Ch3

Mechanism and rate of solidification of metals and alloys
Solidification of metals and alloys

Introduction

• The solidification of metals and their alloys is an important industrial process.
• Not only do structural alloys start with the casting of ingots for processing into reinforcing bars or structural shapes, but when a metal is welded a small portion of metal near the weld melts and resolidifies.
• It also serves as a model to represent first order phase transformations in general.
Solidification of metals and alloys

METAL CASTING
QUICKEST
LEAST EXPENSIVE
ROUTE
TO A
NEAR NET SHAPE PRODUCT
Solidification of metals and alloys

Starting work material is either a liquid or is in a highly plastic condition, and a part is created through solidification of the material.

- Solidification processes can be classified according to engineering material processed:
  - Metals
  - Ceramics, specifically glasses
  - Polymers and polymer matrix composites (PMCs)
Solidification of metals and alloys

- Metal casting
  - Expandable-mold Casting
  - Permanent-mold Casting
  - Permanent-Mold Casting
    - Variations of Permanent-Mold Casting
      - Die Casting
      - Centrifugal Casting
  - Other molding
    - Extrusion
    - Injection Molding
    - Special Molding for PMC
Simple Diffusion-dependent PT

Free Energy, $G$

Temperature, $T$

$\Delta G_f$

Solid

Liquid

undercooling $\Delta T$

$T_f$
Simple Diffusion-dependent PT

- Example: solidification of a pure element

Solidification is undoubtedly the most important processing route for metals and alloys. Consider a pure metal. At the fusion temperature $T_f$, $\Delta G = 0$ so that:

$$\Delta G_f = \Delta H_f - T_f \Delta S_f = 0 \text{ or } \Delta H_f = T_f \Delta S_f$$

where $\Delta H_f$ is the latent heat of fusion and $\Delta S_f > 0$ for melting.

For any temperature other than $T_f$,

$$\Delta G = \Delta H - T \Delta S = \Delta H_f - T \Delta S_f = \Delta S_f (T_f - T) = \Delta S_f \Delta T$$

where $\Delta T$ is under cooling

The driving force is therefore proportional to the under cooling because the latent heat and the entropy of fusion do not vary much with temperature.
Solidification of metals and alloys

Nucleation

The small clusters of crystallized solid forming from a liquid metal. These arise due to the random motion of atoms within the liquid.

- **Homogeneous Nucleation** – precipitation occurs within a completely homogeneous medium

- **Heterogeneous Nucleation** – precipitation may occur also on the surfaces, which separate different media, e.g. walls of the reactor
Homogeneous Nucleation

By assuming that solid phase nucleates are spherical ‘clusters’ of radius, $r$, one can define the excess of free energy change for a single nucleus, $\Delta G_{(r)}$:

$$\Delta G_{(r)} = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma_{SL}$$

where $\gamma_{SL}$ is the solid/liquid interfacial energy.

The critical radius $r^*$ (defined as the radius at which $\Delta G_{(r)}$ is maximum) is given by:

$$r^* = \frac{-2 \gamma_{SL}}{\Delta G_v} = \frac{-2 \gamma_{SL}}{\Delta H_v \Delta T}$$

The associated energy barrier to homogeneous nucleation, $\Delta G^*$ is:

$$\Delta G^* = \frac{16 \pi \gamma_{SL}^3}{3 \Delta G_v^2} = \frac{16 \pi \gamma_{SL}^3 T_m^2}{\Delta H_v^2 \Delta T^2}$$

Important: the temperature-dependence of these terms are: $r^* \propto 1/\Delta T$ and $\Delta G^* \propto 1/\Delta T^2$

Higher under cooling – easy to form new phase!!
Homogeneous nucleation occurs when there are no special objects inside a phase which can cause nucleation.

- For instance, when a pure liquid metal is slowly cooled below its equilibrium freezing temperature to a sufficient degree, numerous homogeneous nuclei are created by slow-moving atoms bonding together in a crystalline form.
Gibbs Free Energy

- \( G = U - TS \)

- where \( U \) = Internal Energy, \( T \) = Absolute Temperature, and \( S \) = Entropy

- Materials Scientists refer to the difference in \( G \) between the old and new phases as the *driving force* for the phase transformation.

- The release of heat when a metal solidifies indicates that the crystalline phase has a lower Gibbs Free Energy, \( G \), than the liquid.

- At the equilibrium freezing temperature the Gibbs Free Energy of the liquid and the crystalline phase are equal.
Energies Involved in Homogeneous Nucleation

(1) Volume free energy

\[
\frac{4}{3} \Pi r^3 G_v
\]

(2) Surface energy

\[
4 \Pi r^2 \gamma
\]
Critical Radius

\[ \Delta G = \frac{4}{3} \Pi r^3 G_v - 4 \Pi r^2 \gamma \]

To find the minimum

\[ \frac{d(\Delta G)}{dr} = 0 \]

\[ r^* = -\frac{2\gamma}{\Delta G} \]
Energies Involved in Homogeneous Nucleation

\[ \Delta G_s = \text{surface free-energy change} = 4\pi r^2 \gamma \]

\[ \Delta G_T = \text{total free-energy change} \]

\[ \Delta G_r^* = \text{retarding energy} \]

\[ \Delta G_v = \text{volume free-energy change} = \frac{3}{4} \pi r^3 \Delta G_v \]
Heterogeneous Nucleation

- Heterogeneous nucleation occurs when there are special objects inside a phase which can cause nucleation.
Heterogeneous Nucleation

- Let us consider that a solid cluster forms on a mould wall. In this case, one can define the excess of free energy change for a nucleus, $\Delta G_{(r)}$ as follows:

$$
\Delta G_{(r)} = V \Delta G_v + A_{SL} \gamma_{SL} + A_{SM} \gamma_{SM} - A_{SM} \gamma_{ML}
$$

Note that as compared to homogeneous case two new interface should be taken into account i.e. solid-mould and liquid mould.

- It can be shown that the critical radius $r^*_{\text{het}}$ for heterogeneous nucleation is equal to $r^*_{\text{hom}}$:

$$
r^*_{\text{het}} = \frac{-2 \gamma_{SL}}{\Delta G_v} = r^*_{\text{hom}}
$$

- And:

$$
\Delta G_{\text{het}}^* = \frac{16 \pi \gamma_{SL}^3}{3 \Delta G_v^2} S(\theta) = \Delta G_{\text{hom}}^* S(\theta)
$$

where $S(\theta)$ is a geometrical factor and $\theta$ is a wetting angle:

$$
S(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4}
$$

Heterogeneous Nucleation is Faster than Homogeneous Process!!
Critical Radius of Nuclei VS. Undercooling

Nuclei are stable in this region.

Embryos form in this region and may redissolve.
The overall nucleation rate is a product of two opposite working factors:
- the driving force for solidification increases with T decrease;
- while the diffusion that is responsible for the clustering process decrease with T decrease.

These explain the “knee-shaped” nature of the transformation curve with maximum at some value below $T_f$. 
Overall Transformation Rate-Temperature Diagram

- The overall transformation rate is a product of two factors:
  - nucleation;
  - growth, which is thermally activated process, typically described by Arrhenius function.

PT rate achieves maximum at some T below \( T_f \)!!
A pure metal solidifies at a constant temperature equal to its freezing point (same as melting point).

Figure 10.4 - Cooling curve for a pure metal during casting
Solidification of Pure Metals

- Due to chilling action of mold wall, a thin skin of solid metal is formed at the interface immediately after pouring.
- Skin thickness increases to form a shell around the molten metal as solidification progresses.
- Rate of freezing depends on heat transfer into mold, as well as thermal properties of the metal.
Most alloys freeze over a temperature range rather than at a single temperature

- (a) Phase diagram for a copper-nickel alloy system
- (b) associated cooling curve for a 50%Ni-50%Cu composition during casting
Solidification Time

- Solidification takes time
- Total solidification time $TST = \text{time required for casting to solidify after pouring}$
- $TST$ depends on size and shape of casting by relationship known as Chvorinov's Rule

Chvorinov's Rule

$$TST = C_m \left( \frac{V}{A} \right)^n$$

where $TST = \text{total solidification time}$; $V = \text{volume of the casting}$; $A = \text{surface area of casting}$; $n = \text{exponent usually taken to have a value} = 2$; and $C_m$ is $\text{mold constant}$
Mold Constant in Chvorinov's Rule

- $C_m$ depends on mold material, thermal properties of casting metal, and pouring temperature relative to melting point.
- Value of $C_m$ for a given casting operation can be based on experimental data from previous operations carried out using same mold material, metal, and pouring temperature, even though the shape of the part may be quite different.
Solidification of Pure Metals

- A thin skin of solid metal is formed at the cold mold wall immediately after pouring.
- Skin thickness increases to form a shell around the molten metal as solidification progresses.
- Rate of freezing depends on heat transfer into mold, as well as thermal properties of the metal.

Randomly oriented grains of small size near the mold wall, and large columnar grains oriented toward the center of the casting (Dendritic growth).
Dendrite Growth
Characteristic grain structure in an alloy casting, showing segregation of alloying components in center of casting.
Shrinkage of a cylindrical casting during solidification and cooling: (0) starting level of molten metal immediately after pouring; (1) reduction in level caused by liquid contraction during cooling (dimensional reductions are exaggerated for clarity in sketches)
(2) reduction in height and formation of shrinkage cavity caused by solidification shrinkage; (3) further reduction in height and diameter due to thermal contraction during cooling of the solid metal (dimensional reductions are exaggerated for clarity in our sketches)
Solidification Shrinkage

- Occurs in nearly all metals because the solid phase has a higher density than the liquid phase.
- Thus, solidification causes a reduction in volume per unit weight of metal.
- Exception: cast iron with high C content
  - Graphitization during final stages of freezing causes expansion that counteracts volumetric decrease associated with phase change.
Shrinkage Cavity

Depression in surface or internal void caused by solidification shrinkage that restricts amount of molten metal available in last region to freeze

- Some common defects in castings: (d) shrinkage cavity
Pin Holes

Formation of many small gas cavities at or slightly below surface of casting

- Common defects in sand castings: (b) pin holes
Directional Solidification

- To minimize damaging effects of shrinkage, it is desirable for regions of the casting most distant from the liquid metal supply to freeze first and for solidification to progress from these remote regions toward the riser(s)
  - Thus, molten metal is continually available from risers to prevent shrinkage voids
  - The term *directional solidification* describes this aspect of freezing and methods by which it is controlled
Rapid Solidification \((10^5 \text{ K/s})\)

Rapidly cool or quench to produce amorphous or glassy structure (metallic glass)
Rapid Solidification

- Cooling Rate $>10^4$ - $10^7$ °K/s
- By processes such as: Atomization, melt spinning, roller-quenching or plasma spray or laser or electron beam surface treatment
- Non-eqm phase, no thermo. Restrictions, exceed solubility limits, melt solidifies without any chem changes.
- Crystalline or amorphous (improved mech. properties)
- Microsegregation-free structures
- Using powder metallurgy to process the materials.
Micro-segregation

(a) Schematic diagram of inclusion formation during dendritic growth: (a) inclusions being pushed; (b) inclusions being entrapped.
Macro-segregation

Macrosegregation refers to variations in composition that occur in alloy castings or ingots and range in scale from several millimeters to centimeters or even meters. These compositional variations have a detrimental impact on the subsequent processing behavior and properties of cast materials and can lead to rejection of cast components or processed products. Macrosegregation is present in virtually all casting processes, including continuous, ingot, and shape casting of steel and aluminum alloys, iron casting, casting of single-crystal superalloys, semisolid casting, and even growth of semiconductor crystals. Because of the low diffusivity of the solutes in the solid state and the large distances involved, macrosegregation cannot be mitigated through processing of the casting after solidification is complete.
Solidification Shrinkage Types

Shrinkage porosity can appear within a casting in a number of ways depending upon the solidification temperature range (T_L - T_S) and the effectiveness of risering. The type of shrinkage observed in castings can be broadly separated into two classes, macroshrinkage and microshrinkage. Macroshrinkage defects can be seen by the unaided eye and microshrinkage defects require a microscope to observe. There are two types of shrinkage within each class, shrinkage which can be observed externally on the casting surface and shrinkage which is observed internally after sectioning. Schematic examples of each of these defects is shown below:
30 mil.tons Al

Molten Steel

Ladle

Tundish

Submerged Entry Nozzle

Mold

Meniscus

Liquid Pool

Support roll

Spray Cooling

Solidifying Shell

Metalurgical Length

Torch Cutoff Point

Strand

Non-ferrous alloy

Steel

1000 mil.tons Fe

Slab
Process:

safety
productivity

Product:

correct shape
no cracks
no porosity
desired composition
desired structure

PROCESS SCHEME
Simulation of macrosegregation formation in a large steel casting, showing liquid velocity vectors during solidification (left) and final carbon macrosegregation pattern (right).
Semi-Continuous casting of Aluminum Alloys, Free machining brass

![Diagram of semi-continuous casting process]

- Tundish
- Water Cooled Mold
- Water Spray
- Liquid Sump
- Solid Casting
- Base Block