# Physical metallurgy of aluminium alloys

VED PRAKASH

## SYNOPSIS

*The service behaviour of metals and alloys is closely related to the microstructures which are developed during the various metallurgical treatments during their transition from the molten state to the final finished product. A precise knowledge of the nature of these structures is therefore of primary importance to the metallurgist who is required to produce materials with widely different properties to meet various technological requirements. During the last decade considerable progress has been made in the understanding of various stages of phase precipitation in metals particularly in aluminium alloys as effected by various precipitation controlling factors such as alloy composition, trace element additions, quenching rates, specimen size, plastic deformation and complex heat-treatments. These studies have been made possible by the introduction of electron microscopy in the metallurgical research and development of the vacancy hypothesis. The present paper describes the structural changes which take place in important aluminium base alloys as revealed by such studies and their effect on properties of technological importance.*

ALUMINIUM is essentially a soft and weak metal which has to be strengthened by alloying with suitable elements. The elements which are added to aluminium in appreciable quantities to increase its strength and improve other properties are surprisingly limited to only four, namely, magnesium, silicon, copper and zinc. These are added singly or in combination. It may be observed that these elements are situated close to aluminium in the periodic table. Magnesium and silicon are its close neighbours in the second period while copper and zinc are close neighbours of aluminium in the next period. Out of these four elements magnesium has a greater atomic diameter (3·1906 Å) than aluminium (2·857 Å), while silicon, copper and zinc have smaller atomic diameters: 2·345 Å, 2·551 Å and 2·659 Å respectively. The differences in the atomic diameters of these elements and that of aluminium are within 15% and therefore alloying elements Mg, Si, Cu and Zn are favourably placed for forming substitutional solid solutions with aluminium. No element is known to have complete miscibility with aluminium in the solid state. Of all the elements zinc has the greatest solid solubility in aluminium with a maximum of 66·4 atomic per cent, while magnesium, copper and silicon have much lower solubilities i.e. 16·3, 2·48, and 1·59 atomic per cent respectively. These elements show a decrease in solubility with decreasing temperature (Fig. 1). This decrease from appreciable concentrations at elevated temperatures to relatively low concentrations at room temperature is the fundamental characteristic that provides the basis for increasing substantially the hardness and strength of aluminium alloys by solution heat-treatment and subsequent precipitation ageing operations. This method of heat treatment of aluminium alloys was first discovered by a German scientist Alfred Wilm and subsequently elaborated by Merica Waltenberg, Wanga and Scott[2] by studying the basic principles underlying precipitation hardening.

Magnesium, copper and zinc form compounds with aluminium which have dominant control on the hardening behaviour of these alloys. The compounds formed in case of magnesium and copper are $Mg_2Al_3$ and $CuAl_2$ respectively. The compound formation is disputed in case of zinc but there are strong indications that a metastable phase of f.c.c. structure does form during

Dr Ved Prakash, Scientist, National Metallurgical Laboratory, Jamshedpur.

the ageing of aluminium zinc alloys. When these four alloying elements are present in combination they may form binary and ternary compounds. When magnesium and silicon are present together in aluminium a stable compound of $Mg_2Si$ generally forms in addition to the parent $Mg_2Al_3$ and $CuAl_2$ compounds. Similarly, $MgZn_2$ and $Mg_2Zn_{11}$ may also form when the alloy is based on Al-Mg-Zn compositions. In the quaternary system Al-Cu-Mg-Zn isomorphous compounds $CuMg_4Al_6$ and $Mg_3Zn_3 Al_2$ have been detected apart from $Mg_2Zn_{11}$ and $Cu_6Mg_2Al_5$. These latter isomorphous compounds form continuous solid solutions that come into equilibrium with aluminium solid solution over a limited range of concentrations.

Rates of diffusion in the solid solutions are much slower than in the liquid solutions. Thus, depending upon the rates of solidification, equilibrium phase boundaries are displaced to varying degrees with the formation of non-equilibrium solid structures. These structures frequently include non-equilibrium constituents and cored solid solutions. The non-equilibrium con-

stituents include non-transformed or incompletely transformed intermetallic compounds. Indeed, equilibrium is not always desirable because preferred characteristics are often developed under non-equilibrium conditions.

Non-equilibrium structures also form, as a rule, rather an exception in quenched aged alloys. Though the solubility of the four alloying elements Mg, Si, Cu and Zn decreases with decrease of temperature, it is possible to retain them in solution on fast quenching. Due to differences in solubility at room and high temperatures the solute atoms try to precipitate out as compounds discussed above under suitable conditions of ageing. The precipitation of equilibrium phases in the aluminium alloys is generally not a straight forward step but involves a series of structural changes.[3] The first stage of these changes has been identified in most of the alloys as rejection of solute atoms on preferred planes to form zones, the zones giving rise to metastable and stable phases. The zones and metastable phases maintain coherency with the aluminium lattice and as these grow in size the interface between zones or metastable phases and aluminium solid solution is appreciably strained and therefore hardened. The maximum strengthening effect depends on the number, size, shape and distribution of zones or a metastable phase which in turn are determined by the concentration of alloying elements and time and temperature of ageing.[4] The dependence of hardness on number of zones is shown in Fig. 2. The shapes of zones and metastable coherent phases are important because they determine the number of slip planes that can be obstructed by a given volume fraction of the precipitate.[5] Their number increases in the order sphere-disc-rod. The shape of zones depends upon the relative diameter of solute and solvent atoms. Guinier[6] was able to show by X-ray diffraction techniques that spherical zones exist in alloys of small atom-size differences, e.g. Al-Ag, Al-Zn, Al-Zn-Mg and precipitation occurs on {111} Al matrix planes. The zones form in the shape of discs or plates when there is a great difference in the atomic sizes as in Al-Cu. The preferred direction of precipitation of such zones is <100> with {100} habit planes. The different models for zones are shown in Fig. 3. Needle or rod type zones form in Al-Mg-Si alloys of composition lying close to AlMg$_2$Si. The zones are composed of layers of one row of silicon atoms bounded by two rows of magnesium atoms. This type of zones were named stringlets by Geisler and Hill and are 10–20 Å wide and 100 Å long. Maximum strengthening is produced when the particles are about 100 Å dia. and interspaced at 100–150 Å. Marked softening occurs when the coherent phases become non-coherent or increase in size or acquire coarser distribution.

During room temperature ageing or during the early stages of ageing at intermediate temperatures of quenched aluminium alloys based on Mg, Si, Cu, Zn additions, zones are the first structures which are formed. The formation of zones proceeds with velocities 10[7] times the self-diffusion rate of solute atoms.[8] To resolve this difference, vacancy-assisted diffusion has been invoked. It is supposed that the vacancies are created when the alloy is heated to solution tem-
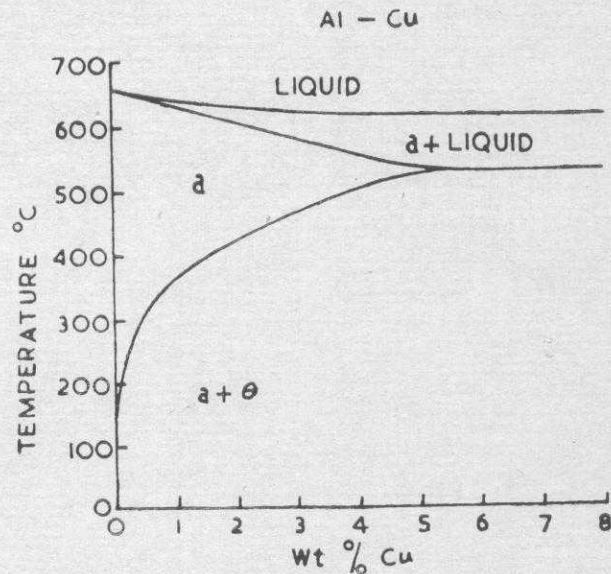


**1**  *The equilibrium phase diagram of the system aluminium-copper*

perature. These thermally generated excess vacancies are retained during quenching and help in the diffusion of solute atoms to nucleation sites which are additionally created by their condensation. The concentration of quenched-in vacancies depends upon the relative difference in the atomic sizes of solute and solvent atoms. When the solute diameter is appreciably smaller than that of the solvent e. g. Al-Cu, the vacancies are mobile and available for promoting the
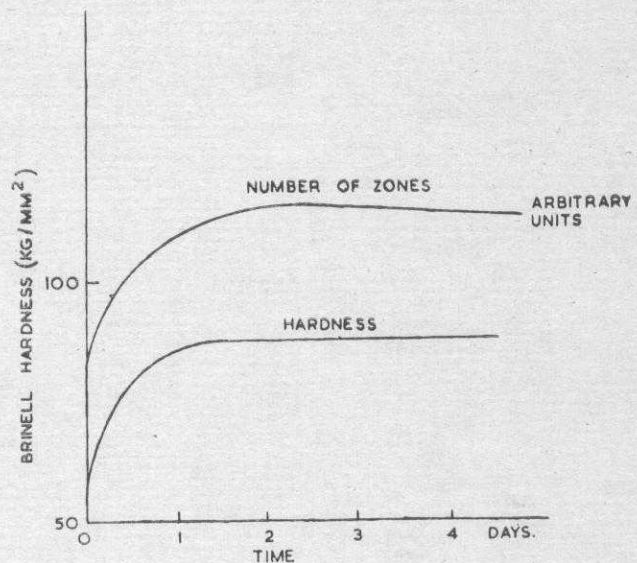


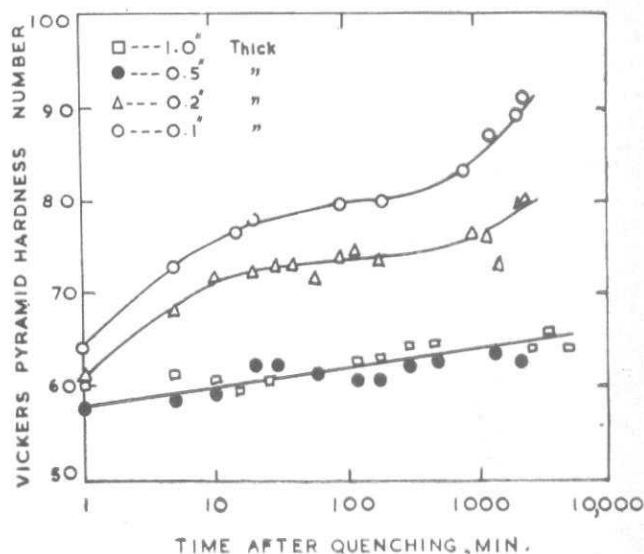**2**  *Variation of the number of zones and of hardness during the age hardening of Al-Cu alloy*

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MODEL OF THE G.P. ZONE ACCORDING
TO V. GEROLD.
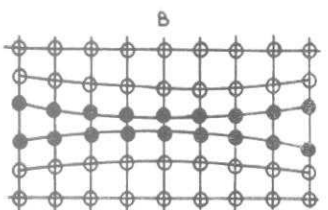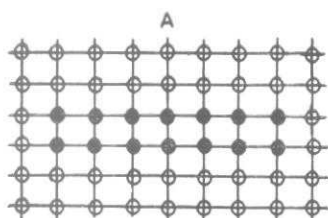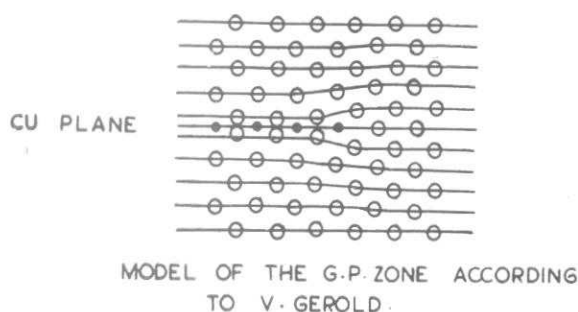


SCHEMATIC OF A ZONE (A) WITHOUT
DISTORTIONS. (B) WITH DISTORTIONS.

**3** *Different models for zones*



**4** *Effect of specimen thickness (in.) on the hardening of specimens solution treated for 24 hrs. at 520°C, quenched in iced water and aged at 40°C*

diffusion. The vacancies are immobilized and diffusion made slower if the solute diameter is larger than the solvent as in Al-Mg. This has obvious bearing on the extent of precipitation strengthening which is more in Al-Cu than in Al-Mg.

The concentration of quenched-in vacancies also depends upon the quenching speeds, specimen size, quenching bath temperature, solution temperatures adopted. The specimens quenched in air harden at a slower rate than the water quenched specimens. During air cooling the excess vacancies get annealed out and only fewer vacancies are left to assist diffusion. Similarly, as specimen size increases, hardening rate decreases appreciably (Fig. 4) for the same reasons. The massive thick specimens cool at slower rates than the thinner specimens and therefore are left with fewer vacancies. For the same reasons the higher the solution temperature and the greater the speed of quenching, the faster will be the rate of zone formation and the greater the speed of hardening. This in fact is the case. The effect of specimen size on quench-ageing of Al-Cu alloys is shown in Fig. 4.

Small amount of impurities present may interact with vacancies to suppress the zone formation and therefore decrease room temperature hardening. Metals like Cd, Sn. In when present up to 0.1% in aluminium-copper base alloys completely suppress room temperature ageing but accelerate artificial ageing by a factor of 3 to 8.[12] These impurities invariably have greater atomic diameter than aluminium. To lower the free energy of the alloy the impurity atoms associate with vacancies and thus bind them to their positions. There are therefore no free vacancies to take part in zone formation. This fact has been used in developing Al-Cu alloys doped with cadmium.[13] Since such alloys will not age at room temperature the necessity of storing samples at low temperature to minimize room temperature hardening is eliminated for fabrication work. However, to avail of the full effect of cadmium the alloy must not contain high concentration of magnesium which precipitates out cadmium. In alloy containing magnesium such as Al-Mg, Al-Zn-Mg, silver[14] has been reported to have the same effect as cadmium in magnesium free aluminium base alloys.

When zones have reached an equilibrium size after natural ageing for some time there is no further increase in hardness observed. For further hadening, the alloys require to be heated to elevated temperatures to form higher structures. These phases generally possess structures of true precipitates and grow in three dimensions when they remain coherent with the matrix

they increase the strength. When coherency is lost and precipitates grow in size loss of strength takes place. These structural changes are described below for each alloy.

## Aluminium-magnesium alloys [15, 16]

As the solid solution of Mg in Al is cooled, the solubility of Mg decreases from 18.9 atomic per cent at 450°C to 2.1 atomic per cent at 100°C and this is accompanied by the rejection of $Al_3Mg_2$ phase from the $\alpha$-solid solution. In the quench-aged alloys formation of $\beta$ is preceded by intermediate phase $\beta'$ in the grains. The hardness curves against tempering time at a given temperature shows a broad peak to coincide with formation of $\beta'$. The peak falls off at longer times to reach values slightly lower than the initial hardness.

The heat-treatment of Al-Mg alloys produces no useful technological properties by structural hardening based upon precipitation or ageing. The small hardening observed in these alloys is due to dispersion of $\beta'$ and $\beta$ which act as obstacles to dislocation propagation. In fact locked dislocations have been observed in the electron micrograph, in the immediate vicinity of $Al_3Mg_2$. The $\beta'$ forms in the grain boundaries in 24 hrs at 150°C and then within the grains in 100 hrs. finally evolving into non-coherent $\beta$ after 50 to 100 days. The alloys however, are used due to their superior capacity to resist corrosion. The alloys can be worked up to 7% Mg. The 10% Mg alloys are used as castings only. To avail of the high corrosion resistance of 10% magnesium alloys attempts have been made to make this alloy workable by addition of other elements particularly misch metal etc. but without success.

## Al-Si alloys

Silicon does not form any intermetallic compound with Al. It dissolves to the extent of 1.65% at 577°C to form solid solution which deposits particles of pure silicon below the solid solubility curve. Thus in commercial alloys containing up to 10% silicon there will be two kinds of silicon existing : (i) the one resulting from the decomposition of the $\alpha$-solid solutions (ii) the one produced by direct solidification from the eutectic melt. The two forms are crystallographically similar but differ in form and distribution. The eutectic silicon is generally coarse and mechanical properties are poor.

The eutectic structure is refined by a treatment known as modification.[17] This consists in treating the molten alloys with metallic sodium or sodium fluoride. After modification the alloy usually contains 0.005 to 0.015% Na. The function of the modifying agent is not known, but it effects an astounding refinement of the eutectic, displaces the eutectic composition from 11.7 to 13.7 silicon and decreases the eutectic temperature.[18] The effect is equivalent to super cooling the alloy and in fact quick cooling does tend to refine the structure. The modified 13% Si alloy

has a U. T. S. of 13 tons/sq. in. and elongation 15% in contrast to unmodified alloy which has a U. T. S. of only 8 tons and elongation 5%.

Al-Si alloys are not regarded as heat-treatable. Von Lanker has found that the properties of Al–10% Si alloys are significantly enhanced by quenching from 530°C. Quenching freezes in the vacancies and the precipitation of the silicon from the $\alpha$-Al solid solution produces high toughness (twice that of untreated Al–10% Si)

Al-Si alloys have good resistance to marine corrosion, high degree of fluidity and low shrinkage and enable castings of intricate sections to be made dense and free from cracks.

## Al-Cu alloys

Aluminium-4 to 5% Cu alloys were the first alloys in which the phenomenon of age-hardening was discovered by A. Wiliam in 1911 ; since that time the alloys have been developed so much that they form an outstanding group of heat treatable high strength Al alloys. On casting Al-4% Cu alloy a solid solution of cellular structures is obtained. On quenching at high cooling rates from the solution temperature, copper and vacancies are retained in solution. Some of these vacancies condense to form discs, rings and spirals of diameter about $10^{-5}$ to $20 \times 10^{-5}$ mm and thickness $0.5 \times 10^{-5}$ mm. Copper atoms associate with remaining free vacancies to form clusters which act as nuclei for the formation of G. P. [1] zones on ageing. Thus, quenched hardness of the alloy consists of two components : (1) hardness due to dispersion of dislocation defects, (2) hardness due to solution effects.[20] As the zones increase in size they exercise their effect on hardness of the alloy by introducing coherency stresses. The contribution of hardness from zones is nearly of the same order as that of dislocation defects generated during fast quenching as shown below :

**Hardness data for Al-3.8% Cu alloy**

| A | B | C |
|---|---|---|
| Air cooled from 520°C | Water quenched from 520°C | Aged 30 days at R.T. |
| 50 V.P.N. | 72 V.P.N. | 100 V.P.N. for B<br>75 V.P.N. for A |
| Difference = 22 V.P.N. (B—A) | Difference = 28 V.P.N. (C—B) | Difference 25 V.P.N. (C—A) |

The aged specimens reverted back to their original hardness of 50 and 72 VPN in case of slowly cooled and water quenched specimens when subjected to reversion treatment of 170°C. However when reversion

treatment was carried at 190°C the water quenched and slowly cooled specimens both showed hardness values of 50 VPN. At temperatures of 185 to 200°C dislocation loops and spirals disappear in pure aluminium.

Reversion tests have been employed to determine the solubility temperature of zones.[21] However care should be exercised in interpreting the results. Reversion temperature is considered to be the solubility temperature at which minimum hardness is obtained. This evidently happens when dislocation defects are also dispersed.

When the Al-Cu alloys are aged at higher temperatures GP[1] zones thicken to form three dimensional zones like GP[2] zones. These are responsible for the highest strength obtained in Al-Cu alloys. GP[2] zones subsequently transform into higher structures $\theta$ and $\theta'$ and the alloy undergoes marked softening. The precise temperatures at which different structures are stable are function of ageing duration. At room temperature and up to 110°C and at the early stages of ageing up to 160°C GP[1] is the only structure which is formed. GP[2] zones form at 110 to 130°C, in the latter stages of ageing and early stages at 190°C. $\theta'$ forms up to about 250°C temperature which ultimately transforms to stable non-coherent $\theta$ phase precipitates.

Thus the structural changes taking place can be summarized as below :

$$S.S. \rightarrow GP[1] \; zones \rightarrow GP[2] \; zones \rightarrow \theta' \rightarrow \theta$$
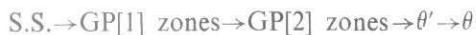
At lower ageing temperatures the lower structures may transform to higher structures but at higher temperatures the lower structures may be completely suppressed in favour of stabler structures.

**Aluminium-zinc alloys**

Binary Al-Zn alloys are of no technological interest due to hot cracking of the casting alloys and great susceptibility to stress-corrosion cracking of the wrought alloys. The alloys however harden by GP[1] zone formation at room temperature. These evolve into GP compounds of f.c.c. structure.[22]
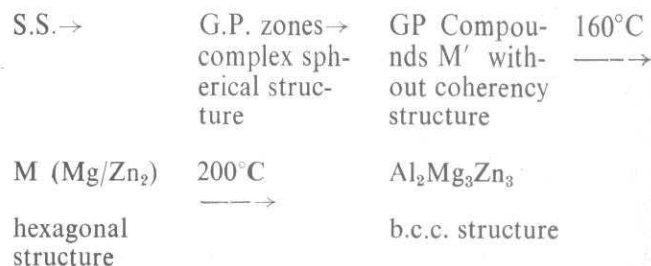
**Complex alloys**

Magnesium is invariably added, singly or in combination to binary Al-Zn, Al-Si, Al-Cu alloys to form ternary and more complex alloys with a view to improve strength, working, casting and corrosion properties. The compounds formed are $Mg_2Cu$, $MgCu_2$, $MgZn_2$, $Mg_2Zn$ and $Mg_2Si$. The complex alloys in which magnesium plays an important role are discussed below :

*Aluminium-zinc-magnesium alloys*

The quenched alloys are $\alpha$-solid solution. Mg and zinc atoms move under the influence of vacancies to form zones in the first 30 minutes at 120°C. Size effects of Mg and Zn are neutralized and the zones formed are therefore spherical, 30 to 50 Å dia. Since the free

energy of formation of $MgZn_2$ is higher, Mg and Zn react eventually. This reaction takes place through a series of stages. First the zones thicken to form platelets which gradually form a Widmanstatten structure. This structure is akin to GP[2] zones in Al-Cu alloys and is designated as M' for $MgZ'n_2$. The lattice constants of this compound are a=4·96 Å, c=8·68 Å. M' forms on $\{111\}_{Al}$ matrix planes and does not introduce coherency stress effects. The hardening effects are thus mainly due to dispersions of M' in $\alpha$-solid solution and are maximum when total number of spherical zones or platelet of M' per cm³ of the alloys is a maximum. When the alloy softens the zones have almost disappeared and M' platelets have thickened. Finally particles of M appear. If softening temperature is near 200°C another ternary compound $Al_2Mg_3Zn_3$ designated as T may form.[24] The structural changes taking place can now be summarized as :

| S.S.→ | G.P. zones→ complex spherical structure | GP Compounds M' without coherency structure | 160°C ———→ |
|---|---|---|---|
| M ($Mg/Zn_2$) | 200°C ——→ | $Al_2Mg_3Zn_3$ | |
| hexagonal structure | | b.c.c. structure | |

Precipitation of M preferentially takes place at the grain boundaries and sub-boundaries ; the regions near the boundaries are therefore deficient in solute and lead to brittleness and intergranular corrosion.

Herenguel has shown that a curve can be drawn in the ternary diagram (Fig. 5) separating compositions liable to intercrystalline corrosion from those which are not so prone to it.[25] During stressing the material fails due to intercrystalline fracture at the denuded regions. To avoid this failure Mg and Zn contents are adjusted and additional elements like Si, Mn, Cr, Cu, Ag are added in small quantities to prevent stress corrosion. Silicon forms additional $Mg_2Si$ zones with magnesium and these zones may have something to do with beneficial effects of silicon added up to about 0·3%.

Chromium and manganese are added individually or in combination to cause general precipitation in order to suppress stress corrosion at denuded zones.[26] Autoradoigraphs have shown that chromium remains inside the grains as discrete particles to cause additional nuclei. Manganese is concentrated partly at places and partly throughout the grains.[26] Manganese also prevents coarse grain recrystallization in quenched extruded products.

A silver addition of about 0·5% dissolves in the solid solution and is very effective in refining the particles in the temperature range of 125–225°C.[27] The precipitates are dispersed more uniformly near the grain boundary. Silver is effective in these respects even in the presence of Cr, Mn, Fe, Si and Ti contained in the commercial alloys. Silver additions also bring about greater hardening response and therefore facilitate
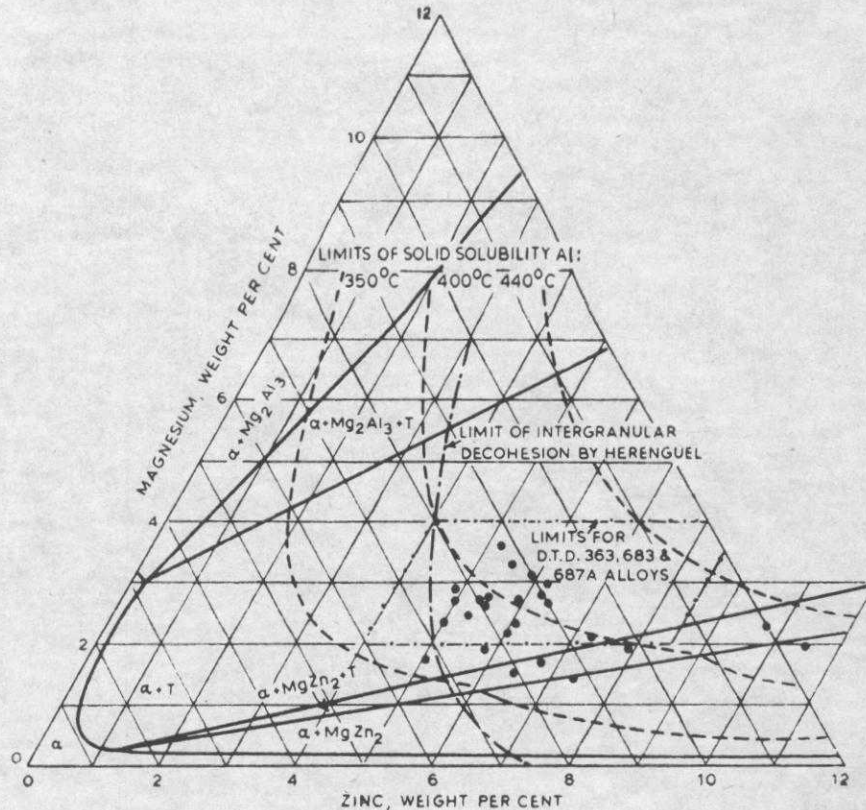
5        Al–Mg–Zn phase diagram (in wt.%), the 200°C section showing the thermodynamically stable phases; $T = Al_2Mg_3Zn_3$. The solid solubility curves at 350, 400 and 440°C give the Mg and Zn contents in wt.% capable of going into solution in $\alpha$-Al. The limit of intergranular decohesion is also plotted. [*J. Inst. Metals*, April 1958, p. 338, Fig. 1.]

nucleation of the precipitates in a finely divided state. These dispersions are stable up to a relatively high temperature, with the result that overageing is avoided.

Copper additions of up to 1% intensify the first stage of ageing (100–235°C) in which G.P. zones develop. The increased hardening is considered to be due to the formation of S phase ($Al_2CuMg$). The combined effects of Ag and Cu are additive and independent of each other.

## Al-Cu-Mg alloys

These are high strength heat-treatable alloys in which copper may vary from 4 to 4·5% and Mg from 0·5 to 1·5%.[28] These may also contain small quantities of iron or Mn~0·3 to 0·8%. High magnesium alloys develop structures based on the ternary compound of $Al_2CuMg$. Magnesium causes acceleration of natural ageing of Al-Cu alloys and it is considered that G.P.(1) zones may contain copper and Mg atoms on {100} Al planes. The sequence of structural changes when Mg content is~1·5 may be written as below:

Solid solution→Clusters of Cu and Mg atoms.→ G.P.(1) zones→G.P. Compounds S′ ($CuAl_2$ Mg)→ S (Cu $Al_2$ Mg)

With lower Mg contents, structures pertaining to Al-Cu binary system are formed in predominant quantities. Wilm's original alloy contained Cu 4·5%, Mg 0·5%, Mn 0·5%. The properties of this alloy has been improved by raising the Mg content to 1·5% and adding about 0·5 to 0·9% silicon to give rise to two separate alloys having compositions (1) Cu 4·5%, Mn 0·6%, Mg 1·5%, (2) Cu 4·4%, Mn 0·8%, Mg 0·5%, Si 0·9%.

The silicon containing Al-Cu-Mg alloys will contain $Mg_2Si$ compound in addition to phases pertaining to Al-Cu, Al-Mg. Al-Cu-Mg systems. Since $Mg_2Si$ has higher melting point the homogenization temperature of quaternary alloys is higher (510°C) than the ternary alloys (495°C). The stable compounds formed are $CuAl_2$, $CuAl_2Mg$, $Mg_2Si$ and $Cu_2lA_5Mg_8Si_6$. These compounds are formed in quenched aged alloys through a series of reactions similar to those which occur in Al-Cu alloys. Due to differences in composition the

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zones and intermediate compounds will be complex but coherent with the Al matrix. Such alloys when tempered at 175°C for 8 hrs. have U.T.S. as high as about 30 tons/sq.in. with elongation of 15%.

Presence of Mn to the extent of 0·3 to 0·8% in these alloys raises the recrystallization temperature after cold work and forms Mn rich compounds which are aligned in bands after extrusion and these seem to prevent recrystallization grain coarsening in the cortical zone.[19] Small amount of Fe present in these alloys combines with Mn to form the Mn rich compounds $Al_2(MnFe)$. Other things being equal Mn containing alloys have higher tensile strength (U.T.S. 24 tons for Mn 0·1%, 32 tons for 0·7% Mn).

### Al-Mg-Si alloys

Non-ageing Al-Si and Al-Mg alloys become heat-treatable when Si and Mg are present together. Si may be present from 0·6 to 1·2% and Mg from 0·6 to 1·0%. These can be homogenized at about 560°C to form α-solid solution which on quenching gives rise to metastable solid solution of vacancies, dislocation defects and solute atoms. On tempering at high temperatures as discussed already needle shaped zones are formed which grow to platelets of $Mg_2Si$. There are no coherency stresses generated during ageing and alloys are hardened due to dispersion effects of precipitates. The mechanical properties are therefore not so high. Sometimes to improve the properties, further copper is added to the extent of 1·5% to create coherency stresses.

The chemical composition and mechanical properties of aluminium alloys used commercially are given in the Table.[19] It may be observed that high tensile strength is obtained after heat-treatment to produce intermediate phases.

### Effect of plastic deformation on precipitation

All metals harden when deformed plastically in cold. This is brought about by (1) fragmentation of grains into smaller grains, (2) generation of dislocation network and vacancies. In age-hardening Al base alloys the effects of precipitation are superimposed. Plastic deformation after quenching in general accelerates the rate of precipitation.[29-31] The time to reach maximum hardness is decreased and the extent of hardening increased. These effects are explained on the basis of assumptions that (1) the formation of nuclei is easier in the strained regions, (2) the distance through which atoms are to diffuse to reach the nucleus is reduced, (3) the diffusion is accelerated due to excess vacancies generated during deformation, (4) dislocation net-work raises the hardness.

The extent to which various structures may be produced, accelerated or decelerated depends upon the amount of deformation to which the alloy is subjected.

Graf and Guinier[29] from the X-ray study of the effect of cold working on zone formation in Al-4% Cu alloys inferred that zone formation is accelerated if the deformation is light. This is also true for Al-Cu-Mg alloys. The small deformations have however, no effect on

**Chemical composition, structure and U.T.S. of some Al alloys**

| Chemical composition Wrought alloys | Structure | Mechanical properties |
|---|---|---|
| 1. 4·0 to 5% Cu, 0·5 to 1·5 Mg, 0-0·9% Si, 0·5-0·8% Mn, 0-0·5% Fe | Intermediate coherent ppts. of Cu $Al_2$, $Cu_4AlMgAl$ in Si-Mg or $Mg_2Si$ | 25·4 tons to 28·6 tons in (quenched and aged condition) |
| 2. 0·6-1·2% Si, 0·6-1·0% Mg, 0·17% Cu max. 0·5-1·0% Mn, 0·4-0·5% Fe | Zones of $Mg_2Si$ type | 14 to 18 tons |
| 3. (a) 5·5-7·5% Zn, 2-2·7% Mg, 1-1·5% Cu, 0·2-0·9% Mn, 0·2-3% Cr | Zones of $MgZn_2$ type | 28·6 to 33·0 |
| (b) 3% Zn, 1·7% Mg, 0·1% Cu, 0·3% Mn, 0·2 % Cr | —do— | 22·2 tons |
| *Cast alloys* | | |
| 4. 4·5% Cu, 0·25% Mg, 0·25% Ti, 0·35% Fe, 0·30% Si | As in No. 1 | 22·0 tons |
| 5. 7-10% Mg, 0·02% Be, 0·1% Max. Cu, 0 003% max. Na, 0·3% max. Fe, 0·2% max. Si (Na, Fe, Si as low as possible), Be is added as deoxidizer. | Quenched and untempered solid solution | 15·9 to 19·0 tons |
| 6. 5% Zn, 0·5% Mg, 0·2% Cu, 0·4% max. Mn, 0·2 % Cr, 0·8% max. Fe, 0·2% Ti. Ti is added in alloys No. 3 and 5 to refine the grains. | Alloy is cast and tempered at 180°C | 14·0 to 16·5 |
| 7. 5·0-10% Si, 0·3-0·6% Mg, 0·1% max. Cu. (5% Si alloy may contain 0·6% Mn). | Zones developing into $Mg_2Si$ quenched and tempered | 11 to 15 |

the zone formation and therefore on the ageing characteristics of Al-Zn-Mg alloys. On the other hand cold work has adverse affect on the response of Al-Cu-Cd alloys to age harden, so that the beneficial effects of trace additions of Cd are lost.[30] In case of Al-Zn-Mg alloys doped with silver the cold working does not affect the ageing rate and also has no adverse effect on ageing as in Al-Cu alloys doped with cadmium.

Large deformation, however, favours the formation of nuclei of the precipitate and thus suppresses preprecipitation in favour of true precipitates. Graf observed that after cold working the precipitates of $\theta'$ become visible at 150°C in comparison to its formation at 200°C in undeformed Al-Cu alloys. The normal structures which are formed at 150°C are G.P. [2] zones. Graf also observed that in a powder of Al-Cu alloy obtained by filling, the $\theta$ phase is formed even at room temperature. In Al-Mg alloys the cold work increases the grain

boundary precipitation of $\beta'$ and $\beta$. These observations can be rationalized on the basis that cold deformation introduces strain ageing effects in age-hardening alloys. The solute atoms get anchored to dislocations and are not free to take part in zone formation.[32] The anchored solute particles give rise to true precipitates on artificial ageing. The basis of the argument is that heavily worked Al-4% Cu alloys do not undergo any reversion and the extent of reversion is dependent upon the deformation.[20]

If cold working is carried out after ageing, the alloys are further hardened. This is due to introduction of sessile dislocations. Maximum hardness is thus obtained by cold working after ageing, and is higher than that given by cold working before ageing. The sessible dislocations produced depend upon the alloying element. Their density increases with increasing solute content and with increasing size factor. With equal solute concentration the density of sessile dislocations is $Cu > Si > Zn > Ag$. Magnesium which has a high size factor is an exception.

The slip band structure of aluminium alloys containing zones, intermediate phases and equilibrium compounds has been examined by Nicholson, Thomas and Nutting.[33] Their work has shown that when the structure consists of G.P.(1) zones, the slip lines are wavy and distributed at random and consist of single steps of large displacements. When G.P. (2) zones are present only a few slip lines of small displacements are seen. When G. P. (2) zones and $\theta'$ are present, the slip lines are more frequent, straight and composed of lamellae. When $\theta$ is the only structure present, the slip lines occur in the solute depleted zones and at the grain boundaries. In specimens containing $\theta'$ and $\theta$, the slip lines are wavy and bent round $\theta$. From these observations it has been concluded that dislocations pass through zones, coherent and partially coherent precipitates but avoid non-coherent phases by a cross slip mechanism.[34]

Subjecting a specimen to fatigue test can be treated equivalent to cold deforming a metal. A passing reference is therefore made on the fatigue strength of aluminium alloys. It is known that the higher the static tensile strength the higher the fatigue endurance of an alloy. This is however not so in case of high strength aluminium alloys. Al-Zn-Mg alloys have higher tensile strength than Al-Cu alloys but show fatigue properties inferior to those of Al-Cu alloys. This abnormal behaviour may be related to the fact that zones and intermediate structures form on {100} planes in case of Al-Cu alloys and on {111} planes in case of Al-Zn-Mg alloys. The slip however, takes place in both the cases on {111} planes. Therefore zones and intermediate phases can react with slip bands in case of Al-Cu alloys to arrest their formation. These structures in the case of Al-Zn-Mg alloys will have no effect on the formation of slip bands as they are formed on the same planes which undergo slipping. This difference can therefore lead to higher fatigue strength of Al-Cu alloys.

### Intermetallic compounds and their effects

Compounds like $Mg_5 Al_8$, $CuAl_2$, $MnAl_6$, $CrAl_7$, $FeAl_3$ are formed when the Al alloys are made from solute elements like Mg, Zn, Mn, Cr, etc. Due to their marked softening effect, these compounds do not play any appreciable role in strengthening aluminium. These phases are invariably hard and brittle at room temperature but show some plasticity when the temperature is raised as shown in the Table I.[35]

TABLE I Hardness of intermetallic compounds at different temperatures

| Compound | Hardness (VPN) at different temperatures | |
| --- | --- | --- |
| | Temperature | V.P.N. |
| $CuAl_2$ | 300°C | 400 |
| | 350°C | 400 |
| | 400°C | 150 |
| | 500°C | 50 |
| $Mg_5Al_8$ | 300°C | 200 |
| | 350°C | 200 |
| | 400°C | 75 |
| | 500°C | 50 |
| $MnAl_6$ | 450°C | 600 |
| | 500°C | 400 |
| $CrCl_3$ | 550°C | 500 |
| $FeAl_3$ | 500°C | 600 |
| $MnAl_4$ | 500°C | 700 |
| $Fe_2Al_5$ | 500°C | 900 |
| $NiAl_3$ | 300°C | 700 |
| | 500°C | 550 |

Compounds like $Cu-Al_2$ and $Mg_5Al_8$ have rather low hardness values which mark the onset of increasing ductility and indicate a softer plastic state near 400°C. These phases therefore give an alloy easily hot workable but with a possible tendency to produce elongated particles of the intermetallic phase. The compounds are brittle below 300°C. Other compounds remain strong near the forging temperature and their constituents would be expected to be brittle under most hot-working conditions. These phases would however confer high temperature stability to the alloys.

These compounds also raise the elastic modulus of aluminium; the increase is proportional to the alloying element forming compounds. The improvement effected has been considered to be due to the relatively high elastic properties of the compounds. Aluminium alloys with high Young's modulus are required in aircraft structures. Table II summarises the elastic properties with respect to alloying percentage.

Addition of magnesium to aluminium therefore lowers the Young's modulus. Chromium additions cause maxi-

TABLE II Young's modulus values of aluminium for weight percentage of added elements

| Element added | Young's modulus (lbs/sq. in × 10⁶) | | | |
|---|---|---|---|---|
| | 1% | 2% | 5% | 10% |
| Magnesium | 9·5 | 9·3 | 9·0 | 8·6 |
| Mg+12% Si | 10·5 | 10·6 | 10·7 | 10·8 |
| Copper | — | 9·7 | 9·8 | 10·3 |
| Silver | 9·3 | 9·6 | 9·8 | 10·3 |
| Iron | 9·3 | 9·5 | 10·3 | 11·2 for 8% Fe |
| Vanadium | 10·2 | 10·4 | 10·6 for 3% V | |
| Chromium | 9·6 | 10·5 | 11·7 | 12·3 for 6% Cr |
| Titanium | 9·6 | 10·0 | 10·5 for 3% Ti | |

TABLE III Electrode potentials of Al solid solutions and constituents

| Solid solution or constituent | Potential | Solid solution or constituent | Potential |
|---|---|---|---|
| Mg₂Al₃ | −1·24 | 99·95Al | −0·85 |
| Al+4MgZn₂ | −1·07 | Al+1Mg₂Si(b) | −0·83 |
| Al+1Zn(b) | −0·96 | Al+1Si | −0·81 |
| Al+4Zn | −1·05 | Al+2Cu | −0·75 |
| MgZn₂ | −1·05 | CuAl₂ | −0·73 |
| CuMgAl₂ | −1·0 | Al+4Cu | −0·69 |
| Al+3Mg | −0·87 | FeAl₃ | −0·56 |
| Al+5Mg | −0·88 | NiAl₃ | −0·52 |
| Al+7Mg | −0·89 | Si | −0·20 |
| MnAl₆ | −0·85 | | |

mum increase in the modulus. These alloys are found to contain $CrAl_7$ compound which has a large proportion of aluminium atoms, and therefore for a given weight of the alloying element they occupy a larger volume as compared to that of the compounds which aluminium forms with many of the other elements. Similarly, high value of Young's modulus in Al-iron alloys is due to formation of $FeAl_3$ and $Fe_2Al_7$. High values of Young's modulus in Al-Ti and Al-V compounds are due to formation of $TiAl_3$ and $VAl_4$ etc.

### Corrosion of aluminium alloys

If a metal is anodic to aluminium, it will corrode. In doing so it can reduce or prevent corrosion of aluminium.[36] This type of action is often used to minimise corrosion and is called cathodic protection. It is however, characteristic of electro-chemical corrosion that it is not generally uniform and is confined to selected area like grain boundaries, imperfections, massive precipitates, places of internal stresses, etc. Therefore the structure of the alloy and composition of phases will be a dominant factor in the control of corrosion. Table III summarises the electrode potential of Al solid solutions and different constituents.[28]

The solutions and constituents situated above 99·5% Al will be anodic to it while those which are below will be cathodic.

As $MnAl_6$ has the same electrode potential as aluminium, therefore Al-Mn alloys are highly resistant to corrosion.

Chromium has little effect on electrode potential of Al. Its addition improves the resistance to stress corrosion and for this reasons it is added in minor quantities to Al-Zn-Mg alloys. Al-Si alloys are corrosion resistant for similar reasons. Al-Mg alloys having solid solution structure and precipitates of $Mg_2Al_3$ will show electro-chemical reaction in which $Mg_2Al_3$ is eaten away as it is more anodic than the solid solution.

Al containing $Mg_2Si$ intermetallic compound is also resistant to corrosion. Mg in solid solution makes the potential more anodic and silicon more cathodic maintaining the electrode potential essentially the same as the potential of Al. More anodic Al-Zn alloys are used as alclad coatings on Al alloys which are cathodic.

Extensive general precipitation throughout the grain boundaries achieved by metallurgical control decreases the rate of electro-chemical attack on the constituents at the grain boundary and slip planes. In this way the composition of solid solution containing precipitates is made uniform at the grain boundaries and in the interior of the grains. To achieve this, small quantities of Cd are added in Al-Cu alloys and Ag, Cr, Mn in Al-Zn-Mg alloys. These elements suppress discontinuous precipitation and cause general precipitation throughout the grains. The precipitated particles are also refined. It is, however, observed that stress corrosion resistance is the highest when the alloys are slightly over aged.[37] The G. P. zones and intermediate structures are more prone to stress corrosion. This is particularly so in Al-Zn-Mg alloys. In specimens aged to contain G. P. zones or intermediate precipitates the tendency is for dislocations to be confined to their original slip planes. In specimens heat treated to contain over-aged precipitates, slip is much more turbulent and is spread over large number of planes as dislocations are forced to by-pass such particles. Observations indicate that a high resistance to stress corrosion cracking is found in materials exhibiting a turbulent slip ; conversely when restricted slip takes place, as in the case of G. P. zones etc. the stress corrosion cracking tendency will be very appreciable.[38] Precipitate-free regions called denuded zones are important in determining cracking resistance but have no controlling influence whatsover on stress

corrosion cracking. In specimens which had the same area of denuded zones but different heat treatment to include zones and intermediate phases in one case and slightly over-aged phases in the other case, the stress corrosion cracking tendency was very different.

## Acknowledgement

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# Discussions

Mr V. K. Agrawal (Hindustan Aluminium Corpn., Renukoot): It is mentioned in the paper that metals like Cd, Sn, In and Ag when present up to 0·1% can completely suppress room temperature ageing and accelerate high temperature ageing by a factor of 3 to 8. In what particular alloy systems have the above phenomena been observed?

Dr Ved Prakash (Author): Cadmium, tin and indium affect the natural and artificial ageing of Al-Cu, Al-Cu-Si, Al-Cu-Zn, Al-Cu-Ni and Al-Cu-Li alloys. The tin and indium additions become ineffective when magnesium is present in these alloys in small quantities as in duralumin. The industrial practice of adding trace elements to improve the properties is therefore confined to cadmium metal only. The presence of cadmium in Al-Cu alloys improves their mechanical strength, working qualities and resistance to stress corrosion.

Ag when present in small quantities improves the strength and stress corrosion resistance of magnesium bearing alloys like Al-Mg and Al-Zn-Mg alloys.

The improvements in the physical and mechanical properties brought about by trace additions of these elements have been related to their ability in causing general precipitation.