2016 Fall

"Phase Transformation *in* Materials"

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Solidification of Pure Metal : Thermal gradient dominant

Solidification of single phase alloy: Solute redistribution dominant

a) Constitutional supercooling

Planar → Cellular growth → cellular dendritic growth → Free dendritic growth

응고계면에 조성적 과냉의 thin zone 형성에 의함
Dome 형태 선단 / 주변에 hexagonal array

T↓ → 조성적 과냉영역 증가
Cell 선단의 피라미드형상/ 가지들의 square array/ Dendrite 성장방향쪽으로 성장방향 변화

성장하는 crystal로 부터 발생한 잠열을 과냉각 액상쪽으로 방출함에 의해 형성
Dendrite 성장 방향/ Branched rod-type dendrite

→ "Nucleation of new crystal in liquid"
성장이 일어나는 interface 보다 높은 온도

b) Segregation

: normal segregation, grain boundary segregation, cellular segregation, dendritic segregation, inversegregation, coring and intercrystalline segregation, gravity segregation

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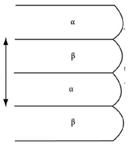
Eutectic Solidification (Kinetics)

: ΔT→ a) formation of interface + b) solute redistribution

How many α/β interfaces per unit length? $\rightarrow 1/\lambda \times 2$



a) Formation of interface: ΔG

For an interlamellar spacing, λ, there is a total of (2/ λ) m² of α/β interface per m³ of eutectic.

$$\Delta G = \Delta\mu \cong \frac{L\Delta T}{T_m} \qquad \rightarrow \Delta G = \Delta\mu = \frac{2\gamma}{\lambda} \times V_m$$

Molar volume

Driving force for nucleation = Total interfacial E of eutectic phase

For very large values of λ, interfacial E~ 0

Total undercooling

$$\lambda \rightarrow \infty, \quad \Delta G(\infty) = \Delta\mu = \frac{\Delta H\,\Delta T_0}{T_E}$$

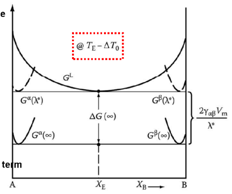
No interface (ideal case)

$$\Delta G(\lambda) = ? = -\Delta G(\infty) + \frac{2\gamma V_m}{\lambda}$$

Interfacial E term

With interface (real case)

Solidification will take place if ΔG is negative (-).



a) All ΔT→ use for interface formation= min. λ

What would be the minimum λ?

Critical spacing, $\lambda^* : \Delta G(\lambda^*) = 0$

최소 층상 간격

$$\Delta G(\infty) = \frac{2\gamma V_m}{\lambda^*} \qquad \lambda^* = +\frac{2T_E\gamma V_m}{\Delta H\Delta T_0}$$

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2) At λ= (∞>) λ (>λ*),

If ∞> λ > λ*, G_α and G_β are correspondingly reduced because less free energy is locked in the interfaces. → $X_B^{L/\alpha} > X_B^{L/\beta}$

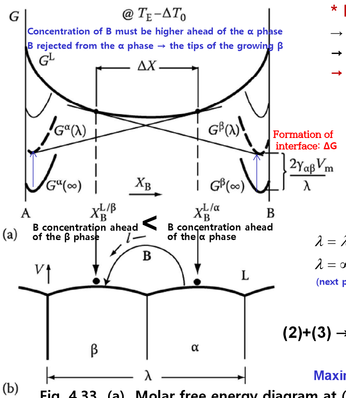


Fig. 4.33 (a) Molar free energy diagram at (T_E - ΔT_0) for the case λ* < λ < ∞, showing the composition difference available to drive diffusion through the liquid (ΔX). (b) Model used to calculate the growth rate.

* Eutectic growth rate, v

→ if α/L and β/L interfaces are highly mobile

→ proportional to flux of solute through liquid

→ diffusion controlled process

$$v \propto D\frac{dC}{dl} \propto (X_B^{L/\alpha} - X_B^{L/\beta})$$

∝ 1/effective diffusion distance.. 1/λ

$$v = k_1 D\frac{\Delta X}{\lambda} \quad (1)$$

$\lambda = \lambda^*, \Delta X = 0$

$\lambda = \infty, \Delta X = \Delta X_0$

(next page)

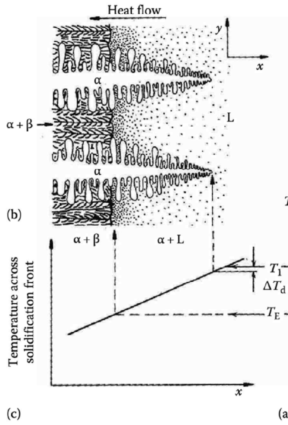
$$\Delta X = \Delta X_0\left(1 - \frac{\lambda^*}{\lambda}\right) \quad (2)$$

$$\Delta X_0 \propto \Delta T_0 \quad (3)$$

(2)+(3) → (1) $$v = k_2 D\frac{\Delta T_0}{\lambda}\left(1 - \frac{\lambda^*}{\lambda}\right)$$

Maximum growth rate at a fixed ΔT_0 → $\boxed{\lambda = 2\lambda^*}$

4.3.3 Off-eutectic Solidification

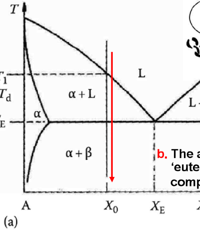


(b) Non-equilibrium solidification

a. primary α + eutectic lamellar

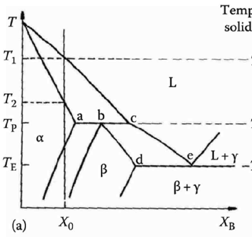
- Primary α dendrites form at T_1. Rejected solute increases X_L to X_E; eutectic solidification follows.
- Coring : primary α (low solute) at T_1 and the eutectic (high solute) at T_E.

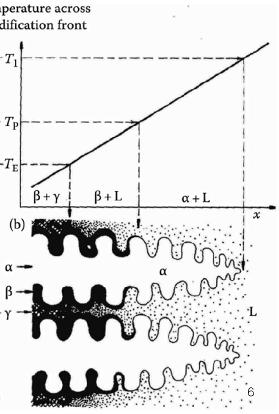
→ in-situ composite materials



b. The alloy solidifies as 100% 'eutectic' with an overall composition X_0 instead of X_E.

4.3.4 Peritectic Solidification





(b) Non-equilibrium solidification

- L + α → β , difficult to complete.
- α dendrites first form at T_1;
  Liquid reaches the composition 'c';
  β forms as the result of the peritectic reaction;
  α coring is isolated from further reaction
  finally β + γ eutectic forms.

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

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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 non-equil. freezing range of the alloy

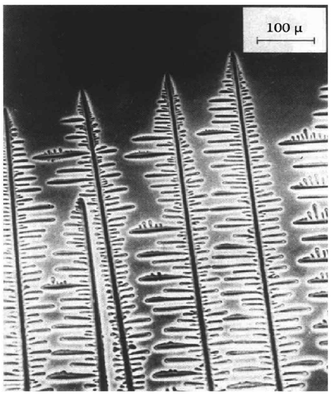


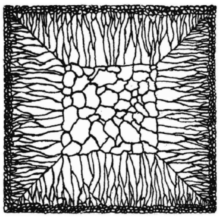
Fig. 4.28 Columnar dendrites in a transparent organic alloy.
(After K.A. Jackson in Solidification, American Society for Metals, 1971, p. 121.)

4.4 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.

1) **If the pouring temp. is low**: liquid~ rapidly cooled below the liquidus temp. → **big-bang nucleation** → **entirely equiaxed ingot structure**, no columnar zone
2) **If the pouring temp. is high**: 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**

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 melted-off dendrite side-arms + convection current

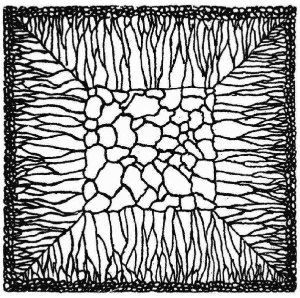
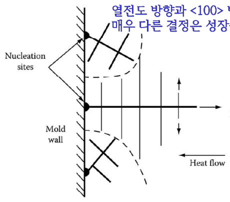


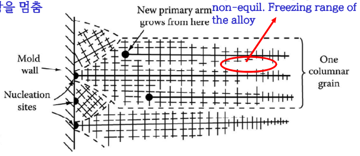
Fig. 4.40 Schematic cast grain structure.
(After M.C. Flemings, Solidification Processing, McGraw-Hill, New York, 1974.)

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.

→ grow fastest and outgrow less favorably oriented neighbors

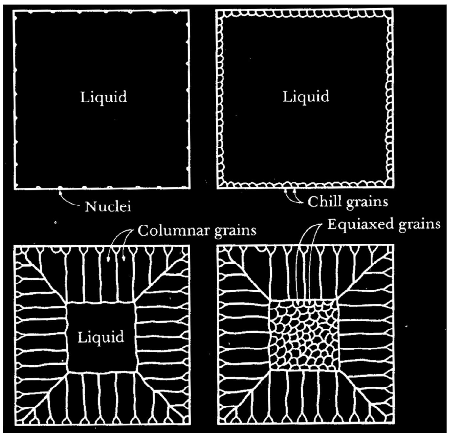

열전도 방향과 <100> 방향이
매우 다른 결정은 성장을 멈춤



Mushy zone (or pasty zone)
depends on temp. gradient and non-equil. Freezing range of the alloy

Fig. 4.41 Competitive growth soon after pouring. Dendrites with primary arms normal to the mould wall, 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.



Q: What kind of segregations exist?

4.4.2 Segregation and Shrinkage in Ingots and Castings

(a) Segregation

- **Macrosegregation :** Large area
  composition changes over distances comparable to the size of the specimen.
- **Microsegregation :** In the secondary dendrite arm
  occur on the scale of the secondary dendrite arm spacing.

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.**

Fig. Simulation of macrosegregation formation in a large steel casting, showing liquid velocity vectors during solidification (left) and final carbon macrosegregation pattern (right).

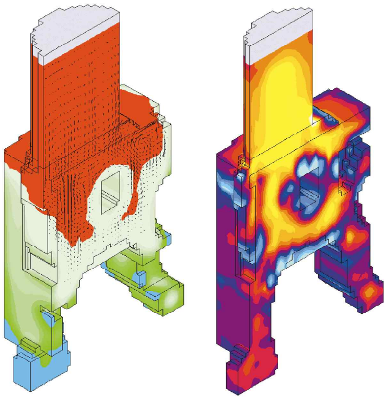


Fig.
Freckles in a single-crystal nickel-based superalloy prototype blade (left) and close-up of a single freckle (right) (courtesy of A. F. Giamei, United Technologies Research Center).

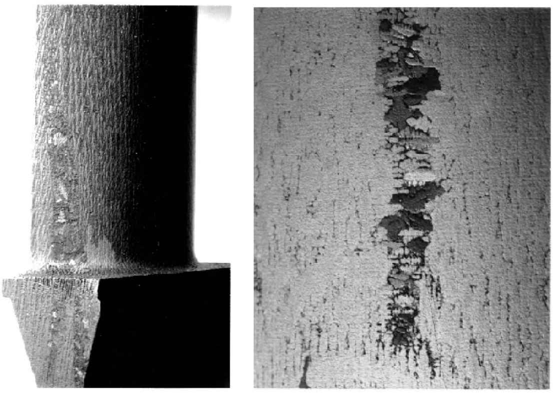
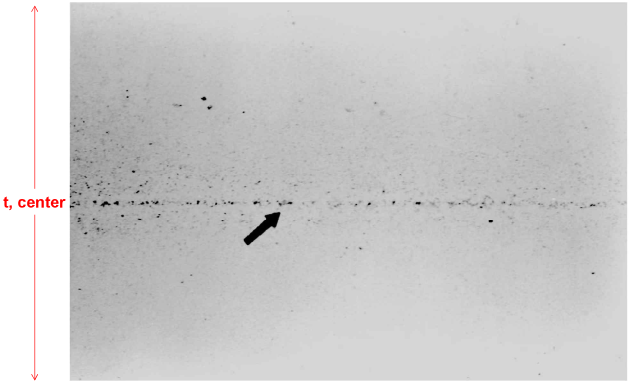
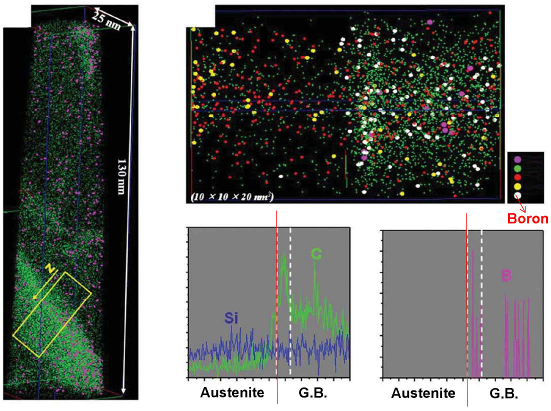


Fig.
Sulfur print showing centerline segregation in a continuously cast steel slab (courtesy of IPSCO Inc.).





The result obtained by APT analysis. (a) 3D Atom map of **Boron steel containing 100 ppm Boron** and (b) composition profile showing **solute segregation within retained austenite and grain boundary**

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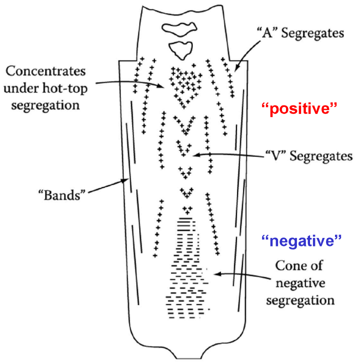
* Segregation: undesiable ~ deleterious effects on mechanical properties

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

→ good control of the solidification process



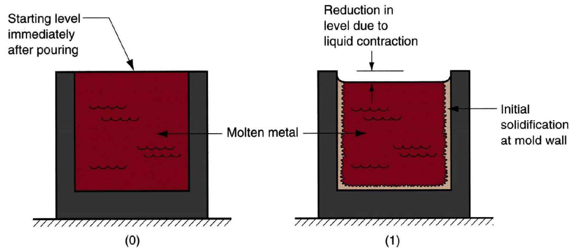
Inverse segregation (역편석): As the columnar dendrites thicken solute-rich liquid (assuming k<1) must flow back between the dendrites to compensate for (a) shrinkage and this raises the solute content of the outer parts of the ingot relative to the center.

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 (초기응고고상)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.)

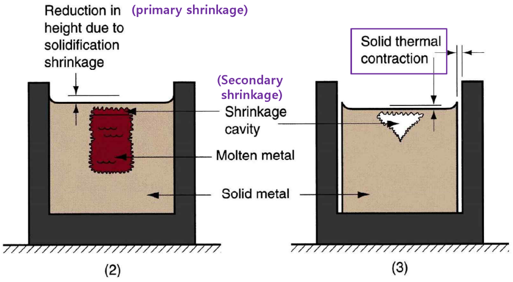
Shrinkage in Solidification and Cooling



* 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).

Q: Shrinkage in Solidification and Cooling?

Shrinkage in Solidification and Cooling

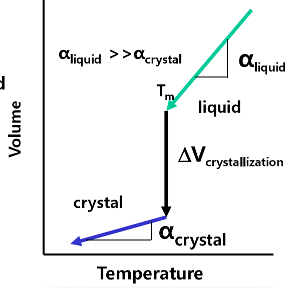


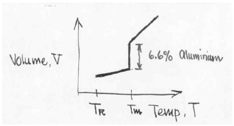
* (2) reduction in height and formation of shrinkage cavity caused by solidification shrinkage; (3) further reduction in height and diameter due to thermal contraction during cooling of solid metal (dimensional reductions are exaggerated for clarity).

(b) Shrinkage

Crystallization is Controlled by Thermodynamics

- Volume is high as a hot liquid
- Volume shrinks as liquid is cooled
- At the melting point, T_m, the liquid crystallizes to the thermodynamically stable crystalline phase
- More compact (generally) crystalline phase has a smaller volume
- The crystal then shrinks as it is further cooled to room temperature
- Slope of the cooling curve for liquid and solid is the thermal expansion coefficient, α





Shrinkage effect

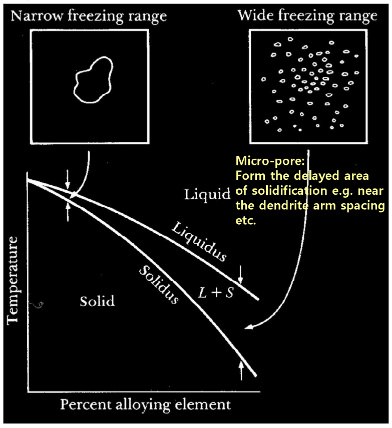
* Formation of Voids during solidification

Central shrinkage:
조성 변화가 크지 않은 주물의 응고 시 주로 응고수축, ΔV 에 의해 발생하는 주물 중심부에 발생

Dispersed Micro-Pore:
상당히 넓은 범위에 분산된 미소기공

외부수축 (몰드 주위) 및 1차수축공 (표면)을 제외하면, 이러한 수축공 결함은 주로 기포 결함임

기포 내에는 철합금에서는 CO, 질소, 산소, 수소 등이, 동합금에서는 수소, 산소, 알루미늄 합금에서는 수소 등의 가스가 존재



Micro-pore: Form the delayed area of solidification e.g. near the dendrite arm spacing etc.

Shrinkage in Solidification and Cooling

- Can amount to 5-10% by volume
- Gray cast iron expands upon solidification due to phase changes
- Need to design part and mold to take this amount into consideration

TABLE 5.1

Metal or alloy	Volumetric solidification contraction (%)	Metal or alloy	Volumetric solidification contraction (%)
Aluminum	6.6	70%Cu–30%Zn	4.5
Al–4.5%Cu	6.3	90%Cu–10%Al	4
Al–12%Si	3.8	Gray iron	Expansion to 2.5
Carbon steel	2.5–3	Magnesium	4.2
1% carbon steel	4	White iron	4–5.5
Copper	4.9	Zinc	6.5

Source: After R. A. Flinn.

* Volumetric solidification expansion: H_2O (10%), Si (20%), Ge

ex) Al-Si eutectic alloy (casting alloy)→ volumetric solidification contraction of Al substitutes volumetric solidification expansion of Si.

Cast Iron: Fe + Carbon (~ 4%) + Si (~2%)

→ precipitation of graphite during solidification reduces shrinkage.

“Dynamic process: importance of isotherm distribution”

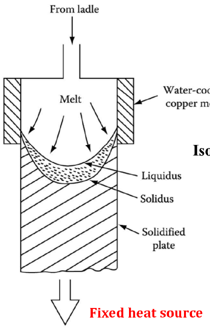


Fig. 4.44 Schematic illustration of a continuous casting process

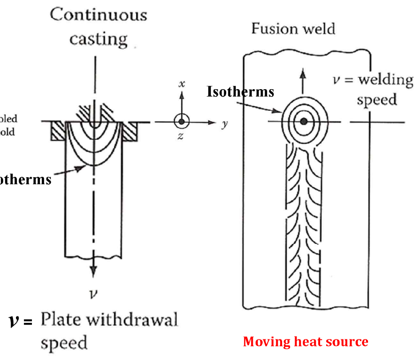


Fig. 4.45 Illustrating the essential equivalence of isotherms about the heat sources in fusion welding and continuous casting

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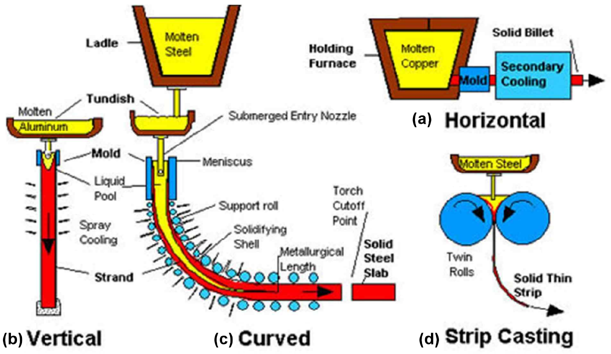
Q: What is continuous casting?

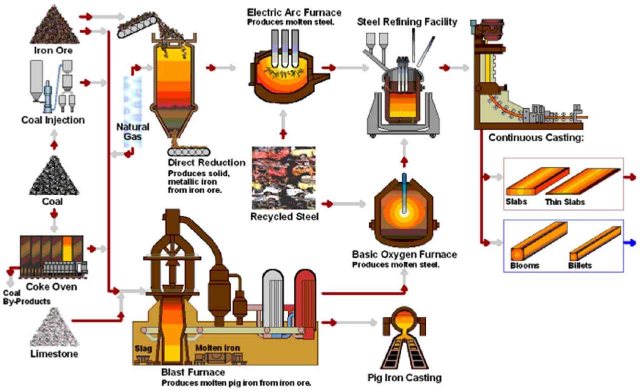
4.4.3 continuous casting

4.4.3 continuous casting: a number of dynamic industrial process

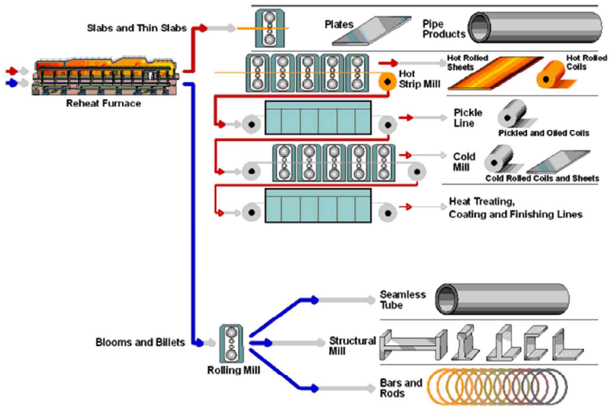
The molten metal is poured continuously into a water-cooled mold from which the solidified metal is continuously withdrawn in plate or rod form. (solid-liquid interface)



4.4.3 continuous casting



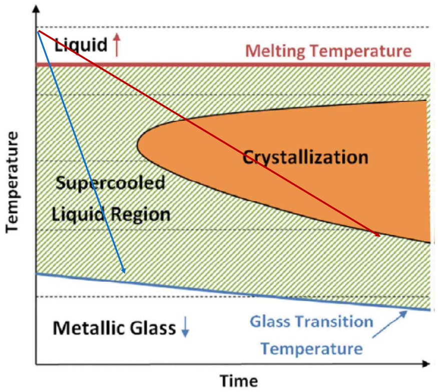
4.4.3 continuous casting



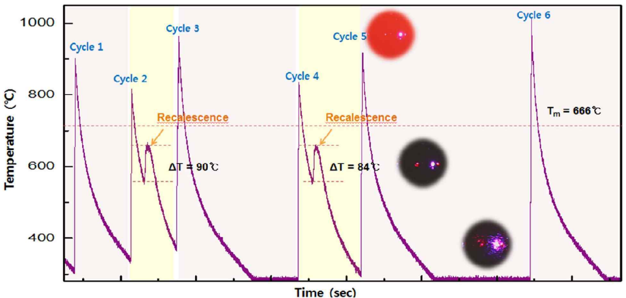
Q: Glass formation?

4.6 Solidification during Quenching from the Melt

Time-Temperature-Transformation diagram



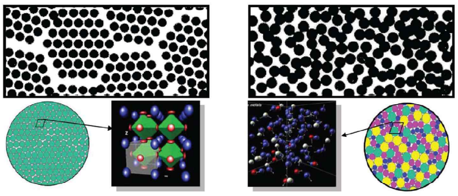
Electrostatic Levitation: cooling curve of Vitreloy 1 system



at KRISS

Structure of Crystals, Liquids and Glasses

Crystals **Liquids, glasses**



Building block: arranged in orderly, 3-dimensional, periodic array

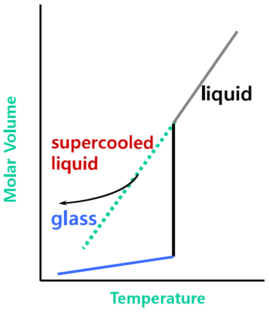
- grain boundaries

nearly random = non-periodic

- no grain boundaries

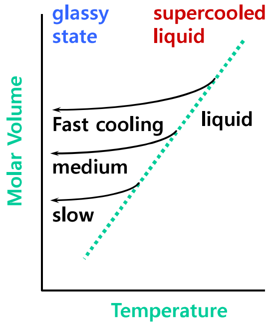
Glass Formation is Controlled by Kinetics

- Glass forming liquids are those that are able to "by-pass" the melting point, T_m
- Liquid may have a high viscosity that makes it difficult for atoms of the liquid to diffuse (rearrange) into the crystalline structure
- Liquid maybe cooled so fast that it does not have enough time to crystallize
- Two time scales are present
  - "Internal" time scale controlled by the viscosity (bonding) of the liquid
  - "External" timescale controlled by the cooling rate of the liquid



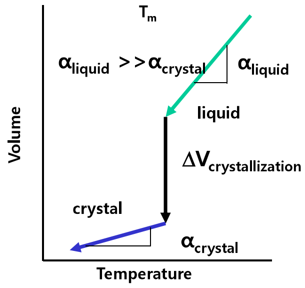
The Cooling Rate Affects the Properties of Glass

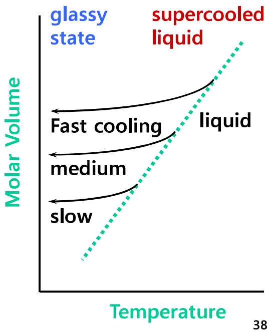
- Faster cooling freezes in the glass at a higher temperature
- The temperature is lowered so fast that the liquid does not have time to relax to the properties at the next lower temperature, glass is formed at a high temperature
- Slower cooling freezes in the glass at a lower temperature
- The temperature is lowered slowly enough that the liquids can relax to properties at lower and lower temperatures, glass is eventually formed at a lower temperature



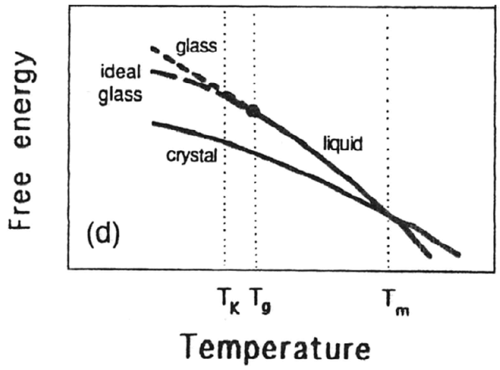
Fundamentals of the Glass Transition

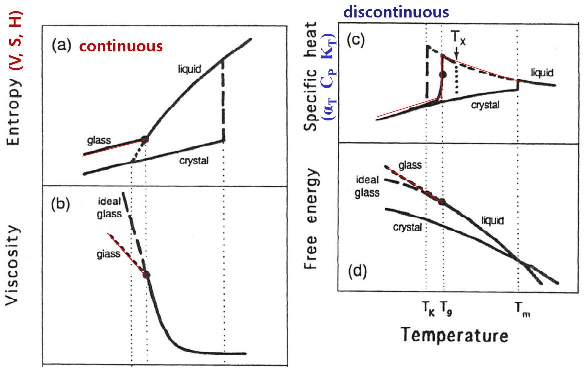
- Melting and Crystallization are Thermodynamic Transitions
- The Glass Transition is a Kinetic Transition





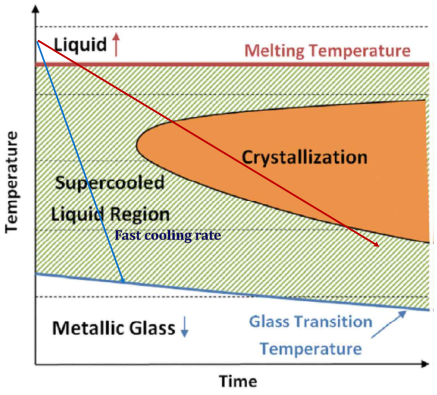
Schematic of the glass transition showing the effects of temperature on free energy





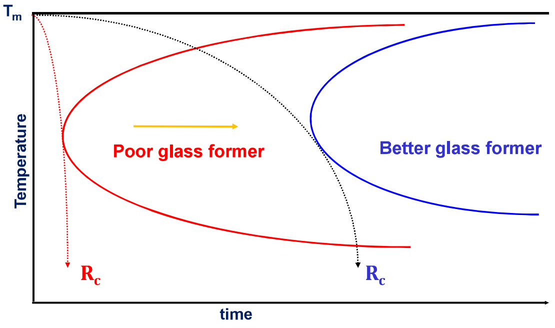
Schematic of the glass transition showing the effects of temperature on the entropy, viscosity, specific heat, and free energy. T_x is the crystallization onset temperature.

Glass formation : (1) Fast Cooling



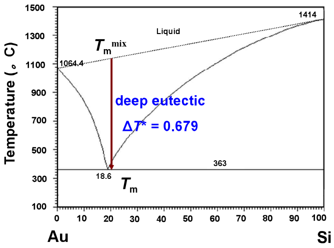
Glass formation : (2) Better Glass Former

GFA $R_c = \frac{\Delta T}{t_n}$ undercooled liquid → crystalline

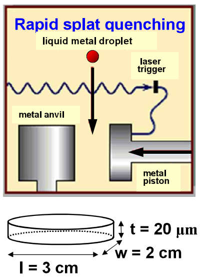


Glass formation : stabilizing the liquid phase

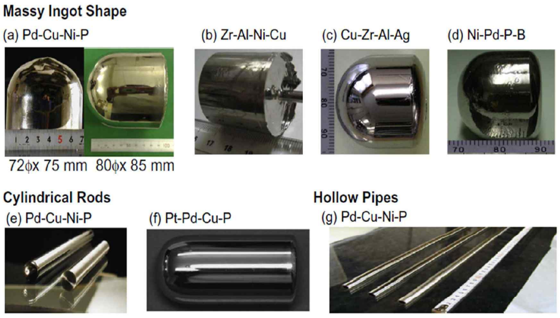
- First **metallic glass** ($Au_{80}Si_{20}$) produced by splat quenching at Caltech by Pol Duwez in 1960.



W. Klement, R.H. Willens, P. Duwez, Nature 1960; 187: 869.

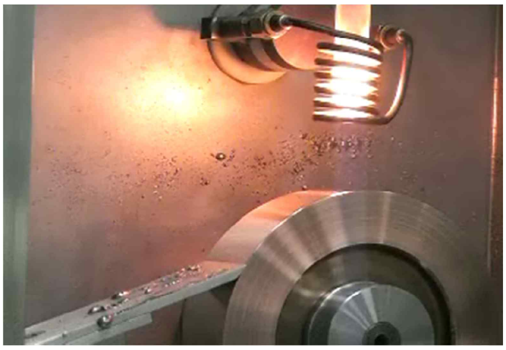


Bulk glass formation in the Pd-/Ni-/Cu-/Zr- element system

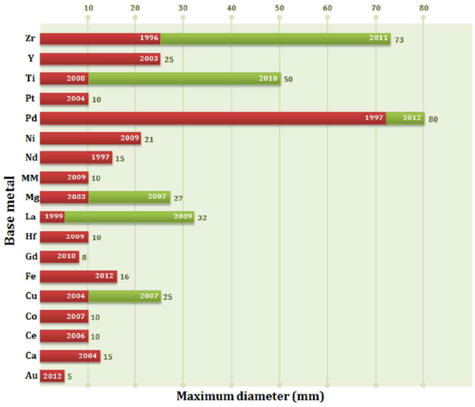


Glass formation: Rapid quenching (~$10^{5\text{-}6}$ K/s) of liquid phase

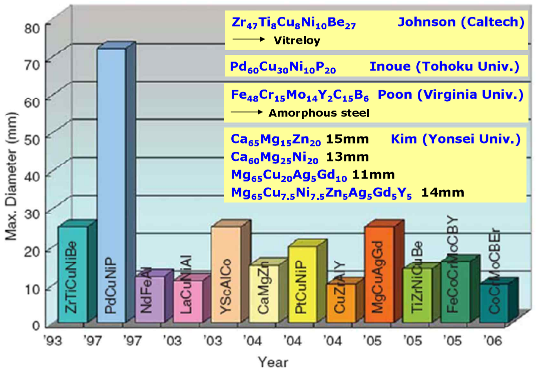
1969 Ribbon type with long length using melt spinner : FePC, FeNiPB alloy



Recent BMGs with critical size ≥ 10 mm



Recent BMGs with critical size ≥ 10 mm



$Zr_{47}Ti_8Cu_8Ni_{10}Be_{27}$ **Johnson (Caltech)**
→ **Vitreloy**

$Pd_{60}Cu_{30}Ni_{10}P_{20}$ **Inoue (Tohoku Univ.)**

$Fe_{48}Cr_{15}Mo_{14}Y_2C_{15}B_6$ **Poon (Virginia Univ.)**
→ **Amorphous steel**

$Ca_{65}Mg_{15}Zn_{20}$ **15mm** **Kim (Yonsei Univ.)**
$Ca_{60}Mg_{25}Ni_{20}$ **13mm**
$Mg_{65}Cu_{20}Ag_5Gd_{10}$ **11mm**
$Mg_{65}Cu_{7.5}Ni_{7.5}Zn_5Ag_5Gd_5Y_5$ **14mm**

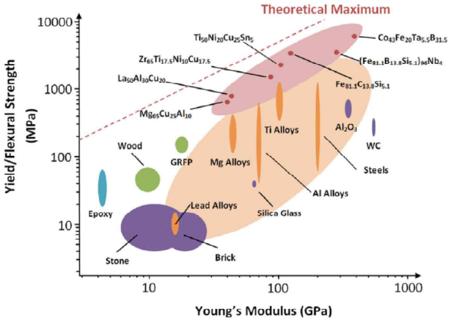
A.L. Greer, E. Ma, MRS Bulletin, 2007; 32: 612.

Q: BMG = The 3rd Revolution in Materials?

The 3rd Revolution in Materials

2. Large elastic strain limit of BMGs

1. High strength of BMGs

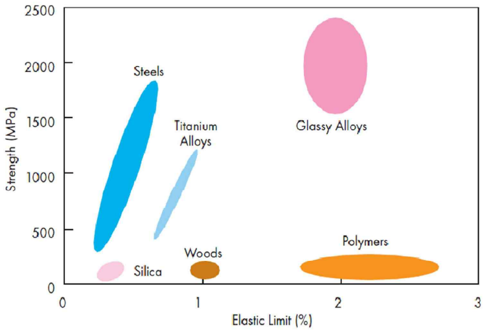


High fracture strength over 5 GPa in Fe-based BMGs

A.L. Greer, E. Ma, MRS Bulletin, 2007; 32: 612.

Metallic Glasses Offer

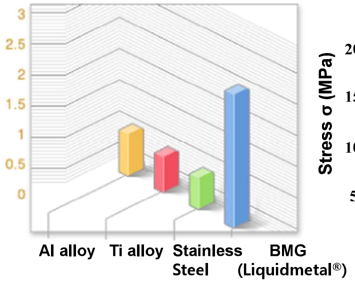
a Unique Combination of "High Strength" and "High Elastic Limit"



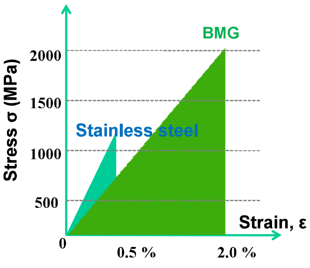
2. Large elastic strain limit of BMGs

Elastic Strain Limit

[as % of Original Shape]

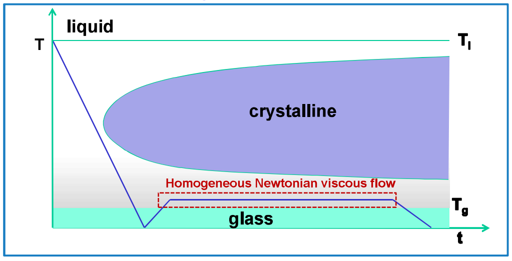


Stress-Strain Curve



3. Processing metals as efficiently as plastics

* Thermoplastic forming in SCLR

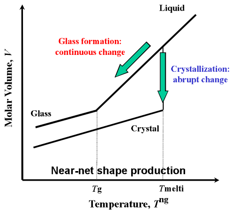


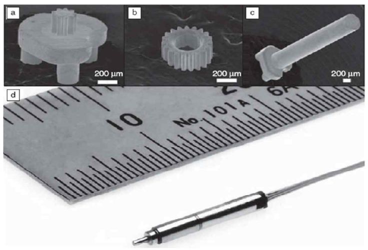
Metallic glass can be processed like plastics by homogeneous Newtonian viscous flow in supercooled liquid region (SCLR).

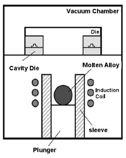
➡ Possible to deform thin and uniform in SCLR

3. Processing metals as efficiently as plastics

(a) Micro-casting

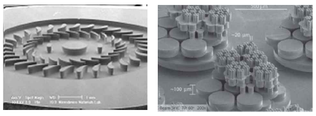






Precision die casting

Precision Gears for Micro-motors



MRS BULLETIN **32** *(2007)654.*

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3. Processing metals as efficiently as plastics

Seamaster Planet Ocean Liquidmetal® Limited Edition

- Superior thermo-plastic formability
  : possible to fabricate complex structure without joints
  - ↳ **Multistep processing can be solved by simple casting**
  - ↳ **Ideal for small expensive IT equipment manufacturing**

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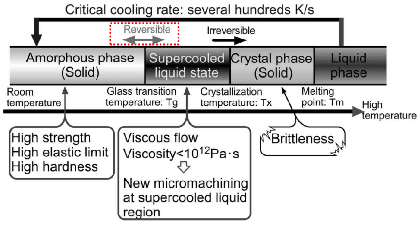
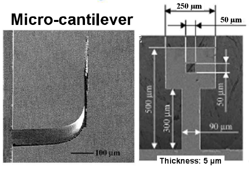
3. Processing metals as efficiently as plastics

(b) Micro-forming



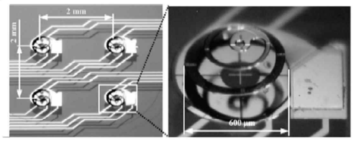
Micro-forming of three-dimensional microstructures from thin-film metallic glass

Micro-cantilever



Thickness: 5 µm

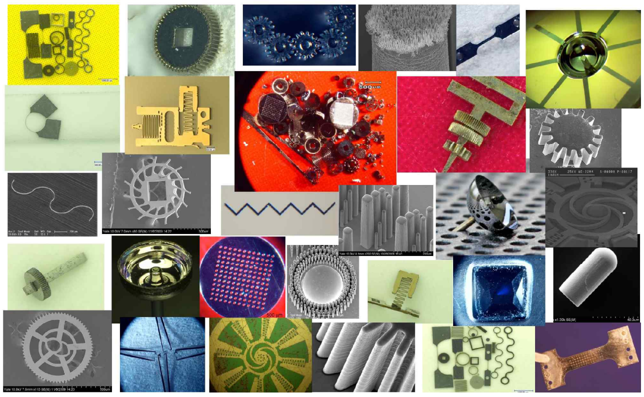
Integrated conical spring linear actuator



Materials Views
www.MaterialsViews.com
ADVANCED MATERIALS
www.advmat.de

Processing of Bulk Metallic Glass

Adv. Mater. **2009**, *21*, 1–32



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3. Processing metals as efficiently as plastics

* Thermoplastic forming in SCLR

$Mg_{65}Cu_{25}Gd_{10}$ metallic glass ribbon

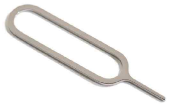
- Drawing sample at 220°C ➡ **Elongation over 1100%**

"Yale professor makes the case for Supercool Metals"

According to Yale researcher Jan Schroers, This material is 50 times harder than plastic, nearly 10 times harder than aluminum and almost three times the hardness of steel."

Apple buys exclusive right for Liquidmetal

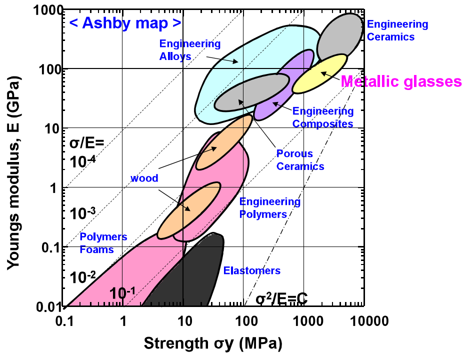
Apple is using Liquidmetal for…



USIM ejector (iphone 4)

Enclosure / Antenna

A new menu of engineering materials



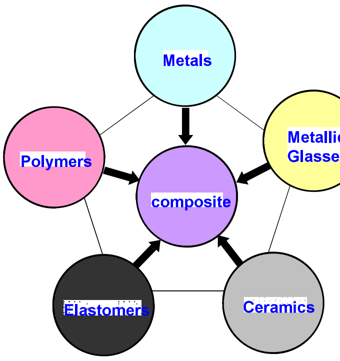
Apple continuing work on Liquidmetal casting techniques…

October 29, 2015

Two New Liquid Metal Inventions Published Today Cover Every Current Apple Product and even Complete Car Panels

Apple's patents cover the use of liquid metal in every imaginable Apple product and even hints that the process described in these inventions could produce complete car panels. That makes you wonder if Apple's Project Titan will be able to take advantage of the liquid metal process for car parts and beyond.

A new menu of engineering materials



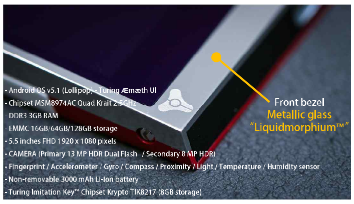
High GFA

High plasticity

higher strength
lower Young's modulus
high hardness
high corrosion resistance
good deformability
⋮

First smart phone with BMG exterior

Turing phone
by Turing Robotics Industries (UK)
with
Metallic glass
"Liquidmorphium™"



- Android OS v5.1 (Lollipop) - Turing Æmæth UI
- Chipset MSM8974AC Quad Krait 2.5GHz
- DDR3 3GB RAM
- EMMC 16GB/64GB/128GB storage
- 5.5 inches FHD 1920 x 1080 pixels
- CAMERA (Primary 13 MP HDR Dual Flash / Secondary 8 MP HDR)
- Fingerprint / Accelerometer / Gyro / Compass / Proximity / Light / Temperature / Humidity sensor
- Non-removable 3000 mAh Li-Ion battery
- Turing Imitation Key™ Chipset Krypto TIK8217 (8GB storage)

"Unhackable"
"Waterproof"
+
"Unbreakable"

The Turing Phone is built with
a pioneering material called Liquidmorphium™,
an amorphous "liquid metal" alloy tougher than
either titanium or steel - so what's in your hand
is as strong as your privacy protection.

from https://www.turingphone.com/

Skip section 4.5 and 4.8 in the text book

* Homework 4 : Exercises 4 (pages 257-259)

until 23th November (before class)

Good Luck!!