

THE UNIVERSITY OF MANITOBA

PRECIPITATION BEHAVIOUR IN THE Al-1.5%Cu-0.75%Mg ALLOY

By

ALOK KUMAR GUPTA

A Dissertation Submitted to the Faculty of
Graduate Studies of the University of Manitoba
in Partial Fulfillment of the Requirements of the Degree of

DOCTOR OF PHILOSOPHY

DEPARTMENT OF MECHANICAL ENGINEERING
METALLURGY

Winnipeg, Manitoba

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ABSTRACT

The precipitation strengthening of Al-Cu-Mg alloys with a Cu/Mg ratio close to 2.2:1 has been attributed primarily to the precipitation of the orthorhombic S' phase. However, very little is known about the precipitation process in dilute Al-Cu-Mg alloy in terms of the kinetic parameters controlling the precipitation rates and the effect of Si additions on them. Therefore, a series of dilute Al-1.5%Cu-0.75%Mg alloys containing 0, 0.23, 0.49, 0.76 and 1.03% Si were chosen to study their precipitation behaviour by transmission electron microscopy (TEM) and differential scanning calorimetry (DSC).

The alloys were solution treated and water quenched, stabilized at room temperature for 48 h and further aged at 130° and 190°C. TEM studies on the Si-free alloy showed that on ageing at 130° and 190°, S' precipitates nucleated on dislocation loops and helical dislocations and grew as rods parallel to $\langle 100 \rangle_M$ matrix directions with a slight tendency to cluster in groups on $\{110\}_M$ matrix planes. These groups of precipitates did not however coalesce to form laths on the $\{110\}_M$ or $\{210\}_M$ matrix planes as has been reported in more concentrated alloys with similar Cu/Mg ratios. The orientation relationships determined from the x-ray investigations were used to simulate a detailed and complete S' phase diffraction pattern which was consistent with the morphology and crystal structure. Measurements of relative changes in lattice parameters suggested that the S' phase is simply a strained version of the equilibrium S phase. With increase in the time of ageing at 190°C the b lattice parameter of the S' phase increased significantly and the c value declined without any change

in the cell volume. Grouping of rods on $\{110\}_M$ fcc matrix planes were explained on the basis of expansion of the b parameter and contraction of the c parameter.

The kinetics of the precipitation processes were studied by using differential scanning calorimetry (DSC). Various exothermic and endothermic DSC peaks were associated with specific precipitation and dissolution processes. Appropriate equations were developed to calculate the heat effects, mole fractions and reactions rates of the processes which occurred at heating rates 5°, 10°, 15° and 20°C/min. The first exothermic (25°-170°C) and endothermic (140°-240°C) peaks were found to be due to precipitation of GPB zones and dissolution of Guinier-Preston-Bagaryatsky (GPB) zones and complexes respectively. The second exothermic (253°-367°C) and endothermic (380°-434°C) peaks were associated with the precipitation and dissolution respectively of the S' phase. Except the process of dissolution of the S' phase, all others were found to be kinematically controlled processes. The dissolution of S' phase was interpreted as a thermodynamically controlled process. All the kinematically controlled processes were analysed for the determination of activation energy for each process using the following relationship

$$\frac{dY}{dt} = f(Y) K_o e^{-Q^*/RT}$$

The expression for $f(Y)$ was $(1-Y)$ for all the peaks analysed. The activation energy, Q^* , and the value of K_o for the precipitation and dissolution of GPB zones were determined to be 55.6 kJ/mole, $5.7 \times 10^5 \text{ s}^{-1}$, 123.9 kJ/mole and $1.1 \times 10^{10} \text{ s}^{-1}$ respectively. These results were found to be in good agreement with the published

information. The Q^* and K_o values for the precipitation of the S' phase were 129.9 kJ/moles and $2.7 \times 10^9 \text{ s}^{-1}$ respectively.

The addition of Si $\geq 0.49\%$ caused the formation of insoluble particles. The back scattered scanning electron microscopic images of the polished sections of the alloys showed the presence of very small particles of nearly spherical shape at the grain boundaries of the alloys except the one that contained 0.23% Si. Alloys with 0.76 and 1.03% Si also contained large particles of well defined geometrical shapes. The volume percentage of insolubles in the 1.03% Si alloy was 1.34. An electrolytic technique was used to extract the insolubles from the matrix. The extracted particles were analysed by energy dispersive x-ray analysis in SEM. They contained $20.6 \pm 0.4\%$ Cu, $32.6 \pm 0.4\%$ Mg, $30.2 \pm 0.4\%$ Si and $16.6 \pm 0.1\%$ Al by weight. X-ray diffraction analysis of these particles showed that they have a hexagonal structure with a and c parameters of $1.036 \pm 0.004 \text{ nm}$ and $0.404 \pm 0.004 \text{ nm}$ respectively. The insoluble particles were identified as the quaternary phase, Q. Ageing for extended periods of time at 190°C did not alter the composition or morphology of the insoluble particles. The presence of insoluble particles changed the solute contents of the matrix so that the Cu, Mg and Si contents 1.45, 0.63 and 0.39% respectively in the 0.49% Si alloy to 1.16, 0.05 and 0.44% in the 1.03% Si. The Cu/Mg ratio also changed from 2 in 0.23% Si alloy to 23 in 1.03% Si alloy.

The Al-1.52%Cu-0.74%Mg alloy which retained 0.23% Si in solid solution exhibited precipitation of the S' phase like the Si free alloy. At Si concentrations of 0.49% and greater, the matrix became depleted in solute due to the formation of the Q phase

($\text{Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$) and the subsequent precipitation behaviour changed. The TEM microstructure of the aged alloy containing 0.49% Si showed three kinds of precipitates. One of them was found to be plate shaped θ' phase while the other two had small needle-like and square shaped morphology. The alloy containing 1.03% Si also showed plate type θ' phase along with needle-like and dot shaped precipitates. Ageing of this alloy for extended time (1000 h) at 190°C resulted in a more complex structure.

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Finally, I pursued the Ph.D. program to fulfill the ambitions of my parents. I wish to dedicate this thesis to them.

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CHAPTER I

INTRODUCTION

The resistance to plastic deformation of metals and alloys is generally improved by three methods; namely, cold working, solid solution strengthening and introducing particles of a second phase. Many modern high strength alloys are based on the use of one or more of these methods of strengthening. The first two of these techniques have been known since ancient times, but the latter did not become known until the early 19th century. Wilm,⁽¹⁾ while searching for an aluminum alloy which could be strengthened by quenching from elevated temperature, in a manner similar to that used for steel, discovered that hardness of an Al-Cu-Mg-Mn alloy increased when it was quenched from elevated temperatures. The extent of hardening depended upon time and temperature of ageing. These observations were different from those made on steels and gave birth to the phenomenon of "age hardening". The fundamental reasons for age-hardening of aluminum alloy remained unknown to Wilm.⁽¹⁾ However, Mercia, Waltenberg and Scott⁽²⁾ suggested later that hardening observed in aluminum alloys resulted due to their resistance to deformation by slip caused by "submicroscopic dispersion" of the second phase particles formed throughout the grains as a result of ageing for a sufficient period of time at a particular temperature.

Since that time many more alloy systems have been developed which can be hardened by the precipitation of second phase particles. However, progress in the understanding of the microstructural changes during ageing remained a mystery until sophisticated techniques like

x-ray diffraction and electron microscopy were developed. Use of these techniques has resulted in a significantly improved understanding of the process of precipitation hardening. Nevertheless it cannot be regarded as being a completely understood phenomenon until two goals suggested by Kelly and Nicholson⁽³⁾ are met. Firstly, the number and arrangement of precipitates that are formed after a given alloy is aged at a given temperature for a given period of time must be predictable by its phase diagram and the properties of the individual elements. Secondly, yield stress and work hardening properties of the alloy must be capable of being predicted. This is not yet possible even for less complex alloys despite the availability of theoretical models and a wealth of experimental data.

Understanding and predicting the effects of minor or trace elements on the precipitation process in alloys have been another goal that has been pursued during the last 30 years. Although trace element effects are being widely studied, only limited progress has been made in establishing the rules governing their behaviour. In some cases the trace element effect appears unique to a particular alloy system, whereas in others the same trace elements may simulate precipitate nucleation in several systems. The effect of trace elements on aluminum alloys has been reviewed by Hardy and co-workers.⁽⁴⁾

The Al-Cu-Mg alloys are capable of age hardening and retaining their age hardened strength at relatively high temperatures.⁽⁵⁾ Some of these alloys are widely used for various industrial applications.⁽⁶⁾ It has been shown that for alloys having a Cu/Mg ratio close to 2, ageing causes an increase in strength of as much as 275% due to precipitation of the S' phase.⁽⁷⁾ Small additions of Si increase

the strength of these alloys by about 350%.⁽⁷⁾ Silicon containing alloys like AA 2038 are being considered as possible alternative sheet materials for automotive applications.⁽⁸⁾ Because of the high potential of the Al-Cu-Mg alloys, the precipitation behaviour in these alloys was selected for investigation in this study. The silicon free and silicon containing (0.25, 0.50, 0.75 and 1.03%) Al-1.5%Cu-0.75%Mg alloys have been examined by transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) in order to characterize the crystallography, precipitation kinetics and effects of small additions of silicon. It is hoped that a little understanding of the phenomena occurring during age hardening of these alloys will result in the development of alloys having improved and predictable properties.

CHAPTER II

LITERATURE REVIEW

The theory of solid state precipitation reactions has been discussed by Christian⁽⁹⁾ and Martin and Doherty⁽¹⁰⁾ and critically reviewed by Russell.⁽¹¹⁾ The literature dealing with precipitation in aluminum alloys has also been reviewed by Hardy and Heal⁽¹²⁾ in 1954, Kelly and Nicholson⁽³⁾ in 1963, Mondolfo⁽¹³⁾ in 1976, Lorimer⁽¹⁴⁾ in 1978 and Shchegoleva⁽¹⁵⁾ in 1982. In the review presented here an outline of the theory of solid state precipitation reactions and the precipitation behaviour in binary Al-Cu and Al-Mg alloys and ternary Al-Cu-Mg alloys will be presented. The literature on the effects of the small additions of solute to ternary Al-Cu-Mg alloys will also be included. Emphasis will be given on the recent developments in our understanding of precipitation processes in the above mentioned alloys.

2.1 THEORY OF PRECIPITATION IN SOLIDS

Precipitation in the solid state in alloys occurs by thermally activated atomic movements. It can be expressed as:



where α' is a metastable supersaturated solid solution, β is a stable or metastable precipitate and α is a more stable solid solution with the same crystal structure as α' , but with a composition closer to the equilibrium composition of α_e (Fig. 2.1). The decomposition of a phase into one or more phases may be divided into three stages:

- (i) creation of nuclei of the new phase by concentration and structural

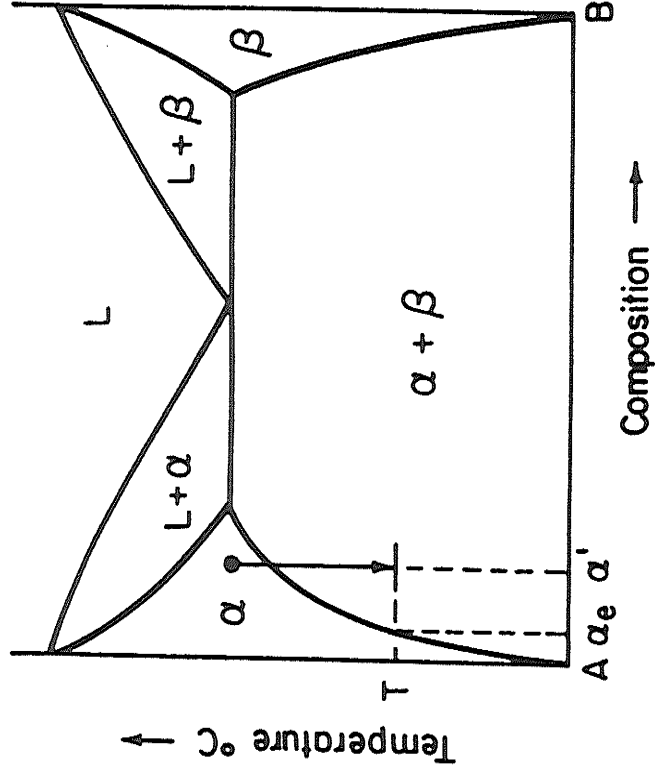


Fig. 2.1 Schematic equilibrium diagram representing precipitation of β from supersaturated α' at temperature T .

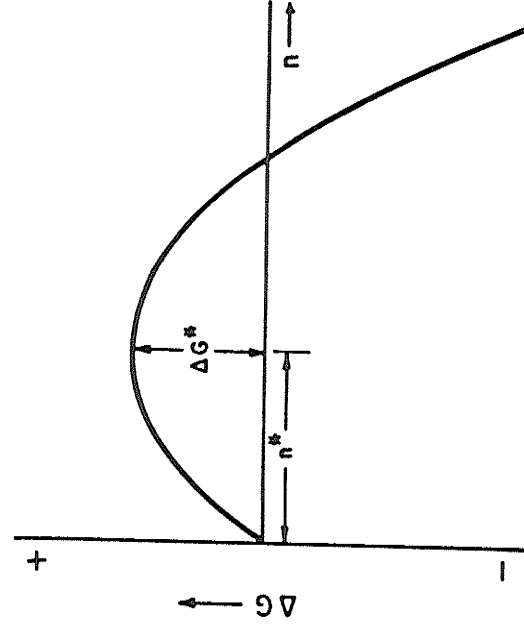


Fig. 2.2 Free energy (ΔG) of a precipitate as a function of the number of atoms it contains (n)

fluctuations, (ii) growth of the nuclei directly from supersaturated medium and (iii) growth of larger particles at the expense of smaller ones when the particles have reached appreciable size and the degree of supersaturation in the matrix has become negligible. The first two stages of precipitation are called nucleation and growth respectively. The third stage is called coarsening.

2.1.1 Nucleation of Precipitates

Nucleation is the formation of a microscopic volume of the product phase β in the parent α' phase. Creation of the nucleus is associated with the formation of a surface between β and α' . Hence the total free energy change associated with the nucleation process is given by:

$$\Delta G = a \sigma n^{2/3} + (\Delta g_c + g_e) n V \quad (2.2)$$

where, ΔG - free energy change

a - shape factor

σ - surface energy of β/α' interface per unit area

n - number of atoms

g_e - elastic strain energy (per unit volume of β) associated with nucleus

Δg_c - chemical free energy/unit volume of β

V - atomic volume of nucleus

The variation in ΔG with n is shown in Fig. 2.2. The condition for continued growth of the embryo is that the number of atoms it contains should exceed n^* , i.e. $(\frac{d\Delta G}{dn})_{n=n^*} = 0$. Hence,

$$n^* = \left[\frac{2 a \sigma}{-3V (\Delta g_c + g_e)} \right]^3 \quad (2.3)$$

and

$$\Delta G^* = 1/3 \sigma n^{*2/3} \quad (2.4)$$

For a spherical nucleus of radius r , the surface area is given by $4\pi r^2 = an^{2/3}$ and $n = \frac{4\pi r^3}{3V}$, Hence

$$r^* = \frac{2\sigma}{- (\Delta g_c + g_e)} \quad (2.5)$$

$$\text{and} \quad \Delta G^* = \frac{16 \pi \sigma^3}{3 (\Delta g_c + g_e)^2} \quad (2.6)$$

The chemical free energy term is negative below the equilibrium temperature and increases almost linearly with undercooling. The rate of nucleation $\dot{N}_V$ is given by,

$$\dot{N}_V = \omega C_o \exp \left\{ - \frac{\Delta G^*}{kT} \right\} \exp \left\{ - \frac{\Delta G_m^*}{kT} \right\} \quad (2.7)$$

where, ω = factor that includes vibration frequency and area of nucleus

C_o = number of atoms per unit volume in the nuclei

k = Boltzman's constant

ΔG_m^* = activation energy for migration of atoms

The values of ω and ΔH_m^* are assumed to be independent of temperature, but ΔG^* is strongly dependent upon temperature. (16)

$$r^* \propto \frac{1}{\Delta T} \quad \text{and} \quad \Delta G^* \propto \frac{1}{(\Delta T)^2} \quad (2.8)$$

Fig. 2.3(a) shows the variation of the two exponential terms in Equation 2.7, T_e in the Figure is the equilibrium solvus temperature above which α' is single phase. The term $\exp \{\Delta G^*/kT\}$ is the potential concentration of nuclei which is essentially zero until a critical undercooling, ΔT_c , is reached, below which the term rises very rapidly. On the other hand, the term, $\exp \left(\frac{\Delta G_m^*}{kT} \right)$ is essentially the atomic mobility factor and decreases rapidly with decreasing temperature. The combination of these terms, i.e. the homogeneous nucleation rate is shown in Fig. 2.3(b). Maximum nucleation rate is obtained after a finite undercooling. During precipitation the nucleation rate is initially low, then generally rises and finally decreases as the mean concentration of solute atoms in the matrix decreases.

The chemical free energy change Δg_c in Equation 2.6 is given by $(\Delta G_n/V)$, where ΔG_n is the change in free energy for a mole of precipitate and V is molar volume. ΔG_n is given as

$$\Delta G_n = (G_\beta - G_0) - (X_\beta - X_0) \left(\frac{\partial G}{\partial X} \right)_{X_0} \quad (2.9)$$

The value of ΔG_n can be obtained from the free energy versus composition diagram as shown in Fig. 2.4. If the composition of α is greater than the spinodal composition $\left(\frac{\partial^2 G}{\partial X^2} = 0 \right)$, spinodal decomposition may first take place. For example, if the composition of α is X'_0 , α of composition X_β may form by spinodal decomposition before the formation of the β phase.

The shape of the nucleus is governed by its surface energy and strain energy. The free energy of the nucleus is minimal with respect to its shape. When the atomic size difference is small

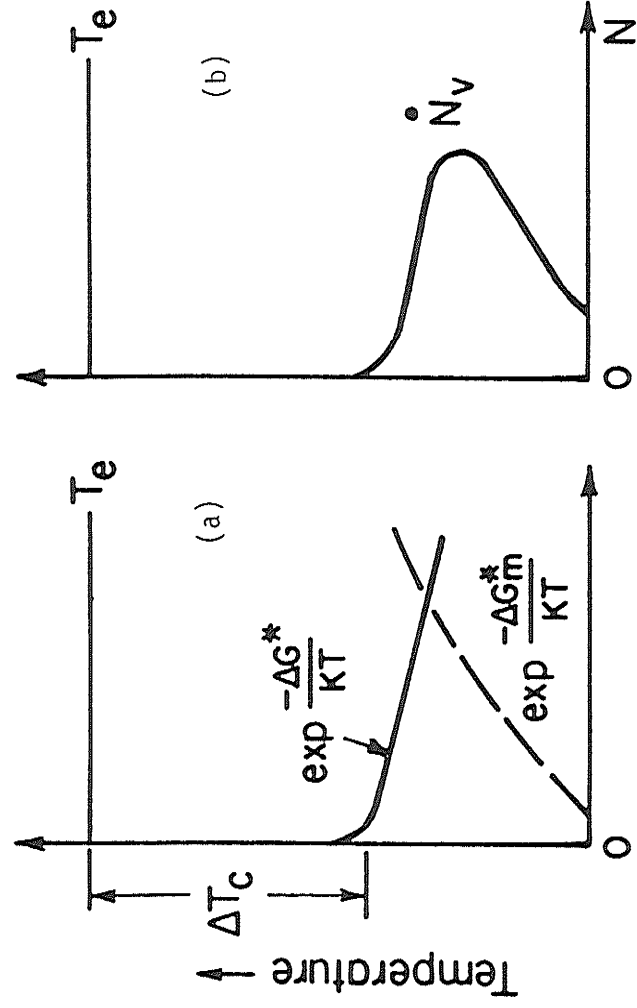


Fig. 2.3 Variation of the rate of homogeneous nucleation with undercooling (16)

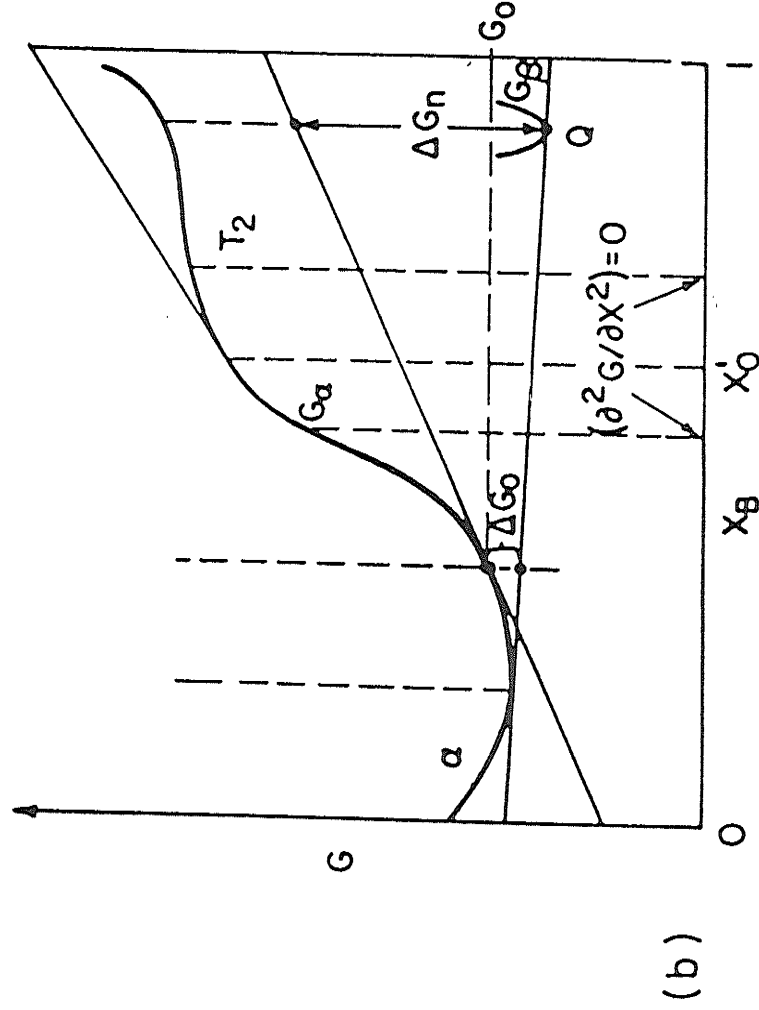
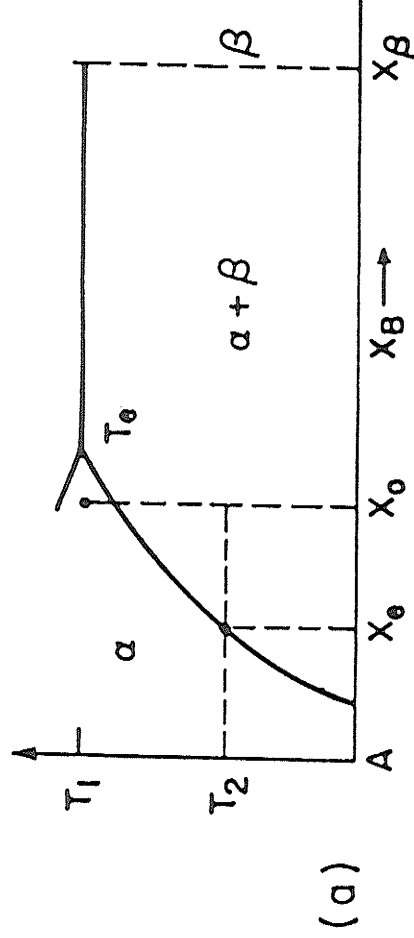


Fig. 2.4(a) Schematic phase diagram showing precipitation at T_2 from supersaturated alloy of composition X_0

(b) Variation of the free energies of phases with composition at temperature T_2 and determination of the molar free energy change due to precipitation, ΔG_n

($\leq 3\%$) spherical GP zones are formed. But at higher misfits ($> 5\%$) plate shaped zones are formed. The largest strain due to lattice misfit is usually along the matrix direction of lowest elastic modulus. For example, in the face centred cubic lattice of aluminum $\langle 100 \rangle$ directions are the ones of minimum modulus, and the GP zones form as discs perpendicular to these directions. The strain energy of the nucleus increases faster than the interfacial energy term until the point is reached where the free energy of the system is lowered by the loss of coherency. GP zones in Al-Zn and Al-Ag alloys are exceptions to this type of behaviour. In these systems, the atomic mismatch between solute and solvent atoms is less than two percent and the strain energy is less than the surface energy. GP zones in such systems form in spherical clusters in order to minimize surface energy.

2.1.2 Growth of Precipitates

Martin and Doherty⁽¹⁰⁾ have reviewed the growth of precipitates in detail. The likely limiting factors for the growth of precipitates in solid solutions are the rates at which the atoms are brought to or removed from the interface by diffusion and the rates at which they cross the interface. The interface reaction is likely to be a slower step during early stages of growth, since diffusion distance tends to be zero in this situation. At later stages, however, diffusion is likely to be the rate controlling step since the continuous removal of solute from the solution reduces the concentration gradient, which is the driving force for diffusion.

For the growth of spherical precipitates of radius $R^{(9)}$,

$$R = \alpha (D t)^{\frac{1}{2}} \quad (2.10)$$

where, D is the volume diffusion coefficient and α is a function of super saturation. A similar expression has been deduced for planar precipitates,

$$S = \alpha (D t)^{\frac{1}{2}} \quad (2.11)$$

where S is the half thickness of planar precipitates.

Nuclei are usually bounded by a combination of coherent, semi-coherent and smoothly curved incoherent interfaces. Generally the incoherent interfaces are highly mobile. The precipitates grow by the movement of these interfaces. The shape that develops during growth depends on the relative rates of migration of the interfaces.

2.1.3 Transformation Kinetics

The overall transformation can be represented by plotting temperature for a given fraction transformed (Y) as a function of time. This is called a TTT diagram (Fig. 2.5). For precipitation reactions $\alpha' \rightarrow \alpha + \beta$, Y at a given temperature is defined as the volume of β at a time t divided by the final volume of β . The value of Y varies from 0 to 1.

Among the factors that determine $Y(t, T)$ are the nucleation rate and the growth rate. If the quenched metastable α is allowed to transform at a constant temperature, nuclei will form in the alloy. One possible sequence of events shown in Fig. 2.6(a) is that nuclei form throughout the transformation process so that at any given time a wide range of sizes of particles exist. Another possibility is that all nuclei form at the beginning of the transformation as shown in Fig. 2.6(b). If all potential nucleation sites are consumed in the process, "site saturation" is said to occur. In Fig. 2.6(a) Y

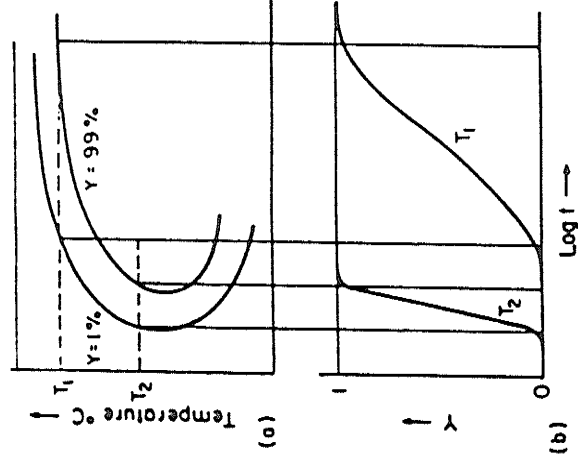


Fig 2.5(a) The time-temperature transformation diagram
 (b) Transformed fraction (Y) vs. time plots at two different temperatures (16)

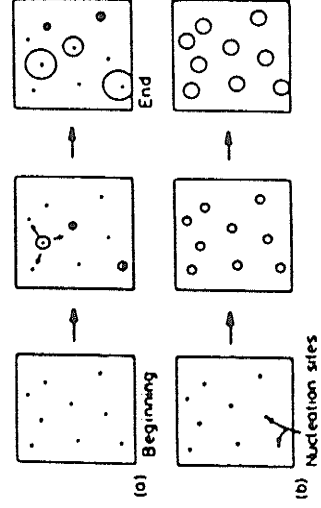


Fig. 2.6(a) Nucleation at constant rate during the whole transformation
 (b) All nuclei appear at the beginning of transformation (16)

depends upon the nucleation rate and the growth rate, while in Fig. 2.6(b), Y depends only on the number of nucleation sites and the growth rate. In both cases the overall fraction transformed can be represented by the following: (9)

$$Y = 1 - \exp(-Kt^n) \quad (2.12)$$

This is known as the Johnson-Mehl-Avrami equation, where n is a numerical exponent whose value may vary from ≈ 1 to 4. If there is no change in the nucleation mechanism, n is independent of the transformation temperature. The constant K on the other hand depends on the nucleation and growth rates and is therefore very sensitive to the transformation temperature. It can be shown that the rate constant is $K^{1/n}$ and

$$K^{1/n} = K_o \exp \{ - Q^*/RT \} \quad (2.13)$$

where, Q^* is the activation energy. It is the value of Q^* which determines the rate of transformation at a given temperature.

2.1.4 Factors Influencing the Activation Energy of Transformation

2.1.4.1 Interfacial Energy

Assuming constant homogeneous nucleation rate and constant growth rate, it can be shown that $n = 4$ and

$$K^{1/n} = K' \exp \left(- \frac{\Delta G_m^* + 0.25 \Delta G_H^*}{kT} \right) \quad (2.14a)$$

Hence,

$$Q^* \approx \Delta G_m^* + 0.25 \Delta G_H^* \quad (2.14b)$$

$$\text{and from Equation (2.6), } \Delta G^* \propto \frac{\sigma^3}{(\Delta g_c + g_e)^2} \quad (2.14c)$$

It is evident from these equations that the interfacial energy is one of the barriers to nucleation. This barrier can be minimized if the interfacial energy is small. Thus, metastable precipitates capable of forming coherent interfaces can have lower values of Q^* and precipitate in preference to the stable precipitates. The GP zones are often the first precipitates to form because of their low surface energy, typically $10\text{--}30 \text{ mJ/m}^2$ as compared with 500 mJ/m^2 for larger intermediate precipitates.⁽⁹⁾ The volume free energy change for GP zone formation is also small as shown in Fig. 2.7. It may be noted that the free energy change accompanying the transformation of an alloy of composition α_0 into GP zones of composition α_{GP} and matrix of composition α_1 is $(G_1 - G_0)$. Similarly the transformation to θ' is driven by the volume free energy change $(G_3 - G_0)$. Although at equilibrium, θ phase has the largest thermodynamic driving force Δg_c , it also has the greatest interfacial energy due to the incoherent nature of the interface. GP zones have a very low value of surface energy and hence they precede the formation of the equilibrium and intermediate precipitates, provided the alloy is quenched below the appropriate metastable GP zone solvus. At high ageing temperatures, the equilibrium phase may form because it is the only phase with a negative Δg_c term at that temperature.

2.1.4.2 Strain Energy

Coherent precipitates are associated with elastic strains. Equation (2.14b) and (c) show that elastic strain energy increases the activation barrier to transformation as the positive value of g_e reduces the magnitude of the negative Δg_c . The transition of the

coherent state to the incoherent state takes place when the magnitude of the strain energy increases with the growth of the coherent phase.

At some stage it becomes energetically more favourable for the interfacial misfit to be accommodated by dislocations lying on the interface. This phenomenon is called loss of coherency. There are several mechanisms in which coherency may be lost and some of these are illustrated in Fig. 2.8 and are described in detail by Martin and Doherty⁽¹⁰⁾ and Porter and Easterling.⁽¹⁶⁾

2.1.4.3 Heterogeneous Nucleation Sites

From the expression for ΔG^* (Equations (2.6) and (2.8)), it can be seen that if nucleation is to be made easier at lower degree of undercooling, the chemical free energy term must be increased in magnitude. In supersaturated solid solutions various non-equilibrium defects such as vacancies and interstitials, dislocations, stacking faults, twin boundaries, grain boundaries, etc. which are present in the system, are expected to increase the free energy of the system. Creation of a nucleus on any of these sites results in the destruction of defects which causes the free energy of the system to decrease. This in turn reduces the activation energy required for nucleation to occur in the system. Details of the nucleation process in heterogeneous sites have been described by Christian,⁽⁹⁾ Martin and Doherty⁽¹⁰⁾ and Porter and Easterling.⁽¹⁶⁾

2.1.4.4 Quenched-in Vacancies

As shown in Fig. 2.9⁽¹⁷⁾ the equilibrium concentration of vacancies increases exponentially with temperature. The equilibrium

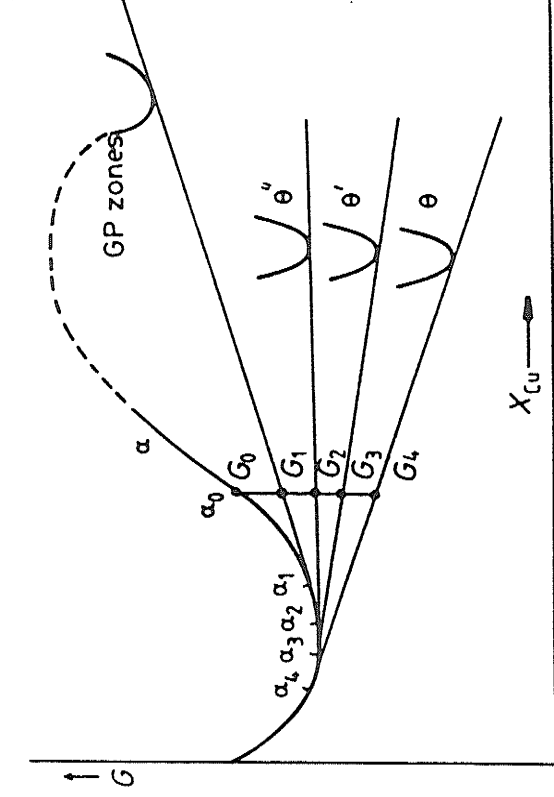


Fig. 2.7 A schematic molar free energy diagram for the Al-Cu system

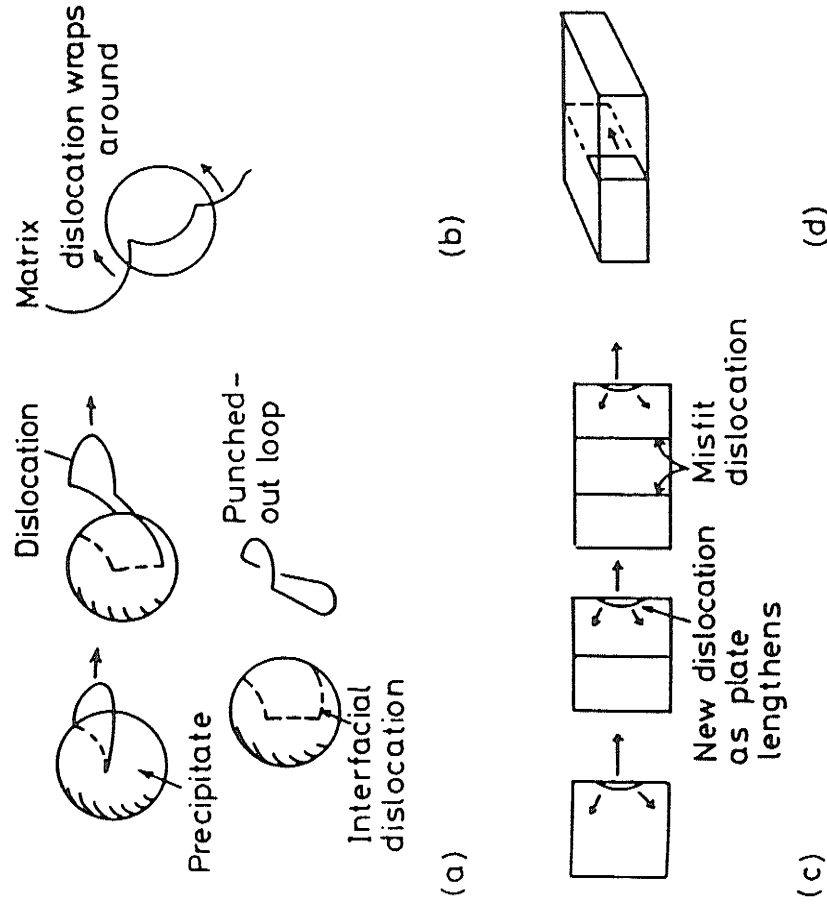


Fig. 2.8 Mechanism of coherency loss

- (a) Dislocation punching from interface
- (b) Capture of matrix dislocation
- (c) Nucleation at edge of plate as plate lengthens
- (d) Loop expansion by vacancy condensation in the precipitate

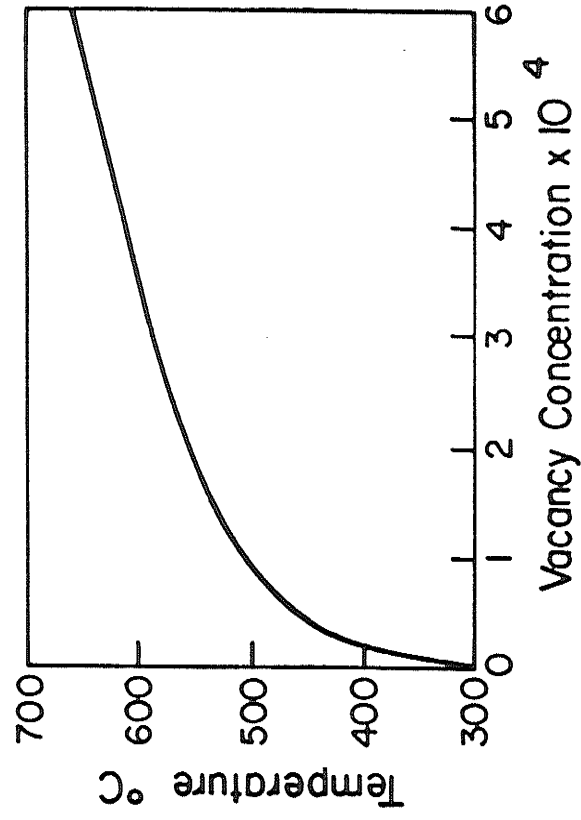


Fig. 2.9 Variation of the equilibrium concentration of vacancies in aluminum with temperature⁽¹⁷⁾

concentration of vacancies is relatively high at the solution temperature and much lower at the ageing temperature. When the alloy is rapidly quenched from the solution treatment temperature to lower temperatures, the high concentration of vacancies present at the solution treatment temperature is quenched-in. The excess vacancies influence the precipitation reaction by providing sites for heterogeneous nucleation and by enhancing diffusion rates at the ageing temperatures.

The quenched-in vacancies in the alloy have a tendency to form small vacancy clusters, dislocation loops and helical dislocations. In dilute Al-Ge and Al-Si alloys, vacancy loops are formed during quenching and the precipitates sequentially form heterogeneously on these dislocation loops.^(3,18,19) Katz and Ryum⁽²⁰⁾ reviewed the precipitation processes in various Al-alloys and found that on quenching dilute Al-alloys the vacancy clusters form, which on up quenching serve as nuclei for the precipitation process. On the other hand, on up quenching concentrated alloys GP zones may form and serve as nuclei for the transition phases. On the basis of studies by Askedale (as quoted by Katz and Ryum)⁽²⁰⁾ on Al-Mg alloys and by Westengen and Ryum⁽²¹⁾ on Al-Mg-Si alloys, Katz and Ryum proposed that vacancy clusters nucleated during quenching, or immediately following quenching, act as sites for nucleation of intermediate precipitates in all alloys in which GP zones do not form due to instability or low solute supersaturation.

Dislocation loops are formed by the collapse of vacancies and they appear on {111} planes. Some loops also lie on {100} and {110} planes as predicted by Kuhlman-Wilsdorf.⁽²²⁾ The loops can

grow by absorbing excess vacancies at the ageing temperature and provide sites for heterogeneous nucleation. The S' precipitates in Al-Cu-Mg alloys⁽²³⁾ and β' in Al-Mg alloys⁽²⁴⁾ are examples of this type of nucleation.

The screw dislocations already present in alloys can absorb excess vacancies by progressive climb to form helical dislocations and provide sites for heterogeneous nucleation.⁽²⁵⁾ The θ' phase in Al-Cu alloys, γ' phase in Al-Ag alloys, and S' phase in Al-Cu-Mg alloys are all found to form on helical dislocations. The addition of solute to aluminum may reduce the effective vacancy supersaturation in the quenched specimen below the level that is necessary for the prismatic loops to be nucleated. The excess vacancies can then only migrate to dislocations to form helices.⁽²⁶⁾

The diffusion rates at the ageing temperatures are greatly enhanced due to quenched-in vacancies and clustering of solute atoms takes place seven or eight orders of magnitude faster than that expected from extrapolation of high temperature diffusion data. In dilute alloys the binding energy between solutes and vacancies may be appreciable. For example, Panseri et al.⁽²⁷⁾ and Christian⁽⁹⁾ report that a solute vacancy cluster may move at an appreciable rate gradually acquiring more solute atoms and vacancies. In this way the quenched-in vacancies may assist diffusion in alloys.

The literature related to increase in diffusion rate due to quenched-in vacancies, has been reviewed by Kelly and Nicholson.⁽³⁾ Due to high diffusivity of the quenched-in vacancies it is very difficult to avoid losing vacancies in the vicinity of grain boundaries and interfaces. This has an important effect on the distribution

of precipitates that form in the vicinity of the grain boundary or interfaces on subsequent ageing. The causes and effects of precipitate free zones (PFZ) at grain boundaries have been reviewed in detail by Starke.⁽²⁸⁾

2.1.5 Formation of Transition Phases and the Precipitation Sequence

Because of changes in the value of Q^* due to various factors discussed in the last section, the rate of precipitation of many metastable phases becomes appreciable compared with that of the stable phase. The intermediate transition phases also help with nucleation of other transition phases. The nucleation of intermediate precipitates at GP zones has been examined in detail by Marth et al.⁽²⁹⁾ Russell⁽³⁰⁾ has shown that change in the free energy associated with the incoherent precipitation is increased by the incorporation of vacancies which relieve the transformation strains. Marth et al. have also shown that the presence of GP zones provides an effective surface for nucleation and makes available a significant amount of GP zone-matrix interfacial energy which reduces the interfacial energy component of the activation energy barrier to nucleation.

Russell and Aaronson⁽³¹⁾ have attempted to summarize the factors affecting the sequential nucleation of precipitates. The early transition phases are predicted to nucleate preferentially at the precipitate matrix interfaces of their predecessors. The reduction in activation energy occurs after initial precipitation of solute atoms. Most of the examples of precipitation sequence cited in the literature were found to be in agreement with this prediction. Baur⁽³²⁾ and Phillips⁽³³⁾ have demonstrated that an in situ transformation from

GP zones to θ'' occurs during isothermal growth. However, some serious objections to the general applicability of sequential nucleation theory have been raised. In the Al-Cu system GP zones form homogeneously, but there is no clear experimental evidence for θ'' being nucleated at GP zones. It has been shown that θ' nucleates on dislocations.⁽¹⁴⁾ Suzuki and Kimura⁽³⁴⁾ demonstrated that θ' is also nucleated on some types of vacancy clusters.

Westengen and Ryum⁽²¹⁾ showed that β'' and β' phases in the Al-Mg-Si system developed continuously from homogeneously nucleated GP zones. However, β phase never nucleated on β' , but rather as plates or cubes on vacancy-solute atom clusters. Lendvai et al.⁽³⁵⁾ also found that vacancy-solute atom clusters are formed in these types of alloys during quenching.

The precipitation reactions in Al-Zn-Mg systems are probably most complex among aluminum alloys. Many investigators⁽³⁶⁻³⁸⁾ have demonstrated that there are two types of GP zones in these alloys. One of these two types is rich in vacancies and probably is best regarded as a vacancy-solute cluster while the other is the GP zone. On up quenching the intermediate η' -phase or the T-phase is nucleated on the vacancy-solute atom clusters, while GP zones are reverted.

On the basis of observation made on different Al-alloy systems, it is evident that precipitation kinetics are quite different from those advocated by Russell and Aaronson.⁽³¹⁾

During or immediately following quenching from the homogenization temperature, two clustering reactions may take place; clustering of solute atoms form GP zones and clustering of vacancies into vacancy clusters. The two clustering reactions are interdependent

through the diffusivity of solute atoms and vacancies. On subsequent ageing the GP zones grow and internal ordering takes place within them. On up quenching the GP zones dissolve either partially or completely, depending upon whether the up quench temperature is below or above the GP zone solvus.

Katz and Ryum⁽²⁰⁾ have proposed a model to generally explain the decomposition of aluminum alloys after quenching and the subsequent nucleation of intermediate precipitates. On quenching from the solution temperature two types of clusters are formed and the subsequent behaviour of these two types depends upon the particular alloy system and alloy composition. In dilute Al-Si and Al-Ge alloys for example, no zones form after quenching to a low temperature (T_q , Fig. 2.10). During ageing, only the vacancy clusters are stable, and they act as a nuclei for Si and Ge precipitates. Al-Cu and Al-Zn-Mg alloys, however, would behave more as X_B^{II} in Fig. 2.10. Precipitation reactions occurring on up quenching depend on the length of time spent at T_q (Fig. 2.10) and whether the ageing temperature is above or below the GP zones solvus. The vacancy clusters grow slowly at low ageing temperatures but are much more stable on up quenching than GP zones and are able to act as nucleation sites for semi-coherent and fully coherent precipitates. Precipitate free zones are formed around vacancy sinks, as a critical vacancy concentration is required for the formation of vacancy clusters. It can be concluded that the vacancy clusters contain both solute atoms and vacancies and some kind of crystallographic character. The critical temperature for nucleation of these defects, which is dependent on the solution temperature, is approximately 20-40°C for Al-Zn-Mg alloys and 0-20°C for Al-Mg-Si

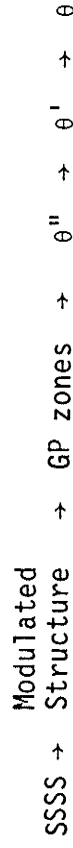
alloys.

This model, then, is a combination of Lorimer and Nicholson's theory and the one first proposed by Ryum.⁽³⁸⁾ It is an attempt to produce a unifying theory, capable of explaining the mechanisms of nucleation of intermediate precipitates in all aluminum alloys.

The TTT diagram of a system which may have many transition phases is shown in Fig. 2.11. This diagram clearly illustrates that, depending upon the ageing temperature, a number of possible sequences of precipitation may be observed. By modifying TTT curves of phases, the precipitation sequence may be altered.

2.2 PRECIPITATION IN THE BINARY Al-Cu ALLOY

The decomposition of a supersaturated solid solution (SSSS) of copper in aluminum depends on the alloy composition, ageing temperature and time. Based on x-ray diffraction, TEM and field ion microscopy (FIM), the following precipitation sequence has been established.⁽³⁹⁾



Each succeeding precipitate in this sequence is in metastable equilibrium with the aluminum-rich matrix below its solvus (Fig. 2.12).

The development of many modern research techniques has led to a much better understanding of the precipitation processes in these alloys. However, there is considerable disagreement about the detailed atomic arrangements of GP zones and the relationship between GP(I) and GP(II) zones, and the GP zones and the intermediate precipitates.

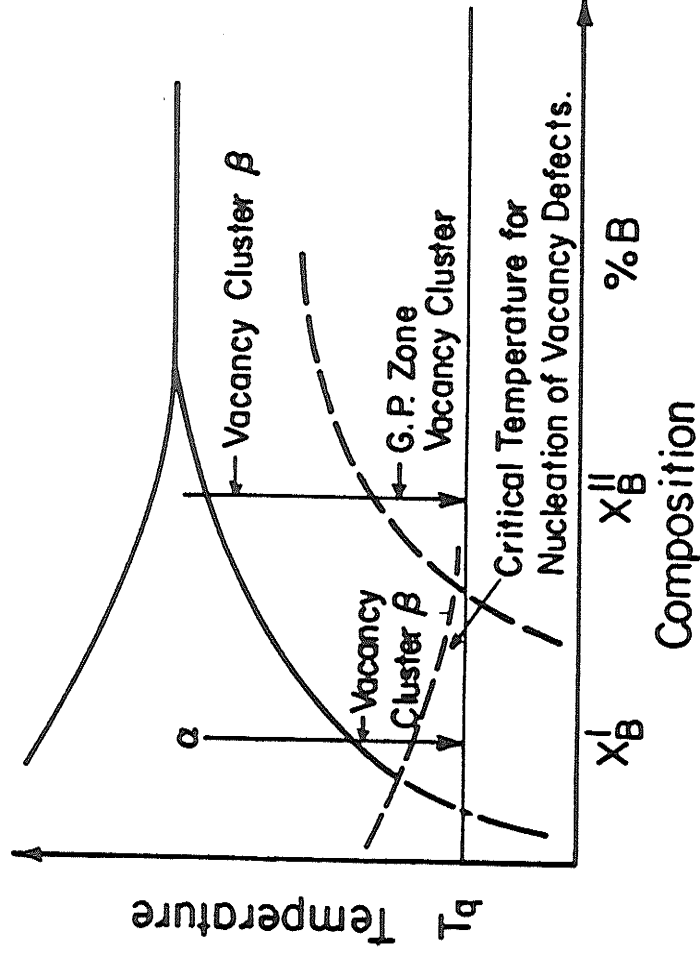


Fig. 2.10 Schematic phase diagram illustrating the different way in which an alloy of composition X_B may decompose, following quenching to T_q and subsequent ageing at a higher temperature (20)

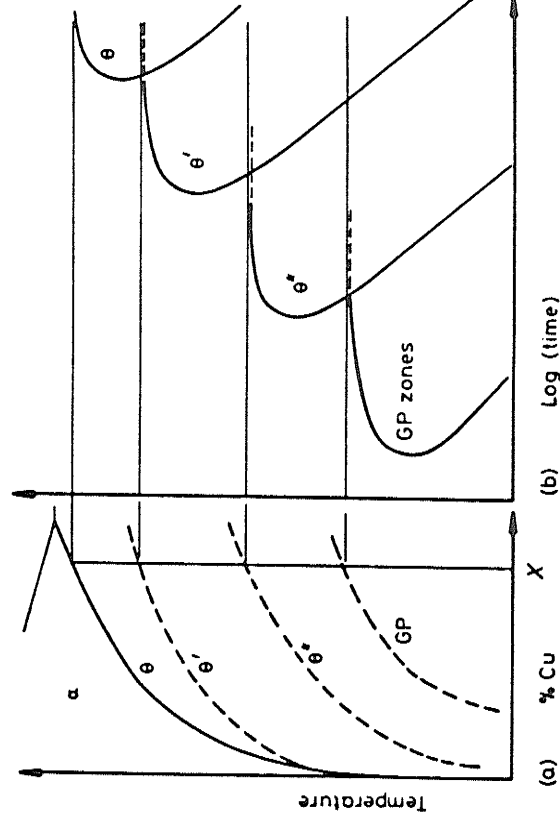


Fig. 2.11(a) Metastable solvus lines in Al-Cu alloys (schematic)
(b) Time for start of precipitation at different temperatures for alloy X in (a) (16)

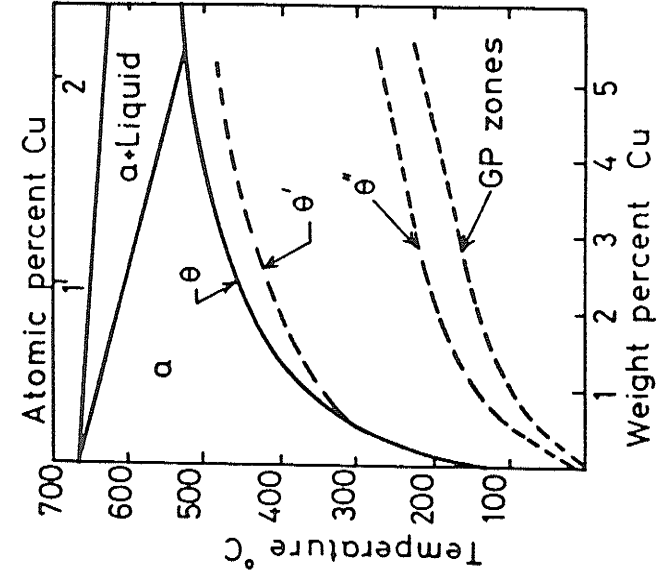


Fig. 2.12 Metastable solvus curves for GP zones, θ , θ' and θ'' precipitation (16)

2.2.1 GP(I) Zones

Copper rich clusters in quenched and aged Al-Cu alloys are known as GP zones. Numerous investigations have been carried out on the kinetics of zone formation (see for example Sanderson⁽⁴⁰⁾). Turnbull⁽⁴¹⁾ has made several suggestions regarding zone formation including spinodal decomposition and pipe diffusion through moving dislocations. Lorimer and Nicholson⁽⁴²⁾ favour homogeneous nucleation of GP zones. Naudon and co-workers⁽⁴³⁾ and Rioja and Laughlin⁽⁴⁴⁾ have presented evidence for spinodal decomposition. Rioja and co-worker in a TEM study on a room temperature aged Al-1.7%Cu alloy have reported modulated structures consisting of copper rich and poor regions which resulted in continuous formation of GP zones. However, when an alloy was aged at 130°C the GP zones nucleated directly from the solid solution. Thus, they concluded that the formation of GP zones in Al-1.7%Cu alloy occurs by spinodal mechanism between 20-130°C. This observation has been supported by Matsubura and Cohen⁽⁴⁵⁾ and Desarmot and Quere.⁽⁴⁶⁾

GP zones are detected as streaks in x-ray or electron diffraction patterns parallel to $\langle 100 \rangle$ matrix directions.⁽⁴⁷⁾ The structure of such zones therefore, is characterized by segregation of Cu atoms on (100) matrix planes and the strain fields induced by coherency of zones with the matrix. Several models (illustrated in Fig. 2.13) have been proposed for the structure of zones.⁽⁴⁸⁻⁵²⁾ The generally accepted model is that due to Gerold.⁽⁴⁹⁾ It describes GP zones as single layers of Cu atoms coherent with the (100) matrix planes and forming disc shaped particles. The strain associated with disc shaped particles decreases linearly until it vanishes at the

fifteenth plane from the zone. Nicholson and Nutting⁽⁵⁴⁾ in a TEM study were able to resolve and detect disc shaped zones, 4-6 Å thick and ≈ 90 Å in diameter on $\{100\}_M$ matrix planes of an Al-4%Cu alloy aged for 16 h at 130°C. Later, Phillips^(33,55) used bright field and lattice imaging techniques to study the GP zone structure in an Al-3%Cu alloy aged at 130°C. A direct correspondence between $\{200\}_M$ lattice fringes and atom planes was assumed and measurements were made to determine the strain field surrounding individual zones. These were found to be complex; most exhibited one or two oscillations between the first and the tenth $\{002\}_M$ planes and the exact nature of the displacement varied from zone to zone. The displacement field measurements did not fit either Gerold's or Toman's model of a zone, but were closer to Toman's, while the contrast in the image was interpreted as consistent with the copper monolayer model of Gerold.

Yoshida, Cockayne and Whelan⁽⁵⁶⁾ used the weak beam electron microscopy to investigate plate-like GP zones in aluminum alloy with 1.48 and 3.97%Cu aged at 80°, 100° and 130°C. GP zones were imaged under a variety of diffraction conditions and some common features were noticed under each condition. In dark field images with the value of deviation parameter $|S| \leq 1.1 \times 10^{-2} \text{ Å}^{-1}$ the zones appeared as pairs of bright lines with a spacing which depended on the value of deviation parameter. The comparison with the computed image agreed well with the observed zones and supported Gerold's model. However, strain around the $\{200\}$ planes was observed to be higher, that is, 0.2 rather than 0.1 for adjacent planes as predicted by Gerold's model.

Field ion microscopy is also being used to study the structure of GP zones.⁽⁵⁷⁻⁵⁹⁾ Abe et al.⁽⁵⁷⁾ have suggested that the GP zones

have complex shapes with inhomogeneity in their thickness which is in close agreement with the structure proposed by Auvray et al.,⁽⁵³⁾ although Mori and co-workers⁽⁵⁸⁾ have reported only single layer of Cu atoms on {100} planes.

Auvray et al.,⁽⁵³⁾ using diffuse x-ray intensity measurements and computer simulations, suggest that the GP zone state is a mixture of single and multilayer regions with (001) faces (Fig. 2.13(e)). The GP zone state is rather complex, unlike previous models. They have suggested that these multilayer zones are due to overlap or initiation of GP(II) zones before ordering. This is appreciably different from the accepted model of GP(I) zone. Matsubura and Cohen⁽⁶⁰⁾ in an investigation on Al-Cu alloys confirmed the presence of single layer and multilayer pure Cu zones on {100} matrix planes. They also found that strain around GP(I) zones oscillates with distance from them and vanishes near the fourth or fifth Al plane. In a recent study⁽⁵⁹⁾ using FIM, Hono and co-workers confirmed results of Matsubura and Cohen on the presence of single and multilayer zones. Phillips⁽⁵⁵⁾ using lattice imaging techniques has also reported the presence of zones two atom layers thick and a zone density of $1.3 \times 10^{14} \text{ cm}^{-3}$ in the quenched material. Several investigators have used high resolution electron microscope to observe GP zones in Al-Cu alloys.⁽⁶¹⁻⁶⁴⁾ Sato et al.⁽⁶¹⁾ in a study using the lattice imaging technique have confirmed the presence of the multiple Cu-rich layer structure and also have shown that these various periodic structures are composed of several Cu-rich layers and Al (200) planes which are different and more complex than GP(I) and GP(II) structures. Sato and Takahashi⁽⁶³⁾, in a further study, found that periodicity of these

complex atypical structures is similar to that of a θ' precipitate. Moreover, these complex structures transform more smoothly to the θ' precipitate as a result of ageing.

Most investigations in the last six years have shown the presence of multilayer complex zones. Their existence has, however, become questionable as they have high strain energy. Several studies^(53,59) suggest that these zones may grow from single layer to multilayer zones. Hono et al.⁽⁵⁹⁾ have related their existence to a pre-precipitation stage in these alloys. It is now increasingly clear that GP zones form by spinodal decomposition. Therefore the zones are expected to be formed through concentration fluctuation and, in early stages of the precipitation, the interface of the precipitates (Cu clusters) must be diffused. It is also suggested that if these clusters continuously grow into GP zones, it is probable that these zones, formed at room temperature, are multilayer on (001) planes. Moreover, the ratio of the number of multilayer to single layer GP zones must depend upon ageing temperature and time.

The stability of GP zones has been studied recently using calorimetry.⁽⁶⁵⁻⁶⁷⁾ Zahra et al.^(65,66) have found that the results of reversion experiments carried out by Beton and Rollason⁽⁶⁸⁾ accurately describe the solubility limits of GP zones in alloys excepting those with Cu contents less than 1%. For these alloys it was found that the results of Beton and Rollason were below the true values. The maximum temperature for stability of GP zones in an Al-4%Cu alloy was found to be 170°C. In another calorimetric investigation, Papazian⁽⁶⁷⁾ found good agreement with the results of Beton and Rollason.

Yoshida⁽⁶⁹⁾ studied the distribution and size of GP zones

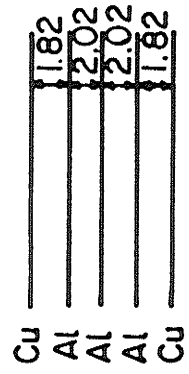
using the weak beam technique and found that GP(I) zones show normal distribution even in the transient stage from GP(I) to GP(II) zones. It was suggested that nucleation and growth of GP zones was due to the random walk of solute atoms, although Cu atoms could be supplied from the compression side near the edge of GP zones.

2.2.2 GP(II) Zones or (θ'') Phase

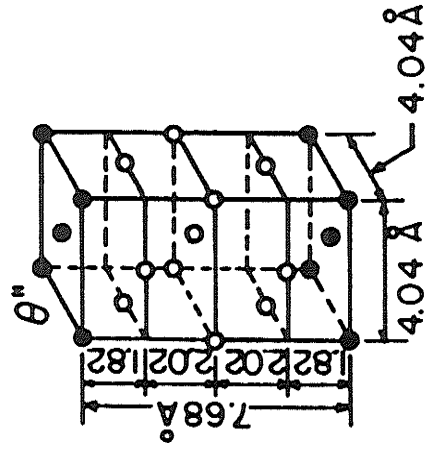
After longer ageing time and at higher temperatures (130°-170°C), the streaks in diffraction patterns transform into well defined intensity maxima. The precipitate at this stage is designated as θ'' .^(48,70) The structure of θ'' proposed by Guinier⁽⁴⁸⁾ does not fit the diffuse intensity maxima measurement along [h00] direction in reciprocal space.⁽⁷¹⁾ Another model proposed by Gerold⁽⁴⁹⁾ suggested two pure Cu {100} layers separated by three Al layers (Fig. 2.14(c)). The interplanar spacings involving Cu planes are 0.182 nm and those involving only Al planes are 0.202 nm. The structure which is usually accepted is tetragonal (Fig. 2.14(b)) with $a = 0.404$ nm and $c = 0.79$ nm. The orientation relationship with the matrix is

$$(001)_{\theta''} \parallel (001)_M ; [001]_{\theta''} \parallel [001]_M$$

The composition of θ'' was deduced to be about 17%Cu by comparing the θ'' lattice parameter with that of splat quenched fcc alloys.⁽⁷²⁾ Silcock and co-workers⁽⁴⁷⁾ and Gerold⁽⁴⁹⁾ showed that the c parameter varies with ageing time and temperature. The model of Gerold for θ'' has been verified by the x-ray measurements of Baur,⁽⁷³⁾ the weak beam study by Yoshida et al.⁽⁵⁶⁾ and the high voltage lattice imaging study of Satoh and Takahashi.⁽⁶³⁾ Satoh and Takahashi



(a)



(b)

Fig. 2.14 (a) Schematic diagram of a model of GP(II) zones⁽⁴⁹⁾
 (b) A θ'' unit cell

suggest θ'' to be a distinct phase structure which is different from single layer GP(I) zones. Recent single crystal x-ray work on the structure of the θ'' showed that the generally accepted structure of θ'' is probably quite correct and that multilayer arrays of (θ'') may account for 20% of zones in alloys aged to produce GP(I) zones. ⁽⁷⁴⁾

There is considerable argument about the ambiguous nomenclature, GP(II) vs. θ'' . It arises from the debate, whether θ'' is to be considered a phase distinct from GP zones or whether the zone and θ'' are considered as two stages of development of one phase. There have been two arguments for θ'' to be designated as a distinct phase: (i) θ'' has a distinct ordered crystal structure, and (ii) the existence of two stage ageing processes and the possibility of complete reversion of GP zones before the formation of θ'' . Gaylor and Parkhouse⁽⁷⁵⁾ distinguished θ'' from GP zones metallographically and argued on this basis that θ'' is a distinct phase. Nicholson and co-workers⁽⁷⁶⁾ noted that "... GP(II) was best described as a coherent intermediate precipitate rather than a zone, since it has a definite crystal structure.... and that ... Guinier's symbol for the θ'' phase was preferred". On the other hand, the experimental observations by direct lattice imaging in HVEM, weak beam microscopy, FIM, and DSC suggest continuous change from GP(I) to θ'' . Phillips⁽⁵⁵⁾ used lattice imaging and suggested that "there is a continuous structure progression from monolayer zones, to groups of parallel staggered zones, to GP(II) to θ' platelets". Papazian⁽⁶⁷⁾ in his DSC study on 2219 Al alloy found that transformation of GP(I) zones to θ'' were not abrupt, but rather more evolutionary in nature. He concluded that θ'' is not a required transitional step in the ageing sequence

and is consistent with the concept of θ'' as a regular spaced array of monolayer GP zones that evolve during long term ageing.

Yoshida et al.⁽⁵⁶⁾ have suggested a definite sequence for formation of GP(II) from GP(I) zones. As shown schematically in Fig. 2.15 the extra layer of copper atoms are envisaged to nucleate and grow on either side of the two main layers. This would be a state intermediate between a two layer GP(II) and a multilayer GP(II) zone. Finally, GP(II) zones may become ordered and approach θ'' precipitate structures. In another investigation⁽⁶³⁾ on Al-4%Cu alloy, it was found that GP(I) and GP(II) with typical structures, are formed predominantly as pre-precipitates in the early stage of ageing and that GP(I) zones grow into GP(II) zones. They also found that the GP(II) zone structure agreed well with Gerold's model. The GP(II) zones nucleate at the edge of Cu-rich layer, thicken and transform continuously to the semi-coherent θ' phase loosing coherency gradually.

Matsubura and Cohen⁽⁶⁰⁾ found that the GP(II) zones or θ'' are on the average five layers thick, and consist, as in the GP(I) zones, of essentially pure Cu. The structure is tetragonal, not because of ordering, but because of constraint imposed by the matrix. The structure is thus suggested to be identical with GP(I) zones except for the thickness of the precipitate. Moreover, they argued on the basis of the study due to Matsubura, Wu and Cohen⁽⁷⁷⁾ that the extra peaks which supposedly characterize the GP(II) or θ'' state can be detected even at ageing times that are assumed to produce only GP(I). These extra peaks are due to the thickness of the GP(II) zones in the later processes rather than a unique structural difference between GP(I) and GP(II).

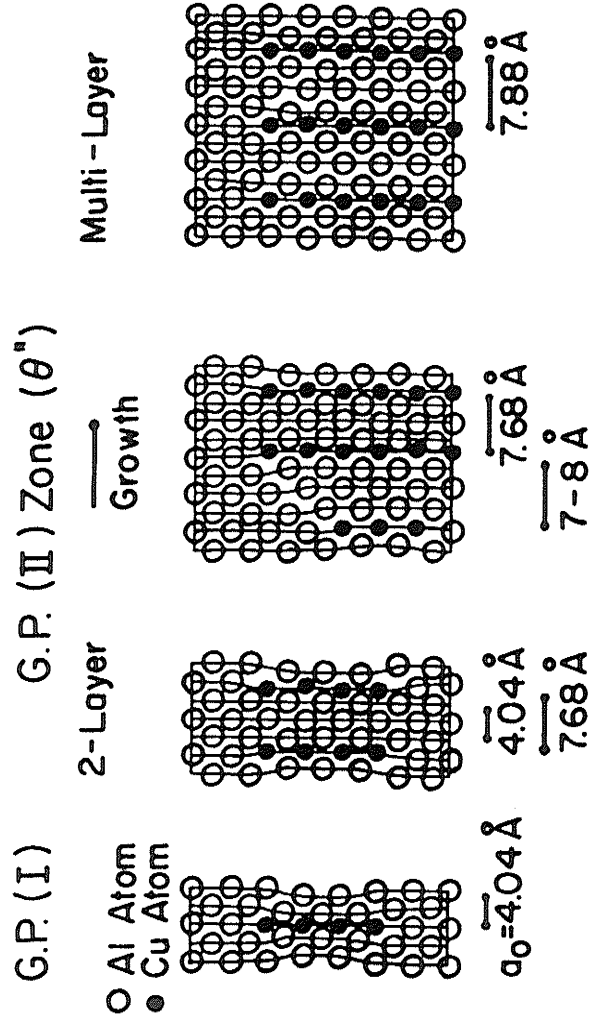


Fig. 2.15 Schematic diagrams of models of GP(I) and GP(II) zones (56)

Hono and co-workers⁽⁵⁹⁾ have recently distinguished multilayer GP(II) or θ'' from single layer GP(I) zones. Schematic views of (001) planes containing multilayer GP(I) zones and GP(II) zones or θ'' are shown in Fig. 2.13(e). Multilayer zones have no spacing among the Cu rich layers, so that the zones are observed to have a thickness of a few atomic layers, while θ'' has a structure suggested by Gerold. Hence "images of multilayer zones might represent θ'' or GP(II) zones". In light of these observations, it appears that GP(II) or θ'' in the later stage of ageing is not very different from GP(I) zones other than in thickness.^(59,60) Results of various studies on the structure of GP(II) or θ'' have been summarized in Table 2.1.

The possibility of complete reversion of GP zones after formation of GP(II) or θ'' has been studied widely by two step ageing techniques. The solvus for GP zones determined by resistivity measurements⁽⁷⁹⁾ is vastly different from that obtained by x-ray and hardness measurements.^(47,68,80) Also the theoretical estimates made by Merzinger⁽⁸¹⁾ are quite different from those of Baur.⁽⁷³⁾

The most widely quoted GP zone and θ'' solvi are those determined by the hardness-reversion experiments of Beton and Rollason.⁽⁶⁸⁾ Their results were, however, accurate for a high level of Cu content. Nakamura et al.,^(82,83) in a study on Al-1.7 at %Cu alloy, investigated solvus curves for GP zones and θ'' using the nuclear magnetic resonance (NMR) technique. They found that the precipitation of the GP(I) zone mainly occurs in substage a_1 (Fig. 2.16). At the end of substage a_1 at which the precipitation of the GP(I) zone is much slowed down, the formation of θ'' becomes active. It results in a decrease in the solute concentration of the matrix

Table 2.1 Summary of structural studies for GP(II) zones.

Reference Number	Authors	Type of Measurements	Results
78	Guinier	X-ray	Al: (1/6 Cu + 5/6 Al): Cu: (1/6 Cu + 5/6 Al): Al: 2.10: 1.85: 1.85: 2.10 Å
49	Gerold	X-ray	Two Cu layers separated by three Al layers (Cu: Al: Al: Al: Cu); 1.82: 2.02: 2.02: 1.82 Å
54	Nicholson & Nutting	TEM	Consisting of alternate Cu and Al layers.
55	Phillips	TEM	Two Cu rich layers separated by 6-14 Å.
56	Yoshida et al.	TEM	Gerold's model.
57	Abe et al.	FIM	Two Cu or Cu rich layers separated by matrix layers.
63	Sato & Takahashi	TEM	Two Cu rich layers separated by 3 matrix layers and few multilayer and complex layer structures.
64	Yoshida et al.	TEM	Two Cu rich layers separated by 2 or 3 matrix layers and unexplicable structures.
74	Wu et al.	X-ray	GP(II) state is an ordered array of Cu rich and Al layers.
58	Mori et al.	FIM	Two Cu rich layers separated by 3 Al layers.
60	Matsubura & Cohen	X-ray	GP(II) zone is on average 5 layers thick. Cu rich and multilayer regions are always present. Upon ageing there are fewer thin zones but more thick zones. Designation GP(I) and GP(II) is unnecessary.
63	Hono et al.	FIM	Multilayer zones with no matrix layer spacing might be

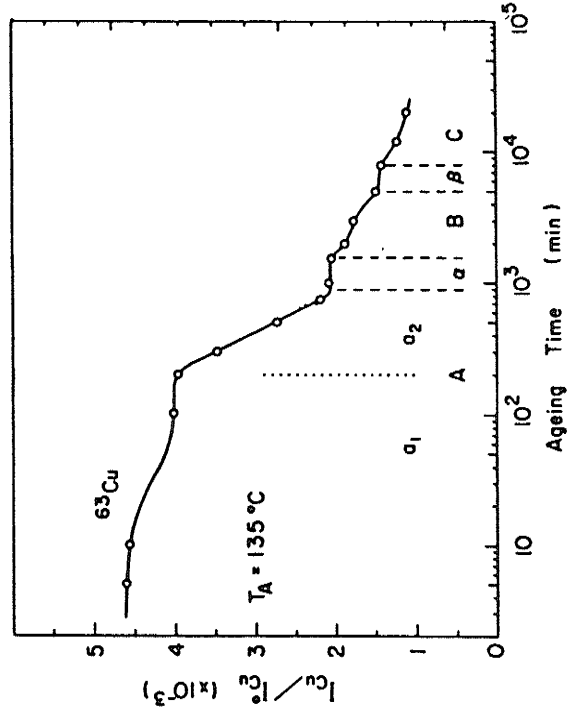


Fig. 2.16 The copper intensity curve for a solution treated Al-1.7at%Cu alloy aged at 135°C⁽⁸²⁾

in sub-stage a_2 . However, once solute concentration reaches the solvus of the GP(I) zone, the existing GP(I) zones begin to dissolve. The plateau α comes to an end when all the GP(I) zones are exhausted, and thereafter the solute concentration in the matrix is again decreased with further precipitation of θ'' . Recently, Matsubara and Cohen⁽⁶⁰⁾ have shown that the appearance of the plateau in resistivity (or hardness)^(80,68) curves for times which were thought to be incubation periods for GP(II) zones is in fact related to the coarsening process of GP(I) zones. Different solvus curves presented earlier are merely an expression of the differences in zone thickness for different ageing times as these solvi were determined by reversion experiments.

In spite of the availability of results of detailed studies carried out by TEM, x-ray scattering, FIM, hardness measurements, NMR and DSC on the structure and properties of zone development, it is not possible to unambiguously establish whether θ'' is a distinct phase from GP(I) zones or whether the GP(I) zone and θ'' are to be considered as two stages of development of one phase. As pointed out by Lorimer,⁽¹⁴⁾ there is general agreement that the θ'' forms from the preceding GP(I) zones. Evidence for this comes from several sources. Eto and co-workers⁽⁸⁴⁾ have found that tensile stress applied in the [001] direction of an Al-Cu single crystal favours formation of GP(II) zones preferentially on [100] and (010) variants. On subsequent ageing without stress some variants are preferentially found for the transformation of θ'' , indicating a definite relationship between the two phases.

2.2.3 The θ' Phase

The x-ray diffraction studies have shown that the θ' has a body centred tetragonal CaF_2 type lattice structure with parameters, $a = 0.404 \text{ nm}$, and $c = 0.58 \text{ nm}$.^(47,49,78) It has the same composition as equilibrium compound θ (CuAl_2). This structure is considered as a modification of the LI_0 super lattice in which two of the copper atom positions are vacant. The orientation relationship with the matrix is:

$$(001)_{\theta'} \parallel (001)_M ; [110]_{\theta'} \parallel [110]_M .$$

Fig. 2.17 shows the arrangement of aluminum and copper atoms in the CuAl_2 lattice. The size of the θ' phase precipitates depends upon the time and temperature of ageing and ranges from 10 to 600 nm or more in length with a thickness of about 10-15 nm.⁽³⁾

There are two points of view concerning nucleation of the θ' phase. Many experimental observations indicate that the θ' phase forms from GP(II) zones and is a continuous process.⁽⁸⁵⁻⁸⁷⁾ On the other hand, many other investigators⁽⁸⁸⁻⁸⁹⁾ have reported that θ' nucleates independently on certain preferential sites like dislocations, subgrain boundaries, regions near active slip planes and vacancy clusters. Lorimer,⁽¹⁴⁾ in a recent review, ignored the former point of view and advocated that θ' preferentially nucleates on dislocations and is able to relieve misfit around the periphery of the plates. This is in support of the observations of Headly and Hren⁽⁹⁰⁾ and theoretical predictions of Russell and Aaronson.⁽³¹⁾ Lorimer has also proposed that subsequent nucleation and growth may occur in an autocatalytic fashion (Ref. 11, p. 269). This theory holds that the

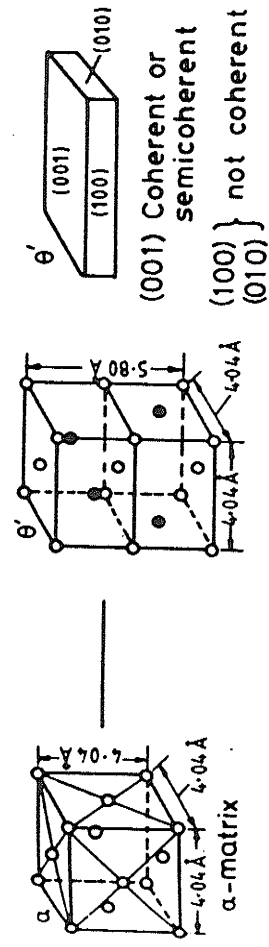


Fig. 2.17 Crystal structure and shape of the θ' precipitates

stress field around a particular θ' plate may aid in the nucleation of the other plates at a region nearby.

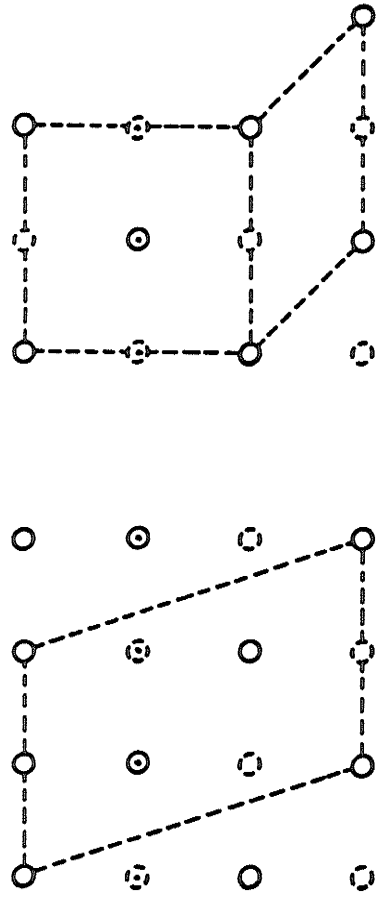
Many recent investigations suggest that θ' evolves out of the θ'' phase as a result of ageing. The stress ageing experiments of Eto et al.⁽⁸⁴⁾ have shown that prolonged two step ageing treatments yield the same variants of the θ'' and θ' as were initially present in the GP (Cu) zones strengthened microstructure. This observation was further confirmed by the x-ray diffraction and high resolution microscopic study of Takahashi and Sato.⁽⁹¹⁾ Their results suggest that θ' may nucleate at either GP(I) zones or θ'' precipitates. Phillips⁽⁵⁵⁾ and Sato and Takahashi,⁽⁶³⁾ through electron microscopic studies, have supported this view and demonstrated that as ageing proceeds the GP(II) zones or θ'' grow, thicken and transform continuously to the semi-coherent θ' phase and continuously lose coherency. Clearer evidence about the nucleation of θ' has come from HVEM study by Suzuki and Kanno⁽⁹²⁾ on the Al-4%Cu alloy. They show that θ' nucleates mainly on dislocation loops leading to homogeneous distribution of θ' in an as-quenched and aged alloy while on direct ageing both homogeneous and heterogeneous distribution are observed depending upon available nucleation sites for θ' . It appears therefore, that θ' phase may nucleate at many different sites depending upon the prehistory of the material.

The loss of coherency due to the formation of dislocations at the interface of θ' has been studied by many investigators.⁽⁹³⁻⁹⁵⁾ Weatherly and Nicholson⁽⁹⁴⁾ have shown by contrast experiments in electron microscope that the broad faces of θ' plates are fully coherent at lower ageing temperatures and may contain widely spaced misfit

dislocations at higher ageing temperatures. Moreover, the structure of the planar interface contains misfit dislocations of the type a $\langle 100 \rangle$. Nemoto et al.⁽⁹⁵⁾ and Vaughan⁽⁹⁶⁾ confirmed these results through high voltage electron microscopic studies and x-ray diffraction. Laird and Aaronson,⁽⁹³⁾ however, found that dislocation arrays at the interface are due to plastic deformation accompanying transformation. In a recent study using lattice imaging of θ' , Sato et al.⁽⁹⁷⁾ observed complicated contrast effects which they related to the loss of coherency of θ' with the matrix.

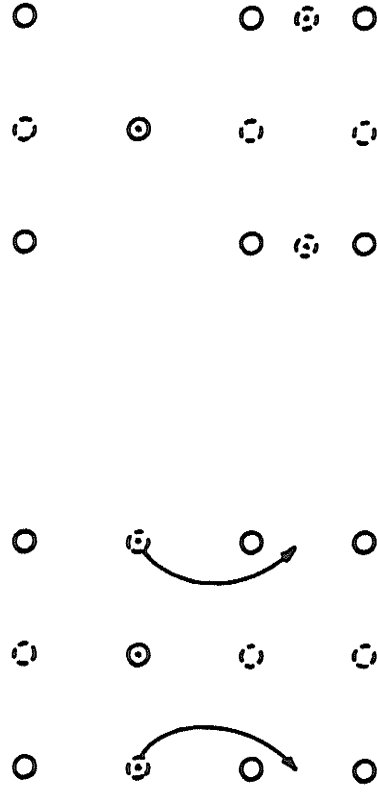
Various studies^(93,98-101) have shown that the precipitates of θ' plates grow by a diffusional lengthening process. Sankaran and Laird⁽⁹⁸⁾ have suggested that the strain field around the growing plate influences the diffusional field and growth rate. During initial growth and coarsening, the coherent broad faces are immobile with respect to normal migration under the full range of driving forces available. This has been emphasized by both Laird and Aaronson⁽⁹³⁾ and Weatherly.⁽¹⁰²⁾ These interfaces move perpendicular to the habit plane by the lateral movement of ledges and the growth of precipitates takes place by ledge mechanism.⁽¹⁰³⁾ The heights of these ledges were proposed to be small multiples of c parameters, i.e. 20 nm.⁽⁹³⁾ Weatherly and Sargent's⁽¹⁰⁴⁾ study, by contrast, determined ledge step height to be 1.5-6.5 nm using TEM, which is somewhat larger than predicted by Laird and Aaronson. Bouazra and Reynaud⁽¹⁰⁵⁾ recently determined the values to be 0.29 and 2 nm using the convergent beam electron diffraction pattern and lattice plane imaging technique. The overall length and thickness of θ' precipitates grow continuously with square root of ageing time.⁽¹⁰¹⁾

Recently, Dahmen and Westmacott⁽¹⁰⁶⁾ have proposed a model of precipitate plate growth of θ' in Al-4.0%Cu alloy similar to the principles of conservative and non-conservative growth ledges proposed for {100} plate precipitate in Pt-C.⁽¹⁰⁷⁾ Fig. 2.18(a) is the [010] projection of the fcc lattice sites and Figs. 2.18(b) and (c) show the schematic representation of the transformation of the matrix to the body centred tetragonal (bct) unit cell of θ' . The total transformation can be visualized as consisting of two simple steps: (i) the shear vector of homogeneous transformation is $a/2 \langle 100 \rangle$ and may be envisaged as the passage of the partial dislocation with this burgers vector (Fig. 2.18(b)); (ii) the shuffles indicated in Fig. 2.18(c) are necessary to obtain the final bct arrangement shown in Fig. 2.18(d). The two steps describe the simplest way to achieve the structural part of the transformation. Solute diffusion is still necessary to accomplish the compositional part of the transformation. It is a homogeneous transformation. Lattice sites are conserved during the process, and the transformed and untransformed unit cells are separated by the shear vector $a/2 \langle 100 \rangle$ of the transformation. Dahmen and Westmacott have also mentioned that θ' can grow in a heterogeneous or non-conservative growth mode. This is illustrated in Fig. 2.19. Here the number of the lattice sites are not conserved and the sheared shell in Fig. 2.19(a) may be sheared by vector $a/2 \langle 100 \rangle$ and expanded to transform to the θ' structure the addition of Cu atoms at the sites indicated in Fig. 2.19b. This will "create" extra sites by leaving behind vacancies in the fcc lattice sites. The result is the formation of a $1/2$ unit cell of θ' (Fig. 2.19(c)) as opposed to the unit cell formed by the conservative process. These two processes are building



(a) Lattice Correspondence

(b) Shear



(c) Shuffle

(d) Structure

Fig. 2.18

[010] projection of the conservative fcc to θ' transformation. Full circles represent atoms at $Y = 0, 1$ and broken circles are atoms at $Y = 1/2$. Circles with dot in centre show a possible positioning of the Cu atoms. In (a) a 6-atom unit cell is outlined in the fcc lattice. The same cell is shown in (b) where the $a/2$ [100] shear component is resolved onto one plane. In (c) shuffles necessary after the shear are indicated.

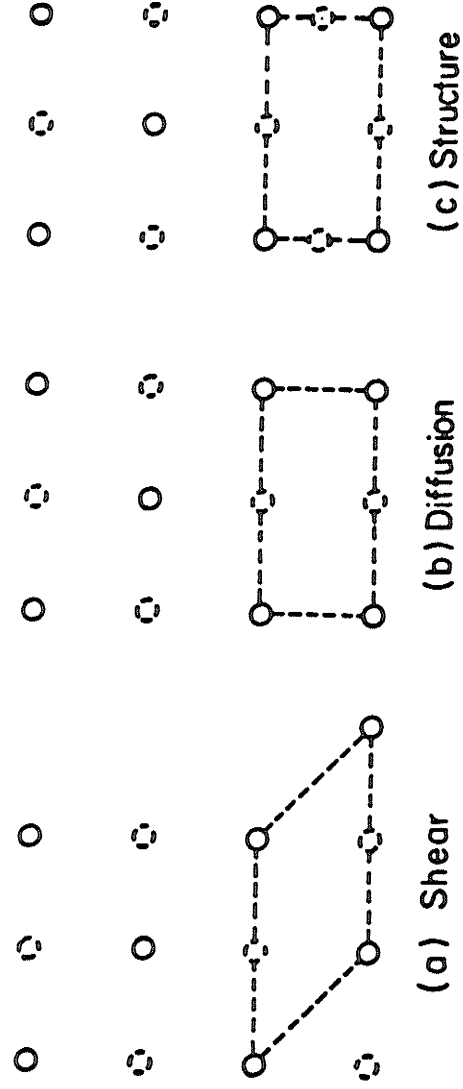


Fig. 2.19 [010] projection of the non-conservative fcc to θ' transformation with symbols as used in Fig. 2.18. The cell outlined in (a) is sheared into the AAA stacking by $a/2$ [100] shown in (b), and diffusion of Cu into the sites marked with arrows completes half a θ' unit cell as shown in (c) (107)

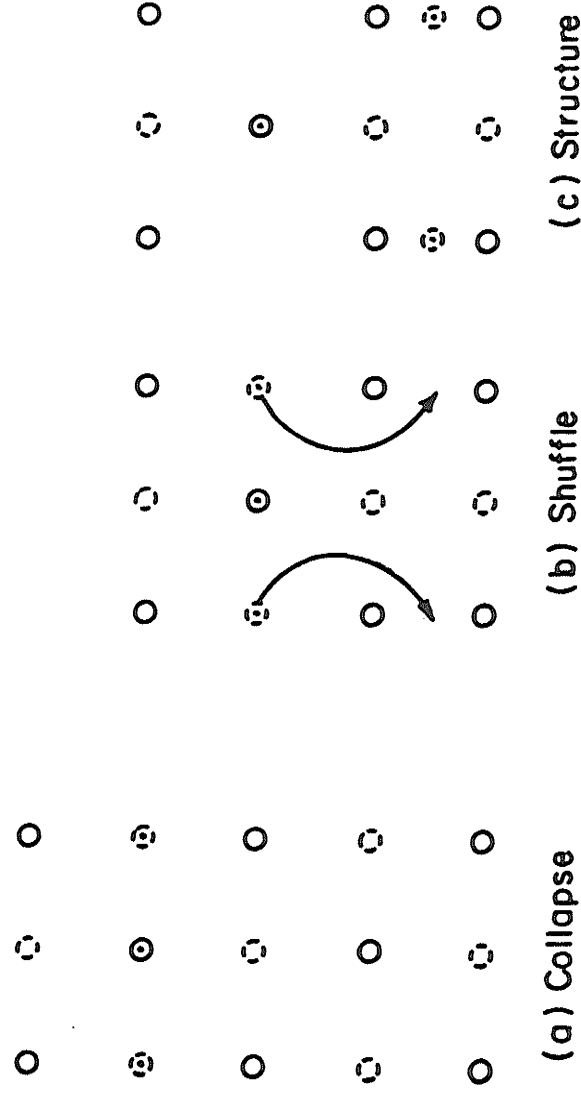


Fig. 2.20 [010] projection of non-conservative transformation from θ'' to θ' using symbols as in Fig. 2.18. In a θ'' precipitate of composition Al_3Cu a layer of vacancies condensing on the line indicated in (a) changes the local stoichiometry to Al_2Cu and produces a layer of AAA stacking. A shuffle of Cu atoms (b) completes the full θ' cell (c) (107)

blocks for the structural transformation that describes the precipitation of θ' in Al-Cu alloys. Multiple growth steps are made up of the combination of these two building blocks. In addition to studying θ' formation from solid solution, Dahmen and Westmacott also proposed a model for θ' formation from θ'' . They have suggested that in non-conservative ledge growth there is emission of vacancies. However, collapse of vacancies is also possible in the Al-Cu system during transition from θ'' to θ' as shown that in Fig. 2.20. The structural transformation is essentially the same as shown in Fig. 2.20(a). Dahmen and Westmacott compared these models with the results of several studies and found them to be in agreement with the available experimental data.

After an extended period of ageing, antiphase boundaries are observed in the ordered precipitates and are found to increase with increase in ageing time.⁽¹⁰⁸⁾ Kajiwara⁽¹⁰⁹⁾ observed striations in θ' precipitates in samples aged at 240°C for 4 days. He interpreted the striations to be stacking faults.

2.2.4 The θ Phase (CuAl_2)

The phase, θ (CuAl_2), is the final product of decomposition of the supersaturated solid solution, Al-Cu. It has a body centred tetragonal lattice (space group $I14/mcm$) with lattice parameters $a = 0.6054$ nm and $c = 0.4864$ nm. The arrangement of atoms in the unit cell is shown in Fig. 2.21. Guinier⁽⁷⁸⁾ investigated the orientation relationship of θ phase with the matrix and categorized it as follows:

$$\text{Group I} \quad : \quad [001]_{\theta} \parallel [001]_M ; [100]_{\theta} \parallel [110]_M$$

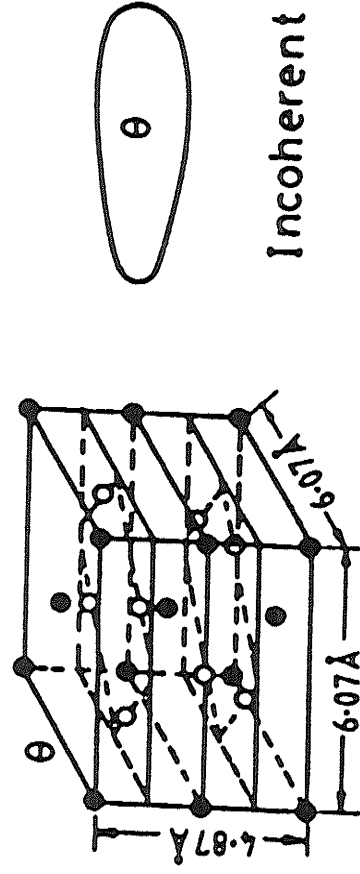


Fig. 2.21 Structure and shape of θ phase in Al-Cu alloys

Group II/III: $[001]_{\theta} \parallel [110]_M$; $[100]_{\theta} \parallel [001]_M$

Group IV/V: $[001]_{\theta} \parallel [001]_M$ with $[100]_{\theta}$ making an angle of $\pm 20^\circ$ with $[100]_M$

In addition to these Vaughan and Silcock⁽¹¹⁰⁾ have summarized more crystallographic relationships reported by other investigators.

An atomic fit at the interface between precipitate and matrix leads to a low value of interfacial energy and low activation energy for nucleation. The large number of orientation relationships gives rise to different kinds of precipitate morphology. The θ phase can form from θ' , or directly from the matrix with somewhat different orientation relationships.⁽¹¹⁰⁾ Direct formation of θ from θ' by rearrangement of atoms has been suggested.^(4,85,86) Maximum amount of θ' is present when θ begins to form and θ' disappears when the amount of θ is maximum.⁽¹¹¹⁾ However, most of the investigators accept independent nucleation and growth near or with θ' phase (for example, Heimendahl and Wasserman⁽¹¹²⁾ and Laird and Aaronson⁽⁹³⁾). The difference in suppositions on nucleation of θ phase is due to absence of an easy manner in which the perfect fcc lattice can rearrange into a perfect (Al_2Cu) lattice.⁽¹¹³⁾ Shchegoleva⁽¹¹³⁾ has proposed a model in which θ may be formed from a perfect fcc lattice as a result of small atomic displacements. The phase that appears may contain periodically distributed stacking faults which disappear as a result of ageing. However, it appears that nucleation of θ phase, like θ' , depends upon the prehistory of the material.

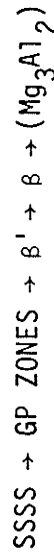
Heterogeneous nucleation of this phase also occurs at grain boundaries. Orientation relationships presented above, however, do not correspond to grain boundary precipitates.⁽³⁾ Vaughan and

Silcock⁽¹¹⁰⁾ have noted that additional abnormal orientations are obtained from these phases at grain boundaries. At longer ageing time the grain boundary precipitates drain the solute from nearby regions and narrow precipitate free zones (≈ 0.25 nm) are formed.⁽¹¹⁴⁾

The lengthening kinetics of θ precipitates have been studied in detail by Laird and Aaronson.⁽¹¹¹⁾ They found that growth is controlled by volume interdiffusion of aluminum and copper in the matrix.

2.3 PRECIPITATION IN THE BINARY Al-Mg ALLOY

The Al-Mg equilibrium diagram exhibits extensive solid solubility at the Al-rich end (Fig. 2.22). An alloy quenched from the α phase field shows the following precipitation sequence⁽¹⁴⁾



2.3.1 GP Zones

It can be seen from the solvus curve of GP zones in Fig. 2.22 that the critical temperature above which these zones do not form is very low (47°-67°C). Formation of GP zones occurs within seconds from quenching in high energy areas (grain boundaries, dislocations, etc.).⁽¹³⁾ Dager et al.⁽¹¹⁵⁾ in an x-ray study on Al-12%Mg alloy aged at room temperature reported them to be spherical. They are very small in size during initial stages of ageing at room temperature (1.0-1.5 nm dia.) and most of the quenched-in vacancies remain around them as clouds. As a result there is little strain and no appreciable hardening. Upon continued ageing at room temperature

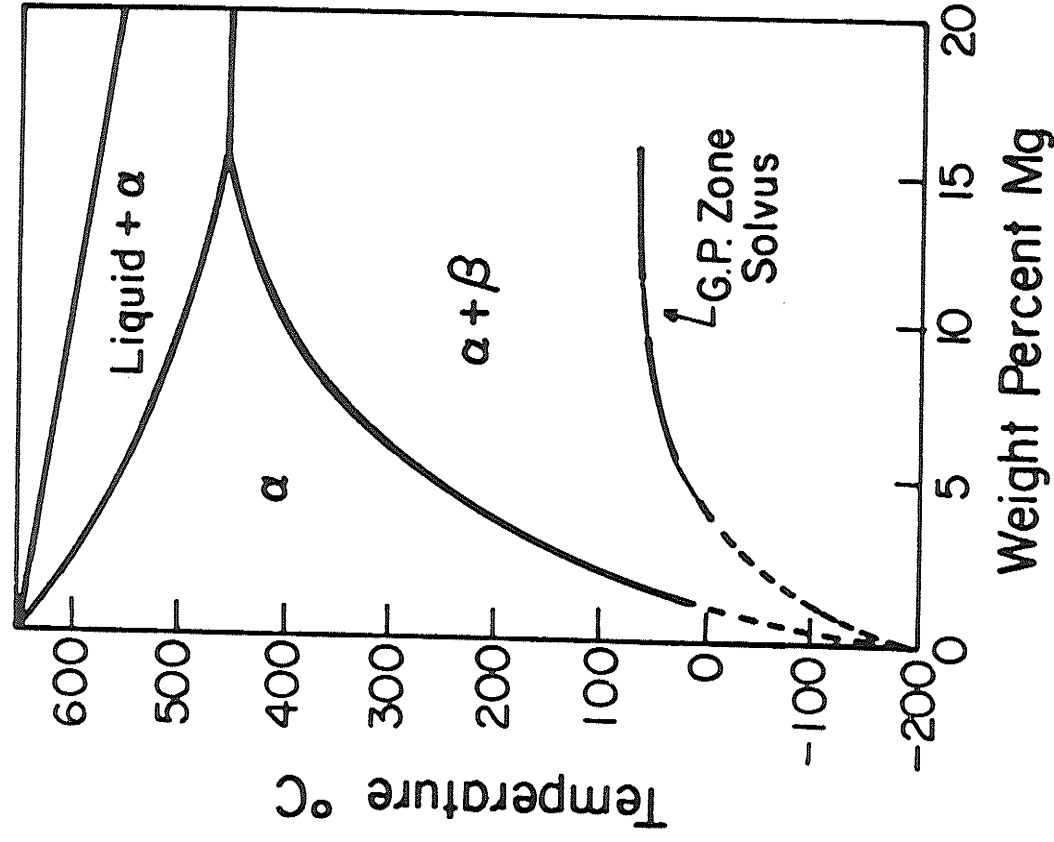


Fig. 2.22 Al-Mg equilibrium diagram to which the GP zone metastable boundary has been added⁽¹⁴⁾

these zones grow to up to 10 nm diameter. Bernole et al. (116,117) used TEM to detect coherent Mg rich zones of density of approximately 10^{17} m^{-3} in an Al-10.0%Mg alloy which had been aged at room temperature for 13 years.

Boudili et al. (118) used TEM and x-ray small angle scattering to study Al-9.5 and 14.8% Mg alloys aged at 20°C. They have reported that the dilute alloy decomposed to form ordered GP zones with the Li_2 (Al_3Mg) superstructure. The concentrated alloy decomposed to produce a modulated structure in the $\langle 100 \rangle$ directions which they interpreted as evidence of spinodal decomposition.

2.3.2 The β' Phase

This phase has a hexagonal crystal structure with $a = 0.1002 \text{ nm}$ and $c = 0.1636 \text{ nm}$ (13) Saulnier and Mirand (119) have reported the particles of the β' phase to be irregularly shaped plates formed on $\{100\}_M$ planes of an Al-12%Mg alloy aged at 120°C. Bernole (120) has carried out an extensive x-ray and TEM investigation of the precipitation behaviour of β' and β phases in an Al-10.0%Mg alloy. It is reported that β' phase nucleates heterogeneously on dislocations. It is often surrounded by extensive dislocation debris and, at the later states of ageing it is internally faulted on $\{10\bar{1}0\}$ planes. After ageing for 20 h at 200°C or 5 h at 250°C, irregular plates up to 0.5 mm thick were observed on $\{100\}_M$. The plates were usually oval shaped and elongated along $\langle 100 \rangle_M$. The orientation relationship between the β' plates and the aluminum matrix was reported by Bernole to be:

$$(0001)_{\beta'} \parallel (001)_M ; [01\bar{1}0]_{\beta'} \parallel [110]_M .$$

2.3.3 The β Phase

The equilibrium β phase (Mg_3Al_2) has a fcc crystal structure with $a = 2.824 \text{ nm}^{(121)}$ Bernole⁽¹²⁰⁾ reported that β phase forms preferentially at grain boundaries and at the matrix/ β ' interface. Both plate and lath morphology were reported and the former exhibited the following orientation relationship:

$$(111)_{\beta} \parallel (001)_{\text{M}} ; [110]_{\beta} \parallel [010]_{\text{M}} .$$

2.4 PRECIPITATION IN THE TERNARY Al-Cu-Mg ALLOY

The Al-rich corner of the Al-Cu-Mg equilibrium diagram is shown in Fig. 2.23(a). The isothermal section of the ternary diagram shows that phases which may be in equilibrium with Al-rich terminal solid solution, are θ , S, T and Mg_2Al_3 . The composition and crystal structures of these phases are listed in Table 2.2.

It can be seen from Fig. 2.23(b) that the formation of different phases due to ageing depends upon the Cu/Mg ratio. Results of various studies on high purity alloys are summarized in Table 2.3. When the Cu/Mg ratio is 0.46, T' (Al_6CuMg_4) precipitates form along with S' (Al_2CuMg) phase. However, an increase in Cu/Mg ratio to 2.2 results in precipitation of only the S' phase. On further increase in the Cu/Mg ratio, θ' (CuAl_2) phase forms along with the S' phase.

The Al-Cu-Mg alloys having a Cu/Mg ratio of 2.6 form pseudo-binary Al- $\text{Al}_2\text{CuMg(S)}$ system⁽¹²⁴⁾. Bagaryatsky⁽¹²¹⁾ and Silcock⁽¹²²⁾ used x-ray diffraction techniques to show that the decomposition of the supersaturated solid solution (SSSS) of the pseudo-binary alloy takes place in the following general sequence.

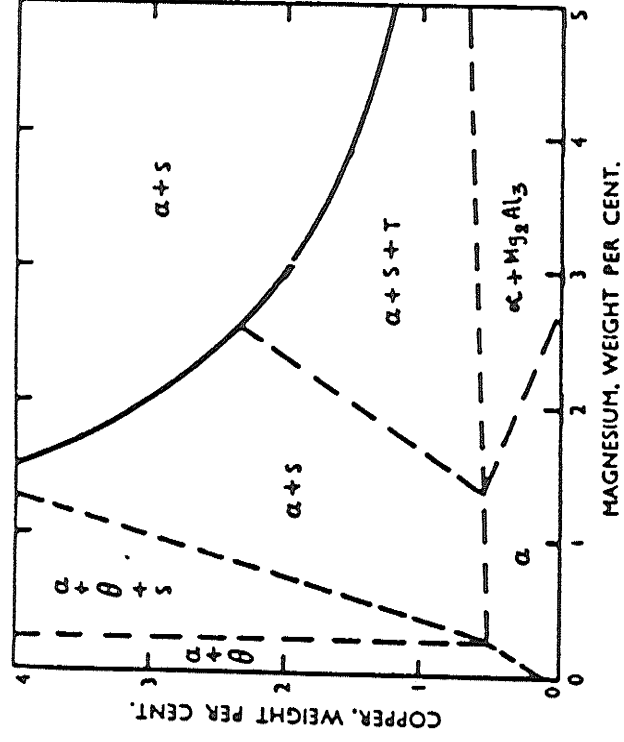
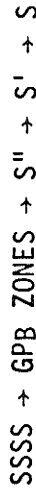


Table 2.2 Phases present at the aluminum corner of Al-Cu-Mg equilibrium diagram (Isotherm 430°C)⁽¹²⁴⁾

Phases	Composition	Crystal Structure
T	Al_6CuMg_4	Cubic
S	CuMgAl_2	Orthorhombic
θ	CuAl_2	bct
β	Mg_2Al_3	Cubic

Table 2.3 Summary of published information on the ageing characteristics of high purity ternary Al-Cu-Mg alloys

S. No.	Alloy composition (wt%)			Phases reported after ageing at temp. T		Ref. Nos.
	Cu	Mg	Cu/Mg Ratio	Phases	T (°C)	
1	0.96	2.10	0.46	S + T	200	125
2	2.00	1.10	1.82	S	200	125
3	2.7	1.36	1.98	S	325	94
4	3.3	1.58	2.08	S'	190	126, 127
5	1.29	0.69	2.2	S'	190	122
6	3.15	1.52	2.2	S'	190	122
7	2.00	0.9	2.2	S'	200	128
8	3.00	1.15	2.61	S'	180-240	129-131
9	2.5	0.5	5.0	S' + θ'	190	151
10	3.53	0.48	7.00	S' + θ'	190	122
11	1.71	0.33	7.00	S' + θ'	190	122
12	3.3	0.27	12.22	S' + θ'	230	132



2.4.1 GPB(I) Zones

Most of the early work, notably by Bagaryatsky⁽¹²¹⁾ indicated that room temperature ageing of Al-Cu-Mg alloys caused the formation of clusters of atoms composed of 1 Cu, 1 Mg and several Al atoms. Silcock⁽¹²²⁾ termed these clusters of atoms GPB zones, in honour of Bagaryatsky, and in order to distinguish them from the GP zones observed in binary Al-Cu alloys. Many models have been proposed to describe the crystal structure of GPB zones.^(122,129,130,133,134) Gerold⁽¹³³⁾ has suggested that these are regions of an ordered CuAuI type phase with tetragonal lattice in the initial stages of ageing. Silcock⁽¹²²⁾ has shown the GPB zones to be an ordered phase with a tetragonal lattice. Shchegoleva and Buynov⁽¹³⁴⁾ determined the structure of the zones to be similar to the S'' phase and preferred to call them S'' phase instead of GPB zones. Alekseyev et al.⁽¹²⁹⁾ however, have presented a different model for GPB zones. They have suggested that GPB zones have the same crystal structure as equilibrium S phase and a lattice isomorphous to the matrix. Mondolfo⁽¹³⁾ has shown the arrangement of atoms in the GPB zone lattice as shown in Fig. 2.24 which also illustrates its crystallographic relationship with the matrix. In a recent study⁽¹³⁵⁾ which used hardness, Laue x-ray diffraction and high resolution microscopy to study the precipitation behaviour of the Al-4%Cu-1.5%Mg alloy, it was concluded that the GPB zones are divided into two zones, namely GPB(I) and GPB(II). The GPB(I) zones have a random arrangement of atoms while GPB(II) zones

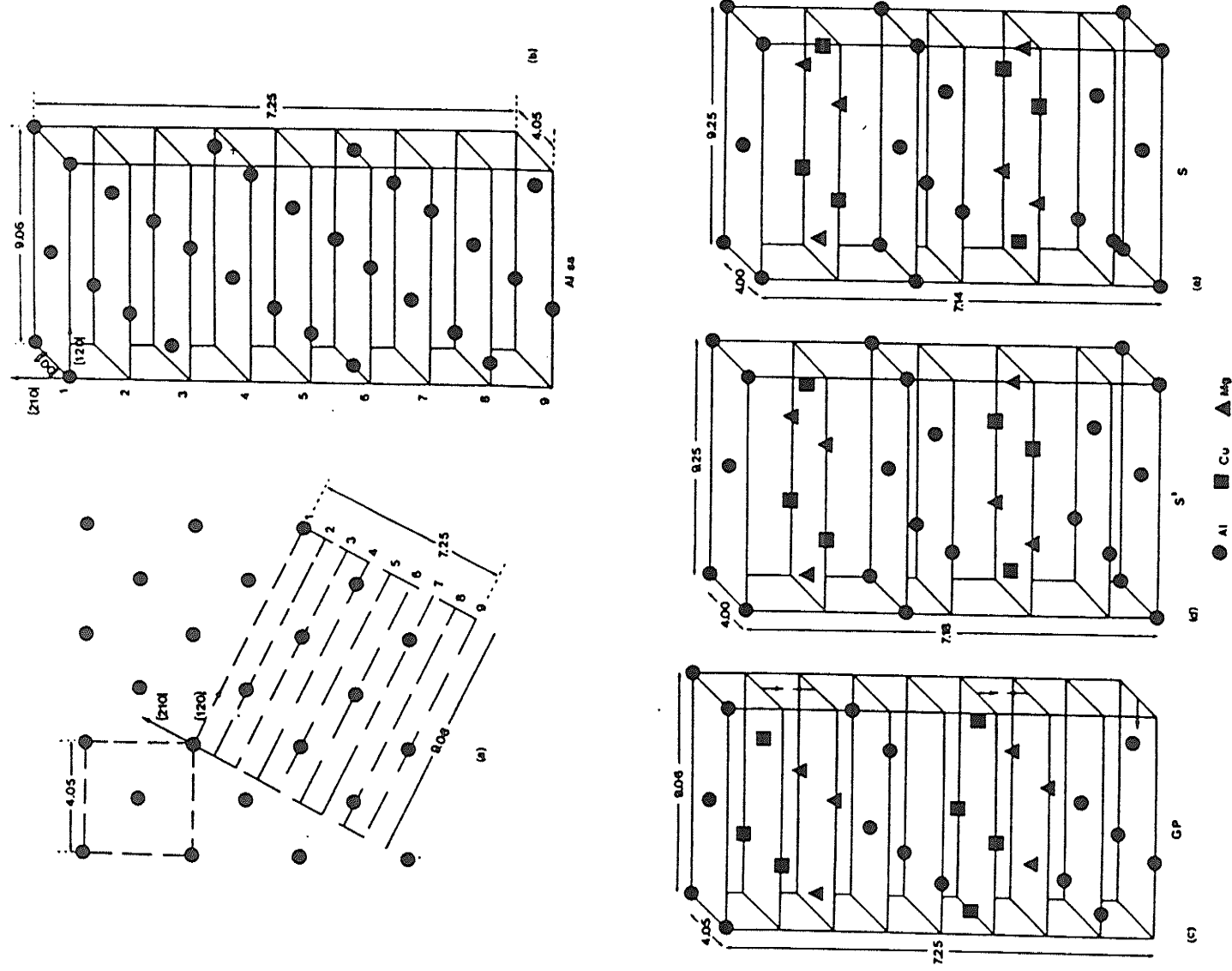


Fig. 2.24 Formation of S phase from supersaturated solid solution. (a) the relative orientation of the precipitate with respect to the matrix; (b) Al solid solution; (c) GPB zones; (d) S' phase; (e) S phase₍₁₃₎

are similar to the S' phase and have an ordered arrangement of atoms. The GPB(II) zones are rod shaped, lying parallel to $\langle 100 \rangle$ matrix direction.

Gerold and Haberkorn⁽¹³³⁾ considered the zones to be spherical while Alekseyev et al.⁽¹²⁹⁾ reported equiaxial particles with a minimum size of 7.0 nm. Most of the investigators, for example Silcock,⁽¹²²⁾ suggest GPB zones to be cylindrical particles lying along $\langle 100 \rangle_M$ directions. She found the zones to be 2.0 nm in diameter and 4.0 nm long.

The zone formation in an Al-3%Cu-1%Mg alloy has been examined by Pabi and Mallik⁽¹³⁶⁾ using a resistivity technique. It was reported that quenched-in vacancies were strongly bound to the solute atoms or zones. Consequently, a slow reaction should be maintained for several weeks during room temperature ageing.⁽¹³⁷⁾ Cho⁽¹³⁸⁾, using resistivity, hardness and TEM, confirmed the presence of the slow reaction in the Al-2%Cu-1.1%Mg alloy. It was also shown that pre-precipitation in this alloy occurs in three different stages; (i) GPB zone formation during quenching and ageing for less than 1 min (known as fast reaction); (ii) GPB zone formation in the early stages of ageing below 200°C (known as slow reaction), and (iii) GPB(II) zone formation in the early stages of ageing at about 250°C.

When the concentration of solutes is increased at the same Cu/Mg ratio the density of dislocation loops and helices increases. Consequently, the rate of GPB zone formation is high in alloys with a higher solute content for a given Cu/Mg ratio.⁽¹³⁸⁾ The rate of zone formation is critically related to the ageing temperature. Cho⁽¹³⁸⁾ studied an Al-2%Cu-1.1%Mg alloy and found that the rate of

GPB zone formation is highest when ageing is carried out at a temperature between 70°-120°C.

The GPB zone solvus curve has been determined by many investigators.^(68,126,138) Beton and Rollason⁽⁶⁸⁾ determined the reversion temperature of GPB zones to be 260°C using hardness experiments and this was confirmed by Sen and West.⁽¹²⁶⁾ Cho,⁽¹³⁸⁾ on the basis of his resistivity measurements on Al-2%Cu-1.1%Mg alloy, found that reversion rate of zones is very slow up to 230°C, while at 240°C it increases anomalously and zones dissolve in 7 min. He concluded that the thermal stability of the GPB zones in Al-Cu-Mg alloys is higher than their counterpart in Al-Cu alloys. DSC curves of Al-3.15%Cu-1.52%Mg alloy due to Howie,⁽¹⁴²⁾ support the observation of Cho.

The solubility curves of GPB(I) zones have not been widely studied. They can be represented by an equation of the type⁽⁶⁸⁾

$$\log [X] = A - K/T$$

where X is solute concentration, A and K are constants, and T is absolute temperature.

2.4.4.2 GPB(II) Zones (or S" Phase)

In an x-ray study on Al-4.0%Cu-1.2%Mg, Lambot⁽¹⁴⁰⁾ observed a "checkerboard" pattern which could not be explained. Bagaryatsky⁽¹²¹⁾ associated this pattern to the presence of a distinct phase, named S", which has a slightly distorted equilibrium S structure, but with different matrix coherence. Silcock,⁽¹²²⁾ using the x-ray diffraction technique on low temperature aged Al-Cu-Mg alloy single crystals did

not observe any structure resembling the S" as reported by Bagaryatsky. However, a new structure termed GPB(II) zone was observed after ageing at elevated temperatures (i.e. $\geq 240^{\circ}\text{C}$). These zones were larger in size and sharper in shape than GPB(I) zones. Wilson and Partridge⁽²³⁾ and Weatherly⁽¹⁴¹⁾ using TEM technique also did not observe S" phase after ageing at 190°C . On the other hand, Althof et al.,⁽¹⁴³⁾ using TEM, observed S" particles 1.0 nm wide and 5.0 nm long in a naturally aged sample. Schegoleva and Buynov,⁽¹³⁴⁾ in an x-ray study on Al-3.0%Cu-1.15%Mg alloy, inferred that a cluster of solute atoms with internal ordering is formed on quenching this alloy. They called it S" phase instead of the GPB zones mentioned in Section 2.4.1. The S" phase is cylindrical in shape and is formed at the very beginning of isothermal ageing. During the initial period of ageing, the S" phase particles grow in length but do not alter in diameter. In later stages, however, diameter is also increased and causes strong elastic distortion of cylindrical symmetry within the matrix. In another study, Schegleyeva and Buynov⁽¹³⁴⁾ determined the crystal structure of S" phase and proposed that it has a peculiar structure with abnormal orientation relationships with the matrix. Cuisat and co-workers,⁽¹⁴⁴⁾ in a study of an aged Al-2.8%Cu-1.4%Mg alloy by TEM, confirmed the presence of S" phase during the initial stages of ageing. They also reported that S" phase contains antiphase domains within the structure. Takahashi and Sato⁽¹³⁵⁾ in a high voltage lattice imaging study reported the presence of ordered rod shaped GPB(II) zones lying in $\langle 100 \rangle$ matrix. They pointed out that these zones have a crystal structure similar to that of the S phase.

In spite of a detailed study carried out by several workers,

as presented in this and the previous section, the crystal structure of GPB zones is not unambiguously established.

2.4.3 The S' Phase

The crystal structure of S' phase is orthorhombic with lattice parameters $a = 0.404$ nm, $b = 0.925$ nm, and $c = 0.718$ nm. The stoichiometric formula of this phase is reported to be CuMgAl_2 (Fig. 2.24). From x-ray investigations, S' has been found to form with the following orientation relationship^(121,122)

$$[100]_{S'} \parallel [100]_M ; [010]_{S'} \parallel [021]_M ; [001]_{S'} \parallel [\bar{0}1\bar{2}]_M$$

giving a total of 12 possible orientations in the matrix.⁽⁹⁴⁾ A detailed study on the nucleation and growth of S' phase was carried out by Wilson and Partridge.⁽²³⁾ An Al-2.5%Cu-1.5%Mg alloy aged at 190°C was examined by TEM, and S' precipitates were found to nucleate heterogeneously on dislocations. The precipitates grew as laths on $\{210\}_M$ planes in $\langle 100 \rangle_M$ directions. Corrugated sheets of precipitates are formed by laths which have a common $\langle 100 \rangle$ growth direction and which form on alternating $\{210\}$ planes (Fig. 2.25). At low magnification these sheets appear to be large precipitates on $\{110\}_M$ planes. Wilson and Partridge also showed that deformation of the alloy prior to ageing had the effect of refining S' precipitate distribution.

Alekseyev and co-workers⁽¹³⁰⁾ proposed a model to explain the coherency loss in Al-Cu-Mg alloys. According to this model the coherency of S' phase is lost along the b-axis and accompanied by an absorption of excess vacancies. Alekseyev et al. have also explained

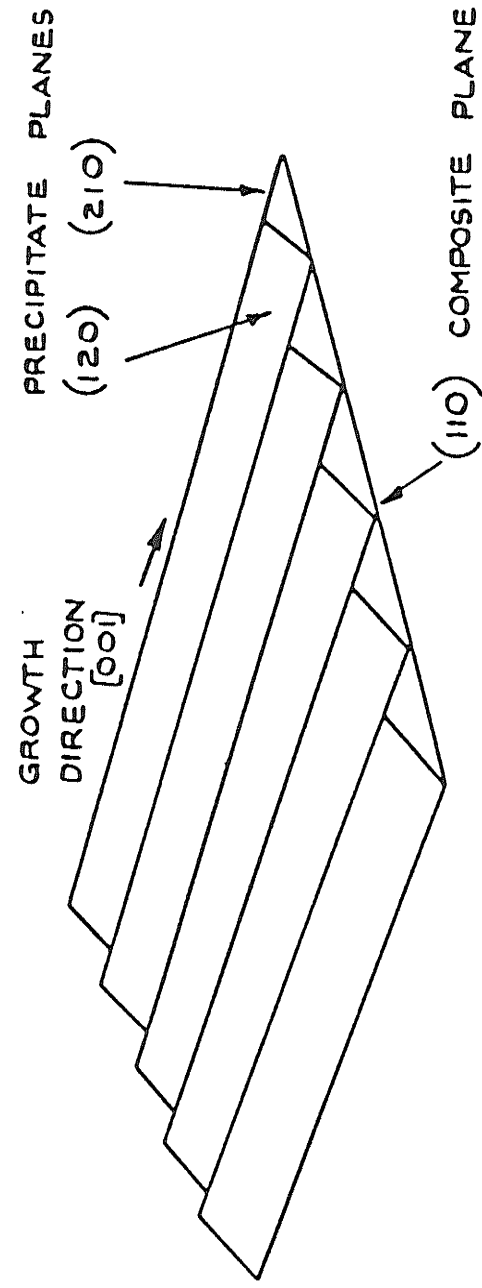


Fig. 2.25 The formation of a composite precipitate sheet on a (110) plane by the growth of precipitate plates in the [001] direction

the development of S' particles. As a result of ageing, the GPB zones (4.0 nm) grow in size along $\langle 021 \rangle_M \parallel \langle 010 \rangle_{S'}$ (b-direction) with simultaneous flattening in the $(01\bar{2})_M \parallel (001)_{S'}$ plane. (129) After a certain size the mismatch between the precipitate particles and matrix becomes zero along the b-direction and the particles lose coherency. Growth in c-direction is difficult because the elastic strain due to "shear mismatch" between phase and matrix is greater. The growth remains most rapid in a-direction and the S' acquires the shape of laths.

The kinetics of coarsening in an Al-2.0%Cu-1.1%Mg alloy aged at 200°C and 230°C has been studied using TEM. (145) The coarsening of S' precipitates takes place by Ostwald ripening and the distribution of precipitates remains uniform. Cho⁽¹⁴⁵⁾ also showed that the diffusion coefficient ($D_{Cu-Mg} = 7.03 \times 10^{-14} \text{ cm}^2/\text{sec}$ at 200°C) calculated from kinetic analysis, was 10^3 times the diffusion coefficient of Cu and Mg in pure aluminum. The aspect ratio of lath shaped S' precipitates increased with temperature and time.

2.4.4 The S Phase

The S phase is orthorhombic (space group CmCm) with lattice parameters⁽¹⁴⁶⁾ $a = 0.400 \text{ nm}$, $b = 0.923 \text{ nm}$ and $c = 0.714 \text{ nm}$ (Fig. 2.24). It has the same orientation relationship with the matrix as S' phase.

Weatherly and Nicholson⁽⁹⁴⁾ studied the loss of coherency of lath shaped S precipitates in Al-2.7%Cu-1.36%Mg alloy aged for 24 h at 325°C. They found that S-laths lost coherency by first attaching the matrix dislocations to the lath/matrix interface. It was followed by the formation of an array of dislocation loops with

Burgers vector of type $a/2$ [101] spaced along the length of the laths. The average spacing of the loops was 26.0 nm compared to a value of 17.0 nm if there was complete relief of misfit. They also found that S phase loses coherency less rapidly than do the θ' plates in Al-4.0%Cu alloy. For example, after 4 days of ageing at 260°C, many θ' plates in Al-4.0%Cu alloy started to lose coherency, whereas after 25 days at the same temperature most of the S laths in Al-2.7%Cu-1.5%Mg alloy were still coherent.

Sen and West⁽¹⁵³⁾ studied the influence of various factors on the precipitation of S phase in an Al-3.3%Cu-1.6%Mg alloy aged at 260°C after various conditions of initial quenching, pre-ageing and plastic deformation. They found that a reduction in the quenching rate slightly reduced the subsequent hardening on ageing which was accompanied by a slight coarsening of S laths. Cold working accelerated the subsequent ageing and refined the S lath size, as a result of enhanced nucleation on dislocations. The pre-ageing treatment had both positive and negative effects on hardening depending upon the pre-ageing temperature, which was related to the supersaturation condition. They also found that the coarsening of S phase follows the Lifshitz-Slyozov-Wagner (LSW) theory of coarsening.

2.4.5 The Distinction Between S' and S Phase

It was stated in Section 2.4.3 that the crystal structures of both S' and S phase are orthorhombic and their lattice parameters are close to each other. Silcock⁽¹²²⁾ found that distinction between these two phases is very slight and somewhat arbitrary. Wilson and Partridge⁽²³⁾ found that S' and S phase have the same crystal structure

as S phase but with slightly different lattice parameters. Alekseyev et al.⁽¹³⁰⁾ agree that the S' phase has the same crystal structure as S phase but suggest that the S' phase has "broken coherency" along the b-axis. Wilson⁽¹²⁷⁾ also attempted to differentiate between S and S' precipitates by their morphologies. He identified S' phase as lath shaped precipitates formed at lower ageing temperatures and S phase as massive precipitates observed in specimens aged at higher temperatures. Thus, there appears to be no clear cut distinction between the S and S' phases.

2.4.6 Effect of Precipitation on Hardness and Tensile Properties

The effect of precipitation on hardness of high purity Al-Cu-Mg alloys have been measured by several investigators. Hardy⁽⁴⁾ showed that hardness of high purity Al-Cu-Mg alloys is strongly dependent on the heat treatment of the alloy (Fig. 2.26) and its solute content (Fig. 2.27). Silcock,⁽¹²²⁾ in an x-ray diffraction study of Al-3.15%Cu-1.5%Mg alloy, related the observed changes in hardness with ageing time at different temperatures to the microstructural changes. Fig. 2.26 due to Silcock⁽¹²²⁾ correlates the hardness with various precipitating phases in this alloy.

Very little information is available on the tensile properties of the high purity Al-Cu-Mg alloys. However, it is expected that the tensile strength would also behave in a similar manner to the hardness. Wilson et al.⁽⁷⁾ have reported that the 0.2% yield strength of quenched Al-2.5%Cu-1.2%Mg alloy increases by 140% due to ageing for 90 min at room temperatures. They attributed this increase in strength to the formation of GPB zones. Further ageing at 190°C for

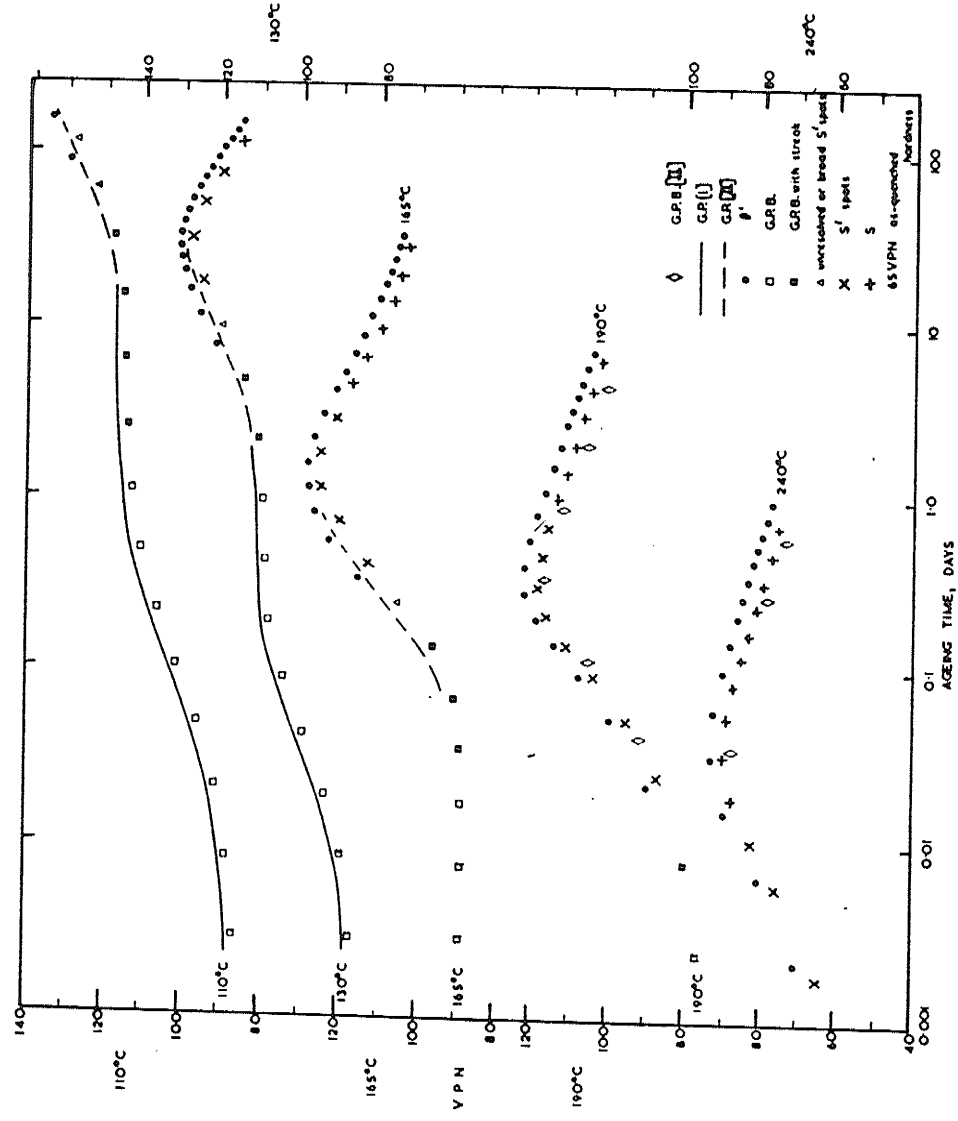


Fig. 2.26 Structures occurring at various points on the hardness curve for acetone - quenched and aged Al-3.53% Cu-0.48% Mg alloy₍₁₂₂₎

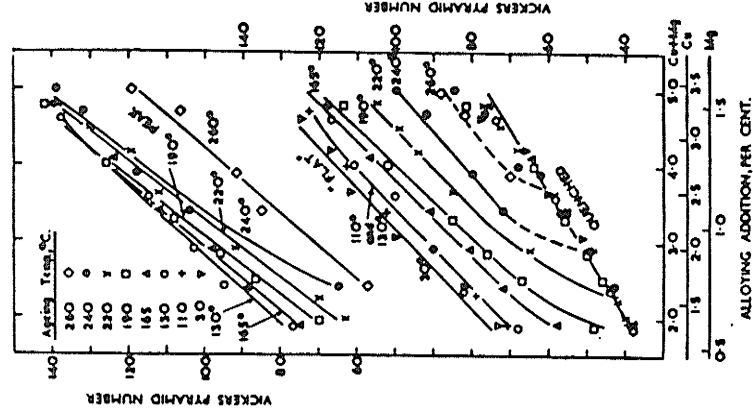


Fig. 2.27 Effect of solute contents on the quenched, flat, and peak hardness values of alloy with a Cu/Mg ratio of 2.2:1(4)

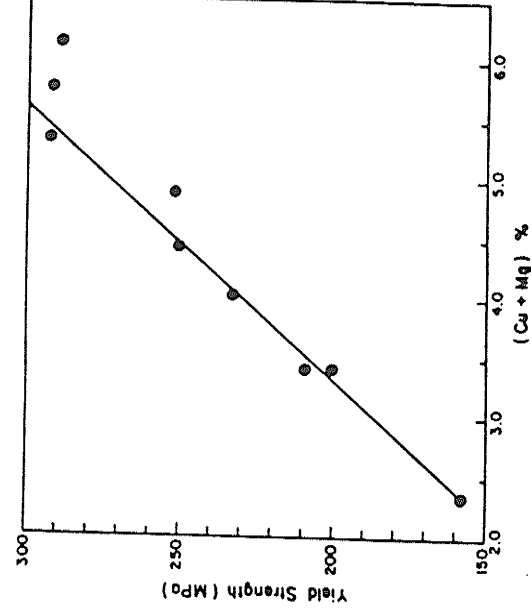


Fig. 2.28 Effect of solute content on the yield strength of Al-Cu-Mg alloys aged for four days at room temperature (167)

16 h resulted in precipitation of S' phase and increased 0.2% yield strength by 200%.

Robinson and Hunter⁽¹⁴⁷⁾ measured the tensile properties of a series of Al-Cu-Mg alloys aged at room temperature for 4 days. Their results are plotted in Fig. 2.28. It shows that the yield strength of the alloys increases linearly with the increase in the total solute content up to 5.25%. This is consistent with the hardness results of Hardy⁽⁴⁾ as shown in Fig. 2.27.

2.5 EFFECT OF SMALL QUATERNARY ADDITIONS ON THE PRECIPITATION BEHAVIOUR OF Al-Cu-Mg ALLOYS

The addition of small amounts of solutes to various aluminum alloys has been shown to modify the precipitation reaction appreciably. Several mechanisms by which solutes may modify the precipitation behaviour have been recognized.⁽¹⁶⁹⁾ Some of these are listed below:

- (1) Interaction with vacancies which leads to a reduction in the rate of lattice diffusion of substitutional elements,
- (2) Modification of the interfacial energy between the precipitate and the matrix and the rate of nucleation.
- (3) A change in free energy relationship in an alloy system, so that precipitation of different phases is favoured.
- (4) Segregation to grain boundaries and inhibition of discontinuous precipitation, nucleation, etc.

These effects of small additions are generally valid but there are no rules which govern the behaviour of individual solutes.⁽¹⁰⁾ Most of the early work on the effects of small addition of solutes on the Al-Cu-Mg alloy system has been reviewed by Hardy.⁽⁵⁾

2.5.1 Silver

Addition of silver to Al-Cu-Mg alloys has been widely studied by many investigators.^(123,132,148,150-153) Polmear⁽¹⁴⁸⁾ has shown that alloys based on the Al-Cu-Mg system are greatly affected by the addition of silver although it has almost no effect on the Al-Cu alloy. The silver atoms interact with vacancies to reduce the GPB zone formation and improve mechanical properties. Sen and West⁽¹⁵³⁾ observed a similar increase in peak hardness when silver was added to the alloy, Al-3.2%Cu-1.5%Mg. Studies on a wide range of ternary and quaternary alloys showed that the addition of silver increased the hardening rate, when ageing was conducted in the medium temperature region. This was attributed to the formation of a uniformly distributed BCC Mg₃₂(AlZn)₄₉ type phase.^(123,126,150) Sen and West⁽¹²⁶⁾ postulated that the silver atoms are somehow responsible for trapping vacancies and hence fewer dislocation loops formed in the quaternary alloy. With fewer nucleation sites, formation of S phase is restricted and the T phase is formed. Silver also promotes the formation of an entirely new phase. Aultz and Vietz⁽¹⁵²⁾ observed GPB(II), S' and θ' precipitates in an Al-2.5%Cu-0.5%Mg alloy aged to peak hardness at 200°C. The addition of 0.5% Ag to this alloy resulted in the formation of a new precipitate along with a fairly small amount of lath shaped S-precipitate. The new phase was a hexagonal shaped plate type precipitate formed on {111} matrix when ageing was done at a temperature between 135°-350°C. Chester⁽¹⁵¹⁾ and Aultz and Vietz⁽¹⁵²⁾ found the new phase has a hexagonal crystal structure with lattice parameters $a = 0.496 \text{ nm}$, $c = 0.848 \text{ nm}$ and it is oriented with $[00.1]_{\text{hex}} \parallel [111]_M$ and $[10.0]_{\text{hex}} \parallel [\bar{1}10]_M$. The same phase was observed in

Al-4.4%Cu-0.27%Mg-0.7%Ag alloy by Taylor et al.⁽¹³²⁾

2.5.2 Transition Elements, Ti, Mn, Fe and Ni

Cho et al.⁽¹⁵⁴⁾ studied the influence of Ti, Mn and Fe addition on Al-Cu-Mg alloys by DSC and TEM. They have reported that the addition of Mn causes the rate of GPB zone formation to increase and that this effect becomes pronounced by the addition of Ti. Conversely, Fe reduces the rate of GPB zone formation. The combined addition of Fe, Mn and Ti increases the rate of GPB zone formation by small amounts, but the nucleation and growth of S' is reduced considerably.⁽¹⁵⁴⁾

Wilson and Forsyth⁽¹⁵⁵⁾ studied the effect of 1% Fe and 1% Ni addition on the age hardening characteristics of Al-2.5%Cu-1.2%Mg alloys using TEM and tensile testing techniques. They found that the addition of both solutes reduced the ability of this alloy to age harden. The solutes combined with Cu and Al atoms to form insoluble phases and reduced the Cu content of the solid solution. The combined (1% Fe and 1% Ni) addition of both the elements, however, restored the age-hardening capability of the alloy by forming a Ni/Fe rich phase with little copper in it.

2.5.3 Silicon

Wilson and Partridge⁽²³⁾ have shown that the effect of the addition of 0.25% Si to an Al-2.5%Cu-1.5%Mg alloy is similar to that of cold work prior to ageing, namely, the S' phase becomes more finely dispersed. In a subsequent paper, Wilson⁽¹²⁷⁾ studied the effect of Si addition in detail and concluded that a strong binding energy

between Si atoms and vacancies reduced the number of dislocation loops and also decreased the diffusion rate of solute in this alloy. This resulted in a decreased rate of GPB zone formation, and a higher density and more uniform dispersion of S' precipitates. This observation was further confirmed by Cho et al.⁽¹⁵⁴⁾ Wilson⁽¹²⁷⁾ has further reported that addition of 0.24% Si to the alloy also causes a strong bonding between solute atoms, vacancies and GPB zones, so that the stability of the zones is enhanced and the temperature at which S' could be formed is raised.

Suzuki et al.⁽¹²⁸⁾ observed increases in hardness of Si containing Al-2.0%Cu-0.9%Mg alloy isochronically aged at different temperatures for 100 min (Fig. 2.29). They reported that the increase in hardness of the aged ternary alloy is due to the change in aged microstructure that had three kinds of precipitates in contrast to the one type of precipitate formed in the Si free alloys. Moreover, addition of 0.5% Si to dilute Al-2.0%Cu-0.9%Mg alloy promoted the precipitation of θ' and suppressed the precipitation of S' phase. These results have not been confirmed so far by any other investigator. Suzuki et al. have further reported that the addition of Si to a concentrated alloy (Al-4.0%Cu-1.8%Mg) has the tendency to lower the peak aged hardness.

The complex effect of Si may be rationalized in terms of the Al-Cu-Mg-Si phase diagram. Two sections through the Al-Cu-Mg-Si system at 1.4% Cu and at constant temperature and pressure are shown in Fig. 2.30.^(156,157) The presence of many phases in the aluminum corner of the equilibrium diagram at 520°C and at 175°C should be noted. This suggests that ageing of a supersaturated solid solution

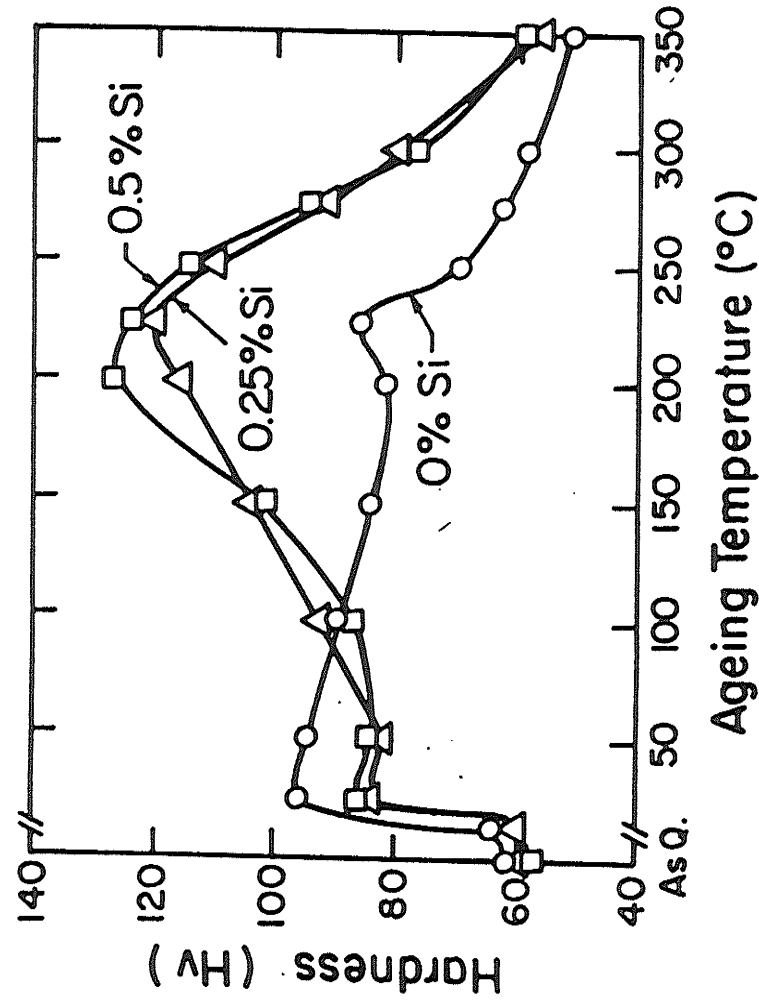


Fig. 2.29 Hardness vs. ageing temperature curves of Al-2% Cu-0.9% Mg alloys having different Si contents. Specimens were solution-treated at 505°C for 1 h, quenched into iced water and isochronally aged for 100 min (128)

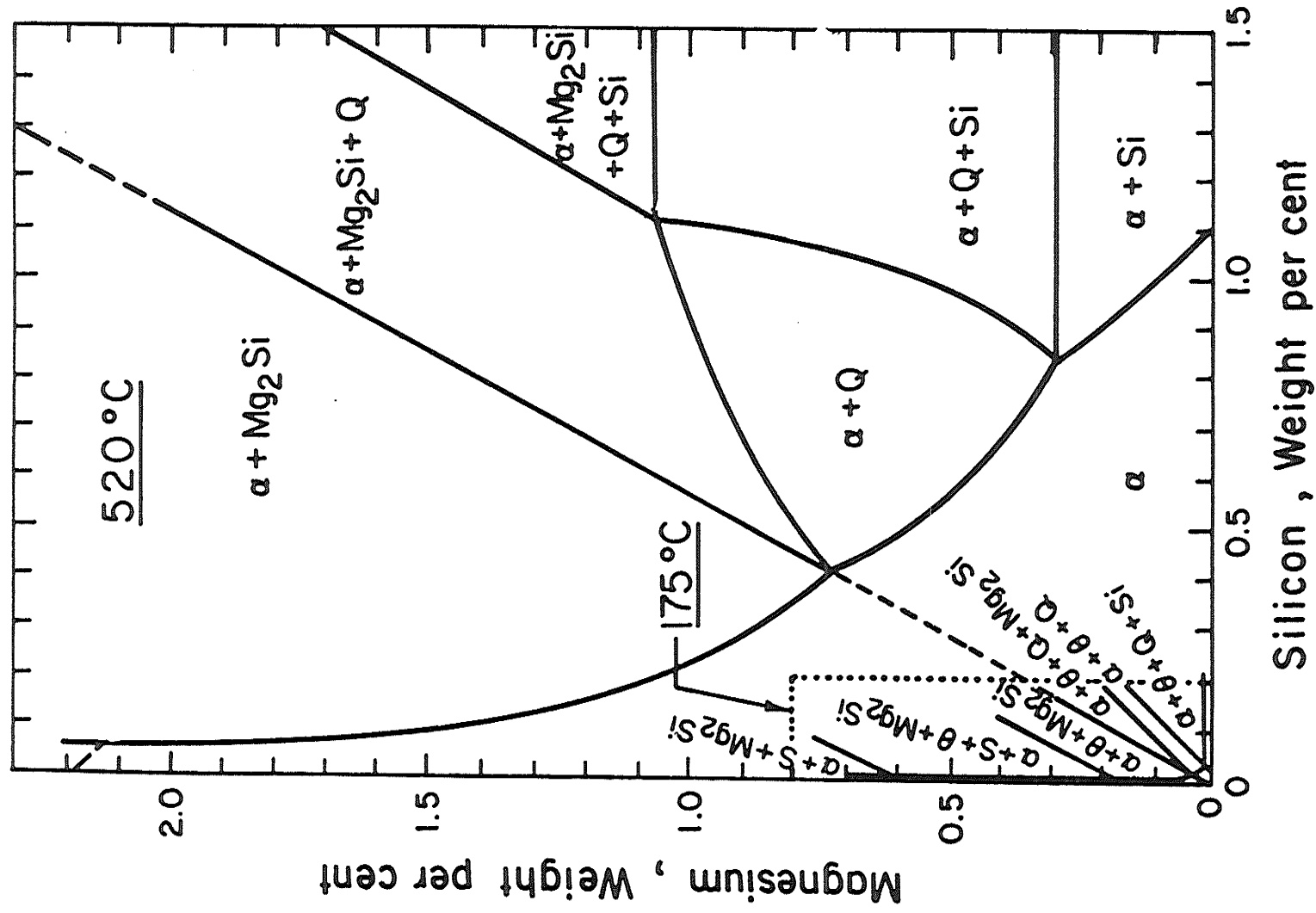


Fig. 2.30 Sections at 1.4% copper of the isotherms of the Al-Mg-Si-Cu system at 520°C and 175°C(156)

at 175°C may cause the precipitation of many types of phases. These are: (i) CuMgAl_2 - S type; (ii) CuAl_2 - θ type; (iii) Mg_2Si - β type and (iv) $\text{Cu}_2\text{Mg}_8\text{Si}_6\text{Al}_5$ - Q type. The type of phase precipitates on ageing is known to depend mainly upon the Cu/Mg and Mg/Si ratio in the alloy. (13) The ageing behaviour of alloys in which the Cu content is at or above the solubility limit (4-5% Cu) and Mg and Si are present in small amounts or in the proportions to form Mg_2Si , is very similar to the Al-Cu alloys. (13)

The second group of alloys has a Cu/Mg ratio of at least 2.5 and usually a low (< 0.2) Si content, so that most of the Mg is combined with copper to form CuMgAl_2 . The ageing characteristics of this second group of alloys differ only slightly from those of ternary Al-Cu-Mg alloys. Moreover, if Si is present, the Mg/Si ratio for the formation of the CuMgAl_2 must be above 1.73, i.e. there must be more Mg in alloys than the amount necessary for the formation of Mg_2Si . If there is more copper than the amount necessary to form this compound, CuAl_2 will be formed. (13)

The third group of alloys in which copper is very low ($< 0.4\%$) or Mg content is decidedly higher than the Si content, the ageing characteristics correspond to those of ternary Al-Mg-Si alloys. (13)

The fourth group comprises the alloys in which the Cu content is approximately one half of Mg and Si content is the same as or higher than the Mg content. The age hardening of these alloys is mainly due to the precipitation of $\text{Cu}_2\text{Mg}_8\text{Si}_6\text{Al}_5$ phase.

The amount of Si present at a fixed Cu/Mg ratio will determine the type of phase that will form on ageing. If Mg/Si ratio is exactly equal to 1.73, all the Mg and Si will combine to form Mg_2Si . On the

other hand, if Mg:Si ratio is precisely 1.08, all the Mg and Si would combine with copper to form the quaternary phase $\text{Cu}_2\text{Mg}_8\text{Si}_6\text{Al}_5$, with the excess copper being present as CuAl_2 . If the ratio of Mg to Si is between 1.08 and 1.73, some Mg_2Si will also be present. If it is below 1.08, there will be an excess of Si.⁽¹³⁾ Table 2.4 summarizes the phases observed in the quaternary Al-Cu-Mg-Si alloys on ageing at elevated temperatures.

Fig. 2.29 shows that the addition of 0.25 to 0.5% Si increases the hardness of Al-2.0%Cu-0.9%Mg alloy by about 50%. A similar observation has been made by Wilson et al.⁽¹²⁷⁾ They found that 0.25% Si in the alloy containing 2.5% Cu and 1.27% Mg can increase the yield strength by 75% on ageing at 190°C. Thus, Si additions appear to have a potential to increase strength of Al-Cu-Mg alloys.

2.6 SCOPE OF THE PRESENT WORK

The review of literature presented in the earlier sections shows that the precipitating phase in the ternary Al-Cu-Mg alloys with a Cu/Mg ratio close to 2.2 is S'. However, very little is known about the precipitation process in alloys with low solute concentrations. The kinetic parameters that control the precipitation rates have not at all been investigated. The distribution of the S' phase in the matrix and the unusual electron diffraction effects of the S' phase have also not been understood. In addition, very little work is done on the effects of increasing the amount of Si additions on the Al-Cu-Mg alloys although Si is a promising additive. In view of these factors the low solute containing Al-1.5%Cu-0.75%Mg alloy was chosen to study its precipitation behaviour by TEM and DSC

Table 2.4 Summary of published information on the ageing characteristics of Al-Cu-Mg alloys containing silicon

Item #	Alloy Composition (wt%)				Ratio Mg/Si	Phases reported	Ref.
	Cu	Mg	Si	Cu/Mg			
1	2.42	1.25	0.24	2.08	5.2	CuMgAl ₂	127
2	2.39	1.23	0.26	1.94	4.73	CuMgAl ₂	127
3	2.00	0.900	0.25	2.2	3.6	CuMgAl ₂ + Mg ₂ Si + unknown x	128
4	2.00	0.900	0.50	2.2	1.2	CuAl ₂ + Cu ₂ Mg ₈ Si ₆ Al ₅ + unknown x	128
5*	4.00	0.8	0.8	5.0	1	CuAl ₂	158
6*	1.34	0.65	0.94	2.06	.69	CuMgAl ₂ + β	8
7*	2.39	0.42	0.24	5.69	1.75	CuAl ₂	159
8*	4.00	0.89	0.90	4.5	1	CuAl ₂	160
9*	2.50	1.3	0.70	1.9	-	CuMgAl ₂ + β	160

* Commercial alloys

techniques. An attempt was made to understand the crystallography and morphology of the S' phase and establish the kinetics of the overall precipitation process. The effects of Si additions (0.25, 0.50, 0.75 and 1%) on the precipitation behaviour were also examined.

CHAPTER III

EXPERIMENTAL TECHNIQUES AND PROCEDURE

3.1 MATERIALS AND PROCESSING

As-cast ingots, ($23 \times 15 \times 2 \text{ cm}^3$) of high purity aluminium alloys, whose chemical composition is given in Tabel 3.1, were supplied by the Aluminium Company of Canada. In order to prepare homogeneous and equilibrated specimens of the alloys, $3 \times 15 \times 2 \text{ cm}^3$ pieces were cut from each alloy and homogenized at 530°C for 48 h. The homogenized specimens were skimmed, upset forged and hot and cold rolled. About 70% reduction in area was given by hot rolling at 500°C in a number of passes. After each pass the specimen was annealed at 530°C for 10 min. The hot rolled alloys were equilibrated at 530°C for 12 h and water quenched to room temperature.

The equilibrated material was cold rolled ($\approx 80\%$) and used for preparing specimens for metallographic, differential scanning calorimetry (DSC), and transmission electron microscopic (TEM) studies. The specimens for the extraction of insoluble particles were prepared from the equilibrated material. Specimens for TEM were cut from cold rolled sheets, solution treated and quenched to room temperature. Different solution treatment temperatures were used in order to obtain approximately the same grain size in all the alloys. The solution treated specimens were aged at room temperature for 48 h which was followed by ageing at 130°C and 190°C for various lengths of time in an oil bath and an air furnace, respectively. The ageing temperatures were stable to $\pm 2^\circ\text{C}$. Specimens for optical and scanning electron microscopy (SEM) were cut from cold rolled sheets and solution

Table 3.1: Chemical composition of alloys.

Alloy #	Composition, Wt %			
	Cu	Mg	Si	Al
1	1.53	0.79	-	Bal.
2	1.52	0.74	0.23	Bal.
3	1.51	0.75	0.49	Bal.
4	1.54	0.75	0.76	Bal.
5	1.52	0.77	1.03	Bal.

treated at 530°C for 1 h. Some of the solution treated specimens were aged at room temperature followed by ageing at 130°C and 190°C for various lengths of time.

During the course of this investigation it was necessary to prepare a synthetic compound containing 19.3% Cu, 36.5% Mg, 30.2% Si and 14.0% Al for structural studies. Appropriate amounts of high purity (99.999%) elements, Cu, Mg, Si and Al, were melted in an induction furnace in an argon atmosphere. The as cast compound was vacuum sealed in a quartz tube and solution treated at 530°C for 300 h. The single phase structure of the compound was confirmed by optical and scanning electron microscopy.

3.2 EXTRACTION OF INSOLUBLE PARTICLES

Some of the alloys were found to contain insoluble particles. In order to identify and characterize them, $5 \times 5 \times 40 \text{ mm}^3$ size specimens were used for electrochemical extraction of the insoluble particles. They were solution treated at 530°C for 6 h and water quenched. The solution treated specimens were stabilized at room temperature by ageing for 48 h and then further aged at 190°C for various lengths of time.

The precipitate particles were extracted by electrolytically dissolving the matrix of the heat treated specimens in a 2.5 wt% KI-methanol bath.⁽¹⁴²⁾ An aluminium strip kept inside the periphery of the 500 ml beaker containing about 300 ml of solution served as a cathode and a polished and cleaned bar of the specimen ($5 \times 5 \times 40 \text{ mm}^3$) suspended in the centre of the beaker served as the anode. A magnetic stirrer was continuously used during the anodic

dissolution which was carried out at 2-5 volts for 20-24 h at a current density of 40-80 mA/cm². Upon complete dissolution of the specimen the electrolytic bath was treated with 40 ml saturated aqueous solution of disodium ethylenediamine tetracetate (EDTA) for settling the suspended particles and the complex which formed during the electrolytic process. The clear liquid at the top was discarded and the remaining residue was treated with 40 ml of 50% HCl.⁽¹⁶¹⁾ The contents were centrifuged and decanted. The residue was washed thoroughly in distilled water and methanol several times and dried in an oven at 40°C.

3.3 OPTICAL MICROSCOPY

The alloy specimens were mechanically polished and etched with dilute Keller's etchant (1% HF, 1.5% HCl, 2.5% HNO₃ and 95.0% H₂O) to reveal the microstructure and the grain size of the specimens.⁽¹⁶²⁾ Some of the specimens were also etched with the saturated molybdic acid containing 10% HF in distilled water to reveal the grain size and the insoluble particles present in the alloys.⁽¹⁶³⁾ The ASTM intercept method⁽¹⁶²⁾ was used to measure the grain size of the alloys in a Lietz Tas Plus image analysis system.

3.4 ELECTRON MICROSCOPY

3.4.1 Transmission Electron Microscopy

The transmission electron microscopic studies were carried out on a Philips 300 Transmission electron microscope operated at 100 kV.

The TEM specimen of different alloys (1.2 mm thick) were

abraded on different grades of SiC paper to a thickness of 0.1-0.2 mm. Discs of 3 mm diameter were punched out and thinned in a Tenupol jet thinning unit using a solution of 5% perchloric acid in methanol as the electrolyte. Electropolishing was carried out at -60°C at 12.5 volts and at a current density of 18-20 mA/mm². As soon as hole formation was indicated the specimen was quickly taken out, washed in ethanol-methanol and dried. When the specimen was left in electrolyte for more than a few seconds, copper tended to deposit on the specimen. The thin foils stored in dessicators remained free from oxides and could be re-examined after periods of several months.

3.4.2 Scanning Electron Microscopy

The mechanically polished and unetched metallographic specimens were examined in the back scattered mode in a JEOL-840 scanning electron microscope equipped with TN-5500 energy dispersive analysis (EDS) system.

3.4.2.1 Chemical Analysis

The EDS spectra from particles in metallographic specimens visible in the back scattered mode were used for rapid chemical analysis and to observe the effect of ageing. The electrochemically extracted insoluble particles were placed on a carbon replica supported on a Be-grid. In order to avoid inclusion of x-rays generated by the specimen holder, the Be-grid was placed on a carbon block which rested on a brass SEM specimen holder. Several EDS spectra were obtained

from different particles at different accelerating voltages and detector positions to optimize the spatial resolution of the x-ray signals and the efficiency of the production of characteristic x-rays. Generally for an efficient production of the x-rays the energy of electrons striking the specimen should be ≈ 2.5 times the energy of the particular characteristic x-ray. The x-ray spectra were obtained in the spot mode of the SEM from suitable locations in the extracted insolubles and particles visible in the metallographic specimens. The peaks in the x-ray spectra were identified and quantitative analysis was carried out by using Tracor Northern micro quantitative analysis (MICRO Q) program based on K-ratio and ZAF correction procedures. This program requires spectra from pure metal standards of interest which are acquired under similar conditions as unknown to give accurate chemical analysis.

3.4.2.2 Volume Fractions of Insoluble Particles

The volume fractions of insoluble particles were determined from bulk metallographic specimens of the alloys using back scattered images. The images were stored on a disk and analysed by using Tracor Northern Stored Image Analysis (SIA) program.

3.5 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The Du Pont 910 DSC instrument was used in this investigation. It consists of a cell base module connected to the 9900 programmer recorder. The DSC Cell plug into a cell base. A schematic diagram of the calorimeter cell is shown in Fig. 3.1. The cell employs a constantan disc as its primary means of heat transfer to the sample

DSC CELL CROSS — SECTION

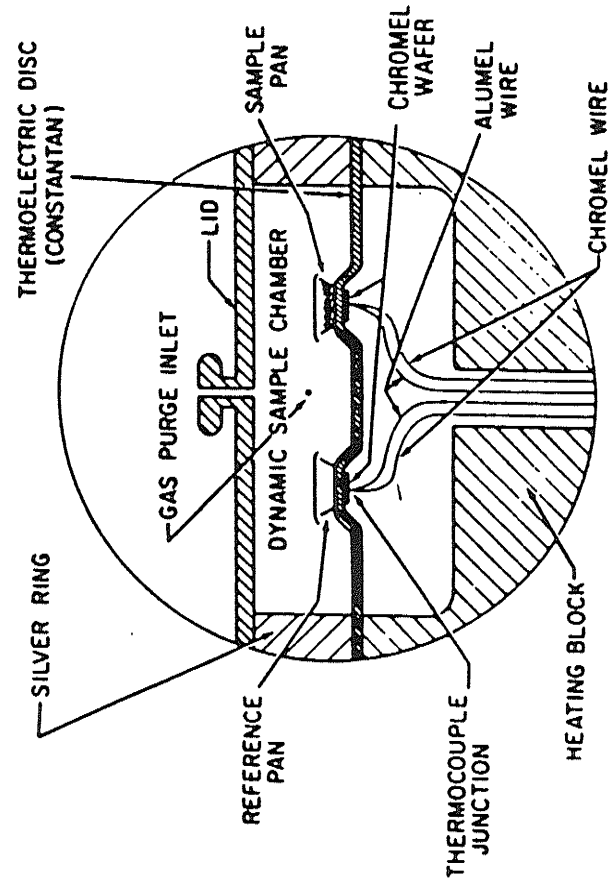


Fig. 3.1 Schematic diagram of the DSC cell

and reference positions, and as one element of the temperature measuring thermocouple. The samples and a reference are placed in pans which sit on raised platforms on the constantan disc. Heat is transferred through the disc and up into the sample and reference via the sample pans. The differential heat flow to the sample and reference is monitored by chromel-constantan area thermocouples formed by the junction of constantan disc and chromel wafer which covers the underside of the platforms. Chromel and alumel wires are connected to the underside of the chromel wafers, and the resultant chromel-alumel thermocouple is used to directly monitor the sample temperature. Hence, deviations from the programmed temperatures can be directly detected. The temperature of the environment of the sample is controlled by a sophisticated feedback control temperature programmer with its own thermocouple system located in the silver heating block. Purge gas is admitted to the sample chamber through an orifice in the heating block wall positioned midway between the two raised platforms. The purge gas enters the cell base at the rear and is preheated by circulation through the block before entering the sample chamber at the block temperature.

Specimens for use in the DSC were prepared from cold rolled strips ($\approx 80\%$) by cutting 5 mm dia discs in a spark cutting machine in order to avoid deformation.⁽¹⁶⁴⁾ The specimens were solution treated and water quenched. Appropriate ageing heat treatments were given to some of them. Heating rates of 5°C/min, 10°C/min, 15°C/min and 20°C/min were used. During each run, dry nitrogen at the rate of 30 ml/min was passed through the cell to avoid oxidation. Each experiment was performed twice and maxima and minima in the curves

were found to be reproducible to within $\pm 2^\circ\text{C}$. The overall shape of the DSC curve was also found to be highly reproducible.

3.6 X-RAY DIFFRACTION

The x-ray diffraction patterns from the extracted precipitate particles and the polished metallographic specimens of solution treated and quenched alloys were obtained using a 114.6 mm Debye-Scherrer camera with Ni-filtered $\text{Cu K}\alpha$ radiation at 40 kV. The specimens were exposed for about 8 h. The 'd' spacing of each reflection was calculated by the standard procedure used for powder diffraction analysis and the corresponding intensity was estimated by visual examination.

The reflections due to the insoluble particles were identified by comparing them with the reflections due to the synthetic quaternary compound. The lattice parameters of the alloys and the electrochemically extracted insoluble particles were determined by using a standard computer program based on the Cohen's least square method.⁽¹⁶⁵⁾ The Nelson-Riley extrapolation technique was also used to determine lattice parameters of the bulk alloys and extracted particles. Both methods gave similar results.

3.7 DENSITY MEASUREMENTS

The densities of the alloys were calculated from their respective lattice parameters. The density of 4.03 gm/c.c. for the synthetic quaternary compound was determined by measuring the loss of weight of a sample of the compound in a liquid. Ethyle iodide was found to be a satisfactory liquid for this purpose. In order to overcome errors due to internal porosity, the compound was finely

crushed, examined under a binocular microscope and transferred to a small container. The crushed pieces held in the container were evacuated in a vacuum chamber and the ethyle iodide was transferred into the container. A thin metal wire was used for suspending the container in the ethyle iodide. The length of the wire that was immersed in the liquid was always kept constant. This procedure and prolonged evacuation produced reproducible results. The density of liquid was also determined by weighing an Al block in distilled water and ethyle iodide. The densities of the liquid and the quaternary compound were measured at the same temperature. Atmospheric pressures noted and corrections due to air density were made. (166,167)

CHAPTER IV

PRECIPITATION IN THE Al-1.53%Cu-0.79%Mg ALLOY

4.1 MICROSTRUCTURAL CHARACTERIZATION

Specimens of the Al-1.53%Cu-0.79%Mg alloy were solution treated at 460°C for 10 min and water quenched. The optical micrograph (Fig. 4.1) of the as quenched specimen showed insoluble free single phase microstructure with an average grain size of $\approx 160 \mu\text{m}$. The as quenched specimens were then room temperature aged for 48 h followed by ageing at 130° and 190°C for various lengths of time. The microstructure of the aged specimens were examined by transmission electron microscopy.

4.1.1 Initial Stages of Ageing: Defect Structure and GPB Zones

Transmission electron microscopic studies showed that the solution treated and quenched specimen as well as those aged at room temperature for 48 h and further aged at 130°C up to 600 h and at 190°C upto 4 h contained appreciable amounts of quenched-in defects. A typical TEM micrograph obtained from a specimen aged at room temperature for 48 h shows the presence of dislocation loops and helical dislocations (Fig. 4.2). The latter have formed due to condensation of vacancies on the screw dislocations whereas the former form by condensation of vacancies into collapsed discs (Fig. 4.3) during or immediately after quenching from solution treatment temperature. The formation of dislocation loops has been discussed by Kuhlman-Wilsdorf⁽²²⁾ and Embury and Nicholson.⁽¹⁶⁸⁾ They have suggested that the Burgers vector of the dislocation loops is $a/2 \langle 110 \rangle$ and

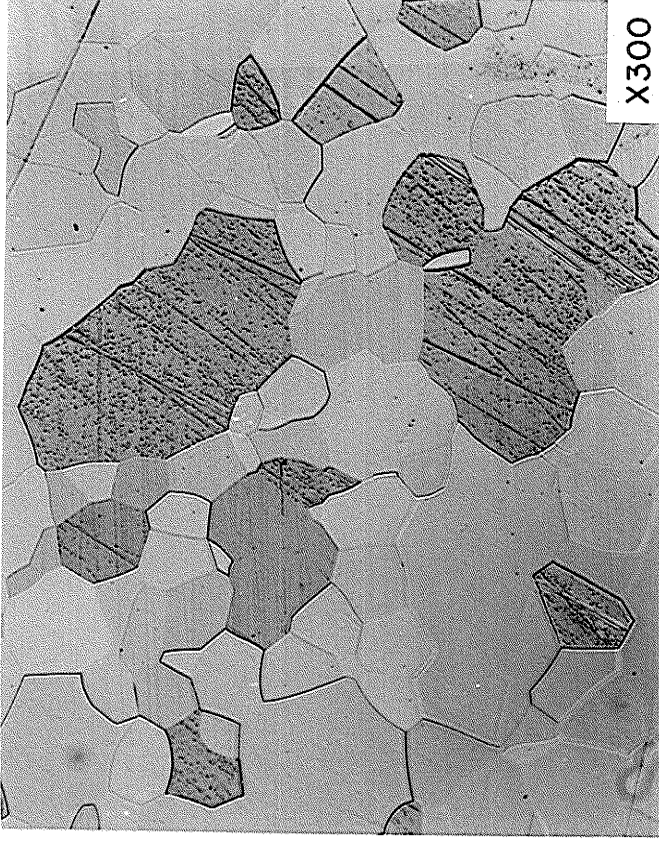


Fig. 4.1 Optical micrograph of the solution treated and water quenched Al-1.53%Cu-0.79%Mg alloy

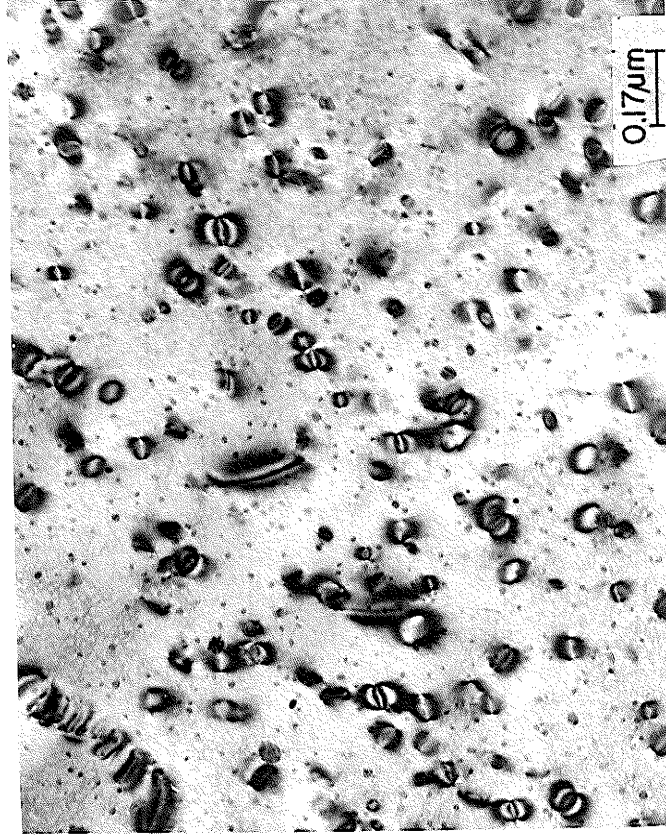


Fig. 4.2 Bright field image of the Al-1.53%Cu-0.79%Mg alloy aged at room temperature for 48 h

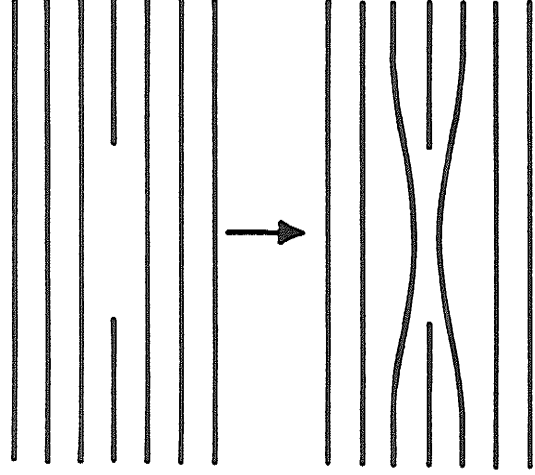


Fig. 4.3 The formation of a dislocation loop by the collapse of a disc of vacancies₍₂₂₎

they lie on $\{110\}_M$ planes. The presence of dislocation loops in the present alloy indicates that considerable amount of excess vacancies were retained during quenching. The thickness of the foil was estimated to be about 1500 Å. For this thickness of foil, the vacancy concentration was estimated to be of the order of $\approx 10^{-4}$. This value is similar to the values of the quenched-in vacancy concentration in pure aluminum⁽¹⁶⁹⁾ and ternary Al-3.2%Cu-1.5%Mg alloys.⁽¹⁷⁰⁾ Further ageing of the stabilized specimens up to 24 h at 130°C (Fig. 4.4) increased the size of dislocation loops, but the estimated vacancy concentration was not very much different from that in room temperature aged specimen. Increase of ageing time to 192 h and 288 h at 130°C seems to have caused the alignment of the loops along $\langle 100 \rangle_M$ direction and increased their sizes. These two factors have been interpreted to suggest that the dislocation loops have been decorated by solute atoms (Fig. 4.5). Ageing beyond 384 h showed clearly the presence of precipitate particles associated with dislocations (Fig. 4.6). Ageing of room temperature aged samples at 190°C produced decorated dislocation in them during the first 30 min of ageing. Further ageing for 2 h produced larger and fewer dislocation loops and helical dislocations (Fig. 4.7), while after 4 h of ageing specimens showed the presence of fine visible precipitates associated with dislocations (Fig. 4.8).

Wilson⁽¹²⁷⁾ and Horiuchi et al.⁽¹⁷¹⁾ have suggested that these excess vacancies assist the diffusion of Cu and Mg complexes. The sum of the atomic diameters of Cu (0.2556 nm) and Mg (0.3196 nm) is approximately twice that of the atomic diameter of aluminum, so that the formation of Cu-Mg complexes in equiatomic 1:1 ratio may

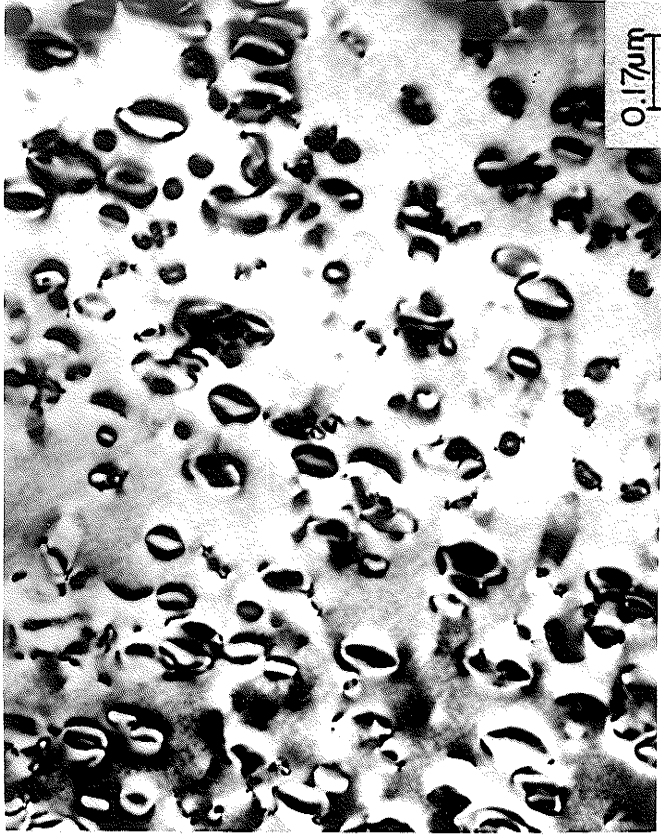


Fig. 4.4 Bright field image of the Al-1.53%Cu-0.79%Mg alloy aged at room temperature and further aged at 130°C for 24 h

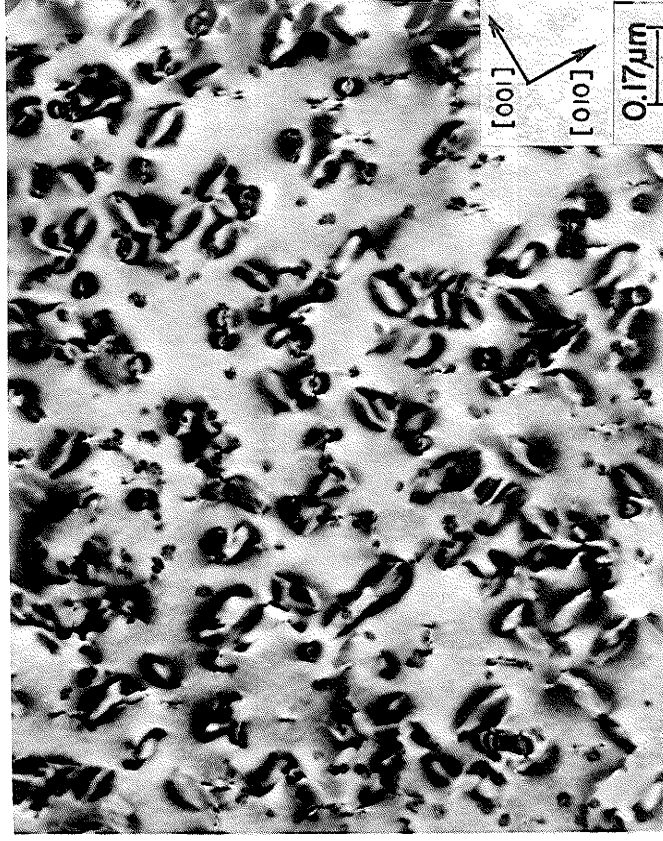


Fig. 4.5 Bright field image of the Al-1.53%Cu-0.79%Mg alloy aged at room temperature for 48 h and further aged at 130°C for 288 h



Fig. 4.6 Bright field image of the Al-1.53%Cu-0.79%Mg alloy aged at room temperature for 48 h and further aged at 130°C for 600 h

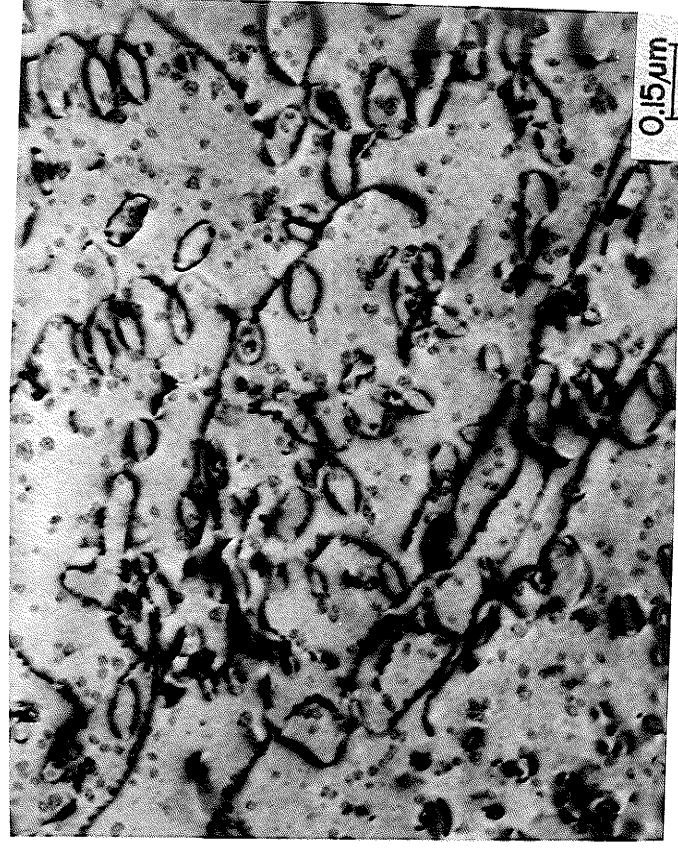


Fig. 4.7 Bright field image of the Al-1.53%Cu-0.79%Mg alloy aged at room temperature for 48 h and further aged at 190°C for 2 h

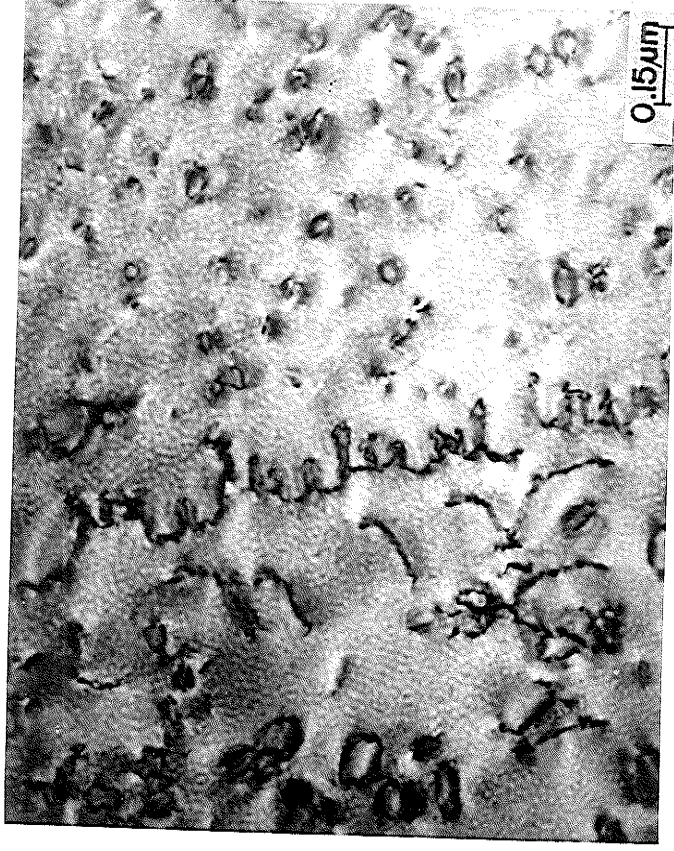
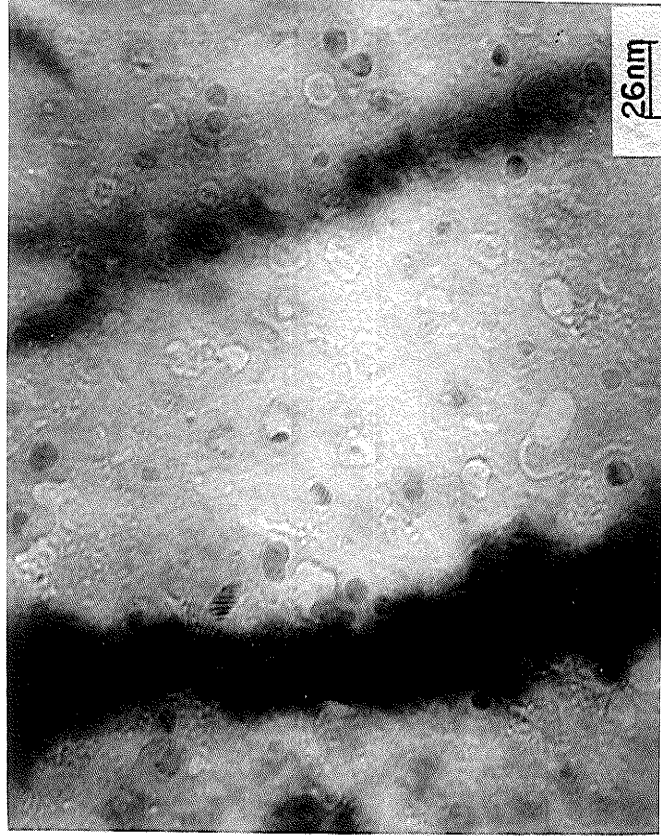


Fig. 4.8 Bright field image of a specimen aged at room temperature for 48 h followed by ageing at 190°C for 4 h.

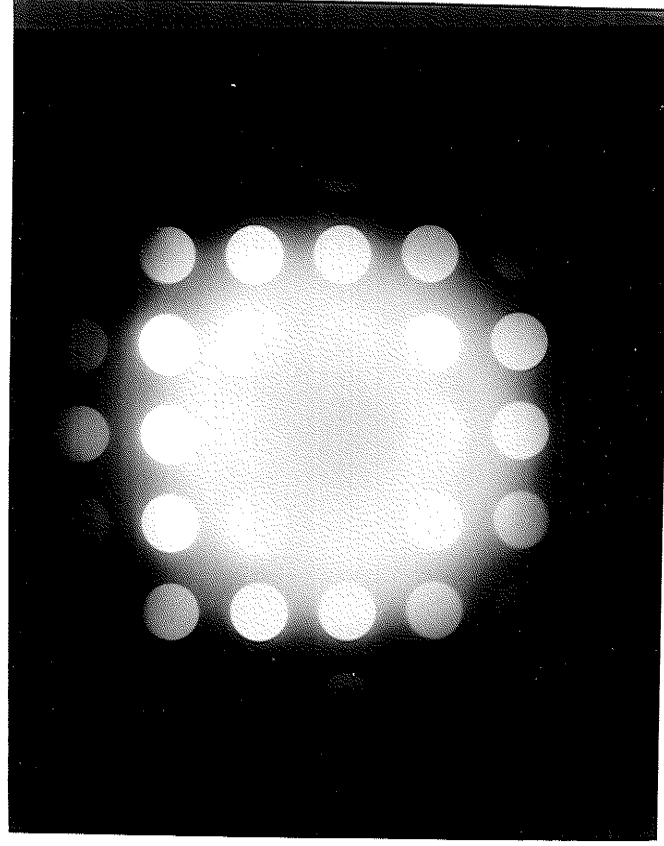
be expected to reduce lattice strain.⁽¹⁷⁰⁾ Therefore, one might also expect GPB zones to be formed in the initial stages of ageing of this alloy. These zones are too small to be resolved in the Philips 300 transmission electron microscope used in this investigation. Thus, a few specimens of the alloy were examined in the JEOL-200 FX transmission electron microscope operated at 200 kV. A typical micrograph obtained from a specimen aged at 130°C for 16 h is shown in Fig. 4.9(a) with its SADP in Fig. 4.9(b). The microstructure shows GPB zones fringes suggesting them to be cylindrical, (10-20 Å in diameter) and lying along $\langle 100 \rangle_M$ direction. These observations are consistent with the x-ray studies of Bagaryatsky⁽¹²¹⁾ and Silcock⁽¹²²⁾ who reported them to be of cylindrical shape (1-2 nm dia) lying along $\langle 100 \rangle_M$ directions. High resolution lattice imaging studies of Takahashi and Sato⁽¹³⁵⁾ also showed similar results.

4.1.2 Formation of the S' Phase

The first clear indication of the presence of second phase particles were seen in specimens aged for more than 384 h at 130°C and 4 h at 190°C. A typical bright field image obtained from a specimen aged for 4 h at 190°C is shown in Fig. 4.10(a). The precipitate particles are not clearly visible, however, strain field contrast, which could be due to the presence of coherent precipitate is observed. The coherency strains also gave the surface a mottled appearance. The presence of precipitate particles was confirmed by the presence of faint streaks (encircled) in the SAD pattern shown in Fig. 4.10(b). These streaks are parallel to $\langle 100 \rangle_M$ direction. Further ageing of the specimens at 190°C resulted in the growth of these particles (Fig.



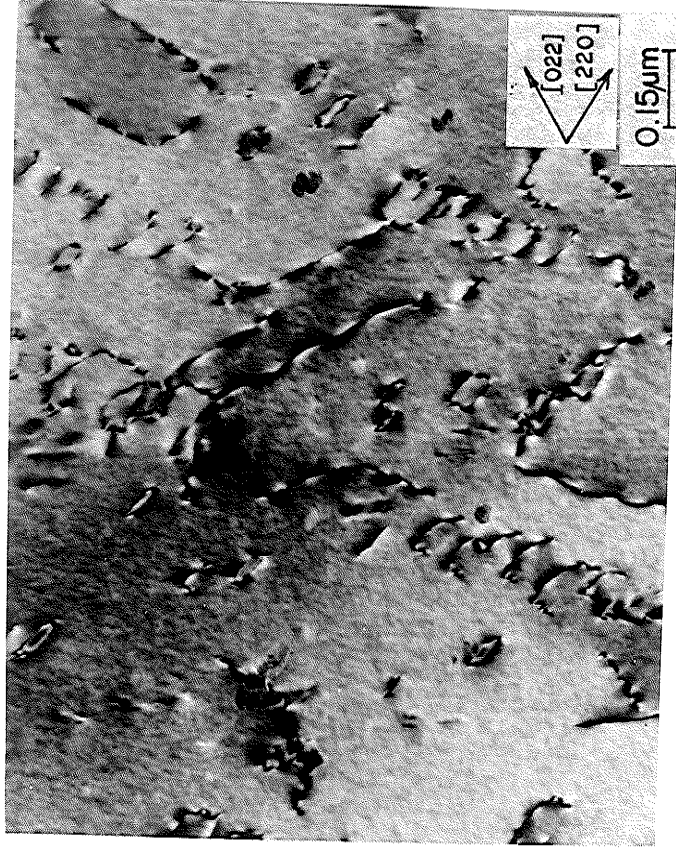
(a)



(b)

Fig. 4.9 (a) Bright field image of the Al-1.53%Cu-0.79%Mg alloy aged at room temperature for 48 h and further aged at 130°C for 16 h

(b) The corresponding SAD pattern



(a)



(b)

Fig. 4.10 (a) Bright field image of the Al-1.53Cu-0.79Mg alloy aged at room temperature for 48 h and further aged at 190°C for 4 h

(b) The SAD pattern of (a). The streaks due to precipitates are encircled

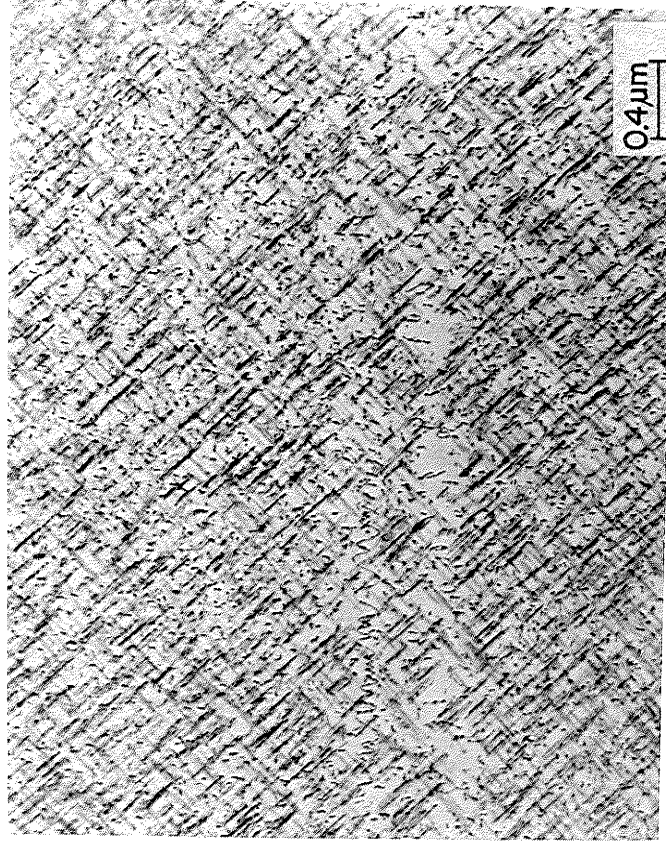
4.11(a)) and the SAD pattern showed definite precipitate reflections in Fig. 4.11(b). The precipitate reflections can be indexed as due to the orthorhombic S' phase by a method discussed in Section 4.1.2.2. The advanced stage of ageing at 130°C for 768 h also showed similar features (Fig. 4.12(a) and (b)). The identification of the precipitates is in agreement with the conclusions of an x-ray diffraction study by Bagaryatsky⁽¹²³⁾ and Silcock⁽¹²²⁾ on Al-Cu-Mg alloys with a Cu/Mg ratio of 2.2:1.

4.1.2.1 Nucleation of the S' Phase

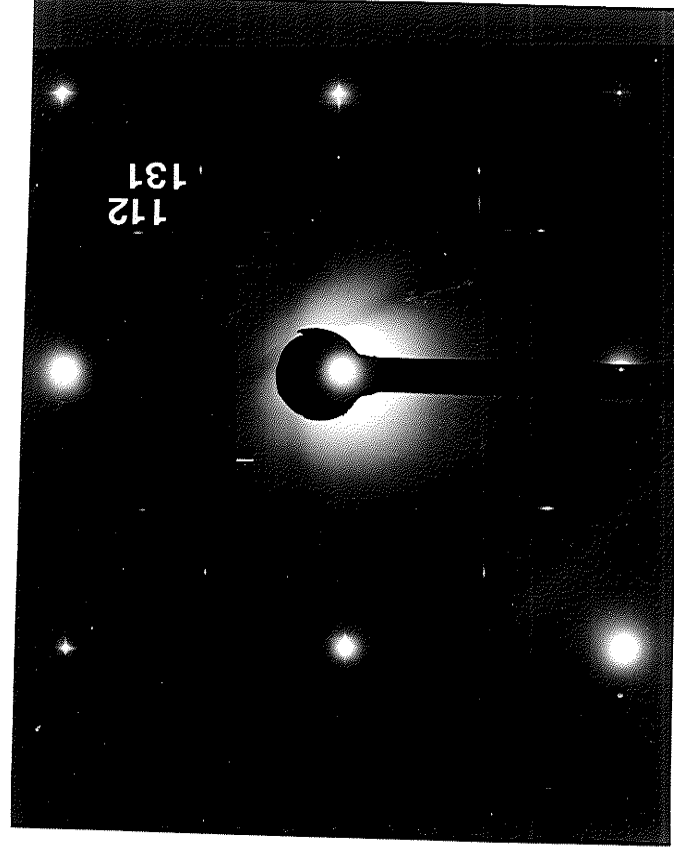
The bright field image obtained from a specimen aged for 600 h at 130°C showed the S' phase to be associated with dislocations (Fig. 4.13(a) and (b)). it can be more clearly seen in Fig. 4.14 which is a micrograph of a specimen aged at 130°C for 288 h. The S' phase has nucleated on (110) planes with a tendency to grow along [001] direction. This observation is consistent with the models of Alekseyev et al.⁽¹³⁰⁾ shown in Fig. 4.15 and of Wilson and Partridge.⁽²³⁾ The S' precipitates also nucleate on helical dislocations as evidenced by the trace of helical dislocation on the micrograph shown in Fig. 4.11(a). Thus, it can be concluded that dislocations are primarily responsible for the nucleation of the S' phase.

4.1.2.2 Theoretical Prediction of the Electron Diffraction Pattern of the S' Phase

A typical example of the microstructure of a specimen aged for 168 h at 190°C is shown in Fig. 4.16(a) with its SAD pattern in Fig. 4.16(b). The analysis of the SAD pattern due to matrix suggests



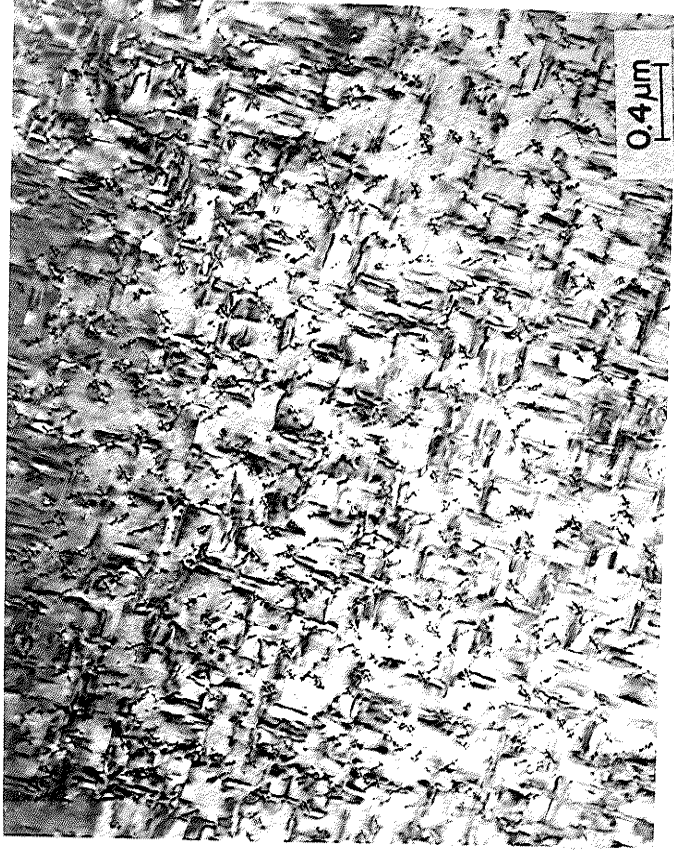
(a)



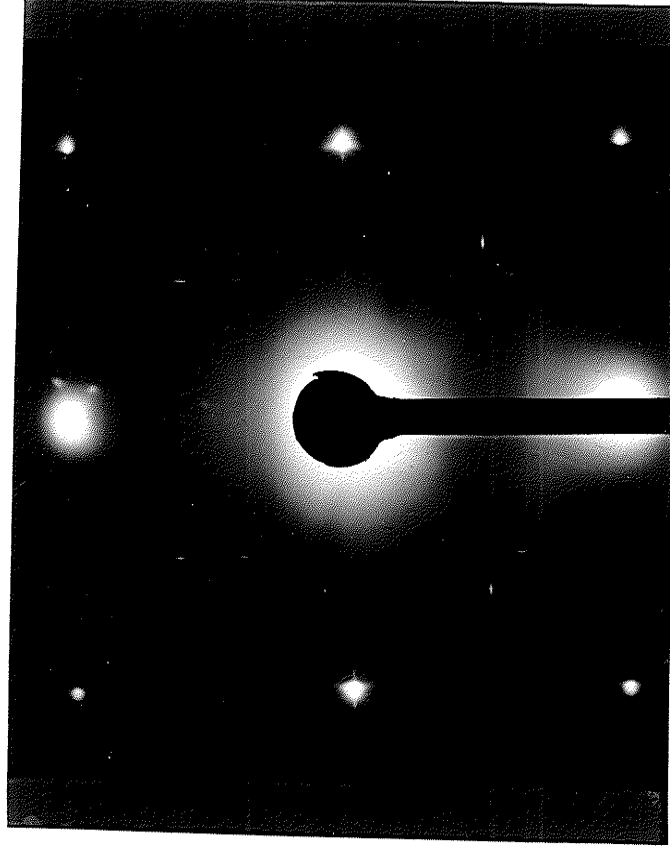
(b)

Fig. 4.11 (a) Bright field image of the Al-1.53%Cu-0.79%Mg alloy aged at room temperature for 48 h and further aged at 190°C for 6 h. The traces of helical dislocation are visible

(b) The SAD pattern of (a)



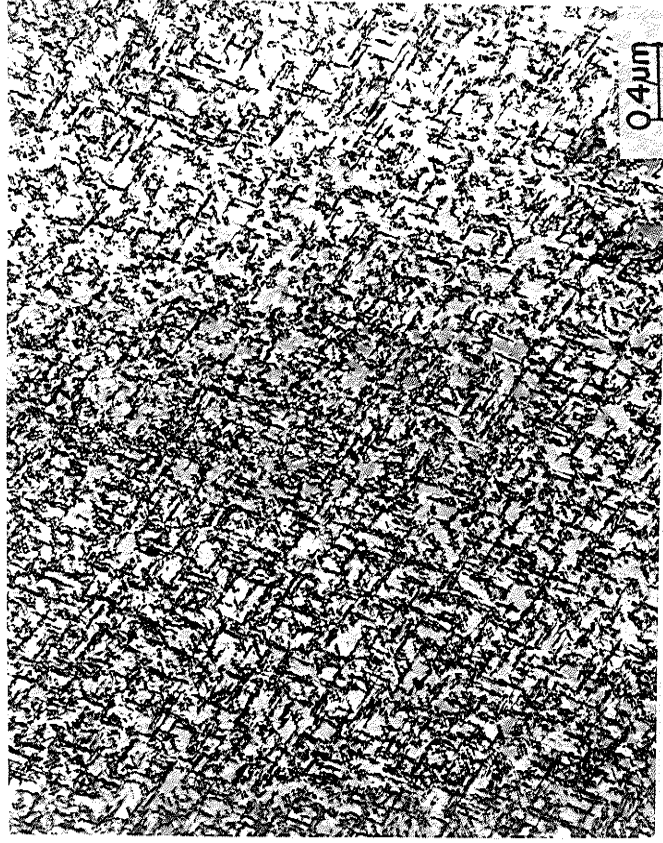
(a)



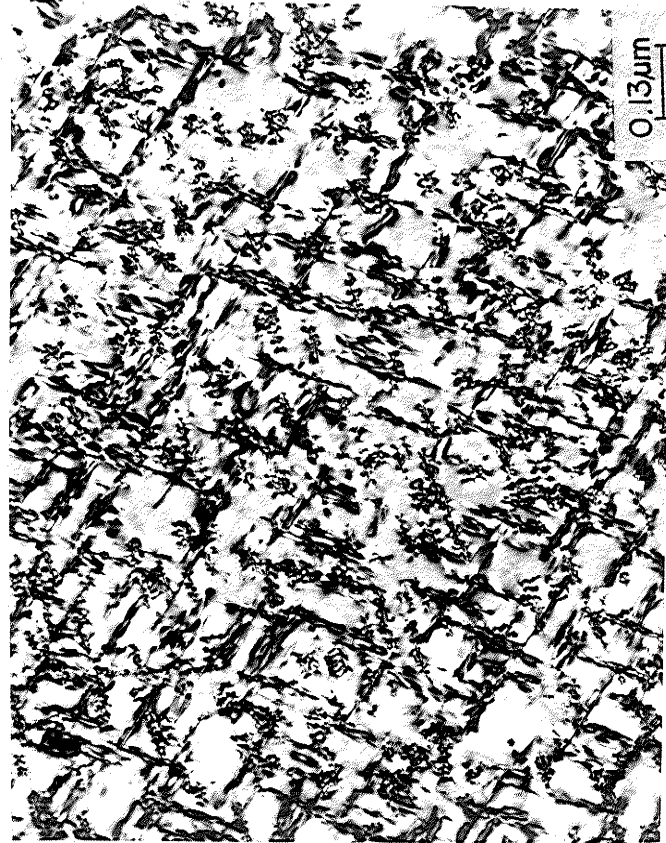
(b)

Fig. 4.12 (a) Bright field image of the Al-1.53%Cu-0.79%Mg alloy aged at room temperature for 48 h and further aged at 130°C for 768 h

(b) The SAD pattern of (a)



(a)



(b)

Fig. 4.13 (a) Bright field image of the Al-1.53%Cu-0.79%Mg alloy aged at room temperature for 48 h and further aged at 130°C for 600 h

(b) Same area as in (a) at a higher magnification

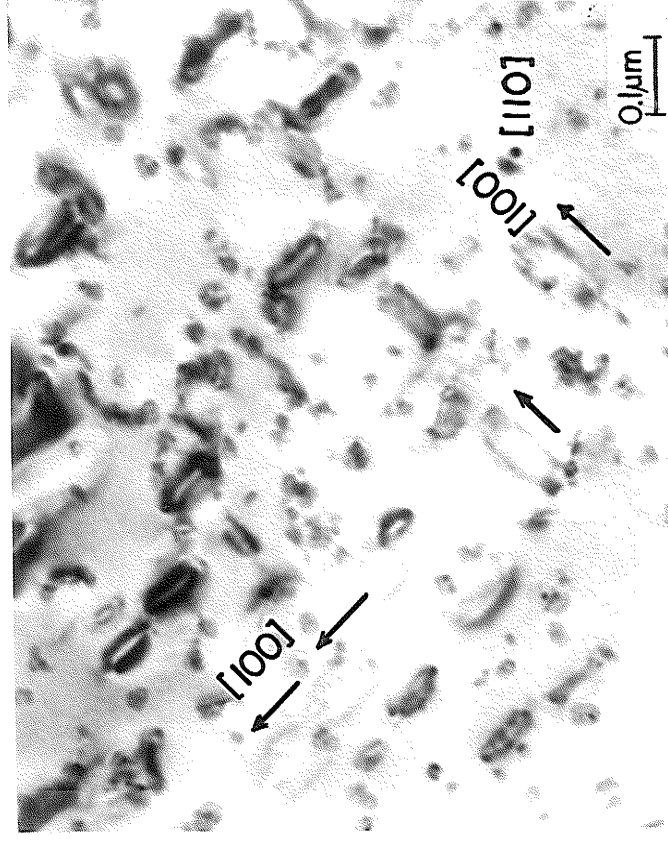


Fig. 4.14 Bright field image of the Al-1.53%Cu-0.79%Mg alloy aged at room temperature for 48 h and further aged at 130°C for 288 h. Nucleation of the S' phase on loops is marked by arrows

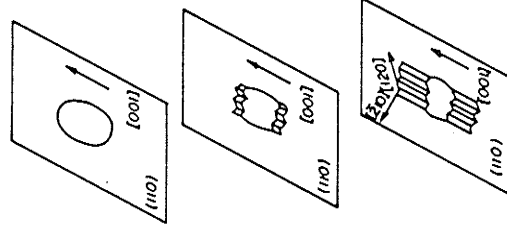
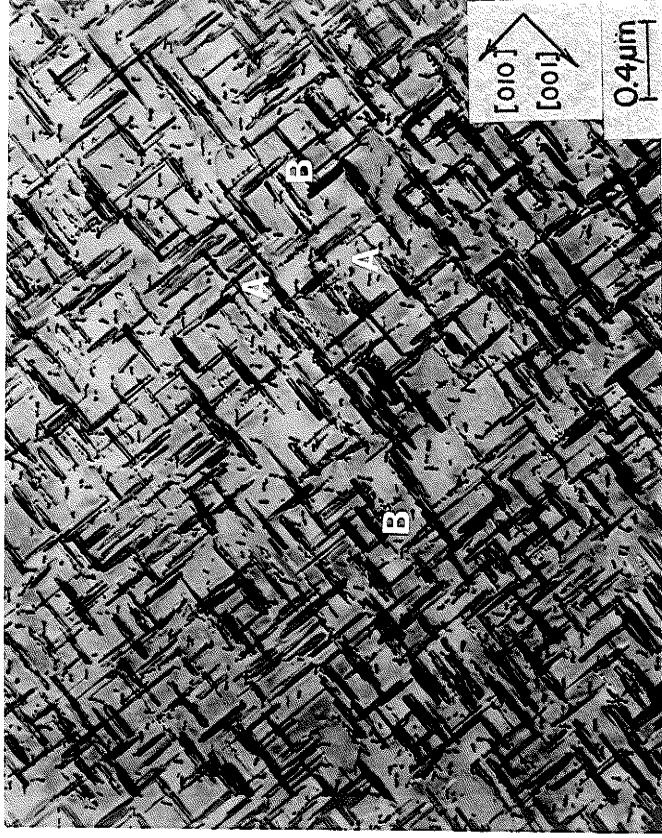
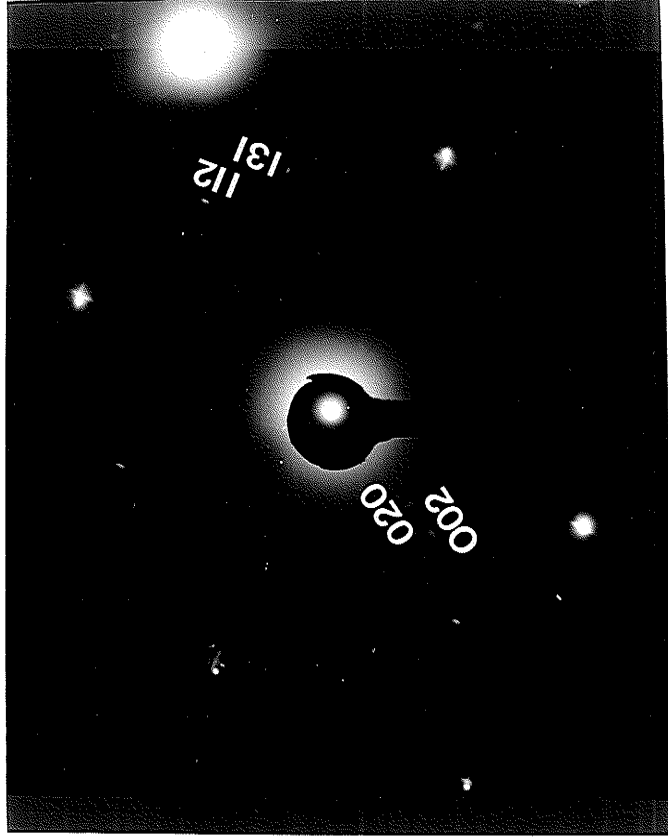


Fig. 4.15 Schematic diagram of a suggested sequence for the nucleation of the S' phase (130)



(a)



(b)

Fig. 4.16 (a) Rod shaped S' precipitates in the Al-1.53%Cu-0.79%Mg alloy aged for 168 h at 190°C. Groups of 'end on' precipitates parallel to $\langle 110 \rangle$ and $\langle 100 \rangle$ are marked A and B, respectively

(b) SAED pattern from an area similar to that shown in (a). {020}, {002}, {112} and {131} reflections of the S' precipitates are marked

the thin foil to be in $[100]$ orientation, however, the diffraction pattern due to the precipitates is very complex. The SAD pattern can be interpreted by simulating a theoretical diffraction pattern using known orientation relationships as described below.

The following orientation relationships between S' and the matrix were established by Bagaryatsky⁽¹²¹⁾ and Silcock⁽¹²²⁾ using the x-ray diffraction technique,

$$[100]_{S'} \parallel [100]_M ; [010]_{S'} \parallel [021]_M ; [001]_{S'} \parallel [\bar{0}12]_M$$

If the $[100]$ direction of a single crystal of fcc matrix phase is parallel to the $[100]$ direction of S' phase, four possible variants of S' are possible. This occurs because there are four $\langle 021 \rangle$ matrix directions which are at 90° to $[100]_M$ and can become 'c' direction of S' phase. These directions are $[\bar{0}12]_M$, $[021]_M$, $[\bar{0}21]_M$ and $[012]_M$. These four orientations are referred to as variant 1, 2, 3 and 4 respectively. Since there are three $\langle 100 \rangle_M$ axes which can be chosen as parallel to $[100]_{S'}$, there are a total of 12 possible crystallographic variants of the S' phase from a single crystal of matrix phase. The four variants 1, 2, 3 and 4 which arise from the matrix-S' orientation relationship of $[100]_M \parallel [100]_{S'}$ are shown in a stereogram in Fig. 4.17.

Based on the structure of the S' phase its strongest reflections are expected to be 131, 020, 200, 111 and 112. Considering the variants with $[100]_M \parallel [100]_{S'}$ only those $g_{S'}$, reciprocal lattice vectors of S' phase, lying almost perpendicular to the $[100]_M$ beam direction will be able to satisfy the Bragg diffraction condition. The simplest way to check this condition is to form a transformation

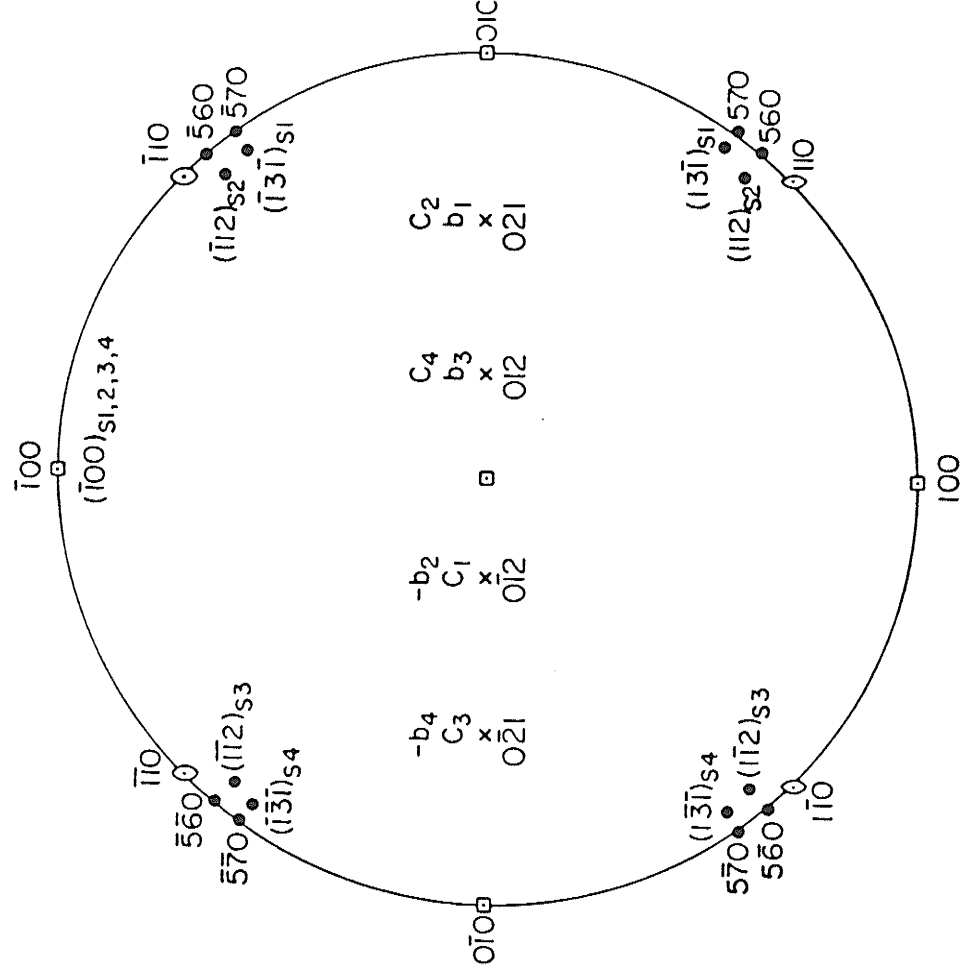


Fig. 4.17 Stereogram showing the b and c axis directions of four orthorhombic S' variants sharing a common 'a' axis direction parallel to $[100]$ in the parent cubic crystal. The directions of g_S , vectors for $\{112\}_S$, and $\{131\}_S$, reflections from the four variants are also shown (round brackets). The matrix directions are unbracketed

matrix to convert plane normals in the S' phase to the directions referred to as the face centred cubic matrix phase. In the S' phase the (h, k, l) plane normal is parallel to the direction [h/a, k/b, l/c]_{S'}. Thus for variant 2, expressing the S' phase plane normals as row vectors,

$$[100]_M \rightarrow [100]_{S'}$$

$$\left[\frac{01\bar{2}}{\sqrt{5}}\right]_M \rightarrow [010]_{S'}$$

$$\left[\frac{02\bar{1}}{\sqrt{5}}\right]_M \rightarrow [001]_{S'}$$

the transformation matrix is:

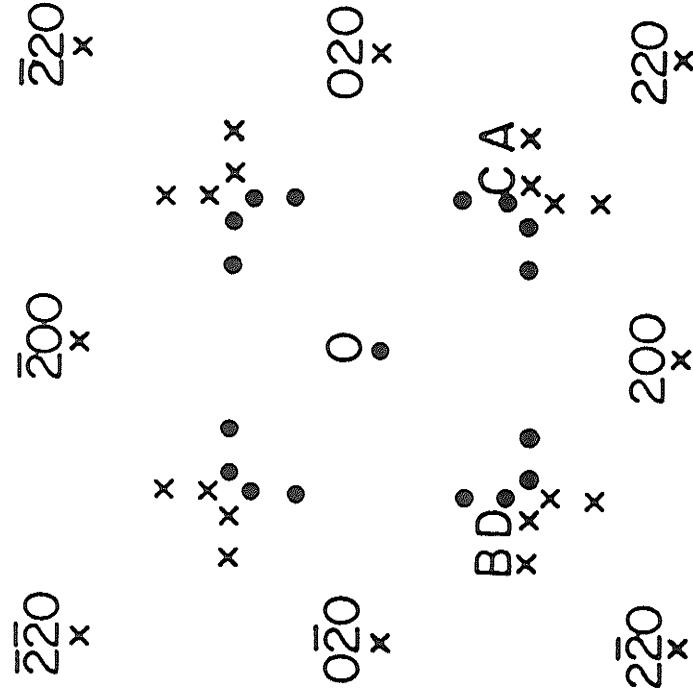
$$S' \approx M = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1/\sqrt{5} & -2/\sqrt{5} \\ 0 & 2/\sqrt{5} & 1/\sqrt{5} \end{vmatrix}$$

For this variant only the strong reflections (112)_{S'} and (1 $\bar{1}$ 2)_{S'} have g_{S'} vector nearly perpendicular to [001]_M. They are parallel to the unit normals [0.6398, 0.7651, 0.726]_M and [0.6398, 0.7651, 0.0726]_M which are calculated to be lying at $\mp$ 4.16° respectively from the (001)_M plane. Similarly for variant 4, (131)_{S'} and (131)_{S'} are the only visible reflections lying at $\mp$ 2.5° to the (001)_M plane. These g_{S'} vectors are lying sufficiently close to the foil plane to give Bragg reflections. For variant 3, (11 $\bar{2}$)_{S'} and (1 $\bar{1}$ 2)_{S'}, are favoured reflections and (131)_{S'} and (131)_{S'} are favoured reflections for variant 1. These eight reciprocal lattice vector directions are also plotted on the standard stereographic projection in Fig. 4.17. It is observed that the {112}_{S'} vectors have projections in the (001)_M plane close to [560]_M, [560]_M, [560]_M and [560]_M and the {131}_{S'} vectors close to [570]_M, [570]_M, [570]_M and [570]_M.

There are also four similar S' phase variants with $[010]_M$ $\parallel$ $[100]_{S'}$, and these will produce diffraction spots rotated about $[001]$ by 90° relative to the $[100]_M$ $\parallel$ $[100]_{S'}$ variants discussed above.

The stereogram in Fig. 4.17 shows the directions of all the $g_{S'}$ vectors lying in, or close to, the $(001)_M$ plane. The simulated diffraction pattern of Fig. 4.18 was constructed by plotting lines parallel to these $g_{S'}$ vectors through the centre of the pattern and placing diffraction spots at a distance from the origin proportional to the length of the $g_{S'}$ vector under consideration. The crosses mark primary reflections and the solid circles show precipitate double diffraction spots caused by strong matrix reflections. The reflections A, B, C and D represented by crosses are primary reflections due to the S' phase. The origin of these primary reflections is given in the Table included in Fig. 4.18. The primary and double diffraction spots around the "forbidden" $\{110\}_M$ reflections give a characteristic grouping of 8 diffraction spots due to the S' phase. The theoretical diffraction pattern is in close agreement with the observed diffraction pattern shown in Fig. 4.16(b). The presence of double diffraction spots depends critically upon the value of the deviation parameter S_g which is governed by the thickness of the foil and the angle of tilt. Tilting of the $\{001\}_M$ foil weakens the matrix reflections and causes some of the double diffraction spots shown in Fig. 4.16(b) to disappear - which is in agreement with observations reported by Chester.⁽¹⁵¹⁾

The four variants with $[001]_M$ $\parallel$ $[100]_{S'}$ are simple to analyse since for these 4 variants, S'-phase $g_{S'}$ vectors of the type $(0\ k\ 1)_{S'}$,



A	$(1\bar{3}\bar{1})_1, (131)_4$	Angle COD = 100.5°
B	$(1\bar{3}1)_1, (1\bar{3}\bar{1})_4$	Angle AOB = 109.5°
C	$(112)_2, (1\bar{1}\bar{2})_3$	
D	$(1\bar{1}\bar{2})_2, (112)_3$	

Fig. 4.18 Interpretation of diffraction pattern with [001] matrix beam direction. The crosses represent primary reflections while solid circles are double diffraction spots. The variants contributing to reflections A, B, C and D are listed in the Table below

will lie in the $(001)_M$ foil plane. The strong S' reflections of this type are expected to be, in order of decreasing intensity, 020 , 002 , 042 , 022 and 021 . Their predicted positions on the $(001)_M$ great circle can be calculated using the appropriate rotation matrix. These variants 9, 10, 11 and 12 have $[001]_M \parallel [100]_{S'}$. For variant 9 with $[210]_M \parallel [010]_{S'}$ and $[\bar{1}20]_M \parallel [001]_{S'}$ the matrix which transforms S' g-vectors to directions referred to the matrix axes is,

$$S \approx M = \begin{vmatrix} T & 0 & 0 & 1 \\ 2/\sqrt{5} & 1/\sqrt{5} & 0 \\ 1/\sqrt{5} & -2/\sqrt{5} & 0 \end{vmatrix}$$

For variant 9 the in-foil unit vector from the $(0\ k\ 1)_{S'}$ plane is parallel to:

$$\frac{1}{\sqrt{5}} \left[\left(\frac{2k}{b} + \frac{1}{c} \right), \left(\frac{k}{b} - \frac{2l}{c} \right), 0 \right]_M$$

Thus $(020)_{S'}$ $\parallel$ $(210)_M$ for variant 9 and it does not overlap $(002)_{S'}$ reflections from other variants. Overlapping reflections do not in fact occur for variants 9, 10, 11 and 12. The S' reflections $(002)_{S'}$ and $(020)_{S'}$ are marked on the diffraction pattern of Fig. 4.16(b). The $(002)_{S'}$ reflection comes from variant 9 and the $(020)_{S'}$ from variant 12, as their $g_{S'}$ vectors being parallel to $[\bar{1}20]_M$.

Recently, Cusiat, Duval and Graf⁽¹⁴⁶⁾ have attempted to interpret the "superlattice" spots in Fig. 4.16(b) as periodic antiphase domain satellites rather than being due to double diffraction. However, they did not show convincing evidence of the presence of periodic antiphase domain images to support their interpretation. It is,

therefore, concluded that satellite spots in Fig. 4.16(b) are due to double diffraction phenomenon as had been earlier suggested by Weatherly and Nicholson⁽⁹⁴⁾ and Hirsch, Howie, Nicholson, Pashley and Whelan.⁽¹⁷²⁾

4.1.2.3 Analysis of SAD Patterns and Morphology of the S' Phase

In order to confirm the theoretical predictions of simulated diffraction pattern and to study morphological development of the S' phase, bright field and centred dark field (CDF) images were examined and lattice parameters were measured from SAD patterns obtained from specimens aged for various times at 190°C.

4.1.2.3.1 Morphology From Bright Field Images

In the bright field image of an $(001)_M$ foil (Fig. 4.16(a)), rods of the S' phase parallel to $[010]_M$ and $[100]_M$ directions in the plane of the foil and perpendicular to the foil $[001]_M$ are clearly visible. These rods are circular in cross-section with a diameter of ≈ 90 Å. This dimension is consistent with the streaking of the $(020)_{S'}$ and $(002)_{S'}$ reflections in Fig. 4.16(b) in $[120]_M$ and $[210]_M$ directions. Despite the long ageing time of 168 h at 190°C the rods have not coalesced to form laths, although there is some tendency for rods to group together parallel to (110) and $(\bar{1}10)$ matrix planes and occasionally parallel to (100) and (010) matrix planes. These features are most clearly seen in the four "end-on" variants. The average length of the rod is ≈ 90 Å, giving a rod volume of $\approx 1.146 \times 10^7 \text{ Å}^3$. By observing the projections of the rod images in a $\{110\}_M$ foil, the foil thickness was estimated to be 1525 Å.

4.1.2.3.2 Interpretation of Centred Dark Field (CDF) Images

The analysis in Section 4.1.2.2 clearly implies that CDF images formed using the diffraction spots A and B of Fig. 4.18 will show variants 1 and 4 of S' phase, while C and D will light up variants 2 and 3. Figs. 4.19(a), (b), (c) and (d) show CDF images using the A, B, C and D reflections shown in Fig. 4.18, while Figs. 4.19(e) and (f) are taken from $(002)_{S'}$ and $(020)_{S'}$ spots shown in Fig. 4.16(b). The CDF images from all six reflections highlight S' rods parallel to [100] matrix directions. Since both B and A reflections come from the same two variants, 1 and 4 they light up some identical rods in the images, which are marked with X in Figs. 4.19(b) and 4.19(a). Similar common features occur in the images using reflection D and C from variants 2 and 3 and marked Y in Figs. 4.19(d) and 4.19(c). Some rods in Fig. 4.19(a) are, however, also weakly visible in Fig. 4.19(c), and are marked X1. Similarly, some strongly lit rods in Fig. 4.19(c) also appear weakly in Fig. 4.19(a) and are marked Y1. Less obvious "ghosts" are observed between Fig. 4.19(c) and 4.19(d). Great care was taken not to shift the specimen as the different CDF images were formed from the diffraction pattern shown in Fig. 4.20(a). Fig. 4.20(b) shows the bright field image. The weak coincidences arise because the diffraction aperture had a reciprocal lattice diameter of $\approx 0.018 \text{ \AA}^{-1}$, which is close to the $0.017 \text{ \AA}^{-1}$ separation of the spots B-D and C-A in Fig. 4.18. This fact together with the 90° A diameter of the rods and their associated $0.011 \text{ \AA}^{-1}$ diameter reldiscs, did not allow spot C to be isolated without including part of the reldisc of spot A to give weak ghosts of A rods in Fig. 4.19(c). The CDF images formed using the diffraction spots $(002)_{S'}$ and $(020)_{S'}$



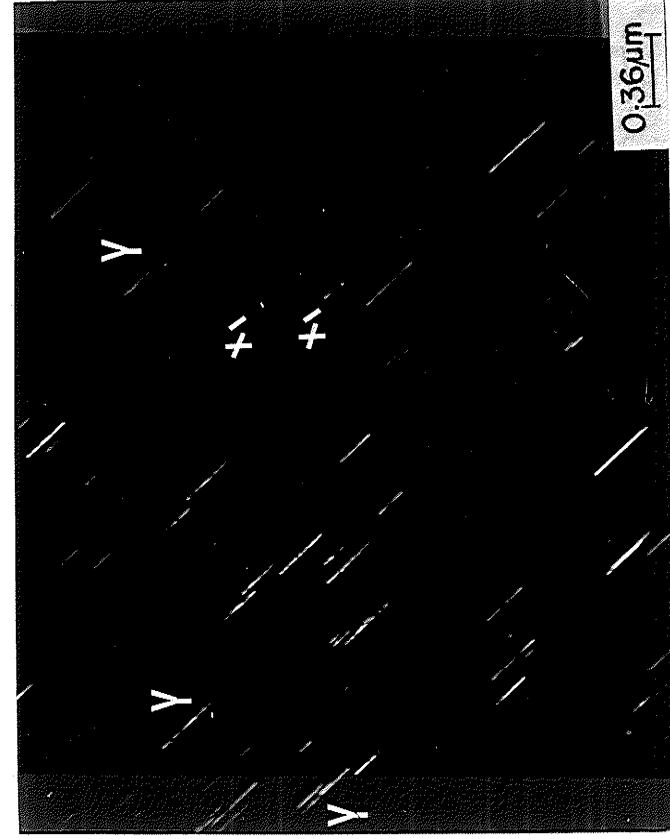
(a)



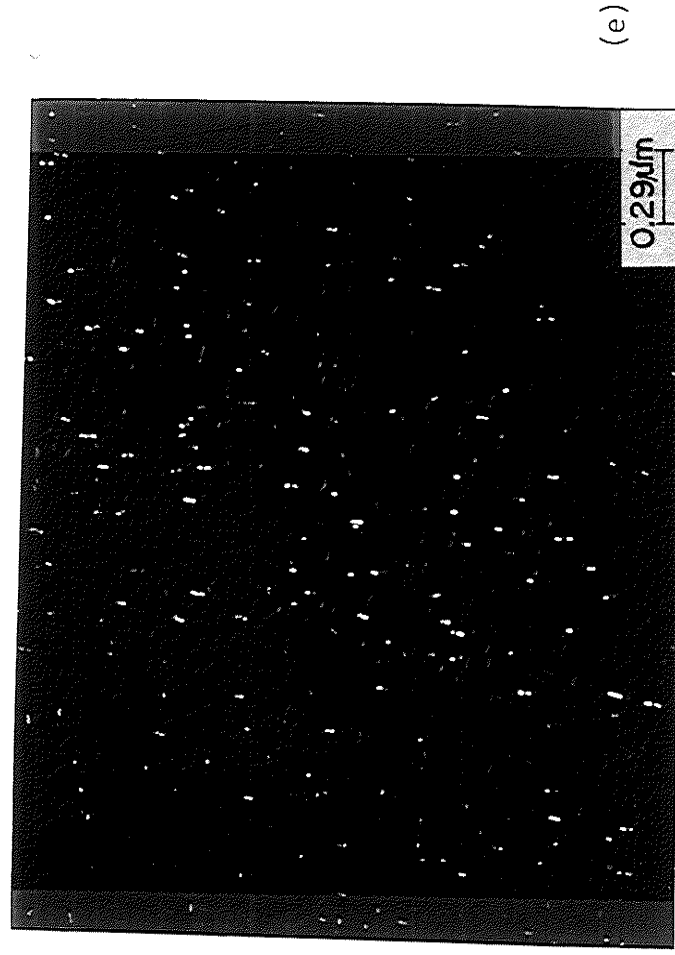
(b)



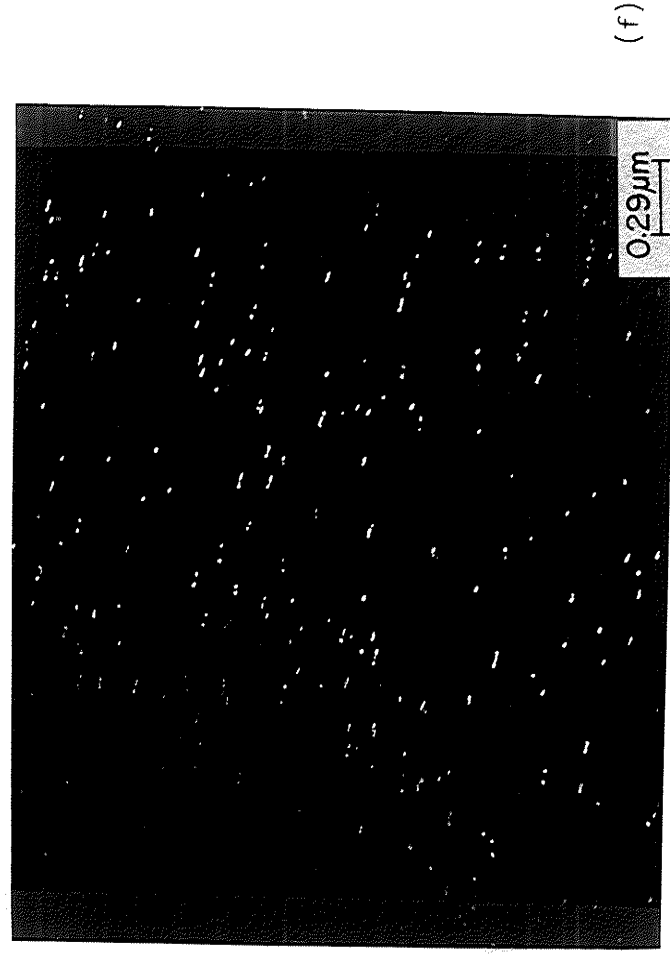
(c)



(d)



(e)



(f)

Fig. 4.19 Centred dark field images of the alloy aged for 168 h at 190°C. (a), (b), (c) and (d) are taken with the A, B, C and D reflections shown in Fig. 4.18, while (e) and (f) are taken with $\{002\}_S$ and $\{020\}_S$, shown in Fig. 4.16(b).

Some of the precipitates (marked X) are common to (a) and (b). Similar features (marked Y) are common to (c) and (d). Rods in (a) which appear weakly in (c) are marked X1 and rods in (c) weakly appearing in (a) are marked Y1

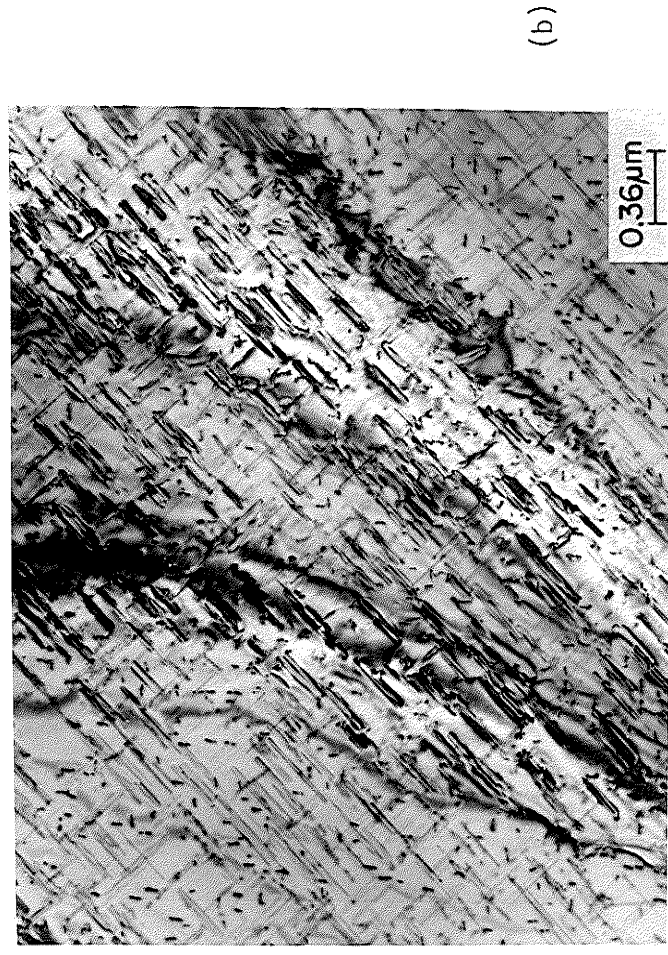


Fig. 4.20 (a) SAD pattern used to produce the centred dark field images of Fig. 4.19. (b) is a bright field image from the same pattern

of Fig. 4.16(b) show "end on" image rods from variants 9 and 12 respectively. The CDF image of Fig. 4.19(e) shows that the rods grouped in $[110]$ matrix direction are perpendicular to those in Fig. 4.19(f). Both the reflections $(002)_{S'}$ and $(020)_{S'}$ do not overlap since they come from two different variants.

Despite the slight tendency to form groups of $\langle 100 \rangle_M$ rods parallel to $\{011\}_M$ planes, the extensive lath formation noted by Wilson and Partridge⁽²³⁾ was not found in these alloys.

4.1.2.3.3 Effect of Ageing on the Lattice Parameters of the S' Phase

The values of the S phase lattice parameters used in the present analysis were those given by Perlitz and Westgren⁽¹⁴⁶⁾ for $Al_2(CuMg)$. Small deviations from these values will not affect the conclusions presented here but can be of interest in determining the coherency strain between the matrix and precipitate. Unless special precautions are taken (Hirsch et al.)⁽¹⁷²⁾ it is usually not possible to determine the lattice spacing to an accuracy better than 0.1% using thin film electron diffraction techniques. Using the pattern in Fig. 4.16(b), however, the relative spacing between the aluminium matrix and the S' phase has been determined by measuring the spot position, to an accuracy of $\approx 0.5\%$. Referring to Fig. 4.18, the distance between A and B is proportional to the g vector for $(062)_{S'}$ planes and between C and D for $(024)_{S'}$. The equivalent row of spots parallel to A, B, C, and D, on the other side of the origin, is separated by a distance proportional to $(200)_{S'}$. The $g_{S'}$ vector for $(200)_M$ is proportional to half the distance between $(200)_M$ and $(\bar{2}00)_M$ reflections. Measuring these distances means that it is not necessary

to measure across the centre of the diffraction pattern to find distances proportional to the $g_{S'}$ vectors $(062)_{S'}$, $-AB$, $(024)_{S'}$, $-CD$ and $(200)_{S'}$, - row spacing. The distance AB is heavily weighted in the b parameter and the distance CD in the c parameter, which in combination with the row spacing and depending only on a , gives increased accuracy in the a , b , c determinations. Assuming that the value a_0 of the matrix phase remains unchanged at 4.05 Å, this allows the S' parameters to be determined using the aluminium spacing $a_0 = 4.05$ Å as an internal standard which does not depend on the operating conditions of the microscope. Because the S' phase vectors $[131]$ and $[112]$ lie $\pm 2.50^\circ$ and $\pm 4.16^\circ$ respectively out of the $(001)_M$ plane, the AB and CD distances are divided by the correction factors $\cos 2.5^\circ = 0.999$ and $\cos 4.16^\circ = 0.997$ respectively, to give true, rather than the projected, $g_{S'}$ values which appear when reldiscs associated with (001) rods intersect the Ewald sphere. Table 4.1 gives value of a , b and c following a range of ageing times at 190°C . The 6 h ageing time gives values close to the completely coherent parameter of $a = a_0$, $b = \sqrt{5} a_0$ and $c = 4 a_0 \sqrt{5}$.⁽²³⁾ As ageing proceeds the b parameter increases significantly but the c value declines and the cell volume shows no significant change. After 560 h the parameters are close to the equilibrium values of $a = 4.00$ Å, $b = 9.23$ Å and $c = 7.14$ Å reported by Perlitz and Westgren⁽¹⁴⁶⁾ for Al_2CuMg . Although an accuracy significantly better than $\approx 0.5\%$ is not claimed, the increase in b and the decrease in c with ageing time are clearly demonstrated by the measurements.

Parallel neighbouring rods growing as different variants probably reduce the matrix strain energy between the rods. Thus, for example, a variant 1 rod parallel to $[100]_M$ expands in the $[021]_M$ - b

Table 4.1: Values of the orthorhombic S' phase parameters a, b, c assuming a matrix fcc parameter of 4.05Å. The values expected for complete matrix coherence are also shown.

Aging Time at 190°C	Lattice Parameter (Å)			Unit Cell Volume Å ³
	a	b	c	
Perfect coherence	4.05	9.05	7.24	265.7
6	4.05	9.10	7.23	266.3
12	4.05	9.16	7.20	266.9
24	4.05	9.15	7.15	264.8
120	4.05	9.18	7.17	266.7
168	4.04	9.16	7.15	264.4
240	4.04	9.16	7.13	263.9
384	4.04	9.17	7.14	264.3
576	4.04	9.18	7.13	264.3
S phase	4.00	9.23	7.14	263.60

direction after breaking coherency, whereas a neighbouring $[100]_M$ variant 2 would contract in the $[021]_c$ direction. Such nearest combinations will therefore reduce the net matrix strain energy between the rods. In fact, bright field image (Fig. 4.16(a)) does show grouping of rods in $\langle 110 \rangle$ and $\langle 100 \rangle$ directions.

As mentioned earlier, extensive lath formation was found by Wilson and Partridge⁽²³⁾ and Weatherly and Nicholson.⁽⁹⁴⁾ This observed difference could be related to the higher 2.52% Cu and 1.27% Mg content of the alloy of the above investigators compared with 1.53% Cu and 0.79% Mg of the present alloy. This means that there will be fewer nucleation sites for the S' phase rods and that lath formation, due to coalescence of the parallel neighbouring rods is less likely to occur. However, with a higher (Cu+Mg) concentration, creating more rod nucleation sites, the growing together of parallel rods to form laths becomes energetically favourable as the strain energy is further reduced by macroscopic shear processes.

4.1.3 The S Phase

The results of this investigation have shown (Section 4.1.2) that the orthorhombic S' precipitates, when initially formed, are coherent with the fcc parent matrix. Later, as ageing proceeds, they show a gradual loss of coherency and causes changes in the lattice parameter b and c without any alteration in the crystal structure. As shown in Table 4.1, the lattice parameter eventually approach the equilibrium cell dimensions of the S phase. Occasionally during TEM study large precipitates were observed on or close to the grain boundaries as shown in Fig. 4.21 which is a bright field micrograph

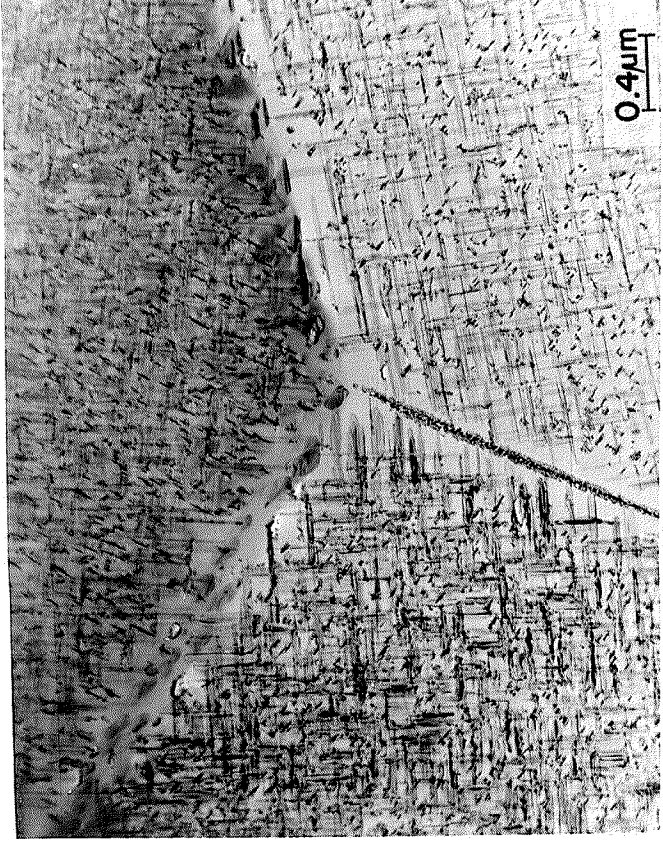


Fig. 4.21 Bright field image of the Al-1.53Cu-0.79Mg alloy aged at room temperature for 48 h and further aged at 190°C for 12 days. Large precipitates of the S phase of grain boundaries are visible

of a specimen aged for 288 h at 190°C. This figure also shows the presence of a precipitate free zone on both sides of the grain boundaries. It is likely that the formation of precipitates at the grain boundary caused a depletion of solute atoms around them, which resulted in the formation of a precipitate free zone. Lloyd⁽⁸⁾ has also observed such precipitates on the grain boundaries of an alloy of a similar composition and has suggested they are equilibrium S phase. However, the S and S' phases have an identical crystal structure and their lattice parameters are also very similar. Therefore, electron diffraction studies in a conventional TEM cannot differentiate between the two. As such, it is probably unnecessary to identify S and S' to be distinct phases as they differ mainly because of the presence of strains in S' phase due to the precipitate environment. In other words, the S' phase is simply a strained version of the equilibrium S phase, which, if extracted from the matrix, would probably relax to S phase. Therefore, if S' is defined as a phase structure before complete equilibrium is achieved, then it would include other definitions suggested by many investigators (Section 2.4.5) based on coherency loss along the b axis⁽¹³⁰⁾ and changes in cell dimensions.^(23,122)

4.2 KINETICS OF PRECIPITATION

4.2.1 Introduction

Differential scanning calorimetry (DSC) has been used in order to gain an insight into the kinetics of the precipitation processes in the present alloy. When a specimen and a reference material are heated in a DSC at a known heating rate, the heat inputs

to the specimen and the reference remains almost the same unless a heat related transformation takes place in the specimen. Depending upon the nature of the transformation process (i.e. precipitation or dissolution), the heat input to the specimen is altered. The rate of heat input to the specimen relative to the reference is directly related to the amount of the transformation product in the specimen. Therefore, the kinetics of precipitation and dissolution of stable and metastable phases can be in principle, estimated from the DSC runs. In the following sections the DSC thermograms have been analysed and the kinetic data have been evaluated.

4.2.2 Theory of DSC Operation

In the 910 differential scanning calorimeter, both the reference and the sample have the same thermal environment and the thermal resistances between the sample and the environment and reference and environment are identical. Hence, the rate of heat input to the sample, $\dot{q}_S^i$, and the reference, $\dot{q}_R^i$ are given by

$$\dot{q}_S^i = (T_S - T_E) C \quad (4.1)$$

$$\dot{q}_R^i = (T_R - T_E) C \quad (4.2)$$

where T_S , T_E and T_R are temperatures of sample, environment and reference respectively and C is the conductance. The rate of heat leakage $\dot{q}''$ from the sample and reference through the purging gas can be written as

$$\dot{q}_S'' = (T_S - T_E) C_g \quad (4.3)$$

$$\ddot{q}_R'' = (T_R - T_E) C_g \quad (4.4)$$

The net heat inputs to sample, $\dot{q}_S$ and $\dot{q}_R$ are obtained from Equations (4.1) to (4.4)

$$\dot{q}_S = (T_S - T_E) C - (T_S - T_E) C_g \quad (4.5)$$

$$\dot{q}_R = (T_R - T_E) C - (T_R - T_E) C_g \quad (4.6)$$

Hence

$$(\dot{q}_R - \dot{q}_S) = (T_R - T_S) (C - C_g) \quad (4.7)$$

The above relation shows that the temperature difference between the reference and the sample is a measure of net energy flow to the reference. The instrument measures the temperature difference and displays as the net flow $\dot{q}$ to the reference. Thus

$$(\dot{q}_R - \dot{q}_S) = \dot{q} E \quad (4.8)$$

where $\dot{q}$ is the instrument reading in mJ/sec and E is a dimensionless cell calibration constant.

The net heat input to the sample and reference are used for heating of the holders and the specimens. Hence

$$\dot{q}_R = \phi C_{h(R)} + \phi C_R \quad (4.9)$$

where ϕ is the heating rate $(\frac{dT}{dt})$ ($^{\circ}\text{C}/\text{sec}$), $C_{h(R)}$ is the heat capacity (mJ) of holder pan for the reference and C_R is the heat capacity (mJ) of the specimen used as the reference.

Similarly,

$$\dot{q}_S = \phi C_{h(S)} + \phi C_S + \dot{Q} M 10^3 \quad (4.10)$$

where $C_{h(S)}$ and C_S are heat capacities of the sample pan and the sample holder respectively, $\dot{Q}$ (J/g-S) is the rate at which heat is absorbed by the specimen due to the reaction occurring in it and M is the mass of the sample in grams. Thus,

$$(\dot{q}_R - \dot{q}_S) = \phi [C_{h(R)} - C_{h(S)}] + \phi [C_R - C_S] - \dot{Q} M 10^3 \quad (4.11)$$

4.2.2.1 Cell Calibration Constant

If one DSC run (1) is performed with both holders empty and a second run (2) is performed with a metal, whose physical properties are known, in the sample pan at the same constant heating rate ϕ , then from Equation (4.11),

$$(\dot{q}_R - \dot{q}_S)_1 = \phi [C_{h(R)} - C_{h(S)}] \quad (4.12)$$

$$(\dot{q}_R - \dot{q}_S)_2 = \phi [C_{h(R)} - C_{h(S)}] + \phi [-C_S] - \dot{Q} M 10^3 \quad (4.13)$$

Hence

$$(\dot{q}_R - \dot{q}_S)_1 - (\dot{q}_R - \dot{q}_S)_2 = \phi C_S + \dot{Q} M 10^3 \quad (4.14)$$

Combining Equation (4.14) with Equation (4.8) and integrating with time,

$$E (\dot{q}_1 - \dot{q}_2) dt = (\phi C_S + \dot{Q} M 10^3) dt \quad (4.15a)$$

$$\text{or} \quad \frac{E}{\phi} \int_{T_1}^{T_2} (\dot{q}_1 - \dot{q}_2) dT = \int_{T_1}^{T_2} C_S dT + M 10^3 \int_{t_{T_1}}^{t_{T_2}} \dot{Q} dt$$

$$= \int_{T_1}^{T_2} C_S dT + M 10^3 Q \quad (4.15b)$$

The value of E can be calculated if T_1 and T_2 are selected such that melting occurs in this range. From the known value of heat of fusion and heat capacity, the DSC cell was calibrated using Indium and lead which melt at 430°C and 327.6°C respectively. The value of E was found to be 1.054.

The variation of E with temperature was tested using a pure block of aluminium in which no reaction transformation takes place in the range $10\text{--}500^\circ\text{C}$. Therefore, $\dot{Q} = 0$ and Equation (4.15a) reduces to

$$E (\dot{q}_1 - \dot{q}_2) = \phi C_S \quad (4.16)$$

using Equations (4.14) and (4.16) and rearranging the above equation,

$$E = \frac{\phi C_S}{[(\dot{q}_R - \dot{q}_S)_1 - (\dot{q}_R - \dot{q}_S)_2]} \quad (4.17)$$

Hence, E could be calculated from the heat capacity of pure aluminium. In order to determine the value of cell constant, the DSC cell was loaded at room temperature. Care was taken to put specimens on the centre portion of the raised part of the DSC platform (Fig. 3.1). The cell was then cooled to a temperature of $\approx 5^\circ\text{C}$ below the temperature at which data was required. The cell was allowed to equilibrate at that temperature for a few minutes. The heating was initiated at a programmed rate of $10^\circ\text{C}/\text{min}$ from the 5°C to the highest temperature at which specific heat capacity information was required. The thermal curve was recorded in the instrument (disc) memory. A minimum of two thermal curves were obtained. In the first run baseline was obtained using empty sample and reference pans as shown in Fig. 4.22.

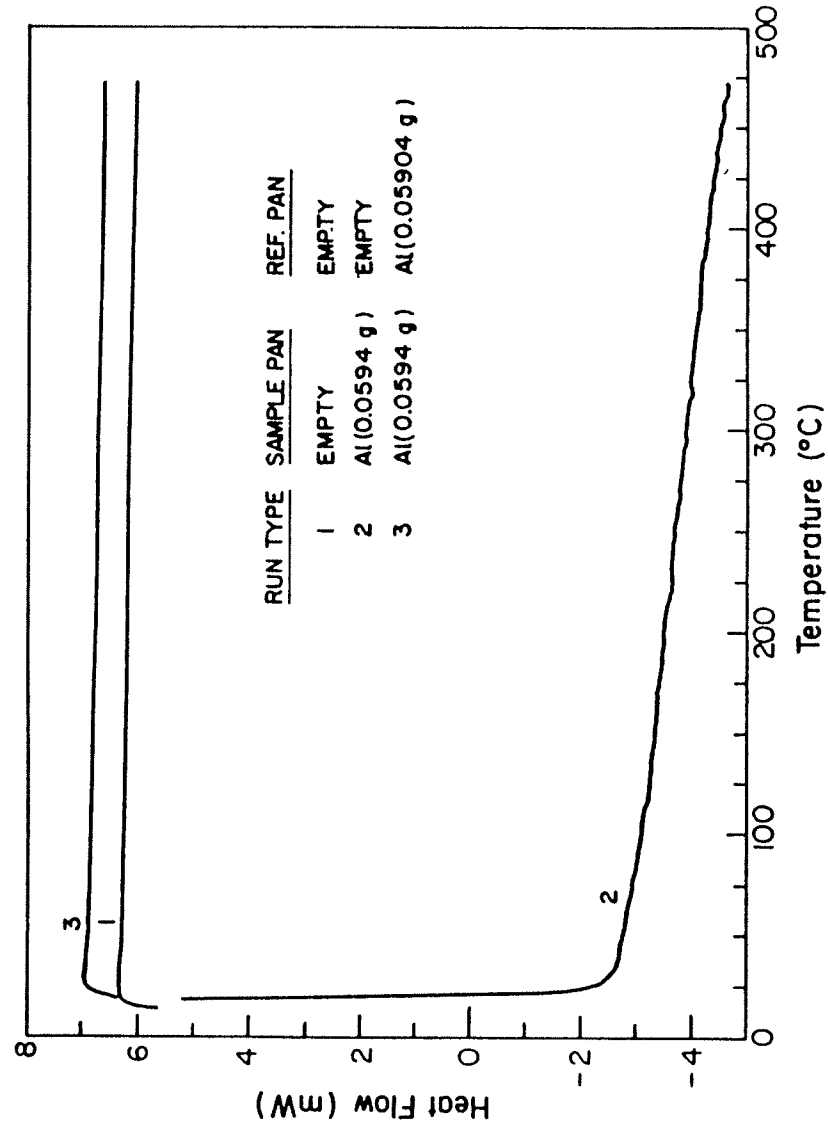


Fig. 4.22 DSC curves obtained from different types of runs carried out at the heating rate, 10°C/min

The same procedure was repeated under identical conditions with a 0.0594 g Al-Block in the sample pan that was used in the first run (Fig. 4.22). The heat capacity of pure aluminum in the sample pan was then calculated by measuring the difference in Y-axis displacement between the sample and blank curves at four different temperatures (Fig. 4.22). The values obtained at different temperatures are listed in Table 4.2. Substituting the values in Equation (4.17) the cell calibration coefficient was determined. The value of E show that over the entire range of temperature, E is constant within $\pm 1.8\%$.

4.2.2.2 Heat Effects of Reactions

The measured heat flow in DSC depends upon the nature of the sample in the two pans. Equation (4.11) describing the difference in heat flow between sample and reference reduces to following under various conditions.

Run type Sample pan Reference pan Relationship

1	Empty	Empty	$E\dot{q}_1 = (\dot{q}_R - \dot{q}_S) = \phi [C_{h(R)} - C_{h(S)}]$ (4.18)
---	-------	-------	--

2	Al	Empty	$E\dot{q}_2 = (\dot{q}_R - \dot{q}_S) = \phi [C_{h(R)} - C_{h(S)}]$ $- \phi C_S$ (4.19)
---	----	-------	--

3	Al	Al	$E\dot{q}_{20} = (\dot{q}_R - \dot{q}_S) = \phi [C_{h(R)} - C_{h(S)}]$ $+ \phi [C_R^{A1} - C_S^{A1}]$ (4.20)
---	----	----	---

4	unknown sample	Al	$E\dot{q}_{21} = (\dot{q}_R - \dot{q}_S) = \phi [C_{h(R)} - C_{h(S)}]$ $+ \phi [C_R^{A1} - C_S^S] - \dot{Q}M0^3$ (4.21)
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Table 4.2 Data used for evaluation of the value of E.
Heating rate 1/6°C/sec

T(K)	325	450	575	725
$C_p^* (A1)(J/g)$	0.053	0.056	0.062	0.064
$(\dot{q}_R - \dot{q}_S)_1 - (\dot{q}_R - \dot{q}_S)_2$ (J/sec)	9.057×10^{-3}	9.647×10^{-3}	10.005×10^{-3}	10.685×10^{-3}
E (calculated using Eqn. (4.17))	0.979	0.975	1.032	0.999

* See Ref. 173

Thermograms obtained from run types 1 and 2 are shown in Fig. 4.22. It is seen from the run type 1 that the $(\dot{q}_R - \dot{q}_S)$ term is positive, implying that the reference pan is absorbing more heat. But the run type 2 yields negative values of heat flow as the amount of material to be heated in the sample pan containing aluminum is more. It results in negative value of the term $(\dot{q}_R - \dot{q}_S)$. When both reference and sample pan contain pure aluminum blocks of approximately the same weight, the DSC curve is expected to be similar to the blank run, represented by curve 1 in Fig. 4.22. The difference in the absolute values of the heat flow is related to the difference between heat capacities of both pans containing the aluminum blocks. Fig. 4.23 shows the DSC run obtained from run type 4. In this run the reference pan contained 0.0594 g aluminum while the sample pan contained 0.05940 g sample of solution treated and quenched alloy. This figure also contains the DSC curve of run type 3 where the same reference (0.0594 g of aluminum) was used and 0.5904g of aluminum was used in the sample pan. As expected, the run type 4 shows endothermic and exothermic heat effects. In order to determine the total heat effects associated with solid state reactions, Equation (4.21) is subtracted from Equation (4.20). Since same reference and sample pans were used in all experiments; on subtraction,

$$\{(\dot{q}_R - \dot{q}_S)_{20} - (\dot{q}_R - \dot{q}_S)_{21}\} = \phi (C_S^S - C_S^{A1}) + \dot{Q} M 10^3 \quad (4.22)$$

Using measured heat flux $\dot{q}$ from Equation (4.8), the above Equation (4.8), reduces to

$$\dot{Q} M 10^3 = E(\dot{q}_{20} - \dot{q}_{21}) - \phi (C_S^S - C_S^{A1}) = E[(\dot{q}_{20} - \dot{q}_{21}) - \frac{\phi (C_S^S - C_S^{A1})}{E}] \quad (4.23)$$

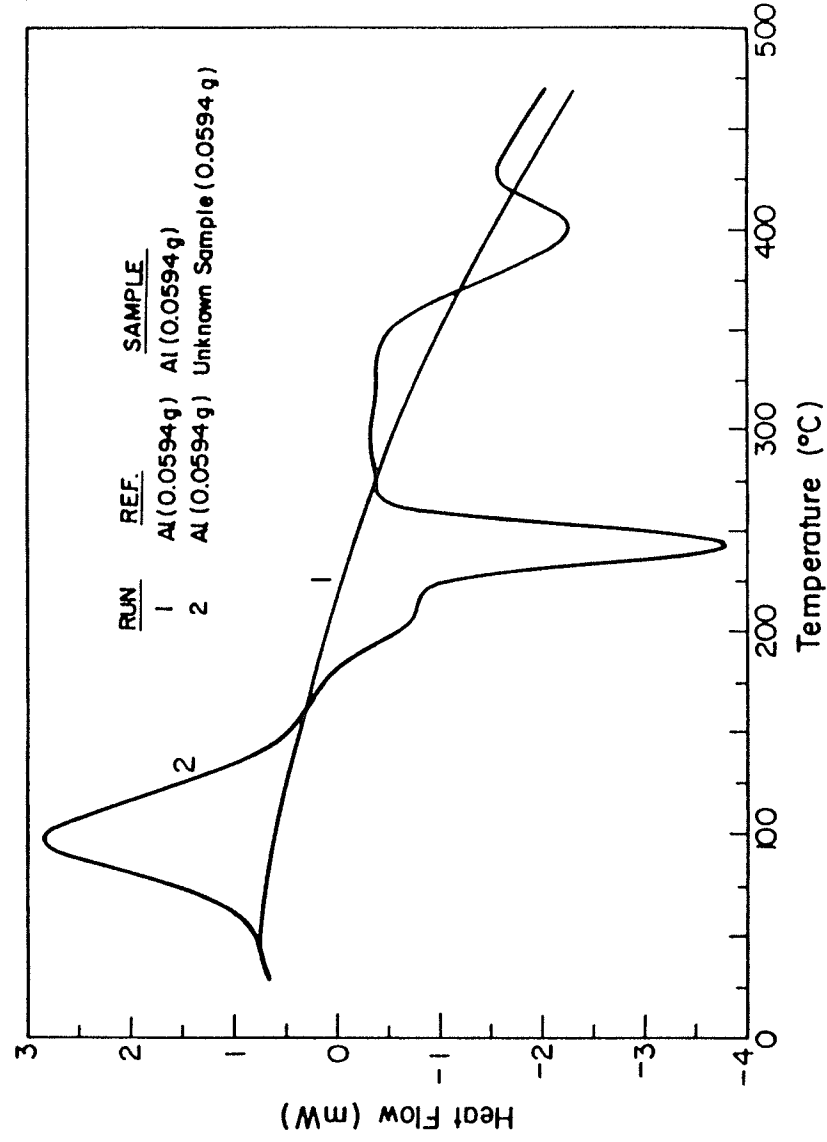


Fig. 4.23 DSC curves obtained with pure aluminum in the reference pan at the heating rate of 20°C/min

Let $A = (\dot{q}_{20} - \dot{q}_{21})$ and $B = \frac{\phi (C_S^S - C_S^{A1})}{E}$, then

$$\dot{Q} \text{ M } 10^3 = E (A-B) \quad (4.24)$$

Firstly, term A in Equation (4.24) was obtained by subtracting the thermograms of run type 3 and 4 (Fig. 4.23). The subtracted curve is shown in Fig. 4.24. Equation (4.24) shows that Q can be obtained after subtracting B from measured value of A. The term B is a correction factor which is due to the difference in the heat capacities of aluminum standard and the sample. The term $\{\phi (C_S^S - C_S^{A1})\}$ can be made very small by choosing the same weight of aluminum in the sample and reference pans. The calculation of errors associated with runs in Fig. 4.23 is shown in Table 4.3. It is found that if Kopp-Neuman rule is assumed, the correction factor is about 0.15 to 0.18 mJ/sec which is very small and is of the same order as estimated from Fig. 4.24.

When there is no reaction occurring during heating then $\dot{Q} = 0$ and the value of B from Equation (4.24) is

$$B = [\dot{q}_{20} - \dot{q}_{21}] \dot{Q} = 0 \quad (4.25)$$

Substituting the value of B in Equation (4.24)

$$\dot{Q} \text{ M } 10^3 = E [(\dot{q}_{20} - \dot{q}_{21}) - (\dot{q}_{20} - \dot{q}_{21}) \dot{Q} = 0] \quad (4.26)$$

The Equation (4.26) obtained above gives corrected values of $\dot{Q}$ during any reaction. The difference between curve 1 when $\dot{Q} = 0$ and the zero line in Fig. 4.24 represents the term B of Equation (4.26). The deviation of curve from zero line at higher temperature (Fig. 4.24, marked X) where alloy is in solid solution is higher by 0.2 mJ/sec.

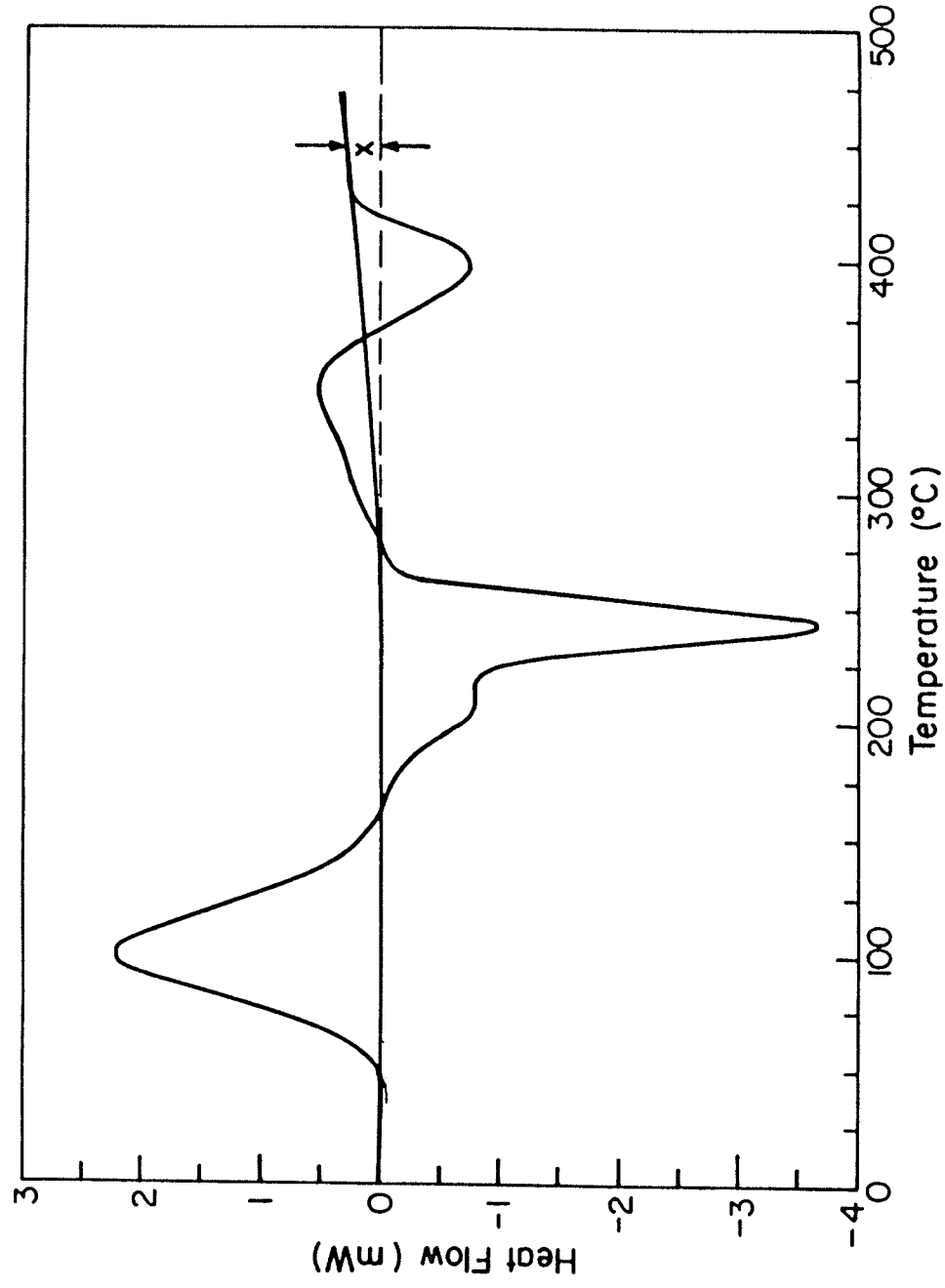


Fig. 4.24 The DSC curve obtained after subtracting curve (1) from (2) of Fig. 4.23

Table 4.3 Data used to estimate the difference between the heat capacities of pure Al and the solid solution of the present alloy

$\left(\frac{dT}{dt}\right) = 1/3^\circ\text{C/sec}$ weight of standard aluminum = 0.0594 gms weight of sample = 0.0594 gms				
Temp(K)	325	450	575	725
C^{Al} (J*/g)	0.9142	0.9692	1.0654	1.1006
C_S^{Al} (J)	0.05430	0.05757	0.06328	0.06538
C_S^{**} (J/g)	0.9052	0.9617	1.0565	1.0912
C_S^S (J)	0.05382	0.05712	0.06275	0.06481
$(C_S^{Al} - C_S^S)$ (mJ)	-0.48	-0.45	-0.53	-0.57
Error = $\frac{\Delta C_S (dT/dt)}{E}$	-0.158	-0.1423	-0.165	-0.180

* See Ref. 173

** Using Kopp-Neuman rule,

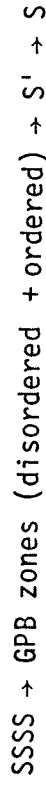
$$C_S^S = C_{pCu} \left(\frac{\text{wt}\%Cu}{100}\right) + C_{pMg} \left(\frac{\text{wt}\%Mg}{100}\right) + C_{pAl} \left(\frac{\text{wt}\%Al}{100}\right)$$

where heat capacities are in J/g

This is approximately the same as that calculated earlier in Table 4.2. Any minor difference arises due to deviation from Kopp-Neuman rule. Table 4.4 shows that the difference in mass of the sample and the aluminum standard, that was used for the DSC run at a heating rate of 5°C/min was maximum when compared with the weights of reference and samples used for the heating runs carried out at 10, 15 and 20°C/min. However, since the heating rate is only 1/4th of that used for calculations in Table 4.3, the errors introduced due to difference in mass of reference and sample for 5°C/min run will be minimal and can be ignored. Fig. 4.25 shows the corrected curves obtained by subtracting the difference between curve of the type 1 and 2 of Fig. 4.24 at 5°, 10°, 15° and 20°C/min. The variation of the heat flow in the curve so obtained represents the true heat effects associated with the solid state reactions. The corrected curves so obtained at different heating rates are shown in Fig. 4.25.

4.2.3 Peak Identification

The transmission electron microscopic studies carried out in this investigation and other studies (121,122,135) show that the supersaturated solid solution (SSSS) of the Al-Cu-Mg alloy with Cu/Mg ratio of 2.2:1 decompose in the following sequence:



It has been suggested that the GPB zones when formed initially, are disordered (GPB(I) zones) which gradually orders to form GPB(II) or S" phase. (135)

A typical DSC curve of a solution treated and water quenched

Table 4.4 Weights of standard and unknown sample used in DSC experiments

Weight of standard Al block (gms)	Weight of unknown in sample pan (gms)	Heating rate (°C/min)
0.0594	0.05976	5
0.0594	0.05956	10
0.0594	0.05946	15
0.0594	0.05940	20

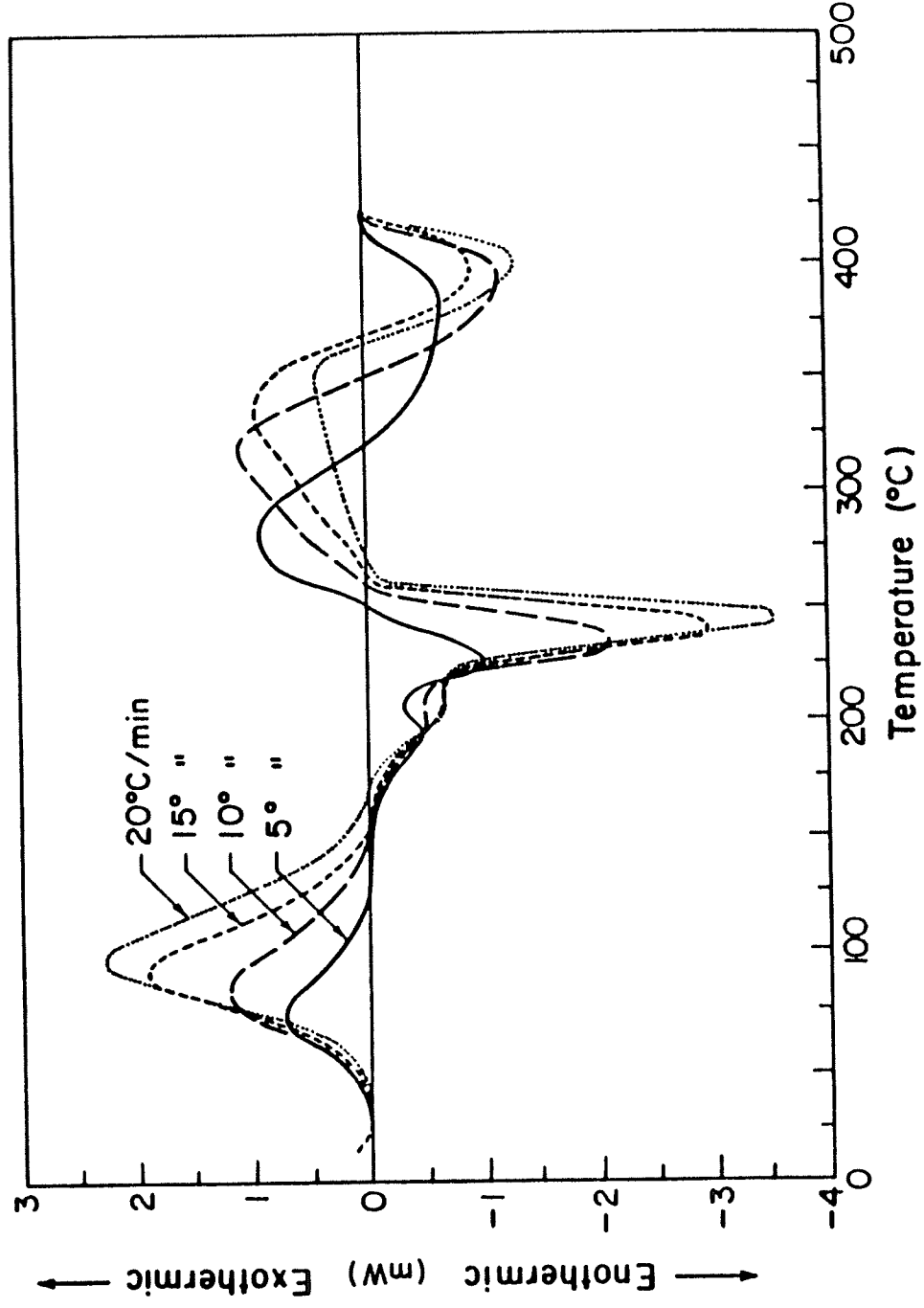


Fig. 4.25 Corrected DSC curves at heating rates of 5°, 10°, 15° and 20°C/min for solution treated and quenched specimens of the Al-1.53%Cu-0.79%Mg alloy

sample is shown in Fig. 4.26(a). The principle features here are: the two exothermic peaks A and F, three endothermic peaks C, D and G and three plateaus B, E and H. These features can be associated with the precipitating phases described above, by using DSC curves of samples aged at 130°C and 190°C. The results of a few selected runs are also shown in Fig. 4.26.

The first exothermic peak in Fig. 4.26(a) found in the as quenched sample may be described as a broad peak in the temperature range 45-143°C is approximately symmetrical around the peak temperature ($\approx 85^\circ\text{C}$). When the sample is quenched from the solution treating temperature it retains excess vacancies in the supersaturated solid solution. During quenching these excess vacancies migrate to sinks and collapse to form dislocation loops (Fig. 4.2). On ageing the quenched-in excess vacancies help in the formation of GPB zones. The first exothermic peak is attributed to GPB zone formation. This is confirmed by the absence of this peak in the DSC curve of a solution treated sample aged at room temperature for 48 h (curve b, Fig. 4.26) as the GPB zones have already formed in this sample.

High voltage electron microscopic studies of Takahashi and Sato⁽¹³⁵⁾ suggest that GPB zones are initially disordered (GPB(I) zones) and become ordered with time. The ordered GPB zones are termed GPB(II) zones. As the process of the formation of GPB(I) and GPB(II) zones is continuous and they occur simultaneously, a single peak is observed for the process. Similar behaviour has been observed in the precipitation of θ'' in Al-Cu alloys.^(67,174) Thompson⁽¹⁷⁴⁾ has suggested that formation of θ'' is not a separate and distinct process, but rather a continuous transformation. No peak will be observed

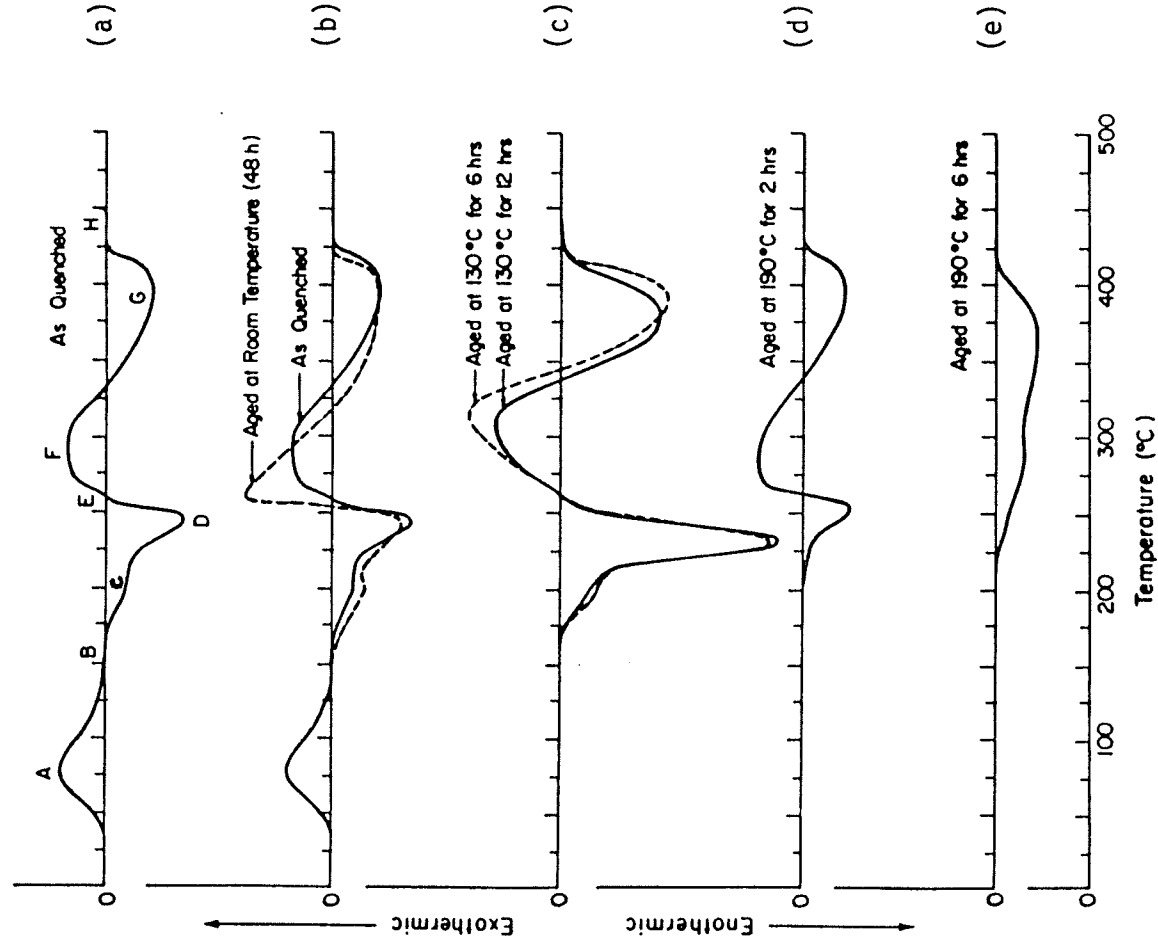


Fig. 4.26 Corrected DSC curves at the heating rate of 10°C/min for the Al-1.53%Cu-0.79%Mg alloy aged at 130° and 190°C

if thickening of GP zones to θ'' occurred by a process of competitive growth. Therefore, it is likely that the first precipitation peak observed in quenched sample is due to the formation of both disordered GPB(I) and ordered GPB(II) zones.

The presence of two minima in first endothermic peak indicates multiple dissolution processes. The DSC curves (c) in Fig. 4.26, for the samples aged at 130°C for 6 and 12 h, clearly show that the first dissolution peak becomes progressively less prominent with an increase in ageing time. It finally disappears after ageing for 24 h at 130°C. The TEM studies have shown that the microstructure of this specimen contains dislocation loops and helical dislocations formed during quenching. Therefore, peak c can be attributed to the dissolution of GPB zones.

The heat effect due to the dissolution (peak area c) is very small. It implies that most of the GPB zones must have interacted with dislocation loops. This is evidenced by the decoration of dislocation loops and appearance of precipitate-like particles on the dislocation loops (Fig. 4.7) (although no diffraction effect was observed). The dislocation loops disappear on precipitation of the S' phase as indicated by the exothermic peak F. The sample aged at 190°C for 2 h (Fig. 4.7) has some dislocation loops and precipitate like structures but no diffraction effects due to the S' phase were observed. Its DSC curve shows a small D peak and a large F peak which is due to the precipitation of the S' phase. Thus, peak D could represent a complex dissolution peak due to the dissolution of GPB zone-dislocation complexes. Also, streaks have been observed in the alloy aged for only 4 h at 190°C (Fig. 4.10(b)). Therefore, nucleation

of S' may also be superimposed on the dissolution of dislocation GPB zone complexes.

The exothermic peak F as indicated in Fig. 4.26 is due to the precipitation of the S' phase as it is absent in the sample containing the S' phase (Fig. 4.26(e)). It can be described as a blunt broad peak occurring within the 265-350°C temperature range. This peak is symmetrical about peak maximum temperature ($\approx 315^\circ\text{C}$).

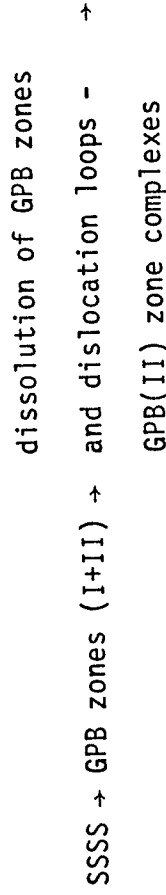
The endothermic peak G shown in Fig. 4.26 is due to the dissolution of the S' or equilibrium S phase. Alloy aged at 190°C for 6 h show only the dissolution peak G (Fig. 4.26(e)). The equilibrium S phase does not show any separate precipitation peak in the DSC curves of all the specimens analysed. It appears that the precipitation of the equilibrium S phase, like the formation of GPB(II) zones, is not a distinct process but rather a continuous process. It is in agreement with the analysis described in Section 4.1.3 based on TEM studies. It seems that the equilibrium S phase is simply a strained version of the S' phase and would not be expected to have a separate precipitation peak. The formation of S'/S phase is complete on ageing a sample for 6 h at 190°C as depicted in Fig. 4.26. The S' precipitation peak has completely disappeared as only a broad dissolution peak is obtained in DSC curve.

The presence of a plateau E in the DSC curve, indicates that the dissolution of GPB zones and precipitation of the S' phase are independent of each other. It implies that the S' phase may be nucleating independently as can be seen in TEM micrograph shown in Fig. 4.14. This plateau disappears in DSC curves (Fig. 4.26(b)) of room temperature aged sample and a number of other samples heat treated

under certain specific conditions (Fig. 4.26(c) and (d)). Such behaviour is possibly related to the overlapping of processes due to dissolution of dislocation loop, GPB zones complexes and precipitation of the S' phase which in turn critically depend upon the aged structures of the samples prior to the DSC run. When an as quenched sample is heated the small GPB(I) and GPB(II) zones are formed and they dissolve prior to the beginning of the S' precipitation peak. But when starting structure already contains GPB zones, then on heating they grow and do not dissolve completely; causing the dissolution peak to overlap with the precipitation peak of the S' phase and causing the disappearance of plateau E. Moreover, the S' peak becomes sharp and shift to a lower temperature indicating that the dislocation loop - GPB zone complexes dissolution process is more dominant compared to the precipitation of the S' phase. However, in curves from aged specimen (curve d) the precipitation of the S' is more dominant in the vicinity of 210°C and pushes the S' peak to a higher temperature. Ageing of samples for 2 h at 190°C shows area under the complex dissolution peak and the S' precipitation peak to decrease as shown in Fig. 4.26 (curve d). At this stage of heat treatment the sample has few dislocation loops, GPB zone complexes and the S' phase and only the remaining S' phase is precipitated. The sample aged for 6 h at 190°C showed (curve e) only a broad dissolution peak related to the S' and equilibrium S phase. The hump seen in dissolution peak is likely to be due to the difference in the dissolution processes of the S' and equilibrium S phases. The presence of B and H indicates that reactions representing peaks A and G are complete.

The DSC results therefore show that the transformation of

quenched supersaturated solid solution on heating takes place in the following sequence:



formation of $\rightarrow$ dissolution of
S' phase S' and S phases

4.2.4 Evaluation of Heat Effects and Reaction Rates from DSC Data

The total heat effect associated with any reaction in a sample of mass 'M' may be obtained by using Equation (4.26),

$$dQ \ M \ 10^3 = E \ [\{ \dot{q}_{20} - \dot{q}_{21} \} - \{ \dot{q}_{20} - \dot{q}_{21} \} \dot{Q} = 0] \frac{dt}{dT} \cdot dT \quad (4.27)$$

Thus, the total heat effect in the temperature range T_i to T can be obtained by integrating Equation (4.27)

$$M \ 10^3 \int_{T_i}^T dQ = \frac{E}{\phi} \int_{T_i}^T [\{ \dot{q}_{20} - \dot{q}_{21} \} - \{ \dot{q}_{20} - \dot{q}_{21} \} \dot{Q} = 0] dT$$

Where T_i is the temperature at which the peak begins. Hence,

$$Q(T) = \frac{E \ A(T)}{M \ 10^3 \ \phi} \quad (4.28a)$$

$$A(T) = \int_{T_i}^T \{ (\dot{q}_{20} - \dot{q}_{21}) - (\dot{q}_{20} - \dot{q}_{21}) \dot{Q} = 0 \} dT \quad (4.28b)$$

$$(Q_{(T)}/E) = A_{(T)}/M \cdot 10^3 \phi \quad (4.28c)$$

Where, $Q_{(T)}$ and $A_{(T)}$ are the heat effect and area under the curve between T_i and T respectively. By using Equation (4.28), heat effect in desired temperature ranges could be determined by dropping a perpendicular as shown in Fig. 4.27. If T_f is the final temperature of the peak then total heat effect is

$$Q = \frac{E A(T_f)}{M \cdot 10^3 \phi} \quad (4.28d)$$

The mole fraction (Y) of the precipitates is related to the heat effects and can be written as:

$$Y = \frac{n}{n_e} \quad (4.29)$$

where n and n_e are number of moles of precipitates per gram of specimen at any temperature T and equilibrium number of moles of precipitate per gram of the alloy respectively. The value of n and n_e can be determined in terms of total heat effect up to a given temperature and the total heat effect under the peak respectively.

The precipitation or dissolution of phases due to heating causes continuous changes in the composition of the matrix. Consequently the heat content of the matrix also changes depending upon the extent of precipitation or dissolution in the matrix. The enthalpy change, ΔH , due to precipitation is given by:

$$\Delta H = H_p \left(\frac{X_m - X'_m}{X_m - X'_m} \right) + H'_m \left(\frac{X_p - X'_p}{X_p - X'_p} \right) - H_m \quad (4.30)$$

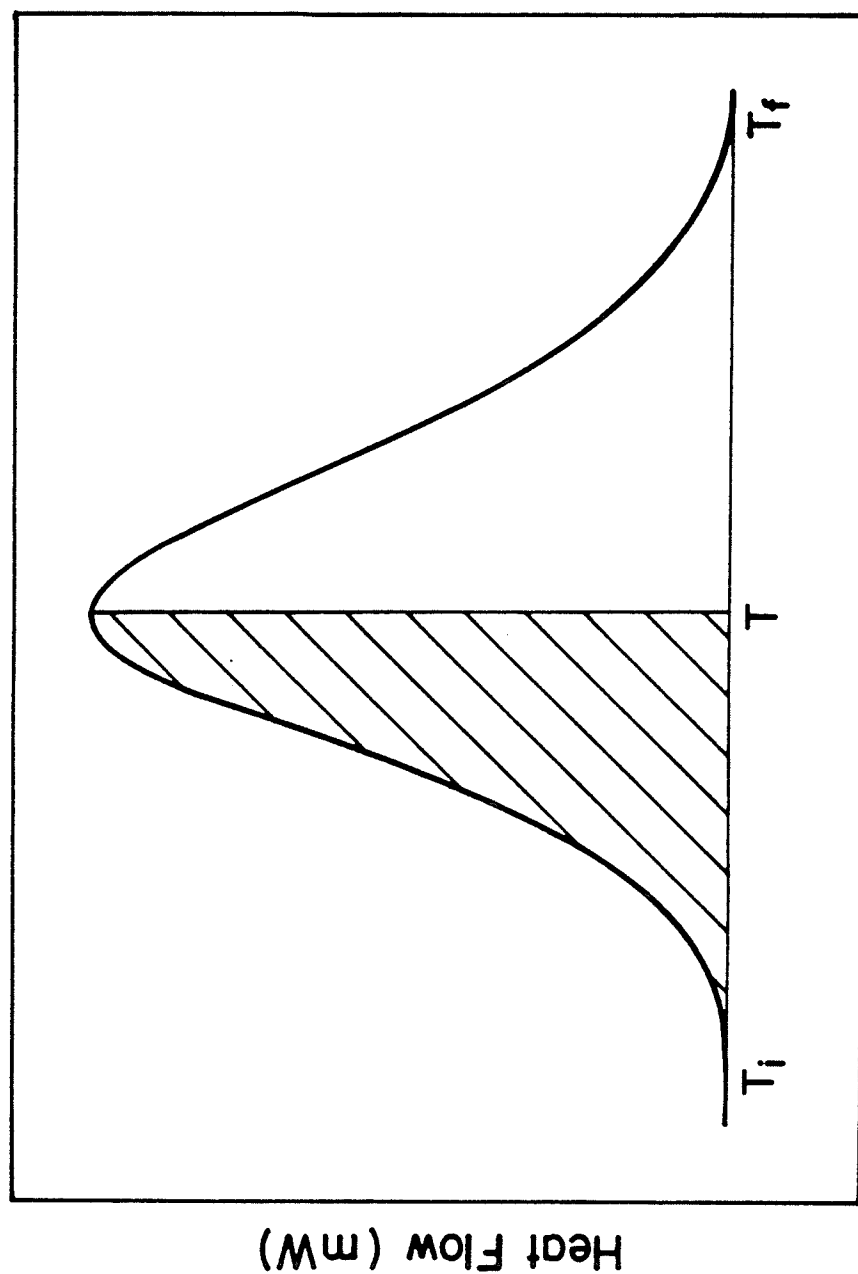


Fig. 4.27 Shaded area in the Figure shows the heat effect within the temperature range T_i to T_f .

where, X_m , X_p and X'_m are the mole fraction of the alloy, precipitate and matrix, respectively while H_m , H_p and H'_m are the corresponding enthalpies. Equation (4.30) can be rearranged to:

$$\Delta H = (H_p - H_m) \left[\frac{(X_m - X'_m)}{(X_p - X'_m)} \right] + (H'_m - H'_m) \left[\frac{(X_p - X_m)}{(X_p - X'_m)} \right] \quad (4.31)$$

Let Q_o be the heat effect per mole of precipitate, hence

$$Q_o = \frac{\Delta H}{\text{Total number of moles of precipitate}} \quad (4.32)$$

Substituting the value of ΔH from Equation (4.30) in (4.32) rearranging and noting that $(X_m - X'_m)/(X_p - X'_m)$ is equal to the number of moles of precipitate,

$$Q_o = (H_p - H_m) - (X_p - X_m) \left(\frac{dH}{dx} \right) X_m \quad (4.33)$$

If it is assumed that compositional change in the alloy associated with precipitation or dissolution of the precipitate is small, then the enthalpy of the matrix is expected to change linearly with the mole fraction of the precipitate according to the following relationship

$$H_m = a + b X_m \quad (4.34)$$

Where 'a' is a constant and b is $\left(\frac{dH}{dx} \right) X_m$. Substituting the value of H_m in Equation (4.33) and solving it yields:

$$Q_o = [H_p - a - b X_p] \quad (4.35)$$

This equation shows that heat effect per mole of precipitate is

independent of temperature and composition of the matrix. Thus, if Q_o is in J/mole, heat effect dQ is given as,

$$dQ = Q_o \, dn \quad (4.36)$$

where, dn is total number of moles of precipitate per gram of the alloy. Total number of moles per gram of the alloy within temperature range T_i and T can be obtained by integrating Equation (4.36) as shown.

$$\int_{T_i}^T \frac{dQ}{Q_o} = \int_{T_i}^T dn \quad (4.37)$$

On substituting value of dQ from Equation (4.27) in (4.37)

$$\int_{T_i}^T dn = \frac{E}{\phi Q_o M 10^3} \int_{T_i}^{T_f} [(\dot{q}_{20} - \dot{q}_{21}) - (\dot{q}_{20} - \dot{q}_{21})\dot{Q} = 0] dT$$

or

$$n(T) = \frac{E A(T)}{Q_o \phi M 10^3} \quad (4.38)$$

Similarly, total number of moles of precipitate per gram of alloy under a given peak from initial to final temperature (T_f) of the peak gives

$$n_o = \frac{E A(T_f)}{Q_o \phi M 10^3} \quad (4.39a)$$

$$\text{where, } A(T_f) = \int_{T_i}^{T_f} [(\dot{q}_{20} - \dot{q}_{21}) - (\dot{q}_{20} - \dot{q}_{21})\dot{Q} = 0] dT \quad (4.39b)$$

The equilibrium number of moles, n_e is a function of temperature. It is given by the following relationship

$$n_e(T) = \left(\frac{1}{w}\right) \left(\frac{X_m - X_e}{X_p - X_e}\right) \quad (4.40)$$

where w is average atomic weight of the alloy.

If the change in X_e over the temperature range of the peak is negligible, one may assume that $n_0 \approx n_e$, i.e. the total number of moles of precipitate per gram is the same as the equilibrium number of moles of precipitate per gram of the sample

$$n_e = \frac{E A(T_f)}{Q_0 \phi M 10^3} \quad (4.41)$$

Therefore, mole fraction of precipitate at any temperature can be determined by substituting the value of n and n_e in Equation (4.29), i.e. total area up to desired temperature T divided by total area under the curve:

$$Y = \left(\frac{E A(T)}{Q_0 \phi M 10^3} \right) / \left(\frac{E A(T_f)}{Q_0 \phi M 10^3} \right)$$

or

$$Y = \frac{A(T)}{A(T_f)} \quad (4.42)$$

The relationship for reaction rate can also be obtained by differentiating Equation (4.29) with respect to temperature T

$$\frac{dY}{dT} = \frac{d}{dT} \left(\frac{n(T)}{n_e} \right)$$

$$\left(\frac{dY}{dT}\right) = \frac{E}{Q_o \phi M 10^3 n_e} \left(\frac{dA(T)}{dT}\right) - \frac{E A(T)}{Q_o \phi M \cdot 10^3 n_e} \left(\frac{d \ln n_e}{dT}\right)$$

$$\left(\frac{dY}{dT}\right) = \frac{E}{Q_o \phi M \cdot 10^3} \left[\frac{1}{n_e} \left(\frac{dA(T)}{dT}\right) - \frac{(X_m - X_p)}{(X_p - X_e)(X_m - X_e)} \left(\frac{dX_e}{dT}\right) \right] \quad (4.43)$$

If change in X_e is assumed to be negligible over the temperature range of reaction peak, then n_e becomes independent of temperature. Therefore the above Equation (4.43) reduces to

$$\left(\frac{dY}{dT}\right) = \frac{E}{Q_o \cdot \phi M 10^3 n_e} \left(\frac{dA(T)}{dT}\right)$$

when $n_o \approx n_e$,

$$\left(\frac{dY}{dT}\right) = \frac{E}{Q_o \cdot \phi \cdot M 10^3 n_o} \left(\frac{dA(T)}{dT}\right)$$

Substituting n_o from equation (4.39)

$$\left(\frac{dY}{dT}\right) = \frac{[(\dot{q}_{20} - \dot{q}_{21}) - (\dot{q}_{20} - \dot{q}_{21})\dot{Q} = 0]}{\int_{T_i}^{T_f} [(\dot{q}_{20} - \dot{q}_{21}) - (\dot{q}_{20} - \dot{q}_{21})\dot{Q} = 0] dT} \quad (4.44)$$

and also,

$$\left(\frac{dY}{dT}\right) = \left(\frac{dY}{dT}\right) \left(\frac{dT}{dt}\right) = \left(\frac{dY}{dt}\right) \phi$$

Using Equation (4.44)

$$\frac{dY}{dt} = \frac{\phi [(\dot{q}_{20} - \dot{q}_{21}) - (\dot{q}_{20} - \dot{q}_{21})\dot{Q} = 0]}{\int_0^T [(\dot{q}_{20} - \dot{q}_{21}) - (\dot{q}_{20} - \dot{q}_{21})\dot{Q} = 0]dT} \quad (4.45)$$

Relationships (4.28a), (4.42), (4.44) and (4.45) derived above give the necessary expressions for determination of total heat effects, mole fraction of precipitates dissolving or precipitating, and reaction rates within desired range of temperatures on DSC curve. All these parameters were evaluated from DSC curves using the Dupont General Utility Program.

4.2.5 Kinetic Analysis

The decomposition rate of any reaction is determined by the temperature and the extent to which the reaction has already proceeded. Under isothermal conditions, the reaction rate depends only upon the fraction transformed^(175,176)

$$\frac{dY}{dt} = K f(Y) \quad (4.46)$$

where $f(Y)$ is a certain function of Y , and K is the rate constant and is a function of temperature. In accordance with the Arrhenius equation

$$K = K_0 e^{-Q^*/RT} \quad (4.47)$$

where K_0 is the frequency factor, Q^* is the molar activation energy, R is the gas constant and T is the absolute temperature. Combining Equations (4.46) and (4.47)

$$\frac{dY}{dt} = f(Y) \cdot K_0 e^{-Q^*/RT} \quad (4.48)$$

or

$$\int_0^Y \frac{dY}{f(Y)} = \int_0^t K_o e^{-Q^*/RT} dt$$

If reaction is isothermal then

$$F(Y) = Kt \quad (4.49a)$$

$$\text{where } F(Y) = \int_0^Y \frac{dY}{f(Y)} \quad (4.49b)$$

If the reaction is non-isothermal then

$$\int_0^Y \frac{dY}{f(Y)} = K_o \int_{T_i}^T e^{-Q^*/RT} \frac{dT}{dT} \quad (4.50)$$

If heating rate is constant, i.e. $\frac{dT}{dt} = \phi$, then

$$F(Y) = (K_o/\phi) \int_{T_i}^T e^{-Q^*/RT} dT \quad (4.51)$$

Since

$$(K_o/\phi) \int_0^Y e^{-Q^*/RT} dT = [F(Y)]_Y = 1 = 0 \quad (4.52)$$

$$\text{and } F(Y) = \left(\frac{K_o}{\phi}\right) \int_0^T e^{-Q^*/RT} dT \quad (4.53)$$

Equations (4.46) to (4.53) can be used for the evaluation of the kinetic parameters for the four reactions occurring in the alloy.

4.2.5.1 Determination of Activation Energy

4.2.5.1.1 The Integral Technique

In Equation (4.53), let, (177)

$$\int_0^T e^{-Q^*/RT} dT = i$$

then,

$$\ln [F(Y)/K_o] = \ln i (T, Q^*) - \ln \phi$$

If at a given heating rate ϕ_j , a given fraction of precipitate Y' is obtained at temperature T_j , then

$$\ln \phi_j - \ln i (T_j, Q^*) = \ln [F (Y')/K_o]$$

For two heating rates 1 and 2, the above equation reduces to

$$\Delta = [\ln \phi_1 - \ln i (T_1, Q^*)] - [\ln \phi_2 - \ln i (T_2, Q^*)] = 0 \quad (4.54)$$

In this equation Q^* is such that ' Δ ' is zero for all pairs of values of ϕ . If the left hand side, Δ , is plotted as a function of Q^* for at least two heating rates, the activation energy corresponding to $\Delta = 0$ is the activation energy of the reaction provided $\log i$ can be calculated. The integral, i , does not have any finite solution. A number of expansions have been proposed for obtaining approximate values of the integral.⁽¹⁷⁷⁾ However, the integral has been numerically evaluated and its values have been tabulated as functions of T and Q^* . Gyulai and Greenhow⁽¹⁷⁷⁾ have shown that $\log i$ varies linearly with Q^* and $1/T$. These data therefore can be used for calculation of the activation energy.

4.2.5.1.2 A New Differential Technique

A new and simple differential technique can be used to evaluate the activation energy. It was mentioned earlier that the non-isothermal data are functions of the heating rate ϕ . Thus, Equation

(4.48) may be written as

$$\frac{dY}{dT} = f(Y) K_o e^{-Q^*/RT} \quad (4.55)$$

Therefore,

$$\frac{dY}{dT} \phi = f(Y) K_o e^{-Q^*/RT}$$

or

$$\ln \left[\left(\frac{dY}{dT} \right) \cdot \phi \right] = \ln [f(Y) K_o e^{-Q^*/RT}] \quad (4.56)$$

If at different heating rates, ϕ_j , temperatures, T_j , corresponding to a constant mole fraction (Y') is determined, then

$$\ln \left[\left(\frac{dY}{dT} \right) \phi_j \right] = \ln [f(Y') K_o] - (Q^*/R) (1/T_j) \quad (4.57)$$

Since $f(Y')$ is a constant, the plot of $\ln \left[\frac{dY}{dT} \phi_j \right]$ against $(1/T_j)$ should give a straight line whose slope should be equal to $-(Q^*/R)$.

4.2.5.2 Determination of the Function $f(Y)$

The expressions for $F(Y)$ or $f(Y)$ can be determined by assuming suitable forms and using experimental data to verify the applicability of these forms. Based on different models several possible forms of $F(Y)$ or $f(Y)$ are available to describe solid state reactions. They can be broadly classified by the shape of the Y - t curve under isothermal conditions as accelerating, sigmoidal or decelerating. (178) In isothermal studies, these shapes serve as a guide in selecting appropriate relationships. Selvaratnam and Garn (179) have given a more sensitive procedure for selecting the appropriate expression.

For the non-isothermal case, however, all of the expressions give

sigmoidal Y-t curves and there is no sensitive procedure for selecting the correct form of $f(Y)$. (178)

Most of the precipitation reactions occur by the process of nucleation and growth while dissolution reactions may be considered as negative growth. Such processes show sigmoidal behaviour. The most probable expressions for $F(Y)$ or $f(Y)$ applicable to such processes are listed in Table 4.5.

Assuming a particular model relation, the appropriate kinetic parameters can be determined.

Model relation 1: This is a general equation for a nucleation and growth type of process, where the value of n is determined by the nucleation and growth processes and the shape of the precipitate. Two techniques can be used to test this model and to determine the value of n and K_o .

(a) Substituting function $f(Y)$ in Equation (4.48)

$$\frac{dY}{dt} = n(1-Y) \left[\ln \left\{ \frac{1}{1-Y} \right\} \right]^{(n-1/n)} K_o e^{-Q^*/RT} \quad (4.58)$$

or

$$\ln \left[\left(\frac{dY}{dt} \right) \left(\frac{1}{1-Y} \right) \right] = \ln n K_o + \left(\frac{n-1}{n} \right) \ln \ln \left(\frac{1}{1-Y} \right) - Q^*/RT \quad (4.59)$$

or

$$\ln \left[\frac{dY}{dt} \cdot \left(\frac{\phi}{1-Y} \right) \right] + \frac{Q^*}{RT} = \ln n K_o + \left(\frac{n-1}{n} \right) \ln \ln \left(\frac{1}{1-Y} \right) \quad (4.60)$$

The value of the activation energy Q^* may be calculated by the techniques given earlier. If the model relation 1 is applicable, the plot of $\left[\ln \left\{ \left(\frac{dY}{dt} \right) \left(\frac{\phi}{1-Y} \right) \right\} + \frac{Q^*}{RT} \right]$ against $\ln \ln \left(\frac{1}{1-Y} \right)$ for a given heating rate ϕ , would be linear. The values of n and K_o would be determined

Table 4.5 Most probable expressions for solid state reactions in the present alloy

S. No.	Model relation	Expression for		
		$f(Y)$	$F(Y)$	Y
1	Johnson-Mehl Eqn. ⁽⁹⁾	$n(1-Y)$ $[\ln \frac{1}{1-Y}]^{n-1/n}$	$[\ln (\frac{1}{1-Y})]^{1/n}$	$1-e^{-Kt^n}$
2	Johnson-Mehl Eqn. ⁽⁹⁾	$(1-Y)$	$\ln (\frac{1}{1-Y})$	$1-e^{-Kt}$
3	3 dimensional ⁽¹⁸⁰⁾ diffusion Eqn.	$\frac{3(1-Y)^{2/3}}{2[1-(1-Y)^{1/3}]}$	$[1-(1-Y)^{1/3}]^2$	-
4	General Sigmoidal ⁽¹⁷⁷⁾ relation	$Y^r (1-Y)^m$	-	-

from the slope and intercept of the plot.

(b) Substituting $F(Y)$ from model relation 1 (Table 4.5) in Equation (4.53)

$$\left[\ln \left(\frac{1}{1-Y} \right) \right]^{1/n} = \frac{K_0}{\phi} \int_0^T e^{-Q^*/RT} dT \quad (4.61)$$

Since $\int e^{-Q^*/RT} dT = i$

$$\text{or} \quad \left[\ln \left(\frac{1}{1-Y} \right) \right]^{1/n} = \frac{K_0}{\phi} i \quad (4.62)$$

$$\text{or} \quad -\log i = \log \left(\frac{K_0}{\phi} \right) - \frac{1}{n} \log \ln \left(\frac{1}{1-Y} \right) \quad (4.63)$$

Using a predetermined value of Q^* $-\log i$ may be plotted against $\log \ln \left(\frac{1}{1-Y} \right)$ for a given heating rate ϕ . A straight line so obtained would verify validity of the model relation 1. The slope and intercept of this curve would yield $(-1/n)$ and $\log \left(\frac{K_0}{\phi} \right)$ respectively.

Model relation 2: This is a special case of model relation 1 where $n = 1$. The test techniques described below yield relationships to determine K_0 and verify the validity of the model.

(a) For $n = 1$, Equation (4.60) reduces to the following

$$\ln \left[\left(\frac{dY}{dT} \right) \left(\frac{\phi}{1-Y} \right) \right] = \ln K_0 - \left(\frac{Q^*}{R} \right) \left(\frac{1}{T} \right) \quad (4.64)$$

If $\ln \left[\left(\frac{dY}{dT} \right) \left(\frac{\phi}{1-Y} \right) \right] V/S (1/T)$ plot is linear, the validity of the model relation 2 becomes justified. This plot also yields the value of Q^* .

(b) For the present model the Equation (4.63) reduces to the following:

$$-\log i = \log \left(\frac{K_0}{\phi} \right) - \log \ln \left(\frac{1}{1-Y} \right) \quad (4.65)$$

For a given value of ϕ , $-\log i$ plotted against $\log \ln \left(\frac{1}{1-Y} \right)$ should

yield a straight line of slope, 1, and intercept (K_0/ϕ).

Model relation 3: This is a three dimensional diffusion controlled equation originally developed to describe the kinetics of solid state reactions in powders. (180) It has been found to be applicable to the precipitation and dissolution kinetics of GP zones in 2219 and 7075 aluminum alloy. (181)

Substituting $f(Y)$ in Equation (4.48)

$$\frac{dY}{dt} = \frac{3(1-Y)^{2/3}}{2[1-(1-Y)^{1/3}]} K_0 e^{-Q^*/RT} \quad (4.66)$$

$$\text{or} \quad \left[\frac{dY}{dt} \cdot \frac{2[1-(1-Y)^{1/3}]}{3(1-Y)^{2/3}} \right] = K_0 e^{-Q^*/RT} \quad (4.67)$$

Taking natural log of both sides,

$$\ln \left[\frac{dY}{dt} \cdot \frac{2[1-(1-Y)^{1/3}]}{3(1-Y)^{2/3}} \right] = \ln K_0 - \frac{Q^*}{R} \left(\frac{1}{T} \right) \quad (4.68)$$

For a given value of ϕ , the plot $\ln \left[\frac{dY}{dt} \cdot \frac{2[1-(1-Y)^{1/3}]}{3(1-Y)^{2/3}} \right]$ VS $(1/T)$ should be linear if model relation 3 is applicable. The plot would also yield the value of Q^* .

Model relation 4: This is a general equation yielding a sigmoidal behaviour. Such a relationship has been proposed for the precipitation reactions. (178)

Substituting $f(Y)$ in Equation (4.48)

$$\left(\frac{dY}{dt} \right) = Y^r (1-Y)^m K_0 e^{-Q^*/RT} \quad (4.69)$$

Rearranging,

$$\left[\left(\frac{dY}{dt} \right) (\phi/e^{-Q^*/RT}) \right] = Y^r (1-Y)^m K_0$$

Taking ln of both sides

$$\ln \left[\left(\frac{dY}{dT} \right) \frac{\phi}{e^{-Q^*/RT}} \right] = \ln K_0 + r \ln Y + m \ln (1-Y)$$

it reduces to

$$\frac{\ln \left[\left(\frac{dY}{dT} \right) \frac{\phi}{e^{-Q^*/RT}} \right]}{d \ln Y} = r - m \left(\frac{Y}{1-Y} \right) \quad (4.70)$$

For a given value of ϕ , if the plot of $\Delta \{ \ln [\left(\frac{dY}{dT} \right) \left(\frac{\phi}{e^{-Q^*/RT}} \right)] \} / \Delta (\ln Y)$ against $[Y/(1-Y)]$ is linear, the model relation 4 is applicable. The intercept and slope would then yield values for r and m .

On the basis of the formulations described in this section, various peaks observed in the DSC curves of as quenched samples were analysed to obtain the kinetic parameters.

4.2.5.3 The GPB Zones Precipitation Peak

The representative thermograms of the GPB zones precipitation peaks obtained from the present alloy in the as quenched condition at the four heating rates, are shown in Fig. 4.28. The peak characteristics and the total heat effects associated with this peak are listed in Table 4.6. The value of E used for calculation of Q was 1.054.

Table 4.6 shows that the total heat effect Q decreases only slightly with increasing heating rate indicating that the net amount of GPB zone formation is independent of heating rate. The absence of overlap of this peak with next dissolution peak (Fig. 4.26(a)) suggests that the precipitation of these zones is completed during

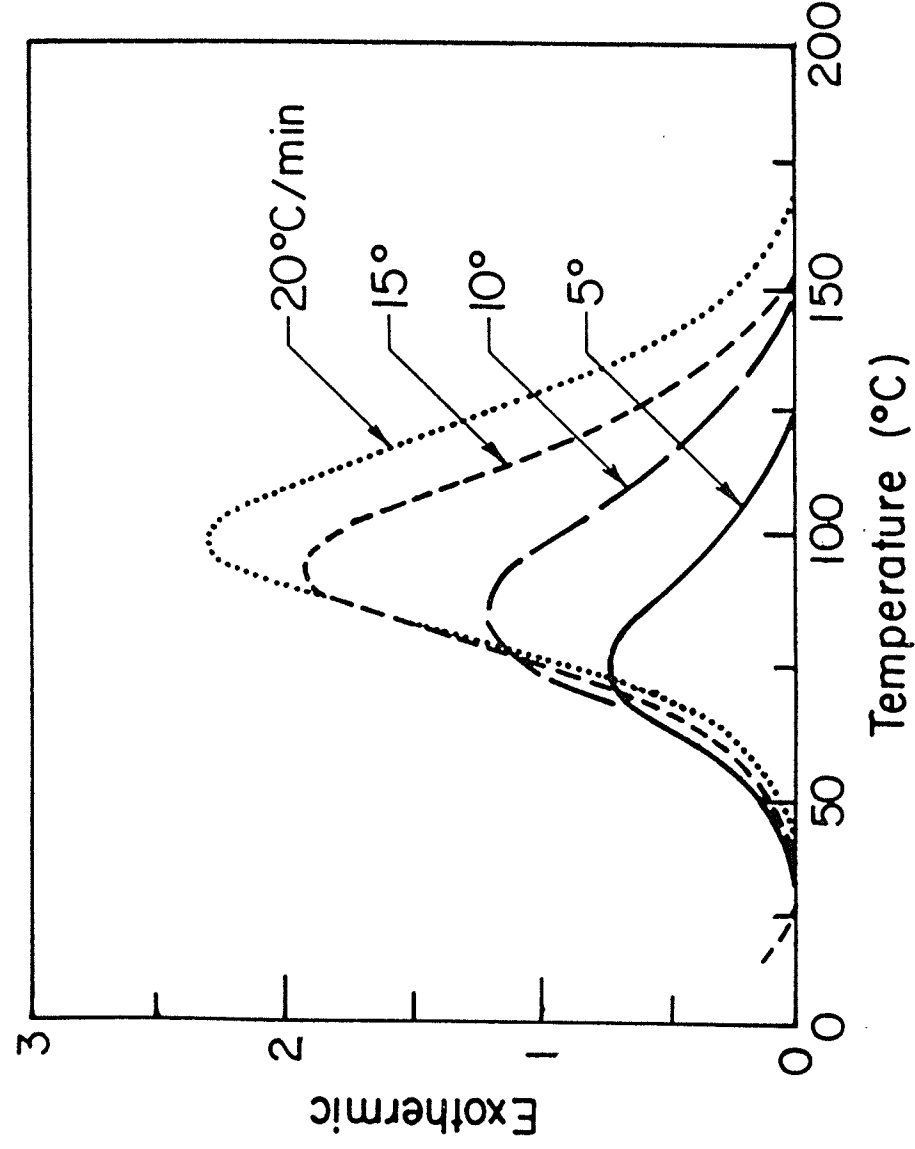


Fig. 4.28 GPB zone precipitation peaks in the solution treated and quenched Al-1.53%Cu-0.79%Mg alloy at different heating rates

Table 4.6 Peak characteristics and total heat effects due to GPB zones precipitation peak at different heating rates

Heating Rate (°C/min)	Total heat effect Q J/g)	Peak temperature (°C)			Maximum rate, $(\frac{dY}{dT}) \times 10^3$
		Beginning	Maximum	End	
5	6.69	25.41	73.81	142.09	23.74
10	6.52	26.05	84.6	152.56	28.75
15	6.52	34.19	93.25	157.08	20.74
20	5.99	44.52	99.70	170.36	23.30

the DSC run. The comparison of the thermograms in Fig. 4.28 shows a systematic shift in the peak temperature from 73.8° to 99.7°C, indicating the process to be kinetically dominated. In order to determine the kinetics of this process the mole fraction (Y) of the precipitates and their rates of formation with respect to temperature were determined (Section 4.2.4.1). These data are listed in Table 4.7.

The plots in Figs. 4.29(a) and 4.29(b) show the variations of the mole fraction Y and the rates of GPB zone formation with temperature. The Y-T curve is sigmoidal in shape and shifts to the right hand side with an increase in heating rates. The initial stage is characterized by a very low rate of transformation which increases and goes through a maximum with the progress in transformation. The values of reaction rate then decreases, becomes zero at the end of the transformation. The rate of transformation depends upon heating rate as shown in Fig. 4.29(b). At low heating rate it is slow and increases at higher heating rates (10°, 15° and 20°C/min).

The activation energy Q^* was calculated by the differential and integral techniques using the data plotted in Figs. 4.30(a) and 4.31. Three plots were made after Equation (4.57) corresponding to three values of Y, 0.25, 0.5 and 0.825. Fig. 4.30 shows that the variation is linear. The slopes of all the three straight lines plotted by least square method gave the value of the activation energy Q^* to be 55.61 ± 0.13 kJ/mole. Following Equation (4.54) plots of Δ vs. Q^* (Fig. 4.31) were also made to obtain the activation energy. The value of Q^* corresponding to $\Delta = 0$ was calculated to be 52.3 ± 0.96 kJ/mole. Values obtained by both the techniques are in

Table 4.7: DSC data obtained from GPB zones precipitation peaks at various heating rates.

S. No.	Temp. _T (°C)	Total heat effect up to temp. T (Q/E) (J/g)	Mole Fraction Y	$\frac{dY}{dT} \times 10^3$ /°C	Heating rate °C/min
1	40.00	0.0679	0.0107	1.9940	5
2	50.00	0.3192	0.0503	6.6265	
3	60.00	0.9634	0.1519	14.5281	
4	70.00	2.1504	0.3390	22.6385	
5	75.00	2.8909	0.4557	23.6254	
6	85.00	4.2559	0.6709	18.6496	
7	105.00	5.2397	0.8259	12.2495	
8	110.36	5.8411	0.9207	7.1028	
9	119.64	6.0459	0.9530	4.8614	
10	126.43	6.2451	0.9844	2.0131	
11	141.43	6.3078	0.9943	0.0912	
12	142.09	6.3443	1.0000	-	
1	44.96	0.0576	0.0095	1.6025	10
2	55.00	0.2338	0.0387	4.8475	
3	65.04	0.6754	0.1119	10.2558	
4	75.08	1.4919	0.2472	17.0263	
5	85.12	2.6549	0.4399	20.6316	
6	95.16	3.8299	0.6346	17.3868	
7	104.76	4.6978	0.7784	12.6395	
8	115.24	5.3506	0.8866	8.2327	
9	124.84	5.7305	0.9495	5.0278	
10	135.82	5.9509	0.9861	2.1032	
11	142.74	6.0131	0.9964	0.8613	
12	151.90	6.0346	0.9999	-	
13	152.56	-	1.0000	-	
1	45.08	0.0242	0.0039	0.7246	15
2	54.92	0.1194	0.0193	2.5096	
3	65.08	0.3747	0.0606	6.1074	
4	75.24	0.9129	0.1476	11.7361	
5	85.08	1.8146	0.2935	18.3653	
6	94.92	3.0266	0.4895	20.7158	
7	104.76	4.1836	0.6766	16.9731	
8	112.06	4.8635	0.7866	13.0888	
9	120.00	5.4025	0.8738	9.2119	
10	129.21	5.8234	0.9418	5.6827	
11	134.60	5.9833	0.9677	3.9748	

S. No.	Temp. (°C) T	Total heat effect up to temp. T (Q/E) (J/g)	Mole Fraction Y	$\frac{dY}{dT} \times 10^3$ /°C	Heating rate °C/min
12	141.27	6.1062	0.9876	2.0455	
13	147.94	6.1650	0.9970	0.8124	
14	156.51	6.1832	1.0000	-	
15	157.08	6.1832	-	-	
1	55.00	0.0231	0.0041	0.9604	
2	65.00	0.1386	0.0241	3.3792	
3	75.00	0.4450	0.0784	7.8255	
4	85.00	1.0522	0.1853	14.2282	
5	95.00	2.0191	0.3555	19.5638	
6	105.36	3.1768	0.5593	19.1192	20
7	115.36	4.1464	0.7301	14.9397	
8	125.00	4.8273	0.8500	9.9598	
9	135.00	5.2687	0.9272	5.7802	
10	145.00	5.5098	0.9696	2.8812	
11	154.64	5.6223	0.9894	1.2805	
12	165.00	5.6714	0.9981	0.4268	
13	170.36	5.6794	0.9995	0.1423	
14	171.60	5.6794	1.0000	-	

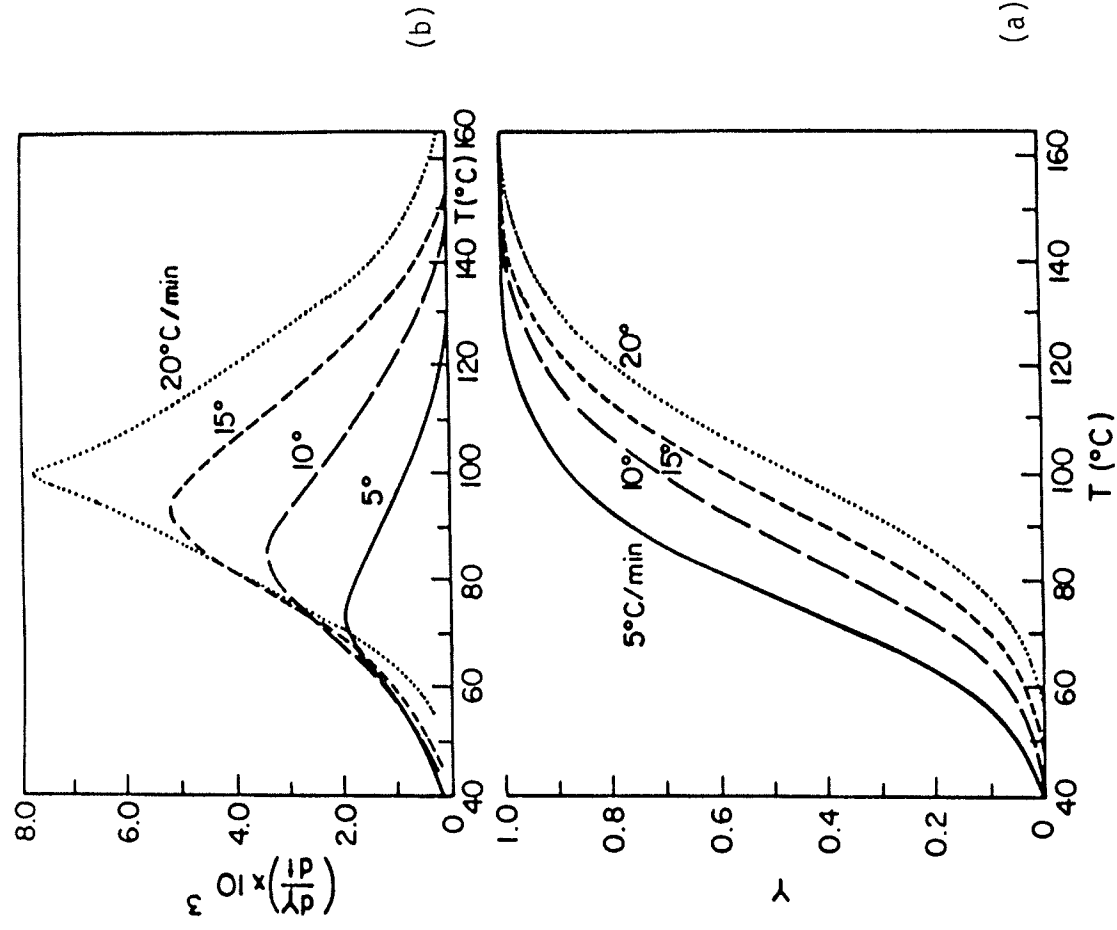


Fig. 4.29 (a) Y versus temperature plots for the GBP zone precipitation peak at different heating rates
(b) Variation of $\left(\frac{dY}{dT}\right)$ with temperature at different heating rates

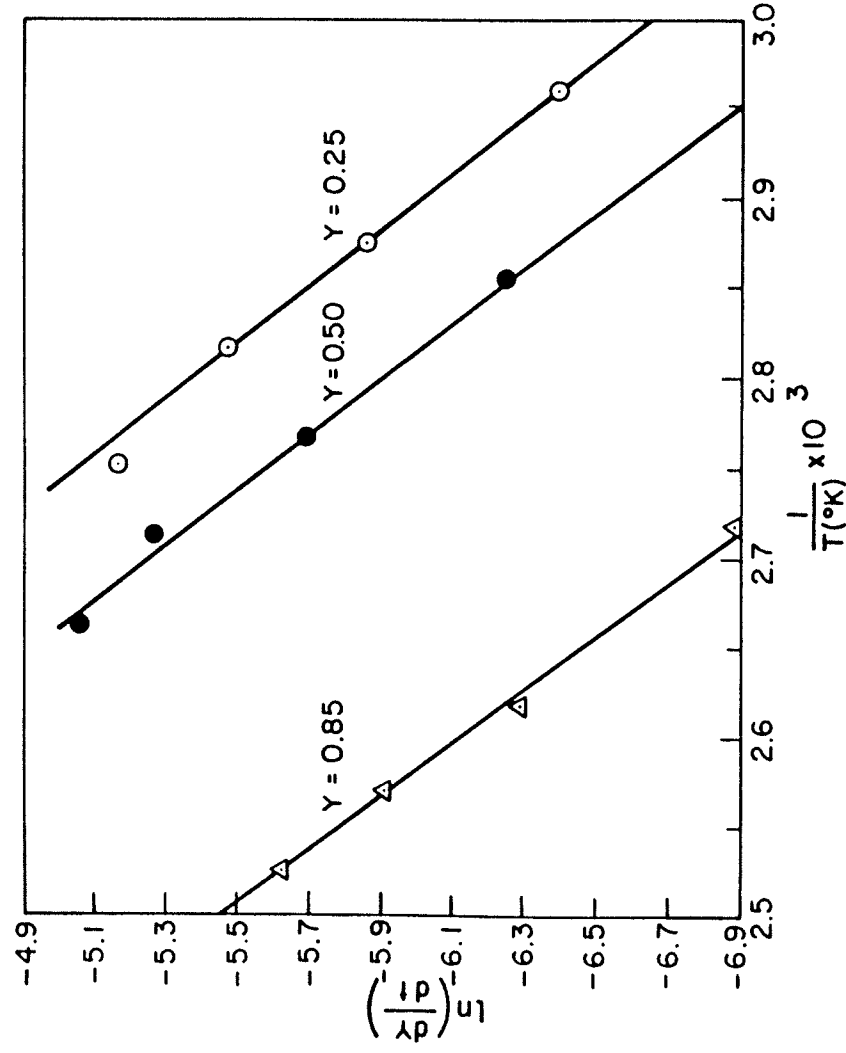


Fig. 4.30 Activation plots for the GPB zone precipitating peak after Equation (4.57)

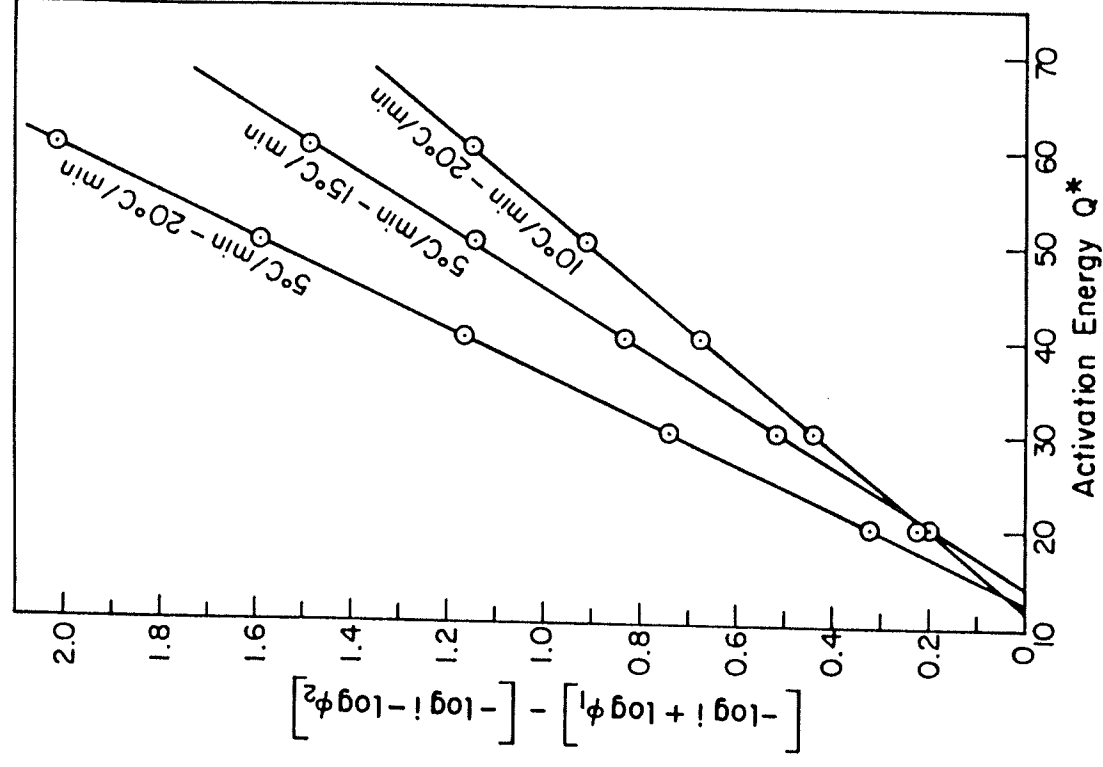
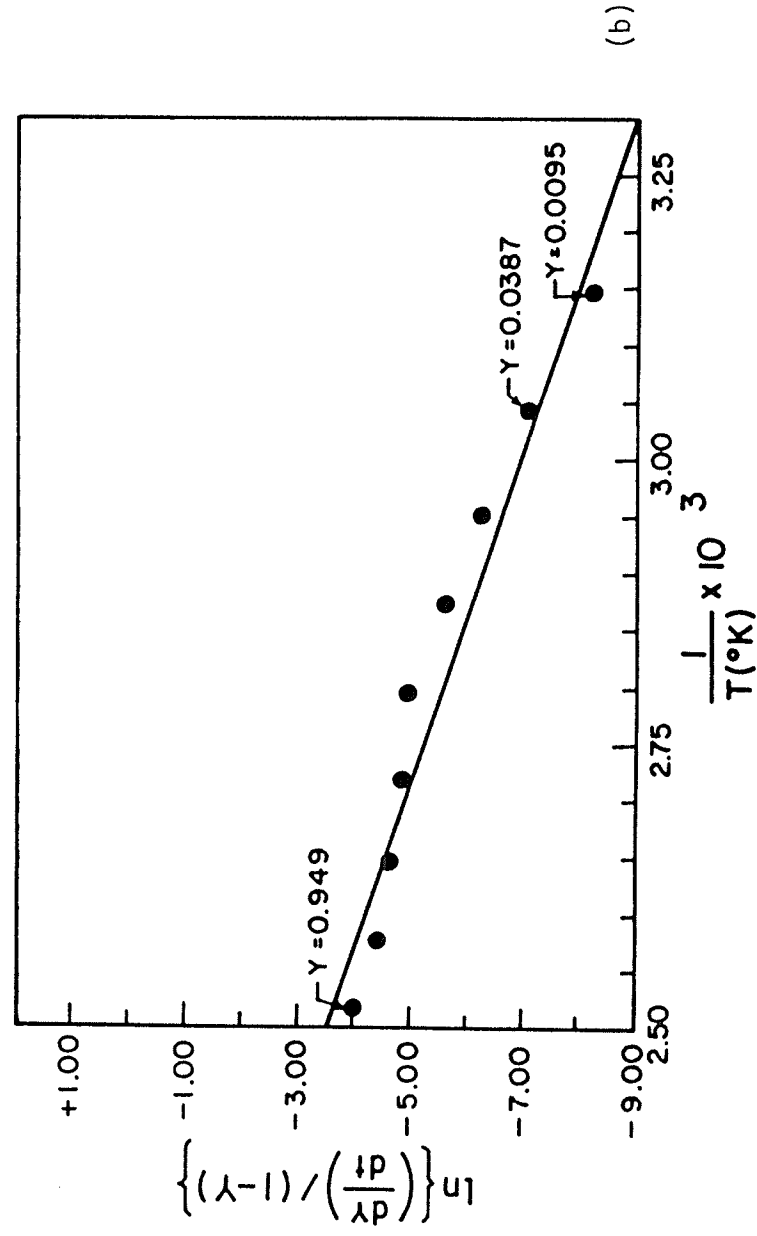
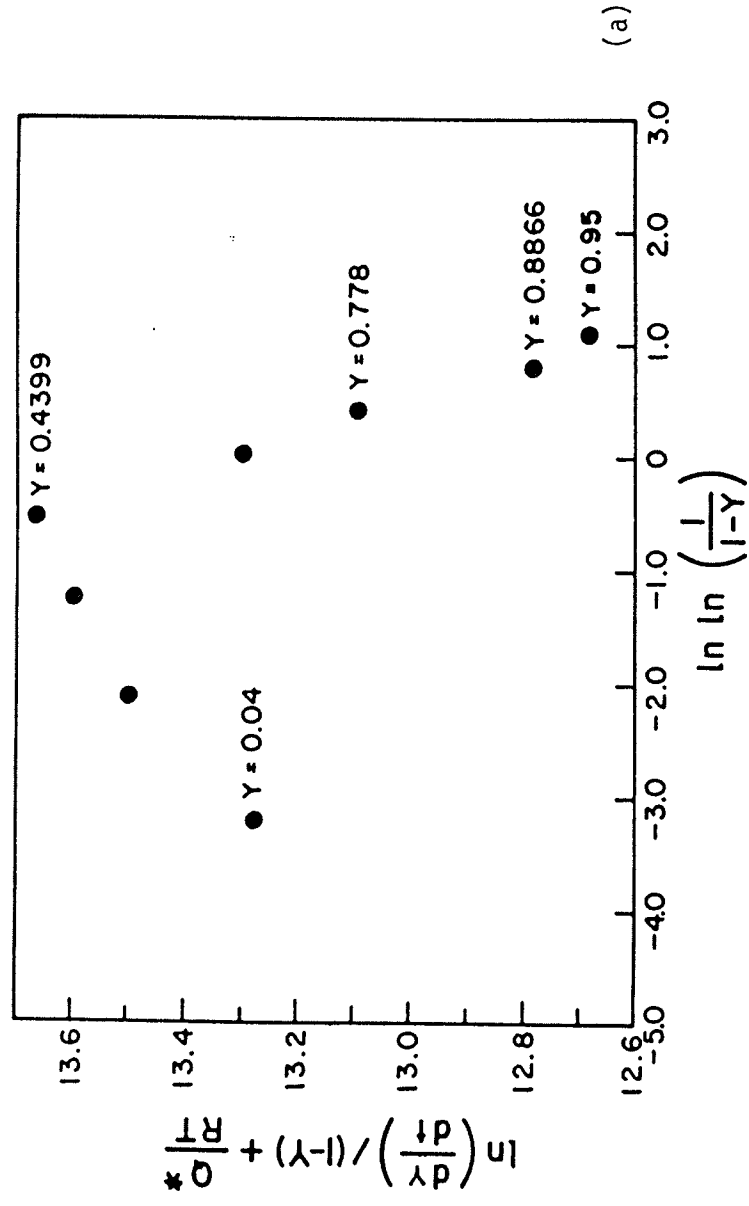


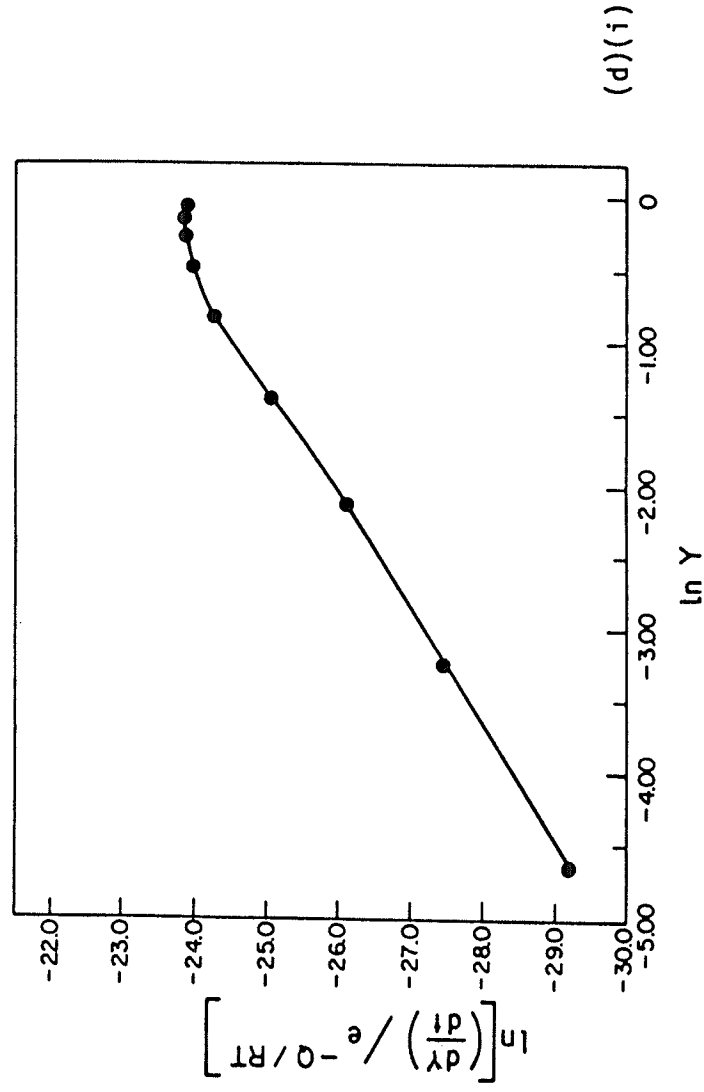
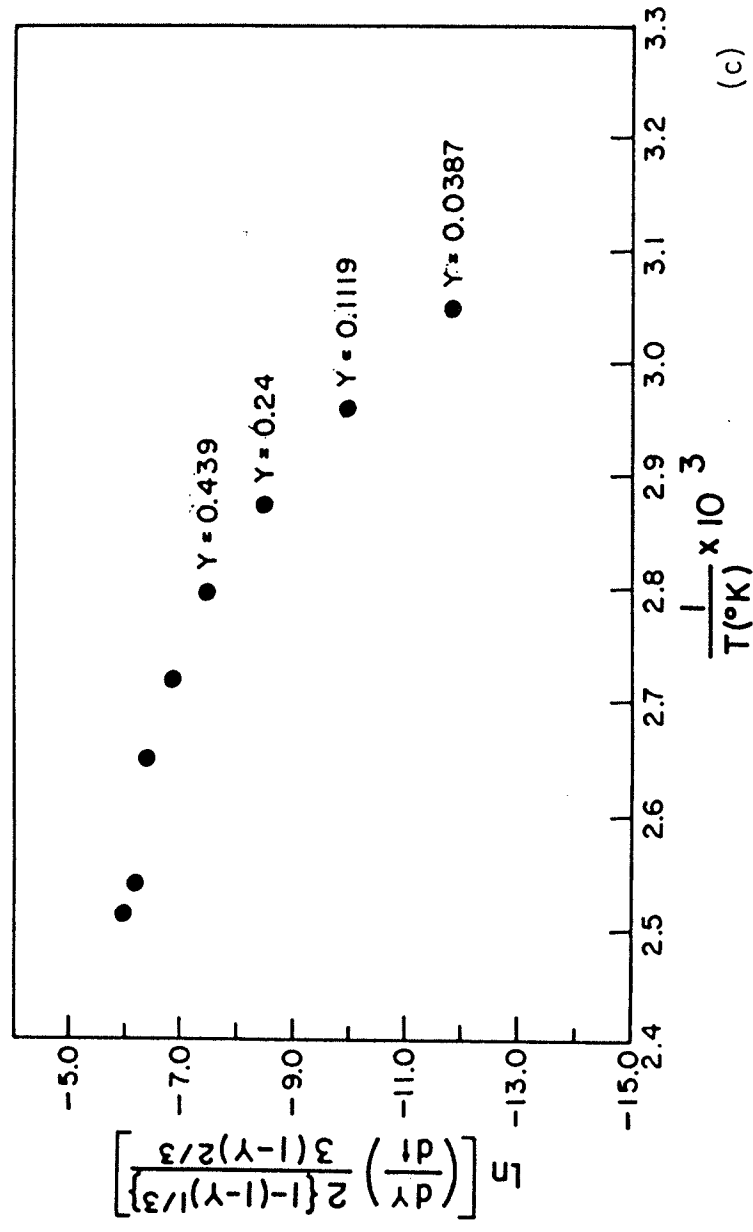
Fig. 4.31 Activation plots for the GPB zone precipitation peak after Equation (4.54)

excellent agreement with each other.

Using the activation energy $Q^* = 55.6$ kJ/mole and the experimental data listed in Table 4.7, various curves were plotted (Figs. 4.32(a) to (d)) to verify the validity of the expressions (Table 4.5). The best fit of the experimental data is obtained with the model relation 2 over a wide range of the values of Y from 0.009 to 0.95.

The GPB zones precipitation peak exists in between 25° - 170°C depending upon the heating rate. The rate of their formation is maximum within 74° - 100°C and the total heat effect associated with the peak is 6.5 J/g. These results are in excellent agreement with the resistivity measurements of Cho⁽¹³⁸⁾ on Al-2.0%Cu-1.1%Mg alloy who reported that the rate of GPB zone formation is maximum within 70° - 120°C with associated total heat effect of ≈ 6 J/g. A value of 64 kJ/mole for the activation energy has been found from resistivity data obtained with the Al-4.2%Cu-1.4%Mg alloy.⁽¹⁷¹⁾ This is close to the activation energy of 55.6 kJ/mole found in this investigation. This value is consistent with the value expected for the formation of GPB zones. When the alloy is quenched from solution treatment temperature vacancies collapse to form dislocation loops (Fig. 4.12) and appreciable amounts of excess vacancies are quenched-in. The excess vacancies diffuse to sinks as a result of ageing. Consequently, these quenched-in excess vacancies enhance the diffusion of solute required for the formation of GPB zones.⁽¹⁸²⁾ Since excess vacancies are present, the activation energy for diffusion of solutes would be equal to the activation energy for migration of vacancies. The migration energy of vacancies in Al-Cu alloys has been reported⁽¹⁸³⁻¹⁸⁵⁾ to be in the range 41.8 - 66.9





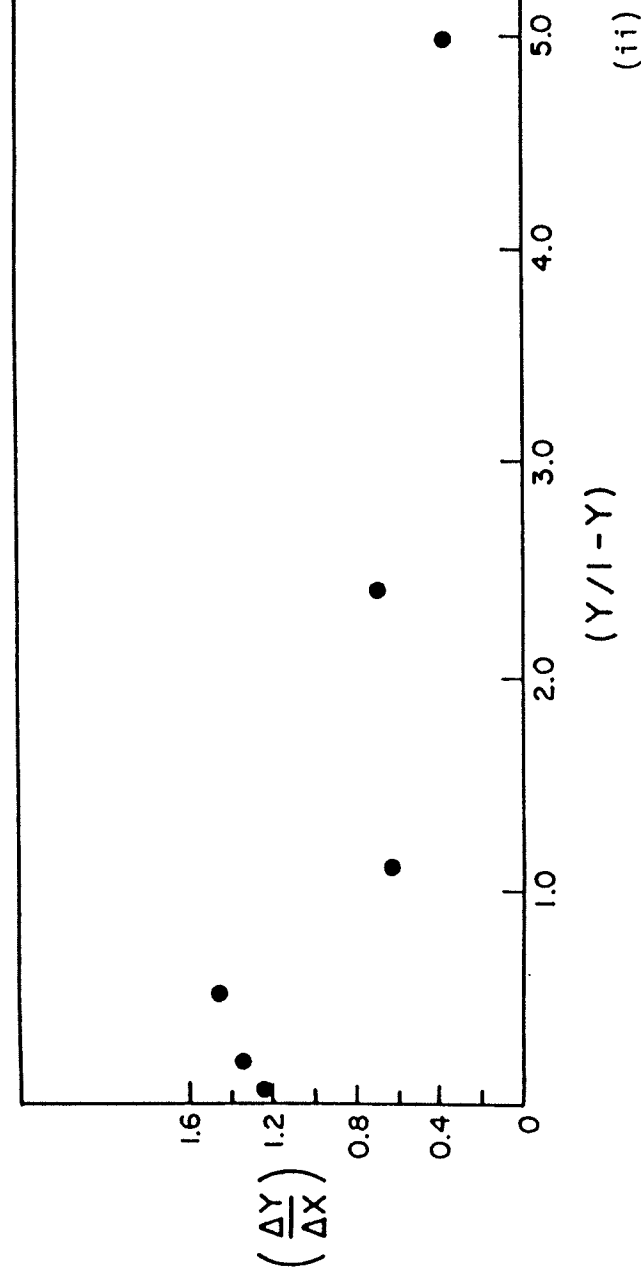


Fig. 4.32 (a) The plot of $\{\ln (\frac{dY}{dt})/(1-Y) + \frac{Q^*}{RT}\}$ against $\ln (\frac{1}{1-Y})$ after Equation (4.60)
 (b) The plot of $\ln \{(\frac{dY}{dt})/(\frac{1}{1-Y})\}$ against $1/T$ after Equation (4.64)
 (c) The plot of $\ln [(\frac{dY}{dt}) \frac{2\{1-(1-Y)^{1/3}\}}{3(1-Y)^{2/3}}]$ against $1/T$ after Equation (4.68)
 (d)(i) The plot of $\ln [\frac{(dY/dt) \times 10^{-3}}{e^{-Q^*/RT}}]$ against $\ln Y$ after Equation (4.70)
 (ii) The plot of $(\frac{\Delta Y}{\Delta X})$ against $Y/(1-Y)$

kJ/mole. The value of activation energy of 55.6 kJ/mole experimentally determined in this study is in excellent agreement with the range of activation energies for migration of vacancies.

The plots in Figs. 4.32(a)-(d) to test expression for function $f(Y)$ in rate equation clearly showed that model relations 1, 2 and 4 do not give linear plots and are not applicable to the kinetics of GPB zone formation. However, the plot (Fig. 4.32(b)) after the model relation 2 gives good fit and explains the kinetics of GPB zone formation. It should be noted that slope of this line in Fig. 4.32(b) (Equation (4.64)) yields a value of activation energy which is in excellent agreement with the calculated value from the activation plots (Figs. 4.30 and 4.31). The linearity of the curve extends over the wide range $Y = 0.0095$ to $Y = 0.95$. The value of K_0 calculated from the intercept of the best least square line with slope -6.7 is 5.7×10^5 .

As mentioned in Section 4.1, the GPB zones are cylindrical in shape. The process of GPB zone formation is diffusion controlled. If nucleation occurs in the early stages and the growth of cylindrical zones occur in radial directions, the radius of zones is given by:

$$R = \alpha (Dt)^{1/2} \quad (4.71)$$

where α is a constant, the exponent of Johnson-Mehl equation becomes 1.

The function $f(Y)$ determined in the present study, is $(1-Y)$. It yields the following equation for GPB zone formation

$$Y = 1 - e^{-kt} \quad (4.72)$$

when the exponent of t is indeed 1.

The kinetic analysis shown above suggests that the formation of GPB zones is controlled by the enhanced diffusion of solute atoms due to the quenched-in vacancies and the increase in the amount of GPB zones may be visualized as taking place by radial growth of cylindrical zones. The kinetics of zone formation is represented by Equation (4.47) where

$$K = 5.7 \times 10^5 e^{-55600/RT}$$

The kinetic parameters are listed in Table 4.8.

4.2.5.4 The First Dissolution Peak

The dissolution peaks obtained from DSC runs at different heating rates are shown in Fig. 4.33. The overall peak is a combination of a minor and major peaks. These two peaks are referred to as subpeak 1 and 2 respectively. The total heat effects and the characteristics of this multiple peak are listed in Table 4.9. It may be noted from Table 4.9 that both sub peaks 1 and 2 shift to higher temperatures with increasing heating rates. This suggests that this dissolution process is kinetically dominated, similar to the precipitation of GPB zones. However, peaks tend to overlap each other. The total area A_1 associated with peak 1 was estimated by doubling the peak area obtained from the initial to peak minimum temperature. The fraction,

$$(1-f) = \frac{A_1}{(A_1 + A_2)} \quad (4.73)$$

where, $(A_1 + A_2)$ is the total area under the composite peak. It is to be noted from Table 4.9 that the area fraction of peak 1 is almost constant for all heating rates except the slowest one which is higher.

Table 4.8 Summary of the kinetic parameters for the precipitation process

PEAK	1st EXOTHERMIC	1st ENDOTHERMIC	2nd EXOTHERMIC	2nd ENDOTHERMIC
Nature of the peak	GPB precipitation	Sub peak 1 GPB dissolution	Sub peak 2 complex dissolution	S' precipitation S' dissolution
Q* (kJ/mole)	55.6	123.9	209.5	129.9
K _o	5.7 x 10 ⁵	1.1 x 10 ¹⁰	2.7 x 10 ¹⁸	2.6 x 10 ⁹
f(Y)	(1-Y)	(1-Y)	(1-Y)	(1-Y)
				-

Table 4.9: Characteristics and total heat effects of the GPB zones dissolution peak at different heating rates.

Heating Rate () °C/min. Q (J/g)	Total heat effect (1-f) = Area of subpeak 1 Total area under peak	Peak temperatures (°C)						Maximum Rate		
		Subpeak 1			Subpeak 2					
		Beginning	Minimum	End	Beginning	Minimum	End	Subpeak 1	Subpeak 2	
5	8.1916	0.40	142.25	196.16	-	-	227.57	253.06	-	29.561 × 10 ⁻³
10	7.9545	0.26	151.29	200.30	-	-	234.37	265.08	-	28.752 × 10 ⁻³
15	7.2420	0.28	156.24	207.03	-	-	241.24	272.16	-	29.930 × 10 ⁻³
20	5.9359	0.24	173.33	209.32	-	-	243.49	275.67	-	29.282 × 10 ⁻³

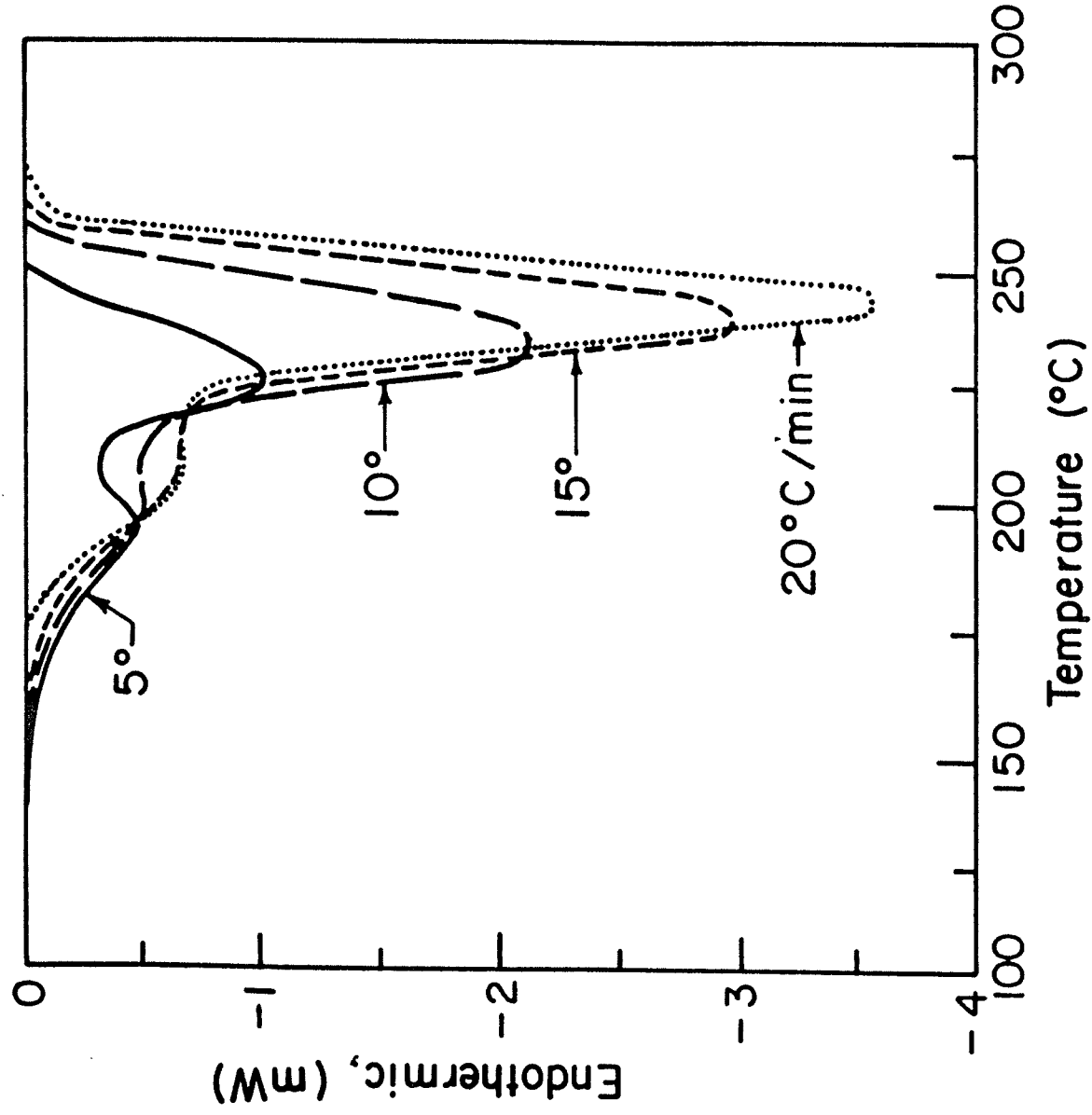


Fig. 4.33 The complex dissolution peak obtained from solution treated and water quenched Al-1.53Cu-0.79Mg alloy at different heating rates

If the area fraction $(1-f)$ of peak 1 is assumed to be constant for 10° , 15° and $20^\circ\text{C}/\text{min}$, then Y_1 the fractional change of the process occurring under peak 1, may be written after Equation (4.42)

$$Y_1 = \frac{A(T)}{A_1} \quad (4.74a)$$

Rearranging,

$$Y_1 = \frac{A(T)}{(A_1 + A_2)} \frac{A_1}{(A_1 + A_2)} \quad (4.74b)$$

Writing Y for the experimental value, $Y = \frac{A(T)}{(A_1 + A_2)}$,

$$Y_1 = \frac{Y}{(1-f)} \quad (4.74c)$$

The rate, is then,

$$\left(\frac{dY_1}{dT}\right) = \left[\left(\frac{1}{1-f}\right) \frac{dY}{dT}\right] \quad (4.75)$$

Similarly, for peak 2, the mole fraction and the rate at any temperature T can be written as

$$Y_2 = \frac{A(T)^{-A_1}}{A_2} = \frac{Y}{f} + \frac{(f-1)}{f} \quad (4.76)$$

$$\text{and} \quad \frac{dY_2}{dT} = \frac{1}{f} \left(\frac{dY}{dT}\right) \quad (4.77)$$

(a) Analysis of sub peak 1

For sub peak 1, Equation (4.55) becomes

$$\frac{dY_1}{dT} = f(Y_1) K_0 e^{-Q^*/RT}$$

Substituting from Equations (4.74) and (4.75)

$$\frac{1}{(1-f)} \frac{dY}{dT} \phi = f \left(\frac{Y}{1-f} \right) K_o e^{-Q^*/RT}$$

Hence,

$$\ln \left[\left(\frac{dY}{dT} \right) \phi \right] = \ln [(1-f) K_o] + f \left(\frac{Y}{1-f} \right) - \frac{Q^*}{RT} \quad (4.78)$$

Since, f is constant for the heat rates 10° , 15° and $20^\circ\text{C}/\text{min}$, then plot of $\ln \left[\left(\frac{dY}{dT} \right) \phi \right]$ vs, $(1/T)$ should be linear for peak 1 and slope should yield the value of Q^* . Table 4.10 lists the various experimentally determined parameters. The variation of Y with temperature T at different heating rates is shown in Fig. 4.34. The activation energies for the sub peak 1 was calculated using Equation (4.78) for $Y = 0.09$ (Fig. 4.34). Fig. 4.35 shows the activation plot. The slope of best straight line in Fig. 4.35 gives a value of 123.9 kJ/mole for sub peak 1. The point for heating rate $5^\circ\text{C}/\text{min}$ is shown for comparison.

The kinetic expression which is likely to govern the non-isothermal kinetics of dissolution peak 1 was assumed to be the same as that applicable to GPB zones precipitation peak. Therefore, Equation (4.64) is applicable to sub peak 1. For sub peak 1, Equation (4.64) becomes,

$$\frac{dY_1}{dT} \phi = (1-Y_1) K_o e^{-Q^*/RT} \quad (4.79)$$

Substituting Equations (4.74c) and (4.75), and rearranging,

$$\left(\frac{dY}{dT} \right) e^{-Q^*/RT} = C_1 - (K_o/\phi) Y \quad (4.80)$$

Table 4.10: Data obtained from GPB zones dissolution peak from DSC run at all the choosen heating rates.

S. No.	Temp. _T (°C)	Total heat effect up to temp. T (Q/E) (J/g)	Mole Fraction Y	$\frac{dY}{dT} \times 10^3$ /°C	Heating rate °C/min
1	165.00	0.1145	0.0147	1.5707	5
2	175.00	0.3200	0.0412	3.8583	
3	185.00	0.7630	0.0982	7.6064	
4	195.00	1.5521	0.1997	11.8505	
5	205.28	2.4006	0.3089	7.4686	
6	210.00	2.6705	0.3436	7.5237	
7	215.00	3.0230	0.3390	11.4371	
8	220.00	3.6352	0.4677	19.7876	
9	225.00	4.5406	0.5842	25.4924	
10	230.00	5.5566	0.7150	25.9058	
11	235.00	6.4843	0.8343	21.2207	
12	239.72	7.1514	0.9202	14.6065	
13	245.00	7.5899	0.9766	6.8898	
14	252.78	7.7718	0.9998		
15	253.06	7.7718	1.0000		
1	174.60	0.1142	0.0151	1.5617	10
2	184.92	0.3123	0.0414	3.6441	
3	194.84	0.6962	0.0922	6.4472	
4	205.16	1.2500	0.1663	7.0078	
5	215.08	1.7945	0.2378	8.0356	
6	221.60	2.6506	0.3524	18.3804	
7	229.76	3.5469	0.4700	26.2866	
8	234.92	4.6439	0.6153	28.7520	
9	240.08	5.7359	0.7600	26.2252	
10	245.24	6.6396	0.8798	18.9945	
11	250.00	7.1823	0.9517	10.6783	
12	255.16	7.4539	0.9877	3.5506	
13	264.29	7.5461	0.9999	-	
14	265.08	7.5466	1.0000	-	
1	185.12	0.1853	0.0269	2.5847	15
2	200.00	0.6239	0.0908	6.3444	
3	214.88	1.3397	0.1950	6.7555	
4	230.36	2.3837	0.3469	18.2107	
5	237.50	3.5687	0.5194	28.5791	
6	245.24	5.1397	0.7480	27.6099	
7	254.76	6.4907	0.9447	13.5406	

S. No.	Temp. (°C) T	Total heat effect up to temp. T (Q/E) (J/g)	Mole Fraction y	$\frac{dy}{dT} \times 10^3$ /°C	Heating rate °C/min
8	263.10	6.8379	0.9952	1.4686	
9	272.02	6.8705	0.9999	-	
10	272.17	6.8707	1.0000	-	
1	184.76	0.0387	0.0069	1.3402	
2	194.92	0.1845	0.0327	3.9012	
3	204.76	0.4757	0.0845	6.2419	
4	214.92	0.8517	0.1512	6.4840	
5	225.08	1.2573	0.2233	8.6095	
6	234.92	2.0566	0.3652	22.8420	20
7	239.05	2.6811	0.4761	29.8641	
8	243.49	3.4833	0.6185	32.5546	
9	247.94	4.2779	0.7596	29.5942	
10	254.92	5.1989	0.9232	16.1423	
11	260.32	5.5185	0.9799	5.5959	
12	265.40	5.6058	0.9954	1.3452	
13	274.60	5.6315	0.99996	0.1883	
14	275.67	5.6316	1.00000	-	

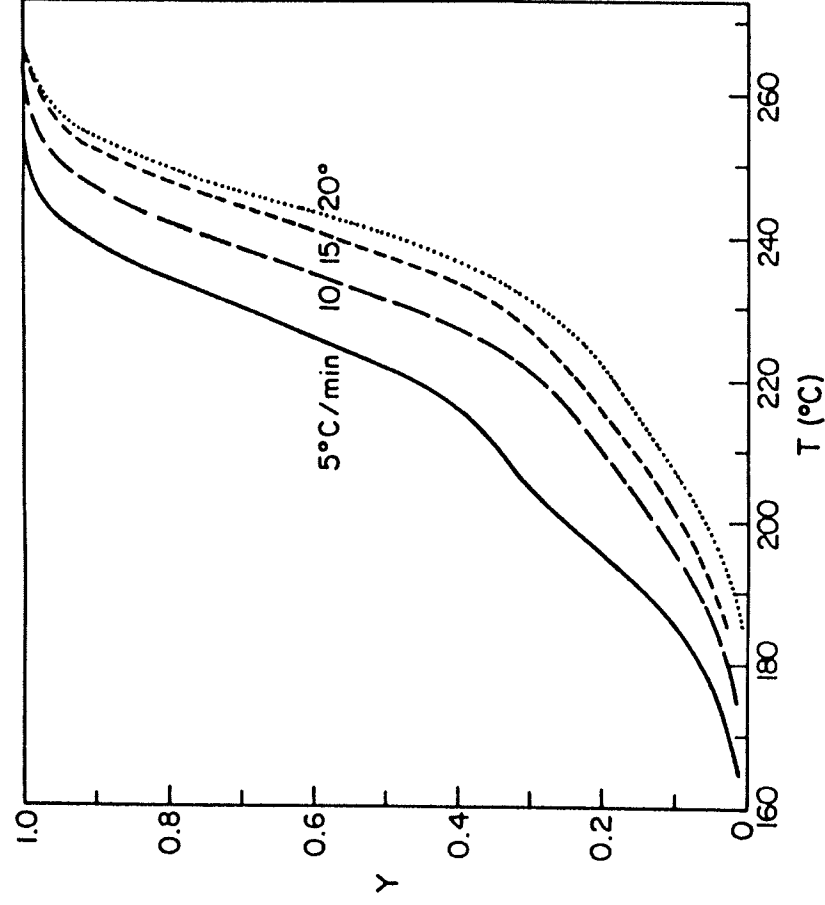


Fig. 4.34 Y versus temperature plots for the complex dissolution peak at different heating rates

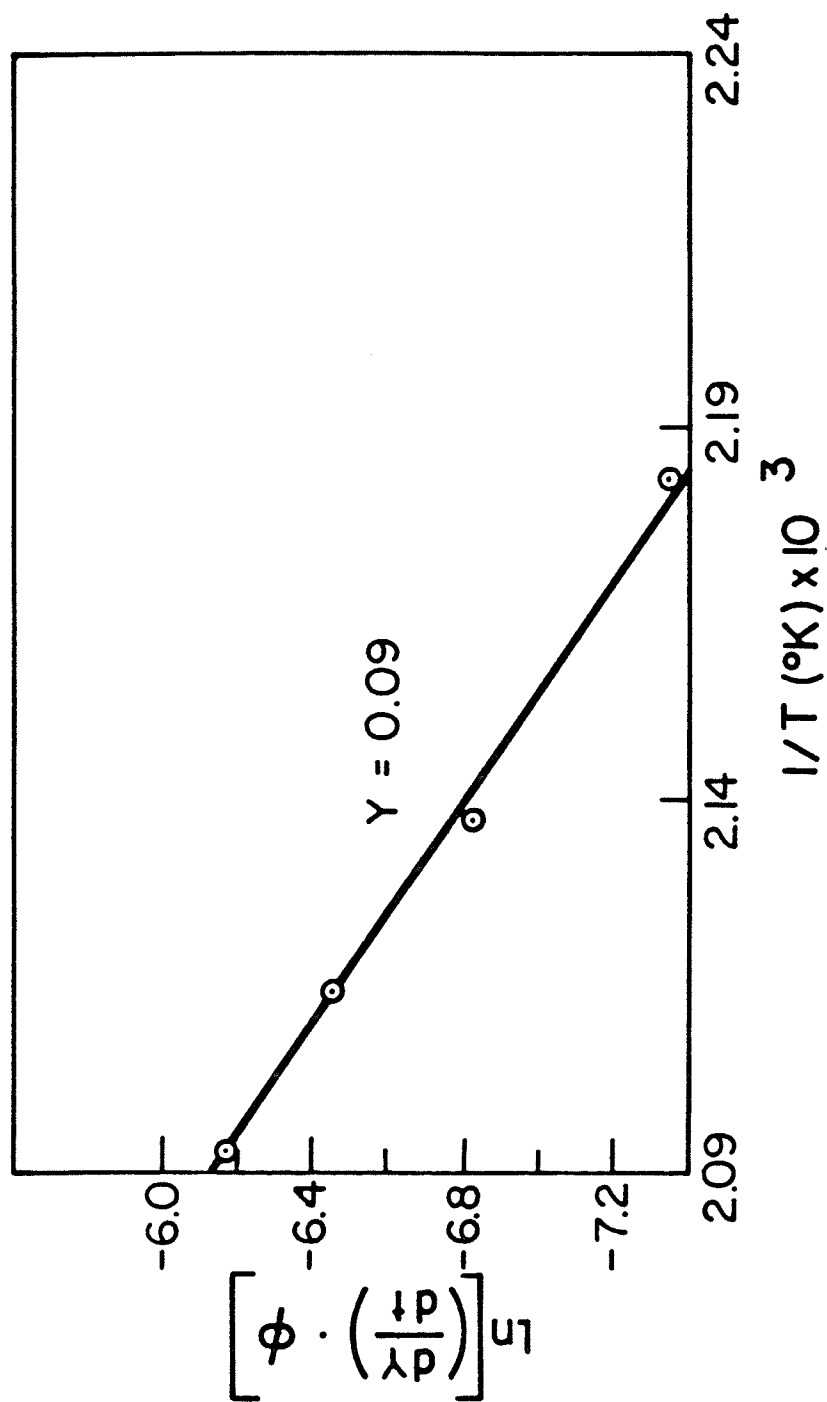


Fig. 4.35 Activation plot for sub peak 1 of the complex dissolution peak after Equation (4.78)

Where C_1 is a constant. Plots $\left[\frac{dY}{dT} e^{-Q^*/RT}\right]$ against Y obtained for sub peak 1 should be linear. However, the narrow range of Y and small values of $\left(\frac{dY}{dT}\right)$ associated with sub peak 1 were not adequate for a satisfactory analysis. The plot shown in Fig. 4.36 is approximately linear and yields a value of K_0 to be 1.1×10^{10} .

This endothermic peak between $140^\circ\text{--}240^\circ\text{C}$ is attributed to the dissolution of GPB zones which were formed in the temperature range of $25^\circ\text{--}170^\circ\text{C}$. As shown in Fig. 4.26(c), this peak is present in the specimen even after ageing for 6-12 h at 130°C . Therefore, during this stage quenched-in excess vacancies are unlikely to be present and dissolution process will be controlled by the diffusion of solutes. Therefore, the activation energy for diffusion of solutes should be equal to the activation energy required for the formation and migration of vacancies. The value of 109.6 kJ/mole for vacancy diffusion determined in Al-1.7%Cu alloy is in a reasonable agreement with the measured activation energy of 123.9 kJ/mole . This result is also consistent with a value of 125.5 kJ/mole determined for the dissolution of GP zones in AA 2219 (6.2% Cu, 0.28% Mn, 0.20% Fe, 0.1% Si, 0.16% Zr, 0.09% V, 0.06% Ti, 0.08% Zn and $< 0.02\%$ Mg alloy).⁽¹⁸¹⁾

Errors involved in determination of function $f(Y)$ for this peak are expected to be large because of small values of Y and $\left(\frac{dY}{dT}\right)$ involved. The data listed in Table 4.9 show that the heating rate of 5°C/min gives the highest possible values of Y and (dY/dt) . Thus, this heating rate is best suited for the determination of the function $f(Y)$. The plot for determination of the function $f(Y)$ in Fig. 4.36 shows $f(Y)$ to be approximately equal to $(1-Y)$. The value of K_0 of

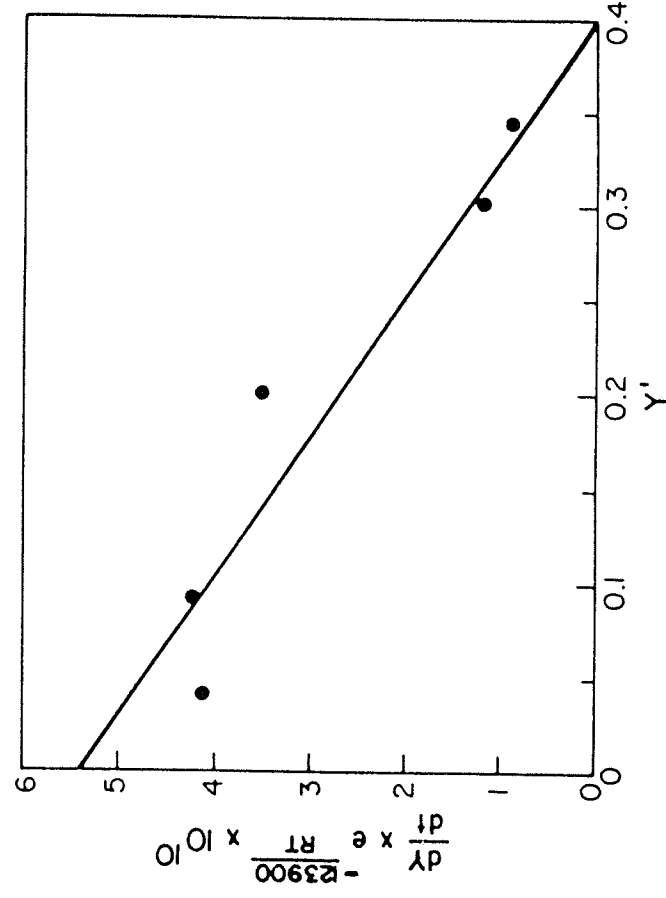


Fig. 4.36 The plot of $\left(\frac{dY}{dt} e^{-\frac{123900}{RT}} \times 10^{10}\right)$ versus Y' , after Equation (4.80)

1.1×10^{10} determined from the slope of this curve is consistent with the value of 3.5×10^{12} reported by Papzian⁽¹⁸¹⁾ for dissolution of GP zones in 2219 alloys. When $f(Y)$ is equal to $(1-Y)$,

$$Y = 1 - \exp(-Kt) \quad (4.81)$$

As pointed out earlier, the value of exponent of t equals to 1 is expected when cylindrical particles of GPB zones dissolve by diffusion of solute atoms. Thus, the GPB zones dissolution process may be considered as radial shrinkage of cylindrical GPB zones by diffusion. The kinetic parameters are listed in Table 4.8.

(b) Analysis of sub peak 2

Sub peak 2 can be analysed in the same manner as sub peak 1 described above. The equation for determination of Q^* of sub peak 2 becomes

$$\ln \left[\frac{dY}{dT} \phi \right] = \ln \left[f K_o \left\{ \left(\frac{Y-1}{f} \right) + 1 \right\} \right] - \left(\frac{Q^*}{R} \right) \frac{1}{T} \quad (4.82)$$

The slope of the best straight line through data points in Fig. 4.37 yields a value of 209.5 kJ/mole for Q^* .

Assuming that the function, $f(Y)$, applicable to this process is the same as relation 2 of Table 4.5, then

$$\left(\frac{dY}{dT} \right) \phi = (1-Y_2) K_o e^{-Q^*/RT} \quad (4.83)$$

Substituting Equations (4.76) and (4.77)

$$\left(\frac{dY}{dT} \right) e^{-Q^*/RT} = \frac{K_o}{\phi} - \left(\frac{Q_o}{\phi} \right) Y \quad (4.84)$$

The data after this equation were plotted in Fig. 4.38. They are linear and yield the same value as that determined separately by Equation (4.57). The average value of K_o determined from the slope

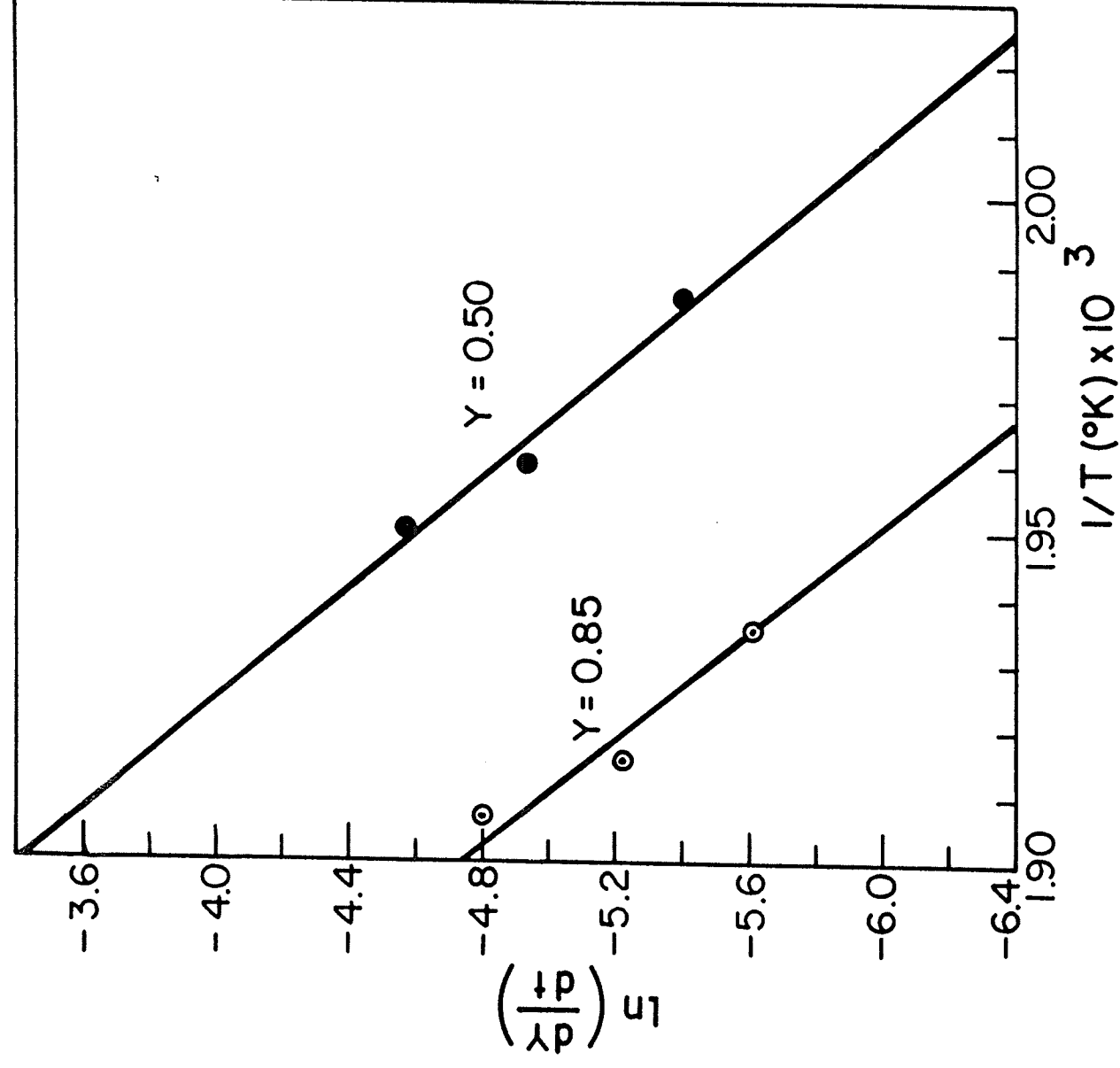


Fig. 4.37 Activation plot for sub peak 2 of the complex dissolution peak at $Y = 0.5$, after Equation (4.82)

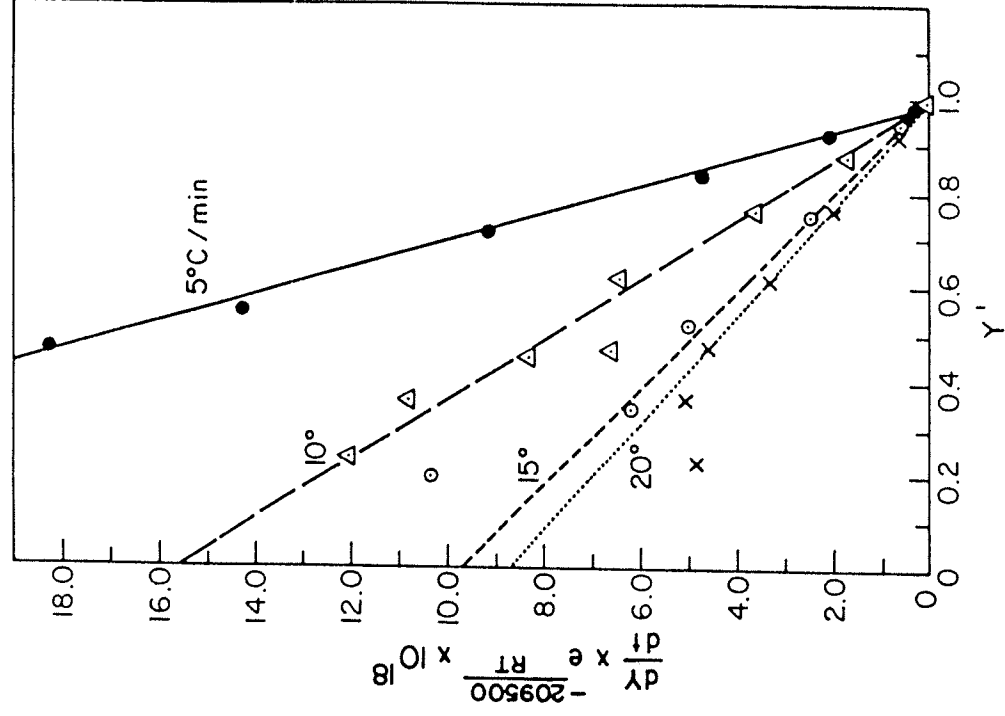


Fig. 4.38 The plot of $(\frac{dY}{dt} \times e^{\frac{RT}{RT}} \times 10^{18})$ against Y' , after Equation (4.84)

is 2.7×10^{18} .

This sub peak occurs between 200°-275°C and appears to be very complex. It can be noted from Fig. 4.26 that this peak is present in the alloy aged up to 4 h at 190°C. The TEM results reported in Section 4.1 clearly showed various microstructural changes, like decoration of dislocation loops, formation of precipitate like complex and nucleation of S' phase, which occur when alloy is aged for times ≤ 4 h at 190°C. It means that all these microstructural changes occur in the range of this peak. Cho, (138) on the basis of resistivity measurements on Al-2.0%Cu-1.1%Mg alloy has also reported microstructural changes around the temperature range of this peak. Thus, the exact nature of the microstructural changes occurring in dissolution process are not very clear. However, GPB zones-dislocation complexes do disappear in this temperature range. The complexity of this peak is evident from the fact that only a small fraction of the GPB zones must have interacted with dislocations and dissolve in the temperature range of sub peak 2. The rest of the GPB zones must have interacted with dislocations and dissolve in the temperature range of sub peak 2. Therefore, the value of Q^* , $f(Y)$ and K_0 determined for this sub peak are only empirical parameters and may not have other significance.

4.2.5.5 The S' Precipitation Peak

Fig. 4.39 shows thermograms due to the precipitation of the S' phase for all the heating rates. It is interesting to note that there is a continuous transition of this peak into the following dissolution peak. It means that, unlike precipitation of GPB zones, precipitation of S' is immediately followed by its dissolution. Total

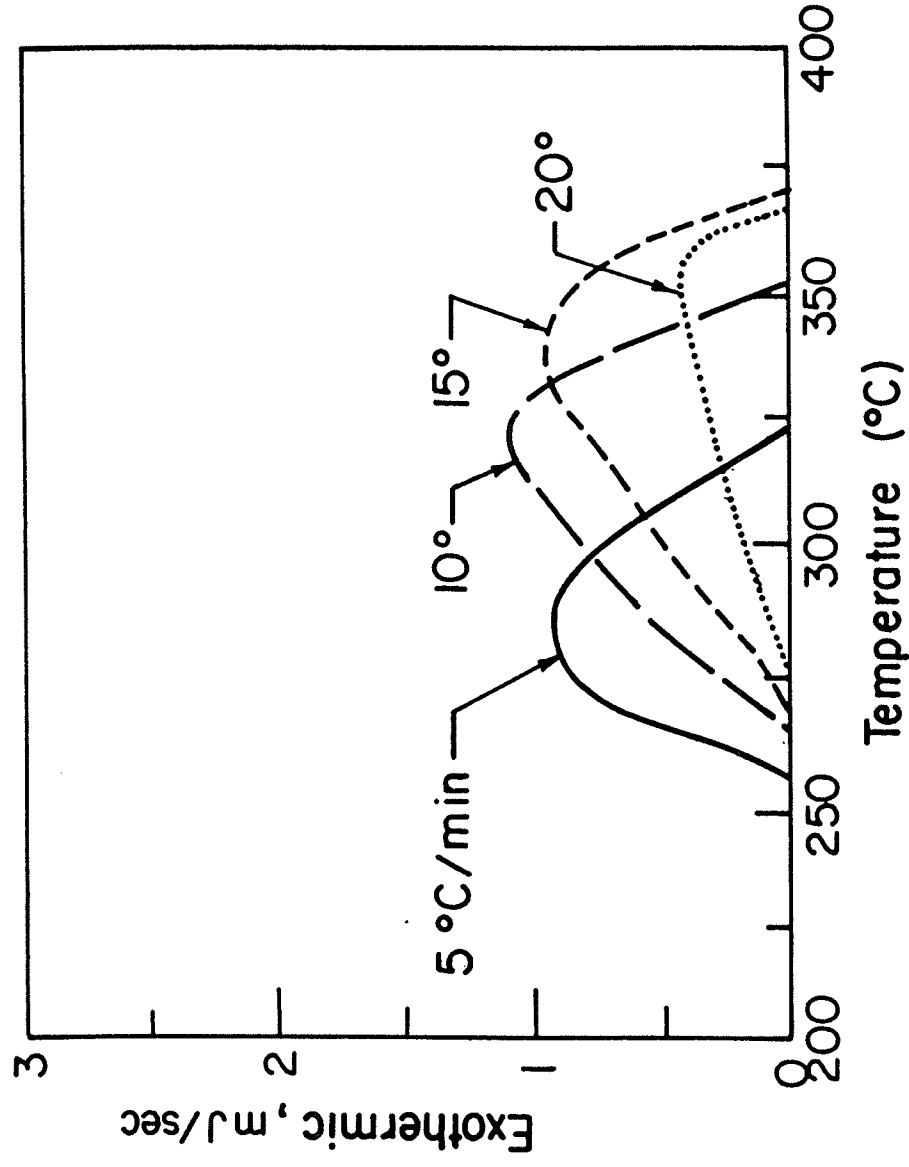


Fig. 4.39 The S' precipitation peaks of the solution treated and water quenched Al-1.53%Cu-0.79%Mg alloy at different heating rates

heat effects associated and temperature characteristics of the precipitation peaks are listed in Table 4.11.

Table 4.11 shows that the peak temperature and the range increase with heating rate, but the total heat effect decreases considerably with increase in heating rate. In the case of the previous peaks the heat effects had remained constant. Fig. 4.40 schematically illustrates the precipitation of a compound of composition X_p from a supersaturated solid solution of composition X_M . When an alloy of matrix composition X_M is heated at a pre-programmed rate ϕ_1 , the precipitates begin to form at temperature T_i and the composition of the matrix approaches (dashed lines) the solvus line. When the solvus line is reached $A(T_f)$, the precipitates start dissolving. The dissolution of the precipitate starts immediately after point A as the diffusivity of the solute elements is quite high at that temperature. This is suggested by the absence of a plateau in the DSC curve (Fig. 4.26(a)). On the other hand, if the transformation takes place at a lower temperature then the rate of transformation is initially higher, but it diminishes with an increase in temperatures as the free energy difference decreases and becomes very small near the solvus temperature. Therefore, the precipitation is followed by an incubation period prior to the dissolution process. Such a situation is observed in the precipitation and dissolution of GPB zones as indicated by a plateau (B) in the DSC curve (Fig. 4.26(a)). Fig. 4.40 shows that at any temperature n_e is proportional to $(X_p - X_e)$ as $(X_p - X_e)$ is usually large. For a heating run n_o is proportional to n_e at T_f . When heating rate is increased from ϕ_1 to ϕ_4 , T_f increases and n_e at T_f decreases. Therefore, n_o decreases. Thus, n_o would

Table 4.11 Total heat effects and temperature characteristics of the peak at different heating rates

Heating rate (°C/min)	Total heat effects Q (J/g)	Peak temperature (°C)			Maximum rate $(\frac{dY}{dT}) \times 10^3$
		Beginning	Maximum	End	
5	8.2431	253.16	282.88	319.85	66.69
10	5.5086	264.88	318.49	348.52	83.64
15	3.3612	271.83	337.29	364.09	92.26
20	1.2619	275.20	340.43	367.74	92.54

decrease with increase in heating rate if T_f is on the solvus curve where solubility increases rapidly with increase in temperature. Such behaviour was observed in this investigation.

Under such conditions the value of n_e cannot be assumed to be the same over the temperature range of transformation. In this case n_0 is assumed to be close to the average value of n_e over the temperature range of the transformation. This average value would of course depend upon the heating rate ϕ . With this assumption, the kinetic analysis of the whole process could be done in the usual manner.

Table 4.12 lists all the experimental data obtained from the S' precipitation peak. The mole fraction of the S' phase transformed at different heating rate over the entire range of the peak temperature, is plotted in Fig. 4.41. The Y-T curves are sigmoidal in shape and shift to a higher temperature with an increase in heating rate. The activation energy of this process was calculated by using both differential and integral techniques. The data points obtained were too scattered to give any definite value of Q^* . It means that the value of n_0 , initially assumed to be the average value of n_e , is in fact very different. This exothermic peak is due to the precipitation of the S' phase. TEM results have shown that the S' particles are rod shaped. Thus, growth of these rod shaped particles may be expected to satisfy Johnson-Mehl type expression where the value of the coefficient, n , is equal to 1 for both diffusion controlled parabolic radial growth and diffusion controlled linear axial growth.⁽⁹⁾ In order to test this supposition $f(Y)$ was assumed to be $(1-Y)$ and appropriate plots were made. Such plots, given in Fig. 4.42 for both

Table 4.12: DSC data obtained from the S' precipitation peak at different heating rates.

S. No.	Temp. T (°C)	Total heat effect up to temp. T (Q/E) (J/g)	Mole Fraction Y	$\frac{dY}{dT} \times 10^3$ /°C	Heating rate °C/min
1	260.12	0.1906	0.0244	8.6268	5
2	270.24	1.4416	0.1843	20.0572	
3	280.36	3.1946	0.4085	23.1074	
4	290.48	5.0116	0.6408	21.6901	
5	300.00	6.4776	0.8283	16.7297	
6	310.12	7.4956	0.9584	8.6576	
7	319.64	7.8207	0.9999	-	
8	319.85	7.8207	1.0000	-	
1	274.80	0.1264	0.0242	5.5570	10
2	284.72	0.5386	0.1032	9.5411	
3	294.64	1.1213	0.2146	12.5287	
4	305.06	1.9057	0.3646	16.0310	
5	315.48	2.8757	0.5502	18.9537	
6	325.40	3.8797	0.7424	18.6389	
7	335.32	4.7442	0.9078	13.2670	
8	345.24	5.1967	0.9944	3.3089	
9	348.21	5.2262	0.9999	-	
10	348.52	5.22612	1.0000	-	
1	285.22	0.1017	0.0319	5.1197	15
2	295.14	0.3144	0.0986	7.9254	
3	305.06	0.6044	0.1895	10.2380	
4	315.48	0.9887	0.3101	12.8469	
5	325.40	1.4543	0.4561	16.4057	
6	334.82	1.9877	0.6234	18.4595	
7	344.74	2.5711	0.8063	17.1465	
8	355.16	3.0420	0.9540	9.8513	
9	360.12	3.1588	0.9906	4.4299	
10	363.59	3.1886	0.9999	-	
11	364.09	3.1886	1.0000	-	
1	290.48	0.0474	0.0396	5.7649	
2	304.76	0.1837	0.1535	9.5657	
3	320.24	0.3853	0.3220	12.6608	
4	335.12	0.6523	0.5450	17.0216	
5	350.00	0.9745	0.8143	17.5842	

S. No.	Temp. (°C) T	Total heat effect up to temp. T (0/E) (J/g)	Mole Fraction Y	$\frac{dY}{dT} \times 10^3$ /°C	Heating rate °C/min
6	358.33	1.1244	0.9396	12.0978	20
7	366.67	1.1956	0.9990	1.4066	
8	367.74	1.1967	1.000	-	

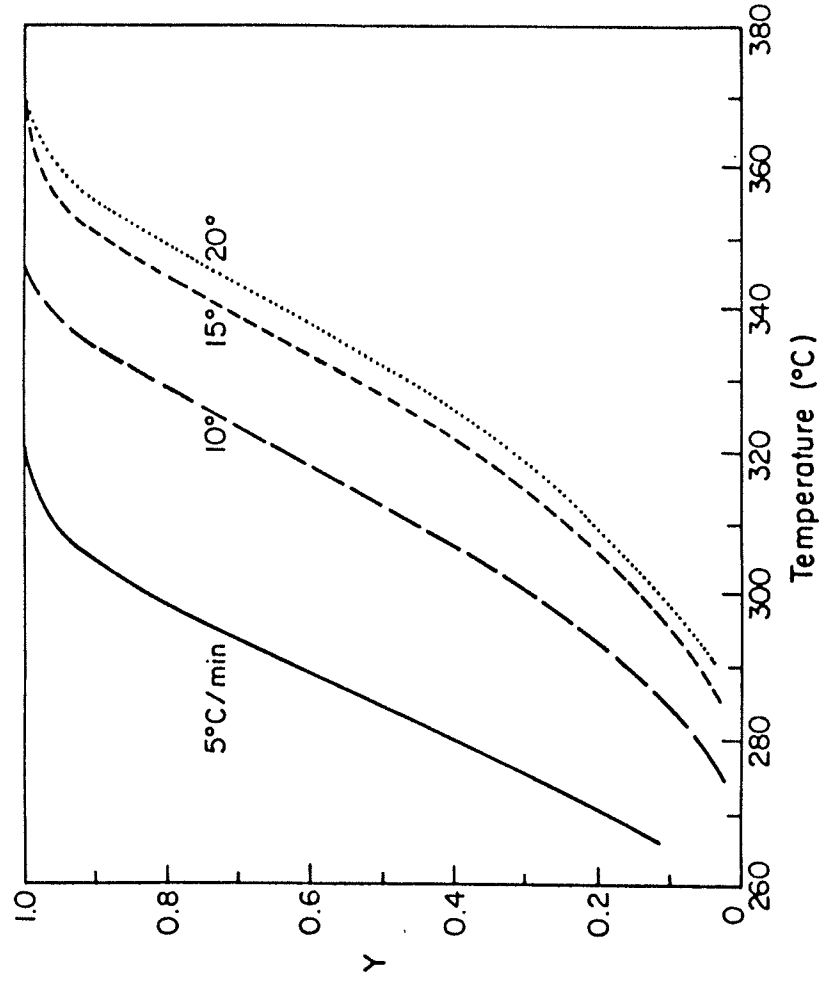


Fig. 4.41 Y versus temperature plots from the precipitation of S'

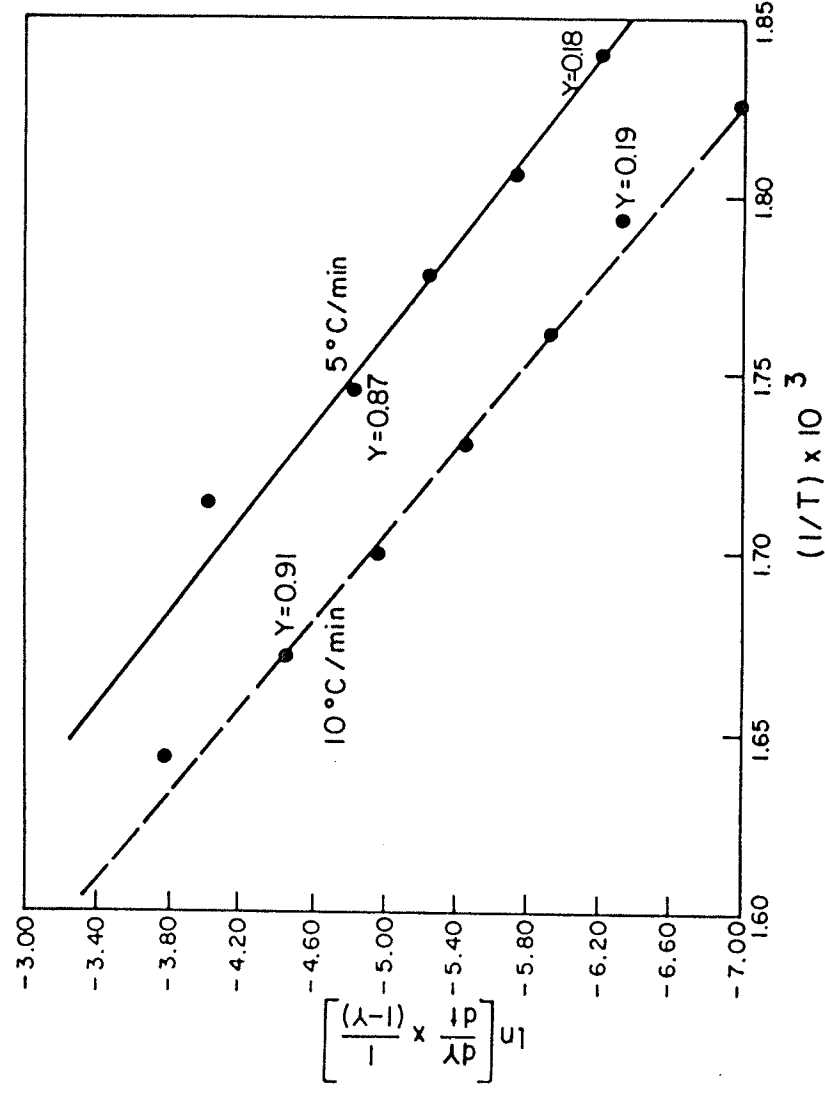


Fig. 4.42 $\ln \left[\frac{dY}{dt} \times \frac{1}{1-Y} \right]$ versus $(1/T)$ plots after Equation (4.64) for the S' precipitation peak

5° and 10°C/min heating rates are linear over a wide range of volume fractions. Similar plots for higher heating rates yielded considerable scatter most likely because of uncertainty in the value of n_e . These plots (Fig. 4.42) yield average values of activation energy Q^* of 129.9 kJ/mole which is close to the activation energies required for the diffusion of solute atoms. This value of activation energy is also consistent with 117.1 kJ/mole reported for the formation of the θ' phase in AA 2219 alloy.⁽¹⁸¹⁾ The K_0 value of 2.55×10^9 is very close to 3×10^9 found for precipitation of the θ' phase in AA 2219.⁽¹⁸¹⁾ The kinetic parameters of the precipitation of the S' phase are listed in Table 4.3.

4.2.5.6 The S' Dissolution Peak

Fig. 4.43 shows the S' dissolution peaks for all the heating rates. Table 4.13 lists characteristic temperatures and total heat effects associated with these peaks. It can be seen that the value of Q decreases and the entire peak shifts only slightly while the temperature range remains approximately constant with an increase in the heating rates. Various experimentally determined parameters related to this peak are listed in Table 4.14. The mole fraction of the S' phase dissolved as a function of temperature is plotted in Fig. 4.44(a).⁽⁹⁾ The curves are sigmoidal in shape and shift slightly to higher temperatures when heating rate is increased from one to the other. The initial stage of these curves is characterized by a higher rate of dissolution and reaches a maximum on further transformation. Then the rate of transformation diminishes towards the end of the dissolution process. Fig. 4.44(a) also shows that

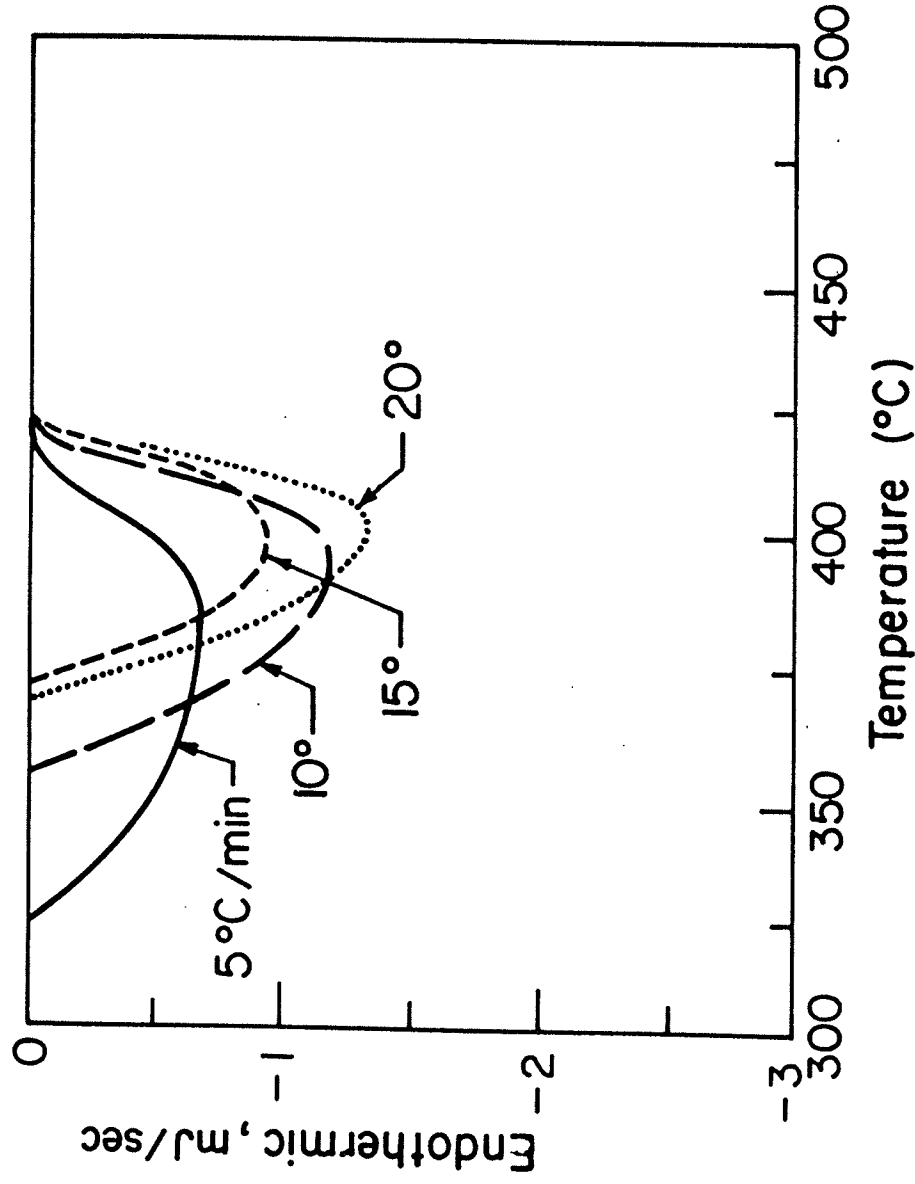


Fig. 4.43 The S' dissolution peak of the solution treated and water quenched Al-1.53%Cu-0.79%Mg alloy at different heating rates

Table 4.13: Characteristic temperatures and total heat effects associated with the dissolution of the S' precipitates.

Heating Rate (°C/min)	Total heat effect Q (J/g)	Peak temperature °C		Maximum $\frac{dY}{dT} \times 10^3$ /°C	$(T_i - T_f) = \Delta t$
		Beginning (T _i)	Minimum Final (T _f)		
5	9.5316	380.36	380.38	419.85	15.134
10	6.4250	384.92	392.60	425.40	20.930
15	3.8977	389.88	399.80	430.06	26.660
20	1.8113	398.81	399.59	434.40	28.520
					35.59

Table 4.14: Data obtained from the S' dissolution peak at different heating rates.

S. No.	Temp. (°C) T	Total heat effect up to temp. T (Q/E) (J/g)	Mole Fraction Y	$\frac{dY}{dT} \times 10^3$ /°C	Heating rate °C/min
1	329.76	0.2542	0.0281	5.1159	5
2	340.48	0.9654	0.1068	9.3259	
3	350.00	1.8836	0.2083	11.6708	
4	359.52	2.9706	0.3285	13.3228	
5	370.24	4.3556	0.4816	14.6551	
6	380.36	5.7426	0.6350	15.1347	
7	390.48	7.1126	0.7865	14.3095	
8	400.00	8.2346	0.9106	11.1378	
9	409.52	8.9161	0.9859	4.2100	
10	419.05	9.0433	0.9999	-	
11	419.85	9.0433	1.0000	-	
1	355.16	0.1353	0.0222	5.7841	10
2	365.08	0.6965	0.1143	12.3944	
3	375.00	1.5980	0.2621	17.0762	
4	384.92	2.7370	0.4490	19.9964	
5	394.84	4.0000	0.6562	20.7946	
6	404.76	5.1970	0.8526	17.3797	
7	415.18	5.9822	0.9814	6.4219	
8	425.10	6.0958	0.9999	-	
9	425.40	6.0958	1.0000	-	
1	372.52	0.1368	0.0370	8.9137	15
2	379.96	0.4785	0.1294	15.9591	
3	389.88	1.2116	0.3276	23.5600	
4	399.90	2.1537	0.5824	26.6561	
5	409.72	3.0787	0.8325	21.5626	
6	419.64	3.6225	0.9796	6.6216	
7	425.10	3.6928	0.9986	0.7640	
8	429.56	3.6981	0.9999	-	
9	430.06	3.6981	1.0000	-	
1	375.00	0.0610	0.0355	8.9340	20
2	382.84	0.2469	0.1436	18.0246	
3	390.38	0.5267	0.3065	25.0777	
4	398.81	0.9246	0.5380	28.5260	
5	406.25	1.2791	0.7443	25.0777	
6	414.68	1.5810	0.9199	14.4980	

S. No.	Temp. (°C) T	Total heat effect up to temp. T (Q/E) (J/g)	Mole Fraction Y	$\frac{dY}{dT} \times 10^3$ /°C	Heating rate °C/min
7	421.63	1.6953	0.9865	4.2319	
8	432.04	1.7185	0.9999	-	
9	434.40	1.7186	1.0000	-	

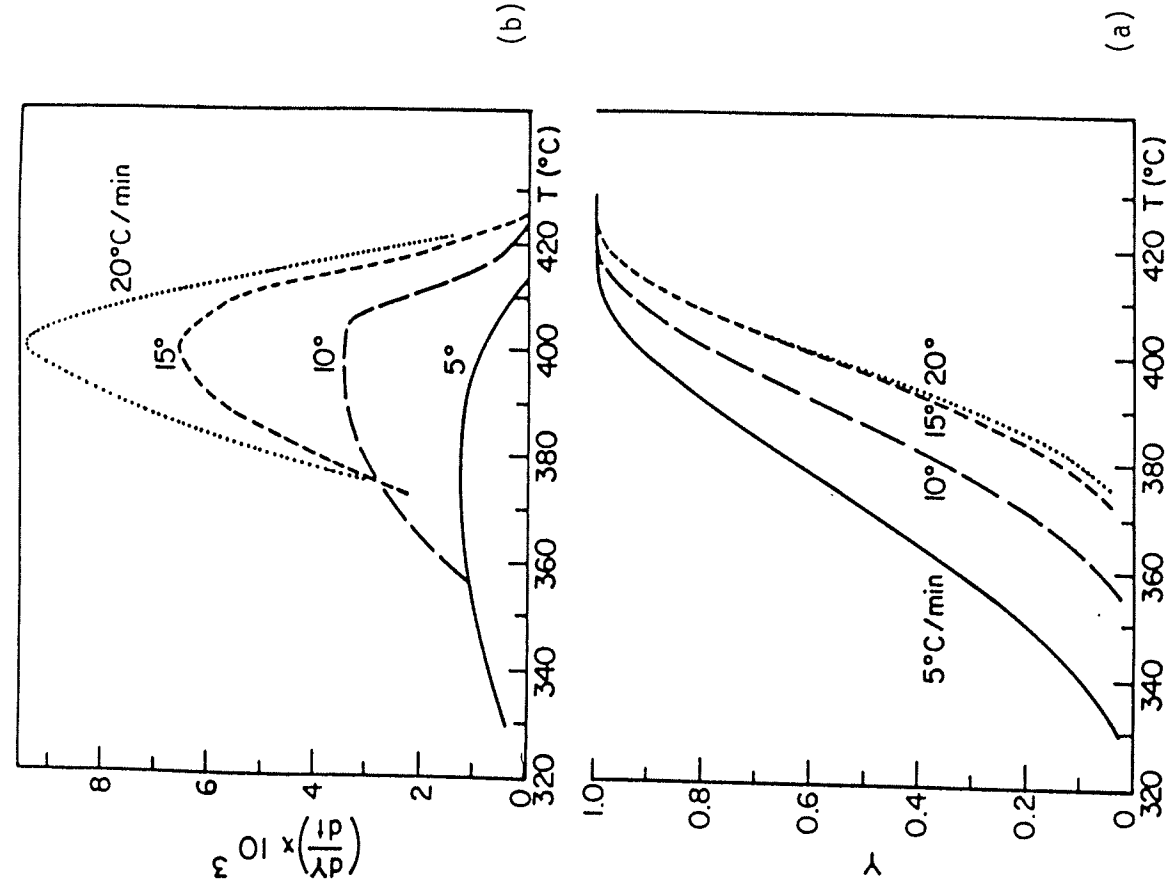


Fig. 4.44 (a) Y versus T curve for the S' dissolution peak
 (b) Variation of $\left(\frac{dY}{dT}\right)$ with temperature at different heating rates

at higher heating rates (20°C/min) the curves overlap when roughly 70% of the S' has dissolved into the matrix. There is a slight shift in peak position when heating rate is increased from 5° to 10°C/min. However, when heating rate is increased from 15° to 20°C/min, the peak positions are identical (Table 4.13). This is clearly demonstrated by plots of $(\frac{dY}{dt})$ against (T) in Fig. 4.44(b). It shows that maximum rates are insensitive to temperature. These results suggest that the dissolution process is not controlled by kinetics but rather by thermodynamics, i.e. the amount of precipitates which needs to go into solution under equilibrium condition is independent of heating rates.

In the expression

$$Y = \frac{n}{n_e}$$

for the dissolution process at a certain fixed temperature, n is the amount of precipitate which has gone into the solution and n_e is the amount of the precipitate which should go into solution under equilibrium conditions. n and n_e are shown in Fig. 4.45. It is clear from the schematic diagram that n_e is very small at a temperature close to the start of the dissolution peak. Since n_e is small, all of it may dissolve and equilibrium composition of matrix will be approached. If the rate is high, i.e. temperature is high enough, the rate of heat absorption would simply be proportional to n_e . This process would be a thermodynamically controlled process.

In order to test this further it was assumed that n_e in the kinetic expression for dissolution is $n_o g$ where g is a constant. On this basis an analysis of the experimental data was attempted. In

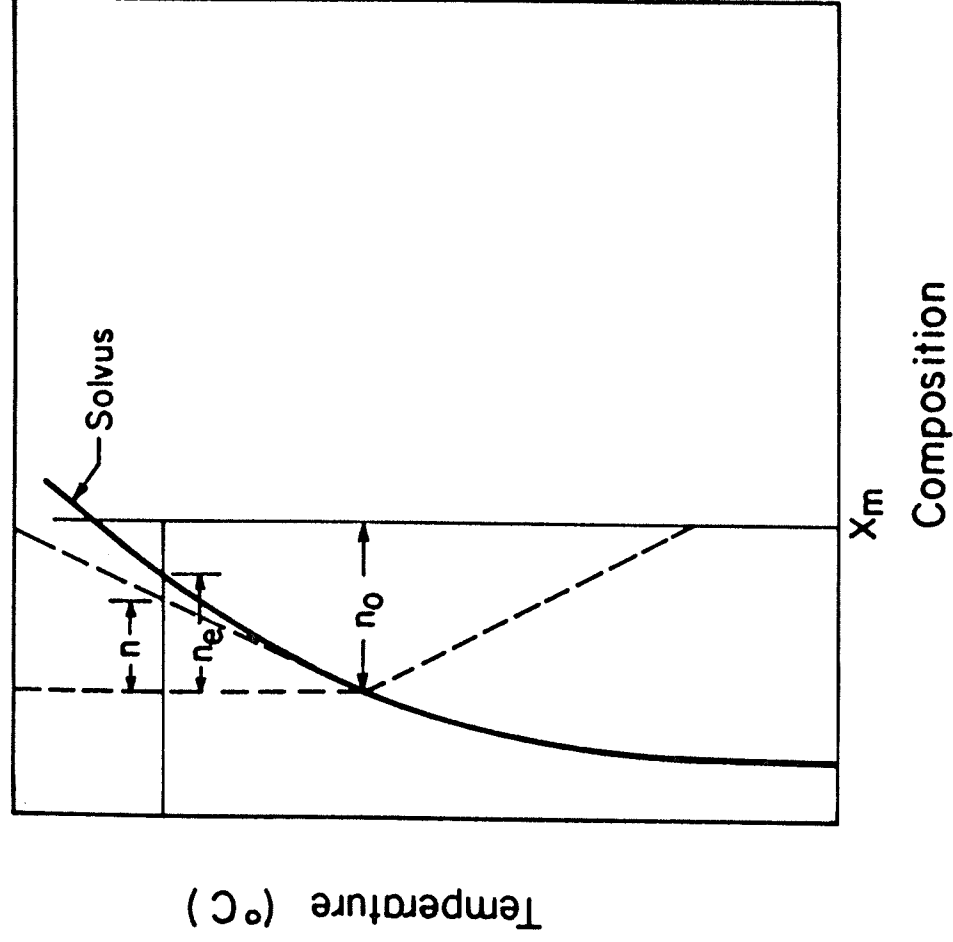


Fig. 4.45 Schematic diagram showing the variation of the composition of the matrix on heating

order to estimate activation energy, Q^* , plots were made after Equations (4.54) and (4.57). The plots show a considerable scatter in the data and no definite value of Q^* could be determined. The model relation 2 (Table 4.5) was also tested by making suitable plots. For some of the heating rates the plots were almost linear, but the slopes were very high. Therefore, it is concluded that the dissolution of S/S' is a thermodynamically controlled rather than a kinetically controlled process.

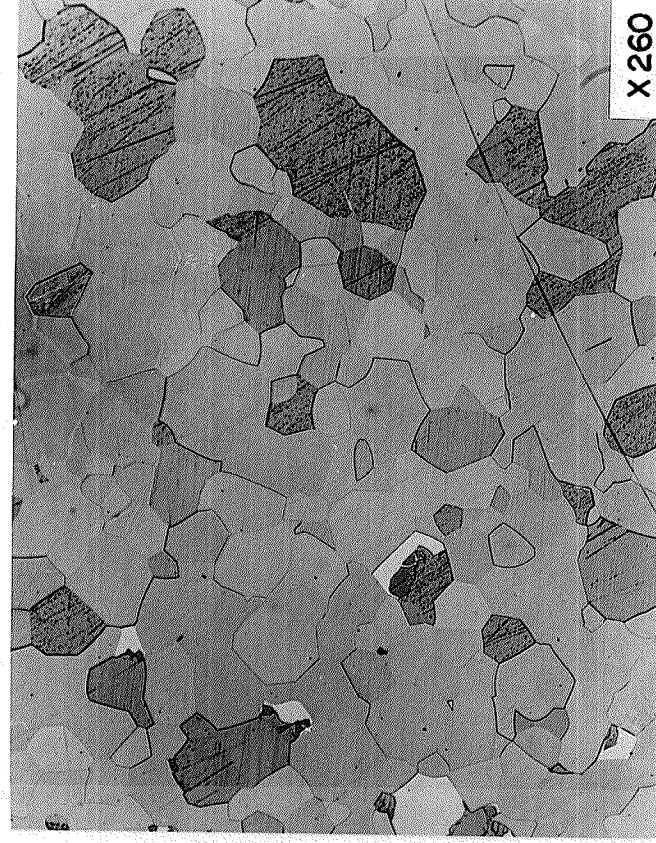
CHAPTER V

EFFECTS OF Si ADDITIONS ON THE Al-1.50%Cu-0.75%Mg ALLOY

The Al-1.50%Cu-0.75%Mg alloys containing various amounts (0, 0.23, 0.49, 0.76 and 1.03%) of Si were homogenized, solution treated and aged. The effects of Si addition were evaluated using results of optical, transmission and scanning electron microscopy and DSC techniques.

5.1 THE INSOLUBLE PHASE IN Si CONTAINING ALLOYS

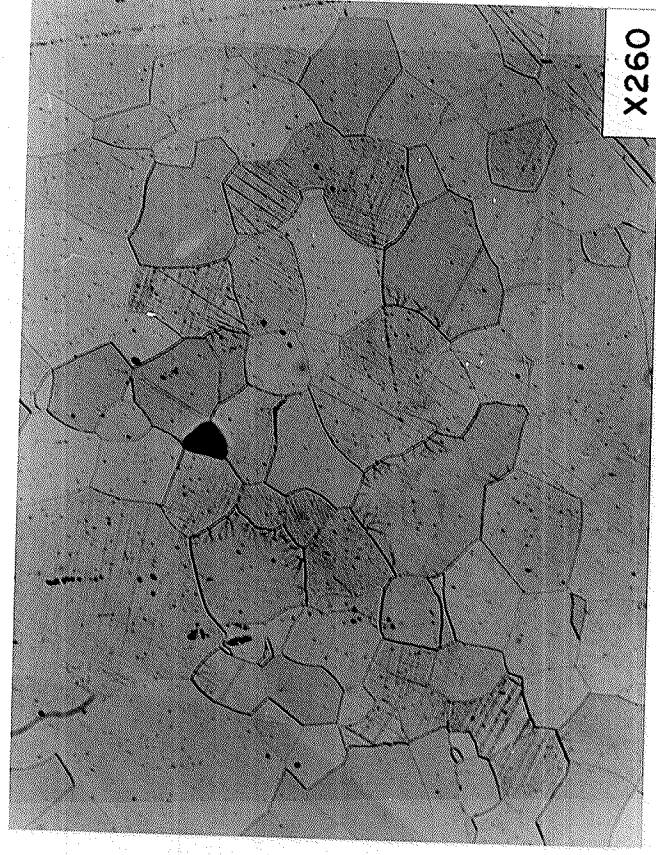
The optical microscopic observations suggested the presence of insoluble particles in alloys containing $\geq 0.49\%$ Si under all conditions of the heat treatment. The amounts of insolubles increased with an increase in Si content as shown in Fig. 5.1(a) - (e). At higher magnification the micrograph in Fig. 5.2, which is obtained from an alloy containing 1.03%Si, shows the insoluble particles to have well defined geometrical shapes. The Al-Cu-Mg-Si alloys depending upon their composition may contain one or more of the CuMgAl_2 (S), Mg_2Si (β), Si, CuAl_2 (θ) and $\text{Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$ (Q) phases as insoluble particles.⁽¹⁵⁶⁾ Suzuki et al.⁽¹²⁸⁾ have not reported the presence of any insoluble particles in high purity Al-2.0%Cu-0.9%Mg-0.5%Si alloy. However, there is evidence for the presence of insolubles in commercial aluminum alloys. Lloyd⁽⁸⁾ has observed large as well as submicron size dispersoids containing Fe, Mn, Si and Al in a solution treated and aged alloy containing 1.34% Cu, 0.65% Mg, 0.94% Si, 0.29% Mn, 0.26% Fe and 0.013% Ti. Bonfield and Datta⁽¹⁵⁸⁾ and Kowatschewa et al.⁽¹⁸⁶⁾ have also observed insolubles in the



(a)

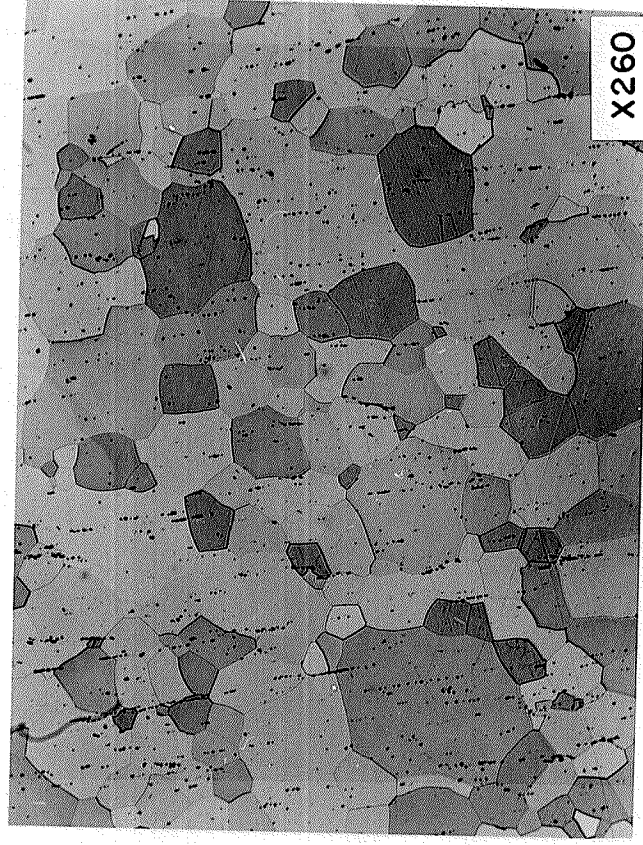


(b)



(c)

X260



(d)

X260

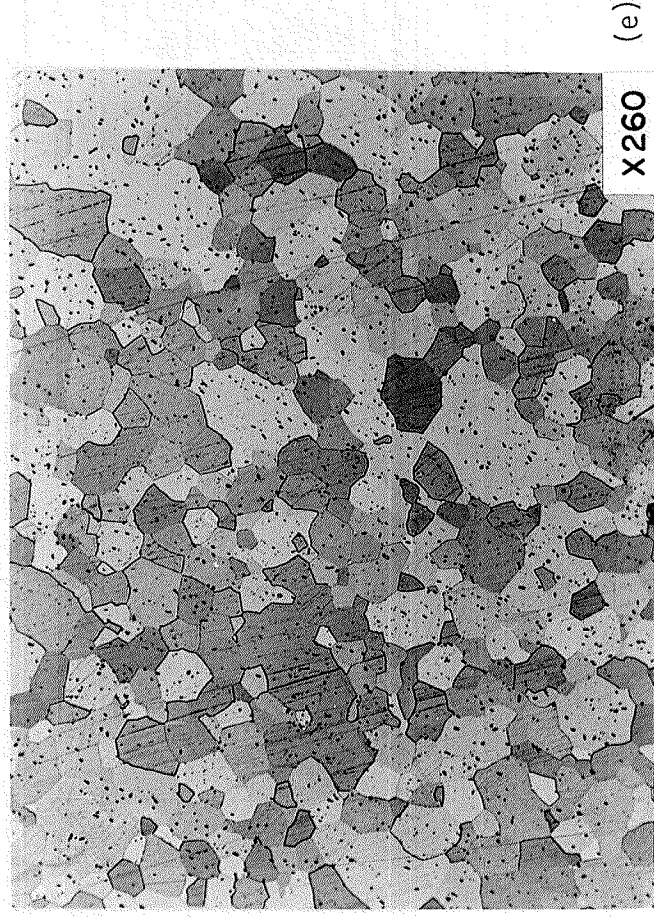


Fig. 5.1 Optical micrographs of alloys solution treated at 530°C for 1 h and water quenched. (a) Si free, (b) 0.23% Si, (c) 0.49% Si, (d) 0.76% Si and (e) 1.03% Si

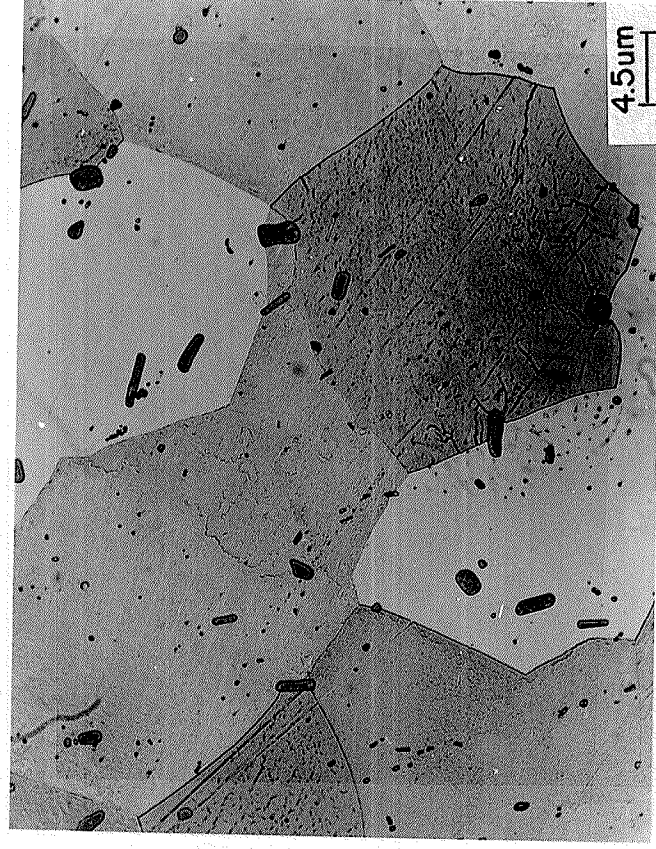


Fig. 5.2 Optical micrograph of the Al-1.52%Cu-0.77%Mg-1.03%Si alloy solution treated at 530°C for 1 h and water quenched showing insoluble particles

Al-4.0%Cu-0.8%Mg-0.7%Mn-0.5%Fe alloy and commercial alloys containing 12 to 22% Si respectively. Thus, the presence of the insoluble particles and their characteristics in high purity Al-Cu-Mg-Si alloys have not been established. The insolubles observed in the present study are likely to affect various properties such as grain size and the precipitation behaviour of the alloys.

5.1.1 Effects of the Insolubles on the Grain Size of the Alloys

The decrease in the grain size due to progressive addition of Si, as observed in Section 5.2, is due to the presence of the insoluble particles. The presence of large particles induce local deformation around them during processing, and act as nucleation sites for recrystallization. The disperse particles that are at grain boundaries impede boundary migration and inhibit recrystallization and grain growth. (187-189)

Zener's (190) model for the interaction of the grain boundaries with spherical particles is shown in Fig. 5.3. The total pull of the particle on the grain boundary, f , is given by:

$$f = 2\pi r \sigma \cos \theta \sin \theta \quad (5.1)$$

where, r is the radius of the second phase particle,

σ is the surface tension and

θ is the angle between equilibrium position of the boundary

and the vector σ

The force ' f ', also a drag force, is maximum when $\theta = 45^\circ$ and hence

$$f = \pi r \sigma \quad (5.2)$$

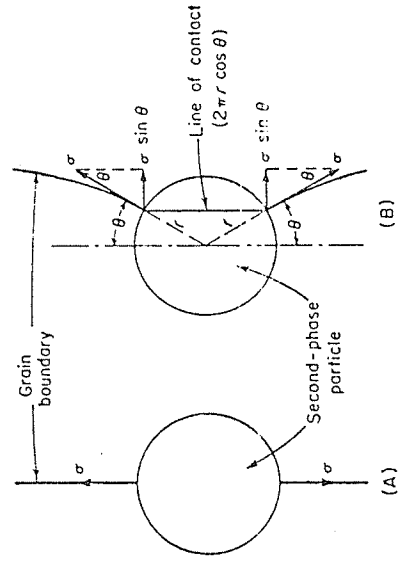


Fig. 5.3 Schematic diagram showing interaction between a grain boundary and a second phase particle

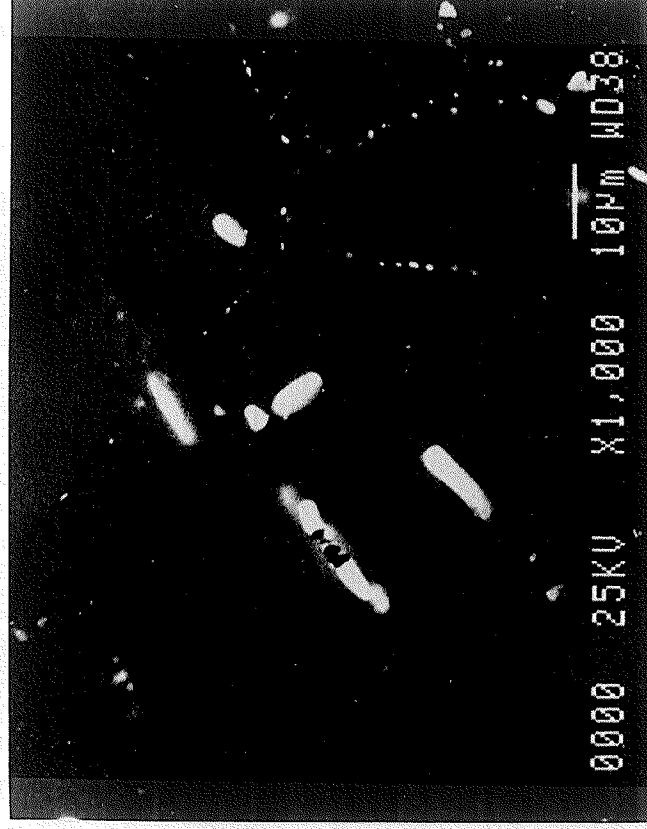


Fig. 5.4 Back scattered image of 1.03% Si alloy aged at 190°C for 65 days

Fig. 5.2 shows how the grain boundary is dragged around the particles. The alloy containing 0.76% Si also showed similar features. Thus, the drag force is directly related to the size of the particles.

The effect of second phase particles in hindering grain boundary motion becomes greater and more effective if present in abundance. Therefore, it is likely that the decreased grain size with increasing amount of Si is due to change in size, shape, distribution, volume fractions and characteristics of particles themselves.

5.1.2 Morphology and Distribution of Insolubles

The optical micrographs of solution treated and quenched specimens of the 0.49, 0.76 and 1.03% Si alloy show the presence of a large number of insoluble particles (Figs. 5.1 and 5.2). Some of the particles may be too small to be resolved. Therefore, the morphology and distribution of the insoluble particles in all the alloys were examined in the scanning electron microscope in the back scattered mode. The distribution of insolubles in the 1.03% Si alloy solution treated, quenched and aged for 65 days at 190°C is shown in Fig. 5.4. The shapes of the particles within the grains are either nearly cylindrical or oval or irregular. Heavy cold working and extended ageing could have caused the particles to be free from sharp edges, as shown in Fig. 5.5 of a 1.03% Si alloy aged for 48 h at room temperature. The sizes of these particles are in the range of about a few to ten microns. Much smaller and nearly spherical insoluble particles are uniformly distributed along the grain boundaries (Fig. 5.4). The alloy with 0.76% Si showed grain boundary particles which



Fig. 5.5 Back scattered image of insoluble particles showing perfectly rounded edges

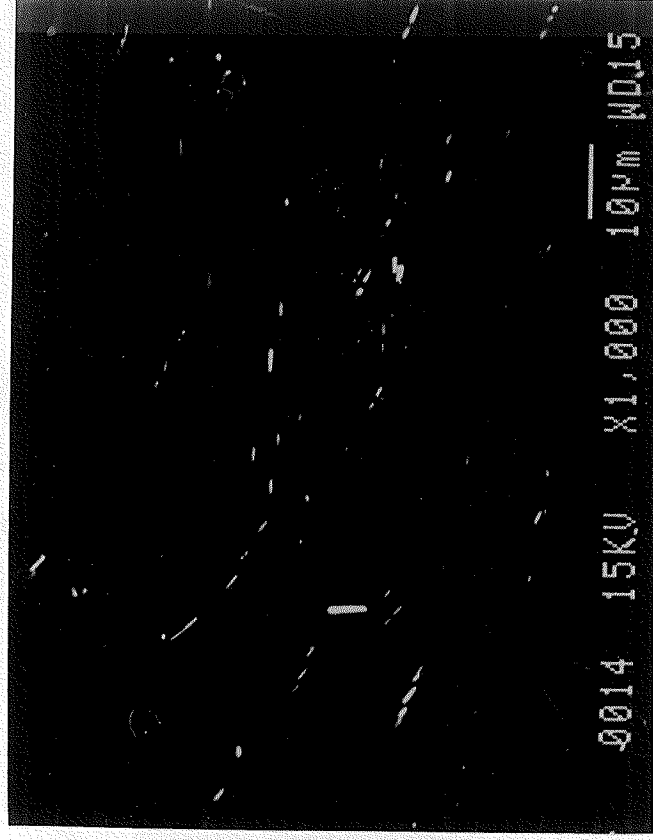


Fig. 5.6 Back scattered image of a 0.76% Si alloy aged at room temperature for 48 h

were similar to those found in 1.03% Si alloys. Alloys with 0.76% Si also contain cylindrical particles within the grains (Fig. 5.6). The maximum size of the particles observed in these alloys was of the order of 5 μm . As the Si content decreased, the number of the particles in the matrix and at the grain boundaries decreased, but the size of the particles at the grain boundaries remained unchanged. This is shown in Fig. 5.7(a) for 0.49% Si alloy. Nearly spherical particles of approximately 1.5 μm diameter are present at the grain boundaries. Much smaller and nearly spherical particles are observed within the matrix (Fig. 5.7(a)). In a few areas these particles appear to align themselves along certain directions. Such a distribution could be the result of extensive cold deformation given to these alloys prior to solution heat treatment. The Si free alloy and alloy with 0.23% Si did not show the presence of insoluble particles.

5.1.3 Volume Percentages of the Insoluble Particles

The volume fractions of the insoluble particles measured in the 0.49, 0.76 and 1.03% Si alloys are plotted in Fig. 5.8. The variation of the fraction of insoluble particles seem to be non-linear. It shows that the volume percentage of the insoluble phase increased due to the addition of Si to these alloys. The solubility of Si in these alloys is estimated to be about 0.35% by extrapolating the curve shown in Fig. 5.8. This is consistent with the observation that the alloy with 0.23% Si had no insoluble particles in them.

5.1.4 Energy Dispersive Analysis of the Insoluble Particles

The chemical composition of the insoluble particles was

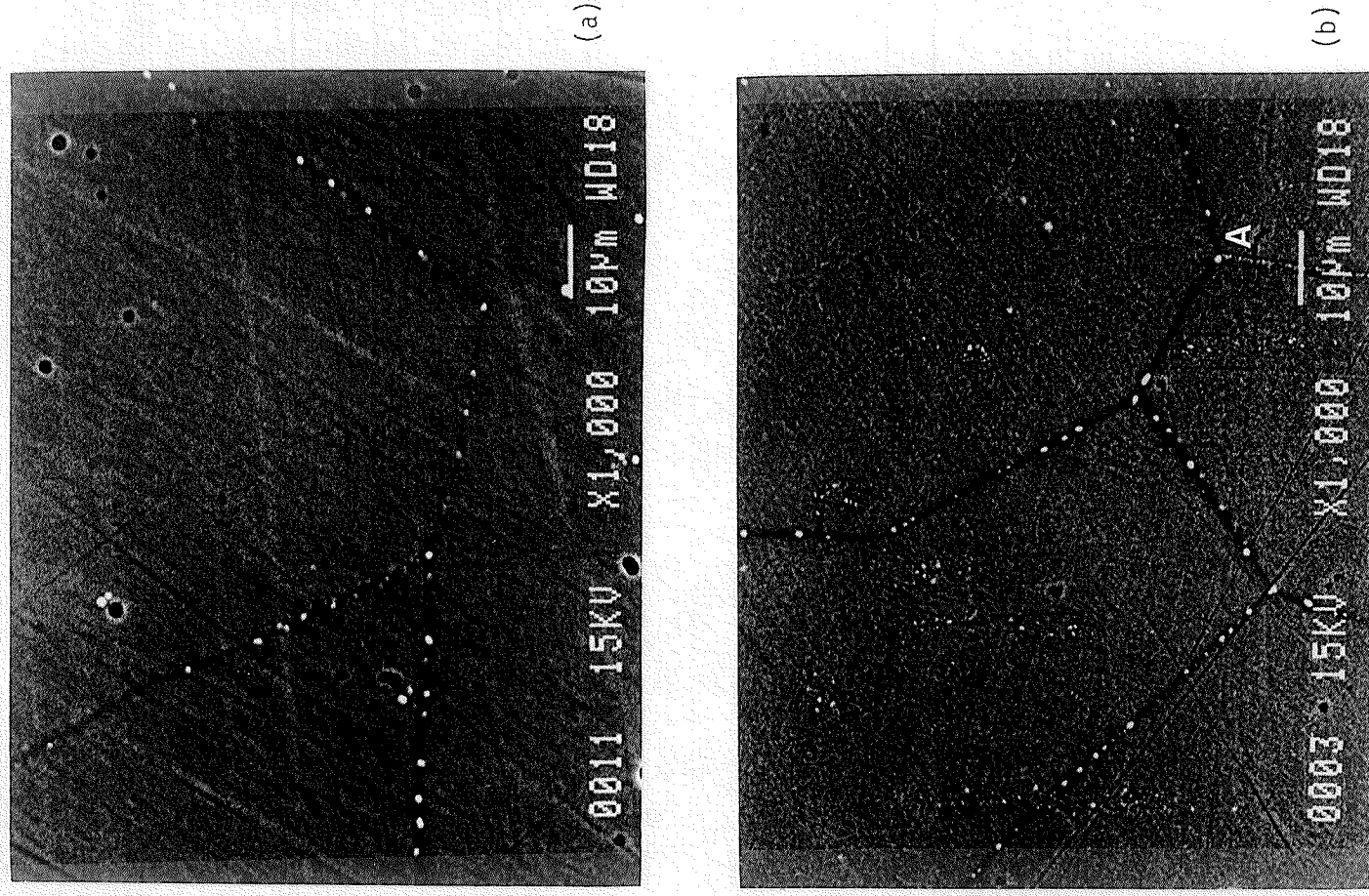


Fig. 5.7 The back scattered images of 0.49 Si alloy
(a) solution treated and aged for 48 h at room temperature
(b) solution treated and aged for 65 days at 190°C

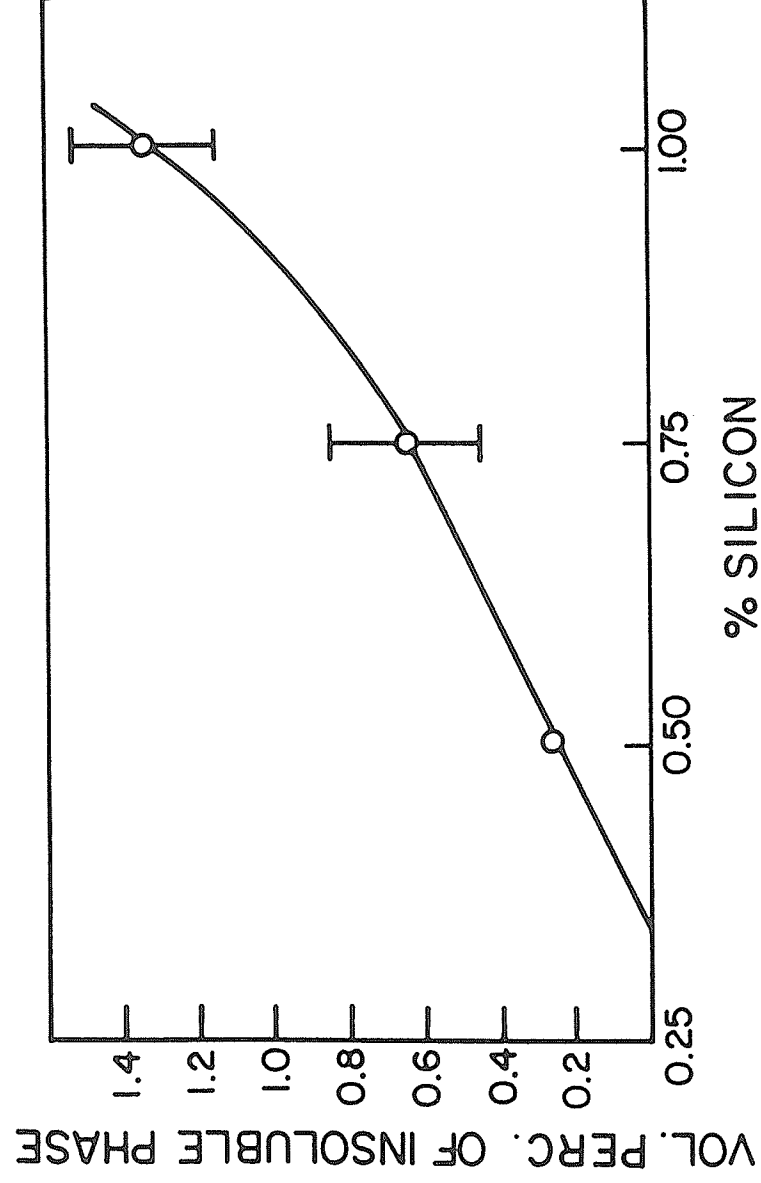


Fig. 5.8 Variation of the volume percentage of insolubles with Si content of the alloy

determined by energy dispersive x-ray analysis (EDS) in SEM. Many x-ray spectra were obtained from large electrolytically extracted particles and insolubles present in the metallographic specimens of all the Si bearing alloys. The results are presented in the following sections.

5.1.4.1 Analysis of the Extracted Particles

A typical x-ray spectrum, obtained at an accelerating voltage of 12 kV from a large particle (Fig. 5.9), electrolytically extracted from the 1.03% Si alloy aged at 190°C for 144 h, is shown in Fig. 5.10. The x-ray energy peaks are identified to be due to Cu, Mg, Si and Al. Thus, the insoluble is a quaternary compound with Cu, Mg, Si and Al in it.

The accelerating voltages used to obtain spectra influence the spatial resolution of the x-ray signals, the efficiency with which characteristic x-ray are excited from the atoms of the specimen and the absorption. The energies of characteristic K_{α} x-rays from the constituent elements of the insoluble particles, Cu, Mg, Si and Al are 8.04, 1.235, 1.739 and 1.486 keV respectively. Generally, for an efficient production of x-rays the energy of electrons striking the specimen should be about 2.5 to 3 times the energy of the particular characteristic x-ray. However, 25 keV electrons which are appropriate for the production of K_{α} radiations of copper cause an excessive fluorescence and absorption of x-rays from the lighter elements Mg, Si and Al, which cannot be corrected adequately by the usual correction procedures. The energy of Cu L β x-ray (0.95 keV) is of the same order as those of Mg K_{α} and Al K_{α} . Therefore, the use of CuL β radiation

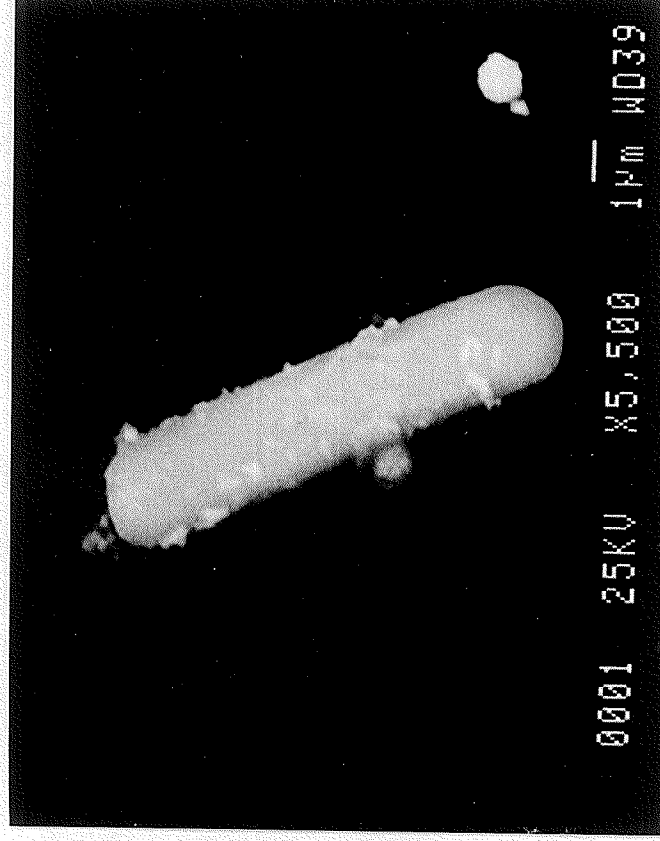


Fig. 5.9 One of the insoluble particles extracted from 1.03% Si alloy aged for 6 days at 190°C

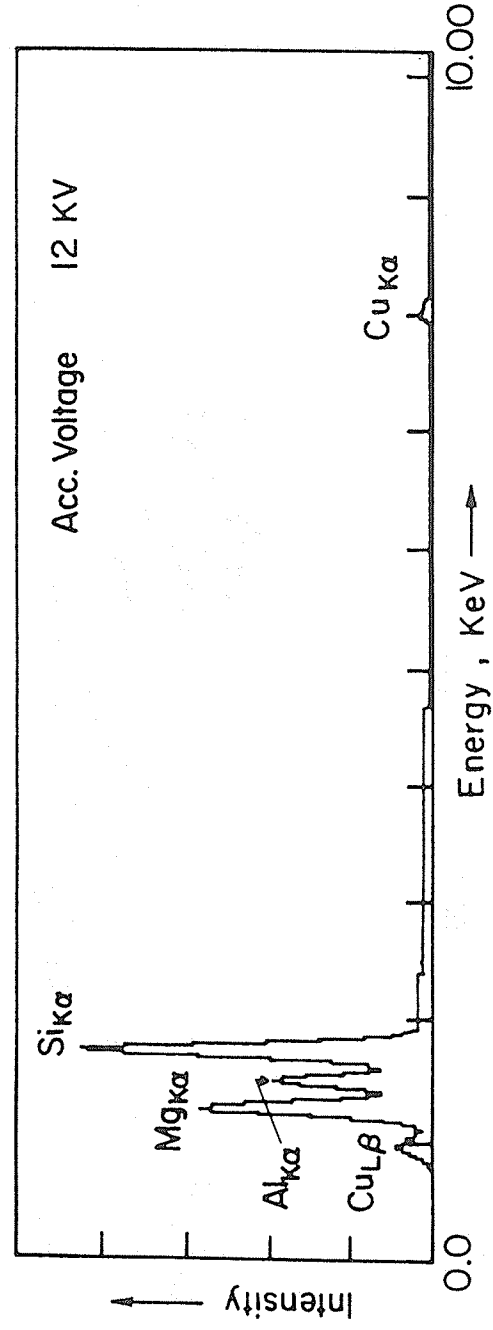


Fig. 5.10 X-ray emission spectrum from an insoluble particle electrochemically extracted from 1.03%Si alloy aged for 6 days at 190°C

instead of Cu K_α should allow the use of an electron beam of lower energy. Unfortunately, it was found that when the energy of the electron beam was less than 10 keV the production of Bremsstrahlung x-rays was excessively high in the vicinity of 1.0 keV region of EDS spectrum. Therefore, in order to determine the optimum accelerating voltage, a number of x-ray spectra from an isolated particle were acquired at 10, 12, 15 and 25 kV accelerating voltages. Quantitative chemical analysis using ZAF correction procedure of Tracor Northern and pure metal standard spectra acquired at the same kV, electron beam current and working distance as the unknown, were carried out. The results are given in Table 5.1. It is seen that 10, 12 and 15 keV electrons yield nearly the same compositions which are significantly different (2.5 to 4.5%) from that observed at 25 kV accelerating voltage. Therefore, it was decided to use accelerating voltages of 10, 12 and 15 kV and use CuL_β , MgK_α and AlK_α x-rays to carry out the chemical analysis. The average values of all measurements made on a number of particles of a given specimen were calculated. The composition of particles in quenched and other heat treated alloys are listed in Table 5.2 along with scatter in the data. It was not possible to extract adequate amounts of insoluble particles from lower Si bearing alloys. But large isolated particles in the bulk specimens of these alloys could be analysed by EDS techniques as discussed below.

5.1.4.2 Analysis of particles in the Bulk Specimens

Insoluble particles in the bulk specimens of Si bearing (0.49 - 1.03%) alloys in solution treated as well in aged conditions, were analysed. All the spectra obtained from large particles were

Table 5.1: Analysis of isolated particle at different accelerating voltages.

Analysis #	Accelerating Voltage (kV)	Composition (Wt %)		
		Cu	Mg	Al
1	10	21.8 $\pm$ 1.4	32.7 $\pm$ 0.5	30.5 $\pm$ 0.7
2	12	20.9 $\pm$ 0.3	33.7 $\pm$ 0.2	30.3 $\pm$ 0.5
3	15	22.1 $\pm$ 0.1	32.9 $\pm$ 0.1	29.7 $\pm$ 0.6
4	25	18.5 $\pm$ 0.5	29.0 $\pm$ 0.5	34.9 $\pm$ 0.6

Table 5.2: EDS X-ray analysis of extracted insoluble particles and the synthetic compound.

	Aging Time, at 190°C (days)	Composition (Wt %)		
		Cu	Mg	Al
103% Si Alloy	0	20.6 $\pm$ 0.4	32.2 $\pm$ 0.4	30.2 $\pm$ 0.4
	6	20.8 $\pm$ 0.3	33.8 $\pm$ 0.3	30.4 $\pm$ 0.3
	24	21.2 $\pm$ 0.5	35.0 $\pm$ 0.9	29.8 $\pm$ 0.7
Synthetic Compound	-	18.9 $\pm$ 0.3	36.2 $\pm$ 0.3	29.8 $\pm$ 0.2

similar (Fig. 5.11) and showed the presence of the Cu, Mg, Si and Al. The composition obtained (Table 5.3) from these insoluble particles are expected to have the least interference from the matrix. This is supported by the observation that EDS analysis of large particles in bulk specimen of 1.03% Si alloy is in good agreement with that of particles electrochemically extracted from the same alloys (Table 5.3). All the spectra obtained from large particles ($\approx 10 \mu\text{m}$) occasionally seen in 0.76% Si alloys were similar and showed the presence of Cu, Mg, Si and Al. The spectra from small particles were not identical with those obtained from the extracted particles (Fig. 5.12) due to the interference from the matrix.

X-rays produced due to the interaction of electrons with the specimen characterize the elements rather than the phases of the excited volume. If it is assumed that the intensity of element i is approximately proportional to the mass of the element i , then a mathematical expression to determine the actual composition of the precipitate can be derived. If W_i and W_m are the weight of insolubles and matrix respectively in the excited volume, then weight fraction, x , can be written as:

$$x = \frac{W_m}{W_i} \quad (5.3)$$

Let,

$W_{\text{Cu}}^e, W_{\text{Mg}}^e, W_{\text{Si}}^e, W_{\text{Al}}^e$ be the weight fractions of elements measured in the excited volume,
 $W_{\text{Cu}}^i, W_{\text{Mg}}^i, W_{\text{Si}}^i, W_{\text{Al}}^i$ be the weight fractions of elements actually present in the insolubles and

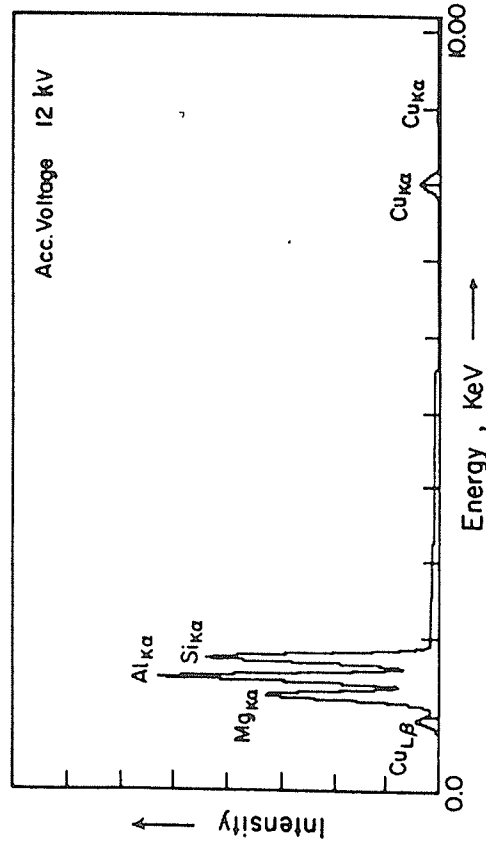


Fig. 5.11 X-ray emission spectrum from a large insoluble particle embedded in the matrix of the 1.03% Si alloy

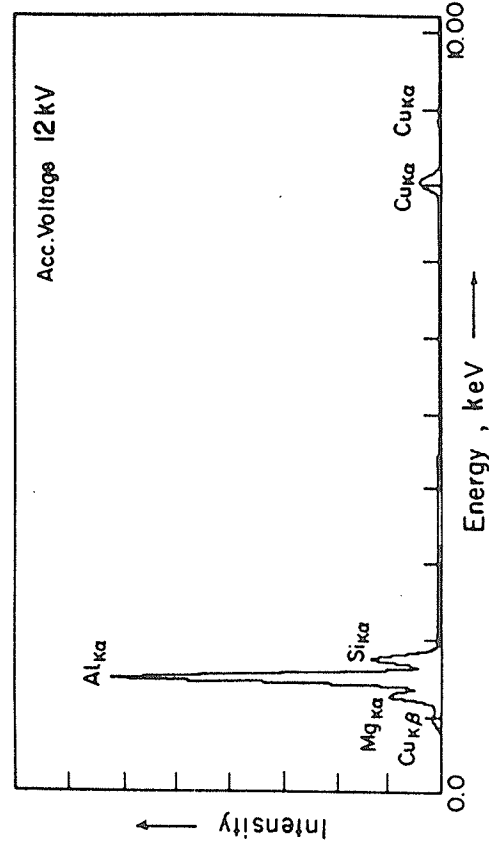


Fig. 5.12 X-ray emission spectrum from a small insoluble particle embedded in the matrix of the 1.03% Si alloy

Table 5.3: Composition of large particles in the bulk specimen of the 1.03% Si alloy.

Heat Treatment	Composition (Wt %)			
	Cu	Mg	Si	Al
As quenched	17.0 ± 0.2	35.5 ± 0.1	30.7 ± 0.2	16.7 ± 0.4
Aged at 190° C, for 65 days	17.0 ± 0.2	35.0 ± 0.3	30.3 ± 0.2	17.6 ± 0.2

$w_{Cu}^m, w_{Mg}^m, w_{Si}^m, w_{Al}^m$ be the weight fractions of elements actually present in the matrix.

Then,

$$w_{Cu}^e = \frac{w_i w_{Cu}^i + w_m w_{Cu}^m}{(w_i + w_m)} = \frac{w_{Cu}^i + x w_{Cu}^m}{1 + x} \quad (5.4)$$

which simplifies to $w_{Cu}^i = w_{Cu}^e (1+x) - x w_{Cu}^m$

$$w_{Mg}^i = w_{Mg}^e (1+x) - x w_{Mg}^m$$

$$w_{Si}^i = w_{Si}^e (1+x) - x w_{Si}^m$$

Where, weight fraction is $\frac{X_i A_i}{\sum X_i A_i}$, X_i is the atom fraction and A_i is the atomic weight. In order to utilize this method, a standard analysis from an extracted particle was performed. Once measurements on particles embedded in a matrix and the matrix are made, the above equations could be used by assuming the value of x . The value of x depends upon the orientation of the particle in the matrix and could be different even if the spectra along the length of the same insoluble are acquired. Since alloys in this investigation are dilute, the second term on the right hand side of the above equations can be ignored. The results of the analysis performed using relation (5.4) on many particles are shown in Table 5.4.

The analyses of smaller particles present in the bulk specimens of Si bearing alloys showed their composition to be similar to those obtained from large particles and agreed well with that of particles electrochemically extracted from the 1.03% Si alloys. The data in Table 5.2 and 5.4 suggests that the effect of electrochemical

Table 5.4 The compositions obtained for smaller insolubles present in bulk specimen of 1.03% Si alloy

Analysis	Heat treatment	Composition (wt%)				Weight fract. of matrix x
		Cu	Mg	Si	Al	
1	As quenched	18.3	35.0	30.6	16.1	0.11
2		18.8	34.7	30.0	16.5	0.25
3		18.8	35.2	29.8	16.2	0.33
Average		18.6 ± .2	34.9 ± .2	30.1 ± .3	16.3 ± .4	
4	Aged for 65 days at 190°C	18.02	35.56	31.20	15.2	0.1
5		17.06	36.00	30.76	16.15	0.06
Average		17.54	35.8	30.98	15.675	

dissolution on the composition of the insolubles is negligible. Thus, the analysis of the insoluble particles in 0.49 and 0.76% alloy were routinely carried out. All the analyses showed similar composition of the particles with those of 1.03% Si alloy.

It is seen from the analysis of insolubles electrochemically extracted and in bulk alloys, that they are of a quaternary phase containing Cu, Mg, Si and Al. The partial quaternary phase diagram (Fig. 2.30) for the Al-Cu-Mg-Si system presented by Collins⁽¹⁵⁶⁾ suggests that the insoluble phase containing all these elements could be Q. Phragman⁽¹⁹¹⁾ has given the analysis of the Q phase to be 20.6% Cu, 31.8% Mg, 31.4% Si and 16.2% Al. However, Mondolfo⁽¹³⁾ found that the chemical composition of Q phase is in the range of 14-17% Cu, 28-30% Mg, 27-29% Si and 30-24% Al. Later, he reported (1976) the work of Schrader who found the Q phase to contain 19.2% Cu, 33.0% Mg, 32.1% Si and 15.7% Al. It appears from the data that the Q phase is stable over a range of compositions. The composition of insolubles found in this investigation (Table 5.2) is within the range of the compound of Q phase as reported by other investigators.

The synthetic single phase quaternary compound which was prepared for crystal structure studies was also analysed by EDS technique under the same operating conditions as were used for analysis of insoluble particles. The composition is listed in Table 5.2 for comparison. It is seen that the composition determined by the EDS technique is in close agreement to the bulk wet chemical analysis (19.3% Cu, 36.5% Mg, 30.2% Si and 14.00% Al) of the compound. It also shows that the analysis of the extracted particles corresponds to that of the synthetic single phase compound.

5.1.5 Crystal Structure of the Insolubles

The x-ray powder diffraction pattern analyses of the extracted insoluble particles are shown in Table 5.5 which contains the d-spacings and estimated relative intensities of all the observed reflections. Phragman⁽¹⁹¹⁾ has reported that the Q phase has a hexagonal structure with $a = 1.032$ nm and $c = 0.405$ nm. As the space group of this compound is uncertain it is not possible to predict the expected diffraction lines in the powder diffraction pattern. Therefore, the quarternary single phase compound of a composition close to that of the Q phase was analysed by x-ray powder diffraction. The 'd' values of diffraction lines from this compound are listed in Table 5.5. Assuming this compound to have the hexagonal structure suggested by Phragman, the values of lattice parameters a and c were calculated by using the Nelson-Riley function and Cohen's least square method.⁽¹⁶⁵⁾

In the Nelson-Riley method the value of the lattice parameter 'a' calculated from (h K 0) lines were plotted against the Nelson-Riley function (Fig. 5.13(a)) and the best value of 'a' was obtained by regression analysis. Using this value of a , the values of c were calculated from the rest of the (h K l) lines and plotted against the Nelson-Riley function (Fig. 5.13(b)). The best value of c was obtained by regression analysis. The values of a and c were also calculated by using a computer program based on the Cohen's least square method. Both these methods gave similar results which are listed in Table 5.6. They agreed well with those reported by Phragman⁽¹⁹¹⁾ ($a = 1.032$ nm and $c = 0.404$ nm). The synthetic compound is therefore considered to be the quarternary phase Q. The reflections and intensities of extracted insolubles compared agree very well with

Table 5.5: X-ray diffraction data obtained from the particles extracted from the 1% Si alloy solution treated and aged at 190°C for various lengths of time and the synthetic quaternary compound (19.3% Cu, 36.5% Mg, 30.2% Si and 14.0% Al).

Line	Synthetic quaternary compound		As quenched		Aged for 6 days		Aged for 10 days		Aged for 24 days	
	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
1	8.932	MS	9.029	M	8.972	M	8.957	M	8.951	MS
2	5.181	S	5.183	S	5.195	S	5.193	S	5.188	S
3	4.480	MS	4.472	MS	4.490	MS	4.478	M	4.474	M
4	3.659	S	3.675	S	3.664	M	3.658	S	3.662	S
5	3.385	MW	-	-	3.384	M	3.384	M	-	-
6	3.156	W	-	-	-	-	3.144	M	3.142	MW
7	-	-	3.006	S	3.002	S	2.988	S	-	-
8	2.593	VS	2.597	M	2.599	VS	2.574	S	2.591	VS
9	2.485	MS	2.482	M	2.487	MW	2.488	M	2.487	M
10	2.396	MS	2.399	MS	2.404	M	2.377	M	2.400	M
11	2.298	VW	-	-	-	-	2.289	W	-	-
12	2.176	VW	-	-	2.183	W	2.175	W	2.177	W
13	2.117	S	-	-	2.121	S	2.122	S	2.121	S
14	2.065	MS	2.083	S	2.071	S	2.087	S	2.081	S
15	2.010	S	2.017	S	2.022	S	2.020	S	2.015	M
16	1.961	VS	1.959	VS	1.968	VS	1.964	VS	1.961	VS
17	1.829	M	-	-	1.830	M	1.828	M	1.831	M
18	-	-	1.800	VS	1.803	VS	1.811	S	1.802	S
19	1.562	MW	1.564	W	1.560	W	1.571	W	1.564	W
20	1.497	MW	-	-	1.498	MW	-	-	1.495	VW
21	-	-	1.429	MW	1.432	MW	-	-	1.438	W
22	1.404	S	1.405	MW	1.397	M	1.411	M	1.403	S
23	1.353	W	1.353	VW	-	-	1.360	VW	1.356	MW
24	1.294	M	-	-	-	-	-	-	1.298	MW
25	-	-	1.276	S	1.281	M	1.281	MW	1.278	MW
26	1.247	M	1.247	M	1.252	M	1.254	M	1.249	MW
27	1.222	M	1.220	MS	1.224	M	1.224	MW	1.223	MW
28	0.8259	VW	0.8256	W	0.8263	W	0.8266	W	0.8266	W
29	0.8056	VW	0.8059	W	0.8056	W	0.8061	W	0.8056	W
30	0.7818	VW	0.7816	W	0.7812	W	0.7816	W	0.7811	W

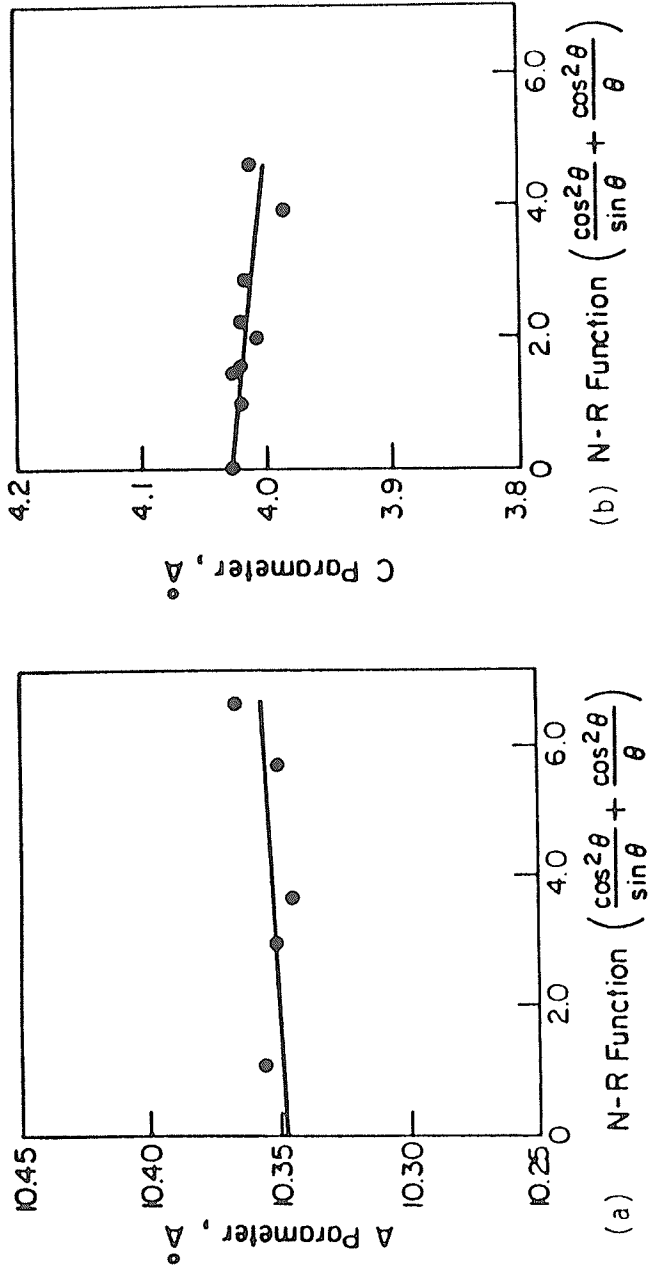


Fig. 5.13 (a) Extrapolation of measured lattice parameter 'a' against N-R function
(b) Extrapolation of measured lattice parameter 'c' against N-R function

Table 5.6: Lattice parameters of electrochemically extracted insoluble particles and the synthetic quaternary compound.

	Ageing Time at 190°C (days)	Lattice parameters (nm)	
		a	c
1.03% Si Alloy	0	$1.036 \pm .004$	$0.404 \pm .004$
	6	$1.036 \pm .009$	$0.404 \pm .004$
	10	$1.035 \pm .009$	$0.405 \pm .004$
	24	$1.036 \pm .011$	$0.403 \pm .011$
Synthetic Compound	-	$1.036 \pm .006$	$0.402 \pm .001$

those of the single phase quaternary compound. No extra reflections were observed, confirming that all the insoluble particles represent the single phase quaternary compound Q. Thus, based on the lattice parameter measurements and chemical composition, it can be concluded that the insoluble in Si bearing Al-Cu-Mg alloys are particles of the hexagonal quaternary phase, Q.

5.1.6 Effect of Ageing at 190°C

Morphologies of the insoluble particles in a large number of aged Si bearing alloys were investigated by SEM in a back scattered mode. Ageing up to 1560 h did not affect the size and distribution of these particles. A few of the grain boundaries, (such as the one marked A in Fig. 5.7(b)) were decorated by small and uniformly spaced particles. These particles may have resulted due to precipitation as they were not found in the solution treated condition of alloys.

The insolubles electrochemically extracted from specimens aged for 144, 240 and 576 h have been analysed by EDS. The results listed in Table 5.2 show that these particles have nearly the same composition as those observed in solution heat treated specimen. That is to say, no significant change in composition occurred on ageing. Large insoluble particles present in a bulk specimen aged for 1560 h were also analysed by EDS. This result (Table 5.3) also does not show any significant change in composition. The somewhat lower copper content yielded by the EDS analysis of particles in the bulk specimens may be attributed to absorption of x-rays of lighter elements by the matrix. The lattice parameters of the insolubles electrochemically extracted from samples aged for 144, 240 and 576 h were also measured.

These data listed in Table 5.6 do not show any measurable change in lattice parameters due to ageing. Thus, ageing at 190°C does not influence either the chemical composition or the structure to an appreciable extent.

The insensitivity of crystal structure, composition and distribution of insolubles to ageing at 190°C for up to 1560 h is not unexpected. The solution heat treated specimens contain Q phase which is in equilibrium with the matrix at the solution heat treatment temperature. At the ageing temperature, it is possible that primarily the transition phases precipitate in preference to Q phase. Small amounts of the precipitating phase Q are expected to deposit on the existing insoluble particles. This mode of precipitation is unlikely to affect the composition, lattice parameter or morphology of insoluble to any appreciable extent. The precipitation behaviour in these alloys will be discussed in separate sections.

5.2 EFFECTS OF INSOLUBLE PARTICLES ON THE SOLUTE CONTENTS OF THE

MATRIX

The presence of insoluble particle of Q phase in alloys containing (0.49, 0.76 and 1.03%) Si is likely to change the precipitation behaviour of these alloys by altering the matrix composition. The percentage of solute atoms in the matrix, α , in equilibrium with the insolubles determined by the volume fraction x_c of the insoluble compound. If w_i and w_i^c are the weight fractions of solute i in the alloy and the insoluble compound respectively, the weight fraction of the solute in the matrix w_i^α is given by the following expression:

$$W_i^\alpha = W_i - \left(\frac{x_c}{1-x_c} \right) \left(\frac{\rho_c}{\rho_\alpha} \right) (W_i - W_i^c) \quad (5.5)$$

where ρ_c and ρ_α are the densities of the insoluble compound and the matrix respectively.

The measured volume percentages of the insoluble compounds in all alloys are listed in Table 5.7 and plotted in Fig. 5.8. The insoluble compound has the same composition and the same hexagonal structure in all the three high Si alloys (Section 5.1.4). The density of the compound (ρ_c) was taken as that of the synthetic quaternary compound of the Q phase. The density was measured by using both immersion methods (Section 3.7). The experimentally determined density of the compound was found to be 4.03 gm/cc. The density of the matrix (ρ_α) of all the alloys were evaluated using the measured lattice parameters listed in Table 5.7. The experimentally determined density of the compound (ρ_c) and the weight fractions of the solutes in the alloy were substituted in Equation (5.5) and the value of w_i^α were calculated by several iterations.

The concentration profiles of solutes in the matrix in equilibrium with insoluble compound at 530°C are plotted in Fig. 5.14. On the basis of the Si concentration, the solubility of Si in the Al-1.50%Cu-0.75%Mg alloy at 530°C can be estimated by determining the point of intersection of the unsaturated and saturated concentration profiles. It is estimated from the extrapolated lines in Fig. 5.14 that the solubility of Si in the ternary Al-1.50%Cu-0.75%Mg alloy is about 0.3%. Fig. 5.14 shows that the Si concentration in the matrix changes only slightly when Si contents of the alloy are increased from 0.49 to 1.03%. This is due to the formation of insolubles. The insolubles cause a reduction in the concentration of Cu and Mg in

Table 5.7: Experimentally calculated parameters to determine w_i

Alloy composition (wt %)			Volume Fraction	Lattice Parameter	Density ρ_α	Composition of matrix in equilibrium with Q at phase		
Cu	Mg	Si Al	X_c	a (Å)	(gm/cc)	Cu	Mg	Si Al
1.53	0.79	- Bal.	0	4.0513	2.7152	1.53	0.79	- Bal.
1.52	0.74	0.23 Bal.	0	4.0508	2.7165	1.52	0.74	0.23 Bal.
1.51	0.75	0.49 Bal.	.230	4.0492	2.7201	1.45	0.63	.39 Bal.
1.54	0.75	0.76 Bal.	0.604	4.0490	2.7210	1.37	0.44	0.50 Bal.
1.52	0.77	1.03 Bal.	1.34	4.0494	2.7200	1.16	0.05	0.44 Bal.

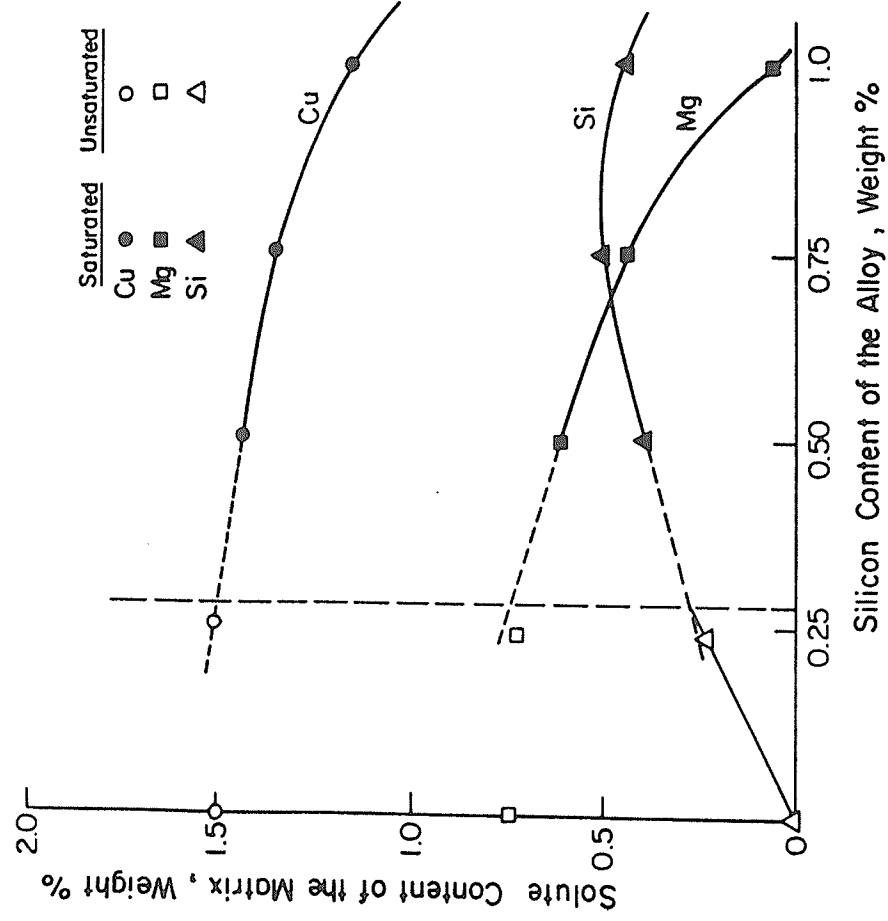


Fig. 5.14 Variation in the solute content of the matrix with increase in Si content of the alloy

the matrix. Consequently, the Cu/Mg ratio in the matrix changes drastically from 2 to 23 as the amount of Si in the alloy increases from 0.23 to 1.03%. A number of investigators have found that the nature of precipitating phase and its precipitation kinetics changes with an increase in Cu/Mg ratio.^(4,122) Thus, an increase in the Si content should cause an appreciable depletion of solutes and therefore precipitation behaviour would be modified by an increase in the Si content.

The solubility of Si in the Al-1.50Cu-0.75%Mg alloy can be estimated from the solubility curves. When the matrix contains 1.5% Cu and 0.75% Mg, the equilibrium Si content obtained from Fig. 5.14 is about 0.3%. Thus, Si up to $\approx .3\%$ will remain in solid solution in alloy containing 1.50% Cu and 0.75% Mg. The addition of excess Si would only go to the formation of Q phase beyond this range.

Equation (5.5) may be rearranged in the following way,

$$(1-x_c) = \frac{(W_i - W_i^\alpha)}{W_i [1-(\rho_c/\rho_\alpha)] + \left(\frac{\rho_e}{\rho_\alpha}\right) W_i^c - W_i^\alpha} \quad (5.6)$$

The above relationship suggests that the volume fraction of the insoluble phase is linearly related to the difference in solute content of the matrix and the solid solution α . The plot in Fig. 5.15 shows this relationship and the internal consistency of the data.

The variation of solubility with an increase in Si content in the Al-1.52Cu-0.75%Mg alloy may be understood with the help of the schematic phase diagram shown in Fig. 5.16. This diagram refers to constant temperature and constant pressure. The weight percentages of Cu, Mg and Si are represented by the three cartesian coordinates.

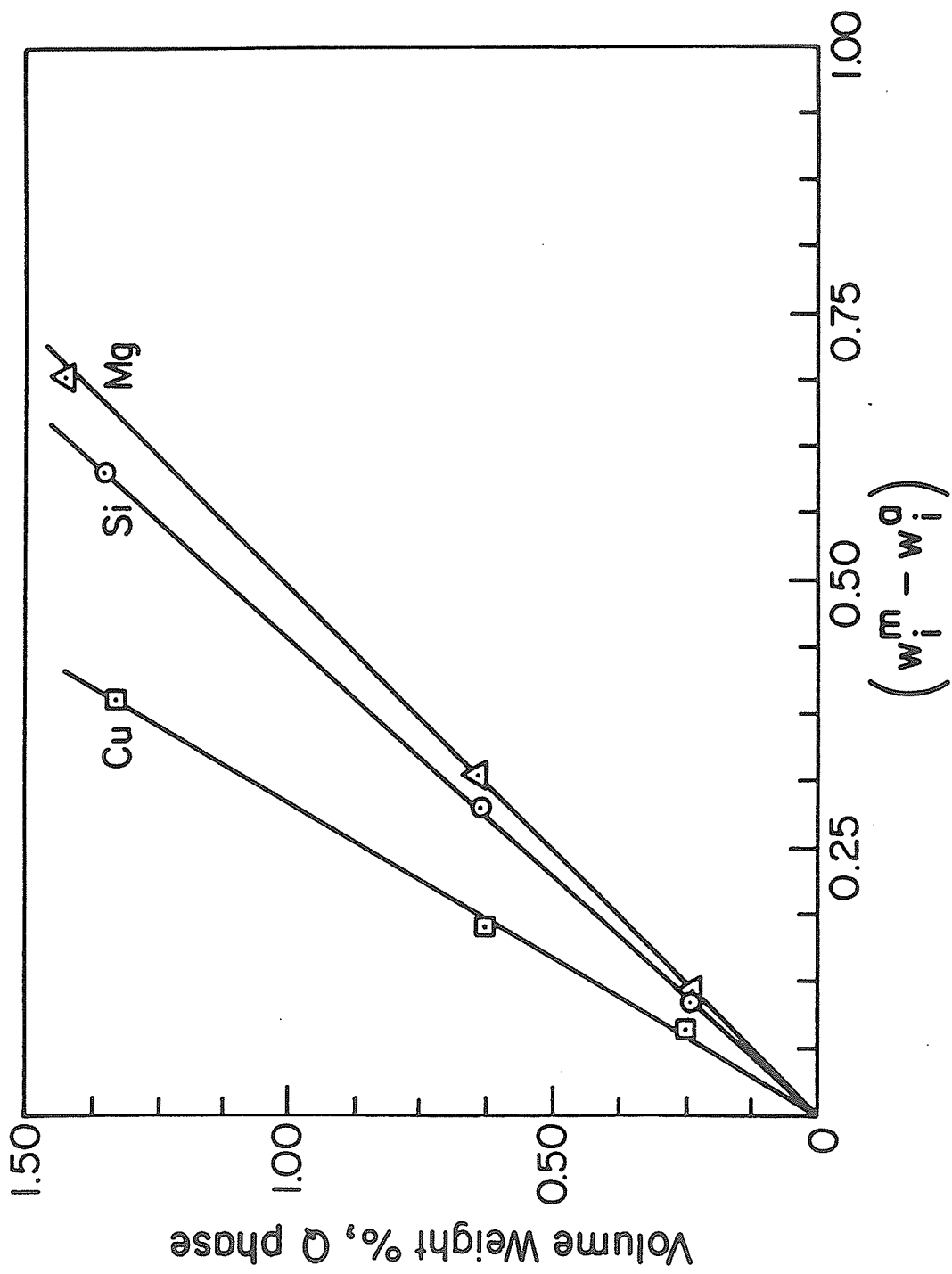


Fig. 5.15 Variation in the solute content of the matrix with increase in the volume fraction of the Q phase

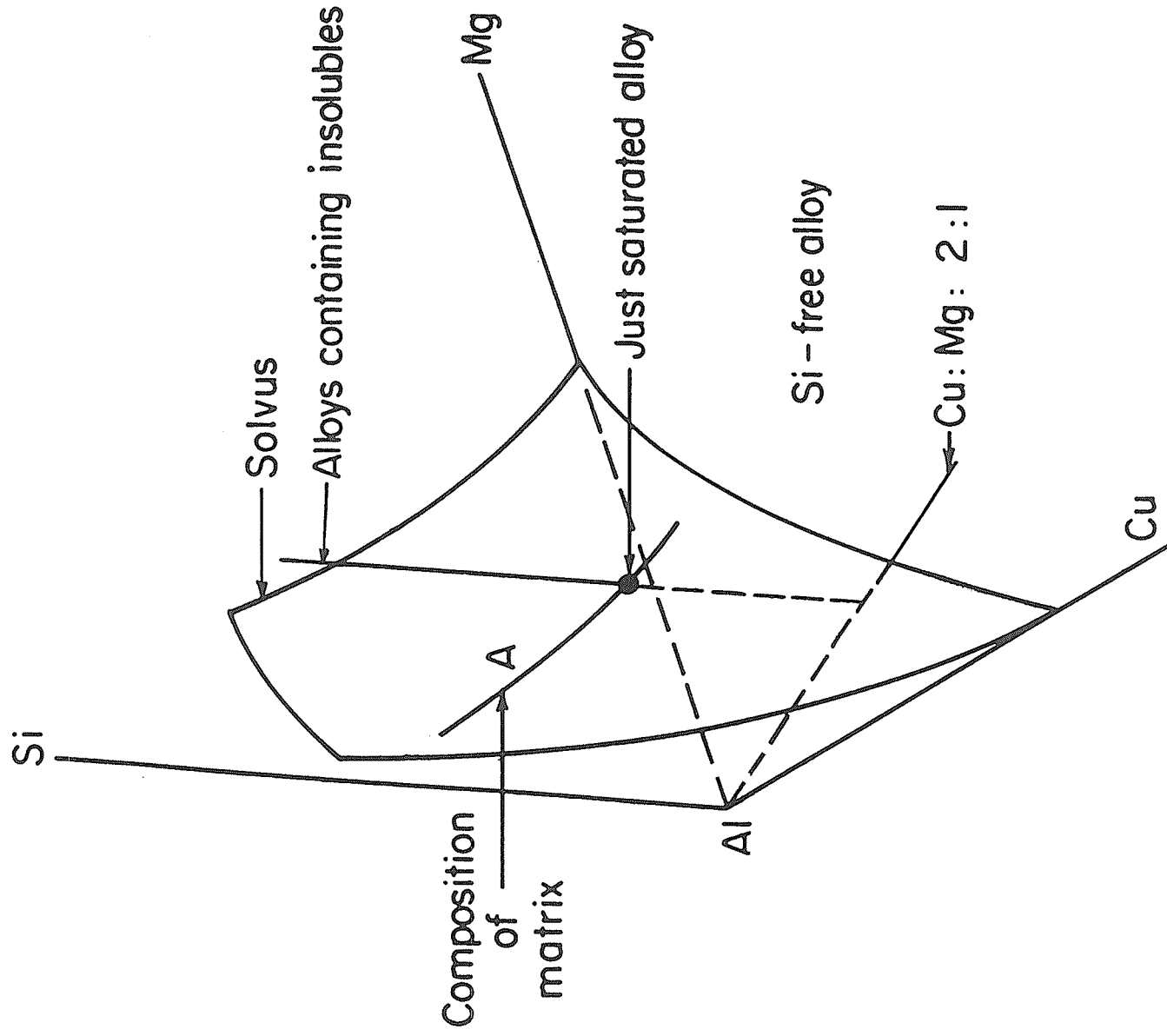


Fig. 5.16 Schematic diagram showing multicomponent equilibrium in a two phase field of the Al-Cu-Mg-Si alloys at constant temperature and pressure

The solvus is given by a curved surface. In this diagram the alloys of a constant Cu/Mg ratio are represented by a plane perpendicular to the plane containing the Cu and Mg axes. A line on this plane parallel to the Si axis represents the Al-1.50%Cu-0.75%Mg alloys with increasing Si content. The composition representing the intersection of the solvus and the line representing the Si containing alloys show the solubility of Si in the present alloy. The line A on the solvus gives the composition of the matrix in equilibrium with the insolubles. The composition plotted in Fig. 5.14 represents matrix composition along line A.

5.3 PRECIPITATION BEHAVIOUR IN THE INSOLUBLE FREE

Al-1.52%Cu-0.74%Mg-0.23%Si ALLOY

The concentration profiles of the matrix of the Si containing alloys show (Fig. 5.14) that the Al-1.5%Cu-0.75%Mg alloy can retain up to 0.3% Si in solid solution. Optical and scanning electron microscopic studies also showed that the alloy containing 0.23% Si does not have any insoluble particles in its matrix. The presence of Si in the alloy is likely to alter the precipitation by reason other than the changes in the concentration of Cu, Mg and Si due to the formation of the insolubles.

It was demonstrated in the last chapter that changes in the precipitation behaviour can be studied by the DSC technique. A typical DSC curve of a solution treated and water quenched sample of the 0.23% Si alloy is shown in Fig. 5.17. The principle features of this curve are the same as the ones obtained from the Si free alloy (Fig. 4.26) and can be interpreted in exactly the same manner. The

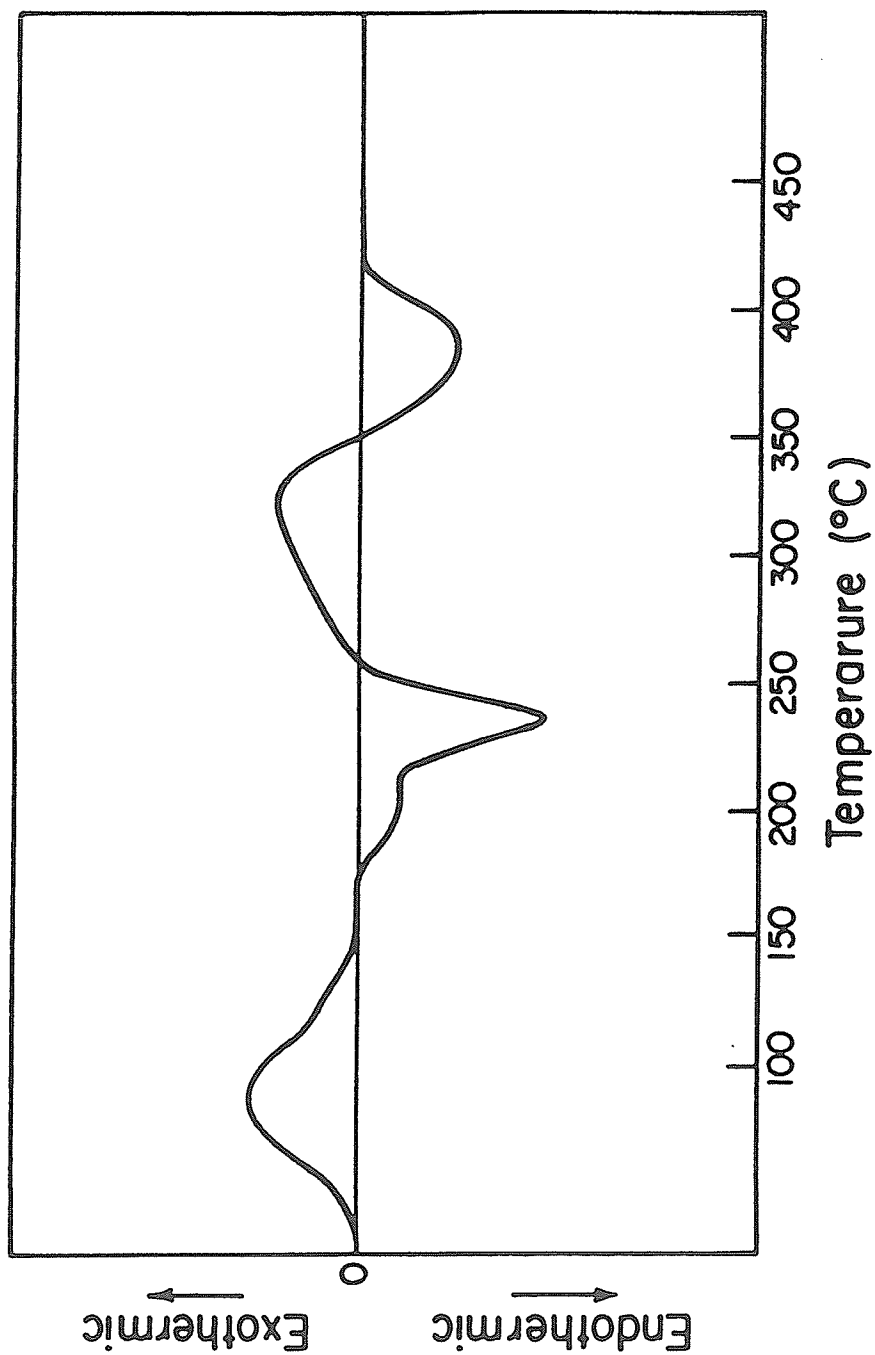


Fig. 5.17 DSC curve of a solution treated and quenched
Al-1.52%Cu-0.74%Mg-0.23%Si alloy at the heating
rate of 10°C/min

peak positions and total heat effects associated with the peak in the Si free and 0.23% Si alloys have been listed in Table 5.8. The only significant changes appear to be the shifting of the initial temperatures of the GPB zone precipitation and dissolution peaks to higher temperatures. Results of the DSC runs obtained with specimens aged at 130° and 190°C showed precipitation behaviour similar to that observed in the Si free alloys.

In order to confirm the results of the DSC studies a number of samples aged at 190°C were examined in the transmission electron microscope. A typical electron micrograph (Fig. 5.18(a)) shows the microstructure of the specimen aged at 190°C for 240 h and the corresponding SAD pattern is shown in Fig. 5.18(b). Similar to Si free alloy, the precipitate particles are rod shaped and lie parallel to the $\langle 100 \rangle$ matrix direction and the SAD pattern can be indexed as belonging to the orthorhombic S' phase.

5.4 EFFECTS OF AGEING ON THE INSOLUBLE CONTAINING 0.49, 0.76 and

1.03% Si ALLOYS OF Al-1.50%Cu-0.75%Mg

The solubility curves of Fig. 5.14 show that the addition of Si results in alteration of the overall matrix composition of the alloy due to the precipitation of insoluble particles of the Q phase. One would therefore expect significant changes in the subsequent precipitation behaviour of these alloys. In order to explore this possibility, alloys containing 0.49, 0.76 and 1.03% Si were examined using DSC and TEM.

Table 5.8: Peak characteristics of insoluble free alloys.

Alloy	Al-1.52% Cu-0.75% Mg	Al-1.52% Cu-0.74% Mg-0.23% Si
i) GPB zone precipitation peak heat effect Q (J/g)	6.52	6.40
Peak temperature (°C)		
- initial	26.05	34.52
- maximum	84.60	85.89
- final	152.56	148.00
ii) Complex dissolution peak Heat effect Q (J/g)	7.95	7.01
Peak temperature (°C)		
- initial	151.29	175.00
- minimum A1-A2	200.30 - 234.37	200.00 - 234.71
- final	265.00	261.00
iii) S' precipitation peak Heat effect Q (J/g)	6.50	4.64
Peak temperature (°C)		
- initial	264.88	261.90
- maximum	318.49	327.6
- final	348.52	347.00
iv) S' dissolution peak Heat effect Q (J/g)	6.42	5.43
Peak temperature (°C)		
- initial	384.92	350.00
- minimum	392.60	385.0
- final	425.40	420.00

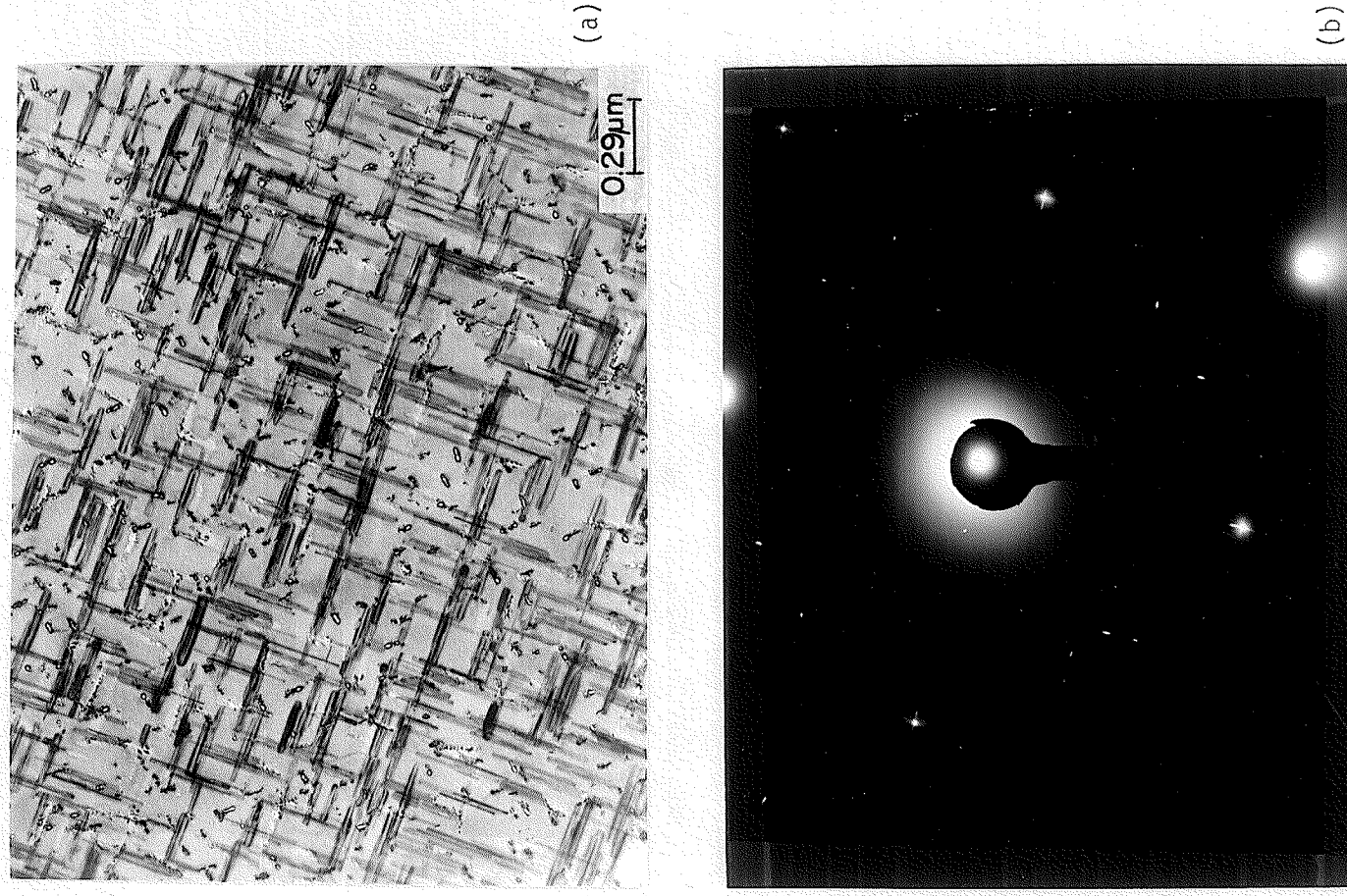


Fig. 5.18 (a) Bright field image of an Al-1.52%Cu-0.74%
Mg-0.23%Si alloy aged at 190°C for 240 h
(b) SAD pattern of (a)

5.4.1 Kinetic Investigations

The non-isothermal precipitation kinetics were investigated by DSC. Fig. 5.19 shows the DSC curves of solution treated and quenched insoluble containing 0.49, 0.76 and 1.03% Si alloys obtained at a heating rate of 10°C/min. The DSC curves of the solution treated and quenched insoluble free alloys containing 0 and 0.23% Si have also been included for comparison purposes. It is obvious that the DSC curves of insoluble containing alloys are radically different from those of insoluble free alloys. The peak positions and their shapes are different and multiple peaks appear at higher temperatures. Furthermore, the DSC curves of the three insoluble bearing alloys differ from each other at higher temperature. This is further illustrated by the DSC curves in Figs. 5.20 and 5.21 obtained from the alloys containing 0.49% and 1.03% Si respectively. The DSC curve of as quenched 0.49% Si alloy in Fig. 5.20 shows a broad and complex multiple precipitation/dissolution peak D compared with well defined peaks found in the 1.03% Si alloy (Fig. 5.21(d)). However, on further ageing of room temperature aged (48 h) alloys, the complex peak D of 0.49% Si alloy becomes well defined and is similar to the one seen in Fig. 5.21 (peak D) for 1.03% Si alloy. Such a behaviour of 0.49% Si alloy suggests that the transition phases are likely to be different in the 0.49% and 1.03% Si bearing alloys. The precipitation peaks, A and C and the dissolution peak B in the DSC curves of the alloys containing 0.49 and 1.03% Si exhibit the same peak temperature ranges and a similar behaviour on ageing. The initial precipitation peak A (Figs. 5.20 and 5.21) which occurs within the temperature range $\approx 50^{\circ}\text{--}150^{\circ}\text{C}$ becomes smaller in a specimen aged at room temperature

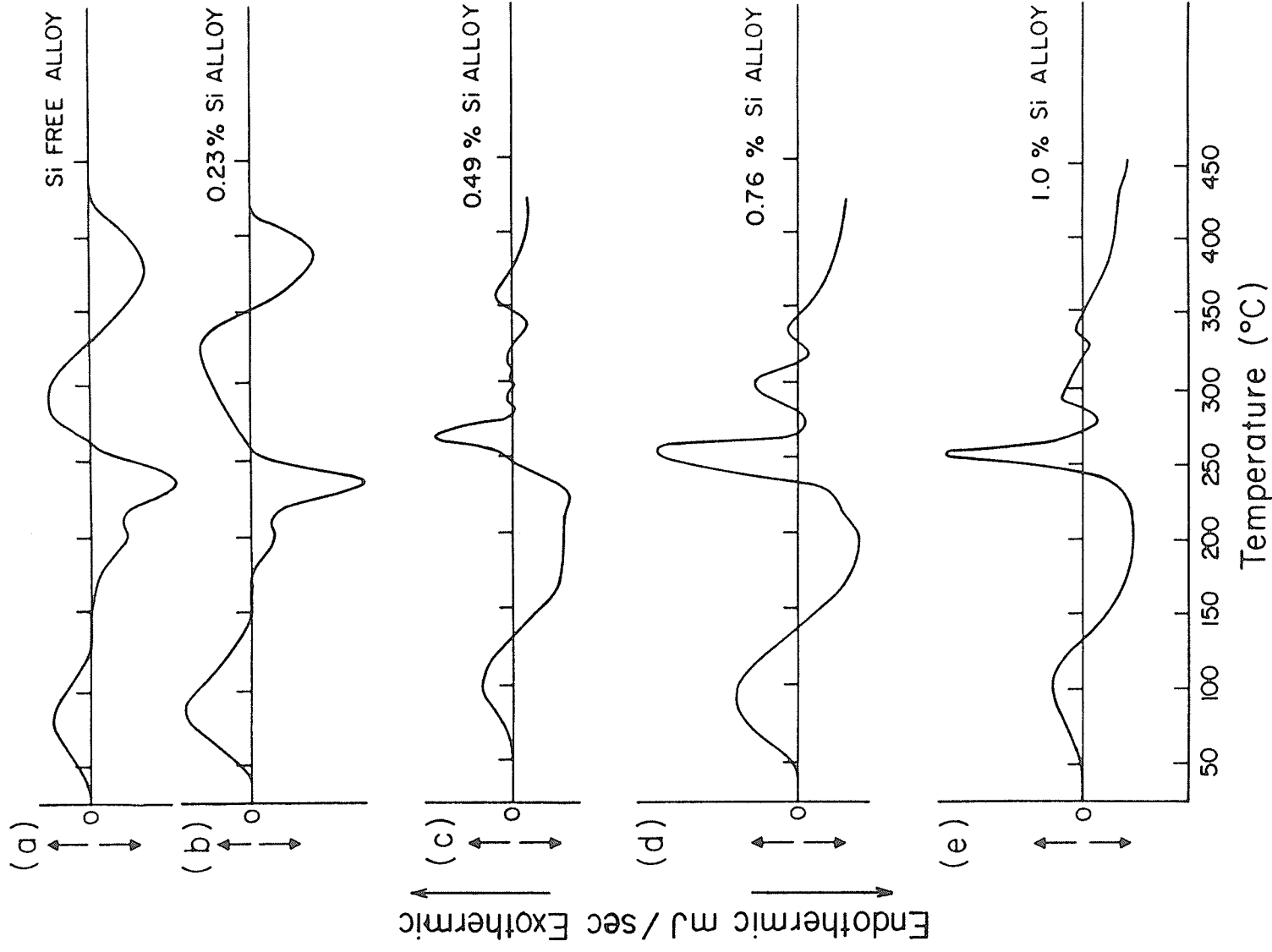


Fig. 5.19 DSC curves obtained from solution treated and quenched specimens of 0, 0.23, 0.49, 0.76 and 1.03% Si alloys at the heating rate of 10°C/min

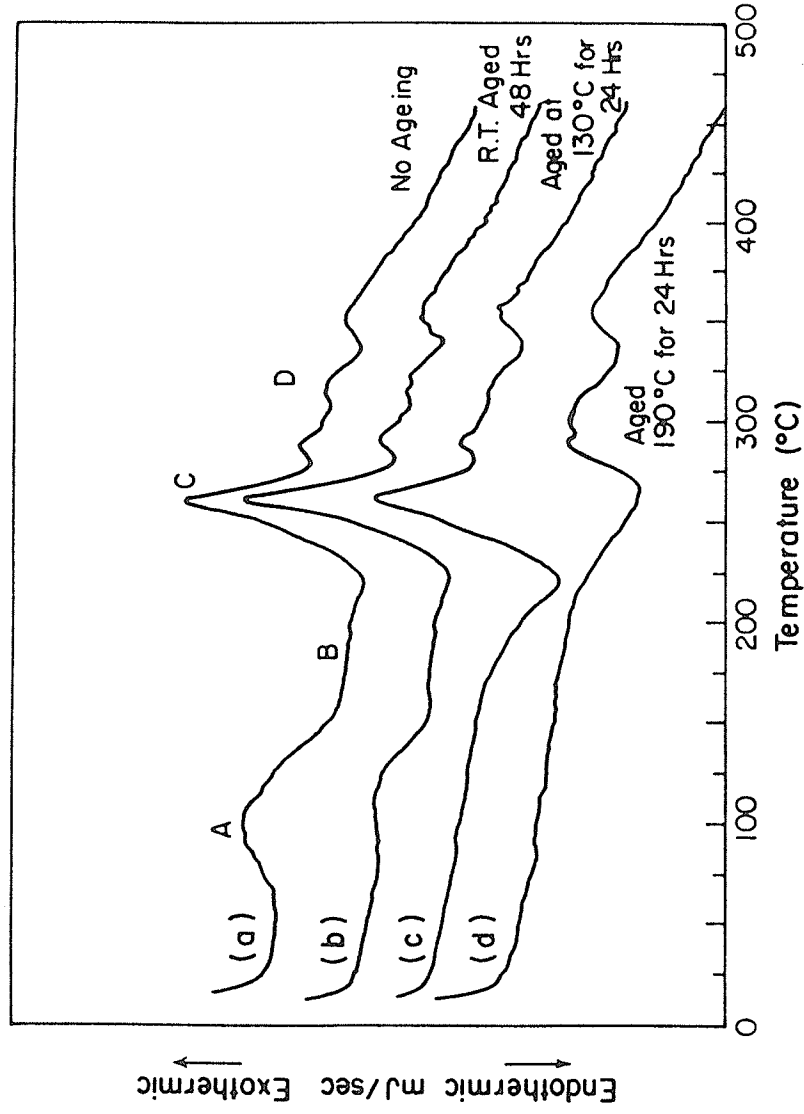


Fig. 5.20 DSC curves obtained at the heating rate of 10°C/min from specimens of the 0.49%Si alloy heat treated under various conditions

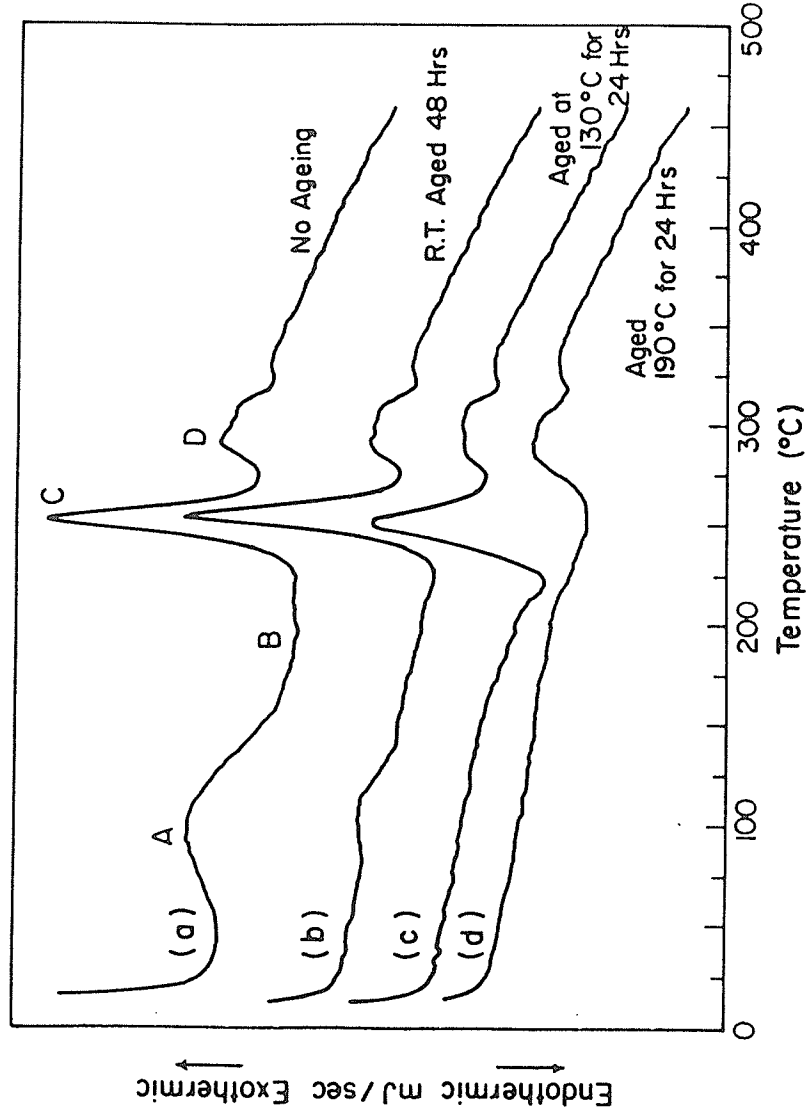


Fig. 5.21 DSC curves obtained at the heating rate of 10°C/min from specimens of the 1.03% Si alloy heat treated under various conditions

for 48 h and finally disappears on further ageing in the sample aged at 130°C for 24 h. The precipitation process related to peak C was found to be completed in the alloys after ageing for 48 h at room temperature and further ageing at 190°C for 24 h. The DSC curve thus obtained showed a broad dissolution peak in place of the precipitation peak C. It indicates that the precipitation process occurring in C is complete after 24 h at 190°C.

In all the three alloys (0.49, 0.76 and 1.03% Si), the first exothermic peak is most likely due to precipitates which form at room temperature. The second endothermic peak is due to the dissolution of these precipitates. The precipitates responsible for peak 'C' occurs in all the alloys aged for 24 h at 190°C. Beyond this the precipitation process seems to be very complex and may involve several phases in the 0.49 and 1.03% Si alloys.

5.4.2 Microstructural Studies

Microstructural changes which occur during ageing of 0.49 and 1.03% Si alloys were investigated in a transmission electron microscope.

5.4.2.1 The Al-1.51%Cu-0.75%Mg-0.49%Si Alloy

The solution treated and quenched 0.49% Si alloy showed isolated and helical dislocations. A typical micrograph in the weak beam condition is shown in Fig. 5.22. The presence of isolated and helical dislocations instead of vacancy loops observed in the Si free alloys suggests the reduction in the mobility of vacancies during quenching. As discussed earlier for the 0.23% Si alloy (Section 5.3),

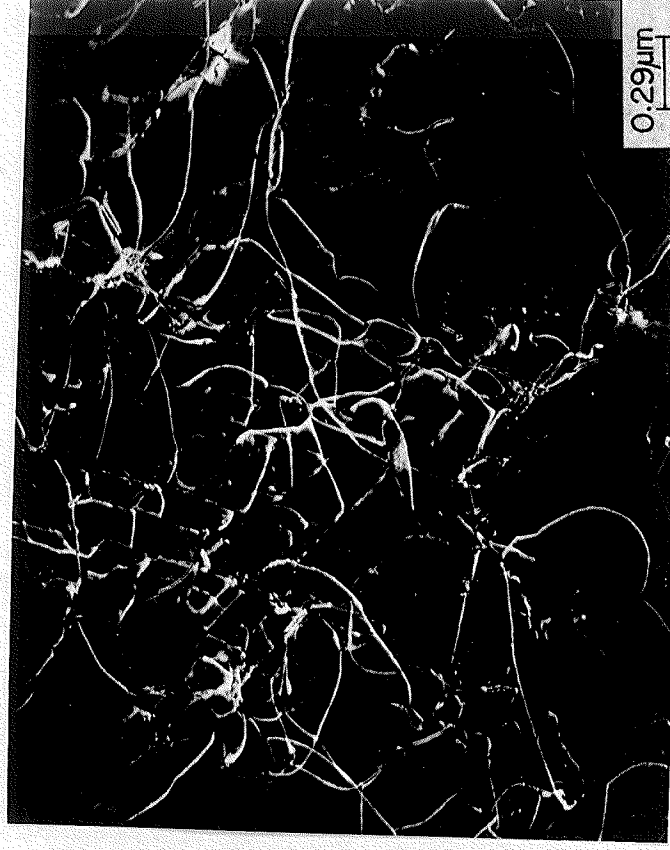


Fig. 5.22 Weak beam image of the solution treated and quenched Al-1.52%Cu-0.74%Mg-0.49%Si alloy

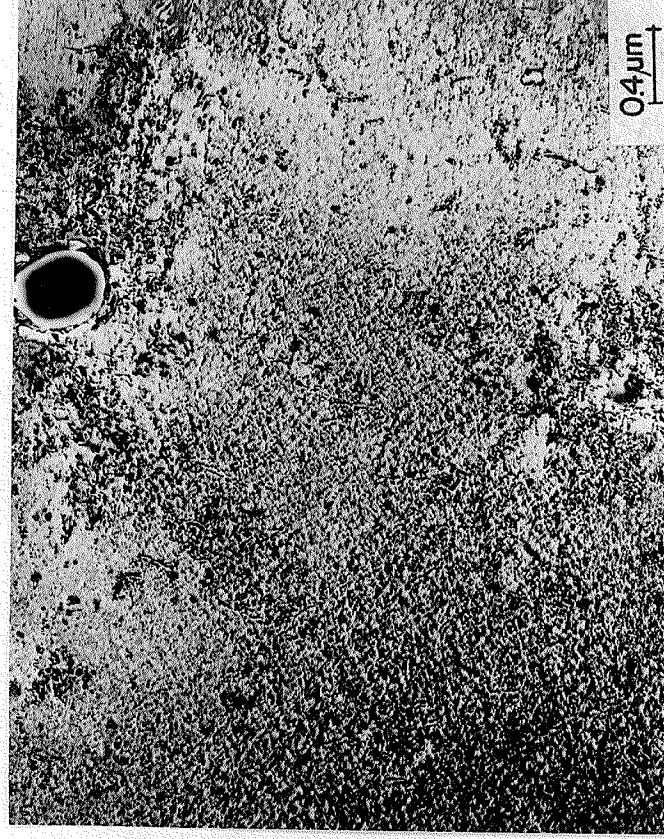


Fig. 5.23 Bright field image of Al-1.52%Cu-0.74%Mg-0.49%Si alloy aged at room temperature for 48 h and further aged at 190°C for 24 h

the increase in the Si content of the matrix (Fig. 5.14) is expected to reduce the mobility of vacancies. The dislocations observed in the quenched alloy became fewer in number with an increase in the ageing time and were observed until 24 h of ageing at 190°C as shown in Fig. 5.23.

The first clear sign of precipitation was observed in a specimen aged at room temperature for 48 h and further aged at 190°C for 6 h as shown in Fig. 5.24(a) with its SAD pattern in Fig. 5.24(b). The SAD pattern (Fig. 5.24(b)) in the (100) foil orientation showed streaks in the $\langle 100 \rangle$ matrix direction. The precipitates are on planes perpendicular to the plane of foil as seen in Fig. 5.24(a). The dark patches near some of the precipitates are most probably due to strain contrast. The microstructure and SAD pattern in Fig. 5.24(a) and (b) were not observed in either Si-free or 0.23% Si alloys. Further ageing at 190°C for 24 h showed intensity maxima in the SAD pattern (Fig. 5.25) around the (110) matrix direction which is characteristic of the precipitate phase θ' . A typical microstructure is shown in Fig. 5.23. Thus, the microstructure shown in Fig. 5.23 suggests that the peak C in the DSC curve (Fig. 5.21) is associated with the formation of θ' phase rather than S' found in insoluble free alloys. The peak A of the DSC curve (Fig. 5.21) therefore, is likely to be due to precipitation of GP zones rather than GPB zones.

The microstructure of a specimen aged at room temperature for 48 h and further aged for 384 h at 190°C is shown in Fig. 5.26(a) and (b). The thin foils observed are in (100) orientations. The bright field images (Fig. 5.26(a) and (b)) represent complex microstructures and showed plates and small needle shaped precipitates,

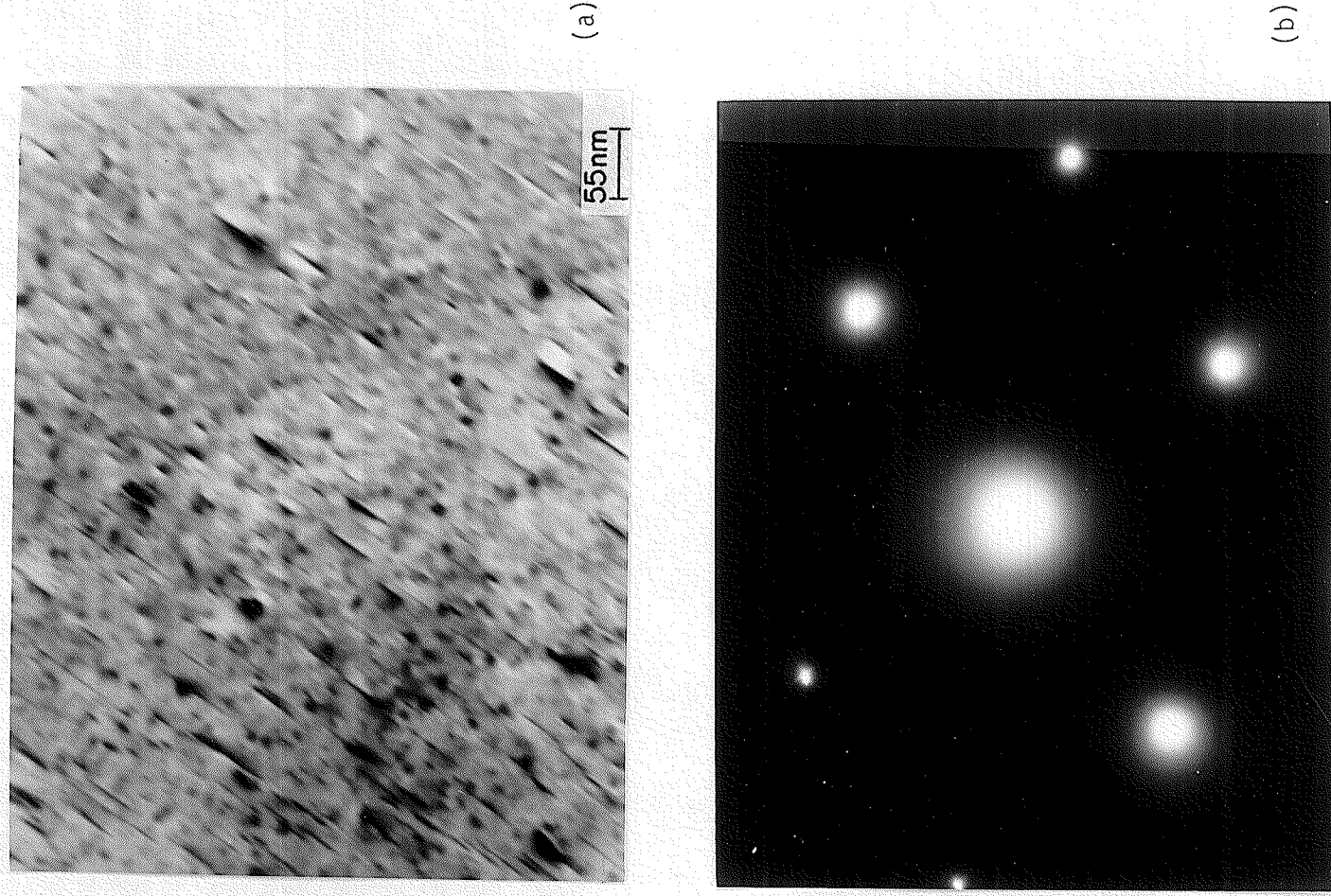


Fig. 5.24 (a) Bright field image of Al-1.52%Cu-0.74%Mg-0.49%Si alloy aged at room temperature for 48 h and further aged at 190°C for 6 h
(b) SAD pattern of (a)



Fig. 5.25 The SAD pattern of the structure similar to that shown in Fig. 5.23

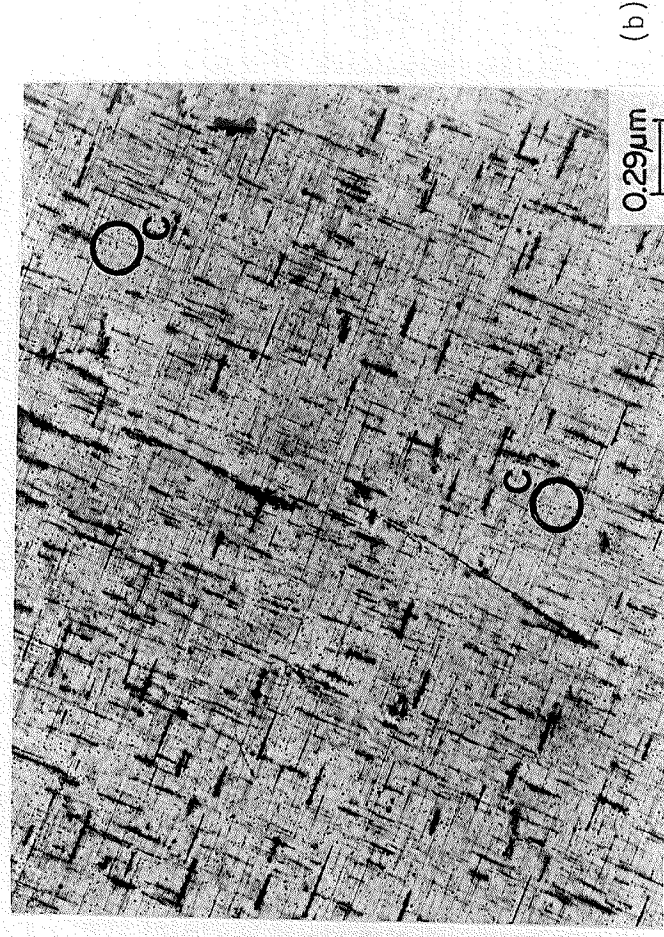
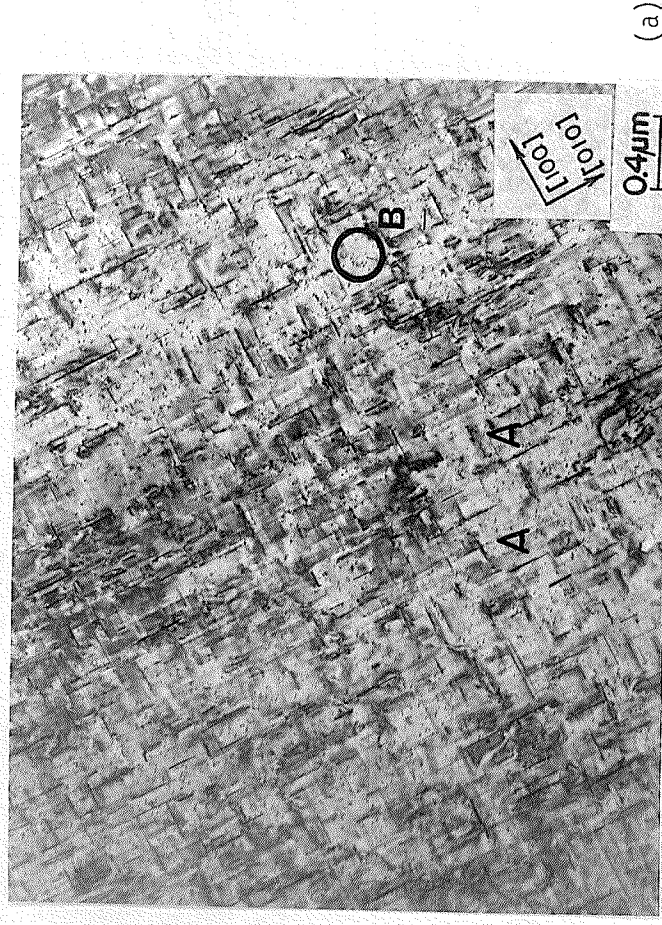


Fig. 5.26 Bright field images of the Al-1.52%Cu-0.74%Mg-0.49%Si alloy aged at room temperature for 48 h and further aged at 190°C for 384 h

- (a) Plate-like precipitates parallel to $\langle 100 \rangle_M$ (marked A) and small needle-like precipitates (marked B) are clearly visible
- (b) Small square shaped precipitates (marked C) are visible in this figure

marked as A and B respectively. Another dot-like precipitate (marked C) in Fig. 5.26(b) was also found in some areas of the foil. A SAD pattern obtained from the structures similar to the ones in Fig. 5.26 is shown in Fig. 5.27(a) which is more fully developed than that in Fig. 5.25. The observed SAD pattern is completely different from the one shown in Fig. 4.16(b), obtained from microstructure containing S' phase. The characteristic grouping of four spots around a centre spot at the centre of $\{110\}$ matrix direction is due to the presence of θ' phase. The reflections due to θ' are marked as A, B and C in a schematic diagram shown in Fig. 5.27(b). However, other reflections D and E in Fig. 5.27(b) remained unidentified. The centre dark field image with the spot, marked A in Fig. 5.27(b) is shown in Fig. 5.28(a). The reflection A highlights one orientation of θ' phase parallel to the $\langle 100 \rangle$ matrix direction. The reflection C could not be isolated from A and B and gave a composite CDF image of all the orientations of θ' phase shown in Fig. 5.28(b). Some of the additional precipitates visible in Fig. 5.28(a) and (b) are possibly due to overlapping of their reflections. The CDF images obtained from D and E reflections showed small needle-like precipitates perpendicular to each other. A typical example is shown in Fig. 5.28(c) obtained with reflection D of Fig. 5.27(b). The precipitates lie parallel to the matrix direction. Tilting of the specimen in the microscope by a few degrees resulted in the D and E reflections becoming more intense and diffused and the corresponding CDF image showed small precipitates both on the grain boundaries and within the matrix. A typical CDF image of an area close to the grain boundary and within the matrix is shown in Fig. 5.28(d) and (e) respectively.

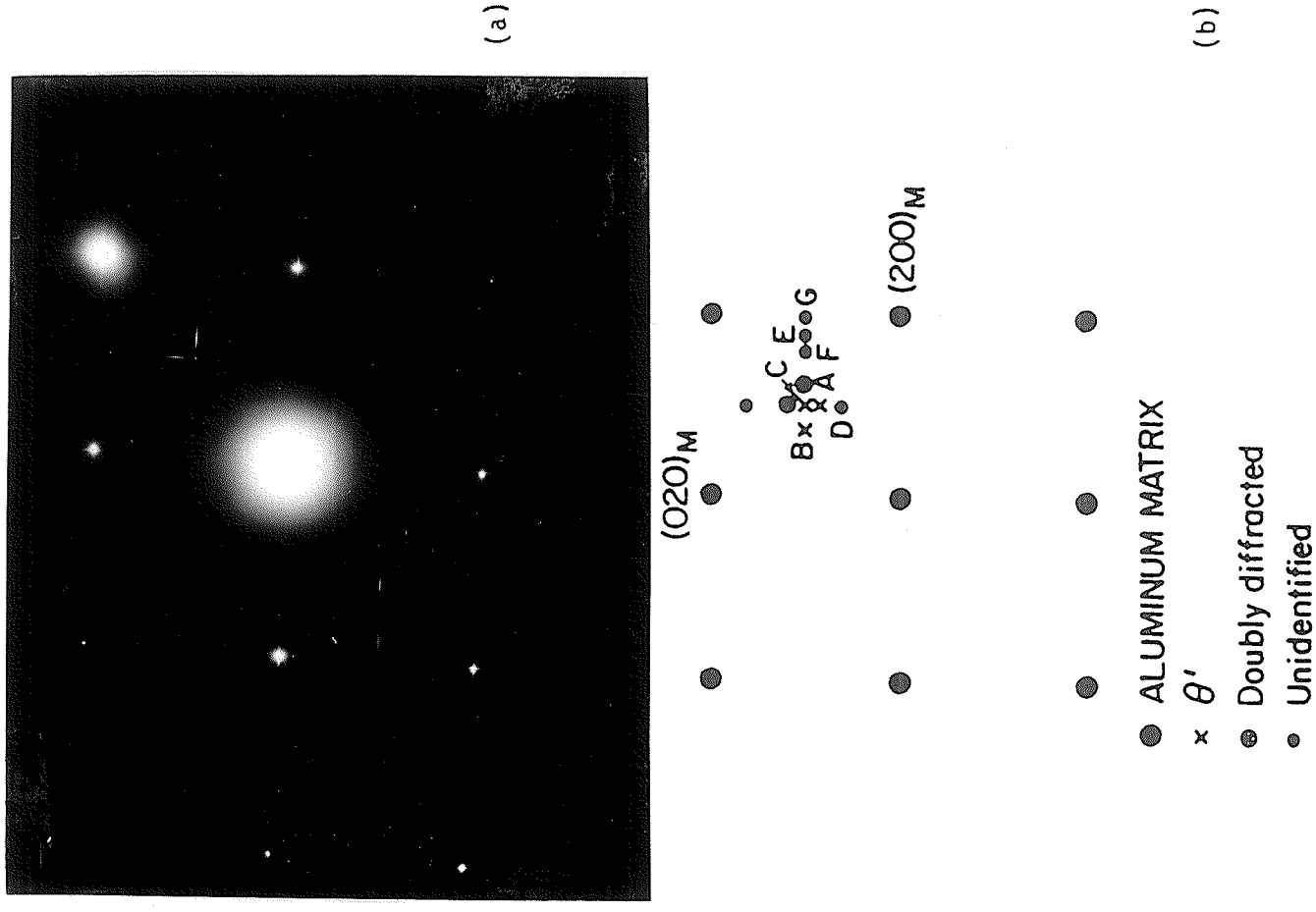
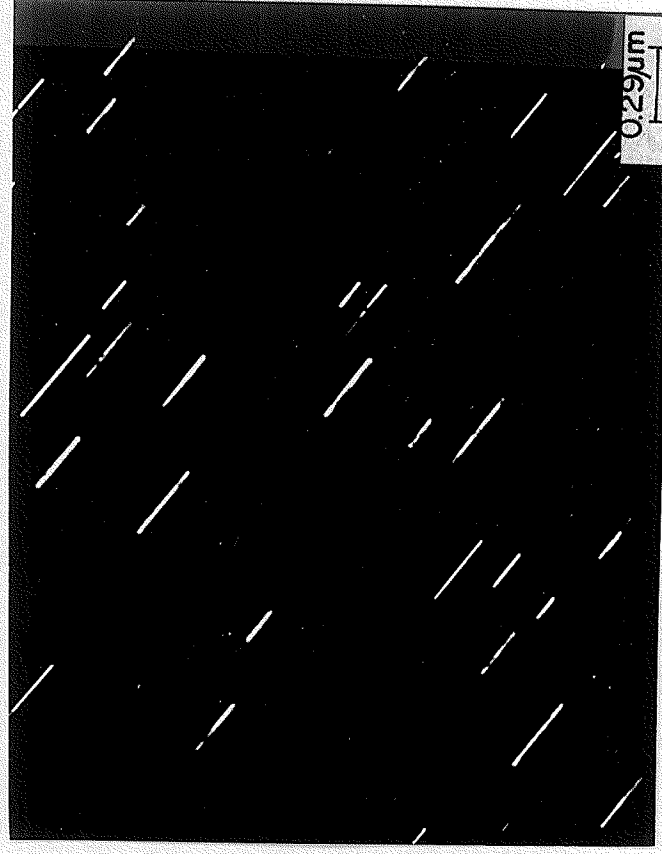
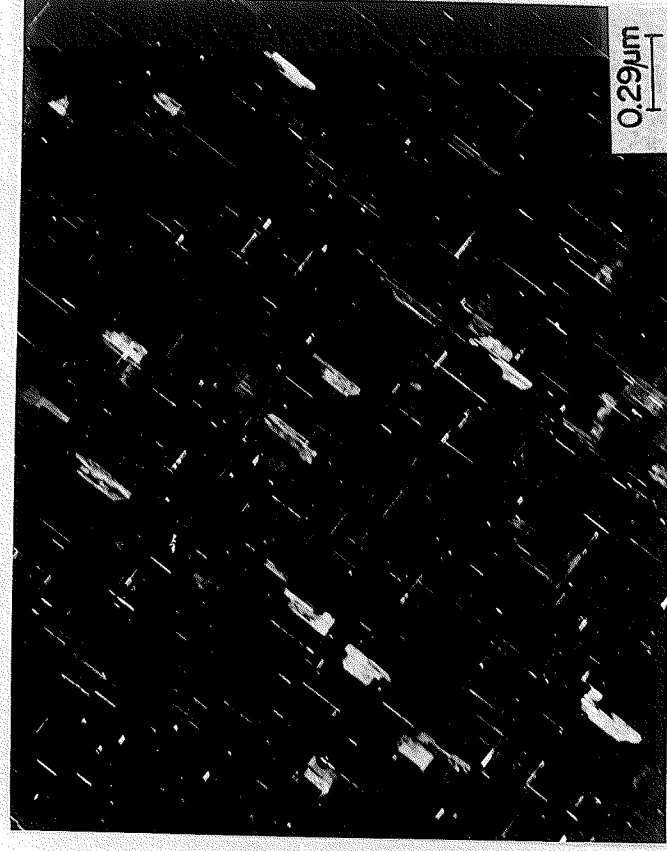


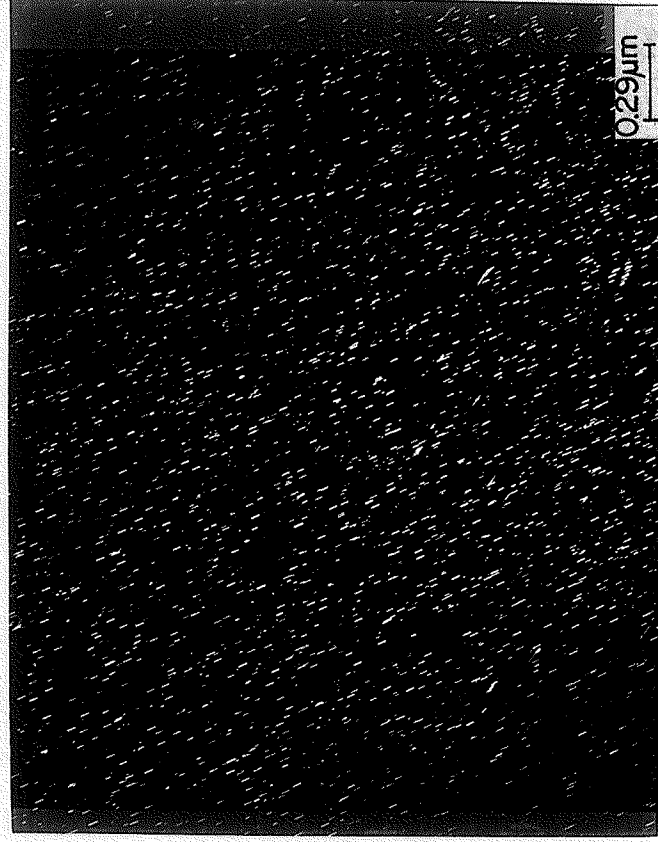
Fig. 5.27 (a) The SAD pattern from the microstructure similar to that shown in Fig. 5.26
(b) Schematic representation of the SAD pattern in (a). The reflections A, B and C correspond to $(0\bar{1}1)_b$, $(101)_a$ and $(110)_c$ reflection of θ' phase in a, b and c orientations respectively. The reflection E is due to the needle-like precipitate while F and G are due to the square type precipitates



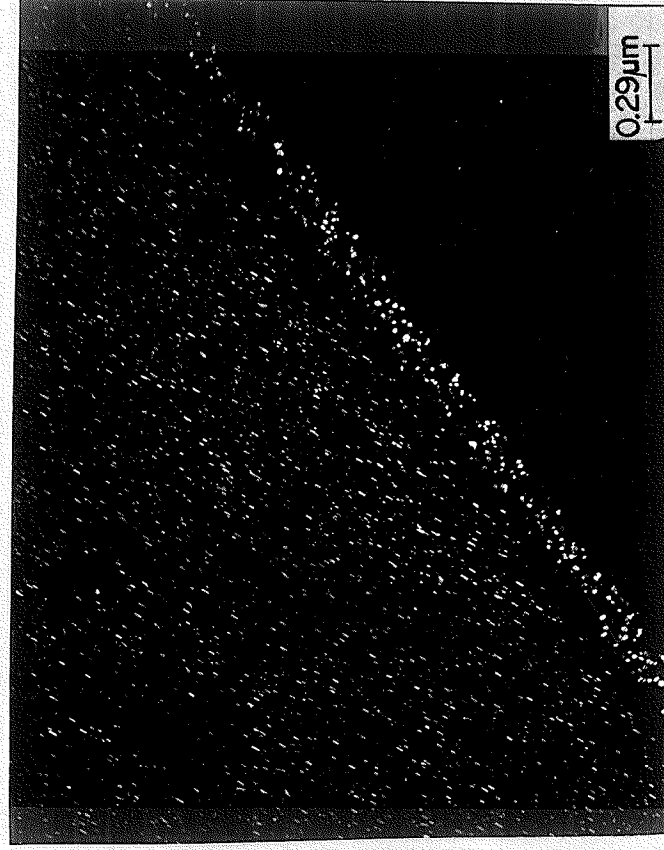
(c)



(d)



(c)



(d)

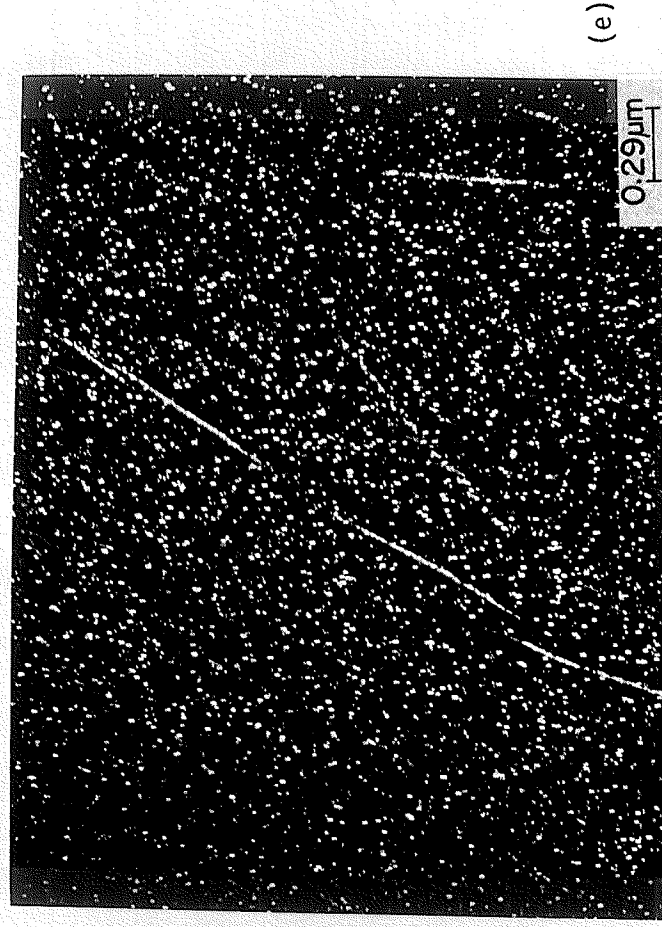


Fig. 5.28 CDF images obtained by using reflections of SAD pattern in Fig. 5.27

- (a) Image due to spot A. The precipitates lie along $\langle 100 \rangle_M$ direction
- (b) Composite image of A, B and C reflections. The precipitates are plate θ' phase
- (c) Image due to reflection D. Small needle-like precipitates are visible
- (d) Small square precipitates at the grain boundary. Image is due to reflection G of Fig. 5.28(b)
- (e) Composite image obtained for reflection E and G of Fig. 5.28(b)

The above CDF image analysis of the SAD pattern clearly shows the presence of three types of precipitates in the 0.49% Si alloy. Suzuki et al. (128) have also found the presence of three different kinds of precipitates, θ' , unknown cubic X and needle-like Q' , in an Al-2.00%Cu-0.9%Mg-0.5%Si alloy after ageing for 168 h at 200°C. However, in the present alloy, only θ' could be identified. The crystal structures of the other two peaks are not known, therefore, it is not possible to identify them individually. However, there does seem to be three distinct precipitates present in the aged specimens. The multiple precipitation of these three phases may be the cause of the complex high temperature peaks found in the DSC curves of 0.49% Si alloy.

5.4.2.2 Precipitation in Al-1.52%Cu-0.77%Mg-1.03%Si Alloy

The solution treated and quenched specimen of 1.03% Si alloy showed the presence of tangled dislocations (Fig. 5.29). This is expected as the Si content of the matrix hardly changes (Fig. 5.14) on addition of Si. The first indication of the presence of precipitate particles was observed in a specimen aged for 48 h at room temperature and further aged at 190°C for 6 h. A typical micrograph and its SAD pattern are shown in Fig. 5.30(a) and (b). The microstructure shows very fine precipitate particles which gives almost continuous streaks parallel to the $\langle 100 \rangle$ matrix direction (Fig. 5.30(b)). Further ageing up to 24 h at 190°C caused these streaks to develop intensity maxima in the SAD pattern around the centre of the $\{110\}$ matrix direction as illustrated in Fig. 5.31(a). The corresponding bright field TEM image showed traces of helical dislocations and fine precipitate

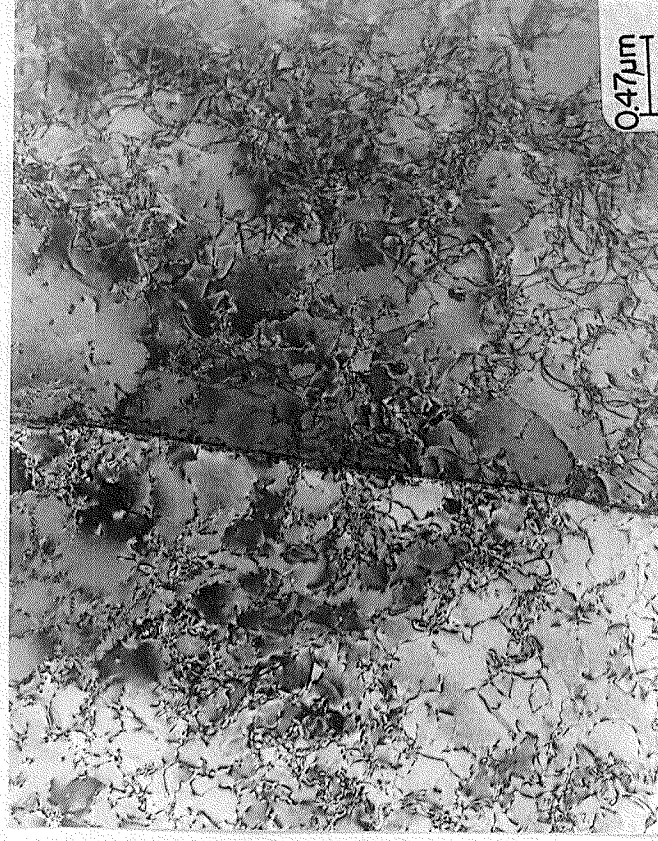


Fig. 5.29 Bright field image of solution treated and quenched
Al-1.52%Cu-0.77%Mg-1.03%Si alloy

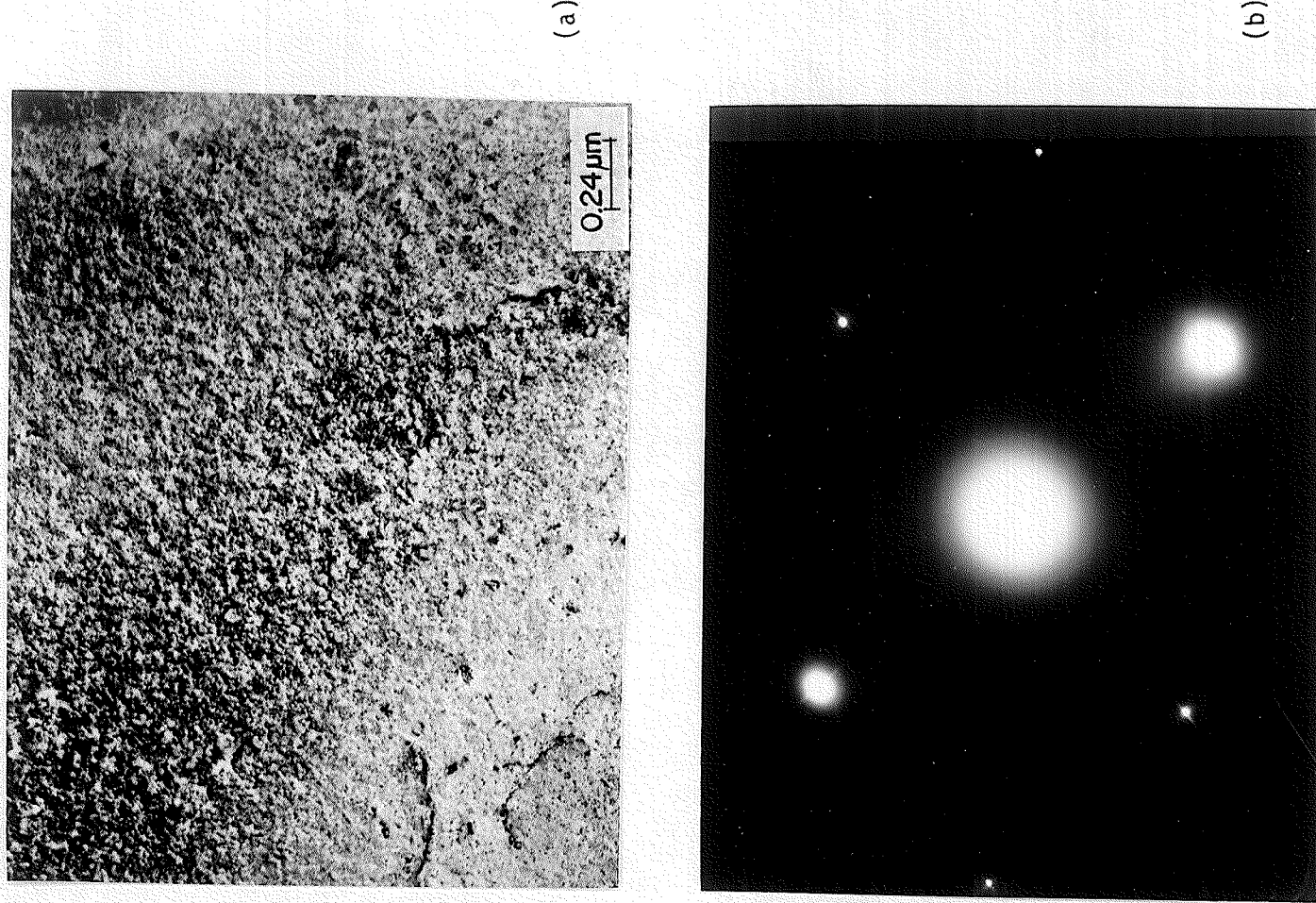
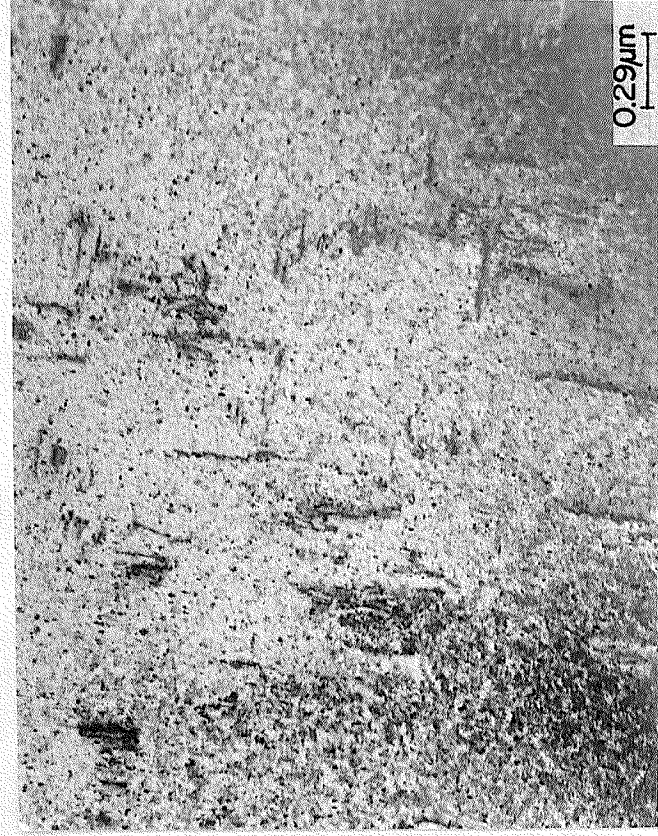


Fig. 5.30 (a) Bright field image of Al-1.52%Cu-0.77%Mg-1.03%Si alloy aged at room temperature for 48 h and further aged at 190°C for 6 h
(b) Corresponding SAD pattern



(a)



(b)

Fig. 5.31 (a) Bright field image of the Al-1.52%Cu-0.77%Mg-1.03%Si alloy aged at room temperature for 48 h and further aged at 190°C for 24 h
(b) SAD pattern of (a)

particles (Fig. 5.31(b)). The ageing of specimens for 24 h at 190°C results in the precipitation of θ' phase. This is similar to the behaviour of the 0.49% Si alloy. Thus, peak C of the DSC curve of 1.03% Si alloy (Fig. 5.21) is attributed to the precipitation of θ' phase and therefore, the first exothermic peak is likely to be due to formation of GP zones (Fig. 5.21, 6 h at 190°C).

The microstructure of a fully aged specimen, aged for 120 h at 190°C is shown in Fig. 5.32(a) with its SAD pattern shown in Fig. 5.32(b). The bright field image shows fine dot shaped particles (A), faint needle-like particles (B) and plate-like (C) particles of θ' phase. Overageing of the alloy (1536 h at 190°C) caused the SAD pattern to become well defined, but increasingly complex as can be seen in Fig. 5.33(a) and (b), which is the bright field micrograph and SAD pattern of a specimen aged at 190°C for 1536 h. This SAD pattern is not the same as that of overaged 0.49% Si alloy (Fig. 5.27(a)). Therefore, microstructure of the overaged 1.03% Si alloy contains phases which are different from those present in the overaged 0.49% Si alloy. The DSC curves for the two alloys are therefore different at high temperatures. It has been reported that an increase in Cu/Mg ratio beyond 2.0 can give rise to the precipitation of θ' phase.^(122,123) The presence of Si in Al-Cu-Mg alloys changes the composition of the matrix and thereby alters the Cu/Mg ratio up to 23.0 in 1.03% Si alloys. The precipitation of θ' may therefore be expected in Si bearing alloys as observed in both 0.49 and 1.03% Si alloys.

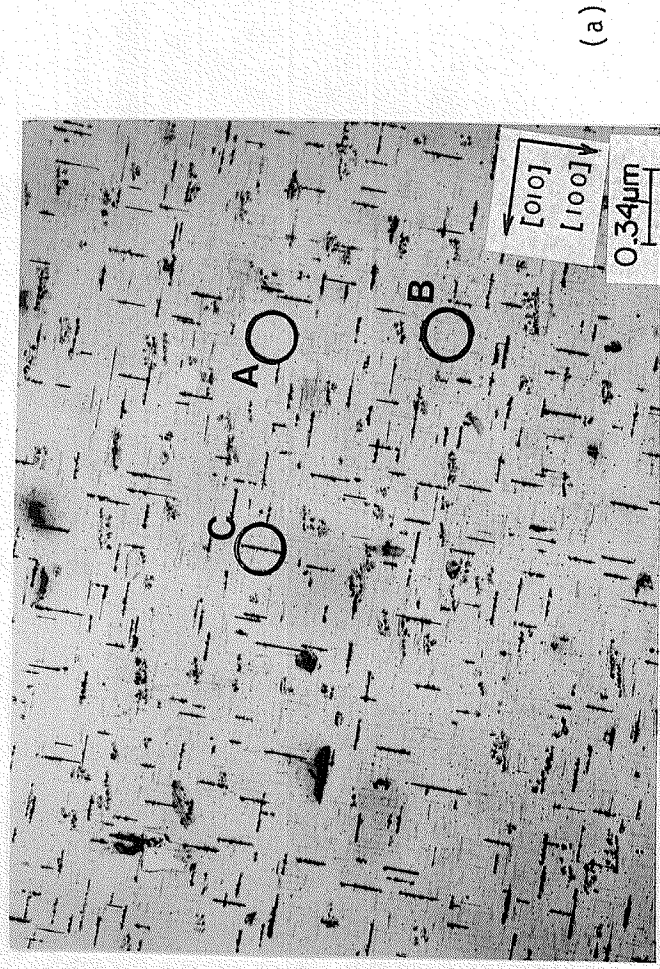
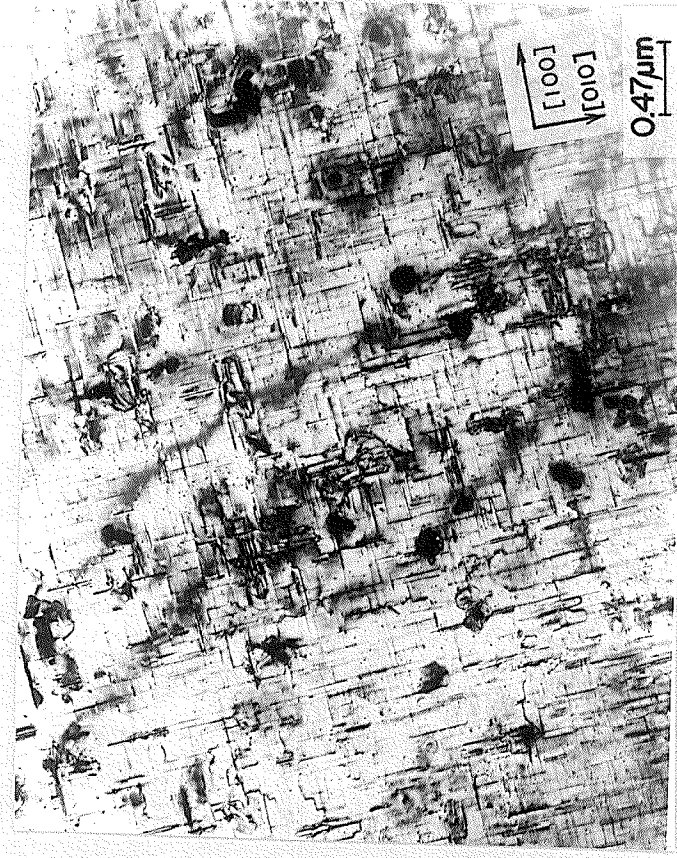
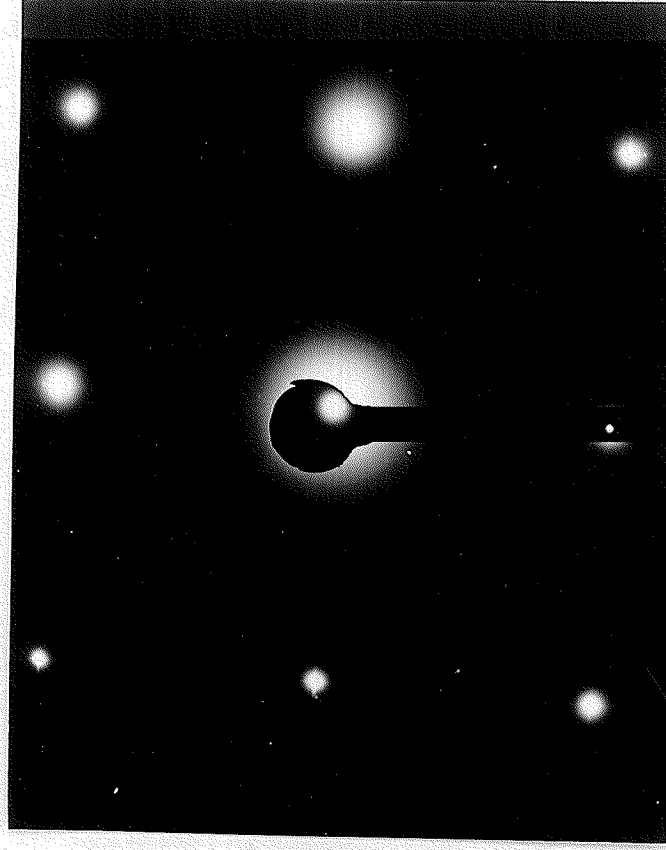


Fig. 5.32 (a) Bright field image of the Al-1.52Cu-0.77Mg-1.03Si alloy aged at room temperature for 48 h and further aged at 190°C for 120 h. Faint needle-like (marked A), dot shaped (marked B) and plate-like θ' (marked C) precipitates are visible

(b) SAD pattern from a microstructure similar to that shown in (a)



(a)



(b)

Fig. 5.33 (a) Bright field image of the Al-1.52%Cu-0.77%Mg-1.03%Si alloy aged at room temperature for 48 h and further aged at 190°C for 1536 h
(b) Corresponding SAD pattern

CHAPTER VI

SUMMARY AND CONCLUSIONS

6.1 THE Al-1.53%Cu-0.79%Mg ALLOY

- (1) The Al-1.53%Cu-0.79%Mg alloy was solution treated at 460°C, water quenched, aged at room temperature for 48 h and further aged at 130° and 190°C for various lengths of time. Transmission electron microscopic and differential scanning calorimetric experiments were carried out to evaluate the microstructures and the kinetics of the precipitation process.
- (2) The as quenched microstructure showed the presence of dislocation loops and helical dislocations. Ageing up to 4 h at 190° and 600 h at 130°C resulted in a reduction in the density of dislocation loops and helical dislocations and an increase in the size of the loops.
- (3) Ageing for more than 4 h at 190°C and 384 h at 130°C resulted in the nucleation of rod shaped precipitates of the S' phase on dislocation loops and helical dislocations.
- (4) In order to interpret the SAD pattern of the S' phase, a theoretical diffraction pattern was simulated. The method involved the use of orientation relationships of the S' phase with the fcc parent matrix, determined by x-ray diffraction techniques by other investigators and transformation of the g_s vectors of the product phase into unit normals referred to as matrix phase. This method also accounted for the g_s vectors which did not exactly satisfy the Bragg conditions. The technique is applicable to any system where the orientation

relationship is known with a reasonable degree of certainty.

(5) Centred dark field images from selected reflections in SAD pattern showed that the S' phase grew as rods in $\langle 100 \rangle_M$ directions. Connected lath formation was not found although there was a slight tendency for rods to line up in unconnected groups parallel to $\{110\}_M$ and $\{100\}_M$ planes.

(6) Relative changes in the lattice parameters of the S' phase suggested that S' is simply a strained version of equilibrium S phase which, on loss of coherency, relaxes to the equilibrium S phase. With increase in the ageing time at 190°C the b lattice parameter of the S' phase increased significantly and the value of c lattice parameter declined without any significant change in cell volume. Grouping of rods on $\{110\}_M$ fcc planes were explained on the basis of the expansion in b parameter and contraction in c parameter.

(7) The kinetics of precipitation and dissolution of stable and metastable phases were established from DSC runs. In order to analyse DSC thermograms various exothermic and endothermic peaks were identified. Suitable equations were developed and used to calculate heat effects, mole fractions and reaction rates of the processes which occurred at heating rates of 5°, 10°, 15° and 20°C/min.

(8) The kinetic analysis of the peaks were carried out by using the following relationship

$$\frac{dY}{dt} = f(Y) K_0 e^{-Q^*/RT}$$

On the basis of the expression a new differential technique

was developed to calculate activation energy Q^* for various precipitation and dissolution processes. The values of Q^* , calculated from this technique, were found to be consistent with those obtained using the integral technique. Several probable forms of function $f(Y)$ were tried using the experimental data and the best expression was determined for each peak of the DSC curves of as quenched alloys at different heating rates.

- (9) The precipitation of GPB zones occurred in the temperature range 25°-170°C and gave rise to an exothermic peak. The rate of formation of GPB zones was found to be maximum within 74°-100°C and the total heat effect associated with this peak was 6.5 J/g of this alloy. The activation energy, Q^* , for the formation of GPB zones was 55.6 kJ/mole, which is comparable with the activation energy required for the migration of vacancies. This result suggested that GPB zones formed by quench-in vacancy assisted diffusion of solute atoms. The function $f(Y)$ was $(1-Y)$. It suggested radial growth of cylindrical zones. The kinetics of GPB zones formation may be represented by

$$Y = 1 - e^{-Kt}$$

$$\text{where } K = 5.7 \times 10^5 e^{-(55600/RT)}$$

- (10) The dissolution of GPB zones occurred between (140°-240°C) and was manifested as an endothermic sub peak 1. The activation energy for GPB zones dissolution was 123.9 kJ/mole, which is consistent with the activation energy required for the formation and migration of vacancies. The function $f(Y)$ was $(1-Y)$ and the value of K_0 was 1.1×10^{10} . The $f(Y)$ function is consistent

with the dissolution of cylindrical particles of the GPB zones.

(11) The reactions which occurred between 200°-275°C and gave rise to the second exothermic sub peak were due to the interaction of GPB zones with dislocation loops. They were too complex and could not be analysed.

(12) The precipitation of rod shaped S' precipitates occurred between 253°-367°C and gave rise to an exothermic peak. The activation energy for the process was 129.9 kJ/mole and the function $f(Y)$ was $(1-Y)$. The value of K_0 was 2.56×10^9 . These results were consistent with other studies. The dissolution of S phase was found to be insensitive to variation in heating rate and was thermodynamically controlled.

6.2 EFFECT OF Si ADDITIONS

(1) The Si containing alloys Al-1.52%Cu-0.74%Mg-0.23%Si, Al-1.51%Cu-0.75%Mg-0.49%Si, Al-1.54%Cu-0.75%Mg-0.76%Si and Al-1.52%Cu-0.77%Mg-1.03%Si were examined by using TEM, SEM, DSC and other techniques in both solution treated and aged conditions.

(2) Addition of Si $\geq 0.5\%$ caused formation of insoluble particles. Small particles of nearly spherical shape were found along the grain boundaries in all the alloys except the one containing 0.23% Si. Large rounded particles were also found within the grains. The volume fraction of the insolubles in the alloy with 1.03% Si content was 1.34. The energy dispersive analysis on both the electrochemically extracted particles and particles embedded in the matrix gave the chemical composition

$20.6 \pm 0.4\%$ Cu, $32.6 \pm 0.4\%$ Mg, $30.2 \pm 0.4\%$ Si and $16.6 \pm 0.1\%$ Al by weight. The x-ray diffraction analysis showed them to have hexagonal structures with lattice parameters of $a = 1.06 \pm .004$ nm and $c = 0.406 \pm 0.004$ nm. The insolubles were found to be particles of the hexagonal Q phase. The morphology, composition and lattice parameters were not influenced by ageing at 190°C up to 1534 h.

(4) The addition of 0.23% Si did not produce any insolubles and the precipitation behaviour of the alloy remained unchanged. The only difference was a slight retardation in the rate of precipitation of GPB zones.

(5) The presence of insolubles reduced the grain size and altered the matrix composition considerably. The concentration profiles of solutes in the matrix at different percentages of Si showed that the Al-1.50%Cu-0.75%Mg alloy retains $\approx 0.35\%$ Si in solid solution. When the Si content is increased beyond $\approx 0.3\%$, insoluble particles appear and the Cu, Mg and Si contents of the matrix changed from 1.45, 0.63 and 0.39% in the 0.49% Si alloy to 1.16, 0.05 and 0.44% in the 1.03% Si alloy, respectively. The Cu/Mg ratio in the matrix changed drastically from 2.0 in 0.23% Si to 23 in 1.03% Si alloy.

(6) Addition of greater than 0.49% Si caused changes in the defect structure of the solution treated and quenched alloys. The microstructure showed the presence of isolated helical dislocations in 0.49% Si alloy while the alloy with 1.03% Si showed tangled dislocations. Ageing of the 0.49% Si alloy at 190°C resulted in the formation of three kinds of precipitates.

One of them was found to be plate shaped θ' phase while the other two were needle-like and square shaped precipitates. The crystal structure of the latter two precipitates could not be determined. Ageing of the alloy containing 1.03% Si also showed plate type θ' phase along with needle-like and dot shaped precipitates. Ageing of this alloy for 1000 h at 190°C resulted in a more complex microstructure.

6.3 SUGGESTIONS FOR FUTURE WORK

The results of the present investigation suggest that further work needs to be done in a number of related areas in order to fully understand the behaviour of the Al-Cu-Mg alloy. High resolution microscopic studies may be done in order to understand the distinction between GPB(I) and GPB(II) zones, the mechanism of their formation, the nature of the interaction between the zones, and the dislocation and dislocation GPB zone complexes.

All the precipitates which are induced by Si addition should be identified and their precipitation kinetics should be investigated.

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