

Precipitation from Solid Solutions

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Summary: Precipitation from solid solutions and supersaturated solutions is a very important process as it plays an important role in the structure and properties of metals/alloys. This process is used widely in the metallurgical engineering to obtain desired mechanical properties. The phenomena under discussion has great practical significance, for they make possible the precipitation or age hardening of metals, an extremely important way of hardening of metals, especially in commercial strengthening of non-ferrous alloys, e.g. aluminum and magnesium alloys. This review discusses precipitation and its effects on hardening in solid solutions and saturated solid solutions.

Keywords: Precipitation, Solid solutions, Hardening, Commercial strengthening, Steel aluminum alloys.

Introduction

Precipitation and Precipitation hardening are very important phenomena as they are equally useful in Chemistry (Solid State), Physical Metallurgy and Solid State Physics. Precipitation reactions are of great significance in metals and alloys. This occurrence in different ways in different alloys when one form changes into a mixed form system as a conclusion of cooling (quenching) from elevated temperatures. [1-8]. In simple words, the precipitation of a solid form from a liquid is controlled by a balance or equilibrium between the thermodynamical driving force and the energy penalty for creating new solid-liquid surface interfaces. This phenomenon controls the size and shape of the precipitates.

Since we are going to discuss solid solution strengthening (hardening) and precipitation strengthening, it is advisable to define the two terms. Bob Jarrett of State University of New York has defined them nicely in ResearchGate Question Answer session. Solid solution strengthening is the result of alloying a metal at the same time as remaining within the single form region of the phase diagram. The limited strain of the alloy atoms in the host matrix provides resistance for dislocation movement - raising the strength of the alloy. Precipitation strengthening results when the addition is higher than its solubility in the host matrix. To get the strengthening effect from the precipitates, the alloy is heated over the solution temperature of the second form, while remaining in the solid state. After a satiate, the alloy is aged less the solution temperature. Homogeneous nucleation of the precipitate form results in a fine circulation of the secondary form (Fig. 1) - and the resulting

dislocation barriers and higher strength (Fig. 2). For examples, Al-Cu, Al-Mg, Ni gamma/gamma key superalloys, maraging steels. In short solid solution strengthening is a single phase system and precipitation strengthening it has at least two phases, where the precipitate(s) are the reinforcing phase i.e. precipitating titanium carbide particles from an Al-Ti alloy, as defined by Milton Manrique of Simon Bolivar University in Search Gate.

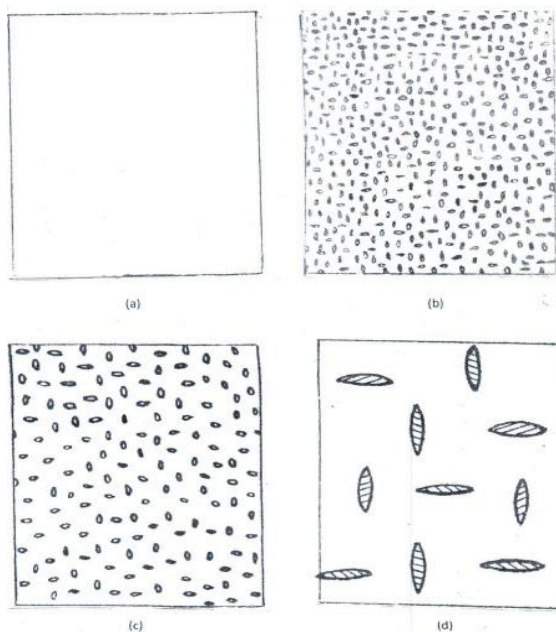


Fig. 1: (a) Homogenous solid solution (b) Age hardened at low temperature (c) age hardened at medium temperature (d) Age hardened at high temperature (schematic).

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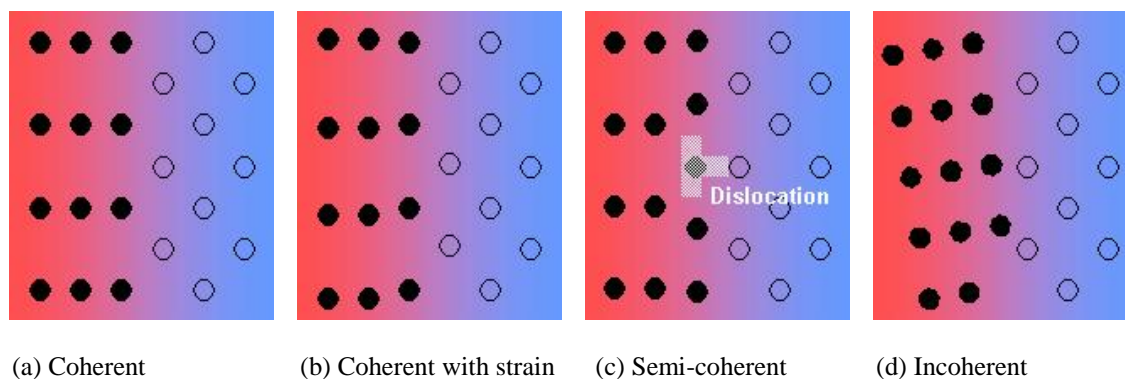


Fig. 2: Various types of interfaces between solid phases, viz (a) Coherent (b) Coherent with strain (c) Semi coherent (d) Incoherent.

It must be kept in mind that the precipitation of a solid form from a solid parent form is similar [9]. The various type of interface between the matrix- the precipitate viz.

1. Coherent – There is ideal match up of the lattices of both the lattices.
2. Coherent with strain – There is a reasonable possibility for there to be some strain with the interface of the two lattices because of imperfect matching. The strain energy increases with the size of growing precipitate, and there is a transition to a semi coherent interface.
3. Semi-coherent interface – The introduction of dislocations reduce the strain energy, but they themselves contribute to the energy of the system.
4. Incoherent interface – There is no matching the interfaces. (Fig.3) shows the above mentioned 4 situations. When the two phases match better, the interfaced energy is minimized. Incoherent interfaces have energy and are comparatively mobile due to the relatively larger freedom of the motion of the atoms. The shape of the precipitate is powerfully influenced due to the stresses present in the parent phase as the precipitates grow strongly. If the precipitate is modeled as an ellipsoid of revolution, the graph (Fig. 4), shows how the strain energy is related to the shape [2]. The growth of precipitates as disc or plates is usually preferred. Studies have shown that a precipitate is likely to have several coherent and some incoherent interface with the matrix. The incoherent interfaces have larger mobility leading to faster growth in these directions. It is the anisotropy growth that leads to plate and disc morphologies and the bounding coherent interfaces will be comparable to the crystallographic phases in the parent matrix.

Theoretical Background

Departure from equilibrium is often extreme in the case of phase changes that occur in solid alloys, since activation energies for solid-state reactions are typically high, and the diffusion and atomic rearrangement involved in them are relatively slow. Precipitation of a secondary phase from a primary solid solution is a very common example of such a phase change, and one of great importance as it is usually accompanied by significant changes in the properties of alloy in which it occurs. One of these properties is hardness, and hence the name, precipitation hardening. In the process which gives precipitation harden, usually at relatively low temperatures, much complex change may occur before the actual precipitation, and the details differ in the variety of alloys which have been so far investigate by many workers.

The precipitation reaction : Supersaturated $\alpha \rightarrow \alpha + \beta$ is commonly produced by first annealing a sample at a high temperature in the region where its equilibrium structure is a single homogeneous solid solution, and then quench to a lesser temperature, where the solid solution is only metastable. The course of subsequent isothermal transformation may then be followed by measuring any suitable physical property. If age-hardening occurs, the strength and hardness of the alloy are found to increase with time at the ageing temperature, and changes occur in electrical resistance and other properties. The basic situation required for age-hardening is thus a solid solution of limited extent having a solubility limit which varies with temperature.

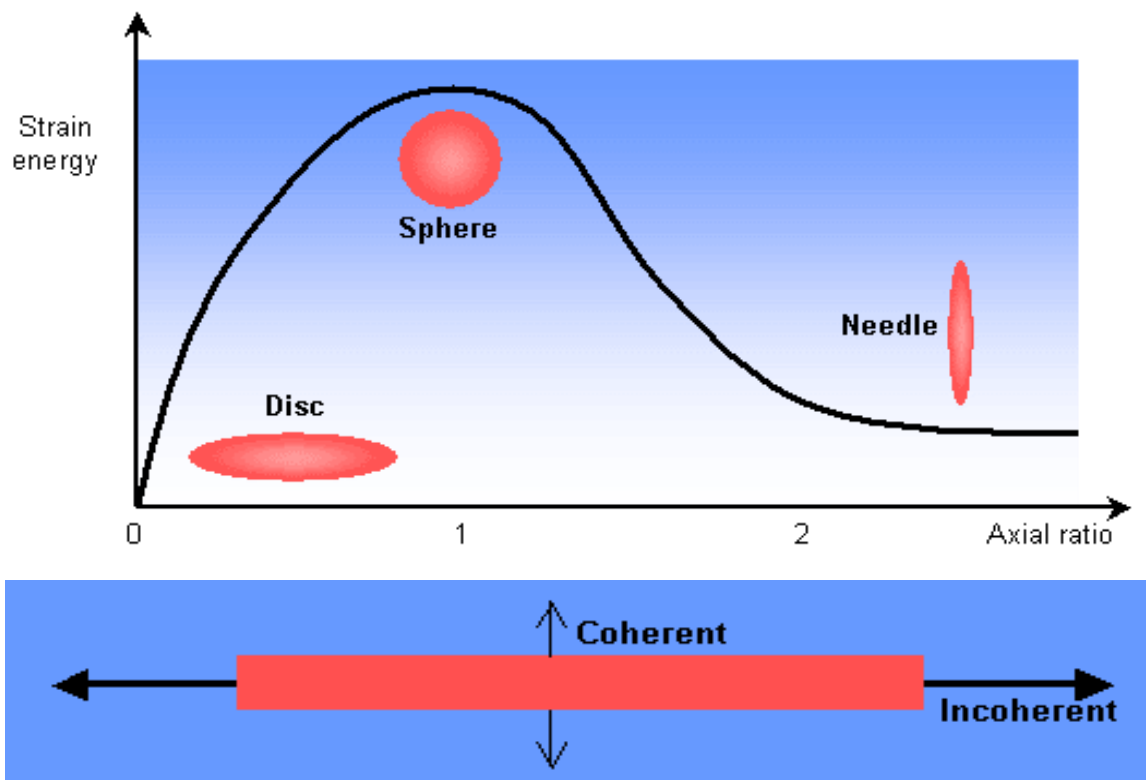


Fig. 3: (a) Precipitate growth as discs or plates. A precipitate particle usually has some coherent and some incoherent interfaces with the matrix. The anisotropy leads to plate and discs morphologies. (b) the bonding coherent interfaces will be parallel to crystallographic plates in the matrix. [2].

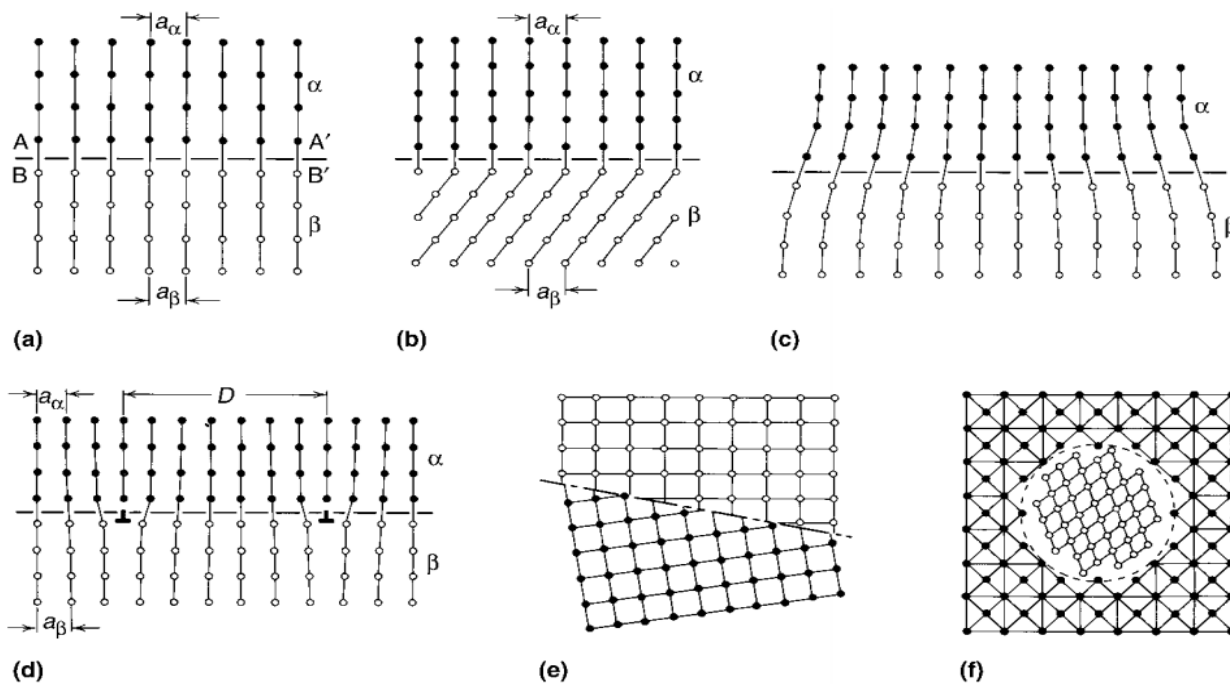


Fig. 4: Different types of interfaces: (a) and (b) are fully coherent, (c) and (d) are semi-coherent, lattice strain showing the presence of dislocations and (e) and (f) are coherent [1].

Alloy system	Parent phase and lattice(a)	Precipitate phase and lattice(a)	Crystallographic relations
			(precipitate phase described first)
Ag-Al	Al solid solution; fcc	γ (Ag_2Al); hcp	$(0001) \parallel (111), [11\bar{2}0] \parallel [\bar{1}10]$
	Al solid solution; fcc	γ' (transitional); hcp	$(0001) \parallel (111), [1120] \parallel [110]$
Ag-Cu	Ag solid solution; fcc	Cu solid solution; fcc	Plates $\parallel \{100\}$; all directions \parallel
	Cu solid solution; fcc	Ag solid solution; fcc	Plates $\parallel \{111\}$ or $\{100\}$; all directions \parallel
Ag-Zn	β (BAgZn); bcc	Ag solid solution; fcc	$(111) \parallel (110), [110] \parallel [111]$
	β (BAgZn); bcc	γ ($\gamma\text{Ag}_5\text{Zn}_8$); bcc	$(100) \parallel (100), [010] \parallel [010]$
Al-Cu	Al solid solution; fcc	θ (CuAl_2); bct	Plates $\parallel (100); (100) \parallel (100), [011] \parallel [120]$
	Al solid solution; fcc	θ' (transitional); tet	$(001) \parallel (100), [010] \parallel [011]$
Al-Mg	Al solid solution; fcc	β ($\beta\text{-Al}_3\text{Mg}_2$); fcc	Plates first $\parallel \{110\}$; later probably $\parallel \{120\}$
Al-Mg-Si	Al solid solution; fcc	Mg_2Si ; fcc	Plates $\parallel \{100\}$
Al-Zn	Al solid solution; fcc	Nearly pure Zn; hcp	Plates $\parallel \{111\}$; $(0001) \parallel \{111\}, [11\bar{2}0] \parallel \langle 110 \rangle$
Au-Cu (b)	Au-Cu solid solution; fcc	α_1' (AuCu I); ord fct	$(100) \parallel (100), [010] \parallel [010]$
Be-Cu	Cu solid solution; fcc	γ_2 (γBeCu); ord bcc	G-P zones $\parallel \{100\}$; later γ_2 with $[100] \parallel [100], [010] \parallel [011]$
0.4C-Fe	Austenite (γFe); fcc	Ferrite (αFe) (proeutectoid); bcc	$(110) \parallel (111), [111] \parallel [110]$
0.8C-Fe	Austenite (γFe); fcc	Ferrite in pearlite; bcc	$(011) \parallel (001), [\bar{1}00] \parallel [100], [0\bar{1}1] \parallel [010]$
	Austenite (γFe); fcc	Ferrite in upper bainite; bcc	$(110) \parallel (111), [110] \parallel [211]$
		Ferrite in lower bainite; bcc	$(110) \parallel (111), [111] \parallel [110]$
1.3C-Fe	Austenite (γFe); fcc	Cementite (Fe_3C); ortho	Plates not $\parallel (111)$; $(001) \text{Fe}_3\text{C}$ \parallel to plane of plate
Co-Cu	Cu solid solution; fcc	αCo solid solution; fcc	Plates $\parallel \{100\}$; lattice orientation same as parent matrix
Co-Pt(b)	Pt-Co solid solution; fcc	α'' (CoPt); ord fct	Plates $\parallel \{100\}$; all directions \parallel
Cu-Fe	Cu solid solution; fcc	γFe (transitional); fcc	Cubes $\{100\}$; lattice orientation same as parent matrix
		αFe ; bcc	Plates $\parallel \{111\}$; lattice orientation random
Cu-Si	Cu solid solution; fcc	β (ζ Cu-Si); hcp	Plates $\parallel \{111\}$; $(0001) \parallel (111), [1120] \parallel [1\bar{1}0]$
Cu-Sn	β phase; bcc	Cu solid solution; fcc	$(111) \parallel (110), [1\bar{1}0] \parallel [111]$
Cu-Zn	β (CuZn); bcc	Cu solid solution; fcc	$(111) \parallel (110), [110] \parallel [111]$; variable habit; plates or needles $\parallel [556]$
	β (CuZn); bcc	γ ($\gamma\text{Cu}_5\text{Zn}_8$); ord bcc	$(100) \parallel (100), [010] \parallel [010]$
	ϵ ($\epsilon\text{Cu-Zn}$); hcp	Zn solid solution; hcp	$(1014) \parallel (1014), [1120] \parallel [1120]$
Fe-N	Ferrite (αFe); bcc	γ_1 (Fe_4N); fcc	$(112) \parallel (210)$
Fe-P	Ferrite (αFe); bcc	δ (Fe_3P); bct	Plates $\parallel (21,1,4)$
Pb-Sb	Pb solid solution; fcc	Sb solid solution; rhom	$(001) \parallel (111), [100] \parallel [110]$

Fig. 5: Crystallographic relations between precipitate and parent phases in selected soil systems [1].

To recall the essential facts pertaining to the process of precipitation, the starting point and the final one are well known. The initial stage is the supersaturated solid solution before quenching. The dissolved atoms replace some of the atoms of the solvent at the points of a definite lattice. It is generally considered that the distribution of the atoms is completely random, and that the lattice defects such as distortions, are relatively weak (Fig. 5). These assumptions are only an approximation, and it was proved later that, in some cases, the dissolved atoms had a tendency to segregate to form very small nuclei (Fig. 6). Thus, the first stage in the procedure of precipitation from a solid solution consists in the development of segregates of solute atoms which comprise stable region having a chemical composition dissimilar from the average composition of the solid solution. Within these regions the atoms

are situated at the average lattice points of the random solid solution. The region may be produced on ageing, or possibly at the temperature of solution treatment or during the quench, and the aggregates may have associated with them a larger or smaller number of vacant lattice sites than will be found in an equal volume of matrix.

The final stage is obtained by a very long annealing at such a temperature that equilibrium is reached in a reasonable time. The alloy then consists of a matrix which is a saturated solid solution, much poorer than the initial one. Imbedded in this matrix are the grains of the precipitate indicated by the equilibrium diagram (Fig. 7).

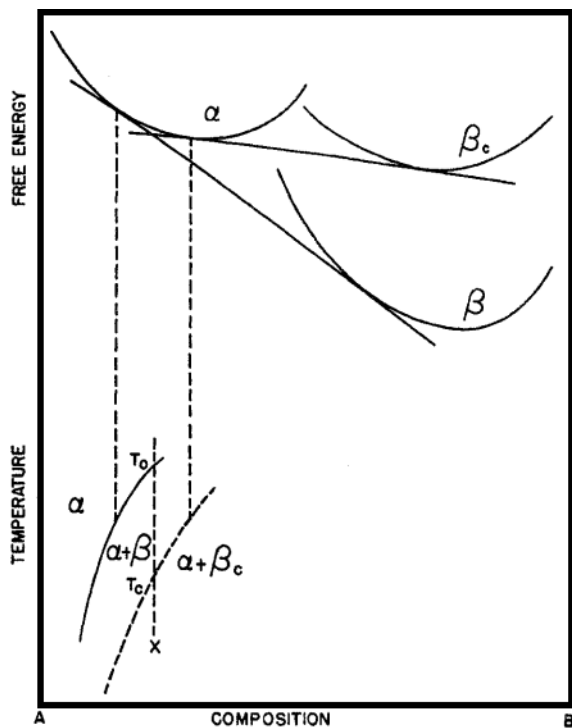


Fig. 6: Phase diagram for non coherent- β_c phase (solid lines) and coherent β_c phase (dashed lines)[3].

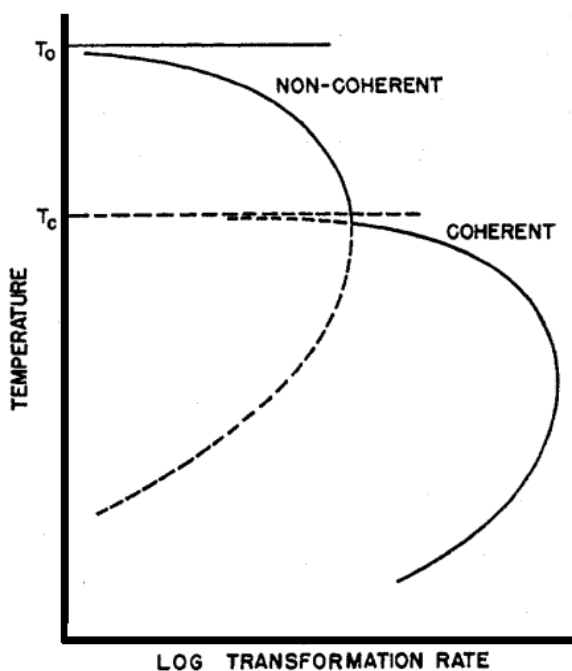


Fig. 7: Relative transformation rates for non-coherent and coherent precipitates (schematic) [3].

For simplicity, one can consider the transformation in which the crystal of the initial solid solution retains its identity up to the end of the precipitation. Its external shape and its orientation remain unchanged, which is generally very small. That means that there is no complete reorganization of the atoms, but only a rearrangement of solute atoms in a practically fixed lattice.

In such a case, if annealing is made at progressively lower temperature, the processes are slower and slower. However, according to the equilibrium diagram, one would expect no change except in the kinetics of the transformation. Nevertheless, the precipitation phenomena are generally profoundly changed. The first possible change is the occurrence of another type of precipitate. Micrographs and X-ray patterns make them easily visible. If the annealing temperature is kept in a range narrow enough always to have the same precipitate, e.g. $\text{Al}_2\text{Cu}(\theta')$ in an Al-Cu alloy, it is found that at a given temperature and after a short annealing, numerous small precipitates are visible. After a long annealing, large and less numerous precipitates are found (Fig. 1).

Microscopic examination of a supersaturated solution shows that it is convenient to distinguish the following modes of precipitation:

- Continuous or General
- Discontinuous or Cellular
- Coherent Precipitation of Metastable Phases
- Formation of Segregates, or Guinier-Preston Zones

The third and fourth processes are rather complex and occur mainly at low temperatures, and it is advisable to have a look at the continuous and discontinuous modes of direct precipitation first.

A supersaturated solution during its transition towards the equilibrium state shows, when examined microscopically, that there are two possible types of phenomena. In the first, intact regions of the matrix and regions decomposed by precipitation are placed side by side; the volume of the two-phase region increases with time. This is called discontinuous precipitation. In this process the precipitated regions generally grow from the edges of the grains and consume the crystal progressively. The crystals of original matrix become a matrix of precipitate and new crystals of an impoverished matrix. Generally there is no orientation relation between the new and the initial crystals. Decomposition is governed by the nucleation and the

nuclei of the precipitate grow by the diffusion of atoms dissolved in the matrix. Here it should be kept in mind that there is a disorganization of the matrix crystal at first and, then, complete reorganization of the atoms around the nuclei. The sharp change in structure occurs without intermediate stages, the disorder is usually limited to narrow regions along the interface between the matrix and the precipitated solution. The disordered domains are too small to be detected.

In continuous precipitation, as in the most widely studied Al-Cu alloys, the precipitate appears simultaneously throughout the matrix crystal, although its rate may show marked variations from one region to another. There is a rigorous orientation relationship between precipitate and matrix. The matrix crystal remains unchanged in its exterior shape and orientation. There is only a slight variation of the parameters as a consequence of the variation of composition. Thus it is possible to conclude the process takes place by atomic movements within the framework of the lattice of the matrix.

There are, however, structural changes in the solid solution before any precipitation appears. These structural changes involve an important fraction of the total volume so that they produce detectable X-ray diffraction effects. In addition, there are very marked variations in the physical and mechanical properties. This early stage is termed as pre-precipitation.

A homogeneous solid solution, when quenched, does not decompose immediately, and a supersaturated solution is obtained at room temperature. However, the physical properties of the quenched alloy change with time, either at ordinary temperature or during an anneal at a temperature much lower than the homogenizing temperature.

During the anneals at these lower temperature the optical microscope reveals no second phase in the bulk of the crystal in the beginning at least. Occasionally there are a few grains of precipitate along the boundaries. This, however, is far too rare to be responsible for the important changes of the properties. Observations with the electron microscope using ordinary replica techniques also do not reveal a second phase. There are only indications of heterogeneities in the matrix. [9].

There are two possibilities for explanation the changes in physical property during ageing. One may assume either that the alloys contain precipitates so fine that they are not visible, or that the solid

solution pass through a state of pre-precipitation characterize by a different atomic structure.

The first idea is the basis for the first theory of age-hardening by Mercia and Geisler, see Guinier [9]. According to Geisler, there is a sequence of stages during the evolution of the alloy corresponding to the progressive growth of the precipitated particles. According to this theory, the first nucleus is formed by the clustering of a few dissolved atoms; this nucleus then grows into a needle directed along an important crystallographic axis. The needle is subsequently transformed into a thin platelet parallel to a reticular plane. Finally, this platelet becomes a grain, which is large enough in three dimensions to give diffraction spots.

The sequence theory of Geisler has been discussed in detail by Guinier [10] and he has demonstrated that this theory, in its strictest form, is unacceptable in the case of Al-Cu.

The idea now generally accepted is that the variation in the property of the solid solutions in the pre-precipitation phase are cause by heterogeneities in the distribution of the dissolved atoms; however, this occurs without the presence of two distinct phases. The excess dissolved atoms have a affinity to produce a clusters or "zones" which are incorporated in the matrix, which always have submicroscopic dimensions and whose composition is that of the matrix, more or less deformed. Thus, a zone generally could be defined as a small region of crystalline irregularity in the matrix resultant from a variation in composition and possibly from displacement of the atoms external of the nodes of the average matrix. The essential characteristics of the zone, which justify its distinction from that of a very small precipitate, are that it does not have a well-defined lattice, and it does not have precise boundaries. The simplest hypothesis is to assume that the atoms remain at the points of the lattice of the matrix, (Fig.8). Such is the ideal zone, because the lattice is not, or very little, deformed. Generally, however, a gathering of dissolved atoms inevitably produces strong distortions of the lattice. In the zone, the atoms are then removed from the matrix points, (Fig. 9), but it is characteristic of the structure of the zone that they do not reach any regular arrangement. In other words, the structure of the zone may be regarded as a more or less strongly distorted lattice. The distortions may vary from the centre to the periphery of the zone in proportion to the concentration of the dissolved atoms. Therefore, the zone has no well defined boundaries. There is a ideal coherence between the zone and surrounding matrix. Such a structure can exist only if all the atoms of the

zone, upto its centre, are strongly influenced by the lattice of the matrix. It means that only very small zones can be constant, especially if the displacements from the ideal positions are appreciable. The order of magnitude of the observed zones is 100 Å or less. The shapes of the zones are different in various alloys. Zones have been found in Al-Cu alloys for the first time, and are then generally known as Guinier-Preston (G.P.) zones, after the two workers who independently first discovered them. [9, 10].

Both spherical and plate-like zones have been detected in aluminum alloys, and Guinier has suggested that the shape of the zone depends on the relative diameters of solute and solvent atoms. Thus, solutes like silver and zinc, which have atomic diameters very similar to aluminum, give rise to spherical zones, whereas a solute like copper, which

has a diameter 10% smaller than that of aluminum, forms plate-like zones. Here in the latter case, the strain-energy considerations preclude the formation of spherical zones.

The size of a G.P. zone is higher than the resolving power of an advance electron microscope, but the ordinary etching techniques do not reveal them directly. The application of the thin film transmission technique was pioneered by Castaing [7] although it now has been concluded that some of his photographs were wrongly interpreted. A thin film transmission micrograph of the first detectable zones in Al-Cu alloys was presented by Nicholson and Nutting [8] for the first time.

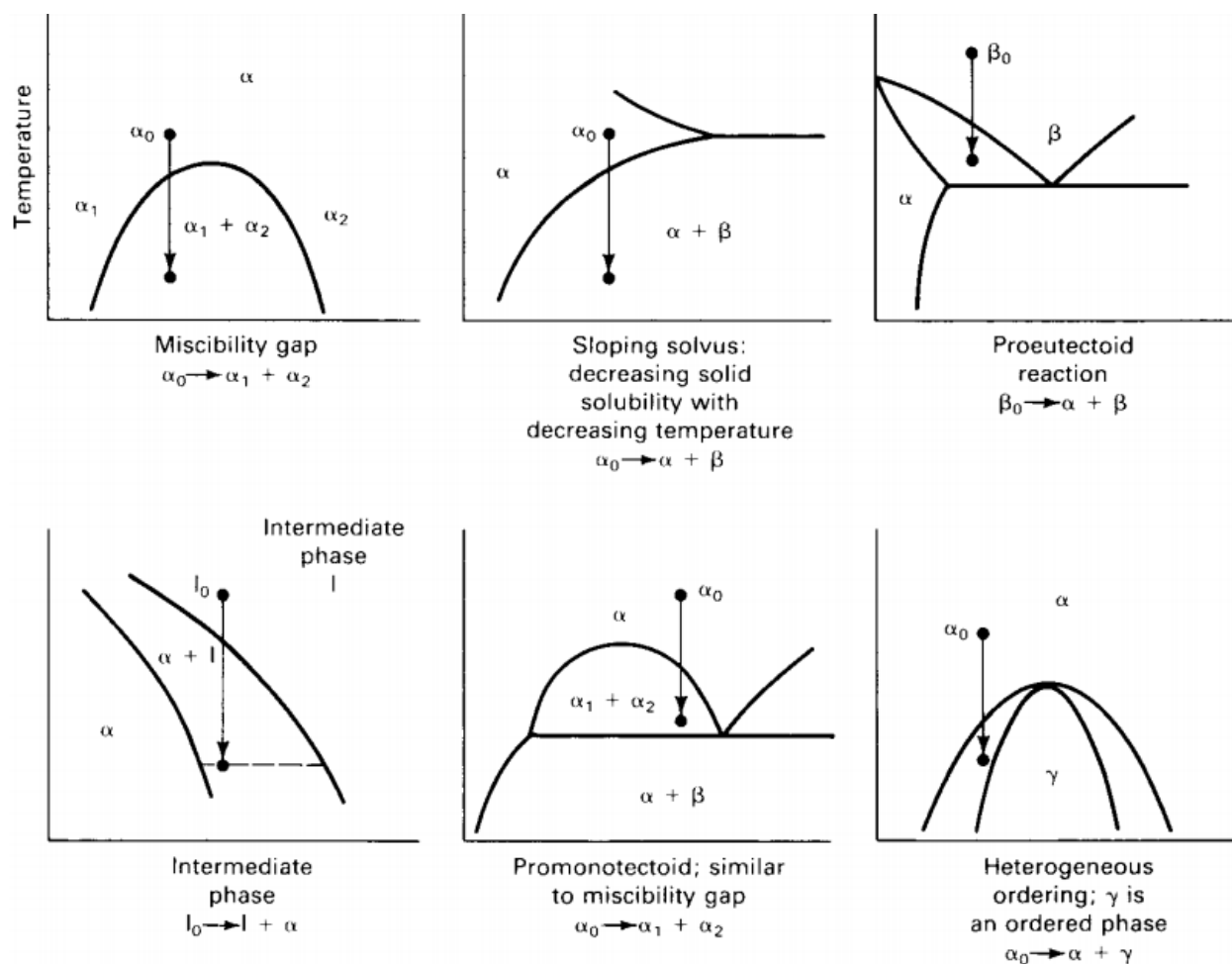


Fig. 8: Equilibrium phase diagrams illustrating various conditions for precipitation of a second phase. In all cases, the matrix of the two phase product has the same crystal structure as the initial one phase parent, but with a different equilibrium composition (α , β or D) [1].

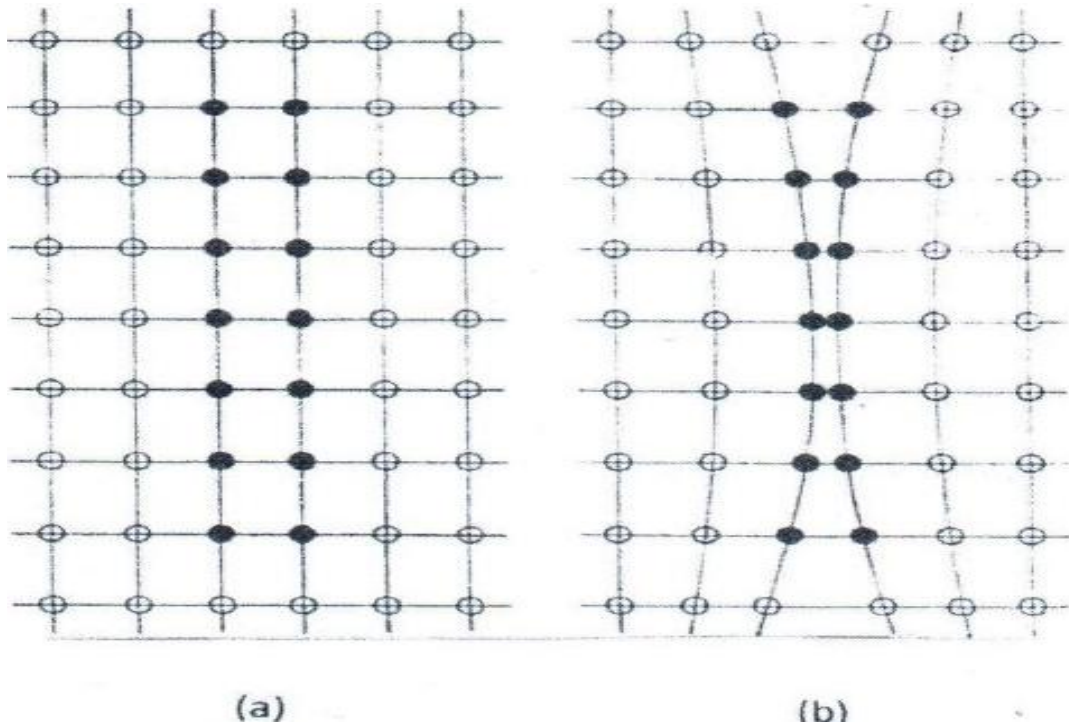


Fig. 9: (a) atoms remain at the points of the lattice (b) in the zone, the atoms are then removed from the matrix points [10, 11].

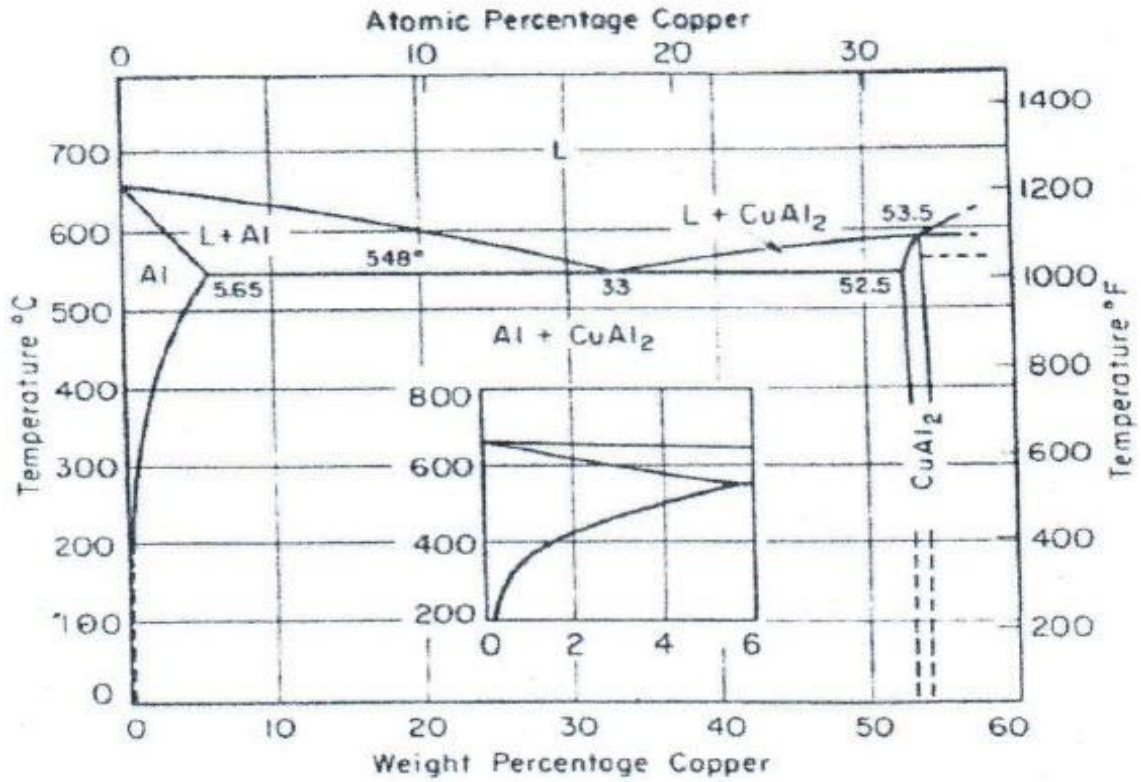


Fig. 10: Phase diagram of Al-Cu alloy.

Even though quite a few alloys are now known to be able to get improved mechanical properties through precipitation hardening (Fig.10), most of the earlier work, for decades, has been on Al-Cu alloys for their useful industrial application. Hence some reference to this alloy.

Descriptive Account of Precipitation in Al-Cu Alloys

In 1938 Guinier [9] and Preston [10] independently announced new experimental results from X-ray studies of Al-cu alloys and their interpretations were in remarkable good agreement. Since then, extensive work has been done on these alloys, and precipitation structures which are responsible for hardening have been studied. Most of the work has been done on Al-4%Cu alloys and extensive X-ray diffraction studies of this alloy have helped to deduce the sequence of precipitation. The following sequence has been given by Guinier [11] and Preston [12] and Silcock, Heal and Hardy [13].
Supersaturated solid solution \rightarrow
G.P. zones $\rightarrow \Theta''$ (or G.P.II) $\rightarrow \Theta'$ $\rightarrow \Theta$ (CuAl₂)

Of these four stages, two correspond to true precipitates of composition CuAl₂, called the Θ'' or G.P.II zone. The first type of zone is the G.P.I zone, (Fig.11) [1].

It should be mentioned here, before discussing the precipitating structures in detail, which many workers have attempted to associate the

sequence with the structures observed in the electron microscope using oxide replica technique. Thomas and Nutting [14] deduced the following stages:

- Circular white spots ca. 200 Å in diameter associated with G.P. zones.
- Aligned white spots on {100} matrix planes corresponding to Θ'' .
- Definite white plates on {100} matrix planes indicating the formation of Θ' phase.
- Large irregular white patches indicating the equilibrium Θ (CuAl₂) phase.

These results, however, are only in good agreement with the X-ray sequence in stages (c) and (d), i.e. when the alloy has completely precipitated. The disagreements are that stage (b) coincides with the precipitation of Θ' according to the X-ray results, and stage (a) suggests that the G.P. zones are spherical whereas strong X-ray evidence shows them to be disc-shaped. Recent thin foil technique results are in good agreement with the X-ray results, and stages (b) and (c) both represent the Θ' precipitate and there seems to be no structural significance in the change from aligned white spots to continuous plates. The most probable explanation of the isolated white spots in stage (a) is that they are small surface precipitates of Θ' formed by the diffusion of copper from the supersaturated matrix. [15].

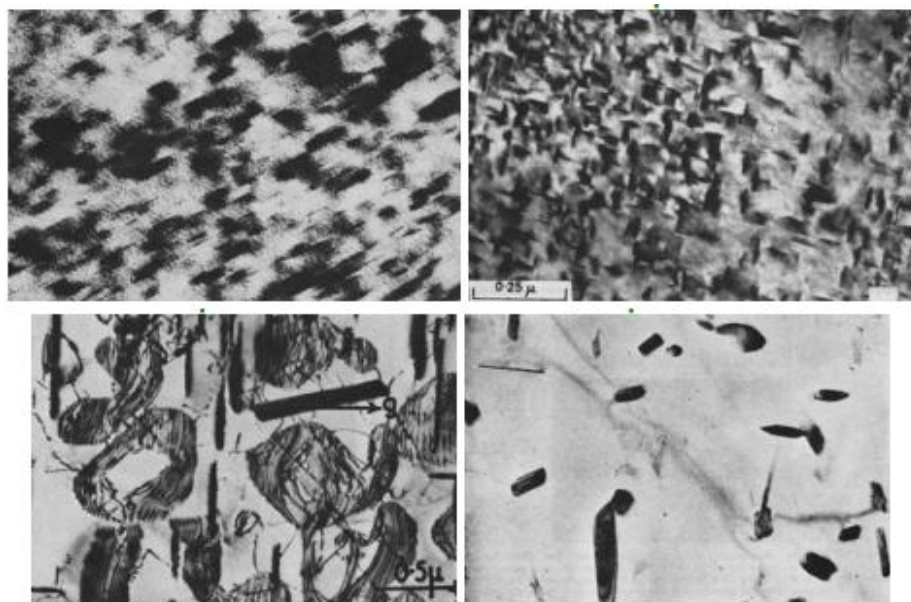


Fig. 11: Decomposition of solid solution (parallel matrix) into new phases of different compositions (precipitates) and the depleted matrix. Transmission electron micrographs of precipitation sequence in Al-Cu alloys. (a) Guinier-preston zones at 72,000x (b) Θ'' at 63,000x (c) Θ' at 18,000x (d) Θ at 8,000x.

The process of clustering (formation of the precipitates) can be summarized as: The supersaturated alloy, obtained on quenching a homogeneous solute, decomposes during or immediately after quench, and the solute atoms segregate to form clusters. These clusters grow until they give rise to X-ray diffraction effects typical of G.P. zones. There is no effective nucleation barrier to the formation of these clusters so the process takes place entirely by competitive growth which is determined by vacancy flux. The initial stages of clustering take place by the motion of vacancy-solute atom pairs and are governed by activation energy rather less than E_M , the activation energy of migration of a single vacancy. This explains the anomalous high diffusion rate, first pointed out by Jagodzinski & Laves [16-21]. The later stages have a rather high activation energy, ca. 1 eV in Al alloys, which is still less than that for solute diffusion (ca. 1.4 eV). Thus a non-equilibrium number of vacancies remain in the lattice and may be associated with the clusters. The process which controls the diffusion may be the migration of solute-vacancy examples or the emission and absorption of vacancies from zones. The majority of the excess vacancies, introduced by quenching, migrate to sinks, such as grain boundaries and dislocations, to give a characteristic dislocation structure, viz. helical loops etc.

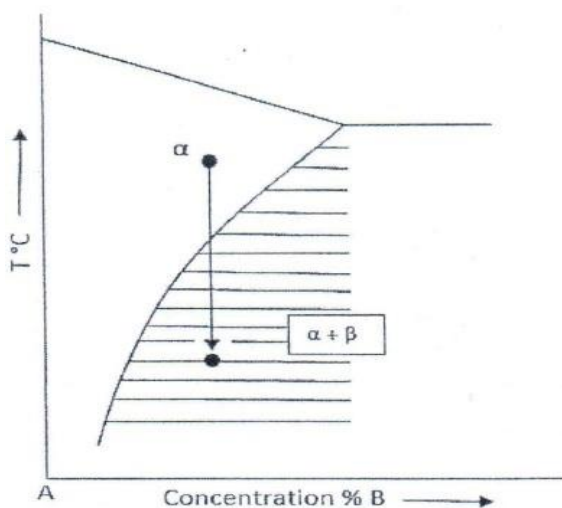


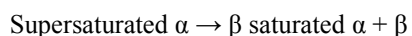
Fig. 12: phase relations for precipitation. The solid phase β precipitates from the solid solution α on cooling (arrow).

Mechanism of Precipitation (Thermodynamical Background)

Hardy & Heal and Newkirk [7.b and 8.b] have discussed in details the various theories dealing with precipitation in supersaturated solutions. Later Brook [15] discussed all the work on mechanism of

precipitation upto 1963. We will confine the discussion here to some relevant facts about Al-Cu alloys, with the main emphasis on thermodynamics and kinetics of precipitation.

Precipitation, as we know, is a decomposition of solid solution (the parent matrix) into a new phase of different composition (the precipitate) and the initial solid solution with lesser solute concentration (the depleted matrix), (Fig.12). The reaction is represented by an equation of the type:



The phase diagram merely defines the initial and final equilibrium states. It does not define the path by which the reaction progresses but only the thermodynamically stable conditions. Now the only requirement for a precipitation reaction is that the solid solubility decreases with temperature. This decrease may be as great as from 50%B type atoms soluble at the high temperature to a few percent soluble at low temperatures, or the change may be a small fraction of a percent.

Now the atoms of the solute are distributed at random throughout the lattice of the solvent in a solid solution. If the solution is of substitutional type the solute atoms B occupy lattice positions occupied by solvent A atoms in pure solvent. In interstitial type B atoms occupy positions between the lattice sites of the solvent A lattice (as do carbon atoms in Fe lattice). On atomic scale the difference in atomic sizes creates the solid-solution type of lattice distortion in which the interatomic distance varies from point to point with fluctuations in concentration; this distortion being the chief factor controlling solid solution hardness. The atoms are in a constant motion and are activated by thermal agitation or vibration and move from point to point of the lattice by atomic interchange or by migration to unoccupied lattice sites. The potential barrier (that is the minimum energy an atom must possess to be capable of interchange) is nearly independent of temperature but varies considerably with the solute concentration. The intensity of the lattice bonds in the neighborhood of a solute atom and the activation energy for diffusion are altered and, thus, the rate of diffusion. The variation of rate of diffusion D with temperature may be expressed by the equation:

$$D = Ae^{-Q/RT}$$

where A is a constant, Q is the activation energy for diffusion, R is the gas constant, and T is the absolute temperature. With the decrease in T there must be a rapid decrease in D and, therefore, the rate of diffusion would control the rate of precipitation to a

great extent at low temperature where mobility is low.

Fink and Smith, see Newkirk [8.b], have considered the problem of atomic distribution in solid solutions and of monetary regions of high solute concentrations at high temperatures. These regions or groups are not stable and the immediate disintegration of these is imminent. Fink and Smith calculated the probability of occurrence of various numbers of solute atoms in certain size groups for the ideal case from Poisson's formula:

$$P_j = \frac{\epsilon^j e^{-\epsilon}}{j!}$$

where J is the number of solute atoms in a group and ϵ is the average number of solute atoms in a group. They found that the probability of the occurrence of a group of atoms of Al and Cu in the proportion to form CuAl_2 decreased very rapidly as the size of the group increased. Mehl and Jetter in Geisler [5] pointed out that Poisson's formula was only an approximation and that derivations occurred from the ideal distribution which presumably came chiefly from interaction energies between solvent and solute atoms. This would make the existence of such groups as rich in copper as CuAl_2 even momentarily in the structure of matrix unconceivable. It would be rather expected that such groups would have the regular atomic arrangements and appropriate lattice dimensions of Θ' (CuAl_2), a structure intimately related to the matrix. This is supported by the X-ray diffraction analysis of quenched alloys.

A solid solution, immediately after quenching, might be expected to exhibit the state of fluctuation in existence just before the quench and then in time of approach the state of grosser fluctuation characteristic of lower temperature. No definite information about the state or the rate of change is known for a real system and one has to consider a number of factors, such as imperfections and conditions at grain boundaries etc. In these cases the crystallographic lattice is in a disrupted condition in the internal surfaces and the diffusion rates may be faster or the activation energy for nucleation is smaller, and the rate of growth of the new phase may be fast process.

Now the decomposition of supersaturated solution and formation of precipitates occurs by a mechanism involving nucleation and growth. At temperatures below the solvus curve, a solid solution is no longer structurally stable but tends to reject solute atoms from its own lattice. In doing so, i.e. on precipitation of the new phase, the free energy of the system decreases to a minimum at equilibrium. The

driving force in the reaction is this decrease in free energy. In an ideal case the change in free energy consists of two terms, the positive one which increases with particle size, and the negative one which decreases with particle size. The first is proportional to the surface of the nucleus and the latter is proportional to the volume of the nucleus. The summation of the two shows that the free energy increases with particle size upto a specified size, the stable nucleus size, and then decreases. The temperature dependence of the initial rate of nucleation N has been expressed by Becker by the relationship:

$$N = C \cdot \exp \left(-\frac{Q+A}{kT} \right)$$

where Q is the diffusion activation energy, C a constant, and A is the work of nucleation and is a function of temperature. It should be mentioned here that the work of nucleation and the stable nucleus size depend upon degree of supersaturation. With increasing degree of supersaturation the work of nucleation and stable nucleus size decreases (Fig.13). At constant concentration the rate of nucleation goes through a maximum with temperature since Q is independent of temperature and A increases markedly with increasing temperature.

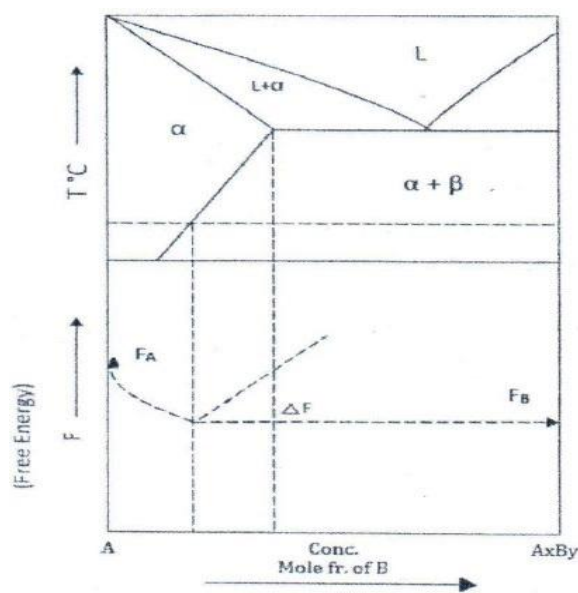


Fig. 13: Change in total free energy ΔF on precipitation of precipitates from supersaturated solution of precipitates from supersaturated solution of Al-Cu type alloy system. F_A & F_B = free energy of pure components. ΔF = Free energy change on precipitation.

The mechanism of nucleation has been the subject of much speculation. Dehlinger in Geisler [5] has

talked of certain groups of atoms, complexes, arising in the supersaturated solution which have the capacity to grow, and only with time and in certain regions do they finally attain the concentration and space lattice of the equilibrium precipitate. Fink & Smith in Geisler [5] assumed that the first nuclei are the resultant rearrangement of atoms in the groups rich in solute that were retained from the solution heat treatment. Mehl & Jetter in Geisler [5] believed the theory of Fink & Smith, and pointed out that the formation of the first nuclei did not require any change in the matrix composition, is formed purely by shearing processes (Fig. 14) and does not require any diffusion from the matrix. Later, Turnbull in Geisler [5] applied the theories of Volmer, Becker and Döring to the problem of incubation period and proposed that nuclei are formed by a sequence of bimolecular processes in which stable-size embryos change in size by fluctuations. The important point of this process is that embryo at all sizes has a characteristic orientation relationship with the matrix in which it forms. This relationship is due to a state of coherency between the lattice of the nucleus and that of matrix. The coherency relationship may also cause a preferred shape and orientation of the precipitate particles, particularly in early stages of formation. The state of coherency, since it allows a lower interfacial energy between the precipitate and the matrix, promotes the formation of a structure which, though not the most stable precipitate structure, forms with a lower free energy of activation than does the final precipitate structure.

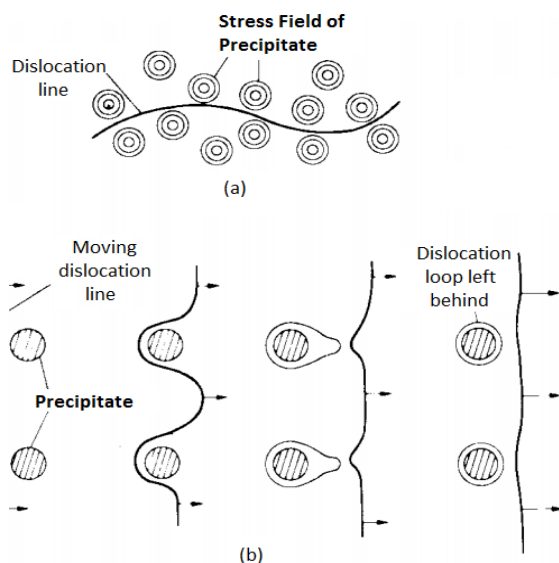


Fig. 14: Schematic representation of a dislocation, (a) curling round the stress fields from precipitates and (b) passing between widely spaced precipitates [28].

The free energy F ($F = H - TS$) of a system containing growing particles in a surrounding matrix

can be thought of as composed of 3 components : a volume free energy term, a surface free energy term and a strain energy term.

$$F_{\text{precipitate}} = F_{\text{vol.}} + F_{\text{surf.}} + F_{\text{strain}}$$

F_{surface} is an extra energy term and arises due to the formation of a new phase and the subsequent interface; the atoms between the precipitate and the matrix possess higher energy than the atoms of the matrix and the precipitate. F_{strain} is a result of elastic strains due to the difference in volumes of the precipitate and the matrix. When the precipitate particle is very small, $F_{\text{surf.}}$ dominates and may lead to the formation of the transition lattice. As the particle grows, the $F_{\text{vol.}}$ and F_{strain} terms become important in determining its free energy. When the particle becomes large enough so that the last two terms overcome the first, the crystal tends to transform to a crystal structure which is more stable, but which is surrounded by higher energy interface than the previous coherent interface.

In Al-Cu alloys the contribution of F_{surface} (or rather $\Delta F_{\text{surface}}$), the change in surface energy term due to the appearance of a new phase) is limited when coherent G.P. zones are formed. It is due to the concentration gradient between the G.P. zones and the matrix. The greater is the difference in volumes of the precipitate and the matrix, the more important is the influence of ΔF_{strain} . In Al-Cu alloys, this is determined by the difference in atomic radii of the two components. Furthermore, according to Nabarro [15-B], these strains govern the form of precipitate and the planes of matrix on which it lies. A plate-shaped precipitate has the lowest strain energy. Since the strain energy depends upon the volume of the precipitate, the formation of a smaller number of larger precipitates does not reduce the total strain energy of the precipitating system. The “chemical” free energy change, which is the driving force for precipitation, depends upon the degrees of supersaturation, and decreases as precipitation proceeds. Therefore, unless the strain energy is reduced in some way, the process of precipitation must eventually stop. Thus, the chemical free energy change must be larger than the sum of the surface free energy term and the strain energy term. If the precipitate breaks away from the matrix and forms a non-coherent precipitate (such as the equilibrium phase Θ in CuAl alloy), the strain free energy change term vanishes and the influence of the surface free energy change term is large. Even though the increment in chemical free energy change is larger when the equilibrium precipitate is formed than that when G.P. zones are formed, the G.P. zones are formed earlier due to the lower free energy of activation, which in fact is due to the low

contribution of the lower surface energy change and lower strain energy change. The intermediate precipitate, Θ' , could also be formed earlier than the equilibrium precipitate due to a lower contribution of surface free energy change. However, here the strain energy change is lowered due to the partial break-away of coherency by dislocations absorbed at precipitate-matrix interface.

Precipitations in many alloys, especially in Cu-Al alloys, have been thoroughly discussed by Meijering [22], Beton and Rollason [23], Hornbogen [24-27], Silcock and Heal [19], Laird and Aaronson [20].

The presence of small amount of these elements can increase or decrease precipitation in a number of alloys. For example Co, Ni and Fe reduce nucleation in Cu-Be alloys. Small amount of Cd, Li, In, Sn etc have a remarkable influence upon the ageing characteristics of Al-cu alloys [29, 30, 34, 35]. Hardy [21] said that the effect was due to changes which the third element imposed upon the precipitate-matrix relationship rather than to changes in the solid solution [31-35]. Certain elements cause an increased response to ageing by lowering the activation energy for nucleation.

Kelly and Nicholson pointed out [25] that when supersaturated Al-cu alloys are quenched they give rise to the formation of dislocation loops (Fig. 15) and fine precipitates, G.P. zones, even at very low temperatures and that this happened without any incubation process. The necessary conditions were to be determined thermodynamically by the spinodal curve which was obtained from the points of inflection on the free energy-composition curve. These points of inflection are represented by P and Q in (Fig.16) and at these points $d^2F/dc^2 = 0$. The sign of parametric d^2F/dc^2 also determined the sense of diffusion coefficient D [25] since

$$D = \frac{D_0 \cdot C(1-C)}{RT} \cdot d^2F/dc^2$$

where C is the solute concentration and D_0 involves the statistical probability of a phase change.

Inside the spinodal curve d^2F/dc^2 is negative, i.e. less than zero, and random concentration differences in the solid solution will be accentuated. That is to say that D is negative and uphill diffusion takes place; there is no nucleation barrier. The transformation occurs over the whole crystal. Between the spinodal and the phase boundary d^2F/dc^2 is positive, that is D is positive, and random concentration differences will tend to even out downhill or normal diffusion. Hence there is a

nucleation barrier which must be overcome before precipitation can take place [35].

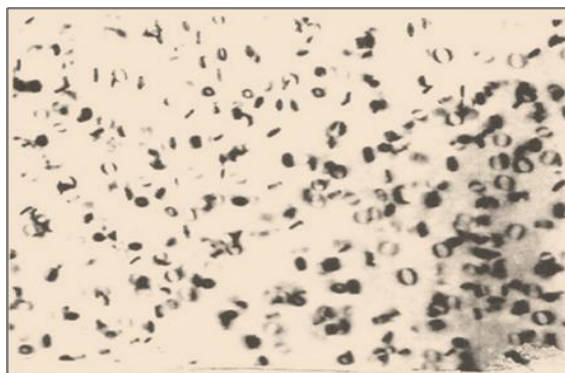


Fig. 15: Al+ 4% Cu, as quenched. Dislocation loops (X27, 200) [28].

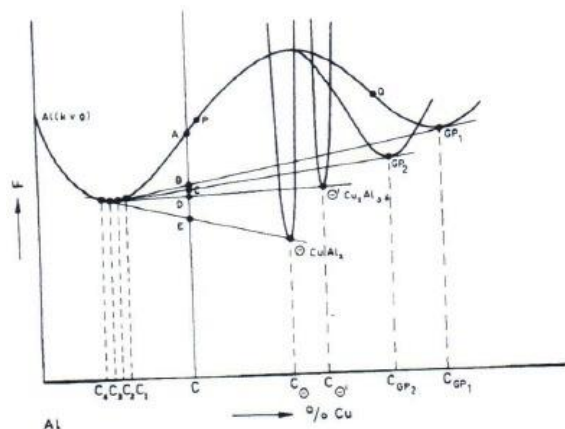


Fig. 16: Schematic free energy- concentration diagram for Al- Cu alloys [27].

The formation of clusters (G.P. zones) in Al-Cu alloys takes place above the spinodal [26] and Meijering [22] has obtained the value of d^2F/dc^2 to be greater than zero for an Al-5.7 w% Cu at 0°C. Cahn in Kelly and Nicholson [25] calculated that due to the effect of F_{strain} , the spinodal curve is shifted towards lower temperatures. He says that this depressed spinodal was the real spinodal of the coherent phase and was applicable to the formation of G.P. zones in Al-Cu alloys. This is explained by the decrease in energy of domain boundaries owing to the presence of dislocations due to the difference in diameters of the Al and Cu atoms.

The formation of clusters of fine particles (zones) above the spinodal could be explained in terms of nucleation and growth. There is a clustering or concentration fluctuations of copper atoms in the time the specimen is quenched and the first

measurements are made [36-38]. The embryos so formed lower the critical nucleus size because the excess vacancy concentration lowers the activation energy of nucleation, as suggested by Hornbogen [24]. If the critical nucleus size is reduced to be smaller than the size of embryo, there is a decrease in free energy and precipitation takes place. Since the excess vacancies are still active, further nucleation of fine zones takes place. It is to be noticed that while clusters or zones are forming, there is a saturation of solute atoms in the matrix.

The whole mechanism of precipitation can be summarized briefly as follows. The decomposition of supersaturated solid solutions occurs by a mechanism involving nucleation and growth. Kuhlmann-Willsdorf [28] suggested that the first stage in the precipitation process is the formation of instable large clusters of solute atoms and instable large vacancy clusters. These regions could be formed at the homogenizing temperature or possibly during quenching. As precipitation proceeds, these clusters might collapse to form dislocation loops. This was confirmed by Hirsch and colleagues [28] by electron micrographs of quenched aluminium which showed prismatic loops a few hundred Angstrom in diameter. Shear strains are minimized if the precipitates grow as thin plates. Further growth of the precipitates results in a progressive loss of coherency by the introduction of surface dislocations and vacancies until ultimately the interface resembles a large angle boundary; the precipitates now becoming non-coherent. The modes of formation growth of precipitates result in the greatest rate of fall in free energy of the system.

There seems to be little basic difference between the mechanism of precipitation in simple binary alloys and in those containing a third addition. The unit processes, including nucleation, growth, transition lattice formation, etc. apply as well to simple binary alloys and to ternary alloys. We could simply say that the addition of ternary elements alters the kinetics of precipitation profoundly but not the nature of precipitation.

The following possible effects due to trace element additions could be taken into consideration:

- a) Trace elements might increase the nucleation rate of a particular phase or vice versa.
- b) They might increase the supersaturation of solute at the ageing temperature.
- c) They might reduce inter-facial energy by diffusing to the matrix/precipitate inter-face.
- d) They might concentrate at grain boundaries and thus effect the precipitation.
- e) The atomic size of these elements may influence the precipitation behavior as it should cause the opposite distortion of the matrix to that of the solute, and preferably be of as numerically large a size factor as consistent with adequate solution.
- f) The trace element, by entering into the precipitate structure, may lower its free energy and make it more likely to precipitate.
- g) The effect of valence of solute element on binding energy between a solute atom and a vacancy could be an influential factor.
- h) The trace element may nullify or modify the effect of other trace elements already present in the alloy.

Coring of Solid Solutions

“The most common and most obvious departure from equilibrium that occurs among solid solutions is coring, the appearance of crystals that vary significantly in composition from centres (or cores) to their surfaces. Coring results from the fact that, in general, the first material to freeze as an alloy melt cools is distinctly richer in one or the other of its components than the average for the alloy as a whole, and from the further fact that diffusion rates in solid metals are relatively low, so that a composition gradient established during freezing of a solid-solutions crystal may not be completely eliminated during its subsequent cooling to room temperature” [39-46].

We want to point out there have been some very informative articles on precipitation and precipitation from solid solutions. To name a few:

- a) Precipitation by J.L. Meijering in Topics in Physical Metallurgy, Edited by A. Q. Khan and M. J. Brabers, Elsevier Sequoia S.A. Lausanne, Switzerland (1972). Meijering has nicely discussed the thermodynamics of precipitation from unstable and metastable solid solutions. The role of interfaces and vacancies in precipitation kinetics is reviewed.
- b) “Precipitation from solid solution” by J.C. Fisher, J.H. Hollomon and J.G. Leschen in ACS Publications, “Industrial and Engineering Chemistry, Vol. 44,6, 1323-1327 (1952). According to the authors, elastic strain can be present in particles that precipitate from solid solution and in the surrounding parent phase as well. When the nucleation theory is modified to include the effects of elastic distortion, most of

the characteristics of precipitation from solid solution can be accounted for. The article is concerned primarily with the nucleation of precipitates, and only secondarily with their growth. The possibility of coherent nucleation is perhaps the most striking feature of solid-solution precipitation, and is discussed in some detail. Precipitation in solids differs from that in liquids and vapors largely by the possibility of coherency relationships between the parent and precipitating phases. The free energy per unit area of coherent interfaces is very small, and coherent precipitates form whenever the free-energy change of the transformation is sufficient to provide the elastic coherency strain. Many observations of the types of precipitates that form in various temperature ranges and of the mechanical property changes that accompany precipitation can be understood in terms of coherent and non-coherent precipitation."

- c) "The kinetics of precipitation from supersaturated solid solutions", by I. M. Lifshitz and V.V. Slyozov, *J.Phys. Chem. Solids*, Vol. 19, Nos ½, Pergamon Press (1961).

"An analysis is made of the process whereby diffusion effects can cause the precipitation of grains of a second phase in a supersaturated solid solution. The kinetics of this type of grain growth are examined in detail. Some grains grow, only to be later dissolved; others increase in size and incorporate further grains that they encounter in so doing. This latter phenomenon of coalescence is discussed in a new "kinetic" approximation. Formulate are given for the asymptotic grain size distribution, for the number of grains per unit volume and for the supersaturation as a function of time. The effects of anisotropy, strain, crystalline order and the finite size of the specimen are allowed for. It is pointed out that for a material that can be said to be "supersaturated with vacancies", the discussion can be applied to the vacancies as solute "atoms" which cluster together to form internal cavities. The practical case of a real, finite crystal is here important, because the vacancies can in general also escape to the surface. A special analysis is made of this example, and the results are applied to the theory of sintering". The article is rather difficult to understand due to a very large number of mathematical equations [45-47].

- d) "Structures by Precipitation from Solid Solutions" by Mario Epler, *ASM Handbook*, Vol. 9, Metallurgy & Microstructures, Editor G.F. Vander Voort (2004). (6 pages).

"PRECIPITATION REACTIONS are of great importance in engineering alloys. This general phenomenon occurs in many different alloy systems when one phase (for example γ in steel) transforms into a mixed-phase system (such as $\gamma + \alpha$ in steel) as a result of cooling from high temperatures. The solid-state reaction results in a phase mixture of matrix phase and precipitates that nucleate and coarsen. The matrix may share a similar crystal structure to the parent phase, but has a different composition and often a dissimilar lattice parameter, while the precipitated phase may differ in crystal structure, composition, lattice parameter, and degree of long-range order. The resultant properties of the alloy after precipitation are a direct result of the type, size, shape, and distribution of the precipitated phase".

- e) "Precipitation from Supersaturated Solid Solution", (In *Phase Transformations*) by J.W. Christian, from "Physical Metallurgy", Ed. By R.W. Cahn, North-Holland Publishing Company (1970) [48].

Precipitation from Supersaturated Solid Solution

"The precipitation reaction supersaturated $\alpha \rightarrow \alpha + \beta$ is usually produced by quenching the specimen from a high temperature where its equilibrium structure is a single solid solution to a low temperature where the solid solution is only metastable. The course of the reaction may then be followed by measurements of any suitable physical property, although direct measurements of volume transformed using metallographic or X-ray methods are to be preferred to indirect measurements, such as electrical resistivity. The improvement in mechanical properties which occurs when the alloy is held at a relatively low temperature (age-hardening) usually precedes any visible microstructural changes, and when precipitation is evident with an optical microscope, the alloy is often found to have softened again.

The results of all investigations show that it is convenient to distinguish three modes of precipitation – continuous, discontinuous and low temperature processor". "Precipitation Hardening", in *Physical Metallurgy Principles* by Robert E. Reed-Hill, Van Nostrand, USA (1968) [48]

"*Nucleation of Precipitates*. How nuclei form and start to grow during precipitation is a subject of great interest. It is, however, very complicated and difficult to resolve in specific

commercially important alloys. In many cases, it is believed that the precipitate phase does not originate in its final structure, but form in intermediate crystal structures which later transform into the final structure. The nature of these processes is difficult to determine because of the extremely small size of the precipitate particles at the time of their nucleation, or even when they have grown to the point where the alloy is at the point of maximum hardness. Usually the particles only become visible under a microscope when the metal is well advanced into the overaging stage. The nature of precipitate particles in a given alloy system can only be deduced from indirect evidence obtained from X-ray-diffraction studies or from considerations based on changes in the physical properties of the alloys that occur during the progress of precipitation. One of these properties, hardness, which is our primary concern, has already been discussed. Another is the electrical resistance of metals. The orderly motion of electrons through a crystal, which constitutes an electrical current, is made more difficult when the crystal has a second component in solid solution. In other words, the resistance of a metallic solid solution increases with the concentration of solute. In general, the electrical resistance of the solid solution will decrease as the concentration of the solute decreases. The progress of precipitation can be followed with the aid of resistivity measurements”.

The book contains useful information on precipitation hardening and related topics. “Precipitates from solid solutions”, DOITOMS University of Cambridge, Teaching and Learning Packages (1017).

Precipitates from Solid Solution

“The precipitation of a solid phase from a liquid matrix is governed by a balance between the thermodynamic driving force and the energy penalty for creating new solid-liquid surface interfaces. This determines the size and shape of the precipitates. The precipitation of a solid phase from a solid parent phase is very similar.

There are various types of interface between solid phases:

- a) *Coherent* – there is perfect registry of the lattices.
- b) *Coherent with strain* – it is quite likely for there to be some strain with the interface, due to imperfect matching. The strain energy increases with the size of the growing particle, and there is a transition to a semi-coherent interface.

- c) *Semi-coherent interface* – the introduction of dislocations reduces the strain energy (but they themselves contribute to the energy of the system).
- d) *Incoherent* – there is no matching of the interface.

In general, the interfacial free energy will be minimized with better matching of the two phases. Incoherent interfaces have high energy and are relatively mobile because of the greater freedom of atomic motion.

The stresses present in the parent matrix as the precipitate grows strongly influence the shape of the precipitate”. ‘Precipitation Hardening in “Alloy Series, Harper Brothers, Publishers, New York, USA (1956) [49-50].

Precipitation Hardening

Departures from equilibrium are often extreme in the case of phase changes that occur in solid alloys, since activation energies for solid-state reactions are typically high, and the diffusion and atomic rearrangement involved in them are relatively slow. Precipitation of a secondary phase from a primary solid solution is a common example of such a phase change, and one of great industrial importance because it is usually accompanied by significant changes in the properties of the alloy in which it occurs. If uncontrolled, these changes may be an expensive nuisance or a serious service hazard; if controlled they may often be used to produce in the alloy an advantageous combination of properties that would not otherwise be attainable.

The important series of duralumin-type aluminum alloys afford an excellent example of the effects of controlled departure from equilibrium with regard to precipitation of a secondary phase, and of the application of these controlled departures to a useful adjustment of alloy properties.

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