KMU 496
MATERIALS SCIENCE AND
TECHNOLOGY III

CHAPTER 9
PRINCIPLES OF SOLIDIFICATION

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- Of all the processing techniques used in the manufacturing of materials, ***solidification*** is probably the most important.
- All metallic materials, as well as many ceramics, inorganic glasses, and thermoplastic polymers, are liquid or molten at some point during processing.
  - Like water freezes to ice, molten materials solidify as they cool below their freezing temperature.
- The solidification of metallic, polymeric, and ceramic materials is an important process to study because of its effect on the properties of the materials involved.

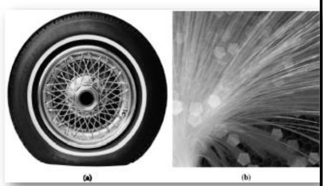
PRINCIPLES OF SOLIDIFICATION

- We will study the principles of solidification for ***pure metals***.
- We will learn:
  - Technological sigificance
  - Nucleation
  - Growth mechanisms
  - Cooling curves
  - Cast structure
  - Solidification defects
  - Casing processes for manufacturing components

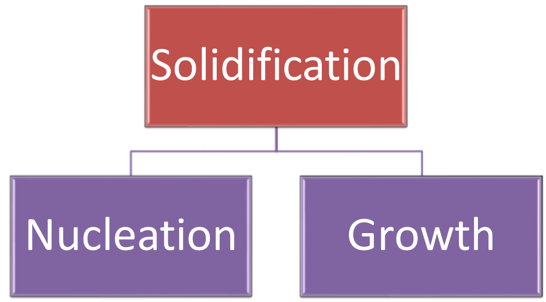
Technological Significance

- Industry uses the solidification process as:
  - Primary processing: Processes involving casting of molten metals into ingots or semi-finished useful shapes such as slabs.
  - Secondary processing: Processes such as rolling, extrusion, etc. used to process ingots or slabs and other semi-finished shapes.

An image of a bronze object. This Canteen (bian hu) from China, Warring States period, circa 3rd century BCE (bronze inlaid with silver). (*Courtesy of Freer Gallery of Art, Smithsonian Institution, Washington, D.C.*)



(a) Aluminum alloy wheels for automotives, (b) optical fibers for communication. (*Courtesy of PhotoDisc/Getty Images.*)



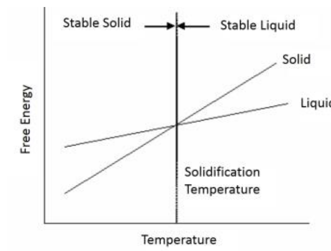
Technological Significance

- We also use solidification for processing inorganic glasses.
- High-quality optical fibers and other materials, such as fiberglass, are also produced from the solidification of molten glasses.
- Many thermoplastic materials such as polyethylene, polyvinyl chloride, polypropylene are processed into useful shapes using process that involves melting and solidification.
  - Therefore, solidification is an extremely important technology used to control the properties of the materials.

Nucleation

- Nucleation - The physical process by which a new phase is produced in a material. In another words, nucleation refers to the initial stage of formation of one phase from another phase.
  - It also refers to the formation of the first nanocrystallites from molten material.
  - For example, as water begins to freeze, nanocrystals, known as nuclei, form first.
- Undercooling - The temperature to which the liquid metal must cool below the equilibrium freezing temperature.
  - The liquid solidifies when cooled below the solidification temperature.
  - The resulting structure in the solidification process affects the *mechanical properties*.
  - Particularly *grain size* and *shape* can be controlled by solidification.

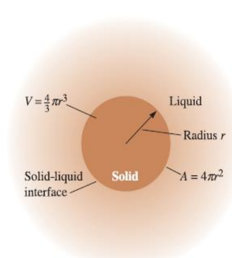
- The most important factor in the formation of internal structure in the materials is energy.
- One of the main features of physical nature is the increase in stability in a body with reduced energy.
- Systems always tend to become more stable by directing towards their energy-reducing way.



- When the temperature decreases further from the solidification point, the increasing energy difference makes the solid more stable.
- The energy difference between the solid and the liquid is the free energy per unit volume = ΔG_V

- We expect a material to solidify when the liquid cools to just below its freezing temperature.
- Because the energy associated with the crystalline structure of the solid is less than the energy of the liquid.
- The energy difference betwen the liquid and the solid is the free energy per unit volume ΔGv and is the driving force for solidification.

- When a solid forms, a solid-liquid interface is created, a surface free energy σ_{sl} is associated with this interface.
- Thus the total energy change ΔG:

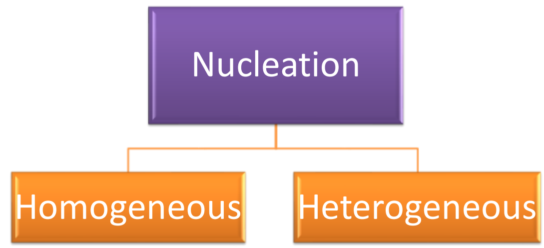


$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \sigma_{sl}$$

Surface area ⇧

Surface free energy ⇧

- Critical radius (r*) - The minimum size that must be formed by atoms clustering together in the liquid before the solid particle is stable and begins to grow.
- Nucleation occurs when small solid particles become embryo from liquid.
  - An embriyo is a tiny particle of solid that forms from the liquid as atoms cluster together.
  - The embriyo is unstable and may either grow into a stable nucleus or redissolve.



- The total free energy of the solid-liquid system changes with the size of the solid.
- The solid is:
  - an *embryo* if its radius is less than the critical radius,
  - a *nucleus* if its radius is greater than the critical radius.

Homogeneous Nucleation

- This theory was discovered by Volmer-Weber in 1925.
- It is the simplest form of nucleation.
- Homogeneous nucleation is possible with extreme cooling of the liquid.

TABLE 9-1 *Values for freezing temperature, latent heat of fusion, surface energy, and maximum undercooling for selected materials*

Material	Freezing Temperature (T_m) (°C)	Heat of Fusion (ΔH_f) (J/cm³)	Solid-Liquid Interfacial Energy (σ_{sl}) (J/cm²)	Typical Undercooling for Homogeneous Nucleation (ΔT) (°C)
Ga	30	488	56×10^{-7}	76
Bi	271	543	54×10^{-7}	90
Pb	327	237	33×10^{-7}	80
Ag	962	965	126×10^{-7}	250
Cu	1085	1628	177×10^{-7}	236
Ni	1453	2756	255×10^{-7}	480
Fe	1538	1737	204×10^{-7}	420
NaCl	801			169
CsCl	645			152
H_2O	0			40

Homogeneous Nucleation

- The latent heat of fusion represents the heat given up during the liquid-to-solid transformation.
- As the undercooling *increases*, the critical radius required for nucleation *decreases*.

Homogeneous Nucleation

- Homogeneous nucleation occurs when the undercooling becomes large enough to cause the formation of a stable nucleus.
- The size of the critical radius r* for homogeneous nucleation is given by

$$r^* = \frac{2\sigma_{sl}\, T_m}{\Delta H_f\, \Delta T}$$

- ΔH_f is the latent heat of fusion per unit volume
- T_m is the equilibrium solidification temperature in Kelvin
- $\Delta T=(T_m-T)$ is the undercooling when the liquid temperature is T

Example 9.1. Calculation of Critical Radius for the Solidification of Copper

Calculate the size of the critical radius and the number of atoms in the critical nucleus when solid copper forms by homogeneous nucleation. Comment on the size of the nucleus and assumptions we made while deriving the equation for radius of nucleus.

Example 9.1 SOLUTION

From Table 8-1:

$$\Delta T = 236°C \quad T_m = 1085 + 273 = 1358 \text{ K}$$

$$\Delta H_f = 1628 \text{ J/cm}^3$$

$$\sigma_{sl} = 177 \times 10^{-7} \text{ J/cm}^2$$

$$r^* = \frac{2\sigma_{sl} T_m}{\Delta H_f \Delta T} = \frac{(2)(177 \times 10^{-7})(1358)}{(1628)(236)} = 12.51 \times 10^{-8} \text{ cm}$$

Example 9.1 SOLUTION (Continued)

The lattice parameter for FCC copper is $a_0 = 0.3615$ nm $= 3.615 \times 10^{-8}$ cm

$$V_{\text{unit cell}} = (a_0)^3 = (3.615 \times 10^{-8})^3 = 47.24 \times 10^{-24} \text{ cm}^3$$

$$V_{r^*} = \tfrac{4}{3}\pi r^3 = (\tfrac{4}{3}\pi)(12.51 \times 10^{-8})^3 = 8200 \times 10^{-24} \text{ cm}^3$$

The number of unit cells in the critical nucleus is

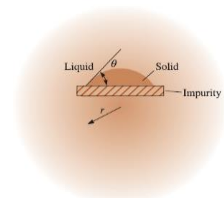
$$\frac{8200 \times 10^{-24}}{47.24 \times 10^{-24}} = 174 \text{ unit cells}$$

Since there are four atoms in each unit cell of FCC metals, the number of atoms in the critical nucleus must be:

$$(4 \text{ atoms/cell})(174 \text{ cells/nucleus}) = 696 \text{ atoms/nucleus}$$

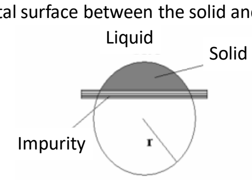
Heterogeneous Nucleation

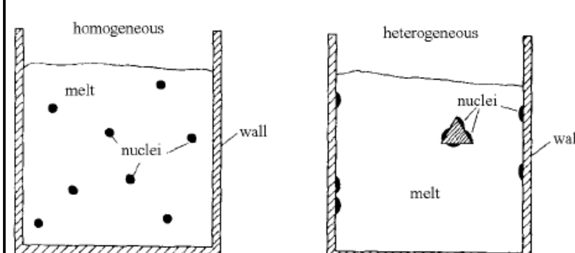
- Much less undercooling is required to achieve the critical size, so nucleation occurs more readily.
- This process is dependent on the contact angle (θ) for the nucleating phase and the surface on which nucleation occurs.



Heterogeneous Nucleation

- Except in controlled laboratory experiments, homogeneous nucleation never occurs.
- Instead, impurities in contact with the liquid, either suspended in the liquid or on the walls of the container that holds the liquid, provide a surface on which the solid can form.
- Relatively few atoms must cluster together to produce a solid particle that has the required radius of curvature.
- Now, a radius of curvature greater than the critical radius is achieved with very little total surface between the solid and liquid.





Rate of Nucleation

- The rate of nucleation is a function of *temperature*.
- Prior to solidification, there is no nucleation and at temperatures above freezing point, the rate of nucleation is *zero*.
- As the temperature drops, the driving force for nucleation *increases*; however, as the temperature decreases, atomic diffusion becomes *slower*, hence slower the nucleation process occurs.

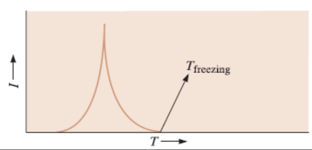
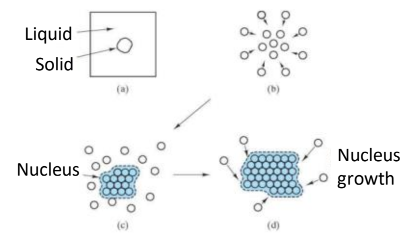


Figure 9-5
Rate of nucleation (*I*) as a function of temperature of the liquid (*T*).

Growth Mechanisms

- Once the solid nuclei of a phase forms, growth begins to occur as more atoms become attached to the solid surface.
- Growth is the physical process by which a new phase increases in size. In the case of solidification, this refers to the formation of a stable solid particle as the liquid freezes.



GROWTH MECHANISMS

Growth Mechanisms

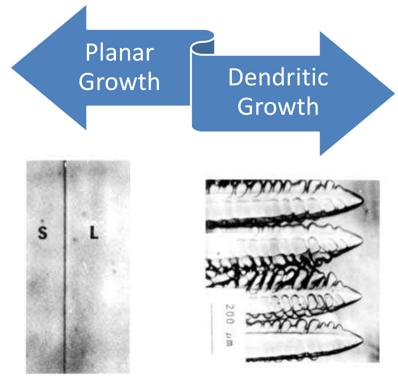
- The nature of the growth of the solid nuclei depends on how heat is removed from the molten material.
- In the solidification process, two types of heat must be removed:
  - the specific heat of the liquid
  - the latent heat of fusion

The manner in which the latent heat is lost determines the growth mechanism!!!

Growth Mechanisms

- The specific heat is the heat required to change the temperature of a unit weight of the material by one degree.
- The specific heat must be removed first,
  - either by radiation into the surrounding atmosphere or,
  - by conduction into the surrounding mold, until the liquid cools to its freezing temperature.

Growth Mechanisms



Growth Mechanisms

- The latent heat of fusion must be removed from the solid-liquid interface before solidification is completed.
- The manner in which we remove the latent heat of fusion determines
  - the material's growth mechanism and
  - final structure of a casting.

Planar Growth

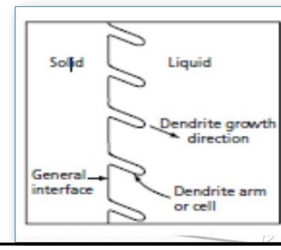
- It is the smooth growth of solid-liquid interface during solidification *without any extreme cooling*.
- During solidification, the *latent heat of fusion* is removed by *conduction* from the solid-liquid interface.

Planar Growth

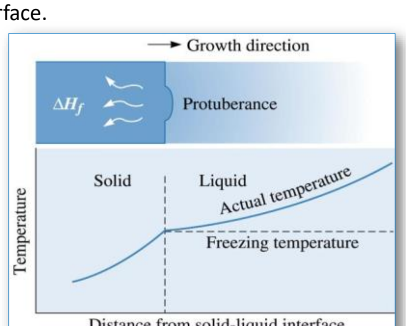
- When *a well-inoculated liquid* (i.e., a liquid containing nucleating agents) cools under equilibrium conditions, there is no need for undercooling since heterogeneous nucleation can occur.
- The temperature of the liquid is greater than the freezing temperature. The temperature of the solid is at or below the freezing temperature.
- During solidification, the latent heat of fusion is removed by conduction from the solid-liquid interface.

Dendritic Growth

- When the *nucleation is poor*, the liquid has to be undercooled before the solid forms.
- Under these conditions, a small solid proturbance called a *dendrite*, which forms at the interface, is encouraged to grow since the liquid ahead of the solidification front is *undercooled*.



- When the temperature of the liquid is above the freezing temperature, a protuberance on the solid-liquid interface will not grow, leading to maintenance of a planar interface.



Dendritic Growth

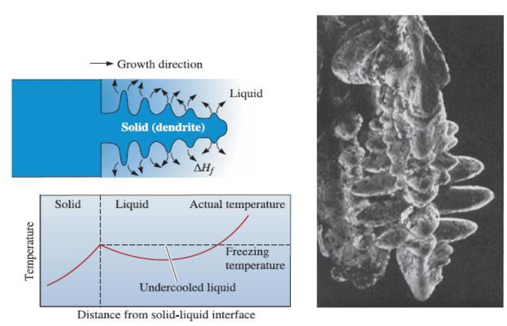
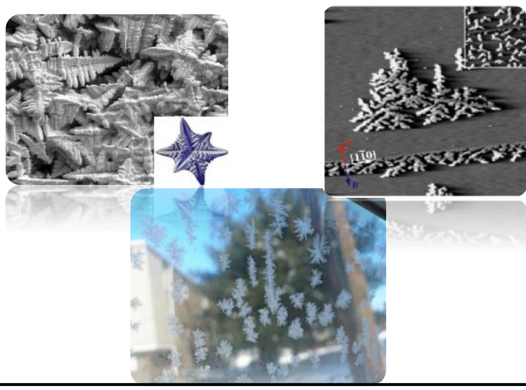
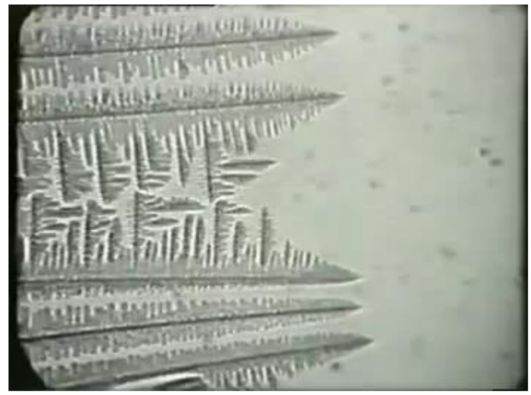


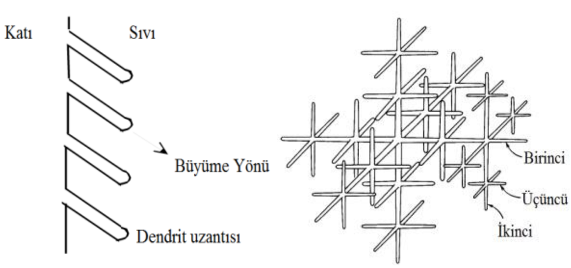
Figure 9-4 (a) If the liquid is undercooled, a protuberance on the solid-liquid interface can grow rapidly as a dendrite. The latent heat of fusion is removed by raising the temperature of the liquid back to the freezing temperature. (b) Scanning electron micrograph of dendrites in steel (× 15). (*Reprinted courtesy of Don Askeland.*)

Dendritic Growth





Dendrit Formation



In planar growth → Vessel or mold absorbs heat

In dendritic growth → Subcooled liquid absorbs heat

Solidification Time and Dendrite Size

- The rate at which growth of the solid occurs depends on the *cooling rate*.
- A higher cooling rate produces *rapid solidification*, or *short solidification times*.
- The time t_s required for a simple casting to solidify completely can be calculated using **Chvorinov's rule**:

$$t_s = B\left(\frac{V}{A}\right)^n$$

V: volume of the casting
A: surface area of the casting in contact with the mold
n: constant (usually about 2)
B: mold constant

The mold constant depends on the *properties* and *initial temperatures* of both the metal and the mold.

- The solidification time affects the size of the dendrites.
- Dendrite size is characterized by measuring the distance between the secondary dendrite arms.
- The **secondary dendrite arm spacing (SDAS)** is reduced when the casting freezes more rapidly.

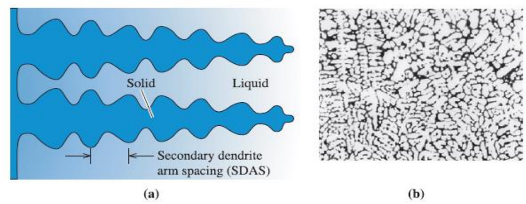


Figure 9-5 (a) The secondary dendrite arm spacing (SDAS). (b) Dendrites in an aluminum alloy (× 50). *(From ASM Handbook, Vol. 9, Metallography and Microstructure (1985), ASM International, Materials Park, OH 44073-0002.)*

Example 9-2 ***Redesign of a Casting for Improved Strength***

Your company currently is producing a disk-shaped brass casting 2 in. thick and 18 in. in diameter. You believe that by making the casting solidify 25% faster the improvement in the tensile properties of the casting will permit the casting to be made lighter in weight. Design the casting to permit this. Assume that the mold constant is 22 min/in.^{2} for this process and $n = 2$.

- The secondary dendrite arm spacing (SDAS) is related to the solidification time by

$$SDAS = kt_s^m$$

m and k are constants depending on the composition of the metal

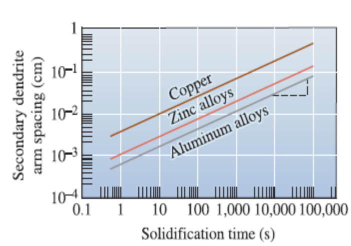


Figure 9-6 The effect of solidification time on the secondary dendrite arm spacings of copper, zinc, and aluminum.

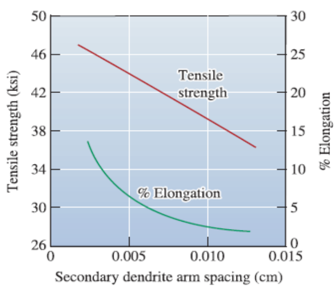


Figure 9-7
The effect of the secondary dendrite arm spacing on the mechanical properties of an aluminum casting alloy.

Example 9-5 *Design of an Aluminum Alloy Casting*

Design the thickness of an aluminum alloy casting with a length of 12 in., a width of 8 in., and a tensile strength of 40,000 psi. The mold constant in Chvorinov's rule for aluminum alloys cast in a sand mold is 45 min/in^2. Assume that data shown in Figures 9-6 and 9-7 can be used.

Example 9-3 *Secondary Dendrite Arm Spacing for Aluminum Alloys*

Determine the constants in the equation that describe the relationship between secondary dendrite arm spacing and solidification time for aluminum alloys (Figure 9-6).

COOLING CURVES

Cooling Curves

- A cooling curve shows how the temperature of a material decreases with time.

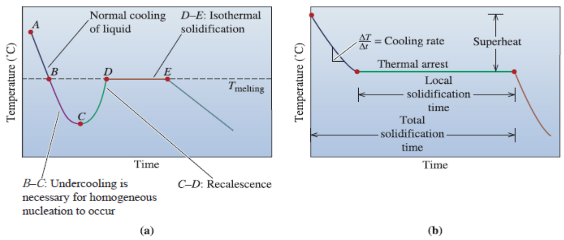
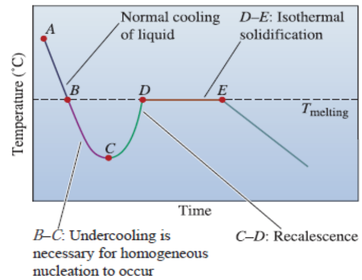
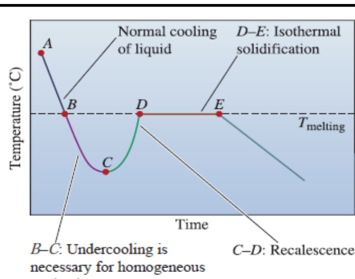


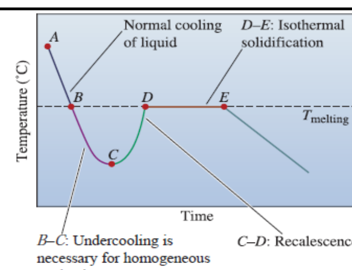
Figure 9-8 (a) Cooling curve for a pure metal that has not been well-inoculated. The liquid cools as specific heat is removed (between points *A* and *B*). Undercooling is thus necessary (between points *B* and *C*). As the nucleation begins (point *C*), latent heat of fusion is released causing an increase in the temperature of the liquid. This process is known as recalescence (point *C* to point *D*). The metal continues to solidify at a constant temperature ($T_{melting}$). At point *E*, solidification is complete. The solid casting continues to cool from this point. (b) Cooling curve for a well-inoculated, but otherwise pure, metal. No undercooling is needed. Recalescence is not observed. Solidification begins at the melting temperature.



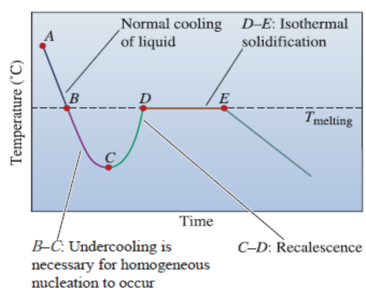
- As nucleation begins (point *C*), latent heat of fusion is given off, and the temperature rises.
- This increase in temperature of the undercooled liquid as a result of nucleation is known as *recalescence* (point *C* to *D*).



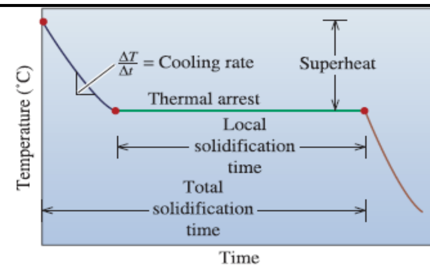
- The difference between the pouring temperature and the freezing temperature is the superheat. The heat is extracted by the mold until the liquid reaches the freezing temperature (point *B*).
- If the liquid is not well-inoculated, it must be undercooled (point *B* to *C*).



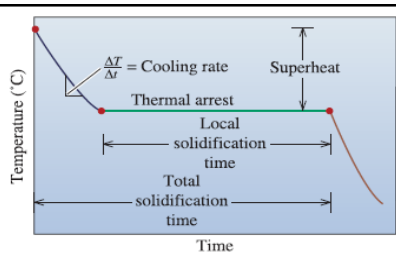
- Solidification proceeds isothermally at the melting temperature (point *D* to *E*) as the latent heat given off from continued solidification is balanced by the heat lost by cooling.
- This region between points *D* and *E*, where the temperature is constant, is known as the *thermal arrest*.



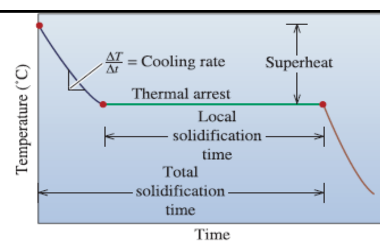
- At point *E*, solidification is completed, and the solid casting cools from point *E* to room temperature.



- The latent heat keeps the remaining liquid at the freezing temperature until all of the liquid has solidified and no more heat can be evolved.
- Growth under these conditions is *planar*.



- If the liquid is well-inoculated, the extent of undercooling and recalescence is usually very small and can be observed in cooling curves only by very careful measurements.
- If effective heterogeneous nuclei are present in the liquid, solidification begins at the *freezing temperature*.



- **Total solidification time:** The time required to remove both the specific heat of the liquid and the latent heat of fusion.
- **Local solidification time:** The time required to remove only the latent heat of fusion at a particular location in the casting.
  - It is measured from when solidification begins until solidification is completed.

CAST STRUCTURE

Cast Structure

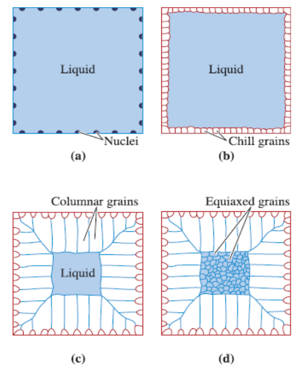
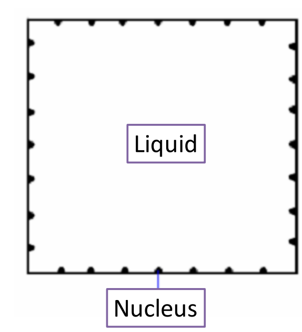


Figure 9-9
Development of the ingot structure of a casting during solidification: (a) nucleation begins, (b) the chill zone forms, (c) preferred growth produces the columnar zone, and (d) additional nucleation creates the equiaxed zone.

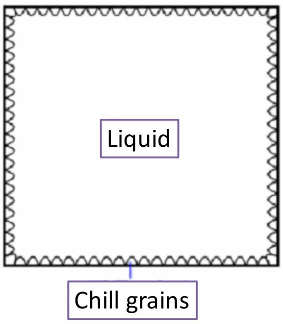
Cast Structure

- Molten metals are often poured into molds and permitted to solidify.
- The mold produces a finished shape, known as a ***casting***.
- In other cases, the mold produces a simple shape called an ***ingot***.
- An ingot usually requires extensive plastic deformation before a finished product is created. A *macrostructure* consists of three regions:
  - *Chill zone*
  - *Columnar zone*
  - *Equiaxed zone*

Initiation of Nucleation

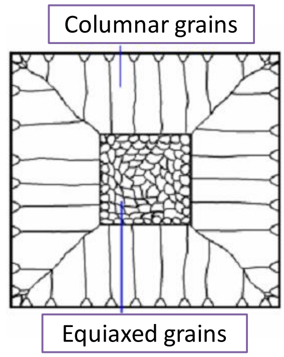


Chill Grain Formation



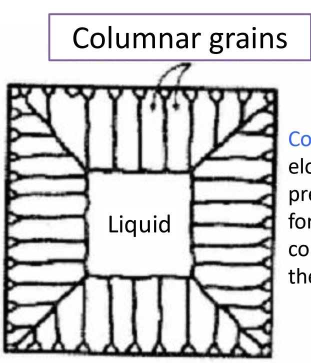
Chill zone: A region of small, randomly oriented grains that forms at the surface of a casting as a result of heterogeneous nucleation.

Equiaxed Grain Formation



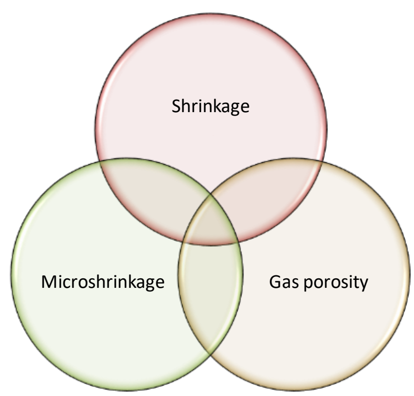
Equiaxed zone: A region of randomly oriented grains in the center of a casting produced as a result of widespread nucleation.

Columnar Grain Formation



Columnar zone: A region of elongated grains having a preferred orientation that forms as a result of competitive growth during the solidification of a casting.

Solidification Defects



Shrinkage

- Contraction of a casting during solidification. Often, the bulk of the shrinkage occurs as cavities.

- Almost all materials are more dense in the solid state than in the liquid state.
- During solidification, the material contracts, or shrinks, as much as 7%.

Shrinkage

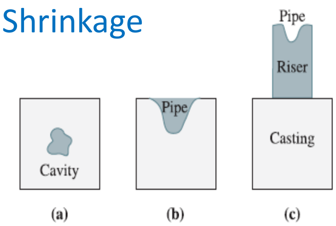


Figure 9-11 Several types of macroshrinkage can occur, including cavities and pipes. Risers can be used to help compensate for shrinkage.

- Shrinkage can occur as different types.
- If solidification begins at all surfaces of the casting, shrinkage occurs as cavities.
- If one surface solidifies more slowly then the others, shrinkage occurs as pipes.
- To control these problems, risers can be used.

Shrinkage

TABLE 9-2 *Shrinkage during solidification for selected materials*

Material	Shrinkage (%)
Al	7.0
Cu	5.1
Mg	4.0
Zn	3.7
Fe	3.4
Pb	2.7
Ga	+3.2 (expansion)
H_2O	+8.3 (expansion)
Low-carbon steel	2.5–3.0
High-carbon steel	4.0
White Cast Iron	4.0–5.5
Gray Cast Iron	+1.9 (expansion)

Note: Some data from DeGarmo, E. P., Black, J. T., and Koshe, R. A. Materials and Processes in Manufacturing, *Prentice Hall, 1997.*

Shrinkage

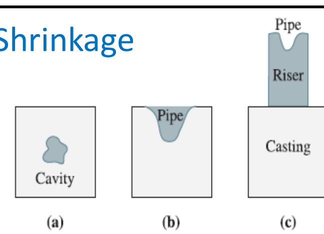


Figure 9-11 Several types of macroshrinkage can occur, including cavities and pipes. Risers can be used to help compensate for shrinkage.

- Riser must freeze after the casting !!!
- Chvorinov's rule can be used to help design the size of the riser.

Example 9-6 *Design of a Riser for a Casting*

Design a cylindrical riser, with a height equal to twice its diameter, that will compensate for shrinkage in a 2 cm × 8 cm × 16 cm, casting (Figure 9-12).

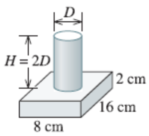
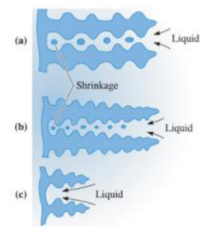


Figure 9-12
The geometry of the casting and riser (for Example 9-6).

Microshrinkage (Interdendritic shrinkage)

- Fast cooling rates may reduce problems with **interdendritic shrinkage**; the dendrites may be shorter, permitting liquid to flow through the dendritic network to the solidifying solid interface.



Microshrinkage (Interdendritic shrinkage)

- Small, frequently isolated pores between the dendrite arms formed by the shrinkage that accompanies solidification.
- This consists of small shrinkage pores between dendrites.

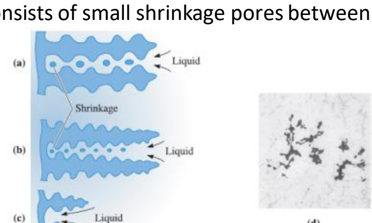


Figure 9-13 (a) Shrinkage can occur between the dendrite arms. (b) Small secondary dendrite arm spacings result in smaller, more evenly distributed shrinkage porosity. (c) Short primary arms can help avoid shrinkage. (d) Interdendritic shrinkage in an aluminum alloy is shown (× 80). (*Reprinted courtesy of Don Askeland.*)

Gas Porosity

- Bubbles of gas trapped within a casting during solidification, caused by the lower solubility of the gas in the solid compared with that in the liquid.
- Many metals dissolve a large quantity of gas when they are molten.
  - Aluminum, for example, dissolves hydrogen.
  - The excess hydrogen that cannot be incorporated in the solid metal forms bubbles that may be trapped in the solid metal, producing *gas porosity*.

Gas Porosity

- The amount of gas that can be dissolved in molten metal is given by *Sievert's law*:

$$\text{Percent of gas} = K\sqrt{p_{gas}}$$

- p_{gas} is the partial pressure of the gas in contact with the metal and
- K is a constant which, for a particular metal-gas system, increases with increasing temperature.

- The amount of a gas that dissolves in a metal is proportional to the partial pressure of the gas in the surroundings.

SOLUTION

We can solve this problem in several ways. In one approach, the liquid copper is placed in a vacuum chamber; the oxygen is then drawn from the liquid and carried away into the vacuum. The vacuum required can be estimated from Sievert's law:

$$\frac{\%\,O_{initial}}{\%\,O_{vacuum}} = \frac{K\sqrt{p_{\,initial}}}{K\sqrt{p_{\,vacuum}}} = \sqrt{\left(\frac{1 \text{ atm}}{p_{vacuum}}\right)}$$

$$\frac{0.01\%}{0.00001\%} = \sqrt{\left(\frac{1}{p_{vacuum}}\right)}$$

$$\frac{1 \text{ atm}}{p_{vacuum}} = (1000)^2 \quad \text{or} \quad p_{vacuum} = 10^{-6} \text{ atm}$$

Example 9-7 *Design of a Degassing Process for Copper*

After melting at atmospheric pressure, molten copper contains 0.01 weight percent oxygen. To ensure that your castings will not be subject to gas porosity, you want to reduce the weight percent to less than 0.00001% prior to pouring. Design a degassing process for the copper.

Summary

- Transformation of a liquid to a solid is probably the most important phase transformation in applications of materials science and engineering.
- Nucleation produces a critical-size solid particle from the liquid melt. Formation of nuclei is determined by the thermodynamic driving force for solidification.
- Homogeneous nucleation requires large undercoolings of the liquid and is not observed in normal solidification processing. By introducing foreign particles into the liquid, nuclei are provided for heterogeneous nucleation.

Summary

- In solidification from melts, the nuclei grow into the liquid melt. Either planar or dendritic modes of growth may be observed.
- In planar growth, a smooth solid-liquid interface grows with little or no undercooling of the liquid. Dendritic growth occurs when the liquid is undercooled.
- Rapid cooling, or a short solidification time, produces a finer dendritic structure and often leads to improved mechanical properties of a metallic casting.

Summary

- By controlling nucleation and growth, a casting may be given a columnar grain structure, an equiaxed grain structure, or a mixture of the two.
- Porosity and cavity shrinkage are major defects that can be present in cast products.
- In commercial solidification processing methods, defects in a casting (such as solidification shrinkage or gas porosity) can be controlled by proper design of the casting and riser system or by appropriate treatment of the liquid metal prior to casting.

Summary

- Chvorinov's rule is used to estimate the solidification time of a casting.
- Metallic castings that have a smaller interdendritic spacing and finer grain size have higher strengths.
- Cooling curves indicate the pouring temperature, any undercooling and recalescence, and time for solidification.

Any Questions?