Rapid Solidification: Fundamentals and Modeling

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CHAPTER
FOUR

RAPID SOLIDIFICATION: FUNDAMENTALS
AND MODELING

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ABSTRACT

Rapid solidification can produce materials with superior, and sometimes astonishing, physical and mechanical properties. This has led to many advanced materials processing techniques such as melt atomization, thermal spray coatings, melt-spinning, laser melting and resolidification, and high-energy beam treatment of surfaces, to name a few. Because of large melt undercooling and very high rate of solidification, the rapid solidification processes inherently involve nonequilibrium kinetics of phase change and coupled transport of energy and species. This coupling ultimately determines the phase selection, microstructure formation and final properties of the rapidly solidified materials. The fundamentals of rapid solidification, and recent progress made in modeling of these processes are reviewed in this article. Both single component and alloy materials are considered, and the issues related to thermodynamics of rapid solidification, nucleation and growth kinetics of crystalline phase, planar interface stability, dendritic growth theory, and microsegregation are discussed. Thermal transport models incorporating the basic principles of rapid solidification and their integration with kinetics models are presented. Special features of theoretical results are discussed in detail, particularly, for phase selection and microstructure formation in atomized powders, pulsed laser processing, and melt-substrate quenching.
NOMENCLATURE

\( a_0 \)
interatomic distance

\( \beta \)
thickness of splot or deposit

\( C \)
solute concentration

\( C_0 \)
initial solute concentration

\( C_p \)
specific heat

\( C_{SR} \)
solid composition at maximum recrystallization temperature

\( D \)
mass diffusivity

\( d \)
average grain density, Eq. (113)

\( E_i \)
exponential integral function, \( E_i = \int \exp(-z/x)dz \)

\( f \)
fraction of interfacial sites where attachment can occur

\( f_s \)
solid fraction in mushy zone

\( f_{s,r} \)
fraction of solid formed at dendrite tip, Eq. (89)

\( f_{SR} \)
solid fraction at maximum recrystallization temperature

\( G_C \)
gradient of solute concentration in the liquid

\( G_L \)
gradient of temperature in the liquid at the interface; free energy of liquid

\( G_S \)
gradient of temperature in the solid at the interface; free energy of solid

\( G_{eff} \)
effective temperature gradient at the interface, Eq. (61)

\( \Delta G_A \)
activation energy for diffusion

\( \Delta G_c \)
nucleation barrier, Eq. (10)

\( \Delta G_{LS} \)
free energy difference between the liquid and solid phases

\( \Delta G_m \)
free energy change when a nucleus is formed in the melt, Eq. (8)

\( \Delta G_V \)
free energy change per unit volume

\( h \)
interfacial heat transfer coefficient

\( H_r \)
convection-radiation parameter, \( h(\sigma T_m^3) \)

\( \Delta H_m \)
heat of fusion

\( i \)
transient nucleation rate, Eq. (29)

\( i_{SS} \)
steady-state nucleation rate, Eq. (11)

\( I_v \)
Ivansov function, \( I_v(P) = P \exp(P)E_1(P) \)

\( K \)
thermal conductivity

\( k \)
nonequilibrium partition coefficient

\( k_g \)
equilibrium partition coefficient

\( k_f \)
frequency factor, Eq. (31)

\( L \)
latent heat

\( L_e \)
Liew's number

\( m_L \)
nonequilibrium liquidus slope

\( m_m \)
equilibrium liquidus slope

\( N \)
conduction-radiation parameter, \( K(4\sigma T_m^3b) \); number of nuclei

\( N_a \)
Avogadro's number

\( N_t \)
total number of atoms in the melt

\( \nu \)
Pascal number \( V_R / (2D_L) \)

\( P(t) \)
intensity of the laser pulse

\( Q \)
heat flux of a laser beam

\( q \)
cooling rate of a volume element, Eq. (101)

\( R \)
ideal gas constant; reflectivity

\( R_t \)
radius of dendrite tip

\( r \)
radius of nucleus or spray droplet

\( r_c \)
critical nucleus radius

\( r_0 \)
initial droplet radius

\( \Delta S_m \)
entropy of fusion

\( \Delta S_{LS} \)
entropy difference between liquid and solid phases

\( T \)
temperature

\( T_G \)
gas temperature

\( T_g \)
glass transition temperature

\( T_m \)
equilibrium freezing temperature

\( T_N \)
nucleation temperature

\( \Delta T_0 \)
frosting range of an alloy, \( \Delta T_0 = -m_cC_d(1-k)k \)

\( t \)
time

\( u_s \)
speed of sound

\( V \)
temperature or tip velocity

\( V_{abs} \)
absolute stability velocity, Eq. (62)

\( V_C \)
characteristic velocity of interface movement of binary alloy, Eq. (35)

\( V_D \)
interfacial diffusive velocity

\( V_m \)
molar volume

\( x \)
space coordinate

\( y \)
coordinate normal to the substrate

Greek Symbols

\( \alpha \)
thermal diffusivity

\( \beta \)
extinction coefficient of the medium

\( \delta \)
amplitude of disturbance in stability analysis

\( \Gamma \)
Gibbs-Thomson coefficient

\( \Gamma_Z \)
Zeldovich factor

\( \eta \)
Viscosity; heat flux parameter, Eq. (68)

\( \kappa_B \)
Boltzmann constant

\( \kappa_D \)
optical thickness of the layer, \( \beta b \)

\( \lambda \)
wavelength

\( \lambda_1 \)
primary dendrite spacing

\( \lambda_2 \)
secondary dendrite arm spacing

\( \mu \)
chemical potentials of liquid

\( \mu_1 \)
chemical potentials of solid

\( \mu_t \)
linear kinetics coefficient

\( \nu \)
characteristic atomic jump frequency

\( v_0 \)
vibration frequency of atoms
1 INTRODUCTION

Solidification from liquid to solid is an important process that to a large extent determines the final structure of the material produced and its properties [1]. Although conventional process of casting can be dated centuries ago, rapid solidification processing is a recently developed process, only about 40 years old. Duwez and his co-workers [2] accidentally discovered it when they were conducting experiments to examine the effect of very high cooling rate on metallic melts during solidification. They developed the so-called gun technique in which a small volume of molten metal was expelled out of a nozzle, atomized to small droplets, and impacted on a colder substrate to form flakes. Because of very small thickness of the flake, heat was very quickly transferred from the flake to the substrate and the melt was rapidly solidified. The rapidly solidified material was found to have astonishing physical and mechanical properties. This triggered a great scientific curiosity among material scientists and engineers that has led to the development of present-day rapid solidification technology.

Following Anantharaman and Suryanarayana [3], the salient features of the rapidly solidified materials in comparison with the conventionally cast materials can be summarized as follows: (1) substantial extension of solid solubility of one or more metals in the other, (2) extreme refinement of the grain size in the solidified metals and alloys, (3) considerable reduction in segregation in the solidified alloys, (4) formation of new metastable crystalline phases, and (5) formation of metallic glasses. All of these result in materials with advanced physical (thermal, electrical, and mechanical) properties. Suryanarayana et al. [4] has divided the rapid solidification (RS) effects into two categories: constitutional and microstructural. Constitutionally RS allows large departures from the equilibrium constitution, which results in large extensions of solid solubility, formation of metastable crystalline phases and metallic glasses, and retention of disordered crystalline structures in normally ordered materials and intermetallic compounds. The microstructural effects include change of morphology and refinement of the dimensions of microstructural features such as the size, shape, and locations of phases present, with much reduced effect of solute segregation.

After its discovery, RS emerged as a widely investigated research topic, with most of the early work motivated by either the process development or material characterization. Jones [5–6] and Anantharaman and Suryanarayana [3] have presented excellent reviews and exhaustive bibliographies of the research performed to that date, on the processes that involve RS phenomena and the materials produced by using these processes. Material aspects of RS processes have been discussed in great detail by several authors in an engineering guide book edited by Srivatsan and Sudarshan [7]. The processes and characteristics of the rapidly solidified ceramics have been reviewed by Jacobson and McKittrick [8].

It is now well understood that the unique features of rapid solidification result from the nonequilibrium phase transformation in the presence of large melt undercooling and fast solidification rate. The importance of nonequilibrium kinetics in rapid solidification has stimulated extensive research in this area and significant progress has been made in developing an understanding of the phenomena underlying the RS processes. Issues related to both thermodynamic and kinetic aspects of rapid solidification including kinetics of crystalline nucleation and growth have been addressed [9–13]. Physical mechanisms have been analyzed both quantitatively and qualitatively for some unique phenomena such as solute trapping and solubility extension, metastable phase (glass) formation, and banded structures. Although most of the early efforts on rapid solidification fundamentals were focused on the formation of metallic glasses, significant efforts have been made in recent years to study the rapid solidification of crystalline materials [14].

Since rapid solidification processes involve high-temperature molten states, transport of momentum, heat, and species critically influence the characteristics of the final materials produced. Scientific researchers and industrial engineers now fully realize that a better understanding of transport phenomena in RS processes is necessary for the design and improvement of these processes. For example, extensive studies have been performed to quantify the cooling rate that promotes rapid solidification, and to characterize the thermal contact resistance between the melt being quenched and the substrate surface [5–6, 15]. Fluid dynamics of RS processes has also been focus of many studies, such as splat formation after a molten droplet impacts on a solid substrate in thermal spray deposition [16–18], and flow of the melt in melt-spinning and planar flow casting [19–21]. Except in few cases, most of the transport phenomena studies have considered only the equilibrium conditions in their treatment of melt/solid phase-change.

Efforts were made to include the nonequilibrium effects of solidification in some early models for rapid solidification; for example see Ruhl [22] and Shingu and
Ozaki [23]. It was Levi and Mehrabian [24], however, who for the first time, integrated the nonequilibrium kinetics of rapid solidification into a heat transfer theory to develop a model for atomized powders. In addition Mehrabian [25] presented an excellent review of the early efforts on modeling of rapid solidification, including the physics, basic equations, and governing parameters. An update of the efforts on RS modeling was documented recently by Gutierrez-Miravete [26] and Wang and Prasad [27]. Nonequilibrium thermodynamics of an undercooled melt, and nucleation and growth phenomena with special emphasis on the conditions that promote metastable phases, were examined in detail by Feuerbacher [28] and Herrlach [29] who made excellent effort to connect nonequilibrium phenomena with the materials produced.

Although the research on materials and thermodynamics aspects of RS processes has been reviewed extensively, its relationship with coupled heat and mass transfer in the solidifying melt and substrate is not well understood. The primary objective of this review paper is to take a broader view of rapid solidification processes, examine the complex physical phenomena associated with these processes and present theoretical models developed thus far. Emphasis is placed on thermal and species transport, and phase change under the conditions of nonequilibrium kinetics and thermodynamics. The paper also presents the state-of-the-art of theoretical models that can provide important information on nucleation, interface instability, growth kinetics, and microstructural formation of the RS processes.

The paper is organized in ten sections. Following this section, Section 2 describes briefly the important rapid solidification processes and techniques classified by their heat transfer behavior and solidification conditions. Section 3 then provides a brief review of the physical models and mathematical formulations commonly used for rapid solidification processes. Important issues such as nonequilibrium kinetics of crystalline nucleation and growth, solidification morphology and microstructure formation, and microsegregation are also introduced in Section 3, and then presented in detail in Sections 4, 5, and 6, respectively. Applications of various kinetics models to the modeling of a variety of rapid solidification processes are introduced in the subsequent sections: phase selection and microstructure formation in atomized powders in Section 7, pulsed laser processing in Section 8, and melt-substrate quenching in Section 9. The emphasis is always on modeling efforts that integrate fundamental theories of rapid solidification into heat and mass transport formulations. The paper finally ends with concluding remarks.

2 PROCESSES AND TECHNIQUES

Fundamentally, rapid solidification can be achieved in two ways [5–6], one by imposing a large melt undercooling prior to solidification, and the other, by producing a very high rate of solidification. Large melt undercoolings can be achieved by melt dispersion, melt atomization, containerless (such as levitation) cooling, and flux method. In the first two cases, the melt is dispersed or atomized into small droplets so that the impurity particles in the melt can be isolated into only a small fraction of the melt volume. In the last two cases, the melt is undercooled and therefore can achieve a large melt undercooling prior to solidification. However, in containerless and flux methods, the bulk melt is cooled down slowly, generating a large melt undercooling [28–29]. Once a large undercooling is produced, the melt starts nucleating, and the rapid solidification is initiated with the crystalline phase quickly growing into the undercooled melt with a high speed, a process called recrystallization.

RS by high rate of solidification has also been achieved in many applications, such as by withdrawing a sufficiently thin melt specimen at a very high velocity through a controlled temperature gradient as in the directional solidification; see Ludwig and Kurz [30]. A high rate of solidification can also be produced when a very steep temperature gradient exists across the solid/liquid interface, such as in laser surface melting and resolidification.

However, many of the RS methods use both of the above basic mechanisms. The best example is the melt-substrate quenching in sput cooling, thermal spray deposition, and melt-spinning. In these processes, a thin molten layer is brought into contact either intermittently or continuously with a cold substrate. Large undercooling can be achieved in the melt near the substrate prior to solidification due to very high rate of heat transfer. In these processes, a high rate of solidification is maintained during (almost) the entire process because of both the large melt undercooling and high temperature gradient between the melt and the substrate.

A wide variety of rapid solidification processes have been developed in the last 40 years. The most widely used classification of these processes, due to Jones [5], is based on the methods to produce melt: (1) spray methods involving fragmentation of melt into droplets prior to quenching, (2) chill methods preserving continuity of the melt up to and during quenching, and (3) surface methods which involve rapid melting and resolidification of a surface layer. Detailed discussions on various rapid solidification methods can be found in various review articles, monographs, and books [1–8]. A few selected RS processes are described here to make the discussion on fundamentals and modeling relevant and easy to follow. No attempt is made to discuss in detail the technical issues concerning various RS processes. Only a brief introduction is presented to illustrate the most common features of the processes. The emphasis is on heat transfer characteristics of rapid solidification and their effect on microstructure evolution of the rapidly solidified solid.

2.1 Melt Atomization

Melt atomization is the process with the highest potential for exploitation of the microstructural benefits that can be achieved through rapid solidification processing [3, 24]. Significant melt undercooling can be achieved in atomized droplets by breaking up a molten stream of liquid into small spheres using gas or water jets. Various metastable phases can then be formed under the condition of large melt undercooling with a variety of microstructures. For example, rapidly solidified powders of Al–8wt%Fe exhibit four distinct microstructures: microcellular α-Al, cellular α-Al, α-Al + Al₃Fe eutectic, and Al₃Fe primary intermetallic structure [31]. The formation of the metastable phase Al₃Fe and its eutectic with stable α-Al is primarily due to the large melt undercooling achieved in small size droplets. Metast-
able phases are also formed in electro-hydrodynamically (EHD) atomized \( \text{Al}_2\text{O}_3 \) ceramic powders [32].

Several methods have been devised to generate atomization of bulk melts [3, 6, 8]. Gas atomization is perhaps one of the most commonly used atomization techniques in which one or more high-velocity jets of air or some other gases impinge on a molten metal stream exiting a nozzle. In practice, nitrogen, hydrogen, argon, and air have all been used for various reasons, and a mixture of these gases and helium is also effective. The melt stream breaks into small droplets that solidify in flight by convective and/or radiative heat transfer. The cooling rate depends on the particle size, with higher rates associated with smaller droplets. Gas-atomized powders are smooth and spherical. A wide range of alloys, including superalloys, high-alloy steels and aluminum alloys are commonly atomized using the gas atomization [3, 8].

Water atomization is similar to gas atomization except that water jets are used instead of gas. The water pressure used for this purpose is generally higher than the pressure employed in gas atomization and the angle of impingement is smaller. Water atomization has been used extensively to make powders of tool and low-alloy steels, copper, tin, and iron [3].

One of the special atomization methods is EHD atomization which employs an electron beam generated by the thermionic emission of electrons from a heated filament [8]. The beam is focused on the tip of a thin rod or wire connected to a high positive potential (20–30 kV). The tip is melted and forms a meniscus, which becomes unstable when the voltage exceeds a critical value. A steady stream of droplet is then generated and ejected into a chamber. Levi et al. [32] have extended this technique to produce ceramic powders such as \( \text{Al}_2\text{O}_3 \).

### 2.2 Laser Surface Melting and Resolidification

Laser-induced surface melting, often stated as “laser annealing,” is an RS process that has attracted extensive research. Originated as a method to remove implantation damage in semiconductor silicon wafer [33], the laser surface melting has become an important process that has significantly improved our understanding of thermodynamics and kinetics of metastable and nonequilibrium phase formation during rapid solidification [11, 34]. In laser processing, a laser beam of extremely high power density (higher than \( 10^{10} \text{ W/m}^2 \)) is concentrated in a small area, typically 0.1–1.0 mm in diameter, for very short duration of time less than \( 10^{-3} \text{ s} \). A very thin melt layer, from less than one micron to hundreds of microns, can then be formed, and it is in direct contact with its own crystalline phase. As soon as the laser is turned off or moved away, rapid solidification of the melt layer starts because of the large temperature gradient generated in the bulk substrate.

Two different types of lasers, pulsed and continuous-wave, have been used [35]. The former is used in a stationary mode, while the latter is used in a rapid scanning mode. If such scanning is combined with slow transverse translation of the laser beam, then successive strips of melted material can cover the entire surface. The melted layer solidifies immediately after the heat source moves on or after it has been switched off because the liquid layer is in good thermal contact with the bulk of the material.

Practical applications of laser surface melting include the following [35–38]: (1) surface remelting to reconstitute, homogenize, and refine in order to achieve special material properties at the surface, (2) surface alloying in which preplaced or injected alloying materials are incorporated into the surface, (3) particle injection in which dispersed second phase is incorporated, without being melted, into the remelted zone at the surface, (4) surface cladding in which a metal or alloy is fused onto the underlying material with a minimum of dilution by the underlying material, and (5) laser layer technique for joining amorphous materials to produce thick foils. Laser surface treatment has been found to increase resistance to fatigue, erosion and wear. Recently laser processing has emerged as one of the most promising techniques for rapid prototyping using sintering powders layer by layer [39].

### 2.3 Splat Cooling or Gun Technique

The gun technique was an early method developed to generate rapid solidification [2]. It involved ejecting the melt, generally by a high-pressure gas onto a substrate. Various improved versions have since been developed, but the basic principle remains the same: Atomize the melt into small droplets and then quench them on a cold substrate usually made of copper. Splats are formed after the droplets impact on the substrate. Extensive studies have been made on the phase, microstructure, and properties of the rapidly solidified materials produced by splat cooling [5, 6].

### 2.4 Thermal Spray Deposition

Thermal spray deposition can be viewed as an industrial version of splat cooling [40]. In this process the stock powders are fed into a plasma or combustion torch where the powders heat up, melt, and accelerate. High-speed molten droplets then impact on a material (substrate) surface and spread to form pancake shaped splats. Millions of such splats pile up together to form a coating. Free standing forms can also be made using this method. Since a high velocity of tens to hundreds of meters per second can be achieved, very thin splats can be formed, leading to rapid solidification.

Figure 1 shows an SEM picture of a single splat of yttria-stabilized zirconia formed on a smooth steel substrate at high temperature. In practice, there can be severe splashing and thus splats of very irregular shapes can be formed. This is true especially when the substrate surface is rough and its temperature is low. How to prevent melt splashing during spray is an important research topic. Typical microstructure of splat is columnar grains as shown in Figure 2, an optical micrograph of an air plasma sprayed Mo coating on a steel substrate [40]. Most of the splats in this picture show columnar grains grown in the direction normal to the interface, along the direction of heat flux. It is now well known that columnar growth depends on the contact condition, and epitaxial-like growth has also been observed when a good contact can be
achieved, as shown in Figure 3. Depending on heat transfer conditions, a cellular structure may also develop in one single grain of the splat as shown in Figure 4.

2.5 Free-Jet and Planar Flow Melt-Spinning

Melt-spinning is the most commonly used method to produce long and continuous ribbons. There are several different versions of melt-spinning technique, two most important ones are the free-jet melt-spinning (FJMS) (Fig. 5a) and planar flow casting (Fig. 5b) [41]. FJMS involves directing a molten metal jet onto a cold, spinning wheel on which a puddle is formed. Ribbon is solidified in the puddle, dragged out, and then expelled from the surface of the wheel. Melt can also be ejected onto the inner surface of a rapidly rotating wheel. The radial acceleration...
stabilized and the disturbance in melt by the gas boundary layer and surface roughness of the wheel is greatly reduced.

A variety of microstructures, from pure columnar grains to pure equiaxed grains, have been observed in the melt-spun ribbons. For example, pure columnar grains, like those observed in the splats by thermal spray, have been observed in thick nickel-base superalloy ribbons with cellular and dendritic structures [41–42]. Pure equiaxed dendrites are seen to exist in Al–Fe systems [43]. Quite often, the melt-spun ribbons show multilayer structures: a segregation-free columnar layer near the wheel surface and a cellular or dendritic equiaxed layer near the air surface, as shown in Figure 6 [44]. Occasionally an equiaxed microcellular, chill-zone-like, structure may appear underneath the columnar layer near the wheel surface. Such complex microstructure formation results mainly from a lower rate of interfacial heat transfer and a larger ribbon thickness, compared to the splats formed in gun techniques and thermal spray deposition.

3 FUNDAMENTALS OF MATHEMATICAL MODELING

Liquid-solid phase change has been traditionally treated as a pure thermal problem that primarily concerns with the latent heat released at the solidification interface under local thermal equilibrium. The assumption of local equilibrium provides the necessary conditions at the interface, through the use of equilibrium phase diagram of materials. Extensive efforts have been made in recent years to address various
solidification issues such as the crystalline nucleation and growth morphologies, and develop improved transport models for solidification processes, particularly for casting [45–52]. Local equilibrium at the moving interface is still considered as an important condition. It is assumed that there exists a small nucleation barrier (i.e., solidification starts at a temperature very close to the equilibrium freezing temperature), an infinite fast growth kinetics (i.e., no interface undercooling), and a well-defined solidification path corresponding to the equilibrium phase diagram.

The analysis of rapid solidification, on the other hand, needs to address the issues of nucleation and selection of various phases, which requires the introduction of nucleation theory of both stable and metastable phases into the model. It is also possible that several phases may form simultaneously, and one phase may grow over the other. Therefore the growth kinetics of various crystalline and amorphous phases must be incorporated into the theory. This is important because the melt may get undercooled during the growth even if there is no nucleation barrier at the beginning of the process, especially for the materials with slow growth kinetics such as the intermetallic compounds. In the case of alloys, the solute partitioning is significantly influenced by the melt undercooling and growth kinetics, and hence the effect of solute trapping must be accounted for by the model. The solidification morphology (planar, columnar, or equiaxed dendritic) is also greatly influenced by the nonequilibrium nature of rapid solidification processes [27, 53]. The theory must therefore allow for different mechanisms of latent heat release due to the variations in growth morphologies, and consider transition from one structure to another.

In this section we first review the historical development of rapid solidification modeling, the efforts made to incorporate various nonequilibrium phenomena into the model, and our understanding of RS processes. Modeling of selected rapid solidification processes is also described in brief.

3.1 Historical Development of Rapid Solidification Modeling

For the simplest case of equilibrium solidification without the melt flow, the solution of classical Stefan problem provides useful information on solidification rates [54]. Recent research on solidification modeling has focused on the prediction of solid microstructure by accounting for the melt flow and complex solidification morphology [45–51]. All of these studies, however, assume local equilibrium at the liquid/solid interface.

To explain various experimentally observed phenomena in rapid solidification, Ruhl [22] simply lowered the interface temperature in his numerical analysis of splat cooling, and attempted to simulate the nonequilibrium solidification of an undercooled melt. His results are believed to be seen in the literature. However, Ruhl did not consider kinetics effects. A similar approach was later used by Shingu and Ozaki [23] to model the splat cooling. They used the information on crystalline growth kinetics to determine the interface velocity at given melt undercooling conditions. Attempts were made to predict the conditions of glass formation and melt undercooling by comparing the kinetics-determined interface velocity with that calculated by the thermal model with a lowered solidification temperature at the interface.

The importance of nonequilibrium kinetics in rapid solidification modeling was first demonstrated by Levi and Mehrabian [24]. They introduced the crystalline growth kinetics into their thermal transport model to define the melt-solid interface, and predict recrystallization with a large increase in interface temperature during the solidification of an undercooled melt. The nucleation process was simplified by assigning a nucleation temperature and a planar interface was assumed between the melt and the solid. Cooling conditions resulting in an isothermal droplet (also called as Newtonian cooling) as well as two-dimensional variations of temperature in the droplet were considered to predict recrystallization. The significance of Levi and Mehrabian's work lies in the fact that it showed for the first time the importance of solidification kinetics that was always ignored. Later Clyne [55] generalized the model of Levi and Mehrabian [24] to apply it to splot cooling and melt-spinning where thin melt layers exist in direct contact with the cold substrates. Clyne also presented a methodology for the inclusion of nucleation kinetics into a thermal model to predict the nucleation temperature that may be below the equilibrium freezing temperature. The classical nucleation theory and interface kinetics theory were also incorporated into a one-dimensional model by Wood and Geist [56] who simulated the melting and resolidification of a semiconductor substrate irradiated by a nanosecond or picosecond pulsed laser. Complex nonequilibrium solidification and phase selection phenomena were predicted by this model. These initial studies on rapid solidification modeling have been followed by more complex kinetics models and sophisticated numerical techniques.

3.2 Physical Models for Rapid Solidification Processes

The requirement of very high rate of heat transfer in rapid solidification has kept its application limited to simple geometries with very small dimensions at least in one direction. The majority of RS processes can be categorized based on three simple geometries: planar, radial, and spherical [55] (Fig. 7), although three-dimensional effects exist in most of these configurations. For example, a spherical geometry can be adopted to describe the rapid solidification of an atomized droplet if one assumes that only one crystalline nucleus nucleates on the surface of the droplet. Processes such as spray deposition, splot cooling, melt-spinning, and surface melting, on the other hand, can be simulated as a first approximation by a one-dimensional planar geometry, if one ignores the two- and three-dimensional effects of melt-spraying and solidification. Figure 8 shows a schematic of the sequence of physical phenomena in splat cooling or spray deposition when a molten droplet impacts on a solid substrate. After impact the melt droplet deforms and spreads to form a liquid splash. If the impact velocity is very high, the spreading may complete far before the nucleation and solidification take place at the contact interface. In this case, the spreading and rapid solidification can be treated separately [16–17, 57]. However, if the impact velocity is moderate or low, solidification takes place simultaneously with the
spreading. A coupled treatment of melt spreading and solidification must be adopted under such conditions [18, 58–59]. Also, as shown by Wan et al. [59], the coupling between spreading and solidification is a strong function of substrate thermal diffusivity (or Peclet number), droplet Reynolds number, and thermal contact resistance between the melt and substrate. It is therefore difficult to prescribe any simple criterion for the velocity at which spreading becomes independent of rate of heat transfer and solidification. The reader should refer to the work of Majdheis [57], Zhang [58], and Wan et al. [59] on spreading, solidification, and heat transfer coupling between the splat and substrate.

In thermal spray coating the particle velocity is generally very high, up to 300 m/s, and hence a decoupled treatment of melt-spreading and rapid solidification may be a good approximation [59]. In this case rapid solidification can be modeled by assuming a thin layer of molten liquid suddenly brought in contact with a cold substrate [60–61]. As a first approximation, this kind of physical model can also be used to simulate the melt-spinning process, particularly, for planar flow casting (PFC) [55, 60]. In PFC, the ribbon can be considered as a thin sheet, since the dimensions in moving and transverse directions are very large compared to the puddle height and ribbon thickness. Similarly, in high-intensity laser surface melting, the thickness of the melt layer is much smaller than the laser beam diameter.

In a decoupled model, the thin melt layer, subsequent to spreading, is cooled down at a high cooling rate, leading to significant melt undercooling before nucleation. In most cases crystalline phase or phases nucleate on the substrate surface because of a low temperature there and also because of the catalytic effect of the substrate on nucleation. In some rare cases the crystalline phases also nucleate in the bulk melt, such as if the substrate induces very weak catalytic effects. Once the crystalline phase nucleates on the substrate, it covers the substrate surface very quickly, and the entire crystalline phase then grows in the direction normal to the substrate, a direction in which the heat is transferred out. This kind of solidification, also called columnar growth, shows a columnar structure in the solidified material. However, if the nucleation occurs in bulk melt, an equiaxed growth takes place. In many RS processes both of these growth phenomena can occur simultaneously. For example, in melt-spinning, a transition from initial columnar growth to equiaxed growth has often been observed if the thickness of the ribbon is large (see Fig. 6). In the case of a columnar growth, either a planar, cellular, dendritic morphology, or a mixture of them may develop at the solid/melt interface depending on the heat transfer conditions. After solidification the solid phase transformation can also play an important role in the development of microstructure. All of these can severely complicate the mathematical treatment.
To model rapid solidification processes accurately and reliably, mathematical models must be able to describe the various physical phenomena as described above. Not only the heat transfer but also the mass transfer, nucleation kinetics, crystalline growth kinetics, and solidification dynamics all need to be accounted for by the model.

3.3 Formulation for a Thin Liquid Layer in Contact with a Cold Substrate

As noted above, several important RS processes can be simplified as a thin layer of molten metal suddenly brought in contact with the substrate, as shown in Figure 9. Since the thickness in such conditions is much smaller than the other two dimensions, the transport of heat and mass can be considered one-dimensional in both the deposited layer and the substrate [55, 60]. However, a thermal contact resistance between the layer and the substrate must be considered, which can be introduced through an interfacial heat transfer coefficient, \( h \) [15, 62–63]. The mathematical formulation then depends on the melt/solid interface morphology as described below.

3.3.1 Planar Interface Solidification. The governing equations for planar interface solidification of a binary alloy system (Fig. 10a) can be written as

- Temperature,

\[
\rho_j C_{p_j} \frac{\partial T_j}{\partial t} = \frac{\partial}{\partial y} \left( K_j \frac{\partial T_j}{\partial y} \right)
\]  
(1)

- Concentration,

\[
\frac{\partial C_j}{\partial t} = \frac{\partial}{\partial y} \left( D_j \frac{\partial C_j}{\partial y} \right)
\]  
(2)

Figure 10  (a) Planar solidification; (b) dendritic solidification. Wang et al. [69].

where subscript \( j \) stands for the substrate, solidified material, or melt. (No mass diffusion equation needs to be solved in substrate.)

There exist four unknown parameters at the moving solid/liquid interface: interface velocity, \( V_i \), interface temperature, \( T_i \), and solute concentrations of liquid (\( C^L_i \)) and solid (\( C^S_i \)). The conservation laws for energy and mass provide the conditions

\[
\rho_L V_i L = K_S \frac{\partial T_S}{\partial y} \bigg|_i - K_L \frac{\partial T_L}{\partial y} \bigg|_i,
\]  
(3)

\[
(C^L_i - C^S_i) V_i = D_S \frac{\partial C_S}{\partial y} \bigg|_i - D_L \frac{\partial C_L}{\partial y} \bigg|_i.
\]  
(4)

Two other conditions can be obtained from the consideration of nonequilibrium crystalline growth kinetics of alloys. Baker and Cahn [64] call them the "response functions," which, in a general form, can be represented by

\[
f_1(V_i, T_i, C^S_i, C^L_i) = 0
\]

\[
f_2(V_i, T_i, C^S_i, C^L_i) = 0
\]  
(5)

The specific forms of these functions depend on the thermodynamics and kinetics considerations. In the case of local equilibrium, these response functions can be obtained from pure thermodynamic analyses. The interface temperature then relates to solute concentrations through solidus and liquidus curves of the equilibrium phase diagram. In RS processes, the solidification kinetics plays a critical role, and as a
result the response functions are very complex. Detailed discussions on various forms of response functions will be presented in Section 4.

3.3.2 Columnar Cellular or Dendritic Solidification. Columnar cellular or dendritic solidification involves complex shapes of the solid/melt interface, and explicit tracking of this interface is not an easy task, nor practical for engineering modeling. Traditionally these problems have been treated by considering the solid-liquid region as a solid-liquid mixture or a porous medium (i.e., a mushy zone) with varying effective properties [45–51, 65]. This allows one to avoid the complexity of the solid-melt interface geometries. If convection in the melt is neglected, no macroscopic segregation of the constituents needs to be considered, which leads to a macroscopic heat transport equation as

\[
\rho_l C_v \frac{\partial T_i}{\partial t} = \frac{\partial}{\partial y} \left( K_v \frac{\partial T_i}{\partial y} \right) + \rho_v L \frac{\partial f_s}{\partial t}
\]

(6)

where \( f_s = 0 \) in the liquid, \( f_s = 1 \) in the solid, and \( f_s = f(T, C, y, t) \) in the mushy zone. For alloy solidification with localized equilibrium conditions, Clyne [65] has shown that the functional form of \( f_s \) can be derived from the analysis of microscale solute redistribution between cells or dendrites. For example, for extremely slow solidification condition, the level-rule can be used to derive a relationship between the solid fraction and temperature in the mushy zone:

\[
f_s = \frac{1}{1 + k_e \frac{T - T_m}{T - T_L}}
\]

(7)

where \( k_e \) is the equilibrium partition coefficient, \( T_L \) is the equilibrium liquidus temperature corresponding to the melt concentration \( C_0 \), and \( T_m \) is the equilibrium freezing temperature of the solvent. It should be noted that Eq. (7) is derived by assuming that the liquidus and the solidus curves are linear such that the equilibrium partition coefficient can be considered constant. More complex relationships for \( f_s \) can be derived based on microsegregation analysis in the mushy zone by taking into account the effect of finite solute diffusion and nonequilibrium solidification kinetics. A brief summary of recent progress in this area is presented in Section 6.

It should be pointed out that alloy solidification has become an important research topic recently because of its applications in traditional metal processing. Significant progress has been made in the last two decades to model such complex solidification processes. Sophisticated models have been developed to accommodate various complex physical mechanisms of mushy zone solidification including melt convection and macrosegregation. Excellent reviews of modeling of alloy solidification have been presented by Rappaz [46], Beckermann and Wang [50], Prescott and Incropera [51], and others, but mainly for solidification under local equilibrium conditions.

Interested readers should refer to these articles as well as the bibliographies cited there. Here we will focus on only nonequilibrium solidification.

Important length scales that govern cellular or dendritic solidification include the dendrite tip radius, primary dendrite arm spacings, secondary dendrite arm spacings, and so on. Models based on microscale heat and mass transfer and solidification kinetics have been developed to approximate these parameters. These models can be incorporated into the above macroscopic transport equations, Eqs. (1), (2), and (6), as supplementary correlation or boundary conditions [46, 50], leading to the so-called macro- and micromodeling of solidification.

Significant progress in macro- and micromodeling of rapid solidification has been made by employing successfully the dendritic models developed by Kurz, Trivedi, and their co-workers [13] together with the above transport model (Fig. 10b). By employing the microscale dendritic model as a boundary condition at the dendrite tip-melt interface, the macro/micro-model can determine the dendrite tip radius and the transition of solidification morphology from planar to dendritic growth, and vice versa [66–69]. In this treatment an artificial interface enveloping the dendrite tips is considered as a moving interface, with the mushy zone behind the tips considered as a mixture. At this artificial tip-melt interface, the dendritic solidification is governed by five different parameters: tip temperature, tip velocity, solute concentrations of liquid and solid at the tip, and tip radius. Response functions similar to Eq. (5) can be derived using the microscale dendritic tip growth dynamics. Sections 5 and 9 present a detailed review of these functions and some typical results.

3.4 Other Kinetics Issues

There are several other kinetics issues that need to be addressed to complete the mathematical description of RS processes. The first important issue is to determine the conditions at which the crystalline nucleation takes place and solidification starts. This question must be answered before the solidification model can be employed. Crystalline nucleation in a molten liquid is a complex physical phenomenon and has not been well understood thus far. However, several phenomenological models have been developed in the last one hundred years. In rapid solidification the formation of metastable phase(s) becomes another important issue. Phase selection among stable and metastable phases, in most cases, is determined by the nucleation kinetics. A nucleation kinetics model together with heat and mass transfer formulation can provide information on initial nucleation temperature, \( T_N \), defined as the temperature when the first nucleus appears, as well as on the number and distribution of nuclei. A brief review of nucleation kinetics is provided in Section 4.

During solidification many different interface morphologies develop depending on the solidification conditions, leading to a variety of microstructures. Transition from one morphology to another can be considered through the interface stability theory. Planar interface stability theories have advanced significantly in recent years, and several criteria are now available to determine the interface velocity at which a planar interface will be broken down, and more complex cellular or dendritic struc-
3.5 Numerical Scheme and Iteration Procedure

Several numerical techniques have been developed to solve phase-change problems. Most of these methods can be categorized into two groups: interface tracking (two-domain) method and single-domain method. In the former case, the solid and melt regions are considered separately and coupled through the moving interface. The interface is continuously tracked during the solidification process. In the single-domain method, the solid and liquid phases are considered as one domain with different physical properties. Generally, the enthalpy equation instead of temperature equation is solved and the solid/liquid interface is traced back from the enthalpy-temperature relationship. The single-domain method is especially convenient for alloy solidification where a mushy zone exists between the solid and melt, and it therefore has been widely used in conventional alloy solidification modeling [46–51].

Early works of Levi and Mehrabian [24] and Clyne [55] both employed the enthalpy formulation in a single domain to solve for the temperature field. Since the temperature was unknown and dependent on the interface velocity, explicit tracking of the interface was used in both of these studies. In Levi and Mehrabian’s work, the interface was traced back from the enthalpy-temperature relationship, while in Clyne’s method, a local heat source was added at the node where the interface was located. Since both of these methods cannot accurately predict the interface location and temperature, which are strongly related through kinetics relationship, Wang and Matthys [60] have proposed an explicit interface tracking method through element subdivision. A numerical scheme based on coordinate transformation has been developed recently by Wang et al. [70] to immobilize the solid-liquid interface in the computational domain and track it implicitly. The coordinate transformation is particularly useful in the case of rapid planar alloy solidification where a very thin concentration boundary layer exists in front of the interface, and therefore extremely fine grids are required to resolve the segregation of solute species. For planar rapid solidification, the interface tracking method seems to be a natural choice because of the existence of a distinct solid-liquid interface. This review will focus only on the physical issues of nonequilibrium solidification. Readers interested in the details of the numerical methods should refer to the original papers cited here.

Extensive research efforts have been made in recent years to develop special numerical algorithms to simulate solidification in single and multiple component systems, particularly, suitable for multidimensional problems. Although rapid solidification modeling is currently limited to one-dimensional systems and does not require very sophisticated numerical techniques to be used, it is expected that as RS modeling advances these algorithms, particularly adaptive methods [71], will be very helpful in modeling two- and three-dimensional coupled macro and micro problems.

4 KINETICS OF CRYSTALLINE NUCLEATION AND GROWTH

Two fundamental issues in solidification are the nucleation and growth of crystalline phases. Thermodynamic consideration dictates whether a process can or cannot take place, but it is the kinetics that controls the rate of the process. In most of the conventional solidification processes, nucleation and growth kinetics of crystals are usually under an implicit assumption of the local thermodynamic equilibrium during solidification. Under such conditions, stable crystalline phases form immediately after the melt temperature has reached the equilibrium freezing temperature (for alloys, the equilibrium liquidus temperature at the given concentration). Crystal growth kinetics is also neglected since the phase-change process is controlled only by the removal of latent heat. As a result conventional melting and solidification problems have been conveniently treated as pure thermal problems with moving boundaries. Rapid solidification, on the other hand, is a highly nonequilibrium process, so kinetics of crystalline nucleation and growth are extremely important issues in this case and must be incorporated into the model. A summary of the research performed on rapid solidification theory, which includes crystalline nucleation and growth kinetics, is provided here, starting with the concepts of melt undercooling and metastable phase formation.

4.1 Melt Undercooling and Metastable Phase Formation

Because of altered chemical, structural and/or morphological forms, rapid solidification and other nonequilibrium processes invariably experience competition among various metastable states, which leads to the development of novel microstructures [12]. Thermodynamically, phase transformation can occur only when there exists a strong driving force, which in the case of solidification is the difference between the Gibbs free energies of the solid and the melt, and this is proportional to the melt undercooling (Fig. 11). During cooling of a molten material, its temperature first meets the equilibrium freezing temperature of the stable solid phase, for example, \( T_m \) for stable phase \( \alpha \). If the temperature is further lowered, the melt is considered to be undercooled with an undercooling \( \Delta T_u = T_m - T \). At temperature \( T < T_m \), the solid \( \alpha \) phase has a lower free energy than the corresponding liquid phase. The difference of the free energy, \( \Delta G_{\alpha} = G_\alpha(T) - G_m(T) \), between the liquid and \( \alpha \) phase then leads to phase transformation from the melt to the solid \( \alpha \) phase. If the undercooled melt can be further cooled below the equilibrium freezing temperature of phase \( \gamma \) \( (T < T_{\gamma}) \) without the nucleation of phase \( \alpha \), the melt will be undercooled relative to the metastable \( \gamma \) phase. Then there is a free energy driving force available for the phase transformation from the liquid phase to the solid \( \gamma \) phase, \( \Delta G_{\gamma} = G_\gamma(T) - G_m(T) \). At this temperature it is possible to form both the stable \( \alpha \) phase and the metastable \( \gamma \)
phase. The selection of the final phase(s) will, however, depend on the nucleation kinetics of each phase. A metastable phase may form instead of a stable phase if the nucleation prefers metastable conditions, although the stable phase has a higher driving force than that of a metastable phase, $\Delta G_{\text{m}} > \Delta G_{\text{s}}$. If the melt can be further cooled down to a very low temperature and both $\alpha$ and $\gamma$ phases cannot be formed, then the metastable $\gamma$ phase or even a metallic glass (amorphous phase) will be formed [28].

### 4.2 Nucleation Kinetics

In most conventional solidification processes, crystalline nucleation takes place with very little melt undercooling because of the catalytic action of the impurities in the melt. In most of these cases a stable phase therefore is selected. A large melt undercooling can be achieved only under special solidification conditions, as described in Section 2.

#### 4.2.1 Classical Nucleation Theory

In the classical approach, nucleation is considered as a thermal-activation process in which the solidlike clusters are formed in the undercooled melt due to thermal fluctuations. The formation of these solidlike clusters implies an energy reduction by the transformation of a volume fraction of the system from the undercooled state of higher energy melt to the solid state of lower energy. The formation of a solidlike cluster also means that energy is gained to build an interface between the solid and melt. Assuming for simplicity a spherelike geometry of the clusters, the Gibbs free-energy change due to the formation of a cluster of radius $r$ can be written as [72]

$$\Delta G_n = -\frac{4}{3} \pi r^3 \Delta G_{\text{LS}} + 4\pi r^2 \sigma$$

(8)

where $\sigma > 0$ is the melt-crystal interfacial energy and $\Delta G_{\text{LS}}$ is the Gibbs free-energy difference between the melt and solid at the given undercooled temperature. Since the terms in Eq. (8) for volume and interface contributions have different dependence on $r$, $\Delta G_n$ exhibits a positive maximum value $\Delta G_c$ at a critical radius $r_c$, as shown in Figure 12. The critical Gibbs free-energy difference, $\Delta G_c$, therefore forms an activation barrier against crystallization and is generally called the nucleation barrier. For $r < r_c$, the interface-to-volume ratio is large and the interface energy dominates. Such a cluster is called an embryo, and it is unstable and decays spontaneously. On the other hand, a cluster of radius larger than $r_c$, termed a nucleus, can lower its free energy by growing, and thus initializes crystallization. The critical nucleus radius $r_c$ can be obtained by differentiating Eq. (8) with respect to $r$:

$$r_c = \frac{2\sigma}{\Delta G_{\text{LS}}}$$

(9)

which leads to the Gibbs free energy for nucleation barrier as

$$\Delta G_c = \frac{16\pi \sigma^3}{3\Delta G_{\text{LS}}}$$

(10)

Figure 12 Change in free energy as a function of the cluster radius. There exists a critical radius $r_c$ when $\Delta G_c$ is maximum.
Following the work of Volmer and Weber [73] and Becker and Döring [74] on nucleation of liquid from vapor, Turnbull and Fisher [75] introduced a steady-state, homogeneous nucleation theory for solid crystal nuclei from an undercooled melt. It can be expressed as [29]

\[ I_{SS} = N_i \frac{k_B T}{h} \Gamma_z \exp \left( -\frac{\Delta G_a}{k_B T} \right) \exp \left( -\frac{\Delta G_c}{k_B T} \right) \]  

(11)

where \( I_{SS} \) is the nucleation frequency, \( N_i \) is the total number of atoms in the undercooled melt and is on the order of Avogadro's number, \( \Delta G_a \) is the activation energy for interatomic diffusion in the liquid, \( k_B \) is the Boltzmann constant, \( h \) is the Planck's constant, and \( \Gamma_z = [\Delta G_a/(3\pi k_B T)]^{1/2} \) is known as the Zeldovich factor. According to Eq. (11), the nucleation rate \( I_{SS} \) is governed by two exponential terms. At high temperatures, in the vicinity of the equilibrium freezing temperature (i.e., at small undercoolings), the second exponential term containing the nucleation barrier for the formation of critical nuclei dominates. While at low temperatures, particularly in the vicinity of the glass temperature (i.e., at high undercoolings), the first exponential term, which takes into account the atomic diffusion process, controls the nucleation frequency.

For a quantitative estimate of nucleation rates it is often assumed that \( \Delta G_a \) corresponds to the activation energy for atomic self-diffusion [24, 29]. The diffusion coefficient \( D_L \) is generally correlated with the melt viscosity, \( \eta \), via the Einstein-Stokes relation [29]

\[ D_L = \frac{k_B T}{6\pi \eta a_0} = \frac{a_0^2 \nu}{\eta} \]  

(12)

where \( a_0 \) is a typical atomic diameter and \( \nu \) is a characteristic atomic jump frequency,

\[ \nu = \nu_0 \exp \left( -\frac{\Delta G_a}{k_B T} \right) \]  

(13)

The coefficient \( \nu_0 \) denotes the vibration frequency of the atoms and is in the order of \( 10^{12} \) to \( 10^{13} \) Hz. The Einstein-Stokes relationship correlates the macroscopic magnitude of \( \eta \) with the microscopic magnitude of \( D_L \). Equation (11) then reduces to

\[ I_{SS} = \frac{K \Gamma_z}{\eta(T)} \exp \left( -\frac{\Delta G_c}{k_B T} \right) \]  

(14)

For a typical value of \( \Gamma_z = 1/20 \), Turnbull [76] simplified the equation to

\[ I_{SS} = \frac{10^{36}}{\eta(T)} \exp \left( -\frac{\Delta G_c}{k_B T} \right) \]  

(15)

Since the viscosity \( \eta \) changes by about 15 orders of magnitude between the glass temperature and the equilibrium freezing temperature, a quantitative estimation of viscosity is crucial for the determination of the nucleation frequency.

The temperature dependence of viscosity in an undercooled metallic melt is an unresolved issue. Often an Arrhenius-like expression is used with a fixed activation energy for viscosity flow, \( \Delta G_n \) [29, 77]:

\[ \eta = \eta_0 \exp \left( -\frac{\Delta G_n}{k_B T} \right) \]  

(16)

Such Arrhenius-like expressions should be able to describe the viscosities of the systems with strong covalent bondings, where the viscous flow requires breaking of the directional bonds. On the other hand, in metallic systems one expects more or less pronounced isotropic bondings. In such cases the Vogel-Fulcher-Tammann expression

\[ \eta(T) = \eta_0 \exp \left( -\frac{B}{T - T_{00}} \right) \]  

(17)

is considered to be more appropriate [29, 77]. Equation (17) implies that the viscosity diverges if the temperature approaches the ideal glass temperature \( T_{00} \). For metallic melt, an approximation is given by Thompson and Spaepen [78] as

\[ \eta = 10^{-3.3} \exp \left( \frac{3.34 T_m}{T - T_g} \right) \]  

(18)

and the glass transition temperature is assumed as \( T_g = 0.25 T_m \) [76].

One critical parameter in nucleation theory is the melt-crystal interfacial energy, \( \sigma \). Experimental determination of \( \sigma \) is very difficult and therefore several models have been proposed to estimate its value \( \sigma \). In regard to the structural aspects of \( \sigma \), Spaepen [79] has obtained an expression for interfacial energy as

\[ \sigma = \alpha \frac{\Delta S_m T}{(N_a V_m)^{1/3}} \]  

(19)

where \( \Delta S_m \) is the entropy of fusion, \( N_a \) is the Avogadro's number, \( V_m \) is the molar volume, and the factor \( \alpha \) represents the structure of the solid. In the case of bcc structure, \( \alpha = 0.71 \), whereas in the fcc or hcp structure, \( \alpha \) is taken as 0.86 [80].
4.2.2 Heterogeneous Nucleation  Homogeneous nucleation is an intrinsic process, and the nucleation threshold depends exclusively on the thermodynamic properties of the material such as the interface energy and the Gibbs free-energy difference between the liquid and solid. In practice, heterogeneous nucleation plays a more dominant role. Foreign phases such as container wall, metal oxides at the melt surface, and impurity particles in the melt, all participate in the nucleation process. Therefore heterogeneous nucleation is an extrinsic process and can be significantly influenced by the process conditions.

The kinetics of heterogeneous nucleation can be described by a modification to the barrier for homogeneous nucleation, $\Delta G_C$. The modification needs to account for the different interfaces and modified critical nucleus volume involved in the crystal formation. For a spherical cap model as illustrated in Figure 13, the evaluation of critical free-energy difference, $\Delta G_C^{\text{het}}$, for heterogeneous nucleation yields [72]

$$\Delta G_C^{\text{het}} = \Delta G_C^{\text{hom}} f(\theta) = \frac{\Delta G_C^{\text{hom}} (2 - 3 \cos \theta + \cos^3 \theta)}{4}$$  (20)

where the contact angle $\theta$ is calculated based on the interfacial energies as

$$\cos \theta = \frac{\sigma_{mm} - \sigma_{cs}}{\sigma_{cm}}.$$  (21)

Over the variation in $\theta$ ranging from complete wetting to nonwetting, $f(\theta)$ varies from 0 to 1. This change in nucleation barrier has significant influence on the nucleation rate. In addition, the atoms involved in the nucleation process will be the ones that are in direct contact with the foreign surface(s) where the surface catalytic effect is strong. Under such conditions the rate of heterogeneous nucleation can be written as [29]

$$J_{SS}^{\text{het}} = N_A \frac{k_B T}{h} \Gamma_c \exp \left( - \frac{\Delta G_a + \Delta G_c f(\theta)}{k_B T} \right)$$  (22)

where $N_A$ is the number of the atoms located at the interface to the substrate.

It should be pointed out that the spherical cap model, a classical description of heterogeneous nucleation, represents the situation that is often unrealistic or even unphysical [12]. For example, it is clear that the nucleus height will approach atomic dimensions before complete wetting is achieved as $\theta$ is reduced. In fact, for the spherical cap model, this condition is applicable when $\theta < 30^\circ$. Therefore, for high nucleant potency that is often of interest in theoretical analysis, there is clearly a breakdown in the above continuum model. Moreover, the conditions adopted in the idealized models are those of a flat substrate and a clean liquid substrate interface without, for example, segregation. It is well known that on the length scale of nucleus, many substrates are not atomically flat but contain various steps and other features that can act as preferred nucleation sites. Similarly the assumption of a pristine liquid-substrate interface cannot be expected to be valid in general. Although some modifications to the model to treat simple topographic features such as steps have been reported, the consideration of real surface topography and its influence on nucleation energetics have not been worked out in detail. Moreover a real surface involves a distribution of sites of different topographic features and nucleation energetics which must be incorporated into an overall kinetics expression for varying rates. The implication is that there may not be a single nucleation frequency, $I$, but rather a distribution of frequencies based on the distribution of sites and their associated energetics and kinetics. Moreover the situation depicted in the classical model is that of a static interface. This is also not a realistic view, especially during solidification where continuous cooling is involved and dynamic interfaces that change the shape and position are of importance.

4.2.3 Nucleation in Binary Alloys. In binary systems, the crystalline nucleus can have a composition different from that of the melt, and both the free energy difference between the melt and the crystal (per unit volume of crystal) and the solid-liquid interfacial energy are therefore composition dependent. Thompson and Spaepen [78] have proposed a method for calculating the composition of the nucleating crystal as well as the free-energy difference between the liquid and solid phases. The composition of the nucleating crystal is chosen in such a way that the free-energy difference is maximized. The free-energy change per unit volume, associated with forming a small amount of solid of composition $C_A^S$ out of the melt is given by

$$\Delta G_V = \frac{C_A^S \Delta \mu_A + (1 - C_A^S) \Delta \mu_S}{V_m}$$  (23)

where

$$\Delta \mu_A = \mu_A^L - \mu_A^S$$

$$\Delta \mu_S = \mu_S^L - \mu_S^S$$  (24)

Figure 13  Schematic for heterogeneous nucleation on a flat and smooth substrate surface. $\theta$ is the contact angle between the crystal and the substrate surface.
with \( \mu_1^A, \mu_1^B, \mu_2^A, \) and \( \mu_2^B \), are the chemical potentials of components A and B in liquid and solid phases, respectively, and \( V_m \) is the average molar volume of the solid, assumed to vary linearly between the molar volumes \( V_m^A \) and \( V_m^B \) of the pure solid systems:

\[
V_m = C_S^A V_m^A + (1 - C_S^A) V_m^B
\]

(25)

If we assume that the solid composition at nucleation, \( C_{NS} \), is given by the largest difference in free energy, \( \Delta G_V \) between the liquid and solid states, then \( \Delta \mu^A = \Delta \mu^B \) and

\[
\Delta G_V = \frac{\Delta \mu^A}{V_m}
\]

(26)

For given composition dependence of the liquid and solid free energies, one can then calculate the solid nucleus composition and free energy of nucleus formation as functions of the initial liquid composition, \( C_L \), and undercooling \( \Delta T = T_L - T \). An example was given by Thompson and Spaepen [78] who have derived the relationships for \( C_{NS} \) and \( \Delta G_V \) for an undercooled melt at temperature \( T \) based on regular solution models. Recently Zhang [81] has carried out similar calculations for more general binary systems.

The crystal-melt interfacial energy, \( \sigma \), for a binary alloy can be estimated using the same relationship as derived by Spaepen, Eq. (19), except that the composition-dependent molar volume and molar entropy of fusion of the alloy have to be used. For example,

\[
\Delta S_m = C_S^A \Delta S_m^A + (1 - C_S^A) \Delta S_m^B
\]

(27)

Furthermore, unless specific data are available, it can be assumed that the composition dependence of glass transition temperature \( T_g \) is weak and can be approximated by

\[
T_g = 0.25(C_L^A T_m^A + (1 - C_L^A) T_m^B)
\]

(28)

based on the suggestion made by Turnbull [76], that is, \( T_g \approx 0.25 T_m \) in pure metals.

4.2.4 Transient Effect. The expressions for nucleation rate obtained above are based upon the assumption of a quasi-stationary cluster distribution function. This implies that the distribution function can follow changes in the system very rapidly, so that at all times the cluster distribution function has its instantaneous equilibrium value. However, during rapid cooling this condition can be easily violated. In such processes the cooling time can be so short that there is not enough time to establish the dynamic equilibrium in the disturbed cluster system. This can lead to deviations from the quasi-stationary cluster distribution function and result in significant transient effects. Fujino et al. [82] have studied the transient effects of nucleation in rapid solidification using the classical nucleation theory as summarized in the following paragraph.

In classical nucleation theory, the time-dependent effects mainly come from the transient behavior of the nucleation rate which is characterized by the time necessary for the cluster distribution in liquid phase to attain an equilibrium value. The transient nucleation rate is related to the steady-state nucleation rate, \( I_{SS} \), as [83–84]

\[
I = I_{SS} \left[ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left( -\frac{m^2 t}{\tau} \right) \right]
\]

(29)

where \( \tau \) is the transient time given by Fujino et al. [82],

\[
\tau = \frac{4}{\pi^3 k_p^* \Gamma_2^2}
\]

(30)

where \( k_p^* \) is the frequency factor corresponding to the absorption rate of a single atom to a critical nucleus of \( n^* \) atoms, and in the case of heterogeneous nucleation, is given by

\[
k_p^* = \frac{6 D L_2 n r c(1 - \cos \theta)}{\lambda^2}
\]

(31)

where \( \lambda \) is the atomic jump distance. Fujino et al. [82] have carried out the calculation for transient nucleation of rapidly solidified pure iron with different contact angles. The transient time decreases with decreasing contact angle and is smaller than \( 10^{-10} \) s if the melt undercooling is larger than \( 50 \) K. Transient nucleation effects in rapid solidification have also been investigated by Reiss and Katz [85] and Lin et al. [86].

4.2.5 Recent Development in Nucleation Kinetics Theory. The preceding discussion on crystal nucleation is based on the classical nucleation theory (CNT) that assumes an infinitely thin interface between the crystal and the melt. Recent computer simulations, however, indicate that the nuclei are nearly "all interface," and therefore the assumption that the thickness of the interface region is very small compared to the size of the nuclei (i.e., capillarity approximation in CNT) may not be valid. The error introduced by this assumption can be corrected by using the so-called diffuse interface theory (DIT) which assumes a finite width of the solid-liquid interface between the nuclei and melt. Spaepen [87] has presented a detailed account of the physics of the crystal-melt interface and proposed a generic model to determine the crystal-melt interfacial surface energy. Granasy [88–89], on the other hand, has proposed a much simplified treatment that seems to produce quite satisfactory results.
for crystal nucleation in an undercooled melt [90]. The diffuse interface theory provides a nucleus size-dependent interfacial energy, in contrast to CNT which assumes a constant interfacial energy. A detailed description of the diffuse interface theory can be found in the papers by Granasy [88–89] and Spaepen [87].

4.3 Crystalline Growth Kinetics for Pure Materials

Once a crystal is nucleated in an undercooled melt, it starts to grow by attaching more and more atoms to the nucleus. The classical kinetic rate theory provides a phenomenological model for this crystalline growth process as [91–92]

\[ V = a_0 v f \exp \left( -\frac{\Delta G_s}{k_B T} \right) \exp \left( -\frac{\Delta S_{LS}}{k_B} \right) \left[ 1 - \exp \left( -\frac{\Delta G_{LS}}{k_B T} \right) \right] \]  (32)

where \( a_0 \) is the average jump distance on the order of an interatomic distance, \( v \) is the atomic vibration, or attempt frequency, and \( f \) is the fraction of interfacial sites where the attachment can occur. The value of \( f \) is close to unity for “rough” crystal-melt interfaces such as in metals, but it is small for “smooth” interfaces.

The atomic movement during the crystallization can be either diffusion or collision limited. The classical kinetic rate theory assumes a diffusion-limited growth where the motion of an atom from the liquid to the crystal requires a rearrangement similar to that for a diffusive jump in the liquid. For diffusion-limited growth, \( \Delta G_s \) corresponds to the free activation energy for liquid diffusivity. The growth in concentrated metallic alloys and systems with large crystalline unit cells belongs to the diffusion-limited growth. The crystallization of oxide glasses and other covalent materials also falls into this category [91]. For some elemental metals, the experimental measurements have, however, shown much larger growth velocities than the maximum velocity predicted by the diffusion-limited growth model [93]. A collision-limited growth mechanism can describe this kind of crystalline growth. In this case the activation barrier \( \Delta G_s \) approaches zero [92], and the maximum crystalline growth velocity is limited only by the rates of impingement of atoms with the crystal surface, which is scaled by the speed of sound [93]. It should be noted that three orders of magnitude difference in growth velocities is predicted by the two growth models.

Although no rigorous theories are available to guide the selection of the model for a given material, some common wisdom has been outlined for both single-component systems and alloys by Aziz and Beottinger [94]. For example, the collision-limited growth is believed to be applicable to the pure metals, while the diffusion-limited growth is better suited for those materials with complex molecular structures such as ceramics. Regardless of this uncertainty in the selection of the atomic movement mechanism, the validity of the transient rate theory is supported by several experiments [29, 91]. Further qualitative confirmation of this theory has been provided by the molecular dynamics modeling of melting and solidification of silicon.

### Table 4.1 Linear Kinetics Coefficients for Selected Materials.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Al</th>
<th>Cu</th>
<th>Ni</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_m )</td>
<td>K</td>
<td>933.6</td>
<td>1356</td>
<td>1728</td>
<td>1941</td>
</tr>
<tr>
<td>( \Delta H_m )</td>
<td>J/mole</td>
<td>( 1.05 \times 10^4 )</td>
<td>( 1.3 \times 10^4 )</td>
<td>( 1.7 \times 10^4 )</td>
<td>( 1.5 \times 10^4 )</td>
</tr>
<tr>
<td>( \Delta S_{m/R} )</td>
<td>—</td>
<td>1.35</td>
<td>1.15</td>
<td>1.19</td>
<td>0.9</td>
</tr>
<tr>
<td>( \mu_s )</td>
<td>m/s</td>
<td>4688</td>
<td>3485</td>
<td>4036</td>
<td>5230</td>
</tr>
<tr>
<td>( \mu_k )</td>
<td>m/s-K</td>
<td>1.74</td>
<td>0.94</td>
<td>0.85</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Source: Wang and Matthys [96].

Equation (32) provides a relationship between the interface velocity and interface conditions (e.g., the temperature for pure materials, and temperature and concentration for alloys). If the interface temperature is not too far away from the equilibrium freezing temperature, Eq. (32) can be approximated by a linear kinetics model for pure materials as

\[ V = \mu_k (T_m - T) \]  (33)

where \( \mu_k \) is the linear kinetics coefficient. For pure metals with a collision-limited growth, \( \mu_k \) can be estimated as [92, 96]

\[ \mu_k = \mu_s \exp \left( -\frac{\Delta S_m}{R} \right) \frac{\Delta H_m}{RT_m^2} \]  (34)

where \( \mu_s \) is the speed of sound in the melt. Using Eq. (34), Wang and Matthys [96] have obtained the values of \( \mu_k \) for a range of pure metals (Table 1). For materials with complex structures, \( \mu_k \) can be estimated using the interfacial diffusion velocity \( V_0 \) instead of \( \mu_s \).

4.4 Crystalline Growth Kinetics for Alloys

Crystalline growth of an alloy shows much more complexity than that of a pure material. Besides considering the movement of the interface, one also needs to account for the solute redistribution across the interface. Nonequilibrium growth kinetics of alloys should therefore provide relation between the interface velocity and interface conditions with the consideration of solute partitioning [11]. The primary effect of alloying on the interface velocity is to reduce the driving free energy for the growth of metastable solute-trapped material. As a first approximation, one can assume that a relationship similar to that in the continuous growth model, Eq. (32), for a pure material with a rough crystal/melt interface still holds for alloy kinetics. The free-energy difference between the melt and solid phase as well as the activation energy barrier should be solute concentration dependent [97]. A simplified expression for the growth kinetics of alloy solidification can then be written as
\[ V = V_c \left[ 1 - \exp \left( -\frac{\Delta G_{LS}}{RT} \right) \right] \]  

(35)

where \( V_c \) represents the maximum growth velocity with an infinite driving force, which again, can be scaled as the speed of sound, \( u_s \) for the collision-limited growth and the interface diffusion velocity, \( V_D \) for the diffusion-limited growth.

The free-energy change \( \Delta G_{LS} \) of forming an infinitesimal amount of solid with composition \( C_s \) from liquid with composition \( C_L \) at temperature \( T \) can be obtained from Baker and Cahn [64]:

\[ \Delta G_{LS} = \Delta \mu^A (1 - C_S) + \Delta \mu^B C_S \]  

(36)

For dilute alloys the changes in chemical potentials across the solidification front are given by

\[ \Delta \mu^B = RT \ln \left( \frac{C_S C_I^i}{C_L C_S} \right) \]  

(37)

and

\[ \Delta \mu^A = RT \ln \left( \frac{(1 - C_S)(1 - C_I^i)}{(1 - C_L)(1 - C_S)} \right) \]  

(38)

Equation (36) can then be written as

\[ \Delta G_{LS} = RT \left[ C_S \ln \left( \frac{C_S C_I^i}{C_L C_S} \right) + (1 - C_S) \ln \left( \frac{(1 - C_S)(1 - C_I^i)}{(1 - C_L)(1 - C_S)} \right) \right] \]  

(39)

By defining a nonequilibrium partition coefficient, we have

\[ k = \frac{C_S}{C_L} \]  

(40)

Now, assuming straight liquidus and solidus lines for binary alloys, we can further simplify Eq. (39) for free-energy difference \( \Delta G_{LS} \) to [98]

\[ \frac{\Delta G_{LS}}{RT} = \left( \frac{1 - k_e}{m_L^i} \right) (T_m + m_L^i C_L - T) + C_L \left[ (k_e - k) + k \ln \left( \frac{k}{k_e} \right) \right] \]  

(41)

where \( m_L^i \) is the slope of the equilibrium liquidus curve and \( k_e \) is the equilibrium partitioning coefficient.

Substituting Eq. (41) into Eq. (35) and employing the Fourier expansion, we obtain the linear kinetics equation for dilute binary alloys [98]:

\[ V = \mu_k (T_m + m_L C_L - T) \]  

(42)

with the slope of the nonequilibrium liquidus curve as

\[ m_L = m_L^e \left[ 1 + \frac{k_e - k + k \ln(k/k_e)}{1 - k_e} \right] \]  

(43)

where \( \mu_k \) is the linear kinetics coefficient of the solvent and can be calculated from Eq. (34).

The nonequilibrium partitioning coefficient, \( k \), can be obtained using the solute transport model in the interfacial region. For example, based on Henry’s law, Aziz and Kaplan [97] have obtained an expression for \( k \) as

\[ k = \frac{V a_0 / D_i + \kappa_e}{1 + V a_0 / D_i - [(1 - \kappa_e)C_L/100]} \]  

(44)

where \( D_i \) is the interface diffusion coefficient and

\[ \kappa_e = \frac{k_e (100 - C_S^i)}{100 - C_S^i} \]  

(45)

For dilute binary alloys with a constant equilibrium partition coefficient, \( k_e \), Eq. (44) reduces to the familiar form for \( k \) as [99]

\[ k = \frac{k_e + V / V_0}{1 + V / V_D} \]  

(46)

where \( V_0 \) is the interface characteristic diffusion velocity, \( V_D = D_i / a_0 \).

One of the consequences of rapid solidification is “solute trapping,” which occurs when the solute elements do not have sufficient time to be diffused away from the interface and are thus trapped in the solid. Solute trapping in rapid solidification can result in a partition coefficient that is much larger than its equilibrium value, \( k > k_e \) when \( k_e < 1 \). From Aziz’s model, it is evident that the higher the interface velocity, the larger the nonequilibrium partition coefficient (if \( k_e < 1 \)). When the interface velocity is much larger than the interface diffusion velocity, \( k \) approaches unity and
the “partitionless” solidification can occur; that is, \( k = 1 \) even when \( k_e < 1 \). When \( k = 1 \), the alloy solidification is similar to that of a pure material.

If the liquidus or solidus curves are not straight lines, the partitioning coefficient \( k_e \) does not remain constant and the relationships above cannot be used. For dilute binary alloys, Carrard et al. [100] have proposed a methodology to determine the interface temperature from the equilibrium liquidus curve as

\[
T = g(C_L^e)
\]

(47)

where \( g(C) \) is a fitted polynomial function of concentration. The equilibrium solute concentration \( C_L^e \) at the interface is a function of the interface velocity and nonequilibrium concentration \( C_L \). It can be determined from the free-energy variation of phase change at the interface,

\[
C_L^e = C_L \left( 1 + \frac{k_e - k(1 - \ln k/k_e)}{1 - k_e} \right) + \frac{V}{V_c(1 - k_e)}
\]

(48)

with \( k_e(T) \) as a function of the interface temperature.

For concentrated alloys or intermetallic compounds, the liquidus and solidus curves become strongly nonlinear. Trivedi and Kurz [101] have proposed a simple treatment for such cases by assuming an idealized phase diagram composed of a piecewise linear solidus and liquidus curves.

5 SOLIDIFICATION MORPHOLOGY AND MICROSTRUCTURE

Microstructure evolution in solidification is mainly controlled by nucleation and growth of crystalline phases. If nucleation takes place in the bulk melt, equiaxed structure will be formed. However, in many rapid solidification processes, nucleation takes place on foreign surfaces, resulting in columnar solidification morphologies. Mostly transition from columnar to equiaxed solidification takes place at the later stage of the process if the melt layer is thick. Important issues in columnar solidification are when the planar interface is stable, how the cells or dendrites grow, and what are the important microstructure length scales such as tip radius, and primary and secondary arm spacings.

5.1 Solidification Morphology and Interface Stability

Selection of solidification morphology is critical, since different morphologies lead to different geometric configurations of the melt-solid interface, and as a result, different microstructures. Additionally different solidification morphologies are associated with different latent heat release mechanisms that can greatly affect the thermal transport during solidification. Three basic solidification morphologies are planar interface, columnar cellular or dendritic, and equiaxed dendritic, which have all been observed in rapidly solidified solids. Generally, a planar or a columnar dendritic growth is expected in surface melting and resolidification, an equiaxed dendritic growth in melt atomization, and a mixture of two or three different morphologies in melt-substrate quenching.

Planar interface solidification is expected under two extreme conditions: very slow and very fast interface movements. For example, very slow interface movement is observed in most single-crystal growth processes, such as Czochralski pulling [102] and some unidirectional solidification processes [1]. On the other hand, a planar solidification has also been observed in several rapid solidification processes where the interface velocity is very high [103–106]. The conditions under which a stable planar interface can exist can be determined from the stability analysis.

A rigorous linear stability analysis for the growth of a planar interface was first performed by Mullins and Sekerka [103]. They examined the stability of a planar interface moving with a constant velocity by imposing an infinitesimal perturbation,

\[
Z = \delta(t) \sin \omega X
\]

(49)

where \( Z \) is the coordinate in the direction of interface movement with \( Z = 0 \) at the interface, \( X \) is the coordinate parallel to the interface, \( \delta \) is the amplitude, \( \omega \) is the wave number (= \( 2\pi/\lambda \)), and \( \lambda \) is the wavelength. The stability of the planar interface then depends on the sign of \( \delta \dot{\delta} \), where \( \dot{\delta} \) is the rate of change of the perturbation amplitude. The planar interface will be stable if \( \delta \dot{\delta} < 0 \) and will be unstable when \( \delta \dot{\delta} > 0 \). The marginal stability condition holds at \( \delta \dot{\delta} = 0 \). This condition can be met when the following condition is satisfied [104]:

\[
-\Gamma \omega^2 + m_L G_c \xi_L - (K_L G_L \xi_L + K_S G_S \xi_S) = 0
\]

(50)

where

\[
\xi_L = \frac{\omega_L - (V/\omega_L)}{K_S \omega_S + K_L \omega_L}
\]

(51)

\[
\xi_S = \frac{\omega_S + (V/\omega_S)}{K_S \omega_S + K_L \omega_L}
\]

(52)

\[
\xi_U = \frac{\omega_U - (V/D_L)}{\omega_U - (V/D_L)(1 - k)}
\]

(53)

and
\[
\omega_C = \frac{V}{2D_L} + \left[ \left( \frac{V}{2D_L} \right)^2 + \omega^2 \right]^{1/2} \tag{54}
\]

\[
\omega_L = \frac{V}{2\alpha_L} + \left[ \left( \frac{V}{2\alpha_L} \right)^2 + \omega^2 \right]^{1/2} \tag{55}
\]

\[
\omega_S = -\frac{V}{2\alpha_S} + \left[ \left( \frac{V}{2\alpha_S} \right)^2 + \omega^2 \right]^{1/2} \tag{56}
\]

\[
\tilde{K}_L = \frac{K_L}{K_S + K_L} \tag{57}
\]

\[
\tilde{K}_S = \frac{K_S}{K_S + K_L} \tag{58}
\]

where \( \Gamma \) is the Gibbs-Thomson constant, \( G_C \) is the concentration gradient in the melt ahead of the interface, \( G_L \) and \( G_S \) are the temperature gradients in the liquid and solid, respectively, at the interface.

A general stability criterion can then be derived from Eq. (50) [104]:

\[
m_{L}(G_C)_{eff} - G_{eff} \leq \Gamma \omega^2 \tag{59}
\]

where

\[
(G_C)_{eff} = G_C \xi_C
\]

\[
G_{eff} = \tilde{K}_L G_L \xi_L + \tilde{K}_S G_S \xi_S
\]

Equation (59) represents a general condition for planar interface stability, predicting both the low and high velocity limits of stability. In the case of rapid solidification, it can predict the absolute stability condition for the growth from an undercooled alloy melt as well as for the constrained growth with a positive temperature gradient ahead of the interface.

Based on this stability analysis, two primary instability mechanisms have been identified for a planar interface: a negative temperature gradient and the solute piling up (for alloys) in front of the interface in the melt. In the case of a high interface velocity, the capillary effect stabilizes the interface again, leading to the so-called absolute stability. The planar interface solidification in RS processes results from this absolute stability. The absolute stability velocity can be derived from Eq. (59) as [104–106]

\[
V_{abs} = s_C V_{abs}^C + s_T V_{abs}^T \tag{62}
\]

with

\[
V_{abs}^C = \frac{D_L m_L (k - 1) C_0}{\Gamma \kappa^2} \tag{63}
\]

\[
V_{abs}^T = \frac{\alpha_L \Delta H_m}{\Gamma C_P} \tag{64}
\]

and the coefficients \( s_C \) and \( s_T \) given by

\[
s_C = \max \left[ \frac{4k[-1 + (1 + Y^2/Le^2)^{1/2}]}{(Y^2/Le^2)[2k - 1 + (1 + Y^2/Le^2)^{1/2}]}, \frac{1}{Le} \right] \tag{65}
\]

\[
s_T = \max \left[ \frac{4b[n[-1 + (1 + Y^2)^{1/2}] + b(n - 1)[a + (a^2 + Y^2)^{1/2}]}{Y^2[a + (a^2 + Y^2)^{1/2} + b(1 + Y^2)^{1/2}]}, \frac{1}{Le} \right] \tag{66}
\]

with

\[
a = \frac{\alpha_L}{\alpha_S}, \quad b = \frac{K_L}{K_S}, \quad Le = \frac{\alpha_L}{D_L}, \quad Y = \frac{2\alpha_L \omega}{V} \tag{67}
\]

Since the solutal diffusivity for most materials is three or four orders of magnitude lower than the thermal diffusivity, \( Y/Le \) is generally very small, which reduces Eq. (65) to \( s_C = 1 \).

A heat flux parameter \( \eta \) has been introduced by Ludwig [105] to define the amount of released latent heat at the interface that flows into the undercooled melt:

\[
\eta = -\frac{G_L K_L}{V \Delta H_m} \tag{68}
\]

where a minus sign is added indicating a negative melt temperature gradient \( G_L \) in front of the interface.

For a given material, \( a \) and \( b \) are fixed (e.g., \( a = 0.53 \) and \( b = 0.45 \) for Al–2wt%Cu) and \( s_T \) is only a function of \( \eta \). Figure 14 shows the variation of \( s_T \) with \( \eta \) for
5.2 Cellular and Dendrite Growth Theory

Whenever a planar interface reaches unstable conditions, cellular or dendritic growth is followed, leading to complex microstructure in the solidified materials. If the growth conditions are not very far from the stability criteria, cellular structures will be developed with cells growing into the melt. For the cases where the conditions significantly depart from the stability condition, dendritic growth will prevail. Extensive research has been conducted to understand and model such complex cellular/dendritic growth [13, 107-108]. In most cases dendritic growth involves two coupled phenomena [108]: (1) steady-state propagation of the tip region accounting for the formation of the main or primary stem and (2) strongly time-dependent crystallization of the secondary and tertiary branches. The characteristic length scales involved in cellular or dendritic growth include [107] the tip radius \( R_t \), the primary spacing (\( \lambda_p \)) between the cells or dendrite trunks, and the secondary arm spacings, \( \lambda_s \) (for dendrites). Significant progress has been made on the modeling of dendritic tip growth during the last three decades. A brief review of dendrite tip growth models is presented here.

As noted in Section 3, there are five unknown tip parameters for dendritic solidification (Fig. 15): tip temperature, tip velocity, solute concentrations of liquid and solid at the tip, and tip radius. (For an array of dendrites, the sixth parameter is the primary dendrite spacing, which cannot be accounted for if each dendrite tip is treated independently.) The tip radius is an important length scale for dendritic solidification, and has to be determined by the model. The energy balance condition, Eq. (3), and nonequilibrium partition model, Eq. (44 or 46), provide two equations, other three equations are obtained from the generic steady-state dendritic growth theory, as described by Kurz and Trivedi [13].

At the dendrite tip, thermodynamic and kinetic considerations lead to a relationship among the tip parameters as [13]

\[
T_t = T_m + m_L C_L = \frac{2T_t}{R_t} - \frac{V_t}{\mu_k}
\]

Equation (62) shows that the absolute stability velocity consists of two parts, the solute absolute stability velocity, \( V_{abs} \), and the thermal absolute stability velocity, \( V_T (\eta, a, b) V_{abs} \). Generally, \( V_{abs} \) is several orders of magnitude larger than \( V_T \) [104]. The absolute stability velocity lies between \( V_{abs} \) and \( V_{abs} + V_T \) since \( 0 \leq s_T (\eta, a, b) \leq 1 \). In the case of directional solidification with a positive temperature gradient in the melt, the entire latent heat released at the interface flows into the solid, \( \eta = 0 \) and \( s_T = 0 \), leading to the absolute stability velocity equals to \( V_{abs} \). On the other hand, when the interface grows into an undercooled melt with a constant solid temperature, all of the latent heat is transferred into the melt, \( \eta = 1 \) and \( s_T = 1 \), resulting in an extremely high absolute stability velocity \( V_{abs} \) equal to \( V_{abs} + V_T \). In the latter case a stable planar interface is not possible because of an extremely large value of \( V_{abs} \) for example, \( 5.67 \times 10^4 \) m/s for Al–2 wt% Cu [106]. An interesting characteristic to note is that a stable planar interface may still exist in a crystal growing into an undercooled melt if a large temperature gradient is produced in the solid that makes \( \eta \) < 1, especially if \( \eta \) is reduced below 0.6 forcing \( s_T \) to approach zero. The implication is that the stability of a planar interface during rapid solidification is strongly dependent on the heat transfer conditions across the melt and the substrate. The linear stability theories, however, do not provide a complete solution of the problem, and a heat and mass transfer model must be used to obtain additional information on Ludwig's
The third term on the right side of Eq. (69) represents the Gibbs-Thomson undercooling. For planar interface solidification, $R_t$ approaches infinity and the Gibbs-Thomson undercooling is zero.

The solute concentration at the tip can be determined from the Ivantsov solution for a steady-state, paraboloidal shape tip:

$$C_L = \frac{C_0}{1 - (1 - k) Iv(Pe_t)}$$

(70)

where $C_0$ is the bulk liquid composition, $Iv(Pe_t)$ is the Ivantsov function, and $Pe_t$ is the tip solutal Peclet number equal to $V_t R_t/2D_L$. The solid composition at the dendrite tip is then $C_S = kC_L$.

The last equation needed is obtained from the marginal stability condition that sets the tip operating criterion. It is postulated that the dendrite tip grows at the margin of stability and the tip radius is equal to the wavelength of the fastest growing instabilities to be formed under local growth conditions [109]. The lower limit of perturbation wavelength of a planar front is generally employed to simplify the problem. A generic form that is applicable to a variety of solidification conditions can be used to determine the dendrite tip radius:

$$R_t = \left( \frac{\Gamma}{\sigma^*} \right)^{1/2} \left( m_L G_C \xi_C - \frac{K_L G_L \xi_L + K_S G_S \xi_S}{K_L + K_S} \right)^{1/2}$$

(71)

where $\sigma^* = 0.02533$ is the stability constant, $G_C$ is the composition gradient ahead of the tip, and $\xi_C, \xi_L$, and $\xi_S$ are the special functions as defined by Eqs. (51) to (53). The composition gradient $G_C$ can be determined from the solute balance condition at the tip:

$$G_C = -\frac{V_t C^*_l (1 - k)}{D_L}$$

(72)

Equations (69) through (72) constitute a unified dendrite growth theory for any given thermal conditions of the system represented by the temperature gradients $G_t$ and $G_S$ in the liquid and solid regions, respectively [69].

### 5.3 Transition from Dendritic to Planar Solidification

The dendritic growth theory implicitly considers the transition from dendritic to planar growth by employing the marginal stability conditions of the dendrite growth. Transition between the two solidification modes can be determined by inspecting the sign of the quadratic terms within the square root in Eq. (71).

$A = m_L G_C \xi_C - \frac{K_L G_L \xi_L + K_S G_S \xi_S}{K_L + K_S}$

(73)

When $A$ is positive, a stable dendritic solidification will occur. If $A$ is negative, then no real solution can exist for the dendrite tip radius, and therefore dendritic solidification is not possible and a planar solidification is expected. Since the first term in Eq. (73) is always positive, the sign of $A$ depends on the second term representing $G_{eff}$, Eq. (61). If $G_{eff}$ is negative, $A$ will always be positive and a stable dendritic solidification will be expected. If $G_{eff}$ becomes positive, then depending on the absolute values of the two terms, $A$ may be either positive or negative. A transition from dendritic to planar solidification will take place as $A$ changes from a positive to a negative value, and vice versa.

Two special cases are worth mentioning here, one the free dendrites growing into an undercooled melt (so-called LKT model, proposed originally by Lipton, Kurz and Trivedi [110]), and the other constrained dendrite growth with a positive temperature gradient in both solid and liquid (KGT model by Kurz, Giovanola and Trivedi [111]). In free dendrite growth with no temperature gradient in the solid, $G_S = 0$ and $G_L = -\rho_L LV_t/K_L$, and thus Eq. (61) leads to

$$G_{eff} = -\frac{\xi_L, \rho_L, LV_t}{K_L + K_S}$$

(74)

which is always negative, indicating a stable dendrite growth. (For extremely high velocity, $\xi_L$ is zero, and a stable planar interface exists as shown by Trivedi and Kurz [104].) Figure 16a shows the dendrite tip radius as a function of tip velocity for free dendrite growth under various initial melt undercoolings (a high velocity results from a large melt undercooling). As shown in the figure, the dendrite tip radius can be obtained for the entire velocity spectrum from $10^{-3}$ to $10^5$ m/s, or even wider. In this case the model predicts transition from a solutal dendrite to a thermal dendrite when the velocity increases from a low to a high value, as illustrated by the sudden increase in dendrite tip radius as shown in the figure [13]. The thermal dendrites result from a strong solute trapping at a high-growth velocity.

On the other hand, for constrained dendrite growth under a strong positive temperature gradient, $G_{eff}$ is positive and $A$ may become negative, leading to a planar interface solidification. As shown in Figure 16b for a given effective temperature gradient, $G_{eff} = G_L$, the dendritic solidification exists only for a limited velocity range. Beyond that, the stable planar interface solidification will take place. (There exists also the transition between the cellular and dendritic growth with branches. The present analysis does not make any distinction between these two growth modes [107].) The lower tip velocity limit corresponds to the constitutional supercooling stability condition, whereas the upper limit relates to the absolute stability condition. This prediction is in agreement with the measurements for directional solidification and laser surface melting [13, 29].
5.4 Banded Structure

A banded microstructure has been observed in many rapidly solidified alloys. It is composed of alternating light and dark bands lying parallel to the solidification front (Fig. 17). The dark bands correspond to a spatially periodic precipitate structure, either cellular or eutectic, and the light bands correspond to microsegregation-free regions. Banded structures have been observed in many RS processes such as atomized powders, melt-spun ribbons, and laser-treated surfaces, although most of the research in this area has been performed on laser surface melting [112–114].

A banded structure was first observed by Sastry and Suryanarayana [115] as an isolated phenomenon. Since then this structure has been found as a common microstructural characteristic of many alloys solidified under growth conditions that approach absolute stability [114]. Detailed experimental studies in Ag–Cu, Al–Cu, and Al–Fe have shown that the dark bands have a precipitate structure, either cellular-dendritic or eutectic, depending on the alloy composition, which is similar to the precipitate structure observed at lower growth rates preceding the appearance of the banded structure. In contrast, the light bands have a microsegregation-free structure similar to the one observed at large growth rates following the disappearance of the banded structure.

According to the classical Mullins-Sekerka linear stability analysis of the planar interface discussed above, one would expect a cellular-array structure to form at the velocities just below the absolute stability limit, \( V_{bs} \), beyond which the planar interface will be completely stable. At velocities above \( V_{bs} \), a planar interface leading to a microsegregation-free structure would be expected. This type of structure pattern has actually been observed by Boettinger et al. [116] in sufficiently dilute Ag–Cu alloys. However, at larger concentrations of Cu, banded structures are observed for a range of growth rate between the cellular and microsegregation-free solidification. In several other alloys such as Al–Fe, banded structures persist even at very dilute alloy compositions.

Figure 16  Dendrite tip radius versus tip velocity: (a) LKT model for free dendrite growth and (b) KG model for constrained dendritic growth. Note the transition of solidification morphology in constrained growth. Wang et al. [69].

Figure 17  Banded structure in Al–4wt%Fe alloy formed of single-phase planar growth (light) and cellular dendritic growth (dark) at 0.7 m/s. Kertz and Trivedi [114].
stability theory. On the other hand, Jönsson [120] argues that the bands are due to the solute drag effects. Interested readers are referred to these papers for details.

5.5 Primary Dendrite Spacing

Dendrite arm spacings (primary and secondary) are important length scales that determine the microstructure of the solidified materials. Some basic features of the primary dendrite spacings have been observed experimentally [121]: (1) The primary dendrite spacing goes through a maximum as the growth rate is increased, and (2) at high-growth rates the variation in primary spacing has a logarithmic relationship with the growth rate (linear on a log-log plot), and (3) in the high-growth rate regime, the temperature gradient significantly affects the primary spacing, even though it has no effect on the dendrite tip radius and initial secondary dendritic arm spacings.

Analytical models have been developed to predict the primary arm spacings [1, 122–123]. Hunt’s model [122] is based on the two major assumptions: (1) A dendritic interface with side arms can be approximated as a smooth steady-state interface, and (2) the temperature and liquid composition in the direction normal to the primary dendritic growth direction are constant. With these assumptions, Hunt obtained the following relationship between the tip radius, \( R_i \), and the primary dendrite spacing, \( \lambda_i \) [122],

\[
\frac{G_i \lambda_i^2}{R_i} = -4\sqrt{2} \left[ m_L C_i^*(1 - k) + \frac{D_i G_i}{V_i} \right] \tag{75}
\]

The dendrite tip radius can be obtained from the dendrite growth model. For example, Hunt (1979) has used the following simplified form:

\[
R_i = \left[ \frac{\Gamma D_i}{\sigma V_i k \Delta T_0} \right]^{1/2} \tag{76}
\]

He has also assumed that \( G_i D_i / V_i = m_L C_i^* (1 - k) \) which may be true in most cases for the dendrite growth. Substituting these into Eq. (75), we obtain

\[
\lambda_i = \left[ \frac{32 \Gamma}{\sigma k} \right]^{1/4} \left[ \frac{\Gamma D_i k}{V_i} \right]^{1/4} V_i^{1/4} G_i^{1/2} k^{1/2} \Delta T_0 \tag{77}
\]

where \( \Delta T_0 = -m_L C_i^* (1 - k)/k \) is the freezing range. Equation (77) shows that the primary dendrite spacing decreases with an increase in the velocity or temperature gradient.

Kurz and Fisher [1], on the other hand, have assumed that the dendrite or cell shape corresponds to an ellipsoid whose half major axis is equal to the length of the...
dendrite and whose minor axis is equal to the primary spacing, and they have obtained

\[ \lambda_i = [342]^{1/3} \Gamma D_i k^{1/4} V_i^{-1/4} G_i^{-1/2} \Delta T_i^{1/4} \] (78)

Equation (78) shows identical dependence on velocity, temperature gradient, and freezing range (\(\Delta T_0\)) as in Eq. (77) obtained by Hunt. However, the coefficients are quite different, much smaller in Eq. (78).

As pointed out by Hunt and Lu [124], these analytical models are oversimplified and the expressions may be of right form but do not accurately describe the process. These authors have developed a numerical model that represents more realistic physics. The model describes both steady and transient growth of an array of axisymmetric cells or dendrites. They use the finite difference technique in their model to solve the solute transport equation in the melt, which is done by neglecting the diffusion in the solid. They include heat flow by assuming a moving linear temperature profile. The surface energy and surface energy anisotropy of the solid-liquid interface are incorporated. Steady-state solutions have been obtained for a wide range of spacings. The results show that the cells occur at small spacings while the dendrites exist at large primary spacings [125]. They have observed that the dendrites always grow near the "marginal stability" condition for any spacing, but the cells approach marginal stability condition only if the spacing is large. The dendrite tips show parabolic profiles, whereas the cell tips are more spherical with the radius of curvature increasing as the spacing increases. The model also includes the spacing selection procedure by considering a number of cell/dendrites. It is assumed that the lower limit of spacings for both cells and dendrites is defined by the array stability limit at which one member of the array is overgrown by the surrounding members of the array. New cells are produced by tip splitting, and new primary dendrites are produced by the growth of a tertiary arm, which leads to the prediction of the upper spacing limit. Since the model is unable to treat the dendrite arms, Hunt and Lu [124, 126] assumed that the maximum dendrite spacing limit is twice of the array stability limit. The upper and lower spacing limits define the narrow range of spacings very similar to that observed experimentally. The results agree well with the experimental data for low velocity directional solidification [126] as well as with the measurements for laser surface melting with a high interface velocity [125]. Based on their numerical data, Lu and Hunt [124] have also derived some analytic expressions for the lower limit of primary spacings for selected materials. For example, the nondimensional primary spacing for cells, \(\lambda_i^c\), and dendrites, \(\lambda_i^d\), are given as [123]

\[ \lambda_i^c = 8.182 \cdot 10^{-4.25} V^{-0.39} (V' - G')^{-0.3} \Delta T_i^{-0.5} (1 - V')^{-1.4} \] (79)

\[ \lambda_i^d = 0.15595 V^{-0.73} (V' - G')^{0.75} G^{-0.6028} \] (80)

\[ \Delta T_i' = \frac{G'}{V'} + \left(1 - \frac{G'}{V'}\right) \left[a_c + (1 - a_c) V^{-0.45}\right] \quad (81a) \]

\[ a_c = 5.273 \cdot 10^{-3} + 0.5591 k - 0.1865 k^2 \] (81b)

\[ a_d = -1.31 - 0.1555 \log_{10}(G') - 0.7589 \cdot 10^{-2} \log_{10}(G')^2 \] (81c)

\[ G' = \frac{G_i \Gamma k}{\Delta T_0^2} \]

\[ V' = \frac{V_i \Gamma k}{D_i \Delta T_0} \] (81d)

\[ \lambda_i^c = \frac{\lambda_i^c \Delta T_0}{\Gamma k} \]

\[ \lambda_i^d = \frac{\lambda_i^d \Delta T_0}{\Gamma k} \]

Equations (79) and (80) give the lower limit of cell and dendrite spacings. The upper limit should be about twice the lower one [124].

Recently Ma and Sahm [123] have developed a new analytical model for primary spacing in directional solidification which looks very promising at least for the low velocity growth. The model assumes a paraboloid-shape dendrite core with the tip having a curvature radius corresponding to the dendrite tip radius. Behind the tip, the side arms are assumed to grow out of the core and the arms of the neighboring dendrites touch each other. The primary spacing between the dendrites are then the sum of the core radius and twice the arm's length. The core diameter is approximated as twice the dendrite tip radius, \(R_c\), which is then determined from the dendrite growth models, such as those discussed in Section 5.2 (e.g., Eq. 71) with certain approximations. Ma and Sahm have also derived an analytical expression for the primary spacings for both dendritic and cellular growth under steady directional solidification conditions [123],

\[ \lambda_i^c = 2\pi k D_i \Gamma \Delta T_0^{1/4} \left(1 - \frac{V_{ci}}{V}\right)^{3/4} G^{-1/2} V^{-1/4} \] (82)

\[ \lambda_i^d = 4\pi \left(\frac{D_i \Gamma}{k \Delta T_0}\right)^{1/2} \left(1 - \frac{V_{ci}}{V}\right)^{-1/2} \] (83)

with \(V_{ci}\) as the critical velocity over which the interface will break down to form a cellular structure due to constitutional supercooling.
\[ V_{os} = \frac{GD_t}{\Delta T_0} \]  \hfill (84)

It should be noted that all of the above models have been derived for steady-state, directional solidification. In RS processes the melt-solid interface velocity changes significantly during solidification. Moreover the interfacial growth may be subject to the effect of melt flow. Nevertheless, these models serve as first approximations to estimate the primary spacings of the cells or dendrites.

6 MICROSEGREGATION IN RAPID SOLIDIFICATION

Microsegregation critically influences the mechanical and physical properties of the solidified materials. It has therefore attracted extensive research efforts in recent years. Microsegregation analysis also provides important relationships between the solid fraction in a mushy zone and the local solidification conditions, which are important for the macroscopic thermal analysis of the process. Battle [127] has presented an extensive review of the various models developed to understand and simulate the microsegregation in a solidified solid. The basic philosophy of how a microsegregation model can be incorporated into a model for alloy solidification using the equilibrium phase diagram has been outlined by Clyne [65].

The simplest model for microsegregation between the two dendrite arms has been proposed by Scheil [128], which is based on a local equilibrium condition at the solid/liquid interface. The Scheil equation assumes a complete mixing in the melt with no solid diffusion, no mass flow in or out of the volume element, and no curvature effect. For a control volume element between the two planar dendrite arms, as shown in Figure 19, the solute concentration in the solid can be expressed as follows:

\[ C_s = k_s C_L = k_s C_0 (1 - f_s)^{k-1} \]  \hfill (85)

where the equilibrium partition coefficient, \( k_s \), is assumed to be constant. Employing the equilibrium phase diagram data with

\[ T = T_m + m_L C_L \]
\[ T_L = T_m + m_L C_0 \]  \hfill (86)

the solid fraction can be obtained as

\[ f_s = 1 - \left( \frac{T - T_m}{T_L - T_m} \right)^{1/(k-1)} \]  \hfill (87)

where \( T \) is the temperature of the control volume element, assumed to be uniform over the entire element. The macroscopic temperature in the mushy zone can be obtained by solving the heat transfer equation, Eq. (6). Substituting Eq. (87) into (6), we can solve for the temperature at each point in the solidification domain. Several modifications have been proposed to relax the assumptions made by Scheil, leading to more sophisticated microsegregation models as reviewed by Battle [127].

Most of these microsegregation models still use local equilibrium condition at the solid-liquid interface by transforming the equilibrium phase diagram data to a \( T_s \) relationship, and are therefore not valid for rapid solidification. Nonequilibrium kinetics has strong effects on microsegregation of solute. Indeed, the rapidly solidified alloys show quite different segregation patterns from that of the conventionally cast materials. For example, an inverse distribution of solute is observed in rapidly solidified alloys with the center of the dendrite having the same composition as that of the original melt [129–132]. Sarreala and Abbaschian [133] have proposed three physical mechanisms that can alter the microsegregation pattern under rapid solidification conditions: (1) second phase reduction due to tip temperature depression, (2) eutectic temperature depression, and (3) melt undercooling prior to nucleation. A summary of microsegregation models developed to take into account the nonequilibrium effects is presented next.

6.1 Analytical Models

Solaris and Biloli [134] were probably the first to introduce the tip undercooling into an analytic microsegregation model. However, the model came under severe criticisms because it lacked solute conservation [133, 135]. Sarreala and Abbaschian [133] later modified this model to satisfy the solute conservation condition. The tip melt undercooling was also introduced through the dendrite tip growth model of Burden and Hunt [136]. The modified model is
\[ C_s = k_2 C_L \left( \frac{(1 - f_S)}{(1 - f_S^0)} \right)^{k_2 - 1} \]  

where \( f_S^0 \) represents the fraction of solid formed at the tip temperature \( T \), with composition equal to \( k_2 C_L \). Based on the mass balance at the tip, we can write,

\[ f_S^0 = \frac{C_L - C_0}{C_L(1 - k_2)} \]  

(89)

The model still assumes a complete mixture of solute in the melt, which may be true near the root area of the dendrite, but cannot apply near the tip, especially when the solidification is fast.

Giovanoa and Kurz [135] have developed an analytical model by considering a solute boundary layer near the tip region. The model considers two compatible functions for concentration-versus-fraction solid relationship: one for the transient in the region around the dendrite tips and the other for the region of complete liquid mixing of the interdendritic liquid. These authors have employed an empirical relationship for the transient region around the tips:

\[ f_s = a_1 C_s^2 + a_2 C_s + a_3 \quad 0 \leq f_s \leq f_x \]  

(90)

and have used a truncated Scheil equation for rest of the region:

\[ f_S = 1 + (f_X - 1) \left( \frac{C_S}{C_X} \right)^{1/(k-1)} \quad f_x \leq f_s \leq 1 \]  

(91)

The solute concentration at the tip is determined by the dendrite tip growth model, and the constants \( a_1, a_2, a_3, f_x, \) and \( C_X \) are determined from the conditions such as mass conservation, continuity conditions at the transition, and so on. The model-predicted solute distributions between the cells are in good agreement with the experimental observations in laser scanned surface of Ag-15wt%Cu substrate by Bendersky and Boettinger [137].

Recently McCarthy and Blake [138] introduced a simplified version of the above model by simplifying the treatment of the \( C_s - f_s \) relationship in the tip region. They have used the truncated Scheil equation over the entire cellular region and assigned tip concentration a value determined from the dendrite growth theory. The solid fraction at the tip, \( f_x \), is calculated from the mass balance condition as

\[ f_x = \frac{(C_0 - C_s)}{(1 + \frac{k}{1 - k})} \]  

(92)

where the nonequilibrium partition coefficient \( k \) is determined based on the tip velocity. It should be pointed out that both of the above models are valid only for moderate growth rate, for example, \( V_x < 0.05 V_{obs} [66] \).

If the melt is significantly undercooled, local recrystallization can be expected around the dendrite tip. The recrystallization leads to partitionless solidification with solute-richest tips as revealed by the experiments of Kattamis [129], Petev et al. [131], Munitz and Abbaschian [132]; see Figure 20. Behind the dendrite tip, solute partitioning takes place due to slowing down of the solidification rate. Kattamis [129] was the first to analyze this kind of microsegregation problem and has proposed an analytical model. The model divides the entire solidification process into three stages with the solute concentration separately related to the solid fraction in each stage. In the first stage, partitionless solidification takes place before the melt temperature recrystallizes to the equilibrium liquidus temperature:

\[ C_s = C_0 \quad 0 \leq f_s \leq f_s^0 \]  

(93)

Figure 20  Experimental observation of solute rich core in rapid dendritic solidification: Compositional line profiles of Ni concentration along line AB for four samples with 0, 30, 60, and 130 K melt undercooling. Munitz and G. Abbaschian [132]
where $f_0^0$ is determined from the energy balance condition of adiabatic recalcience that raises the melt temperature to the solidus temperature:

$$ f_0^0 = \frac{C_p}{L} (T_s - T_N) \quad (94) $$

where $C_p$ is the average specific heat of the undercooled melt, and $T_N$ is the initial melt temperature. As the temperature recalcices above the solidus, partitioning begins at the interface and solidification continues with the solid decreasing in solute until the maximum recalcence temperature (i.e., the equilibrium liquidus temperature) is reached. Beyond this point it follows the conventional solidification process with no melt undercooling. The solute concentration versus solid fraction during and after recalcience are given by

$$ C_s = C_0 + \frac{L}{m_s C_p} (f_s - f_0^0) \quad f_0^0 \leq f_s \leq f_{SR} \quad (95) $$

$$ C_s = C_{SR} \left( 1 - \frac{f_s - f_{SR}}{1 - f_{SR}} \right)^{k-1} \quad f_{SR} \leq f_s < 1 \quad (96) $$

where $f_{SR}$ and $C_{SR}$ are the solid fraction and solute composition at the maximum recalcence temperature. This model has been used by Kattamis [129] as well as by Petes et al. [131] and Munitz and Abbaschian [132]. A fairly good match between the model predictions and experimental measurements has been reported.

The Kattamis model tends to overestimate the amount of partitionless solidification. Munitz and Abbaschian [132] attribute such overestimation to the use of several simplifying assumptions in the model which include (1) adiabatic solidification during recalcience, (2) negligible solid state diffusion, (3) no remelting, (4) no curvature effect, and (5) uniform temperature throughout the system during recalcience. Among them, the last two assumptions are probably the most critical. At the dendrite tip the curvature effects significantly depress the melting temperature and reduce the extent of the partitionless solidification. During recalcience the fast release of latent heat can lead to a significant increase in the solid/liquid interface temperature and produce a large temperature gradient in the system, which can further contribute to the error in the estimated partitionless solidification. In addition nonequilibrium phenomena such as solute trapping may also have important effects.

Kattamis model can be improved by including these effects. For example, instead of partitionless solidification, the solidified at the early stage of recalcience should have a concentration of dendrite tip under the local growth conditions. The early recalcience should end with the dendrite tip temperature instead of solidus temperature as in Eq. (94). With these considerations a modified Kattamis model can be written as [139]

$$ C_s - C_s^0 \quad 0 < f_s < f_0^0 \quad (97) $$

with

$$ f_0^0 = \frac{C_p}{L} (T_i - T_N) \quad (98) $$

and

$$ C_s = C_s^0 + \frac{L}{m_s C_p} (f_s - f_0^0) \quad f_0^0 \leq f_s \leq f_{SR} \quad (99) $$

$$ C_s = C_{SR} \left( 1 - \frac{f_s - f_{SR}}{1 - f_{SR}} \right)^{k-1} \quad f_{SR} \leq f_s < 1 \quad (100) $$

where $m_s$ is the slope of the nonequilibrium solidus curve. In the original Kattamis model an equilibrium condition is assumed at the solid-liquid interface after the tip recalcies as well as a complete mixing in the melt. In reality, nonequilibrium conditions will always exist at the solid-liquid interface, and a solute boundary layer will be developed in front of the interface, namely noncomplete mixing. In addition, if the solidification rate is small after recalcience, the solid diffusion may alter the final solute distribution in the solidified material. These effects can be incorporated into the model only if a numerical approach is adopted.

### 6.2 Numerical Models

Several numerical models have been developed to study the solute redistribution and microsegregation in dendritic solidification. Battle [127] has presented a comprehensive review of such efforts. Most of the early efforts focused on the numerical solutions of diffusion equations with nonuniform physical properties, coarsening phenomena, effect of nonlinear phase diagram characteristics, and so on. Recently, the effect of tip undercooling and eutectic undercooling, particularly, in the case of rapid solidification, has also been included in the numerical model. Voller and Sundarraj [140] have summarized the appropriate parameters and conditions for a comprehensive microsegregation model. Their model considers the variations of both mass and domain due to coarsening as well as the variation of density during solidification. It also takes into account the melt undercooling at the dendrite tip and at the eutectic front, although the tip undercooling is based on Burden and Hunt's model which is valid for only small rate of solidification. A special numerical treatment of melt undercooling in the tip region has been proposed by Sarreal and Abbaschian [133]. They consider the solid diffusivity at an artificially high value (e.g., that of liquid) until the temperature has reached the tip temperature. Beyond which the solid diffusivity is reset to its physical value. In this way the model allows to predict a uniform composition in the tip region.
Kraft et al. [141] have recently developed a much more comprehensive microsegregation model that accounts for a broad range of physical phenomena of dendritic solidification including coarsening and tip melt undercooling. Numerically they have adopted a similar method to that employed by Voller and Sundarraj [140] in order to introduce the initial uniform composition in the dendrite tip region. Kraft et al. [142] have also presented a detailed analysis of the effects of using various dendrite growth models.

Although the numerical models above account for the melt undercooling at the tip, they are valid only if the melt undercooling is small, or under a large positive temperature gradient such as the constrained growth. Under these conditions the solute boundary layer develops ahead of the solid-liquid interface but the thermal field remains uniform at the micro level. Local recalceneces takes place wherever the dendrites grow into a significantly undercooled melt, leading to a solute-rich tip and a large temperature gradient in the region. Therefore thermal diffusion equation must be solved in addition to solute diffusion equation to take into account the temperature buildup at the solid-liquid interface due to local recalcenecence. Wang et al. [143] were the first to introduce such local recalcenecence effect into the microsegregation model. Recently the model has been extended to the cylindrical geometries [70, 144]. These authors have introduced a special numerical treatment to predict the early partitionless solidification as observed by Kattamis [129] and Abbaschian and his co-workers [131-132]. Advanced dendrite growth models are employed to determine the tip growth conditions including the tip temperature, velocity, radius, and solute concentration, as well as the initial profiles of solute concentration and temperature around the tip [144]. The model is then used to analyze the solute distribution in a melt-spun Al-Cu ribbon. A very good agreement has been achieved between the model predictions and the experimental measurements by Masur and Flemings [145].

The model by Wang et al. [144] is based on the Brody-Flemings plate or cellular volume element between two dendrites or dendrite arms (primary or secondary) (Fig. 19) [145]. No coarsening is permitted, no solute is allowed in or out of the volume element, and heat is removed from the volume element only through an average rate of volumetric cooling, \( q \). Physical properties of the melt and solid are considered constant except the solute diffusivity that varies with the temperature. It is further assumed that only steady-state growth takes place at the tip whose shape is paraboloidal and a dendrite growth model can be used to predict the tip conditions. Solute trapping and nonequilibrium kinetics are introduced into the model and eutectic temperature depression is accounted for by a linear kinetics law [140-141]. Wang et al. [144] have also assumed that the eutectic reaction occurs only when the solid-liquid interface temperature reaches the metastable eutectic temperature and the solidification then takes place under the metastable conditions. The solute redistribution is calculated during the eutectic reaction and the subsequent solid cooling, but within the single phase region only.

With the above assumptions and the coordinate system shown in Figure 21, the heat and mass diffusion equations in a plate or cellular volume element for a binary alloy can be written as:

\[
\frac{\partial T}{\partial t} = \frac{1}{r^3 \partial r} \left( a \gamma^2 \frac{\partial T}{\partial r} \right) - q \tag{101}
\]

and

\[
\frac{\partial C_j}{\partial t} - \frac{1}{r^3 \partial r} \left( D_j(T) \gamma^3 \frac{\partial C_j}{\partial r} \right) \tag{102}
\]

where \( r \) is the direction normal to the axis of the dendrite, subscript \( j \) represents the solid and liquid phases, and exponent \( n \) is a constant; \( n = 0 \) representing the platelike dendrites and \( n = 1 \) the cellularlike dendrites. The source term \( q \) in Eq. (101) accounts for the average volumetric heat sink due to cooling, and it is currently an input parameter.

The effect of nonequilibrium kinetics is introduced at the solid-liquid interface, taking into account the effect of solute trapping and linear crystalline growth kinetics as outlined in Section 3 for a planar interface. The capillary undercooling in the dendrite tip region and behind the tip is also considered. The model imposes an adiabatic condition at both ends (\( r = 0 \) and \( r = 2 \)), where \( \lambda \) is the spacing between the...
dendrites or dendrite arms) of the volume element. Zero gradient conditions are used for solute diffusion at the boundaries because no solute is allowed to enter or leave the control volume.

The free dendrite growth (LGK) model [110] is used to determine the tip conditions as well as the temperature and solutal fields around the tip. In particular, the microsegregation analysis starts with the solid-liquid interface at the location equal to the dendrite tip radius, \( R_t \), with temperature and solute concentration in the solid (0 \( \leq r \leq R_t \)) being equal to the temperature and solute concentration of the solid at the tip, respectively. Because of solute buildup the solute concentration around the dendrite tip is different from that in the melt far from the tip. As a first approximation the initial solute distribution in the melt is assumed as the profile along the direction normal to the dendrite axis at the location where the radius of the dendrite in the same normal direction is equal to \( R_t \). Temkin [147] has derived the profile as

\[
\frac{C_L(r) - C_0}{C_L^* - C_0} = \frac{E_1[(r/R_t)Pe_c]}{E_1(Pe_c)} \quad \text{for} \quad R_t \leq r \leq \frac{\lambda}{2}
\]

(103)

where \( r \) is the distance in the melt from the center of the dendrite and \( E_1 \) is an integral exponential function. Equation (103) predicts a large concentration gradient in the liquid ahead of the solid-liquid interface for high Peclet numbers. For free dendrites growing into a significantly undercooled melt, the local recalculation will lead to a nonuniform temperature distribution around the tip. The Ivanov solution similar to Eq. (103) can then be used to determine the initial nonuniform temperature profile in the volume element.

Wang et al. [144] have used this model to predict the solute distribution within a cell in a melt-spun Al-4.5wt%Cu ribbon. The cylindrical coordinate system (i.e., \( n = 1 \)) is chosen to fit the experimental conditions. The initial melt undercooling is assumed to be 15 K to impose a high-solute concentration of the solid at the tip, since the experimental data show a higher-solute concentration in the cell center (about 1.6 wt%) than that of the equilibrium value (0.78 wt%). Figure 22 shows a comparison between the model calculations and the experimental data reported by Masur and Flemings [145]. A good agreement has been obtained for \( q_t = 4 \times 10^6 \) K/s during solidification and \( q_t = 200 \) K/s during solid cooling (solid line). The cooling rate also agrees well with the estimate by Masur and Flemings [145]. Figure 22 also shows the prediction by Scheil model. A large difference is observed between the Scheil model and the experimental data, demonstrating the effect of rapid solidification.

The effect of initial melt undercooling on solute segregation can also be investigated by the model, as shown in Figure 23. As is expected, the larger the undercooling of the melt, the wider is the solute-rich core region. Figure 23 also indicates that once the local recalculation is completed, the solute redistribution is mainly controlled by the external cooling rate and the effect of initial melt undercooling is significantly decreased. A comparison with predictions made by Kattamis model and the modified nonequilibrium Kattamis model at high melt undercoolings is shown in Figure 24. It is evident that the nonequilibrium analytical model has
succeeded in predicting the main characteristics of microsegregation in rapidly solidified materials.

7 RAPID SOLIDIFICATION OF_ATOMIZED POWDERS

Atomization is one of the most promising techniques for large-scale production of rapidly solidified materials for structural applications [148]. As noted earlier, in atomization processes, the more potent heterogeneous nucleation catalysts are isolated in a small fraction of the total volume, thus allowing most of the droplets to achieve significant undercooling prior to nucleation. This leads to the formation of various metastable phases and fine structures in the atomized particles. Efforts of modeling on atomization are focused on phase selection and microstructure development.

7.1 Modeling of Nucleation in Atomized Powders

An analysis of the relative roles of heat transfer, nucleation, and growth on the evolution of microcrystalline structures in metal powders within the current limitations of kinetics models has been presented by Levi [77]. It is generally acknowledged that nuclei can form only during the initial transients when the overall cooling rate decreases rapidly from its value at the beginning of nucleation to zero at the onset of recrystallization. At the start of solidification, the solid-liquid interface velocity is finite, but its area, determined by the critical nucleation radius, is very small. Therefore the rate of heat extraction dominates the latent heat release and the droplet temperature drops further below nucleation temperature, $T_N$. During this period the formation of additional nuclei competes with the growth of existing nuclei. However, both of them increase the rate of latent heat release by increasing the interfacial area, until it overcomes the external heat extraction and recrystallization begins.

Levi [77] has developed a model for nucleation which couples the heat transfer formulation (lumped heat transfer method assuming a uniform temperature in the droplet) with the classical homogeneous nucleation and continuous growth kinetics. The model simulates the thermal history of a molten droplet and calculates the associated grain size evolution in the early stages of solidification. A finite-difference method is used to solve the transient temperature variation of the droplet.

For a small molten particle flying in a gas environment of temperature, $T_0$, the droplet temperature before the start of nucleation can be calculated from [77]

$$\frac{T - T_G}{T_0 - T_G} = \exp\left(-\frac{3h}{\rho C_p r_0} t\right)$$

(104)

where $T_0$ is the initial temperature, $r_0$ is the initial radius of the droplet, and $h$ is the heat transfer coefficient between the particle and the surroundings gas which is assumed to be a constant (i.e., independent of time and temperature) and can have both convective and radiative components. The convective heat transfer coefficient, $h_c$, can be calculated using an empirical relationship such as

For radiative heat transfer in the vacuum, the Stefan-Boltzmann relationship can be used to obtain a radiative heat transfer coefficient, $h_r$, as

$$h_r = \frac{\sigma \varepsilon (T^4 - T_0^4)}{T - T_G}$$

(106)

where $\varepsilon$ is the surface emissivity of the droplet and $\sigma$ is the Stefan-Boltzmann constant. In most of the gas atomization processes for low-melting point materials, $h_r$ is much smaller than $h_c$, and hence the radiative effect can be neglected. Under such conditions Eq. (104) can predict the variation of the droplet temperature with time.

In the vacuum where convective heat transfer is negligible, a strong temperature-dependent radiative heat transfer needs to be considered. When the radiation dominates, the temperature of the droplet can be determined from [86]
\[
\frac{dT}{dt} = -\frac{3}{r_0 \rho C_p L} \left[ \sigma (T^4 - T_G^4) \right]
\]

(107)

After the first nucleus appears in the droplet, the crystalline growth begins and the latent heat is released, which can be treated as a heat source:

\[
(\rho C_p)_c \frac{dT}{dt} = -\frac{3h}{r_0} (T - T_G) + \rho L \frac{df_s}{dt}
\]

(108)

In the equation above, \( f_s \) is the solid fraction based on the nuclei in the droplet at the time considered [77]:

\[
f_s = \sum_{i=1}^{N} \left( \frac{r_i}{r_0} \right)^3
\]

(109)

To derive Eq. (109), it is assumed that there are \( N \) nuclei in the droplet and that each nucleus has a spherical shape with a radius, \( r_i \). The number of nuclei at an infinitesimal time interval, \( \Delta T \), is given by

\[
\Delta N_i = J(T, f_s, r_0) \Delta t
\]

(110)

and the total number of nuclei in the droplet at time \( t \) is

\[
N(t) = \sum_i \Delta N_i
\]

(111)

Levi employed the classical homogeneous steady-state nucleation theory to calculate the rate of nucleation, \( J \), as described in Section 4.1 through the quantity, \( I_{ss} \), in Eq. (11)

Once the nuclei form, they are assumed to grow as spheres whose radii, \( r_i \), increase at each time step:

\[
r_i(t + \Delta t) = r_i(t) + V_i(t) \Delta t
\]

(112)

with the crystal growth velocity \( V_i(t) \) determined from the continuous growth model, Eq. (32), modified to include the capillary effect. Levi's model also takes into account the remelting of some nuclei formed at lower temperatures as the temperature of the droplet increases rapidly during the recrystallization [77].

Once the growing nuclei start impinging upon each other, the geometrical model for the interface and its relationship to the fraction solid breaks down. Levi's model sets a limit at a fraction solid of 74%, corresponding to the maximum packing of \( N \) spheres in a spherical droplet. It determines the melt undercoolability (i.e., the largest melt undercooling), nucleation temperature, total number of nuclei and grains in the droplet, and the average grain size, \( d_s \), defined as

\[
d_s = 2r_0 \left( \frac{\pi}{3\sqrt{2N}} \right)^{1/3}
\]

(113)

The model was first used to study the nucleation feature of atomized Al and Ni powders, as shown in Figure 25. This figure shows that the total number of grains is a strong function of the droplet diameter and material properties. For a given material, there is an upper limit on the number of grains that can be produced.

### 7.2 Phase Selection in Atomized Powders

The preceding nucleation model has been successfully used to explain the nucleation and phase selection behavior of the EHD atomized Al2O3 powders. Alumina is an industrially important ceramic that can have a variety of metastable crystalline phases. For example, in thermal plasma sprayed aluminum oxide coatings, the metastable \( \gamma \) phase is commonly produced instead of stable \( \alpha \) phase [149–150]. However,
in atomized powders, only $\alpha$-alumina exists in coarse powders (Levi 1988), for example, with diameters larger than 10 $\mu$m. TEM analysis of many finer (< 10 $\mu$m) powders shows a host of metastable microstructure including amorphous powders and metastable crystalline phases such as $\delta$, $\gamma$, and 0. Amorphous alumina has also been observed but only in very fine particles, whose diameters are in the range of 100 nm or smaller [32].

This motivated Levi [32] to introduce phase selection mechanisms in his nucleation model, which he then applied to the EHD atomized $\text{Al}_2\text{O}_3$ powders. He considered three important phases, stable $\alpha$ phase and metastable $\delta$ and $\gamma$ phases. Catalytic effects of impurity at the surface were introduced into the model through a contact angle. In Levi's model, once the melt is cooled down to a particular phase freezing temperature, that phase starts being nucleated. If the melt is cooled down to the lowest melting temperature of the three phases, all three phases may nucleate. The phase for which the first nucleus appears is the phase being selected. Levi predicted that in $\text{Al}_2\text{O}_3$, the $\gamma$ phase is the preferred crystalline phase across the entire particle size range when the nucleation is homogeneous (i.e., the wetting angle $\theta = 180^\circ$). On the other hand, the $\alpha$ phase is selected when strong catalysts are present (e.g., $\theta = 30^\circ$), the catalyst being equally active with respect to all three phases. A kinetic hierarchy of phase selection for $\text{Al}_2\text{O}_3$ powders can be constructed using this model if one assumes that an identical catalytic potency (contact angle) exists for all three phases (Fig. 26). After comparing their predictions with experimental observations, Levi et al. [32] concluded that the nucleation catalysts for alumina phases should fall in the range of $50^\circ < \theta < 55^\circ$.

Levi et al. [32] have also incorporated into their model the solid state transformation of the solid $\gamma$ phase to the solid $\alpha$ phase after recaelsecence. Figure 27 shows the calculated thermal histories of 1 $\mu$m $\text{Al}_2\text{O}_3$ droplets cooled down from the equilibrium freezing temperature $T^*_m$ with different nucleation temperature of $\gamma$-$\text{Al}_2\text{O}_3$ based on the assumed potency of the nucleation sites. As is evident, active catalysts cause nucleation at lower undercoolings and a distinct period of quasi-isothermal solidification close to the freezing point of $\gamma$ phase. During this time period an extensive transformation from the solid $\gamma$ phase to the solid $\alpha$ phase can be expected. On the other hand, if the catalytic effect is not strong ($\theta > 75^\circ$), a hypercooling temperature ($T^*_m$) will be reached, and there will be no isothermal solidification period. As a result the metastable phase formed due to rapid solidification will be maintained.

Similar models have been developed by other researchers to analyze the phase selections in atomized powders of many different kinds of materials. For example, Lin et al. [86] investigated the microstructures and phase selection of submicron EHD atomized iron-nickel powders. For Ni concentration of less than 50 at%, the selection of different microstructures is dominated by the competition between the metastable bcc and the stable ccp phases, with the metastable bcc phase having the highest nucleation temperature. This is in agreement with their experimental observation for alloys of up to 40 at% nickel. Recently Volkmann et al. [151] have employed the classical nucleation models to analyze the nucleation and phase selection in undercooled Fe–Cr–Ni melts, a ternary system.

![Figure 26](image1.png) Model-predicted kinetic hierarchy of phase selection in $\text{Al}_2\text{O}_3$ based on nucleation preference, assuming the same catalytic potency (contact angle $\theta$) for all three phases. Levi et al. [32].

![Figure 27](image2.png) Thermal histories of 1 $\mu$m $\text{Al}_2\text{O}_3$ droplets containing different nucleation catalysts for the $\gamma$ phase. Note the reduction in the high-temperature exposure as the activity of the catalyst decreases. Levi et al. [32].
7.3 Rapid Solidification of Metal Powders

In the case of a small droplet, a single crystalline nucleation event takes place on the surface of the droplet, and solidification starts in a columnar dendritic fashion. Levi and Mehrabian [24] have studied this phenomenon for pure aluminum, considering the nucleation event in the form of a spherical cap occurring at the droplet surface with the assumption that a planar solid-liquid interface follows the axisymmetric geometry, as shown in Figure 28. The melt undercooling was introduced prior to solidification with a given nucleation temperature, and the subsequent nonequilibrium solidification was analyzed by incorporating the nonequilibrium kinetics conditions into the heat transfer model. They used Turnbull's continuous growth model, Eq. (32), to account for the nonequilibrium kinetics effect at the interface. A free parameter, \( \beta \), as proposed by Cahn et al. [152], was introduced in the model to treat the uncertainties of the kinetics modeling. Both Newtonian and non-Newtonian cooling conditions were considered. Since in the latter case, a temperature difference exists in the droplet, a two-dimensional, axisymmetric energy equation was solved based on a bipspherical coordinate system using a finite difference method. The model calculations show four different regimes during the solidification of an atomized pure metal droplet: undercooling of the liquid, recalescence, quasi-equilibrium solidification near local interfacial equilibrium, and cooling of the solid powder.

7.4 Rapid Solidification of Alloy Powders

Levi [153] has extended his model to treat the rapid solidification of binary alloy powders with a planar solid/liquid interface, assuming no temperature difference in the droplet. He assumes that the solidification starts at a prescribed nucleation temperature at the single nucleation event at the droplet surface. As in the previous model, the interface is shaped like a spherical cap and grows with a symmetry axis defined by the nucleation point and its antipode. The continuous growth model, Eq. (32), is employed to correlate the interface velocity with the free-energy variation, which is calculated based on a subregular solution thermodynamics model. Levi examined the solute redistribution for various aluminum alloys under different thermal conditions using the Aziz's solute trapping model, Eq. (46).

As Boettinger et al. [31] have pointed out, several solidification morphologies are possible in atomized alloy powders. Figure 29 shows three basic morphologies: planar, cellular, and dendritic. Figure 29a shows the case where coarse dendrites sweep across the droplet. This corresponds to the case of small rate of solidification and small melt undercooling. In contrast, Figure 29b presents the case where an early planar interface develops into a cellular structure at the late stage of solidification. Sometimes the early solidification is characterized by a microcellular form as shown in Figure 29c. The Levi's model, as discussed above, is valid only for the early stages of Figure 29b, with a planar interface sweeping the entire droplet under the condition of Newtonian cooling.

The variation of solidification morphology shown in Figure 29b and Figure 29c corresponds to the so-called two-zone structure as observed by Boettinger et al. [31] in rapidly solidified powders of Al–8wt%Fe and by Chu et al. [43] in melt-spun ribbons: zone A and zone B. Zone A, which shows a very weak response to chemical etching, has been identified as a microcellular structure of α-Al by transmission electron microscopy and believed to be formed during the recalescence stage with a
large initial undercooling. Zone B, which is highly sensitive to chemical etching, has the microstructure formed after recrystallization.

The stability of a planar interface in a highly undercooled atomized droplet has been addressed by Salas and Levi [154]. They found that a stable planar interface can sustain at early stages because of the strong solute trapping that can occur due to a high solidification velocity during recrystallization. At the early stages of solidification, the dimensions of the marginally stable perturbations are larger than that of the interface, and perturbations smaller than the critical one can be stabilized by capillarity. Both contribute to a stable planar interface. As the rate of solidification decreases, and the solute partitioning becomes more and more important, the planar interface breaks down to the cellular growth. A transition from a planar to cellular structure then takes place as shown in Figure 29b.

Boettinger et al. [31] have proposed a simplified cooling model for cellular/dendritic solidification of atomized droplets. They have introduced the LGK dendritic growth model [110] to determine the relationship between the dendrite tip velocity and the melt undercooling. The following relationship is obtained for Al-8wt%Fe:

\[ V_t = 1.49 \times 10^{-4} \Delta T^{2.84} \text{ (cm/s)} \]  

Boettinger et al. [31] assume that the thermal fields from adjacent dendrite tips overlap significantly. Therefore one can treat the motion of an advancing array of dendrite or cellular tips as an instantaneous isothermal smooth surface which releases an effective latent heat \( L_t \), taken as 70% of the latent heat of the material. By using the equation above together with the adiabatic recrystallization condition (i.e., the latent heat released during solidification used for heating the droplet), the model can be used to calculate the fraction of microcellular structure in the particles. The LGK dendritic growth model also provides information on the tip radius. These calculations compare favorably with the cell spacings observed in the case of microcellular and cellular zones.

A more sophisticated model for cellular-dendritic solidification in a gas-atomized Al-8wt%Fe alloy droplet, after a single nucleation event on the surface, has been developed by Kim et al. [68]. These authors use the numerical method of Levi and Mehrabian [24] to solve the energy equation and track the solid-liquid interface movement. At the moving interface they have implemented the scheme proposed by Boettinger et al. [31]; that is, the motion of an advancing array of dendrite or cellular tips is treated as an instantaneous isothermal smooth surface. However, they neglect the detailed dendrite geometry and assume a very small thickness of the mushy zone, such that all of the latent heat is released only at an imaginary interface enveloping the cell tips in the model. This assumption can result in an overestimation of the local recrystallization effect.

Kim et al. [68] have employed the dendritic growth model to define the tip parameters of the microcellular or cellular growth. A velocity-versus-temperature relationship is derived based on the KGT dendritic model when free dendrites grow into an undercooled melt. The transition from thermal dendrites to solutal dendrites, which may introduce an oscillatory solidification and a highly branched structure, is smoothed out by a continuous transition between the solutal dendritic growth and thermal dendritic growth. Using this model, Kim et al. have successfully identified the relative roles of initial undercooling (before the onset of nucleation), droplet size, and rate of heat removal from a droplet (by external cooling) on microstructure evolution of α-Al, which is the most stable phase.

8 NONEQUILIBRIUM MELTING AND RESOLIDIFICATION IN PULSED LASER PROCESSING

Because of their high-energy intensity, lasers are being increasingly used in special applications in materials processing including surface treatment, cutting, drilling, machining, and profiling. Since lasers induce phase transformation at the surface (from solid phase to liquid phase, or from solid phase to vapor phase), they can be used to drastically modify the surface composition and microstructure. Although a wide variety of laser processing has been invented in recent years, early efforts were focused on high-temperature rates that could be achieved by rapidly melting a thin layer in perfect contact with its own large body, a process named laser surface melting. Because of the high solidification rate involved, and the possibility of improving the surface structure, and hence its properties, the laser surface melting process is now being widely used [35–39]. A method of laser surface melting and resolidification has also become important in the study of nonequilibrium solidification kinetics of crystal growth at high velocities, it allows extremely high cooling rates to be achieved, up to 10^{12} K/s. Several review articles have been written on laser processing technologies and basic principles of laser-material interactions [14, 35–39, 155–156]. Here we present a brief review of the effort made to model one special laser processing technique, surface melting by pulsed laser, in order to illustrate how the nonequilibrium kinetics has been incorporated into the heat transfer model to simulate this process.

Pulsed laser processing has been widely used to study the mechanisms of nonequilibrium kinetics and solute trapping by making measurements of the melt depth during the process from which one can deduce both the melting and solidification velocities [11, 34]. For example, the interface velocity measurement in the experiments with pulsed laser surface melting and resolidification confirmed the theory of collision-limited growth [93]. The laser melting technique has also been used to study the dependence of solidification morphology and microstructure development on interface velocity. These experiments have been of great help in verifying the theoretical models for rapid solidification [14, 113].

In laser surface melting the substrate heats up when the laser is fired at the surface, with the melting starting when the surface temperature reaches the melting point. As the substrate is further irradiated, the liquid layer thickens and the surface temperature keeps increasing (in some cases, until the vaporization takes place). Even after the laser is turned off, the melting continues because of the melt superheat until the
melted layer reaches a depth at which the heat flux from the melt into the solid-liquid interface becomes equal to that from the interface into the solid. At this point the interface stops and the melt begins to resolidify. In real situations the process is quite complicated because of the irregular geometry of the melt pool and the complex solidification morphologies.

Recently significant efforts have been made to develop models for laser surface melting and resolidification. These models are generally based on several simplifying assumptions, which include [96] the following: (1) the substrate can be treated as a semi-infinite solid maintained at a uniform temperature and composition, (2) the cross section of the laser beam is much larger than the depth into the substrate over which significant temperature changes occur, (3) the melt pool is shallow so that convective effects can be neglected and only diffusion (of both heat and mass) needs to be taken into account, (4) in most cases a stable planar solid-liquid interface exists during both melting and resolidification, which excludes bulk nucleation in the liquid region. The first assumption is easy to justify and understand. The second and fourth assumptions are also met, in practice, in pulsed laser surface melting, which make the one-dimensionality of the model acceptable. However, a uniform laser beam is not readily achievable; hence the third assumption is only an approximation of the real condition. In addition the absorption and reflection of light from a material is not strictly a surface phenomenon, and some penetration of the laser radiation may affect a significant fraction of the molten layer. This requires the consideration of laser-melt interaction at the microscopic level, which is emerging as an area of special research interest [157–158].

Hsu et al. [159] developed the first numerical model for laser surface melting, considering a semi-infinite substrate subjected to a constant heat flux for a given period of time. The model was used to examine the basic characteristics of the process, such as the interface velocity, maximum melt depth, and temperature history of the surface layer. Since the model was developed for continuous CO₂ lasers, the melting layer thickness was rather large and local equilibrium conditions were imposed at the solid-liquid interface. Later the model was extended to two-dimensional conditions [160] and alloy systems with mushy zone [161]. Again, local equilibrium was assumed during the solidification.

A model for pulsed laser processing was developed by Baeri et al. [162] who solved the heat conduction equation using a finite difference method. This model has been widely used for data processing in laser annealing of dopant-implanted silicon films, from which one can obtain the value of nonequilibrium partition coefficient [11, 34]. The model, however, decouples the temperature and concentration at the interface, and a constant velocity is considered to solve the concentration distribution in the film after it is resolidified.

A more comprehensive model that includes nonequilibrium melting and solidification has been developed by Wood and Geist [56] for pulsed laser processing of multilayer silicon thin films. The model introduces the nucleation and growth kinetics of crystalline phases using the so-called state diagrams based on the temperature-enthalpy relationships for nonequilibrium phase change. The model accounts for the laser energy penetration into the thin film through an energy source term, \( S \), in the heat transfer equation as

\[
S(x, t) = [1 - R(x, t)] P(t) x \exp(-\alpha x) \tag{115}
\]

where \( x \) is the space coordinate into the thin film from the surface, \( P(t) \) is the intensity of the laser pulse, and \( \alpha \) is the absorption coefficient. Since the reflection of light from a material is not purely a surface phenomenon, the reflectivity \( R(x, t) \) is a function of both space and time. However, \( R \) has been generally treated as a surface parameter and is considered a function of the temperature and phase of the materials. Except for the solid-state lasers where the intensity is nearly a Gaussian function, \( P(t) \) is a complex function and causes difficulty in realistic modeling. Therefore, in most of the numerical treatments, only a Gaussian form has been used. The above equation (115) for laser energy penetration is only valid when the absorption coefficient \(\alpha\) is a constant. For semiconductor materials under long-wavelength radiation, \( \alpha \) may be a complex function of doping concentration and temperature. It is evident that a more generalized form of energy source is needed to model the complex laser surface melting.

Equation (115) has been used by Xu et al. [163–164] to model the pulsed Excimer laser melting of thin polysilicon films. They employed a linear kinetics relationship at the planar solid/liquid interface with the kinetics coefficient for polysilicon as \( \mu = 0.1 \text{ m}^2/\text{K} \), and they predicted the melt depth and its duration times, which agree well with their measurements. Solute diffusion was later included in the model (decoupled from heat diffusion) to treat the dopant redistribution in thin films [165].

Experiments and modeling have also been performed to study the pulsed laser treatment of bulk materials. For example, MacDonald et al. [92] have investigated the effect of picosecond pulsed laser on bulk noble metals, Au and Cu. They have employed the collision-limited growth model to formulate nonequilibrium melting and resolidification. The model predicted significant solid overheating during melting and melt undercooling during solidification.

All of the above models deal primarily with the pure or doped semiconductor materials. Since the dopant concentration in semiconductor materials is generally very small, the thermal problem can be decoupled from solute diffusion without introducing much error, and the interface velocity obtained from the thermal analysis of pure materials can be used to calculate the solute diffusion with nonequilibrium solute partition.

In the case of bulk alloy materials, the planar interface temperature is related to solute concentration through kinetic relationships as described in Section 4.4. For dendritic solidification, the tip-melt interface relationships can be described only through more complex response functions. Nonequilibrium effects of solute trapping have been considered by Kar and Mazumder [166] through Aziz's model, Eq. (46), to study the laser cladding of Ni-Cr alloy. However, solute diffusion was decoupled from the temperature field, since a constant interface temperature was employed.
Recently Wang and Matthey [96] have developed a model for pulsed laser surface melting of bulk alloys in which the interface advancements and solute partitioning at the interface are kinetically coupled. Collision-limited growth kinetics relationships are employed to determine the linear kinetics coefficients of pure metals. Both solid overheating during melting and melt undercooling during resolidification have been considered in this model. These authors have also used Aziz’s model [99], Eq. (46), for solute trapping. However, the laser heating is treated only through a constant flux during the pulsed time duration. A numerical method based on implicit finite difference and solid-liquid interface immobilization using coordinate transformation is implemented to solve the resulting nonlinear moving boundary problem for heat and solute diffusion. An efficient iteration scheme and a nonuniform grid are employed to treat the unknown interface parameters and large solute gradients in front of the interface.

The model-predicted typical interface velocity during the laser surface melting of a pure aluminum is shown in Figure 30 for three different heat fluxes within the typical range of nanosecond pulsed lasers, $8 \times 10^{10}$, $10^{11}$, and $2 \times 10^{11}$ W/m$^2$, and 35 ns duration pulse. In Figure 30 the vertical axes represent the interface velocity, the positive values in the upper part of the graph represent the melting phase, and the negative values represent resolidification. Figure 30 also shows the corresponding levels of overheating and undercooling. As we can see, the maximum value of solid overheating is reached very quickly after the laser is fired. Melting then continues with a gradual decrease in solid overheating. As the melt layer thickens, the interface velocity slows down until the laser is turned off (indicated by arrows on the graph). Beyond this point the melting velocity drops much faster, and more so in the case of a lower heat flux. As expected, for a given exposure time, the larger the heat flux, the higher is the peak velocity and the thicker is the melt pool.

Melting stops when the heat flux from the melt to the solid-liquid interface equals that from the interface to the solid. Once the heat flux into the solid from the interface exceeds that from the melt to the interface, the melt begins to resolidify. As is evident from the figure, the solidification velocity first increases after the resolidification starts because of the diminishing melt superheat, reaches a peak value and then starts decreasing as the bulk material heats up. Similar to the peak rate of melting, the maximum solidification velocity is a function of the laser flux. The larger the laser flux, the smaller is the maximum solidification velocity (e.g., 4.7 m/s compared to 25.1 m/s when the input heat flux decreases from $2 \times 10^{11}$ to $8 \times 10^{10}$ W/m$^2$).

With the finite phase change kinetics (e.g., a linear kinetics coefficient $\mu_k = 1.74$ m/s for pure aluminum), the model is also able to predict the corresponding interface overheating and undercooling, as shown in Figure 30. (Note that solid overheating during melting is shown as positive values and melt undercooling during solidification as negatives in Figure 30.) As we can see, significant solid overheating and melt undercooling are possible under these heat flux conditions. For example, a maximum solid overheating during melting of about 87 K is obtained for $Q = 2 \times 10^{11}$ W/m$^2$, and a maximum melt undercooling of about 14 K for $Q = 8 \times 10^{10}$ W/m$^2$. It should be noted that this model does not account for nucleation. As a result the solid overheating and melt undercooling result only from the melting or crystalline growth processes. A large solid overheating or melt undercooling at the interface has to be generated to maintain a high rate of melting or solidification because the model considers only finite kinetics.

Figure 31 shows the departure of the interface temperature from its equilibrium value for pure metals (Al, Cu, Ni, Ti) as a function of the interface depth nondimensionalized by the maximum melt depth, for a fixed input flux, $Q = 2 \times 10^{11}$ W/m$^2$, and exposure time, $\Delta t = 35$ ns. As expected, the material properties have strong effects on melting and resolidification. A large variation in solid overheating, and hence in melting velocity, takes place during the melting of Al, Ni, and Cu, whereas the variation is small for Ti, especially in the early stages of melting. During resolidification, only small variations in melt undercooling are seen for Al, Ti, and Ni, while it is much larger for Cu. A higher thermal conductivity of copper leads to a larger undercooling (i.e., the larger rate of solidification) and larger solid overheating at the interface in this case, except during the very beginning of the melting process when the kinetics dominate. For aluminum, however, a relatively large thermal conductivity is counterbalanced by a larger kinetics coefficient, resulting in the smallest undercooling. Its low melting temperature, on the other hand, significantly influences the solid overheating. Although experimental data are not available for a direct comparison, as noted earlier, significant solid overheating and melt undercooling have been observed in laser surface melting of noble metals [92].
Figure 31  Deviation of the interface temperature from its equilibrium value as a function of the solid-liquid interface location nondimensionalized by the maximum melt depth (d_melt) during laser surface melting of four pure metals: Al (d_melt = 3.33 μm), Cu (0.73), Ni (0.60), and Ti (0.56). Note the different vertical scales for melting and solidification (Q = 10^11 W/m^2, Δα = 35 ns, T_{in} = 300 K). Wang and Matthey [96].

Figure 32 shows the effect of initial Cu concentration on the interface velocity during melting of dilute Al–Cu alloys under the same processing conditions (Q = 10^11 W/m^2 and Δα = 35 ns). As discussed above, the treatment of an alloy is complicated on two counts: First, the solute partitioning at the interface leads to solute diffusion, which makes the mathematical analysis much more complicated. Second, the kinetics model must include the nonequilibrium liquidus slope n_L and nonequilibrium partition coefficient k, both of which are strong functions of the interface velocity.

The effect of solute on melting is reflected by its influence on melting temperature: 933.6 K for pure metal and concentration-dependent values for binary alloys: 921.7 K for C_0 = 2 wt% and 903.9 K for C_0 = 5 wt%. As shown in Figure 32, the variation in the melting temperature has little effect on melting before the laser is stopped. However, the melting does not stop instantaneously because of the melt superheat. Evidently the lower the melting temperature (i.e., for Al–5wt%Cu), the more superheated the melt gets and the larger is the melt depth.

As the melt starts to resolidify, the solidification velocity shows much more complex behavior in the case of alloys (Fig. 32); the rate of resolidification shows a small local maximum and then decreases very fast. After achieving a minimum, the interface velocity quickly increases first and then decreases gradually to almost quasi-steady behavior. Figure 32 shows a strong effect of solute concentration; the larger the solute concentration, the larger is the maximum interface velocity.

9 MELT-SUBSTRATE QUENCHING

Many rapid solidification processes including melt-spinning and thermal spray deposition involve molten materials quenched on cold substrates. These processes are characterized by a large melt undercooling prior to solidification and afterward a fast solidification rate because of the large amount of heat transfer from the solidifying molten material to the substrate during the entire solidification time.

9.1 Melt Undercooling, Nucleation, and Phase Selection

Classical nucleation theories have been frequently used to determine the melt undercooling and subsequent crystalline nucleation and phase selection, even though the
quantitative accuracy of the models remains an unresolved issue. Only few studies have been reported that address the issues of melt undercooling, nucleation, and phase selection in melt-substrate quenching [55, 167–168]. Clyne [55] was the first to consider the nucleation process in melt-spinning. He considered the heterogeneous, steady-state nucleation, as described in Section 4.2, in the first volume element of his one-dimensional heat transfer model in order to calculate the number of nuclei. Clyne defined the time when the first nucleus appears as the nucleation time, \( t_N \), which is the solution of [55]

\[
V_1 \int_0^{t_N} I_{SS}(T) \, dt = 1
\]  
(116)

with \( V_1 \) as the volume of the first element. The temperature of the first element at \( t_N \) is then defined as the nucleation temperature, \( T_N \). In a one-dimensional model, the volume \( V_1 \) depends on the surface area of the element considered in the model. Clyne found that this area (in the range of 100 µm²) could be varied by several orders of magnitude without affecting the results in any significant manner. Since no data were available on the contact angle, \( \theta \), for the selected materials, Clyne’s model could predict only the qualitative trend of nucleation and melt undercooling as functions of \( \theta \). For example, his results show that the nucleation temperature \( (T_N) \) is insensitive to the cooling rate over the range of \( \theta \) considered by him, while the melt undercooling is mainly controlled by the contact angle.

In Clyne’s model, the classical nucleation theory is used to determine the initial nucleation temperature. Once the first nucleus appears, the implementation of nucleation model is stopped and the solidification model is invoked. Recently Robert et al. [167–168] have extended this model to investigate the formation of nuclei at the substrate surface and subsequent grain distribution and microstructure formation in the splat with application to thermal spray coatings. They considered a thin alumina splat quenched on a steel substrate. A one-dimensional heat transfer model, as discussed in Section 3.3.1, was used to model the superheated melt layer suddenly brought in contact with the substrate. Since the alumina has several metastable phases available when the melt is significantly undercooled, a phase selection mechanism was considered based on the work of Levi [77]. Among the stable phase \( \alpha \) and two metastable phases \( \gamma \) and \( \delta \) that are competing, the phase that has the lowest nucleation barrier was selected as the final phase. The model also accounted for the growth of each nucleus after it appears, and the latent heat released due to the growth of nuclei was included as a source in the energy equation. The melt temperature considered in the nucleation theory was that of the first element near the substrate, and a linear growth law was used to calculate the nucleus surface velocity based on this melt temperature. As nucleation continued, the surface area available for generating new nuclei decreased, and when 67% of the splat surface in contact with the substrate was covered by nuclei, the nucleation stopped.

Robert et al. [168] performed calculations for an alumina splat of 1 µm thickness and 100 µm diameter with a uniform temperature of 3000 K quenched on steel. The interfacial heat transfer coefficient was chosen as \( 10^8 \) W/m²-K. Figure 33 shows typical results for nucleation temperature as a function of the contact angle. It is evident that the large contact angle leads to a low nucleation temperature, namely large melt undercooling. Figure 33 also shows the effect of contact angle on phase selection under the condition that the surface has the same effect on three phases. As shown in this figure, the stable \( \alpha \) phase nucleates at a higher nucleation temperature when the contact angle is small \( (\theta < 37^\circ) \), which implies a strong surface catalytic effect on nucleation. If the surface catalytic effect is weak (i.e., has a large contact angle), the metastable \( \gamma \) phase is nucleated at a low nucleation temperature with large melt undercooling. The metastable \( \delta \) phase appears when the contact angle has a value between 37° and 48°.

Robert et al. [68] have calculated the grain density (i.e., number of nuclei per unit area) as a function of the contact angle, as shown in Figure 34. When the contact angle is small, the stable \( \alpha \) phase nucleates a large number of nuclei which result in a high grain density. A rather small number of nuclei form when the nucleation becomes difficult as in the case of metastable \( \gamma \) phase. Figure 34 shows that the surface temperature (or cooling rate) also has a strong effect on grain density.

Since the grain density and nucleation temperature depend strongly on the contact angle, its value must be chosen carefully for the model to be realistic. Unfortunately, no data are available in the literature. An attempt to estimate \( \theta \) was made by Robert et al. [168] by comparing the predicted and measured values of grain density and average grain size with the assumption that each nucleus grows into a grain, an assumption probably realistic for extremely thin splat and fast rates of solidification. The grain density was obtained from a statistical analysis of the atomic force microscopy (AFM) pictures of the splat top surface, as shown in Figure 35 for an alumina splat collected on a \( \gamma \)-alumina substrate. The substrates were heated to 573 K before
spraying. Figure 36 shows a comparison between the experimental and predicted grain size distributions, and it is evident that a good agreement can be achieved if an appropriate value of $\theta$ is used. Figures 35 and 36 show a slightly higher number of large grains than what the model predicts, probably because of the grain coarsening not included in the model. Robert et al. have examined several alumina splats sprayed over different substrate materials all maintained at 573 K, and they found that the contact angle are $78^\circ$, $73^\circ$, and $66^\circ$ when the $\gamma$-phase is formed on a steel, a $\alpha$-alumina substrate, and a $\gamma$-alumina substrate, respectively.

9.2 Nonequilibrium Solidification of a Pure Material Quenched on a Substrate

Melt-substrate quenching of pure metals has been analyzed extensively. A model to predict recrystallization with a temperature inversion has been developed by Clyne [55]. It incorporates a diffusion-limited kinetics model into the heat transfer formulation and uses a local heat source method to solve the corresponding moving boundary problem. To calculate more accurately the interface velocity and temperature, both of which are strongly coupled through the kinetics relationship such as Eq. (32), Wang and Matthys [60] have developed an interface tracking method based on element subdivisions. They performed an extensive parametric study of splat cooling of pure aluminum melt on various substrates using both the linear and exponential diffusion-limited kinetics models [169–170] and hence investigated the roles of solidification kinetics and external heat transfer under both low and high melt undercooling conditions. Zhang and Atrens [171], on the other hand, have used a power law kinetics model to relate the interface velocity with the interface melt undercooling. Recently Fryd and Hattel [172] have employed similar models to study the melt-spinning of 12Cr–Mo–V steel.

The importance of nonequilibrium kinetics in modeling of melt-substrate quenching can be illustrated by Figures 37 and 38 [169]. Figure 37 provides a comparison between the temperature predictions made by the equilibrium model and a model that incorporates nonequilibrium kinetics at the solid-liquid interface for an aluminum splat on a copper substrate. Figure 38 shows the calculated interface velocity for two different thicknesses. As can be seen, the nonequilibrium model (with 100 K melt
undercooling at nucleation) predicts recrystallization during the early stages of solidification with an inverse temperature profile in the melt, namely a negative temperature gradient in the melt near the surface. Because of the fast rate of local dissipation of latent heat into the undercooled melt, the solidification during recrystallization is kinetics controlled, resulting in a very fast rate of solidification as shown in Figure 38. The interface velocity, however, drops quickly as the solid-liquid interface is heated up. Finally, the interface velocity reaches a very low value which is controlled by the rate of heat transfer. The equilibrium model, on the other hand, predicts a slow increase in the rate of solidification at the beginning and then remains almost constant during the entire process.

Figure 39 shows the temperature history of a splat at three locations in the splat (bottom, mid-height, and top) and for two undercooling levels [170]. A strong effect of recrystallization is evident from the rapid increase in temperature of the solidified solid and melt near the interface as solidification takes place. Figure 39 also shows that increasing the undercooling at nucleation decreases the total solidification time, the time needed to solidify the whole splat after nucleation, from about 100 to 35 μs. This substantial reduction in solidification time is important because it facilitates the preservation of some of the beneficial consequences of recrystallization such as refinement of microstructure and metastable phase formation [24, 28].

Recently Yao et al. [173] have studied the nonequilibrium solidification of a semitransparent material with internal absorption and emission in the melt layer. They found that internal thermal radiation helps the removal of latent heat and increases the solidification velocity. Figure 40 shows the calculated nondimensional interface velocity for a semitransparent thin liquid rapidly solidified in a vacuum environment. As can be seen in the figure, the dimensionless interface velocity in all cases starts at 0.5 when the solidification is initiated, a value dictated by the preset nucleation temperature. This high interface velocity drops immediately due to recrystallization. For an opaque material (κ₀ → ∞) the recrystallization is followed by a quasi-equilibrium solidification process with the interface velocity decreasing slowly. If the optical thickness, κ₀, of the material is small enough, for example, κ₀ = 1 or 5, the interface velocity is accelerated after the initial recrystallization before it reaches a maximum because of the internal radiation.

Since the internal radiation depends on optical properties of the material, the extent of melt undercooling during later stages of solidification strongly depends on the optical thickness, as shown in Figure 41, which presents the temperature profiles when the interface advances to S = 0.25 (where S is the dimensionless coordinate with S = 0.5 as the symmetry line). As can be seen, the melt is undercooled in all cases with the opaque material having the smallest melt undercooling. Decreasing
9.3 Nonequilibrium Solidification and Microstructure
Development of Binary Alloys

Several attempts have also been made to model the rapid solidification and microstructure development of alloys in spray deposition and melt-spinning. Issues that need to be addressed in this case include crystalline nucleation of alloys, solidification morphology and transition, and microstructure. Mostly the nucleation in the bulk melt has been ignored, and it is considered only at the substrate surface by a given
nucleation temperature. This simplification has been justified based on the uncertainty of the classical nucleation model, as discussed in Section 4.2. Most of the alloy melt-quenching processes take place in cellular-dendritic solidification regimes near the absolute stability conditions. This makes the modeling of alloy rapid solidification in melt-substrate quenching and prediction of microstructure development much more challenging than that of the pure materials.

Evans and Greer [174] were probably the first to consider the rapid planar interface solidification of alloys through a heat and mass diffusion model in a melt-substrate system, together with the nonequilibrium crystalline growth kinetics conditions at the moving interface as described in Section 4.4. They employed the Clyne’s local source method [55] and studied a binary nickel-alloy system. Later Wang and Matthis [175] employed a coordinate transformation method to treat the thin concentration boundary layer ahead of the interface and to determine more accurately the interface parameters, velocity, temperature, and solute concentrations. Both studies assumed a stable planar interface during the solidification, which is valid only when the interface velocity is high and the initial melt undercooling is small [106].

Since exact tracking of the details of the solid-liquid interfaces in mushy zone during cellular-dendritic solidification is extremely difficult, and is not feasible with the present-day numerical techniques, a simplified treatment of dendritic solidification is commonly employed [45–51, 65], as noted in Section 3.3.2. Flood and Hunt [176] were the first who studied the nonequilibrium dendritic solidification in melt-substrate quenching by considering a thin layer of molten metal subjected to convective cooling on the surface. The most important development in the model by Flood and Hunt [176] is to introduce a velocity-versus-temperature relationship at the tip-melt interface based on a dendrite growth theory. In their original model Flood and Hunt derived such relationship based on the dendrite growth model of Burden and Hunt [136]:

\[ V = C_i(T_L - T_i)^2 \]  

(117)

where \( C_i \) is a constant and \( T_L \) is the liquidus temperature. In their model Flood and Hunt have employed the Scheil equation truncated at the dendrite tip temperature to obtain the solid fraction-temperature relationship in the mushy zone. With such treatments the nonequilibrium dendritic solidification reduces to a thermal problem with the interface velocity expressed in terms of the interface temperature, similar to the nonequilibrium, planar interface solidification models.

More realistic microsegregation models that include various nonequilibrium effects have been developed recently, as summarized in Section 6 and introduced into the heat transfer models of melt-substrate quenching [135, 138]. These models have also improved the treatment of the dendrite tips by taking advantage of the recent progress in dendrite growth theories.

For example, Granasy and Ludwig [66] developed a dendritic growth model for planar flow casting to study the microstructure development in melt-spun ribbons. In this model the tip velocity-temperature relationship was obtained from Jönsson [120], and the microsegregation model of Giovanola and Kurz [135] was used to derive the function \( f_c = f(T) \). A thermal banded structure was predicted by Granasy and Ludwig.

McCarthy and Blake [138] have also developed a dendritic solidification model for melt-quenching. They employed the truncated Scheil equation as the microsegregation model for mushy zone, but a new truncation condition was used to guarantee the solute conservation. The tip velocity-temperature relationship was obtained from the KGT model [111] but was kept limited to only small melt undercoolings (less than 30 K) before the transition to the thermal dendrites due to strong solute-trapping effects, see Figure 16a.

One common feature of all of the above heat transfer and dendritic solidification models is that the predetermined relationships between the tip velocity and temperature are employed to solve the macroscopic energy equation. Since these relationships are derived for only special macroscopic thermal conditions, they do not account for the variations of the macroscopic thermal characteristics during the process. Therefore these models may be acceptable for the processes in which a quasi-steady condition can be maintained such as the process of laser scanning but not for melt-substrate quenching where the solidification velocity undergoes significant changes. In these processes the thermal environments in the early stages of the process are quite different from that in the later part of the process. A universal velocity-temperature relationship is therefore not adequate to reflect such strong dynamic variations. In addition the solidification morphologies can also vary significantly during the solidification process and so cannot be accounted for by these models.

It is therefore highly desirable to develop a fully integrated micro-macro model for dendritic solidification in melt-quenching. Recently some progress has been made in this direction. Instead of using a predetermined temperature-velocity relationship like the ones used by most researchers, Wang et al. [69] have introduced a full dendritic tip growth model of Kurz and Trivedi [13] into the heat transfer model to calculate both macroscopic temperature field and microscale dendrite tip growth conditions simultaneously. The model also considers the transition from dendritic to planar interface solidification implicitly.

### 9.4 Integrated Micro-Macro Dendritic Solidification Model for Melt-Quenching

Following Flood and Hunt [176], Wang et al. [69] assume that all dendrites grow under similar conditions so that a periodic condition can be imposed between the two dendrite tips and an imaginary planar interface can be drawn to envelop the tip; see Figure 10b. To avoid the complexity of mushy zone and following Kim et al. [68], the dendrite region is assumed to be thin, so the latent heat is released only at the tip-melt interface. This assumption can be easily relaxed by introducing a microsegregation model presented in Section 6. With these assumptions, the dendritic solidification can be described by a macroscopic heat equation, such as Eq. (1), with a moving interface that is the location of the dendrite tips. The movement of the dendrite tips is not constrained by a predetermined temperature-velocity relationship as discussed in
Section 9.3. Instead, the microscopic dendrite tip model of Kurz and Trivedi [13], as discussed in Section 5.2, is employed:

\[ T_i = T_m + m_l C^l_T - \frac{2 \Gamma}{R_i} - \frac{V_i}{\mu_k} \]  

(118)

with

\[ C^l_T = \frac{C_0}{1 - (1 - k) I \sqrt{\rho_c}} \]  

(119)

\[ R_i = \left( \frac{\Gamma}{\sigma^*} \right)^{1/2} \left( m_l G_C C^l_T - \frac{K_L G_L S_L + K_S G_S S_S}{K_L + K_S} \right)^{1/2} \]  

(120)

and

\[ G_C = -\frac{V_i C^l_T (1 - k)}{D_L} \]  

(121)

This dendrite tip growth model involves two macroscopic variables, the temperature gradients at the melt-tip interface, \( G_L \) and \( G_S \), in the melt and solid regions, respectively. For given \( G_L \) and \( G_S \), Eqs. (118) to (121) can be used to calculate other tip parameters. The two temperature gradients are the parameters that introduce the effect of macroscopic thermal transport on microscale dendrite tip growth. Theoretically, the microscopic dendrite tip model provides the necessary moving tip-melt interface condition with which the macroscopic heat equation can be solved to determine \( G_L \) and \( G_S \). However, the macroscopic temperature gradients must be specified in order to solve the dendrite model. Therefore an integrated treatment is needed in which both micro and macroscopic equations are solved simultaneously. In addition, since the interface stability criterion is implicitly built into the above dendritic growth model through the term in the square root of Eq. (120), as discussed in Section 5.3, the model can also detect the change of the solidification morphology from dendritic to planar, and vice versa.

Wang et al. [69] have used this model to simulate the rapid solidification of a 5 \( \mu \)m thick molten Al-4.5wt\%Cu splat quenched on a copper substrate, the initial melt being at 983.6 K and the substrate at 300 K. The nucleation temperature, \( T_N \), and the interfacial heat transfer coefficient, \( h \), are treated as free parameters. Figure 42a shows typical predictions for dendritic tip radius when \( h = 10^7 \text{ W/m}^2\text{K} \) and the melt undercooling varies from 50 to 250 K. In all cases the initial tip radius is small, 0.15 \( \mu \)m for 250 K and about 0.32 \( \mu \)m for 50 K. As the solidification progresses, the tip

![Figure 42a](image)

**Figure 42** Effect of melt undercooling on microstructure formation in an Al-4.5wt%Cu alloy splat quenched on a copper substrate: (a) Dendrite tip radius and (b) interface velocity. Note the transition from dendritic solidification to planar solidification. Wang et al. [69].
radius increases, with the rate being a strong function of melt undercooling. A higher initial melt undercooling leads to a lower rate of increase in the tip radius. Eventually the tip radius becomes so large that the dendritic growth becomes unstable and planar interface solidification follows. The extent to which the dendritic solidification occurs strongly depends on the initial melt undercooling.

The corresponding velocity of the interface, for both dendritic and planar interface growths, is shown in Figure 42b. The variation of the interface velocity as shown in this figure is very similar to that observed for planar interface solidification of pure metals and binary alloys [169, 174–175]. A high interface velocity is achieved at the beginning of solidification because of a large melt undercooling. Recrystallization then follows due to the heating of the undercooled melt by the release of latent heat. Eventually kinetic effects fade away as the melt undercooling diminishes and the solidification is controlled by heat transfer, as illustrated by an identical interface velocity for varying initial melt undercooling.

One interesting phenomenon revealed by the model of Wang et al. [69] is the oscillatory behavior of planar interface solidification when \( h \) is in the range of \( 2 \times 10^6 \leq h \leq 8 \times 10^9 \) W/m²K, as shown in Figure 43 for the case of \( h = 6 \times 10^9 \) W/m²K; all other conditions are the same as in Figure 42. The transition from dendritic to planar interface solidification takes place at about 2.2 µm location. A small perturbation occurs at this point due to transition, but it is stabilized immediately, and a stable planar interface growth continues until about 2.6 µm where a small oscillation is observed first which then quickly develops into a large amplitude oscillation. The oscillatory behavior (almost identical amplitudes and frequencies) is independent of the mesh size; it is considered to be a real physical phenomenon. Such oscillatory solidification leads to the formation of a solute band, namely a periodic variation of solute distribution. For the conditions considered here, the solute concentration in the solid varies from a minimum of 4.12 wt% to a maximum of 6.0 wt% with a maximum band width of about 0.19 µm. The appearance of such solute band agrees well with the band structure theory discussed in Section 5.4.

The most important feature of the Wang's model is that it can help to construct a microstructure map for an alloy splat quenched on a cold substrate. To demonstrate this, they have chosen the interfacial heat transfer coefficient, \( h \), and initial melt undercooling at nucleation, \( T_{L} - T_{N} \), as two controlling process parameters, and have generated a microstructure-process map as shown in Figure 44. As one can see, different structures are predicted for different combinations of these two variables. For the case with a high \( h \) and a large melt undercooling at nucleation, \( T_{L} - T_{N} \), the splat is a two layer structure: a dendritic structure in the region close to the substrate followed by a planar interface growth region. For very low values of \( h \), the entire splat is dendritic. In this case, if the melt undercooling is large, large thermal dendrites will be developed in the region close to the substrate followed by small size solutal dendrites. However, if the melt undercooling is small, only solutal dendrites will be present. Banded thermal and solutal dendrites structure may also develop when a transition from thermal dendritic growth to solutal dendritic growth occurs in an intermediate melt undercooling.

![Figure 43](image1.png) Oscillatory planar interface solidification after transition from the dendritic growth: Solute concentration in the solid at the interface. Wang et al. [69].

![Figure 44](image2.png) Schematic of a microstructure map for Al−4.5wt%Cu splat quenched on a copper substrate. Multiple layer structures with varying bands can exist. Wang et al. [69].
10 CONCLUDING REMARKS

Traditionally liquid-solid phase-change has been considered as a pure thermal problem. However, it is now well understood that such treatment is not valid for many industrial solidification processes. A brief review of the fundamentals of rapid solidification processes has shown that the various nonequilibrium phenomena influence critically the microstructure of the rapidly solidified materials, and consequently their properties. Kinetics issues such as crystalline nucleation, nonequilibrium growth of crystals including the solute trapping, interface stability, solidification morphology and transition, and microsegregation must be considered in analyzing these processes. Although significant advances have been made in describing mathematically the kinetics of rapid solidification processes, many of the RS features cannot be modeled today because of the lack of physical understanding and difficulty with developing mathematical expressions. Also it is very difficult to conduct measurements in these processes, and data on thermophysical properties that are critical to realistic modeling remain scarce.

Advancements have also been made in developing special numerical techniques as well as the methodologies to couple macroscopic heat and mass transfer with microscopic solidification. Integrated models have been built and applied to analyze the physical phenomena of rapid solidification of metal droplets to produce atomized powders, pulsed laser treatment of material surfaces, and melt-substrate quenching. However, these models remain one-dimensional, although most of the processes are at least two-dimensional if not three-dimensional.

This review has dealt with only the basic issues of rapid solidification. Several other important but more complex phenomena have not been discussed here because of the space limitation—rapid eutectic solidification [177–178], equiaxed solidification due to bulk nucleation, and transition from columnar to equiaxed growth [179–180], to name a few. Recently progress has also been made on rapid solidification of peritectic system [181]. In addition only simplified phase diagrams for binary systems with stable solids and liquids lines have been considered here. In reality the phase diagrams can be very complex and may involve multiple components as well as nonlinear behavior. Thermodynamic models are needed to provide more accurate descriptions of the equilibrium phase diagrams, particularly, in complex systems [182].

The models described in this article are all deterministic. Recently probabilistic models based on either the Monte Carlo method [183] or the cellular automation technique [184] have been shown to simulate the growth of both columnar and equiaxed grains during rapid solidification. Hon and his co-workers [185–186] employed such probabilistic models using the cellular automation technique to simulate the microstructure development in melt-spun ribbons. This has opened up a new direction for modeling of rapid solidification processes and microstructure development.

Rapid solidification is an emerging field from both applications and fundamentals in science. The industrial applications are expected to grow significantly in the future as its use in changing the material characteristics locally. More research is needed to develop a better understanding of these processes and to build more realistic models.

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REFERENCES


107. R. Billia and R. Trivedi, Pattern Formation in Crystal Growth, in *Handbook of...*


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