grain boundary weakness is expected.

Problems Associated with PM Processing.

Oxide problems chronically plague PM work. Based on fractographic examination (Fig. 7.11-13), significant oxides appear to exist in the present alloys and are expected to be detrimental to mechanical properties, especially ductility. These problems may be solvable through processing to minimize exposure to air and moisture, and through use of large extrusion ratios to break up any oxide particles. A cleaner alloy should result in improved properties for both of the
compositions studied in this work.

Similarly, contamination by foreign alloy powders is not uncommon in PH. Iron particles such that seen in Fig. 7.12 are extremely undesirable from the standpoint of stress concentration. Corrosion enhancement is another potential deleterious effect. These contamination problems are usually minimized through care in cleaning the atomizing apparatus.

7.4. SUMMARY

The addition of zirconium to Al-Li alloys provides for significantly increased strength and toughness (toughness as measured by yield strength/elongation combination). The zirconium acts by 1) preserving a very small grain size throughout processing, and 2) forming the beneficial δ” phase. The very fine grain sizes of these alloys result in yield strength increases of an estimated 13 kai (90 MPa) and 18 kai (125 MPa) for the low Zr and high Zr alloys, respectively, over a coarse-grained alloy.

The value of the δ” phase is two-fold. The phase is effective in its resistance to shearing by dislocations, thereby providing increased strength and dispersing slip. This increase is accounted for by an increased APB energy associated with the presence of Zr in the precipitate. The APB energy should vary with Li:Zr ratio in the phase. The presence of δ” appears to directly contribute 10 to 20 kai (70 to 140 MPa) in yield strength aside from grain size effects. The δ” phase is also stable in δ’-precipitate free zones, providing strengthening in these weakened areas and averting the low ductility associated with grain boundary failure.
CHAPTER EIGHT
PROPERTIES OF δ''

8.1. INTRODUCTION

The results of Chapter 6 show that δ'' contains a substantial fraction of both Li and Zr. The properties of the phase are therefore expected to differ markedly from those of Al₃Li and Al₃Zr. The δ'' may exhibit different thermodynamic behavior, volume fraction precipitate, or physical and mechanical properties. In turn, alloy properties may be modified. These properties of δ'' can be expected to vary with phase composition.

This chapter presents and discusses anticipated properties of δ'' calculated as a function of Li and Zr content. The discussion focuses on both fundamental characteristics of δ'' and the relationship of these properties to the physical metallurgy of the Al-Li-Zr system.

8.2. THE CALCULATION OF δ'' PROPERTIES

8.2.1. Volume Fraction δ''.

The substitution of Li for Zr in Al₃Zr provides a means for increasing the volume fraction second phase without the problems associated with producing large Zr supersaturations. For a given mole fraction of Zr available to precipitate as Al₃(LiₓZr₁₋ₓ), the volume fraction second phase increases with x as follows:

\[ f_{δ''} = \frac{1}{f_{Al₃Zr}} \]  \hspace{1cm} (8.1)

where \( f_{Al₃Zr} \) is the volume fraction Al₃Zr available from the given Zr
level. The curve of Figure 8.1 illustrates the effectiveness of Li substitution in increasing the fraction of precipitate.

8.2.2. Lattice Misfit and Interfacial Energy.

The lattice misfit for $\delta''$ can be expected to vary with Li:Zr ratio by the rule of mixtures as given in Figure 5.10. The low misfit associated with the Li-rich compositions will thus lead to a low associated strain energy. At the same time, a low misfit is believed to contribute to a low interfacial energy for coherent precipitates [95].

8.2.3. Thermodynamic Properties.

Values of entropy and enthalpy for the precipitation of $\delta''$ can be estimated as follows. Thermodynamic values are calculated for the formation of L1$_2$-ordered Al$_3$Zr, Al$_3$Li and $\delta''$ from Al$_3$Zr and Al$_3$Li in the disordered state.

Enthalpy

Several models of first-order type ordering reactions have been developed, and in each case the enthalpy change associated with ordering is directly related to the critical ordering temperature ($T_C$) of a phase [52]. The best thermodynamic analysis of L1$_2$ ordering appears to be the quasi-chemical, tetrahedral model of Yang and Li [52,93]. Their model results in the following relationship for L1$_2$ structures:

$$\Delta H = 1.072 \, R \, T_C \quad (8.2)$$

where $\Delta H$ is the enthalpy change per mole of A$_3$B, and $R$ the gas constant. Using $T_C = 738$ K for $\delta'$ (Appendix A), and $T_C = 1855$ K for Al$_3$Zr (Chapter 7), the enthalpy of ordering can be calculated as:
Figure 8.1 Volume fraction δ" versus δ" composition, assuming a given level of Zr available for precipitation. Normalized to volume fraction Al₃Zr.
\[ \text{Al}_3\text{Li} \quad \Delta H = 6,580 \text{ Joules/mole} \]
\[ \text{Al}_3\text{Zr} \quad \Delta H = 16,540 \text{ Joules/mole} \]

In the perfectly-ordered \( \text{Al}_3(\text{Li},\text{Zr}) \) phase, there are no \text{Li}-\text{Zr}
nearest neighbor pairs. Thus, considering a nearest-neighbor pair-wise
potential model, the \( \Delta H \) associated with the ordering of \( \delta'' \) is simply a
weighted average of the \( \Delta H \) values for the binary phases. The enthalpy
associated with the formation of \( \text{Al}_3(\text{Li}_x,\text{Zr}_{1-x}) \) can then be given, in
\[ \text{Joules/(mole } \delta'' \text{)}, \quad \text{as:} \]

\[ \Delta H_{\delta''} = -16,540 + 9960x. \quad (8.3) \]

Entropy

The critical ordering temperature, \( T_C \), for an L1_2-ordered phase is
that temperature for which the reaction

\[ \text{A}_3\text{B}_{\text{ord}} := (\text{A} \times \text{B})_{\text{fcc-as}} \quad (8.4) \]

has an associated free energy change, \( \Delta G \), of zero. Thus

\[ \Delta G = \Delta H + T\Delta S = 0. \quad (8.5) \]

Combining Eqns. 8.2 and 8.5 and setting \( T = T_C \), we arrive at an entropy
of ordering, \( \Delta S_0 \), of 8.916 Joules/(mole K) for the ordering reaction.*

*The entropy change associated with the DO\text{23}-ordering of \( \text{Al}_3\text{Zr} \) has been
calculated as \(-15 \text{ Joules/(mole K)} \) [94]. However, such a large value for
entropy of ordering leads to a critical ordering temperature for the
phase of \( -1103 \text{ K} = 830^\circ \text{C} \), which is low by more than \( 752^\circ \text{C} \) according to
the established phase diagram (Fig. 2.3). Thus, even though the
configurational component of entropy for the DO\text{23} and L1_2 structures is
the same, the value of \( \Delta S \) from [94] for the DO\text{23} phase will be
disregarded in favor of the value for L1_2 structures from Yang and Li as
calculated above.
The additional configurational entropy term for $\delta''$, due to having two species, Li and Zr, on the minor sublattice, is positive and is readily calculated. There are an Avogadro's number of Li-Zr sublattice sites per mole of $\delta''$. The configurational term is thus equal to the ideal $\Delta S$ of mixing for Al$_3$Li and Al$_3$Zr. The configurational entropy term for Al$_3$(Li$_x$Zr$_{1-x}$) is then,

$$\Delta S'_{\text{conf}} = -R(x \ln x \ast (1-x) \ln(1-x))$$

after Gaskell [96]. The prime is used to indicate the term is due to the presence of two species on the sublattice rather than to the configurational entropy associated with L1$_2$ ordering.

Gibbs Free Energy

The free energy of the $\delta''$ phase can now be described as:

$$\Delta G = -16,540 + 9960x$$

$$-T[-15 - R(x \ln x \ast (1-x) \ln(1-x))]$$

in Joules/mole, where $x$ describes composition of the phase as Al$_3$(Li$_x$Zr$_{1-x}$). The free energy as a function of composition at various temperatures is portrayed in Figure 8.2. Minima in free energy are associated with increasing Li content as the temperature increases, moving from $x \approx 0.125$ at $T = 300^\circ$C to $x \approx 0.325$ at $T = 1500^\circ$C. More relevant to the present work is the equilibrium composition at the SHT temperatures of $450^\circ$C ($x \approx 0.15$) and $500 - 580^\circ$C ($x \approx 0.2$).

8.2.4. Critical Ordering Temperature.

It must be recognized that the additional configurational entropy
Figure 8.2. Free energy of the \( \delta \)" phase as a function of temperature and composition. Standard states are disordered Al-25 at.%Li and Al-25 at.%Zr.
resulting from the two species on the sublattice of the ordered phase would also be applicable if the phase were in the disordered state. Thus the "additional term" does not tend to stabilize the ordered phase at high temperature in an alloy of the "stoichiometric" Al₃(Li,Zr) phase composition, since the disordered phase is "stabilized" to the same extent. The Yang and Li relationship between ΔH and T_C (Eqn. 8.2) should therefore be valid for the ternary phase.

The above argument implies a linear dependence of critical ordering temperature on the composition variable "x". The T_C for all compositions of Al₃(Liₓ,Zr₁₋ₓ) can then be obtained by combining Eqns. 8.2 and 8.3:

\[
T_C = 1855 - 1117x \quad ^\circ\text{K}
\]
\[
1582 - 1117x \quad ^\circ\text{C}
\]  
(8.8)

8.2.5. Anti-phase Boundary Energy

The (111) APB energy for Ll₄ structures is directly related to the ordering energy, and thus to the enthalpy of formation and the critical ordering temperature, as discussed in Chapter 7. As given earlier (Eqn. 7.4), the (111) APB energy can be given for δ" as:

\[
\psi_{APB} = 2.37 \times 10^{-24} T_C \quad \text{joules/A}^2
\]  
(8.9)

where T_C is given in degrees Kelvin. Combining Eqns. 8.8 and 8.9, we obtain:

\[
\psi_{APB} = 440 - 265x \quad \text{ergs/cm}^2
\]  
(8.10)

The influence of the APB energy on deformation behavior has been discussed in Chapter 7.
8.2.6. Nucleation Behavior

The free energy change associated with the solid state homogeneous nucleation of a coherent precipitate can be described as

\[ \Delta G = (4/3) \pi r^3 \Delta G_v + 4\pi r^2 \gamma \]  \hspace{1cm} (8.11)

where \( r \) is the embryo radius, \( \Delta G_v \) is a volume free energy term and \( \gamma \) is the interfacial energy. The volume free energy is composed of chemical and strain energy components:

\[ \Delta G_v = \Delta G_{\text{chem}} + \Delta G_{\varepsilon} \]  \hspace{1cm} (8.12)

The chemical free energy for \( \delta'' \) can be obtained from Eqn. 8.7 or Fig. 8.2. Conversion to a volume basis is obtained by multiplying by the molar volume ("41 cm\(^3\)/mole \( \delta '' \)). The strain energy, \( W \), of a spherical precipitate in an isotropic matrix is given as [97]:

\[ W = 6\mu_\alpha C_6 \varepsilon^2 V_B \]  \hspace{1cm} (8.13)

where \[ C_6 = \frac{3 K_B}{3K_B + 4\mu_\alpha} \]

where \( \mu \) is the shear modulus, \( \varepsilon \) is the misfit strain, \( V_B \) is the volume of the precipitate, and \( K \) is the bulk modulus. (Note that with spherical symmetry, Eqn. 8.13 applies to coherent as well as incoherent precipitates [97]). The volume strain energy density is then

\[ \Delta G_{\varepsilon, v} = 6\mu_\alpha C_6 \varepsilon^2 \]  \hspace{1cm} (8.14)

Both components of \( \Delta G_v \) are thus seen to decrease in value when Li is initially added to Al\(_3\)Zr. \( \Delta G_{\text{chem}} \) decreases as given in Fig. 8.2, and \( \Delta G_{\varepsilon} \)
is reduced as $\varepsilon^2$ with $\varepsilon$ as given in Fig. 5.10. Changes in $C_6$ with $\delta^+$ composition are regarded as second order.

The interfacial energy, $\gamma$, can also be expected to be reduced as the misfit is reduced [95]. Thus all terms of $\Delta G$ are reduced with Li additions to Al3Zr.

Furthermore, the critical radius for nucleation is given as

$$r^* = -\frac{2\gamma}{\Delta G_v} \quad (8.15)$$

and the activation energy for nucleation as

$$\Delta G^* = \frac{16 \pi \gamma^3}{3(\Delta G_v)^2} \quad (8.16)$$

The partial substitution of Li for Zr in Al3Zr is thus seen to favor the thermodynamics of nucleation. Smaller critical radii are to be expected, as is a lower activation energy.

The nucleation rate is dependent upon both the activation energy $\Delta G^*$ and diffusivity of the elements:

$$I = A D_x \exp\left(-\frac{\Delta G^*}{RT}\right) \quad (8.17)$$

The substitution of Li for Zr has been shown to reduce $\Delta G^*$. In addition, the diffusivity of Li is very much greater than that of Zr (See Table 2.2). Thus the effect of Li substitution into Al3Zr should result in smaller critical nuclei and a more rapid homogeneous nucleation rate at all temperatures.
8.3. DISCUSSION

The calculations presented above suggest the strong influence which Li substitution may have on the Al₃Zr phase and on alloys containing δ'". A very basic influence on mechanical properties will be through the volume fraction δ". The beneficial effects of hard second phases in strengthening an alloy and in dispersing slip are related to the volume fraction of the phase. Indeed, the strengthening effects have been calculated to be proportional to the square root of the volume fraction for both cutting and looping behavior [63]. Thus, there is interest in increasing the volume fraction of hard, Zr-rich precipitate.

The curve of Figure 8.1 illustrates the effectiveness of increasing the Li:Zr ratio in δ" in increasing the volume fraction of δ". This increase in volume fraction of second phase is provided without the problems associated with producing very large Zr supersaturations, yet may provide equivalent strengthening and slip dispersion. If the δ" is sufficiently resistant to shear, then its effect on deformation behavior will be equivalent to that of Al₃Zr. (Such resistance to shearing has been discussed in Chapter 7.) For compositions and precipitate distributions where Orowan looping is characteristic, an increase in strengthening proportional to the square root of the values given by the curve of Figure 8.1 can be expected. An alloy containing only Al₃Zr precipitates would require a Zr content of 2.5 wt.% to produce the same volume fraction second phase as an alloy of 1.0 wt.% Zr containing δ" with a 6:4 Li:Zr ratio (x = 0.6).

The interfacial energy of δ" is difficult to estimate, but may be expected to be less than that of Al₃Zr, based on the concept that a
smaller misfit is associated with a smaller interfacial energy [95]. The chemical energy associated with Li-Al bonds at the interface must be considered as well, and this effect may be positive or negative on the interfacial energy. Considering the very small δ'-matrix interfacial energy, it is likely that the chemical contribution due to Al-Li bonds will be to reduce the δ''-matrix interfacial energy.

The free energy of the δ'' phase is significantly reduced as the Li content goes from zero to x ≈ 0.2, as shown in Figure 8.2. The minimum δ'' free energy occurs at x ≈ 0.15 at 450°C, and at x ≈ 0.2 at 500-580°C. This minimum free energy results from a competition of enthalpy and entropy factors. The enthalpy magnitude is largest (negative) for no Li in the phase, while the configurational entropy is a maximum at Li:Zr = 1.

The resulting minimum free energy at x ≈ 0.2 is also the composition of δ'' which was determined by image calculation techniques in Chapter 6 for the 580°C/15 h SHT. This 580°C heat treatment is believed to result in the δ'' composition closest to equilibrium of the heat treatments examined. (With this heat treatment the δ'' has spheroidized significantly more than with the other heat treatments, with no filamentary or large aspect ratio precipitates.) Thus the δ'' composition with the minimum free energy appears to have been produced during the 580°C SHT.

The calculations presented above show that surface energy effects, chemical free energy and strain energy all should contribute to ease of homogeneous nucleation of δ'' containing at least some Li. Unfortunately, the experimental evidence does not allow for a testing of this proposal.
Discontinuous precipitation appears to remain the dominant mode of precipitation of the $\delta''$ phase.

8.4. SUMMARY

The presence of Li in $\delta''$ has been calculated to have profound effects on various properties of the phase when compared to Al$_3$Zr, including chemical free energy and strain (mismatch) energy effects. The minimum chemical free energy appears at a Li:Zr ratio of approximately 2:8 (i.e., $x \approx 0.2$ in Al$_3$(Li$_x$Zr$_{1-x}$)) for the solution heat treat temperatures examined in this study. The same 2:8 ratio was ascertained experimentally by image calculation methods of Chapter 6 for the SHT resulting in $\delta''$ compositions believed to be closest to equilibrium (580°C/15 h).
CHAPTER NINE

SUMMARY AND CONCLUSIONS

In the present study it was proposed that the Li2-ordered Al3Zr and
Al3Li phases might show partial or total inter.solubility, and that the
production of an Al3(Li,Zr) phase might prove valuable in improving the
problems of low ductility and fracture toughness of Al-Li alloys.
Indeed, it has been shown that the Al3(Li,Zr) phase, which we call δ'',
can be produced with a wide range of Li:Zr ratios. Precipitates of δ''
appear to reduce the two major causes of low ductility in Al-Li alloys,
that is, alip localization due to shearable precipitates, and
precipitate-free zones along high angle grain boundaries.

The alloys analyzed in this study, Al-2.34Li-1.07Zr and Al-2.19Li-
0.12Zr (by wt.%), were vacuum atomized at ~1000°C, the 400°C superheat
being necessary for dissolution of Zr at the 1% level into the melt. The
atomized powder was vacuum-hot-compacted and extruded. Samples were
solution heat treated at 450-580°C for various times and aged at 190°C.

The Zr supersaturation produced during atomization was preserved
until extrusion. The δ'' phase precipitated during the extrusion and
solution heat treatment. The precipitation occurred discontinuously, as
6 nm diameter filaments, and through a normal nucleation-and-growth
process. The discontinuous process appears to be the predominant
mechanism of precipitation. During aging treatment, the Al3Li phase, or
δ', precipitates heterogeneously at the δ''-matrix interface, completely
wetting the δ'', producing a unique "composite precipitate" of cores of δ''
surrounded by envelopes of δ'. These envelopes of δ' grow in thickness
with aging time. In areas devoid of δ'', the δ' precipitates in the
normal manner, that is, homogeneously and spherically.

Analysis of Li content of δ" is not feasible by the usual microanalytical techniques. A method was developed whereby superlattice dark-field images were calculated and comparisons were made with actual images of the composite precipitates under various imaging and heat treatment conditions to ascertain the Li:Zr ratio in the δ". The Li:Zr ratio varies from 2:8 to 6:4, depending upon heat treatment and precipitation mechanism (discontinuous versus normal nucleation and growth).

A thermodynamic model of free energy for the Al₃( resp. to ) phase as a function of x, or composition, was developed. The model predicts a minimum chemical free energy at x = 0.15 (at 450°C) to x = 0.2 (at 500-580°C). After the 580°C/15 h SHT, a value of x = 0.2 (i.e., Li:Zr = 2:8) was determined experimentally, suggesting the δ" had reached its equilibrium composition. It is believed that the more Li-rich δ" produced under other SHT conditions did not attain an equilibrium composition due to the slow kinetics of Zr diffusion.

The low toughness of Al-Li alloys is believed to be due to 1) slip localization due to the sheartable nature of the δ' precipitate, and 2) δ'-precipitate-free zones (PFZ) which form at high-angle grain boundaries during aging. The presence of the δ" phase at least partially solves both of these problems: 1) the δ" phase appears very resistant to shear under conditions where δ' is sheared, and 2) δ" is stable in the δ'-PFZ, providing a strengthening of this soft region. The increased strength of δ" is believed to be due to a large (111) antiphase boundary energy.

The mechanical properties of the high-Zr alloy are significantly improved over the low-Zr alloy. At equivalent ductility, the high-Zr
alloy has a 20 ksi (140 MPa) advantage in yield strength over the low-Zr alloy. At equivalent strength levels the high-Zr alloy has ~2 to 3 times the elongation. The improvement in properties can be attributed in part (~5 ksi) to a refined grain size, and primarily to the characteristics of the $\delta''$ phase as described in the preceding paragraph.

The major conclusions of this work are as follows:

1. Al-Li-Zr alloys containing up to 1.1 wt.% Zr are readily produced by vacuum atomization resulting in the Zr being preserved in solid solution.

2. An Al$_3$(Li,Zr) phase precipitates in the Al-Li-Zr system at high temperatures, i.e., the solution heat-treat temperatures typical for Al-Li binary alloys. This phase, which we call $\delta''$, is L1$_2$-ordered and coherent with the matrix with a cube-cube orientation relationship with the matrix.

3. The $\delta''$ precipitates discontinuously during extrusion and solution heat treatment, resulting in very fine filaments of diameter of approximately 6 nm. In areas without the filaments, $\delta''$ precipitates in a normal nucleation and growth manner during SHT. The precipitates coarsen slowly with extended heat treatment.

4. A method of compositional analysis using dark-field image calculation has been developed for use in the analysis of Li:Zr ratio in $\delta''$. This method is especially useful since the standard methods of microanalysis, energy-dispersive X-ray analysis and electron energy loss spectroscopy, are either not applicable or very difficult to apply to the analysis of Li in $\delta''$. 

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5. The composition of the $\text{Al}_3(\text{Li}_x\text{Zr}_{1-x})$ phase varies with heat treatment and precipitation mechanism such that $x$ has values from 0.2 to 0.6.

6. The $\delta''$ serves as a preferred nucleation site for $\delta'$ during aging. The $\delta'$ completely wets the $\delta''$, forming "composite" precipitates composed of a $\delta''$ core enveloped by a layer of $\delta'$.

7. The $\delta'$ nucleates with perfect epitaxy on the $\delta''$, i.e., the Li-containing sublattice is continuous across the $\delta'-\delta''$ interface.

8. The $\delta''$ phase is stable in $\delta'$-precipitate-free zones.

9. The high-Zr alloy exhibits significant improvements in strength and ductility over the low-Zr alloy. The improvement is attributed to a refined grain structure, slip dispersion by the $\delta''$ phase, and a strengthening of the $\delta'$-PFZ's by $\delta''$.

10. Aging of the high-Zr alloy after a 450°C/500 hour SHT produces grooves in the $\delta'$ envelopes. It is proposed that this behavior is due to a partial transformation of $\delta''$ filaments from L1$_2$ to the equilibrium (for $\text{Al}_3\text{Zr}$) DO$_{23}$ or DO$_{22}$ structure during SHT, such that the filament remains primarily L1$_2$ but contains thin slices of DO$_{23}$ or DO$_{22}$.

11. A phase diagram for the metastable $\alpha-\delta'$ system (in the Al-Li binary system) has been constructed which is preferable to the phase diagram presently in general use.
CHAPTER TEN
SUGGESTIONS FOR FUTURE RESEARCH

The results of the present work suggest that other Al-Li-based ternary or higher-order systems may show similar phase transformation phenomena and that improvements in the mechanical properties of these alloys may be realized over those of the Al-Li binary system. The elements of primary interest for additions are those which form precipitates of the L1_2 structure in their respective Al-based binary systems. These elements include Sc, Hf, Mg, and U. An additional alloying element of interest is Ti, which precipitates as the equilibrium Al_3Ti in the D0_22 structure, closely related to L1_2.

The Al_3(Li,Zr) system provides a good arena for testing the analytical abilities of electron energy-loss spectroscopy. Precipitates containing a range of Li levels can be produced, with Li content above and below the estimated minimum detectable mass fraction Li.

The calculation of composite precipitate images using the multislice dynamical calculations would complement the kinematical calculations of the present study. Dynamical calculations would be useful in verification of the applicability of kinematical theory, and might lead to better "resolution" in the compositional analytical capabilities of the image calculation approach.

Image calculations in the present study have been done for precipitates with spherical symmetry, but are readily adaptable for other geometries. Such calculations would be useful in further analysis of the various precipitate morphologies found in the Al-Li-Zr system.
With the goal of improving mechanical properties in Al-Li alloys, a second iteration of alloys, with variations in Li and Zr levels, would be of great interest. Both higher and lower levels of Li and Zr in an alloy could be expected to lead to changes in precipitation behavior and consequently deformation behavior. Tests of actual fracture toughness, such as compact tension or notched tensile tests, would be very desirable for the present alloys as well as any future alloys.
APPENDIX A

COMPUTER PROGRAM FOR IMAGE CALCULATIONS

The following is a listing of the computer program, written in
BASIC, which was used for the image calculations of Chapter 6. Included
is a sample of the output from the program. The program utilizes the
Wordstar word processing program and an Okidata Micro 92 dot-matrix
printer. The gray-scale is user-defined and loaded into the printer
memory before printing the output.

100 REM ************************************************************
120 REM IMAGE CALCULATIONS - COMPOSITE PRECIPITATES
130 REM USING MORROW
150 REM PROGRAM FOR MULTIPLE IMAGES
500 REM ************************************************************
1000 OPEN "O", #1, "B:COMPIMA9"
1100 PRINT#1, ".LH 4"
1120 PRINT#1, ".OP"
1140 PRINT#1, ".PO 0"
1210 FOR CONTRAST = 13 TO 11 GRAY LEVELS ARE WHITE
1300 REM ESTABLISH GRAY SCALE
1320 FOR GN = 0 TO 15
1340 READ GS$ (GN)
1360 NEXT GN
1500 REM ** FIGURE STRUCTURE FACTORS FOR DELTA PRIME AND A132r **
1520 FOR N = 0 TO 1
1540 FOR I = 1 TO 20
1570 READ F(N, I)
1580 NEXT I: NEXT N
1590 REM STRUCTURE FACTORS FOR THE BINARY PHASES- FIRST A132r,THEN A13LI
1592 REM FOR REFLECTIONS N"2 = 1,2,3,4,... FOR SUPERLATTICE
1594 REM REFLECTIONS. (INDICATED AS ZERO IF FUNDAMENTAL!!!!)
1595 DATA 3.037, 2.899, 0, 0, 2.24, 2.07, 0, 0, 1.71, 1.61
1596 DATA 0, 0, 1.406, 1.339, 0, 0, 1.157, 1.118, 0, 0
1597 DATA -2.172, -1.757, 0, 0, -1.084, -0.959, 0, 0, -0.746, -0.697
1598 DATA 0, 0, -0.591, -0.565, 0, 0, -0.502, -0.487, 0, 0
2000 REM ** ASCERTAIN NO. OF IMAGES AND CALCULATE **
2020 READ NUMIM 'NUMBER OF IMAGES
2100 REM ***** CALCULATE IMAGE ****
2120 DIM LS(40)  
2200 FOR ITER = 1 TO NUMIM  
2220 READ RATIO 'FRACTION OF TOTAL RADIUS DOUBLE PRIME  
2240 RE=1000: RC = 1000*RATIO 'RADIUS TOTAL, RADIUS CORE FOR IM CALC  
2260 READ COMP 'x IN A13(Lix, Zr1-x) core  
2280 READ REFL 'IMAGING REFLECTION  
2300 READ R 'TRUE TOTAL PPT RADIUS FOR TOTAL IM INTENSITY  
2305 PRINT#1, "COMPOSITE PRECIPITATE"  
2505 PRINT#1,  
2510 PRINT#1,  
2520 PRINT#1, "CORE IS DELTA", A13(Lix, Zr1-x), WHERE x IS ";COMP  
2525 PRINT#1,  
2530 PRINT#1, "CORE RADIUS = ";R;RATIO; "nm"  
2535 PRINT#1,  
2540 PRINT#1, "TOTAL PARTICLE RADIUS = ";R;"nm"  
2545 PRINT#1,  
2550 PRINT#1, "IMAGING SUPERLATTICE REFLECTION IS";REFL  
2555 PRINT#1,  
2560 PRINT#1, "(CONTRAST LEVEL IS";COMP;";CONTRAST;"", 12 IS ONE LEVEL OF WHITE)"  
2565 PRINT#1,  
2570 PRINT#1,  
2575 REM IN ABOVE THE "@" WILL BE CHANGED TO A "CONTROL Y", WHICH  
2576 REM WORDSTAR USES TO GO INTO GRAYSCALE MODE.  
2577 REM LINES 1100-1140 ARE WORDSTAR COMMANDS RE PAGE OFFSET,  
2578 REM AND LINE HEIGHT (NO GAPS BETWEEN LINES)  
2580 REM  
2590 REM ********** CALCULATE N = H^2 + K^2 + L^2 **********  
2600 A = REFL 'HKL  
2610 B = INT(REFL/10) 'HK  
2620 C = INT(REFL/100) 'H  
2630 N = ((A/10-B)*10)^2 + ((B/10-C)*10)^2 + C^2 'H^2+K^2+L^2="N"  
2640 FP= F(1,N) 'STRUCTURE FACTOR DELTA PRIME  
2650 FDP = F(0,N)*(1-COMP) + F(1,N)*COMP 'F DELTA DOUBLE PRIME  
2800 REM *** FIGURE SCALING INTENSITY IMAX ***  
2820 IMAX = 0 : Y = 0  
2840 FOR X = 0 TO 1070 STEP 5  
2860 IF X^2 >= RC^2 THEN ZCT=0 ELSE ZCT = (RC^2-X^2)^(.5)  
2870 IF X^2 >= RE^2 THEN ZET=0 ELSE ZET = (RE^2-X^2)^(.5)  
2880 TDP=2*ZCT: TP=2*(ZET-ZCT)  
2890 I = (TP+FP+TDP+FDP)^2  
2900 IF ABS(I) > ABS(IMAX) THEN IMAX = I  
2920 NEXT X  
3000 REM ***** CALCULATE IMAGE *****  
3010 FOR Y = 0 TO 1080 STEP 27  
3015 L=Y/27  
3020 LS=(L) = ""  
3040 FOR X = -1080 TO 1070 STEP 27  
3050 XYS=X^2 + Y^2  
3060 IF XYS >= RE^2 THEN I=0:GOTO 5000  
3080 ZET = (RE^2-XYS)^(.5)  
3100 IF XYS >= RC^2 THEN I=(2*ZET+FP)^2: GOTO 5000  
3120 ZCT = (RC^2-XYS)^(.5)  
3140 TDP = 2*ZCT 'THICKNESS DELTA DOUBLE PRIME
TP = 2*(ZET-ZCT) \text{ 'THICKNESS DELTA PRIME}
I = (TP*FP*TDP*FDP)^2 \text{ 'INTENSITY FOR S = 0}
GN = CINT(ABS((I/IMAX)*CONTRAST))
LS(L) = LS(L) + GSS(GN)
NEXT X
NEXT Y
FOR L = -40 TO 40
PRINT#1, LS(ABS(L))
NEXT L
PRINT#1, "\text{REPLACE @ WITH } ^{\text{Y B4 WS PRINTING}}"
PRINT#1, "IMAX = " ; IMAX
PRINT#1, "IMAX * R^2 = " ; IMAX*R^2
PRINT#1, "\text{PA}"
PRINT ITER; "IMAGES DONE AND SENT HOME - ONLY" NUMIM-ITER "LEFT!"
NEXT ITER
END
REM THE FOLLOWING ARE INPUT DATA
REM R-VALUE, "X" (COMPOSITION OF CORE), REFLECTION
REM RADIUS OF TOTAL COMPOSITE PPT IN NM
DATA 10
DATA .30, 0, 110, 100
DATA .30, .2, 110, 100
DATA .30, .4, 110, 100
DATA .30, .6, 110, 100
DATA .30, .8, 110, 100
DATA .40, 0, 110, 100
DATA .40, .2, 110, 100
DATA .40, .4, 110, 100
DATA .40, .6, 110, 100
DATA .40, .8, 110, 100
DATA 0, 0, 0, 0, 0, 0, 0, 0, 0
The following is a sample output from the program. The originals are printed as an 8 inch by 8 inch image. One side of the image has been deleted from the image below in order to show the image at approximately 1X magnification.

\[ R = 0.75, \ g = 100, \ x = 0.2 \]
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PUBLICATIONS


