Phase Diagrams—Understanding the Basics F.C. Campbell, editor

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CHAPTER **16**

Nonequilibrium Reactions—Precipitation Hardening

SOLID-STATE PRECIPITATION REACTIONS are of great importance in engineering alloys. Phase diagram configurations that give rise to precipitation reactions are shown in Fig. 16.1. The reaction occurs when the initial phase composition (e.g., α_0 , β_0 , or I_0) transforms into a two-phase product that includes a new phase, or precipitate. The precipitate phase may differ in crystal structure, composition, and/or degree of long-range order from that of the initial single-phase (parent) phase and the resultant product matrix. The matrix retains the same crystal structure as the initial one-phase parent but with a different equilibrium composition (α , β , or I) and usually a different lattice parameter than the parent phase. This general type of phase change is different from reactions at the invariant points of phase transformation (e.g., a eutectic or peritectic), where any change in temperature or composition results in complete transformation of the parent into a matrix with a different crystal structure.

16.1 Precipitation Hardening

Precipitation hardening is used extensively to strengthen aluminum alloys, magnesium alloys, nickel-base superalloys, beryllium-copper alloys, and precipitation-hardening (PH) stainless steels. Precipitation hardening is a three-step process in which the alloy is:

- 1. Heated to a high enough temperature to take a significant amount of an alloying element into solid solution.
- 2. Rapidly cooled (quenched) to room temperature, trapping the alloying elements in solution.

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Fig. 16.1 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 I). Source: Ref 16.1 as published in Ref 16.2

3. Reheated to an intermediate temperature so that the host metal rejects the alloying element in the form of fine precipitates that create matrix strains in the lattice. These fine precipitate particles act as barriers to the motion of dislocations and provide resistance to slip, thereby increasing the strength and hardness.

There are two requirements for precipitation hardening: (1) the process must result in an extremely fine precipitate dispersed in the matrix, and (2) there must be a degree of lattice matching between the precipitate particles and the matrix (i.e., the precipitate must be coherent).

Particle hardening is a form of particle, or dispersion, hardening where extremely small particles are dispersed throughout the matrix. When a dislocation encounters a fine particle, it must either cut through the particle or bow (loop) around it, as shown schematically in Fig. 16.2.

Particles are usually classified as deformable or nondeformable, meaning that the dislocation is able to cut through it (deformable) or the particle is so strong that the dislocation cannot cut through (nondeformable). For effective particle strengthening (Fig. 16.3), the matrix should be soft and ductile, while the particles should be hard and discontinuous. A ductile matrix is better in resisting catastrophic crack propagation. Smaller and more numerous particles are more effective at interfering with dislocation motion than larger and more widely spaced particles. Preferably, the particles should



Fig. 16.2 Particle strengthening. Source: Ref 16.3



Fig. 16.3 Particle hardening considerations. Source: Ref 16.4 as published in Ref 16.3

be spherical rather than needlelike to prevent stress-concentration effects. Finally, larger amounts of particles increase strengthening.

16.2 Theory of Precipitation Hardening

Precipitation hardening is also known as age hardening or aging, to indicate that the resulting strength increase develops with time. It should be noted that sometimes the term *age hardening* is used to denote alloys that harden on aging at room temperature, while the term *precipitation hardening* is used to denote alloys that must be heated above room temperature for hardening to occur at an appreciable rate. However, in both cases, the hardening mechanism is the precipitation of extremely fine particles, which impedes dislocation movement. A portion of a phase diagram for an aluminum alloy system that has the characteristics required for precipitation hardening is shown in Fig. 16.4. Note that the solvent metal at the left-hand edge of the diagram can absorb much more of the solute metal at elevated temperature than it can at room temperature. When the alloy is heated to the solution heat treating temperature and held for a sufficient length of time, the solvent metal absorbs some of solute metal. Then, when it is rapidly cooled to room temperature, atoms of the solute



Fig. 16.4 Typical precipitation-hardening heat treatment for an aluminum alloy. Source: Ref 16.5 as published in Ref 16.3

metal are trapped as a supersaturated solid solution in the solvent metal. On reheating to an intermediate aging temperature, the supersaturated solution precipitates very fine particles that act as barriers to dislocation movement. Note the effects of different aging temperatures shown in Fig. 16.4. If the metal is aged at too low a temperature (T_1) , the precipitation process will be incomplete and the desired strength will not be achieved, a condition known as underaging. On the other hand, aging at too high a temperature (T_4) also results in lower-than-desired strength because the precipitate particles coarsen, and the alloy is now said to be overaged. Commercial heat treatments are closer to T_2 and T_3 , in which the optimal strength can be obtained in a reasonable aging time. The alloy used in this example is one that requires artificial or elevated-temperature aging. Some alloys will age satisfactorily at room temperature, a process called natural aging.

Alloys that harden by precipitation hardening do so by forming coherent precipitates within the matrix. The first step in the aging process is the congregation of solute atoms in the matrix lattice. These solute-rich regions are called clusters and are the embryos for nucleation. Solute atoms then diffuse to the clusters from the surrounding matrix and convert some of them to nuclei of a new phase. During the early phases of precipitation, the equilibrium phase does not immediately form, but an intermediate crystal structure related to it grows in close contact with the solid solution. As long as there tends to be atomic matching, or coherency, between the transition phase and the matrix, the transition phase will create a local strain field within the matrix. The initial precipitate particles are often not spherical but can be platelike or rodlike in shape. The combination of a fine precipitate size and the localized strain fields is an effective barrier to dislocation movement.

For effective precipitation hardening, either a coherent or semicoherent interface must be present. The lattice distortion produced by a coherent precipitate, which impedes dislocation motion, is illustrated in Fig. 16.5. Once the alloy is overaged, an incoherent interface develops that is accompanied by softening of the alloy. The peak strength is usually attained when the alloy is aged to the point where both particle cutting and particle bowing (looping) of dislocations contribute to the alloy strength (Fig. 16.6). The eventual formation of the equilibrium phase is always energetically favorable. If the aluminum alloy is aged at room temperature, equilibrium may never be achieved. However, when the alloy is aged at elevated temperature, either longer aging times or higher temperatures will result in the formation of the final equilibrium precipitate. Because the equilibrium precipitate is larger and more widely spaced, it no longer imposes a strain field on the matrix and is not nearly as effective in blocking dislocation motion, and the strength properties decrease. The equilibrium phase usually nucleates separately from a transition phase(s) and competes with the less stable transition phase for solute atoms, eventually causing the transition phase to redissolve as its particles get smaller. As the volume fraction of equilibrium phase grows, the sizes of the precipitate particles increase, their numbers decrease, and the distance between particles increases, all allowing easier passage of dislocations. It is important to remember that precipitation-hardened alloys are metastable; equilibrium is always lurking around the corner. All precipitation-hardened alloys will eventually soften if heated to high enough temperatures or if they are exposed to somewhat lower temperatures for long periods of time. This being said, some are extremely stable at elevated temperatures, such as the ordered Ni₃(Al,Ti) precipitate in precipitation-hardened nickel-base superalloys that are used in the hottest portions of jet engines.



Fig. 16.5 Coherent and incoherent precipitates. Source: Ref 16.3



Fig. 16.6 Relative contributions of particle cutting and dislocation bowing. Source: Ref 16.3

Coarsening of the particles occurs because the microstructure of a twophase alloy is not stable unless the interfacial energy is at a minimum. A lower density of larger particles has less total interfacial energy than a higher density of small particles, which provides the driving force for particle coarsening that occurs by diffusion of solute atoms. Thus, the rate of coarsening increases with temperature. Ostwald ripening is the mechanism by which smaller precipitates dissolve, and the solute is redistributed to larger, stable precipitates. Smaller particles have a higher free energy due to increased pressure as a result of their high surface curvature. Reversion occurs when an alloy containing a coherent precipitate, or an intermediate semicoherent precipitate, is heated above its solvus temperature, allowing the particles to redissolve into the matrix.

Precipitate formation is not always uniform. Remember that grain boundaries are high-energy sites, and precipitates often form along the grain boundaries. Some alloys will form discontinuous precipitates at the grain boundaries, in which lamellae of the second phase are interspersed with the solute-depleted matrix. Small additions of nickel or cobalt are used in beryllium-copper alloys to minimize this effect, because it adversely affects mechanical properties.

A number of alloy systems that can be precipitation hardened are given in Table 16.1. Aluminum alloys are one of the most important series of alloys that can be precipitation hardened, including the 2xxx (aluminumcopper), 6xxx (aluminum-magnesium-silicon), 7xxx (aluminum-zinc), and some of the 8xxx (aluminum-lithium) alloys. Some of the copper alloys, in particular beryllium-copper, can be precipitation hardened. The ironand nickel-base superalloys are another particularly important class of precipitation-hardening alloys. In the nickel-base superalloys, the precipitate Ni₃(Al,Ti) has very little lattice misfit with the nickel matrix (< 2%), which produces very low strain energies (~10 to 30 mJ/m²) and provides resistance to overaging for prolonged periods at high temperatures.

Matrix	Solute Cu		Transition structures(a)	Equilibrium precipitate	
Al		(i)	Platelike solute-rich GP [1] zones	θ-CuAl ₂	
		(ii)	Ordered GP [2] zones		
		(iii)	θ" phase		
		(iv)	θ' phase		
Al	Mg, Si	(i)	GP zones rich in Mg and Si atoms	β"-Mg ₂ Si	
		(ii)	Ordered zones of β''		
Al	Mg, Cu	(i)	GP zones rich in Mg and Cu atoms	S-CuAl ₂ Mg	
		(ii)	S' platelets		
Al	Mg, Zn	(i)	Spherical zones rich in Mg and Zn	η -MgZn ₂	
		(ii)	Platelets of η' phase		
Cu	Be	(i)	Be-rich regions	γ-CuBe	
		(ii)	γ' spherical GP zones		
Cu	Co	(i)	Spherical GP zones	β-Co	
Ni	Al, Ti	(i)	γ' cubes	γ-Ni ₃ (AlTi)	
Fe	С	(i)	α' martensite	Fe ₃ C	
		(ii)	α" martensite		
		(iii)	ε carbide		
Fe	Ν	(i)	α' nitrogen martensite	Fe ₄ N	
		(ii)	α'' nitrogen martensite		
(a) GP, Gui	nier-Preston. So	urce: Ref 1	6.6 as published in Ref 16.3		

Table 16.1 Some common precipitation-hardening systems

Nucleation and Growth. Nucleation, growth, and coarsening are important in determining the resultant microstructure of the precipitates and associated mechanical properties. During nucleation, not only is the type of precipitate that forms important, but also the distribution of the precipitates. Distribution of precipitates influences mechanical strength by affecting dislocation motion.

Nucleation can occur either homogenously (uniformly and nonpreferentially) or heterogeneously (preferentially) at specific sites such as grain boundaries or dislocations. Most precipitates involve or require the presence of preferential sites for heterogeneous nucleation, but Guinier-Preston (GP) zones and other fully coherent precipitates (such as Ni₃Al in nickelbase superalloys) nucleate homogeneously. Coherent precipitation occurs when continuity is maintained between the crystal lattice of the precipitate and the lattice of the matrix.

Typical heterogeneous nucleation sites include crystal defects such as grain boundaries, grain corners, vacancies, or dislocations. Heterogeneous nucleation occurs because the elimination of defects and high-energy surfaces (by the nucleation of a new phase) acts to reduce the overall free energy of the system. The rate of heterogeneous nucleation is thus influenced by the density of these irregularities. The free-energy relationships associated with homogenous and heterogeneous nucleation can be described as:

$$\Delta G_{\rm hom} = -V(\Delta G_{\rm v} - \Delta G_{\rm s}) + A\gamma$$
$$\Delta G_{\rm het} = -V(\Delta G_{\rm v} - \Delta G_{\rm s}) + A\gamma - \Delta G_{\rm d}$$

where:

 $\Delta G_{\rm hom}$ is the total free-energy change for homogeneous nucleation $\Delta G_{\rm het}$ is the total free-energy change for heterogeneous nucleation V is the volume of transformed phase $\Delta G_{\rm v}$ is the volume free energy of transformed phase $\Delta G_{\rm s}$ is the volume misfit strain energy of transformed phase $A\gamma$ is the surface area and surface energy term of transformed phase, assuming isotropic $\Delta G_{\rm d}$ is the free energy resulting from destruction of defect

Typical values for surface energy are summarized in Table 16.2, and various interfaces are shown in Fig. 16.7. Faceted interfaces are often coherent, while nonfaceted interfaces are semicoherent or incoherent. As

Table 1	16.2	Surface ener	gies for	different	types	of interfaces
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Fig. 16.7 Different types of interfaces. (a) and (b) Fully coherent. (c) and (d) Semicoherent showing lattice strain and the presence of dislocations. (e) and (f) Incoherent. Source: Ref 16.1 as published in Ref 16.2

long as there is a sufficient density of heterogeneous nucleation sites, homogeneous nucleation will not be favored.

A coherent interface (Fig. 16.7a, b) is characterized by atomic matching at the boundary and a continuity of lattice planes, although a small mismatch between the crystal lattices can lead to coherency strains (Fig. 16.7c). Coherent interfaces have a relatively low interfacial energy that typically ranges from 50 to 200 ergs/cm² (0.05 to 0.2 J/m²).

An incoherent interface (Fig. 16.7e, f) is an interphase boundary that results when the matrix and precipitate have very different crystal structures and little or no atomic matching can occur across the interface. The boundary is essentially a high-angle grain boundary characterized by a relatively high interfacial surface energy (~500 to 1000 ergs/cm², or 0.5 to 1.0 J/m²).

Semicoherent interfaces (Fig. 16.7d) represent an intermediate case in which it becomes energetically favorable to partially relax the coherency strains, which would develop if perfect matching occurred across the boundary by introducing an array of misfit dislocations. These interfaces, which are characterized by regions of good fit punctuated by dislocations that accommodate some of the disregistry, have interfacial surface energies from 200 to 500 ergs/cm² (0.2 to 0.5 J/m²).

Dislocations act as nucleation sites only for semicoherent precipitates. Precipitates forming at dislocations is shown in Fig. 16.8. The formation of semicoherent precipitates usually results in the generation of dislocations as a result of the lattice mismatch. The generation of a dislocation maintains coherency by relaxing the strains that develop because of the difference in the lattice parameter at the interface. Vacancies play several roles in the nucleation of precipitates. Vacancies allow for appreciable diffusion at temperatures where diffusion is not expected. They also act to relieve local strains, allowing for the nucleation of coherent precipitates. Vacancy concentration is dependent on temperature, so it is essential for high quenching rates to not only maintain a supersaturated solid solution but to retain a significant number of vacancies.



Coarsening of the particles occurs because the microstructure of a twophase alloy is not stable unless the interfacial energy is at a minimum. A lower density of larger particles has less total interfacial energy than a high density of small particles, which provides the driving force for particle coarsening. Particle coarsening is driven by diffusion of solute atoms; thus, the rate of coarsening increases with temperature. In some cases, coarsening rates are determined by interface control.

Ostwald ripening is the mechanism where the smaller precipitates dissolve and the solute is redistributed to the larger stable precipitates. The higher solubility of the smaller particles in the matrix is termed the capillary effect and can be seen on a free-energy diagram (Fig. 16.9a). Smaller particles have a higher free energy due to increased pressure because of high surface curvature. The point of common tangent (Fig. 16.9a) therefore occurs at a higher solute concentration.

Growth of precipitates occurs by either movement of the incoherent interfaces or a ledge mechanism where coherency is maintained while thickening due to diffusion. Reversion occurs when an alloy containing GP zones or intermediate semicoherent phase is heated above their respective solvus temperatures and they redissolve into the matrix.

Precipitation Sequences. In many precipitation systems and in virtually all effective commercial age-hardening alloys, the supersaturated matrix transforms along a multistage reaction path, producing one or more metastable transition precipitates before the appearance of the equilibrium



Fig. 16.9 (a) Gibbs free-energy composition diagram and (b) locus of solvus curves of metastable and stable equilibrium phases in a precipitation sequence. (a) The points of common tangency show the relationship between compositions of the matrix phase (C'', C', and C_{eq}) and the various forms of precipitate phases at a given temperature. From this common tangent construction, it can be see that for the small Guinier-Preston (GP) zones, there is a higher solubility in the matrix. (b) Hypothetical phase diagram showing the locus of metastable and stable solvus curves. Source: Ref 16.1 as published in Ref 16.2

phase. The approach to equilibrium is controlled by the activation (nucleation) barriers separating the initial state from the states of lower free energy. The transition precipitates are often crystallographically similar to the matrix, allowing the formation of a low-energy coherent interface during the nucleation process.

Often, the precipitation sequence begins with the nucleation of small, fully coherent phases known as Guinier and Preston zones (discovered independently by Guinier and Preston from x-ray diffraction studies). Guinier-Preston zones are solute-rich clusters resulting from phase separation or precipitation within a metastable miscibility gap in the alloy system. They may form by homogeneous nucleation and grow at small undercoolings or by spinodal decomposition at large undercoolings or supersaturations.

The GP zones are the first to nucleate because of their small size and coherency with the matrix. The interfacial energy term is extremely low, providing a low barrier to nucleation, although the driving force for nucleation may not be as high as for the final phase to form. The GP zones typically take the shape of small spherical particles or disk-shaped particles (Fig. 16.10) that are approximately two atomic layers thick and several nanometers in diameter, aligned perpendicular to the elastically soft direction in the matrix material crystal structure. The GP precipitates generally grow into more stable transition phases and eventually an equilibrium phase.

The phases that nucleate and grow from the GP zones are termed transition phases. They have an intermediate crystal structure between the matrix and equilibrium phase. This minimizes the strain contribution to energy between the precipitate and the matrix, making it more favorable



0.1 μm

Fig. 16.10 Coherent transition precipitates revealed by strain contrast (dark field) in transmission electron microscopy. The specimen is a Cu-3.1Co alloy aged 24 h at 650 °C (1200 °F). The precipitate is a metastable face-centered cubic (fcc) phase of virtually pure cobalt in the fcc matrix. The particles are essentially spherical, and the "lobe" contrast is characteristic of an embedded "misfitting sphere." This strain contrast reveals the particles indirectly through their coherency strain fields. Original magnification: 70,000×. Source: Ref 16.2

in the nucleation sequence than the equilibrium phases, which is incompatible with the matrix and has high interfacial energy. A typical reaction sequence for aluminum-copper systems is shown in Fig. 16.11 and can be written as:

 $\alpha_0 \rightarrow \alpha_1 + \text{GPZ} \rightarrow \alpha_2 + \theta'' \rightarrow \alpha_3 + \theta' \rightarrow \alpha_{eq} + \theta$

where θ' and θ'' are transition precipitates and θ is the equilibrium precipitate. Composition of each phase and the matrix can be determined by the common tangent method applied to Fig. 16.12(a). As each new precipitate forms, the matrix, α , becomes more and more depleted in copper. The GP zones and θ'' precipitates are resolved in transmission electron microscopy (TEM) because of the lattice coherency strains. Each step results in the previously precipitated phase being replaced with the new, more stable phase. Figure 16.12(b) outlines the step reductions in total free energy for reactions in the precipitation sequence. The size of the step reduction is the activation energy for a transformation.



Fig. 16.11 Transmission electron micrographs of precipitation sequence in aluminum-copper alloys. (a) Guinier-Preston zones at 720,000×. (b) θ'' at 63,000×. (c) θ' at 18,000×. (d) θ at 8000×. Source: Ref 16.8 as published in Ref 16.2

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Fig. 16.12 Free-energy plots of precipitation sequence in aluminum-copper alloys. (a) Free-energy curve with common tangent points for phase compositions in the matrix. (b) Step reductions in the free energy as the transformation proceeds. C_{eq} and C_3 , copper content of α_{eq} and α_3 phases; ΔG_1 , activation energy for $\alpha_0 \rightarrow \alpha_1 + GP$; GP, Guinier-Preston. Source: Ref 16.9 as published in Ref 16.2

16.3 Precipitation Hardening of Aluminum Alloys

The process of strengthening by precipitation hardening plays a critical role in high-strength aluminum alloys. Precipitation hardening consists of three steps: (1) solution heat treating, (2) rapid quenching, and then (3) aging at room or elevated temperature.

In solution heat treating, the alloy is heated to a temperature that is high enough to put the soluble alloying elements in solution. After holding at the solution treating temperature for long enough for diffusion of solute atoms into the solvent matrix to occur, it is quenched to a lower temperature (e.g., room temperature) to keep the alloying elements trapped in solution. During aging, the alloying elements trapped in solution precipitate to form a uniform distribution of very fine particles. Some aluminum alloys will harden after a few days at room temperature, a process called natural aging, while others are artificially aged by heating to an intermediate temperature.

Consider the aluminum-copper system shown in Fig. 16.13. The equilibrium solid solubility of copper in aluminum increases from approximately 0.20% at 250 °C (480 °F) to a maximum of 5.65% at the eutectic melting temperature of 550 °C (1018 °F). It is even lower than 0.20% at temperatures below 250 °C (480 °F). For aluminum-copper alloys containing from 0.2 to 5.6% Cu, two equilibrium solid states are possible. At temperatures above the solvus curve, copper is completely soluble, and when the alloy is held at such temperatures for sufficient time to permit diffusion, copper will be taken completely into the α solid solution. At temperatures below the solvus, the equilibrium state consists of two solid phases—solid solution α plus the equilibrium intermetallic compound θ (CuAl₂).



Fig. 16.13 Precipitation hardening of an aluminum-copper alloy. Source: Ref 16.3

If an alloy of aluminum containing 4% Cu is heated to 500 °C (940 °F) and held for 1 h, the copper will go into solution in the aluminum. After solution heat treating, the alloy is quenched in cold water to room temperature to keep the copper in solution. The alloy is then artificially aged at 170 °C (340 °F) for 10 h. During the aging process, very fine particles of aluminum-copper are precipitated and the strength and hardness increase dramatically. Precipitation heat treatments generally are low-temperature, long-term processes. Aging temperatures for aluminum range from 115 to 190 °C (240 to 375 °F) with times between 5 and 48 h.

On quenching, the copper is trapped as a supersaturated solution in the a matrix. There is a strong driving force to precipitate the copper as the equilibrium precipitate θ (CuAl₂). However, in aluminum alloys, precipitation occurs by one or more metastable transition precipitates appearing before the appearance of the final equilibrium phase, with each successive stage lowering the free energy of the system. The transition precipitates are often crystallographically similar to the matrix, allowing the formation of a low-energy coherent interface during the nucleation process. Often, the precipitation sequence begins with the nucleation of small, fully coherent GP zones.

The GP zones are the first to nucleate because of their small size and coherency with the matrix. The interfacial energy term is extremely low, providing a low barrier to nucleation. The GP zones are extremely fine, with sizes in the range of tens of angstroms. The exact shape, size, and distribution of the GP zones depends on the specific alloy and on the thermal and mechanical history of the product. The GP zones typically take the shape of small spherical particles or disk-shaped particles that are approximately two atomic layers thick and 10 nm in diameter, with spacings on the order of 10 nm. Their formation requires movements of atoms over very short distances and their densities can approach 1017 to 1018 cm⁻³. As previously discussed, the GP precipitates then grow into more stable transition phases and eventually the equilibrium phase.

The transition phases that form in aluminum-copper alloys are shown in Fig. 16.14. The transition phases have a crystal structure intermediate between the matrix and the equilibrium phase. This minimizes the strain energy between the precipitate and the matrix, making it more favorable in the nucleation sequence than the equilibrium phase, which is incompatible with the matrix and has a high interfacial energy. A typical reaction sequence for aluminum-copper systems is:

Supersaturated solid solution \rightarrow Clustering \rightarrow GP zones $\rightarrow \theta'' \rightarrow \theta' \rightarrow \theta$

where θ'' and θ' are transition precipitates and θ is the final equilibrium precipitate. While the GP zones are totally coherent with the matrix, the much larger transition precipitates are only semicoherent. As each new precipitate forms, the matrix, α , becomes more and more depleted in copper. The GP zones and θ'' precipitates, also known as GP II zones, can be resolved by a transmission electron microscope because of the lattice coherency strains, as shown in Fig. 16.11. The zones themselves are too small to be resolved but the resulting strain fields can be resolved. Each step results in the previously precipitated phase being replaced with a new more stable phase with a lower free energy.

During heating, the GP zones develop an intermediate precipitate, θ'' , which has a tetragonal structure that forms as plates and maintains coherency with the matrix and further increases the strain in the matrix, providing peak strength levels. On still further heating, θ'' is replaced by a second intermediate precipitate, θ' , which is not coherent with the matrix, and the strength starts to decrease; the alloy is now termed overaged. However, in the highest strength condition, both θ'' and θ' are generally present. Both the precipitate particles themselves and the strains they produce in the lattice structure inhibit dislocation motion, and thus both contribute to strengthening. To maximize strengthening, aging is typically carried out at temperatures between those where precipitation of θ'' and θ' occurs, because this spacing and lattice strain are ideal for hindering dislocation motion. Further heating of the alloy causes θ' to transform to the equilibrium precipitate θ , which is stoichiometric CuAl₂.

The solvus lines for the GP zones and the transition phases can be shown as lines on the phase diagram (Fig. 16.15). This series of lines defines the upper temperature limit of the various transition phases for different con-

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Fig. 16.14 Aluminum-copper precipitation sequence. fcc, face-centered cubic; bct, body-centered tetragonal. Source: Ref 16.8 as published in Ref 16.3

centrations. For example, if aging is carried out above the θ'' solvus but below the θ' solvus, then the first precipitate to form will be θ' .

Guinier-Preston zones will normally develop on aging at room temperature. The fact that this will happen at room temperature is somewhat surprising and can be attributed to a high vacancy concentration. When the

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Fig. 16.15 Aluminum-copper binary diagram with GP₁, θ'' , and θ' solvus lines. Source: Ref 16.8 as published in Ref 16.3

alloy is heated to the solution heat treating temperature, the equilibrium number of vacancies increases as the temperature increases. On quenching, the vacancies become trapped in solution. These excess vacancies are then available to help accelerate the nucleation and growth process.

A series of aging curves for an Al-4% Cu alloy is shown in Fig. 16.16. Reactions carried out beyond maximum strengthening are overaged, because the beneficial effects of precipitation strengthening are lost as the precipitates grow larger in size and spacing. Both the underaged and overaged conditions have lower strengths and hardness levels than the peak aged condition.

In aluminum alloys, precipitate-free zones (PFZs) can occur adjacent to the grain boundaries (Fig. 16.17). The grain boundaries themselves and the interior of the grains contain precipitate particles, but there is a zone adjacent to the boundaries with very few particles. These differences in chemical composition can set up galvanic effects that lead to intergranular corrosion. There are two plausible explanations for PFZs. The first is due to vacancy migration. Grain boundaries are a major sink for vacancies that migrate to the grain boundaries and deplete the areas adjacent to the boundaries of vacancies. The lack of vacancies in these depleted areas inhibits the nucleation and growth of precipitate particles, even though the matrix in these areas contains sufficient solute. The second explanation is that precipitation occurs directly on the higher-energy grain boundaries and the adjacent areas become depleted of solute. There is direct experimental evidence for both of these mechanisms. Special heat treatments are used to minimize the formation of PFZs. Precipitate-free zones can be eliminated by a two-stage heat treatment where nucleation is induced homogeneously at a low temperature, and the precipitates are then allowed



Fig. 16.16 Aging curves for Al-4% Cu alloy. Source: Ref 16.3



Fig. 16.17 Precipitate-free zone (PFZ) in an Al-Zn-Mg alloy. Source: Ref 16.10 as published in Ref 16.3

to grow during the second, higher-temperature aging treatment. In addition, higher solution treating temperatures and faster quenching rates also reduce the PFZ widths. The beneficial effect of a faster quenching rate is shown in Fig. 16.18.

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Fig. 16.18 Precipitate-free zone (PFZ) width as function of quench rate. Source: Ref 16.8 as published in Ref 16.3

16.4 Precipitation Hardening of Nickel-Base Superalloys

Another class of important alloys strengthened by precipitation hardening is the nickel-base superalloys. Superalloys are heat-resistant alloys of nickel, iron-nickel, and cobalt that frequently operate at temperatures exceeding 540 °C (1000 °F). Superalloys are the primary materials used in the hot portions of jet turbine engines, such as the blades, vanes, and combustion chambers, constituting over 50% of the engine weight. In general, the nickel-base alloys are used for the highest temperature applications, followed by the cobalt-base alloys and then the iron-nickel alloys.

Nickel-base superalloys are strengthened by a combination of solidsolution hardening, precipitation hardening, and the presence of carbides at the grain boundaries. The face-centered cubic (fcc) nickel matrix, which is designated as austenite (γ), contains a large percentage of solid-solution elements such as iron, chromium, cobalt, molybdenum, tungsten, titanium, and aluminum. Aluminum and titanium, in addition to being potent solidsolution hardeners, are also precipitation strengtheners. At temperatures above 0.6 $T_{\rm m}$, which is in the temperature range for diffusion-controlled creep, the slowly diffusing elements molybdenum and tungsten are beneficial in reducing high-temperature creep.

The most important precipitate in nickel- and iron-nickel-base superalloys is γ' fcc-ordered Ni₃(Al,Ti) in the form of either Ni₃Al or Ni₃Ti. The γ' phase is precipitated by precipitation-hardening heat treatments solution heat treating followed by aging. The γ' precipitate is an A_3B type compound where A is composed of the relatively electronegative elements nickel, cobalt, and iron, and B is composed of the electropositive elements aluminum, titanium, or niobium. Typically, in the nickel-base alloys, γ' is of the form Ni₃(Al,Ti), but if cobalt is added, it can substitute for some nickel as $(Ni,Co)_3(A1,Ti)$. The precipitate γ' has only approximately a 0.1% mismatch with the γ matrix; therefore, γ' precipitates homogeneously with a low surface energy and has extraordinary long-term stability. The coherency between γ' and γ is maintained to high temperatures and has a very slow coarsening rate, so that the alloy overages extremely slowly, even as high as 0.7 $T_{\rm m}$, where $T_{\rm m}$ is the absolute melting temperature. Because the degree of order in Ni₃(Al,Ti) increases with temperature, alloys with a high volume of γ' actually exhibit an increase in strength as the temperature is increased up to approximately 700 °C (1300 °F). The γ/γ' mismatch determines the γ' precipitate morphology, with small mismatches (~ 0.05%) producing spherical precipitates and larger mismatches producing cubical precipitates, as shown in Fig. 16.19.

Wrought precipitation-strengthened nickel-base superalloys are solution heat treated and then aged to produce the desired properties. Solutiontreating temperatures range from approximately 980 to 1230 °C (1800 to



Fig. 16.19 Microstructure of precipitation-hardened nickel-base superalloy. Source: Ref 16.3

2250 °F), or even up to 1315 °C (2400 °F) for some single-crystal alloys. Long exposure times at solution-treatment temperatures can result in partial dissolution of primary carbides with subsequent grain growth. The solution treatment may be above or below the γ' solvus, depending on the desired microstructure and application. A higher temperature is used to develop coarser grain sizes for creep- and stress-rupture-critical applications, while a lower solution temperature will produce a finer grain size for enhanced tensile and fatigue properties. To retain the supersaturated solution obtained during solution treating, the part is rapidly cooled to room temperature using either gas cooling or water or oil quenching.

Aging treatments are used to strengthen precipitation-strengthened alloys by precipitating one or more phases (γ' or γ''). Aging treatments vary from as low as 620 °C (1150 °F) to as high as 1040 °C (1900 °F). Double-aging treatments are also used to produce different sizes and distributions of precipitates. A principal reason for double-aging treatments, in addition to γ' and γ'' control, is the need to precipitate or control grain-boundary carbide morphology. Aging heat treatments usually range from 870 to 980 °C (1600 to 1800 °F), with times of approximately 4 to 32 h. Either single or multiple aging treatments are then used to precipitate γ' . Like the solution temperature, the aging temperatures and times are selected depending on the intended application. Higher aging temperatures will produce coarse γ' precipitates desirable for creep and stress rupture applications, while lower aging temperatures produce finer γ' precipitates for applications requiring strength and fatigue resistance. In general, lower solution-treating temperatures produce better strength, while higher solution-treating temperatures provide better creep and stress rupture properties.

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