

THE PRECIPITATE SEQUENCE IN SOME ALUMINIUM ALLOYS

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Introduction:

The sequence of metastable phases which occurs during the decomposition of a supersaturated solid solution and the effect of one metastable precipitate on the nucleation and distribution of succeeding precipitates is all important in determining the physical and chemical properties of an alloy. If the first metastable phase formed during the breakdown of a solid solution is homogeneously distributed, as are G.P. zones in aluminium alloys, and if the G.P. zones are effective in nucleating a second metastable phase, then the properties of the alloy will be very different than if there is heterogeneous nucleation of the second phase.

The Al-Zn Alloy System:

The Al-Zn alloy system, with an extensive single phase field and the presence of a metastable miscibility gap into which alloys can be quenched directly from the single phase field is an ideal system for studying the breakdown of supersaturated solid solutions and the succession of metastable precipitates. A portion of the phase diagrams for the Al-Zn system, as given by Goldak and Parr (1), is shown in Figure 1.

The decomposition of Al-Zn alloys has been studied intensively by a large number of investigators using a variety of experimental techniques. Experimental results up to 1963 have been summarized by Kelly and Nicholson (2). X-ray investigations have recently been carried out by Niklewski Spiegelberg and Sunbulli (3), Simerska and Synecek (4) and Rundman and Hilliard (5). Lasek (6) has studied the decomposition of a number of alloys using 'dynamic' electrical resistivity measurements. Carpenter and Garwood (7), Ardell, Nuttall and Nicholson (8) and Jacobs and Pashley (9) have used thin foil electron microscopy to study the decomposition reaction. The studies of dilute (less than 20 at.% Zn) alloys (3,4,5,6,7,9) indicate that these alloys decompose to give the aluminium-rich solid solution and the following series of precipitates:

Spherical G.P. zones \rightarrow rhombohedral $\alpha^1 \rightarrow$
cubic $\alpha^1 \rightarrow$ hexagonal zinc.

However, this series of precipitates does not specify the precipitate sequence, the importance and consequence of which is discussed below.

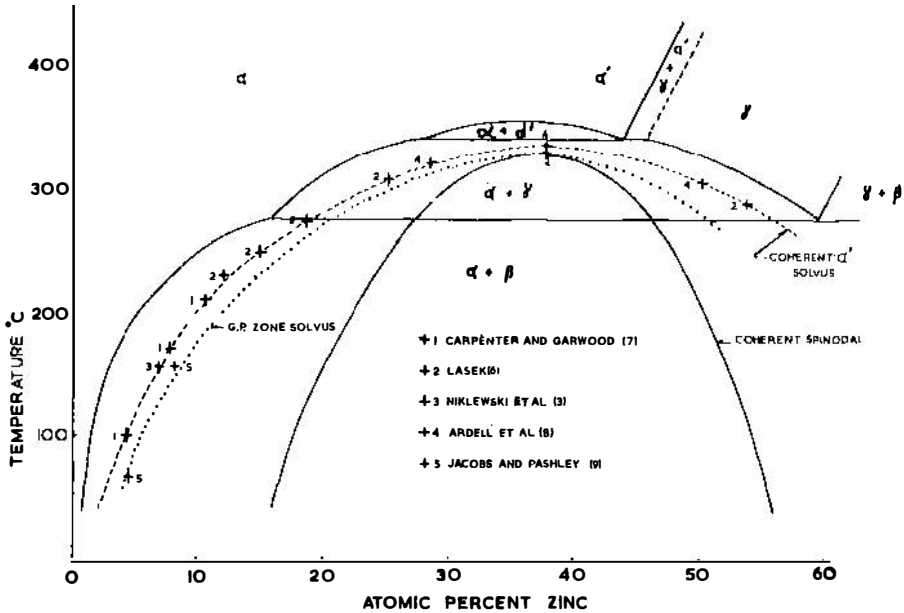


FIG. 1

A portion of the Al-Zn phase diagram taken from the work of Goldak and Parr (1) to which various metastable phase boundaries and the coherent spinodal have been added.

The experimental points of Carpenter and Garwood (7), Niklewski, Spiegelberg and Sunbulli (3) and Lasek (6) have been added to Figure 1. All of these results were obtained during classical "reversion" experiments in which the alloy was quenched, held at a low temperature to allow G.P. zone to form and then up-quenched to "revert" the zones; the results are mutually consistent and are referred to by the respective authors as $T_{G.P.}$, the metastable G.P. zone solvus. Lasek (6) cooled his alloys until he was well below the temperature at which G.P. zones formed and then increased the temperature until his resistivity measurements indicated that a precipitate had dissolved. Carpenter and Garwood (7)

used the technique of Betton and Rollason (10) in which the hardness minima obtained during isothermal ageing is plotted against ageing temperature and any discontinuity is taken as the critical temperature for the reversion of G.P. zones. The techniques of both Carpenter and Garwood (7) and Lasek (6) are indirect and will indicate the correct position of $T_{G.P.}$ only if the G.P. zones do not readily nucleate a more stable phase. Niklewski, Spiegelberg and Sunbuli (3) examined the precipitate dissolution during a classical reversion experiment by a diffuse X-ray scattering technique and interpreted their results as evidence for the dissolution of G.P. zones; their experimental result is also included in Figure 1.

The opposite experiment to reverting a quenched and aged alloy is to quench directly to the ageing temperature. By using this technique (11) it is possible to study the nucleation of G.P. zones without the complications inherent in the interpretation of reversion experiments. Jacobs and Pashley (9) carried out a series of direct quenching experiments on Al- 4.5 and 8.0 at.% Zn alloys. The microstructures of the samples quenched to successively lower temperatures were examined in the electron microscope and the temperature at which the first precipitate was observed, 155°C for the 8.0 at.% Zn alloy and 65°C for the 4.5 at.% Zn alloy, was designated as the critical temperature or $T_{G.P.}^*$ (Figure 2).



FIG. 2

Al- 8.0 at.% Zn alloy direct quenched from 560°C into an oil bath at 160°C showing a homogeneous distribution of precipitate (From Jacobs and Pashley (9)).

* For a discussion of this terminology see reference (8,9) page 94,95.

The results of Jacobs and Pashley are plotted on Figure 1 and they fall well below those obtained using reversion techniques (3,6,7). An explanation of the discrepancy between the reversion and direct quenching results can be given in terms of the precipitation sequence which occurs during a quenching and ageing treatment. When the temperature falls below $T_{G.P.}$ G.P. zones form; the distribution of the zones is homogeneous and it is reasonable to assume that they are homogeneously nucleated. Isothermal ageing at a temperature below $T_{G.P.}$ will result in the growth and subsequent coarsening of the G.P. zones. Simerska' and Synecek (4) have shown that in Al- 12.2 and 15.0 at.% Zn alloys aged below $T_{G.P.}$ the anisotropy of the coherency strains around the G.P. zones produces an internal rhombohedral distortion which gives rise to a change in shape of the G.P. zones from spherical to ellipsoidal. The strain fields in the matrix associated with the change in shape of the zone can be clearly seen in the electron microscope (Figure 3). Subsequent

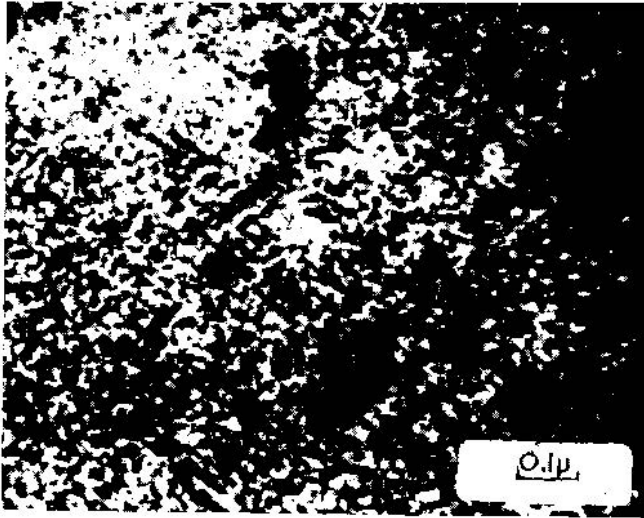


FIG. 3

Al- 4.7 at.% Zn alloy, water quenched from 540°C and aged at 100°C for 24 hours showing small strained precipitates. (From Kelly and Nicholson (2)).

loss of coherency of the zones with the α -matrix, except in the (111) habit plane, leads to the formation of the rhombohedral α^1 phase. The

cubic α' is developed by the breakdown of the partial coherency of the rhombohedral phase. Thus from a homogeneous distribution of G.P. zones a homogeneous distribution of the rhombohedral α' and subsequently of the cubic α' is produced. If the alloy is quenched directly to the ageing temperature then this temperature must be below $T_{G.P.}$ if a homogeneous distribution of G.P. zones or α' is the result. If the alloy is quenched below $T_{G.P.}$, and then aged at a temperature above $T_{G.P.}$ but below the solvus as given by reversion experiments (3,6,7), then the G.P. zones will not revert to a solid solution of zinc in aluminium but will act as nuclei for the formation of α' . Only upon ageing above the metastable α' solvus will "reversion", as determined by indirect measurements, take place. Thus in Figure 1, the results obtained by the reversion experiments (3,6,7) delineate the α' metastable solvus while the direct quenching experiments of Jacobs and Pashley (9) specify $T_{G.P.}$.

The equilibrium β phase is nucleated on dislocations and is present in all quenched and aged samples (Figure 4) but only after prolonged ageing at low temperatures or ageing at elevated temperatures is it a prominent feature of the microstructure.

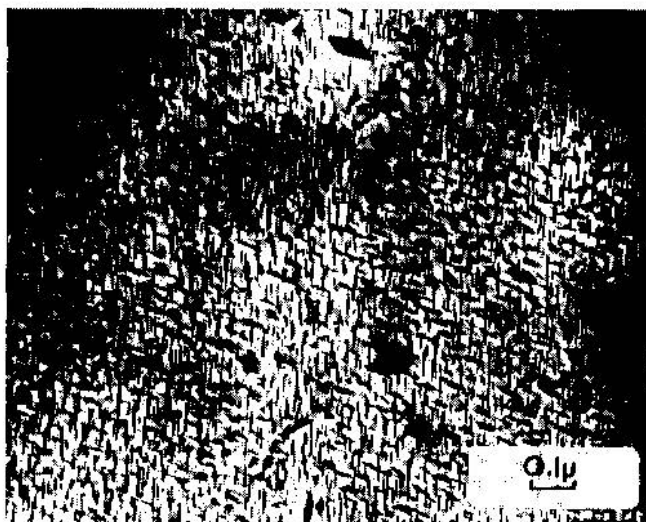


FIG. 4

Al- 4.7 at.% Zn alloy, water quenched and aged at 100°C for 120 hrs. Showing heterogeneous nucleation of zinc-rich β .

The above discussion has been confined to the precipitate sequence in dilute alloys and it is of interest to examine this sequence in more concentrated alloys. Lasek (6) has investigated a large range of alloy compositions and all of his points fall on the same curve, Figure 1. Ardell, Nuttall and Nicholson (8) have carried out a series of direct quenching experiments on 28.4 and 39.3 at.% Zn alloys, and have examined the structures produced in the electron microscope. In both alloys the first phase which was detected was not G.P. zones but α' ; the temperature at which α' was first observed in the 28.4 and 39.3 at.% Zn alloys has been plotted in Figure 1 and these points coincide with the results of Lasek (6). Ardell, Nuttall and Nicholson (8) have designated this temperature as the coherent α' metastable solvus, an interpretation which is consistent with the results discussed above for the dilute alloys. G.P. zones were not detected during any of the direct quenching experiments of Ardell, Nuttall and Nicholson, however the G.P. zone $\rightarrow \alpha'$ transformation would proceed rapidly at the high temperatures investigated (15) and it is unlikely that they would be detected.

Ardell, Nuttall and Nicholson (8) also examined the decomposition of a 59.0 at.% Zn alloy. In specimens quenched and aged at temperatures above 100°C the decomposition product had a lamellar structure while at lower ageing temperatures a granular microstructure was observed which was interpreted as evidence for spinodal decomposition. The small angle scattering results of Rundman and Hilliard (5) on concentrated alloys support this proposal.

The coherent phase boundary as given by Cahn (12) has been included in Figure 1 and, while it is well below the coherent α' metastable solvus, it coincides with metastable G.P. zone solvus as determined by Jacobs and Pashley (9). The excellent correlation between the G.P. zone solvus as determined by the electron microscopy of direct quenched samples and the calculated coherent phase boundary is strong evidence to support the proposal that G.P. zones are formed by a process of homogeneous nucleation and growth and not by spinodal decomposition, as has been suggested (13).

Al-Zn-Mg and Al-Mg-Si Alloys:

The decomposition of Al-Zn alloys is particularly interesting because of the wide range of supersaturations which are obtainable in quenched alloys. The sequence of precipitates which occurs in dilute Al-Zn alloys - the nucleation and growth of G.P. zones followed by the nucleation of an intermediate or equilibrium phase by the G.P. zones - occurs in a number of other aluminium alloys. Al-Zn-Mg and Al-Mg-Si are two alloy systems which have been intensively studied by electron microscopy. Direct quenching experiments have been used to determine the G.P. zone solvus in both alloys (11,14), and a homogeneous distribution of G.P. zones is a prerequisite for a homogeneous distribution of the intermediate, strengthening precipitate. In Al-Zn-Mg alloys the metastable solvus for the intermediate η' precipitate is well above $T_{G.P.}$ (more than 125°C in an Al- 6 wt.% Zn - 3 wt.% Mg alloy as compared to 25°C in an Al-10 at.% Zn alloy). This wide temperature range of the stability of the η' precipitate and a G.P. zone $\rightarrow \eta'$ transition at a G.P. zone size which is readily obtained in a quenched alloy after a short time at room temperature produces a system in which the η' dispersion can be changed markedly by alterations in the size distributions of the G.P. zones. If the 6 wt.% Zn - 3 wt.% Mg alloy is quenched and immediately aged at 180°C ($T_{G.P.} = 170^{\circ}\text{C}$) a fairly coarse distribution of η' and a wide PFZ (precipitate free zone) are formed, (Figure 5a), while if the same alloy is held at 100°C for 15 minutes after quenching but before ageing at 180°C the density of the matrix precipitate is increased and the width of the PFZ is decreased (Figure 5b). In the sample which was quenched and immediately aged at 180°C only a few of the G.P. zones have reached the critical size to act as η' nuclei at 180°C . The effect of the short ageing time at 100°C is to increase the number of G.P. zones greater than this critical size and thus to increase the density of η' formed upon ageing at 180°C . The region adjacent to the grain boundary is particularly sensitive to low temperature treatments because of the decrease in G.P. zone size as the grain boundary is approached due to the variation in diffusivity, and hence size of G.P. zone, associated with the vacancy concentration profile formed adjacent to the grain boundary during the quench (11).



(a)

(b)

FIG. 5

- (a) Al- 5.9 wt.% Zn - 2.9 wt.% Mg alloy water quenched from 465°C and immediately aged at 180°C for 3 hrs.
- (b) as in (a) except held at 100°C for 15 minutes between quenching and ageing at 180°C.

The mechanism of the G.P. zone $\rightarrow \eta'$ transformation has not been studied in detail as has the G.P. zone $\rightarrow \alpha'$ transformation in Al-Zn alloys, although it is probable that a similar "in-situ" reaction takes place.

Al-Ge and Al-Si Alloys:

In the Al-Ge and Al-Si alloys the precipitate sequence is similar to that in Al-Zn alloys but the precipitate series is a short one: the G.P. zones nucleate the equilibrium phase directly (15). In both alloys the temperature must be decreased to below $T_{G.P.}$ during the quench if a homogeneous distribution of precipitate (Ge or Si) is to be formed upon ageing, and in both systems the precipitate can be refined by treatments

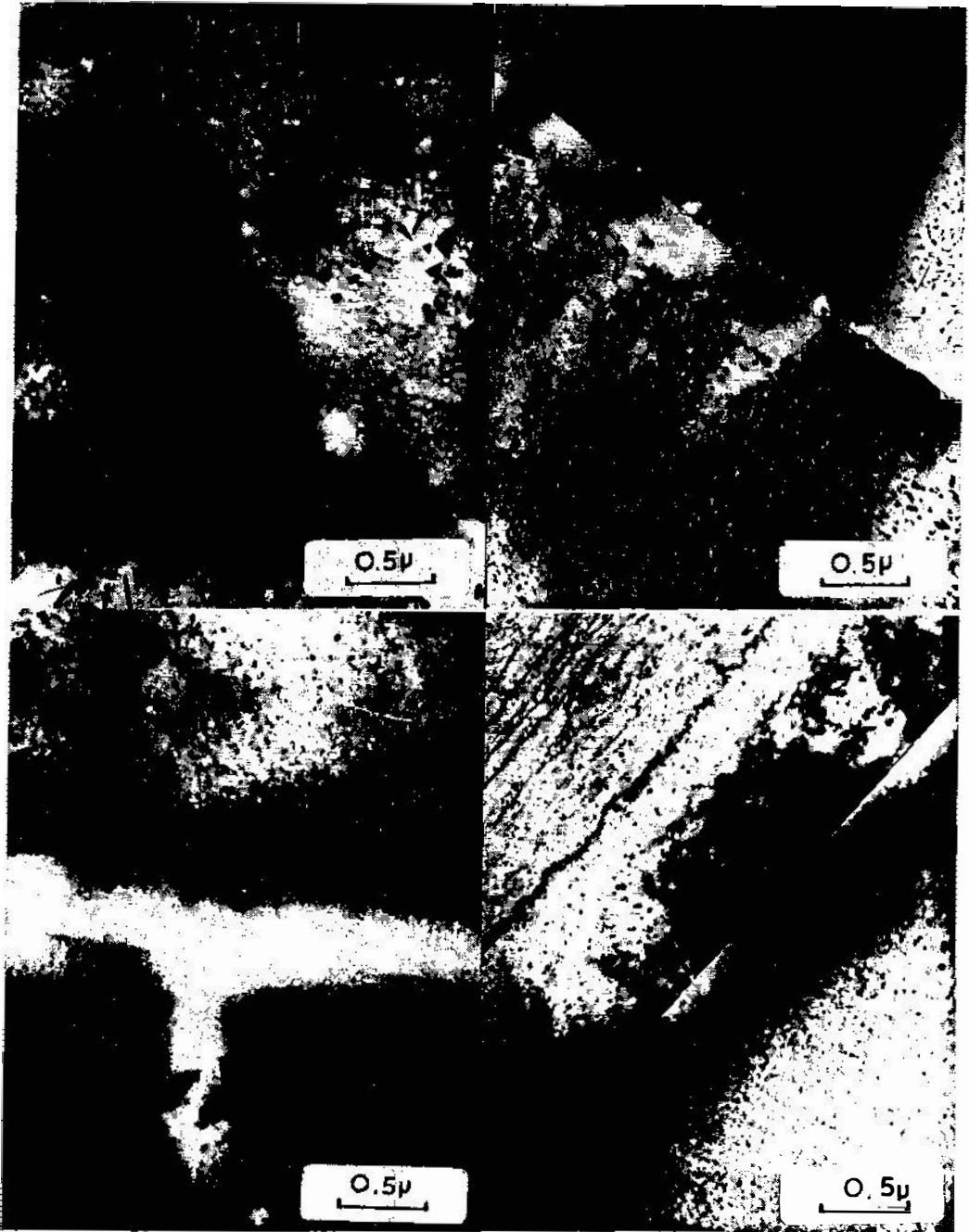


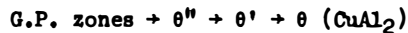
FIG. 6

- (a) Al- 4.5 wt.% Ge alloy water quenched from 450°C and immediately aged at 170°C for 5 hours.
- (b) as in (a) except held at 50°C for 2 hrs. between quenching and ageing.
- (c) Al- 1.2 wt.% Si alloy water quenched from 580°C and immediately aged at 260°C for 30 min.
- (d) as in (c) except held at 100°C for 2 minutes between quenching and ageing.

below $T_{G.P.}$ (Figure 6). The effect of holding treatments below $T_{G.P.}$ has a more dramatic effect on the precipitate distribution in the Al-Si alloy than in Al-Ge. This may be a consequence of Ge having a larger atomic volume than Al while Si is smaller. Gruppen and Sines (16) have proposed that the rate of growth of disk-shaped G.P. zones rich in a solute of larger atomic volume than the matrix should be much slower than when the solute is smaller than the matrix. The interaction of the elastic strain field of the G.P. zone and the vacancies leads to a high concentration of vacancies near the poles of the disk containing larger atoms and hence a reduction in the rate of growth in the plane of the disk, while in a zone containing smaller atoms the vacancies are concentrated at the periphery of the disk and growth in the plane of the disk is enhanced.

Al-Cu Alloys:

Of all of the precipitation hardening aluminium alloys the Al-Cu system is the most thoroughly documented. The series of precipitates formed during the breakdown of the supersaturated solid solution is accepted to be (2)



The G.P. zones are coherent Cu-rich plates on $\{100\}_\alpha$, θ'' and θ' are tetragonal plates on $\{100\}_\alpha$ with lattice parameter $a = 4.04 \text{ \AA}$ and $c = 7.08 \text{ \AA}$, $a = 4.04 \text{ \AA}$, $c = 5.8 \text{ \AA}$, respectively. θ'' is coherent with the matrix while θ' becomes semi-coherent as the plates grow and thicken. The equilibrium precipitate θ is tetragonal, $a = 6.07 \text{ \AA}$, $c = 4.87 \text{ \AA}$ and has a variable orientation relationship with the matrix. Silcock, Hardy and Heal (17) have shown that the reversion temperature for an Al-Cu alloy containing G.P. zones was the same as the limiting temperature for the formation of zones. Beton and Rollason (10) have determined the G.P. zone solvus and the θ'' solvus for a series of Al-Cu alloys which had been held at room temperature for ten days and 130°C for ten days, respectively. The results of these authors are shown in Figure 7 and have been shown by Lorimer and Nicholson (15) to be consistent with the G.P. zone solvus, as determined by direct quenching experiments on an Al-3.9 wt.% Cu alloy.

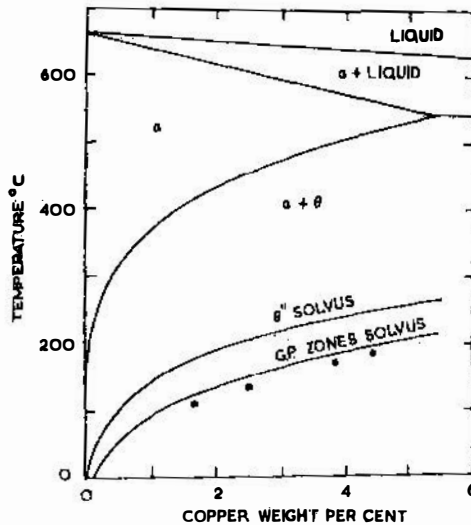


FIG. 7

A portion of the phase diagram for the Al-Cu system showing the metastable phase boundaries for G.P. zones and θ'' (17). The full circles are limiting temperatures for the successive formation of G.P. zones and θ'' (10).

The precipitation sequence in Al-Cu alloys is similar to that described above for the other alloys; G.P. zones must first be nucleated before it is possible to form a homogeneous distribution of θ'' (Figure 8a). If an alloy is directly quenched into the region of the phase diagram between the θ'' solvus and $T_{G.P.}$, only heterogeneous nucleation of θ' takes place. (Figure 8b)



(a)

(b)

FIG. 8

- (a) Al- 3.9 wt.% Cu alloy direct quenched from 525°C into oil at 145°C and aged at 145°C for 5 hrs. showing a homogeneous distribution of θ'' .
- (b) Al- 3.9 wt.% Cu alloy direct quenched to 210°C showing heterogeneous nucleation of θ' on dislocations.

In alloys quenched below $T_{G.P.}$ and aged above $T_{G.P.}$ but below the θ'' solvus G.P. zones will nucleate θ'' and the distribution of θ'' is a function of the size distribution of G.P. zones present when the alloy is up-quenched to the ageing temperature.

θ' is the precipitate which traditionally succeeds θ'' in the precipitate sequence and it is often inferred that θ' is nucleated from θ'' ; the microstructure of an alloy aged for the correct period of time consists

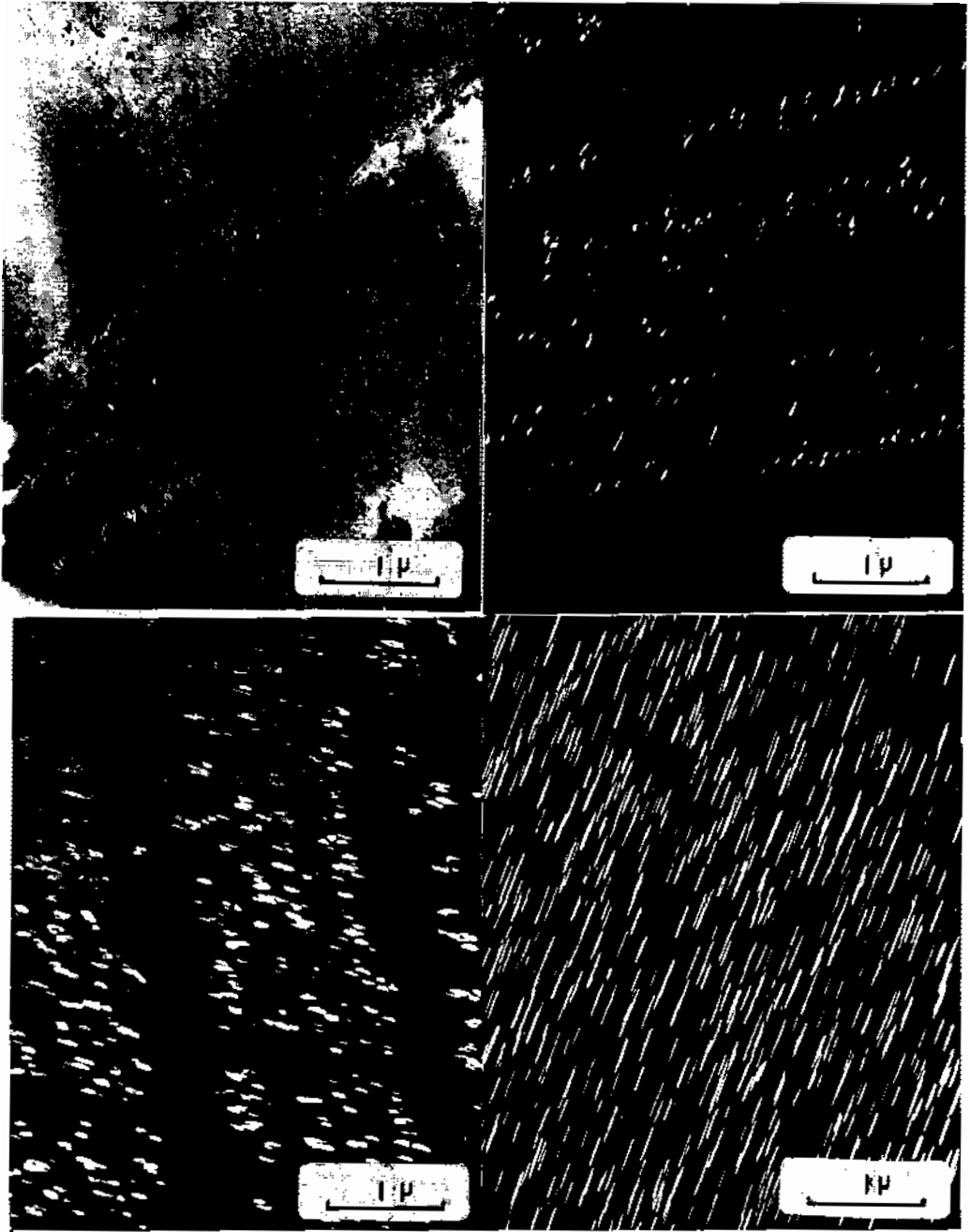


FIG. 9

Al- 3.9 wt.% Cu alloy water quenched from 525°C and aged at 240°C for (a) 0 min. (b) 3 min. (c) 15 min. and (d) 35 min. showing the expansion of θ' into the matrix from the original nucleation sites on dislocations.

of a Widmanstätten array of homogeneously distributional θ' plates. If a specimen containing a homogeneous distribution of θ'' is up-quenched to a temperature above the θ'' solvus the θ'' precipitate dissolves and does not play a direct role in the nucleation of θ' . θ' is nucleated on dislocations and from these sites the regions of θ' expand to fill the volume of the crystal (18), (Figure 9). At temperatures below the θ'' solvus the nucleation and growth of θ' proceeds in the same manner as at higher temperatures. The advancing front of the θ' precipitates is preceded by the dissolution of θ'' , but the θ'' does not play a direct role in the nucleation of θ' (Figure 10).

The nucleation and growth of θ' plates proceeds in the same manner whether θ'' precipitates are present or not; in this way the nucleation of θ' is similar to the nucleation of the hexagonal zinc-rich β phase in dilute Al-Zn alloys and $MgZn_2$ and Mg_2Si phases in Al-Zn-Mg and Al-Mg-Si alloys, respectively. However, the mechanism of the growth of successive θ' plates is different from that of any of the other alloys discussed. Examination of the reaction front of the θ' precipitates reveals that each plate is in close proximity, though usually not in contact, with other θ' plates. The nucleation of one θ' plate is dependent on the previous θ' plate which, in turn, was either nucleated by a θ' plate or by the original dislocation. Close examination of the edge or an expanding θ' band reveals that, while each plate is closely associated with other plates that there is a gap of 50 to 100 Å (Figure 11) between adjacent plates of θ' . The presence of this gap between plates, the initial nucleation event at a dislocation and the nucleation of θ' independent of θ'' is an indication of the importance of the elastic strain energy in the nucleation of θ' and would support an autocatalytic mechanism for the nucleation of θ' plates. Weatherly (19) and Aaronson and Laird (20) have shown that individual θ' precipitates grow by the movement of multi-atomic ledges across the broad faces of the θ' plates. This movement of ledges across the face of the θ' plate would cause a step-wise increment in the strain field in the matrix and trigger the nucleation of another θ' plate. Another possible mechanism for the

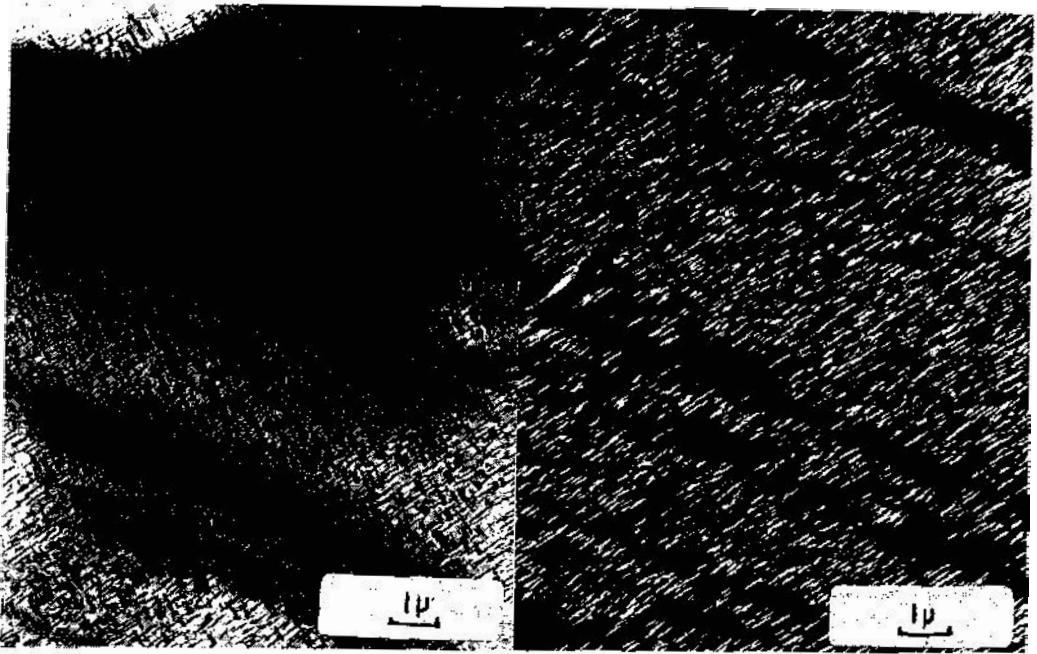


FIG. 10

(a) Al- 3.9 wt.% Cu alloy water quenched from 525°C and aged at 180°C for 45 hrs.

(b) same field as (a) with a θ' reflection. The advancing front of the θ' precipitates is preceded by the dissolution of θ'' .



FIG. 11

Al- 3.9 wt.% Cu alloy water quenched from 525°C and aged at 240°C for 15 min. showing the edge of a band of expanding θ' . The small gaps between some of the θ' plates are arrowed.

nucleation of successive θ' plates is the punching-out of a dislocation by the growing θ' plate and the nucleation of the next θ' plate on this dislocation. However the examination of the growth front of a band of θ' does not reveal any dislocations and the nucleation of one θ' plate usually occurs while the preceeding θ' plate is still coherent with the matrix across the broad faces of the plate and thus the autocatalytic mechanism is favoured.

Conclusion:

In a number of Al- base alloys, including Al-Zn, Al-Zn-Mg, Al-Mg-Si, Al-Ge, Al-Si and Al-Cu, G.P. zones are instrumental in nucleating the succeeding phase and by controlling the size distribution of G.P. zones it is possible to control the dispersion of this phase.

The nucleation of the equilibrium phase is often heterogeneous and independent of the distribution of preceeding precipitates.

In Al-Cu alloys the nucleation of successive plates of θ' is by an autocatalytic mechanism.

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