
4 Growth of the Crystals and Rapid Solidification

4.1 GROWTH OF THE CRYSTALS

There are three well-established mechanisms behind the growth of crystals in pure solids: *continuous*, *lateral*, and *spiral growth*. All three are related to the type of solid/liquid interface and its migration.

The term *continuous growth* originates from the mode of propagation of the diffuse disordered solid/liquid interface, normally to itself, by joining atoms arriving from the liquid at random positions everywhere over the solid surface. This mechanism is characteristic for metallic systems.

In the case of atomic smooth interfaces, characteristic mostly of nonmetallic materials, the *lateral growth* process takes place. This is facilitated by the presence of specific *ledges* and *jogs* and partly filled interface layers. These are preferred sites for the atoms to attach themselves to the solid because of the lower or no increase in interfacial energy compared to that associated with a perfectly flat surface.

The other mechanism affecting crystal growth is *screw-dislocations activity*. The well-known model of *spiral growth*, which has been observed and proven in Mg, Co, Ag, and so on, explains why the experimentally observed growth rate is much higher than the rate predicted by the surface repeated nucleation theory. The exit of screw dislocation at the crystal surface creates a *permanent step (ledge)* of atomic dimensions. When the atoms continuously arrive and attach at equal rate to the step, they make the step rotate around the exit point of the dislocation, but they never remove it. The decrease of angular velocity of rotation away from the dislocation core causes the gradual transformation of the ledge into a permanent spiral, each winding of which lifts the solid surface by one interatomic distance.

The direct observation of crystal growth during the solidification of metals is complicated (if not impossible), because metals as well as many nonmetals are opaque. For this reason, the processes are modeled using a variety of transparent materials and saturated aqua solutions of salts. The phenomena connected with the growth of crystals can be studied in the TEM using a preparation technique called *gold decoration*—vacuum evaporation and deposition of gold on heated fresh cleaved crystals, usually NaCl. Gold particles preferentially attached to the ledges and jogs facilitate the observation of the monatomic steps on the surface.

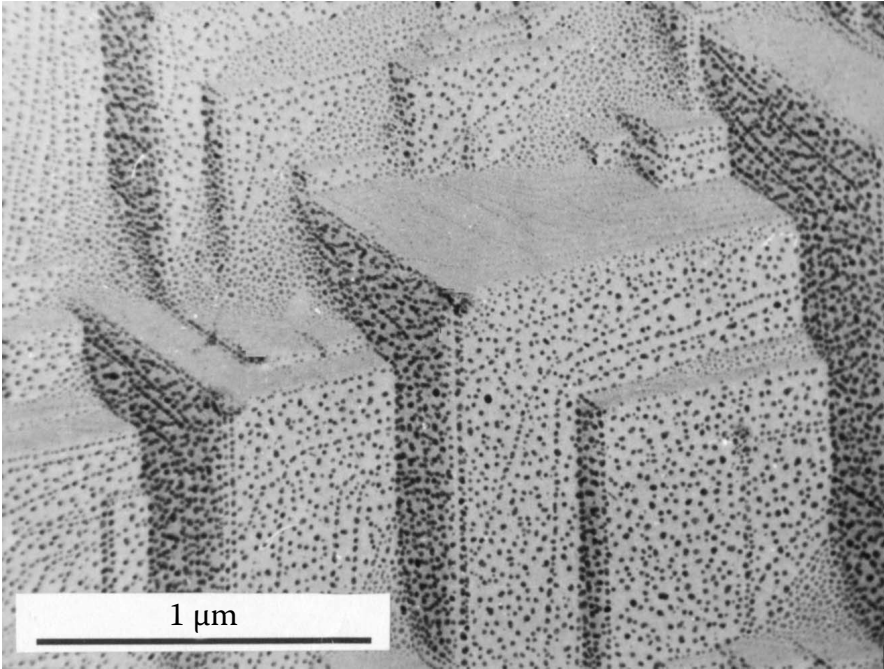


FIGURE 4.1

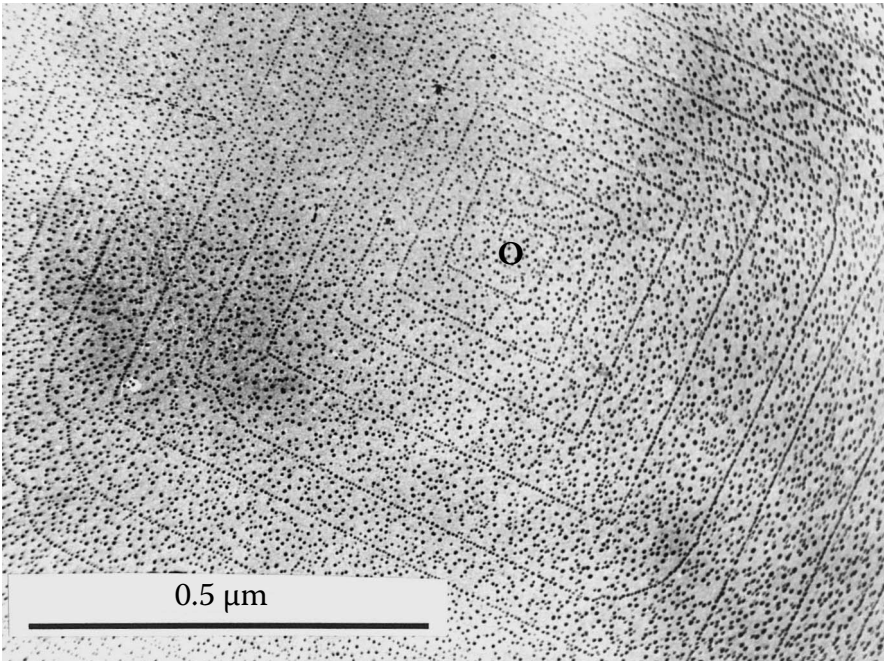


FIGURE 4.2

FIGURE 4.1 *The replica of a cleaved NaCl single crystal shown in this micrograph was prepared by the gold decoration technique. The cleavage has followed the crystal planes of the NaCl cubic crystal lattice and thus the growing ledges. The deposited gold particles subsequently make the ledges clearly visible.*

FIGURE 4.2 *A screw dislocation, which terminated during the growth of the NaCl crystal, has created a ledge on the surface fixed at the exit point O. As the growth proceeded and atoms continuously added to the step, it transformed into a growth spiral. Each winding of the spiral raised the surface of the growing crystal by one interatomic distance.*

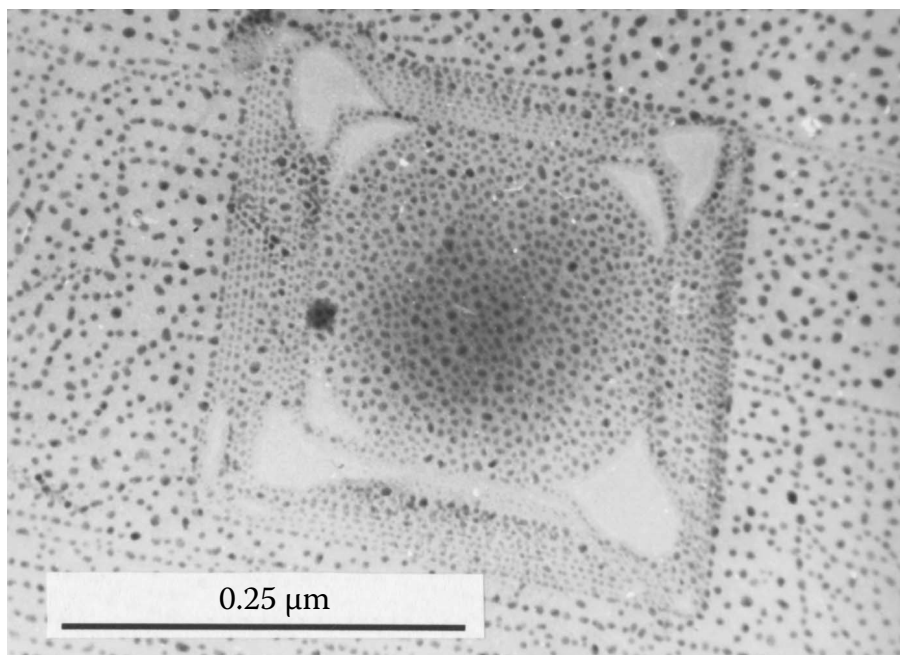


FIGURE 4.3 *This micrograph illustrates the case of spiral growth in which two dislocations of opposite sign participate. The growth steps form a closed planar terrace, which is a part of a conical growth pyramid.*

4.2 RAPID SOLIDIFICATION PROCESS

A rapid solidification process (RSP) requires cooling rates typically in the range 10^4 – 10^7 Ks⁻¹. In practice, different techniques can be utilized to achieve RSP, such as pouring a fine stream of liquid metal onto a rotating chilled cylinder or spraying liquid microdrops onto a cooled (usually copper) substrate. The technique of rapid quenching from a melt of a desired chemical composition is termed *melt spinning*.

The high cooling rate gives undercooling that results in a number of unusual structural effects: a glassy (amorphous) state, refinement of the grains, extended solute solubility in solid state, formation of metastable crystal phases, and lowering of martensitic transformation temperature. These effects are used for the synthesis of new categories of metallic materials, namely, the *amorphous metals* usually referred to as *glassy metals* or *metallic glasses* and the *rapidly solidified microcrystalline alloys*.

Glassy metals are actually multicomponent alloys, produced by RSP, which preserve the short-range order specific to the liquid metal in the solid state. The amorphous, noncrystalline structure ensures unusual and potentially useful physical (magnetic, electrical) and mechanical properties as well as yielding properties that are highly isotropic. Amorphous structure does not contain dislocations and grain boundaries, so the metallic glasses have a high strength and resistance to plastic deformation, wear, and corrosion. The formation of amorphous structure requires a suitable chemical composition (components acting as glass formers) and very fast cooling; the latter limits the maximum thickness of the produced metallic glasses.

Microcrystalline alloys produced by RSP have many advantages compared to conventional alloys, such as improved mechanical properties, reduction or elimination of micro-segregation, and increased solubility in the solid state, which consequently provides a greater strengthening effect on aging. The ultra-fine-grained structure exerts a marked effect on strength and plasticity while serving as a basic microstructure for superplastic deformation.

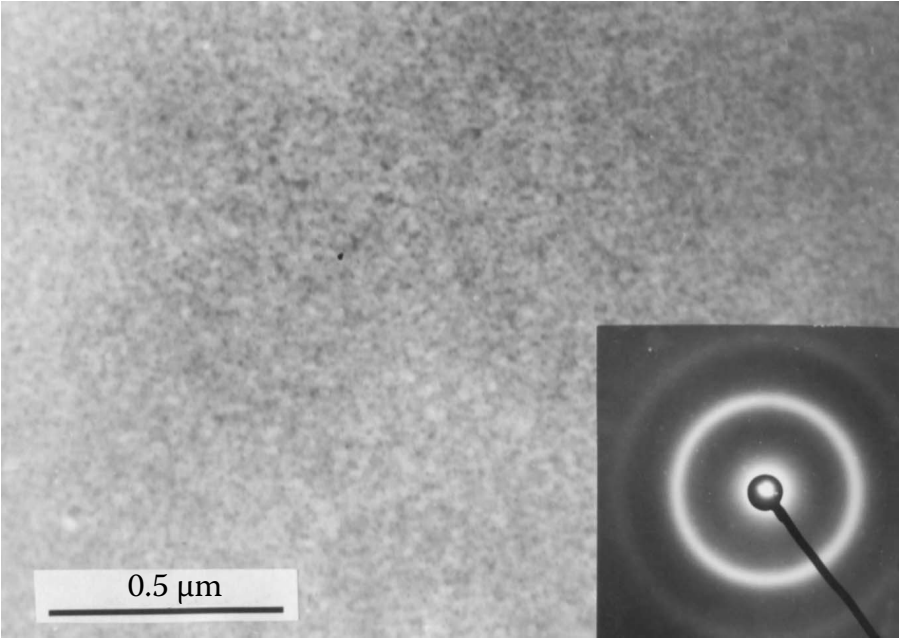


FIGURE 4.4

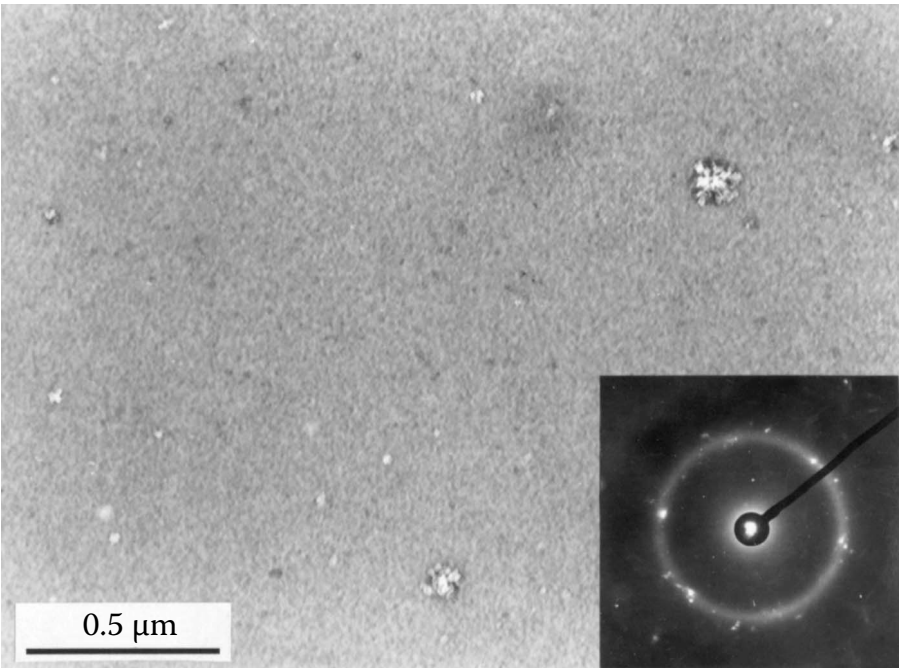


FIGURE 4.5

FIGURE 4.4 An amorphous (glassy) state can be obtained in some metal/metal or metal (Fe, Ni, Co, Mo, Pd)/nonmetal (B, Si, P) systems by undercooling at cooling rates equal to or greater than 10^5 K s^{-1} to suppress the normal crystallization process.

Amorphous Ni-Si-B alloy, melt spun at cooling rate of 10^5 K s^{-1} . The presence of diffuse rings and the absence of diffraction spots in the electron diffraction pattern are an indication of the absence of a crystalline structure, that is, the presence of an amorphous state; see inset to the figure.

FIGURE 4.5 The amorphous (glassy) solid state of alloys is metastable. When such an alloy is heated above some specific temperature for that material, the alloy undergoes a spontaneous crystallization process similar to the crystallization of a molten metal that has been undercooled below its freezing temperature. The nucleation starts at random positions in the amorphous alloy with the formation of single crystals and continues by their growth, which takes on a dendritic form.

Single crystal nuclei in an amorphous Ni-Si-B alloy after heating the alloy for 5 min at 700°C . The appearance of the crystal nuclei immediately changes the nature of the electron diffraction pattern. The newly formed crystal planes produce diffraction spots (reflections) in addition to the diffuse rings obtained from the surrounding amorphous material; see inset to the figure.

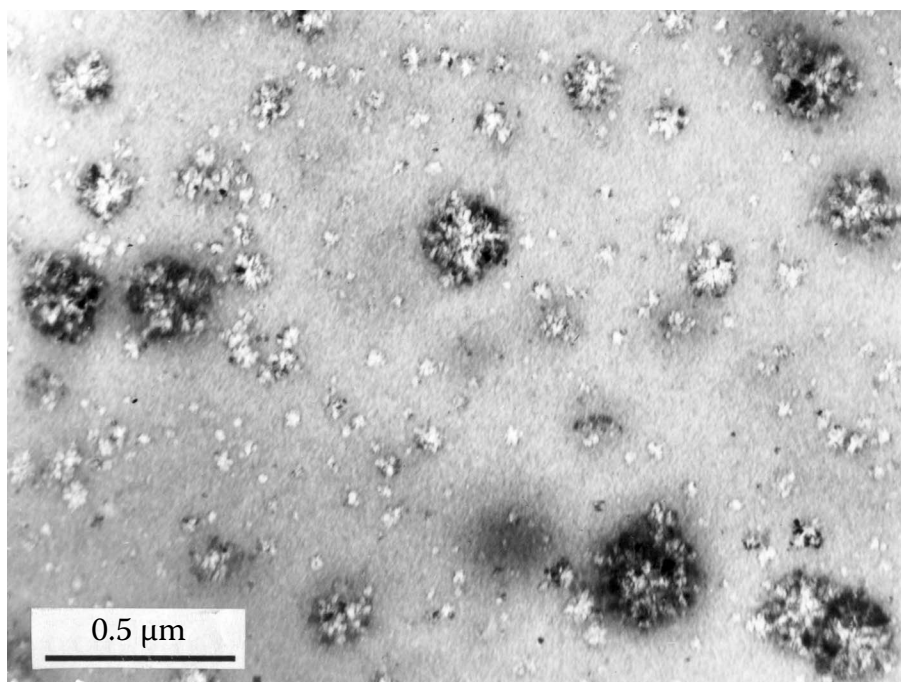


FIGURE 4.6 Crystallization continues during the isothermal heating of a glassy metal by the growth of the existing crystal nuclei and by the formation and growth of new crystal nuclei. Consequently, the number of diffraction spots in the diffraction pattern increases and they start to form rings, typical for the polycrystalline structures.

Crystal nuclei in an amorphous Ni-Si-B alloy after heating the alloy for 10 min at 700°C .

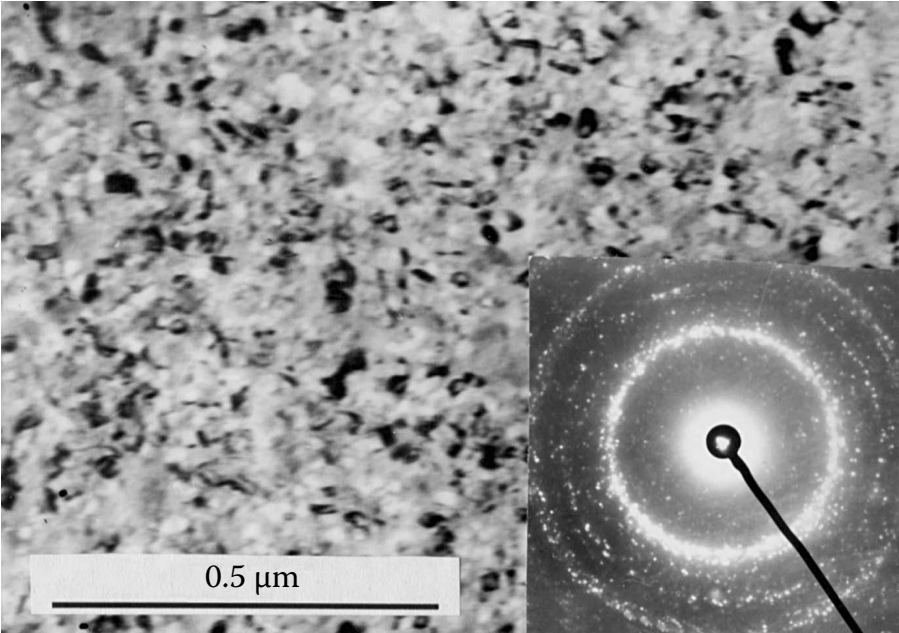


FIGURE 4.7

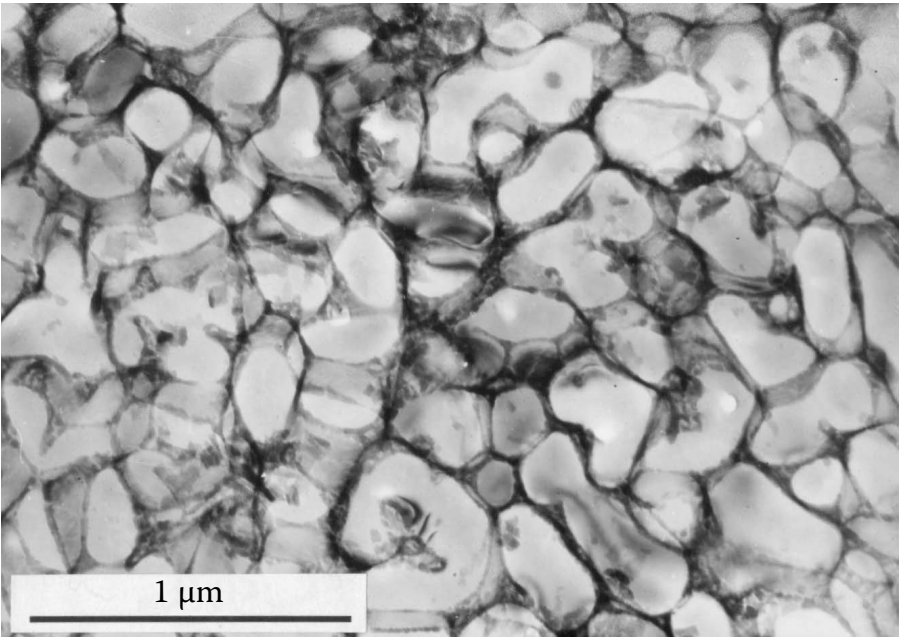


FIGURE 4.8

FIGURE 4.7 The cooling of a liquid metal or alloy at lower rates does not allow an amorphous state to be established but can produce an ultra-fine microcrystalline structure through the simultaneous nucleation of crystals throughout the entire volume of the material.

Microcrystalline Ni-Si-B alloy that was obtained by cooling at a rate of 10^4 K s^{-1} . The rapid quenching has produced randomly oriented microcrystals of a size less than 1 micrometer, which resulted in complete rings of diffraction spots formed from all the grains; see inset to the figure.

FIGURE 4.8 Even when cooled very rapidly, some molten alloys do not freeze in the amorphous state. Instead, they develop a microcrystalline structure with an unusually high super-saturated solid solution, refined grains, and modified morphology of the precipitated phases.

Al-11%Si alloy, quenched from melt on cooled copper substrate. The same alloy conventionally cooled shows a mean diameter of α_{Al} -grains of several tens of micrometers. The rapid cooling refines the grains to several tens of nanometers.

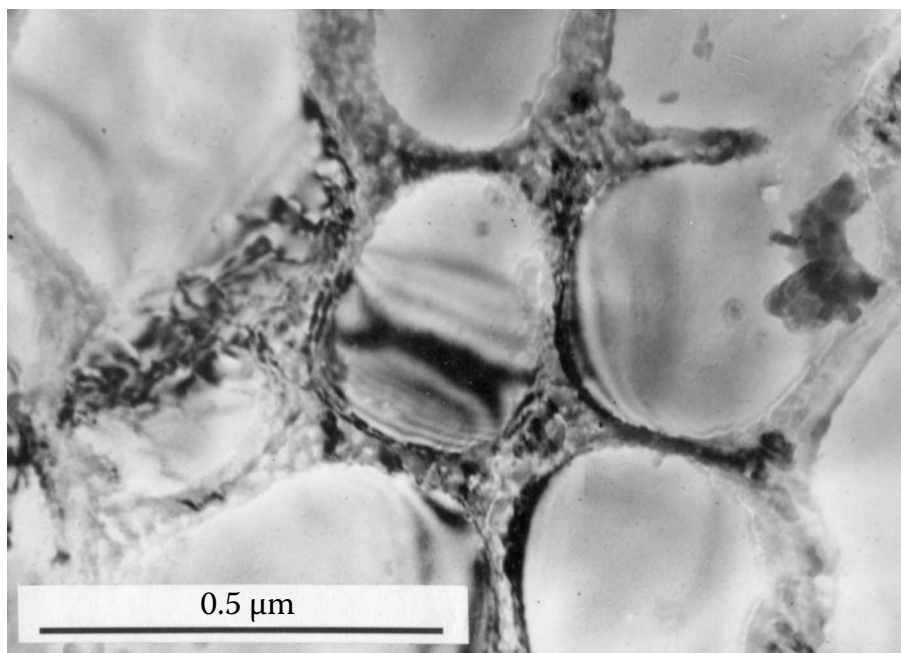


FIGURE 4.9 The rapid solidification of an AlSi alloy dramatically changes the morphology of aluminum-silicon eutectic that borders the ultra-fine grains, even compared to the fine fibrous eutectic in modified alloys.

Al-11%Si alloy, quenched from melt on cooled copper substrate. The size of the rounded silicon particles is reduced to less than several nanometers.