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Advanced Solidification

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: Thermal gradient dominant



Solidification of single phase alloy: Solute redistribution dominant

a) Constitutional Supercooling (C.S.)

Planar \rightarrow Cellular growth \rightarrow cellular dendritic growth \rightarrow Free dendritic growth

Thin zone formation by C.S. at the sol. Interface Dome type tip / (surrounding) hexagonal array $T\downarrow \rightarrow$ Increase of C.S. zone Pyramid shape of cell tip / Square array of branches / Growth direction change toward Dendrite growth direction formed by releasing the latent heat from the growing crystal toward the supercooled liquid Dendrite growth direction/ Branched rod-type dendrite

→ "Nucleation of new crystal in liquid" which is at a higher temp. than the interface at which growth is taking place.

b) Segregation

- : normal segregation, grain boundary segregation, cellular segregation, dendritic segregation, inversegregation, coring and intercrystalline segregation, gravity segregation
- : undesiable ~ deleterious effects on mechanical properties
- \rightarrow subsequent homogenization heat treatment, but diffusion in the solid far to slow
- \rightarrow good control of the solidification process

5.10. Types of Segregation

- * Last discussion on "solute redistribution in single phase alloys"
 - → "Various types of segregation"
- * Segregation: result of rejection of solute at the interface during solidification The difference depends on the rejection direction / distance / solute motion.
- * Segregation

(a) Macrosegregation : Large area composition changes over distances comparable to the size of the specimen.

Four important factors that can lead to macrosegregation

- a) Shrinkage due to solidification and thermal contraction.
- b) Density differences in the interdendritic liquid.
- c) Density differences between the solid and liquid.
- d) Convection currents driven by temperature-induced density differences in the liquid.

(b) Microsegregation : in secondary dendritic arms occur on the scale of the secondary dendrite arm spacing.

1) Normal segregation

- : motion of solute parallel to the direction of solidification
- The form of curve depends on ① equilibrium distribution coefficient k₀, ② the rate
- of R of solidification (or the time-distance relationship if R is not constant), and
- <u>③ the amount of mixing by fluid motion.</u>
- → Actual segregation: depends very much on "sample geometry"

influences both ① solidification rate ② amount of convection

→ difficult to state general rule for predicting the result



→ Oversimplification, because the form of the interface, which depends on the extent of constitutional supercooling, has an important influence on the mixing process.



Fig. 5.42. Extreme cases of normal segregation

2) Grain boundary segregation during the process of solidification

: This is not to be confused with equilibrium segregation at GB.



Fig. 5.43. Conditions for grain boundary segregation

Whose mobility would be high between special and random boundaries? By considering grain boundary structure, (Mobility depending on GB structures)

High energy G.B. \rightarrow relatively open G.B. structure \rightarrow High mobility

Low energy G.B. \rightarrow closed (or denser) G.B. structure \rightarrow Low mobility

^{But,} Ideal \iff Real

2) The other special boundaries are usually more mobile than random high-angle boundary. Why?

If the metal were "perfectly" pure the random boundaries would have the higher mobility.

⇒ Due to differences in the interactions of alloy elements or impurities with different boundaries



Migration rate of special and random boundaries at 300 °C in zone-refined lead alloyed with tin under equal driving forces



<Increasing GB enrichment with decreasing solid solubility in a range of system>

* Solute drag effect

In general,

G_b (grain boundary E) and mobility of pure metal decreases on alloying.

~Impurities tend to stay at the GB.

<u>Generally, ΔG_{b} , tendency of seg-</u> regation, increases as the matrix solubility decreases.

$$X_{b} = X_{0} \exp \frac{\Delta G_{b}}{RT}$$

X_b/X₀: GB enrichment ratio

- Decreases as temp. increases, i.e., the solute "evaporates" into the matrix

Low T or $\Delta \mathbf{G}_{\mathbf{b}} \widehat{\square} \mathbf{X}_{\mathbf{b}} \widehat{\square}$ Mobility of G.B. \square

 \rightarrow Alloying elements affects mobility of G.B.

 X_0 : matrix solute concentration/ X_b : boundary solute concentration

- ΔG_b : free energy reduced when one mole of solute is moved to GB from matrix.
 - \rightarrow The high mobility of special boundaries can possibly be attributed to a low solute drag on account of the <u>relatively more close-packed structure of the special boundaries</u>.

3) Cellular segregation

: after cellular solidification, at the "terminal transient" region

* Temp. and solute distributions associated with cellular solidification.



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1) Note that solute enrichment in the liquid between the cells, and coring in the cells with eutectic in the cell walls.

- Т T_{tir} $T_{\rm E}$ x $X_{\rm S}$ (along BB') $X_{\rm E}$ Xmax Heat flow Isotherm stance on B B ····· Cell $X_{\rm E}$ $\frac{X_0}{k}$ $X_{\rm L}$ (along AA') X_0
- 2) Tips of the cells grow into the hottest liquid and therefore contain the least solute.
- 3) Even if $X_0 << X_{max}$ Solute file up \rightarrow eutectic solidification \rightarrow formation of 2nd phases at the cell wall
- Segregation deceases as a result of diffusion

 during cooling down after solidification
 any subsequent annealing process
 - → but, <u>"dislocation" associated with the solute</u> <u>at the cell walls</u> may tend to stabilize it and limit the homogenizing effect of annealing.

: Almost all work on micro-segregation in alloys has been on cellular-dendritic structure



Fig. 5.44. Distribution of Cu in an Al-4.5% Cu alloy

Cu segregation : light contrast in microradiograph most concentrated close to the plates Fig. 5.45. Segregation in Al-Cu alloy

used Biloni's epitaxial film technique to show the segregation in Al-Cu alloys

Microstructure of as-cast CrFeCoNi-Cu HEA

Alloy fabrication: arc melting \Rightarrow suction casting into 6 mm x 3 mm x 50 mm



Simultaneous study on the two fcc phases under the same irradiation condition

: Almost all work on micro-segregation in alloys has been on cellular-dendritic structure

Quantitative work on the actual distribution of solute has been carried out using electron microprobe technique, with which they were able to establish solute "<u>iso-concentration lines</u>", it is apparent that the plate-like structure is in this case built up of a main stem and coalesced branches. \rightarrow The <u>extremely complicated geometry</u> of the cellular structure makes it very difficult to form realistic theoretical predictions with which to compare the experimental results. \rightarrow "Phase field modeling"



Fig. 5.46. Quantitative results on distribution of solute in columnar dendritic crystal

: Almost all work on micro-segregation in alloys has been on cellular-dendritic structure

But, <u>Flemings and Brody</u> have shown that good agreement with the electron-probe results can be obtained from <u>calculations</u> <u>based on a very simple model</u> (<u>solidification</u> is regarded as taking place inward from <u>two plane "walls"</u> whose spacing is equal to that of the cell walls.

The calculated distribution using

 $C_s = k_E C_0 (1 - g)^{k_0 - 1}$

is shown in Fig. 5.47 for some Al-Cu alloys. Page 140, g=fraction of solidified liquid

- <u>The speed of solidification does not</u> <u>appear explicitly in this solution</u>, because the cell wall spacing depends upon speed.
- Thus, the distribution of solute is independent of speed if it is plotted in <u>the dimensionless form of</u> <u>Fig.5.47.</u>



Fig. 5.47. Calculated distribution of solute 13 between walls of cellular dendritic structure

: Almost all work on micro-segregation in alloys has been on cellular-dendritic structure

 * Maximum concentration (eutectic composition & independent of the rate of solidification) → compared experimental results with theoretical values based on various assumptions



Fig. 5.48. Comparison between calculated and experimental distributions of solute.

: Almost all work on micro-segregation in alloys has been on cellular-dendritic structure

* Flemings and Poirier have shown that the amount of homogenization during cooling can be predicted with reasonable accuracy if the initial distribution is calculated in the manner discussed above. \rightarrow Fig. 5.49.



Fig. 5.49. Experimental and calculated results for homogenization during cooling.

5) Inverse segregation

: occurs when a solute that is rejected during solidification is present at a <u>higher concentration in regions that solidified earlier</u> than in those that solidified later. (=solute moves in the direction opposite to that of normal segregation)

→ Formation mechanism originally proposed by Scheil.

* Shrinkage that in most alloys accompanies solidification may cause motion of the most "solute enriched" liquid in a direction opposite to that of the general solidification front.



* Left of OP line: completely solidified.

 \rightarrow As the region AA solidify, shrinkage takes place, causing the solute enriched liquid at BB to move toward the left.

Liquid

* The effect is larger than might be expected due to the highly enriched composition of the liquid in the terminal transient condition, i.e. when there is only a small amount remaining in a given region.

* General validity of this theory : <u>inverse segregation</u> <u>does not occur in alloys that expand on solidification</u>.

Fig. 5.50. mechanism of inverse segregation

5) Inverse segregation

- * Quantitative approach of inverse segregation (by Kirkaldy & Youdelis) (Assumption1) No shrinkage void → liquid: compensate completely for the shrinkage (Assumption2) Liquid in the interdendritic region is always of uniform composition.
 & it is always in equilibrium with the solid that has just been deposited on dendrite. However, the dendrites are not of uniform composition, since they formed from a liquid of continuously changing composition.
- * This theory describes an alloy system in which enrichment of the liquid is limited by a eutectic composition; the case considered by Kirkaldy and Youdelis was that of the Al-Cu system, of which the relevant part of the diagram is shown in Fig. 5.51.



Fig. 5.51. Part of the phase diagram for the Cu-Al system.

* Good agreement btw theory and experiment in inverse segregation of Al-Cu alloy.



Fig. 5.52. Comparison between experimental and calculated inverse segregation in Al-Cu.

- * Case of Al-Zn system_studied by youdelis & Colton (Fig. 5.53)
 - : somewhat more complicated, because
- a) Assumption of constant k₀ can no longer be regarded as correct,
- b) stepwise integration is used.

However, Fig. 5.54 shows good agreement btw experimental and calculated inverse segregation.



Fig. 5.53. Part of phase diagram for the Al-Zn system

Fig. 5.54. Predicted and measured inverse segregation in Al-Zn.

5) Inverse segregation

- * <u>A much more drastic form of inverse segregation</u> occurs when liquid is sucked out through the boundary QR (the first region to solidify) by a difference of the pressure arising from the separation of the metal from the mold.
- \rightarrow The liquid which has exuded solidifies on surface of the metal btw it and the mold, in the form of small "drops", known as "sweat", which are usually much harder than the neighboring metal due to their high alloy content.



6) Coring and intercrystalline segregation

* The discussion of <u>normal segregation</u> was developed from a <u>macroscopics</u> <u>point of view</u>. \rightarrow However, each crystal is likely to exhibit normal segregation on a <u>microscopic scale</u>; the earliest part of it to form has a lower concentration of solute (unless $k_0 > 1$) than the later parts: "Coring", locally highest solute content

→ found in <u>the terminal regions where two or more crystals</u> grow toward each other and finally form a grain boundary.

5.10 Gravity segregation

* When the mass of liquid is sufficiently large, <u>convection</u> <u>causes motion of the</u> <u>solute away</u> from the limit of the boundary layer.

 \rightarrow If solute changes the density of the liquid, it may set up a convection current that carries it toward the top or the bottom of the space in which the liquid can move.

* This is a type of <u>transverse segregation</u> that is much more significant in large, <u>real system</u> than in the idealized ones discussed in this chapter.

* **Segregation**: undesiable ~ deleterious effects on mechanical properties

→ subsequent homogenization heat treatment, but diffusion in the solid far to slow

 \rightarrow good control of the solidification process



Inverse segregation: As the columnar dendrites thicken soluterich liquid (assuming k<1) must flow back between the dendrites to compensate for (a) shrinkage and this raises the solute content of the outer parts of the ingot relative to the center.

EX) Al-Cu and Cu-Sn alloys with a wide freezing range (relatively low k)

Negative segregation: The solid is usually denser than the liquid and sinks carrying with it less solute (initially solidified one)than the bulk composition (assuming k<1). This can, therefore, lead to a region of negative segregation near the bottom of the ingot. ((b) Gravity effects)

Fig. 4.43 Segregation pattern in a large killed steel ingot. + positive, - negative segregation. (After M.C. Flemings, Scandinavian Journal of Metallurgy 5 (1976) 1.) ²²

Two of the most important application of solidification : "Casting" and "Weld solidification"

Q: What kinds of ingot structure exist?

Ingot Structure

- Chill zone
- Columnar zone
- Equiaxed zone

* Solidification of Ingots and Castings

a lump of metal, usually shaped like a brick.

an object or piece of machinery which has been made by pouring a liquid such as hot metal into a container

Later to be worked, e.g. by rolling, extrusion or forging>> blank (small)

Permitted to regain their shape afterwards, or reshaped by machining

Ingot Structure

- outer Chill zone
 - : equiaxed crystals
- Columnar zone
 - : elongated or column-like grains
- central Equiaxed zone

Chill zone



- Solid nuclei form on the mould wall and begin to grow into the liquid.

- If the pouring temp. is low: liquid~ rapidly cooled below the liquidus temp. →
 big-bang nucleation → entirely equiaxed ingot structure, no columnar zone
- 2) <u>If the pouring temp. is high</u>: liquid~remain above the liquidus temp. for a long time → majority of crystals~remelt under influence of the turbulent melt ("convection current") → form the chill zone
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Columnar zone

After pouring the temperature gradient at the mould walls decreases and the crystals in the chill zone grow dendritically in certain crystallographic directions, e.g. <100> in the case of cubic metals.

 \rightarrow grow fastest and outgrow less favorably oriented neighbors



Fig. 4.41 Competitive growth soon after pouring. <u>Dendrites with primary arms</u> <u>normal to the mould wall</u>, i.e. parallel to the maximum temperature gradient, outgrow less favorably oriented neighbors. Fig. 4.42 Favorably oriented dendrites develop into columnar grains. Each columnar grain originates from the same heterogeneous nucleation site, but can contain many primary dendrite arms.

- 1) In general, the secondary arms become coarser with distance behind the primary dendrite tips.
- 2) The primary and secondary dendrite arm spacing increase with increasing distance from the mold wall.
 (∵ a corresponding decrease in the cooling rate with time after pouring)

Mushy zone (or pasty zone) depends on temp. gradient and nonequil. freezing range of the alloy



Fig. 4.28 Columnar dendrites in a transparent organic alloy.

(After K.A. Jackson in Solidification, American Society for Metals, 1971, p. 121.)

Equiaxed zone

The equiaxed zone consists of equiaxed grains randomly oriented in the centre of the ingot. An important origin of these grains is thought to be <u>melted-off dendrite side-arms + convection current</u>



Fig. 4.40 Schematic cast grain structure. (After M.C. Flemings, Solidification Processing, McGraw-Hill, New York, 1974.)



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Later to be worked, e.g. by rolling, extrusion or forging>> blank (small) an object or piece of machinery which has been made by pouring a liquid such as hot metal into a container

Permitted to regain their shape afterwards, or reshaped by machining

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depends on temp. gradient and non-equil. Freezing range of the alloy

- central Equiaxed zone



Chapter 6 Polyphase solidification

* A diagram relating solubility with temperature for a single pressure (for example, a pressure of one atmosphere) will convey the significant information.



Fig. 6.1. Solubility of hydrogen in copper.

* A diagram relating solubility with temperature for a single pressure (for example, a pressure of one atmosphere) will convey the significant information.

A typical solubility diagram



Fig. 6.2. Solubility of hydrogen in aluminum.

* A diagram relating solubility with temperature for a single pressure (for example, a pressure of one atmosphere) will convey the significant information.

A typical solubility diagram



Fig. 6.3. Hydrogen-Uranium phase diagram.

(b) Bubble formation

- When a metal or alloy containing a gas (such as Oxygen, Nitrogen or hydrogen) in solution solidifies, gas will be rejected at the interface, exactly in the same way as any other solute for which the $k_0 < 1$.
- → If the gas in the liquid was already saturated (i.e. if it was at the limit of solubility for the prevailing pressure at T_m) then it becomes supersaturated as soon as an enriched layer begins to form at the interface. This means that there is more gas in solution than the equilibrium amount, as therefore there is a thermodynamic driving force tending to reduce the gas content.
- → The amount of gas in solution may decrease either by escape of the gas at a free surface, if one is accessible within the range in which the gas can diffuse in the liquid, or by the formation of a gas bubble in the liquid.
- → Formation of gas bubble requires homogeneous or heterogeneous nucleation : "The condition for nucleation of a gas bubble is similar to that for nucleation of a solid phase, except that the effect of the pressure of the gas on its free energy must be considered."

But , a solid-liquid interface should not be an effective nucleant for a bubble;



 $\therefore \cos\theta < -1$

 \rightarrow Surface E of the bubble is increased by contact with the solid-liquid interface.

However, gas bubbles are formed at solid-liquid interfaces.

This location is in part due to the fact that the <u>gas concentration would be</u> <u>highest there during solidification</u>; but it may also be due to the fact that any reentrant in the interface, such as a cell wall, grain boundary, or inter-dendritic space, would have an even higher gas content because of lateral segregation, as shown in Fig. 6.5.

* gas bubbles are formed at solid-liquid interfaces.

In detail, in regions such as A, the terminal transient condition is entered as the 2 walls approach each other; the concentration of solute (in this case, gas rises far above the C_0/k that would occur at a flat interface, and which might not be sufficient to cause nucleation of gas bubbles.



* Experimental observations leave no doubt that gas bubbles are in fact nucleated during solidification, when transport of gas away from the interface by diffusion is not sufficiently fast, in terms of the rate of rejection at the interface, to hold the gas content below the nucleation level.

Fig. 6.5. Conditions for the nucleation of gas bubbles in cell wall.

* Subsequent behavior of bubble;

depends upon whether they float away from the surface or remain attached.

- a) <u>If a bubble escapes from the region</u> where it was nucleated, it may float to the surface of the melt, or it may be trapped by other crystals, in which case its subsequent behavior is similar to that of a bubble that remained at its point of origin.
- b) <u>If the bubble is trapped where it forms</u>, it immediately becomes a "sink" into which gas from the neighboring supersaturated liquid can escape. This sets up a concentration gradient which causes gas to diffuse to the bubble from the surrounding liquid. <u>The bubble there fore grows</u>; but while it is doing so, the <u>interface continues to advance</u>.
- → The relative rates of growth of the bubble and of advance of the interface determine whether the bubble will increase in diameter, remain of constant diameter but increase in length, or be overgrown by the solid.

These three possibilities :



* Growth rate of bubble > Advanced speed of interface → increase of bubble diameter

The diameter of the bubble is maintained in the longitudinal direction

 * Growth rate of bubble ~ Advanced speed of interface
 → Bubble growth progresses in the longitudinal direction while maintaining bubble diameter

* Growth rate of bubble < Advanced speed of interface
→ bubble are trapped in the solid.

Fig. 6.6. Effect of speed of growth of a bubble on its shape and size. 39 (a) Slow growth, (b) intermediate speed, (c) fast growth.

* A bubble that starts by growing (Fig. 6.6a) may reach a size at which the conditions of Fig. 6.6b are satisfied, and a cylindrical bubble becomes stable. The stability of the cylindrical bubble at intermediate speeds, and it breakdown at high and at low speeds, has been demonstrated for water containing dissolved air.

* Cylindrical type of bubble (=wormhole) can easily be seen in ice cubes produced by freezing water containing dissolved air; an example is shown in Fig. 6.7.
→ The bubbles do not nucleate until the ice has grown inward for a few millimeters; this is presumably distance required for the critical supersaturation to be produced.

* Clear ice (=wormhole free ice) can be obtained by causing the water to flow continuously over the freezing interface. This prevents the concentration of dissolved air from reaching the critical level.



Fig. 6.7. Bubbles in ice cube

• Growth of gas bubbles in a solidifyingmetal

The process is essential the same as in water. → The pressure at a point in a solidifying liquid may be lower than would be expected from purely hydrostatic conditions. In the extreme case, a region of liquid may be completely surrounded by solid. Further solidification, accompanied by decrease in volume, would rapidly decrease the pressure, leading to the nucleation of bubbles.



Fig. 6.8. Gas bubbles in a metal.

(c) Formation of compounds by dissolved gases

* A second possible effect of dissolved gasses on solidification is that compounds, such as oxides, may be formed when the gas concentration reaches a high level, especially during the terminal transient stage of solidification.

 \rightarrow Oxide and other inclusions that are often found at grain boundaries in cast metals may have been formed in this way, rather than being present in the liquid prior to solidification. 41

6.2 Eutectics: limited solubility, most fusible (가장 잘 녹는, Greek)

* Most of the discussion of eutectic solidification will be based on binary eutectic.



Fig. 6.9. Phase diagram for the Al-Si system

Fig. 6.10. Phase diagram for the Cu-Mg system



Fig. 6.11. Eutectic phase diagram



ternary eutectic point; liquidus temperature, 239 °C)







* THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

• Isothermal section $(T_A > T > T_B)$





* Quaternary eutectic I $\rightleftharpoons \alpha + \beta + \gamma + \delta$



Fig. Sequence of tie-tetrahedron on cooling through the quaternary eutectic temperature

Polythermal projectin of a quaternary system involving five-phase equilibrium of the type I $\rightleftharpoons \alpha + \beta + \gamma + \delta$ (schematic representation of the Bi-Cd-Pb-Sn quaternary eutectic system).



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