Materials for Mechanical Engineering

Solidification of metals

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Learning Objective

- **Why Does Anything Solidify?**
- **Nucleation**
- **Planar Growth**
- **Dendritic Growth**
- **Cast Structure**
- **Solidification Defects**
- **How to get the fine grain size**

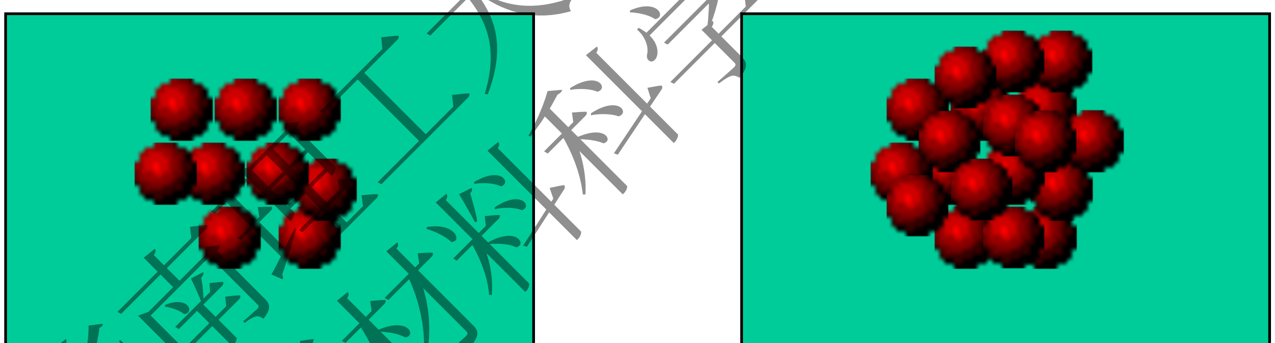
An image of a bronze object. This Canteen (bian hu) China, Warring States period, circa 3rd century BCE (bronze inlaid with silver). (*Courtesy of Freer Gallery of Art, Smithsonian Institution, Washington, D.C.*)

(a) (b)

(a) Aluminum alloy wheels for automotives, (b) optical fibers for communication.

Formation of Nucleii

- Molecules are always bumping into each other – sometimes they stick
- At lower kinetic energies more stick



Why Does Anything Solidify?

- The energy of the crystal structure is less than that of the liquid
- The difference is the volume free energy ΔG_v
- As the solid grows in size, the magnitude of the total volume free energy increases…
- But it is a negative value

But…

- When solids form in a liquid there is an interface created
- The surface free energy, σ, is associated with this interface
- As the solid grows, the total surface free energy increases, and….
- It's a positive value

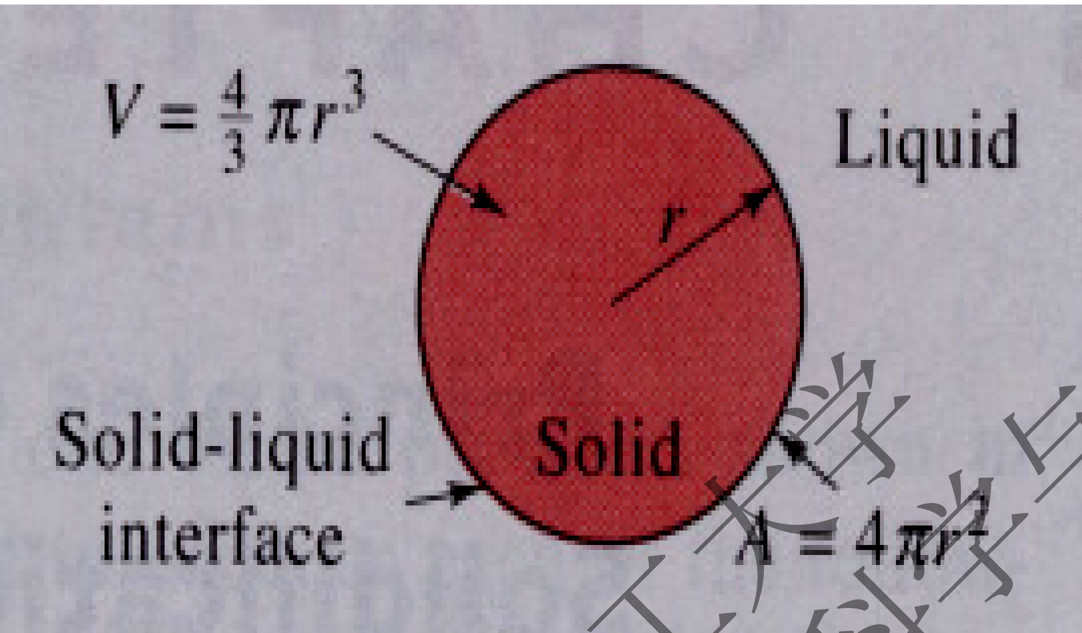
That means…

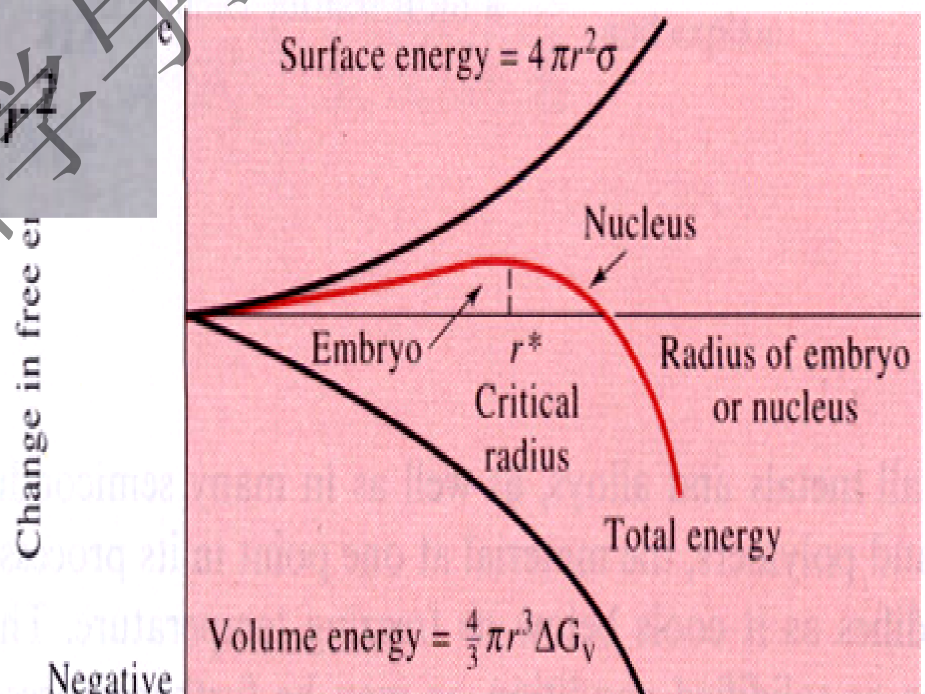
- The total change in free energy for the system is the sum of the two factors.
- $\Delta G = 4/3\ \pi\ r^3 \Delta G_v + 4\pi r^2 \sigma$
- The volume free energy goes up as the cube of the radius
- The surface free energy goes up as the square of the radius

Nucleation

- Nucleation - The physical process by which a new phase is produced in a material.
- 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.
- Undercooling - The temperature to which the liquid metal must cool below the equilibrium freezing temperature before nucleation occurs.
- Homogeneous nucleation - Formation of a critically sized solid from the liquid by the clustering together of a large number of atoms at a high undercooling (without an external interface).
- Heterogeneous nucleation - Formation of a critically sized solid from the liquid on an impurity surface.

Formation of Nucleii





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

Solidification of Metals

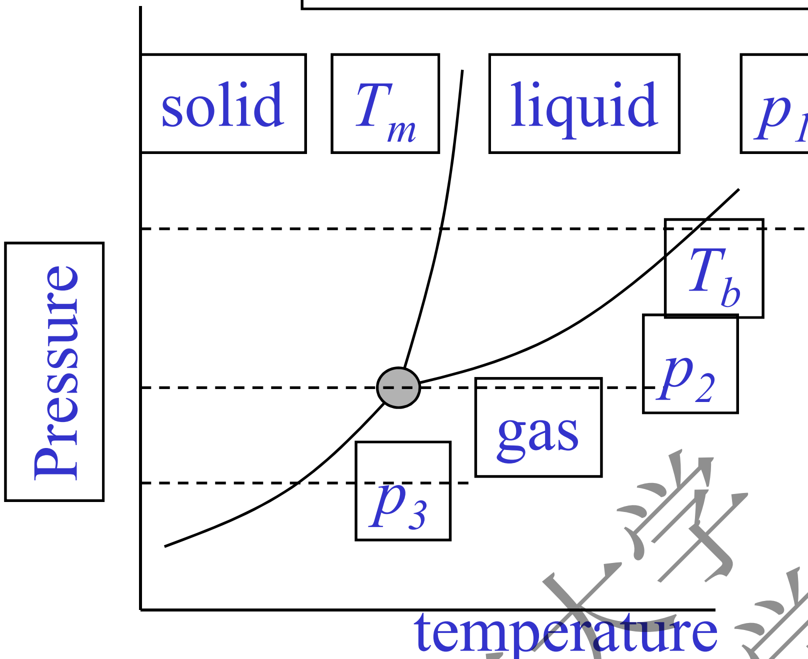
• Most commercial metal objects are frozen from a liquid phase into their final shapes (casting) or immediate forms, called ingots. Other methods: hot pressing, sintering. Thus, the transformation process of liquid to solid (solidification) is important in determining the microstructure of the solid

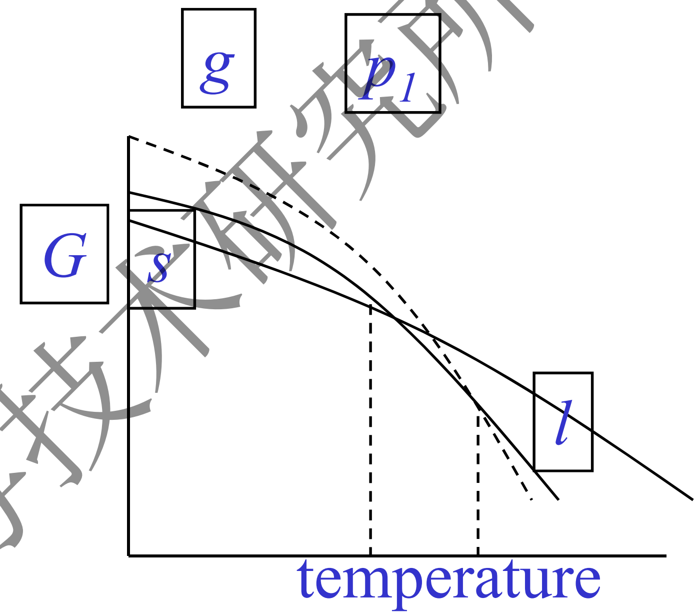
=> affect the properties of the solid.

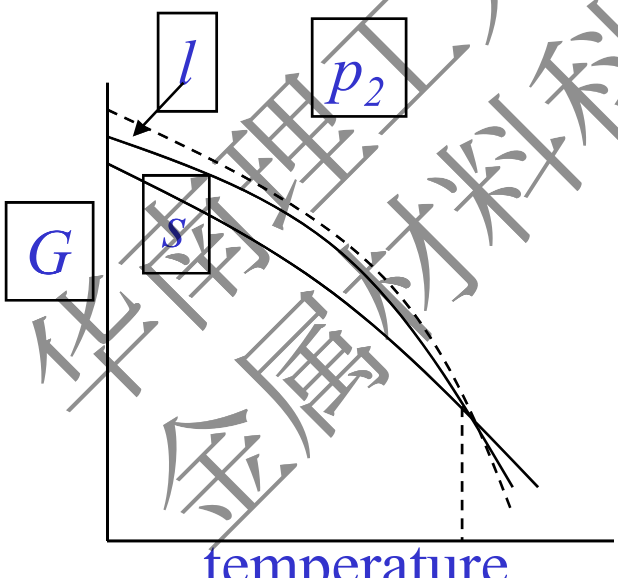
▲ The liquid phase: most of liquid metal alloys are homogeneous liquid phase. The characteristics of liquid metals: (1) no long range order, (2) average separation between atoms is close to solid (small volume changes upon solidification); could be considered as solid with large amount of defects (vacancies); some consider the liquid to be a combo of stable clusters of atoms (short range order is similar to solid), (3) diffusion in liquid is very fast compared to solid, (4) most liquid metals have similar properties (coordination number, electrical and thermal conductivity, etc.); defects in more important in determination of the properties in liquid metal.

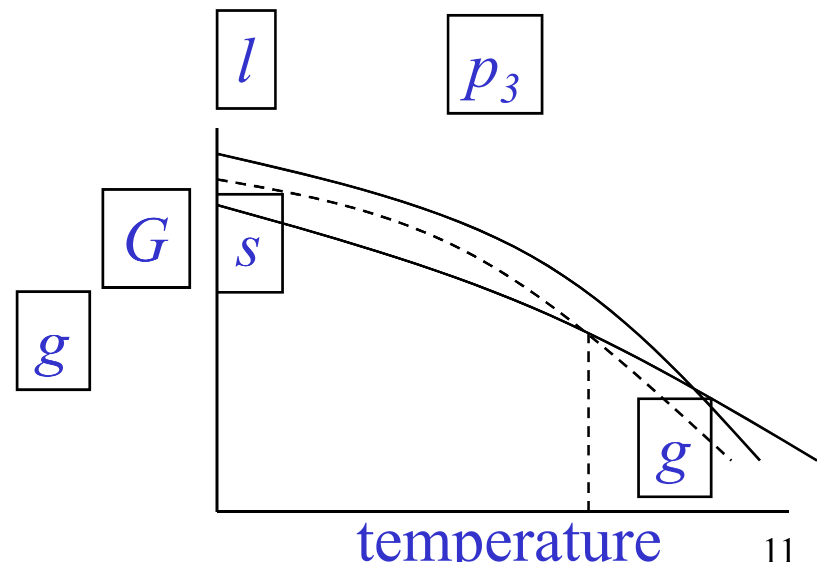
Solidification of Metals

A case of simple liquid to simple solid:



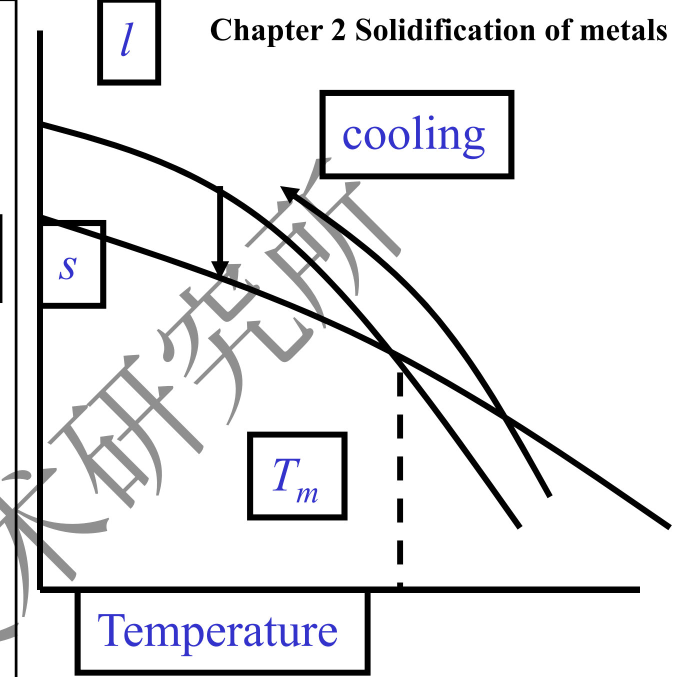


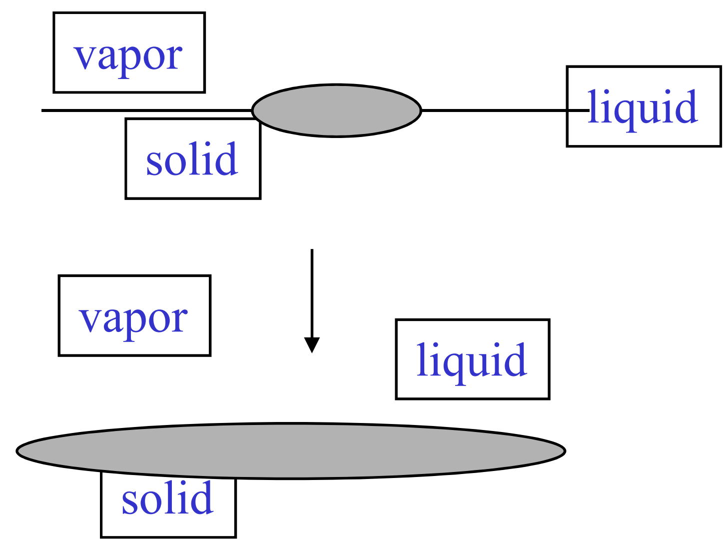




- The solidification or melting of metals occurs by nucleation and growth. The process requires time to achieve especially for solid to form=> if the nucleation is not started yet, but the temperature continue to cool => supercooling => the driving force for nucleation is larger and larger!
- While for heating, the superheating is typically small.
- Typical melting started at the surface and usually $\gamma_{gs} > \gamma_{gl} + \gamma_{ls}$

=> The surface energy could aid nucleation





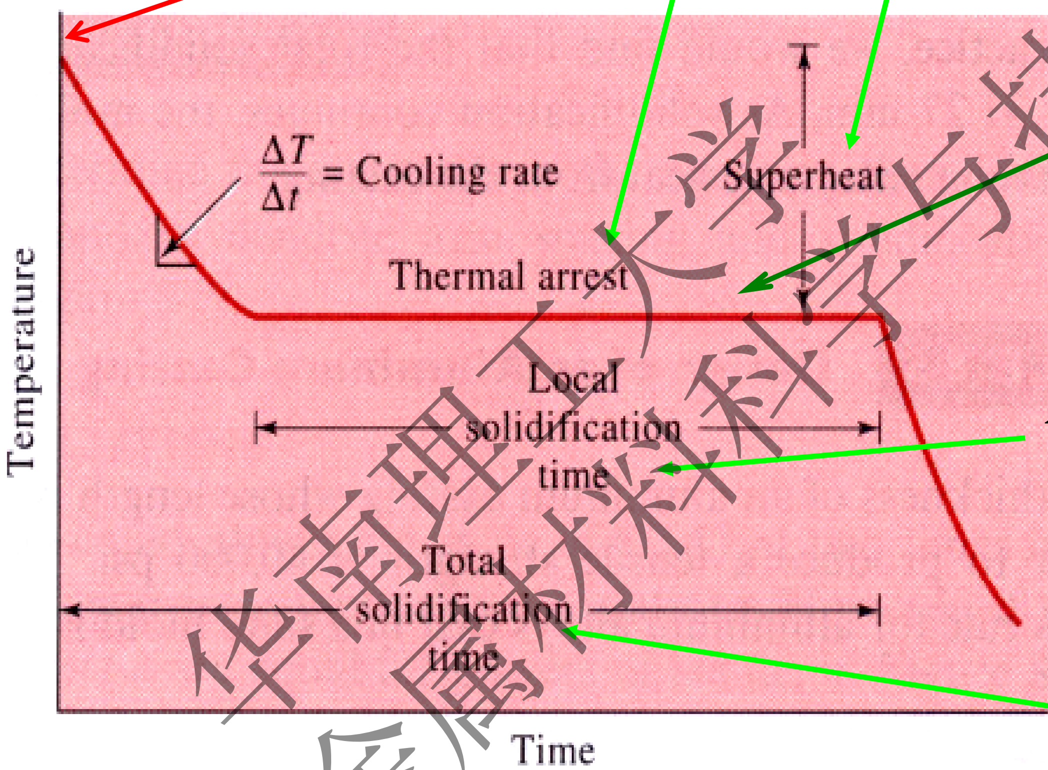
Cooling Curves

constant temperature region on the cooling curve

Pouring Temperature

the difference between the pouring temperature and the freezing temperature

The latent heat keeps temperature unchanged

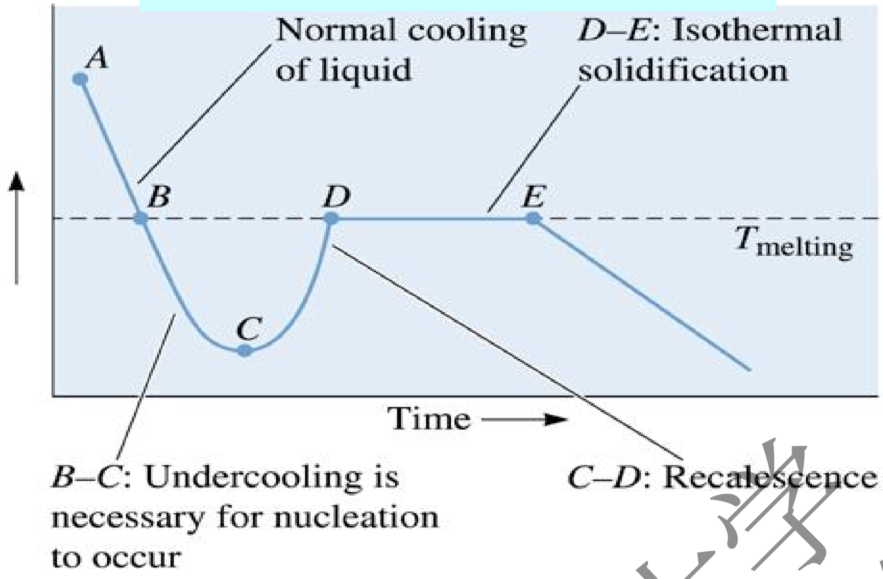


time to remove the latent heat

the time it takes to solidify, from the time you pour the mold

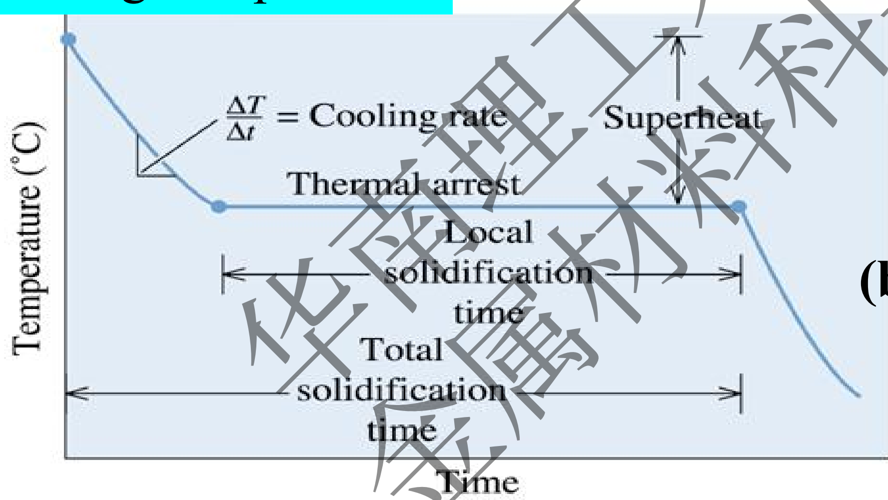
FIGURE 8-9 Cooling curve for the solidification of a pure material.

The latent heat keeps temperature unchanged



(a)

Pouring Temperature

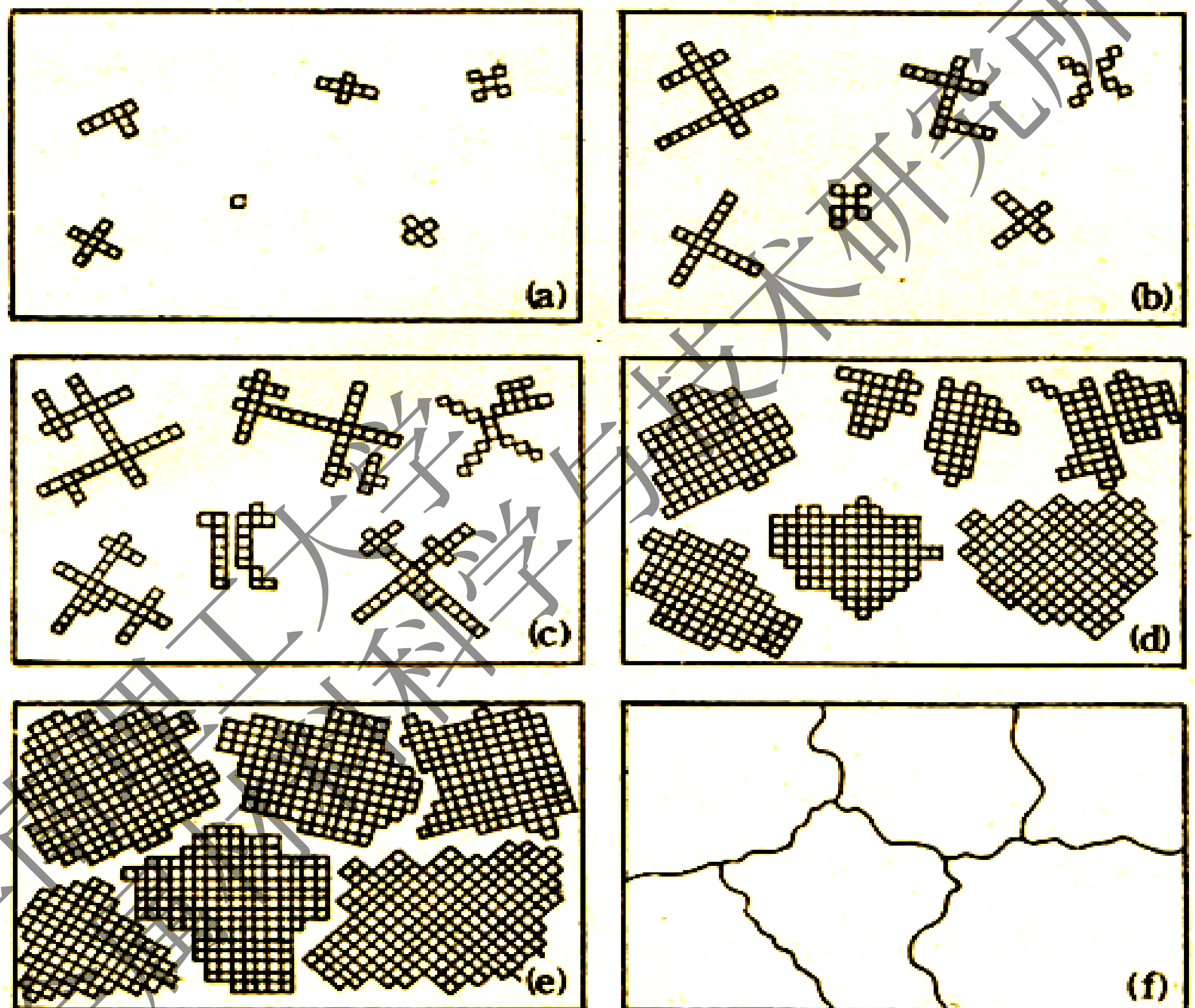


(b)

(a) Cooling curve for a pure metal that has not been well inoculated. Liquid cools as specific heat is removed (betweens 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*). Metal continues to solidify at a constant temperature (T melting). At point *E*, solidification is complete. Solid casting continues to cool from the 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

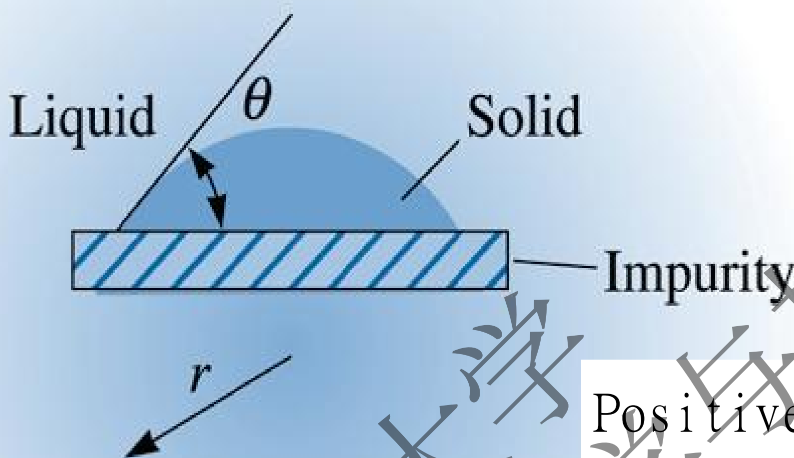
Nucleation and Growth



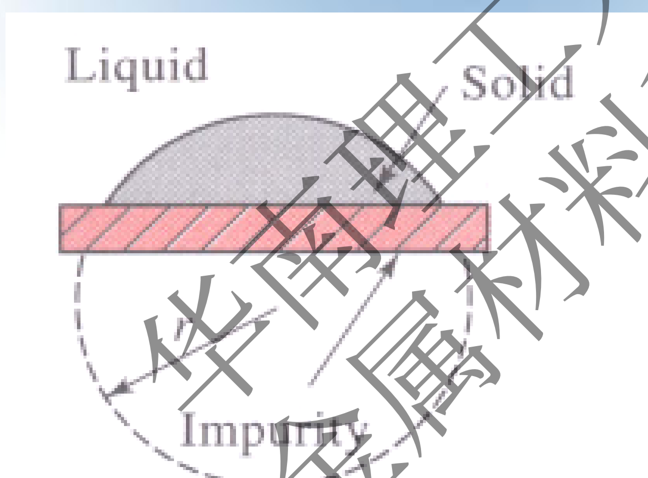
第 1.6 圖　熔融金屬的凝固過程（W. Rosenhein）

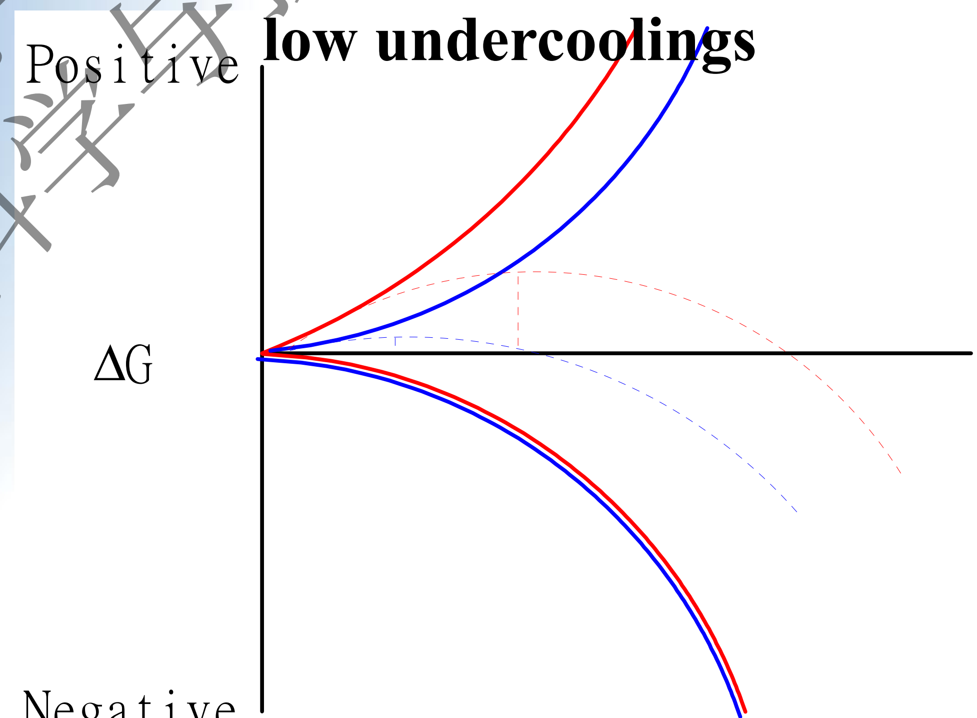
Nucleation

Heterogeneous Nucleation



A solid forming on an impurity can assumed the critical radius with a smaller increase in the surface energy. Thus, heterogeneous nucleation can occur with relatively low undercoolings





Formation of Nucleii

Heterogeneous Nucleation

Grain Size Strengthening: intentionally introduce impurity particles into the liquid, and these tiny particles serve as sites for heterogeneous nucleation. Such particle are called grain refinement.

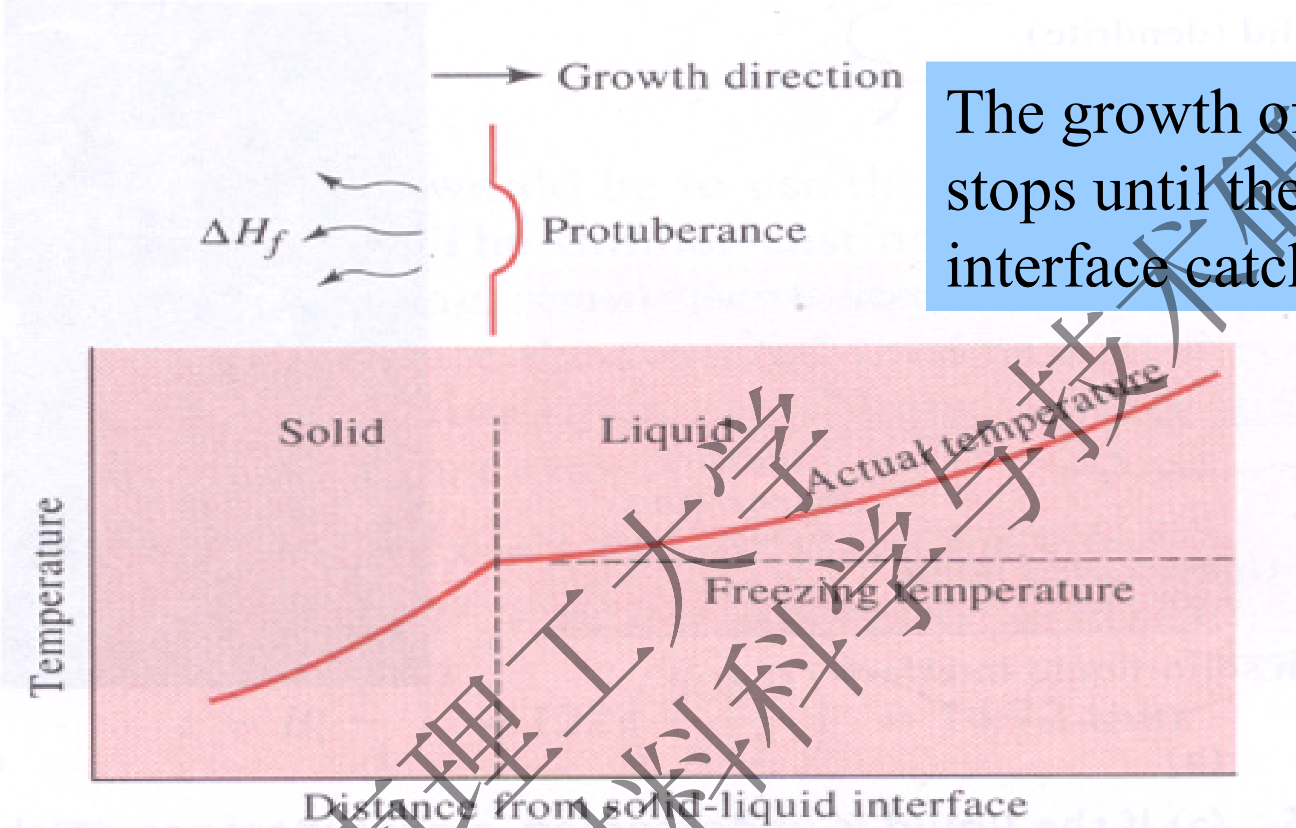
Glasses: for rapid cooling rates, there may be insufficient time for nuclei to form and grow. when this happens, an amorphous or glass solid forms.

Metallic Glasses: cooling rapid of 10^6 °C / s or faster.

- Specific heat - The heat required to change the temperature of a unit weight of the material one degree.
- Solidification front - Interface between a solid and liquid.

Growth

Planar Growth : cools under equilibrium conditions



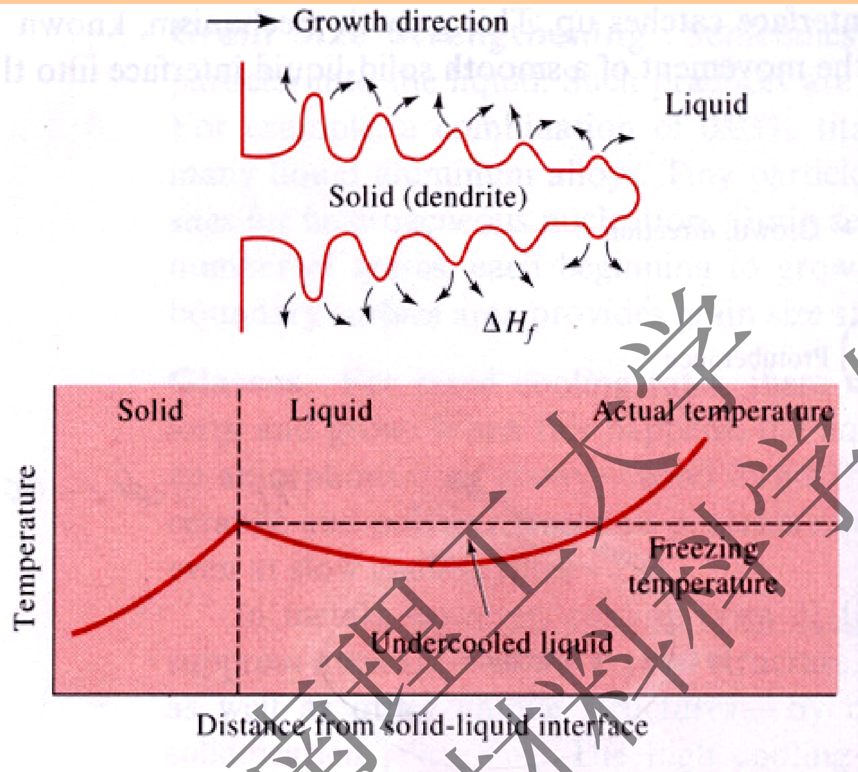
The growth of the protuberance stops until the remainder of the interface catches up.

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 planer interface. Latent heat is removed from the interface through the solid

Growth

Dendritic Growth : under-cool processing

$$\textit{Dendritic fraction} = f = \frac{c\Delta T}{\Delta H_f}, \text{ where } c \text{ is the specific heat of the liquid.}$$



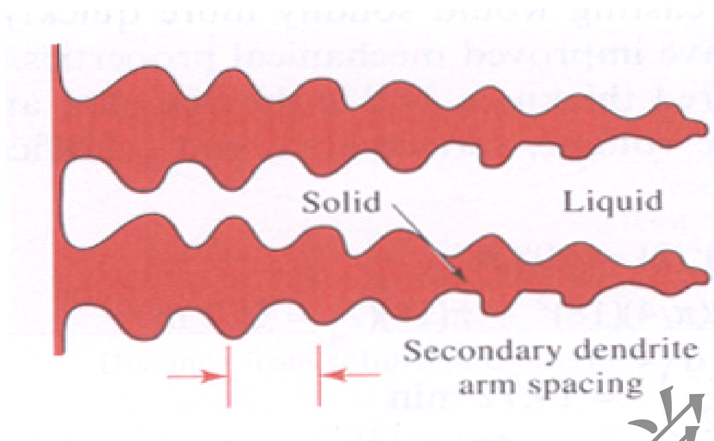
(a)

(b)

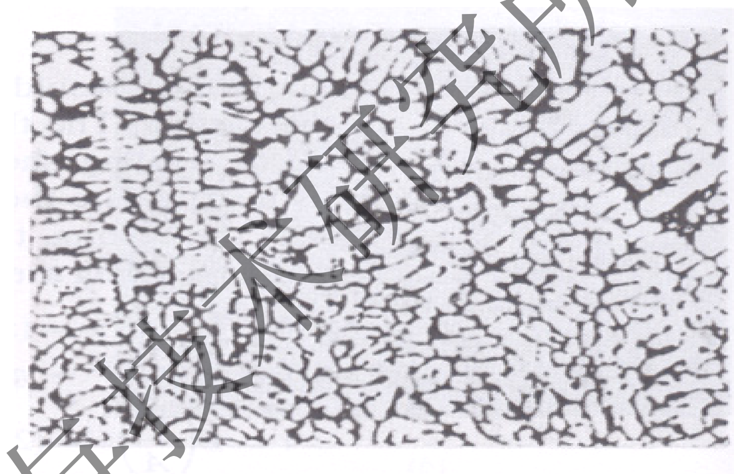
(a) If the liquid is undercooled, a protuberance on the solid-liquid interface can grow rapidly as a dendrite. The latent heat of fusion is removed by raising the temperature of the liquid back to the freezing temperature. (b) Scanning electron micrograph of dendrites in steel (x 15)

Solidification Time and Dendrite Size

Dendritic Growth : under-cool processing



(a)



(b)

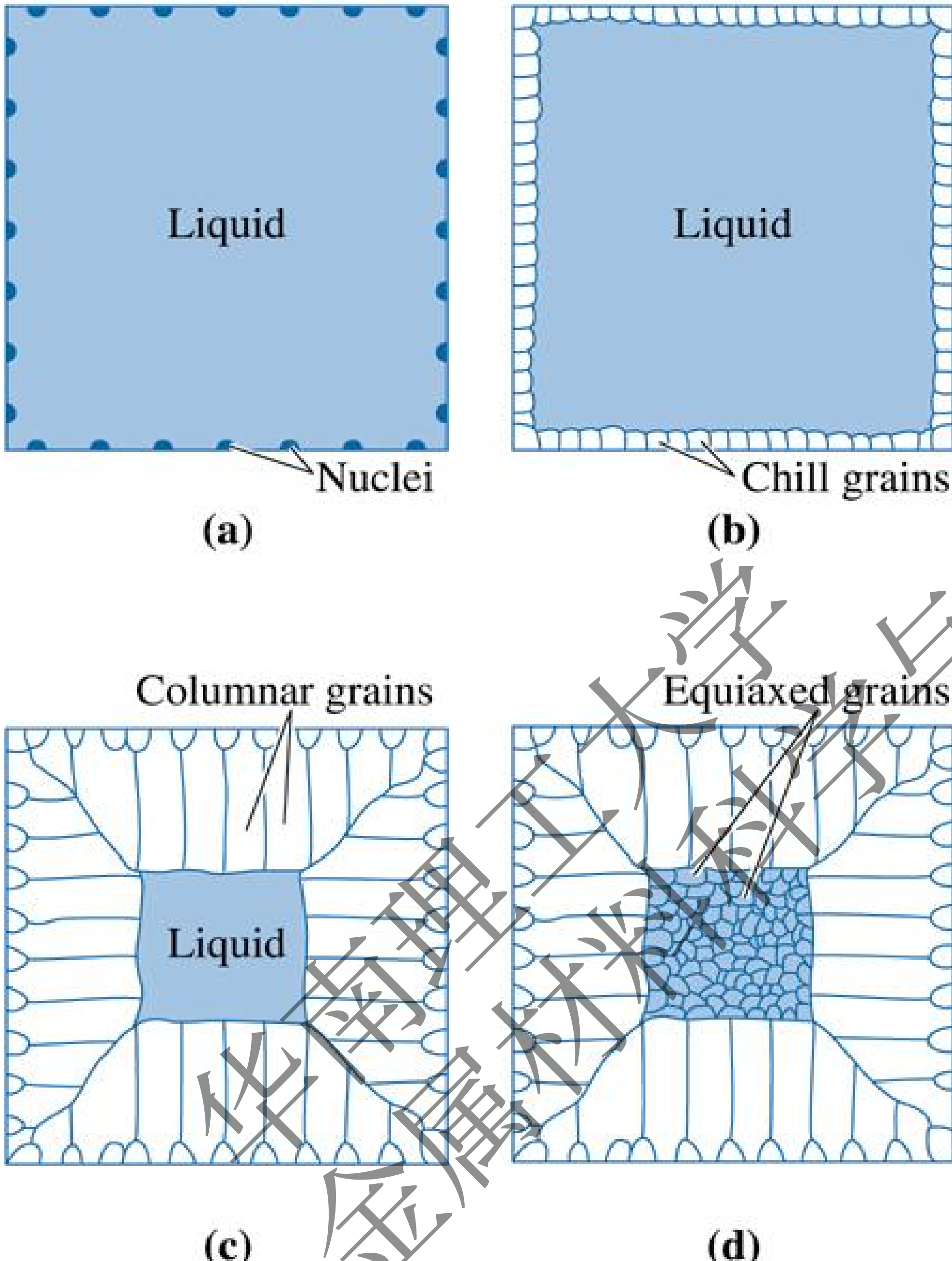
Second Dendrite arm spacing (SDAS) $= kt_s^m$,

where m k is constant, t_s is the time required to solidify completely .

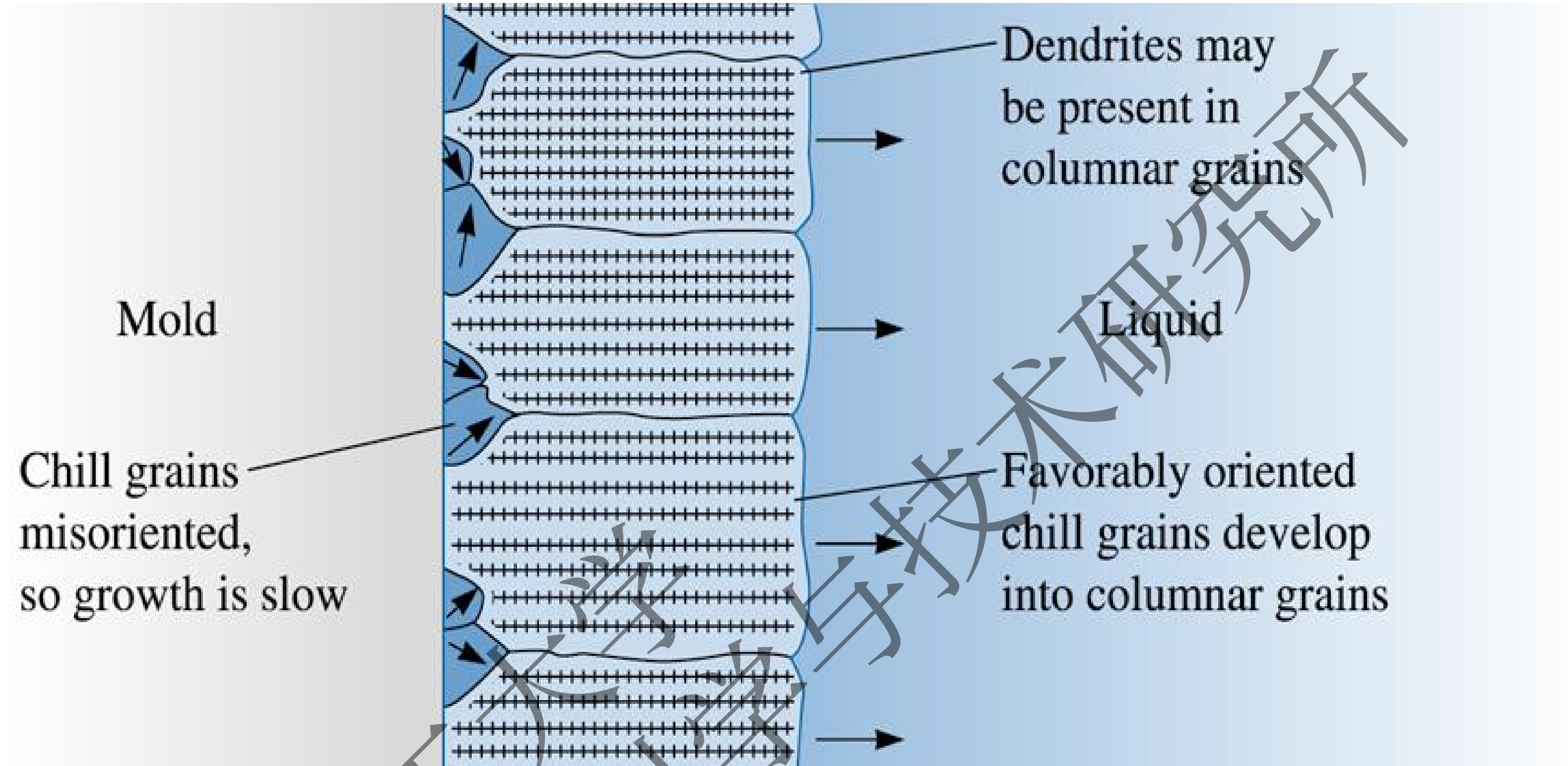
- Chvorinov’s rule - The solidification time of a casting is directly proportional to the square of the volume-to-surface area ratio of the casting.
- Mold constant (B) - A characteristic constant in Chvorinov’s rule.
- Secondary dendrite arm spacing (SDAS) - The distance between the centers of two adjacent secondary dendrite arms.

Cast Structure

- Nucleation begins
- Chill Zone - A region of small, randomly oriented grains that forms at the surface of a casting as a result of heterogeneous nucleation.
- 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.
  - There may be dendrites in the columnar zone
  - Grains grow in preferred directions
- Equiaxed Zone - A region of randomly oriented grains in the center of a casting produced as a result of widespread nucleation.



Development of the ingot structure of a casting during solidification:
(a) Nucleation begins,
(b) the chill zone forms,
(c) preferred growth produces the columnar zone3, and
(d) additional nucleation creates the equiaxed zone



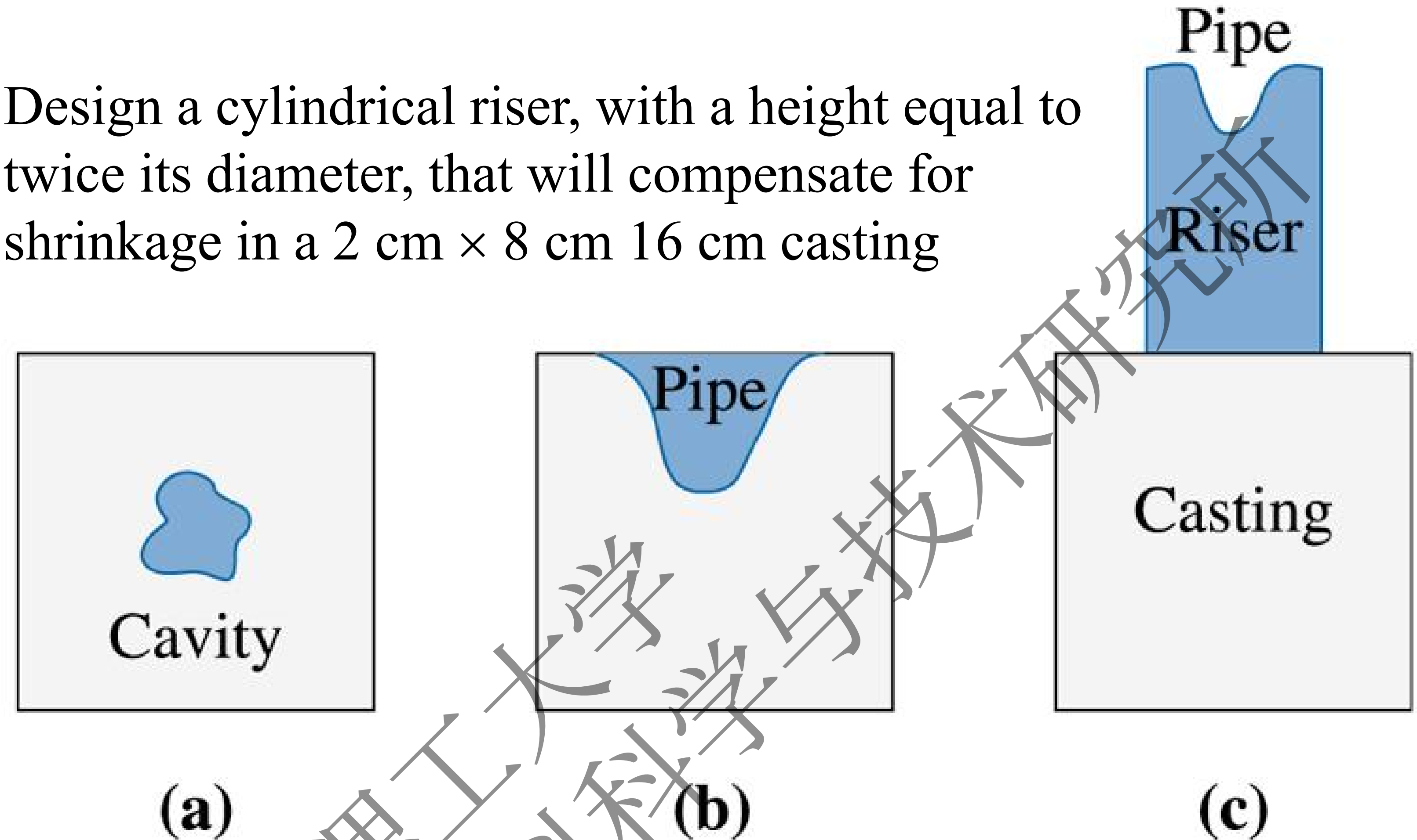
Competitive growth of the grains in the chill zone results in only those grains with favorable orientations developing into columnar grains

Solidification Defects

- Shrinkage Contraction of a casting during solidification.
  - Cavities, Pipes, Control with a riser
- 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.
  - Gas may be dissolved in the melt, then trapped in the solid
- Interdendritic Shrinkage - Small, frequently isolated pores between the dendrite arms formed by the shrinkage that accompanies solidification.

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

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



Several types of macroshrinkage can occur, including cavities and pipes.

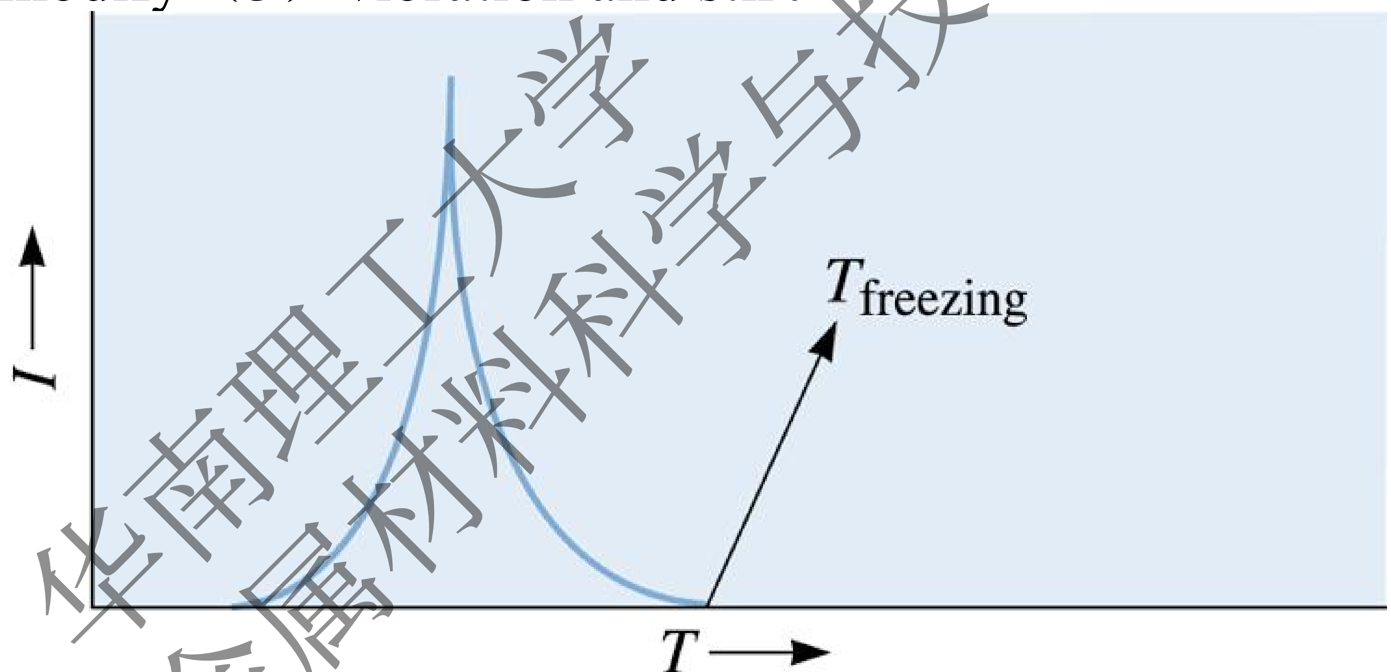
Risers can be used to help compensate for shrinkage

How to get the fine grain size

（1）△T↑:

- T—control the △G and D（diffusion）
- ◆ △T=0，△G=0
- ◆ as V_{cool}↑， △T↑， △G↑， but D↓（maximum）， N↑↑,G↑,fine grain size。
- ◆ as △T↑↑↑，N →0，G→0——amorphous alloy。

（2）modify（3）vibration and stir。



Rate of nucleation *(I)* as a function of temperature of the liquid *(T)*

Grain Sizes

$$N = 2^{n-1}$$

- N: Number of grains
- n: Grain size

Large Grains (Low strength, hardness, and ductility): zinc on the surface of galvanized sheet steels

Small Grains: car bodies, Appliances, and Kitchen utensils

TABLE 1.1

ASTM No.	Grains/mm^2	Grains/mm^3
–3	1	0.7
–2	2	2
–1	4	5.6
0	8	16
1	16	45
2	32	128
3	64	360
4	128	1,020
5	256	2,900
6	512	8,200
7	1,024	23,000
8	2,048	65,000
9	4,096	185,000
10	8,200	520,000
11	16,400	1,500,000
12	32,800	4,200,000