
5 Solid-State Phase Transformations

Solid-state phase transformations play an important role in the development of the structure and properties of metals and alloys. Polymorphic transformations and precipitation reactions are the main types of phase transformations that occur in solids. Well-known examples are the polymorphic transformations of iron, titanium, and cobalt; the hardening of materials by martensitic transformations; and the strengthening (dispersion hardening) by solid-state precipitation. The driving force behind all structural and phase transformations from their start to their completion at a given temperature and pressure is the decrease of the Gibbs free energy. The knowledge of phase transformation mechanisms provides the basis for the theory and practice of the heat treatment and the processing of metals.

According to the classification system based on the physical mechanisms of the reaction and the mode of interphase migration, solid-state phase transformations are divided into two main groups:

- *Diffusional transformations.* These transformations take place by thermally activated atom movement and require diffusion either through the lattice or across a *nonglissile interface*. These transformations are also termed *civilian* due to the uncoordinated atomic movements. The composition of the parent and the product phases may be the same or different. The majority of phase transformations (phase precipitation, eutectoid and massive transformations, ordering) are diffusion controlled.
- *Diffusionless transformations.* No diffusion is involved in these athermal transformations, which are also classified as *military* because of the coordinated movement of the atoms. The phase interface, which must be either coherent or semicoherent, is glissile, and the individual atoms move a distance shorter than one interatomic spacing without changing the neighborhood of the nearest atoms. The product phases preserve the chemical composition of the parent phase. A typical representative of this type of transformation is the martensitic transformation, which is achieved by a shear mechanism.

There are *intermediate transformations* that simultaneously possess the characteristics of both diffusional and nondiffusional reactions. The bainite transformation, which takes place by both a shear mechanism and long-range diffusion, is referred to as intermediate between the martensitic and the pearlitic transformations.

The diffusional processes of phase precipitation are classified as *continuous* or *general* and *discontinuous* or *cellular* depending on the mechanism of the nucleation and growth of the new phase. In a continuous precipitation, the entire matrix is continuously and uniformly depleted of solute elements, thus producing a single

precipitate phase with a random distribution. The discontinuous precipitation starts at grain boundaries or phase interfaces and produces a two-phased structure with a cell morphology.

5.1 CONTINUOUS PRECIPITATION IN AGE-HARDENING ALLOYS

The basic requirement for a precipitation-hardening alloy system is that the solid solubility limit should decrease with decreasing temperature. The precipitation occurs when the alloy, solution treated and quenched to obtain a supersaturated solid solution (SSSS), is allowed to “age” for a sufficient period of time at temperatures below its solvus temperature. The precipitation process is accompanied by changes in the properties of the material. Thus, aging (precipitation hardening) has been used for many years in the commercial heat treatment of numerous engineering alloys.

The precipitation sequence in most age-hardening alloys is complex and multi-stage and usually involves formation of clusters, zones, and several transition phases. Commonly the precipitation reaction is written as $\text{SSSS} \rightarrow \text{clusters} \rightarrow \text{GP-zones} \rightarrow \beta'' \rightarrow \beta' \rightarrow \beta$, where β'' and β' are transition phases and β is the equilibrium phase.

Small *clusters of solute atoms* form in the lattice in the earliest stages of the precipitation sequence. The clusters develop into *Guinier–Preston zones (GP-zones)*—solute-enriched areas with atomic arrangement fully identical with the crystal lattice of the matrix. The nucleation of clusters (zones) and growth of zones occur homogeneously throughout the supersaturated matrix. The presence of excess vacancies in the structure is decisive for the zones’ formation because vacancies provide fast diffusion for solute atoms in the matrix lattice.

Precipitation via *transition (intermediate, metastable) phases* provides a more rapid decrease of the SSSS free energy than by direct transformation to the equilibrium phase. When the SSSS decomposes via transition phases, the activation energy barrier corresponding to each subsequent stage of their precipitation is much smaller in comparison to the barrier associated with the direct precipitation of the equilibrium phase. These phases nucleate heterogeneously on preferred sites such as zones or crystal imperfections because of the lower nucleation energy in the regions of the disturbed atom arrangement. The ability of crystal imperfections to assist nucleation increases in the same order as the energy of the defects associated with the atomic disturbance in their vicinity: vacancy clusters, dislocations, SFs, subgrain boundaries, and grain boundaries.

Continuous precipitation can be microscopically *uniform* or *homogeneous*, when the precipitates are uniformly distributed in the entire volume of the grain. In contrast, *localized* or *heterogeneous*, precipitation occurs when precipitates nucleate heterogeneously on some preferred sites. The latter precipitates are coarse and obtain uneven distribution.

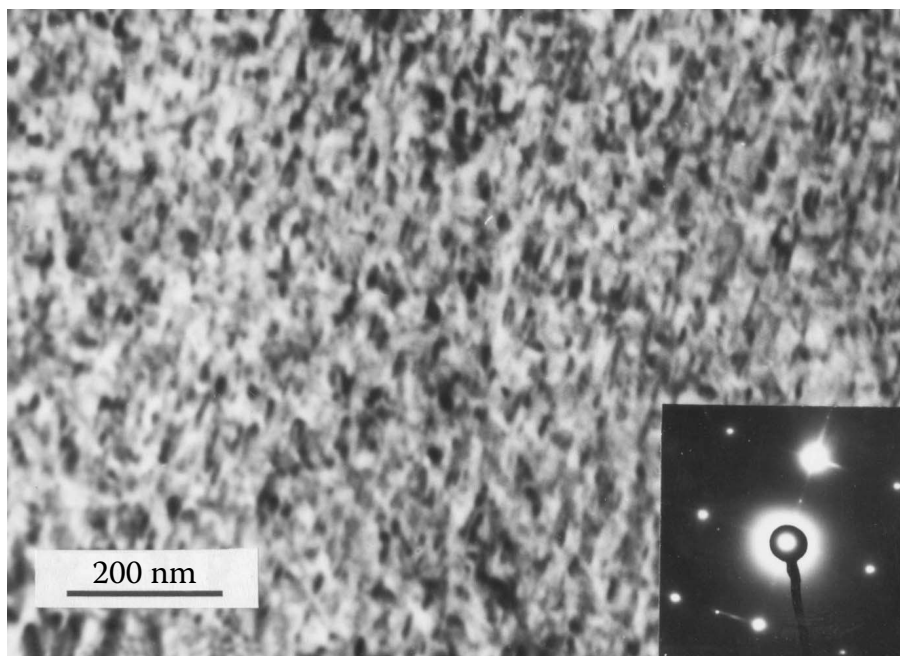


FIGURE 5.1 The number of transition phases in an alloy system depends on the ratio of the solid solution supersaturation to equilibrium phase content. Several intermediate precipitation stages are observed in the Al-Cu system. The first stage for an Al-4%Cu alloy is the homogeneous nucleation of copper-rich zones, which are termed *GP-I zones*. These zones typically are considered to be discs of copper atoms on the {100} planes of the aluminum matrix. Due to their small size, they cannot be directly observed in routine TEMs. The distortion of the crystal lattice around the zone caused by the atomic size difference between the copper and aluminum atoms is very small and thus can be accommodated solely by elastic strains. The only indication for the presence of the zones is the specific roughness of the foil surface, the coherency misfit strain contrast, and the streaking of diffraction spots in a direction normal to {100}_{Al} (see inset). Both the strain contrast and the streaking are derived from the elastic distortion of the crystal lattice in a direction perpendicular to the plane of the zones.

Al-4%Cu, aged to produce GP-I zones.

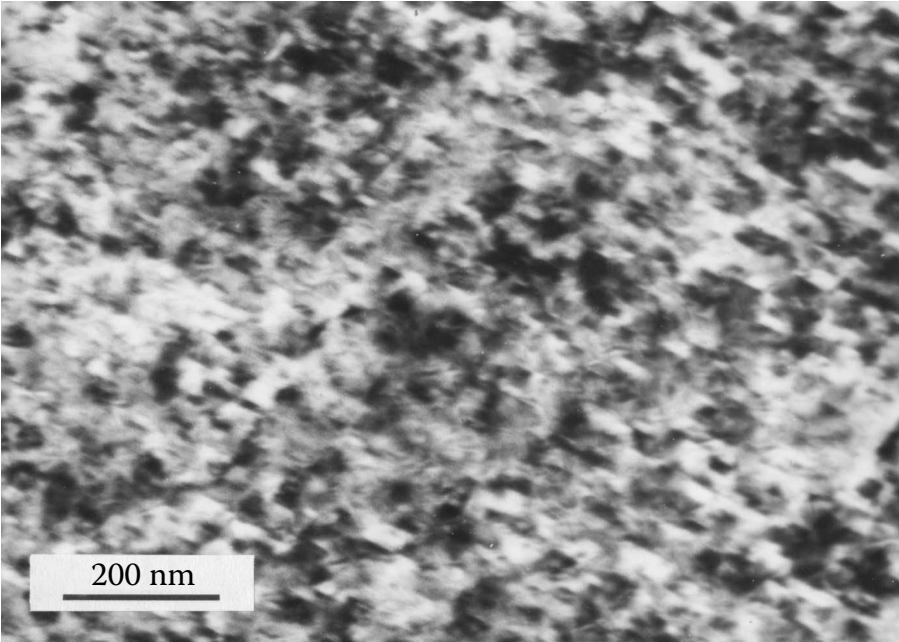


FIGURE 5.2

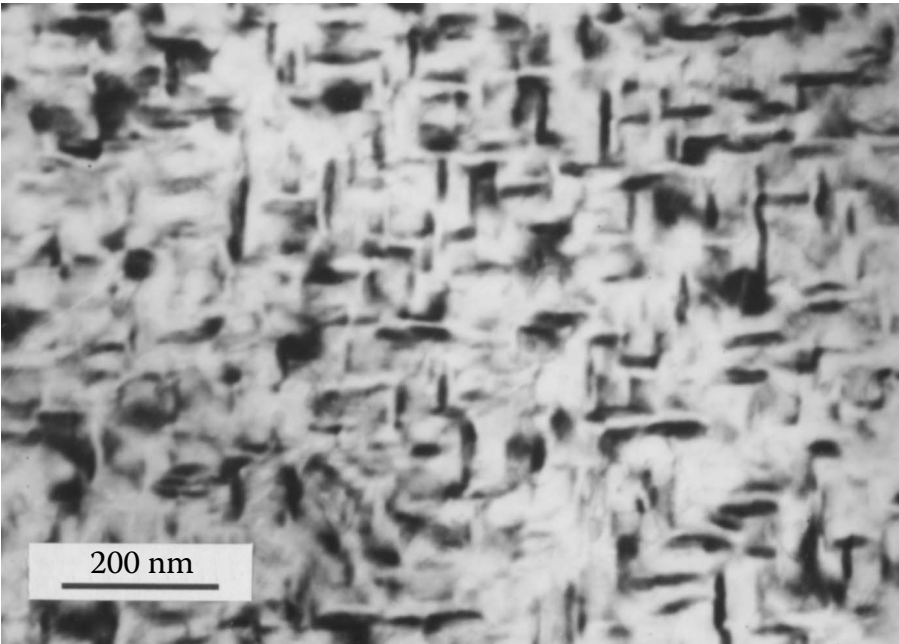


FIGURE 5.3

FIGURE 5.2 The GP-zone stage is characteristic of the precipitation sequence in many engineering aluminum-based alloys, copper-beryllium, and so on. The shape of zones depends on the difference between the atomic diameters of solid solution constituents and can be spherical (Al-Ag, Al-Zn, Al-Zn-Mg), rodlike (Al-Cu-Mg), needle-shaped (Al-Mg-Si), or disc-shaped (Al-Cu, Cu-Be). The size of the zones for each alloy depends on the aging time and temperature.

Al-4%Cu, aged to produce GP-1 zones. The disc-shaped zones lie on $\{111\}_{\text{Al}}$ planes.

FIGURE 5.3 The misfit between the atomic arrangement in the zone and the surrounding matrix increases with aging time due to the increasing content of solute atoms in the zone. The term *zone precipitation* is related mainly to the well-studied aluminum alloys. It applies to the aging process up to the stage when the misfit becomes too large to be compensated solely by elastic strains. In the Al-4%Cu alloy, the zone stage includes formation of *GP-2 zones*, also referred as the *metastable θ'' -phase*. When the diameter of zones reaches about 10 nm, the atomic arrangement of GP-1 transforms into GP-2, which is fully coherent with the fcc lattice of aluminum. θ'' precipitates are larger than the GP-1 zones, being up to ~10 nm thick and 100 nm in diameter.

Al-4%Cu alloy, aged to produce GP-2 zones (metastable θ'' -phase). The shadows around the coherent θ'' -phase are due to the coherency strain fields between the zone and the matrix.

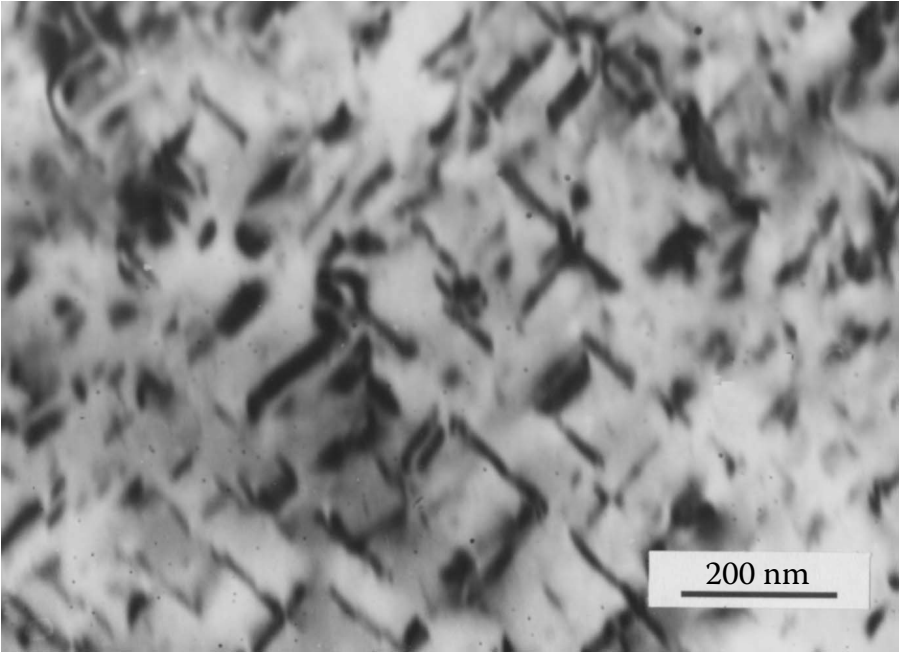


FIGURE 5.4

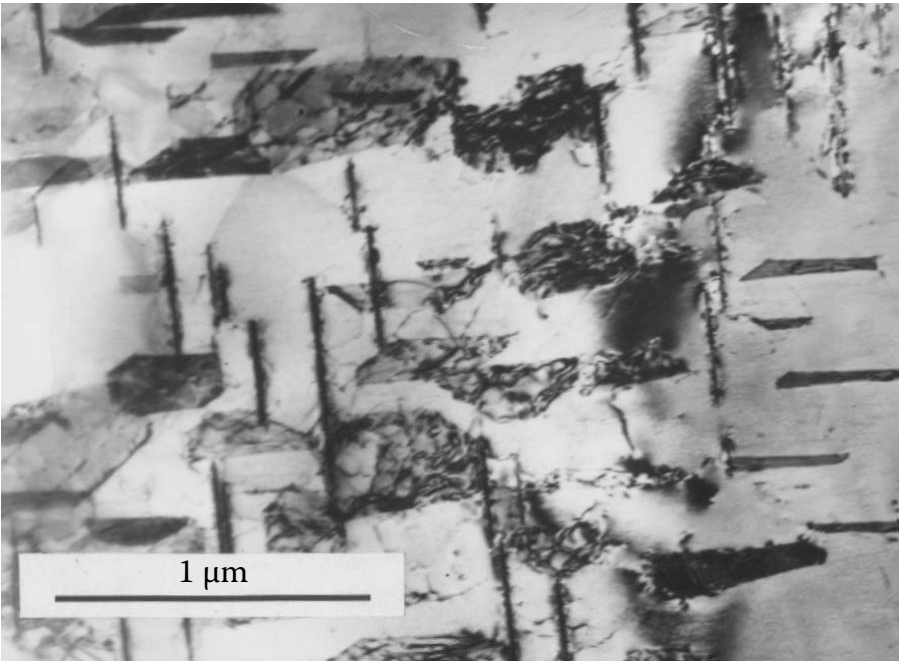


FIGURE 5.5

FIGURE 5.4 Upon aging, the fully coherent θ'' -precipitates (GP-2 zones) become larger and the atomic misfit in some of the crystallographic directions increases. When the size of the precipitates exceeds some critical dimension, the coherency strains and misfit at the matrix/precipitate interface become so large that they have to be compensated by the creation of new phase interfaces containing *misfit dislocations*. If the interfaces in the different crystallographic directions are of mixed type, coherent and noncoherent, the precipitate is defined as being *semicoherent*. The semicoherent θ' phase, with a tetragonal crystal structure, forms continuously from the GP-2 zones by an *in situ* transformation because the structures of these phases are similar.

Al-4%Cu alloy, aged to produce semicoherent θ'' -phase. The dark shadows around the semicoherent θ' -particles are weaker than the shadows around the coherent θ'' -phase (see Figure 5.3) because the latter has more strain associated with it. The interface misfit dislocations around the θ' -particles cannot be resolved.

FIGURE 5.5 Equilibrium phases can be differentiated from the matrix when the number of solute atoms in the enriched zones reaches the concentration of the phase equilibrium of the alloy system. The equilibrium phase in Al-4% Cu alloy is the intermetallic compound CuAl_2 —a noncoherent body-centered tetragonal θ -phase.

Al-4%Cu alloy, aged at high temperature to produce equilibrium θ -phase (CuAl_2) and semicoherent θ' -phase. Notice the absence of strain fields (dark shadows) around the plate-shaped equilibrium θ -particles and the presence of interfacial dislocations accommodating the misfit between the semicoherent θ' -phase and the matrix.

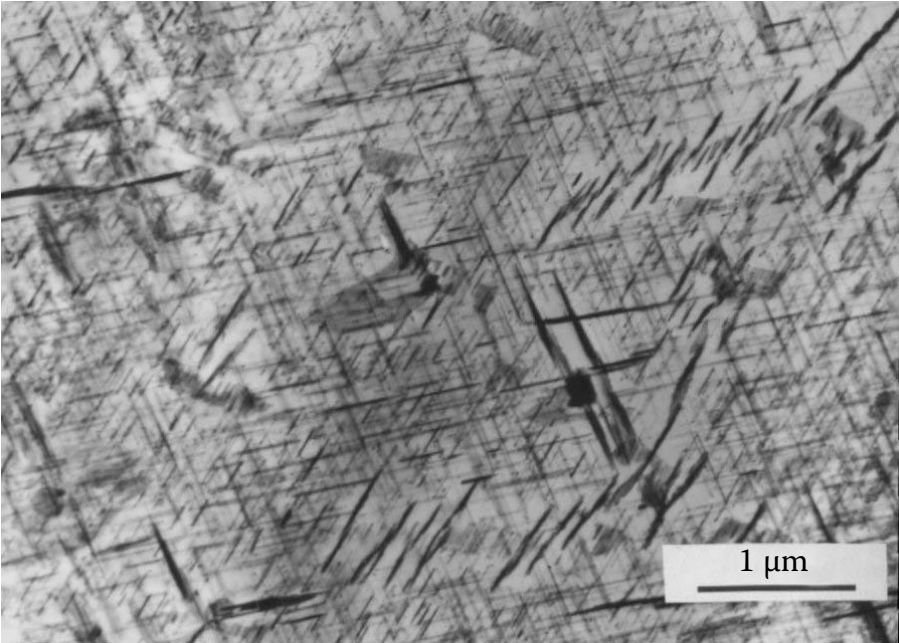


FIGURE 5.6

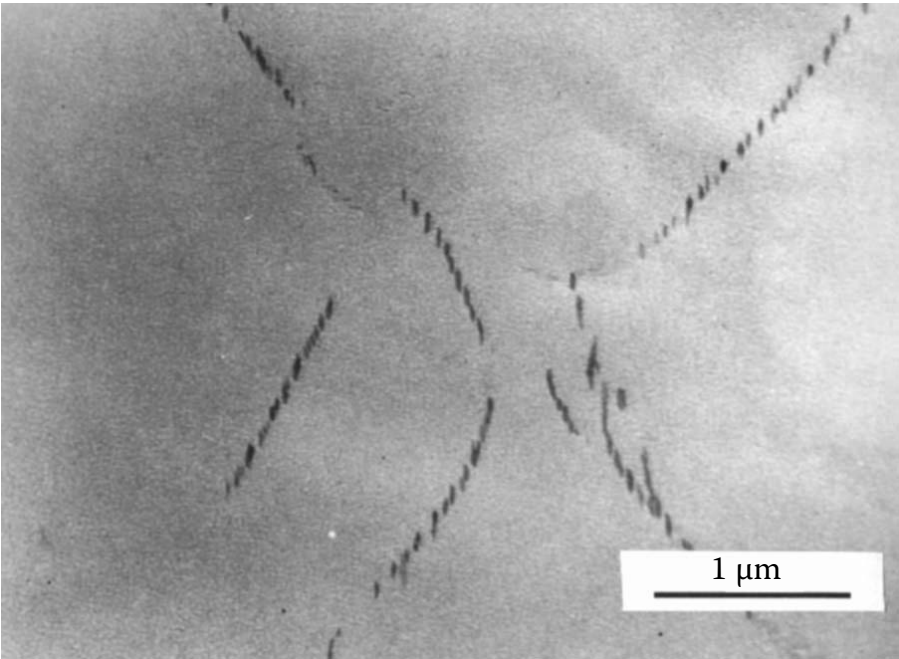


FIGURE 5.7

FIGURE 5.6 In many alloys, the nucleation and growth of phases occurs on preferred matrix planes, called *habit planes*, and under a specific crystallographic orientation relationship with some of the matrix crystal planes or directions. Under these conditions, the new phase usually develops a planar interface with the matrix and takes on a regular geometric shape. In the case of Al-4 Cu, the $\{100\}_{\text{Al}}$ is the habit plane of the GP-1 zones, of the metastable θ'' (GP-2) and θ' phases, and of the equilibrium CuAl_2 phase. This results in the specific morphology, which is referred to as a *Widmanstätten structure*.

Al-4%Cu alloy aged to produce equilibrium θ -phase.

FIGURE 5.7 The nucleation of a second phase at structural irregularities is preferred because a smaller amount of energy is required to create a nucleus of critical size in their vicinity. The heterogeneous nucleation on crystal defects proceeds faster than the homogeneous nucleation in the perfect matrix, but the general decomposition rate is limited by the number of structural irregularities.

Cast alloy Al-6%Cu-0,2%Ti. In this micrograph, heterogeneous precipitation has started at dislocations earlier than homogeneous precipitation in the matrix. The θ -particles decorating the dislocation lines have grown up to 150 nm in size, and still there is no indication of any decomposition in the rest of the matrix.

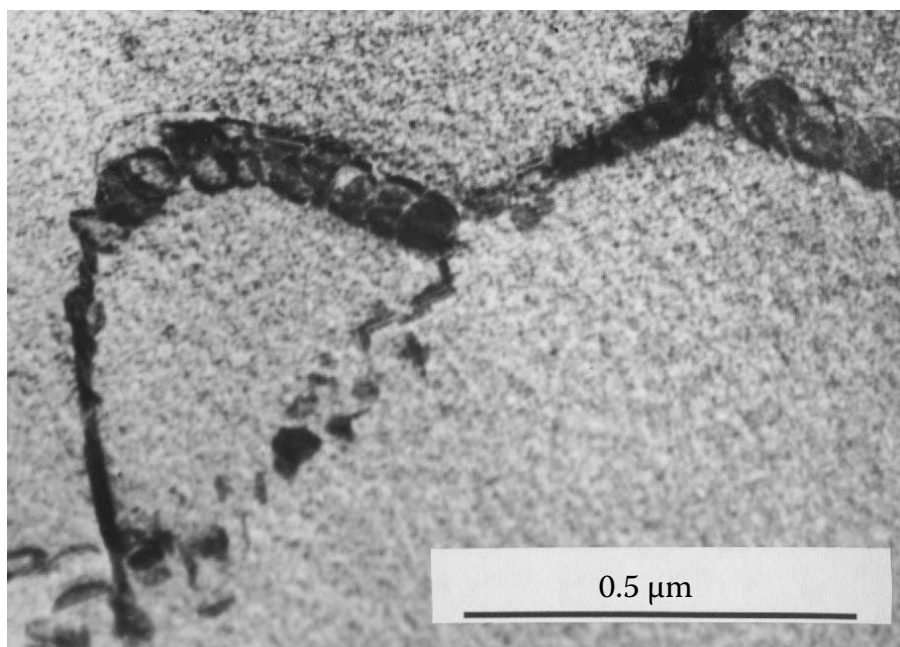


FIGURE 5.8 There are several reasons for dislocations assisting nucleation: (a) the strain field around dislocation lines reduces the total strain energy of the nuclei; (b) the solutes segregated on dislocation lines, the Cottrell atmospheres around dislocations, and the Suzuki atmospheres on the SFs provide enriched sites in the matrix; and (c) the dislocation lines provide fast diffusion paths along the dislocation pipe-shaped core.

Cast alloy Al-6%Cu-0,2%Ti after low-temperature aging. The precipitates of θ' -phase that heterogeneously nucleated on the dislocation lines grow faster than those in the matrix. The contrast in the rest of the volume indicates that the decomposition in the perfect matrix is still at the GP-zones stage.

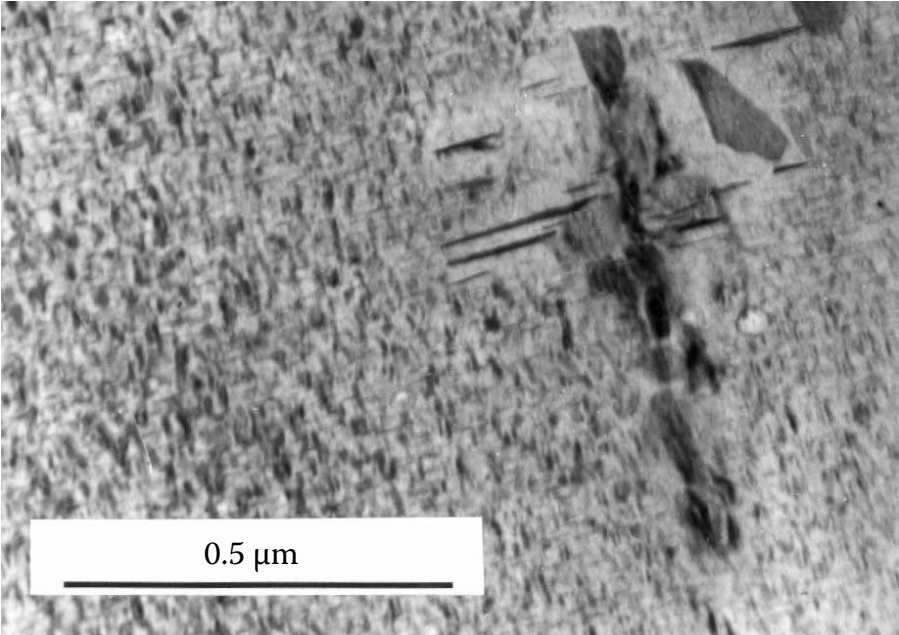


FIGURE 5.9

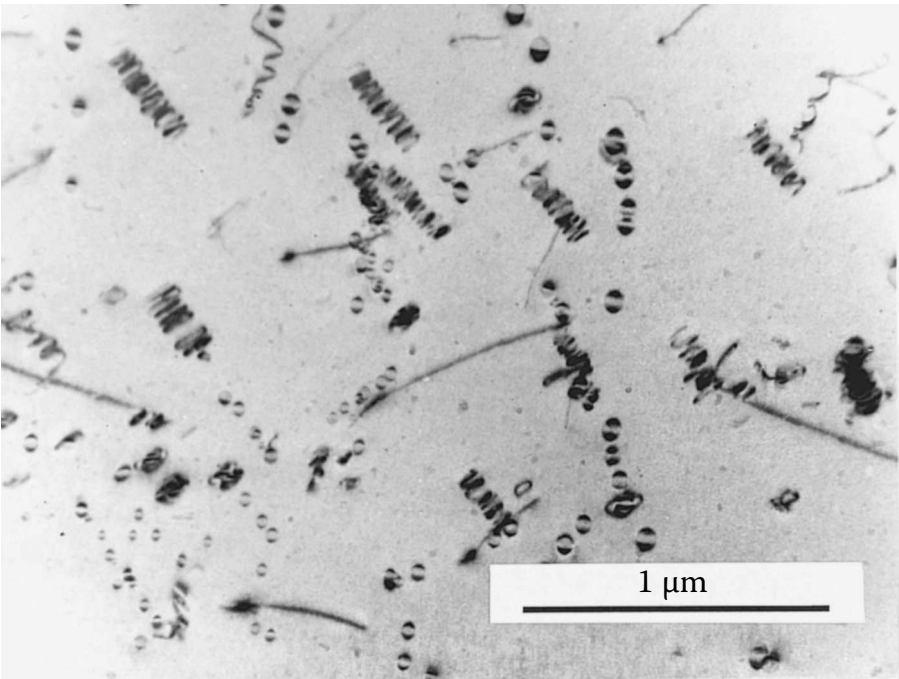


FIGURE 5.10

FIGURE 5.9 The accelerated growth of heterogeneously precipitated phases causes solute depletion at some distance from the particle, which retards the homogeneous decomposition in the surrounding matrix.

Cast alloy Al-6%Cu-0,2%Ti after low-temperature aging. Note the Cu-depleted halo around the heterogeneously precipitated phases and the absence of such a zone around the θ -particles.

FIGURE 5.10 As in the case of homogeneous precipitation, excess vacancies assist the heterogeneous nucleation. The solute atoms are attracted to the dislocation loops that border the complexes of vacancies and to the helical dislocations produced by the interaction of vacancies with screw dislocations. This mechanism of vacancy-assisted heterogeneous precipitation is often observed in aluminum alloys, which are especially susceptible to the quenching-in of excess vacancies.

Al-6%Cu-2%Zn alloy after quenching and subsequent aging. Solute atoms have been absorbed onto the helical dislocations left by quenching and have formed disc-shaped precipitates on each spiral of the helicoids.

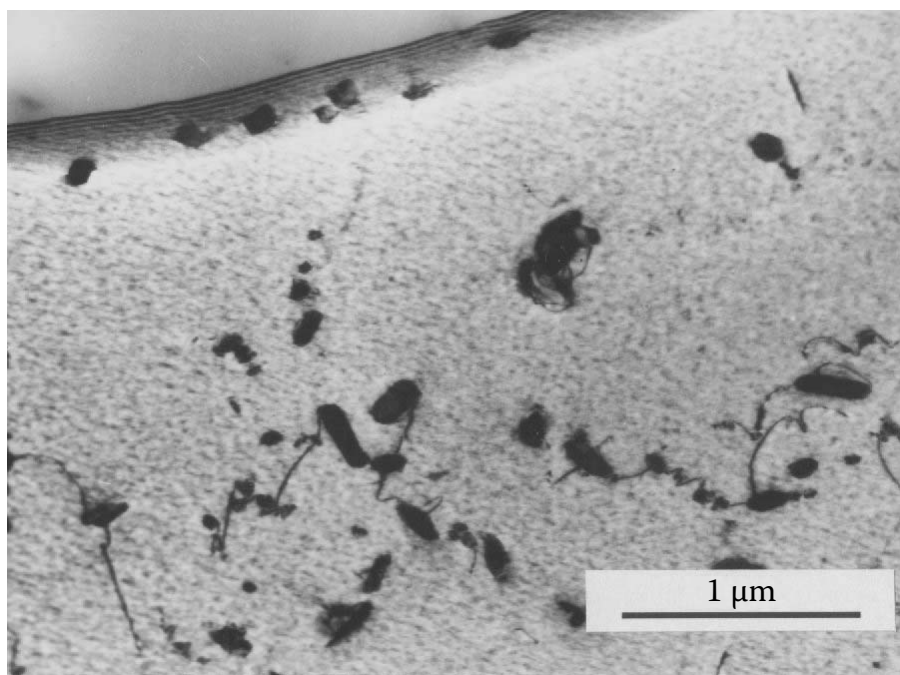


FIGURE 5.11 Grain boundaries are also preferred sites for precipitation. The significant amount of energy that is associated with them can be reduced by boundary segregation of solute atoms, followed by precipitate nucleation and growth. The susceptibility to grain boundary segregation increases with the interfacial energy, that is, with the magnitude of the misorientation across the boundary.

Al-6%Cu-0,2%Ti after quenching and a low-temperature aging. The size of the particles on the grain boundary and on the dislocation lines has reached several hundreds of nanometers, but the decomposition in the matrix is still at the zone stage. This shows once more that the heterogeneous precipitation starts much earlier than the homogeneous precipitation in the matrix.

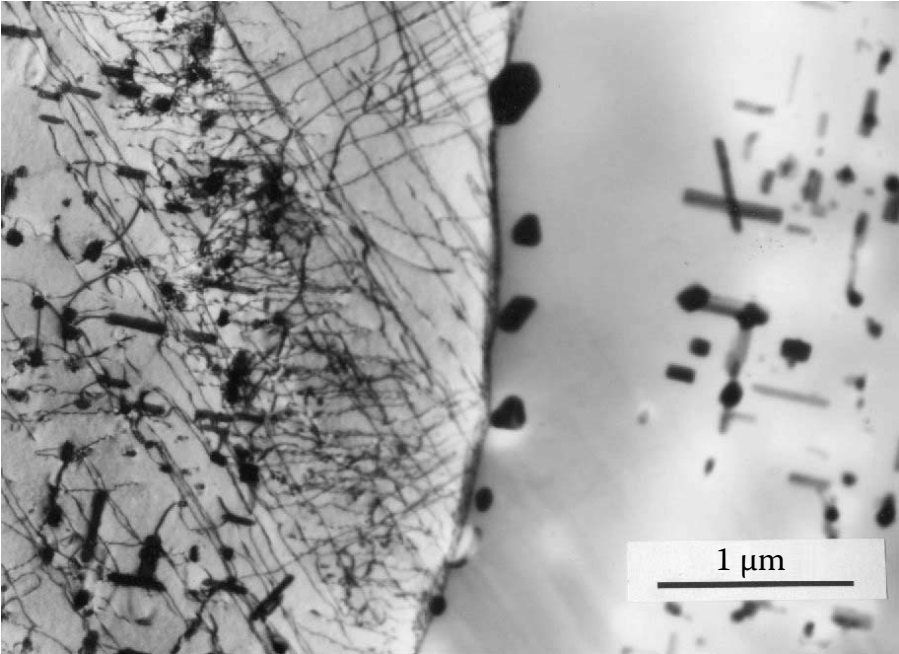


FIGURE 5.12

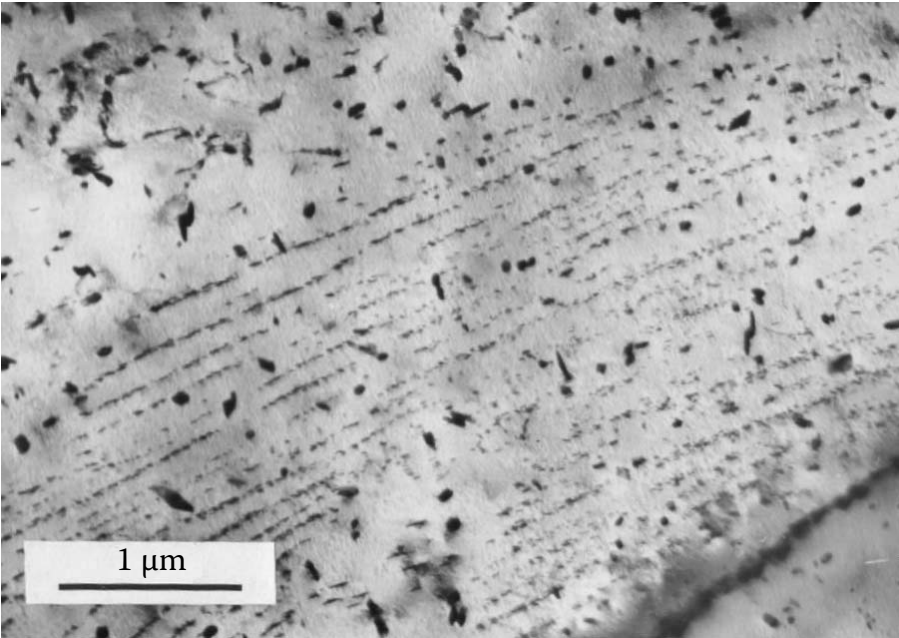


FIGURE 5.13

FIGURE 5.12 Grain boundaries are known to be effective vacancy sinks, and this results in the formation of vacancy-depleted zones around them. On the other hand, the solute atoms from the grain boundary areas are often consumed for heterogeneous boundary precipitation. The more difficult nucleation and growth of phases in the solute-depleted regions causes the formation of a *precipitate-free zone (PFZ)* around such boundaries. PFZs in age-hardened alloys are unwanted due to their detrimental effect on the mechanical properties and corrosion resistance.

Al-6%Cu-0.2%Ti after quenching and a short high-temperature aging. The relatively low rate of cooling from the solid solution temperature for this alloy has promoted grain boundary precipitation and caused the formation of PFZs that are about 1.5 μm wide. Fast cooling during quenching plus prolonged aging at a lower temperature can help to reduce the width of the PFZ.

FIGURE 5.13 Segregation of impurity atoms and precipitation on grain boundaries are often observed at high temperatures. The dragging of boundaries “decorated” with segregated atoms or particles requires too much energy. The only possible mechanism for the boundary to migrate is to bow out between the “decorations” and then to tear away from them. The unrestrained boundary can then move freely only a short distance until new atoms and particles decorate it and stop it. This process can be repeated many times. The precipitates, which have been left behind by the released boundary, indicate the successive positions of boundary during its migration.

Vanadium-alloyed carbon steel after normalization. The austenite-ferrite boundary has been locked by carbon atoms during the polymorphous transformation. Vanadium carbonitrides have had sufficient time to precipitate as a chain along the immobile boundary. The parallel carbide rows seen in the micrograph indicate the successive positions at which the boundary has repeatedly released itself from the precipitates to continue its migration.

5.2 INTERACTION OF DISLOCATIONS WITH SECOND-PHASE PRECIPITATES

Precipitation hardening involves the strengthening of alloys resulting from interaction of dislocations with those precipitates, formed during aging, which are effective obstacles for their free movement. The amount of strengthening achieved by aging of commercial alloys is determined to a large extent by the nature, type, properties, and morphology (size, shape, density, and distribution) of precipitates. Precipitate particles can impede the dislocation motion through a variety of interaction mechanisms, some of which can operate simultaneously. The model of *internal strain hardening* distinguishes two main cases depending on the distribution of the obstacles: (a) the stress fields are closely spaced and the dislocation line has to *curl* between them, or (b) the fields are widely spaced and the dislocation line has to *pass around* them, subsequently leaving a *dislocation loop* around each of them. The change of solvent and solute/neighbor atom arrangement produced by the cutting (shearing) action of the dislocation as it passes through a zone or a coherent precipitate causes *chemical hardening*. The model of *dispersion hardening* applies to the later aging stages when the precipitates are incoherent, they cannot be cut by the dislocation or deformed with the rest of the matrix, and an increase of applied stress is required for the dislocation line to bypass the particles, leaving dislocation loops around them.

The direct study of dislocation–precipitate interactions is rather difficult because the processes occur at the matrix/precipitate interfaces and sometimes are rather difficult to be resolved.

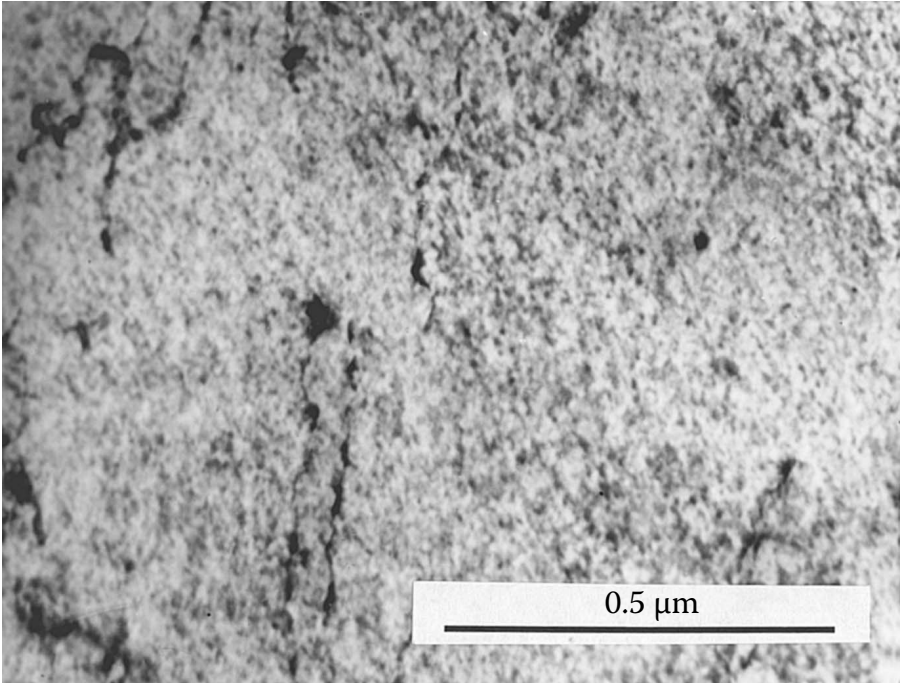


FIGURE 5.14

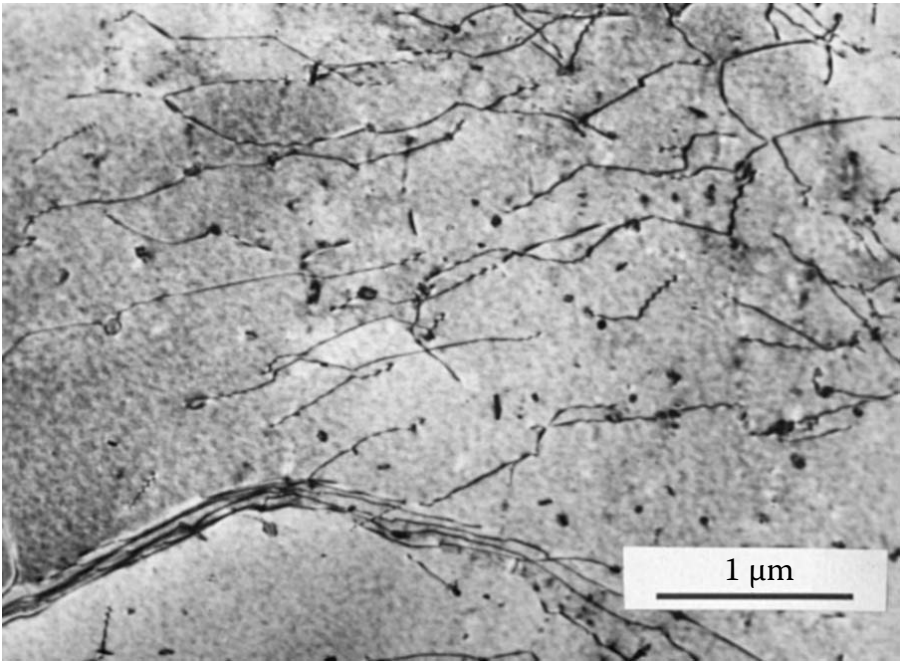


FIGURE 5.15

FIGURE 5.14 Aging treatment, producing a high density of GP-zones or coherent precipitates, results in substantial strengthening because the stress fields around them are effective obstacles to dislocation movement. In Al-4%Cu alloys, GP-2 zones (θ'') are considered to be responsible for the peak strength effect.

Al-4%Cu alloy aged to the GP-zone stage. The internal strain-hardening model is demonstrated in this micrograph by the dislocation lines that have to bow around the zones due to their strain fields.

FIGURE 5.15 The simultaneous formation of zones and precipitation of semicoherent particles guarantees the peak mechanical strength of the alloys because the effect of the strain fields of the zones is superimposed on the effect of the strain fields of the particles.

Al-7%Zn-2%Mg-1%Cu alloy, mold cast. In this micrograph, the dislocation lines have curled due to their interaction with the strain field of the zones while also being additionally “pinned” by the semicoherent particles of the complex intermetallic phases.

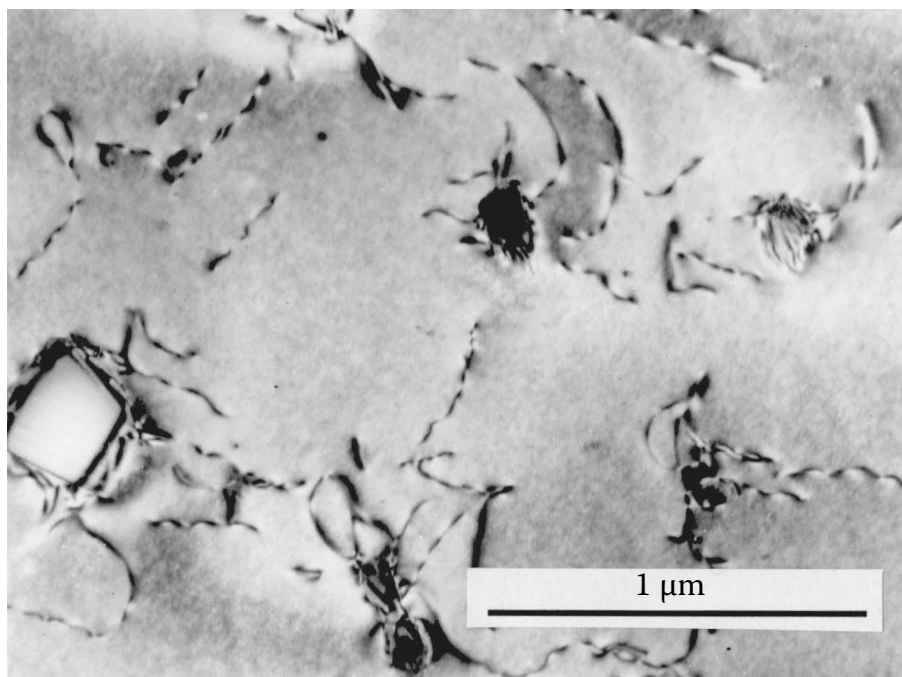


FIGURE 5.16 When the external stress increases and the bowing of the dislocation line becomes large, the dislocation can tear away from the obstacle, leaving a dislocation loop around it.

Al-4%Cu alloy aged to produce θ -phase precipitation. The dislocation loops and the dark shadows produced by the stress fields are clearly visible around the θ -particles.

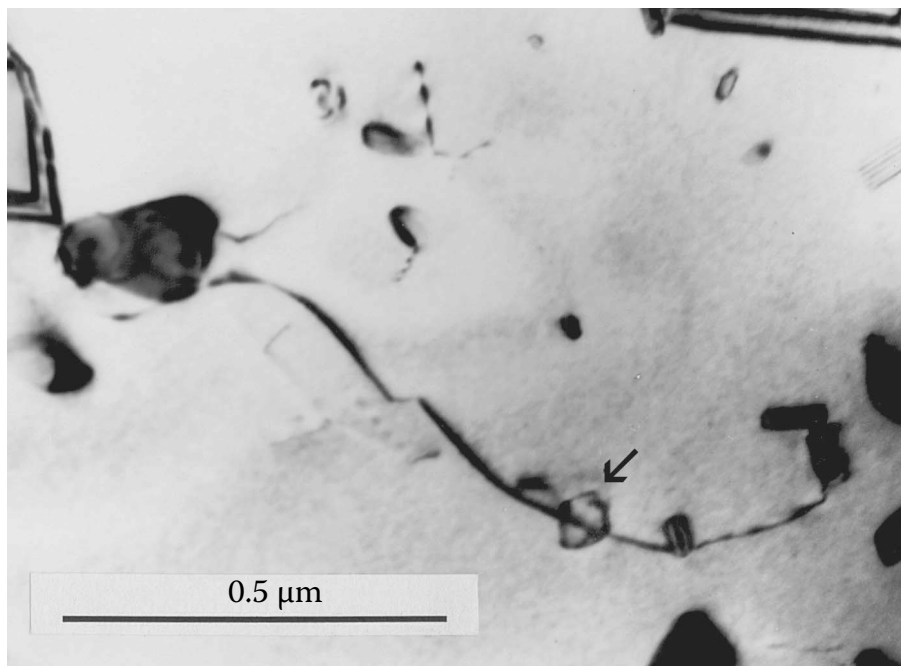


FIGURE 5.17 The cutting of coherent precipitates by dislocations is difficult to study because the sample is three-dimensional, while the recorded TEM image is a two-dimensional representation. Thus, superposition of features in the image can occur.

Low-carbon steel alloyed with vanadium. At first glance, the dislocation line is seemingly cutting through the precipitate indicated by the arrow. More probably it is sliding in a plane over or under the particle. Such a question can often be answered by taking stereo images of the region in question.

5.3 DISCONTINUOUS (CELLULAR) PRECIPITATION

Discontinuous precipitation, also called cellular precipitation, is another mode of transformation, through which the supersaturated solid solution lowers its free Gibbs energy. The decomposition of the supersaturated solid solution α results in transformed regions in the form of *cells* (*colonies*, *nodules*), composed of lamellar precipitates of new equilibrium phase β and *depleted phase* α_1 . The transformation reaction can be written as $\alpha \rightarrow \alpha_1 + \beta$. The phase α_1 has a lower thermodynamic excess of solute and the same crystal structure as the α -phase, but it has a crystallographic orientation different from the orientation of α in the grain, where the cell grows—that is, the α_1 phase inside the cell is reoriented. The two-phase cell (colony) is separated from the surrounding nontransformed parent phase α by a high-angle incoherent interface. The interphase boundary of the growing cell (the cell front) moves into the parent phase with the growing tips of the transformed phases and gradually consumes it, the growth being controlled by boundary diffusion through the colony/parent phase interface. The area of nonconsumed parent phase diminishes with time, thus preserving the initial supersaturation till the completion of the transformation.

The term *discontinuous* originates from the existing concentration gradient at the cell interphase boundary and the abrupt change of both composition (from α to α_1) and orientation of the parent phase when the advancing cell front passes through it. The term *cellular* reflects the morphological characteristics of the reaction products growing as a colony or duplex product regions (cell) with a constant interlamellar spacing, specific for the given temperature, between the two phases inside the colony.

Discontinuous precipitation has been observed in commercial Cu-Be, Cu-Ti, Mg-Al-Zn, Zn-Al, Pb-Sn alloys; nitrogen austenitic steels; and some magnetic alloys under certain, fortunately narrow, ranges of treatment conditions. The discontinuous precipitation reaction is usually unwanted during industrial aging treatments because the nucleation of the noncoherent phase on grain boundaries in the two-phase structure deteriorates the mechanical properties and causes brittleness and higher susceptibility to intercrystalline corrosion.

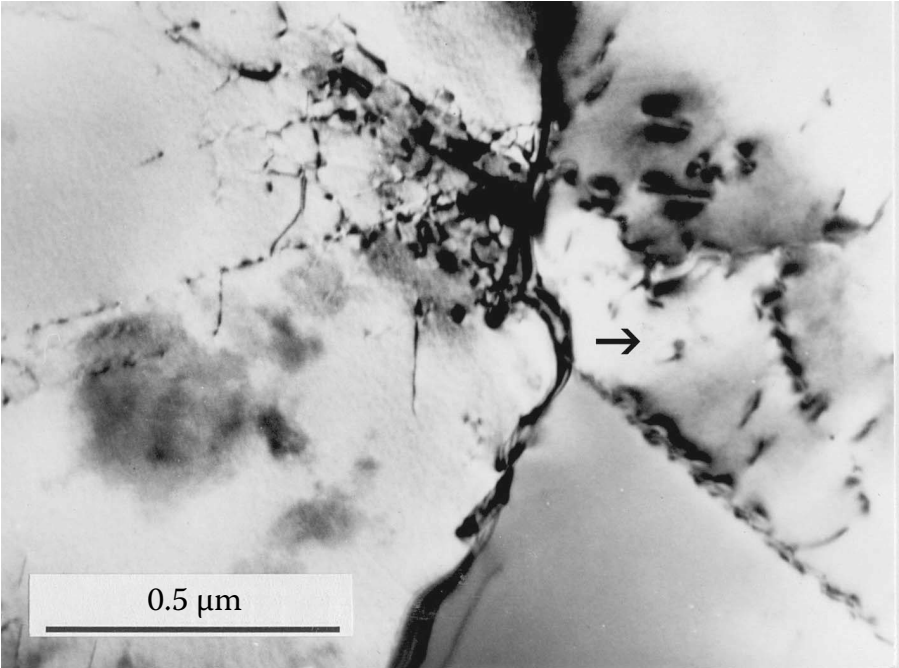


FIGURE 5.18

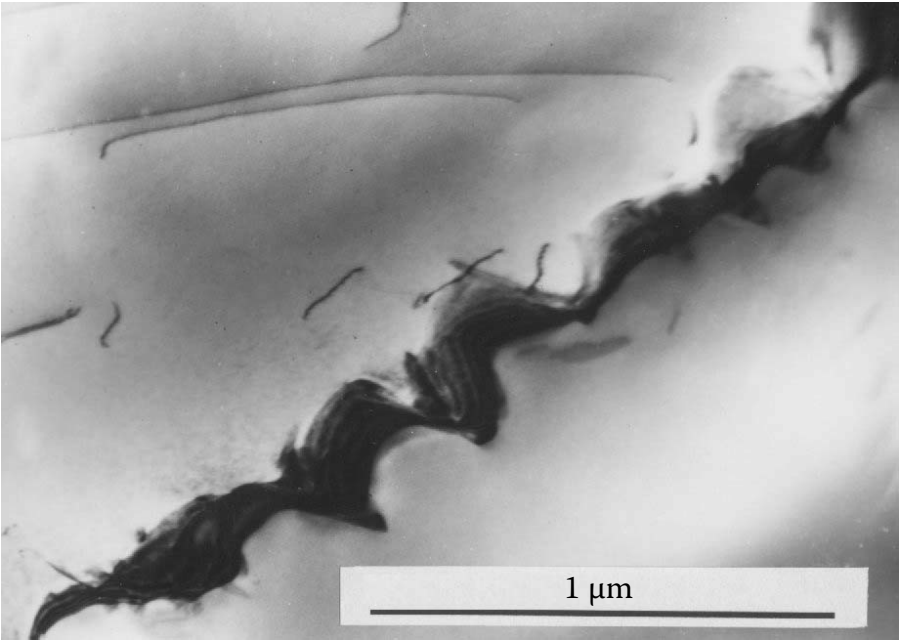


FIGURE 5.19

FIGURE 5.18 The discontinuous precipitation begins with nucleation of platelets of the new equilibrium phase on the boundary. The platelets lie facedown at the boundary; the other broad face of the platelet is semicoherent with the grain into which the precipitation will proceed.

Austenitic nitrogen steel Fe-18Cr-14Mn-0.6N quenched from 1100°C and aged at 650°C for 2 min. The cellular precipitation is observed in the high-nitrogen-alloyed stainless steels in the temperature range 550°C to 850°C. The first nuclei of the new phase (Cr_2N) precipitate on austenite grain boundaries within the first few minutes of aging. The growth direction is shown by the arrow into the austenitic grain.

FIGURE 5.19 The nuclei of the new phase precipitate on the grain boundary at roughly regular intervals and quickly cover its full length. In this way, the preferred nucleation sites are exhausted during the initial steps of the process.

Austenitic nitrogen steel Fe-18Cr-14Mn-0.6N quenched from 1100°C and aged for 5 min at 650°C. The austenitic grain boundary is almost completely covered by platelets of chromium nitride.

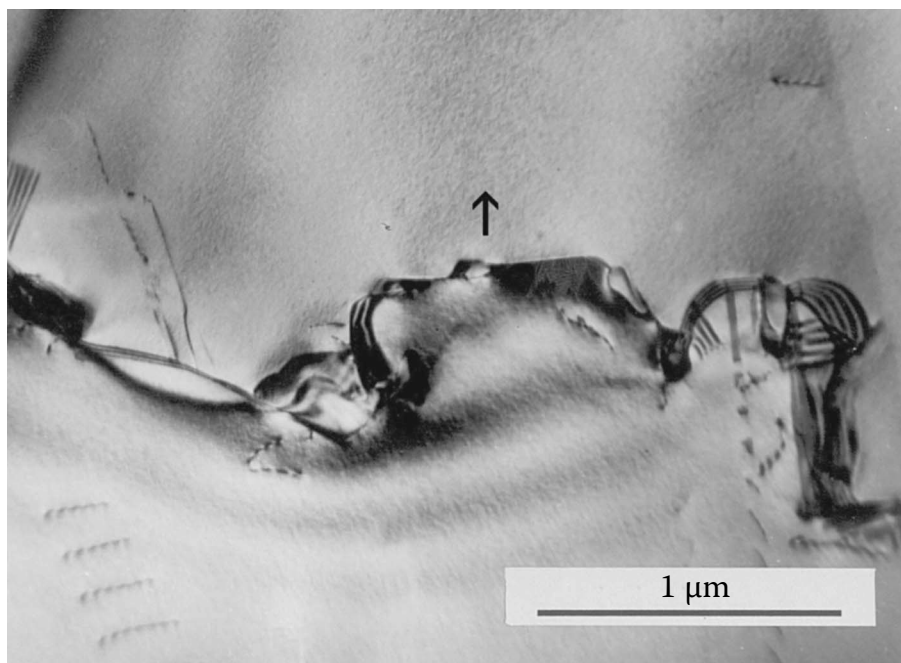


FIGURE 5.20 The broad face of the nuclei of the plate-like phase is parallel to its habit plane. This forces the boundary to bow out between nuclei to remain parallel to this plane during the decomposition.

Austenitic nitrogen steel Fe-18Cr-14Mn-0.6N quenched from 1100°C and aged for 5 min at 650°C. The growth direction is shown by the arrow.

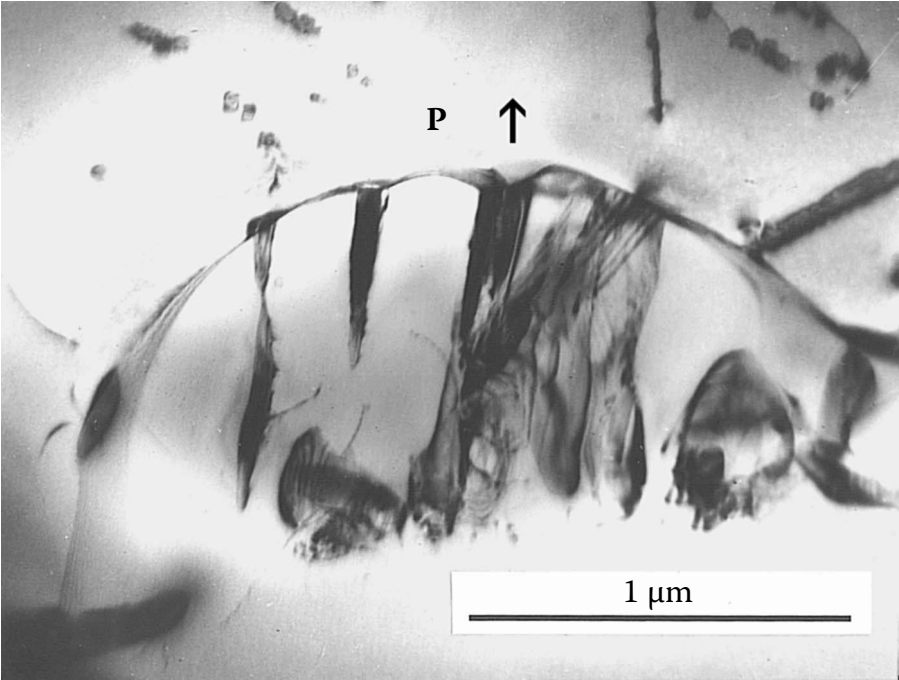


FIGURE 5.21

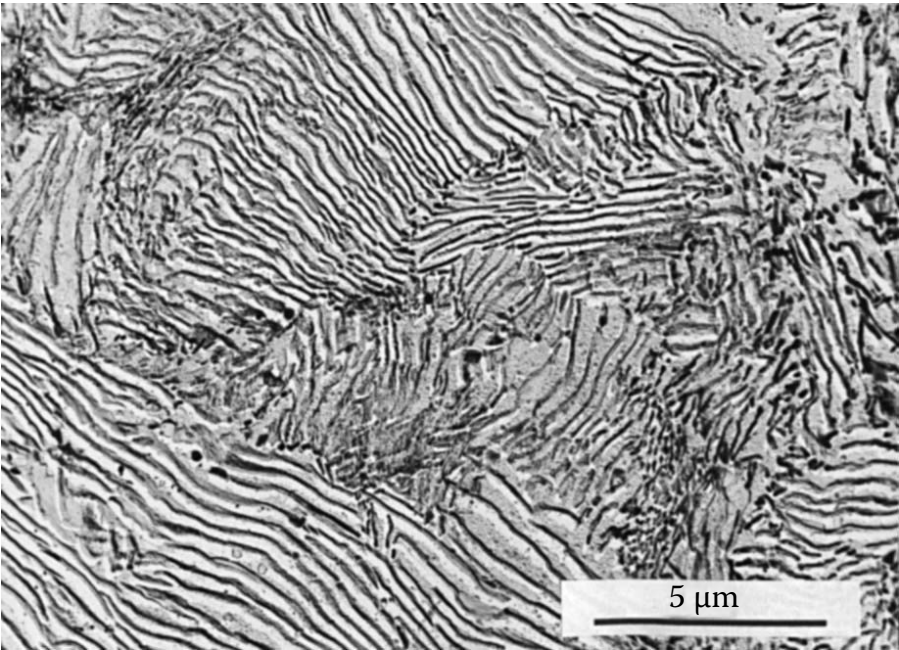


FIGURE 5.22

FIGURE 5.21 Cellular decomposition continues through the cooperative growth of the new precipitated phase and the depleted phase, which are in the shape of parallel lamellae and form cells. The advancing cell front has the structure of a high-angle boundary, which provides effective diffusion path and solute transport even at relatively low temperatures. Thus, the growth rate of the phases is controlled by grain-boundary diffusion.

Austenitic nitrogen steel Fe-18Cr-14Mn-0.6N quenched from 1100°C and aged for 10 min at 650°C. The high-angle boundary between the cell growth front and the parent austenite phase is clearly visible through the high-angle crystallographic misorientation between the transformed austenite lamellae and the grain into which the colony grows, as marked by *P*.

FIGURE 5.22 The morphological characteristics of the discontinuously decomposed alloys are similar to those of colonies of pearlite.

Austenitic nitrogen steel Fe-18Cr-14Mn-0.6N quenched from 1100°C and aged for 60 min at 650°C. Replica. Compare this structure to the pearlite structure in [Figure 5.27](#).

5.4 EUTECTOID TRANSFORMATION

Eutectoid reactions are reversible diffusional transformations that are induced by temperature transitions—cooling or heating through some transformation temperature, which is specific for each alloy system. On slow cooling below the eutectoid transformation temperature T_E , the metastable solid solution *decomposes* into a more stable mixture of two new solid *eutectoid phases*. The formation of phases of different composition is accompanied by a significant redistribution of the constituents, a process that requires *long-range diffusion*.

The eutectoid decomposition of the eutectoid alloy in a standard eutectoid-type phase diagram can be expressed in the form $\gamma_E \rightarrow \alpha + \beta$. The eutectoid morphology is often called *pearlite*, emphasizing with this terminology the main feature of the eutectoid structure—a configuration of alternate lamellae of two product phases.

Eutectoid transformations are found in many alloy systems: the ferrous systems Fe-C, Fe-N, Fe-Cu, and Fe-Nb and the nonferrous Cu-Sn, Cu-Al, Cu-Be, Cu-Si, Zn-Al, Ti-Cr, Ti-Fe, and Ti-Mn. From an engineering point of view, the eutectoid transformations in Fe-C alloys are the most important.

The nucleation of pearlite starts with the formation of a nucleus of either of the two product phases on boundaries of the parent phase (austenite in Fe-C alloys). Either of the two new phases can nucleate first, obeying a definite crystallographic relationship with one of the austenite grains. The nucleation of the second phase occurs adjacent to the first, producing an orientation relationship with it and with the same grain. Both nuclei have an incoherent mobile boundary with the other grain. The nucleation process is repeated sideways while the lamellae of the two phases grow cooperatively and form a *colony* (called also eutectoid grain) of alternating lamellae under this fixed crystallographic relationship. The colony grows radially into the parent austenitic grain with which it does not have an orientation relationship by a boundary diffusion mechanism through the colony/parent phase interface.

The morphologies of the microstructure resulting from the eutectoid decomposition and from the cellular precipitation are microscopically similar—two phases nucleate on grain boundaries and subsequently grow as a common aggregate of alternating lamellae. The main difference is that in the eutectoid reaction the parent phase transforms into a more stable mixture of two different phases, whereas in the cellular precipitation one of the phases in the cell is new, and the other is the same phase but reoriented and depleted.

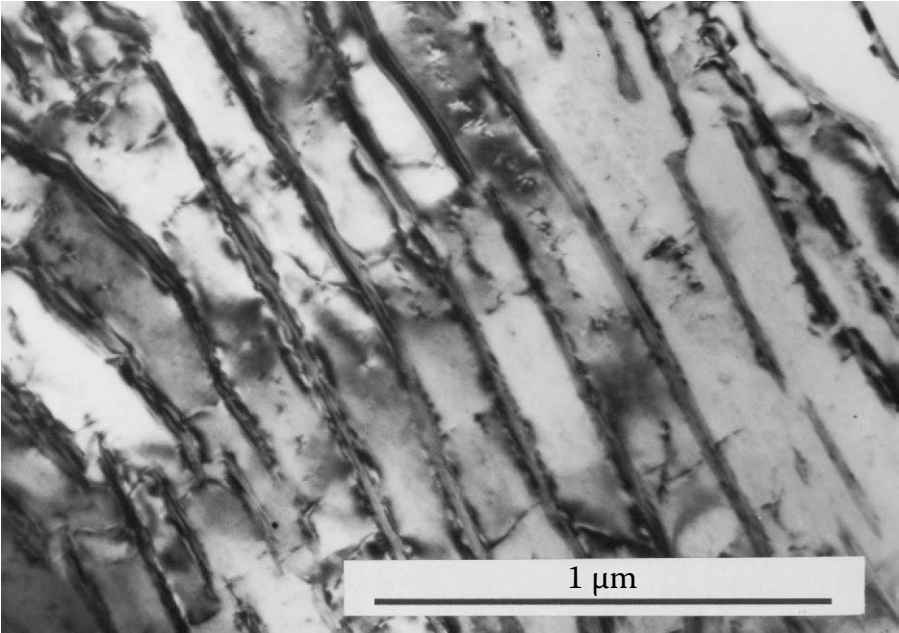


FIGURE 5.23

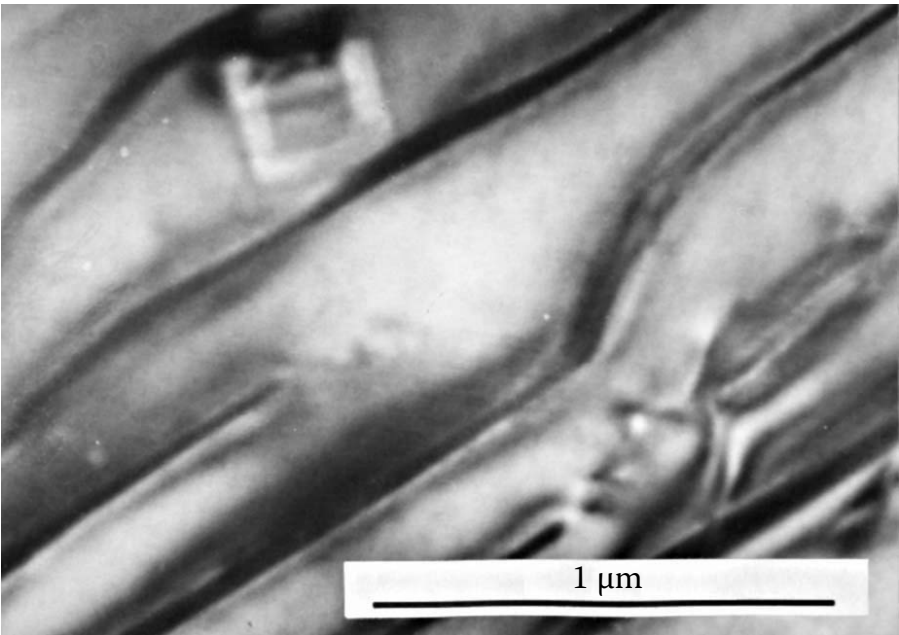


FIGURE 5.24

FIGURE 5.23 During the eutectoid decomposition, the parent phase (austenite) in ferrous alloys undergoes polymorphic transformation: the fcc austenite γ transforms into bcc ferrite α . The eutectoid decomposition in plain carbon steels proceeds according to the reaction $\gamma_{(0.8\%C)} \rightarrow \alpha + \text{Fe}_3\text{C}$ (cementite). The two-phase pearlite is composed of colonies comprising alternate lamellae of cementite and ferrite.

Pearlite in hypo-eutectoid carbon steel 0.25%C. The dark lamellae are cementite, and the light lamellae containing dislocations are ferrite.

FIGURE 5.24 Under isothermal conditions, the growing eutectoid lamellae in all colonies keep a roughly constant interlamellar spacing, which is specific for the transformation temperature and varies inversely with undercooling ΔT below the eutectoid transformation temperature.

Ferrite-pearlitic steel, containing 0.1%C, 0.1%N, and 0.1%V. The growing cementite lamellae change their direction when meeting primary vanadium carbonitride. The constant interlamellar spacing in the colony is restored by formation of additional cementite lamella.

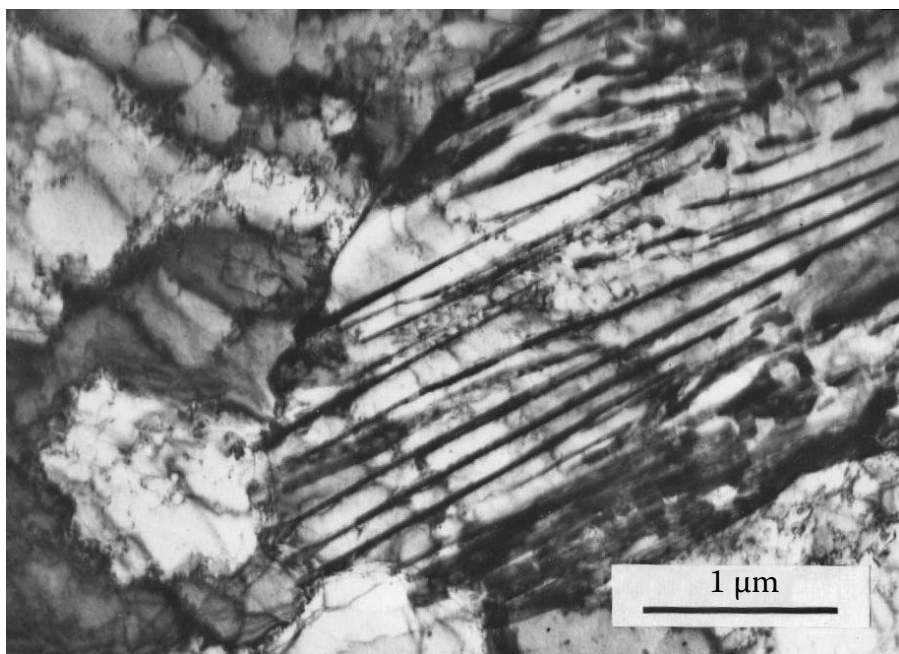


FIGURE 5.25 The rate of growth of the pearlite depends on the undercooling degree. In plain carbon eutectoid steels, the growth rate varies from $0.1 \mu\text{m}\cdot\text{s}^{-1}$ at lower ΔT to $100 \mu\text{m}\cdot\text{s}^{-1}$ at higher ΔT . The higher ΔT contributes to the better mechanical properties of pearlitic steels. This is especially true for the impact strength, which improves from both the smaller colony size and the smaller interlamellar spacing.

Cast carbon steel, containing 0.25%C. The relatively high transformation velocity resulted in eutectoid grains with diameters of several micrometers and a 50 to 100 nm interlamellar spacing.

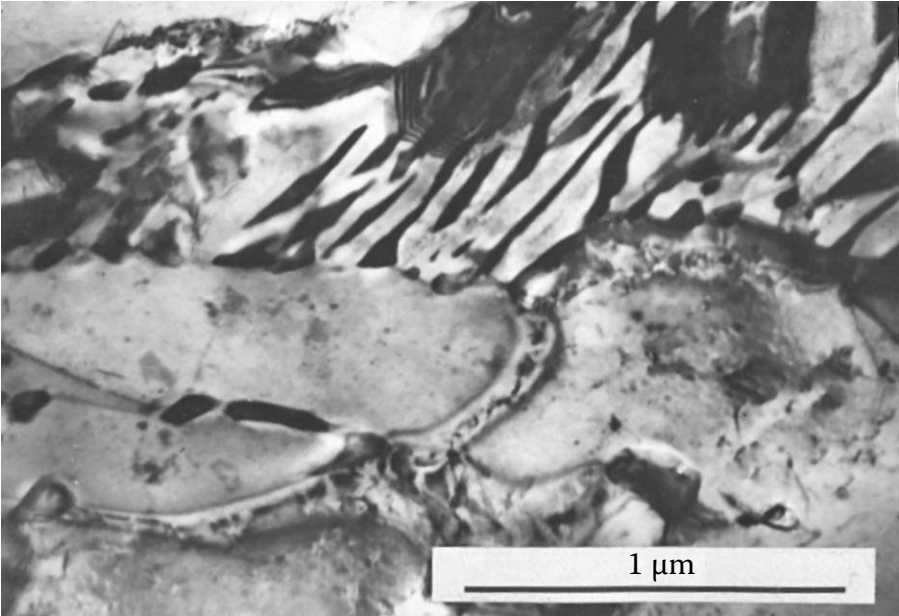


FIGURE 5.26

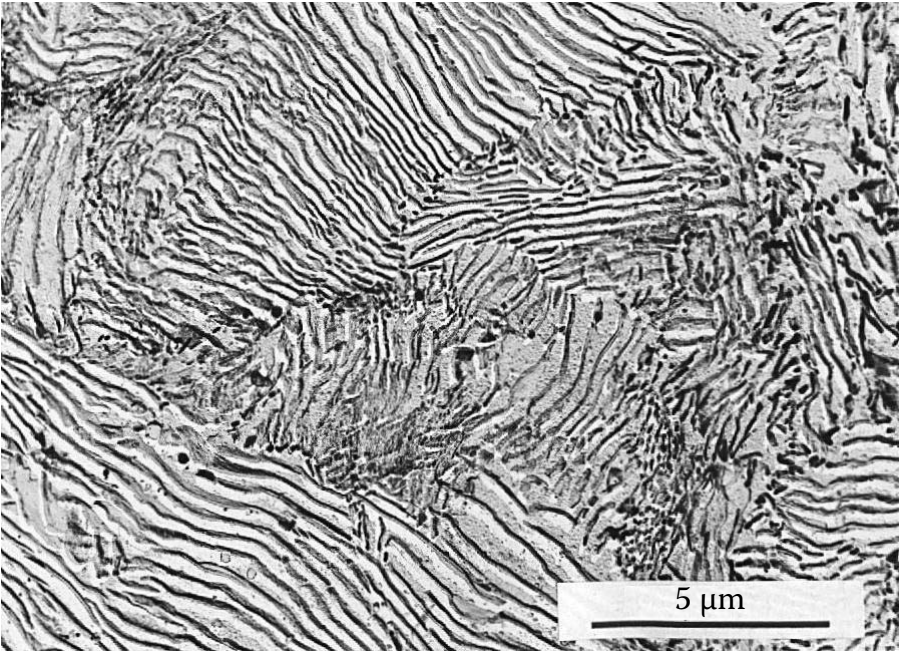


FIGURE 5.27

FIGURE 5.26 The amount of pearlite depends on the transformation time and on the carbon content of the steel. In hypoeutectoid steels, a precipitation of proeutectoid ferrite from austenite precedes the pearlitic decomposition of the remaining austenite, which has reached a eutectoid carbon content.

Low-carbon ferrite-pearlite steel, containing 0.1%C, 0.1%N, and 0.1%V. The ferrite grains contain a small number of short dislocation lines and fine carbonitrides. The high-angle ferrite/ferrite boundaries appear as two parallel lines where they intersect with the foil surfaces. Large cementite particles can be seen precipitated on these boundaries.

FIGURE 5.27 Another factor that influences the pearlite morphology and the pearlitic transformation kinetics, apart from the undercooling ΔT degree and chemical composition, is the size of the prior austenite grains. The smaller grains provide a bigger total length of grain boundaries, a higher number of nucleation sites, a smaller colony size, and a higher growth rate.

Plain carbon eutectoid steel. Replica. Pearlitic colonies have nucleated on all the austenite boundaries and have consumed the whole volume occupied by the fine grains of the parent austenite, thus producing 100% pearlite.

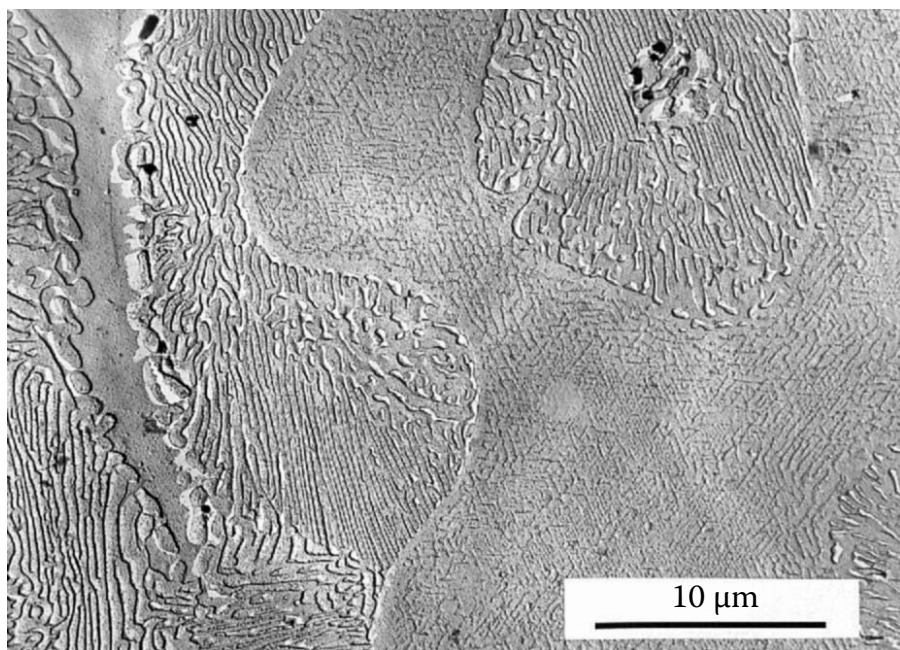


FIGURE 5.28 The eutectoid decomposition is a typical solid-state reaction in Zn-Al alloys. The pearlitic reaction in this case is $\beta \rightarrow \alpha + \eta$, where the high-temperature β -phase decomposes into α -solid solution of Zn in Al and a η -solid solution of Al in Zn.

Cast alloy Zn-27%Al. Replica. The eutectoid decomposition has produced colonies containing lamellae alternately of the α - and η -phases. The sites for the nucleation of the colonies are the grain boundaries and the interfaces of the large primary η -phase boundary precipitates. The rest of the volume has transformed into supersaturated α -solid solution, which has subsequently decomposed during cooling into fine η -needles. The Widmanstätten morphology of the secondary precipitated η -needles is due to the preferred nucleation on the $\{111\}_{Al}$ habit plane.

5.5 MARTENSITIC TRANSFORMATIONS

Martensitic transformations, frequently also called *shear* or *displacive transformations* (because their mechanism involves homogeneous lattice deformations and shear displacements), belong to the diffusionless solid-state transformations. No long-range diffusion is required for the nucleation and growth of martensite, and it inherits the chemical composition of the parent phase. The process does not rely on the assistance of thermal activation; still, for most of the alloys that transform martensitically, the speed of growth of the individual martensite plate is extremely great—it approaches the velocity of sound in solids. The diffusionless, athermal character of the transformation means that from start to completion the individual atoms move only a distance that is smaller than one interatomic spacing in the parent phase. These movements are cooperative and coordinated in a “military” manner that allows the atoms to retain their own original neighbors in the new phase. The military mode of movement of the atoms determines the crystallographic characteristics of the martensite transformation, which are the most distinguishable features from any other transformation. The coordinated structural change requires a fully coherent or semicoherent interface and leads to the establishment of an orientation relationship between the parent and the product lattices.

The term *martensite* was initially introduced to describe the hard structure obtained by rapid quenching of steel from the austenitic region. Nowadays, however, it is used in physical metallurgy as a generic name for the products of the diffusionless transformations. Martensitic transformations are observed in many pure metals with allotropic modifications (Co, Fe, Ti, Zr) and many important engineering materials such as carbon and alloyed steels; iron-based alloys (Fe-Ni, Fe-Mn, Fe-Cr); and nonferrous alloys, such as Cu-Al, (α + β)-Ti alloys, and shape-memory effect alloys (Cu-Zn, Cu-Zn-Al, Cu-Zn-Ni, Ti-Ni). Martensitic transformations can also occur in some types of nonmetallic crystals, some minerals, ceramic inorganic compounds, and even polymers.

The best-known and undoubtedly most significant for engineering practice is the austenite-martensite transformation in Fe-C and Fe-Ni systems, which are basic for steels. This transformation occurs during rapid cooling (quenching) from the austenitic region to temperatures between M_s (the martensite start temperature) and M_f (the martensite finish temperature). Both M_s and M_f are definite temperatures for a given alloy composition but do not depend on cooling rate in a broad range of rates.

The martensite crystals nucleate in austenite as bcc, bct (body-centered tetragonal lattice), or hcp flat crystals. The product of the martensitic transformation in plain carbon steels is a metastable supersaturated solid solution of carbon in α -Fe having bct crystal lattice, the unit cell parameters and the degree of tetragonality (c/a ratio) depending on the carbon content.

The preferred habit plane, usually $\{111\}_\gamma$, and the strict crystallographic relationship between the martensite and austenite crystal lattices determine the planar semicoherent martensite/austenite interfaces. The morphological characteristics of bct and bcc martensite in quenched carbon steels and in carbon-free iron alloys have been adopted as a basis for the classification of martensite into two major types: *plate* (*twinned*) *martensite* and *lath* (*dislocation, massive, packet*) *martensite*. Depending on

alloy composition, the two types differ in their shape, orientation variants, micro- and substructure, and habit plane.

The martensitic structures in nonferrous alloys are classified as plate martensite because of their plate-like shape. They are, however, further divided into two types based on their internal microstructure: *faulted* and *twinned martensite*. The twinned martensite is observed in many nonferrous alloys, such as Cu-Al (containing more than 9.5% Al), Cu-25%Sn, Au-Cd, and Au-Mn, and in Ti-based alloys with Cu, Fe, Mn, Mo, and V. Faulted martensite is observed in Cu-(11–13%)Al, Cu-(22–24%)Sn, Cu-(38–41%)Zn and in Co-based alloys with Fe, Ni, and Al. The *reversible thermo-elastic martensite* transformation running in Cu-Zn, Cu-Zn-Al, Cu-Zn-Ni, Ti-Ni, and Ti-Mo alloys is the physical ground of the *shape-memory* effect and the development of “*smart*” alloys.

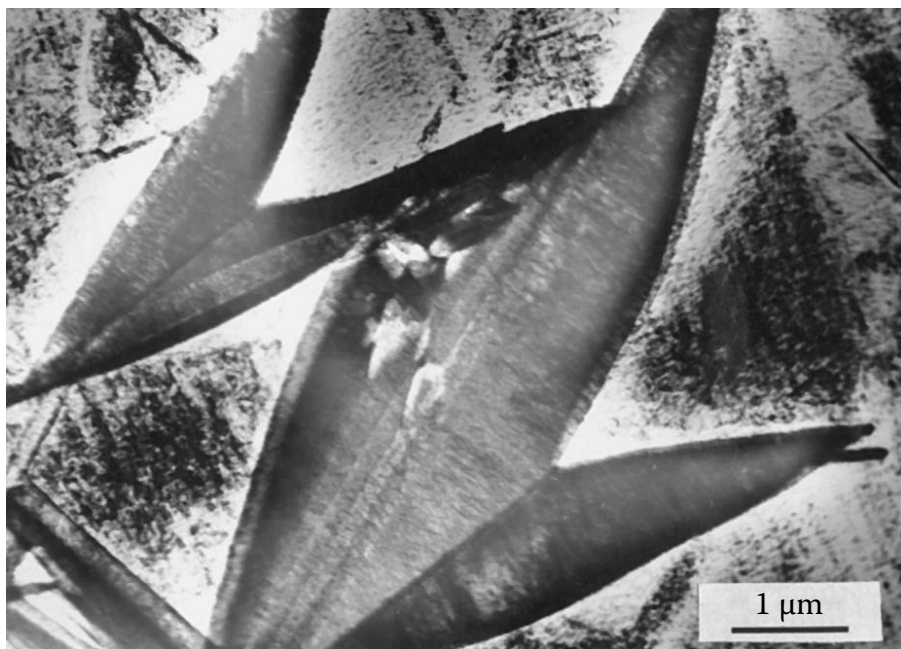


FIGURE 5.29 Plate martensite morphology predominates in high-carbon steels, Fe-Ni alloys (containing more than 28% Ni), and some special steels. The plate martensite has mainly a lens or plate shape. The central part of the lens, called the *midrib* (abbreviation of *middle ribbon*), consists of fine parallel internal twins, which give the name *twinned* to this type of martensite. It has been suggested that due to the crystallographic match between the twins and the $\{111\}_\gamma$ habit plane, the midrib is the first part of the plate to grow. Toward the periphery of the plate, the twins degenerate into complex dislocation arrays.

Plate martensite in Fe-30%Ni alloy, quenched to -196°C (liquid nitrogen temperature). Note the zigzag array of martensite lenses, embedded in retained austenite. The direction of each midrib corresponds to the projection of a $\{111\}_\gamma$ habit plane.

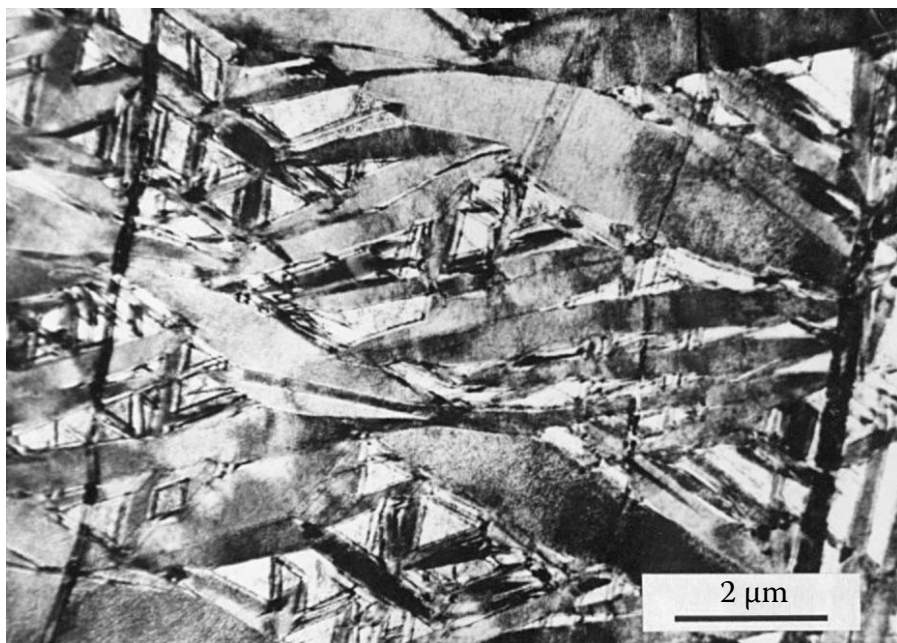


FIGURE 5.30 The typical microstructure after quenching to plate martensite consists of *martensite units*, composed of many zigzag-oriented plates. The length of the plates is restricted either by another martensite crystal or by an austenite grain boundary.

Units of plate martensite in Fe-30%Ni alloy, quenched to -196°C . Each grain contains several martensite units of different direction, but in all units the individual plates lie along the direction of the $\{111\}_{\gamma}$ traces.

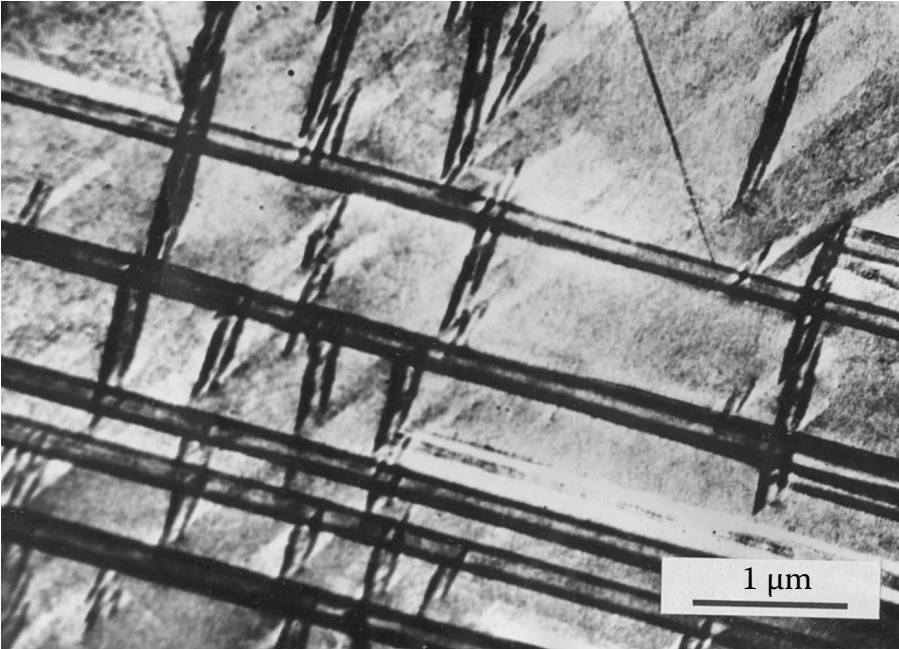


FIGURE 5.31

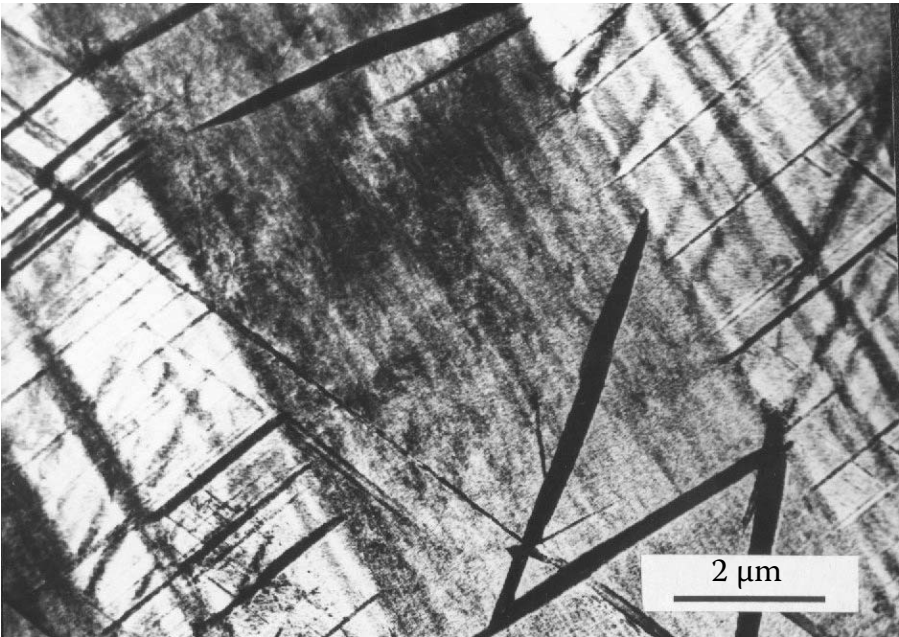


FIGURE 5.32

FIGURE 5.31 Plate martensite develops in some special high-carbon ferrous alloys during cooling to room temperature.

Cast Fe-3%C-30%Cr-15%Mn alloy. The plates of martensite are so thin that they could also be described as needles.

FIGURE 5.32 Needle-shaped plate martensite can be produced by deformation at high strain rates in many alloyed steels of lower carbon content.

Needle-like plate martensite in a shock loaded Fe-0.25%C-14%Mn-3%Cr steel. The martensite needles are surrounded by highly deformed austenite.

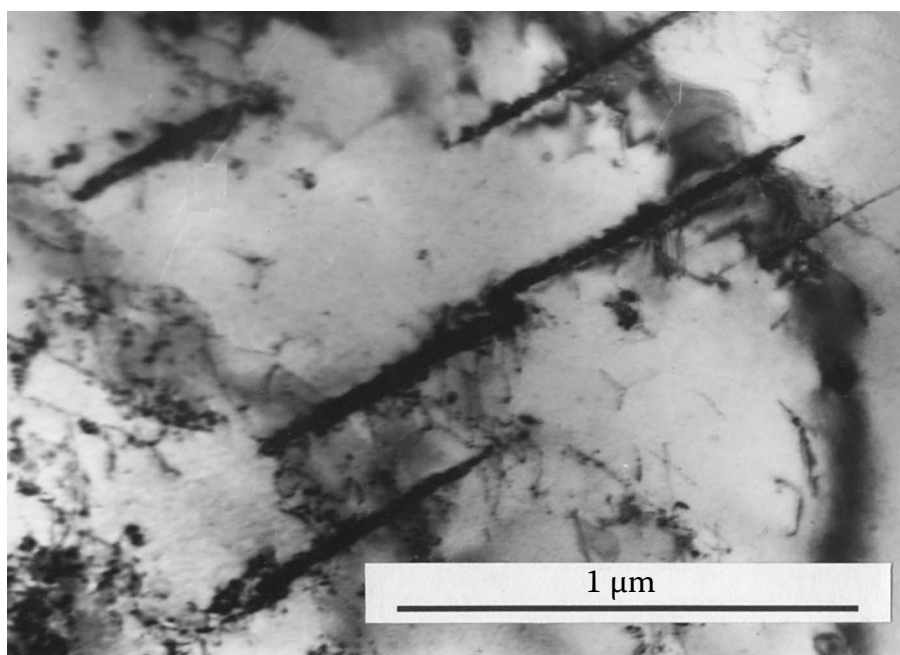


FIGURE 5.33 The cold plastic deformation of iron alloys of relatively high SFE can induce a transformation of the austenite into a *strain-induced martensite*.

Low-carbon steel with 0.25%C cold rolled to a 5% reduction at strain rate $\dot{\epsilon} = 5 \text{ s}^{-1}$. The length of martensite needles is less than 1 μm , whereas their width is less than 10 nm . The interface strain fields and the dislocations accumulated around the needles result from the high strain rate.

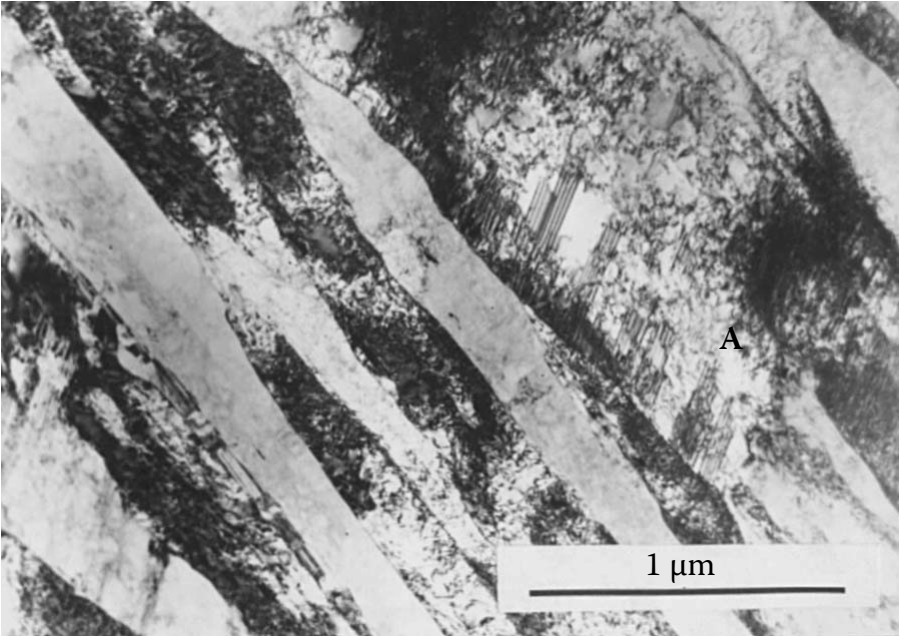


FIGURE 5.34

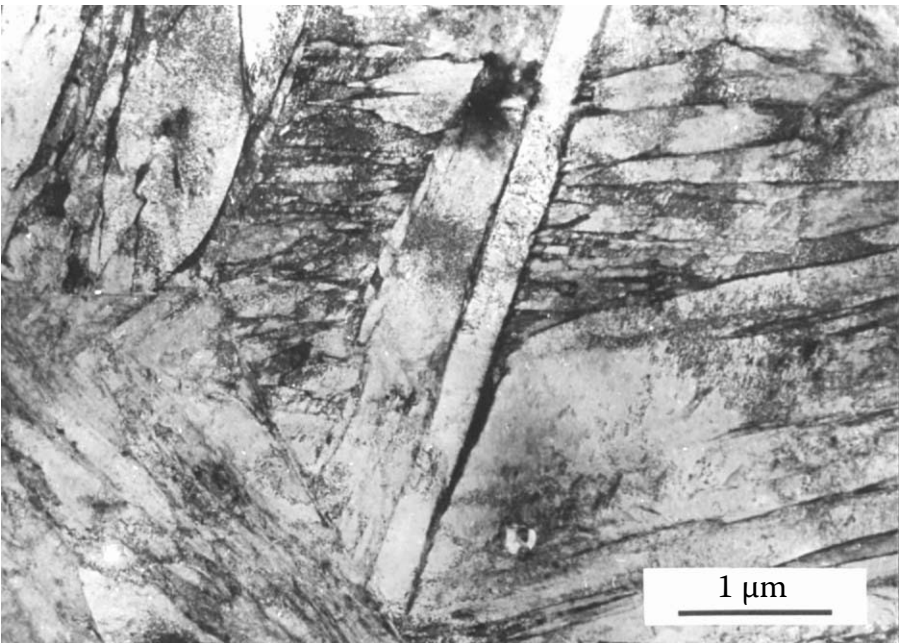


FIGURE 5.35

FIGURE 5.34 *Lath martensite* is the most common martensite morphology. It is observed in quenched low- and medium-carbon steels and in maraging and stainless steels. The lath martensite is referred to as *dislocation martensite* because of the dislocation substructure observed in the laths. It is similar to the substructure of cold-worked steels: the density of dislocations can be about 10^{11} to 10^{12} cm^{-2} , and the dislocations form tangles that separate cells. Some of the tangles develop into low-angle or high-angle boundaries that border the elongated martensite laths. The boundaries are almost straight due to the preferred habit plane and the strict crystallographic relationship between the ferrite and the parent austenite.

Lath martensite in Fe-14Cr-5Ni-3Mo steel. The strong white-black contrast is an indication of the large misorientation angle across the lath boundaries. A roughly 1- μm -thick layer of retained austenite (marked by A) is easily distinguished by the bands of SFs in it.

FIGURE 5.35 The parallel martensite laths are grouped into *martensite units*, the units themselves into larger packets. The terms *packet* or *massive martensite* have been adopted for lath martensite, thus emphasizing the main morphological feature observed when studied in a light microscope.

Packet martensite in a plain carbon steel.

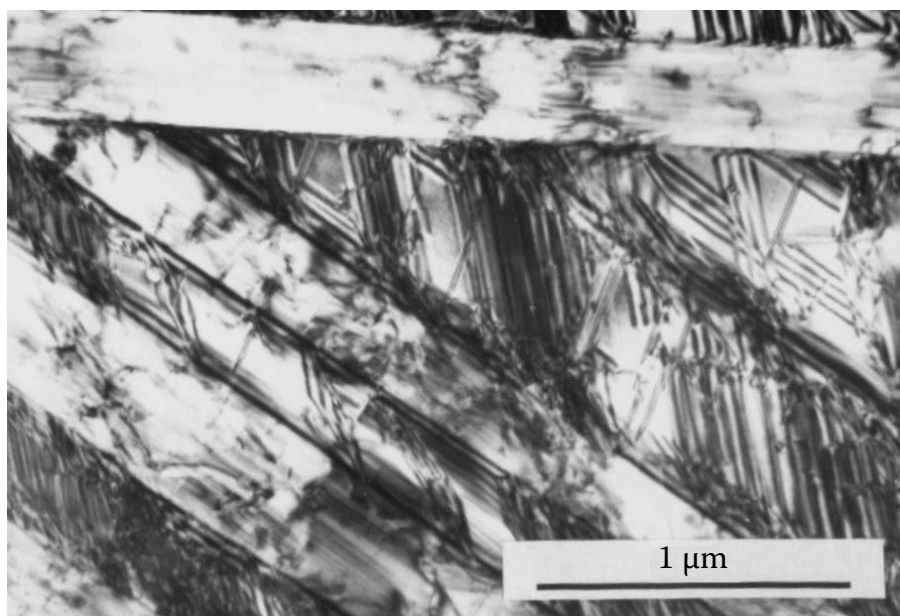


FIGURE 5.36 Cooling to very low temperatures and the plastic deformation of alloys of low SFE such as stainless steels, high-manganese Fe-Mn steels, and some complex alloyed steels induces the transformation reaction γ (fcc) $\rightarrow$ ϵ (hcp). The nonmagnetic ϵ -martensite is also called *sheet martensite* because it forms very thin sheets on $\{111\}_{\gamma}$ planes.

High-carbon Fe-30Cr-15Mn steel, quenched to room temperature. When observed in the TEM, the ϵ -martensite sheets produce the same contrast as SFs—alternating black and white and parallel fringes. The crystallography and the morphology of the SFs and of the ϵ -martensite are identical. They can be distinguished only by the greater thickness of the martensite sheets.

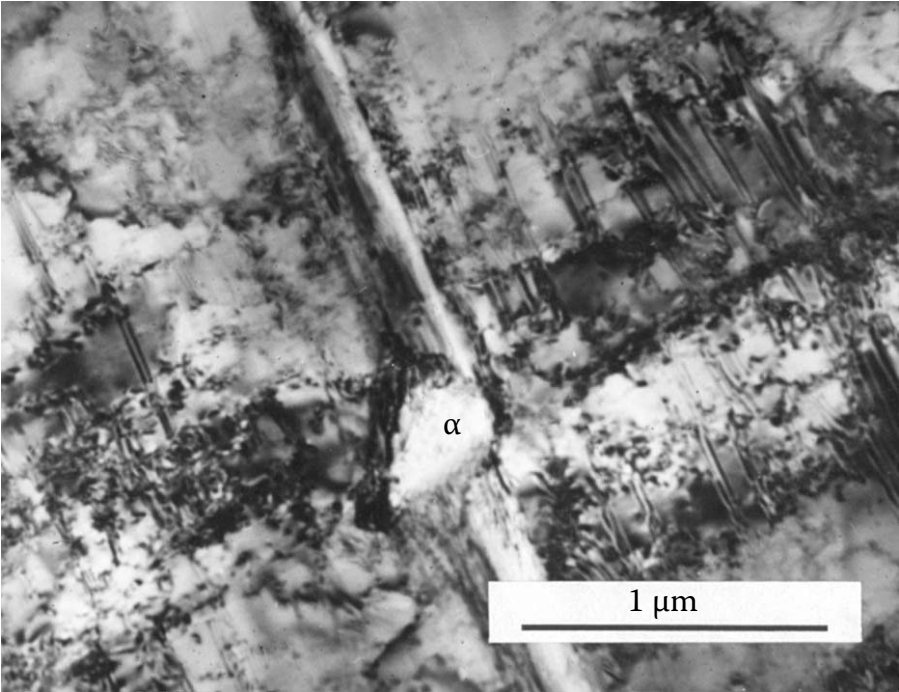


FIGURE 5.37

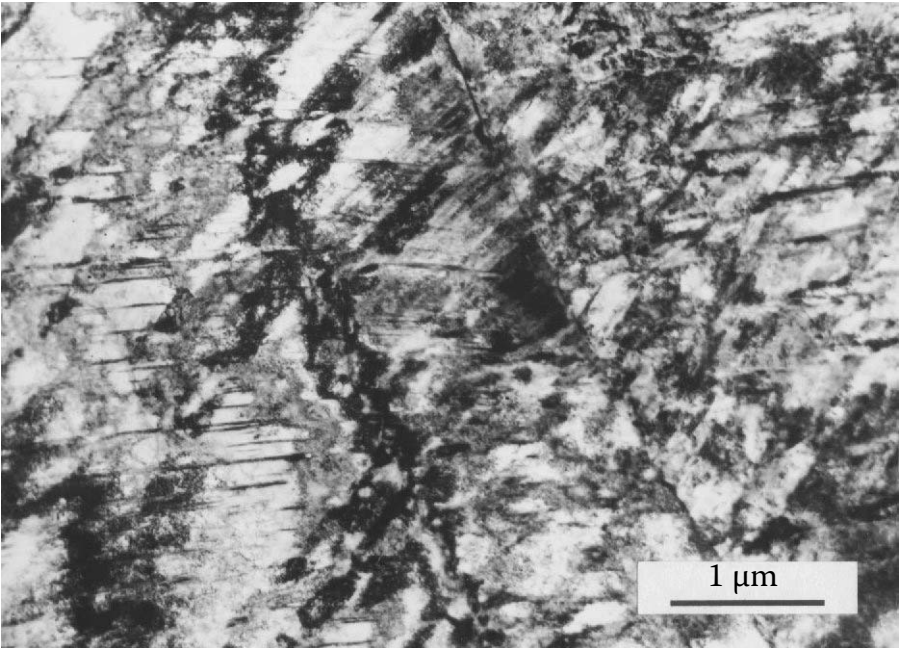


FIGURE 5.38

FIGURE 5.37 The arrangement of atoms produced by the crossing under certain crystallographic conditions of two sheets of ϵ -martensite corresponds to the arrangement of the bcc crystal lattice. These intersections are nuclei for the formation of bcc ferromagnetic α -martensite according to the reaction $\gamma \rightarrow \epsilon \rightarrow \alpha$.

Austenitic Fe-18Cr-9Ni steel, 20% cold rolling. An α -martensite nuclei is indicated by the symbol α .

FIGURE 5.38 The amount of strain-induced ϵ - and α -martensite increases with the amount of deformation.

Fe-18Cr-9Ni stainless steel, 70% cold rolling. The fine martensite laths are embedded in highly faulted austenite.

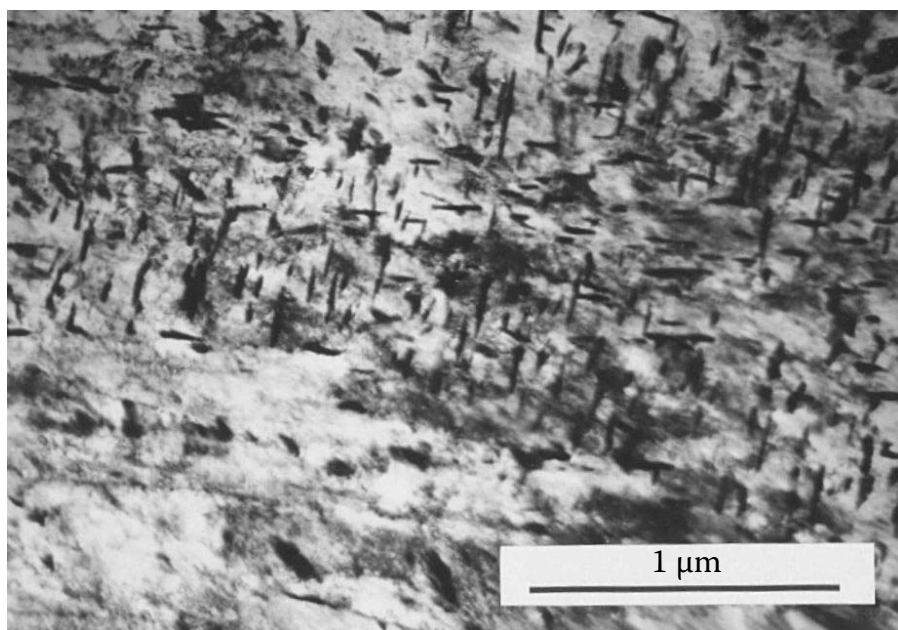


FIGURE 5.39 For most engineering steels and iron alloys, quenching to martensite is not a final heat treatment operation, and a *tempering* is applied. This is a heat treatment process of heating the martensitic steel to temperatures below A_{c1} , aiming to improve toughness, ductility, and even strength. Various structural changes and solid-state reactions take place during tempering of ferrous martensite depending on the temperature and duration of the heat treatment, and on the steel composition. The most important are the segregation of carbon atoms to dislocations, the pre-precipitation clustering and the precipitation of carbides, the decomposition of retained austenite, the recovery of dislocation substructure, and the recrystallization of ferrite plates into recrystallized grains. Many of them overlap, leading to an extremely complicated microstructure.

Tempered martensite in a carbon steel. The fine needle-like carbides that have precipitated in the martensite plates are mutually orientated at an angle of 60° —this angle corresponds to that between $\{011\}_\gamma$ planes, which are the habit planes for cementite precipitation in martensite.

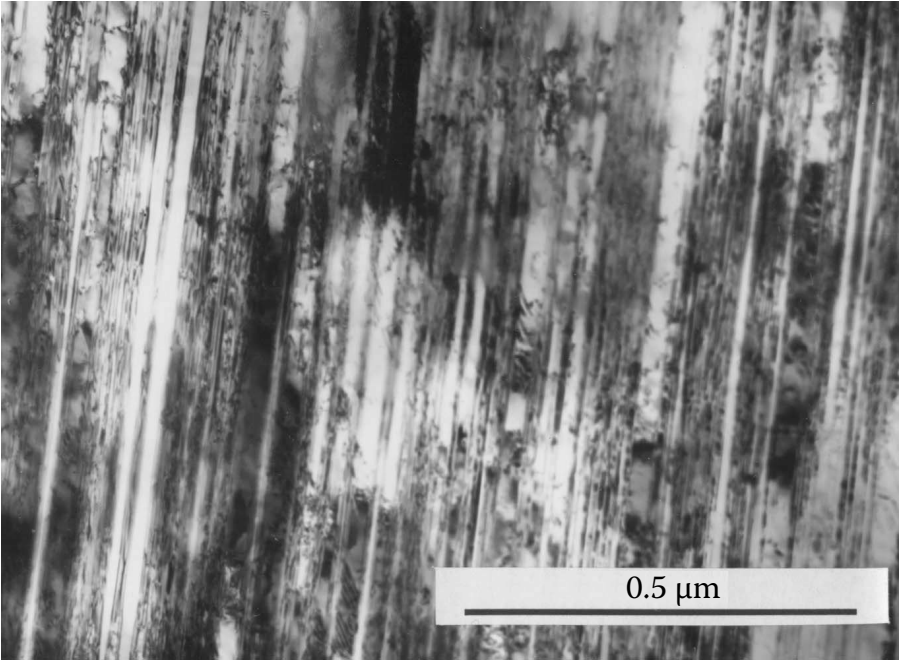


FIGURE 5.40

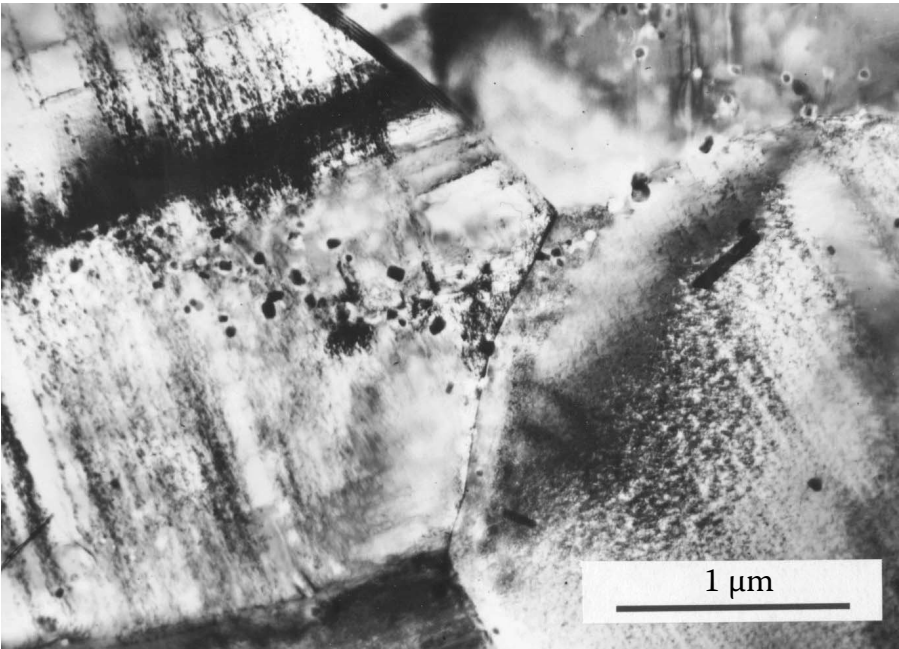


FIGURE 5.41

FIGURE 5.40 The plate martensite in nonferrous metals and alloys forms two morphologies that differ with respect to their internal structure, a feature that can be distinguished in the TEM. The twinned martensite forms plates that consist of fine twin bands separated by bands of nontransformed highly strained matrix.

Twinned martensite in a Cu-3Si-1.5Mn alloy (silicon bronze, Everdur) that was quenched from 900°C. The parallel twin and matrix bands are about 10 nm wide. Fine striations—SFs or secondary twin bands—can be seen in some of the matrix bands.

FIGURE 5.41 The fine structure of faulted martensite is usually defined as consisting of numerous internal faults, but the mechanism of their formation is still uncertain.

Faulted martensite in quenched Cu-26Zn-4Al alloy. The closely spaced striations running across the transformed grains are indicative of the presence of martensite with numerous internal faults, but their character is hard to determine unambiguously.

5.6 THE BAINITE TRANSFORMATION

The bainite transformation occurs in carbon steels at temperatures lower than that of the pearlite reaction and higher than that of the martensitic transformation. The reaction product, termed *bainite*, is a nonlamellar mixture of ferrite of low carbon supersaturation and carbides. The different morphology of the carbide distribution in the upper and the lower part of the bainite temperature range in steels has resulted in the classification of bainite into two groups: *upper bainite*, which is formed in the high-temperature part of the bainite range, and *lower bainite*, which is formed in the low-temperature part of the bainite range. There are differences in mechanical properties and microstructure of upper and lower bainite. Both upper and lower bainite form as aggregates of small plates or laths of ferrite (also called subunits). The carbide phase (cementite) in upper bainite precipitates from the carbon-enriched austenite predominantly between the plates of ferrite, the amount and micromorphology of cementite depending on the carbon content of the alloy. In lower bainite, there are two kinds of much finer carbide precipitates: carbide particles, which precipitate inside the laths of supersaturated lower *bainitic ferrite*, and cementite, which precipitates from the carbon-enriched austenite that separates the plates of ferritic bainite.

The bainite reaction has some characteristics that are typical of the martensitic transformation. For example, the dislocation density in the α -phase of bainite is rather high, although generally not as high as it is in martensite. The bainite transformation produces on the prepolished surface relief effects, that are similar to those resulting from a martensitic transformation, especially in the case of lower bainite and tempered martensite.

On the other hand, as with the austenite-to-pearlite transformation, an incubation period exists for the bainite reaction. A C-curve can be constructed for the bainite transformation on a T-T-T isothermal transformation diagram. Both pearlite and bainite in steels appear as a two-phase product of iron carbide and ferrite. However, the ferrite and carbide phases in bainite do not grow cooperatively like they do in pearlite. The main difference between pearlite and bainite lies in their crystallography. The cementite and ferrite in the pearlite have no specific orientation relationship to the austenitic grain in which they are growing, whereas in upper bainite they do.

The terms *bainite transformation* and *bainite*, which were initially introduced to describe the reaction and its product found in steels during an isothermal transformation, subsequently have been expanded over the years to refer to some nonferrous alloys: β -brass, copper-aluminum, and tin bronzes. The only common feature between bainites in steels and bainites in nonferrous alloys is that they all arise from transformations that are not exclusively civilian or military in character but have some characteristics of both types.

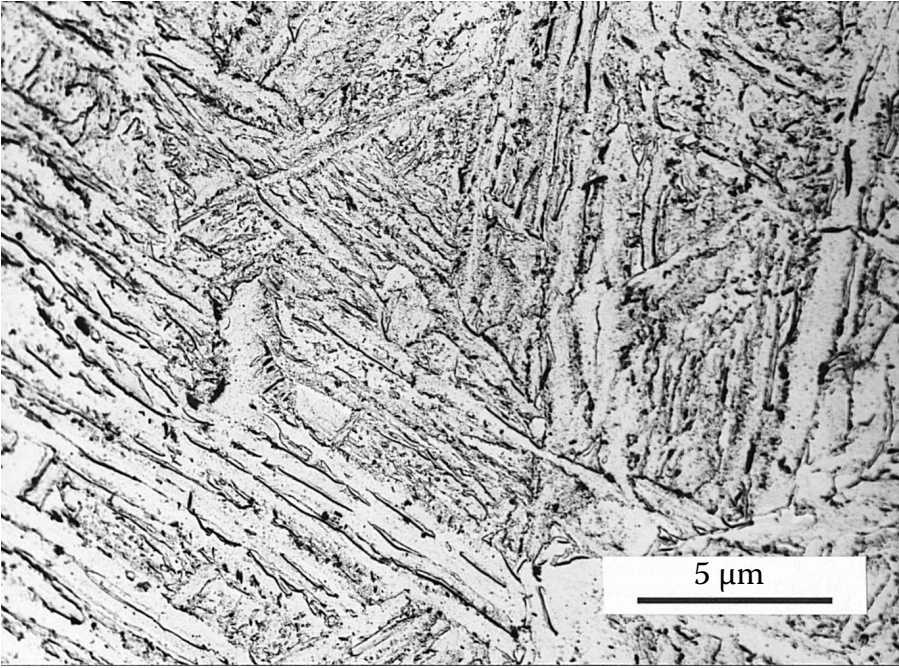


FIGURE 5.42

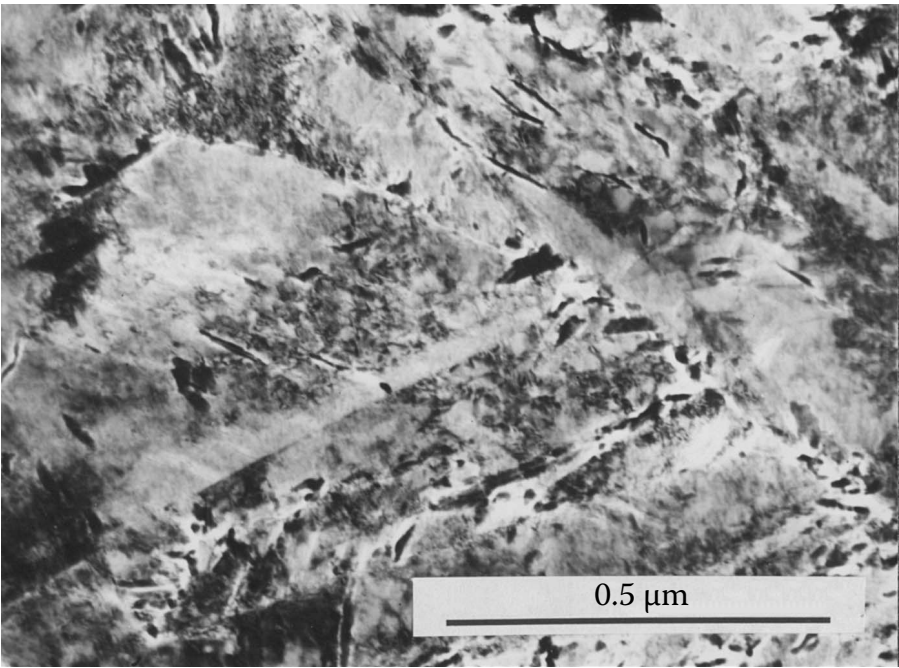


FIGURE 5.43

FIGURE 5.42 When observed at lower magnifications, the structure of lower bainite resembles the structure of lath martensite. The leading reaction is the transformation of austenite into supersaturated ferrite by a shear mechanism, which is typical of a martensitic transformation, followed by precipitation of very fine needle-like carbides in the interior of ferrite laths.

Lower bainite in carbon steel. Replica. Groups of parallel ferrite laths with preferred orientation along $\{111\}_\gamma$ form units in the parent austenite grain.

FIGURE 5.43 Higher-magnification studies reveal the main differences between lower bainite and martensite. The transformation twins that are typical for plate martensite are not present in bainite. The carbides in lower bainite are fine needles that precipitate inside the ferrite in parallel rows as in tempered martensite. In contrast to martensite, whose carbides precipitate on all close-packed crystal planes, lower bainite carbides precipitate predominantly in an identical orientation relationship to the ferrite, that is, about 60° to the direction of the ferrite plate.

Lower bainite in carbon steel. Compare this arrangement of carbides in lower bainite with the tempered martensite shown in [Figure 5.39](#)—the carbides in the martensite lath always show more than one orientation.

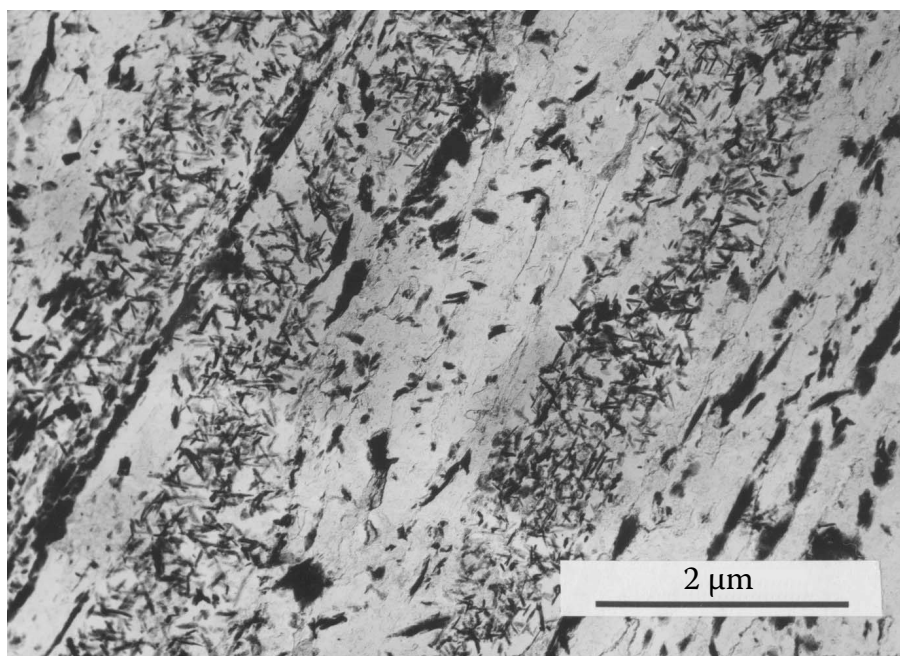


FIGURE 5.44 The differences between the distribution of carbides in lower bainite and martensite can clearly be seen in steels continuously cooled from the austenitizing temperature region at a rate intermediate between the martensite and bainite transformation rate and then tempered for a short time at temperatures close to the start of martensitic transformation.

Steel Fe-0.2C-2Cr, tempered for 8 min at 340°C . The structure is a mixture of plates of lower bainite and martensite. Rod-like carbides (cementite) with a size up to $0.5\text{ }\mu\text{m}$ are observed mainly on interlath boundaries of bainite and in smaller quantities inside the lath interior at an angle of 60° to the lath boundary. The numerous carbides in the adjacent martensite plate are fine needles up to 10 nm long, not more than several nanometers thick, and precipitated in three directions at 60° to the plate boundary.

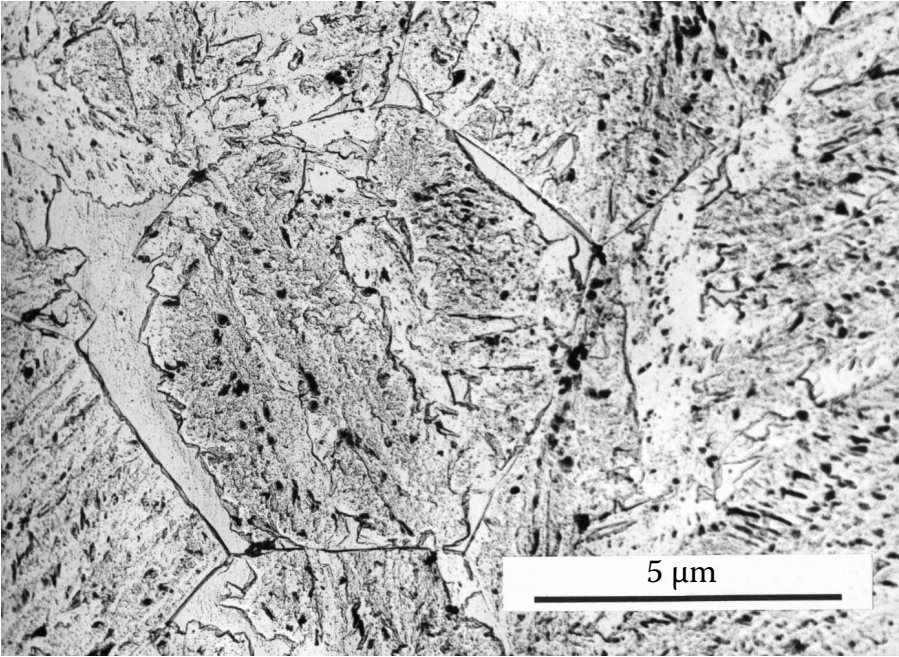


FIGURE 5.45

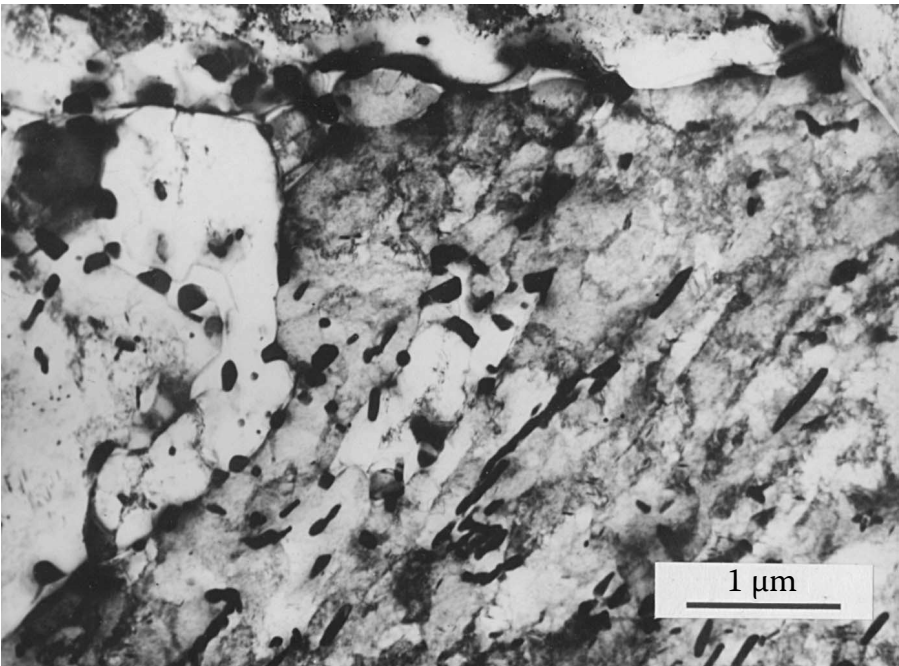


FIGURE 5.46

FIGURE 5.45 Upper bainite is an aggregate comprising ferrite laths and carbides precipitated mainly on lath boundaries. The parallel laths form plate- or feather-shaped regions in the grain. This structure is usually defined as “*feathery*” bainite.

Upper bainite in carbon steel. Replica. The grain boundaries of former austenite grains are covered by some retained austenite, these being the smooth areas in which no carbides are visible.

FIGURE 5.46 The density of dislocations in the interior of the upper bainite laths is rather high, but it is lower than in martensite. The type of boundaries separating laths is also different, being low-angle in the bainite and high-angle in the martensite. The most significant difference is the distribution of cementite particles (Fe_3C): in bainite, they are much larger, precipitate mainly in the interlath regions, and are less dense in the interior of the laths. In steels of higher carbon content, the particles can form nearly a complete carbide film between the laths.

Upper bainite in a carbon steel. High-angle boundaries of former austenite are visible in the upper part, whereas to the left of the micrograph they are covered by relatively large carbides.