Effect of different variables on the precipitate-free zones adjacent to grain boundary regions in conventionally quenched and aged Al-Zn-Mg alloys

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SYNOPSIS

Age-hardenable aluminium alloys are noted for their high strength to weight ratio. Age-hardenable alloys based on the aluminium-zinc-magnesium system possess the highest static strength of known aluminium alloys. A noticeable feature of these alloys is the "denuded zones" or "precipitate-free zones" present at grain boundaries. These zones are soft with respect to the matrix, a fact which adversely affects the resistance of these alloys to stress-corrosion cracking. An attempt has been made in this paper to review the different variables that affect the zone width. A knowledge of these variables would be helpful towards a better understanding of the stress-corrosion behaviour of these alloys. Mehods may then be found out to reduce the susceptibility of these alloys to stress-corrosion cracking.

It is observed that the zone width is strongly dependent on solution treatment temperature, ageing temperature, quenching rate and ageing time. Trace elements like silver, titanium, etc improve the stress corrosion property of these alloys by reducing the zone width. Cold working and the addition of other alloying elements result in a similar improvement. The beneficial effect of copper, manganese and chromium has also been discussed.

THE Eleventh Report to the Alloys Research Committee of the Institution of Mechanical Engineers prepared by Rosenhain, Archbutt and Hanson[1] in 1921, recorded a tensile stress exceeding 40 tons/in^2 in a wrought aluminium alloy containing 20% zinc along with magnesium, copper and manganese but did not recommend this type of alloy for use on account of season cracking. Recognition of the outstanding mechanical properties of Al-Zn-Mg alloys at lower ranges of zinc content was due to work carried out by Sander and Meissner[2] in 1926, which also indicated the significance of corrosion as a factor in cracking under prolonged stressing i.e., stress-corrosion cracking. Inspite of intensive studies over the past 40 years leading to wide adoption by the aircraft industry of alloys of this basic type, relationships between composition, stress level and cracking in service are still undefined.

With the invention of electron-microscopy detailed micro-structural studies have been made by different investigators.[3,4,5] Electron-micrographs clearly indicate that the stress-corrosion susceptibility and the lack of ductility of aged Al-Zn-Mg alloys are normally associated with soft precipitate-free regions adjacent to the grain boundaries. When the alloys are deformed, the precipitate-free zones serve as favourable sites for dislocation movement and this may lead to preferential flow in these regions and ultimately to intercrystalline failure. The maximum difference between the flow stresses of the precipitate-free regions and the grain interiors is produced in alloys aged to peak hardness. Stress concentration effects occur at the grain boundaries and as a result dislocation movement may take place in the precipitate-free regions at applied stresses much below the macroscopic yield stress.

The problem of stress-corrosion cracking, therefore, arises in alloys aged to maximum tensile strength, where there is maximum grain boundary embrittlement. The solution to this problem is, thus, to eliminate the precipitate-free regions next to grain boundaries, whilst at the same time retaining a high mechanical strength. Some possible ways of doing this are :

1. To use single crystals, which of course, is impossible for engineering structure.
2. To reduce the width of the precipitate-free zone to a great extent by the help of proper heat treatment i.e., proper control of solution treatment temperature, ageing temperature, ageing time, quenching rate, etc.
3. To study the effects of some alloying additions.

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4. To fill up the existing precipitate-free regions with dislocations which may act as new nuclei for the precipitates. This may be achieved by plastic deformation prior to ageing.
5. To modify, by the addition of trace elements, the structure of the precipitate phase so that it is nucleated coherently and does not require vacancies.
6. To stabilise, by the addition of trace elements, the vacancy clusters near the grain boundary and to prevent the formation of a vacancy-free zone.

Precipitate-free zone—its meaning and causes of its formation

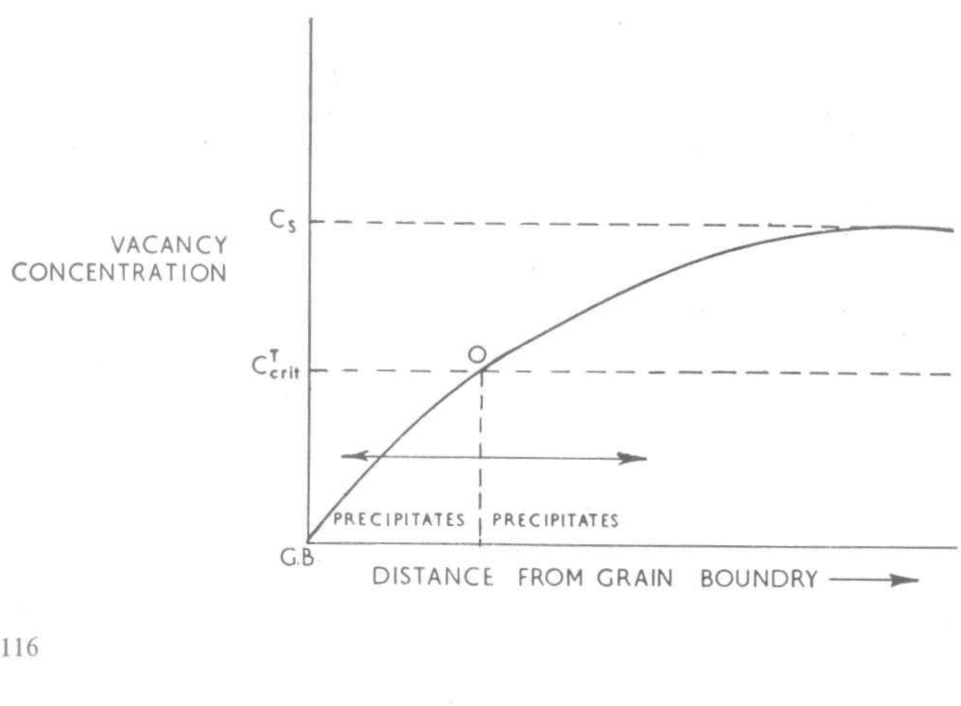
The classical theory of heterogeneous nucleation can be applied to precipitation at grain boundaries. For nucleation at a grain boundary the term $\triangle$f surface in equation 1 must decrease because of the presence of a grain boundary. There may also be some decrease in $\triangle$f strain term. These effects result in a lower value of $\triangle$f which makes possible the nucleation of the equilibrium phase at grain boundaries even at low ageing temperatures. The grain boundary precipitate is then in a lower energy state than the zones or intermediate precipitates formed within the grain and it will, therefore, tend to increase in size during ageing at the expense of intragranular precipitates. In addition, the grain boundary precipitate is frequently nucleated before the intragranular precipitate and is able to draw solute atoms from within the grains. Classical precipitation theory has assumed that these two effects are the cause of the "denuded zone" near grain boundaries. Electron microscopy has shown that this is not always true for the reasons discussed below.

The results of Rosenbaum and Turnbull[6] on Al-Si alloys for the formation of a precipitate-free zone near grain boundaries can be summarised as follows :

1. The width of the precipitate-free zone increases with decreasing quenching rate although the amount of grain boundary precipitation is hardly affected.
2. Precipitates on the edge of the precipitate-free zone are larger than those within the grains suggesting that they are able to draw excess solute atoms from the zone.
3. If the alloy is deformed before ageing, precipitation occurs near the boundary and there is no precipitate-free zone.

It may, therefore, be concluded that in this alloy the "denuded zone" is only denuded of nucleating sites for precipitates and that the solute concentration is the same as that in the supersaturated solid solution within the grains. Therefore, the "denuded zone" is in fact only denuded of vacancies and the phrase "precipitate-free zone" is a better description.

The most practical example showing the above effect has been given by Embury and Nicholson[7] through an experiment involving a double ageing treatment given to a specimen of Al–5·9% Zn-2·9%Mg alloy. The specimen was solution treated, waterquenched, aged for 3 hours at 180°C and then aged for 15 hours at 135°C. The resulting microstructure showed an initial precipitate-free zone width of about ·5μ characteristic of an ageing temperature of 180°C. On subsequent ageing at 135°C fine precipitation occurred inside the previous precipitate-free zone thus reducing the width to $\sim$·25μ which is characteristic of lower ageing temperature in a freshly quenched specimen. The above experiment clearly showed that any explanation of the precipitate-



1 *A schematic illustration of the vacancy concentration profile formed on quenching. C^S is the equilibrium vacancy concentration at the solution temperature T_S and C^T_{crit} is the critical vacancy concentration required to nucleate precipitates at an aging temperature T (From J. D. Embury and R. B. Nicholson).*

free zone in terms of solute denudation must be incorrect since the amount of precipitates is far greater than can be accounted for simply by the decreasing solute solubility.

After quenching from the solution treatment temperature an alloy will be supersaturated with respect to both solute atoms and vacancies, except in the vicinity of vacancy sinks. That the grain boundaries act as vacancy sinks has been demonstrated by the absence of dislocation loops in regions adjacent to the boundaries in drastically quenched aluminium.[8] The distribution of a grain boundary immediately after quenching from solution treatment temperature may, therefore, be expected to be as shown in Fig. 1. The vacancy concentration in the grains C^S is determined by the solution treatment temperature and is simply equal to A exp $\left(\frac{-EF}{KT_S}\right)$

where,

A = entropy factor
E_F = energy of formation of a vacancy
K = Boltzmann's constant
T_S = solution treatment temperature

Westmacott, Barnes, Hull and Smallman[9] have carried out some investigations on aluminium-zinc-magnesium system and reported that a high interaction exists between vacancies and the large magnesium atoms so that vacancies which are retained after the quench will tend to be associated with magnesium atoms. The presence of excess vacancies during ageing seems to be essential to the nucleation process in this system, for there is no reason to suppose that concentration of solute atoms also decreases in the vicinity of the grain boundary. It is believed that the vacancies will not only accelerate the diffusion of solute atoms but also facilitates the nucleation of precipitate by decreasing the value of the strain energy term in the expression.

$$\triangle f = \triangle f \text{ vol.} + \triangle f \text{ surface} + \triangle f \text{ strain} \quad \ldots \quad (1)$$

for the net change in free energy. Thus, a critical concentration of vacancies will be required for the nucleation of precipitate under fixed conditions of ageing.[6] This critical concentration of vacancies has been designated by C^T crit. and shown in Fig. 1 by a horizontal line. Thus, from Fig. 1 it is clear that there will be no precipitates between the grain boundary and the point O in Fig. 1 but nucleation will occur within the grains.

Effect of heat treatment

The simple model in Fig. 1 may be extended in Fig. 2 to show the effects of different solution treatment temperatures, different ageing temperatures and quenching rates. It is known that in addition to point defects formed by thermal fluctuations, point defects may be created in the crystal by other means. One method of producing an excess number of point defect is by quenching from a higher temperature. If temperature is lowered fast enough in the quench, some of the defects in equilibrium at higher temperature may be retained at lower temperature i.e., increase of the solution treatment temperature will increase C^S and the whole vacancy concentration profile will be raised up. On the other hand, a slower quenching rate leads to a greater diffusion distance during quenching and has a lower profile. The reduction in the width of the precipitate-free zone at lower ageing temperatures may be explained by the higher degree of solute supersaturation and the corresponding change in the volume free energy $\triangle$f volume. The critical concentration of vacancies required for nucleation will fall then and the corresponding widths of the precipitate-free zone become a and b.

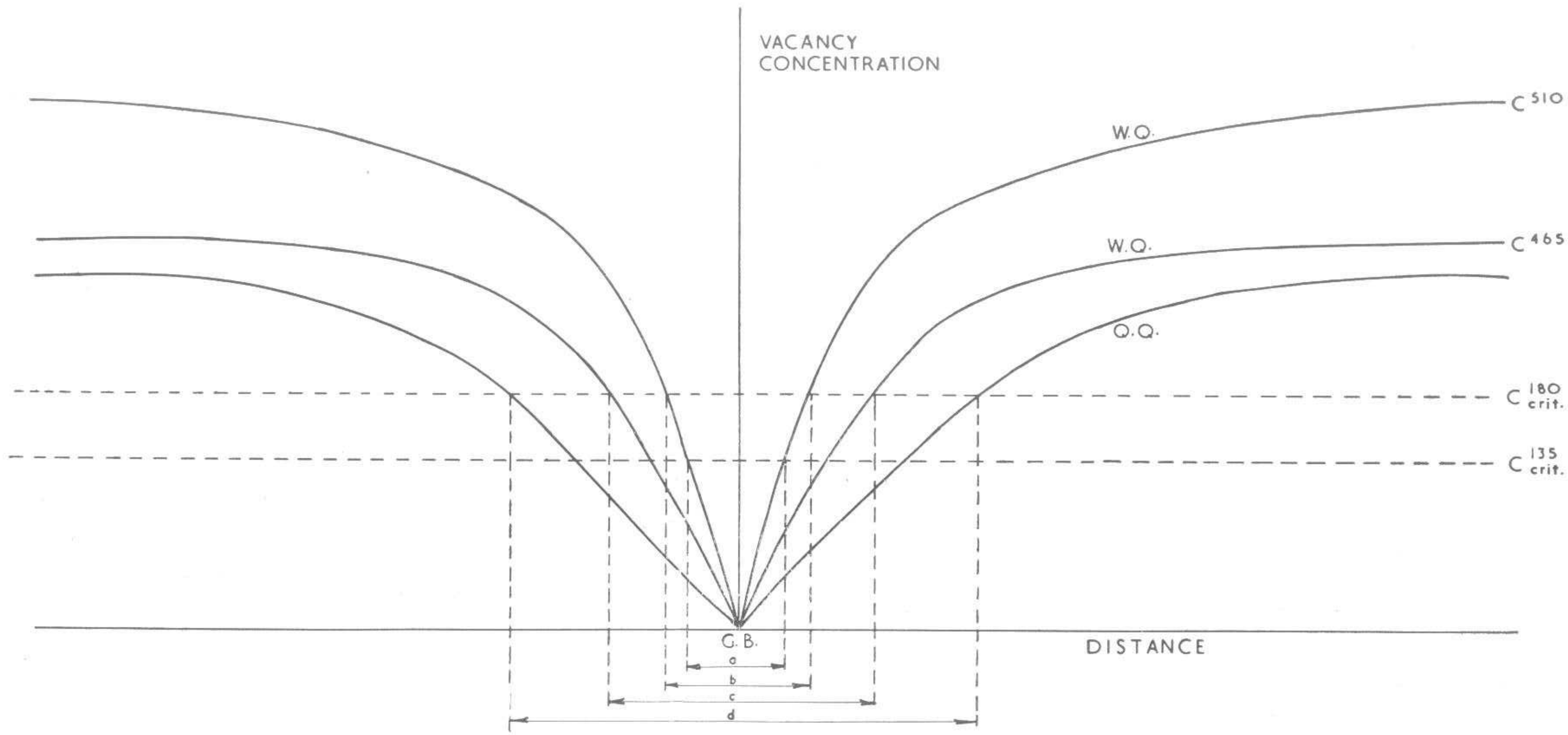
The above discussions explain clearly the raising or lowering of the vacancy concentration profile under different conditions of heat treatment. The predicted precipitate-free zone widths a, b, etc., are shown on the diagram for various heat treatment procedures. Considering an ageing temperature of 180°C it is clear that the model predicts a narrow zone for a higher solution treatment temperature i.e., $b<c$ as shown in Fig. 2.

For a given solution treatment temperature the zone width is narrow at the lower ageing temperatures i.e., $a<b$ (Fig. 2). Both these effects have been found experimentally by Taylor[10] and also by Embury and Nicholson.[7] Finally for constant solution treatment temperature and ageing temperature, a slower quenching rate will give a wider zone i.e., $d>c$ in Fig. 2.

Recent work by Lorimer and Nicholson[11] shows that the ageing time also has a marked effect on the dispersion of precipitates and the width of the precipitate-free zone. They quenched several specimens to below the G–P zone solvus and held there for various times (0·1, 1, 15, 60 min.) before giving a standard ageing treatment of 3 hours at 180°C. They found that a long holding time gave a fine dispersion of precipitates and narrow precipitate-free zone. Experiments with other holding temperatures below 155°C show qualitatively similar results although the rate of refinement of the precipitate and narrowing of the precipitate-free zone is much less at lower holding temperatures and ceases altogether below about –50°C.

Effect of alloying elements

Various alloying elements such as copper, manganese, chromium, titanium, silver, etc. have been added to Al–Zn–Mg alloys by a number of investigators[5,12,13,14,15] in an attempt to reduce the susceptibility of these alloys to stress-corrosion cracking. Polmear[5] has shown through shadowed carbon replica technique that the addition of silver in an Al–2·7%, Zn–2·6%, Mg. –0·5% Cu alloy leads to the removal of the precipitate-free zone completely on ageing for 1 day at 175°C and as expected this results in an increased resistance to stress-corrosion cracking. Chadwick, Muir and Grainger[1] have reported that the addition of copper, chromium and manganese is responsible for the improved stress-corrosion preformance of Al–Zn–Mg alloys but they have mentioned that when manganese is added in the



2 *A comparison of the vacancy concentration profiles for various solution treatment, quenching and ageing conditions. The precipitate-free zone widths depicted are (a) solution at 510°C, water quench, age at 135°C (b) solution at 510°C, water quench aged at 180°C, (c) solution at 465°C, water quench, aged at 180°C and (d) solution at 465°C, oil quench, aged at 180°C (from J. D. Embury and R. B. Nicholson)*

absence of chromium it has no effect on stress-corrosion properties. Roy and Das[13] have confirmed this result but no attempt has been made by these investigators to find out whether any correation exists between stress-corrosion property and the precipitate-free zone. Gantait and Das[14] have worked with Al-Zn-Mg-Cu-Ti alloys and reported the beneficial effect of Ti. The reason for such improvements as they have proposed is that the precipitate is nucleated coherently and does not require vacancies.

Chaudhuri and Das[15] through electron microscopic (oxide replica technique) studies have shown that manganese in presence of copper restricts the precipitate-free zone and hence results in better stress-corrosion properties. They have worked with seven different alloys in each of which the zinc and magnesium contents were kept fixed at 5% and 2·5% respectively. Out of these, one was a ternary Al–Zn–Mg alloy ; two of them were quaternary Al–Zn–Mg–Cu alloys with 0·5 and 1% Cu, while the last four alloys were quinary alloys with different copper and manganese contents. The results are summarised in the following table.

Alloy	Treatment	Thickness of the precipitate-free zone	Time of failure during stress-corrosion testing*
Al-5% Zn-2·5%Mg	Waterquenched from 455°C and aged for 12 weeks at 130°C	0·500μ	48 hours
Al-5% Zn-2·5% Mg-0·5% Cu	,,	0·280μ	96 hours
Al-5% Zn-2·5% Mg-1% Cu	,,	0·255μ	120 hours
Al-5% Zn-2·5% Mg-0·5% Cu-0·5% Mn	,,	0·135μ	240 hours
Al-5% Zn-2·5% Mg-0·5% Cu-1% Mn	,,	0·100μ	312 hours
Al-5% Zn-2·5% Mg-1% Cu-3% Mn	,,	0·030μ	320 hours

* The corrosive solution used during stress-corrosion test was 5% NaCl, 1% HCl and 94% water ; maximum tensile stress developed within the specimens was 10·7 tons/in^2.

From an inspection of the above table it is seen that the role of copper in restricting the formation of the precipitate-free zone is not so prominent in the quaternary alloys as in the case of quinary alloys in which copper and manganese are added together ; stress-corrosion results clearly indicate this behaviour. The improvment in stress-corrosion properties of the Al-Zn-Mg alloys by the addition of copper can be accounted for by the fact that copper increases the particle size and the particle spacing. Thus, deformation slip in the matrix can occur in this alloy earlier during ageing compared to that in the ternary alloy.

Manganese has restricted the formation of the precipitate-free zone adjacent to the grain boundary and consequently has improved the stress-corrosion properties of the alloys possibly due to the following reasons :

(i) The addition of manganese has modified the structure of the precipitate phase so that it is nucleated coherently and does not require vacancies.

(ii) The addition of manganese has stabilised the vacancy clusters near the grain boundary and has restricted the formation of a vacancy-free zone.

Effect of cold work

Deformation either prior to or during the ageing process may be employed to minimise the deleterious effects of precipitate-free regions. The deformation introduces additional nucleation sites for precipitates and hence causes the precipitation to occur close to the grain boundaries, thus tending to eliminate the depleted grain boundary regions. Another beneficial effect of cold working results from the mechanical strengthening of grain boundary regions through work hardening and through the creation of jogs along grain boundaries which reduce the free slip distance.

The work of G. Thomas[16] may be cited as an example to show the effect of cold work on the improvement of the stress-corrosion properties of Aluminium D. T. D. 687 alloys of the following composition : Mg–2·9%, Zn–5·93%, Cu–0·5%, Cr–0·1%, total impurity content (Fe + Si + Ti) —0·48%. He worked with three sets of specimens of which one set was given a direct precipitation treatment at 150°C for various times up to 24 hours. The other two sets were aged for ½ hour at 150°C, deformed 5% and10% respectively by rolling and further aged for total times up to 24 hours at 150°C. After each ageing treatment stress-corrosion tests were carried out and best results were found with specimens of two sets which were deformed, since it was observed that the specimens were unbroken after 100 days in the stress-corrosion test, whereas the average life in the first set was only 12 days.

The evidence of jogged boundary as a result of cold working (50% reduction) prior to ageing of an Al–5·5% Zn–2·5% Mg alloy has been demonstrated by Mcevily, Clark and Bond.[17] So it is evident that the effect of cold work is not only to reduce the precipitate-free zones as demonstrated by Thomas but also to strengthen the grain boundary regions mechanically.

Conclusion

From the above discussions it is evident that the possibilities of improvement of stress-corrosion behaviour in otherwise suitable Al-Zn-Mg alloys warrant attention. While the exploitation of possible ways of (1) finding out a suitable heat treatment procedure, (2) examining the effect of cold work prior to ageing or (3) finding out a suitable combination of alloying elements seems to be promising, the present state of knowledge is too inadequate to give us a suitable method for the improvement of the stress-corrosion properties of Al-Zn-Mg alloys. However, the authors believe that of the methods cited above the addition of suitable alloying elements and the control of their quantities have a great influence on the reduction of the precipitate-free zone adjacent to grain boundaries and hence this would probably be of great significance so far as the direct industrial application of these alloys is concerned.

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Discussions

Mr **V. K. Agrawal** (Hindustan Aluminium Corpn., Renukoot) : It is concluded by the author that Al-Zn-Mg alloys have soft precipitate-free zones adjacent to grain boundaries which may lead to stress-corrosion cracking. I would like to know whether the above observation is true for all the Al-Zn-Mg alloys or for alloys of particular compositions studied by the authors. In alloy D74S, small amount of chromium and manganese is added to prevent discontinuous precipitation and formation of denuded zone and its susceptibility to stress-corrosion is also reported to be low.

Secondly, I would like to know if anybody has determined the solute concentration in the precipitate-free zones adjacent to the grain boundaries.

The observations made by the authors are very interesting and may be of considerable help in the development of Al-Zn-Mg alloys which are of vital importance in a developing country like ours.

In recent years, the Al-Zn-Mg alloys are arousing considerable interest all over the world because of their unique combination of properties like high strength, self-ageing characteristic, good corrosion resistance, excellent weldability and very high strength in the heat affected welded zone as compared to other high strength heat treatable aluminium alloys. Light weight, high strength comparable to that of structural steel and high strength/weight ratio together with excellent weldability and corrosion resistance make these alloys eminently suitable for military as well as civilian structural applications. One representative alloy of this class is Alcan D74S which can be used with advantage for such applications as mobile bridges, high strength dumpers and trucks, etc. to be used at high altitude.

Mr **B. Chaudhuri and** Dr **P. P. Das** (Authors) : The various Al-Zn-Mg alloys studied so far by us and by other investigators have shown soft precipitate-free zones adjacent to grain boundaries. It is always desirable to fix a certain Zn/Mg ratio in these alloys. From theoretical studies it is known that the binding energy between magnesium atoms and vacancies is much greater than that between zinc atoms and vacancies. Hence increased vacancy concentration will be mainly due to magnesium atoms. This will lead to decrease in the precipitate-free zone. It may be possible that by decreasing the zinc content the formation of the precipitate zone may be reduced, but in that case the strength and other properties of the alloys will be lowered. So, attempts have been made to use such a Zn/Mg ratio in these alloys that useful mechanical properties may be obtained with the formation of some precipitate-free zone which is unavoidable but this may later be reduced by the addition of other alloying elements, e.g. copper, chromium, manganese, titanium, silver, etc.

The effect of chromium and manganese in reducing the formation of precipitate-free zone and the susceptibility to stress-corrosion cracking is evidenced in alloy D74S as pointed out by Sri Agrawal.

In reply to the second question, the term 'precipitate-free zones' means zones not denuded with respect to the solute atoms but denuded with respect to vancancies. If any quantitative estimation of solute or vacancy concentration in the precipitate-free zones is to be carried out for assessing the properties of the alloys, it is to be done with respect to the vacancy concentration rather than the solute concentration.

It may, however, be pointed out that no direct estimation of the solute concentration in the precipitate-free zones has probably been carried out; but some indirect measurements have been done by X-ray methods.