
6 Case Studies

Application of TEM in the Solving of Problems in Engineering Practice

Transmission electron microscopy has been applied for more than 50 years as a powerful method for research purposes. Nowadays it is also recognized as a useful technique useful for the investigation of problems arising in engineering practice, especially for the development of new materials, the implementation of new methods for materials processing, and the identification of failures that occur during processing or service.

The main TEM applications are concerned with the following:

1. Phase transformations and structural changes occurring in metals and alloys as a result of the influence of temperature, rate of heating and cooling, and duration of the heat treatment
2. Structural changes occurring during the aging of alloys: precipitation kinetics plus the type, shape, size, volume fraction, and distribution of the strengthening phases
3. Deformation behavior and processes determined by the formation and subsequent changes of the dislocation structure depending on the deformation conditions
4. In-service behavior of alloys—changes in their microstructure under the influence of applied stress, temperature, or environment

6.1 DEFORMATION BEHAVIOR OF NICKEL-SILVER ALLOY IN THE TEMPERATURE RANGE FROM 100°C TO 900°C

A process of edge cracking has been observed during the processing of CuNi10Zn36Mn alloy (Nickel-Silver 10) by hot rolling. Metallographic, scanning electron microscopy (SEM), and TEM observations and mechanical properties testing at elevated temperatures were performed to find the causes for the edge cracking occurrence and to offer a solution to overcome the problem. It was found that a characteristic feature of the deformation behavior of the alloy in the temperature range from 100°C to 900°C was the sharp loss of ductility at 500°C to 550°C. The fracture in this temperature range had a mixed character—brittle and ductile. A TEM investigation of the dislocation structure and the precipitation processes as well as their associated changes over the temperature range from 100°C to 900°C helped to clarify the cause of the minimum in the ductility.

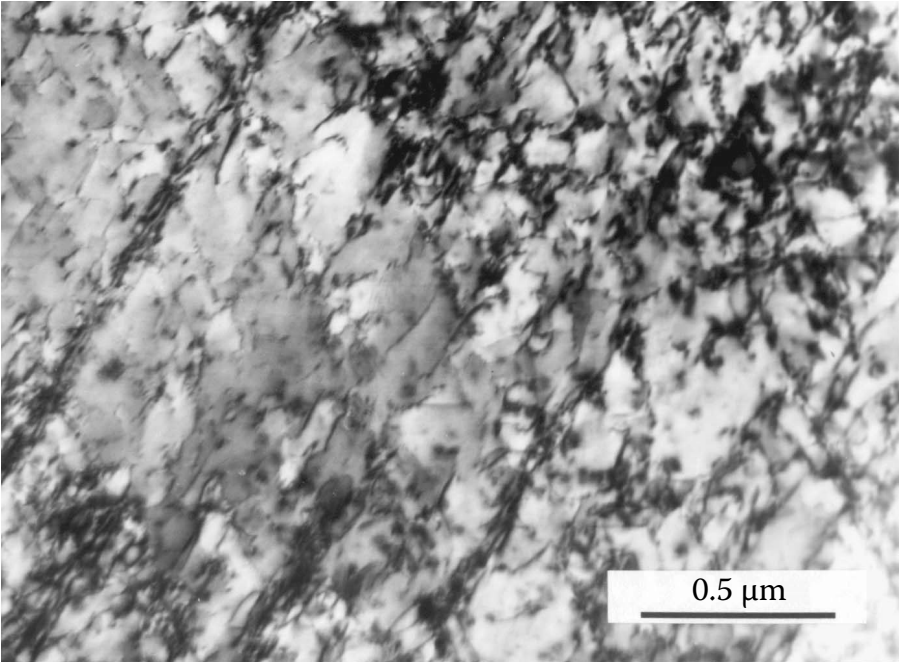


FIGURE 6.1

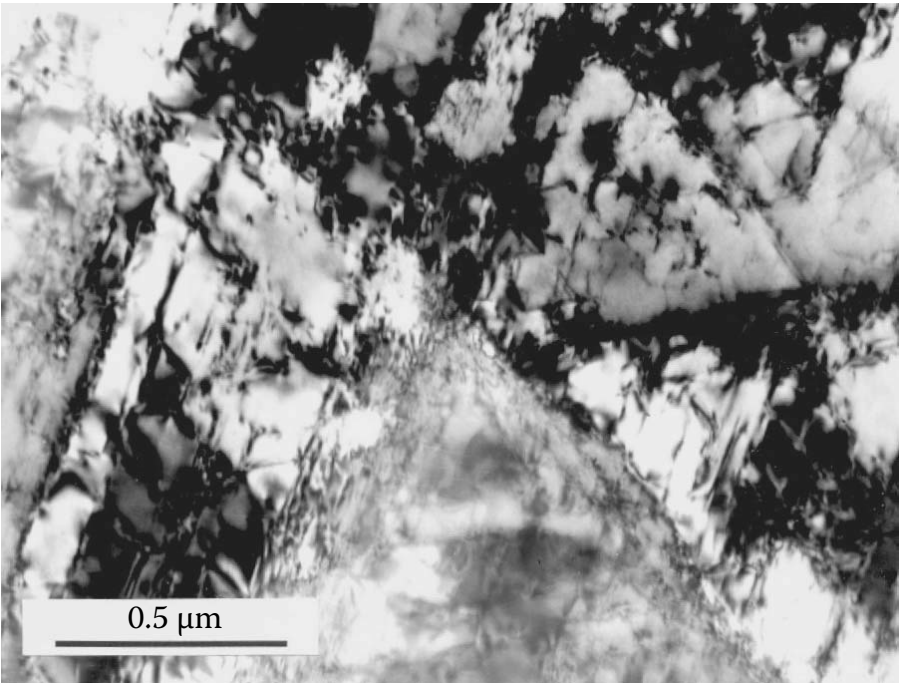


FIGURE 6.2

FIGURE 6.1 *The distribution of dislocations at 100°C is typical of metals of low SFE. The partial dislocations which are separated by ribbons of SF glide in arrows on the close-packed crystal planes of copper.*

FIGURE 6.2 *The planar distribution of dislocations is preserved up to 500°C. The thermally assisted interaction and recombination of dislocations in this temperature range results in formation of deformation bands on the close-packed slip planes.*

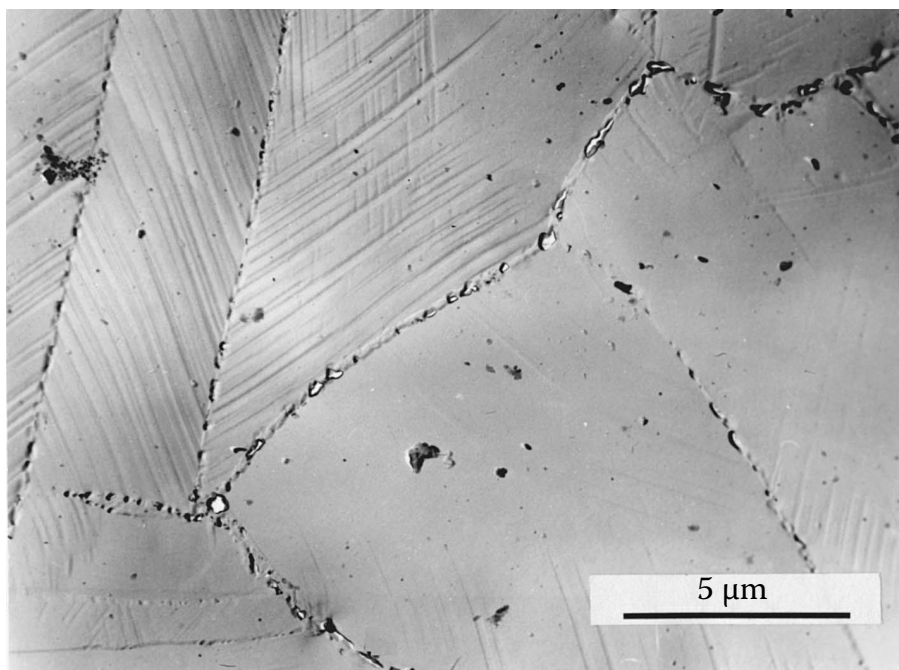


FIGURE 6.3 *The plastic deformation at 500°C is accompanied by accelerated phase precipitation. Numerous particles of tetragonal intermetallic θ -phase (MnNi) precipitate and form chains on both high-angle grain boundaries and coherent and noncoherent twin boundaries, as can be seen in this replica. The precipitates impede the migration of the boundaries, thus lowering the alloy ductility at this temperature.*

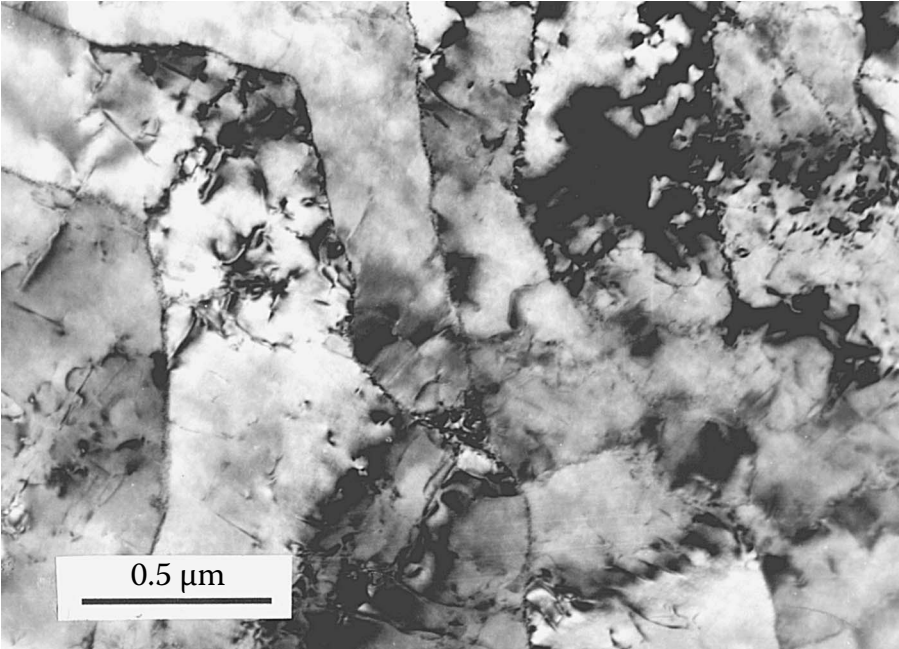


FIGURE 6.4

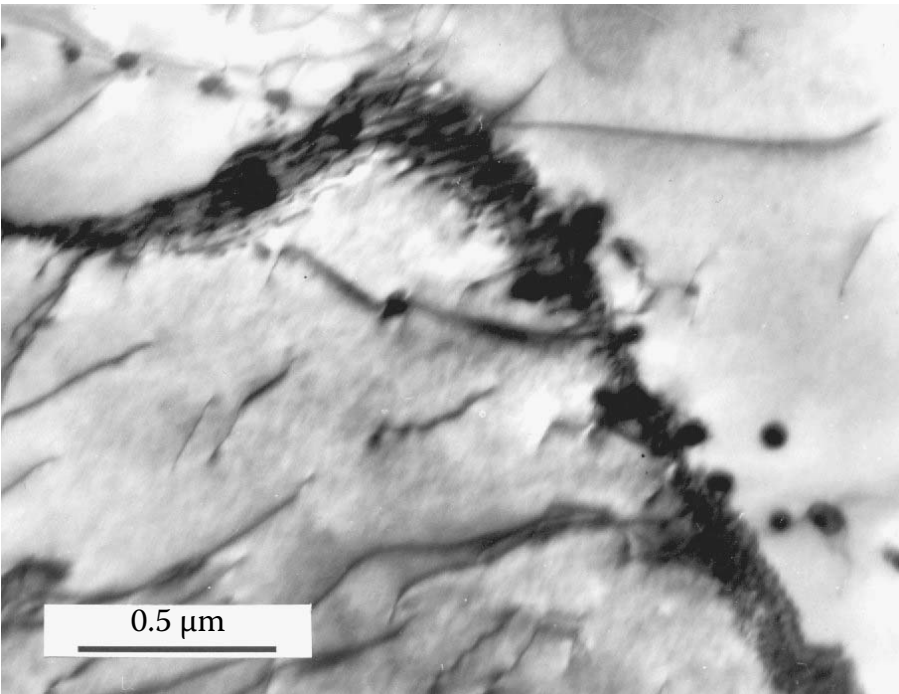


FIGURE 6.5

FIGURE 6.4 At temperatures of 600°C to 700°C, the SFE of the alloy increases and the dislocations move as unit ones. The easy cross-slip and the interaction of the dislocations facilitated by the thermal activation result in the formation of subboundaries and a lower dislocation density. The enhanced diffusion in this temperature range provides for a high mobility of the boundaries and subboundaries, which then are capable of detaching from the precipitates. As a consequence, the ductility of the alloy is restored.

FIGURE 6.5 Very active diffusion processes accompany the deformation at 800°C. The structure is characteristic of dynamic recrystallization: grains of very low dislocation density separated by high-angle boundaries. Isolated θ -particles are present in some of the grains, but because they are not connected to grain boundaries, they cannot impede the migration of the boundaries.

CONCLUSIONS

It was proven that the reason for the loss of ductility and resulting edge cracking was the drop of temperature at the end of the rolling to the temperature range of low ductility. The detrimental effect of the precipitation-induced grain boundary embrittlement was eliminated and the hot workability of the alloy improved by a combination of a grain refinement (modification treatment) and optimization of the hot-rolling temperature-deformation procedure.

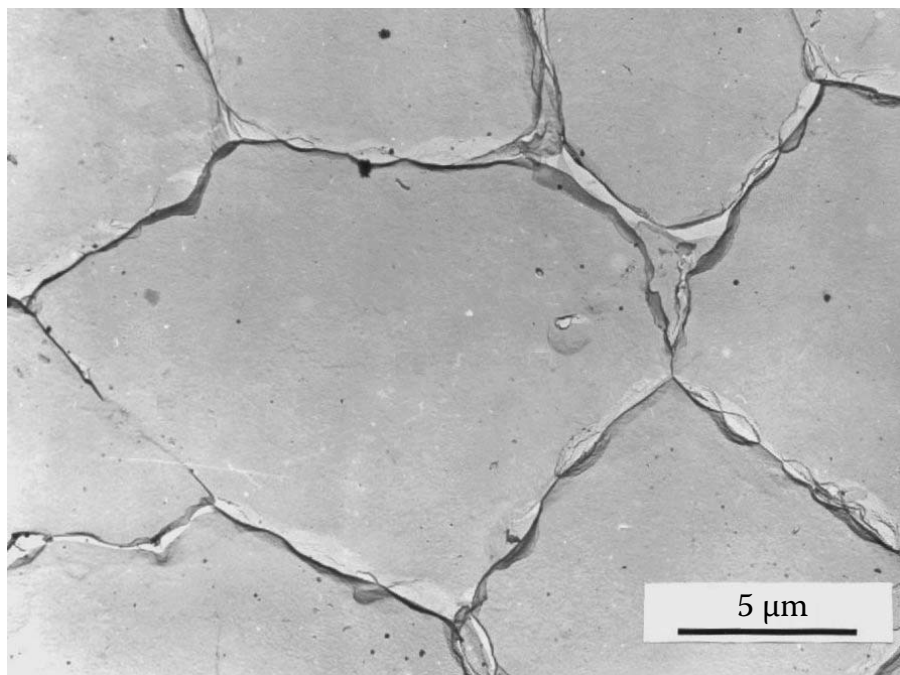


FIGURE 6.6 Replicas prepared from the edge crack zone of the hot-rolled sheets revealed a continuous grain boundary film of coarse precipitates of θ -phase MnNi. This structure corresponds to the structure produced in this alloy by deformation in the low-ductility region covering the temperature range from 500°C to 550°C.

6.2 DISTRIBUTION OF STRENGTHENING PHASES IN PRECIPITATION-HARDENING ALLOYS

The properties of heat-treatable precipitation-hardening alloys are strongly dependent on the distribution of the strengthening phases. The industrial interest in developing technologies for aging and thermomechanical treatments that produce uniform, finely dispersed precipitates in engineering alloys results from the requirements of achieving not only improved mechanical properties but also better corrosion behavior, toughness, fatigue resistance, and so on.

The *solidification conditions* are of great importance to the microstructure and properties of heat-treatable cast alloys. They determine both the type and the morphology of the primary intermetallic phases and thus affect the selection of proper processing parameters (solution treatment and aging temperatures and times) upon which the aging response and the type, distribution, and volume fraction of the strengthening phases depend. The optimal *heat treatment* regimes should be combined with the proper deformation conditions to provide the optimum microstructure and properties of wrought products for a given application. For example, a structure that contains a high density of uniformly distributed coherent or semicoherent fine precipitates provides high strength to aged alloys, whereas the absence of large precipitates on grain boundaries ensures good resistance to intercrystal corrosion, high ductility, and fracture toughness.

The appropriate *thermomechanical treatment* selected for a given alloy is another efficient way to obtain a finer uniform distribution of intermediate precipitates, because the increased dislocation density provides more sites for heterogeneous nucleation of these particles.

TEM studies of the structure of dispersion-hardened alloys facilitate the development and the introduction in practice of new optimal regimes for aging and thermomechanical treatment because they permit the evaluation of the influence of the different processing parameters on the microstructure.

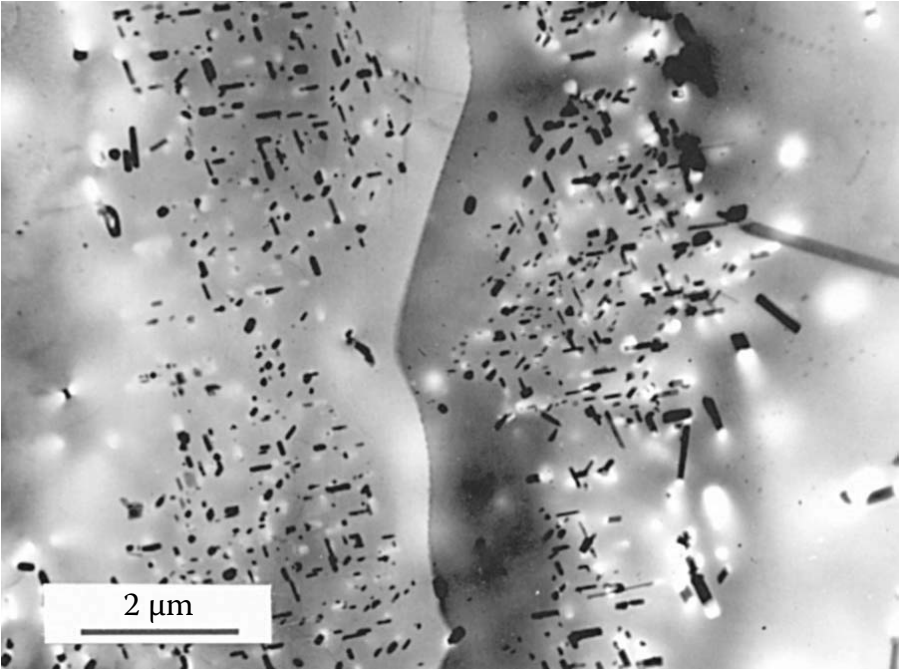


FIGURE 6.7

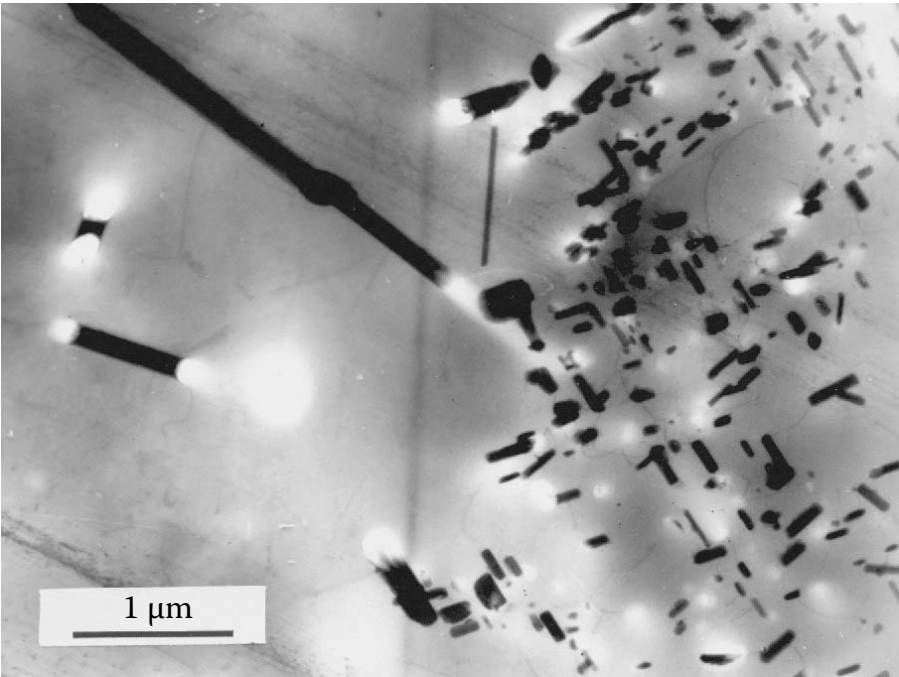


FIGURE 6.8

FIGURE 6.7 Frequently the aging treatment does not produce the desired uniform distribution of strengthening phases. For example, aluminum alloys suffer from the appearance of precipitation-free zones (PFZ)—regions adjacent to grain boundaries where no precipitation has occurred.

Alloy Al-6%Cu-0,2%Ti-0,2%Zr, mold casting with air-cooling, followed by 5 h solution-treatment at 540°C and 12 h aging at 160°C.

FIGURE 6.8 The air-cooling of cast aluminum alloys results in precipitation of coarse intermetallic phases on grain boundaries and solidification of coarse iron-containing needle-like compounds in the grain interior. The coarse needle-like phases are especially dangerous to the mechanical properties of all cast aluminum alloys because they act as stress concentrators and provoke nonuniform distribution of the secondary strengthening precipitations. Most often the inhomogeneous distribution of strengthening phases after aging is due to uneven supersaturation caused by coring and improper quenching regime.

Alloy Al-6%Cu-0,2%Ti-0,2%Zr, mold cast with air-cooling, followed by 5 h solution-treatment at 540°C and 12 h aging at 160°C.

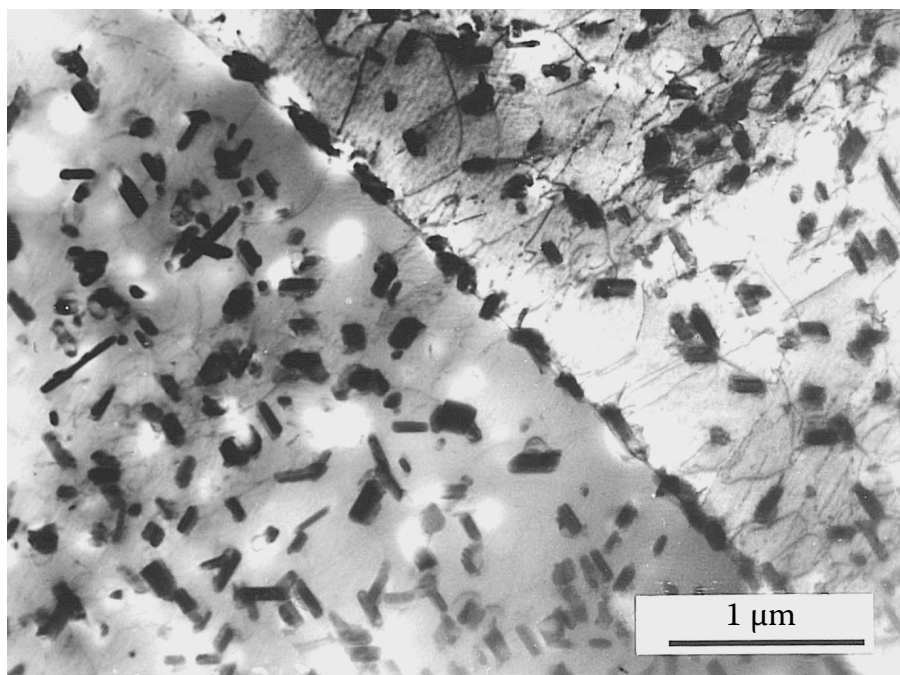


FIGURE 6.9 The amount and the distribution of primary intermetallic phases can be managed by controlling the cooling rate through the mode of casting. Rapid cooling from temperatures just below the solidification temperature results in refined primary precipitates, a higher supersaturation, and a more homogeneous distribution of alloying elements retained in the solid solution. This provides for a shorter aging time and a better aging response, as well as avoiding the formation of unwanted PFZs.

Alloy Al-6%Cu-0,2%Ti-0,2%Zr, die cast and rapidly cooled from 540°C, followed by 5 h solution-treatment at 540°C and 12 h aging at 160°C. The uniform distribution and similar size of the secondary precipitates on the grain boundaries and in the grain interior ensure better mechanical properties compared to the air-cooled casting from the same alloy.

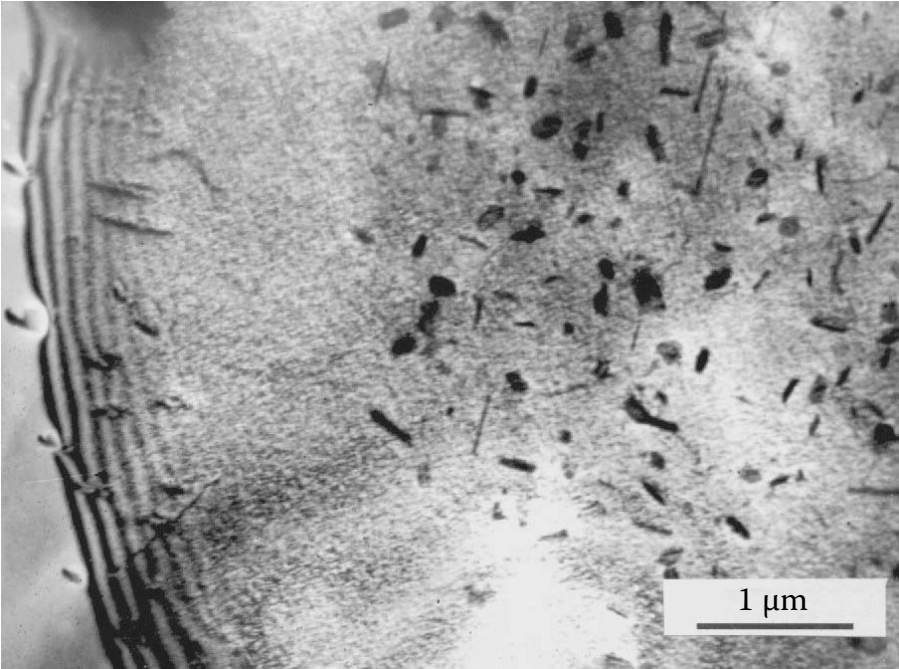


FIGURE 6.10

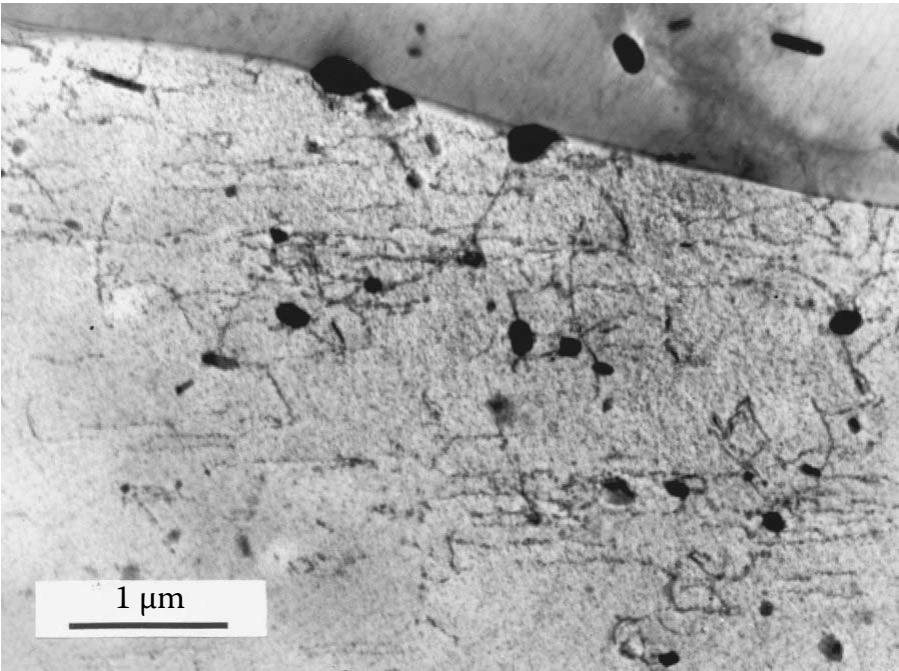


FIGURE 6.11

FIGURE 6.10 The high mechanical strength of this typically wrought aluminum alloy is provided by the disperse precipitation of a rodlike β' -phase (Mg_2Si) and the zone precipitation in the grain interior. The size of the primary intergranular Mg_2Si precipitates is relatively small, but a PFZ about 2 μm wide is seen around the grain boundary. The precipitation of zones occurs throughout the entire grain, including the depleted PFZ region, and this indicates that the zones are composed of mainly copper and chromium atoms.

Alloy 6061 (Al-1%Mg-0.6%Si-0.2%Cr-0.27%Cu), die casting followed by 2 h solution-treatment at 510°C and 12 h aging at 160°C.

FIGURE 6.11 The cold working of a quenched alloy provides numerous sites for subsequent heterogeneous nucleation of intermediate phases. This effect is used in thermomechanical treatments where a controlled degree of deformation is applied prior to aging to improve the properties as well as to accelerate the aging process and to minimize the possible deleterious effect of PFZs in the alloy.

Alloy 6061 (Al-1%Mg-0.6%Si-0.2%Cr-0.27%Cu) cold-forged and then aged for 12 h at 160°C. The heterogeneous precipitation of Mg_2Si in the deformed structure is more uniform, and there are no PFZs. The diminished size of zones, the change of the shape of rodlike Mg_2Si particles to a rounded form, and the presence of some dislocations in the aged structure all contribute to the improved properties of the thermomechanically treated alloy.

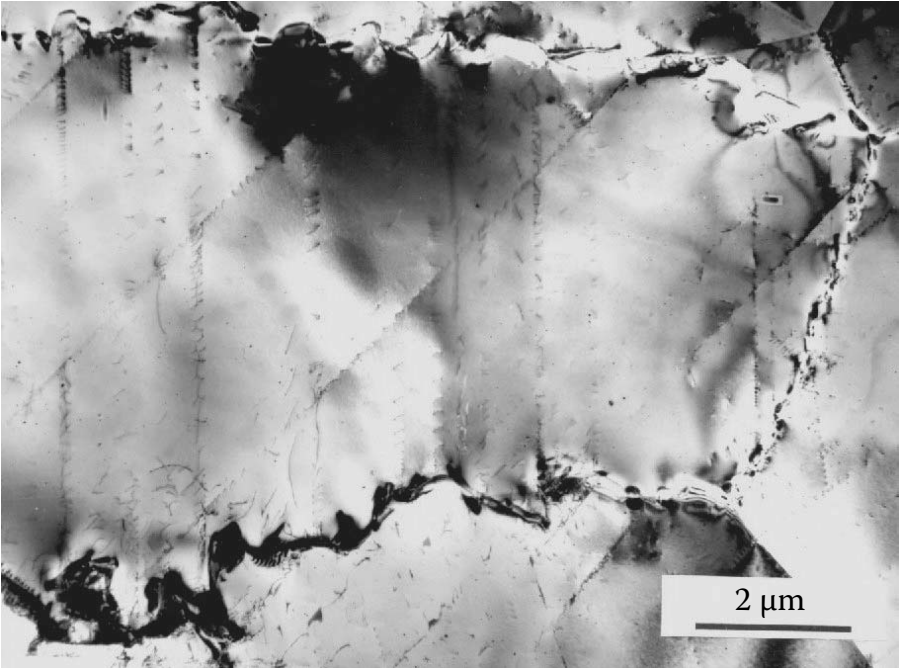


FIGURE 6.12

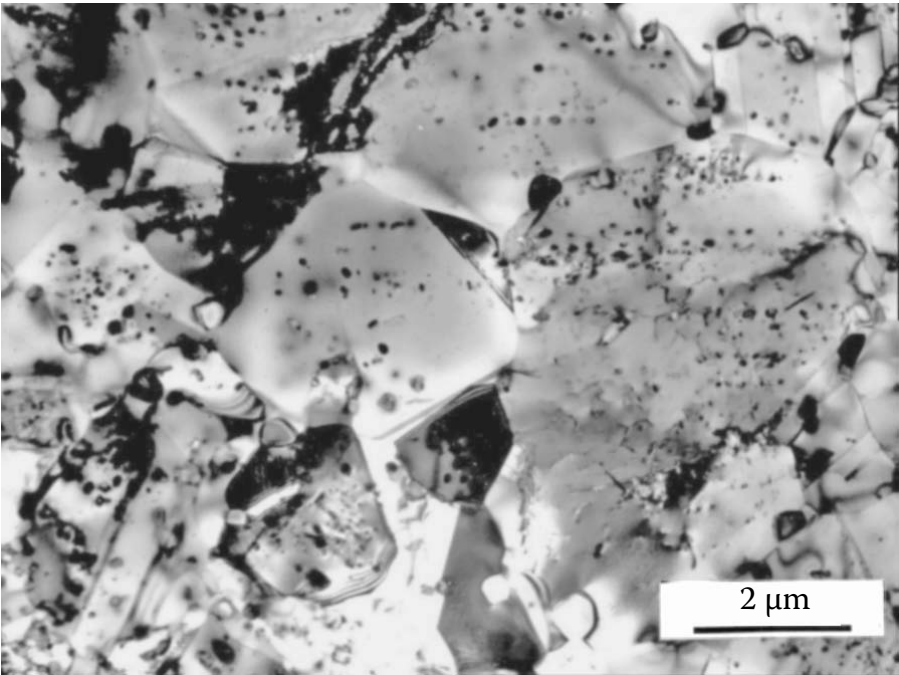


FIGURE 6.13

FIGURE 6.12 The preferential precipitation of phases on the grain boundaries greatly deteriorates the mechanical properties of alloys and can promote intergranular corrosion. This is a serious problem for the high-chromium austenitic stainless steels in the “sensitizing” temperature range from 500 to 900°C in that chromium-rich phases (carbides, nitrides, intermetallics) precipitate on grain boundaries.

Austenitic nitrogen steel Fe-18Cr-14Mn-0.6N, quenched from 1150°C and then tempered for 30 min at 700°C. The most dangerous temperature range for the high-nitrogen austenitic steels lies between 550°C and 850°C, when, supersaturated by nitrogen, austenite decomposes by a discontinuous mechanism. The process starts with the precipitation of Cr₂N particles on grain boundaries (see Chapter 5, Section 5.3).

FIGURE 6.13 The numerous defects of crystal structure introduced by plastic deformation prior to aging serve as centers for second-phase nucleation and can change the precipitation mechanism from localized grain-boundary precipitation to uniform continuous precipitation. Suppression of cellular precipitation by applying severe cold plastic deformation prior to aging is also observed in nonferrous alloys—for example, copper-beryllium.

Austenitic nitrogen steel Fe-18Cr-14Mn-0.6N, quenched from 1150°C, cold worked with 75% reduction, and tempered for 10 min at 700°C. The severe cold work stimulates the precipitation of uniformly distributed globular nitrides in the grain interior. The large number of particles provides numerous recrystallization centers and hence retards grain growth. The final structure of ultra-fine grains and uniformly distributed nitrides provides excellent mechanical properties and good corrosion resistance to the material.

6.3 SPECIFIC FEATURES OF THE STRUCTURE DEVELOPED DURING DEFORMATION IN SUPERPLASTIC STATE

The ability of metallic material to exhibit an extensive plastic deformation—up to 1000% elongation without work hardening—is termed *superplasticity*. Superplasticity is a state used for applying superplastic forming (SPF) and hot sizing to fabricate complex objects and parts for aerospace, automotive, and other applications.

Superplastic behavior is observed in metallic materials in two cases: if they possess an ultra-fine-grained structure (in the case of *structural superplasticity*) or if they undergo a phase transformation during deformation or thermocycling (in the case of *transformation superplasticity*).

The basic deformation mechanism of structural superplasticity is grain boundary sliding. Several preconditions are required to achieve this type of superplasticity: (a) the structure should be fine-grained with high-angle grain boundaries; (b) the grain size should vary from 0.5 μm to not more than several micrometers, a value comparable with the size of subgrains; and (c) the deformation should be carried out under special temperature-strain rate conditions.

The examination of the structural phenomena that underlie the plastic deformation in the superplastic state has to be undertaken on TEM thin foils due to the very finely dispersed structure.

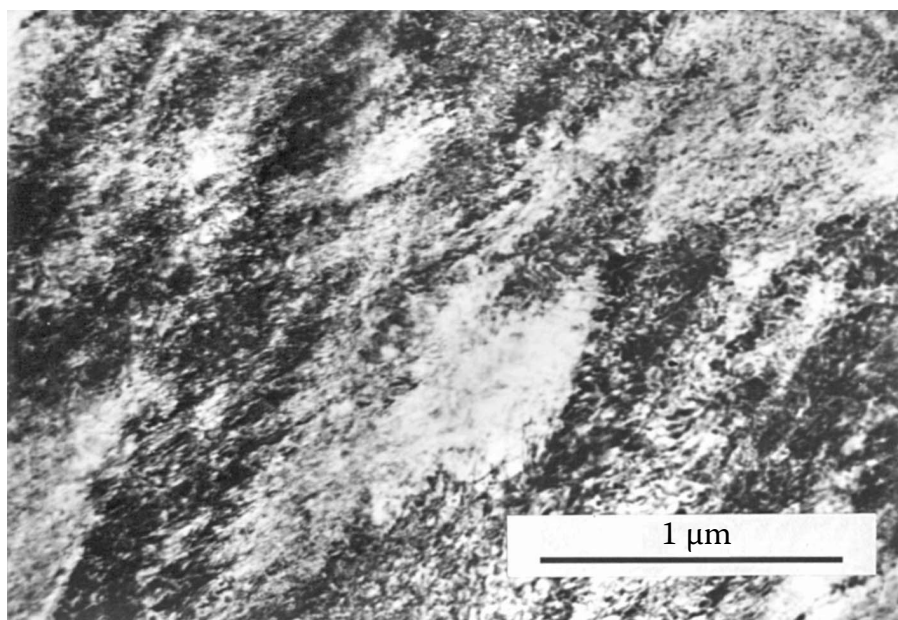


FIGURE 6.14 One of the most frequently used methods to produce an ultra-fine initial structure suitable for deformation in superplastic condition is severe cold deformation followed by a controlled recrystallization annealing. The severely deformed structure provides numerous nucleation sites which are necessary for the future homogeneous precipitation of a second phase.

Austenitic nitrogen steel Fe-18Cr-14Mn-0.6N, after cold rolling to a 75% reduction. The severe plastic deformation ensures the necessary extremely high dislocation density.

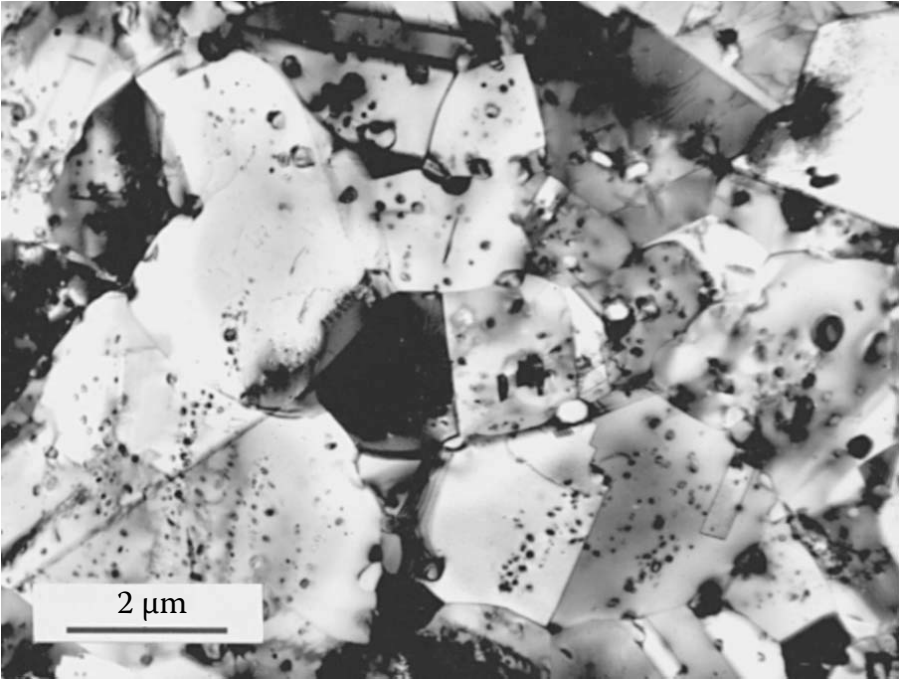


FIGURE 6.15

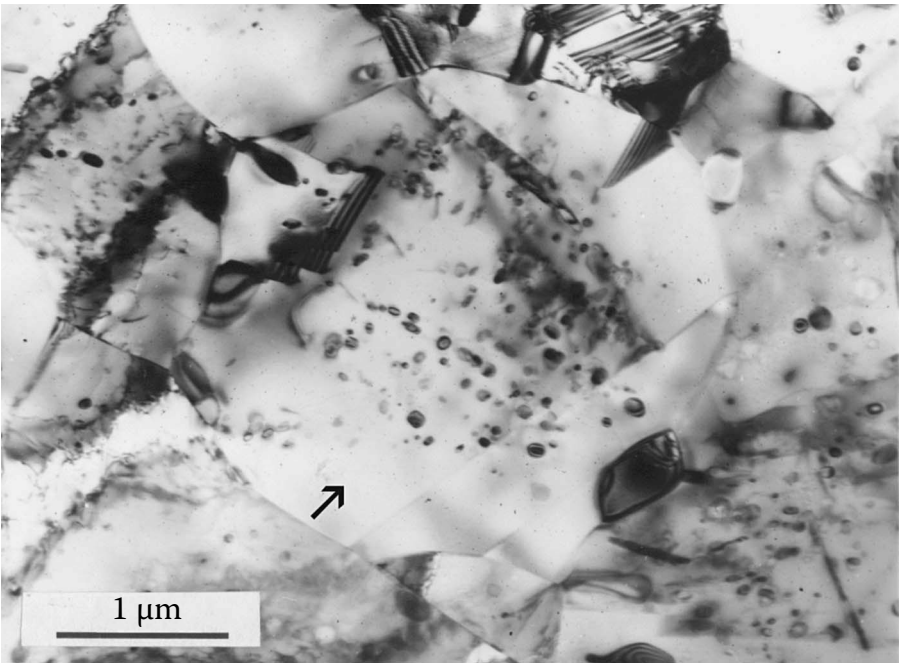


FIGURE 6.16

FIGURE 6.15 Numerous nitride particles precipitate uniformly during the annealing for 60 min at 800°C of the severely deformed austenitic nitrogen steel Fe-18Cr-14Mn-0.6N. The particles ensure numerous recrystallization centers and simultaneously act as barriers for grain growth. As a result, the average diameter of the recrystallized grains is about 3 to 4 μm . The obtained structure is suitable for further deformation in superplastic conditions.

FIGURE 6.16 The fine-grained austenitic nitrogen steel Fe-18Cr-14Mn-0.6N was tensile loaded at a strain rate of $\dot{\epsilon} = 1.10^{-3} \text{ s}^{-1}$ at 800°C up to 100% elongation without fracture. It can be seen from the micrograph that the Cr_2N particles preserve their size during the deformation, thus impeding the migration of grain boundaries and ensuring the stability of the grain size. Note the zones free of particles around grain boundaries that are normal to plastic flow direction (shown by arrow). They arise as a result of the accommodation processes that run in the regions around boundaries but not in the grain interior. Another unique feature of the deformation in the superplastic regime is the absence of dislocations. This shows that the main deformation mechanism does not rely on dislocations in the grain interior.

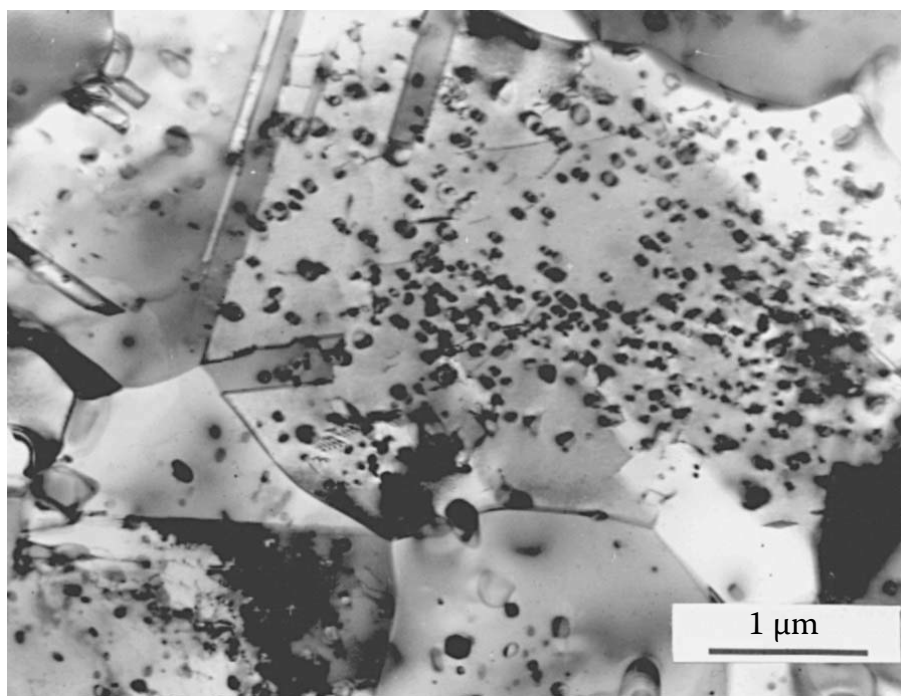


FIGURE 6.17 The elongation of the fine-grained austenitic nitrogen steel Fe-18Cr-14Mn-0.6N under deformation at the same conditions as in [Figure 6.16](#) reached 400% before fracture. The observation of thin foils taken from the region just below the fracture showed the presence of only a few dislocations in the interior of the grains. New elements visible in the micrograph are the slight grain growth and the appearance of vacancy complexes or loops in the interior of the grains.

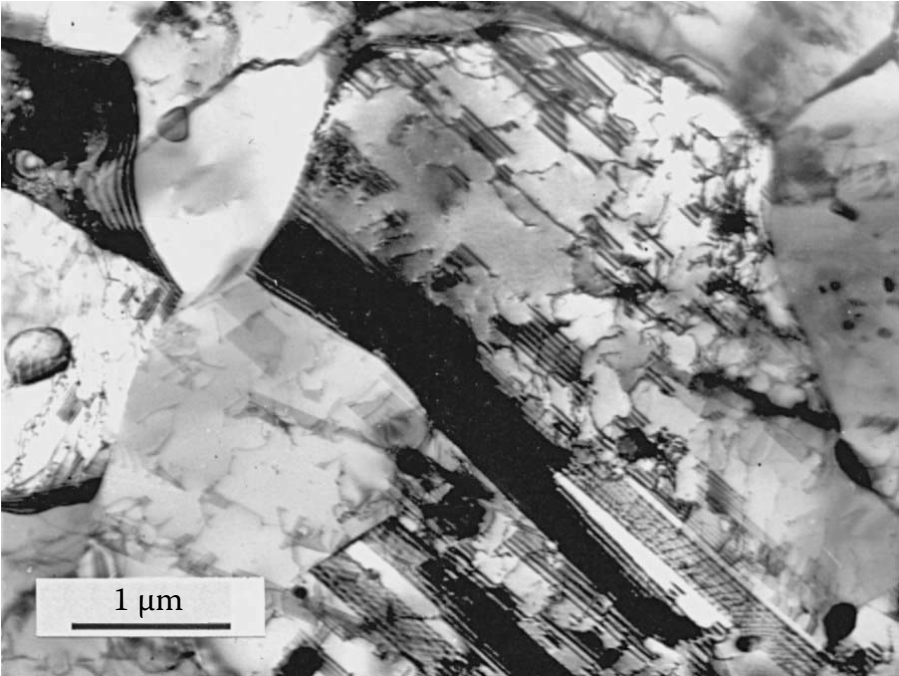


FIGURE 6.18

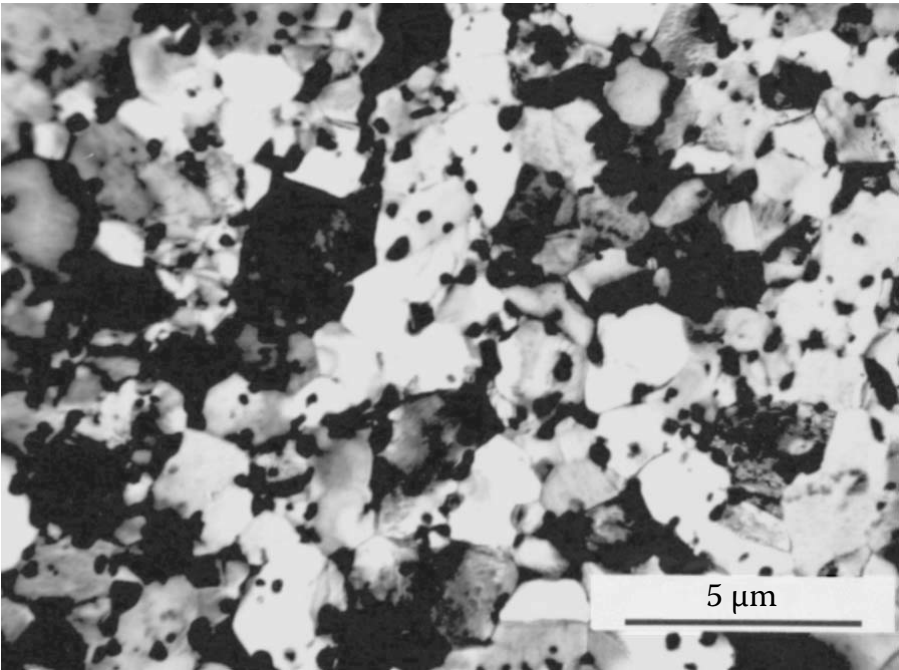


FIGURE 6.19

FIGURE 6.18 *The superplasticity is manifested only in a definite temperature-strain rate deformation range, which is specific to a given alloy. Deformation beyond this range involves grain growth and grain elongation parallel to the flow direction, increase of dislocation density in the grains, and work hardening. These features, which are typical for conventional deformation at elevated temperatures, can be seen in the micrograph of the same fine-grained austenitic nitrogen steel Fe-18Cr-14Mn-0.6N, which was deformed at the same temperature of 800°C but at a higher strain rate of $\dot{\epsilon} = 1.10^{-2} \text{ s}^{-1}$. The fracture has occurred at 80% elongation. The elongated grains with dislocations in their interior are a definite indication of deformation outside the optimum range for superplasticity.*

FIGURE 6.19 *Another method to produce structure with ultra-fine grains necessary for the superplastic deformation is through the thermomechanical treatment of alloys. This method proved itself suitable for the fine-grained Zn-1.2%Mn alloy, in which an average grain size of about 1 μm was obtained by extrusion to an 85% reduction at 275°C. The grain refinement was achieved through the precipitation of a ζ -phase (MnZn_{13} intermetallide) during the deformation.*

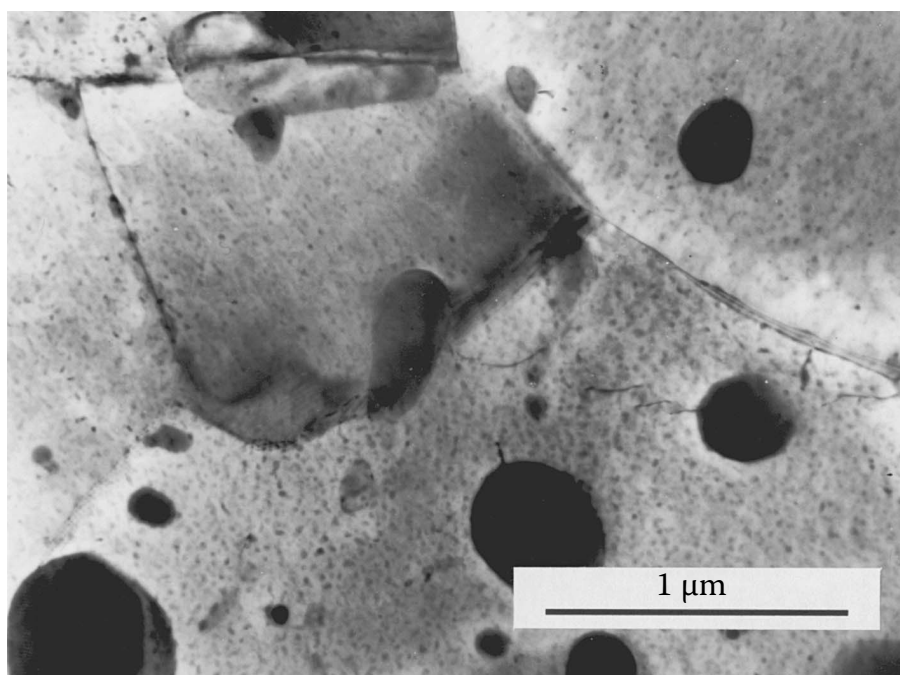


FIGURE 6.20 *The deformation of the ultra-fine-grained Zn-1.2%Mn alloy at a deformation rate $\dot{\epsilon} = 1.10^{-3} \text{ s}^{-1}$ at 300°C ensured an elongation of 680%. The observations of thin foils showed that the principal phenomena controlling the superplastic deformation in these conditions was the plastic flow in the grain-boundary regions. As in the fine-grained austenitic steel (see Figures 6.9 and 6.10), the grain interior of the Zn-1.2%Mn alloy remains almost free of dislocations. The single dislocations present are usually bound to the interfaces of larger MnZn_{13} particles. This shows that the flow is realized mainly by grain boundary slip and that the interfaces of larger precipitates take part in the accommodation process also.*



FIGURE 6.21 A typical feature of the microstructure of ultra-fine-grained Zn-Mn alloys when deformed at temperatures lower than or at a strain rate higher than the optimum for superplasticity is the appearance of vacancy loops in the grains. The appearance of point defects can be explained by insufficient diffusion flow that is unable to ensure the complete accommodation of adjacent grains. This is demonstrated in the micrograph of an ultra-fine grained Zn-0.7%Mn alloy after deformation at a deformation rate $\dot{\epsilon} = 1.10^{-3} \text{ s}^{-1}$ at 300°C. The maximum elongation was only 60%. Note that the shape of MnZn₁₃ particles is not rounded but somewhat faceted and that their size is much larger than in the Zn-1.2%Mn alloy (see [Figure 6.19](#)). Obviously the applied temperature-strain rate interval, which was optimal for the Zn-1.2%Mn alloy, is not suitable for the lower manganese alloy to reach superplastic state.

6.4 THE INFLUENCE OF MODIFICATION AND HEAT TREATMENT ON THE MICROSTRUCTURE OF ALUMINUM-SILICON ALLOY

Proper control over solidification is a first step toward controlling the metallurgical structure, metallurgical quality (soundness, homogeneity), mechanical strength, and physical properties of the castings.

Modification is a term used to denote the addition of “modifying agents”—small quantities of certain elements—to the molten metal to produce melts of better fluidity and feeding characteristics, to achieve better production rates, and finally to obtain castings with improved quality and mechanical properties.

The refinement of the as-cast grain size has proved to bring great benefits to numerous cast and wrought alloys. *Grain refinement* is a term that comprises the decrease in the size of grains or of dendritic cells by controlled additions to the molten metal before casting of “grain refiners,” that is, selected elements in the form of master alloys.

The modification is widely applied to the most important commercial cast Al-Si alloys. In this case, the term *modification* refers to the process of treating or cooling the metal in such a way that the eutectic silicon grows as small, rounded fibrous particles instead of coarse, angular primary grains.

The effect of the cooling rate is limited within the thick sections of the castings, especially in sand or permanent molds. In this case, the modification is accomplished by elemental additions. Foundries have recognized for many years sodium metal or sodium salts and now strontium to be the best modifiers for eutectic and hypoeutectic Al-Si alloys. For example, modification is used to increase the strength and ductility of the non-heat-treatable AlSi12 alloy. Heat treatment of modified Al-Si-Mg alloys provides a further increase in strength.

The structure of Al-Si alloys is usually studied using TEM replicas. This is due to the large difference in the electrochemical properties of the Si and Al phases, which prevents thin foils of good quality from being obtained by the conventional electropolishing technique. Nowadays the invention of ion milling has overcome this limitation.

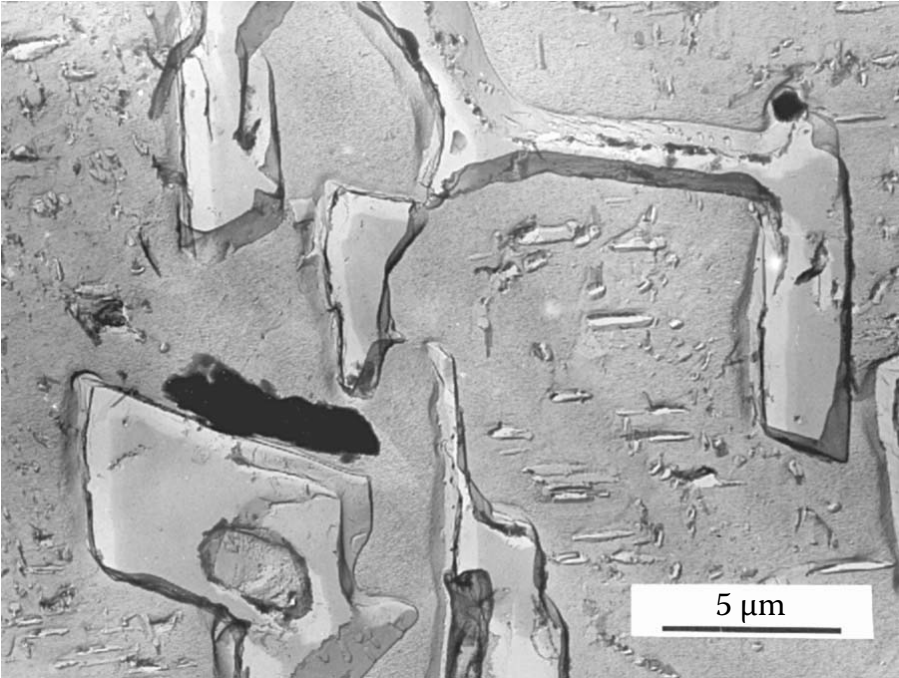


FIGURE 6.22

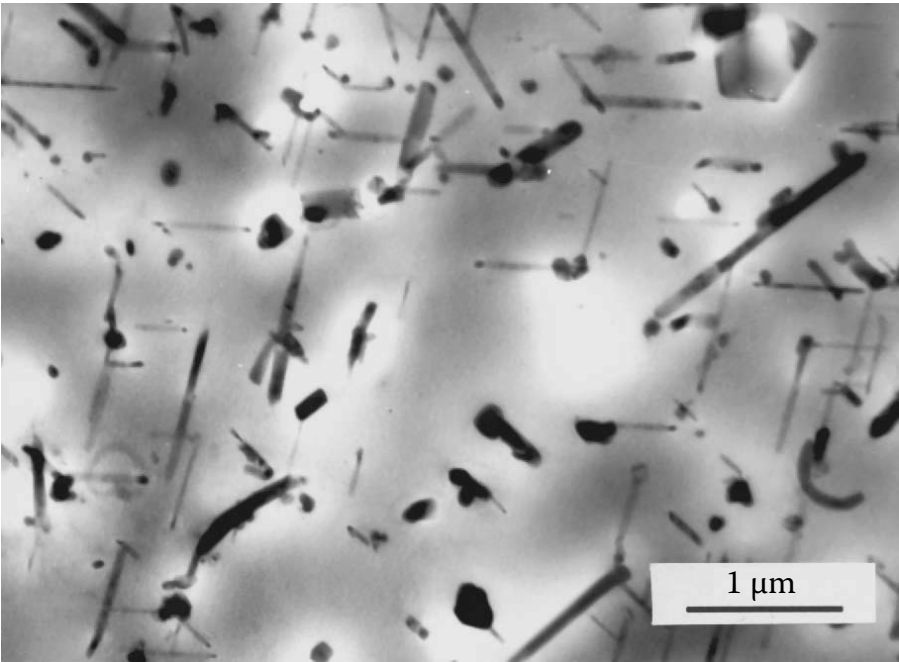


FIGURE 6.23

FIGURE 6.22 *The combined effect of modification and heat treatment on the microstructure was studied in a heat-treatable Al-12%Si alloy containing additions of Mg, Cu, Ni, and Cr. The alloy was developed for counter-pressure casting and intended for service at elevated temperatures. The slow cooling of all cast, nonmodified Al-Si alloys produces, as can be seen in the replica, large dendritic α_{Al} solid solution cells surrounded by coarse eutectic structure built of plate-like silicon particles. The fine needles in the cell interior are intermetallic phases that have precipitated during the slow cooling of the casting.*

FIGURE 6.23 *This micrograph shows a rare observation of small areas of the α_{Al} -solid solution in electropolished thin foil of the same alloy as in Figure 6.22. Several dispersion phases act as strengthening agents: CuAl_2 , Mg_2Si , Cu-Mg-Al , and Al-Cu-Ni . They all precipitate from the supersaturated α_{Al} solid solution in needle-like form and can be differentiated in the TEM using electron diffraction, energy dispersion analysis (EDS), or electron energy loss analysis (EELS). The heat resistance of the alloy is provided mainly by the complex nickel-containing phases.*

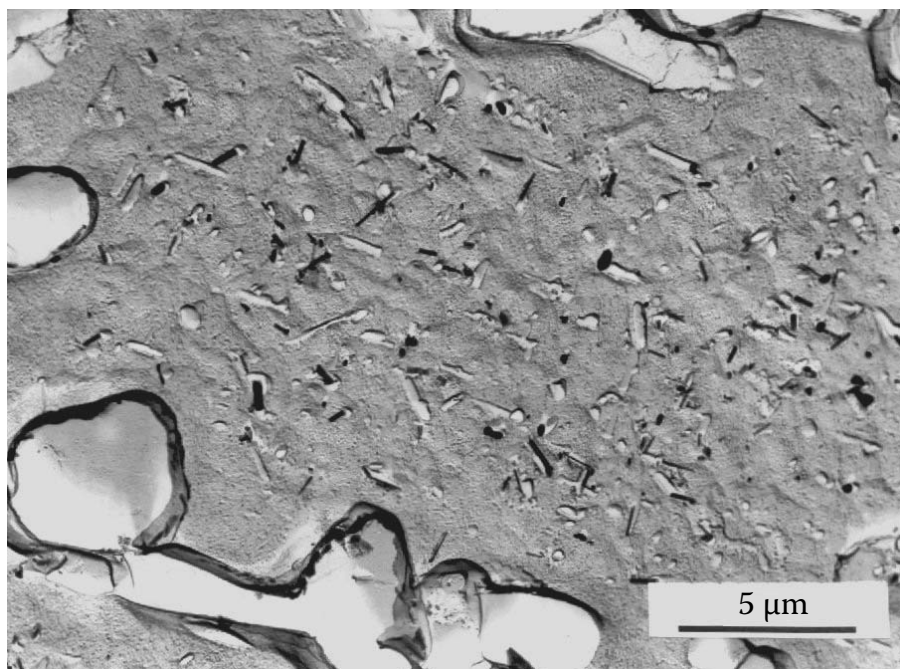


FIGURE 6.24 *High-temperature solid solution heat treatment prior to quenching of all nonmodified Al-12%Si alloys leads to some spheroidization of the silicon particles in the eutectic, but does not influence their size or the dendritic cells' diameter.*

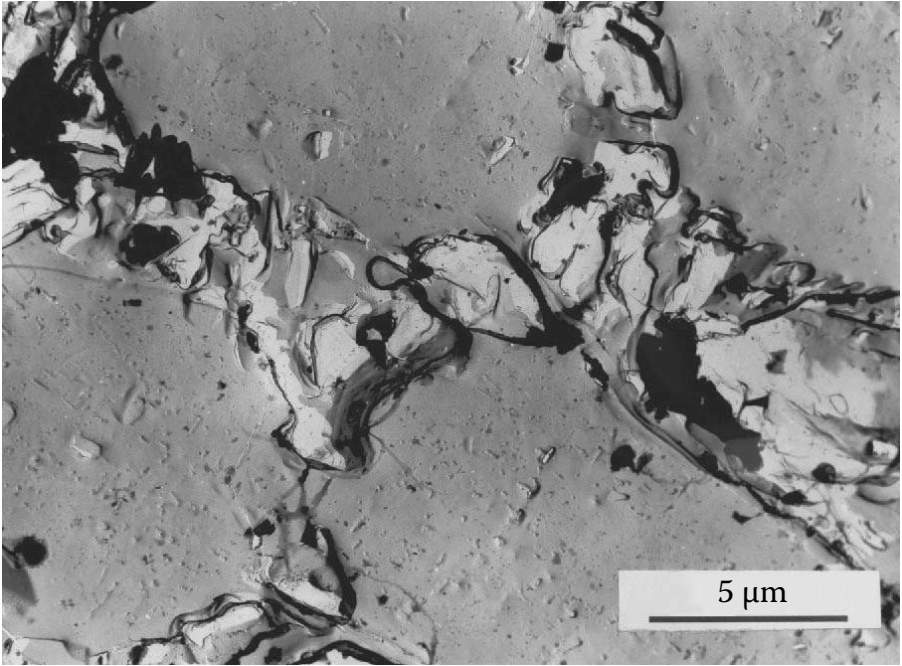


FIGURE 6.25 *The addition of specific quantities of modifying agents—in the form of an Al–Sr-master alloy or sodium salts—alters the shape of the coarse plate-like silicon particles to a rounded form while also restricting their growth. In addition, it causes refinement of dendrite cells. The modified Al–Si eutectic and the refined dendritic cells result in an improved yield strength and especially in an improved elongation of the alloy.*

6.5 SIGMA-PHASE FORMATION IN A DUPLEX STAINLESS CHROMIUM-MANGANESE- NITROGEN STEEL

The prolonged holding of high-alloyed stainless steels at elevated temperatures causes the precipitation of intermetallic compounds, which withdraw a significant amount of the alloying elements (Cr, Mo, Ni) from the austenite. The most serious result of this process is the depletion of austenite of chromium, the latter being the main element that provides the corrosion resistance of the steels. The precipitation of chromium-rich phases occurs at grain boundaries, thereby deteriorating both the mechanical properties and the resistance to intergranular corrosion. The intermetallic phases, which can form in the high-alloyed stainless steels, are designated with Greek letters: σ (sigma), ζ (zeta), and χ (chi). A typical member of this group of phases is the σ -phase—a hard and brittle Fe-Cr intermetallide with a stoichiometry that depends on the chemical composition of the steel.

The mechanism of σ -phase formation is presented here for the duplex Fe-18%Cr-12%Mn-0.03%C-0.2%N steel, but it is representative for all high-chromium-containing stainless steels.

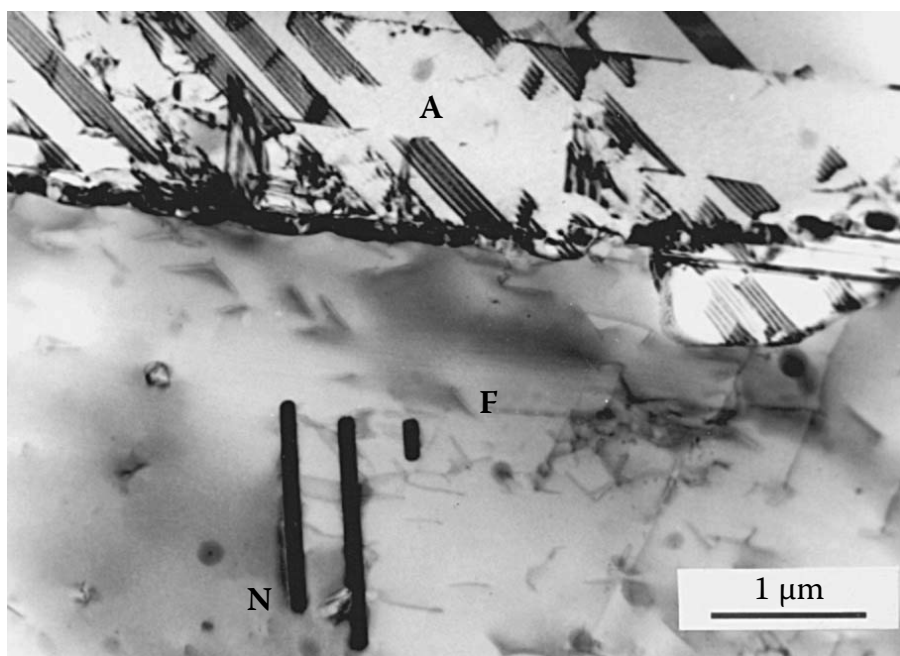


FIGURE 6.26 The structure of quenched nitrogen-alloyed Cr-Mn steels depends on the nitrogen content: they are austenitic at nitrogen content higher than 0.3% and ferrite-austenitic at lower concentrations. The equilibrium solubility of nitrogen in α -iron at 1100°C is less than 0.001%N, which means the ferrite of the low-nitrogen steels is supersaturated with nitrogen and easily decomposes on quenching.

Fe-18Cr-12Mn-0.03C-0.2N steel, quenched from 1150°C. Needle-like Cr_2N particles (marked by N) have precipitated from ferrite (marked by F) during quenching. Austenite (marked by A) has the typical structure of a low-SFE alloy—planar distribution of partial dislocations, separated by ribbons of SFs.

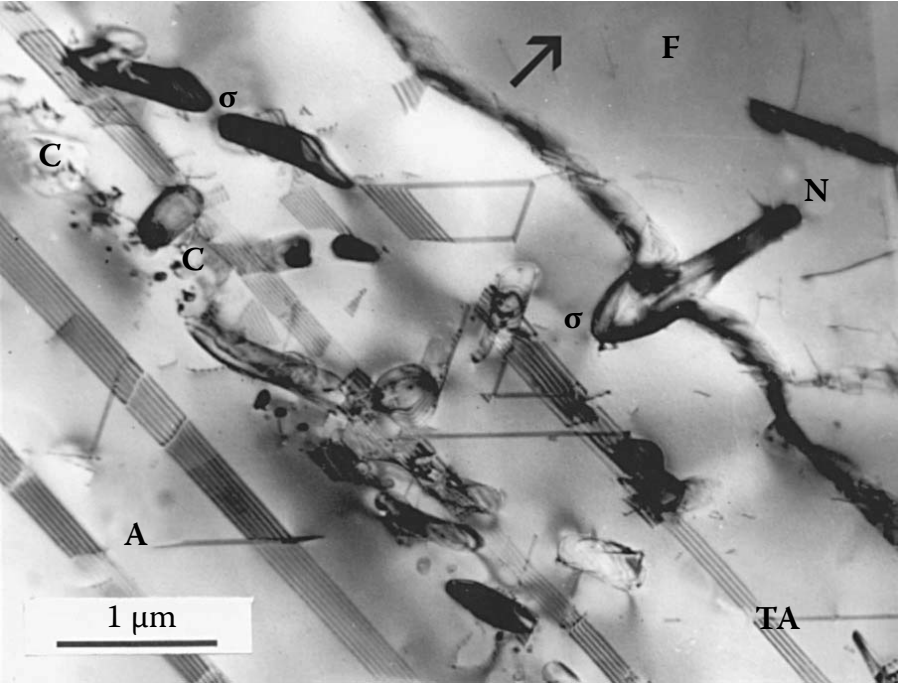


FIGURE 6.27

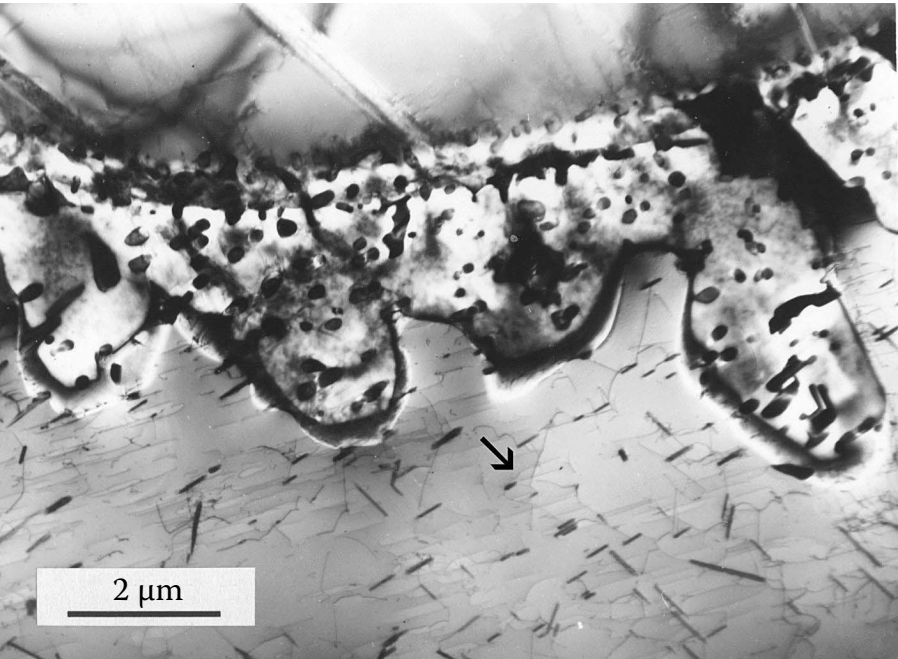


FIGURE 6.28

FIGURE 6.27 When the steel is heated and then held for a prolonged period at a temperature in the range from 550°C to 850°C, disperse chromium-rich $M_{23}C_6$ particles precipitate on the ferrite–austenite boundaries. They consume the chromium from the boundary region, thus inducing transformation of adjacent ferrite (F) into austenite (A). When all available carbon from this region is consumed by the precipitating carbides, decomposition continues by the nucleation and growth of σ -phase in the transformed austenitic grain (TA).

Fe-18Cr-12Mn-0,03C-0,2N steel, quenched from 1150°C and tempered for 30 min at 700°C. The position of the parent austenite-transformed austenite boundary can be seen due to the chain of fine carbides (marked by C). Note the chromium-rich Cr_2N needles (marked by N), which transform directly into σ -plates.

FIGURE 6.28 The precipitation of σ -phase is accompanied by the migration of the new high-angle boundary between the transformed austenite and the parent ferrite. It propagates into ferrite, thus producing a cell of transformed austenite, containing σ -particles.

Fe-18Cr-12Mn-0,03C-0,2N steel, quenched from 1150°C and tempered for 60 min at 700°C. The direction of cell propagation is shown by the arrow.

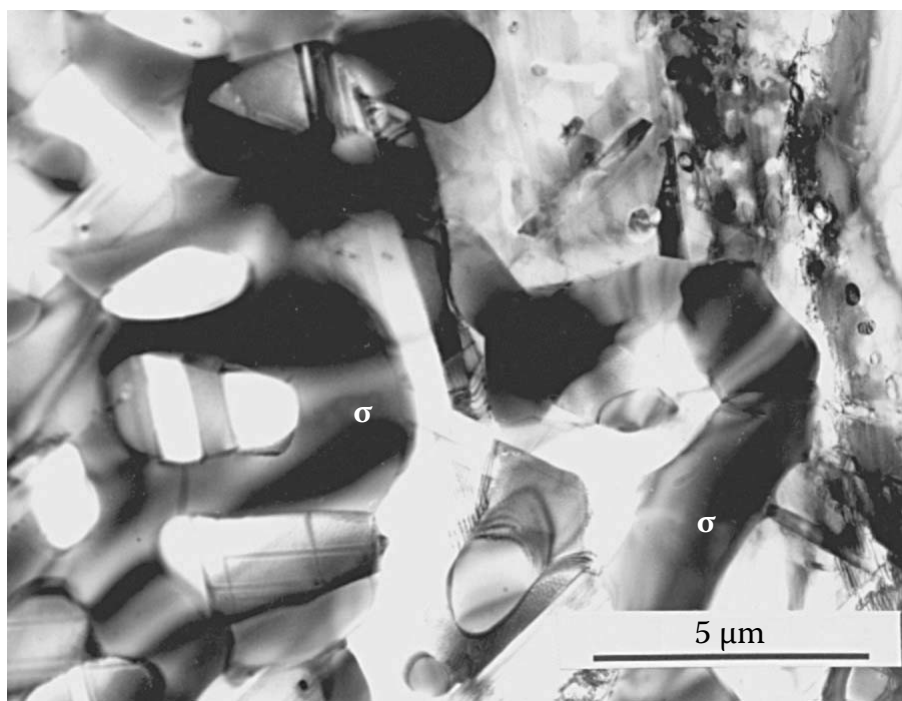


FIGURE 6.29 After a sufficiently long holding period at a higher temperature and with a sufficiently high amount of chromium present, the σ -phase grows in a skeletal form that can occupy all the former ferritic grains.

Fe-18Cr-12Mn-0,03C-0,2N steel, quenched from 1150°C and tempered for 18 h at 700°C.

6.6 CORROSION RESISTANCE OF PARTICULAR STRUCTURE COMPONENTS OF AUSTENITIC STAINLESS STEELS

TEM investigations of thinned foils that have been exposed to the action of a corrosive media can reveal the behavior of particular components of the microstructure to that media as well as permit to study the initial stages of real corrosion processes. This can provide useful information regarding the role of the microstructure and yield a deeper insight into the processes occurring during real service conditions.

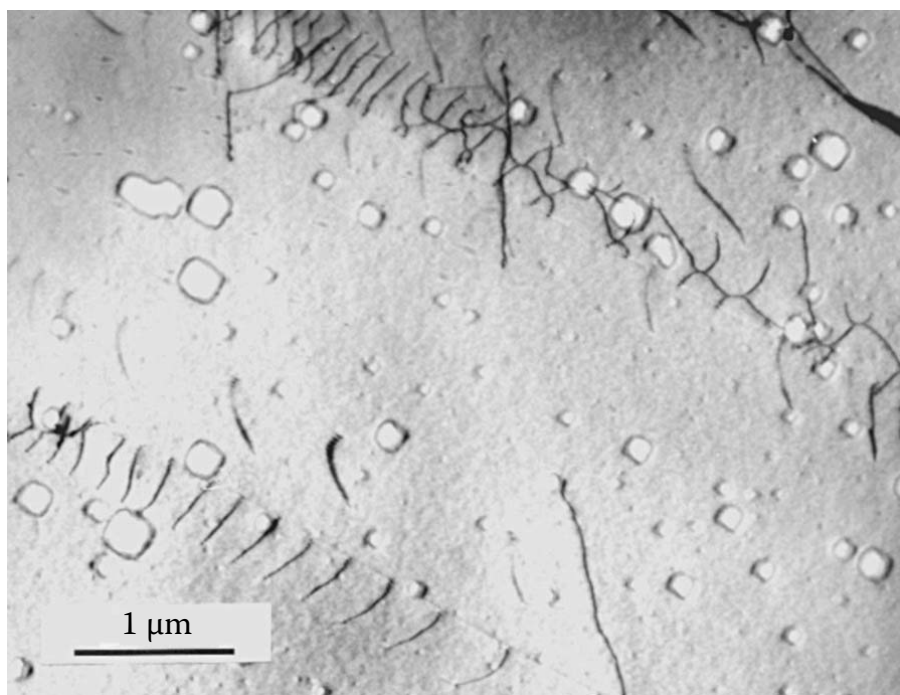


FIGURE 6.30 The term *uniform or general corrosion* covers all nonlocalized processes of physical-chemical interaction at the interfaces between metals and alloys and the environment. The main feature of this type of corrosion is that it develops uniformly over the whole surface of the material.

Fe-18Cr-12Mn-0.03C-0.6N steel, quenched from 1150°C. The thin foil was exposed for 72 h to the action of 6%FeCl₃·6H₂O solution at 20°C. The numerous bright spots on the surface of the thin foil are etched by the aggressive media. Note that they develop independently of the existing dislocations. This means that the individual dislocations have not served as initiating sites for corrosion.

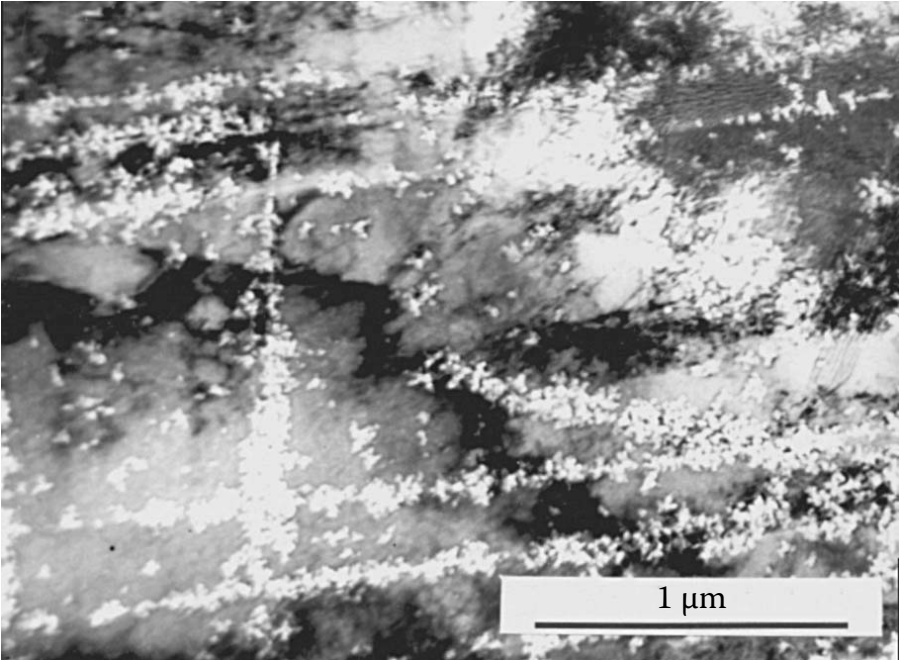


FIGURE 6.31

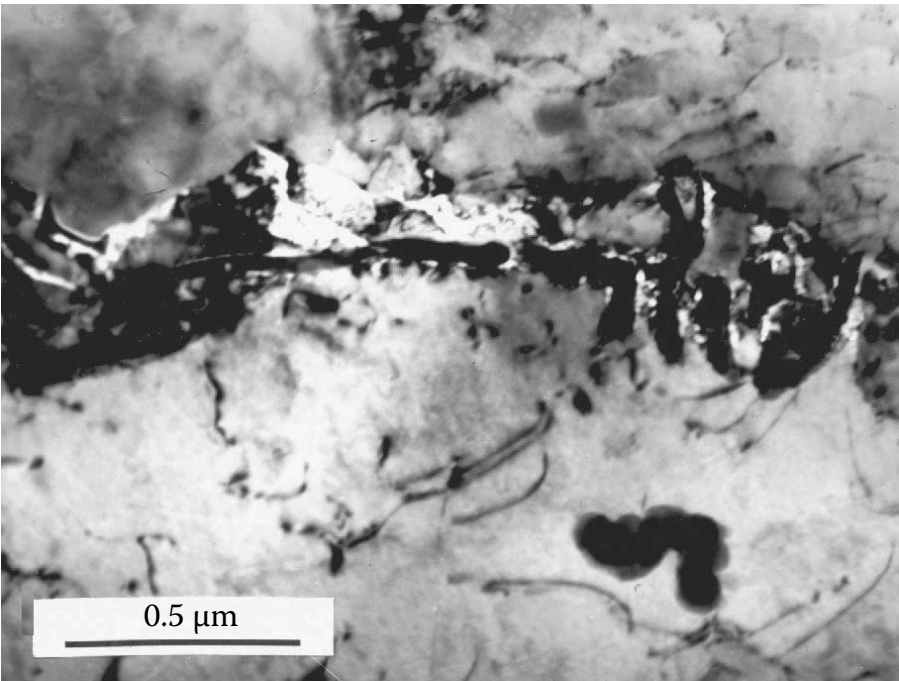


FIGURE 6.32

FIGURE 6.31 *Pitting corrosion* is an extremely dangerous type of electrochemical failure of alloys. This type of corrosion develops in small localized areas (*pits*) where the electrochemical properties of the metal differ from the properties of the surrounding matrix. The enhanced localized anode reaction can be provoked by any chemical or structural discontinuity—nonmetallic inclusions, coarse intermetallic phases, localized defects in the structure, precipitated compounds, and so on. It takes place in metals that rely on passive oxide film for their corrosion resistance (stainless steel falls in this category) in the cases when a break or scratch in the protecting passive film occurs. Regardless of their small size, the pits can be very damaging because they develop in the metal as deep perforations.

Fe-18Cr-12Mn-0,03C-0,6N steel, quenched from 1150°C and 20% cold rolled. The thin foil was exposed for 24 h to the action of 6%FeCl₃·6H₂O at 20°C. The deformation bands produced by dislocation movement during cold rolling differ in their electrochemical characteristics from the properties of surrounding metal and make the metal in the bands susceptible to the formation of pits. The numerous bright spots along the bands shown in this micrograph are pits etched by the corrosive solution.

FIGURE 6.32 Heating of high-alloyed Cr-Ni austenitic steels at temperatures in the “sensitizing range” from 600°C to 700°C causes precipitation of carbides at the grain boundaries. When the carbon content is higher, carbides can form continuous chains along the boundaries. During their growth, they consume significant amounts of chromium from the surrounding matrix, thus producing chromium-depleted zones. This reduced chromium content lowers the corrosion resistance of the material and makes the regions around the grain boundaries and around the intergranular precipitates especially susceptible to *intercrystal (intergranular) corrosion*. This type of corrosion is a very serious problem not only for the austenitic stainless steels but also for another important group of engineering alloys—Al-Cu alloys are the most popular example.

Fe-18Cr-10Ni steel, quenched from 1150°C and tempered for 60 min at 650°C. The thin foil has been exposed for 12 min to the action of boiling 65% HNO₃. The areas around carbides were dissolved by the corrosive media and thus look bright in the micrograph. This indicates the beginning of intergranular corrosion.

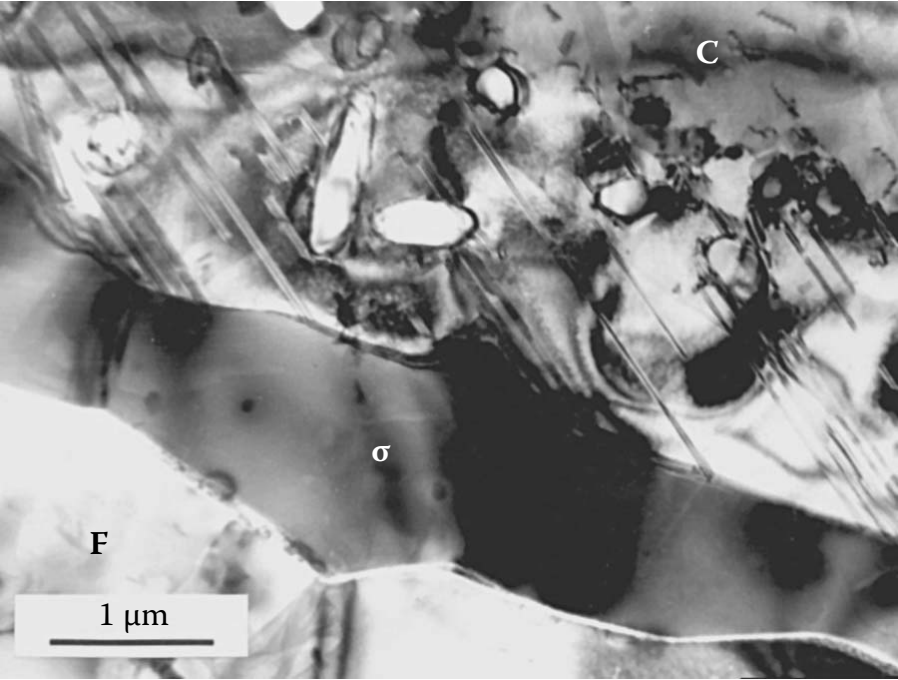


FIGURE 6.33

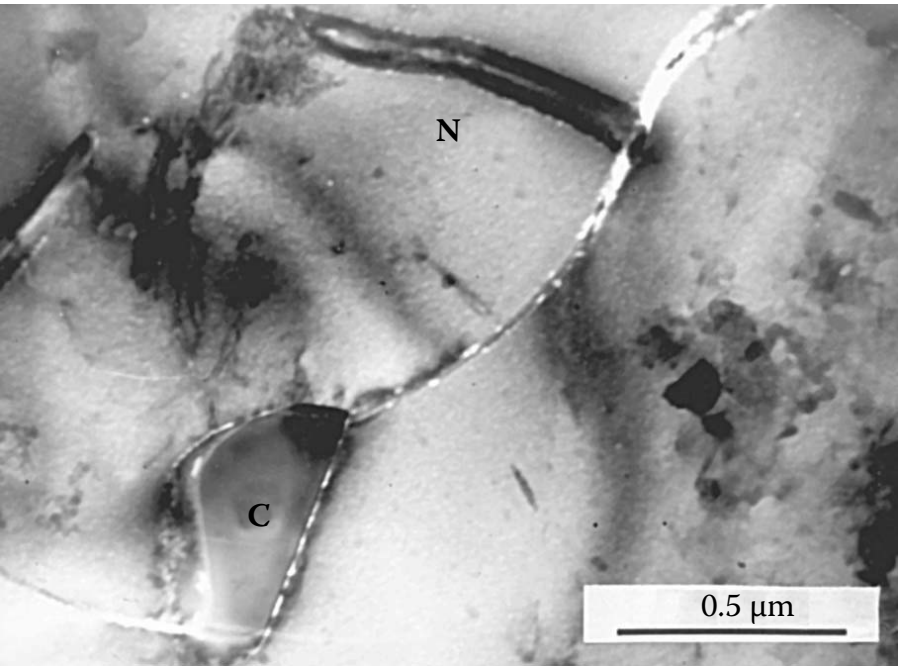


FIGURE 6.34

FIGURE 6.33 The grain boundary precipitation of the chromium-rich σ -intermetallide in the sensitizing temperature range that follows the precipitation of chromium carbides in high-alloy ferrite-austenitic steels leads to enhanced intergranular corrosion, caused again by the chromium-depleted zones around precipitates.

Duplex Fe-18Cr-12Mn-0,02C-0,2N steel, quenched from 1150°C and tempered for 60 min at 700°C. The thin foil has been exposed for 50 min to the action of a boiling solution of CuSO_4 in H_2SO_4 . The most severe corrosion attack is observed at the σ -phase interface with the ferrite grain into which it grows (marked by *F*) followed by the interfaces of carbides (marked by *C*) with the parent austenite grain. This indicates that the chromium depletion is at a maximum around the σ -phase. This is the most serious factor in the susceptibility of the steel to intergranular corrosion.

FIGURE 6.34 The heat treatment of high-nitrogen austenitic steels at temperatures within the sensitizing region causes discontinuous precipitation of chromium nitrides (see Chapter 5, [Section 5.3](#)).

Austenitic Fe-18Cr-12Mn-0,02C-0,45N steel, quenched from 1150°C and tempered for 15 min at 600°C. The thin foil has been exposed for 5 minutes to the action of boiling 65% HNO_3 . The number of chromium nitrides on the grain boundary is relatively low due to the short tempering time, but in spite of this, the short period of corrosive attack has been sufficient to affect the whole length of the boundary. This is due to the grain boundary diffusion-controlled mechanism of nitride nucleation, which causes grain boundary depletion of chromium at a significant distance along the boundary and makes the steel susceptible to intergranular corrosion.

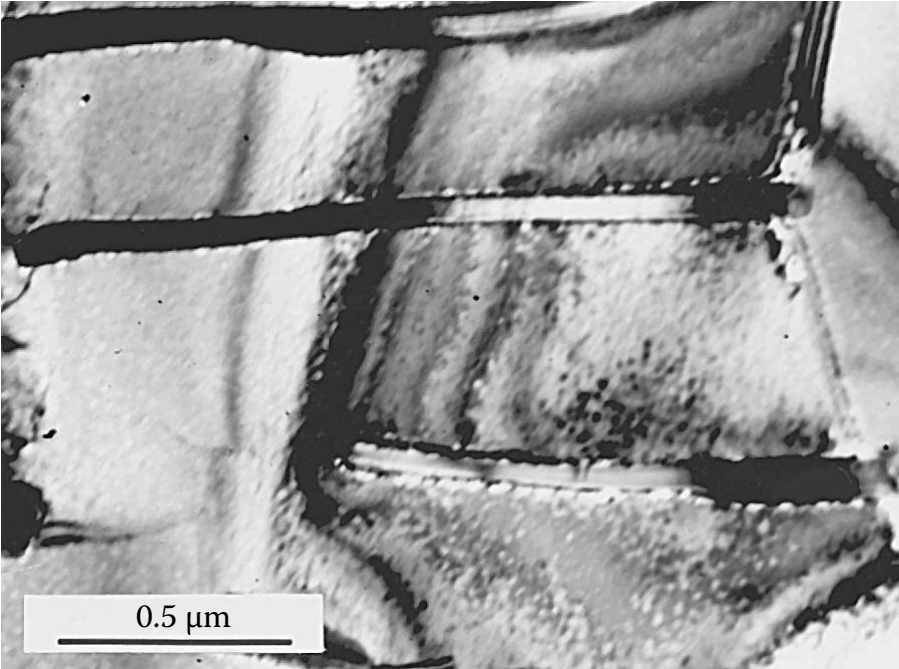


FIGURE 6.35

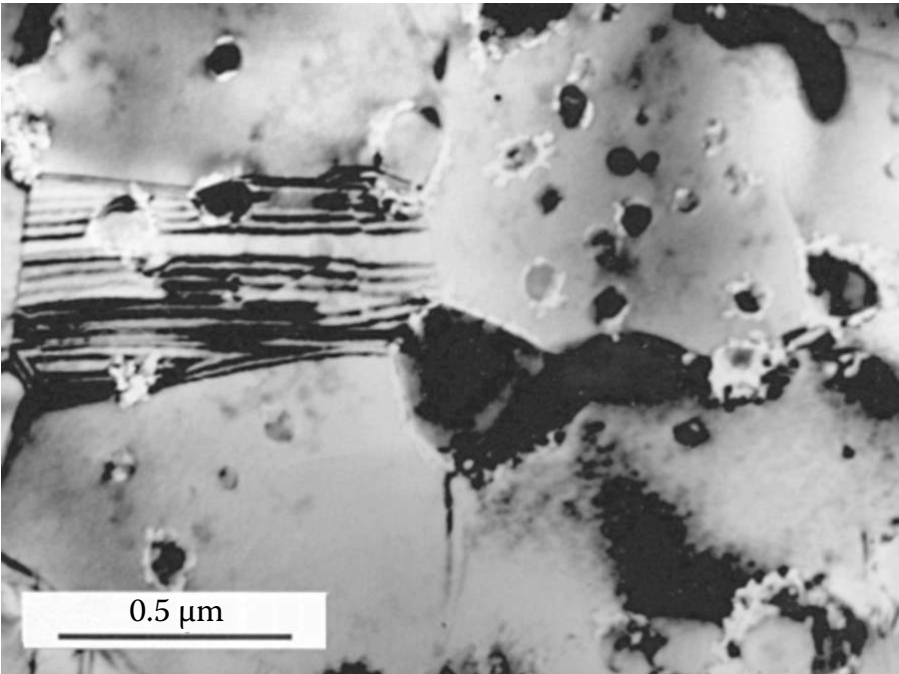


FIGURE 6.36

FIGURE 6.35 A longer tempering duration results in cellular precipitation of lamellar nitride-austenite colonies. The nature of the cellular product (two phases with different composition) and the diffusional mechanism of the cell growth determine the effect of microstructure on the corrosion behavior of the alloy.

Austenitic Fe-18Cr-12Mn-0,02C-0,45N steel, quenched from 1150°C and tempered for 2 h at 600°C. The thin foil has been exposed for 5 min to the action of boiling 65% HNO_3 . The fine perforations throughout the austenite lamellae in addition to the dissolution at the lateral austenite/nitride interfaces indicate that the whole volume of the transformed austenite is susceptible to the action of the aggressive media. This behavior is usually related to general corrosion, but in the high-nitrogen steels the intergranular corrosion dominates even at the stage of 100% cellular decomposition.

FIGURE 6.36 Cold working applied prior to aging helps to avoid the detrimental effect of discontinuous precipitation with regard to both corrosion and mechanical properties of high-nitrogen austenitic steels by changing the decomposition mechanism from a cellular to a continuous one (see Chapter 6, [Section 6.3](#)).

Austenitic Fe-18Cr-12Mn-0,02C-0,45N steel, quenched from 1150°C, cold rolled to a 75% reduction, and tempered for 2 h at 600°C. The thin foil has been exposed for 5 min to the action of boiling 65% HNO_3 . The areas around all the nitride particles and all the grain boundaries were dissolved by the corrosive media, but their large number and large total length prevented the corrosion from being localized. The process developed as a general corrosion rather than as intergranular corrosion.

6.7 CHARACTERIZATION OF FERRITE IN WELDS OF AUSTENITIC STEELS

The microstructural characterization of welds has two purposes: to evaluate the microstructure with respect to the properties of the material as well as with respect to the welding process used. One of the most important objectives of weld characterization is the quantity and the morphology of the ferrite. Besides strength and ductility, the ferrite distribution influences the susceptibility of the weld to solidification cracking, especially in austenitic stainless steels. The application of TEM characterization is particularly useful in the cases of welds with finely dispersed ferrite and with precipitation on the ferrite-austenite boundaries.

TEM replicas were utilized for the investigation of larger areas of the welds while studies of thin foils permitted a more precise characterization of the microstructure, particularly with reference to precipitation and the accumulation of defects in different regions of the weld.

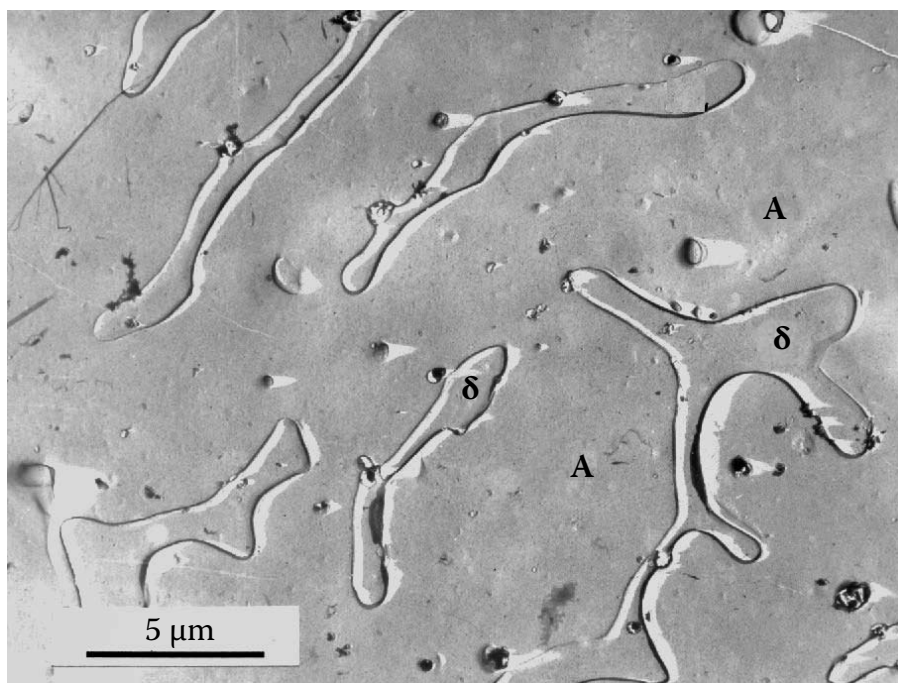


FIGURE 6.37 Replica of the central part of a weld of austenitic stainless steel Fe-18Cr-9Ni. The weld was produced by gas-shielded arc welding without filler. The microstructure of the central part of the weld is columnar austenite with δ -ferrite. This morphology of ferrite, which does not reflect its internal crystalline symmetry, is denoted by the term *allotriomorphic*. Allotriomorphic ferrite typically nucleates at the austenite grain surfaces and forms layers at austenite grain boundaries.

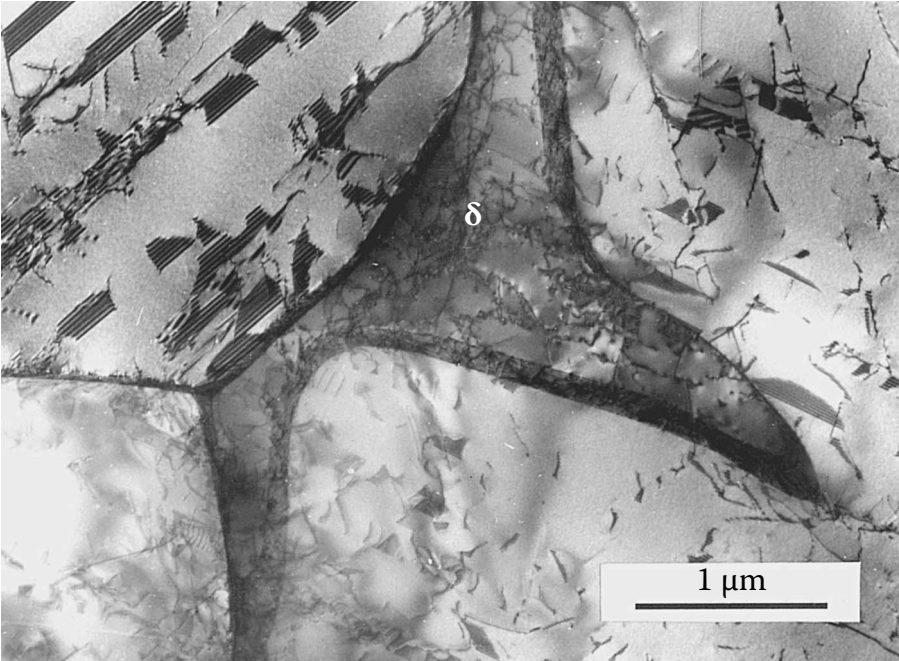


FIGURE 6.38

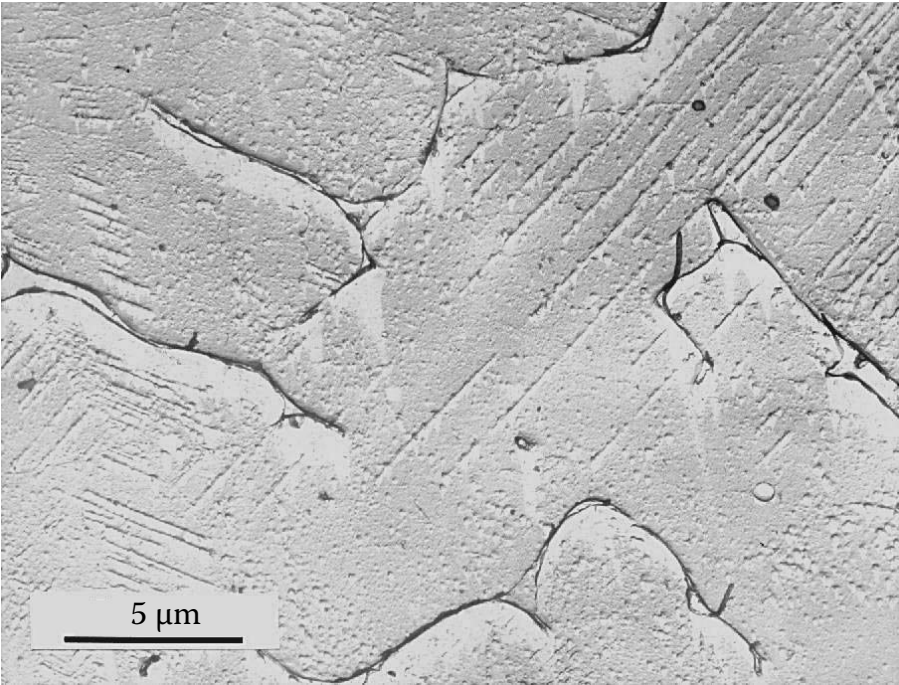


FIGURE 6.39

FIGURE 6.38 *A thin foil prepared from the same area as in Figure 6.37. The grains of austenite can be easily distinguished by the arrow-like arrangement of split dislocations and SFs. The grain of δ -ferrite, which follows the austenite grain contour, contains a three-dimensionally distributed dislocations.*

FIGURE 6.39 *A replica of the same weld, taken from the weld periphery. The microstructure toward the weld periphery becomes dendritic. The quantity of ferrite diminishes, and the ferrite grains get narrower and form elongated streaks along the solidification direction. The straight lines visible in the interior of the austenite are slip lines aligned along the traces of the fcc close-packed planes.*

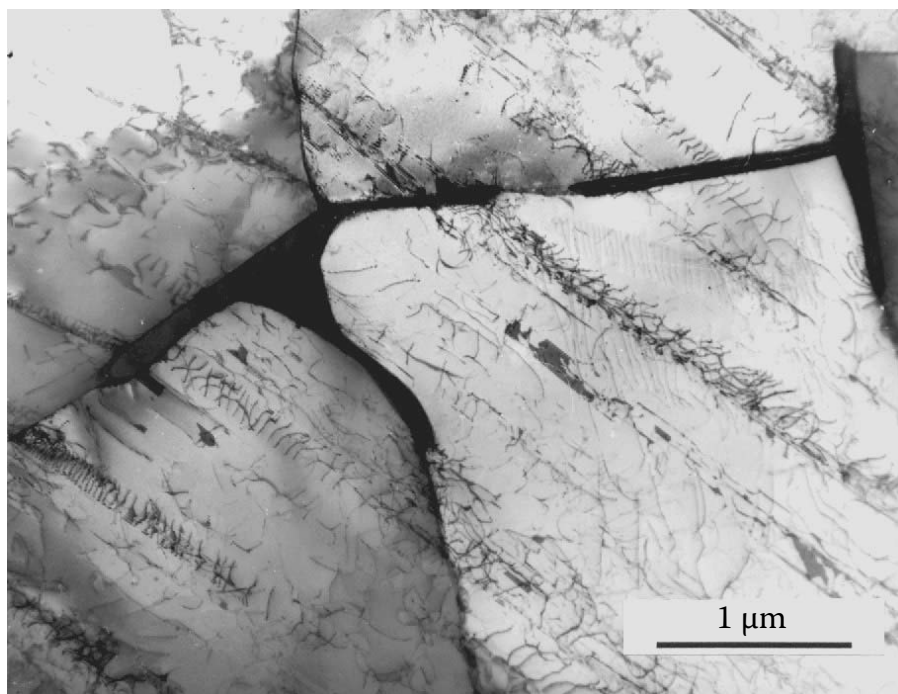


FIGURE 6.40 *Examination of thin foils from the periphery of the weld shows that the straight lines that are visible in the previous replica, Figure 6.39, result from a concentrated movement of dislocations in some slip planes of austenite. The strain arises from the thermal stresses caused by the solidification of the weld. Note that the rows of dislocations pass freely through austenite-austenite boundaries without changing their direction—that is, these are low-angle boundaries.*

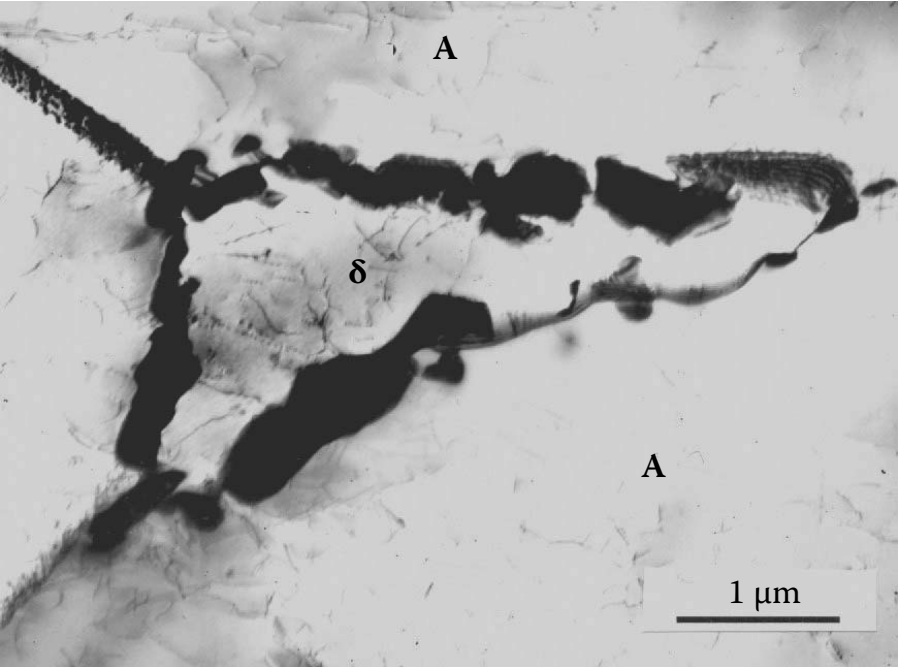


FIGURE 6.41

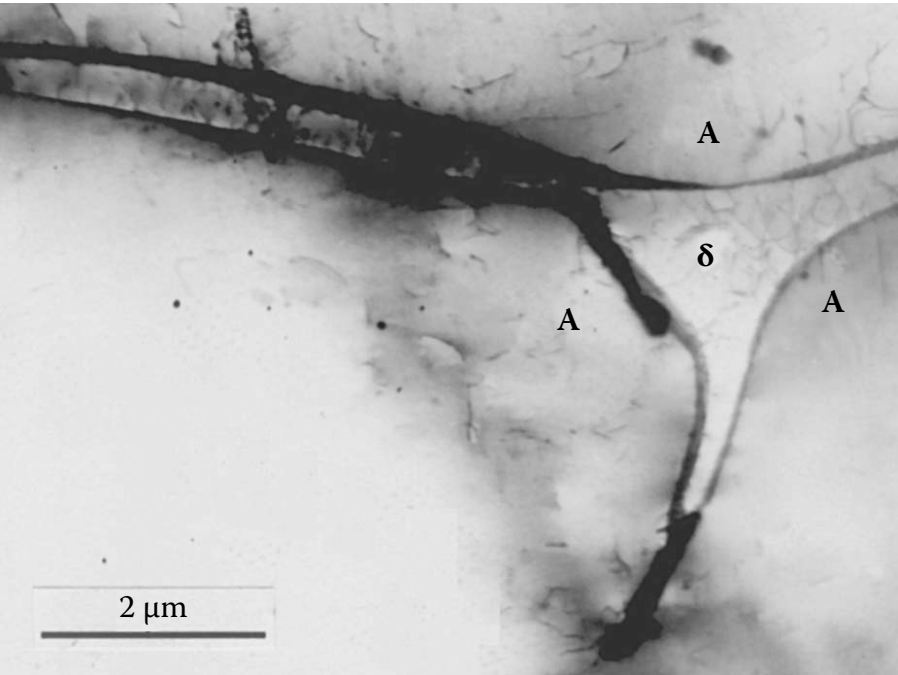


FIGURE 6.42

FIGURE 6.41 Alloying of the base Fe-18Cr-9Ni steel with some additional elements intended to improve corrosion resistance can provoke phase precipitation during the welding. For example, the addition of 2.6%Mo causes precipitation of carbides, followed by growth of intermetallic σ -phase on the ferrite-austenite boundaries of the weld. This precipitation sequence is similar to that occurring in the quenched high-chromium ferrite-austenitic steels in the “sensitizing” temperature range (see Chapter 6, [Section 6.5](#)). The process is very detrimental to the mechanical properties and the corrosion resistance of the welds, especially when the amount of ferrite present is reasonably high.

FIGURE 6.42 The additional alloying of the Fe-18Cr-9Ni alloy with low concentrations of nitrogen (in this case, with 0.16%N) prevents the σ -phase formation but causes unacceptable precipitation of chromium nitrides, which cover a significant length of the ferrite-austenite boundaries. The nitride precipitation runs not only in the weld but also in the heat-affected zone.

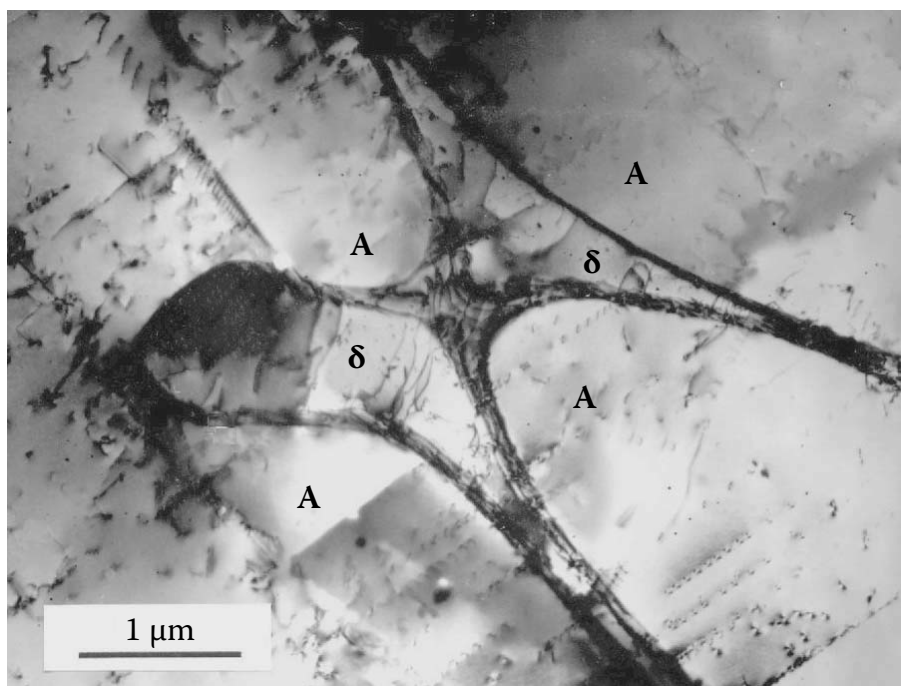


FIGURE 6.43 The combined alloying of the Fe-18Cr-9Ni steel with molybdenum and nitrogen successfully prevents the precipitation of both carbides and of intermetallic phases in all parts of the weld and in the base metal.

Weld of stainless austenitic steel containing 2.9%Mo and 0.16%N, gas-shielded arc welding without filler. Weld center. All grain boundaries of the weld are free of precipitates.