

**MICROSTRUCTURAL CHARACTERISATION
AND PHASE TRANSFORMATIONS
IN QUATERNARY Al-Li ALLOYS**

**A thesis submitted for the degree of
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by

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To the memory of my father

ABSTRACT

A detailed and systematic study of the precipitate phases in the microstructures of a range of 8090 and 8091 (commercial Al-Li based) alloys in both the as-cast and heat treated conditions has been carried out. In addition to the conventional microanalytical techniques (light microscopy, scanning and transmission electron microscopy, energy dispersive x-ray analysis, and x-ray diffractometry), backscattered electron imaging and secondary ion mass spectroscopy have been especially employed to overcome the problem of detecting lithium ($Z = 3$).

These studies have shown that the major second-phase precipitate in as-cast 8090 and 8091 alloys is a quaternary phase of composition: 65.6 Al, 25.9 Cu, 6.3 Mg, and $\approx 2.2\text{Li}$ (wt%), having a simple cubic structure ($a_0 = 1.035$ nm). They also revealed the presence of impurity-based coarse intermetallic phases (AlSiLi , $\text{Al}_6(\text{Fe}, \text{Cu})$) at the grain boundaries. These phases may have a strong influence on the final properties of the alloys.

Studies of the heat treated microstructures have shown that these alloys may be optimally homogenised by annealing at 530°C for 24 hours. In the aged alloys, the co-precipitation of the $\delta'(\text{Al}_3\text{Li})$, $S(\text{Al}_2\text{CuMg})$, and $T_1(\text{Al}_2\text{CuLi})$ phases was demonstrated. The $T_2(\text{Al}_6\text{CuLi}_3)$ -based quaternary phase was also found within the grains of the aged alloys.

Differential scanning calorimetry studies of the as-cast and heat treated 8090 and 8091 alloys revealed the occurrence of liquid-solid and solid state phase transformations similar to those found in ternary Al-Li-Cu and Al-Cu-Mg systems. Therefore, a series of quaternary Al-Cu-Mg-Li alloys with compositions lying in the $\text{Al} - \delta - S$ and $\text{Al} - \delta - S - T$ phase regions were produced and studied in order to determine the influence of the S and T phases on the region of the quaternary phase equilibria which is important to the commercial alloys. These studies have shown that Li is incorporated into the S or T phase to form a phase containing Al, Cu, Mg, and Li; and the presence of Li-bearing phases has some effects on the phase equilibria of the Al-Cu-Mg ternary system.

Finally, the results of the present work have been combined with data available on the constituent Al-Li-Cu and Al-Cu-Mg ternary systems in an attempt to provide a fuller knowledge of the phase transformations which occur within the Al-Li-Cu-Mg quaternary system.

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CHAPTER 1

INTRODUCTION

The addition of lithium to aluminium produces a material with significantly reduced density and increased elastic modulus. These twin features are especially attractive to the aerospace and defence industries where the use of light-weight high strength materials for structural applications is highly desirable.

Early attempts to develop Li-containing aluminium alloys began in Germany in the 1920s and was primarily concerned with the addition of small amounts of lithium to age-hardening alloys in order to improve their strength. In the 1950s, the Aluminium Company of America (Alcoa) developed the commercial alloy AA2020 – an Al-Cu-1%Li alloy; this was followed in the 1960s by the alloys VAD23 (Al-Li-Cu), and 01420 (Al-Mg-2%Li) developed in the Soviet Union. Unfortunately, when used in aircraft structures both the AA2020 and the 01420 exhibited unacceptably low ductility and fracture toughness characteristics and were subsequently withdrawn from commercial use. However, the increasing need over the years for lighter and faster airplanes coupled with the recent threat from carbon fibre composites as likely substitutes for conventional aluminium alloys used in aircraft structures has rekindled interest in re-developing lithium-containing aluminium alloys. Thus, the last 15 years or so have seen an intensive search for a new generation of Al-Li alloys which are at least 10% lighter than, and of comparable or superior properties to, the conventional aircraft alloys.

Research into the new alloys concentrated largely on identifying causes for the brittle behaviour of binary Al-($\approx$ 3wt%)Li alloys and sought to improve their properties primarily through the effect of ternary and higher order alloying additions and precise control of thermal and mechanical treatments. Efforts were also directed at improving the traditional casting methods for aluminium alloys (ingot metallurgy), and also developing new production techniques such as rapid solidification (powder metallurgy) which will produce the desired microstructure and sought to overcome the problems associated with casting lithium. A wide range of alloy systems were investigated, including ternary Al-Li-Cu and Al-Li-Mg and quaternary Al-Li-Mg-Si, Al-Li-Zn-Mg, and Al-Li-Cu-Mg among which the latter emerged as the one capable of consistently

achieving the property targets set for the new alloys. Optimisation of properties within the Al-Li-Cu-Mg system has been achieved through:

- (a) a tight control on alloy composition in order to enable precipitation and distribution of strengthening phases,
- (b) measures to reduce impurity levels especially those of Fe and Si which form insoluble brittle particles, and
- (c) addition of zirconium (and sometimes Ti-Al-B master alloy) for grain refinement and recrystallisation inhibition.

The extensive and detailed work conducted by various researchers on the Al-Li-Cu-Mg-Zr alloy system and the others mentioned above have been adequately reviewed by Peel *et al.* (1,2), Sanders and Starke (3), Flower and Gregson (4), Gregson and coworkers (5) and Reynolds *et al.* (6).

In the last few years, the development within the Al-Li-Cu-Mg-Zr system has successfully led to the registration and commercial production of a number of alloys by the leading aluminium companies. Table 1.1 gives the designation, trade names and chemical compositions of some of the new alloys, together with their producers and the conventional alloys which they are designed to replace (7). Currently, some of these alloys are undergoing flight trials in British, American and French prototype aircraft.

However, the development of the new Al-Li based alloys appears to have been conducted without a proper knowledge of the phase relationships that may exist within the quaternary Al-Li-Cu-Mg system. Being precipitation hardened alloys, phase transformations, particularly, during heat treatment can have significant influence on the behaviour of these alloys. The practice whereby the phase relationships within the quaternary system are considered as a combination of those which exist in the constituent binary and ternary systems has become inadequate with the recently reported occurrence of quaternary phases in these alloys. It is therefore both of academic interest and commercial importance to study the quaternary Al-Li-Cu-Mg system in order to provide detailed information on the phase relationships particularly as they affect the commercial 8090 and 8091 alloys. The main objectives of the present work are therefore:

- 1) to conduct a systematic characterisation of the precipitate phases in the as-cast and heat-treated microstructure of commercial 8090 and 8091 alloys,

- 2) to investigate both the liquid-solid and solid-solid phase transformations that take place in these alloys during solidification and heat treatments,
- 3) to investigate the effect on the phase equilibria existing in the commercial alloys of changes in the composition which may lead to the formation of other phases, e.g. $S(Al_2CuMg)$ and $T(Al_6CuMg_4)$ phases, and
- 4) finally to use the results of this research, together with data available on relevant binary and ternary systems to establish regions of stability for the phases which are present in the 8090 and 8091 alloys.

Table 1.1 Composition Ranges for Commercially Registered Al-Li-Cu-Mg-(Zr) Alloys (Ref. 7).

Aluminum Association designation	Company of origin	Trade Names/ other designations	Chemical composition (weight per cent)											Substitute for
			Li	Cu	Mg	Zr	Si	Fe	Cr	Ti	Zn	Mn	Al	
8090	Alcan/Pechiney	F92 (RAE)	2.20	1.00	0.60	0.04	0.00	0.00	0.00	0.00	0.00	0.00	Bal.	2014-T3 & T851 2024-T4 7475-T73 7075-T73
		DTD --- A (RAE)	to	to	to	to	to	to	to	to	to	to		
		LITAL 'A' (Alcan) CP271 (Pechiney)	2.70	1.60	1.30	0.16	0.20	0.30	0.10	0.10	0.25	0.10		
X8090A	Alcoa	Alithalite A	2.10	1.10	0.80	0.08	0.00	0.00	0.00	0.00	0.00	0.00	Bal.	2024-T3 & T351
			to	to	to	to	to	to	to	to	to	to		
			2.70	1.60	1.40	0.15	0.10	0.15	0.05	0.15	0.10	0.05		
8091	Alcan	DTD --- B (RAE) LITAL 'B' (Alcan)	2.40	1.60	0.50	0.08	0.00	0.00	0.00	0.00	0.00	0.00	Bal.	7075-T76 7475-T76 7050-T7651 7010-T7651
			to	to	to	to	to	to	to	to	to	to		
			2.80	2.20	1.20	0.16	0.20	0.30	0.10	0.10	0.25	0.10		
X8192	Alcoa	Alithalite C	2.30	0.40	0.90	0.08	0.00	0.00	0.00	0.00	0.00	0.00	Bal.	Low density Medium strength
			to	to	to	to	to	to	to	to	to	to		
			2.90	0.70	1.40	0.15	0.10	0.15	0.05	0.15	0.10	0.05		
X8092	Alcoa	Alithalite D	2.10	0.50	0.90	0.08	0.00	0.00	0.00	0.00	0.00	0.00	Bal.	7075-T73
			to	to	to	to	to	to	to	to	to	to		
			2.70	0.80	1.40	0.15	0.10	0.15	0.05	0.15	0.10	0.05		
2090	Alcoa	Alithalite B	1.90	2.40	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	Bal.	7075-T6 7075-T73 (forgings)
			to	to	to	to	to	to	to	to	to	to		
			2.60	3.00	0.25	0.15	0.10	0.12	0.40	0.15	0.10	0.05		
2091	Pechiney	CP274	1.70	1.80	1.10	0.04	0.00	0.00	0.00	0.00	0.00	0.00	Bal.	2024-T351 7475-T7351 7175-T731
			to	to	to	to	to	to	to	to	to	to		
			2.30	2.50	1.90	0.16	0.20	0.30	0.10	0.25	0.10			
	Pechiney	CP276	1.90	2.50	0.20	0.04	0.00	0.00	0.00	0.00	0.00	0.00	Bal.	7050-T6 & T851 7010-T6 & T851
			to	to	to	to	to	to	to	to	to	to		
			2.60	3.30	0.80	0.16	0.20	0.30	0.10	0.10	0.25	0.10		

CHAPTER 2

LITERATURE SURVEY

2.1. Microstructure of Al-Li alloys

For most solutes, aluminium exhibits a relatively low terminal solubility with a result that the characteristic microstructure of cast aluminium alloys consists of Al-rich solid solution primary grains surrounded by a network of one or more second-phase constituents. The primary grain structure will influence the properties of the alloy through:

- (a) their size and shape, and the redistribution of solute(s) during solidification referred to as microsegregation or 'coring'; these features are largely determined by casting conditions; and
- (b) recrystallisation and texture which are developed during thermal and mechanical processing.

For cast aluminium alloys, the solute redistribution during solidification can, very simply, be represented by the Schiel equation:

$$C_s = C_o K (1 - f_s)^{K-1};$$

C_o is the initial concentration of solute in the alloy, $K = C_s/C_L$ is the equilibrium partition coefficient for the solute at the solid-liquid interface and C_s is the concentration of solute in weight fraction (f_s) of solid.

At the start of solidification, $f_s = 0$ and $C_s = C_o K < C_o$ (since $K < 1$ for Al alloys). Thus the first solid to form is lower in solute concentration than the initial alloy. Consequently, the solid that forms in the later stages of solidification becomes progressively richer in solute, resulting in a concentration gradient of the form shown in figure 2.1. Figure 2.1 also represents the linear growth of the dendrite during solidification.

However, a number of simplifying assumptions have been made in deriving the Schiel equation (8–10). In particular, the assumption that there is perfect mixing in the liquid state and no solute diffusion in the solid state is found to be unrealistic. Detailed and more realistic treatments of microsegregation resulting from solidification have been given by Flemings (9) and Kurz and

Fisher (10), and more recently by Kirkwood (8). Microsegregation occurs as a result of non-equilibrium solidification and can be almost totally eliminated by high temperature equilibration (homogenisation).

The development of a fine equiaxed and unrecrystallised grain structure in an alloy greatly enhances mechanical properties. In Al-Li based alloys this is achieved by adding zirconium and/or Ti-Al-B master alloys.

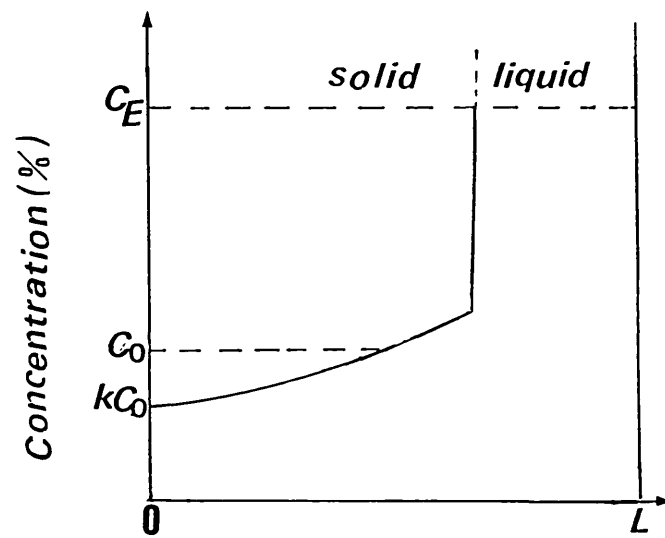


Figure 2.1 Solute distribution within a volume element during solidification (after refs.9, 10).

2.2. Precipitate Phases in Al-Li Based Systems

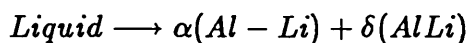
Being precipitation hardening alloys, the nature, size, and distribution of second phase constituents are of utmost importance in developing optimum properties of Al-Li based alloys. These features are determined (a) during casting by factors such as solidification rate, primary grain size, dendrite arm spacing, and solute concentrations; and (b) during thermal and mechanical treatments to which the alloy is subjected.

Usually, the phase diagram provides information regarding the phases that form within an alloy system at known compositions and temperature. Since the phase diagram of the Al-Li-Cu-Mg system is yet to be determined, the practice whereby the quaternary system is regarded as a combination of binary Al-Li and ternary Al-Li-Cu, Al-Li-Mg, and Al-Cu-Mg systems will be adopted for the purpose of this literature survey.

2.2.1. Al-Li Binary System

The extensive research carried out on the Al-Li binary system notably by McAlister (11), Williams and Edington (12, 13), and Baumann and Williams (14–16) has been summarised in the review papers by Williams (17), and Flower and Gregson (4). Although certain inconsistencies still exist between the various results, these studies have led to the determination of the complete phase diagram of the binary system. Figure 2.2 shows a section of the phase diagram up to 20 wt% lithium adapted from McAlister (11). The main features of figure 2.2 may be summarised as follows:

- (a) a maximum solubility of lithium in aluminium of about 14 at % at 600°C which decreases rapidly with decreasing temperature,
- (b) the occurrence of a simple eutectic reaction at 600°C



Thus, only two stable solid phases exist in the Al-corner of the Al-Li system: α -aluminium based solid solution and $\delta(\text{AlLi})$ – a broad intermetallic phase with 45 at% Lithium at 600°C and 55 at% Lithium at 500°C.

The δ phase has been observed to precipitate both in the α - matrix and on high angle grain boundaries after prolonged ageing of the alloy. It has an fcc lattice with $a = 0.6371 \pm 0.001_{\text{nm}}$ and a B32 (NaTi) structure type – determined

by Silcock (18) and confirmed by Noble and Thompson (19). δ precipitates are highly reactive and therefore very difficult to observe. However, the large lattice parameter implies that the α/δ interface is at least semi-coherent and will therefore be associated with dislocations; in transmission electron microscopy (TEM), such dislocation clusters are used to infer the presence of δ particles which have dissolved on thinning. X-ray diffraction studies by Silcock (18) and TEM by Noble and Thompson (19) have given the α/δ orientation relationship as:

$$(100)_\delta // (100)_\alpha; (011)_\delta // (\bar{1}11)_\alpha; (0\bar{1}1)_\delta // (1\bar{1}2)_\alpha$$

with a $\{111\}$ habit plane. As will be seen later, the precipitation of the δ phase in these alloys is detrimental to mechanical properties because of their coarse size and manner of distribution and the precipitate free zones (PFZs) associated with them (12,20).

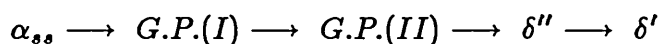
The existence of a metastable δ' (Al_3Li) phase was first reported by Silcock in 1959. The δ' phase is an ordered, fully coherent precipitate having an fcc lattice ($a = 0.4038 \text{ nm}$) and an $L1_2(Cu_3Au)$ structure. It confers on Al-Li alloys their basic precipitation hardening capability; consequently, the mechanism of its formation has been widely investigated.

Early investigators (18,19) only reported δ' precipitation in aged Al-Li alloys. Subsequent studies by Williams and Edington (13), and Ceresera *et al.* (21) reported the presence, in as-quenched alloys, of up to 4.0 nm diameter δ' particles which could be imaged from superlattice spots observed in electron diffraction patterns. More recent and detailed investigations by Baumann and Williams (14–16) have confirmed that the δ' phase is homogeneously precipitated as fine spherical particles in the α -matrix when an aluminium alloy containing more than 1.7 wt% lithium is quenched from the solid solution region.

The δ' solvus shown in Fig 2.3 has been determined from the work of Noble and Thompson (19), Williams and Edington (13), and Nozato and Nakai (22). Also included in Fig 2.3 is the “thermodynamic” δ' solvus (located just below the “apparent” δ' solvus) which was first defined by Williams and Edington (13) and later extended by Ceresera *et al.* (21) and Cocco *et al.* (23). Extrapolating the thermodynamic solvus over the $\alpha + \delta'$ phase field has shown that it is almost coincident with the apparent solvus. This is consistent with the small amount of lattice strain generated by δ' formation (12). Figure 2.3 summarises the results of the recent studies carried out on the Al-Li phase diagram.

The $\alpha + \delta'$ solvus is of a major practical significance as heat treatment of alloys of commercial interest involves compositions and temperatures lying within this solvus. Consequently, several investigations have been carried out to determine its exact nature. Until lately, a simple miscibility gap produced by connecting the experimentally determined α - and δ' - solvi (as shown in Fig 2.3) was generally accepted (24). Recently however, Gayle and Vander Sande (25) have pointed out that such a miscibility gap involving two distinct crystal structures (disordered α and $L1_2 \delta'$) violates thermodynamic restrictions: since the $Al \rightarrow L1_2$ ordering is a first order transformation, it is required that the two phase regions be bounded by two single phase fields. These authors have proposed several possible forms of metastable phase diagrams (25), the more recent of which is shown in fig 2.4(a).

Theoretical calculations by Sigli and Sanchez (26) have predicted a metastable phase diagram which is shown in Figure 2.4(b); it is in good agreement with that determined experimentally by Gayle and Vander Sande. In addition to the $\alpha + \delta'$ solvus, Sigli and Sanchez predicted a second miscibility gap which lies within the $\alpha + \delta'$ phase field. In practical terms, the existence of such a second level of metastability suggests the possibility of δ' formation from Guinier-Preston (G.P.) zones produced by decomposition of the supersaturated solid solution. Nozato and Nakai (22) have proposed the following precipitation sequence:



where the G.P. zones are ordered layers of Li atoms on Al planes and δ'' is a short-range ordered δ' phase of one or two dimensional morphology. Evidence for such a transition has been adduced from the interpretation of data from differential scanning calorimetry which shows low-temperature endotherms and exotherms consistent with G.P. zone formation and dissolution (22,27). No microstructural evidence has, however been obtained for the formation of such G.P. zones either in quenched or aged alloys.

On the other hand, Balmuth (28) has attributed the occurrence of these low-temperature endotherms to the dissolution of fine δ' particles produced on quenching; such δ' particles formed by classical nucleation and growth process would, of course, inhibit G.P. zone precipitation.

During ageing, the homogeneously precipitated matrix δ' particles grow by the transport of solute atoms into the precipitate. The coarsening rate is generally observed to follow the Lifshitz-Slyozov-Wagner (LSW) kinetics and the particle size distribution function $f_{\delta'} \propto (time)^{1/3}$ (4). However, deviations

from the LSW model resulting from alloy composition and/or ageing procedure have been observed. Recent attempts (28–30) to model the particle size distribution under these conditions are discussed in the review paper by Flower and Gregson (4). On the ^{other} hand, δ' can also nucleate on structural defects such as grain boundaries and dislocations. In this case, coarsening during ageing leads to the formation of PFZs. The growth of the PFZs has been observed to also follow a $(time)^{1/3}$ behaviour and has been explained to occur as a result of (a) enhanced lithium diffusion into the δ' particles in these regions, and (b) depletion of vacancies in these regions which act as vacancy sinks (21,31). Recent studies by Gregson and coworkers (32) on the role of vacancies in the nucleation and growth of δ' suggest that the latter is a more important mechanism.

The formation of δ' at grain boundaries is a good example of a discontinuous reaction allowing for such δ' particles to grow at the expense of the homogeneous matrix precipitates. The driving force for such a reaction will be expected to be small in view of the reported small α/δ' surface energy ($0.24 - 0.18 \text{ J/m}^2$). Thus the reaction is easily suppressed by external disturbances such as will be caused by the presence of other lithium-containing phases as in the case of ternary or quaternary alloys. On prolonged ageing, the growth of δ' is observed to terminate rapidly as the equilibrium δ phase forms.

The exact mechanism of δ formation is also not well established. Several workers (13,19) have proposed that the δ' precipitates coarsen and transform to equilibrium δ on prolonged ageing. Schegoleva and Rybalko (33) suggested that this transformation consists in the re-arrangement of the fcc structure to NaTl-type structure by collective shears of groups of $\{111\}$ fcc planes as in the martensitic transformation process. Unfortunately, no diffraction evidence was produced to support this argument. On the other hand, Suzuki *et al.* (34), Venebles *et al.* (35) and Jha *et al.* (31) have produced evidence in favour of δ nucleation independent of δ' and the growth of δ precipitates accompanied by dissolution of surrounding δ' particles. This appears to be the generally accepted process for δ formation in Al-Li alloys.

Table 2.1 Major characteristics of precipitate phases in Al-Li Binary Alloys

Precipitate type	Lattice/Structure	Lattice Parameters (nm)
α -(Al-Li) solid solution	fcc	$a = 0.404$
δ -(AlLi) Equilibrium, intermetallic,	fcc B32(NaTl)	$a = 0.638 \pm 0.001$
δ' -(Al_3Li) metastable, intermetallic	fcc $L1_2(Cu_3Au)$	$a = 0.4038$

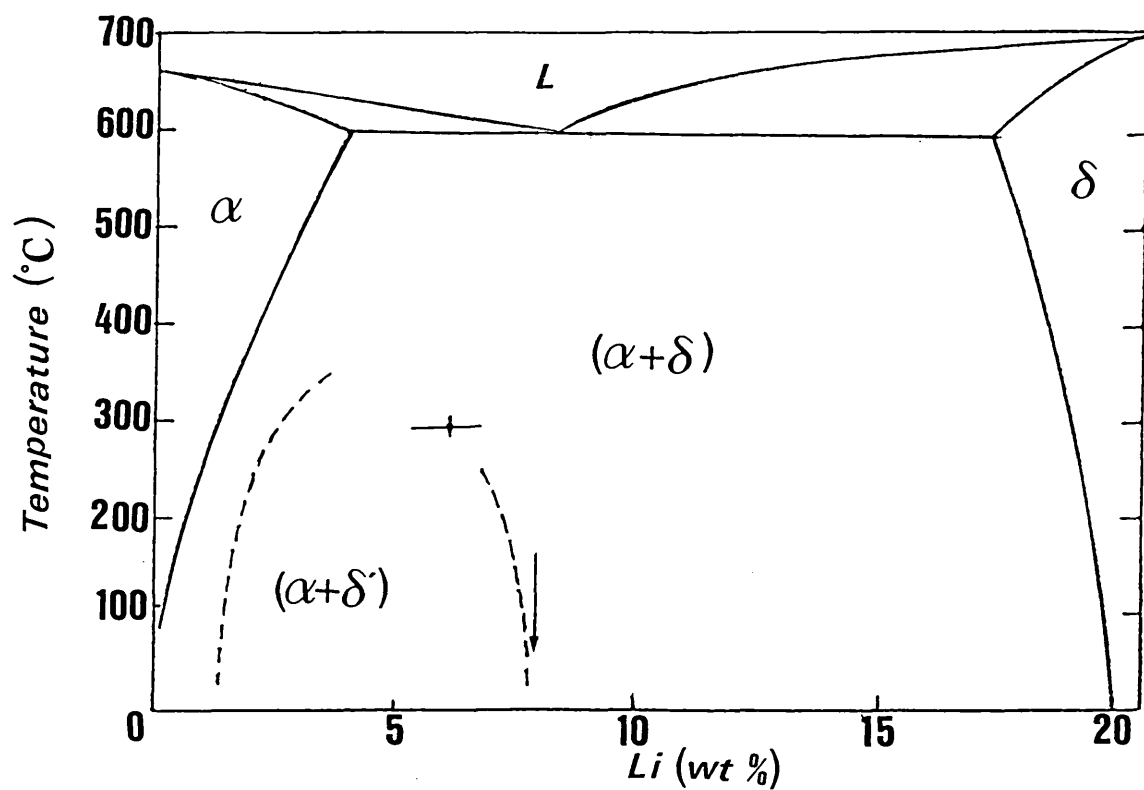


Figure 2.2 Equilibrium Al-Li phase diagram adapted from McAlister(11); dashed lines represent metastable $\delta'(\text{Al}_3\text{Li})$ solvus.

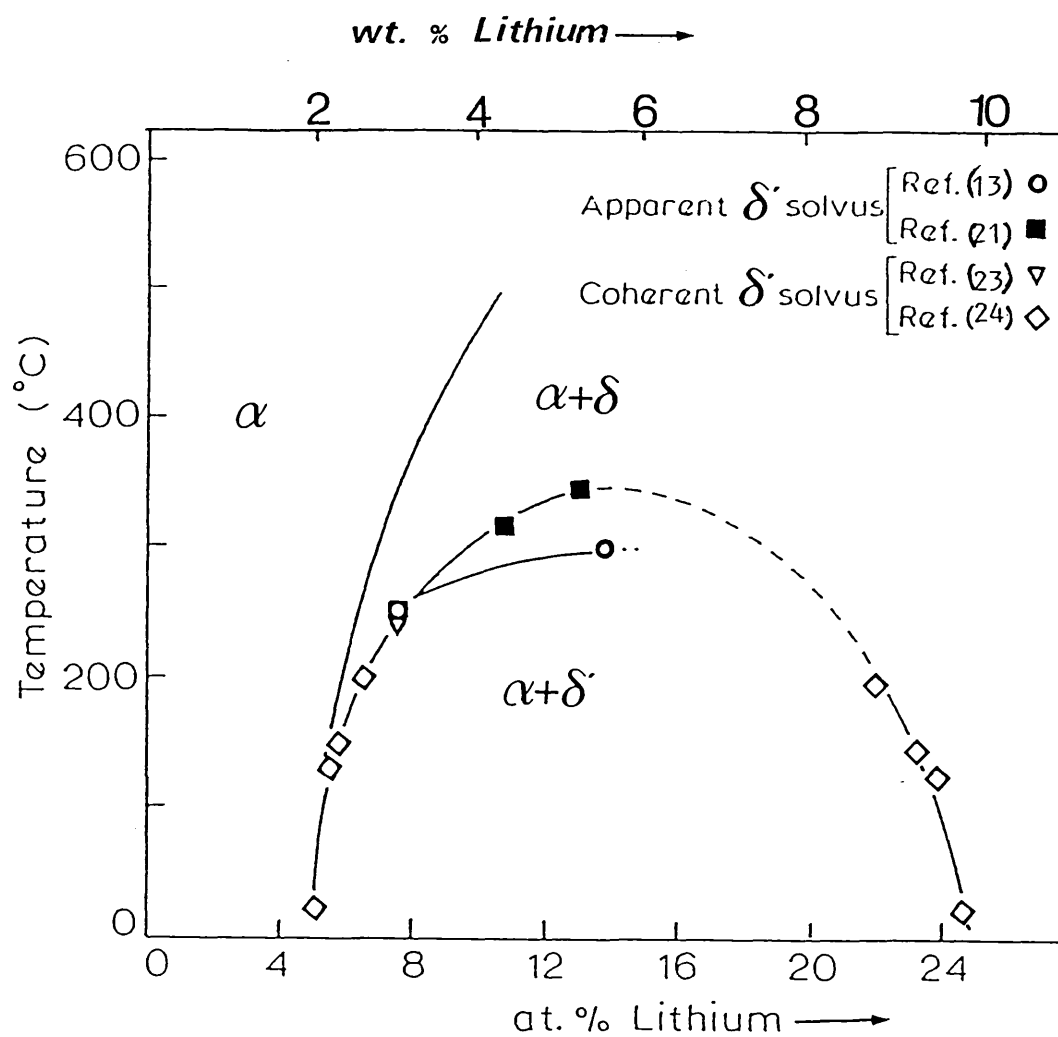


Figure 2.3 Al-Li phase diagram showing the δ solvus, and the apparent and coherent δ' solvi (adapted from Ref.102).

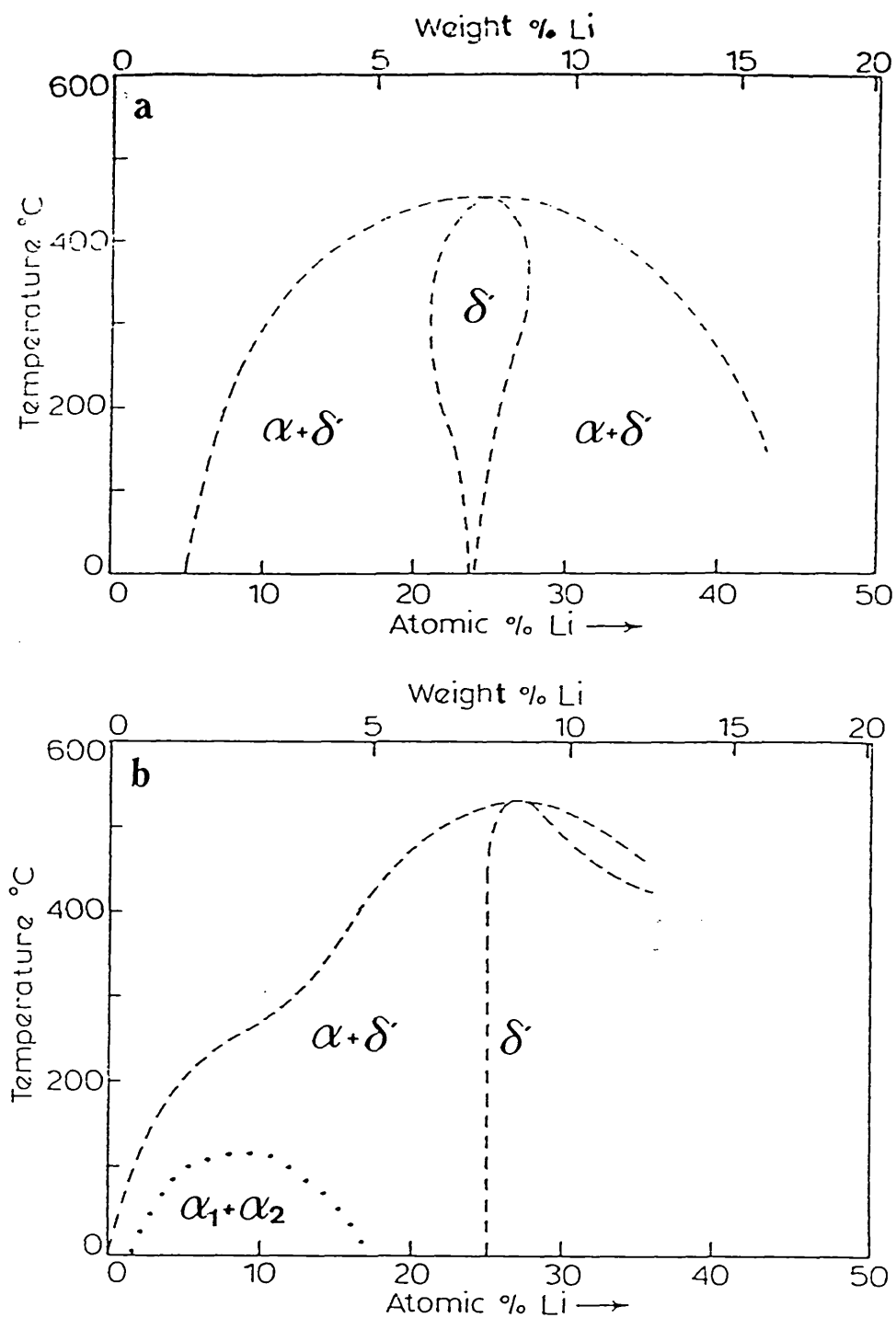


Figure 2.4 The metastable α - δ system

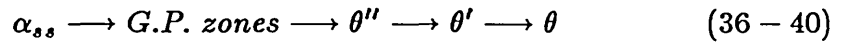
(a) as proposed by Gayle and Vander Sande(25)

(b) as predicted by Sigli and Sanchez(26).

2.2.2. Al-Li-Cu Ternary System

Several phases may precipitate in the ternary Al-Li-Cu system depending on alloy composition and heat treatments. They are essentially based on the constituent binary Al-Li and Al-Cu systems, but also include a number of ternary phases (see table 2.2).

Considering the Al-rich end of the Al-Cu system, the precipitation sequence from supersaturated solid solution has been established as:



The G.P. zones are fully coherent copper rich clusters which have been described by Gerold (36) as a $\{100\}$ plane of copper atoms surrounded by a strain field. θ'' (termed GP(II) zones by Guinier) nucleates heterogeneously on the G.P. zone/ α interface and also consists of ordered layers of Cu and Al atoms on the $\{100\}$ Al plane. Yoshida *et al.* (37) have observed in their study of Al-Cu alloys that the formation of G.P. zones and θ'' is a function of ageing temperature and time.

Silcock (18) demonstrated that in low copper alloys aged at 165°C θ' is the dominant precipitate; while in alloys containing ≥ 2.5 wt%Cu, θ'' predominates at the same ageing temperature. Figure 2.5 shows the Al-rich end of the Al-Cu phase diagram as proposed by Lorimer (40). The major strengthening effect in binary Al-Cu alloys is attributed to the θ'' which transforms to θ' beyond peak ageing. θ' also nucleates heterogeneously at grain boundaries and dislocations during the early stages of ageing and grows at the expense of the G.P. zones and θ'' (as stated above); the particle size could range from 100–6000 nm in diameter and 100–150 nm in thickness.

On prolonged ageing, the equilibrium θ phase nucleates at planar interfaces such as grain boundaries and the θ' /matrix interface and grows as the θ' dissolves. Noble *et al.* (41) have shown that lithium additions to the Al-Cu system in the solid solution range (4.5 wt%Cu, 0.4–1.5 wt%Li) can modify the structure of the G.P. zones and Silcock *et al.* (39) observed that the presence of trace elements such as Cd, In, etc, can suppress θ'' nucleation with a consequent enhancement of θ' precipitation in alloys containing up to 5 wt% Cu and 2.5 wt% Li.

Early work by Hardy and Silcock (42) on the Al-Li-Cu ternary system led to the identification of six stable ternary phases; $T_1(Al_2CuLi)$, $T_2(Al_6CuLi_3)$, $T_B(Al_{7.5}Cu_4Li)$, $R(Al_5CuLi_3)$, and P and Q whose compositions were not

determined. Which of these phases may exist in equilibrium together with the binary δ and θ phases and the Al-solid solution, depends on alloy composition and ageing treatment.

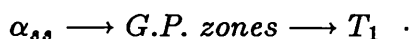
The solid state phase equilibria at 500°C and 350°C proposed by Hardy and Silcock (42) for the Al-rich end of the Al-Li-Cu system are presented in figures 2.6 and 2.7 respectively. Also shown in Figure 2.8 are the regions of different phase formations in alloys aged for 16 hrs at 165°C as determined by Silcock (18). It should be noted that T_2 and T_B do not form at this ageing temperature.

In the solid solution region of these alloys, only matrix δ' particles are precipitated in the as-quenched microstructure. θ' and T_1 precipitates are formed from the early stages of ageing. In the ternary alloys, δ' can also nucleate on θ' particles, forming a coating on the broad face of the θ' particles during ageing (43–46, 82).

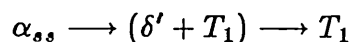
Silcock *et al.* (39) have shown that in alloys containing Li in concentrations close to the solid solution range, the dominant precipitate changed from θ'' to θ' to T_1 as ageing progressed. Whereas, Noble and Thompson (47) observed that in alloys containing > 2.5 wt% Li and 3 wt% Cu, δ' and T_1 precipitates predominate during the early stages of ageing. The hexagonal T_1 phase forms thin plates with $\{111\}$ habit planes and have the orientation relationship:

$$(0001)_{T_1} // (111)_{\alpha}; < 10\bar{1}0 >_{T_1} // < 1\bar{1}0 >_{\alpha} \quad (47)$$

It can form in one of two ways depending on the degree of solid solution supersaturation. In alloys of high copper concentrations ($Cu : Li > 3.0$) T_1 nucleates heterogeneously at G.P. zones formed via classical Al-Cu precipitation sequence:



Whilst in alloys of low copper concentrations ($Cu : Li < 1$) in which the θ'' and G.P. zones are absent, it forms via dissociation of matrix dislocations into Shockley pairs, followed by solute (Cu and Li) enrichment of the intrinsic stacking faults (18, 19). Gregson and Flower (4) have observed that in this case the δ' solvus is in fact exceeded and δ' precipitation precedes the T_1 formation, so that the precipitation sequence is of the form:



Tosten *et al.* (48) and Huang and Ardell (43) have also observed that in high Cu:Li ratio alloys, T_1 can compete with δ' for available lithium and thus grow

at the expense of the δ' during ageing. This leads to the formation of δ' PFZs which are absent in low Cu:Li ratio alloys. However, in such alloys T_1 can again compete with θ' for available copper and grow at the expense of the latter during ageing. Consequently, the volume fraction of the T_1 phase, f_{T_1} , increases significantly with ageing. This contrasts with the case in binary Al-Li alloys where $f_{\delta'}$ increases substantially during ageing. In the overaged alloy, therefore, T_1 is the dominant phase existing in equilibrium together with the binary θ and δ phases and the α -solid solution.

The existence of other ternary equilibrium phases in high copper alloys has been reported. The work of Hardy and Silcock (42) and Schneider and Von Heimendahl (49) seem to suggest that upon prolonged ageing the T_B phase is formed from θ' by diffusion of Li into the latter. T_B thus retains the characteristics of the θ' phase. Hardy and Silcock proposed the following orientation relationship for the T_B phase;

$$(100)_{T_B} // (110)_{\alpha}; (001)_{T_B} // (001)_{\alpha};$$

with a cubic lattice ($a = 0.538$ nm) and C1 crystal structure. Also, Cherkashim *et al.* (50), Casada *et al.* (51) and Rioja and Ludwiczak (52) have observed T_2 precipitation in high copper (2090) alloys. The structure of the T_2 phase was determined as icosahedral exhibiting a five-fold symmetry (51,53,54).

Suzuki *et al.* (55) were the first to suggest the existence of ternary metastable phases in the Al-Li-Cu system. They made their suggestion on the basis of super lattice spots present in electron diffraction patterns which could not be associated with either the θ' or T_1 phase. Later, Rioja and Ludwiczak (52) also from electron diffraction evidence proposed the existence of several metastable phases in aged 2090 alloys (T'_1 , T'_2 , and T'_B) which they suggested were precursors to the corresponding equilibrium phases. An orthorhombic structure of the Pt_2Mo -type was proposed for the T'_1 phase with lattice parameters as shown in Table 2.2 and orientation relationship:

$$(010)_{T'_1} // (110)_{\alpha}; (001)_{T'_1} // (100)_{\alpha}$$

However, several other investigators (39,41,43,44,51) did not find any evidence of the existence of such metastable phases. Huang and Ardell (44) and Casada *et al.* (51) argued that the extra spots observed in electron diffraction patterns can be explained wholly on the basis of the growth mode and orientation of the θ' and T_1 phases, giving rise to streaking which can intersect rational zones in the observed positions of the extra spots.

Table 2.2. Major characteristics of precipitate phases in
Al-Li-Cu ternary alloys

Precipitate type	Lattice/Structure	Lattice parameters (nm)
δ	<i>as in table 2.1.</i>	<i>as in table 2.1.</i>
δ'	"	"
$\theta(Al_2Cu)$ intermetallic	bcc tetragonal	$a = 0.606$ $c = 0.489$
$\theta'(Al_2Cu)$ metastable	bcc tetragonal	$a = 0.404$ $c = 0.580$
$\theta''(Al_2Cu)$	bcc tetragonal	$a = 0.404$ $c = 0.790$
$T_1(Al_2CuLi)$ intermetallic	hexagonal	$a = 0.497$
$T'_1(Al_2CuLi)$ metastable	orthorhombic	$a = 0.288$ $b = 0.860$ $c = 0.406$
$T_2(Al_6CuLi_3)$ intermetallic	icosahedral M35 symmetry	"quasi-lattice constant" $a = 0.51(Ref.55)$
$T_B(Al_{7.5}Cu_4Li)$ intermetallic	cubic (C1)	$a = 0.583$
$R(Al_5CuLi)$ intermetallic	cubic (SG1m-3)	$a = 1.3914$
P undetermined	undetermined	undetermined
Q undetermined	"	"

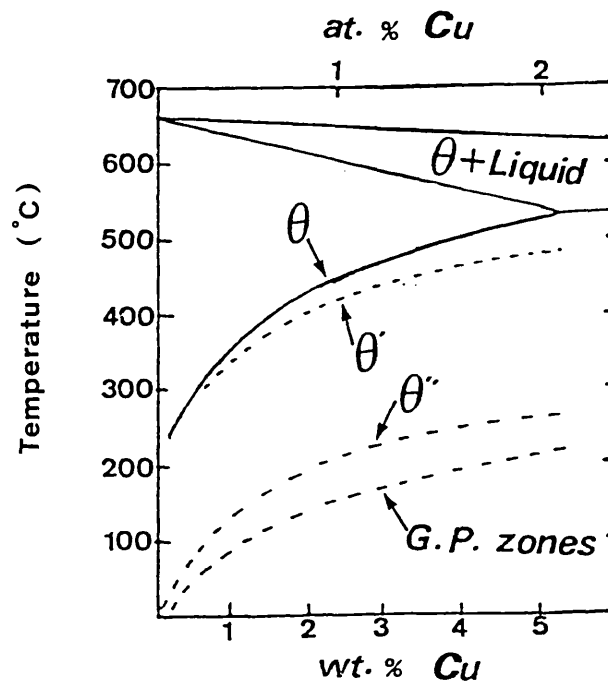


Figure 2.5 The Al-Cu phase diagram with the metastable solvus lines for G.P. zones, θ'' , and θ' (Ref. 40).

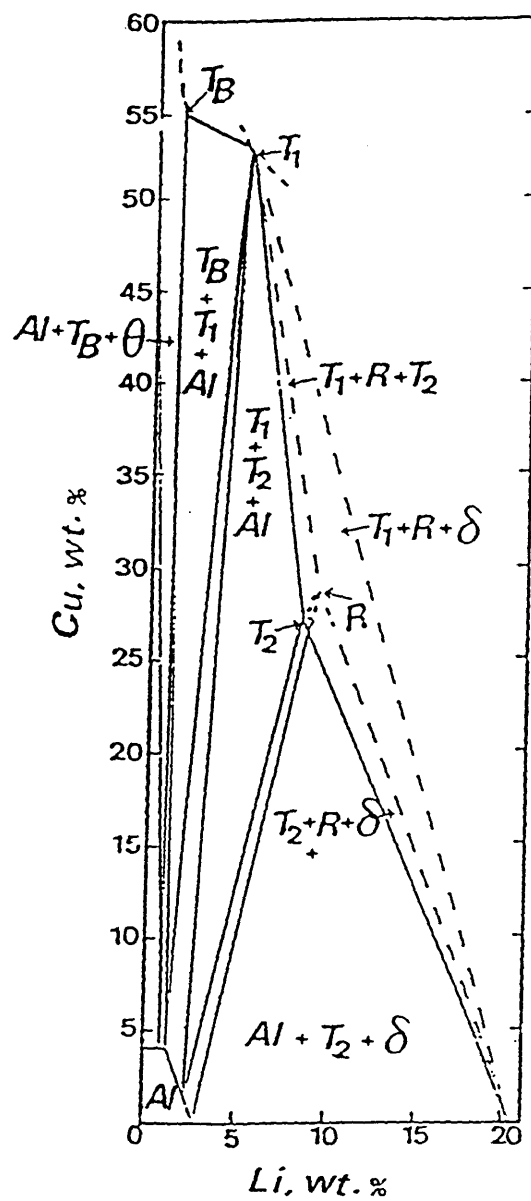


Figure 2.6 Isothermal section of the Al-Li-Cu system:
 Phases identified at 500°C (after Hardy and
 Silcock, 42).

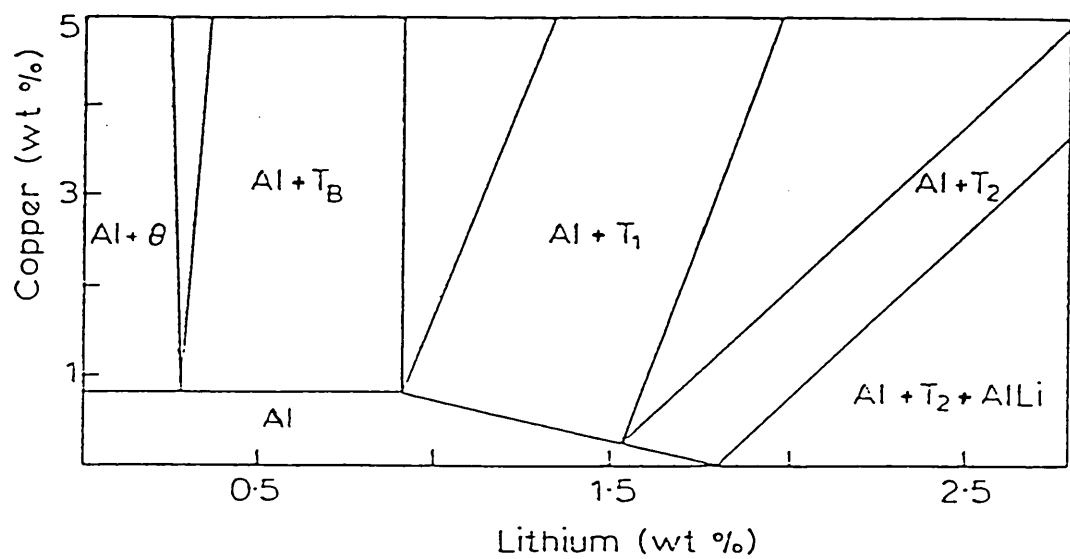


Figure 2.7 Isothermal section of the Al-Li-Cu system:
Phases identified at 350°C (ref. 42).

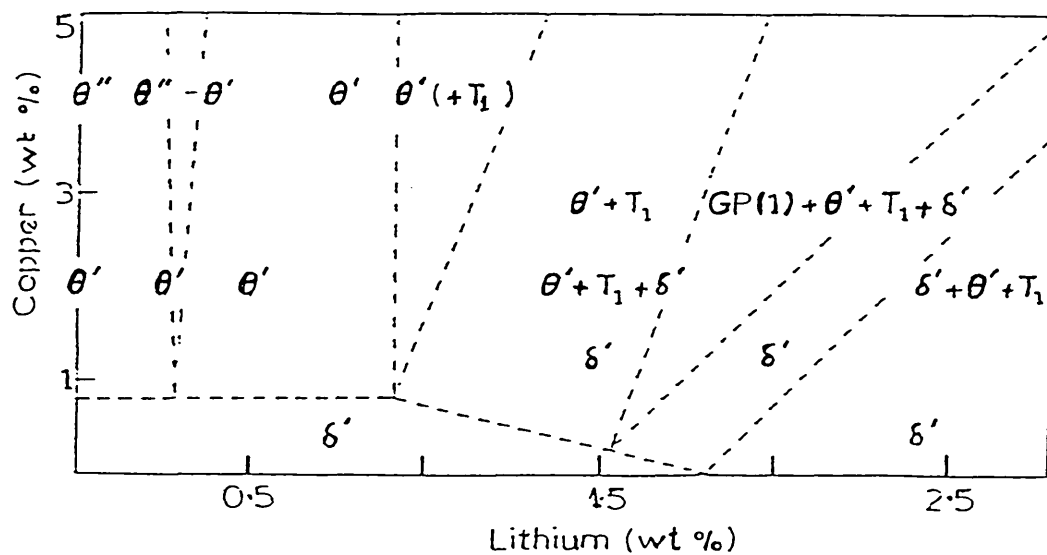
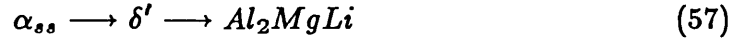


Figure 2.8 Isothermal section of the Al-Li-Cu system:
 Phases identified after ageing at 165°C
 for 16 hrs (after Silcock, 18).

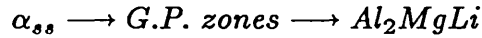
2.2.3. Al-Li-Mg Ternary System

The phases which may precipitate in the Al-Li-Mg system include δ (and δ') from the Al-Li system, $\beta(Al_3Mg_2)$ and $\gamma(Al_{12}Mg_{17})$ from the Al-Mg system and ternary Al_2MgLi (56,57). The β and γ phases are reported to precipitate at higher Mg concentrations than are present in commercial Al-Li based alloys. Figure 2.9 shows a phase section of the Al-Li-Mg system at a typical ageing temperature for Al-Li alloys.

Thompson and Noble (57) have observed that in the early stages of ageing, the microstructures of dilute Al-Li-Mg and Al-Li alloys are very similar; the only observable effect of the magnesium being to reduce the solubility of lithium in Al. Thus, for a given Li content, increasing the amount of Mg results in an increased precipitation of δ' . Upon prolonged ageing however, magnesium was observed to enter into the precipitation reaction via transformation of δ' to Al_2MgLi :



On the other hand, Fridlyander *et al.* (58) have suggested a different precipitation sequence for the Al_2MgLi phase:



but there have not been other studies to support this sequence.

Generally, in alloys containing ≥ 6 wt% Mg, Al_2MgLi precipitates heterogeneously on grain boundaries and matrix dislocations during ageing, leading to the formation of δ' PFZS. Al_2MgLi has an fcc structure with lattice parameter $a = 1.99nm$ and forms as rods with a $< 110 >$ growth direction. Their orientation relationship with the matrix was determined by Noble and Thompson(57) to be:

$$(\bar{1}10)_p // (\bar{1}10)_\alpha; [110]_p // [111]_\alpha$$

Shchegoleva and Rybalko (59) reported the existence of a metastable $S'(Al_2MgLi)$ phase during ageing of the Russian 01420($Al - Mg - Li$) alloy. They proposed a face-centred monoclinic structure for this phase with lattice parameters $a = c = 0.200$ nm, $b = 1.979$ nm, $\beta = 88^\circ 50'$ and orientation relationship:

$$(101)_{S'} // (\bar{1}10)_\alpha; (10\bar{1})_{S'} // (\bar{1}\bar{1}1)_\alpha$$

Clearly, there is close similarity in the lattice parameters and orientation relationship between this phase and the equilibrium Al_2MgLi . It is believed that the Al_2MgLi phase was probably mistaken for the S' phase as no other investigators have reported the existence of such a metastable phase.

Jones and Das (60), Starke *et al.* (61), and Dinsdale *et al.* (62) have attributed the observed increase in strength and ductility resulting from small additions (≤ 2 wt%) of magnesium to Al-Li binary alloys to:

- (a) additional solid solution strengthening by Mg,
- (b) the increased δ' precipitation due to the reduction in solubility of lithium in aluminium, and
- (c) incorporation of Mg into the δ' particles thereby producing stronger precipitates.

The coarse equilibrium Al_2MgLi phase has been shown to have a deleterious effect on ductility and its precipitation is avoided in commercial Al-Li alloys either by keeping the Mg concentration below 2.0 wt% and/or avoiding extended ageing treatments.

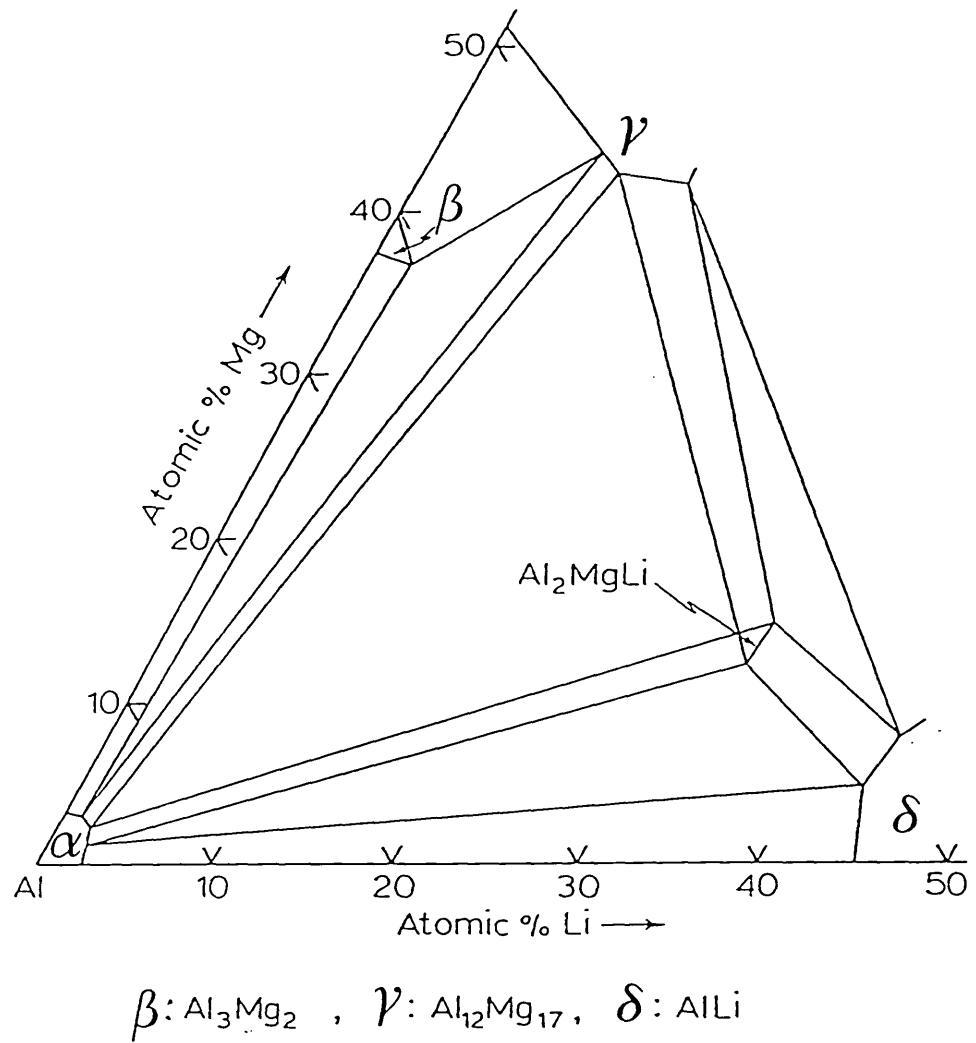


Figure 2.9 Isothermal section of the Al-Li-Mg system at 200°C (after Schürmann and Geibler, 130).

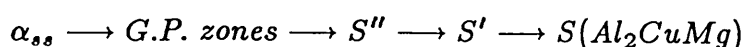
2.2.4. Al-Cu-Mg Ternary System

Al-Cu-Mg alloys were the first precipitation hardenable alloys discovered (A. Wilm, 1906); yet the details of the precipitation processes are not completely understood. However, from the work of Little *et al.* (64), Brommelle and Philips (65), Phragmén (66), Hardy (67) and Silcock and Parsons (68), it is generally accepted that in the Al-corner of this system, the only constituents which may exist in equilibrium with the Al-solid solution are binary $\theta(Al_2Cu)$ and $\beta(Al_3Mg_2)$, and ternary $S(Al_2CuMg)$ and $T(Al_6CuMg_4)$ phases. Figure 2.10 shows the liquidus surface of the Al-Cu-Mg system up to 40 wt% Cu and 40 wt% Mg as determined by Brommelle and Phillips (65). Which of these phases will precipitate at a given temperature will depend upon the Cu:Mg ratio of the alloys. In alloys containing Cu:Mg ratio > 8 , the dominant phase was found to be θ , which precipitates in the same way as in binary Al-Cu alloys (see Section 2.2.2). Hardy (67), Silcock (69) and others have observed that in alloys containing Cu:Mg between 8 and 4, both θ and S phases are formed; while in alloys containing Cu:Mg between 4 and 1.5, S is the dominant phase. The T phase is precipitated in alloys with high magnesium supersaturation. Figure 2.11 shows the phase fields existing in the Al-Cu-Mg system after prolonged ageing at 190°C (4). Within the composition ranges of Al-Li based alloys under commercial development, the ageing reactions involve principally the $\alpha + S$ range of the phase diagram. The $\alpha + S$ system is quasi-binary dividing the Al-rich corner of the system into two partial systems (along the composition ratio 2.6 Cu : 1 Mg (wt %)), in which the reacting phases are:

- (a) α - θ -S eutectic; composition ≈ 33.0 Cu, 6.1 Mg (wt%) at 507°C,
- (b) α -S, T peritectic; composition ≈ 10.0 Cu, 26.0 Mg (wt%) at 467°C.

Under non-equilibrium conditions such as would be met in industrial practice, this last reaction rarely proceeds to completion during solidification, ceasing almost as soon^{as} the S crystals have become enveloped by the T phase. It has been suggested (Little *et al.*, Mirgalovskaya *et al.*) that this phenomenon leads to the formation, in cast alloys, of other ternary phases whose compositions generally lie between those of S and T.

Bagaryatskii (70) reported the existence of two metastable precursors, S'' and S' , to the equilibrium S phase and proposed the following precipitation sequence:



The G.P. zones consist of a segregation of copper and magnesium atoms on $\{210\}$ Al planes and are preferentially precipitated on stacking faults. The S'' are ordered G.P. zones surrounded by a strain field and are coherent with the matrix as they grow in the $\langle 100 \rangle$ Al direction in the form of cylinders. During ageing, there is re-arrangement within the S'' precipitate leading to the formation of S' phase. Bagaryatskii also reported that both S'' and S' have a slightly distorted structure but different precipitate/matrix coherency.

Lorimer (40), Hardy (67), and others could not find any evidence to support the existence of the S'' phase although^a more recent study by Cuisiat *et al.* (71) did indicate its existence.

Silcock (69), and Beton and Rollason (72) have suggested that the G.P. zones in the ternary Al-Cu-Mg system are distinct from those formed in^{the} binary Al-Cu system since they appear to have different compositions.

The S' phase has the same growth direction as the S'' , i.e. $\langle 100 \rangle$ Al directions. They initially grow as rods which, during ageing, widen to form laths. It has been reported (40,70) that equilibrium S phase can form in one of two ways:

- (a) by loss of coherency of the S' phase, particularly, at high ageing temperature.
- (b) by heterogeneous precipitation on the numerous dislocation loops and helices formed as a result of vacancy condensation during quenching.

Both S' and S have the same orthorhombic structure and orientation relationship with the matrix:

$$\langle 100 \rangle_S // \langle 100 \rangle_\alpha; \langle 010 \rangle_S // \langle 021 \rangle_\alpha \quad (75)$$

The lattice parameters are slightly different and are given in table 2.3. The S' phase is one of the major strengthening precipitates in Al-Li alloys and several workers (1,73,74) have demonstrated that a high volume fraction of this phase can be precipitated by increasing the number of heterogeneous nucleation sites via the application of^a pre-ageing stretch. Also, Gregson and coworkers (5,74) have shown that homogeneous (matrix) precipitation of S' can be achieved through the control of alloy composition and ageing treatments.

The T phase has a wide range of homogeneity: 22–27 Cu, 27.5–30.0 Mg (wt%), and is sometimes ascribed either of two formulae Al_6CuMg_4 or Al_5CuMg_4 . In general, it forms at magnesium concentrations > 10 wt% and since at such

Mg levels the equilibrium Al_2MgLi phase also forms in Al-Li based alloys, the precipitation of the T phase is avoided in these alloys. Also, no information is available regarding the mechanism or kinetics of T phase precipitation in Al-Cu-Mg alloys.

Table 2.3 Major characteristics of precipitate phases in
Al-Cu-Mg ternary alloys

Precipitate type	Lattice/Structure	Lattice parameters (nm)
$S(Al_2CuMg)$, intermetallic	orthorhombic	$a = 0.400$ $b = 0.923$ $c = 0.714$
$S'(Al_2CuMg)$, metastable	orthorhombic	$a = 0.404$ $b = 0.925$ $c = 0.718$
$T(Al_6CuMg_4 \text{ or } Al_5CuMg_4)$ intermetallic	cubic $Im\bar{3}(spacegroup)$	$a = 1.428$

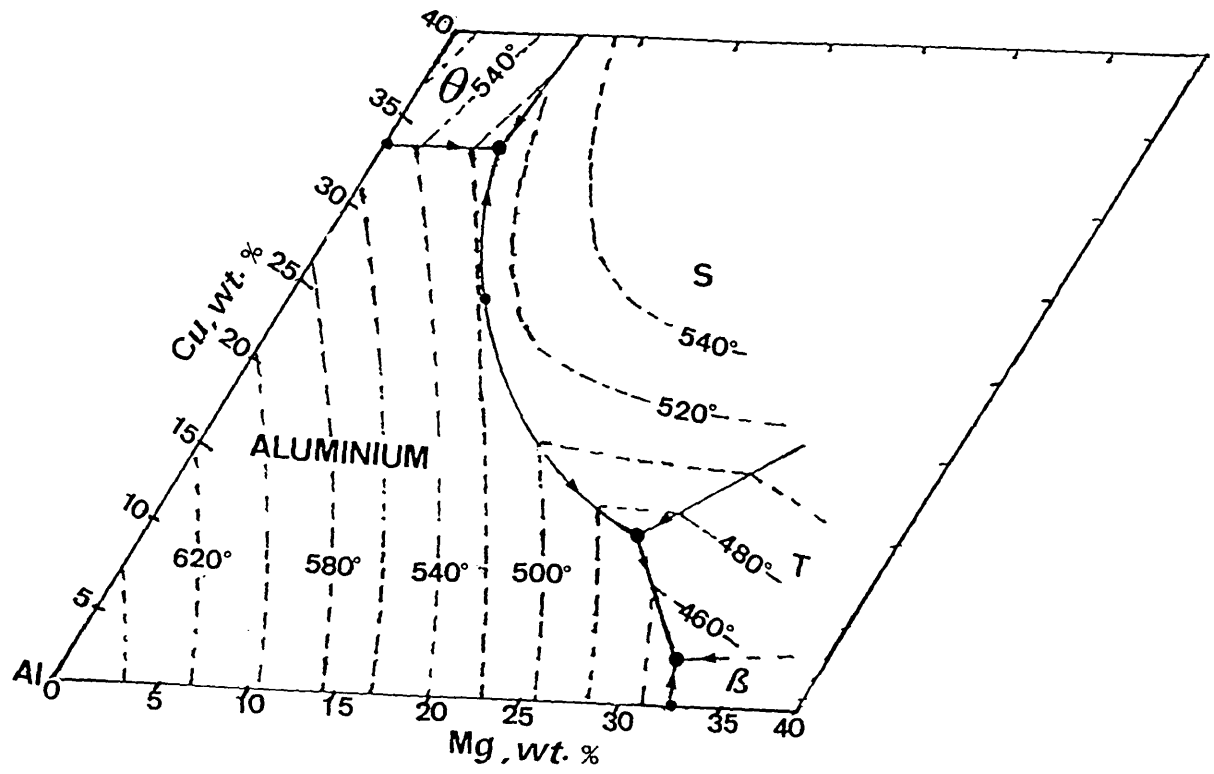


Figure 2.10 The liquidus projection of the Al-Cu-Mg system (after Brommelle and Phillips, 65).

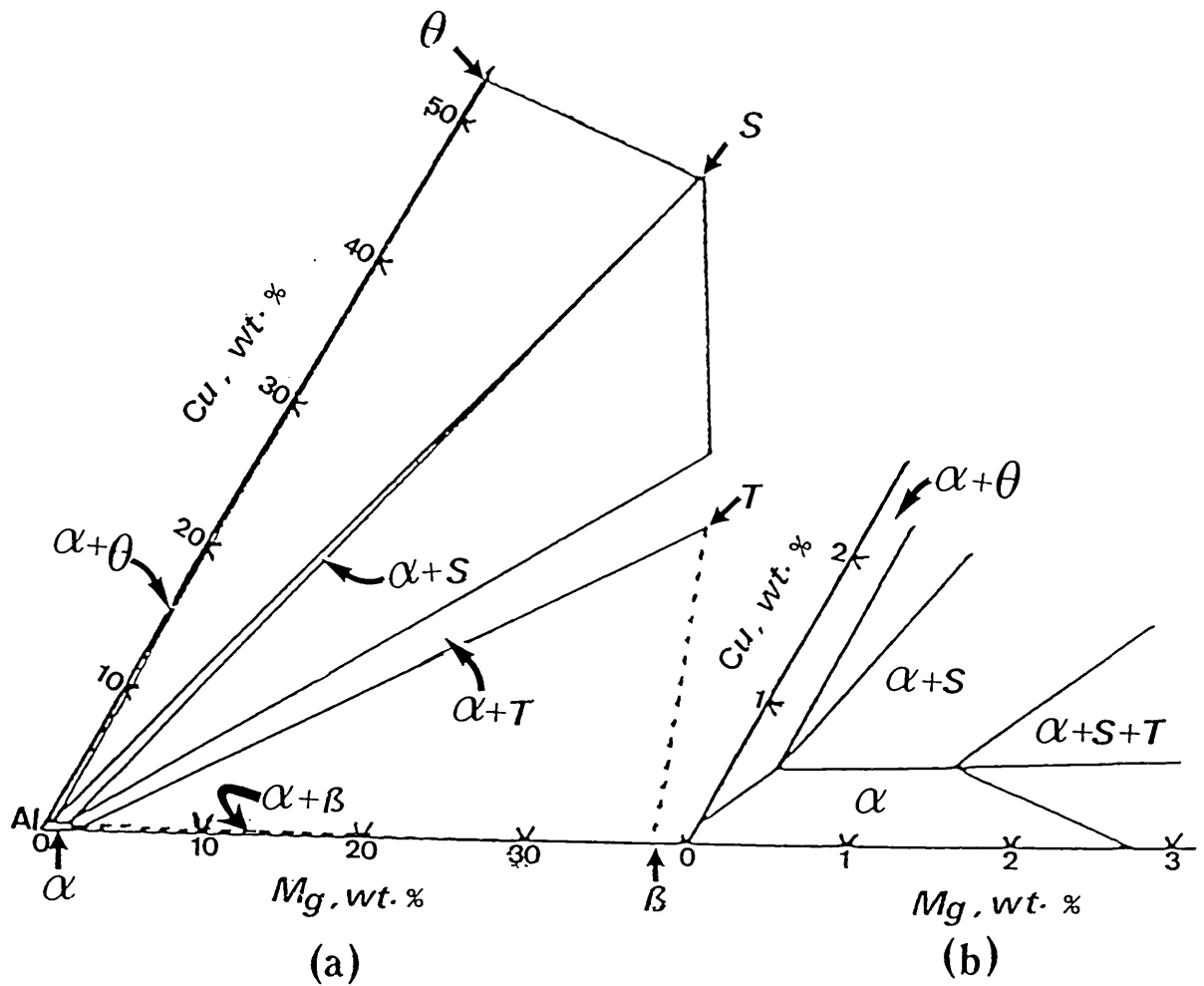


Figure 2.11 (a) The Al-Cu-Mg system (adapted from Refs. 68, 103 and 149): Phase fields correspond to precipitates type observed after extended ageing at 190°C rather than to equilibrium. (b) α - field solubility and adjoining phase fields.

2.2.5 Al-Li-Cu-Mg Quaternary System

There is very little data available on the quaternary Al-Li-Cu-Mg system; no section of the phase diagram has been determined and the precipitation reactions are necessarily very complicated. However, as with other age hardening alloys, the phases that precipitate within the Al-Li-Cu-Mg system are strongly dependent upon alloy composition and heat treatments. Early studies by Peel *et al.* (1), Gregson and Flower (73,75,76) and others (77,78) showed that within the ranges of composition designed for commercial Al-Li based alloys, the major strengthening precipitates in quaternary Al-Li-Cu-Mg alloys are δ' , T_1 and S.

It was generally observed that in these alloys, δ' precipitation preceded the formation of all other phases and occurred in much the same way as in ternary Al-Li-Cu or Al-Li-Mg alloys. The characteristics of the T_1 phase were also found to be essentially the same as in ternary Al-Li-Cu alloys except that magnesium additions appeared to have modified its usual plate-like hexagonal shape to a rounded lath or diamond shape (3,79). No change in crystal structure, lattice parameters or orientation relationship has been observed. However, heterogeneous S precipitation in the quaternary alloys has been observed to be very sluggish compared to the case in ternary Al-Cu-Mg alloys. This is attributed to the absence of dislocation loops and helices upon which S nucleates in quenched ternary alloys. Gregson *et al.* (32,73) and Flower and coworkers (74) have explained that in the Li-containing alloy, the high lithium to vacancy binding energy prevents the condensation of vacancies into dislocation loops and helices upon quenching, thus greatly reducing heterogeneous nucleation sites for S precipitates. This happens in a manner similar to that of Si in Al-Cu-Mg-Si alloys studied by Weatherly (157).

The work of several investigators (1,73,81) has demonstrated that a critical balance in the co-precipitation of the T_1 and S phases is necessary in order to achieve the optimum properties of quaternary Al-Li-Cu-Mg alloys. Peel *et al.* (1) and Gregson and Flower (73) have shown that in alloys containing ≈ 2.5 Li and 1.2 Cu (wt %) , Mg levels of less than 0.5 wt % result in a dominance of T_1 ; while the S phase predominates in the same alloys if the Mg levels are increased to 0.7 wt % (or more). This situation arises since both T_1 and S phase must compete for available copper, so that the driving force for the precipitation of the one phase is reduced if the copper is being consumed in the formation of the other phase.

Peel *et al.* (1), Gregson and Flower (73,76), and Meyer and Dubost (82) have also shown that a high density of S precipitation is more beneficial to

strength and ductility properties in Al-Li based alloys. This was achieved initially by applying a small (1–3%) pre-ageing stretch to the alloys after quenching in order to introduce the high density of dislocations that are necessary for widespread heterogeneous precipitation of S phase. However, this process is not suitable in some commercial practice where alloy products may necessarily be re-solution treated before final ageing. Alternatively, efforts were made to encourage a widespread homogeneous precipitation of S phase. Peel *et al.* (1) found that this can be achieved by extensive ageing treatments which unfortunately not only produce unacceptably coarse precipitates but are also commercially unviable.

Studies by Gregson *et al.* (5,32) and Flower and coworkers (74) revealed that homogeneous precipitation of S phase can be achieved in these alloys through a combination of increased Cu and Mg supersaturation and a high concentration of free vacancies. By a step-ageing process, they found that the vacancies which are originally strongly bound to the lithium atoms after the quench are released as the δ' particles grow at low temperature; such vacancies then go to aid precipitation of S phase. The mechanism by which these free vacancies aid homogeneous S precipitation is not well understood. Gregson *et al.* (32) have suggested two possibilities:

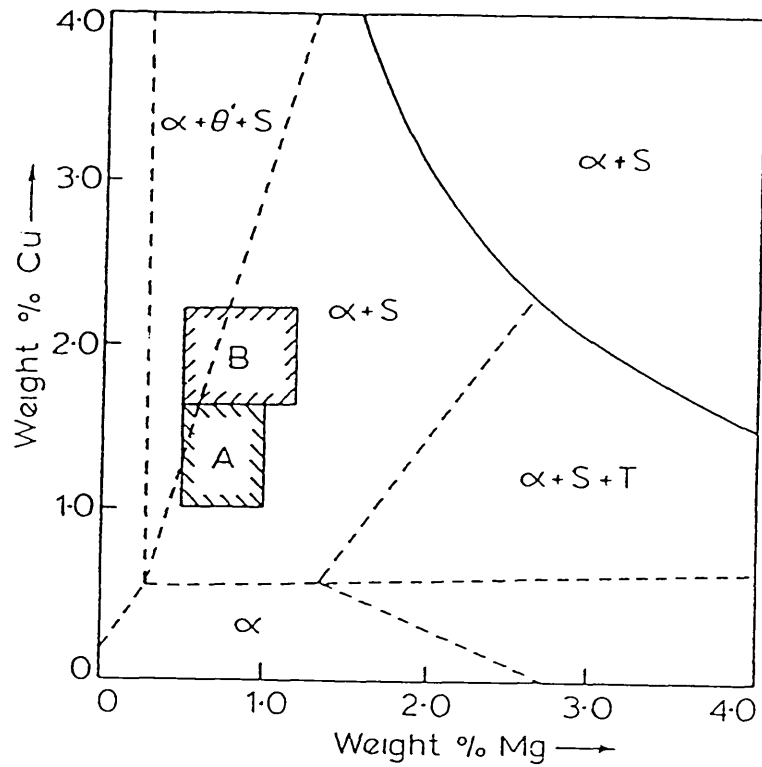
- (a) such free vacancies form clusters (before their condensation) which then provide sites for S precipitation;
- (b) the vacancy clusters so formed become enriched in copper and magnesium atoms during ageing and later develop into S precipitates via a model of the classical G.P. zone type.

In either case, a high vacancy concentration in solution will speed the diffusion of solute atoms required for S precipitation. The increased precipitation of S phase observed in 8091 and 2091 alloys compared to 8090 and 2090 alloys respectively results from the higher $Cu + Mg$ supersaturation in the former.

More recently, a number of quaternary phases have been reported to exist in commercial Al-Li based alloys (81–88). These are generally believed to be:

- (a) an icosohedral I-phase based on ternary $T_2(Al_6CuLi_3)$ with some Mg substituting for Li atoms;
- (b) a crystalline C-phase which Loisseau and Lapasset (87) have suggested is based on ternary $R(Al_5CuLi_3)$, again with some Mg atoms replacing Li atoms.

Both phases are reported to have a “pencil-like” morphology and precipitate largely on high-angle grain boundaries. Lewis *et al.* (83) have also suggested a 530°C solvus for the I-phase. Electron diffraction studies have been conducted to determine the structures of these phases and their orientation relationships with each other and with the matrix (79,84,86,87). However, more work needs to be done in this direction before these phases can be considered fully characterised. In Figure 2.12, the composition ranges (of Cu and Mg) in 8090 and 8091 alloys are shown on the isothermal sections (at 500°C and 190°C) of the Al-Cu-Mg system.



Phase boundaries at 500°C —————
 Possible phase boundaries at 190°C - - - - -
 Boxes represent composition ranges in
 8090 (A) and 8091 (B) alloys respectively

Figure 2.12 Isothermal sections of the Al-Cu-Mg system (after Silcock and Parsons, 68), showing the composition ranges in 8090 and 8091 alloys.

2.2.6. Grain Refining Additions to Al-Li-Cu-Mg Alloys

During the early stages of the development of Al-Li based alloys, a number of transition group elements including Co, Cr, Mn, Ti and Zr were investigated for their effectiveness to refine grains and inhibit recrystallisation in these alloys.

Zirconium additions of between 0.1 and 0.2 wt% were later found to be most efficient in this role, producing a fine unrecrystallised grain structure. The mechanism of grain refinement by Zr has been associated with the presence of fine (20–30 nm dia.), but uneven, dispersions of coherent, metastable $Al_3Zr(\beta')$ particles which precipitate out from the supersaturated solid solution upon quenching. Makin and Ralph (89) and Gayle and Van der Sande (90) have observed that in the as-quenched state the precipitation of the β' particles in Zr-containing Al-Li alloys occurs in essentially the same way as in binary Al-Zr alloys (reported by Nes (91)):

- (a) as fine discontinuous dispersion of spherical particles within the Al matrix;
- (b) as rods, by heterogeneous precipitation, on grain and subgrain boundaries and dislocation loops; the rods are generally orientated in the $\langle 100 \rangle$ Al directions.

The metastable Al_3Zr particles have a cubic ($a = 0.408$ nm) $L1_2$ ordered structure (91) and are therefore isostructural with $\delta'(Al_3Li)$ phase of the Al-Li binary system. The β' /matrix misfit has been measured by Nes (91) as $0.8 \pm 0.1\%$. During ageing, the β' particles act as substrates for heterogeneous nucleation of δ' ; the resulting “composite” precipitate being characterised by a core of Al_3Zr surrounded by an envelope of Al_3Li (25,90,94). Galbraith and Howell (92), and Tosten *et al.* (46) have observed that in these Cu-containing alloys, β' particles also act as nucleation substrates for both θ' and T_1 phases.

The nature of the δ'/β' composite has been extensively studied by several researchers. Gayle and Van der Sande (90) observed that δ' precipitates on the β' particles in such a way that the β' /matrix interface is completely wetted. This was considered to be thermodynamically less favourable than homogeneous precipitation of δ' . However, Gregson and Flower (75), Kim *et al.* (93) and Gayle and Van der Sande (25) suggested that this mode of δ' precipitation would occur if it involved significant reductions in both the strain and interfacial energies that are normally required for heterogeneous nucleation. Indeed, Flower and coworkers have observed that β' particles can induce δ' precipitation at lithium levels which are generally inadequate for homogeneous precipitation.

Recently, there have been several investigations into the possible incorporation of Li into the Al_3Zr particles. This was first proposed by Gayle and Van der Sande (25) on the basis of electron image contrast associated with the β' cores within the composite precipitates. They suggested that these particles are of the form $Al_3(Li, Zr)$ with varying amounts of lithium and zirconium depending on heat treatment. However, other investigators (46,92) could not find any evidence of lithium incorporation into the β' particles and argued that the electron image contrast observed by Gayle and Van der Sande can be in fact explained in terms of the stoichiometry of the $\beta'(Al_3Zr)$ particle and/or its orientation relationship with the matrix. Since lithium cannot be detected by conventional microanalytical techniques, it has been difficult to resolve this controversy. However, Sakurai *et al.* (94) have used the potentially more accurate Atom Probe field ion microscopy technique to analyse β' particles. They reported a substantial amount of Li incorporation into the β' particles, ranging from as much as 5–11 at % in the as-quenched state which then decreases to ≈ 1.5 at% after 30 min of ageing at 200°C. They also reported that the Zr content increases during ageing to between 22–27 at%, i.e. the range of stoichiometry for Al_3Zr . These levels of lithium are much lower than those theoretically predicted by Gayle and Van der Sande which ranges from Li:Zr = 1:4 to 3:2 depending on alloy composition and heat treatments.

The incorporation of Li into Al_3Zr particles is of both theoretical interest and practical importance with particular regard to its effect upon the precipitation and distribution of the δ' phase. For example, Gu *et al.* (95) have reported that alloys containing β' particles age more rapidly. This was attributed to the duplex δ' size distribution which resulted in rapid coarsening; the δ' coated β' particles behaving as a population of larger δ' particles. However, Gregson and Flower have reported that δ' precipitation is unaffected in alloys which contain Zr concentration levels typically employed for grain refinement in Al-Li alloys (< 0.15 Zr wt%). The mechanical properties are therefore unaffected as they are dominated by the much higher volume fraction of homogeneously nucleated δ' precipitates (4).

The results of several investigations have shown that the β' particles inhibit recrystallisation by retarding subgrain boundary migration and coalescence. There is no agreement, however, as to how this is achieved. Rystad and Ryum (96,97) suggested that the coherent nature of the β' particle imparts a high drag force to the recrystallisation front since the β' /matrix interface must change from coherent to semi-coherent as the recrystallisation front passes the precipitate. On the other hand, Starke *et al.* (61) have suggested an alternative

process whereby the β' particle must dissolve and re-precipitate after the recrystallisation front passes it. They observed that although this process may require a high energy, it is nevertheless consistent with experimental observations such as the high recrystallisation temperature associated with β' -containing alloys.

The use of manganese for grain refinement and recrystallisation inhibition was also seriously investigated at the early stages of the development of Al-Li based alloys. Manganese addition results in the precipitation of the dispersoid compound Al_6Mn , which effectively controlled grain size and shape but was found inadequate in preventing recrystallisation (61,98). This was attributed partly to the fact that the Al_6Mn particles were not stable at solution treatment temperatures and partly to the fact that some of the Mn is lost to the formation of coarse impurity intermetallics, such as $Al_{12}(Fe, Mn)_3Si$ or Al_9MnSi , which themselves have deleterious effectson mechanical properties (98). Furthermore, it was observed that during ageing, the Al_6Mn particles promote the precipitation of equilibrium δ phase. However, unlike Zr-rich dispersoids, there is no evidence for interaction between the Al_6Mn particles and the δ' precipitates, nor has there been any study of lithium incorporation into Al_6Mn particles.

Titanium additions, usually in the form of Ti-B-Al master alloys have also been used for grain refinement in Al-Li based alloys. In commercial 8090 and 8091 alloys produced by Alcan International such master alloys, in conjunction with zirconium, have been used most efficiently for grain refinement and recrystallisation inhibition (99). Figure 2.13 shows the effect on the grain size of 8090 alloy, of different ratios of TiBAl master alloy addition after various holding times at 720°C (99).

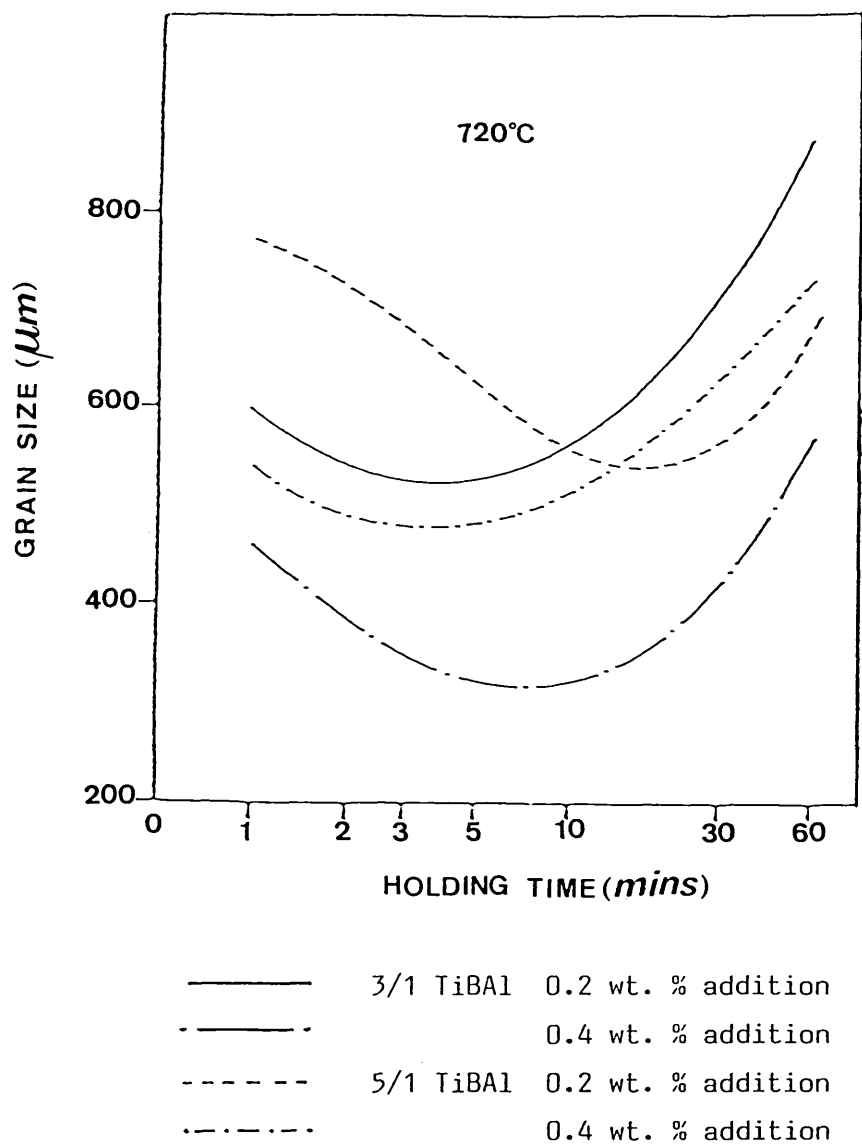


Figure 2.13 The effect of addition rate and titanium content of TiBA1 alloy on grain refinement of Lital A (after Birch, 99).

2.2.7. The Role of Impurity Elements in Commercial Al-Li alloys

All commercial cast and wrought aluminium alloys contain some impurities which are taken in via raw materials and during solidification. Such impurities may appear in the microstructure in their elemental forms, or as coarse insoluble intermetallic compounds which are known to have a strong influence on the ductility, fracture toughness, recrystallisation behaviour, and corrosion resistance of the final products. In this regard, the chief impurity elements in Al-Li-Cu-Mg-Zr alloys are iron, silicon and lithium associated alkali metals, e.g. Na, K, and Ca.

Two Fe-rich phases of average stoichiometries Al_7Cu_2Fe and $Al_6(Fe, Cu)$ have been identified in commercial Al-Li based alloys (100–102). Both are believed to form early in the melt by a peritectic reaction between Al_3Fe and the liquid (103) and generally segregate to high-angle grain boundaries on solidification. The Al_7Cu_2Fe phase may exist over a fairly wide range of composition: from 22.0 Cu, 17.5 Fe, to 32.5 Cu, 14.0 Fe (wt%); it has a tetragonal structure with lattice parameters $a = b = 6.32$ nm, $c = 14.78$ nm. The composition of the $Al_6(Fe, Cu)$ phase varies according to the Fe:Cu ratio in the alloy and heat treatment. It is reported to have an orthorhombic structure with the lattice parameters varying slightly as the Fe:Cu ratio changes. Both the Al_7Cu_2Fe and $Al_6(Fe, Cu)$ phases are insoluble at the solution treatment temperatures for Al-Li alloys ($\approx 530^\circ\text{C}$) and are consequently retained throughout the subsequent thermal and mechanical treatments for these alloys.

Silicon impurity may exist in the elemental form (especially when the magnesium content is low), or form coarse intermetallics such as Mg_2Si , a phase containing Al and Si (which has recently been shown to contain Li as well), or other Al-rich phases containing Fe and Mg as well, e.g. $Al_5Cu_2Mg_8Si$. In their study of the Al-Si-Li system, Hanna and Hellawell(144) have reported that Li depressed the Al-Si binary eutectic point (at 577°C) to a ternary eutectic (at 575°C) involving the Al and Si solid solutions and an AlSiLi phase. On the other hand, Kadaner *et al.*(162) identified the Si-rich ternary phase in Al-Si-Li alloys as $Al_2Si_2Li_3$ with the ternary eutectic temperature at 565°C . The Al, Si, and Li phase is by far the most important silicon impurity in Al-Li alloys. Lewis *et al.* (83) have reported that when the Si content exceeds ≈ 0.08 wt%, this phase forms during solidification and generally segregates at grain boundaries and grain boundary triple points. Since the eutectic temperature is higher than any practicable homogenisation temperature ($530 - 540^\circ\text{C}$) for Al-Li alloys, the Si-rich phase would be retained throughout subsequent thermal and mechanical treatments.

These coarse intermetallic particles sitting on grain boundaries and grain boundary triple points have been shown to have deleterious effects on the mechanical properties of the alloys. For example, the Fe-rich phases are known to promote recrystallisation; Reynolds *et al.* (6) have reported that an increase in the Fe content of 8090 and 8091 alloys from 0.09 to 0.27 wt% reduces their fracture toughness by up to 25%. While Lewis *et al.* (83) have reported that the AlSiLi particles have^a serious adverse effect on the stress corrosion crack resistance of Al-Li alloys. Apart from their direct effect on mechanical properties, these impurity compounds consume substantial amounts of solutes (Li, Cu, Mg) in their formation, thereby reducing the driving force available for the formation of strengthening and dispersoid phases. Attempts are therefore made to keep the iron and silicon levels in commercial Al-Li alloys to the minimum practicable.

Alkali metals such as Na, K, and Ca are easily taken in together with lithium in these alloys. However, unlike lithium, these elements are virtually insoluble in aluminium and usually segregate as grain boundary films after solidification (61,102). Webster *et al.* (105,106) have examined in detail the role of these impurity elements in 8090 and 8091 alloys and concluded that they do not significantly affect the grain structure or precipitation reactions within these alloys. Nevertheless, their concentration must be kept to the minimum practicable as small amounts of Na have been shown to cause intergranular embrittlement in some Al-Mg-Li alloys(61). In principle, by fluxing the melt with chlorine before adding lithium, these alkali metals can be made to precipitate as chlorides. Also, Fe and Si impurities present in these alloys may react with the alkali metals to form dispersoid compounds which may even contribute positively to mechanical properties (61).

2.3. Microstructure and Mechanical Properties

The microstructure developed within an alloy has a strong influence upon its final properties. In Al-Li alloys the microstructural features which may influence mechanical properties include:

- (1) the ^{grain}size, shape and solute distribution within the primary grains; these are largely determined by casting conditions
- (2) the size, volume fraction and distribution of second-phase constituents including:
 - (a) strengthening phases formed from alloying additions
 - b) dispersoid phases due to grain refining additions
 - (c) insoluble intermetallic phases resulting from impurity elements
- (3) the formation and nature of the strengthening phases, and
- (4) the degree of recrystallisation and crystallographic texture.

Most of these features can be (and are) controlled through alloy composition and thermal and mechanical treatments. For the Al-Li based alloys designed for aircraft application the most important mechanical properties include: density, strength, ductility, fracture toughness and fatigue resistance.

2.3.1 Density and Elastic Modulus

Low density and high elastic modulus are the main attraction of Al-Li based alloys in aircraft applications. Peel *et al.* (1) have derived the following formula to calculate density:

$$\rho(\text{g/cc}) = 2.71 + 0.024Cu + 0.018Zn + 0.022Mn - 0.01Mg - 0.004Si - 0.079Li$$

where the atomic symbols represent the concentration of that element in weight percent. Using the above formula, the density ranges for the Alcan alloys are 2.52–2.56 g/cc for 8090 and 2.55–2.58 g/cc for 8091 compared with a typical density of 2.80 g/cc for conventional aluminium alloys; thereby making the former between 10 and 8 percent lighter than the latter. The formula shows clearly the considerable contribution of lithium. In general, for every weight percent lithium addition to aluminium, the density is reduced by about 3% (107).

The influence of alloying additions, in particular lithium, on the elastic modulus (E) is also well established. For each weight percent Li addition to aluminium alloys, E is increased by about 6% (107–109). The 8090 and 8091 alloys have a modulus 10% greater than conventional aluminium alloys (1,81). Several investigators have demonstrated that the elastic modulus of binary Al-Li alloys increases up to peak strength during ageing, beyond which it decreases. This has been attributed to the formation of the metastable $\delta'(Al_3Li)$ phase. Sankaran and Grant (107) have suggested the δ' phase has a high intrinsic modulus due to its ordered nature and this is responsible for the increase in modulus observed in these alloys. Noble *et al.* (108,109) have determined the contributions of lithium in (a) solid solution (ss), (b) $\delta'(Al_3Li)$, and (c) $\delta(AlLi)$, to the elastic modulus in a range of solution treated and aged binary alloys. The results of their study are presented in Figure 2.14(a). For an alloy containing 3 wt% lithium, the total increase in Young's modulus ($E_{ss} + E_{\delta'}$) is $\approx 25\%$.

2.3.2. Strength and Deformation Mechanisms in Binary Al-Li Alloys

The intrinsic strength of a material derives from its resistance to dislocation motion. In precipitation hardened alloys, such as Al-Li binary alloys, this resistance to dislocation motion is offered largely by precipitates and subgrain structure. The basic strengthening mechanism in Al-Li binary alloys is associated with the formation of the metastable, ordered and fully coherent δ' precipitates (60,98,109). Following the work of Decker (110), Noble *et al.* (109) have suggested that the magnitude of the resistance to dislocation motion offered by the δ' particles will depend on:

- (a) the degree of order and of coherency,
- (b) size and distribution,
- (c) difference in modulus between particle and matrix, and
- (d) crystallographic structure of the particle.

The observed increase in strength in these alloys during ageing (up to peak ageing condition) is attributed to the increase in the volume fraction and size of the δ' particles with ageing. However, coherent particles such as δ' are easily sheared by dislocations since the slip systems of the particle and the matrix are coincident. Sanders *et al.* (98) have explained that during ageing as the δ' particles grow (beyond a critical size) and the interparticle distance increases,

less force is required by dislocations to loop round them resulting in the observed decrease in strength beyond peak ageing in binary Al-Li alloys.

Figure 2.14(b) shows the contribution of various mechanisms to strength of Al-Li alloys as determined by Noble *et al.* (109). The authors observed that solid solution strengthening in the binary alloys is minimal probably because of the small difference in size between the aluminium and lithium atoms. On the other hand, Gayle (111) and Baumann and Williams (112) have reported that in systems such as the $\alpha(\text{Al}) - \delta'$ where the particle-matrix misfit energy is small, anti-phase boundary (APB) energy created by dislocation shearing of the δ' particles can in fact act as an extra impediment to dislocation movement and thereby contribute to strength.

Dislocation shearing of the δ' precipitates has been shown to be a major source of the ductility and fracture toughness problems inherent in binary Al-Li alloys (the presence of grain boundary δ and associated δ' PFZs which are also important sources are discussed below). Gayle (111) and Miller *et al.* (81) have reported that in an Al-Li alloy which is strengthened by the coherent, ordered δ' precipitates, dislocations tend to move in pairs (superdislocations). As the first dislocation cuts the particle, it creates a disorder, resulting in an anti-phase boundary (APB). The energy associated with the APB acts as an extra impediment to further dislocation movement. The passage of a second dislocation restores the order disturbed by the first. However, after the passage of a superdislocation on a particular slip plane, the size of the δ' precipitate on that plane is effectively reduced thereby making it easier for more superdislocations to pass on the same plane. Thus, once slip occurs on a particular plane, further slip on that plane is encouraged leading to intense slip planarity. The resultant effect is dislocation pile-up and hence stress concentrations at grain boundaries and grain boundary triple points which in turn open-up cracks and induce intergranular failure during deformation. The consequent effect is the low ductility and fracture toughness of binary Al-Li alloys.

In alloys aged beyond peak strength, Furukawa *et al.* (128,129), Sainfort and Guyot (113), Vasudévan *et al.* (114) and Gregson and Flower (73) have observed dislocation (Orowan) looping around the δ' particles which will be expected to reduce slip coplanarity. However, in this condition, the coarsening of the δ' precipitates has led to the formation of precipitate free zones (PFZs) and the precipitation of the equilibrium $\delta(\text{AlLi})$ phase at grain boundaries. The PFZs act as stress concentration centres and cracks can then nucleate at the grain boundary δ precipitate and propagate intergranularly within the soft PFZs.

2.3.3. Strengthening Mechanisms in Higher Order Alloys

In the early stages of the development of Al-Li based alloys, three major approaches were followed in order to overcome the ductility and fracture toughness problems inherent in binary Al-Li alloys:

- (1) Reducing the propensity towards planar slip by increasing the δ' /matrix misfit. In principle, if the δ' /matrix misfit is made large enough, dislocations would form Orowan loops around the particles rather than shear them (110). Gayle (111) and Baumann and Williams (112) attempted to achieve this by introducing into the Al-Li system other elements such as scandium, silver, gallium, etc, which will be expected to substitute for Al or Li in the δ' (Al_3Li) particle and significantly change the lattice parameter. Unfortunately, these studies were not successful probably for the reason given by the investigators that such elements have lower solubility in aluminium than lithium and therefore largely remain out of solution forming coarse insoluble intermetallics.
- (2) Introducing dispersoid-forming elements which promote grain refinement and inhibit recrystallisation. As discussed in Section 2.2.6., zirconium additions of between 0.1 and 0.2 wt% have been found very efficient in this role. Reducing the grain size means lowering the number of dislocations that can be introduced into a pile-up on a slip plane at a given stress level. This has the effect of lowering the stress concentration across grain boundaries. Also, a uniform and fine dispersion of incoherent, non-shearable β' (Al_3Zr) particles inhibit dislocation cutting of matrix precipitates and strengthen the δ' PFZs. These two factors can consequently change the fracture mode in the alloys from one of low energy intergranular to high energy transgranular. Unfortunately, as reported by White *et al.* (115) and Flower and coworkers, the use of Zr in these alloys leads to the retention of a strong crystallographic texture in both sheet and plate products. The combination of strong texture and coplanar slip has been shown, under certain conditions, to be more susceptible to intergranular failure in underaged alloys (1,116).
- (3) By the co-precipitation of other phases through ternary and higher order alloying additions. As discussed in Section 2.2.4 copper and magnesium have been selected as most suitable additions and at concentration levels that result in the co-precipitation of a number of phases including δ' , T_1 and S' . The work of several investigators including that of Noble *et al.* (41), Harris *et al.* (117,118) Gregson and Flower (73) and Peel *et al.* (1)

has demonstrated that a critical balance in the co-precipitation of the T_1 and S' phases is necessary in order to achieve the optimum properties of these alloys. Figure 2.15 summarises the result of the work of Gregson and Flower on the contribution of various precipitates to the ductility and fracture toughness of a number of Al-Li based alloys after varying ageing treatments. The authors have also shown (76) that a sufficiently dense distribution of homogeneously precipitated S phase will eliminate grain boundary PFZs and disperse slip thus improving mechanical properties. This has been achieved through a fine tuning of alloy composition and precise thermal treatments without the necessity of a pre-ageing stretch.

While these numerous studies have amply demonstrated the beneficial effect of S' precipitation on monotonic properties, the effect on fatigue properties is less well understood. Harris *et al.* (118) and Noble *et al.* (41) have reported that matrix precipitation of S' phase does not appear to improve fatigue properties of 8090 and 8091 alloys; whereas a dense precipitation of S' phase on subgrain boundaries does have beneficial effects on such properties even at elevated temperatures.

In the commercial Al-Li-Cu-Mg-Zr alloys, therefore, the strengthening mechanisms may be summarised as follows:

- (a) τ_s – solid solution strengthening due to Li, Cu, Mg in solution,
- (b) τ_p – precipitation strengthening due to δ' , T_1 , S' and β' phases, and
- (c) τ_B – substructure strengthening due to grain and subgrain boundaries and APB associated with dislocation shearing of precipitates.

Therefore the flow stress of the aged alloys may be given by:

$$\tau_y = \tau_s + \tau_p + \tau_B \quad (81)$$

The magnitude of the contribution from each mechanism differs according to alloy composition. Within the 8090 composition limits, δ' is the main strengthening phase with S' and substructure strengthening approximately equivalent. As the copper level is increased the strengthening due to S' phase increases and in 8091 alloys is larger than that attributable to δ' (81,117). Huang and Ardell (43) have also shown that in 2090 alloys T_1 is the main strengthening phase. Miller *et al.* (81) have shown that substructure contributes significant intrinsic strengthening in these alloys largely by providing a high density of nuclei for the precipitating T_1 and S' phases.

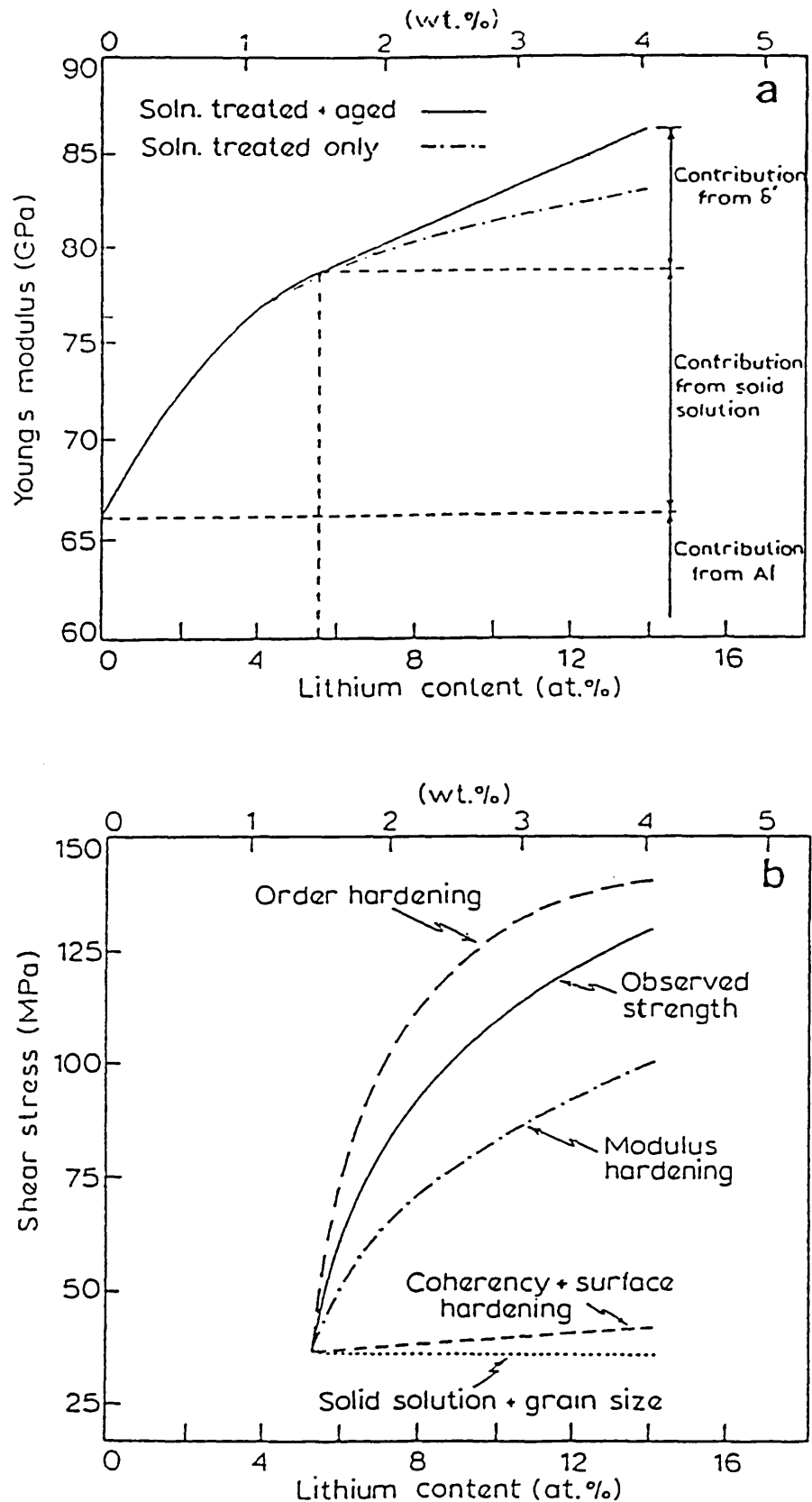


Figure 2.14 Variation of tensile properties with lithium content:

- (a) Young's modulus of solution treated, and solution treated and aged material
- (b) Contribution of different strengthening mechanisms after ageing to near peak strength (after Noble and co-workers, 108, 109).

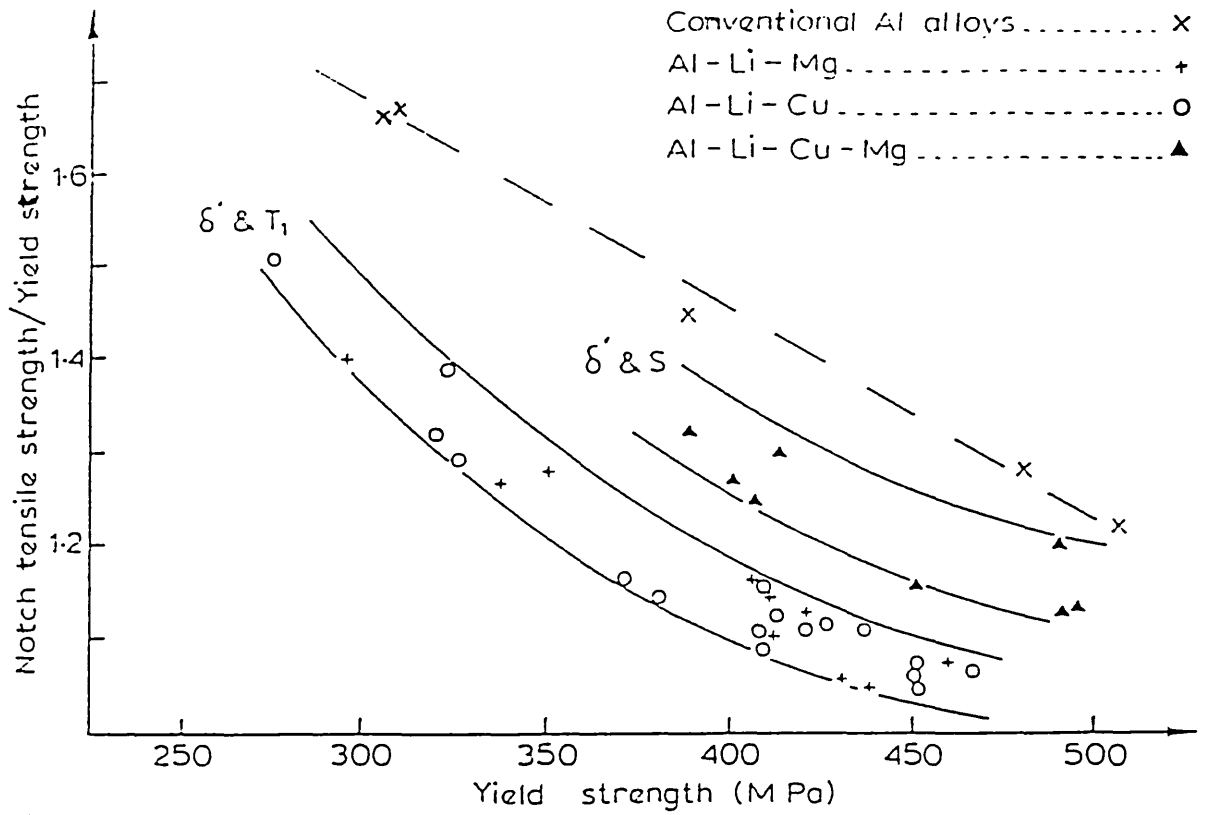


Figure 2.15 A summary of notch tensile strength/yield strength ratio as a function of yield strength for ternary and quaternary Al-Li based alloys (L-T orientation) as compared to 7000 series commercial aircraft alloys (after Gregson, 125).

2.3.4. The Role of Coarse Grain Boundary Precipitates

Coarse grain boundary phases have been shown to play a crucial role in the deformation behaviour of Al-Li alloys. Apart from equilibrium δ phase present in binary alloys ternary and quaternary alloys may precipitate several other phases including the T-type ($Al_xCu_yLi_z$) phases, Al_2LiMg and quaternary I- and C-phases, according to alloy composition. In aged alloys, these phases promote the formation of PFZs in which strain is localised during deformation. Cracks then nucleate at the grain boundaries and propagate within the soft PFZs consequently leading to intergranular failure (61,73,83,119). The Fe- and Si-rich impurity phases which reside at high angle grain boundaries and grain boundary triple points cannot be taken into solution during heat treatment. Studies by Owen *et al.* (100), and others (116,120) have shown that microvoids created around these particles during deformation lead to intergranular failure in these alloys. Also, the lithium-associated alkali metal impurities which generally segregate at grain boundaries have been shown to cause embrittlement (61,82). It is therefore essential to keep the levels of these impurities to the minimum possible in order to achieve the optimum properties of these alloys.

2.4. High Temperature Heat Treatments Of Al-Li Based Alloys

2.4.1 Oxidation at High Temperature

Aluminium and most of its alloys on exposure to air, form a thin protective film on the surface which prevents further diffusion of oxygen into the material so that oxidation which is initially rapid drops off logarithmically. At high temperatures, such as with homogenisation and solution treatment, the oxidation rate for these alloys is observed to be largely parabolic, resulting from the formation of a porous oxide layer. However, investigations by several workers (121–125) have shown that in the case of Al-Li based alloys, oxidation is very rapid and apparently will continue until all the lithium is used up. This behaviour is attributable to the very reactive nature of lithium which forms oxidation products that are highly porous and therefore incapable of acting as a protective layer. Gregson (125) used X-ray diffractometry and electron microscopy to identify the oxidation products in quaternary Al-Li alloy sheet products after heat treatment at 520°C for 15 hours; they comprised a mixture of Li_2O , Li_2CO_3 , $\gamma - Al_2O_3$, Li_5O_8 , LiO , $\gamma - LiAlO_2$ and MgO . The Li-rich oxides are particularly porous and can, in principle, consume all the lithium present in the material. Thus high temperature heat treatment of Al-Li alloys

in air results in the loss of lithium and magnesium from the material, leading to the formation of solute-depleted surfaces.

Ashton *et al.* (121) and Burke and Papazian (124) have demonstrated that the rate of oxidation and therefore the depth of the solute depletion layer depends linearly upon the lithium content of the alloy, the time at temperature, and upon the atmosphere for heat treatment. Figure 2.16(b) shows the effect of atmosphere and time at temperature (542°C) on the depth of solute depletion layer in an Al-Li-Cu-Mg alloy, determined by Ashton *et al.* (121). From this figure, heat treatment for 24 hours at 542°C in laboratory air will result in a lithium depletion layer of approximately 1.00 mm; whereas in dry argon the depletion layer will be only about 0.4 mm. Thus, it is advantageous to conduct high temperature heat treatment of these alloys in an inert gas atmosphere. Also, from Fig 2.16(b), after 4 hours at 542°C in laboratory air, the lithium depletion layer is ≈ 0.3 mm (300 μ m) thick. This compares well with the result of Fox *et al.* (122): 215 μ m thick depletion layer in 8090 sheet product after 4 hours at 530°C. Papazian *et al.* (123) used Nuclear Microprobe Analysis to determine the depth of lithium depletion in 8090 and 8091 alloys and showed that it can be adequately represented by the approximate diffusion equation:

$$\chi = 1.5\sqrt{Dt}$$

The depth of lithium depletion (up to 2/3 the bulk concentration) which they calculated (taking D, diffusivity of lithium in aluminium as 2.5×10^9 cm²/s at 500°C and 5.5×10^{-9} cm²/s at 530°C) for alloys heat treated in air for various times, t, are given in table 2.4.

Field and coworkers (126,127) have tried unsuccessfully to inhibit oxidation in Al-Li alloys through the addition of trace elements such as Be, Ca, and Bi which are known to inhibit oxidation in certain aluminium alloys. Peel *et al.* (1), Ashton *et al.* (121) and Fox *et al.* (122) have shown that the presence of solute depleted layers in Al-Li alloys leads to recrystallisation of the surface layer; and a degradation in surface sensitive properties such as tensile strength, corrosion and fatigue resistance has been observed in sheet products. This has, in effect, caused the time at temperature during solution treatment of such products to be limited; Peel *et al.* (1) have recommended two separate solution treatments of 20 minutes each at 520°C for sheet material. However, the results of the investigations by Ashton *et al.* (121) and Papazian *et al.* (123) have also shown that at the recommended temperature (530°C) and duration (16 hours), bulk samples of Al-Li alloys can be homogenised in ambient air since it is possible to completely scalp-off the solute depleted layer during the usual metallographic grinding and polishing operations.

Table 2.4. Predicted depth of lithium depleted zone after heat treatment in air (after Papazian *et al.* (123)).

Time (t)	500°C $x(\mu m)$	530°C $x(\mu m)$
4 minutes	11	16
16 minutes	24	33
30 minutes	24	45
1 hour	42	63
2 hours	60	87
4 hours	84	126
16 hours	170	250

2.4.2. Homogenisation of Al-Li Based Alloys

The thermal process necessary to develop the desired microstructure and optimum properties of Al-Li alloys begins with homogenisation. This diffusion-controlled process serves to:

- (a) eliminate or reduce microsegregation (coring) in the primary grains which occurs, invariably, in all cast alloys;
- (b) dissolve the low-melting non-equilibrium coarse intermetallic phases;
- (c) precipitate the dispersoid phases such as those containing Zr so that they can perform their role of grain control during subsequent processing.

These changes would bring the alloy closer to its equilibrium state and improve its workability.

The important parameters in the homogenisation treatment are the temperature, time, and to a lesser extent, the atmosphere used for homogenisation. The temperature of homogenisation depends on alloy composition and the final microstructure and properties desired and is usually taken to be $0.9 - 0.95 T_{\alpha}$ where T_{α} is the solidus point of the $\alpha(Al - Li)$ matrix. The homogenisation

time τ depends mainly on the temperature T and the activation energies of the phases present in the alloy, according to the diffusion rate equation:

$$\left| \frac{dm}{d\tau} \right| = D \frac{dc}{dx} ds$$

where $D = A \exp(-Q/RT)$ is the diffusivity of the solute (or second phase particles); dm is the amount diffusing across dc/dx into an area ds normal to dx in the time $d\tau$. A is a constant independent of temperature; T is temperature, R the universal gas constant and Q the activation energy of the reaction.

Thus, at a particular temperature, the dissolution of second phase particles is logarithmic with time, i.e. homogenisation is most intense during the initial stages, and falls to a limiting value beyond which there is no practical benefit to continue. The higher the temperature the less time is required for homogenisation to be completed; but the temperature is kept reasonably below T_α in order to avoid incipient melting. Figure 2.16(a) shows the effect of homogenisation time and temperature on the amount of second-phases present in an 8091 alloy as determined by Ashton *et al.* (121).

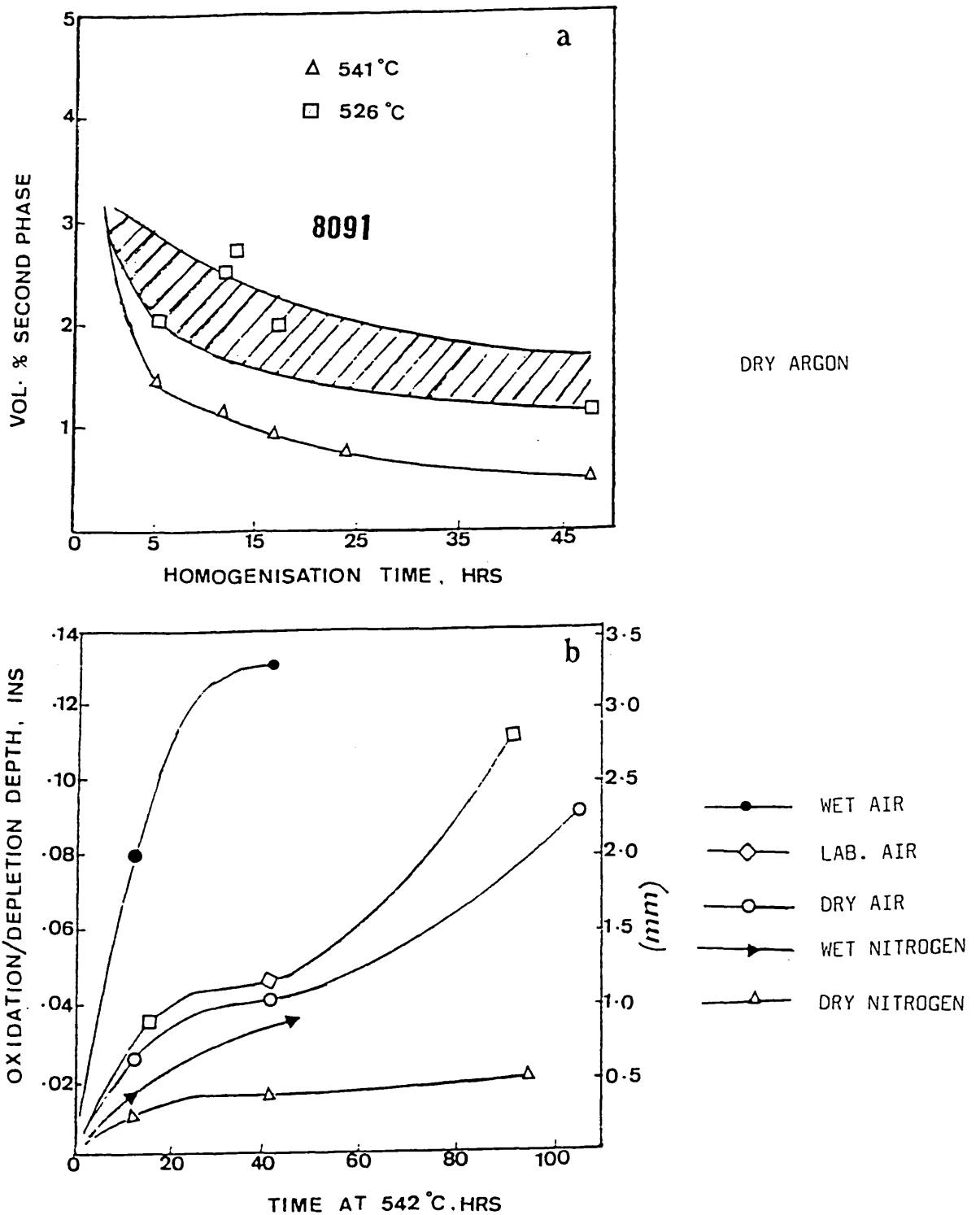


Figure 2.16 (a) The effect of homogenisation temperature and time on second-phase content of 8091 alloy
(b) The effect of homogenisation atmosphere and time on thickness of oxidation/depletion layer of an Al-Li-Cu-Mg alloy (after Ashton et al, 121).

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Introduction

Some combination of the conventional experimental techniques employed in Materials Research – metallography, X-ray diffraction, electron microscopy, energy dispersive X-ray (EDX) analysis, thermal analysis, etc, would normally be found sufficient for microstructural characterisation and phase transformation studies in metallic alloys. However, the study of Al-Li based alloys (especially the as-cast material) presents special problems for the following reasons:

- (1) most of the precipitate phases have low optical contrast and occur in very small volume fractions;
- (2) several of the phases are highly reactive with the atmosphere (due to the presence of lithium) and may therefore change their characteristics during specimen preparation and examination;
- (3) most importantly, energy dispersive X-ray analysis is incapable of detecting lithium.

During this research, therefore, it has been found necessary to employ additional techniques such as backscattered electron imaging in the scanning electron microscope, and secondary ion mass spectroscopy (SIMS) in order to overcome the problems mentioned above.

3.2 Materials

Table 3.1 Designation and Nominal Composition of Alloys Investigated

Sample Code	Alloy Designation	Nominal Composition (wt%)							
		Li	Cu	Mg	Zr	Fe	Si	Ti	Al
A	8090	2.40	1.35	0.61	0.12	0.06	0.18	0.03	Bal.
B	8090	2.45	1.32	0.63	0.12	0.05	0.04	0.038	Bal.
C	8090	2.34	1.27	0.62	0.12	0.04	0.11	0.032	Bal.
D	8091	2.56	1.66	0.73	0.11	0.10	0.13	0.04	Bal.
E	8091	2.49	1.80	0.73	0.13	0.05	0.04	0.055	Bal.
F	Experimental	1.52	24.50	9.10	NA	0.17	0.17	0.003	Bal.
G	"	2.04	26.30	9.40	NA	0.10	0.03	0.001	Bal.
H	"	2.11	21.20	11.80	NA	0.09	0.04	0.002	Bal.
I	"	2.44	13.25	7.38	NA	NA	NA	NA	Bal.
J	"	2.12	22.62	10.10	NA	NA	NA	NA	Bal.

NA —Not Analysed

Two sets of alloys were investigated in the work. The first set coded A – E are commercial 8090 and 8091 D.C. cast ingots produced by British Alcan in their Kitts Green and Chalfont Park foundries. The major differences among this set of alloys are the solute concentrations, particularly (Cu + Mg), and the levels of impurity elements, Fe and Si. It is therefore of interest to observe how these factors influence precipitation within the alloys.

The compositions of the second set of alloys, coded F – J were designed to fall within the Al- δ -S or Al- δ -S-T phase fields in the Al-Cu-Mg-Li quaternary system with very high volume fractions of the Cu and Mg containing phases. Alloys F, G and H were produced as D.C. cast ingots by British Alcan. Alloys I and J were made up in the laboratory by the author, by melting together portions of alloys F, G and H, and 99.99% pure aluminium and/or Al- 3 wt%

Li or Al- 10 wt% Mg binary alloys. The charges were first washed in 10% NaOH solution to remove the oxidised surface layers, then carefully weighed and put in aluminium crucibles. The melting was carried out in a molybdenum resistance wire muffle furnace, under argon atmosphere and cast into $25 \times 30 \text{ mm}^2$ ingots in a copper mould.

3.3. Light Microscopy (LM)

Light microscopy was used as a metallographic technique to investigate the microstructures of both as-cast and heat treated alloys. Specimens with average dimensions $10 \times 10 \times 6 \text{ mm}^3$ were cut from each alloy, mounted on bakelite holders and mechanically ground successively on 220, 400, 800 and 1200 grit SiC abrasive papers. They were then polished successively on $3 \mu\text{m}$ and $0.25 \mu\text{m}$ diamond spray on a short-nap cloth disk. Since Al-Li alloys are quite soft, the specimens needed to be regularly washed in water, cleaned with methanol and dried in-between steps during both the grinding and polishing operations to ensure that flat and scratch-free surfaces are obtained. Each specimen was examined immediately after polishing (to avoid oxidation) in the light microscope, first in the as-polished condition and then after being chemically etched in different solutions. Light micrographs depicting the characteristics of the various precipitates were obtained. Table 4.2 shows the characteristics of the various precipitates in different etchants.

3.4. Scanning Electron Microscopy (SEM)

Specimens for scanning electron microscopy were prepared in the same way as those for light microscopy. They were examined in the as-polished condition first in a JEOL-T200 scanning microscope operating at 25 kV, and then in a JEOL JSM-35CF scanning microscope operating at 20 kV. Electron micrographs of areas of the microstructure containing the precipitate phases were taken in both the secondary electron imaging (SEI), and backscattered electron imaging (BEI), modes of the microscopes. The contrast exhibited by the various phases in the electron images (which are due to both surface topography and atomic number) were used to further characterise the phases.

3.5. Transmission Electron Microscopy (TEM)

Thin foils for transmission electron microscopy were prepared by spark cutting 3 mm diameter discs from ≈ 0.2 mm thick specimens. Before electropolishing, the discs were lightly ground on 1200 grit SiC paper to less than 0.2 mm thickness and washed in both warm water and methanol. The discs were then electrolytically thinned on a Struers Tenupol twin-jet polishing apparatus operating at 20 V and using a solution of 30 volume % nitric acid and 70 volume % methanol, cooled to -30°C . After thinning the foils were thoroughly washed in methanol and dried in warm air and then examined in a Phillips EM301 transmission electron microscope and a JEOL-120CX TEMSCAN transmission/Scanning electron microscope operated at 100 kV. Transmission electron micrographs and electron diffraction patterns of the various precipitates were obtained. It was observed that the TEM examination must be carried out immediately after preparing the foils since in this condition they have^a a strong tendency to oxidise rapidly.

3.6. Energy Dispersive X-ray (EDX) Analyses

3.6.1. EDX in the SEM

Quantitative chemical analysis of precipitates in bulk samples were carried out in the JEOL JSM-35CF scanning microscope which was equipped with a LINK 860 EDX detector. A ZAF software programme was used to correct for atomic number (Z), absorption (A), and fluorescence (F), effects associated with EDX analyses. Several area and spot analyses were carried out on each phase, at different sections of the microstructure and the average values taken as the elemental composition of the phase, given in weight percent.

3.6.2. EDX in the TEM

Quantitative chemical analysis of precipitates in thin foils was carried out in both the JEOL-120CX TEMSCAN and a JEOL 2000FX STEM. These microscopes are equipped with a LINK EDX detector and an accompanying software corrected for atomic number (Z) and absorption (A) effects. Several spot analyses were carried out on each precipitate, at different sections of the microstructure and the average taken as the element composition of the phase, given in weight percent.

3.7. Backscattered Electron Imaging in the Scanning Microscope

The dependence of the backscattered electrons (BE)_{intensity} on atomic number (Z), has been used in this technique to aid in characterising, particularly, the lithium-bearing phases. The technique involved collecting and measuring quantitatively the backscattered signal (S) from the surface of bulk samples of known compositions (hence known Z) to produce a plot of S versus Z . Such a calibration curve is then used to obtain the (mean) atomic number of a phase of unknown composition after measuring the BE signal due to this phase in standardised experimental conditions. Elemental compositions of the phase determined earlier by EDX allowed estimation of the proportion of lithium to be made. The accuracy of the technique depends largely upon the capability to measure the BE signals from both standard and unknown samples under identical experimental conditions. The underlying principles are further discussed in chapter 4.

The backscattered electron image analysis was carried out at the Banbury Laboratories of British Alcan using an ISI-DS130 scanning microscope equipped with a high efficiency Robinson-type backscatterd detector. Quantitative measurements of the output signals were performed by a "Cambridge Technology IMAS" signal processor. This device was coupled to the detector and calibrated to generate backscattered electron images of equal atomic numbers – the so-called iso-atomic number maps.

3.8. Secondary Ion Mass Spectroscopy (SIMS)

Secondary ion mass spectroscopy is principally a surface analysis technique and has been used in this research to overcome some of the problems associated with characterising phases in Al-Li based alloys. SIMS analyses were carried out at Surface Analyses Plc, Ascot, using a CAMECA IMS 4f ion micro-analyser.

Samples of approximately 1 cm^3 were mechanically ground and polished to obtain a smooth surface. In the microscope, the polished surface was sputtered with a mass filtered primary beam of 16 O_2^+ ions with incident energy of 10.5 keV. The primary beam was focused on a $500\text{ }\mu\text{m}$ spot which was rastered over the surface in order to stabilise the secondary ion current and increase yield. Ion micrographs of areas of the sample $250\text{ }\mu\text{m}$ or $150\text{ }\mu\text{m}$ wide were obtained. The image contrast in these micrographs gives qualitative information on the distribution of elements in the microstructure. Line scans across some sections of the microstructure were also obtained to show the distribution of elements in the various phases.

3.9 X-Ray Diffractometry (XRD)

The main advantage of X-ray diffraction over EDX analysis is that it identifies a phase both by its crystal lattice and chemical composition. In the X-ray diffraction pattern produced by a multi-phase material, the intensities of the diffraction lines due to a particular phase indicate the proportion of that phase in the material. So that the pairs of (relative) intensities I , and “ d ” values can lead to a quantitative determination of the phase. However, the procedure for identifying the diffraction lines due to the different phases is necessarily complicated and subject to large errors. For example, valuable data could be lost when diffraction lines due to different phases coincide. The identification of precipitate phases in commercial Al-Li based alloys by X-ray diffraction has been found to present even greater difficulties since these phases occur in very small volume fractions and therefore do not yield sufficient diffraction lines that will permit any meaningful analysis. Fortunately, the situation is different with the experimental alloys and X-ray diffraction has been used to successfully identify a number of phases in these alloys.

A Phillips PW 1130 diffractometer operating at 40 kV and 40mA with CuK_α radiation passed through a Nickel filter was used to obtain the diffraction patterns from samples cut from the alloys. The samples were mechanically ground and polished down to about 16 mm dia. and 5 mm thickness and mounted on the diffraction stage. The scan speed was 0.33 degrees per minute over an incident angle (2θ) range of 10–140 degrees. Details of the identification procedure and the results of the diffraction analyses are presented in chapter 4.

3.10 Differential Scanning Calorimetry (DSC)

DSC studies of the as-cast and heat treated alloys were carried out using a Stanton Redcroft DSC 1500 calorimeter. Specimens for analyses were cut, ground, and polished to a size and shape that ensured good thermal contact with the alumina crucibles used as the DSC cells. The specimens were of an average weight of 30 mg. Alumina powder of equal weight to the specimens was used as the reference material. The specimen and reference material were placed in the DSC cells and heated in high pressure argon atmosphere from room temperature to $\approx 750^\circ\text{C}$ at a rate of $20^\circ\text{C}/\text{min}$. Plots of the heat flow rate (mJ/sec) against temperature ($^\circ\text{C}$) which would indicate any transformations occurring during the heating were obtained for each run. The baseline of the thermal plots was defined as that produced by analysing equal weights of the reference material in both cells of the calorimeter. To determine whether the true temperatures were

being recorded in the experiment, 99.99 % purity aluminium equal in weight to the specimens was analysed in identical conditions. Any difference observed in the melting point (660.4°C) was taken into account when interpreting the results of the DSC studies.

3.11 High Temperature Heat Treatments

High temperature heat treatments were carried out to eliminate coring of the primary grains and re-solutionise the precipitate phases and thus bring the alloys near to their equilibrium state. Any phase transformations which may have occurred during this process were later investigated. All heat treatments were carried out in an air-circulating horizontal tube furnace. Temperatures for heat treatment were determined after thermal analysis of the as-cast alloys; $530 \pm 2^{\circ}\text{C}$ was used for the commercial alloys and between 490 and $510(\pm 2)^{\circ}\text{C}$ was used for the experimental alloys. Holding times ranged between 2 and 48 hours for the commercial alloys and 16 and 144 hours for the experimental alloys. The samples were quenched in ambient temperature water ($10\text{--}18^{\circ}\text{C}$) immediately after being removed from the furnace. In most cases, specimens for heat treatment were sealed in pyrex tubes containing argon gas as a special precaution to prevent high temperature oxidation or loss of lithium and magnesium. Where this precaution was not taken, large specimens (average dimension 1 cm^3) were heat treated so that the oxidised and solute-depleted layers can be scraped off before the specimens are prepared appropriately for the various examinations.

CHAPTER 4

MICROSTRUCTURAL CHARACTERISATION OF CAST Al-Li BASED COMMERCIAL ALLOYS

4.1 Introduction

The severe limitations of conventional investigation techniques for the characterisation of complex Al-Li based alloys (see Section 3.1) have made it necessary to apply a whole range of complementary techniques in the present study. The efficiency of the techniques used (in particular the Backscattered Electron Imaging in the SEM and Secondary Ion Mass Spectroscopy) is demonstrated by the fact that they have produced conclusive evidence regarding the distribution of lithium in the various second-phase precipitates. The use of differential scanning calorimetry to investigate the solidification sequences in these alloys has provided information regarding the basic phase equilibria existing in the quaternary Al-Li-Cu-Mg system and also established appropriate temperatures for subsequent heat treatments which are required to achieve optimum properties of these alloys. Thus the study of the cast alloys is of both academic interest and practical importance. In this chapter the results of a detailed characterisation of the as-cast microstructures of a range of 8090 and 8091 alloys are presented. The alloys are D.C. cast ingots produced by British Alcan via commercial routes. The nominal compositions of the alloys have been given in Table 3.1.

4.2 Experimental Results

4.2.1 Metallography and SEM

The as-cast microstructures of the alloys investigated are shown in the light micrographs of Figure 4.1. Typically, they consist of cellular grains of aluminium solid solution primary phase (α) of average size $\approx 70\mu\text{m}$ surrounded by a network of second-phase precipitates. The dark spots shown in the micrographs are evidence of microsegregation which resulted from non-equilibrium solidification. No noticeable difference was found in the sizes of the primary grains between the 8090 and 8091 alloys.

The nature and distribution of the second-phase constituents are revealed in the light and scanning electron micrographs of Figures 4.2 and 4.3. They are found to comprise six different types which for the purpose of this study have been labelled P(Phase) 1, 2, 3, and so on. The appearance of the various precipitates in light and scanning electron microscopy and their etching characteristics are detailed in Tables 4.1 and 4.2.

P1 – a thick layer of “snake-like” precipitate which dominates the grain boundaries in all the alloys investigated (Fig 4.2(a), (b) and (c)). Visual examination of the microstructures revealed that the amount of this phase is slightly greater in the 8091 alloys than in the 8090 alloys. It was also observed that at grain boundary triple points this phase forms a lamellar eutectic with the aluminium solid solution (Fig. 4.3(a) and (b)).

P2 – large lumps, needles or blades which are found infrequently lying across grain boundaries (Fig. 4.2 (a) - (d)). In alloys C and D they occur largely as lumps while in alloy A, and 8091 alloys D and E they occur mainly as needles and blades with sizes ranging from $5.0\text{--}50\mu\text{m}$ in the maximum dimension.

P3 – coarse angular particles which occur mainly (but not exclusively) at grain boundary triple points (Fig. 4.2(e) and (f)). These particles were found only in the 8090 alloy C.

P4 – large uniquely shaped “composite” precipitates infrequently distributed in the α matrix (Fig 4.3(c) and (d)). These particles of average size $20\text{--}30\mu\text{m}$ in diameter were found only in alloys A and E.

P5 – coarse spherical particles (bright in SEM) of $4\text{--}5\mu\text{m}$ diameter inhomogeneously distributed in the matrix of all the alloys investigated (Fig. 4.3(e)).

P6 – fine spherical particles (dark in SEM) $\approx 2\mu\text{m}$ in diameter which were found both in the matrix and at grain boundaries of the 8090 alloys D and E.

Table 4.1. Description of phases and their appearance in light and scanning electron microscopy.

PHASE	LIGHT MICROSCOPY		SCANNING ELECTRON MICROSCOPY	
	As-polished	Etched (Keller's)	SEI	BEI
α -matrix; cored grains	pale grey	light to pale grey	dark grey	dark grey
P1 – dominant grain boundary (GB) phase	dark grey to light brown	dark brown to black; rough	light to pale grey	light
Lamellar eutectic structure at GB triple points	pale grey	unattacked, slight outlined	pale grey	light
P2 – lumps, needles or blades mainly at GB	brown	dark brown	bright	bright
P3 – very coarse angular particles mainly at GB triple points	grey to light brown	dark grey	dark	dark
P4– very coarse composite particles in matrix	grey core brown shell	dark grey core light grey shell	dark core bright shell	dark core bright shell
P5 – coarse particles in matrix sometimes at GB	not detected	not detected	bright	bright
P6 – fine particles in matrix sometimes at GB	not detected	not detected	dark	dark

Table 4.2 Etching characteristics of phases present
in as-cast alloys.

PHASE	ETCHANT				
	0.5% HF	25 vol % HNO ₃	10 vol % NaOH	Fe(NO ₃) ₃	Conc. NHO ₃
α	light, hardly attacked	light	light to greyish	light, hardly attacked	light, hardly attacked
P1	rough; brown to dark brown	pale grey; turns dark brown after 60 sec in etchant	rough, brown to dark brown	pale grey; hardly attacked even after 60s in etchant	pale grey; turns brownish after 60s in etchant
Lamellar eutectic	light, slightly outlined	light	pale grey with a yellowish tinge	light with a yellow- tinge	light, hardly attacked
P2	grey	dark brown	dark grey	dark grey to brown	dark grey to brown
P3	—	dark grey	—	dark brown	—
P4	—	—	—	—	—
P5	—	—	—	—	—
P6	—	—	—	—	—

Figure 4.1 Microstructures of as-cast alloys: 'cored' aluminium solid solution primary grains (α) and interdendritic network of second-phase precipitates.

Light micrographs (LM), Keller's etch:

(a),(b),and(c) - 8090 alloys A,B,and C respectively

(d) and (e) - 8091 alloys D and E respectively.

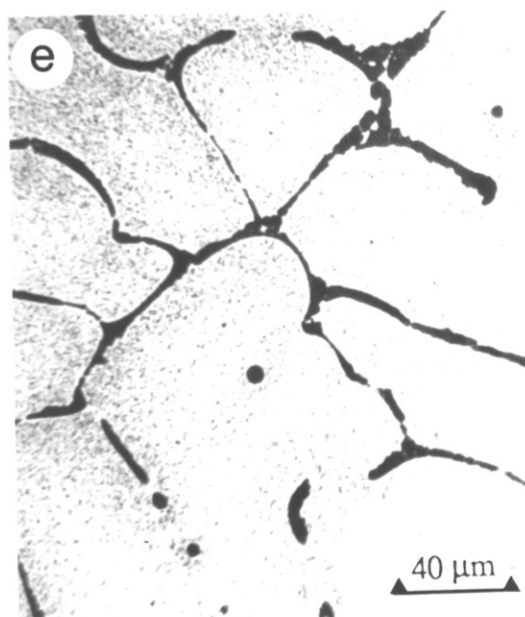
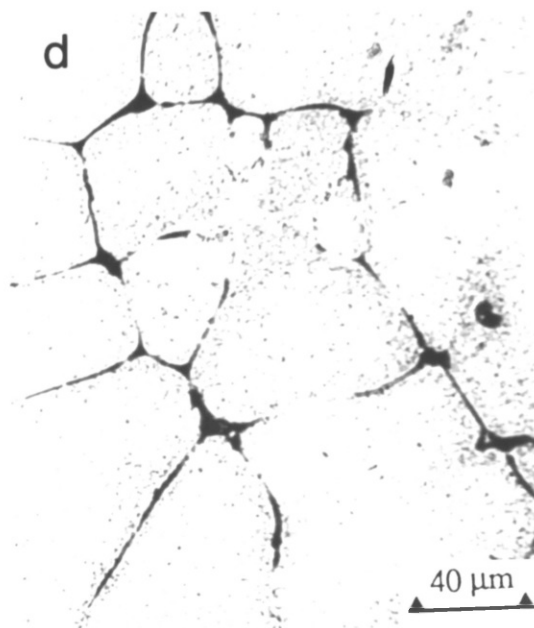
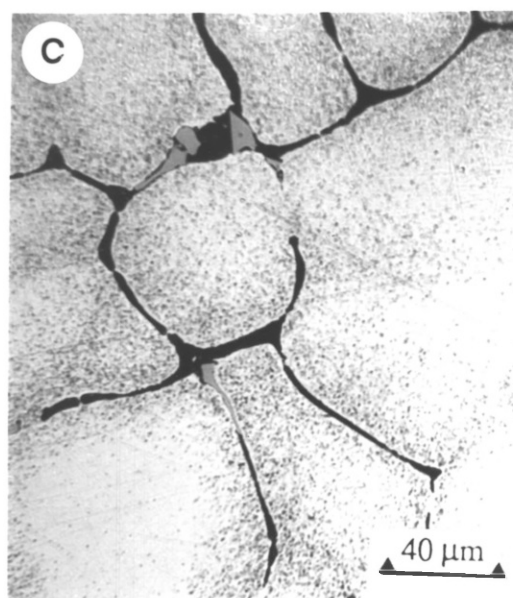
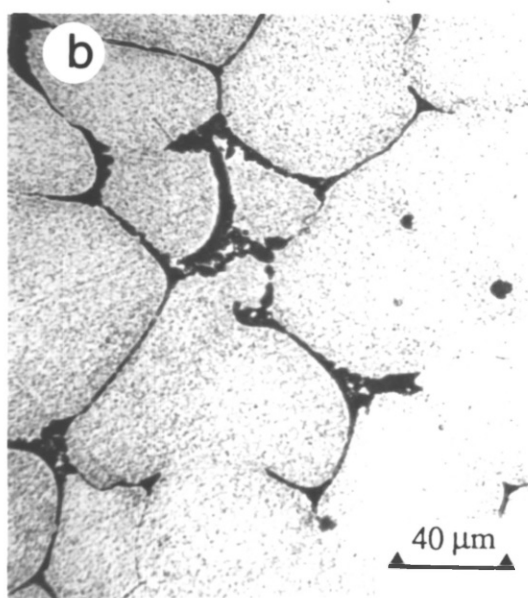
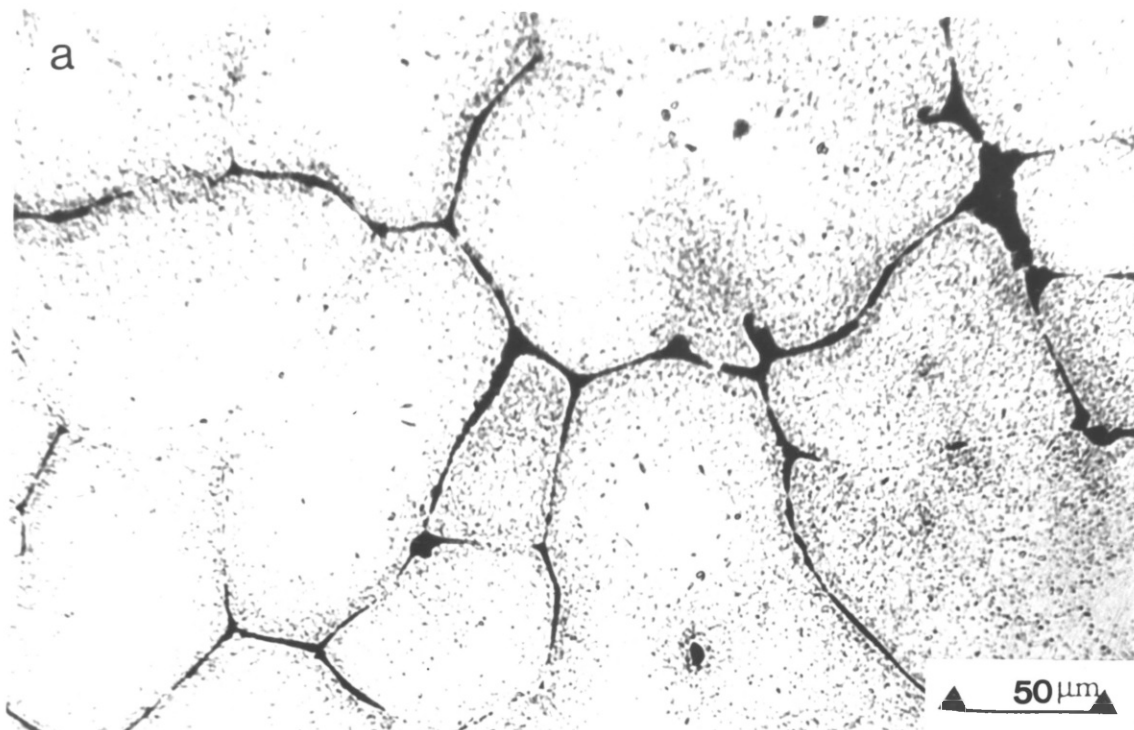


Figure 4.2. Microstructures of as-cast alloys:
second-phase constituents

(a) LM, Keller's etch, (b) Secondary Electron Image (SEI):

P1 - dominant grain boundary phase

P2 - coarse grain boundary particles

(8091 alloy E)

(c) LM, as-polished condition, (d) LM, Keller's etch:

P2 - coarse grain boundary particles

(8090 alloy A)

(e) LM, Keller's etch, (f) SEI:

P3 - coarse grain boundary particles

(8090 alloy C)

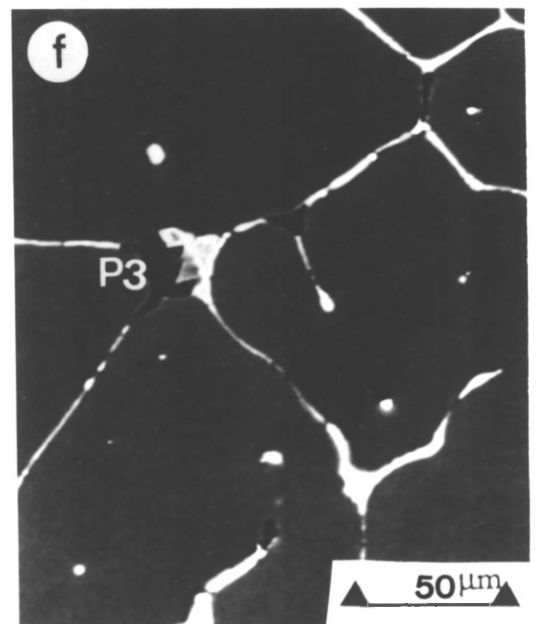
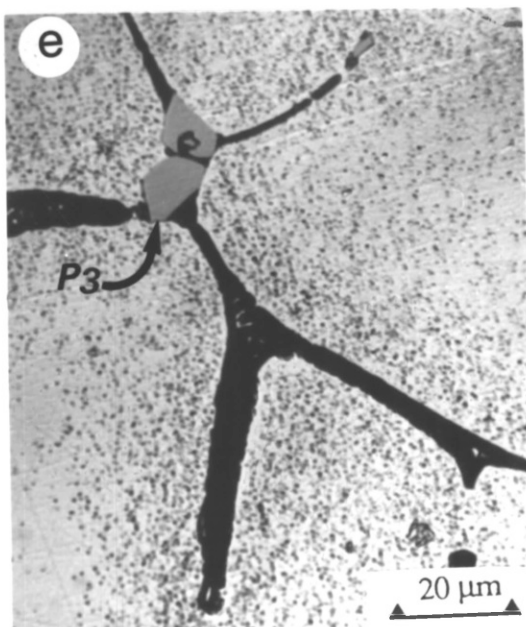
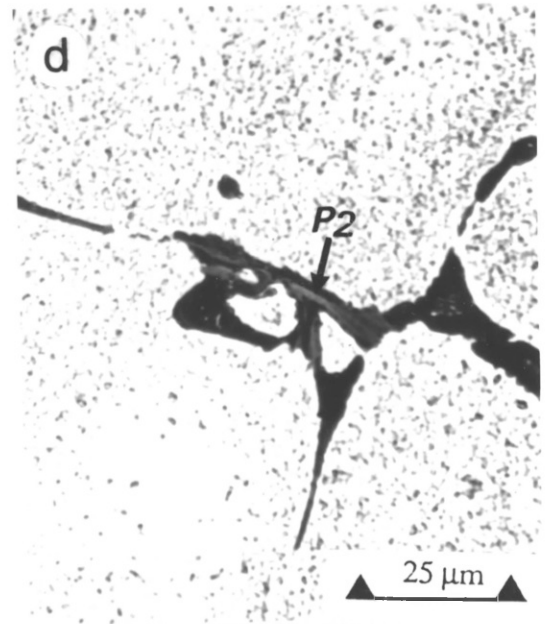
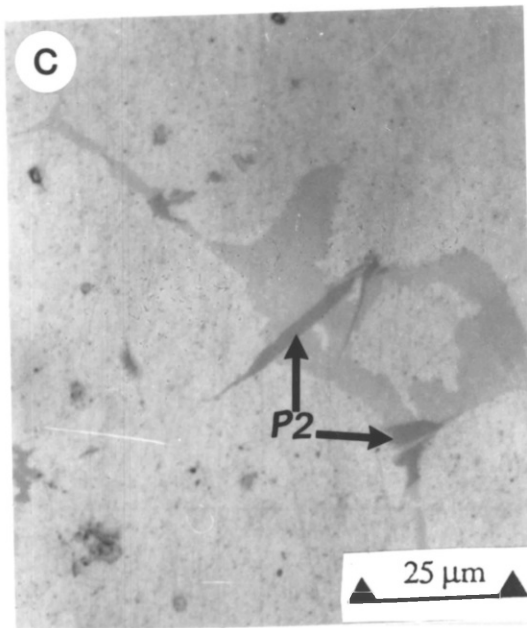
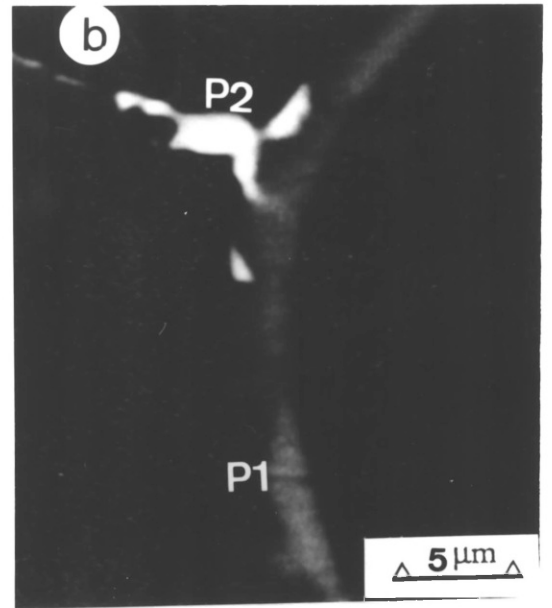
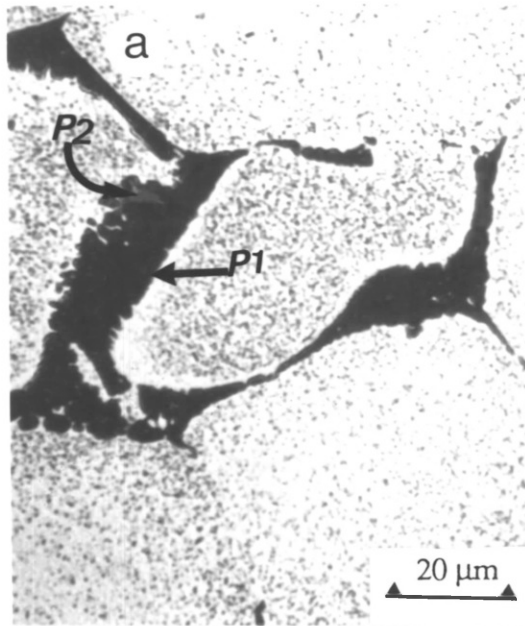
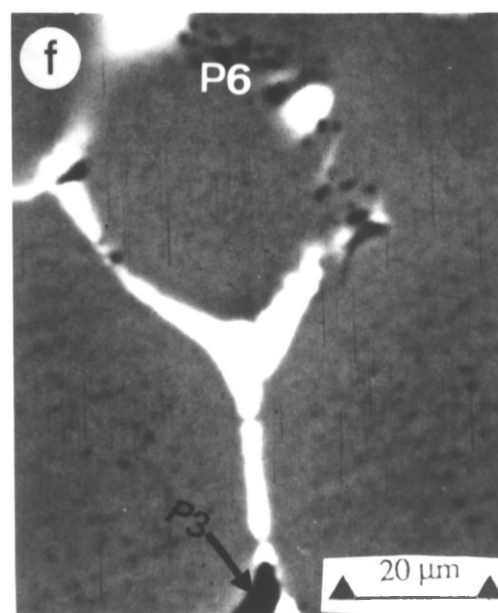
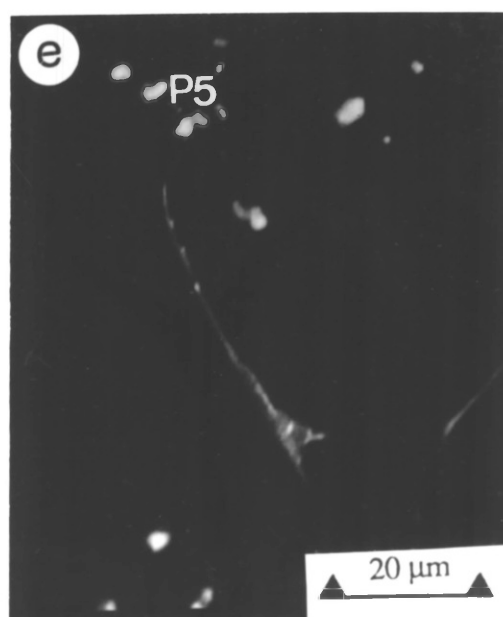
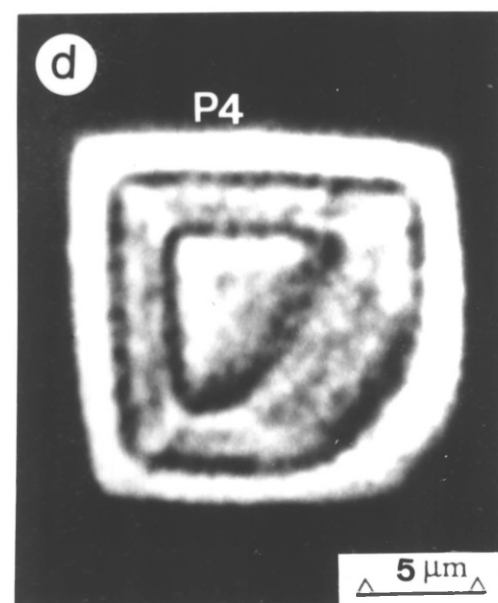
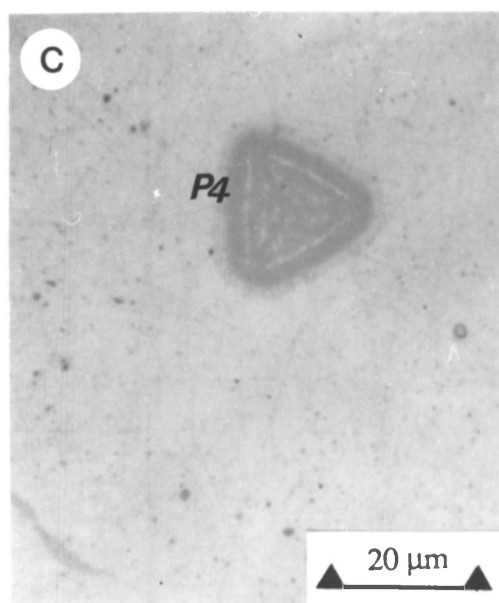
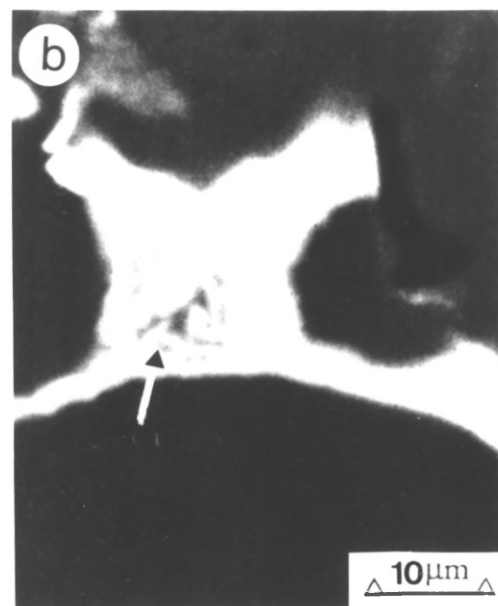


Figure 4.3. Microstructures of as-cast alloys:
second-phase constituents

(a) LM, Keller's etch, (b) Backscattered Electron Image (BEI):
Arrowed - lamellar eutectic at grain boundary triple
points; microstructure overetched in (a) to reveal
eutectic structure (8091 alloy E)

(c) LM, as-polished condition, (d) and (e) SEI:
P4 - large composite matrix precipitates
P5 - coarse spherical matrix precipitates
(8091 alloy E)

(f) BEI:
P3 - coarse grain boundary particle
P6 - fine particles segregated at grain boundary
(8090 alloy C)



4.2.2 EDX in the SEM

The results of EDX analyses carried out on bulk samples to determine the chemical compositions of the various precipitates are presented in Table 4.3. The primary grains are found to contain slightly more solutes (100 - wt%Al) in the 8091 alloys than in the 8090 alloys. This observation (and the greater precipitation of the P1 phase noted earlier) are believed to be due to the higher solute concentrations in the 8091 alloys.

Several of the phases are shown to be due to impurity elements present in the cast alloys. Iron-rich P2 particles which also contain varying amounts of copper, silicon-rich P3 particles, and P6 particles which contain a substantial amount of titanium. The analyses showed evidence of Na and Ca- based particles segregated at grain boundaries. The grain refining zirconium addition is observed to have precipitated both as the large composite particles P4 and the coarse spherical particles P5. The core of the P4 particles is shown to contain about twice as much Zr (≈ 22 wt %) as the envelope (≈ 13 wt %), while the Zr content of the P5 particles is much higher (≈ 27 wt %). The titanium associated with these particles (see Table 4.3) is believed to have resulted from the presence in the matrix of the fine Al-Ti(P6) particles on which the Zr-rich particles appear to precipitate preferentially.

A first indication of the presence (or absence) of lithium in any of the phases can be obtained from the EDX results. When all the elements present in a phase have been analysed, the total composition (in weight %) should add up to 100. Since lithium is not analysed, any shortfall in the total composition may be taken as an indication of the presence of lithium in that phase. Thus the solid solution matrix may be estimated to contain between 1 and 2 wt % Li. There are indications also of lithium presence (≈ 2 wt %) in the P1 phase and in the lamellar eutectic (≈ 7 wt %). The dominant grain boundary phase in as-cast 8090 and 8091 alloys may therefore be a quaternary (AlCuMgLi) phase. The Si-rich particles may be estimated to contain ≈ 3 wt % (11.5 at %) lithium. This value approximates the amount of Li present in the intermetallic particle AlSiLi (11.3 at %). The P4 particles are also shown to contain some amount of lithium; twice as much in the envelope (2.6 wt %) as in the core (≈ 1.4 wt %). There are no indications of lithium presence in the P2(AlFeCu), P5(AlZrTi) and P6(AlTi) precipitates. However, it must be said that this method of estimating low levels of lithium in a phase is largely speculative given that EDX analysis is accurate only to within 2 % of the amount of the element present in a phase.

Table 4.3 Elemental composition (excluding lithium) of phases present in as-cast alloys (determined by SEM-EDX)

Phase	Element (Average composition in wt. %)							Approximate wt. % Li (by difference)	Suspected phase
	Al	Cu	Mg	Zr	Fe	Si	Ti		
α 8090	98.3	—	≈ 0.6	—	—	—	—	1.0	Al solid solution matrix
α 8091	97.0	—	≈ 0.8	—	—	—	—	2.0	
P1	65.6	25.9	6.3	—	—	—	—	2.2	AlCuMg may contain Li
eutectic	74.8	15.4	2.5	—	—	—	—	7.4	$\alpha_{SS} + AlCuMg$ may contain Li and a third phase
P2	66-80	10-16	≈ 1.0	—	23-8	—	—	Nil	Al(Cu,Fe)
P3	54.8	—	—	—	—	42.0	—	3.2	AlSi may contain Li
P4 core	72.7	—	—	21.2	—	—	4.7	1.4	Al(Zr,Ti) complex probably contains Li
P4 shell	81.0	—	—	12.8	—	—	3.7	2.6	
P5	67.0	—	≈ 1.0	27.0	—	—	3.2	≈ 1.0	Al(Zr,Ti)
P6	62-75	14-4	3-2 (and ≈ 3 wt % Na)	—	—	—	18-8	Nil	Al_6Ti

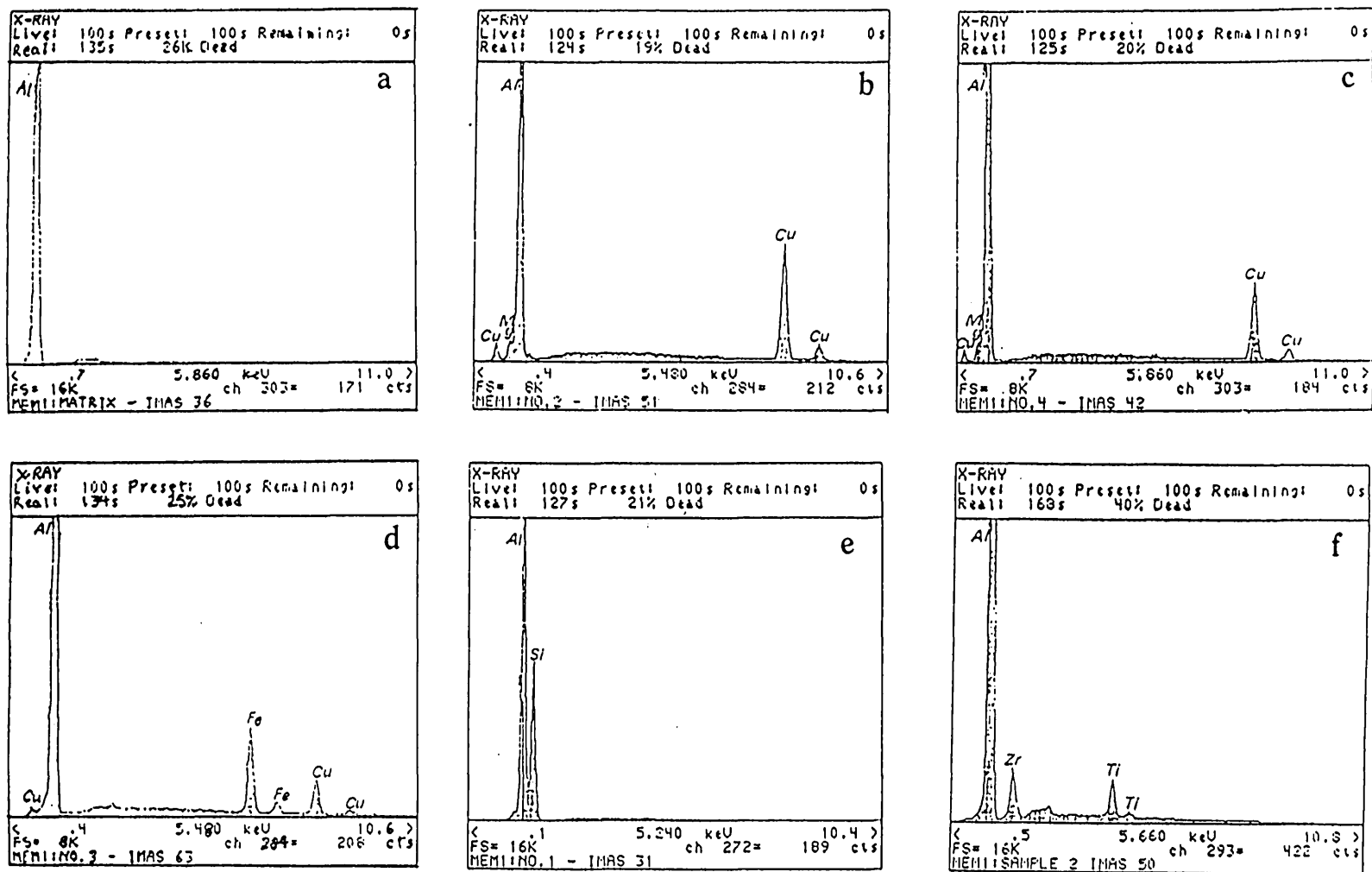


Figure 4.4 X-ray spectra of precipitates present in as-cast 8090 and 8091 alloys:
 (a) Al solid solution, (b) P1, (c) Eutectic, (d) P2, (e) P3, (f) P4 .

4.2.3 TEM and Electron Diffraction

The results of transmission electron microscopy study of the as-cast alloys are set out in the following pages. Besides those precipitates : P1, P2, and P3 (shown in Figs.4.5(a) and (c), 4.6 and 4.7) which have been identified in bulk samples, TEM has revealed the presence of three additional precipitates in the as-cast microstructures:

M1 - which occurs as thin plates (or rods) of lengths ranging from $0.1 - 1.0\mu m$ and possessing three different orientations (labelled 1, 2, and 3 in Fig.4.5 (b)) with respect to the matrix. They were present in the matrix of all the alloys investigated but were noticeably more widely precipitated in the 8091 alloys than in the 8090 alloys. Figure 4.5(e) shows a dark field micrograph imaged using the reflection arrowed in the SAD pattern of Fig.4.5(d). The M1 variant in Fig.4.5(e) is shown to lie along the $\langle 001 \rangle$ matrix directions.

The M2 precipitates occur in the matrix as (near) spherical particles of diameter up to $0.3\mu m$ and have a mottled appearance as shown in Fig.4.5(b). They were present in all the alloys examined but were most commonly found in the 8090 alloy C. The M2 particles appeared too thick to yield clear diffraction patterns for analysis.

Also present in the as-cast microstructures are the hexagonally shaped particles M3 (Fig.4.5(a)) having maximum dimensions ranging from $0.05 - 0.2\mu m$. They occur quite commonly in all the alloys investigated and in the 8090 alloy C were observed to be associated with the Si-rich grain boundary precipitates P3. The M3 particles also appeared to be too thick to yield clear diffraction patterns for analysis.

Electron diffraction studies of the coarse grain boundary precipitates P1 and P2 were carried out using tilting experiments. A series of SAD patterns obtained from P1 by tilting about the $\{h00\}$ row of spots are presented in Fig.4.6. The patterns clearly show a cubic symmetry. However, non-uniformity of the intensities of the diffracted spots is also evident. This may be due to any of a variety of factors : deviations from the exact zone axes; atomic arrangements within the lattice giving rise to superlattice spots; double diffraction spots arising from the matrix or other precipitates; or ^{it} could have arisen from the planar defects associated with the P1 precipitates (see Fig.4.6(a)). This situation has unavoidably introduced some ambiguity into the indexation of the patterns. However, taking the most probable unit cell as the square pattern formed by spots closest to the transmitted beam in Fig.4.6(b), the corresponding planes

will be $\{100\}$ for simple cubic, $\{110\}$ for bcc and $\{200\}$ for fcc lattices. Using any of these reflections as reference, the (hkl) values and angles obtained for the various other spots yielded a simple cubic structure with a lattice constant $a_0 = 1.035\text{nm}$. Details of the analyses are presented in Table 4.4(a).

Figure 4.7 shows a series of SAD patterns obtained from the grain boundary precipitate P2. The patterns are indexed as orthorhombic with lattice constants $a = 0.404$, $b = 0.455$ and $c = 0.515$ (nm). Details of the analyses are given in Table 4.4(b). However, as it has been shown by EDX analyses, the composition (Fe and Cu contents) of the P2 particles may vary from particle to particle. The lattice parameters are therefore expected to vary accordingly.

Table 4.4(a) Electron diffraction data for P1 precipitate

Camera constant $\lambda L = 0.243 \text{ cm.nm}$

Distance from (000) spot R(cm)	d-spacing (nm)	Reflection (hkl)	Lattice parameter a_0 (nm)
0.233	1.043	001	1.043
0.330	0.736	011	1.041
0.525	0.466	012	1.042
0.575	0.423	112	1.036
0.750	0.324	013	1.025
0.875	0.278	123	1.040
0.975	0.249	014	1.027
1.075	0.226	124	1.035
			Ave. 1.035

Table 4.4(b) Electron diffraction data for P2 precipitate

Camera constant - same as above

Distance from (000) spot R(cm)	d-spacing (nm)	Reflection (hkl)
0.793	0.3026	110
1.067	0.2275	020
1.200	0.2025	200
1.717	0.1415	130
1.950	0.1246	132
2.650	0.0916	242
2.950	0.0824	431

Figure 4.5 Transmission electron microscopy of as-cast alloys :
Distribution of precipitates.

- (a) Bright Field (BF) micrograph showing grain boundary precipitated with P1(AlCuMgLi), P3(AlSiLi), and M3 particles (8090 alloy C)
- (b) Matrix of 8090 alloy C precipitated with M1, and clusters of M2 particles. Note the different orientations (3) of the M1 particles labelled 1, 2, and 3.
- (c) Matrix of 8090 alloy A precipitated with P2 (Al-Fe-Cu) particles (BF)
- (d) Matrix of 8091 alloy D precipitated with M1 particles and corresponding SAD pattern: $\langle 001 \rangle$ beam direction. camera constant $\lambda_L = 0.243 \text{ cm.nm}$
- (e) Dark Field (DF) micrograph of (d) imaged using the reflection arrowed in SAD pattern.

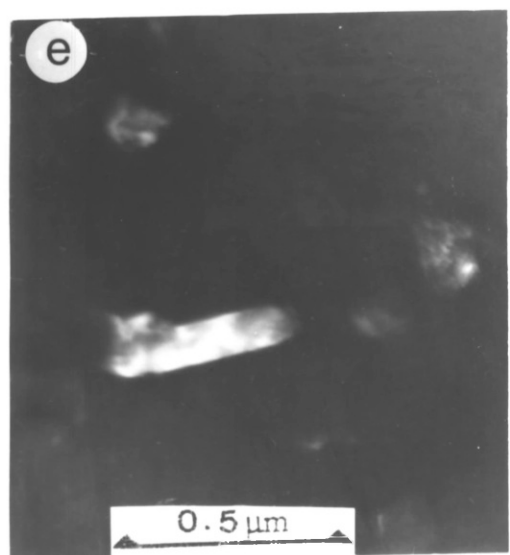
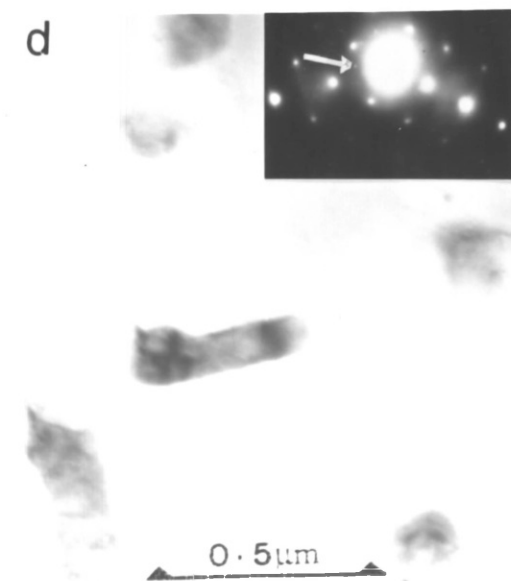
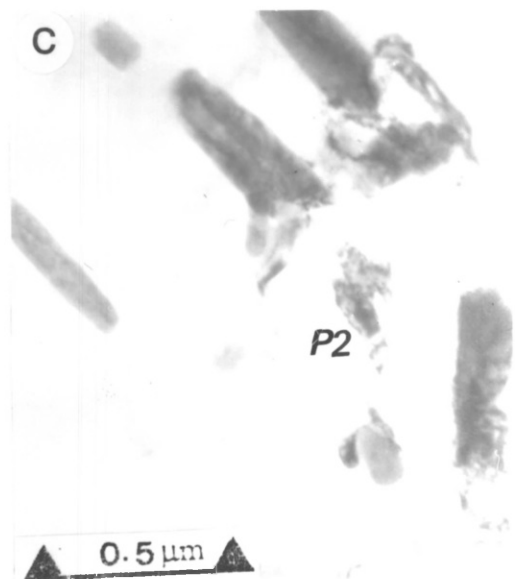
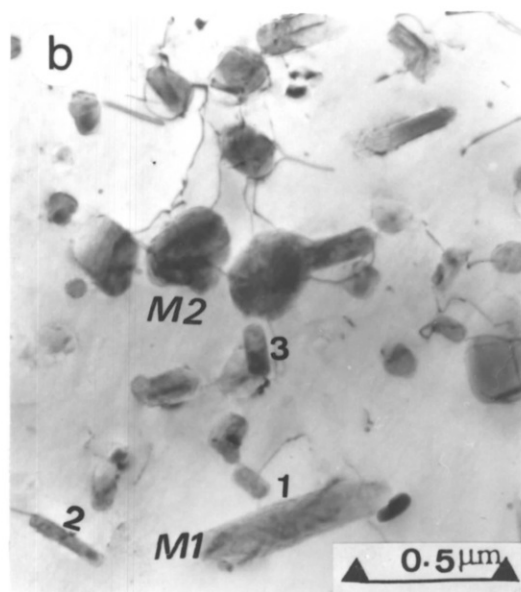
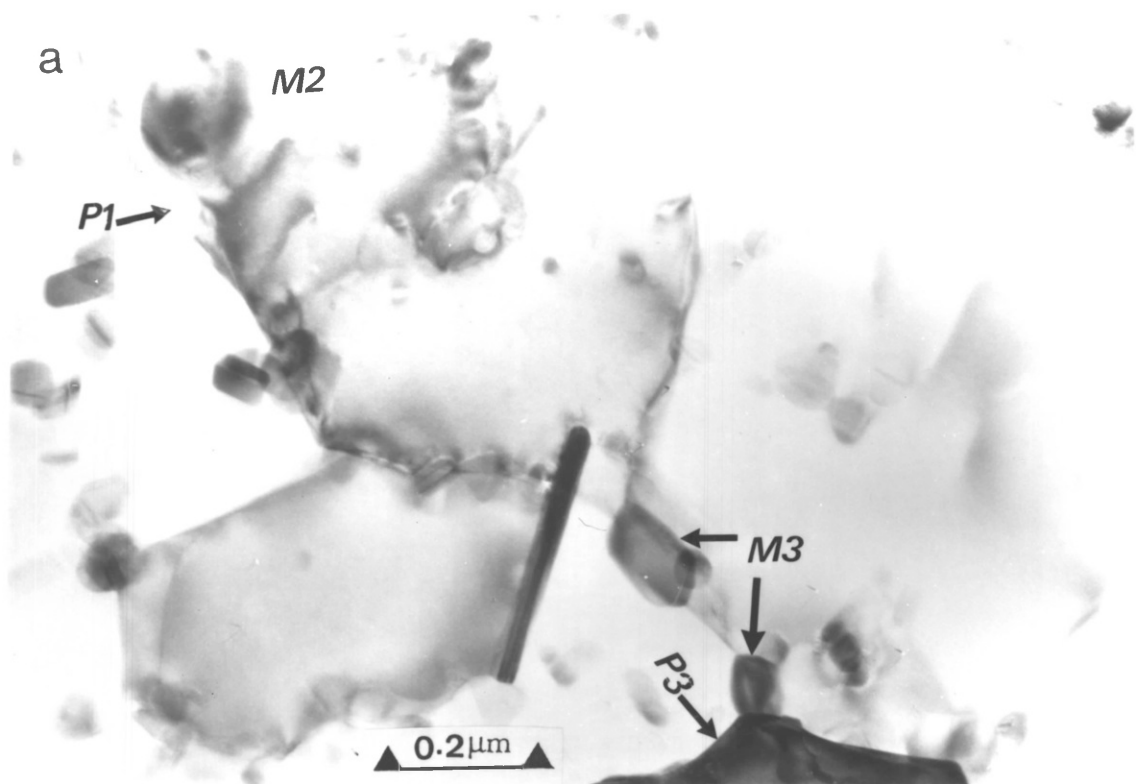


Figure 4.6 Electron diffraction of grain boundary precipitate P1

(a) BF image of P1(Al-Cu-Mg-Li) showing associated planar defects (8090 alloy A).

(b) SAD pattern from P1; $\langle 001 \rangle$ zone axis

(c) SAD pattern from matrix using the same zone axis as (b)

(d), (e) and (f) SAD patterns from P1 obtained by systematic tilting from the $\{h00\}$ row of spots (arrowed in (b)); $\langle 0\bar{4}1 \rangle$, $\langle 0\bar{1}3 \rangle$, $\langle 0\bar{2}1 \rangle$ zone axes respectively.

Camera constant $\lambda_L = 0.243$ cm.nm.

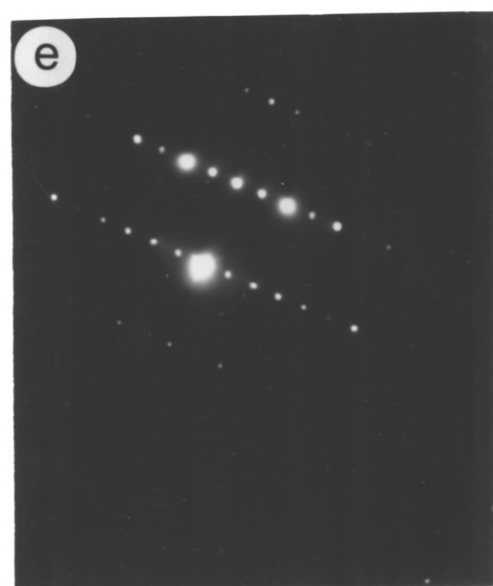
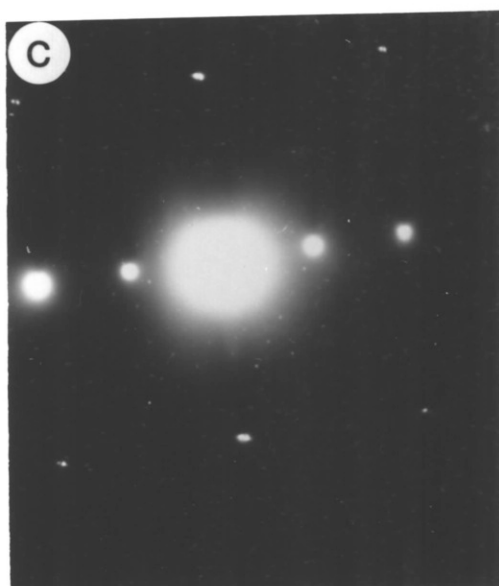
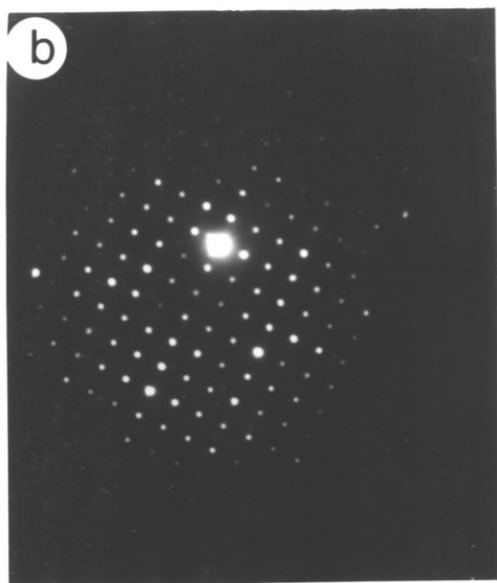
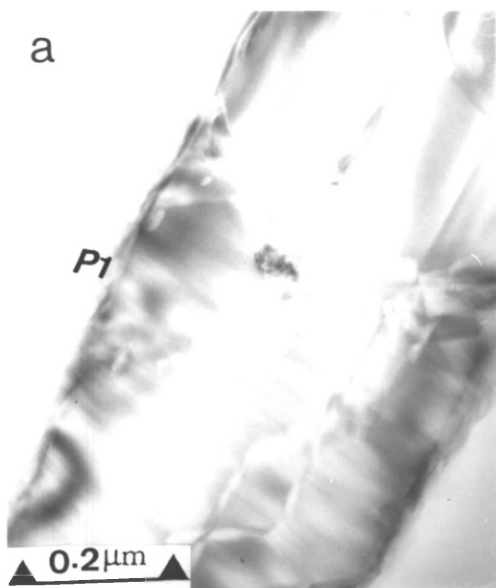
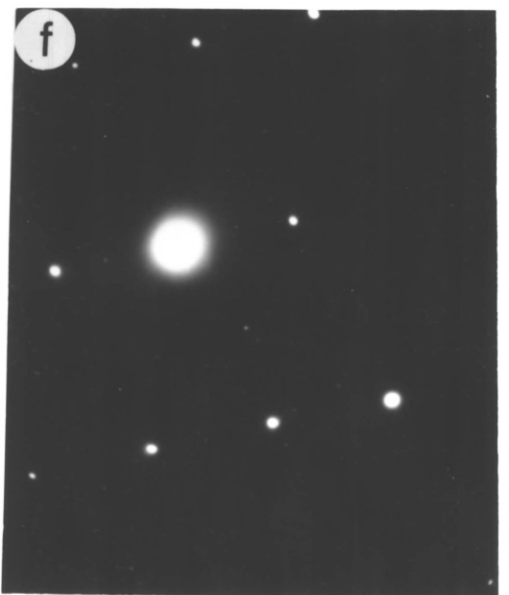
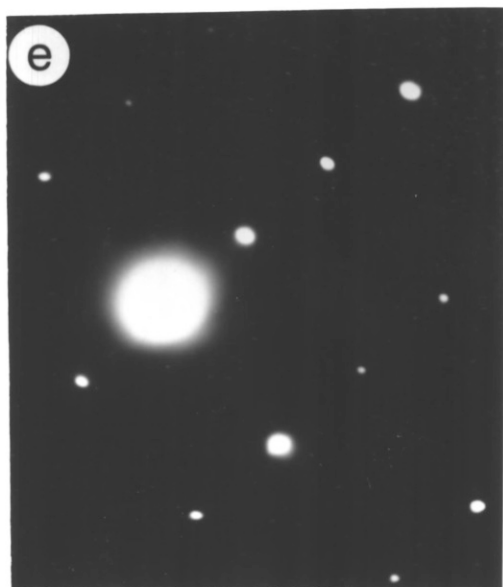
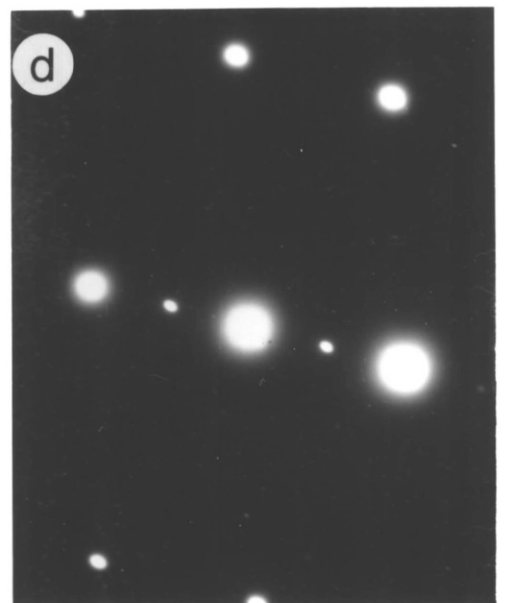
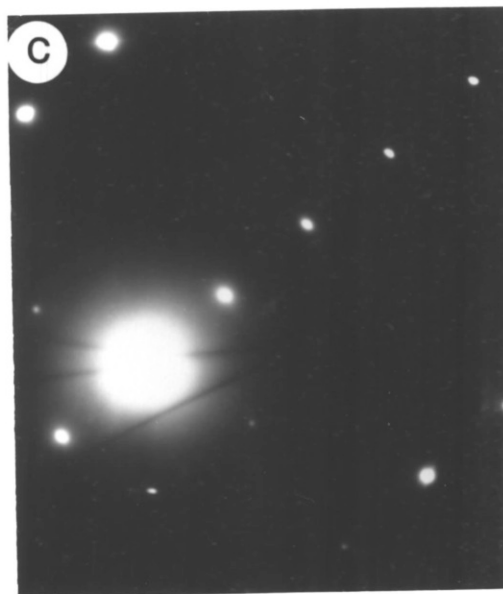
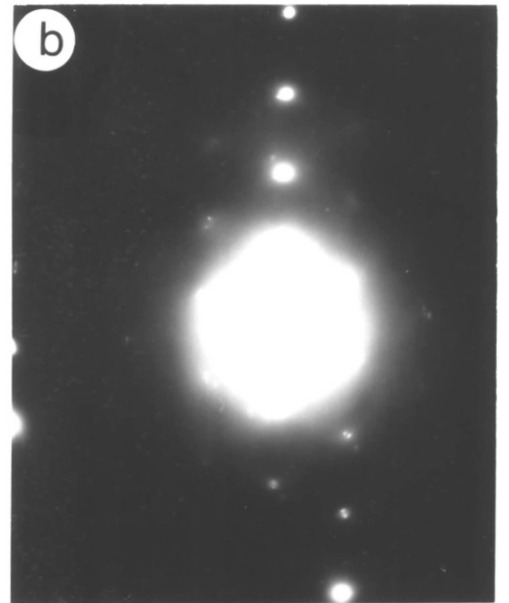


Figure 4.7 Electron diffraction of grain boundary precipitate P2

(a) BF image of P2 particle in 8090 alloy A

(b) - (f) SAD patterns from P2 particle indexed as orthorhombic with lattice parameters $a = 0.404$, $b = 0.455$, and $c = 0.515$ (nm); camera constant $\lambda L = 0.243$ cm.nm.



4.2.4 EDX in the TEM

The results of EDX analyses of the precipitates present in thin foils are presented in Table 4.5 below.

	Average Elemental Composition (wt %)						
Phase	Al	Cu	Mg	Zr	Fe	Si	Ti
P1	64 - 66	26 - 24	7 - 6	-	-	≈1.0	-
P2	64 - 76	15 - 18	≈1.0	-	26 - 9	-	-
P3	53.4	-	≈1.0	-	-	45.6	-
M1	62 - 70	22 - 28	7 - 5	-	-	-	-
M2	70 - 78	13 - 18	5 - 3	-	-	-	-
M3	50 - 62	-	1 - 3	-	-	32 - 38	-

These results confirm that the P1, P2, and P3 precipitates are the same as those identified in bulk samples. In view of the small sizes of the M1, M2 and M3 particles, substantial errors are likely to be involved in the analyses given above. NB: All the analyses are normalised to 100% and thus take no account of any Li content.

4.2.5. Identification of Lithium-bearing phases

In section 4.2.2 a first indication of the presence of lithium in some of the precipitates found in the microstructures of the alloys under investigation was obtained from EDX analyses. In this section, the results of further investigations by techniques especially employed to determine the distribution of lithium in the microstructures are presented.

4.2.5.1. Backscattered Electron Imaging in the SEM

The basis of this technique is the strong dependence of the backscattered electrons generated from the surface of a specimen on the atomic number, Z . The backscattering coefficient defined as

$$\eta = n_B/n_I \quad (4.1)$$

(where n_I is the total number of incident electrons) is related to the atomic number via a simple empirical equation derived by Tomlin and others (131–134):

$$\eta = \frac{1}{6} \ln Z - \frac{1}{4} \quad (4.2)$$

In principle therefore, equation (4.2) can be used to identify a specimen by measuring the number of backscattered electrons n_B generated from the surface of the specimen (since n_I is known). In practice however, the direct measurement of n_B is not possible with present day detectors; rather the intensity (I) of signals produced by the backscattered electrons is measured and quantified in such a way that $I \propto \eta$. Experiments by a number of investigators (135–138) have demonstrated that to consistently achieve this proportionality, a whole range of factors need to be specified and carefully controlled. Ball and McCarthy (135) gave the principal factors as:

- (a) collection efficiency of the detector,
- (b) energy of the incident electrons,
- (c) sensitivity of the signal processing and measuring technique, and
- (d) quality of specimen preparation.

The experimental details involved in the present investigation have been described in Section 3.7. The intensity (IMAS Number) of backscattered signals measured from the surface of a series of specimens of known atomic number

Z (standards) are given in table 4.6. The resulting I versus Z plot which will serve as a calibration curve for specimens of unknown Z is shown in Figure 4.8. The following procedure was adopted to identify the Li-bearing phases in the microstructures of the alloys investigated:

- (1) The intensity (IMAS Number) of the backscattered signal generated from each phase was measured and the corresponding (mean) atomic number $\overline{Z}_m$ obtained from the calibration curve in Figure 4.8.
- (2) The elemental composition (excluding lithium) of each phase determined earlier by EDX was used to calculate the mean atomic number ($\overline{Z}_c$) using the following equation first proposed by Danguy and Quivy (139):

$$\overline{Z}_c = \frac{\sum_i X_i Z_i^2}{\sum_i X_i Z_i} \quad (4.3)$$

where X_i is the proportion of the i^{th} element present in the phase, so that for a binary phase

$$\overline{Z}_c = \frac{X_1}{X_2} Z_1^2 + Z_2^2 / \frac{X_1}{X_2} Z_1 + Z_2 (\text{note that } X_2 = 1 - X_1)$$

Thus within limits of experimental errors, if a phase P does not contain lithium then $\overline{Z}_m(P) = \overline{Z}_c(P)$. On the other hand, the effect of neglecting lithium ($Z = 3$) if it were present in a phase would be an increase in the calculated mean atomic number $\overline{Z}_c$ so that $\overline{Z}_m < \overline{Z}_c$ for all those phases which contain lithium.

The results of these analyses presented in Table 4.7(a) show that lithium may be present in the following phases: the aluminium solid solution (α), the dominant grain boundary phase (P1), the lamellar eutectic, the Si-rich particles (P3) and Zr-rich composite precipitates (P4). Furthermore, the magnitude $|\overline{Z}_m - \overline{Z}_c|$ may be taken as a measure of the amount of lithium present in a phase so that the eutectic phase will contain more Li than the α or P1 phase but less than the P3 phase; while the P4 phase will contain less lithium in the core than in the envelope. For the purpose of comparison, the calculated mean atomic number ($\overline{Z}_c$) of some lithium bearing phases previously identified in ternary Al-Li-Cu and quaternary Al-Li-Cu-Mg alloys are presented in Table 4.7(b). It is observed from this table that the measured mean atomic number of the P1 phase is almost the same as the calculated mean atomic number of the quaternary I-phase. Similarly, $\overline{Z}_m(P3) \approx \overline{Z}_c(AlSiLi)$ and amongst the ternary T-type phases $\overline{Z}_c(T_2)$ is closest to $\overline{Z}_m(P1)$. Relevant conclusions from these observations will be drawn at the appropriate stage during this work.

Table 4.6 Backscattered Electron Signals Measured
from Calibration Specimens

Elements (standard specimens)	Atomic number (Z)	Measured backscattered signal (IMAS number)
Cu	29	100
Ni	28	97
Fe	26	90
Cr	24	83
Ti	22	78
Si	14	41
Al	13	37
Mg	12	32

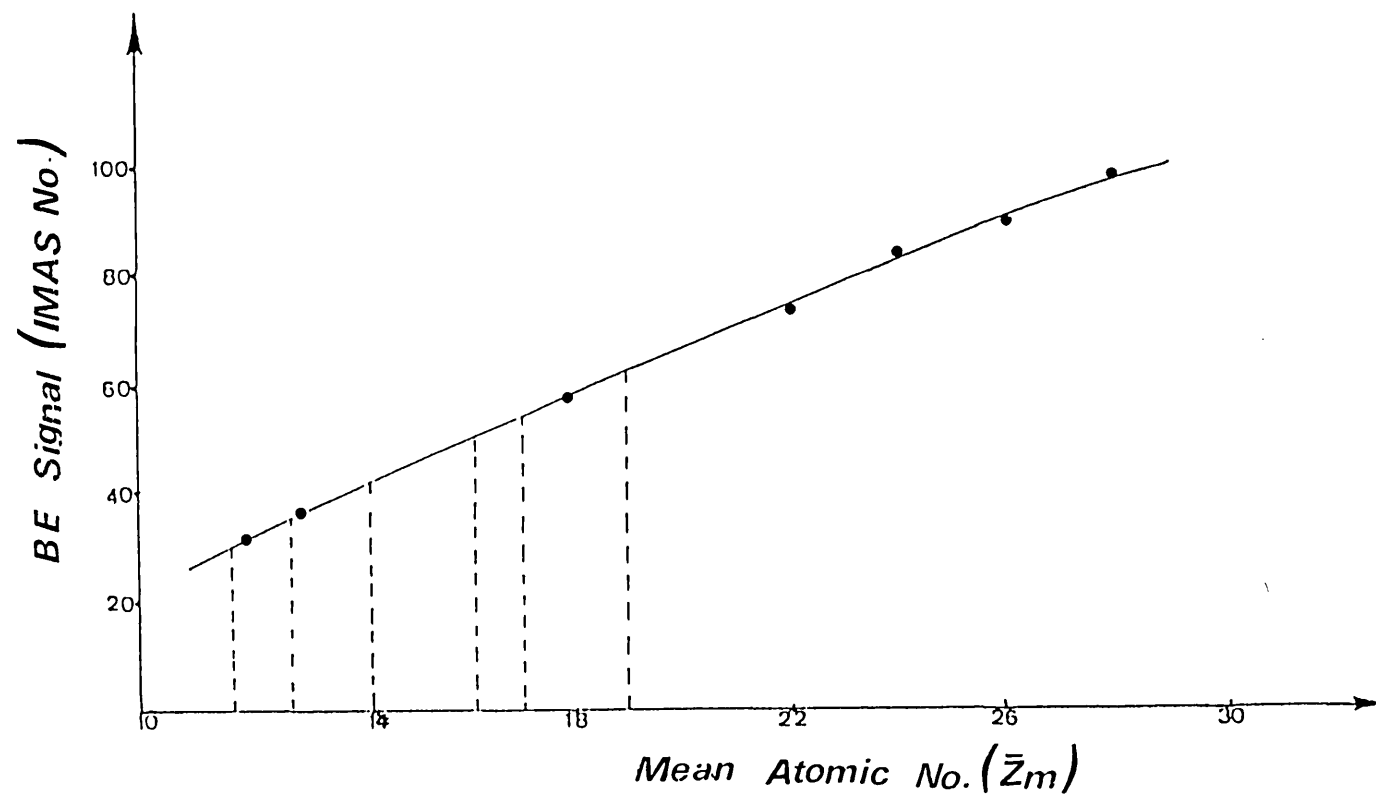


Figure 4.8 Calibration curve for Backscattered Electron Imaging (Atomic Number Measurement).

Table 4.7(a) Comparison of Measured and Calculated Mean Atomic Numbers for Phases Present in 8090 and 8091 Cast Alloys

Phases	Measured Backscattered Electron Signal	Measured Mean Atomic Number (from Fig 4.8) $\overline{Z}_m$	Calculated Atomic Number from EDS $\overline{Z}_c$	$\overline{Z}_m - \overline{Z}_c$
α	36.0	12.70	12.78	-0.08
P1	50.0	16.00	16.73	-0.73
Eutectic	41.70	14.10	15.25	-1.15
P2	61.80	18.80	18.65	+0.15
P3	31.0	11.75	13.37	-1.62
P4 core	50.0	16.00	19.09	-3.09
P4 shell	41.50	14.10	16.92	-2.82

Table 4.7(b) Calculated Mean Atomic Numbers of Some Lithium-bearing Phases identified in Al-Li-Cu and Al-Li-Cu-Mg Alloys

Phase	Calculated Mean Atomic Number ($\overline{Z}_c$)	Comparison with similar phase in present alloys
$T_1(Al_2CuLi)$	20.30	-
$T_2(Al_6CuLi_3)$	16.29	close to P1
$T_B(Al_{7.5}Cu_4Li)$	21.84	-
$R(Al_5CuLi_3)$	16.66	-
$C(AlCuMgLi)$	14.18	-
$I(AlCuMgLi)$	16.10	almost same as P1
$AlSiLi$	11.81	almost same as P3
$Al_2Si_2Li_3$	12.32	-
$S(Al_2CuMg)$	20.01	-

4.2.5.2. Secondary Ion Mass Spectroscopy (SIMS)

The application of SIMS to the characterisation of complex Al-Li based alloys is to take advantage of its ability to directly image all elements ($1 \leq Z \leq 92$) on the surface of bulk samples. The primary aim of this investigation (as in the preceding section) therefore, is to determine the distribution of lithium in the microstructures of 8090 and 8091 alloys. The distribution of other elements present in the alloys has also been determined for the purpose of co-relating them with results obtained in previous investigations. Selected areas of the microstructure of the alloys were imaged to produce ion micrographs of the various elements; and also scanned laterally to produce concentration profiles of the elements (see Section 3.8 for details of experimental technique). Figures 4.9 and 4.10 show ion micrographs obtained from the microstructures of 8090 and 8091 alloys respectively. The intensity (relative to the background matrix) exhibited by an element indicates the concentration of that element in the area of the microstructure imaged. The micrographs show substantial segregation of all the major alloying elements (Li, Cu, Mg) at grain boundaries and grain boundary triple points, with copper present in the highest concentration. This is as expected since there is very little copper in the solid solution matrix.

The lithium distribution maps (Figs 4.9(b) and 4.10(c)) show conclusively that the phases present at the grain boundaries (P1) and at the grain boundary triple points (eutectic) contain substantial amounts of this element. They are therefore confirmed to be quaternary (AlCuMgLi) phase. The Li maps also show evidence of lithium presence in the aluminium matrix. The Al-maps (Figs 4.9(a) and 4.10(b)) show grain boundaries which are dark compared to the matrix, indicating a higher aluminium concentration in the latter.

The Fe distribution map (Fig 4.9(e)) shows that the Fe-rich particles also segregate at grain boundaries. A superposition of this map on the Li, Mg, or Si map shows that the distribution of the Fe-rich particles fits the “gaps” (arrowed) observed in the Li, Mg and Si maps. This implies that the Fe-rich particles do not contain any of these elements. On the contrary, it is observed that the Fe-map completely merges into the Cu-distribution map when superimposed on one another indicating that the Fe-rich particles contain substantial amounts of copper. These observations confirm the results of previous investigations which identified the Fe-rich particles (P4) as an Al, Fe, Cu, phase.

The concentration of Si-rich particles shown in Fig. 4.9(f) is higher than was expected for this alloy which contained only 0.04 wt % Si. One probable and simple explanation for this apparent inconsistency is that the alloy (8091E)

actually contains more than 0.04 % Si and that most of the silicon probably exists in the elemental form rather than forming the Si-rich phase observed in the 8090 alloy C. As expected however, the concentration of Si-rich particles is shown to be higher in the 8090 alloy C (Fig. 4.10(f)) than in the 8091 alloy E. The distribution of the Si-rich particles is shown to indicate that some of them may be associated with lithium.

The line scan profile across an area of the microstructure of 8091 alloy E is shown in Figure 4.11. The peaked sections correspond to distribution of the elements at a grain boundary triple point (1) and at a grain boundary (2) while the more or less flat section corresponds to distribution of the element in the matrix. These observations conform to the trend found in the ion micrographs of Figures 4.9 and 4.10. The Si concentration is shown to be substantially lower than those of the major alloying elements (Li, Cu, Mg), which is as expected.

Figure 4.9. Secondary Ion Mass Spectroscopy(SIMS):
Element distribution maps of second-phase precipitates
in as-cast microstructure of 8091 alloy E

Ion micrographs:

(a) $^{27}\text{Al}^+$

(b) $^7\text{Li}^+$

(c) $^{63}\text{Cu}^+$

(d) $^{24}\text{Mg}^+$

(e) $^{56}\text{Fe}^+$

(f) $^{28}\text{Si}^+$

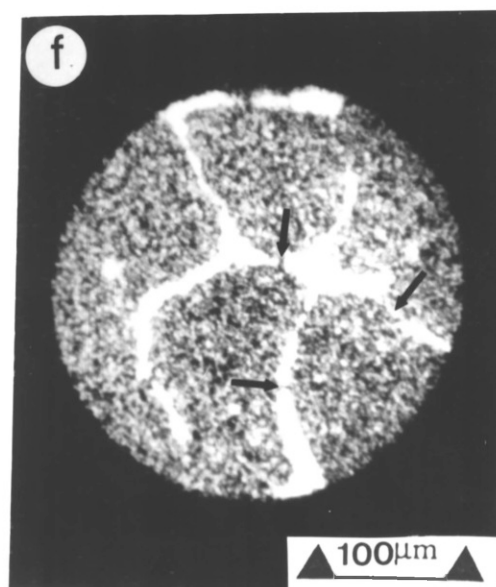
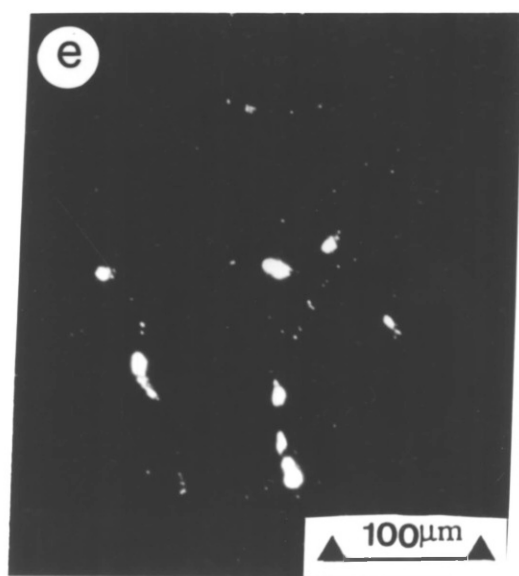
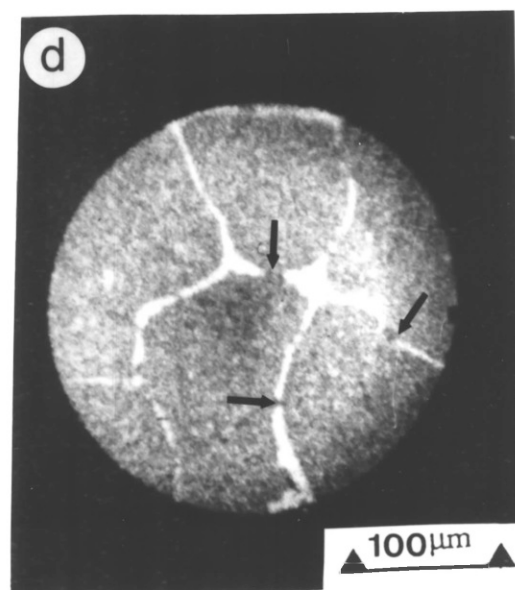
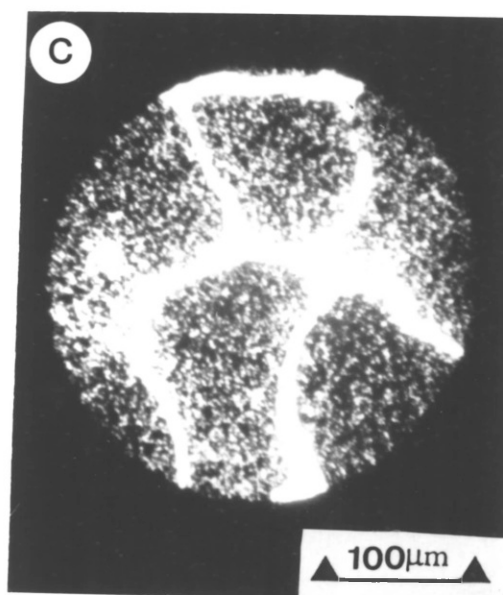
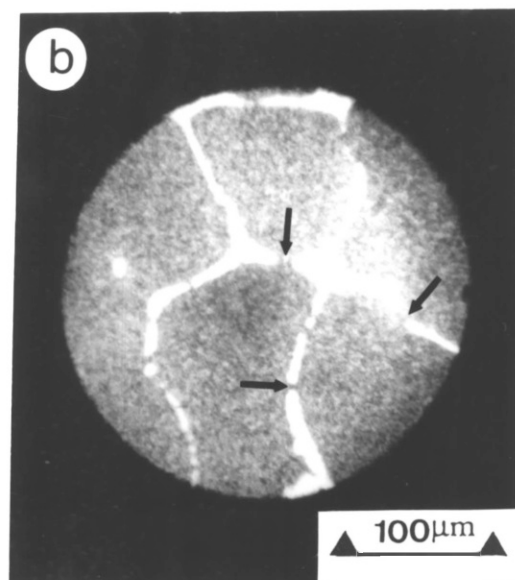
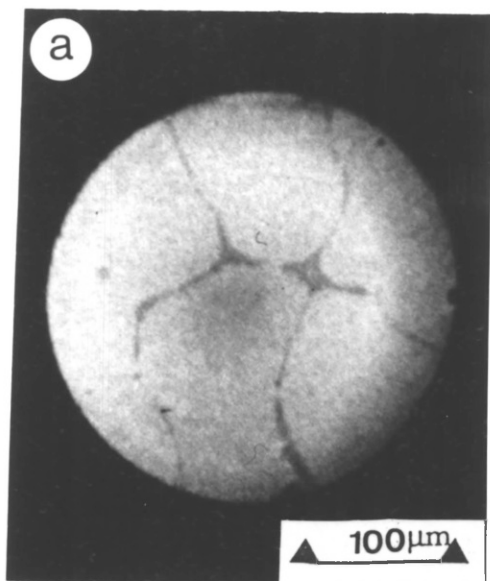


Figure 4.10. Secondary Ion Mass Spectroscopy(SIMS):
Elemental distribution maps of second-phase precipitates
in as-cast microstructure of 8090 alloy C

(a) Optical micrograph

Ion micrographs:

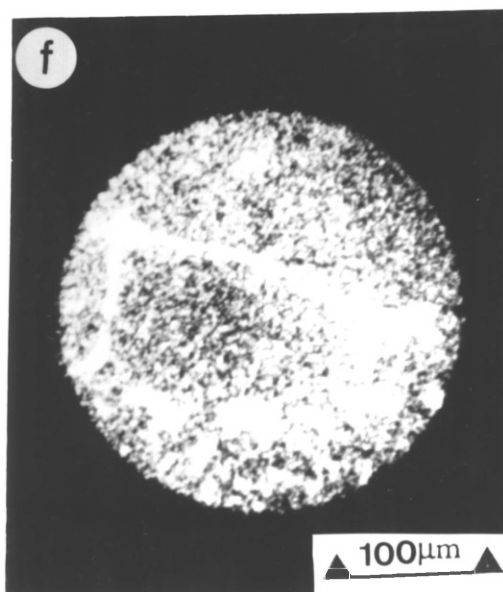
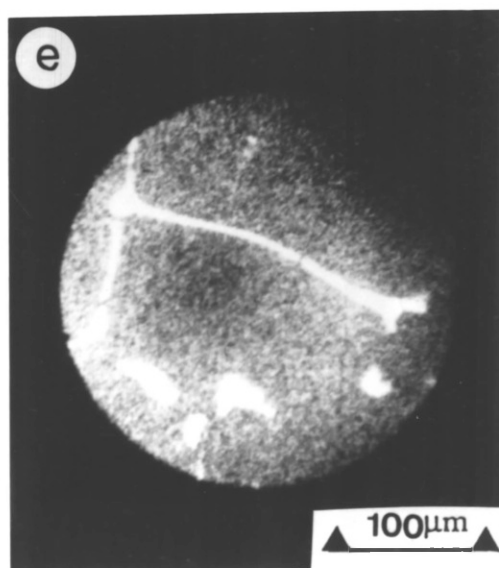
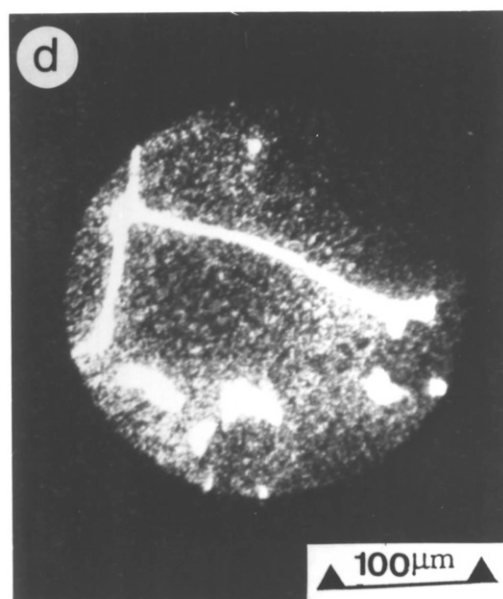
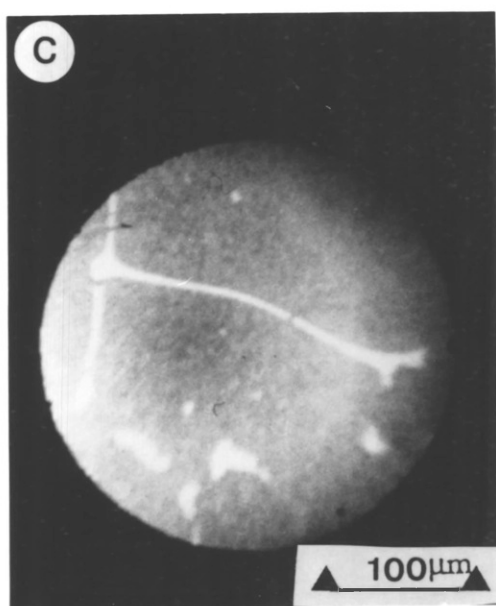
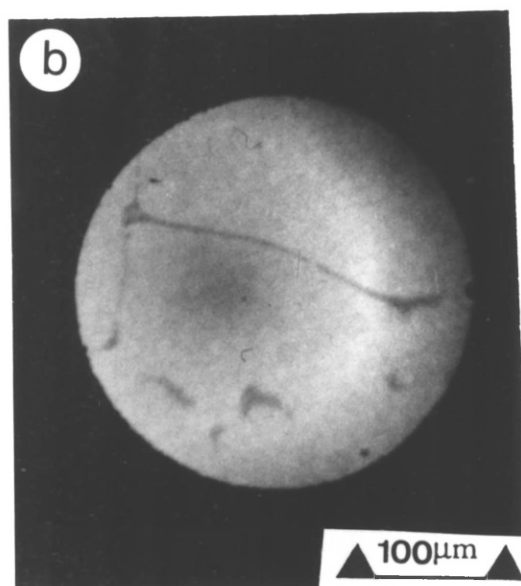
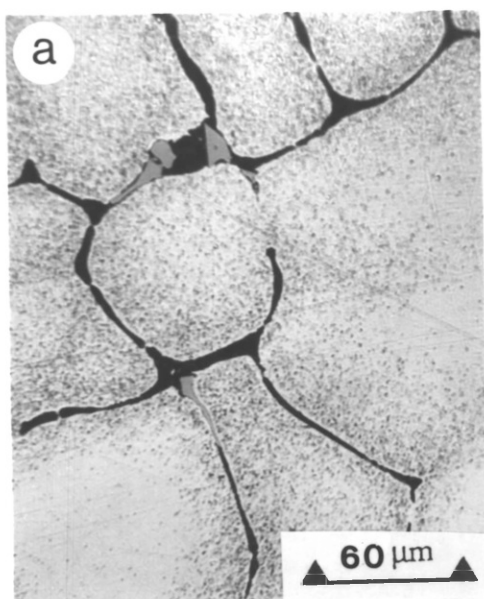
(b) $^{27}\text{Al}^+$

(c) $^7\text{Li}^+$

(d) $^{63}\text{Cu}^+$

(e) $^{24}\text{Mg}^+$

(f) $^{28}\text{Si}^+$



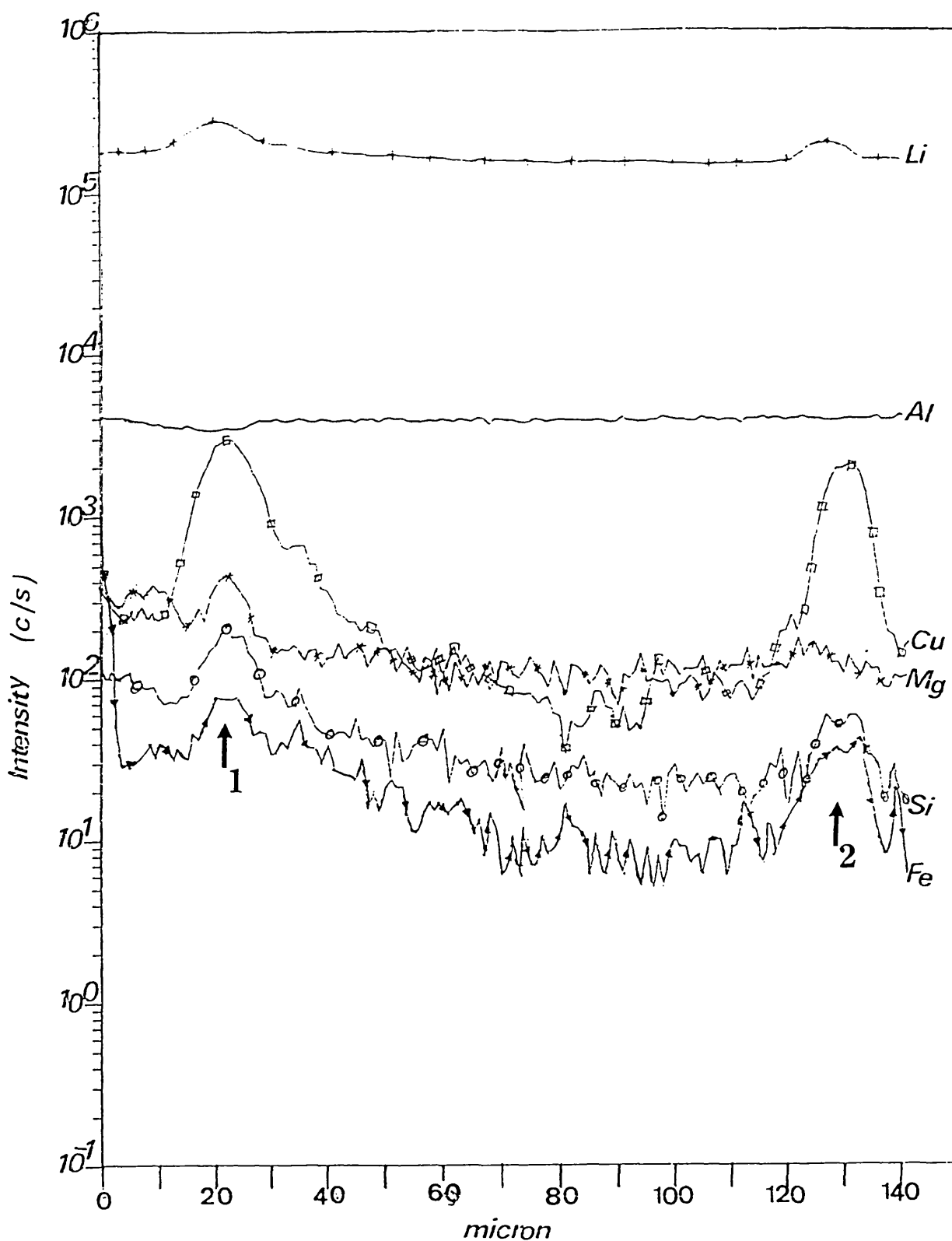


Figure 4.11 SIMS— Line scan across an area of the microstructure of as-cast 8091 alloy E. Peaked sections represent the distribution of elements at a grain boundary triple point (1), and at a grain boundary (2).

4.2.6 X-Ray Diffractometry

X-ray diffraction study of bulk samples of the as-cast alloys did not produce useful results for the identification of second-phase constituents. This is due largely to the low volume fractions of the second-phase precipitates coupled with the inherent complexity in the diffraction analyses of multi-phase alloys (see section 3.9). However, sufficient diffraction lines were obtained from the matrix phase to identify it (in all the alloys investigated) as fcc with a_0 calculated to be 0.4046 nm. The results are presented in table 4.8(a) below. If the amount of other elements in solution (see Table 4.3) is considered negligible, this value of lattice parameter will correspond to ≈ 7.1 at. % (1.8 wt. %) lithium in aluminium solid solution (Ref: Axon and Hume-Rothery(142), Levine and Rappaport(141) and McAlister(11)). N.B: The accuracy implied here (0.0001 nm) is beyond the experimental limit.

Table 4.8(a) X-ray Diffraction Analysis of Matrix Phase
in as-cast 8090 and 8091 Alloys

8090 alloy A		8091 Alloy B		
d(nm)	I/I_0	d(nm)	I/I_0	(hkl)
0.2338	100	0.2338	100	111
0.2023	100	0.2023	100	200
0.1431	95	0.1431	95	220
0.1220	85	0.1220	80	311
0.1169	100	0.1169	95	331
0.1012	85	0.1012	100	400
0.0905	75	0.0905	75	420
0.0827	95	0.0827	65	422

X-ray diffraction also produced evidence for the presence in the as-cast alloys of the equilibrium phase $\delta(\text{AlLi})$. Table 4.8(b) gives the diffraction lines that were identified and are compared with data given in the Joint Committee for Powder Diffraction Studies (JCPDS) file for the compound AlLi. Although the presence

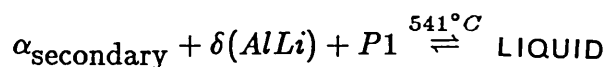
of equilibrium δ in as-cast Al-Li based alloys has not been reported previously, from the phase diagram (Fig. 2.2), its precipitation during solidification in alloys containing up to 2.5 wt % Li is feasible if the cooling rate is sufficiently slow. Such δ phase will precipitate as fine particles at high angle grain boundaries, particularly at grain boundary triple points.

Table 4.8(b). X-ray Diffraction Analysis of δ (AlLi) phase in as-cast 8090 and 8091 alloys

Present Work				JCPDS File		
8090 Alloy A		8091 Alloy D		AlLi phase: fcc $a_0 = 0.638$ nm		
d(nm)	$I/I_0(\%)$	d(nm)	$I/I_0(\%)$	d(nm)	$I/I_0(\%)$	hkl
0.3676	97	0.3677	61	0.365	75	111
0.2265	72	0.2270	69	0.226	100	220
0.1929	60	0.1921	40	0.192	75	311
0.1585	35	—	—	0.158	60	400
0.1431	100	0.1431	100	0.146	60	331
0.1298	49	0.1295	32	0.130	100	422
0.1219	100	0.1219	100	0.122	75	333.511
—	—	—	—	0.112	75	440
0.1012	86	0.1012	38	0.101	85	620
0.0827	100	0.0827	100	0.0827	100	553.731

4.2.7 Differential Scanning Calorimetry (DSC)

DSC studies of the as-cast 8090^{and 8091} alloys have been carried out to provide information regarding the basic phase transformations (solidification sequences) which occur within the quaternary Al-Li-Cu-Mg system and also to determine the appropriate transformation temperatures for subsequent heat treatments of the alloys. The experimental details have been given in section 3.10. Figure 4.12 shows typical DSC traces obtained for 8090 alloy A (a) and 8091 alloy D (b) respectively. It was observed that the DSC traces for all the alloys investigated exhibited identical features. The two obvious features of Fig.4 are a small endotherm occurring at 556°C and a larger one which occurs at 652°C. A check was carried out to determine if there was any difference between the temperatures which are recorded in this experiment and the actual temperatures of the transformations. This was done by analysing an equal weight of 99.99% purity aluminium in identical experimental conditions. The melting point was determined as 672°C, i.e. 11.6°C higher than the actual melting point (660.4°C). The implication is that the transformation temperatures shown in Fig. 4.12 are each higher by this value. The endotherm at $\approx 637^\circ\text{C}$ clearly represents melting of the Al solid solution matrix. Microstructural evidence suggests that the endotherm occurring at $\approx 541^\circ\text{C}$ can only be due to the dissolution of the dominant grain boundary phase P1 (and the triple point eutectic). The transformation sequence will be expected to be of the form:



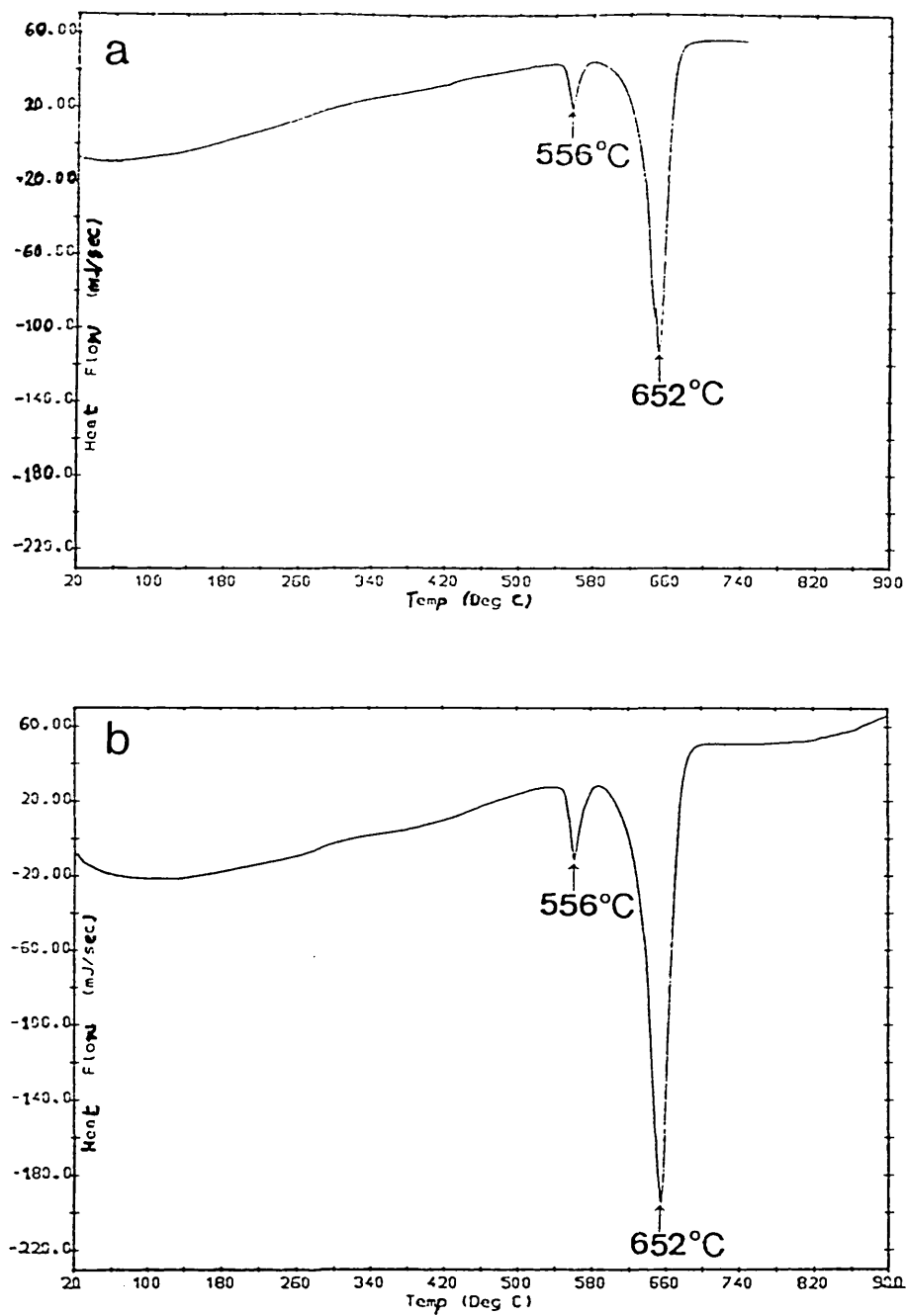


Figure 4.12 DSC traces showing major transformations occurring in as-cast alloys:
(a) 8090 alloy A (b) 8091 alloy D.

4.3 Discussion

The experimental results and observations of the preceding sections are discussed and summarised here in order to present a coherent picture of the characteristics of each of the microstructural features that have been observed in the as-cast 8090 and 8091 alloys.

The Matrix Phase (α)

The matrix phase in all the alloys investigated is aluminium solid solution primary grains which have been shown to contain 1 - 2 wt % lithium and traces of magnesium. The cellular grain structure (Fig.4.1) and the average grain size of $\approx 70 \mu\text{m}$ suggest that substantial grain refinement (resulting from zirconium addition) has occurred during casting. The grains show clear evidence of microsegregation which resulted from non-equilibrium cooling. No difference in the size of the grains was observed between the 8090 and 8091 alloys. X-ray diffraction analysis gave the lattice parameter (a_0) of the fcc matrix as 0.4046 nm which corresponds to $\approx 1.8 \text{ wt } \%$ (7.1 at.%) lithium in Al_{ss} , showing a good agreement with the estimate given by EDX and backscattered imaging technique. The lattice parameter obtained from electron diffraction analysis (section 4.2.3) was 0.4043 nm.

4.3.2 Grain Boundary Precipitates

(1) The Major Grain Boundary Phase (P1)

The grain boundaries in the as-cast 8090 and 8091 alloys have been shown to be largely precipitated with the equilibrium phase P1, whose composition was determined by EDX as: 66 Al, 26 Cu, 6 Mg (wt %). The BEI and SIMS investigations showed clear evidence of lithium presence which has been estimated to be $\approx 2 \text{ wt } \%$. X-ray diffraction did not yield sufficient lines from the P1 phase (largely due to its small volume fraction) for analysis of its structure. However, electron diffraction analysis (Fig.4.6) has shown the structure to be simple cubic with lattice parameter $a_0 = 1.032 \text{ nm}$. TEM also revealed that the P1 precipitate possesses a planar defect structure (Fig.4.6(a)). The temperature of the eutectic involving this phase (and other phases) was determined by DSC studies to be $\approx 541^\circ\text{C}$. The morphology, composition and defect structure of the P1 phase strongly suggest that it is the same as the phase which has previously been reported in heat treated 8090 alloys by Smith(85): 65 Al, 24 Cu, 8 Mg, and by Dubost *et al.*(143): Al, 25 - 29 Cu, 6 - 7.5 Mg, (wt %). Both authors con-

sidered the phase as an extension of the ternary $T_2(Al_6CuLi_3)$ phase with Mg atoms substituting for Li atoms up to the compound formula $Al_6CuLi_{3-x}Mg_x$, where $x \leq 1$. A phase of similar characteristics has been identified by Ball and co-workers(86,88) and Loiseau and Lapasset (84,87) in heat treated 8090 alloys and more recently by Owen(101) and Mukhopadhyay(102) in as-cast 8090 alloys.

The present investigation has produced evidence in support of the relationship between the quaternary phase P1 and the ternary T_2 phase proposed by earlier investigators. Firstly, the mean atomic number of 16.0 measured for the P1 phase is quite close to the 16.29 calculated for the T_2 phase (see section 4.2.5). Secondly, as it will be shown presently, the eutectic reaction at 541°C involving the grain boundary phase P1 is very similar to the one involving the T_2 , δ , and α phases which occurs in Al-Cu-Li alloys.

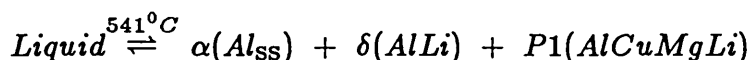
The crystal structure of the grain boundary phase in 8090 alloys has been generating a lot of controversy recently. Smith(85) had used x-ray diffraction to determine the structure as bcc ($a_0 = 1.073 \text{ nm}$), while Mukhopadhyay(102) obtained from electron diffraction studies an fcc structure with a_0 ranging from 1.9 - 2.6 nm . Other investigators notably Ball and co-workers(86,88) and Loiseau and Lapasset(84,87) have used TEM to obtain an icosahedral structure (hence I-phase), exhibiting a characteristic 5-fold symmetry similar to that which had been reported for phases present in rapidly solidified Al-Mn alloys (150). Unfortunately, the structure of the T_2 phase upon which (it is generally agreed) the I-phase is based is also surrounded by controversy. Hardy and Silcock(42) who reported the existence of the T_2 phase could not determine its structure from x-ray diffraction studies. Since then several investigators including Marcus and Elser(151), Cassada *et al.*(51,55), Audier and co-workers(54,152), and Knowles and Stobbs(153) have used electron diffraction to obtain an icosahedral structure for the T_2 phase. Cassada *et al.*(55) obtained a "quasi-lattice constant" of 0.51 nm for the structure. However, Vecchio and Williams(154) in their recent work have suggested that the apparent 5-fold symmetry exhibited by the T_2 phase may have been produced by twinning of microcrystals that make up the T_2 precipitate. They obtained a cubic structure for the phase, $a_0 = 0.40 \text{ nm}$.

In the present study of the grain boundary phase in as-cast 8090 and 8091 alloys by electron diffraction, no evidence of 5-fold symmetry has been found. The variation in intensity of the diffracted spots observed in the SADPs (Fig.4.6) could have been due to any of the factors stated in section 4.2.3. The lattice parameter of 1.035 nm obtained for the phase is close to that (1.073 nm) obtained by Smith(85) for a bcc phase he found at the grain boundaries of heat

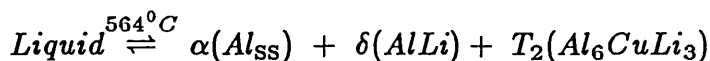
treated alloys of 8090 composition range. It is quite possible for the simple cubic structure to transform to a bcc structure of the same lattice parameter during heat treatment. However, being an equilibrium phase, it should be possible to grow sufficiently large volume fractions of the I-phase to enable x-ray studies to be conducted more easily and determine its crystal structure.

(2) The Grain Boundary Eutectic

The composition of the lamellar eutectic observed at grain boundary triple points (Fig.4.3 (a) and (b)) was determined as: 74 Al, 15 Cu, 2 - 3 Mg (wt %). BEI and SIMS showed that it contained substantially more lithium than the P1 Phase; estimated to be ≈ 8 wt % . Light and scanning electron microscopy showed that the α and P1 phases are both involved in the formation of this eutectic. However, the estimated amount of Li indicates that a third phase, rich in lithium may also be present in the eutectic. This third phase is believed to be the $\delta(AlLi)$ phase which has been identified by x-ray studies (see section 4.2.6). Also, DSC studies of the as-cast 8090 and 8091 alloys have produced evidence to support the occurrence of the invariant reaction:



which is equivalent to the reaction:



in the Al-Cu-Li ternary system. The observable effect of the substitution of Mg for Li in the T_2 phase is to lower the transformation temperature.

In his study of a cast 8090 alloy, Mukhopadhyay(102) also reported the occurrence of a lamellar eutectic involving the Al solid solution and the major grain boundary phase (P1(T)) at grain boundary triple points. He did not however report the presence of the δ phase since in the as-cast alloy, this phase can probably be observed only by x-ray diffraction (the highly reactive nature of the δ particles cause them to dissolve rapidly during the preparation of thin foil specimens for TEM studies).

Loiseau and Lapasset(84,87) have also identified a quaternary crystalline (C-) phase: 70.9 Al, 14.2 Cu, 4.5 Mg (wt %) co-existing with the I-phase at grain boundaries, in heat treated Al-Li based alloys which they investigated. They suggested that this phase is based on the ternary $R(Al_5CuLi_3)$ phase with Mg atoms substituting for Li atoms as was the case between the T_2 and the I-phases. They indexed the structure of the phase as tetragonal (NB: R-phase

is bcc with $a_0 = 1.3914$ nm, Refs.42,50). Such an intergranular C-phase was not observed in the present study of the as-cast 8090 and 8091 alloys.

(3) The Grain Boundary Particles (P2)

The precipitates (P2) which occur as large lumps, needles, or blades at grain boundaries (Fig.4.2 (b), (c) and (d)) have been identified as Al-Fe-Cu based particles formed from iron present as impurity in the cast alloys. SIMS investigation of the microstructures showed clearly that these particles do not contain lithium or any other element. The wide variations in the Fe and Cu concentrations (23 Fe, 8 Cu to 9 Fe, 16 Cu (wt %)) of the particles suggest that they are non-stoichiometric. They may indeed be considered to be based on an unstable Al_6Fe compound which becomes stable by the substitution of Cu atoms for Fe atoms to exist in the equilibrium form $Al_6(Fe, Cu)$. The measured mean atomic number (by backscattered electron imaging technique) of the particles is 18.80 which approximates the calculated value of 18.65 for the average composition: 73 Al, 15 Fe, 13 Cu (wt %). Electron diffraction analysis of the P2 phase (Fig.4.7) has shown that it has an orthorhombic structure with lattice parameters $a = 0.404$, $b = 0.455$ and $c = 0.515$ (nm). Several other investigators (85,101,102) have also identified $Al_6(Fe, Cu)$ particles in Al-Li based alloys containing > 0.04 wt % impurity iron. The Al_7Cu_2Fe phase which has also been reported to occur in some Al-Li based alloys was not found in the as-cast 8090 and 8091 alloys investigated. It may well be that the $Al_6(Fe, Cu)$ phase transforms to Al_7Cu_2Fe during heat treatment as was suggested by Smith(85) or the Al_7Cu_2Fe phase is present only in the copper-rich Al-Li based alloys such as the 2090 and 2091 alloys as was suggested by Mukhopadhyay(102).

(4)

The coarse angular precipitates (P3) which occur mainly at grain boundary triple points (Fig.4.2 (e) and (f)) have been identified as Si-rich particles formed from silicon present as impurity in the cast alloys. The composition: ≈ 54 Al, 42 Si (wt %) determined by EDX gives an Al:Si ratio of 1.29. Backscattered electron imaging showed that the particles contained a substantial amount of lithium, suggesting a stoichiometry of the form $AlSi_{1.29}Li_x$. The mean atomic number of 11.75 determined for the particles is quite close to the value of 11.81 calculated for the compound $AlSiLi$ which has previously been reported by Hanna and Hellawell(144) to exist in Al-Li alloys containing silicon. On the other hand, Degreve *et al.*(138) have also used backscattered electron imaging to characterise similar particles in an Al - 7.8 Si - 4.7 Li alloy. They obtained a mean atomic number of ≈ 12.02 for the Si-rich particles and determined the

stoichiometry as $Al_2Si_2Li_3$ in agreement with Drits *et al.*(146) and Kadaner *et al.*(162) who had previously reported the existence of this compound. Perhaps, in high Si (> 1 wt %) alloys these particles precipitate as $Al_2Si_2Li_3$ while in low Si (< 1 wt %) alloys - such as the commercial Al-Li based alloys - they precipitate as AlSiLi. Unfortunately, although the AlSiLi particles were infrequently observed in TEM, they appeared to be too thick to give a clear diffraction pattern to determine the crystal structure. A probable mechanism for the formation of the AlSiLi particles in the commercial alloys investigated is that when the silicon impurity concentration exceeds a certain level, they precipitate from the melt during solidification.

4.3.3 Coarse Matrix Precipitates

The matrix of the as-cast 8090 and 8091 alloys has been shown to be precipitated with several kinds of particles one of which is the large uniquely shaped “composite” precipitate (P4) shown in Fig.4.3 (c) and (d). The P4 particles have been shown to be rich in zirconium: ≈ 22 wt % in the core and 13 wt % in the shell. The BEI technique showed that they also contain substantial amounts of lithium. These observations are in agreement with the findings of previous investigators (Gayle and Vander Sande(25,90), Sakurai *et al.*(94) and Gregson and Flower(75)): that the Zr grain refining addition in Al-Li alloys precipitates as Al_3Zr particles with a substantial lithium incorporation to exist in the form $Al_3(Zr, Li)$. However, since the $\delta'(Al_3Li)$ precipitates are not known to exist in as-cast alloys, these $Al_3(Zr, Li)$ particles must be distinct from the composite particles which are reported to form by the precipitation of δ' on Al_3Zr particles during heat treatment of the alloys. The $Al_3(Zr, Li)$ particles identified in the present study are believed to have formed simply by Li incorporation into equilibrium Al_3Zr particles which had precipitated from the melt during solidification because of the presence in the alloys of Zr concentrations in excess of its solubility limit in Al (0.05 wt % at 500°C). The unique morphologies exhibited by the $Al_3(Zr, Li)$ particles (Fig.4.3 (c) and (e)) are difficult to explain. They are however thought to have arisen from the initial orientation of the Al_3Zr particles with the fcc Al matrix vis-a-vis the growth direction of the $Al_3(Zr, Li)$ particles (by Li incorporation).

The small spherical precipitates (P5) which are observed to be inhomogeneously dispersed in the matrix were analysed to contain ≈ 27 wt % Zr. Considering the error that may have accompanied the analysis (by EDX) of such small particles sitting in an Al matrix, it is believed that the P5 particles are largely Al_3Zr with little or no lithium incorporation.

Also observed in the matrix are the still smaller spherical particles P6 (shown dark in Fig.4.3 (f)) which have been shown to contain substantial amounts of titanium, (which is) present in the as-cast alloys as a grain refiner. In view of the high reactivity of Al with Ti, the P6 particles probably exist as Al_3Ti or some form of Al-Ti compound. The presence of Ti-rich particles would explain the origin of the titanium associated with some of the other matrix precipitates during EDX analyses (see Table 4.3).

4.3.4 Fine Matrix Precipitates

Transmission electron microscopy revealed a fine dispersion of three different precipitates in the matrix of the as-cast alloys investigated (labelled M1, M2, and M3 in Fig.4.5). The thin plates (or rods) of M1 precipitates have been shown to exhibit three different orientations with the matrix (Fig.4.5 (b)). EDX analysis showed that the composition of the M1 precipitates (62 - 70 Al, 22 - 28 Cu, 7 - 5 Mg (wt %)) is similar to that of the ternary T_2 phase (66 Al, 26 Cu, 8 Li (wt %)) or the quaternary grain boundary phase P1 (but) with a slightly reduced Mg concentration. Loiseau and Lapasset(84,87) have reported the occurrence of an intragranular (I-) phase of similar characteristics in heat treated Al-Li based alloys.

Also, the nearly spherical shape and apparently mottled appearance of the matrix M2 precipitates (Fig.4.5 (b)) correspond to the characteristics of an intragranular phase which has been reported to occur in Al-Li based alloys by Ball and Lagace(86) and Kim *et al*(79). The composition of the M2 particles (70 - 78 Al, 13 - 18 Cu, 5 - 3 Mg (wt %)) is very similar to that of the C-phase identified by Loiseau and Lapasset(84,87). It is probable that in the as-cast 8090 and 8091 alloys the C-phase forms intragranularly. However, since the M2 particles appeared to be too thick, no electron diffraction evidence could be obtained to support the view that they are the same as the C-phase.

The third matrix precipitates (M3) observed in TEM are very fine ($\approx 0.1\mu m$ in the maximum dimension) hexagonally shaped particles. EDX analysis (see section 4.2.4) showed that they contain large amounts of Si (≈ 35 wt %) and occur most commonly in those alloys which contain high concentrations of Si impurity (8090 alloy C). These observations appear to suggest that the M3 particles are either free Si crystals or Si-rich particles such as the AlSiLi observed at grain boundaries.

CHAPTER 5

MICROSTRUCTURAL CHARACTERISATION OF HEAT TREATED Al-Li BASED ALLOYS

5.1 Introduction

Aluminium-lithium based alloys rely on heat treatments to develop their optimum properties. Such heat treatments generally include homogenisation- annealing and ageing. The homogenisation process has been discussed in section 2.4.2. As stated in that section, the operating factors in the process are temperature and time. DSC studies of the as-cast 8090 and 8091 alloys (see section 4.2.7) showed that eutectic melting occurred at $\approx 541^{\circ}\text{C}$. Homogenisation of these alloys must therefore be conducted, at least initially, below this temperature in order to avoid local melting. It was shown in Fig.2.16 (a) that at a given temperature, the dissolution of second-phase precipitates is logarithmic with time so that it is of no practical benefit to extend the homogenisation time beyond a certain limit. Whilst at higher temperatures, shorter times are required to dissolve the same amount of phase. In practice, it is therefore necessary to find the optimum temperature and time that will produce the most effective dissolution of the second-phase precipitates. With the Li-containing aluminium alloys such an optimisation is indeed crucial in view of the necessity to minimize the time at high temperature during which a substantial loss of Li has been shown to occur (see section 2.4.1).

Ageing treatments for Al-Li based alloys are of utmost importance as it is during this process the strengthening phases are precipitated. Consequently, numerous studies have been (and are still being) conducted on the aged microstructures of these alloys, leading to the characterisation of the various precipitates which occur at different compositions, and ageing temperatures and times. Peel *et al.* (1, 2), Gregson and Flower (73,75), and Flower and co-workers (4,32) have established that after solution heat treatment at 530°C and quenching in room temperature water, ageing at 190°C for 24 hrs produces maximum strength in 8090 and 8091 alloys.

In the present study, the 8090 and 8091 alloys have been annealed at temperatures between 530 and 560°C for times up to 48 hrs in order to observe the effect of temperature and time on those phases which were identified in the

as-cast microstructures, and thus establish an optimum homogenisation schedule for the alloys. The aged microstructures have been investigated principally to demonstrate the co-precipitation of the strengthening phases- δ' , S' , and T_1 .

5.2 Experimental Results

5.2.1 Microstructure of Homogenised Alloys

The as-quenched microstructure of the 8090 and 8091 alloys annealed at three different temperatures: 530, 540, and 550 °C for various times: 2, 16, 24, and 48 hrs are shown in Figures 5.1 and 5.2 . They reveal that substantial changes have occurred when compared to the as-cast microstructure shown in Figs.4.1 - 4.3 . Figure 5.1 (a) shows that coring in the solid solution primary grains is eliminated after only 2 hrs at 530°C. It also shows that at this stage the eutectic at the grain boundary triple points (arrowed) has dissolved completely. This is consistent with the fact that the eutectic has the lowest solidus point. The fine dark spots visible in Fig.5.1 (a) and (e) are etching pits caused by slightly over-etching the specimen in order to improve optical contrast. Figure 5.1 (b) shows that after annealing at 530°C for 16 hrs, the major grain boundary phase (P1) has dissolved. Fig.5.1 (c) - (f) show the fully homogenised microstructure, almost completely devoid of the P1 phase. It is observed however that the coarse intermetallic phases (P2 - $Al_6(Fe, Cu)$, P3 - $AlSiLi$, P4 - $Al_3(Zr, Li)$, and P5 - Al_3Zr) identified in the as-cast microstructure have all remained undissolved. After annealing at 530°C for 24 hrs most of the P2 particles are broken down into stringers which decorate the grain boundaries (Fig.5.1 (e)). The P3 particles which are present only in the 8090 alloy C, have remained undissolved even after annealing at 550°C for 48 hrs (Fig.5.1 (c)). The dark areas in the micrograph (arrowed) are pores and cavities which have formed in the microstructure due to over-heating. Annealing at temperatures higher than 550°C for longer times produced a microstructure that is full of such pores and cavities with no effect on the phases. The Zr-rich particles P4 and P5 also remained undissolved in the homogenised microstructure. In fact, it was observed that they were slightly more widely precipitated in these alloys (Fig.5.1 (f)). The micrographs of Fig.5.1 also show that no recrystallisation of the grains occurred within the annealing temperatures and times employed.

Transmission electron micrographs of the fully homogenised (24 hrs at 530°C) and water-quenched alloys presented in Fig.5.2 do not show the coarse intermetallic particles (P2, P3, P4 and P5) which were observed in the light and scanning electron micrographs of Fig.5.1. This is because in the homogenised

alloys these particles are easily polished out during the preparation of thin foil specimens. Quite a few of the particles shown in Fig.5.2 (b) were found unevenly distributed in the matrix of the homogenised alloys. They were too thick to give clear diffraction patterns for analysis; however, EDX analysis (in the TEM) showed that they contained ≈ 42 wt % silicon. They are believed to be the Si-rich particles (M3) present in the as-cast microstructure, which have coarsened during homogenisation. The fine matrix precipitates M1 and M2 which were commonly observed in the as-cast microstructure are conspicuously absent. However, evidence for the precipitation of new phase(s) in the matrix of the homogenised alloys is given by the coherency strain contrast (arrowed) observed in the high magnification micrograph of Fig.5.2 (c), and the superlattice reflections (arrowed) which occur in the SAD patterns of the matrix. Figure 5.2 (c) also shows the presence of a few dislocations (D) - at a particle interface, and voids (V) in the as-quenched microstructure.

The results of bulk EDX analyses (in SEM) of the precipitates found in the homogenised microstructures are presented in Table 5.1. They show that the chemical compositions of most of the phases have not changed significantly during homogenisation. There is however an observable change in the Fe and Cu concentrations of the P2 phase; the latter having decreased from the 10 - 16 wt % range in the as-cast alloys to 3 - 7 wt %, while the former has increased from 23 - 8 in the as-cast alloys to 29 - 18 wt %. Also, there appears to have occurred an ≈ 2 wt % drop in the Mg content of the P1 phase while an increased Li concentration (100 - Total wt %) in the (supersaturated) Al solid solution is barely evident.

Table 5.1 Elemental composition of phases present in homogenised alloys (determined by SEM-EDX)

Phase	Element (Average composition in wt.%)							Approximate wt. % Li (by difference)	Suspected phase
	Al	Cu	Mg	Zr	Fe	Si	Ti		
α	96.4	≈ 1.0	≈ 0.6	–	–	–	–	2.0	Same as in as-cast alloys
P1	68.0	26.0	4.1	–	–	–	–	1.9	„
P2	66 - 73	3 - 7	–	–	29 - 18	1.0	–	Nil	„
P3	52.5	–	–	–	–	44.5	–	3.0	„
P4	66.0	–	–	27.0	–	–	3.3	3.7	„
P5	72.8	–	–	25.2	–	–	2.0	Nil	„

Figure 5.1 Microstructures of homogenised alloys

- (a) Light micrograph (LM) of 8091 alloy E annealed at 530°C for 2 hours showing undissolved grain boundary phase (P1).
- (b) Secondary Electron Image (SEI) of 8090 alloy A annealed at 530°C for 16 hrs showing particles of $P2 - Al_6(Fe,Cu)$ decorating grain boundaries.
- (c) LM and (d) Backscattered Electron Image (BEI) of 8090 alloy C annealed at 550 and 540 °C respectively for 48 hrs. Arrows in (c) indicate pores and cavities resulting from over-heating.
- (e) LM and (f) SEI of 8091 alloy E annealed at 530°C for 24 hrs (optimum homogenisation) showing undissolved intermetallic phase particles.

NB: All light micrographs are etched in Keller's reagent.

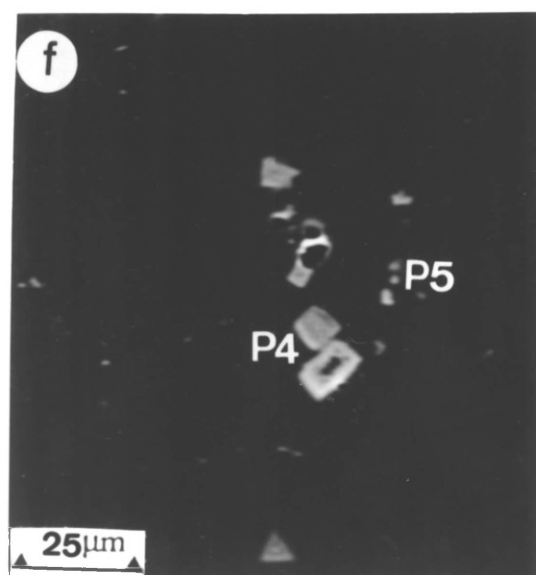
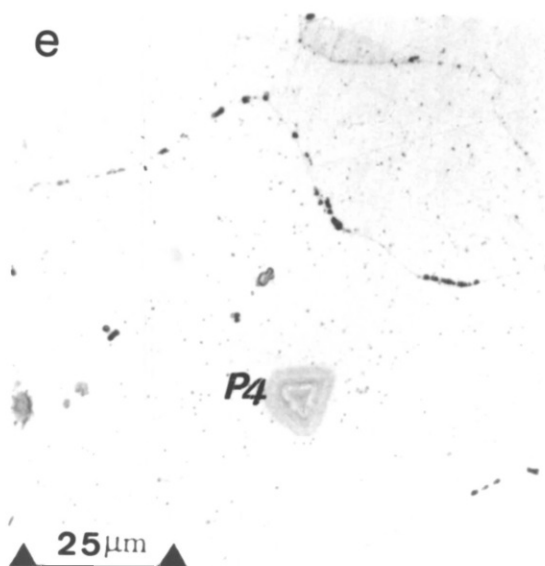
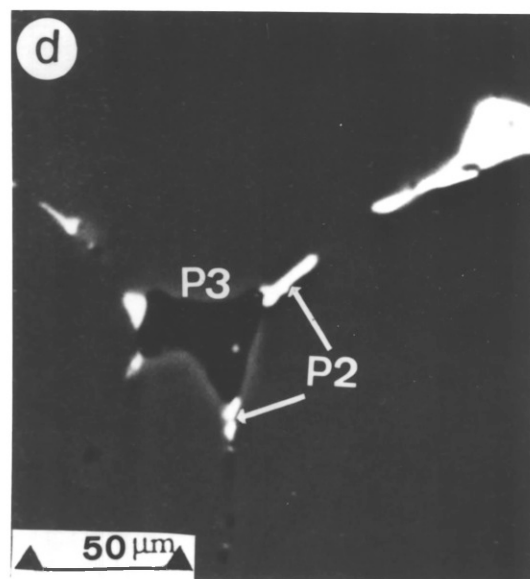
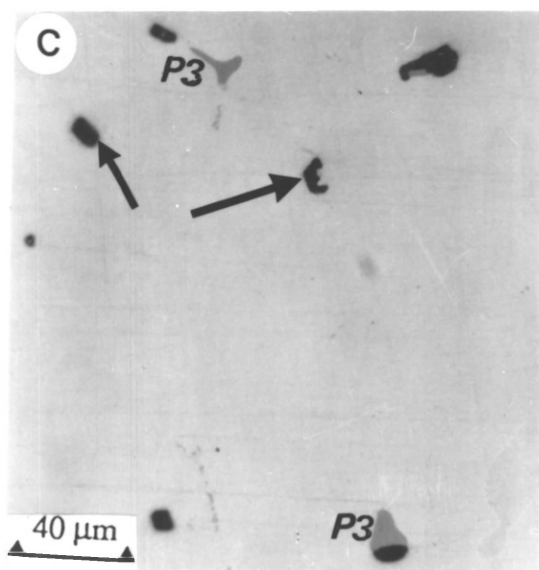
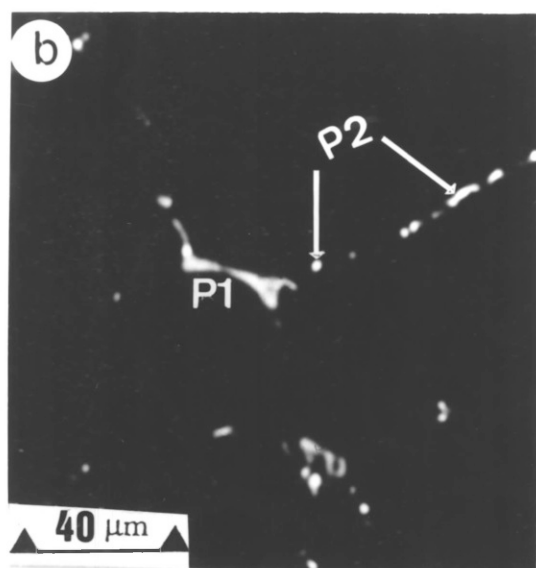
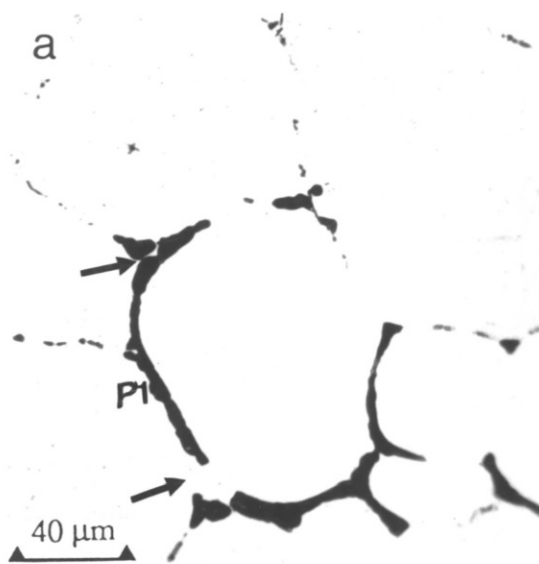
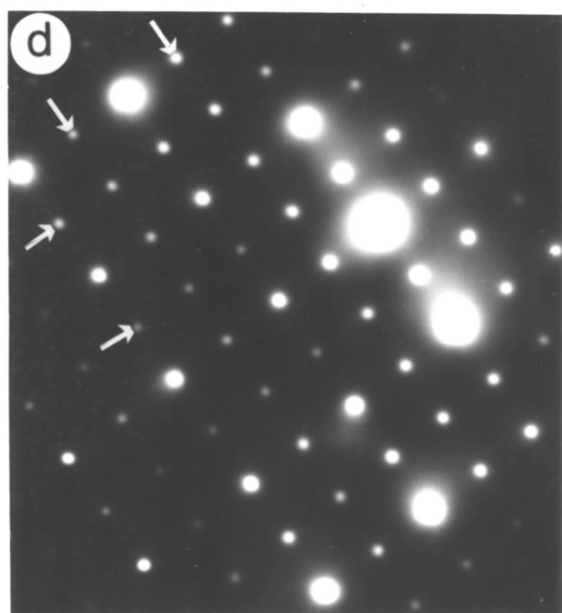
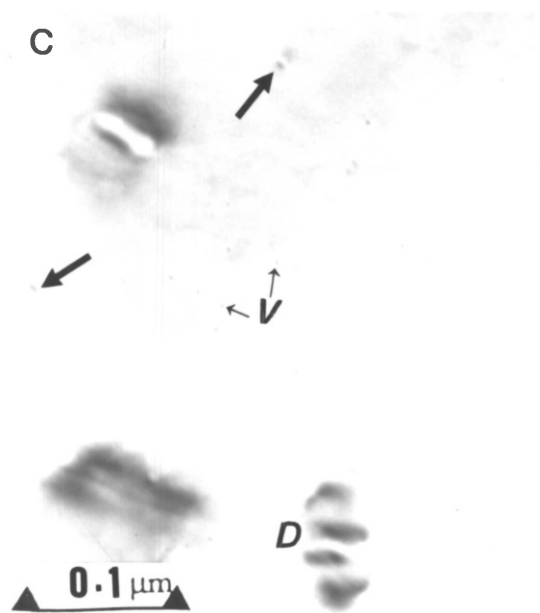
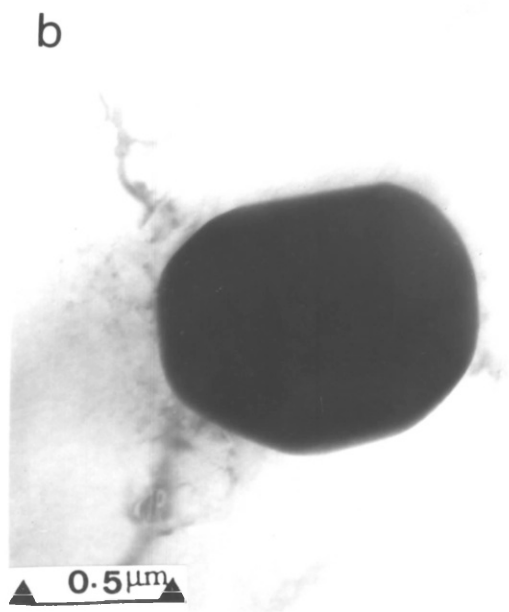


Figure 5.2 TEM of homogenised alloys

Bright Field (BF) micrographs showing (a) bend contours and (b) Si-rich particle in the matrix of 8090 alloy A after annealing at 530°C for 24 hrs and quenched in water at room temperature.

(c) High magnification BF micrograph showing coherency strain contrast (arrowed), dislocations at a particle interface (D), and voids (V) in the matrix of 8090 alloy C after undergoing the same heat treatment as in (a) and (b).

(d) SAD pattern from matrix of the same alloy showing rows of superlattice reflections (arrowed) as evidence for the precipitation of δ' particles in the as-quenched alloy. $\langle 001 \rangle_{Al}$ zone axis.



5.2.2 Microstructure of Aged Alloys

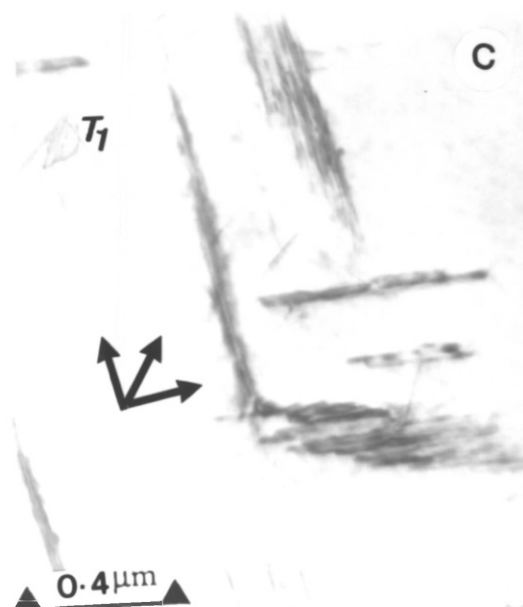
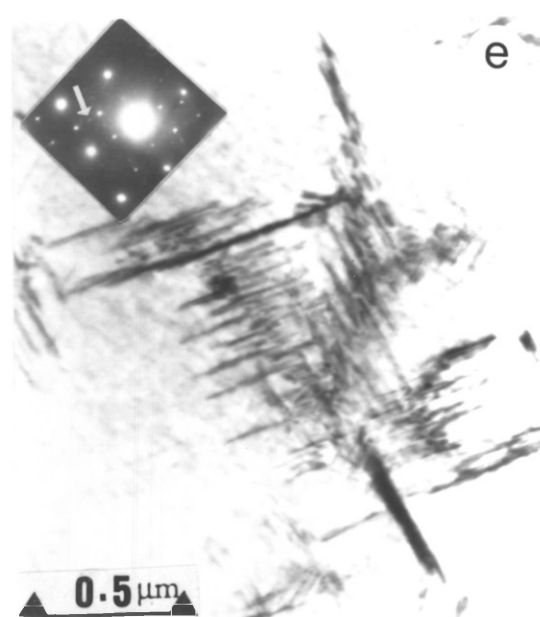
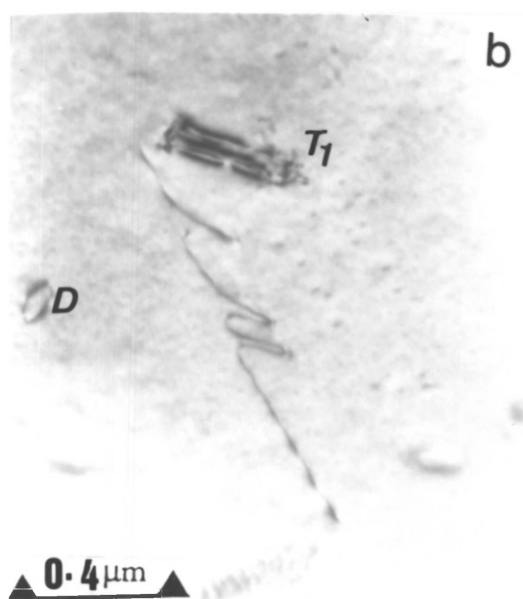
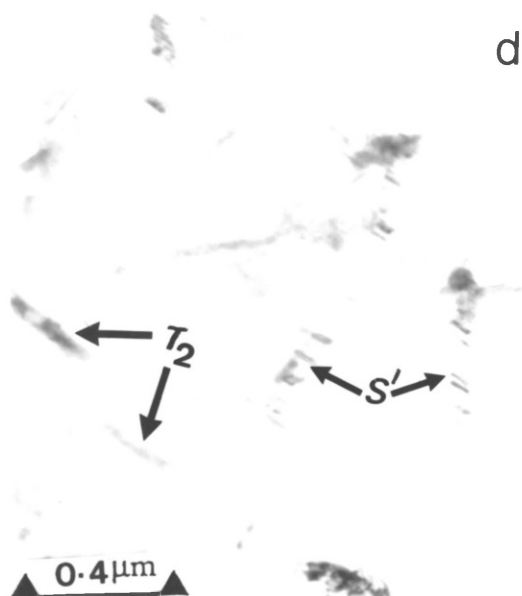
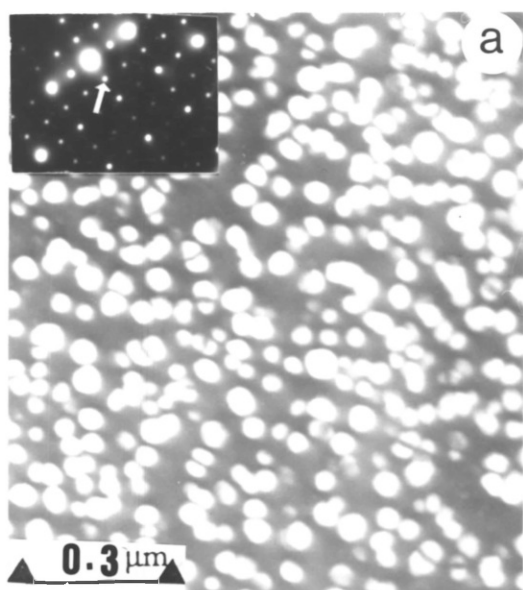
A brief study of the aged microstructure of the 8090 and 8091 alloys has been carried out. The primary purpose was to observe the microstructural evolution from the as-cast and as-quenched conditions and also to compare the results with those obtained by previous investigators.

Light and scanning electron microscopy investigation of the microstructure of the peak-aged alloy (solution heat treated at 530°C , water-quenched and aged at 190°C for 24 hrs) did not reveal any significant difference from those of the as-quenched alloys (Fig.5.1). However, transmission electron microscopy studies have revealed that some precipitation occurred during ageing.

The dark field (DF) micrograph of Fig.5.3 (a) reveals the presence of homogeneously precipitated fine $\delta'(Al_3Li)$ particles in the matrix of the peak-aged 8091 alloy E. The accompanying SAD pattern shows superlattice reflections (arrowed) due to these δ' particles. Figure 5.3 (b) - (f) show a sparse and uneven distribution of heterogeneously precipitated $S'(Al_2CuMg)$ phase and some precipitation of the hexagonal $T_1(Al_2CuLi)$ phase. The T_1 variant shown in Fig.5.3 (b) and (c) exhibits the typical stacking fault contrast observed when viewed from the $\langle 110 \rangle_{Al}$ directions. Some variants of the S' phase (two of which lie perpendicular to each other) are shown in Fig.5.3 (c); while Fig.5.3 (d) shows the characteristic corrugated sheet morphology of the S' phase which, it has been shown (156) is produced by rods of S' nucleating on several $\{210\}$ planes and simultaneously growing in the $\langle 001 \rangle_{Al}$ directions during ageing. Coarsening of the S' laths is observed in Fig.5.3 (e) which shows the microstructure of 8090 alloy C aged for a longer period of 48 hrs. Also visible in Fig.5.3 (d) are the thin-plate precipitates (M1) which were identified in the matrix of the as-cast alloys.

Figure 5.3 TEM of aged alloys

- (a) Dark Field (DF) micrograph (imaged using the $(100)\delta'$ reflection arrowed in SAD pattern) showing the homogeneously precipitated δ' particles in the matrix of the aged 8091 alloy E.
- (b) BF micrograph of the same alloy showing a T_1 precipitate exhibiting stacking fault contrast, and a dislocation loop and helix. $\langle 110 \rangle$ Al directions.
- (c) BF micrograph of the same alloy showing variants (arrowed) of heterogeneously precipitated S' phase and a T_1 precipitate.
- (d) BF micrograph showing the corrugated sheet morphology of the $[210]$ S' variants, and some $M1$ (T_2) precipitates in the matrix of the same alloy as in (a). $\langle 100 \rangle$ Al zone axis.
- (e) BF micrograph showing coarsening of the S' rods into laths in an 8090 alloy C aged for 48 hrs at 190°C .
- (f) DF of (e) imaged using the (112) S' reflection arrowed in SAD pattern. $\langle 001 \rangle$ Al zone axis.



5.2.3 DSC Studies of Heat Treated Alloys

Differential scanning calorimetry studies of the heat treated alloys have been carried out in order to obtain information about phase transformations that may have taken place during the process and to correlate such information with microstructural evidence obtained in earlier studies.

Figure 5.4 shows the DSC traces for (a) 8090 alloy A and (b) 8091 alloy D which have been annealed at 530⁰C for 24 hrs (fully homogenised condition) and quenched in ambient temperature water. In view of the unavoidable time lag between preparing the specimens and start of the DSC analyses, the alloys had undergone a certain amount of natural ageing. As with the as-cast alloys, the traces for the 8090 and 8091 alloys are apparently identical. By super-imposing the DSC traces of the as-quenched alloys on those of the as-cast alloys (Fig.4.12) several new features are readily observed. These are:

A - a slight exotherm occurring between 78 and 125 ⁰C with the peak at 105⁰C

B - an endotherm occurring between 238 and 290 ⁰C with the lowest point at 260⁰C

C - a broad exotherm occurring between 320 and 395 ⁰C with the peak at 360⁰C

D - a very broad endotherm occurring between 400 and 508 ⁰C

In addition, there are the large endothermic troughs F ($\approx$ 640⁰C) which represent melting of the alloys and the small endotherm E occurring at 544⁰C in Fig.5.5 (b) which is caused by melting of residues of the equilibrium grain boundary phase (P1) which have been shown to be present in the homogenised 8091 alloys. It should be noted that the temperatures given above have been adjusted downwards by 12⁰C which, according to earlier studies in section 4.2.7 is the amount by which the recorded experimental temperatures differ from the real transformation temperatures.

Phase transformations in quaternary Al-Li based alloys are necessarily complex and overlapping of transformation temperatures is very probable. Also, thermal fluctuations during the experiment may render weak transformations particularly those occurring at low temperatures undiscernible. These factors make interpretation of the DSC traces rather difficult. However, knowledge of the precipitation in these alloys gained from microstructural studies would suggest that:

- (1) the exothermic reaction A represents coarsening of the δ' precipitates which were formed upon quenching the supersaturated alloy
- (2) the endothermic reaction B represents dissolution of the δ' precipitates as the alloy is heated continually (the δ' solvus has been determined as 270°C by previous investigators)
- (3) the exothermic reaction C represents formation of the S' phase
- (4) the broad endothermic reaction D represents dissolution of the S' phase as the alloy is heated continually.

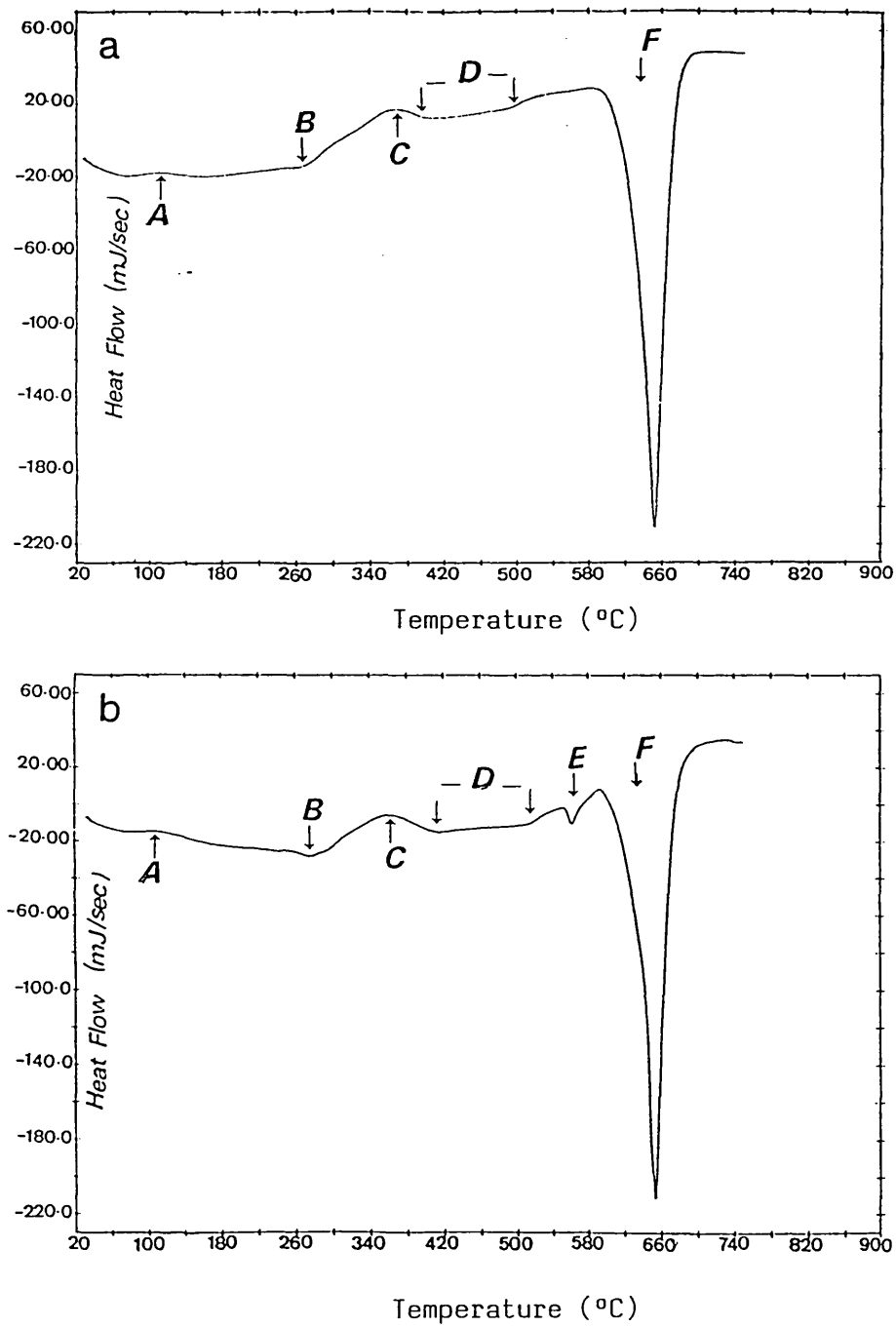


Figure 5.4 DSC traces for (a) 8090 alloy A and (b) 8091 alloy D annealed at 530°C for 24 hrs.

5.3 Discussion

5.3.1 Homogenisation Behaviour of the Second-Phase Precipitates

The results of the present investigation have shown that annealing the 8090 and 8091 alloys at 530°C for up to 24 hrs produces the greatest effect of homogenisation i.e elimination of microsegregation (coring) in the solid solution grains and dissolution of coarse equilibrium phases without causing adverse effects such as incipient melting to the microstructure. However, it was shown that residues of the dominant grain boundary phase P1 were left undissolved (particularly in the 8091 alloys) and all of the coarse intermetallic particles (P2, P3, P4 and P5) were retained in the microstructure even after annealing at 550°C for up to 48 hrs. It was shown also that the morphologies and compositions of the P3, P4 and P5 phases were the same as in the as-cast alloys. Although a change in the composition of the P2 - $Al_6(Fe, Cu)$ particles (increased Fe and reduced Cu concentrations) was observed, it does not suggest a transformation of the phase to Al_7Cu_2Fe as was reported by Smith (85) and Sperry (159). What is clear however is that at high temperature Cu atoms are being rejected from the phase and replaced by Fe atoms - a reversal of the process by which (as was proposed in section 4.3.2) the $Al_6(Fe, Cu)$ particles were formed during solidification. No recrystallisation of the solid solution grains occurred during the annealing of these alloys. It is not known if the presence of these intermetallic particles played any role in this as was suggested by some investigators (61).

The observed reduction in Mg content of the P1 phase seems to suggest that this element was being rejected from the phase during the homogenisation process. This seems to be a reversal of the process by which the P1 phase was formed during solidification i.e. by incorporation of Mg into the T_2 phase. The Mg so rejected would have been taken into the Al solid solution.

The presence of coarse intermetallic particles in the thermally processed alloy (as has been demonstrated here) is likely to have a significant adverse effect on the mechanical properties of the final product.

5.3.2 Precipitation in the Solid State

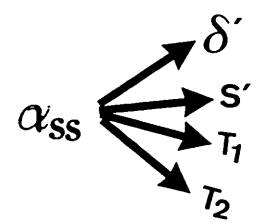
The results of TEM investigation of the as-quenched and aged 8090 and 8091 alloys are in general accord with the work of previous investigators (1,4, 32,73,102) on heat treated Al-Li based alloys.

The presence of submicroscopic δ' particles in the as-quenched microstructure is evident both from the superlattice reflections in SADPs and the existence of the δ' coarsening and dissolution peaks in DSC traces of the as-quenched alloys. This is in agreement with the results of recent studies on the precipitation mechanism of the δ' phase (28,102). The lattice parameter of the fcc δ' particles was determined as 0.404 nm. The dark field micrograph of Fig.5.3 (a) shows the homogeneously precipitated δ' phase in the matrix of the aged 8091 alloy E.

The results of the present study showed clearly that the as-quenched microstructure of the 8090 and 8091 alloys contained very few quenched-in defects such as dislocation loops and helices. In their study of similar alloys, Gregson and Flower and Co-workers (32,73,74) and more recently Ozbilen (158) have shown that this situation is due to the strong binding of the Li atoms to the quenched-in vacancies (Li-vacancy binding energy = 0.26 eV, Ceresara *et al.* (21) in Al-Li binary alloys) which prevents condensation of the vacancies to form dislocation loops and helices. The obvious result of the low density of dislocation loops and helices in the as-quenched microstructure is the sparse and heterogeneous precipitation of the S' phase which habitually nucleates on such defects during ageing of the alloy. The nucleation and growth mechanisms of the S' precipitates have been extensively studied by several researchers including Hardy and Silcock (67,68), Bagaryatskii (70), Lorimar (40), Weatherly (157), Wilson and Partridge (156), and Flower and co-workers (32,73,74).

The T_1 precipitates found in the alloys investigated appear to have formed via the mechanism proposed by Noble and Thompson (19) and supported by Gregson and Flower (4) i.e. dissociation of the matrix dislocations into Shockley pairs, followed by solute (Cu and Li) enrichment of the intrinsic stacking faults. Hence the stacking fault contrast observed in the precipitates (Fig.5.3 (b) and (c)). This result is consistent with the fact that the Cu:Li ratio in these alloys is low (< 1) and the G.P. zones on which the T_1 phase would otherwise have nucleated are absent.

Thus, the co-precipitation of homogeneous δ' and heterogeneous S' and T_1 phases in the microstructure of the aged 8090 and 8091 alloys has been clearly demonstrated in the present study. In addition, it has been shown that the T_2 - based thin-plate precipitates (M1) which were identified in the as-cast alloys are also present in the aged microstructure. The solid state precipitations in these alloys may therefore be summarised as:



The coherency strain contrast observed in the as-quenched microstructure of the alloys (Fig.5.2 (c)) most probably indicates precipitation of the metastable $\beta'(Al_3Zr)$ dispersoid particles.

CHAPTER 6

AN INVESTIGATION OF PHASE EQUILIBRIA IN QUATERNARY Al-Cu-Mg-Li ALLOYS

6.1 Introduction

In the previous two chapters, a systematic characterisation of the microstructure of 8090 and 8091 alloys in both the as-cast and heat treated conditions was carried out. The results of that study revealed that the major second-phase precipitate (P1) in the as-cast alloys is a quaternary Al-Cu-Mg-Li phase which forms a ternary eutectic with the $\alpha(\text{Al}_{\text{ss}})$ and $\delta(\text{AlLi})$ phases at grain boundary triple points. Whilst in the heat treated alloys, the solid state precipitation included binary $\delta'(\text{Al}_3\text{Li})$, ternary $T_1(\text{Al}_2\text{CuLi})$ and $S'(\text{Al}_2\text{CuMg})$, and a quaternary T_2 - based (M1) phase.

The presence of quaternary phases implies that the phase equilibria occurring in these alloys can no longer be adequately represented as a combination of those which occur in ternary Al-Cu-Li and Al-Cu-Mg alloys, as has been the past practice. There is therefore a clear need to further investigate the phase equilibria which exist within the quaternary Al-Cu-Mg-Li system.

In this chapter, the results of a study of the phases present in a number of Al-Cu-Mg-Li alloys in both the as-cast and heat treated conditions are presented. The compositions of the alloys (F - J in Table 3.1) have been selected specifically to fall within the $\alpha(\text{Al})$ - δ - S or $\alpha(\text{Al})$ - δ - S - T phase field, with approximately the same amount of lithium as is present in the commercial 8090 and 8091 alloys. Thus, permitting an investigation of the effect of the presence of lithium on the phase equilibria within the fairly well-understood Al-Cu-Mg system, as well as providing some knowledge of the quaternary phase diagram. The results of the study are discussed in the context of the available data on the constituent ternary systems and an attempt has been made to establish phase fields for the alloys within the quaternary Al-Cu-Mg-Li system.

6.2 Alloy Compositions (excluding Li contents) and Their Predicted Equilibrium Solidification Paths

The compositions of the experimental alloys (excluding Li contents) are shown on the liquidus projection of the ternary Al-Cu-Mg system given in Figure 6.1. Assuming zero solid solubility within the phases, the predicted equilibrium solidification sequences for the zero-lithium alloys are as follows:

Alloy F

The primary solidification product in this alloy would be the Al solid solution (α) phase. As solidification proceeds, the liquid composition reaches the $\alpha + S$ binary eutectic (which precipitates out) and continues down the eutectic valley to the lowest point it can reach on the liquidus surface, either on the $\alpha + S$ binary line or the $\alpha + S + T$ ternary point, where solidification would be completed. However, lack of knowledge of the solidus surface prevents a prediction of the exact point where solidification is completed.

Alloy G

The primary solidification product in this alloy is shown to be the S phase. This would be followed by the $\alpha + S$ binary eutectic and probably the $\alpha + S + T$ ternary eutectic. However, it is not possible to predict the exact point where solidification is completed without knowledge of the solidus surface.

Alloy H

This alloy is positioned on the $\alpha + S$ tie line. The primary solidification products would be a mixture of these two phases. Again, solidification may be completed on the $\alpha + S$ eutectic line or at the $\alpha + S + T$ ternary eutectic point.

Alloy I

The primary solidification product in this alloy is clearly the α (Al) phase; from where solidification would proceed to the $\alpha + S$ binary eutectic and probably the $\alpha + S + T$ ternary eutectic.

Alloy J

The primary solidification product in this alloy is $\alpha(\text{Al})$; this would be followed by the $\alpha + \text{S}$ eutectic and probably the $\alpha + \text{S} + \text{T}$ ternary eutectic.

The predicted equilibrium solidification sequences of the alloys are compared with those obtained from experimental studies of the Li-containing quaternary alloys in section 6.4.3. It should be noted however, that in practice, the solidification of these alloys is unlikely to occur under equilibrium conditions and deviations from the predicted sequences are very probable.

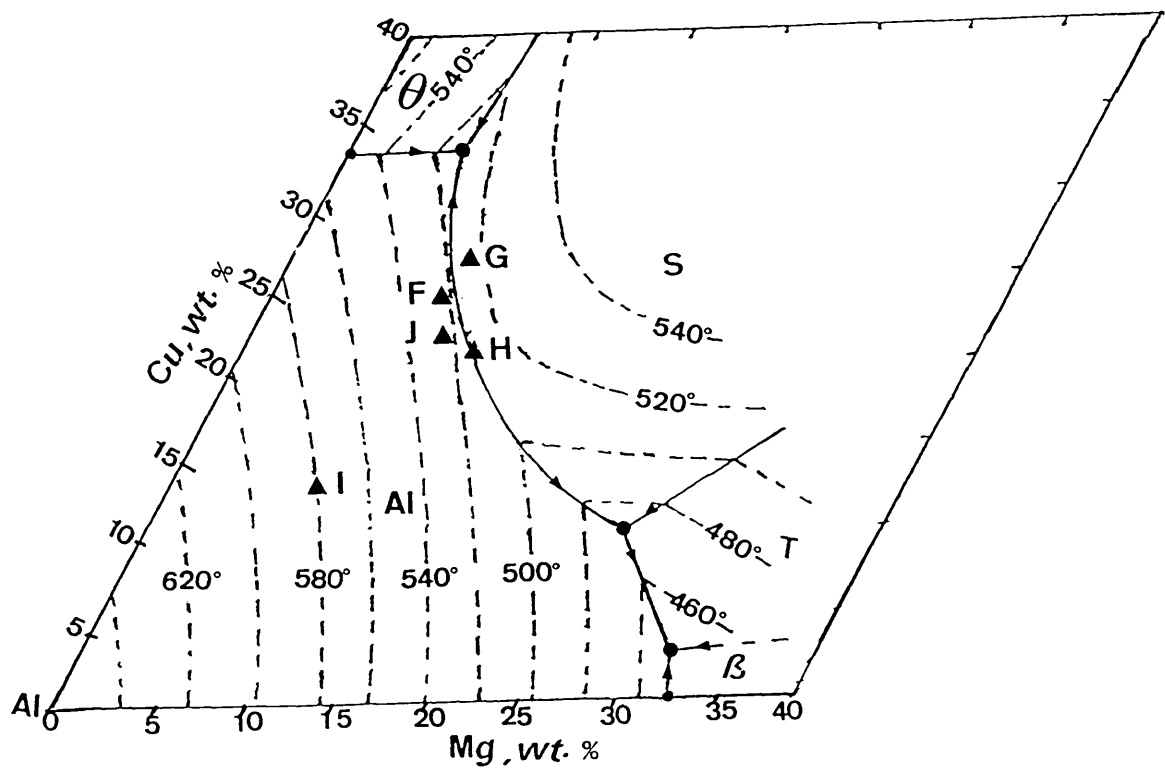


Figure 6.1 The liquidus projection of the Al-Cu-Mg system (after Brommelle and Phillips, 65): showing the compositions (excluding Li contents) of the experimental alloys.

6.3 Experimental Results

6.3.1 Metallography, SEM and EDX Analyses

The results of metallographic and scanning electron microscopy studies, and EDX analyses of the phases present in the as-cast and heat treated Al-Cu-Mg-Li alloys are presented in the micrographs of Figures 6.2 - 6.6, and in Tables 6.1 - 6.6.

Alloy F

Figure 6.2 (a) - (c) show micrographs of the as-cast alloy F (composition: 1.5 Li, 24.5 Cu, 9.1 Mg, 64.5 Al (wt %)). The microstructure consists of a large blocky primary phase F1 (dark in LM, bright in SEM) which also occurs in a secondary form, a coarse phase F2 (bright in LM, dark in SEM) which forms a binary eutectic with the secondary form of F1, a phase F3 (grey in LM, very bright in SEM) which forms a ternary eutectic with F1 and F2, and a fine binary eutectic with F2.

EDX analyses of the elemental compositions of the phases and of the binary and ternary eutectics are given in Table 6.1. An estimation of the amount of lithium present in each of the phases (obtained by subtracting the total weight per cent of all elements analysed from 100) is also given in Table 6.1. As was stated in Chapter 4, this procedure is a convenient way to indicate the presence (or absence) of Li in a phase and does not give the actual amount of Li contained in the phase.

The composition of the F1 phase (both primary and secondary forms) is very similar to that of the ternary S phase ($\approx$ 38 Al, 45 Cu, 17 Mg (wt %)) but there is a strong indication of Li presence too. The composition of the F2 phase shows that it is a solid solution of Cu, Mg (and Li) in aluminium. The F3 phase was too small to be analysed with reasonable accuracy but the high intensity contrast it exhibits in SEM (Fig.6.2 (c)) suggests that it contains more of the higher atomic number element (Cu) than any of the other phases.

DSC studies of the as-cast alloy F (see section 6.3.5) showed that the first melting occurred at $\approx$ 518°C. This alloy was therefore annealed at 510°C for various times in order to observe any changes in the microstructure and compositions of the phases which may result. Figure 6.2 (d) shows the microstructure of the alloy after annealing at 510°C for 24 hours and quenching in water. Some

coarsening of the phases involved in the eutectics is seen to have taken place. Figure 6.2 (e) and (f) show the microstructure of the same alloy after 72 hrs at temperature. Coarsening of the eutectics is now more clearly demonstrated. Furthermore, it is observed that the ternary eutectic involving the F1, F2 and F3 phases has decomposed, leading to a microstructure which consists of well-defined and separate regions of F1 + F2 and F2 + F3 eutectics.

The results of EDX analyses of the elemental compositions of the phases present in the annealed alloy are given in Table 6.6. It is shown that ≈ 5 wt % reduction in the Cu content of the F1 phase has occurred. It is thought that most of the Cu atoms so rejected have gone into the growth (by coarsening) of the F3 phase which can now be analysed to have a composition very similar to that of the ternary S phase with little or no Li incorporation.

The observed decrease in Li content of the F2 phase may suggest that precipitation of Li-rich phases (e.g. $\delta'(Al_3Li)$) has occurred by dissociation of the supersaturated solid solution upon quenching the alloy. However, the phases which are observed in the annealed alloy by light and scanning electron microscopy are believed to be essentially the same as those present in the as-cast alloy F.

Alloy G

The difference in composition between alloys F and G (2.0 Li, 26.3 Cu, 9.4 Mg, 62.1 Al (wt %)) is that the latter is slightly richer in solutes (especially Cu and Li) than the former. Figure 6.3 (a) - (d) show micrographs of the as-cast alloy G. It is observed that the microstructure is very similar to that of as-cast alloy F; consisting essentially of the large blocky primary phase G1, the coarse phase G2 which forms a binary eutectic with (the secondary form of) G1, and the G3 phase which forms a ternary eutectic with G1 and G2, and binary eutectic with G2. However, the volume fractions of the various phases and eutectics appear to be different as compared to the case in alloy F. Firstly, an increased precipitation of the G3 phase is evident. This has resulted in a higher volume fraction of the G2 + G3 eutectic which is generally coarser in this alloy than in alloy F. Secondly, the G1 phase is observed to occur largely in the primary (large blocky) form, at the expense of the secondary form. This has resulted in the formation of lower volume fractions of both the binary and ternary eutectics in which the coarse G1 phase is involved.

The elemental compositions of the phases given in Table 6.2 confirm that they are the same as those which occur in the as-cast alloy F.

Figure 6.3 (e) and (f) show the microstructure of alloy G after annealing at 500°C for 24 hrs and quenched in water. Again coarsening of the binary eutectics and decomposition of the ternary eutectic is shown to have taken place. The results of EDX analyses of the elemental compositions of the phases are given in Table 6.6. The reduction in the Cu content of the G1 phase is much greater (≈ 8 wt %) in this alloy than in the annealed alloy F. However, it still appears as if the same phases are present in both the as-cast and annealed alloy G.

Alloy H

Alloy H (composition: 2.1 Li, 21.2 Cu, 11.8 Mg, 64.8 Al wt %) contains more Mg (and Li), and less Cu than alloys F and G. Figure 6.4 (a) - (c) show micrographs of the as-cast alloy H. The microstructure appears to consist of three phases: H1 - the large blocky primary phase which also exists in the secondary form (dark in LM, brightish in SEM), H2 - the Al solid solution phase which forms a binary eutectic with the secondary H1 phase, and H3 - the coarse phase (darker in LM than the H1 secondary phase) which forms a binary eutectic with H2.

The elemental compositions of the phases are given in Table 6.3. The H3 phase is shown to have a wide range of composition which, in general, is similar to that of the ternary T (≈ 43 -50 Al, 22-27 Cu, 30-27 Mg (wt %)) phase. The H1 phase appears to have a composition between those of the ternary S and T phases (but more towards that of S). There is also an indication of the incorporation of a significant amount of Li into this phase. The Al solid solution (H2) phase in this alloy contains much more Mg (≈ 7 wt %) than in the previous alloys. This is consistent with the higher Mg level in this alloy.

The microstructure of alloy H after annealing at 500°C for 24 and 72 hrs is shown in Fig.6.4 (d) and 6.4 (e) and (f) respectively. Progressive coarsening of the eutectics is evident and after 72 hrs the microstructure appears to consist largely of a binary eutectic. The results of EDX analyses (given in Table 6.6) show that the phases involved in this eutectic are the H1(secondary) and H2 phases.

Alloy I

Alloy I (composition: 2.4 Li, 13.3 Cu, 7.0 Mg, 77.0 Al (wt %)) was made up to have approximately the same composition as the ternary eutectic identified in the as-cast alloy F (see Table 6.1). This was done in order to study, in more detail, the characteristics of the phases involved in that eutectic. Figure 6.5 (a) and (b) show micrographs of the as-cast alloy I. The microstructure is seen to be different from those of the previous alloys. The primary phase (I1) is the Al solid solution phase (bright in LM, dark in SEM) which forms the matrix. There are also: a coarse phase I2 (dark brown in LM, very bright in SEM), and fine precipitates of a third phase I3 (grey in LM, greyish in SEM). All the phases are involved in some sort of eutectic with each other.

The elemental compositions of the phases and of the eutectics are given in Table 6.4. The I2 phase is shown to have a wide range of composition but considering the small size of the precipitates, this may be due to parts of the adjoining phases being picked up during EDX analysis. The I3 phase was too small to be analysed.

Figure 6.5 (c) and (d), and 6.5 (e) and (f) show the microstructure of alloy I after annealing at 500°C for 72 hrs and 30 days respectively. It is observed in both cases that the fine I1 + I3 eutectic has completely dissolved and a greater precipitation and coarsening of the I2 phase has occurred, making the alloy a fairly homogeneous two-phase mixture. The elemental compositions of the phases given in Table 6.6 show that the I2 phase is based on some Al-Cu-Mg ternary phase, probably with some Li incorporation.

Alloy J

Alloy J (composition: 2.1 Li, 22.6 Cu, 10.0 Mg, 65.2 Al (wt %)) was made up to have approximately the same composition as the fine binary eutectic identified in the as-cast alloy F (see Table 6.1). The microstructure of the as-cast alloy J shown in Fig.6.6 (a) and (b) consists of the large blocky primary phase J1 (which also exists in a secondary form), the Al solid solution phase J2 which forms a binary eutectic with the J1 (secondary) phase, and a phase J3 (grey in LM, brightish in SEM) which forms a binary eutectic with J1 and a ternary eutectic with J1 and J2. The volume fraction of the large blocky J1 phase is observed to be higher than in alloy F, G or H.

The results of EDX analyses given in Table 6.5 show that the elemental composition of the J1 phase is close to that of the S phase. There is also an indication of the presence of Li in this phase. The J3 phase was too small to be analysed by EDX in the SEM. The compositions of the eutectics are also given in Table 6.5.

Figure 6.6 (c) - (f) show the microstructure of alloy J after annealing at 500°C for 72 hrs. It is observed that apart from the presence of the blocks of J1, the microstructure consists largely of a binary eutectic of J2 and J1 (secondary) which has coarsened during annealing. The composition of the phases in the annealed alloy (given in Table 6.6) show that they are essentially the same as those in the as-cast alloy J.

Figure 6.2 Microstructure of as-cast and heat treated alloy F

(a) light micrograph (Keller's etch), (b) and (c) secondary electron images showing the phases present in the as-cast alloy.

(d), (e) and (f) light micrographs (Keller's etch), showing microstructure of the same alloy after annealing at 510°C for 24hrs (d) and 72hrs (e) and (f).

(See Tables 6.1 and 6.6 for description and elemental compositions of the phases).

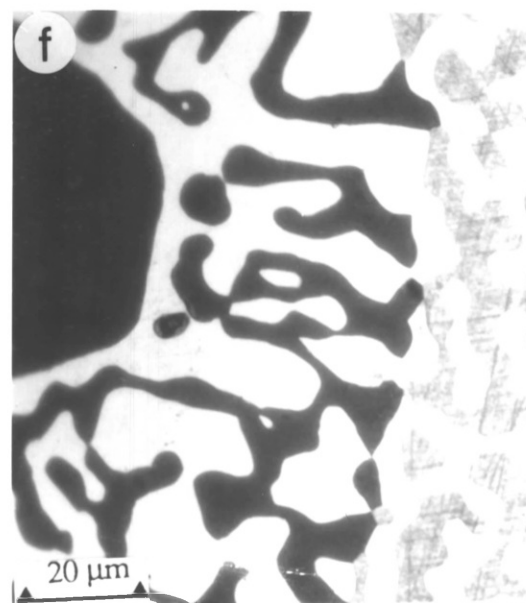
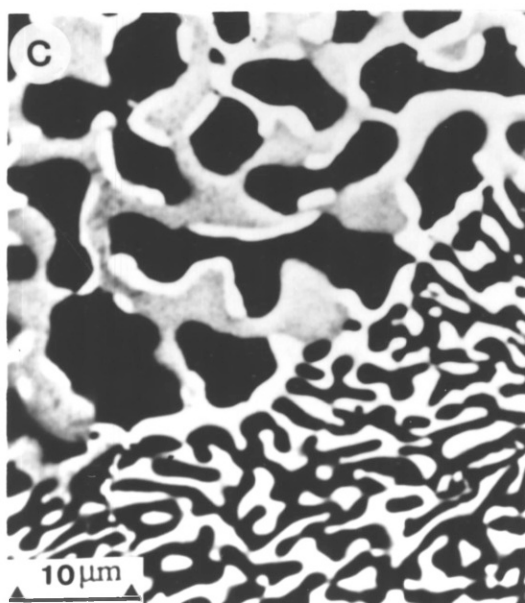
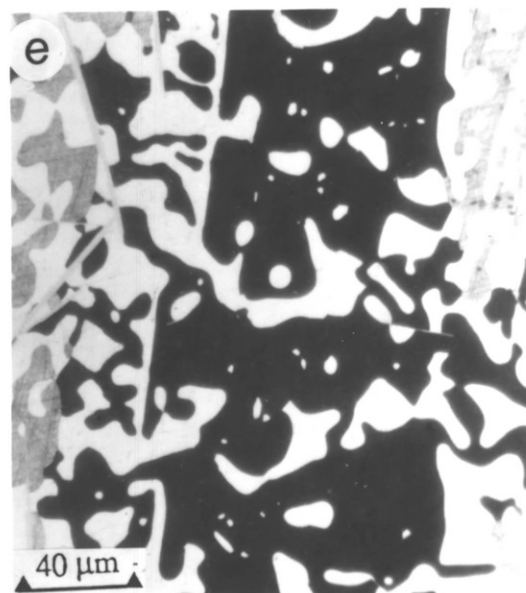
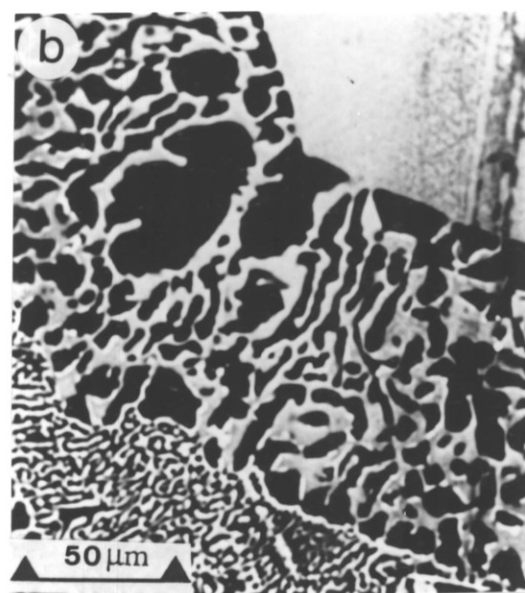
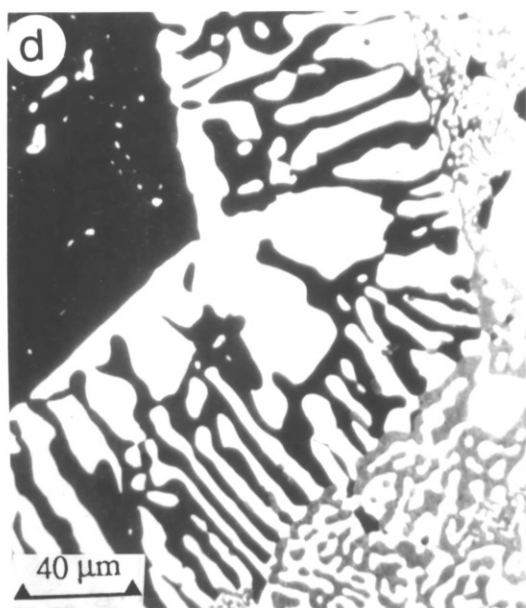
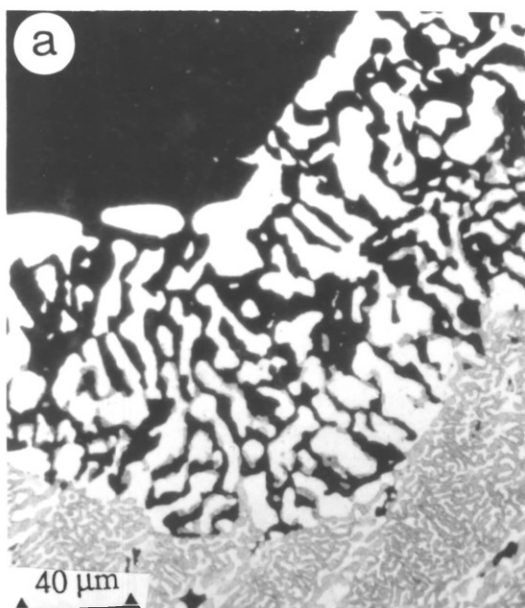


Figure 6.3 Microstructure of as-cast and heat treated alloy G.

Light micrographs (a) as polished (b) Keller's etch showing the phases present in the as-cast alloy

(c) and (d) backscattered electron images of the as-cast microstructure

(e) and (f) light micrographs (Keller's etch) showing microstructure of the same alloy after annealing at 500°C for 24 hrs

(See Tables 6.2 and 6.6 for description and elemental composition of the phases).

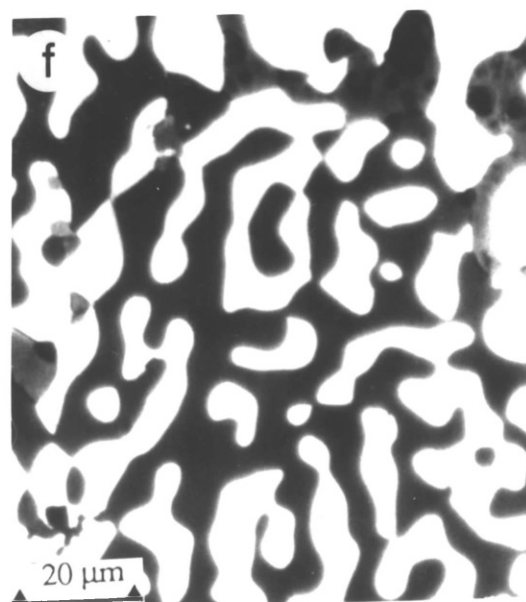
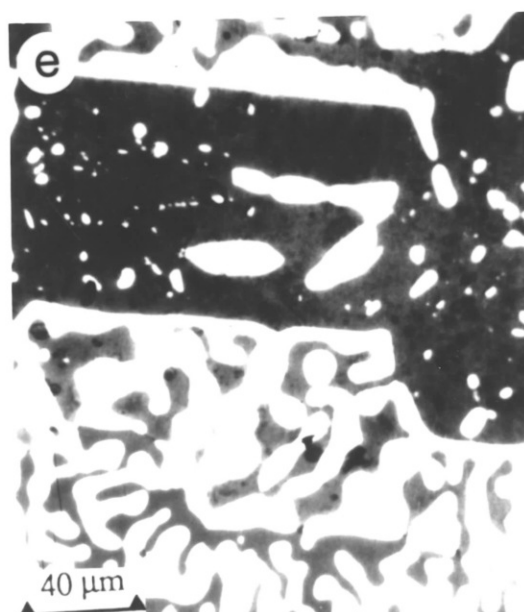
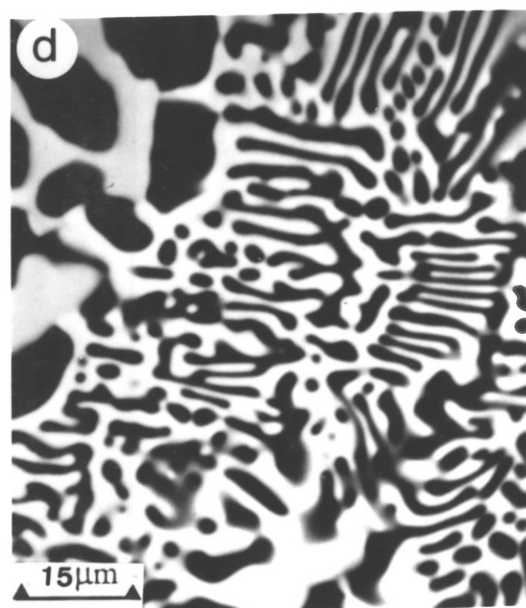
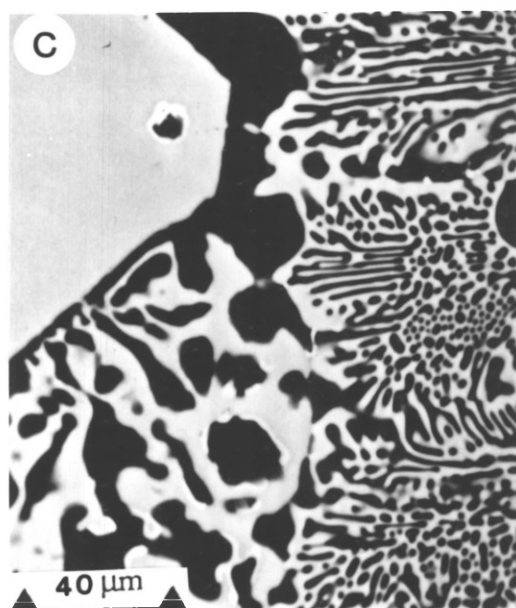
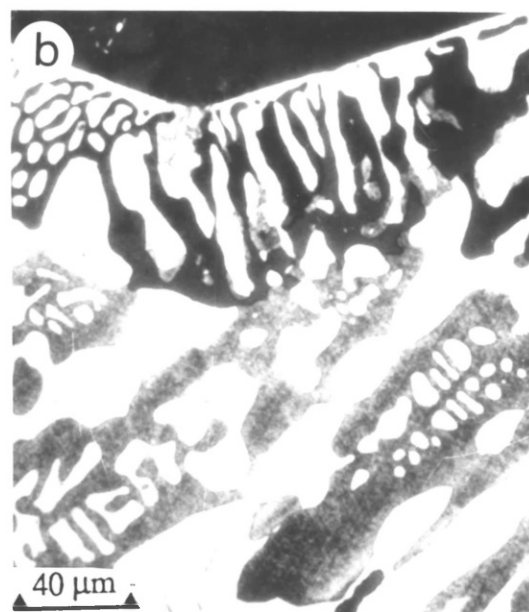
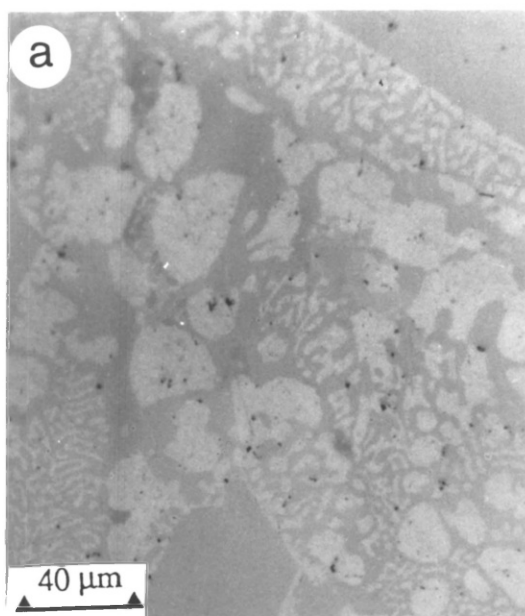


Figure 6.4 Microstructure of as-cast and heat treated alloy H.

(a) and (b) light micrographs (Keller's etch) and (c) SEI showing the phases present in the as-cast alloy.

(d) light micrograph (Keller's etch) showing microstructure of the alloy after annealing at 500°C for 24hrs and quenched in water.

(e) LM (Keller's etch) and (f) SEI, showing microstructure of the alloy after 72 hrs at 500°C.

(See Tables 6.3 and 6.6 for description and elemental compositions of the phases).

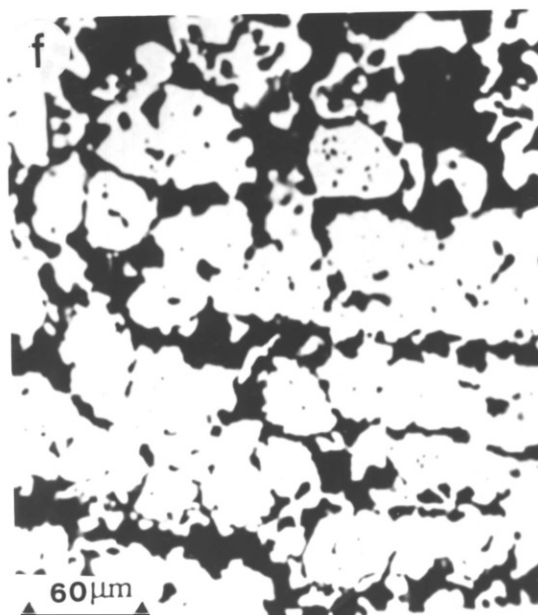
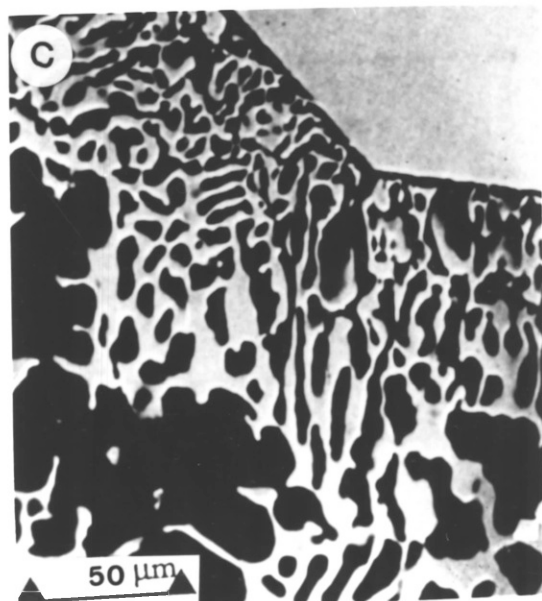
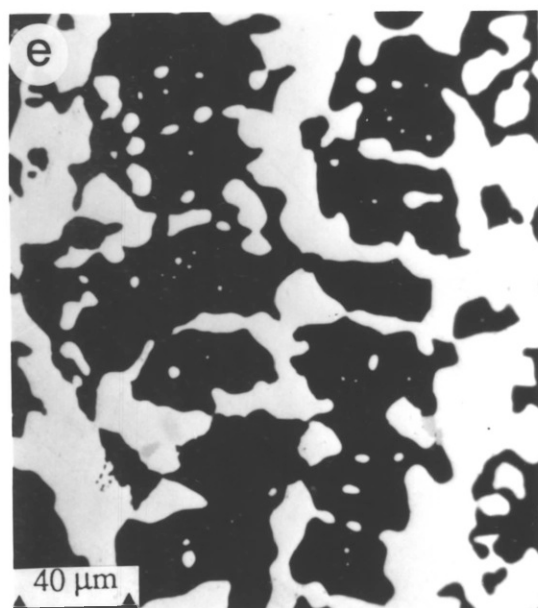
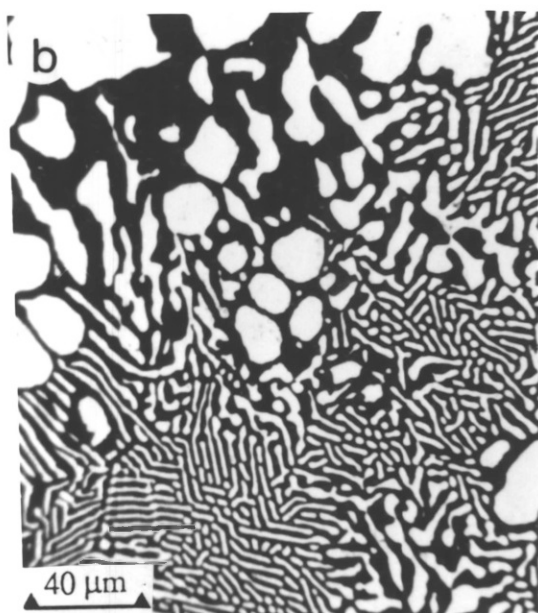
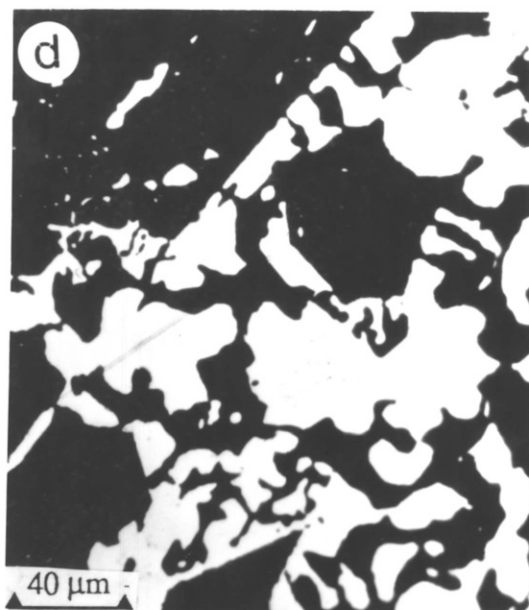
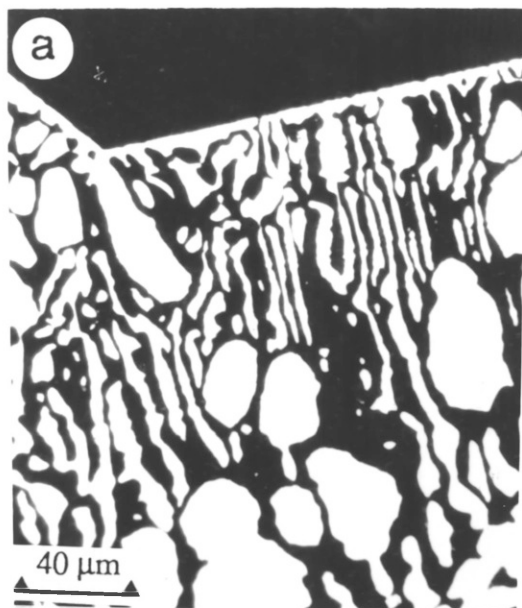


Figure 6.5 Microstructure of as-cast and heat treated alloy I

(a) LM (Keller's etch), (b) SEI showing phases present in the as-cast alloy.

(c) LM (Keller's etch), (d) SEI showing the binary eutectic structure of the alloy after annealing at 500°C for 72hrs.

(e) LM (Keller's etch), (f) SEI showing microstructure of the same alloy after 30 days of annealing.

(See Tables 6.4 and 6.6 for description and elemental compositions of the phases).

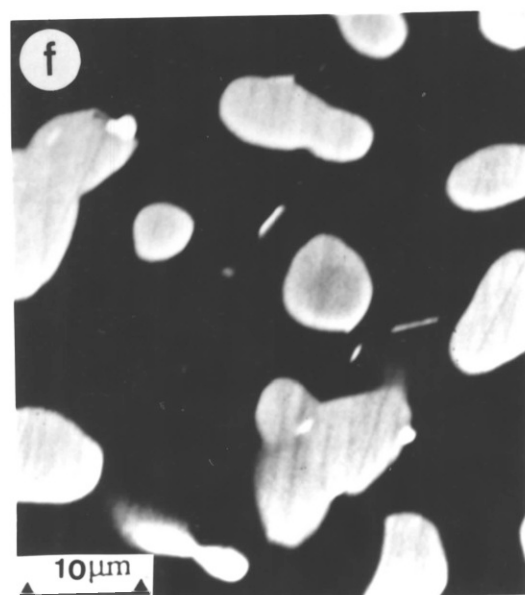
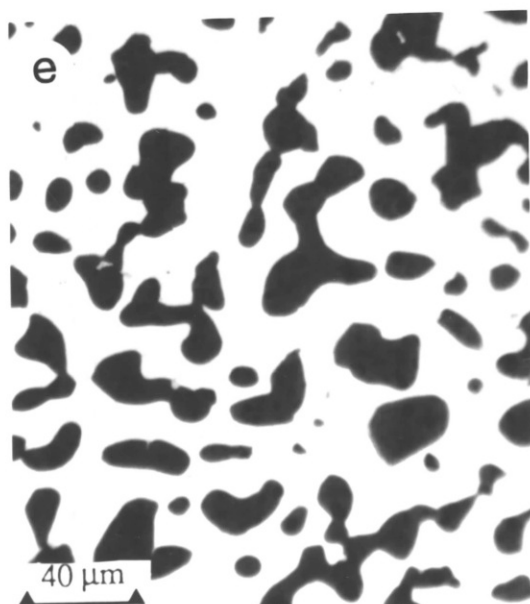
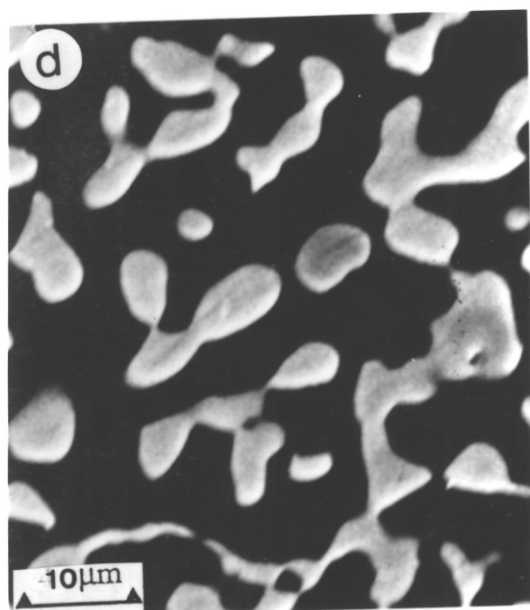
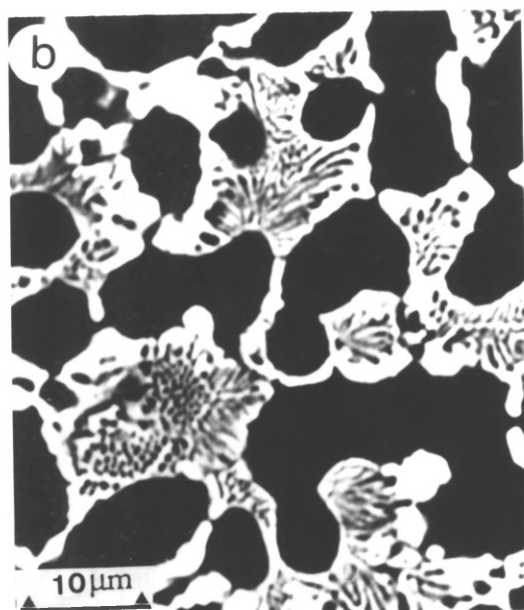
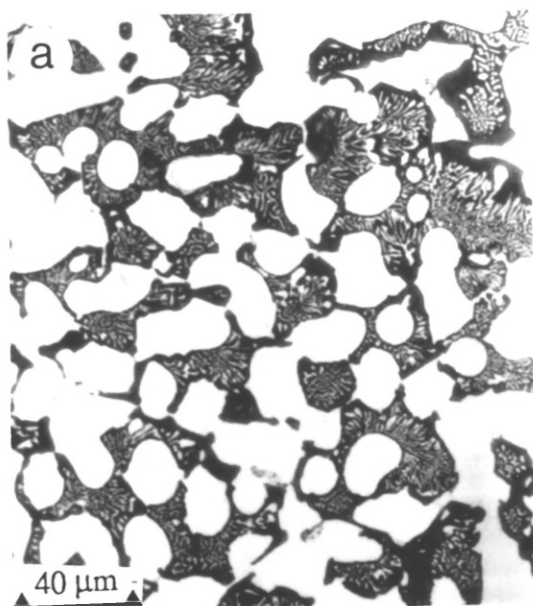


Figure 6.6 Microstructure of as-cast and heat treated alloy J.

(a) LM (Keller's etch), (b) SEI showing phases present in the as-cast alloy.

(c) and (e) LM (Keller's etch), (d) and (f) SEI showing microstructure of the same alloy after annealing at 500°C for 72hrs and quenched in water.

(See Tables 6.5 and 6.6 for description and elemental compositions of the phases).

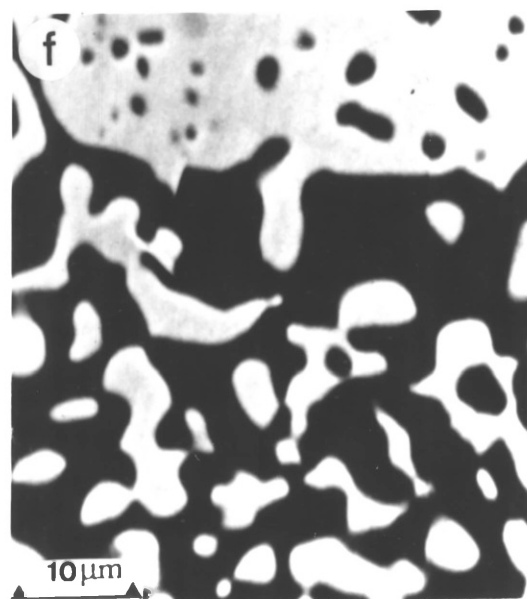
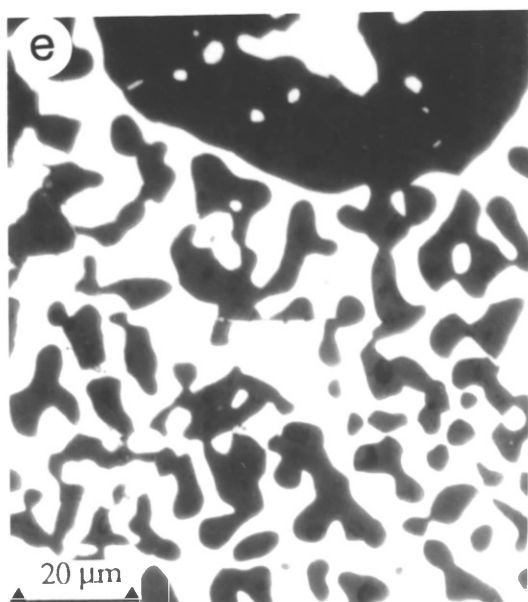
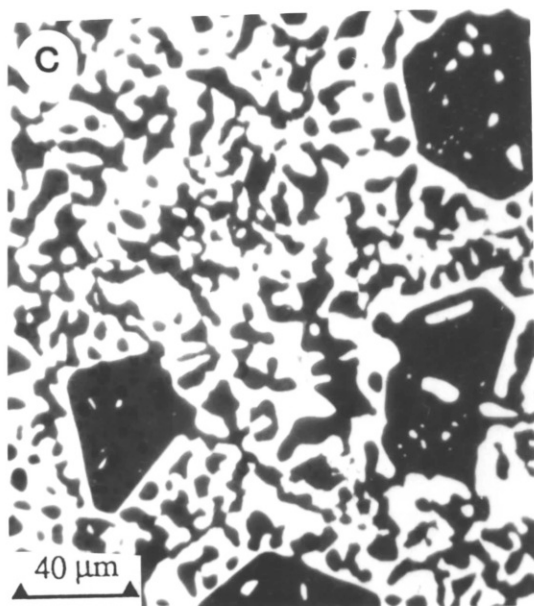
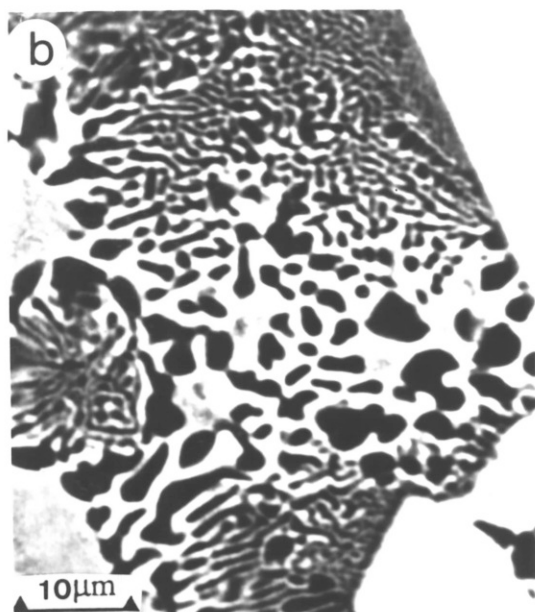
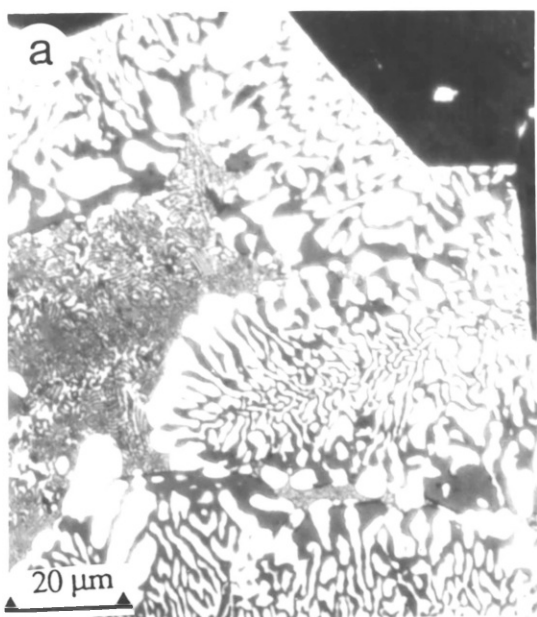


Table 6.1 Characteristics and elemental composition of phases in as-cast alloy F.

Morphology	Appearance in		Average Elemental Composition (wt. %)				Stoichiometry	Probable Phase
	LM (Keller's)	SEM	Al	Cu	Mg	Li (by difference)		
F1 Primary (large blocks) and secondary forms	Dark	Bright	38.7	46.4	14.3	1.3 - 1.8	$\text{Al}_{2.2}\text{Cu}_{1.2}\text{Mg}_{1.0}$	S(Al_2CuMg) based phase with Li incorporation
F2	Bright	Dark	91.5	3.0	2.5	~ 3.0	--	Al solid solution
F3	Grey	Very bright	Not analysed				--	--
Ternary eutectic: F1 + F2 + F3	--	--	79.7	12.7	5.3	~ 2.3	--	--
Binary eutectic: F2 + F3	--	--	61-64	24-25	9-10	~ 2.0	--	--

Table 6.2 Characteristics and elemental composition of phases in as-cast alloy G.

Morphology	Appearance in		Average Elemental Composition (wt. %)				Stoichiometry	Probable Phase
	LM (Keller's)	SEM	Al	Cu	Mg	Li (by difference)		
G1 Primary (large blocks) and secondary forms	Dark	Bright	38.1	46.2	14.2	~ 1.7	$\text{Al}_{2.4}\text{Cu}_{1.3}\text{Mg}_{1.0}$	S(Al_2CuMg) based phase with Li incorporation
G2	Bright	Dark	90.7	3.8	2.3	~ 3.2	--	Al solid solution
G3	Brownish	Bright	Not analysed				--	--
Ternary eutectic: G1 + G2 + G3	--	--	,,				--	--
Binary eutectic: G2 + G3	--	--	,,				--	--

Table 6.3 Characteristics and elemental composition of phases in as-cast alloy H.

Morphology	Appearance in		Average Elemental Composition (wt. %)				Stoichiometry	Probable Phase
	LM (Keller's)	SEM	Al	Cu	Mg	Li (by difference)		
H1 Primary (large blocks) and secondary forms	Dark	Bright	43.3	36.0	17.4	~ 3.3	$\text{Al}_{2.4}\text{Cu}_{0.9}\text{Mg}_{1.0}$	Al-Cu-Mg based phase with Li incorporation
H2	Bright	Dark	89.0	1.4	7.0	~ 2.6	--	Al solid solution
H3	Dark	Brightish	43.5	17-30	26-34	Nil	$\text{Al}_{5.5}\text{CuMg}_4$	T phase
Binary eutectic: H2 + H3	--	--	71-73	14-16	12-14	~ 1.0	--	--
Binary eutectic: H2 + H1	--	--	69.4	17.5	12.2	~ 1.0	--	--

Table 6.4 Characteristics and elemental composition of phases in as-cast alloy I.

Morphology	Appearance in		Average Elemental Composition (wt. %)				Stoichiometry	Probable Phase
	LM (Keller's)	SEM	Al	Cu	Mg	Li (by difference)		
I1 Primary phase	Bright	Dark	91.4	3.0	2.7	~ 2.9	--	Al solid solution
I2 coarse particles	Dark brown	Bright	57-66	18-34	7-16	~ 1.5	--	Al-Cu-Mg based phase with Li incorporation
Coarse eutectic: I1 + I2	--	--	67-72	17-21	6-7	-	--	--
Fine eutectic: I1 + I2 + I3	--	--	65.7	21.1	9.4	-	--	--

Table 6.5 Characteristics and elemental composition of phases in as-cast alloy J.

Morphology	Appearance in		Average Elemental Composition (wt. %)				Stoichiometry	Probable Phase
	LM (Keller's)	SEM	Al	Cu	Mg	Li (by difference)		
J1 Primary (large blocks) and secondary forms	Dark	Bright	43.5	41.4	13.5	~1.6	$\text{Al}_{2.9}\text{Cu}_{1.2}\text{Mg}_{1.0}$	Al-Cu-Mg based phase with Li incorporation
J2	Bright	Dark	91.5	3.9	2.6	~2.0	--	Al - solid solution
J3	Grey	Brightish	Not analysed				--	--
Ternary eutectic J1 + J2 + J3	--	--	70.7	20.6	8.2	~1.0	--	--
Binary eutectic: J2 + J3	--	--	61.1	27.7	11.2	~1.0	--	--

Table 6.6 Elemental composition of phases in heat treated alloys

Alloy/ Heat Treatment	Phase	Elemental composition (wt %)			
		Al	Cu	Mg	Li (by difference)
F annealed at 510 ⁰ C for 72 hrs	F1	40.8	41.5	16.8	1 - 2
	F2	92.7	3.5	2.5	≈ 1.5
	F3	38-42	44.8	17.0	Nil
G annealed at 500 ⁰ C for 24 hrs	G1	41.9	39.0	16.8	≈ 2.3
	G2	91.0	3.8	2.4	≈ 2.5
	G3	-	-	-	-
H annealed at 500 ⁰ C for 72 hrs	H1	42.6	35.9	18.9	≈ 2.6
	H2	89.0	2.3	5.7	≈ 3.0
	H3	43.4	36.6	18.8	≈ 1.0
I annealed at 500 ⁰ C for 72 hrs	I1	93.5	2.9	1.3	≈ 2.3
	I2	44.5	40.3	13.3	≈ 1.9
	I1 + I2	78.0	15.4	4.5	≈ 2.0
I annealed at 500 ⁰ C for 30 days	I1	93.5	3.8	1.0	≈ 2.4
	I2	43.7	42.3	13.3	≈ 1.0
	I1 + I2	78.1	15.2	4.5	≈ 2.2
J annealed at 500 ⁰ C for 72 hrs	J1	43.1	42.2	14.8	≈ 1.0
	J2	92.6	3.5	2.4	≈ 1.3
	J2 + J3	70.1	22.7	6.2	≈ 1.0

6.3.2 Secondary Ion Mass Spectroscopy

The SIMS technique was used to determine the distribution of the elements, particularly of lithium, in the microstructure of the Al-Cu-Mg-Li alloys under investigation. Selected areas of the microstructure were imaged to produce ion micrographs of the various elements. The intensity exhibited by an element (relative to that due to the other elements) is a measure of its concentration in the particular area of the microstructure being imaged.

The ion micrographs of Figure 6.7 show the distribution of the elements (Al, Li, Cu, and Mg) in an area of the microstructure of as-cast alloy F. By comparing the intensities of the elements in the various micrographs, the following observations can be made:

- (a) the F1 phase (both primary and secondary forms) contains significant amounts of Li in addition to high concentrations of Cu and Mg
- (b) the F2 Al solid solution phase contains a substantial amount of Li but very little Cu or Mg
- (c) the F3 phase (greyish in Fig.6.7 (a)) contains almost no Li but very high concentrations of Cu and Mg.

These observations are in agreement with the results of EDX analyses of the phases given in Table 6.1.

Figure 6.8 shows ion micrographs imaged from an area of the microstructure of the as-cast alloy H. The distribution of the elements in the phases follows a trend similar to that observed in alloy F. The presence of significant amounts of Li in the H1 phase is clearly demonstrated. The Al solid solution phase (H2) is also shown to contain a substantial amount of Li but probably less than in alloy F. The ion micrographs also reveal that the coarse phase (H3) contains very little or no lithium. They also show that the H1 phase contains less Cu and more Mg than the equivalent F1 phase in alloy F.

The elemental distribution in the microstructure of as-cast alloy I is shown in the ion micrographs of Figure 6.9. They show that the coarse phase I2 (dark in Fig.6.9 (a)) contains a significant amount of Li. The Al solid solution primary phase (I1) is also shown to contain some Li, probably a little more than in the I2 phase. The I3 phase is shown to contain high concentrations of Cu and Mg.

Figure 6.10 show the distribution of the elements in the microstructure of as-cast alloy J. Here (as in alloys F and H) the J1 phase (both primary and secondary forms) is shown to contain significant amounts of the lithium. The J3 phase (grey in Fig.6.9 (a)) which forms a eutectic with the Al solid solution phase (J2) is shown to contain very little or no lithium.

Figure 6.11 shows concentration profiles of the elements obtained by laterally scanning (across) an area of the microstructure of as-cast alloy H. The sections of the profiles which correspond to different phases in the microstructure are labelled in Fig.6.11. For example, section A showing low Li and high Cu and Mg concentrations corresponds to the H3 phase; section B showing high Li, low Mg and still lower Cu concentrations corresponds to the Al solid solution phase H2; while section C showing high Li, Cu and Mg concentrations corresponds to the H1 phase.

Figure 6.7 SIMS: Ion micrographs showing distribution of elements in the microstructure of as-cast alloy F.

(a) light micrograph (Keller's etch)

Ion micrographs:

(b) $^{27}\text{Al}^+$

(c) $^7\text{Li}^+$

(d) $^{63}\text{Cu}^+$

(e) $^{24}\text{Mg}^+$

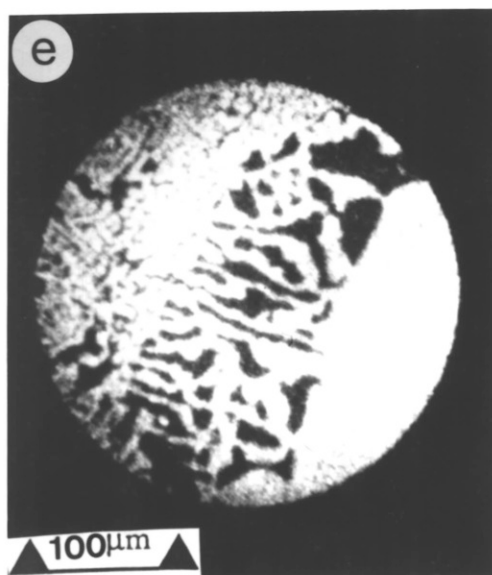
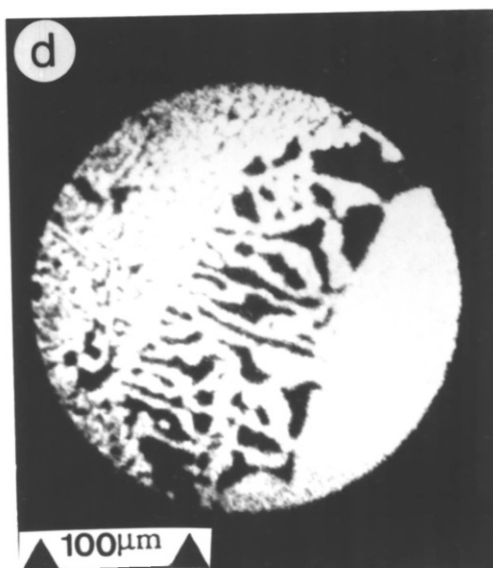
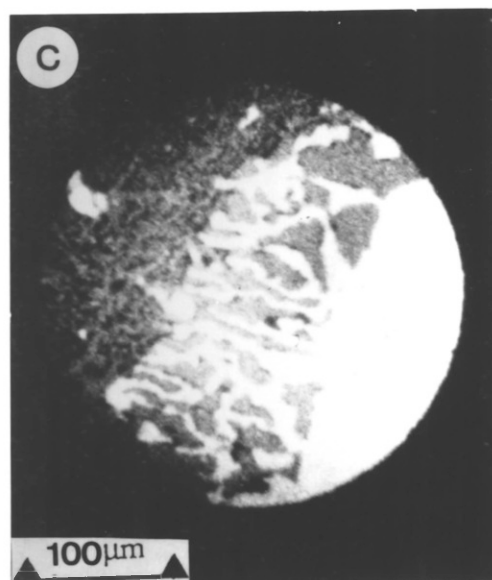
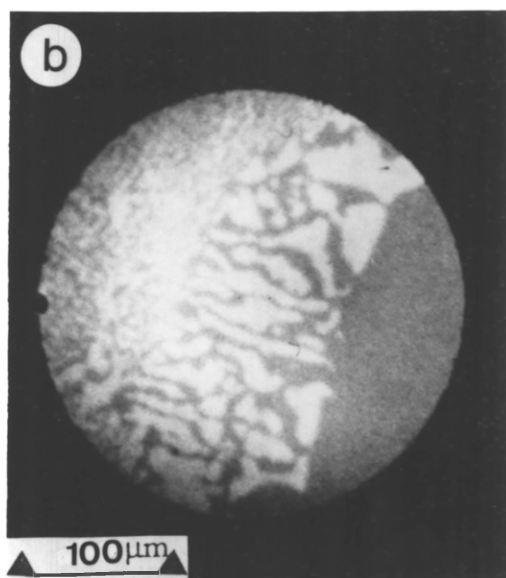
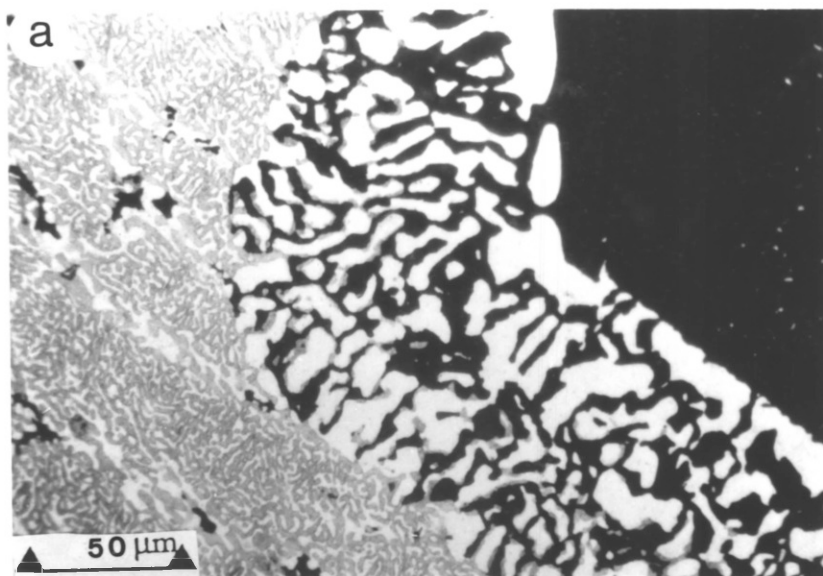


Figure 6.8 SIMS: Ion micrographs showing distribution of elements in the microstructure of as-cast alloy H.

(a) light micrograph (Keller's etch)

Ion micrographs:

(b) $^{27}\text{Al}^+$

(c) $^7\text{Li}^+$

(d) $^{63}\text{Cu}^+$

(e) $^{24}\text{Mg}^+$

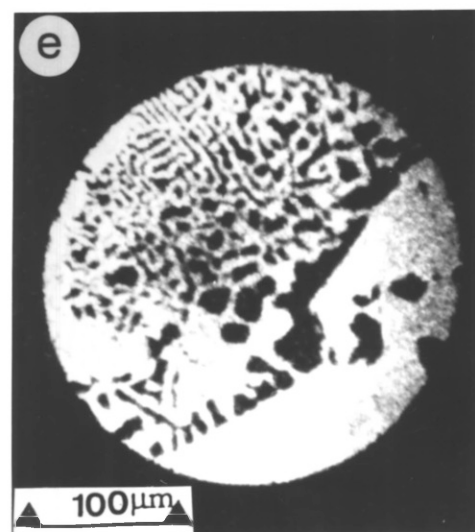
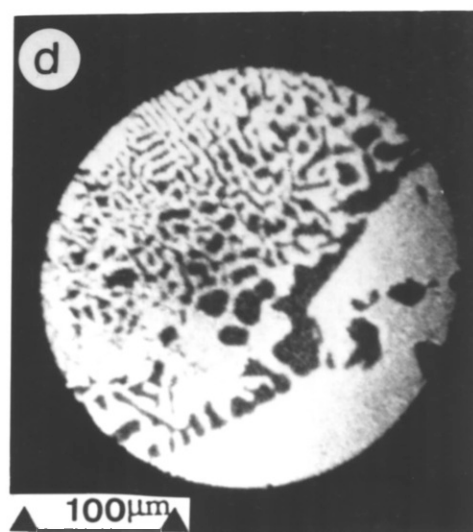
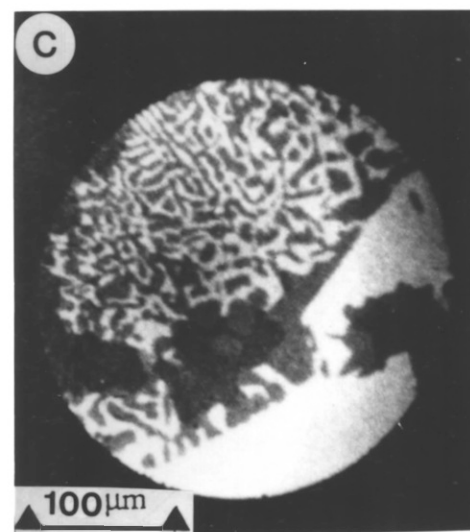
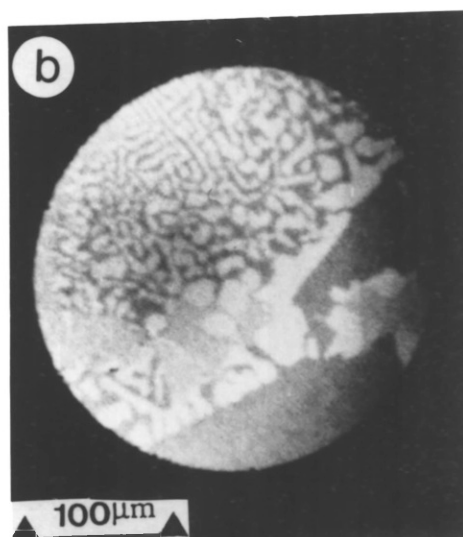
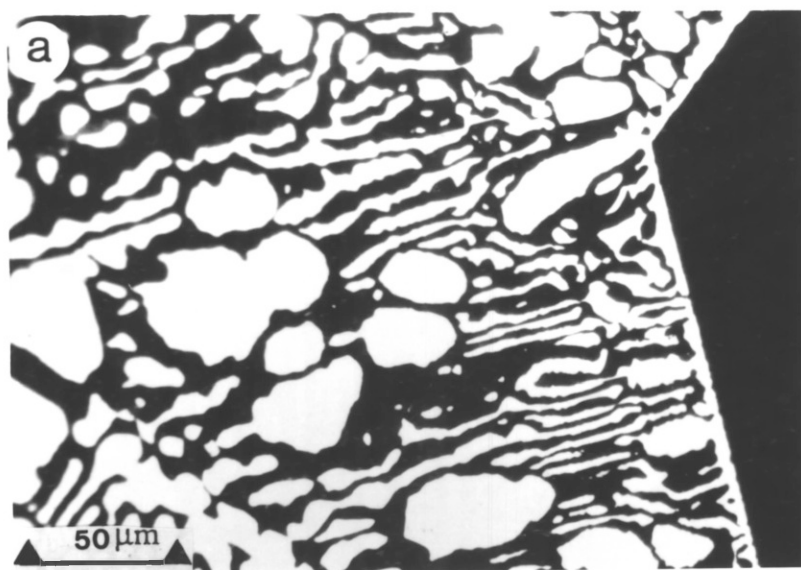


Figure 6.9 SIMS: Ion micrographs showing distribution of elements in the microstructure of as-cast alloy I.

(a) light micrograph (Keller's etch)

Ion micrographs:

(b) $^{27}\text{Al}^+$

(c) $^7\text{Li}^+$

(d) $^{63}\text{Cu}^+$

(e) $^{24}\text{Mg}^+$

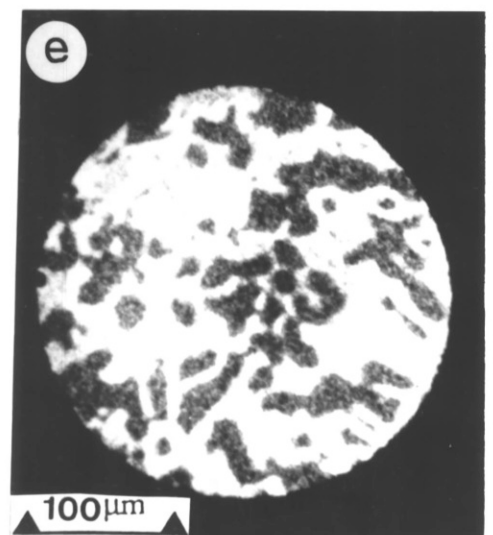
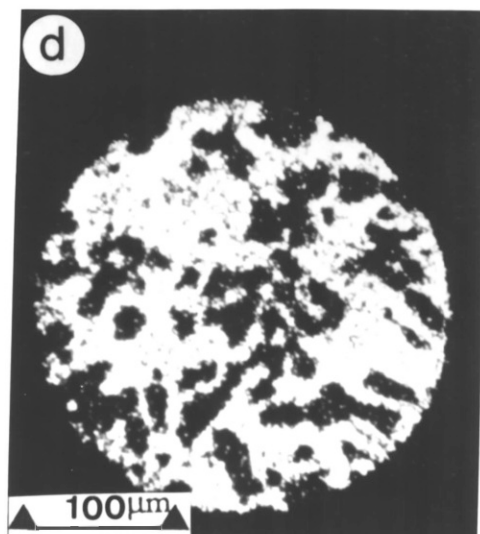
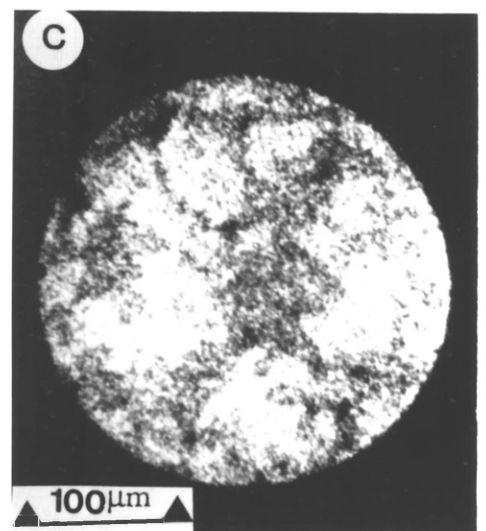
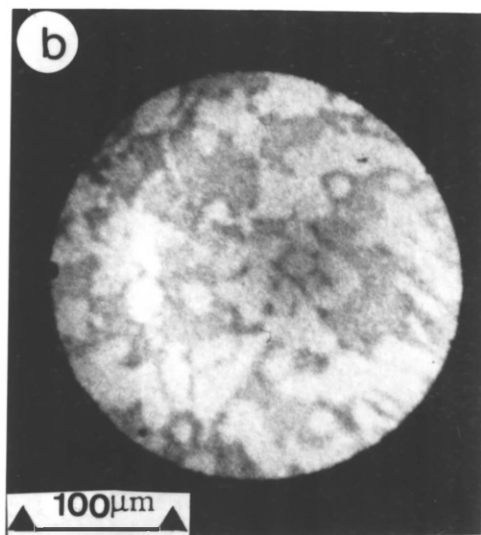
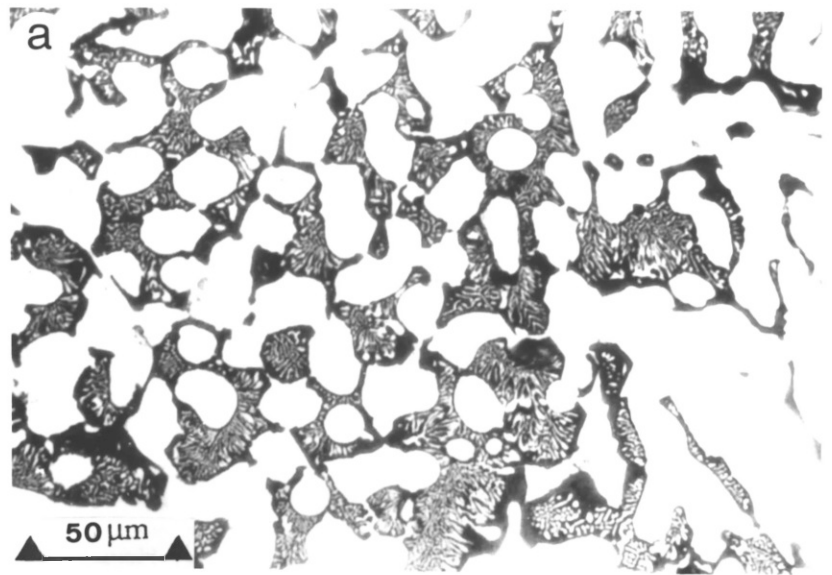


Figure 6.10 SIMS: Ion micrographs showing distribution of elements in the microstructure of as-cast alloy J .

(a) light micrograph (Keller's etch)

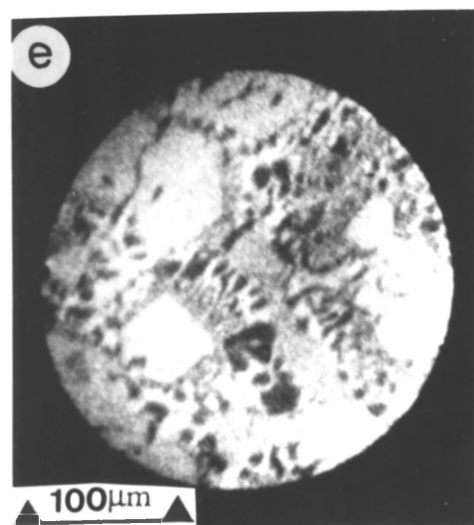
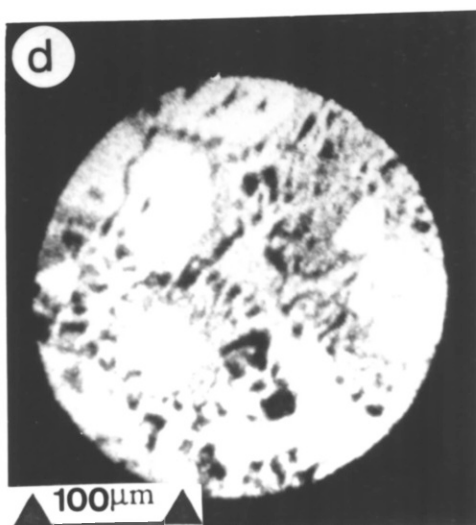
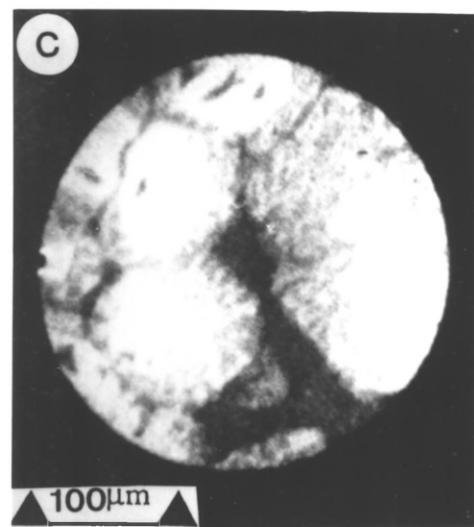
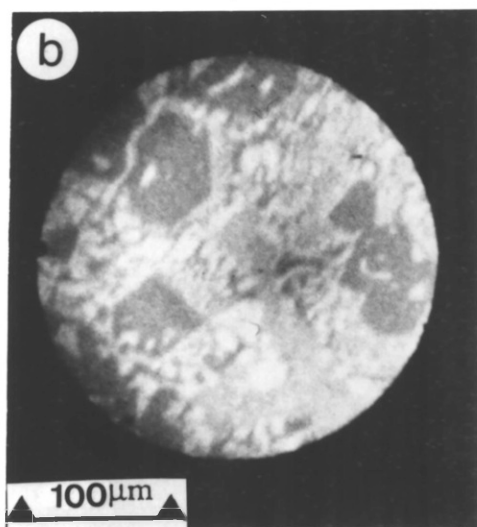
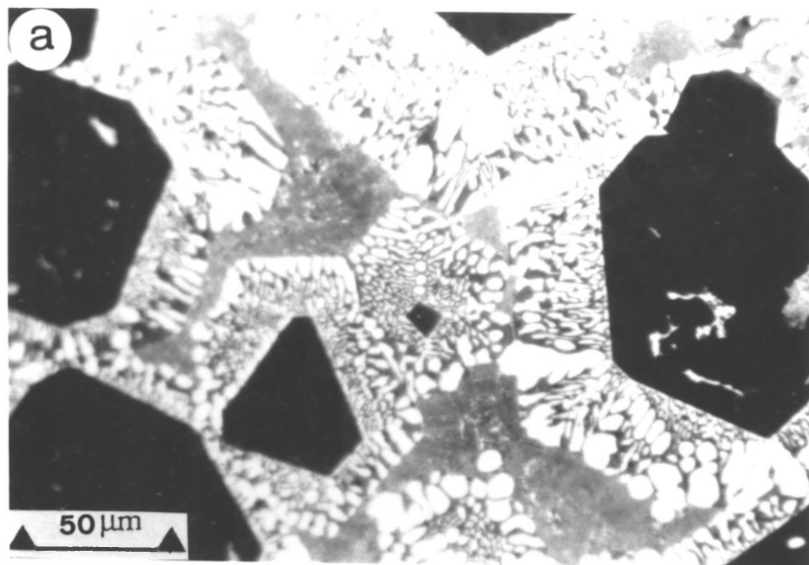
Ion micrographs:

(b) $^{27}\text{Al}^+$

(c) $^7\text{Li}^+$

(d) $^{63}\text{Cu}^+$

(e) $^{24}\text{Mg}^+$



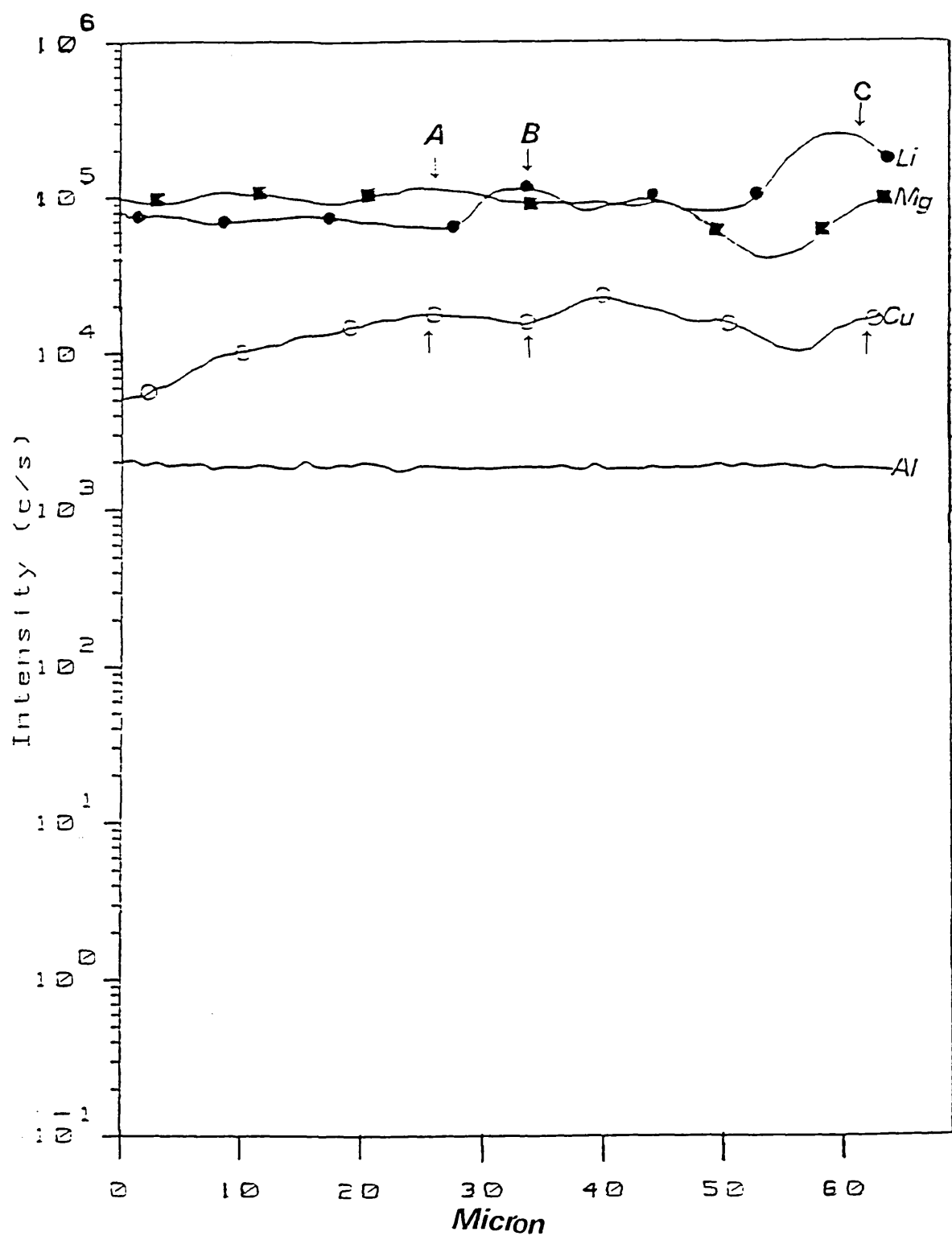


Figure 6.11 SIMS: Concentration profiles of elements across an area of the microstructure of as-cast alloy H. Labelled sections correspond to different phases in the micro-structure.

6.3.3 X-Ray Diffractometry

X-ray diffraction studies of bulk samples of some of the quaternary alloys (in both as-cast and annealed conditions) were carried out to further identify the phases.

Table 6.7 shows the result of diffraction analysis of the as-cast alloy F. By comparing the d-spacings and intensities of the diffracted lines with data from the JCPDS files, three phases were identified: the Al solid solution phase -F2, the $S(Al_2CuMg)$ phase - F3, and the $\delta(AlLi)$ phase which was not detected by LM, SEM or EDX. The calculated lattice constant of the F2 phase is 0.4053 nm. The lines which could not be ascribed to any of the above phases were assumed to belong to the S-based quaternary phase F1. It was not possible to determine the structure of this phase from the x-ray data alone.

Table 6.8 shows the result of diffraction analysis of alloy F after annealing at 510°C for 72 hrs. The same phases were identified to be present as in the as-cast alloy. It was observed however that both the number and intensities of the δ lines were reduced in the annealed alloy. This may be due to partial dissolution of δ during the annealing. It was observed too that the number and intensities of the lines belonging to the quaternary phase have increased, implying a higher volume fraction of this phase in the annealed alloy. Microstructural study has shown this to be the case.

Table 6.9 shows the result of diffraction analysis of the as-cast alloy H. In this alloy, the S phase is absent, being replaced by the cubic $T(Al_6CuMg_4)$ phase with a lattice constant of 1.428 nm. The lattice constant of the Al solid solution (H2) phase in this alloy is 0.4059 nm which is slightly higher than that of alloy F. This is probably due to the increased Mg in solution (≈ 7 wt %) which has the effect of expanding the Al lattice.

Table 6.10 shows the result of diffraction analysis of the as-cast alloy I. The phases identified are the fcc Al solid solution (I1) phase with a lattice constant of 0.4047 nm, the S phase (I3), and the δ phase. The lines belonging to the quaternary phase (I2) are also given in the table.

It is observed that several of the lines belonging to the quaternary phase in the three alloys analysed correspond. This may imply that this phase has the same structure in all the alloys, but the lattice parameter(s) may vary according to its composition in each alloy.

Table 6.7 Phases identified from x-ray diffraction
analysis of as-cast alloy F

F.C.C Al solid solution (α) phase		F.C.C δ (AlLi) phase		Orthorhombic S (Al ₂ CuMg) phase		Lines due to Al-Cu-Mg-Li qua- ternary phase
d-spacing (nm)	(hkl)	d-spacing (nm)	(hkl)	d-spacing (nm)	(hkl)	d-spacing (nm)
0.2337	111	0.3691	111	0.3545	002	0.6316
0.2026	200	0.2239	220	0.3264	111	0.4874
0.1433	220	0.1482	311	0.2818	022	0.4378
0.1222	311	0.1320	422	0.2562	112	0.3940
0.1171	222	0.1222	333	0.2443	130	0.3545
0.1013	400	0.1074	135	0.2312	131	0.2711
0.0929	331	0.1013	026	0.2006	200	0.2239
0.0906	024	0.0914	444	0.1779	221	0.2100
0.0829	224	0.0897	551	0.1704	133	0.1951
		0.0829	553	0.1653	043	0.1882
				0.1629	222	0.1848
				0.1482	241	0.1757
				0.1395	242	0.1629
				0.1334	204	0.1320
				0.1285	224	0.1086
				0.1253	170	
				0.1231	135	
				0.1222	154	
				0.1209	331	

Table 6.8 Phases identified from x-ray diffraction analysis of alloy F annealed at 500°C for 72 hrs

F.C.C Al solid solution (α) phase		F.C.C δ (AlLi) phase		Orthorhombic S (Al ₂ CuMg) phase		Lines due to Al-Cu-Mg-Li qua- ternary phase
d-spacing (nm)	(hkl)	d-spacing (nm)	(hkl)	d-spacing (nm)	(hkl)	d-spacing (nm)
0.2345	111	0.3718	111	0.3274	111	0.5659
0.2036	200	0.2258	220	0.2835	022	0.4916
0.1439	220	0.1930	311	0.2540	112	0.4394
0.1228	311	0.1294	422	0.2453	130	0.3478
0.1181	222	0.1228	333	0.2312	131	0.3104
0.1052	400	0.1129	440	0.1826	220	0.2835
0.0902	024	0.1081	135	0.1520	152	0.2727
				0.1501	061	0.2540
				0.1392	242	0.2487
				0.1292	063	0.2450
				0.1260	170	0.2418
				0.1228	154	0.2381
				0.1202	261	0.2345
				0.1194	006	0.2051
				0.1181	172	0.2036
						0.1967
						0.1907
						0.1891
						0.1619
						0.1550
						0.1406
						0.1352
						0.1327
						0.1260

Table 6.9 Phases identified from x-ray diffraction analysis of as-cast alloy H

F.C.C Al solid solution (α) phase		F.C.C $\delta(AlLi)$ phase		Cubic $T(Al_6CuMg_4)$ phase		Lines due to Al-Cu-Mg-Li qua- ternary phase
d-spacing (nm)	(hkl)	d-spacing (nm)	(hkl)	d-spacing (nm)	(hkl)	d-spacing (nm)
0.2342	111	0.3690	111	0.2447	433	0.4371
0.2030	200	0.2242	220	0.2378	006	0.2720
0.1438	220	0.1300	422	0.2043	236	0.2541
0.1240	311	0.1240	333	0.1959	007	0.2308
0.1175	222	0.1064	135	0.1883	336	0.1401
		0.0915	444	0.1757	554	0.1346
				0.1438	567	0.0934
				0.1385	737	0.0852
				0.1322	468	

Table 6.10 Phases identified from x-ray diffraction
analysis of as-cast alloy I

F.C.C Al solid solution (α) phase		F.C.C $\delta(AlLi)$ phase		Orthorhombic $S(Al_2CuMg)$ phase		Lines due to Al-Cu-Mg-Li qua- ternary phase
d-spacing (nm)	(hkl)	d-spacing (nm)	(hkl)	d-spacing (nm)	(hkl)	d-spacing (nm)
0.2330	111	0.3675	111	0.3252	111	0.5600
0.2033	200	0.1913	311	0.2812	022	0.4342
0.1426	220	0.1568	400	0.2113	023	0.4266
0.1217	311	0.1456	331	0.2017	132	0.3966
0.1168	222	0.1292	422	0.1754	202	0.3434
0.1012	400	0.1217	333	0.1456	223	0.3022
0.0927	331	0.1073	135	0.1394	242	0.2703
0.0903	024	0.1012	026	0.1292	063	0.2365
				0.1282	224	0.2296
				0.1250	170	0.2235
				0.1200	261	0.1951
				0.1185	172	0.1876
				0.1165	064	0.1340
						0.1317

6.3.4 Differential Scanning Calorimetry

The reactions in which the various phases present in the Al-Cu-Mg-Li alloys are involved and the temperatures at which they occur were investigated by DSC.

Figure 6.12 (a) and (b) show, respectively, the DSC traces for the as-cast alloy F and after it has been annealed at 510°C for 72 hrs. (Note that for reasons which were stated in sections 4.2.7 and 5.3, the temperatures shown in Fig.6.12 are each 12°C higher than the actual transformation temperatures). The following features are observed in Fig.6.12 (a):

A - a major endothermic reaction which starts at $\approx 500^{\circ}\text{C}$ with the minimum of the endothermic trough (i.e. the average reaction temperature) at $\approx 512^{\circ}\text{C}$;

B - a second major endothermic reaction which partially overlaps with A and has a minimum at $\approx 525^{\circ}\text{C}$;

C - a third endothermic reaction which also partially overlaps with B with the minimum occurring at 563°C ; and finally

D - a slight endothermic reaction which occurs at $\approx 618^{\circ}\text{C}$.

The results of EDX, SIMS and X-ray diffraction studies have shown that four solid phases ($\alpha(\text{Al}_{\text{ss}})$, δ , S, and a quaternary phase based on S) are present in the as-cast alloy F. Microstructural evidence (Fig.6.2) shows that an $\alpha + \text{S}$ binary eutectic is the last to form during solidification of this alloy. The reaction A occurring at 512°C therefore represents the dissolution of this eutectic during heating of the alloy. This temperature is almost the same as the 518°C at which the $\alpha + \text{S}$ eutectic occurs in Al-Cu-Mg ternary alloys. The microstructure of the as-cast alloy F also showed the existence of a ternary eutectic involving α , S and the coarse quaternary phase F1. Melting of this eutectic is believed to have occurred in the reaction B. A binary eutectic involving the α and the coarse quaternary phase was also observed in the microstructure. The melting of this eutectic is, most probably, represented by the reaction C. Finally, the slight endothermic reaction D occurring at 618°C represents melting of the large blocks of the quaternary phase F1, which at this stage is probably floating in the molten alloy. The similarity of the phases involved in the reactions may explain the overlapping of the endothermic troughs observed in the DSC trace. Evidence of the dissolution of the δ phase was not detected in the DSC traces probably because of their low volume fraction in the alloys.

In the DSC trace for the annealed alloy F shown in Fig.6.12 (b), the reactions A and B are barely distinguishable, while the endothermic trough representing C is considerably reduced. No new reactions are seen to have occurred. The microstructure of the annealed alloy showed that the ternary eutectic involving the α , S, and the quaternary phase decomposed almost entirely while the $\alpha + S$ eutectic grew by coarsening. These observations agree with the trends shown in the DSC trace and are discussed in more detail in section 6.4.2.

The DSC trace for the as-cast alloy H is shown in Figure 6.13 (a). Two major endothermic reactions occurred in this alloy, at 525°C and 563°C respectively. Compared to the trace for alloy F, it is observed that the first endothermic reaction A is absent in alloy H. This observation is consistent with the results of previous studies which showed that the S phase is absent in this alloy, having been replaced by the T phase. Microstructural evidence has also shown that two major eutectics existed in the as-cast alloy H:

- (a) A large volume fraction of a eutectic involving the α , T, and some of the quaternary H1 phases. The reaction occurring at 525°C represents melting of this eutectic.
- (b) A substantial proportion of a second eutectic involving the α and H1 phases. The melting of this eutectic is believed to be represented by the reaction occurring at 563°C.

Finally, as in alloy F, the slight endothermic trough occurring at $\approx 618^\circ\text{C}$, represents melting of the large blocks of the primary H1 phase.

The DSC trace of alloy H after annealing at 500°C for 72 hours is shown in Fig.6.13 (b). The almost indistinguishable forms of the two endothermic troughs is consistent with microstructural evidence which showed that the annealed alloy consisted largely of a eutectic of α and the quaternary H1 phase.

Figure 6.13 (c) show the DSC trace for the as-cast alloy I. It shows clear similarities with those for alloys F and H. The small endothermic reaction occurring at $\approx 510^\circ\text{C}$ represents melting of the $\alpha + S$ binary eutectic which was shown to be present in this alloy in very small amounts. The other three endothermic reactions have their equivalents in both alloys F and H. However, it is observed that the second and last reactions here occurred at slightly higher temperatures - 544°C and 628°C respectively. This may be due to the difference in the relative proportions of the phases which formed the eutectics in the various alloys. The results of the DSC studies of all the alloys are further discussed in section 6.4.2.

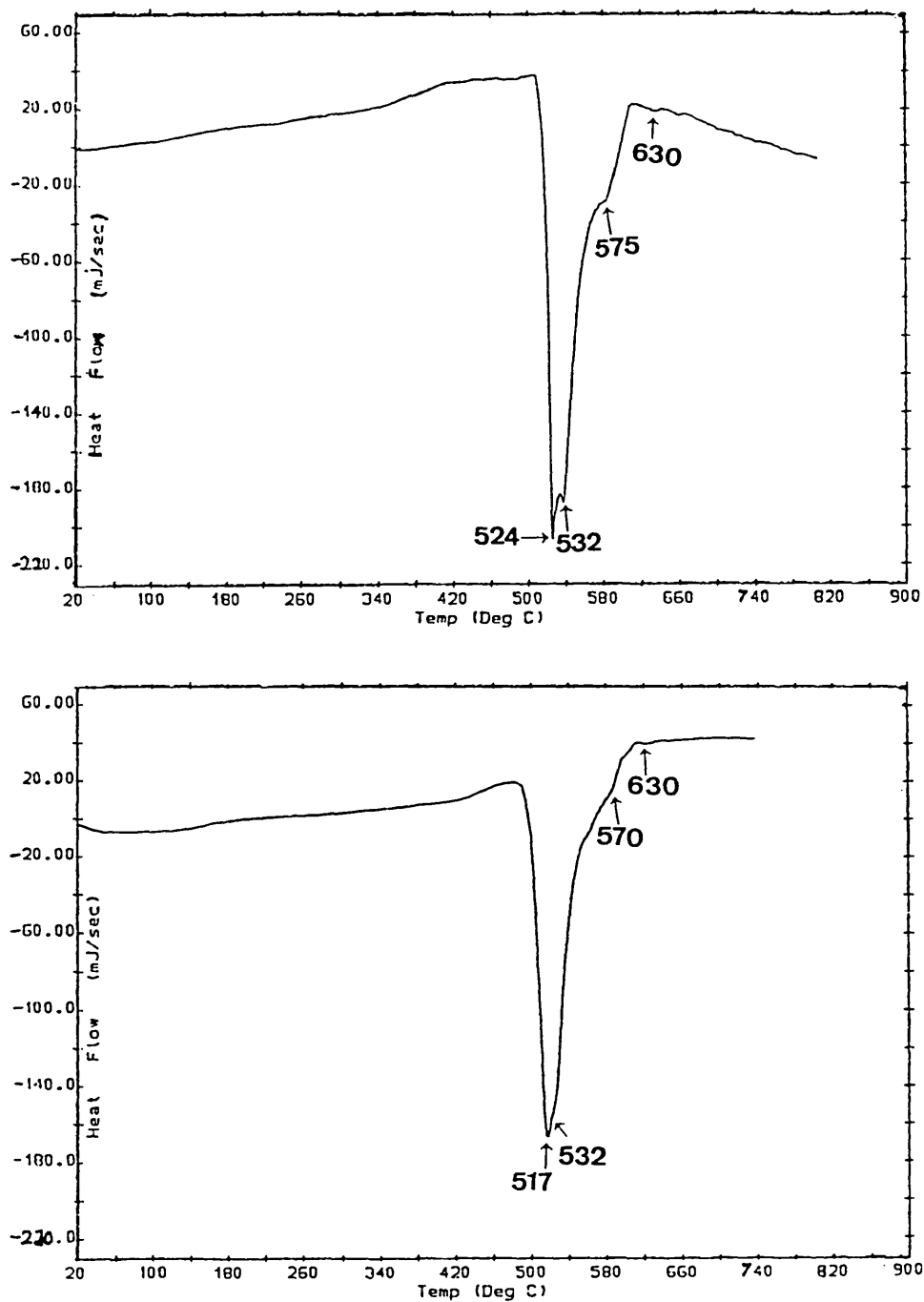


Figure 6.12 DSC traces showing major transformations in alloy F: (a) as-cast condition (b) after annealing at 510°C for 72 hours.

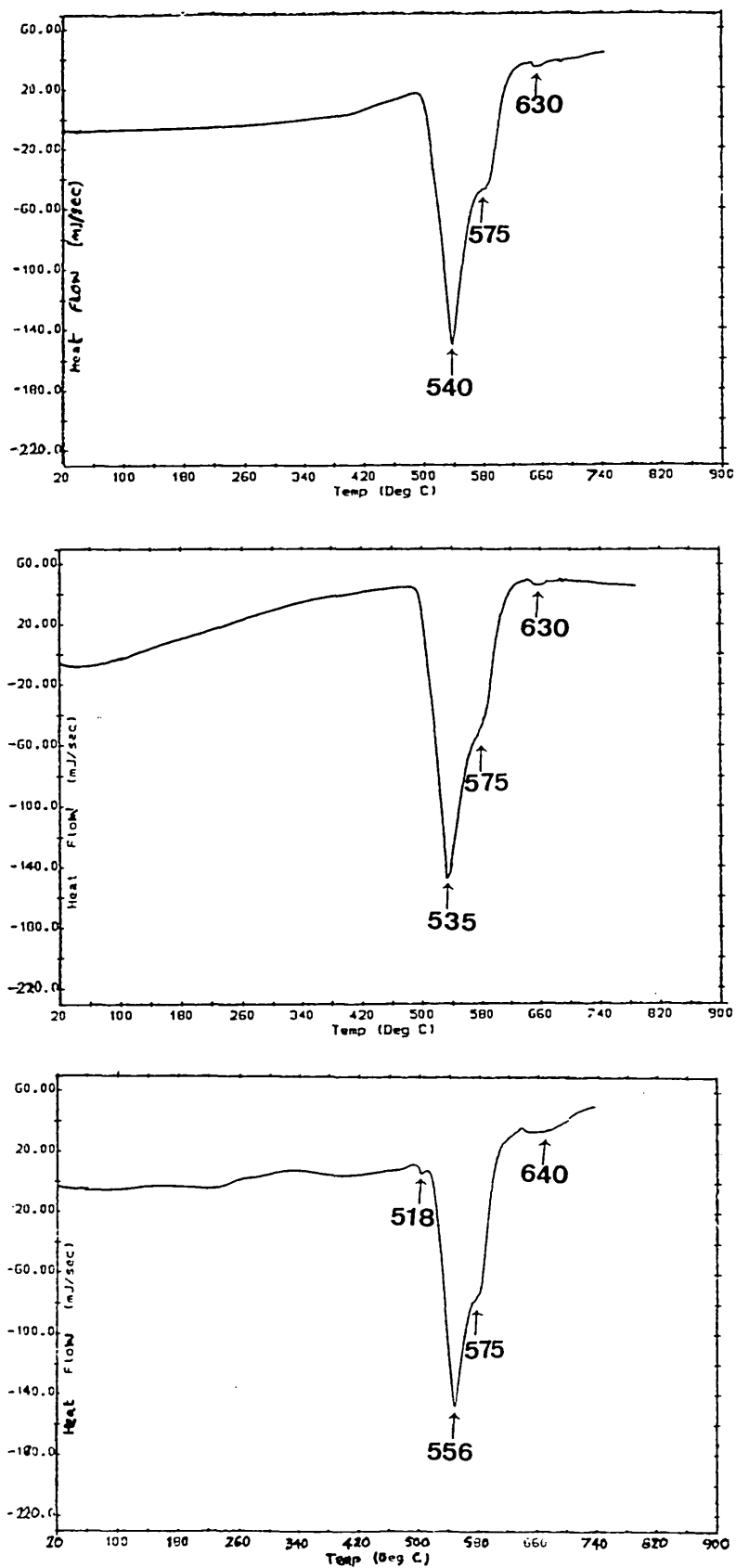


Figure 6.13 DSC traces showing major transformations in
 (a) as-cast alloy H
 (b) alloy H after annealing at 500°C for 72 hrs
 (c) as-cast alloy I.

6.4 Discussion

6.4.1 Characterisation of the As-Cast Alloys

The results of the various studies carried out to characterise the microstructure of the quaternary Al-Cu-Mg-Li alloys have shown that:

- (1) The Al solid solution (α) and the δ (AlLi) phases are present in all the alloys investigated. No visual evidence for the presence of the δ phase was observed in the microstructure of the alloys. A probable explanation for this is that the δ particles were too fine to be observed by light or scanning electron microscopy. Such fine δ particles are unlikely to have formed from the liquid state during solidification. It therefore seems that the δ phase present in the as-cast Al-Cu-Mg-Li alloys was formed by solid state precipitation via dissociation of the supersaturated Al solid solution. This mode of δ precipitation would occur when the alloy is cooled slowly (as in furnace cooling) during solidification (see section 6.4.2 below).
- (2) In the alloys containing high Cu and low Mg levels (F, G, and J), the $S(Al_2CuMg)$ phase is formed while in the high Mg alloy (H) the $T(Al_6CuMg_4)$ phase is formed.
- (3) An Al-Cu-Mg based phase with some lithium incorporation is present in all the alloys investigated. The composition of this phase (excluding Li) particularly in alloys F, G and J, is quite similar to that of the ternary S phase. X-ray diffraction analyses showed that the phase has very similar d-spacings in all the alloys, suggesting that its basic crystal structure may be the same in all the alloys investigated although the lattice parameter(s) may vary according to the variations in compositions of the phase in the different alloys as was revealed by EDX analyses. The results of the various analyses of the Li-containing Al-Cu-Mg phase seem to suggest that it is a solid solution of Li in ternary S phase rather than a true quaternary phase(i.e. formed independently during solidification). Such a situation will be similar to the case in Al-Li based alloys containing low levels of Cu and Mg where Mg atoms are substituted for Li atoms in the ternary $T_2(Al_6CuLi_3)$ phase to form a compound of the formula - $Al_6CuLi_{3-x}Mg_x$ where $x \leq 1$ (see section 4.3.2). For the reason that the Cu and Mg contents of the Li-containing Al-Cu-Mg phase in these alloys are closer to those of the S phase than any other known phase in the Al-Cu-Mg system, this phase will now be referred to as S^* .

In all the alloys investigated excepting I, the S^* phase forms a large volume fraction, occurring both in primary (large blocks) and secondary forms. In the low Cu and Mg alloy I it exists only in the secondary form. The results of the SIMS study (and EDX analyses) suggest that the amount of Li present in the S^* (primary) may be more than is present in the S^* (secondary). This will be consistent with the fact that as the Al solid solution phase is formed, it competes with the S^* phase for the available Li so that the S^* which is formed in subsequent stages of solidification becomes less rich in Li. It also supports the view that the S^* phase is most probably a solid solution of Li in S phase. The SIMS results also suggest that the Li content of the Al solid solution phase in the high Mg alloy H (with ≈ 7 wt % Mg in solution) is less than is present in the other alloys. This observation seems to support the report by previous investigators (56,60) that Mg reduces the solubility of Li in Al.

6.4.2 Solidification Sequences (Liquid-Solid Phase Equilibria) in Cast Al-Cu-Mg-Li Alloys

The complexity of the invariant reactions which are possible within quaternary alloys makes the task of plotting their solidification paths necessarily difficult. However, by combining the results of microstructural, x-ray diffraction, SIMS, and DSC studies, an attempt has been made to plot the solidification sequences of the Al-Cu-Mg-Li alloys being investigated.

Table 6.11 (a) shows what is considered the most probable solidification sequence for alloys F, G and J. The large blocky S^* phase was the first to separate from the liquid. As cooling proceeded, the Al solid solution (α) phase is nucleated, competing during growth with the S^* phase for the available lithium. This led to precipitation of the S^* (secondary) phase which is less rich in Li than the S^* (primary) and hence the $\alpha + S^*$ (secondary) eutectic. As more Li is consumed in the precipitation and growth of the α and S^* phases, the liquid becomes depleted of this element and the ternary S phase is formed, precipitating together with the α and S^* (secondary) phases as the ternary eutectic. Finally, when the liquid is completely depleted of Li, the S phase dominates and the $\alpha + S$ binary eutectic is formed.

It follows from this solidification sequence that the Li content of the Al solid solution phase which forms at the initial stages of solidification will be higher and increasing as solidification proceeds. When cooling is sufficiently slow (as in furnace cooling), some of the Al solid solution phase will become

supersaturated in Li and dissociate, resulting in the precipitation of the fine δ particles:



It needs to be stated that the high reactivity of the δ phase may well have prevented coarse δ particles formed during solidification from being observed by light or scanning electron microscopy. However, solid state precipitation of the δ phase appears to offer a more satisfactory co-relation between the solidification sequences and the microstructures of the Al-Cu-Mg-Li alloys.

In the high Mg alloy H, the S phase is replaced by the T phase and the last product of solidification is an $\alpha + \text{T}$ binary eutectic. Also in this alloy, the volume fraction of the S^* (secondary) phase is very small thereby making the $\alpha + S^* + \text{T}$ ternary eutectic almost indistinguishable from the $\alpha + \text{T}$ binary eutectic. This analysis is consistent with the results of both microstructural and DSC studies.

The microstructure of the low Cu and Mg alloy I was shown to be significantly different from those of the other alloys. The solidification sequence proposed for this alloy is shown in Figure 6.11 (b). The primary phase here is the Al solid solution phase; this may explain the slightly higher temperature (635°C) of the first solidification reaction in this alloy as compared to the case in the other alloys. The S^* phase occurs only in the secondary form and forms a binary eutectic with the α and a ternary eutectic with the α and S phases. Again, the $\alpha + S^* + \text{S}$ ternary eutectic is shown to occur at a slightly higher temperature (544°C) than in the other alloys. This may be due to the predominance of the high temperature α phase in this eutectic. Finally, a very small volume fraction of the $\alpha + \text{S}$ binary eutectic is formed as the last product of solidification.

In all the alloys investigated, the δ phase is believed to have formed via the solid state process described above.

The results of these studies have shown that the solidification sequences in three of the alloys investigated (F, G and J) are identical. This implies that the differences in composition of these alloys (Cu:Mg = 2.7, 2.8, and 2.2 respectively and Cu:Li = 16.1, 12.9 and 10.7 respectively) are not significant to the extent of influencing their basic phase equilibria although they may have led to differences in the volume fractions of the various phases which are formed.

In alloy H (Cu:Mg = 1.8 and Cu:Li = 10.0), the only significant change is the replacement of the S phase by the T phase which may have occurred as a direct result of the higher Mg content (or lower Cu:Mg ratio) of this alloy. Alloy I (Cu:Mg = 1.8, Cu:Li = 5.4) which was made up to have approximately the same composition as the $\alpha + S^* + S$ ternary eutectic in alloy F is shown to have solidified essentially as a mixture of these three phases in varying proportions. It is evident however, that it is the Cu:Mg ratio rather than the Cu:Li ratio which determines the proportions of the various phases that are formed in these alloys.

Table 6.11 (a) Probable solidification sequence in alloys F, G and J

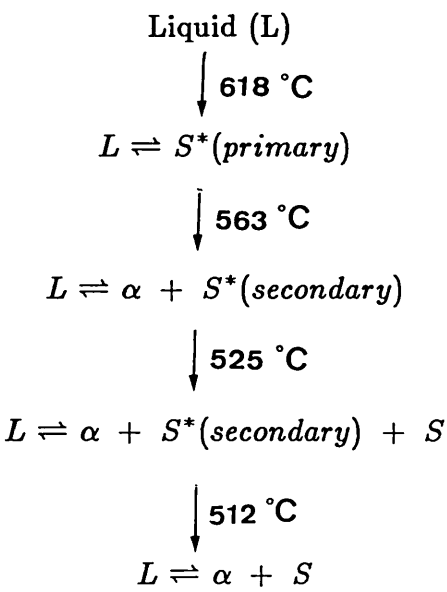
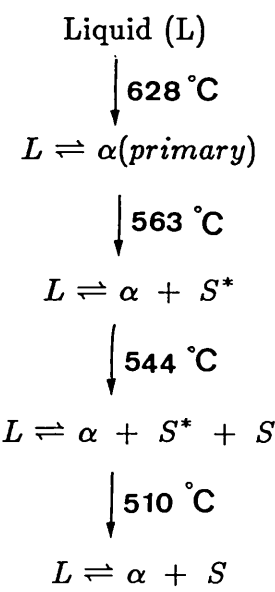


Table 6.11 (b) Probable solidification sequence in alloy I



6.4.3 Comparison of the Phase Equilibria with those Occurring in Ternary Al-Cu-Mg and Al-Cu-Li Alloys and with Data From the Study of the Commercial 8090 and 8091 Alloys

The Al-Cu-Mg System

The predicted equilibrium solidification sequences of the zero-lithium Al-Cu-Mg alloys were given in section 6.2. It was shown that the primary solidification product in alloy F should be the Al solid solution (α) phase, followed by an $\alpha + S$ binary eutectic and probably an $\alpha + S + T$ ternary eutectic. Whereas the primary phase in the Li-containing alloy F has been shown to be an S-based (S^*) phase with Li incorporation, followed by an $\alpha + S^*$ binary eutectic, an $\alpha + S^* + S$ ternary eutectic and an $\alpha + S$ binary eutectic. There are two probable explanations for the discrepancy regarding the primary phase in the two cases:

- (1) Under non-equilibrium conditions, the primary phase in the zero-lithium alloy F could have changed from the predicted α to S. This will not be improbable considering the proximity of the alloy composition to the $\alpha + S$ tie line (see section 6.1).
- (2) The presence of Li may have affected the position of the $\alpha + S$ binary line of the ternary system. For example, pushing it towards lower Mg levels thus putting alloy F on the S side of the line.

In either case, the nucleation of an S primary phase would explain the incorporation of Li into this phase during growth, and the subsequent formation of the $\alpha + S^*$ and $\alpha + S^* + S$ eutectics in the quaternary alloys. However, the completion of solidification in this alloy on a binary ($\alpha + S$) eutectic appears to be inconsistent with what would be predicted under equilibrium conditions where solidification should end with the maximum number of the precipitating phases, i.e. either the ternary eutectic or even a quaternary phase mixture. One way to explain this inconsistency is that during solidification, non-equilibrium conditions have forced the liquid to undercool at the ternary eutectic stage, resulting in the precipitation of the $\alpha + S$ binary eutectic. However, if the S^* phase (both primary and secondary forms) is actually an S phase with some Li dissolved in it as is being proposed in this study, then the alloy F would be basically in a two phase ($\alpha + S$) field and solidification could end with the binary eutectic.

The same interpretation applies to the solidification sequences in alloys G and J. In the high Mg alloy H, following the formation of the S^* phase(s), the Cu and Mg concentrations of the remaining liquid favoured the formation of the T phase instead of the S phase. While the composition of the low Cu and Mg alloy I is sufficiently distant from the $\alpha + S$ binary line for the Al solid solution phase to form as the primary phase.

Thus, the results of the present study seem to suggest that the main effect of the presence of between 1.5 and 2.4 wt % Li in the Al-Cu-Mg alloys is to push the $\alpha + S$ tie line towards lower Mg concentrations with the result that the S phase is formed at lower Mg levels than would be the case in ternary alloys.

The Al-Cu-Li system

The phase equilibria of the Al-Cu-Li system are complex and are still being investigated. Rivlin and Miodownik (147) have from various sources (including Refs. 38,50,148 and 161) compiled a table of the numerous invariant reactions which occur within this system. Those which may be relevant to the low-lithium alloys being investigated in the present study are shown in Table 6.13 below:

Reactions	Temperature (°C)
$L \rightleftharpoons \delta(AlLi) + T_1(Al_2CuLi) + T_2(Al_6CuLi_3)$	640
$L \rightleftharpoons \alpha(Al) + \delta$	596
$L \rightleftharpoons \alpha + \delta + T_2$	564
$L \rightleftharpoons \alpha + \theta(Al_2Cu)$	548
$L \rightleftharpoons \alpha + T_1$	540
$L + \theta \rightleftharpoons \alpha + T_B(Al_5CuLi_3)$	535
$L \rightleftharpoons \alpha + T_1 + T_B$	528

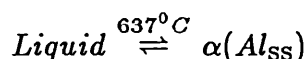
None of these phases, excepting the δ phase, was found in the as-solidified Al-Cu-Mg-Li alloys under investigation. As it has been shown, the Li present in these alloys was taken into solid solution by both the S^* phase and the $\alpha(Al_{ss})$ phase which later dissociated to form the δ phase. The absence of the T-type phases in these alloys is probably due to the high concentrations of Cu and Mg they contained which favoured the formation of phases of the Al-Cu-Mg system rather than those of the Al-Cu-Li system.

The Al-Li-Cu-Mg System

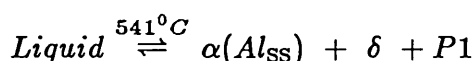
No information was found in the literature on the liquid-solid phase equilibria of the Al-Cu-Mg-Li quaternary system. Indeed, one of the main objectives of the present study is to provide such information and thus a better knowledge of this system.

However, extensive and detailed studies have been (and are still being) carried out by several researchers on the solid state reactions in quaternary alloys of compositions within the ranges designed for commercial Al-Li based alloys (see section 2.2.5). The results of the characterisation of the heat treated 8090 and 8091 alloys carried out in chapter 5 were shown to be consistent with those obtained in previous investigations of similar alloys. The phases identified were : $\alpha(Al_{ss})$, δ' , S' , T_1 , and the quaternary phase based on T_2 .

The characterisation of the as-cast 8090 and 8091 alloys carried out in chapter 4 showed that apart from the dispersoid and impurity based phases, the α , δ and the T_2 -based phases were present. They also showed that two major liquid-solid phase equilibria occurred in these alloys :



and



There is no equivalent of the second reaction in the experimental quaternary alloys which were investigated. This may be due, largely, to the difference in compositions between the two sets of alloys. Although they both contained about the same levels of lithium, the levels of Cu + Mg in the 8090 and 8091 alloys (2 - 2.5 wt %) are far less than are present in the experimental alloys (20 - 36 wt %). Consequently, the Li:Cu ratios in the former (between 1.4 and 1.8) are over ten times greater than in the latter. This therefore, may explain the absence of any of the Al-Cu-Li phases in the high Cu and Mg alloys.

6.4.4 Diagrammatic Representations

To represent the liquid-solid phase reactions shown in Table 6.11 (a) and (b) on two dimensional paper is a rather difficult job. In the first place, the incorporation of lithium into the S^* phase means the composition of this phase lies in

a space. A space model would therefore be required to construct the liquidus projection of the Al-Cu-Mg-Li quaternary system. To do even this requires examining a lot more alloy compositions within the quaternary system than have been examined in the present study. However, the liquidus projections of the constituent ternary systems are shown together in Figure 6.14 to give an indication of the solidification paths of the quaternary alloys investigated. Figure 6.15 shows the composition regions of the commercial (8090 and 8091) and experimental (F - J) Al-Cu-Mg-Li quaternary alloys with respect to the phases which have been identified in the constituent binary and ternary systems.

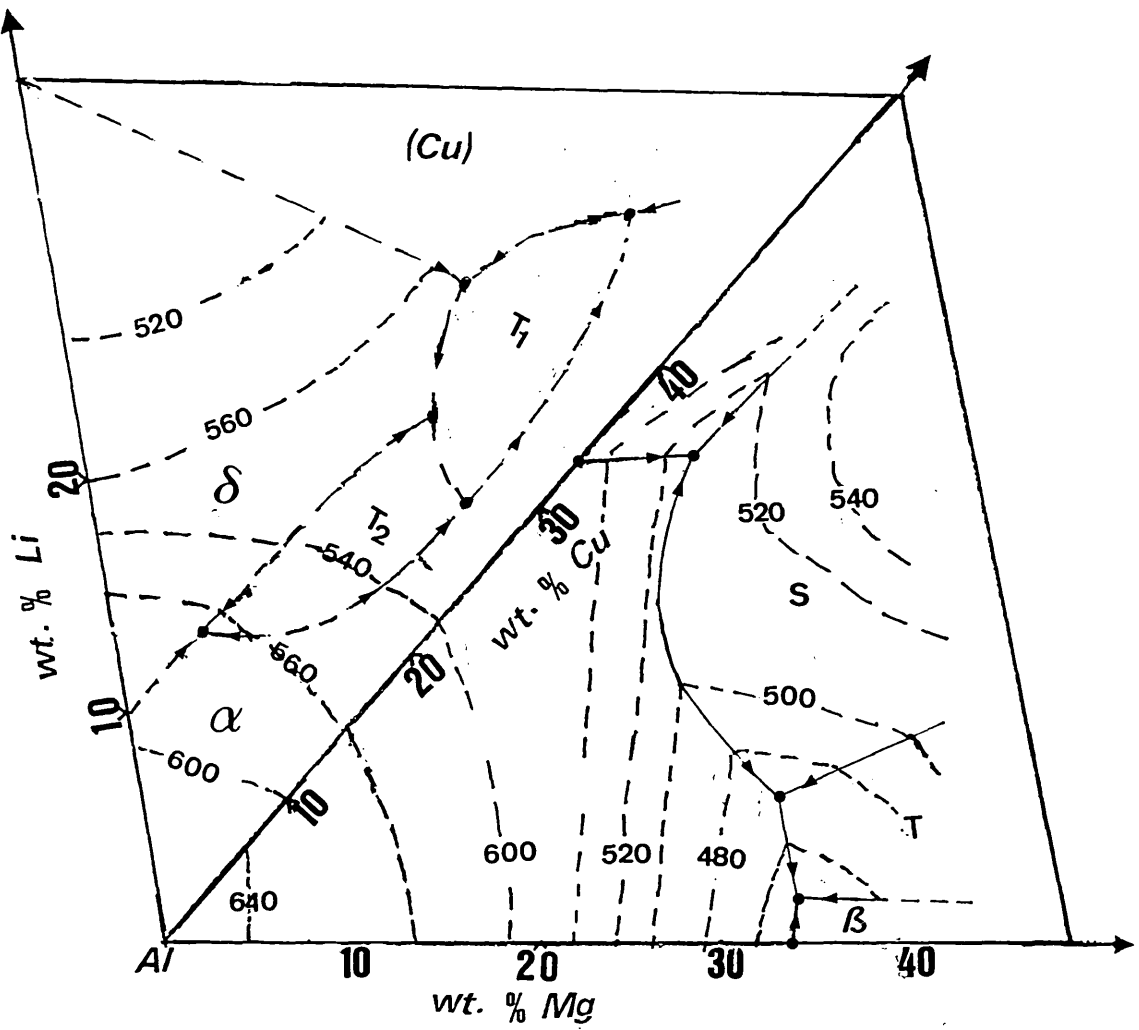


Figure 6.14 The liquidus projections of the Al-Cu-Mg and Al-Cu-Li ternary systems (adapted from Refs. 65 and 147).

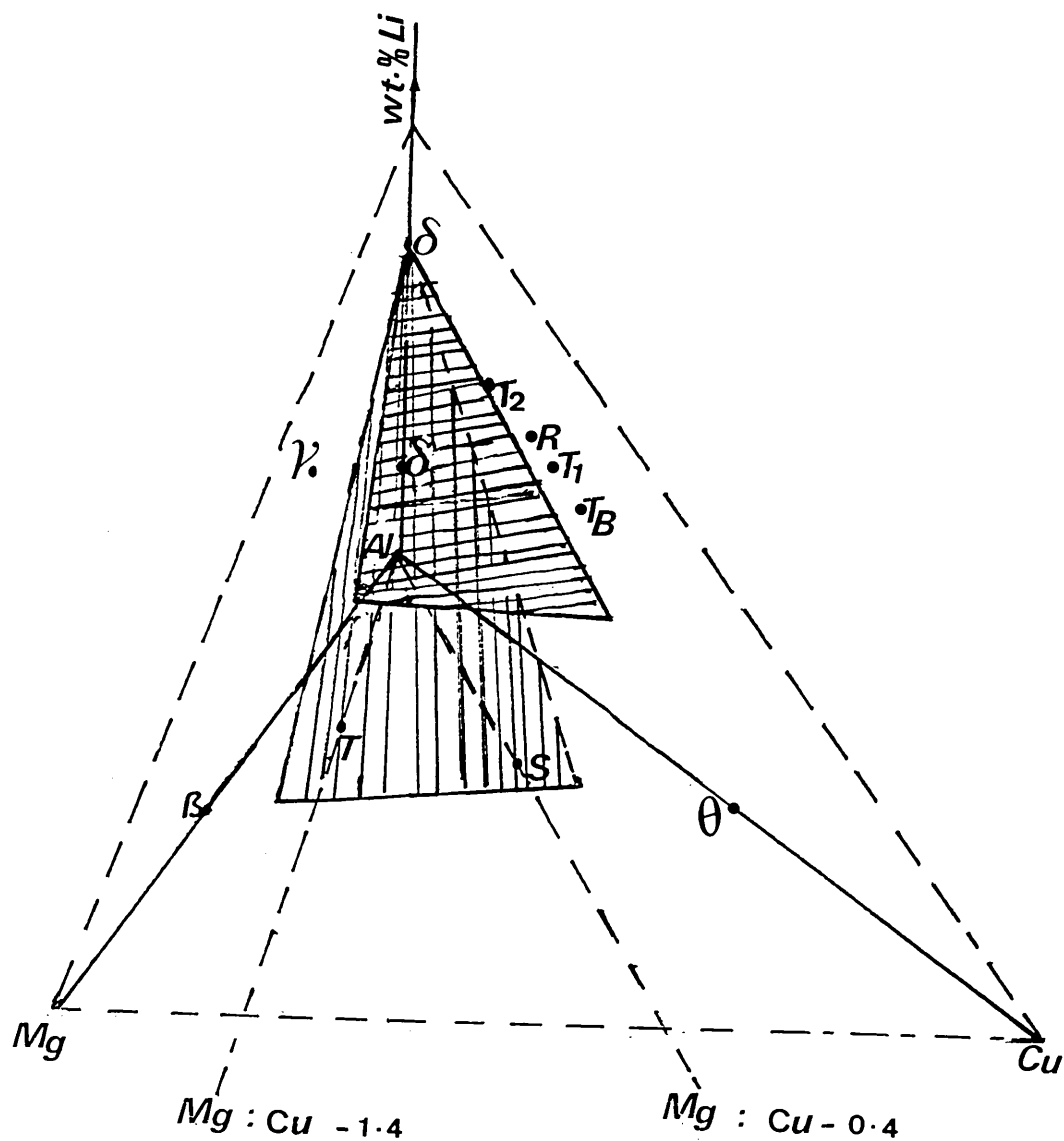


Figure 6.15 Composition regions for the cast Al-Cu-Mg-Li quaternary alloys :

- 8090 and 8091 alloys
- | experimental alloys F - J.

6.4.5 Phase Transformations During Annealing

Characterisation of the microstructure of the alloys after they have been annealed at a temperature ($\approx 500^{\circ}\text{C}$) just below the first eutectic melting have shown that the phases present in the as-cast alloys were stable up to this temperature. Diffusion of atoms during the annealing occurred only on a small scale, resulting in the growth (by coarsening) of some of the existing phases. The changes in the eutectic structures of the alloys which occurred during annealing have been discussed in section 6.3.1.

However, solid state precipitation of new phases may well have occurred in these alloys during annealing. As such precipitations are most probably very fine and of very low volume fractions in the as-quenched microstructure, they could not be detected by any of the techniques of investigation employed in this study. Also, the δ' , S' and T-type phases which were found in the aged microstructure of the 8090 and 8091 alloys may also precipitate upon ageing the Al-Cu-Mg-Li alloys investigated here.

CHAPTER 7

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

7.1 Conclusions

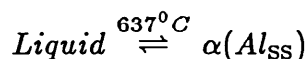
The combination of experimental techniques employed in this research have proved quite successful in characterising the microstructure of the as-cast Al-Li-Cu-Mg alloys which are being studied. In particular, the SIMS and the Backscattered Electron Imaging technique have been found very useful in determining the lithium-distribution in the microstructure of the alloys.

Chapter 4

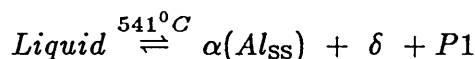
The following conclusions may be drawn from the results of the microstructural and phase transformations studies of the as-cast 8090 and 8091 (Al-Li based commercial) alloys:

- (1) The microstructure of the as-cast 8090 and 8091 alloys consists of cellular grains of an Al solid solution primary phase (α), surrounded by an intergranular network of second-phase precipitates. The primary grains which are cored as a result of non-equilibrium cooling during casting have been refined by the Zr addition to an average size of $\approx 70\mu\text{m}$.
- (2) The major second-phase precipitate in the as-cast alloys is a quaternary phase (P1) of composition: 65.6 Al, 25.9 Cu, 6.3 Mg, and ≈ 2.2 Li (wt %) which forms a lamellar eutectic with the α (Al solid solution) and δ (AlLi) phases at grain boundary triple points. This phase is based on the ternary $T_2(\text{Al}_6\text{CuLi}_3)$ phase with Mg atoms substituting for Li atoms in accordance with the formula: $\text{Al}_6\text{CuLi}_{3-x}\text{Mg}_x$ where $x \leq 1$. Electron diffraction analysis of the quaternary phase showed that it has a simple cubic structure with a lattice parameter $a_0 = 1.035$ nm; no evidence of icosahedral characteristics was observed in this phase as has been suggested by some workers.
- (3) The volume fraction of the quaternary grain boundary phase was observed to be higher in the 8091 alloys than in the 8090 alloys, probably as a direct consequence of the higher solute (particularly Cu + Mg) concentrations in the former alloys.

- (4) Two major impurity-related coarse intermetallic phases ($Al_6(Fe, Cu)$ and $AlSiLi$) were found at the grain boundaries and grain boundary triple points of the as-cast alloys. The structure of the $Al_6(Fe, Cu)$ phase was determined as orthorhombic: $a = 0.404$, $b = 0.455$ and $c = 0.515$ (nm). These coarse particles would need to be re-solutionised during heat treatment of the alloys.
- (5) Coarse particles of Zr-rich equilibrium phases ($Al_3(Zr, Li)$ and Al_3Zr) were found in the matrix of the as-cast alloys. These particles of average diameters $20 - 30 \mu m$ and $4 - 5 \mu m$, respectively, were precipitated as a result of high Zr concentrations (in excess of its solubility limit in Al) in the alloys. They are distinct and different from the Zr dispersoid phases which are precipitated during heat treatment of the alloys. They would also need to be taken into solution during heat treatment.
- (6) In addition to the phases mentioned above, TEM studies of the as-cast microstructure revealed a fine dispersion of intragranular phases. These included precipitates of the T_2 -based quaternary phase (M1) and another phase (M2) with characteristics similar to those of the quaternary C-phase.
- (7) The DSC studies of the as-cast alloys revealed the occurrence of two major liquid-solid phase transformations:



and



Chapter 5

The 8090 and 8091 alloys were heat treated and the resulting microstructures characterised. The solid state phase transformations which occurred in the alloys during heat treatment were investigated by both TEM and DSC. The following conclusions may be drawn from the results of these studies:

- (1) Most of the grain boundary eutectic dissolved after annealing at $530^{\circ}C$ for 24 hours. Residues of the quaternary (P1) phase remained in the microstructure, particularly in the 8091 alloys, even after annealing at higher temperatures for longer times.

- (2) The coarse intermetallic phases ($Al_6(Fe, Cu)$, $AlSiLi$) did not dissolve even after annealing at $550^{\circ}C$ for 48 hrs. The $Al_6(Fe, Cu)$ particles were broken down into stringers which decorated the grain boundaries while the $AlSiLi$ particles were apparently unaffected.
- (3) Studies of the heat treated microstructure suggest that the 8090 and 8091 cast alloys may be optimally homogenised by annealing at $530^{\circ}C$ for 24 hrs. However, the retention of the coarse intermetallic particles in the homogenised microstructure may have a significant adverse effect on the mechanical properties of the final product.
- (4) TEM studies of the homogenised microstructure revealed the presence of only a few quenched-in dislocation loops and helices.
- (5) Evidence from electron diffraction and DSC studies has shown that the metastable $\delta'(Al_3Li)$ particles are nucleated in the as-quenched microstructure after solution heat treatment. This is in agreement with the more recent view on the precipitation mechanism of the δ' phase.
- (6) The solid state precipitation during a typical age-hardening treatment of the alloys (solution treatment at $530^{\circ}C$, water quenched and aged at $190^{\circ}C$ for 24 hrs) included a widespread homogeneous precipitation of the δ' phase, a sparse and heterogeneous precipitation of the S' phase, resulting directly from the very low density of defects in the as-quenched microstructure, and a sparse and heterogeneous precipitation of the T_1 phase. A fine dispersion of the T_2 -based quaternary phase was also present in the aged microstructure.

Chapter 6

The Al-Cu-Mg-Li alloys with high concentrations of Cu and Mg were studied in order to determine the influence of the presence of lithium on the phase equilibria of the ternary Al-Cu-Mg system and to provide more information on the phase transformations which occur within the quaternary system. The following conclusions may be drawn from the results of this study:

- (1) The phases present in the as-solidified Al-Cu-Mg-Li alloys are: an $S(Al_2CuMg)$ -based phase (S^*) with some Li incorporation, an Al solid solution phase (α), the ternary S and T (Al_6CuMg_4) phases, and the $\delta(AlLi)$

phase. No Al-Cu-Li ternary phase was found in these alloys which have Cu:Li ratios of between 5 and 16.

- (2) All the phases (excepting the δ) are involved in the formation of eutectics of various kinds. The volume fractions of the phases, and hence of the eutectics, are determined by the Cu:Mg ratios of the alloys.
- (3) The δ particles were too fine to observe (visually) by light or scanning electron microscopy. This suggests that they may have formed in the solid state via dissociation of the supersaturated Al solid solution which could have occurred during slow cooling of the alloys.
- (4) The S^* phase appears to be an S phase with some Li dissolved in it rather than a 'true quaternary' phase. It forms the primary phase in the alloys with higher Cu:Mg ratios but also occurs in a secondary form.
- (5) The solidification sequences in the Al-Cu-Mg-Li alloys suggest that those in which the S phase dominates (alloys F, G, I and J) are basically in a two-phase ($\alpha + S$) field while the higher Mg alloy (H) in which the T phase is formed is in a three-phase ($\alpha + S + T$) field.
- (6) The presence of between 1.5 and 2.4 wt % Li in the ternary Al-Cu-Mg alloys appears to have enlarged the S phase field (pushing the ($\alpha + S$) binary line towards lower Mg concentrations) with the result that the S phase in the Li-containing alloys is formed at lower Mg concentrations than it would have formed in the ternary alloys. This may have implications for future alloy development within the quaternary Al-Cu-Mg-Li system since the formation of large blocks of primary S (or S^*) phase in these alloys is unlikely to result in improved mechanical properties.
- (7) The formation of high volume fractions of the Li-bearing S^* phase in these alloys appears to have altered the Cu:Mg ratio in favour of the formation of the Mg-rich T phase. That is, the T phase in the Li-containing alloys may form at Mg concentrations lower than it would have formed in Al-Cu-Mg ternary alloys.
- (8) Studies of the heat treated Al-Cu-Mg-Li alloys showed that all the phases present in the as-cast alloys are stable up to 500°C; coarsening by solute diffusion during annealing. However, just above this temperature melting of the various eutectics occurs rapidly and the alloy is destroyed.

7.2 Suggestions For Further Work

- (1) The mode of precipitation of the equilibrium δ phase in the as-cast quaternary alloys is not quite clear because of the difficulty in observing the δ particles by microscopical examination. This has made the interpretation of the solidification sequences in these alloys rather speculative. It may be necessary to know the distribution and size of the δ particles in order to determine their mode of precipitation i.e. whether they are formed in the solid state or from the liquid state during solidification. It is suggested that thin foil specimens of the Al-Cu-Mg-Li alloys be prepared by methods which may not cause the δ particles to erode (e.g ion thinning techniques). This will enable their distribution and size to be determined by transmission electron microscopy.
- (2) It is suggested that TEM studies of the high Cu and Mg alloys be carried out, to identify any fine precipitates which may be present in the microstructure. This may also require thin foil preparation by ion thinning technique to minimize the preferential polishing out of the different phases which occurs during electrolytic jet polishing.
- (3) Phase transformation studies, particularly in complex systems, require several alloy compositions to be examined. In the present study, only a few compositions within the Al-Cu-Mg-Li system have been examined owing to the variety of techniques which were employed. There is therefore a need to examine several more compositions of the quaternary alloys. It is suggested that the new compositions be considerably lower in both Cu and Mg levels in order to bring them closer to the ranges of the Al-Li based commercial alloys.
- (4) Two dimensional representations of the phase equilibria in a 4-component system are necessarily difficult. However, with the increasing application of computer modelling to phase diagrams information from experimental studies such as this one could be used, together with theoretical calculations, to predict phase diagrams which may be useful in alloy development within the Al-Cu-Mg-Li quaternary system. It will be interesting to attempt such phase diagram calculations.
- (5) Finally, the characterisation of the heat treated commercial 8090 and 8091 cast alloys revealed the presence of several coarse insoluble intermetallic equilibrium phases in the microstructure. These phases precipitate at high

angle grain boundaries and are bound to have a deleterious effect on mechanical properties. There is therefore a clear need to (a) further refine the solute contents (particularly the Cu:Mg ratio) of these alloys to prevent or minimize the precipitation of the equilibrium grain boundary Al-Cu-Mg-Li phase without sacrificing the precipitation of the matrix S' and T_1 phases which contribute to strength; and (b) to exercise tighter control on the levels of impurity elements which are taken in during casting of the alloys in order to prevent or minimize the precipitation of the $Al_6(Fe, Cu)$ and AlSiLi impurity-based phases. These measures if implemented may improve the mechanical properties of the cast Al-Li based commercial alloys and thus enhance their competitiveness with other candidate materials for applications in weight-critical structures.

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