2009 spring

Advanced Physical Metallurgy

"Amorphous Materials"

03.04.2009

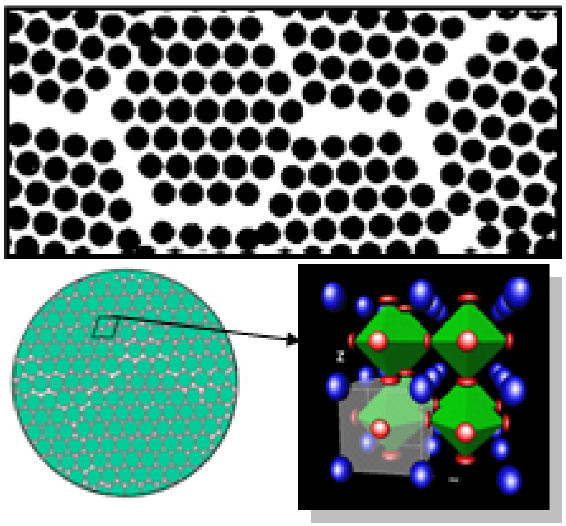
Eun Soo Park

Office: 33-316
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for previous class

- **Amorphous – from the Greek for "without form"**
  not to materials that have no shape,
  but rather to materials with no particular structure

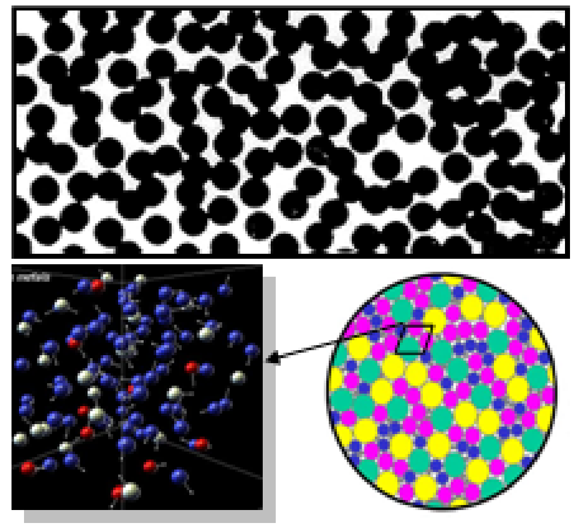
Crystals



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

- **grain boundaries**

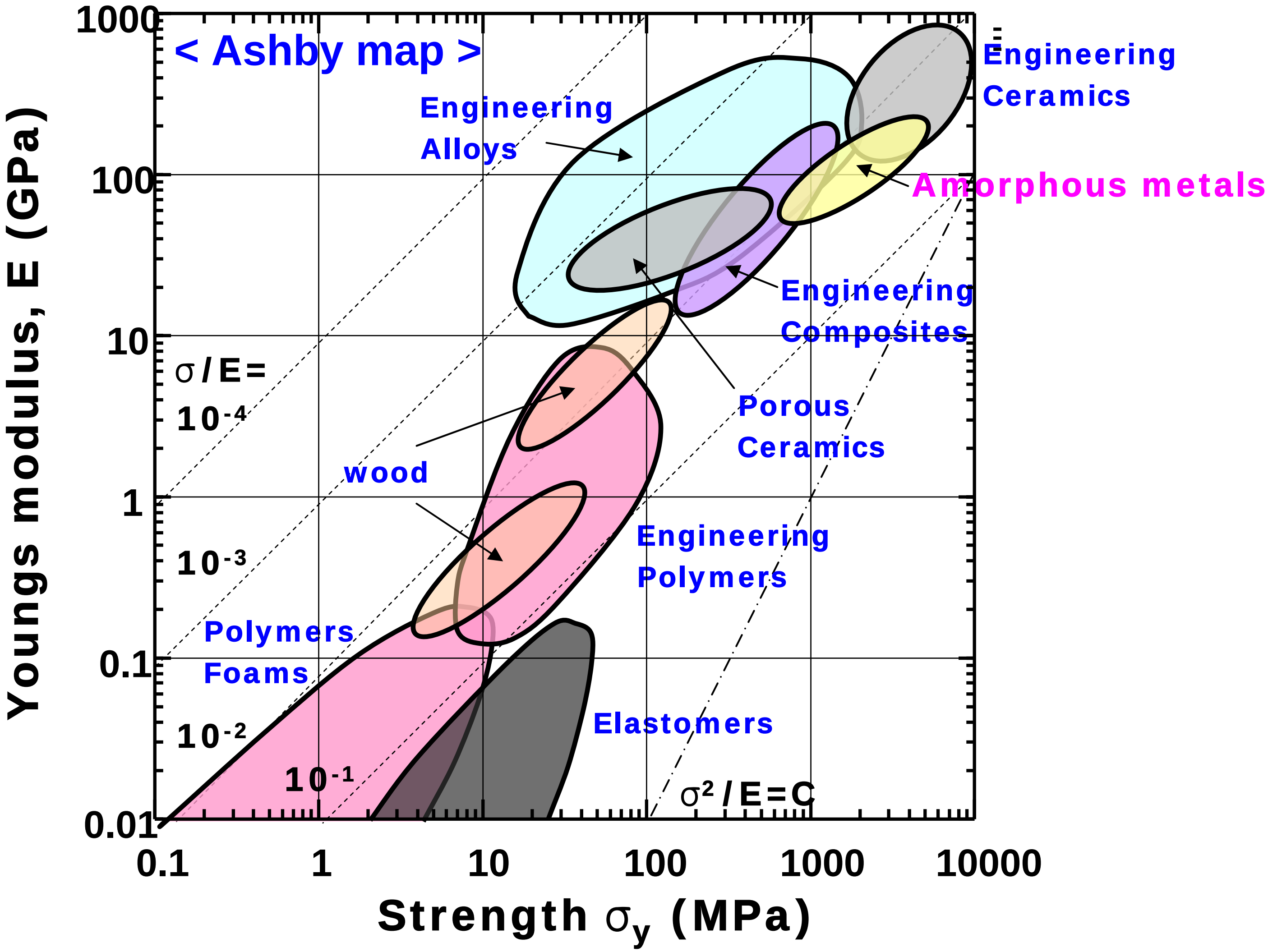
Liquids, glasses



nearly random = non-periodic

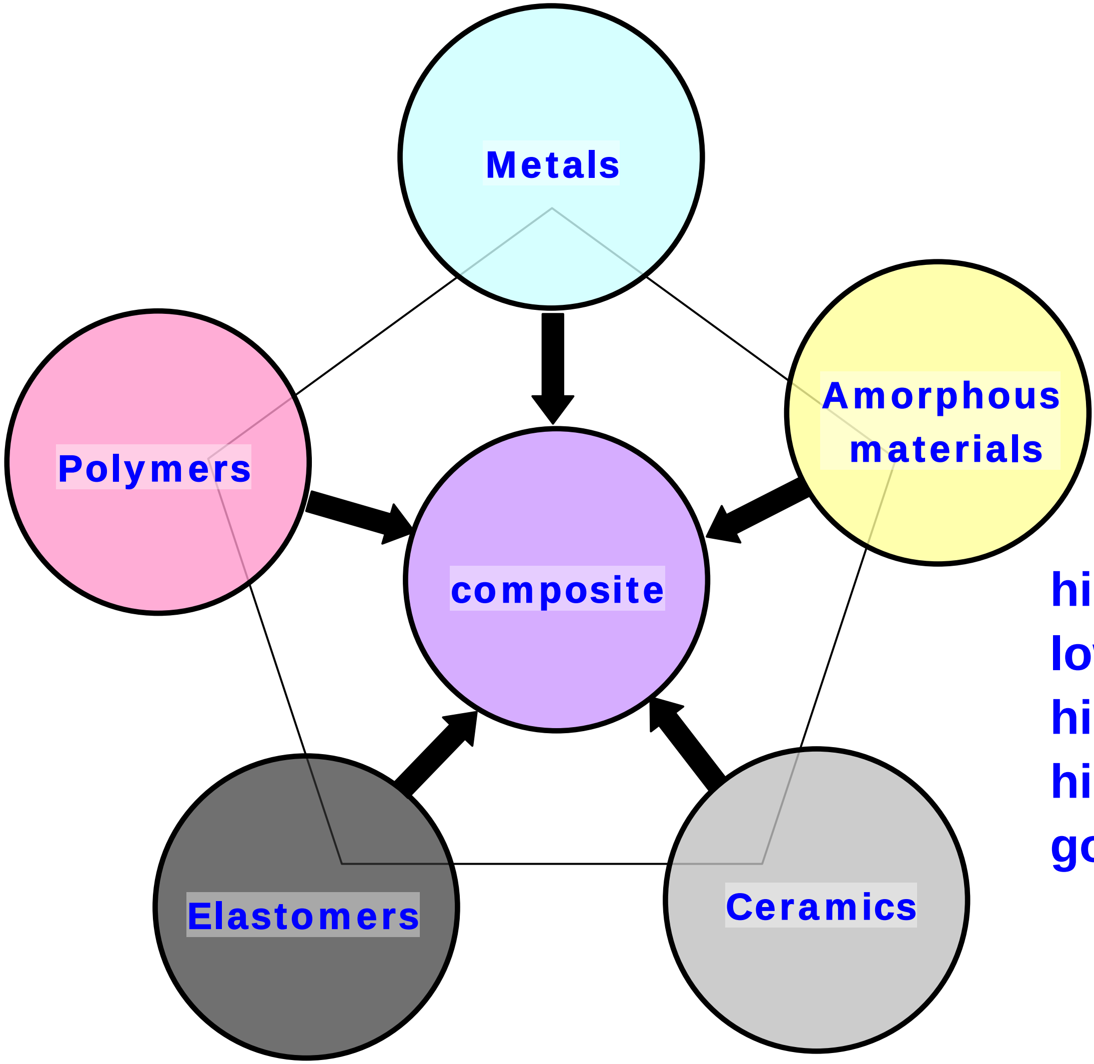
- **no grain boundaries**

Contents for previous class



Contents for previous class

Menu of engineering materials



High GFA

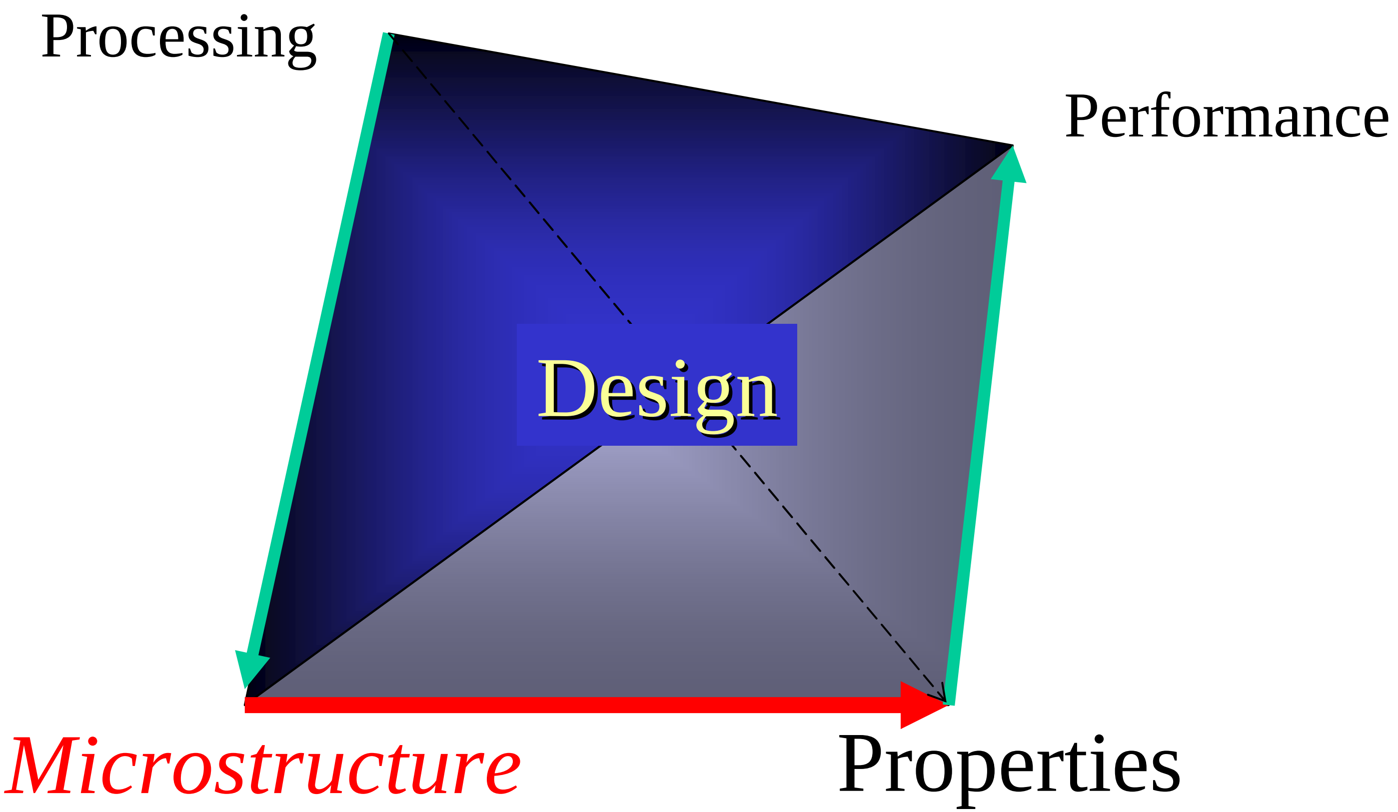
High plasticity

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

⋮

Contents for previous class

Microstructure-Properties Relationships



"Tailor-made Materials Design"

Contents for today's class

Introduction to Amorphous Materials

- **Introduction to Amorphous Materials**
- **Glass Transition Temperature**
- **Glass Formation**
- **History of Amorphous Metals**
- **Unique Properties of Amorphous Materials**

Introduction_amorphous materials

- ***Amorphous materials***

  a wide diversity of materials can be rendered amorphous indeed almost all materials can.

- metal, ceramic, polymer

ex) amorphous metallic alloy (1960)

- glassy/non-crystalline material

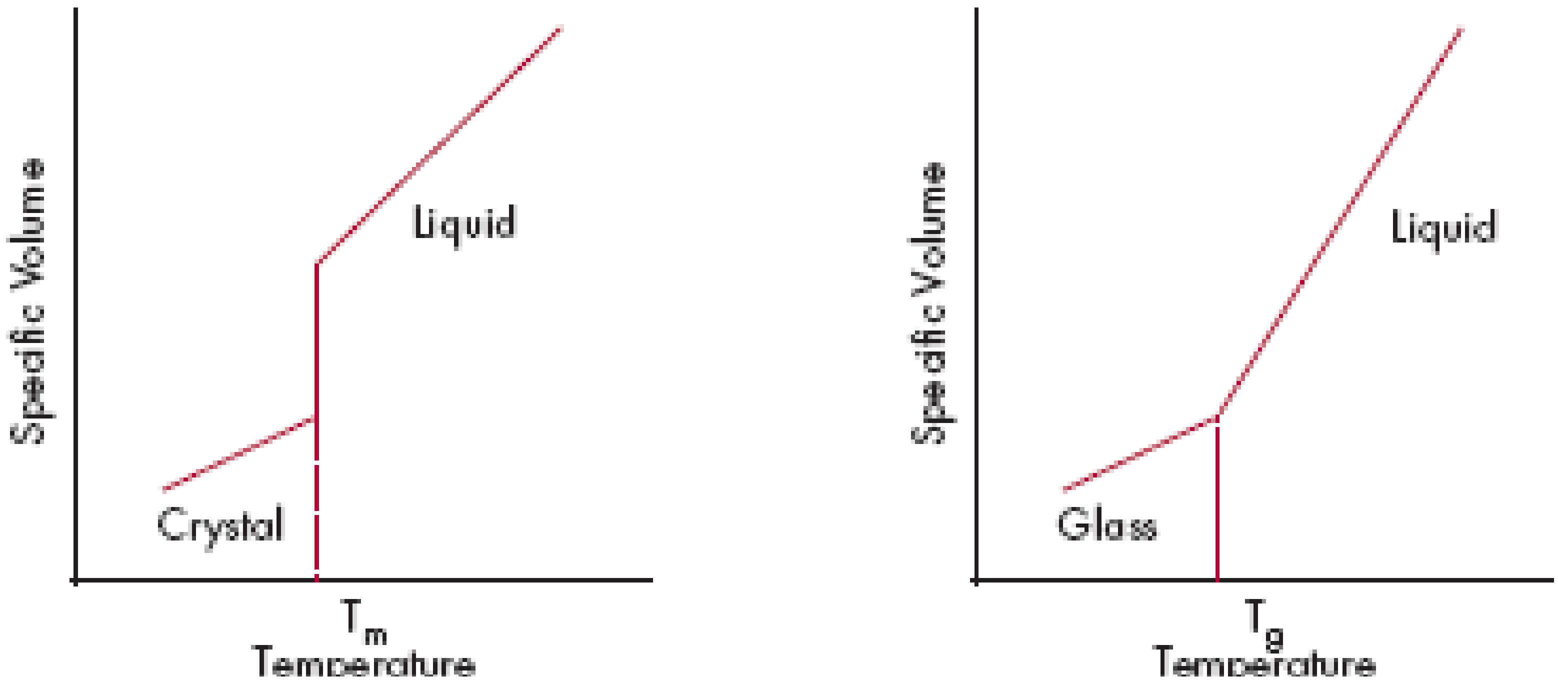
cf) amorphous vs glass

- random atomic structure (short range order)

- rapid solidification from liquid state

- retain liquid structure

Glass: undercooled liquid with high viscosity



Crystal Transition

glass Transition

Figure 4. Liquid-Crystalline Solid Transition (Left) and Liquid-Glass Transition (Right).

Effect of cooling rate on glass transition temperature

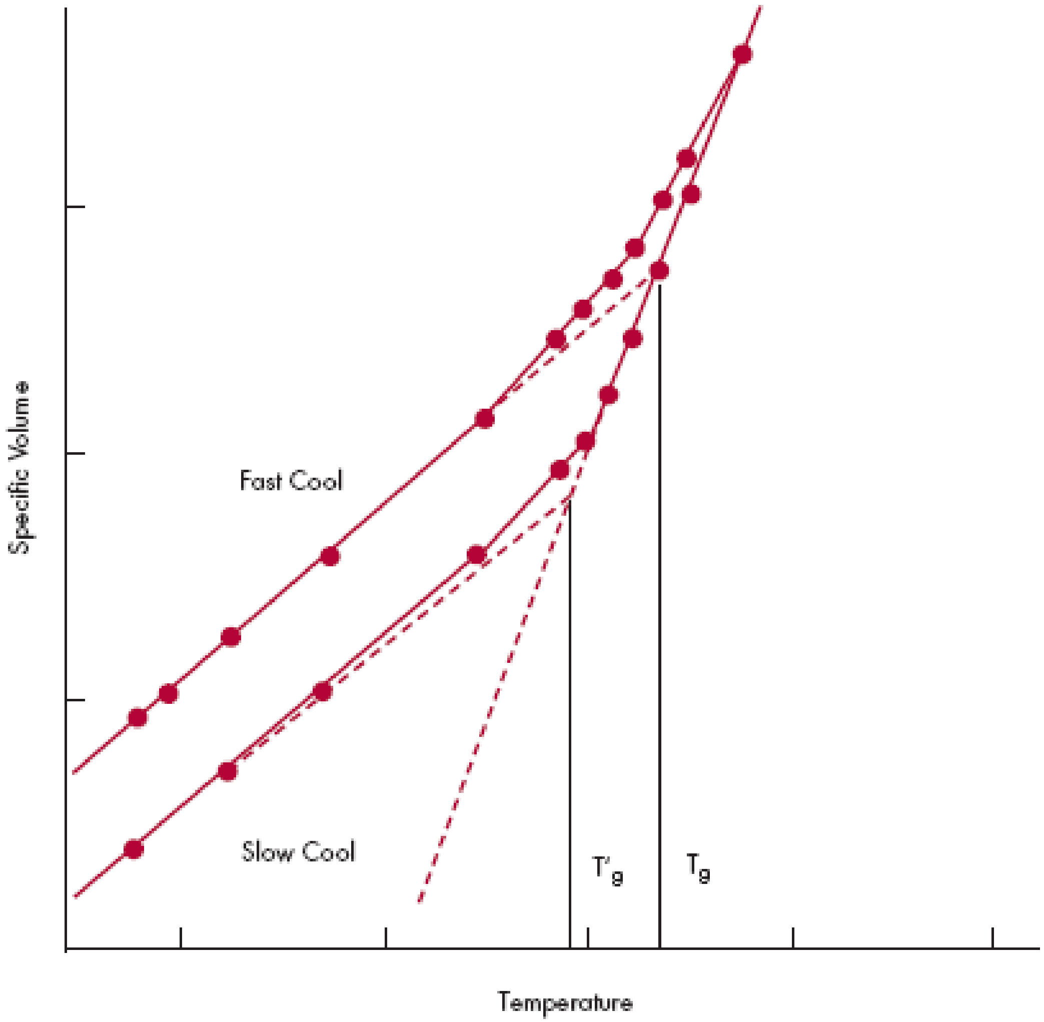


Figure 5. Schematic Representation of the Glass Transition. Note that the Glass-Transition Temperature (T_g) Shifts to a Lower Temperature with Slower Cooling (T'_g).

Introduction_amorphous metals

Definition of metallic glass

- **Noncrystalline metallic solid lacking long-range periodicity of atomic arrangement and showing glass transition.**

Bulk metallic glass (BMG)

- **Metallic glass having a minimum dimension of 1mm which is equivalent to a critical cooling rate of about 10^3 to 10^4 K/s.**

Glass Formation

- **Competing process between retention of liquid phase and formation of crystalline phases**

a. Liquid phase stability

- Stability of the liquid in the equilibrium state (i.e. stable state, Tl)

- Stability of the liquid during undercooling (i.e. metastable state, Tg)

b. Resistance to crystallization

- Nucleation and growth of the competing crystalline phases

Glass formation

Glass formation

Retention of liquid phase

Formation of crystalline phases

Thermodynamical aspect
Small change in free E. (liq.→cryst.)

Kinetic aspect
Low nucleation and growth rates

Structural aspect
Highly packed random structure

- ***Suppression*** **of nucleation and growth of crystalline phase**
- ***Higher*** **degree of dense random packed structure**

➡ ***High glass-forming ability (GFA*** $\propto 1/R_c$ *or* Z_{max}**)**

History: amorphous metal

1934 Vapor deposition

1950 Electro-deposition: Ni-P alloy

: hard & corrosion resistant coating

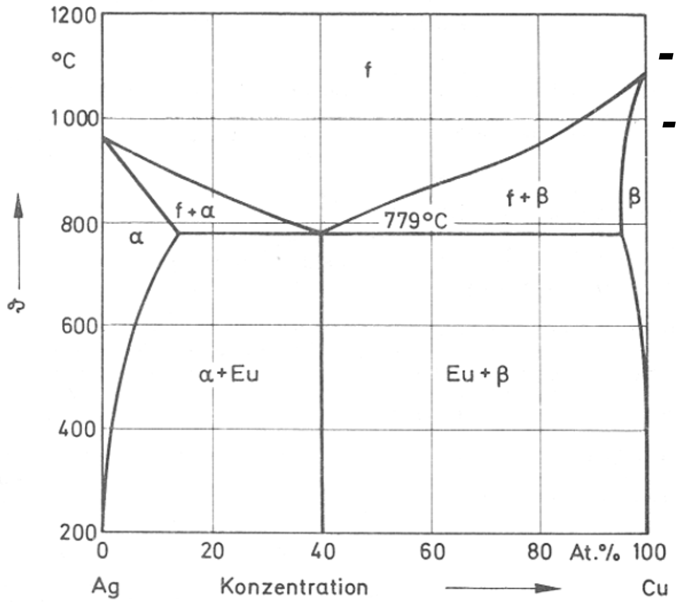
1960 P. Duwez (Caltech)

- quenching: phases stable at high temperature

- retain at R.T. / transform into other metastable phases

- in solid state

- *quenching from liquid state* (breakthrough)



- eutectic system : α + β

- rapid quenching: complete solid solution ?

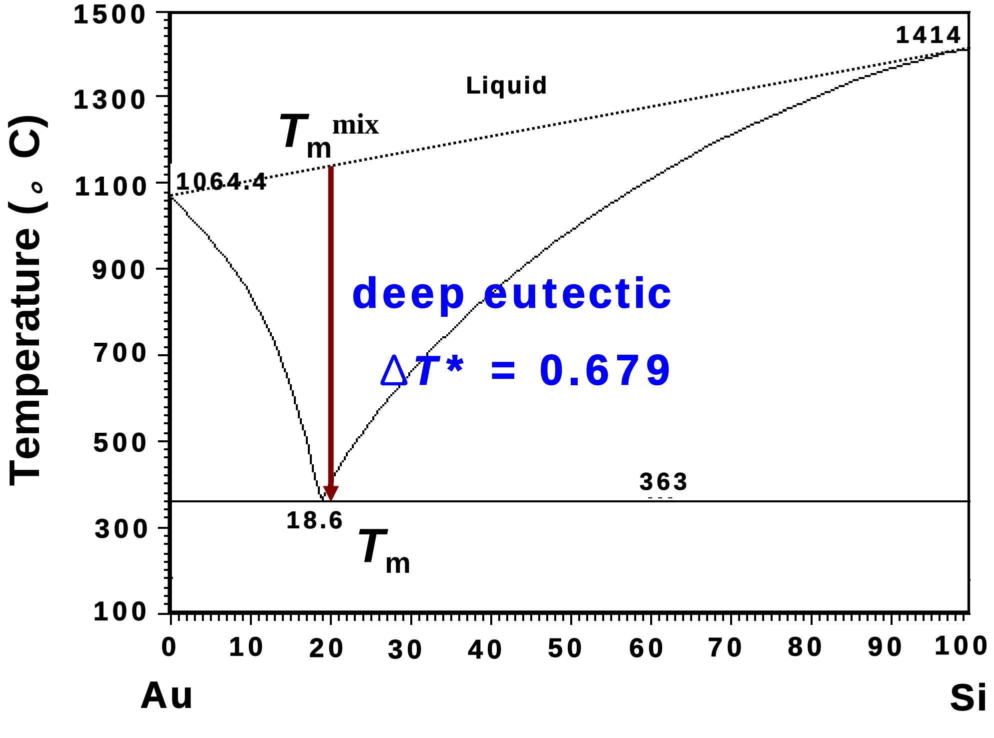
: *Hume Rothery rule*

Formation of solid solution depends on
the size difference, electronegativity, crystal structure.

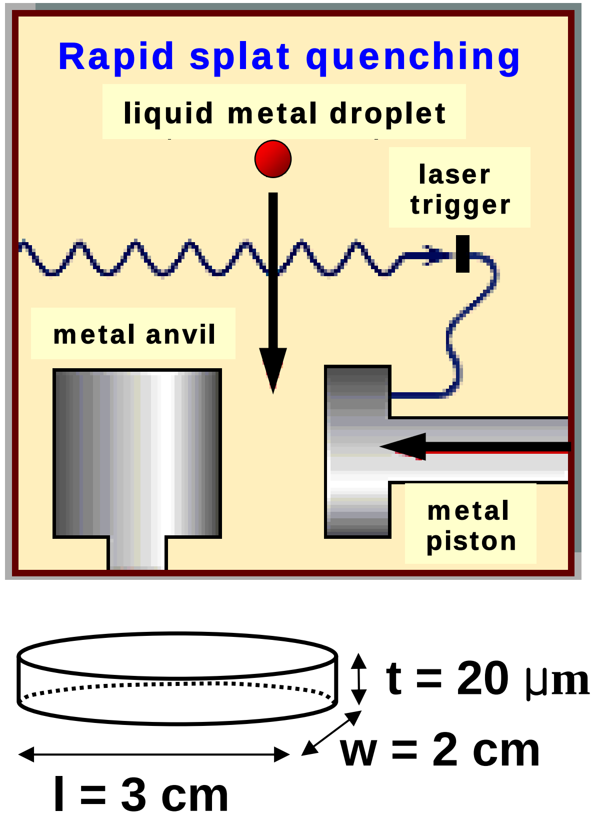
(1959) complete solid solution (but, crystalline)

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.*



Glass formation: stabilizing the liquid phase

- **1969 Ribbon type with long length using melt spinner**

  : FePC, FeNiPB alloy

Bulk formation of metallic glass

- First bulk metallic glass

$Pd_{77.5}Cu_6Si_{16.5}$ (T_{rg}=0.64)

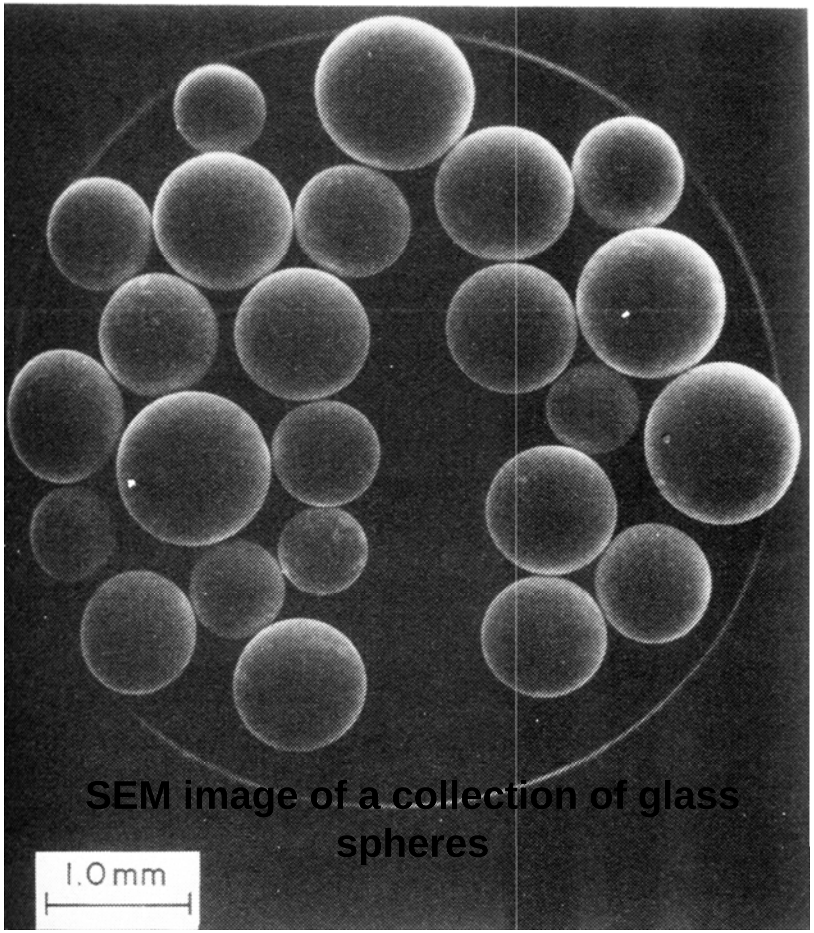
By droplet quenching (CR~800 K/s)

→

Alloy Selection: consideration of T_{rg}

$Pd_{40}Ni_{40}P_{20}$ (T_{rg}=0.67)

Suppression of heterogeneous nucleation



SEM image of a collection of glass spheres

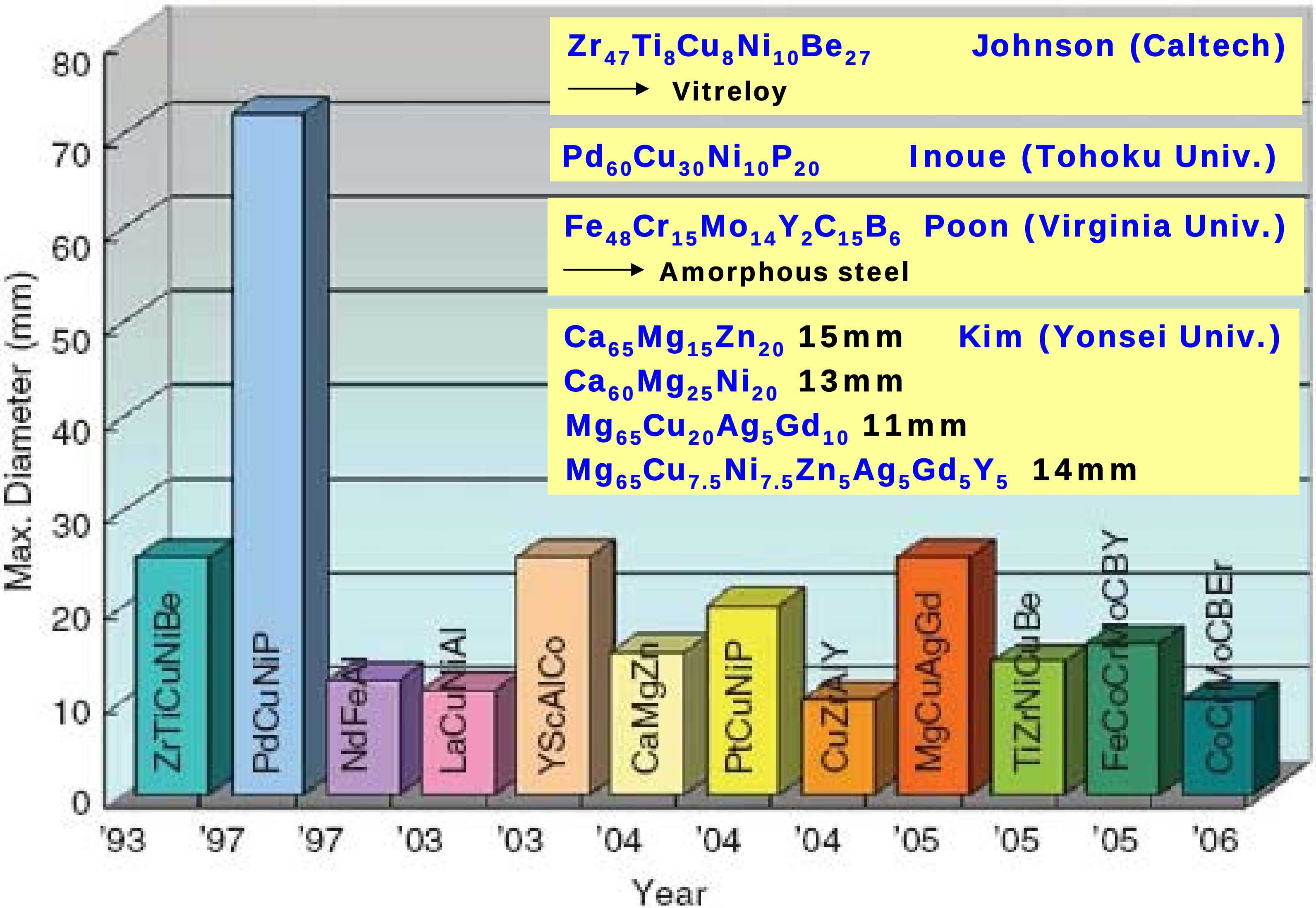
H.S. Chen and D. Turnbull, Acta Metall. 1969; 17: 1021.

- Largest ingot

- minimum dimension 1 cm and mass of 4 g
- Critical cooling rate: ~ 1K/sec.

Drehman, Greer, and Turnbull, 1982.

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.

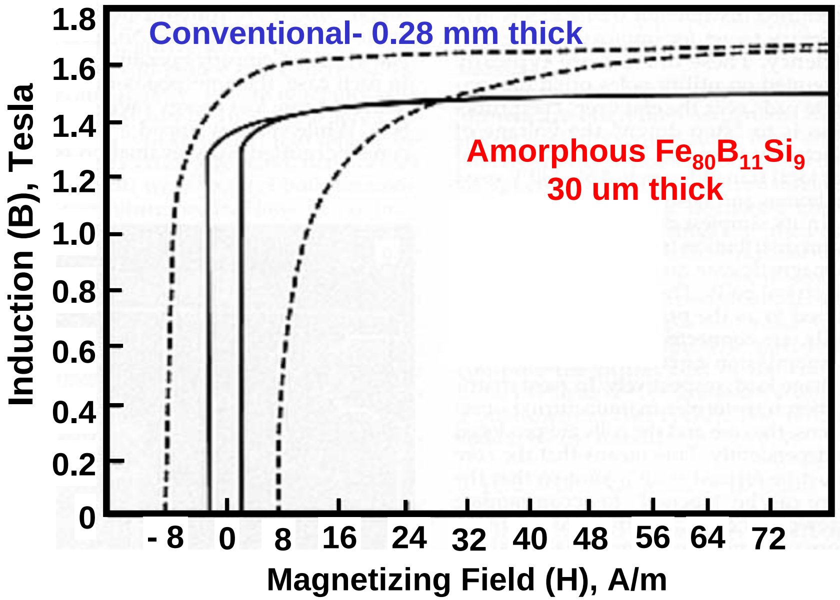
Introduction_Amorphous Materials

- ***Unique Properties*:**

  - not shared by crystalline solids at all

1) very soft magnetic material

- low magnetic loss



Transformers

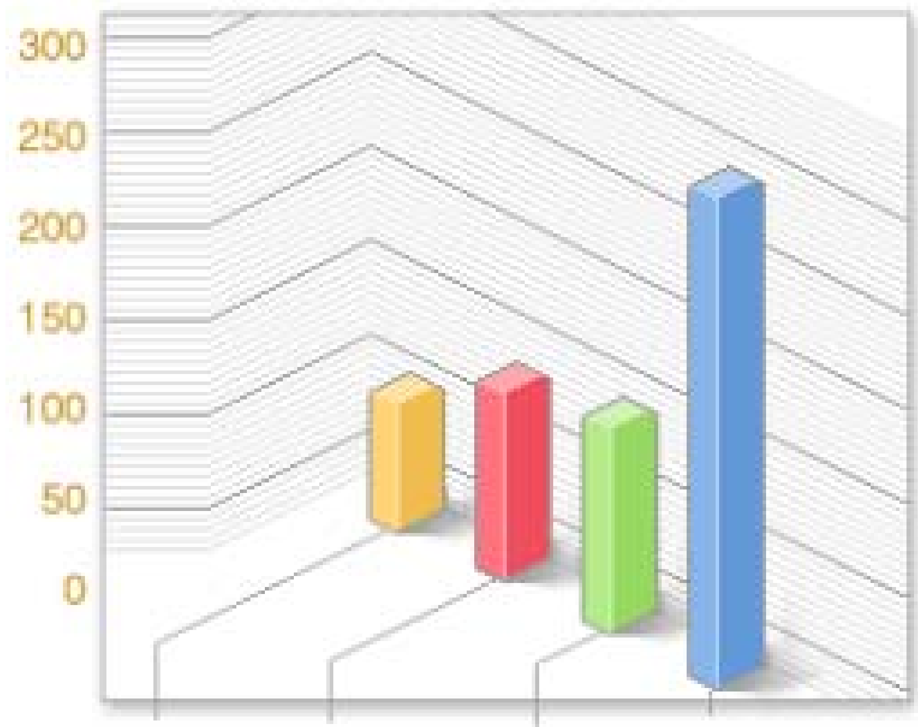
Introduction_Amorphous Materials

- ***Unique Properties*:**

  - not shared by crystalline solids at all

2) very hard, high strength

Yield Strength [1,000 psi]



Al alloy **Ti alloy** **Stainless** **BMG**
(Liquidmetal®)

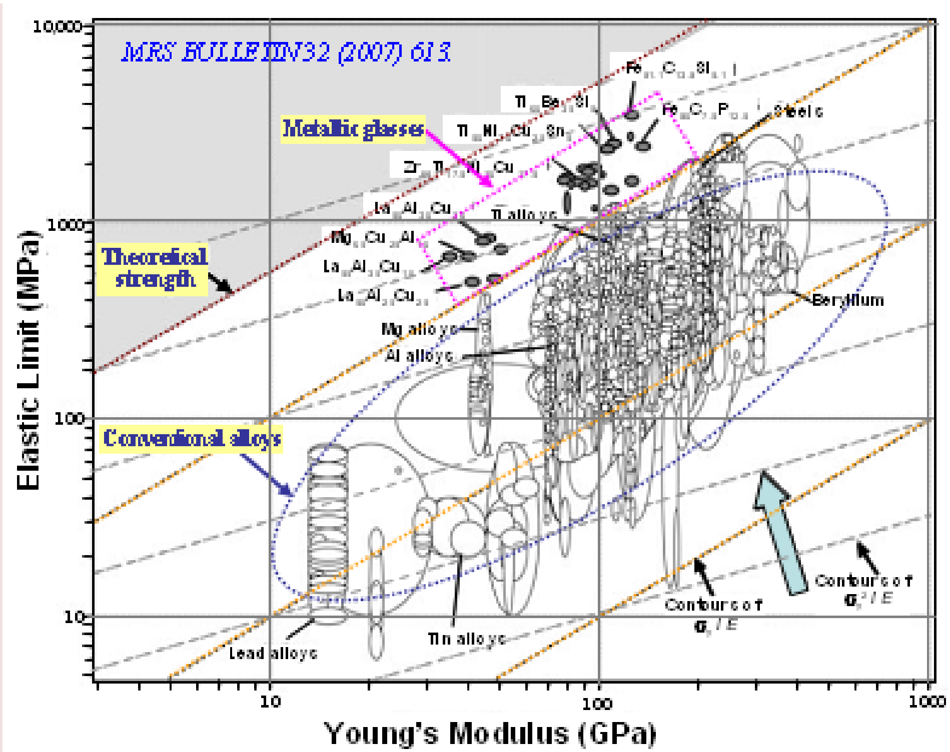
Introduction_Amorphous Materials

- ***Unique Properties*:**

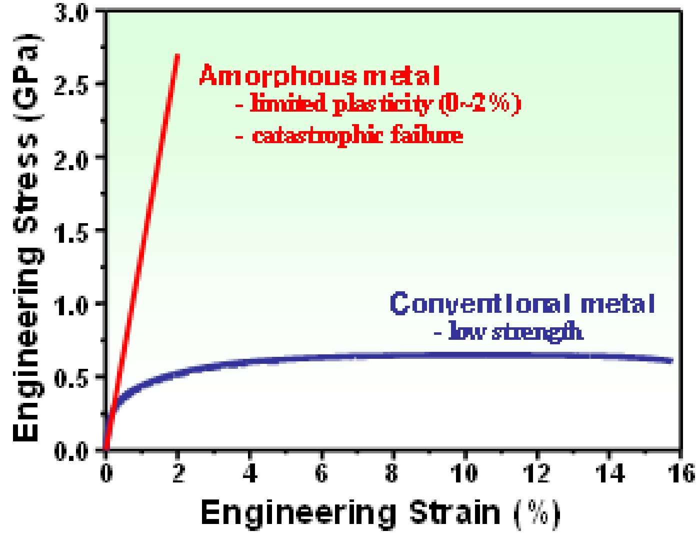
  - not shared by crystalline solids at all

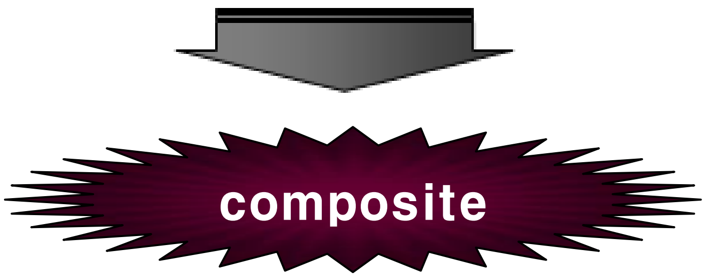
2) very hard, high strength

very brittle



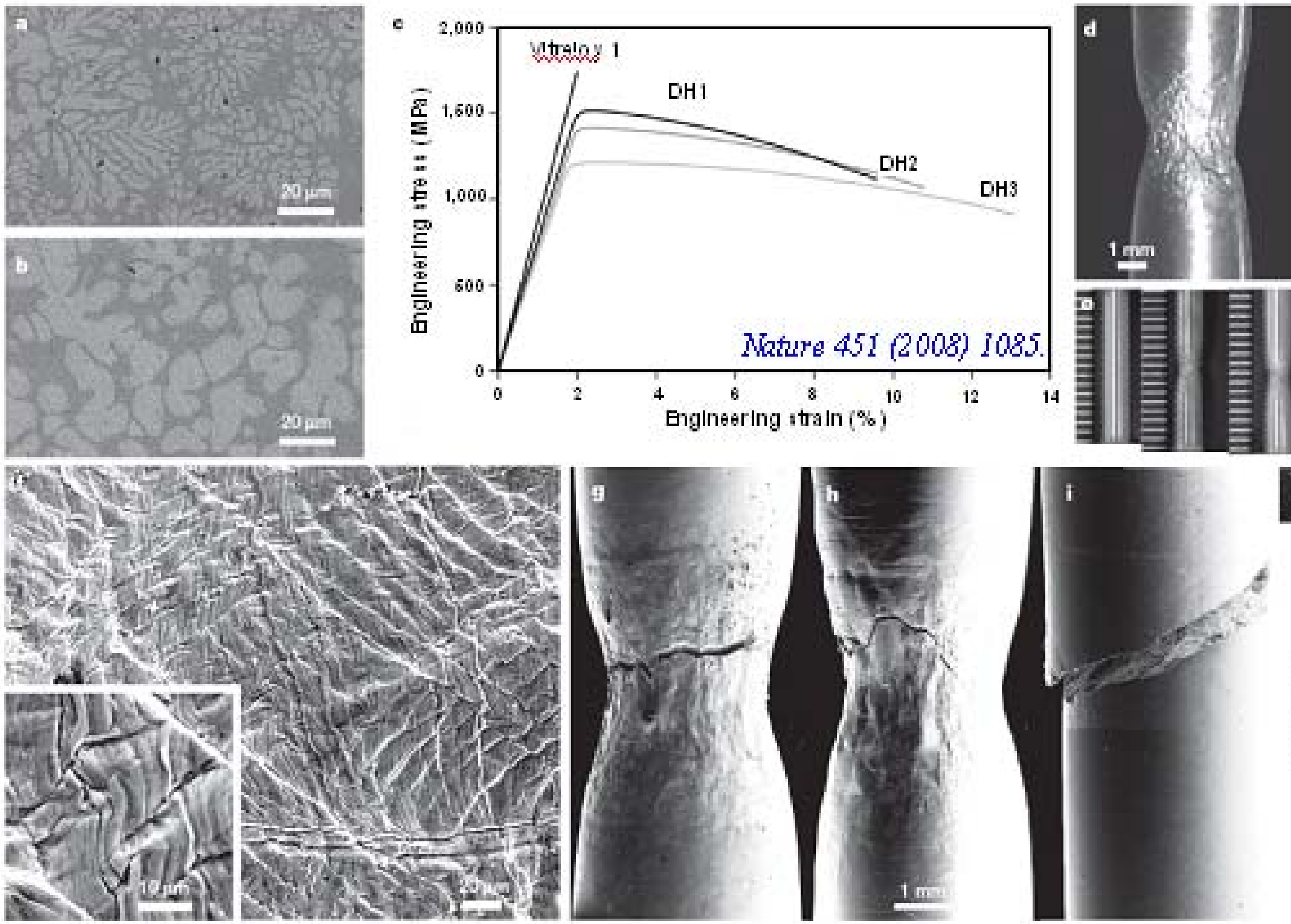
High fracture strength over 5 GPa in Fe-based BMGs





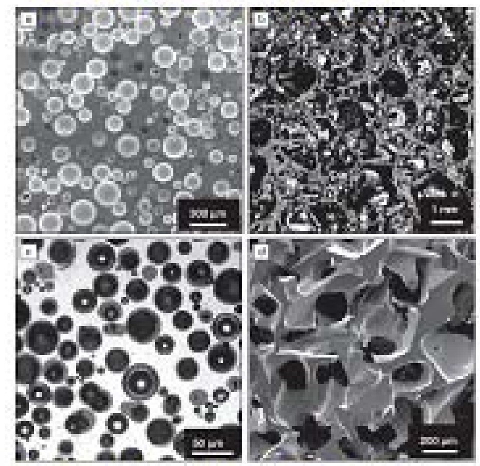
Bulk metallic glass matrix composites

(1) BMG matrix composites

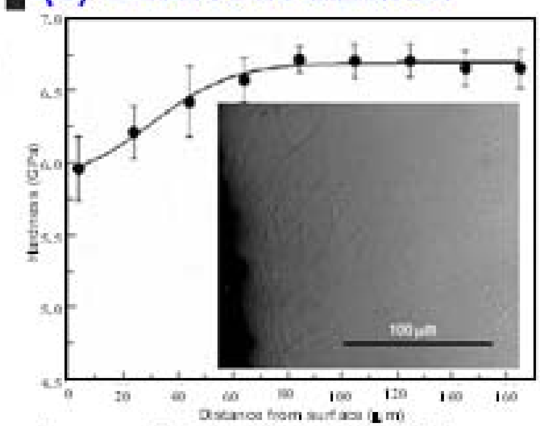


High fracture toughness: > 10 % plastic strain in tensile test

(2) Porous and foamed amorphous metals



(3) Cold-rolled BMGs



By control of residual stress

Nature Materials 5 (2006) 857.

Introduction_Amorphous Materials

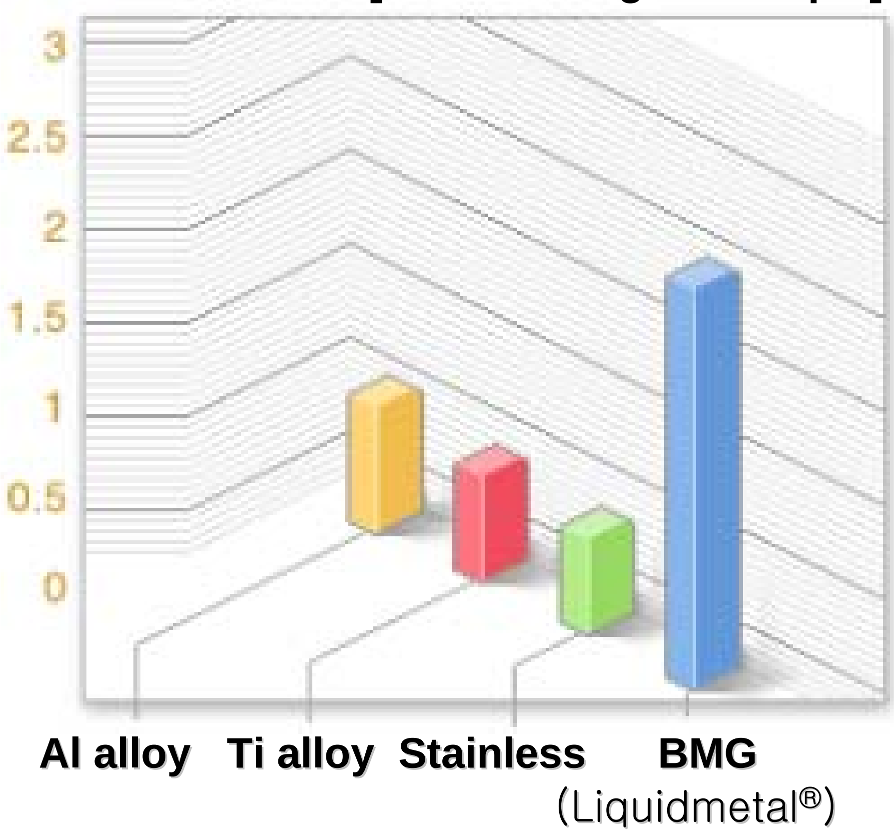
- ***Unique Properties*:**

  - not shared by crystalline solids at all

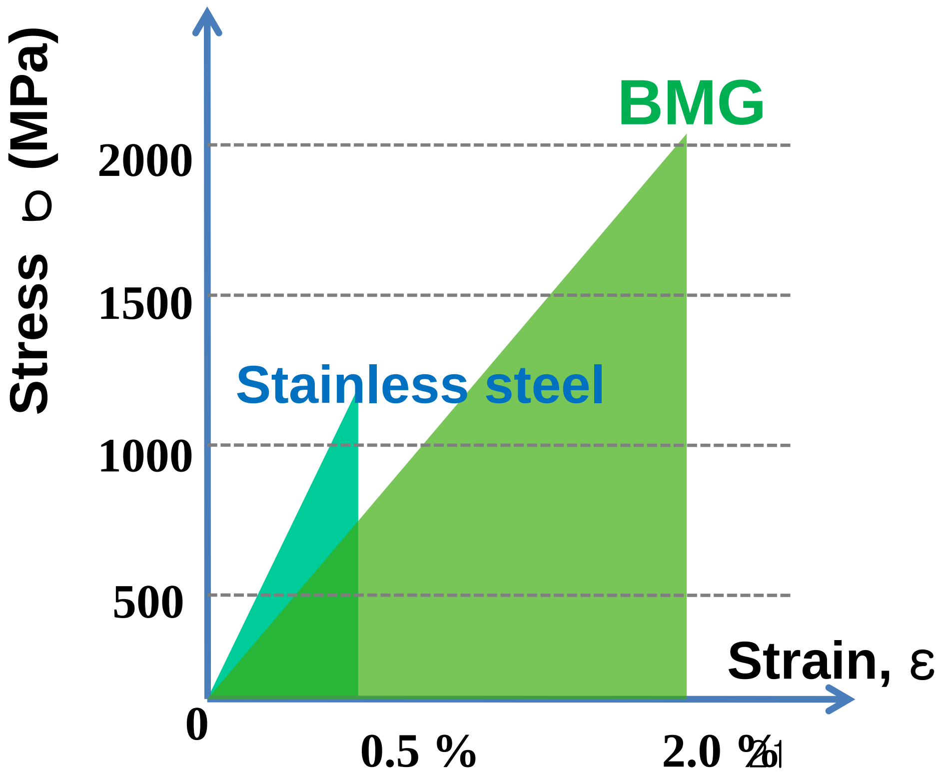
3) large elastic strain limit

Elastic Strain Limit

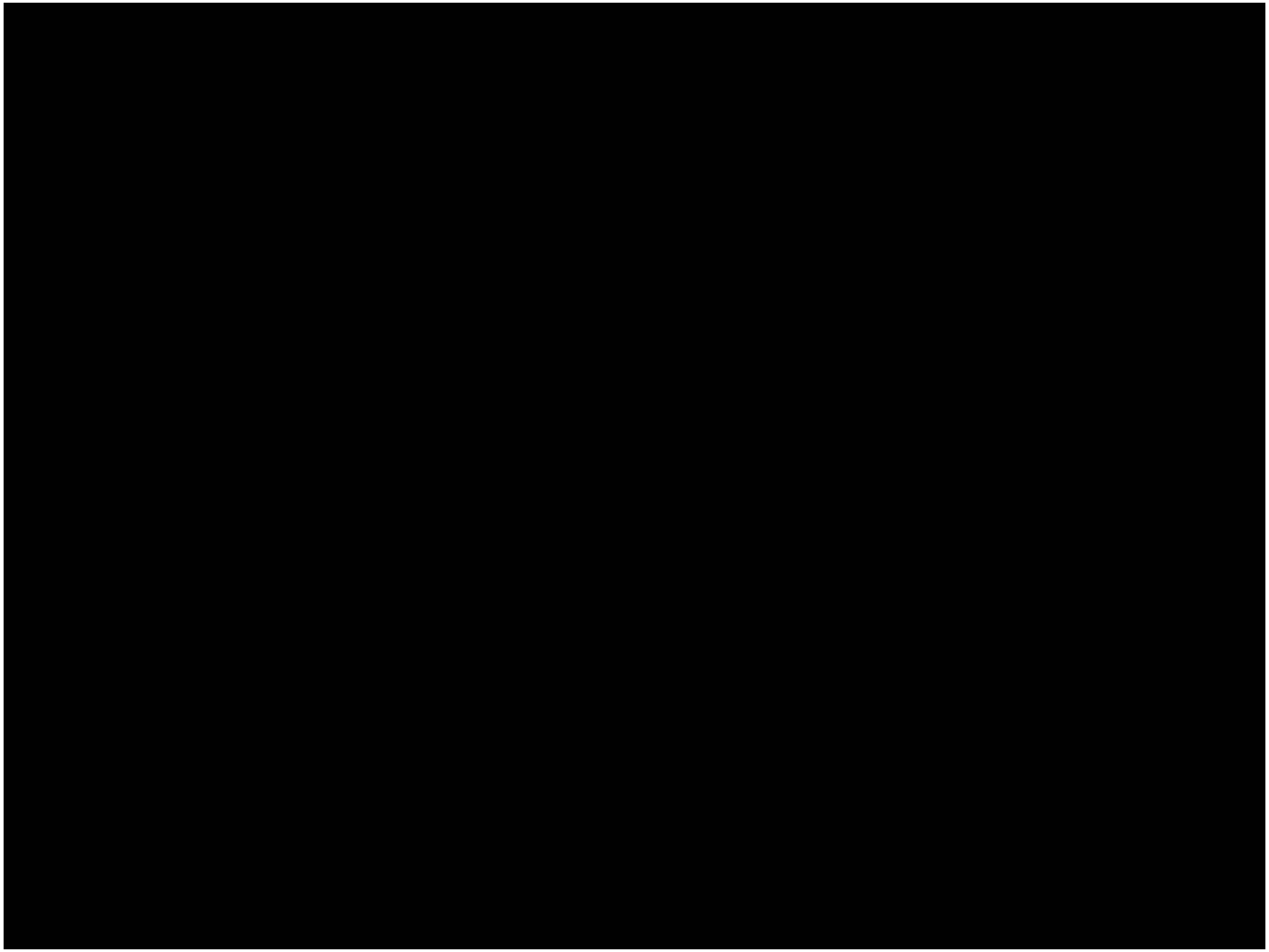
[as % of Original Shape]



Stress-Strain Curve



Bouncing bearing on Liquid Metals



Stainless **BMG** **Ti alloy**

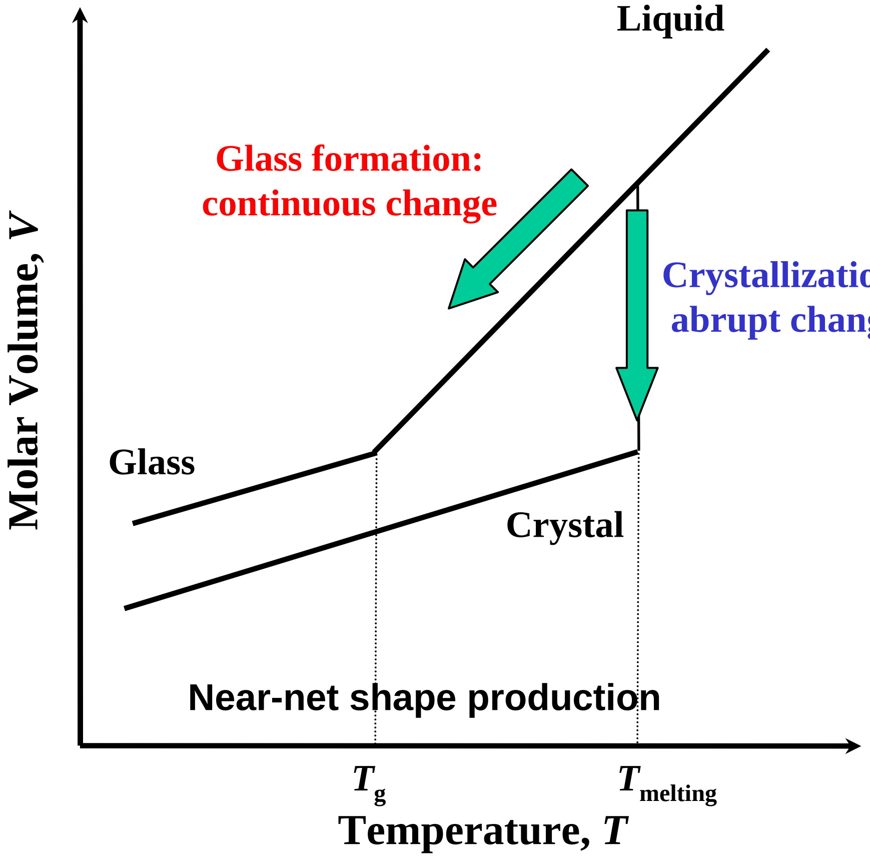
(Liquidmetal®)

Introduction_Amorphous Materials

- ***Unique Properties*:**

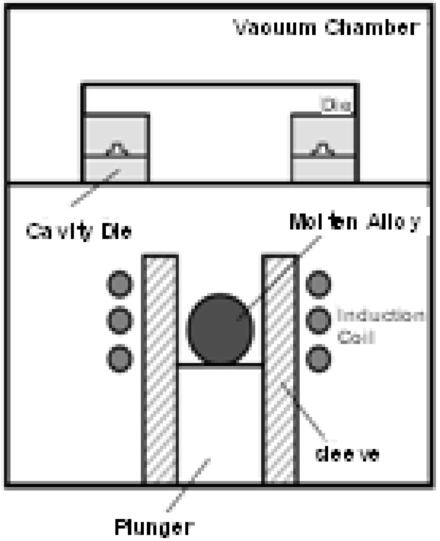
  - not shared by crystalline solids at all

4) thermal expansion coeff.: ~ zero

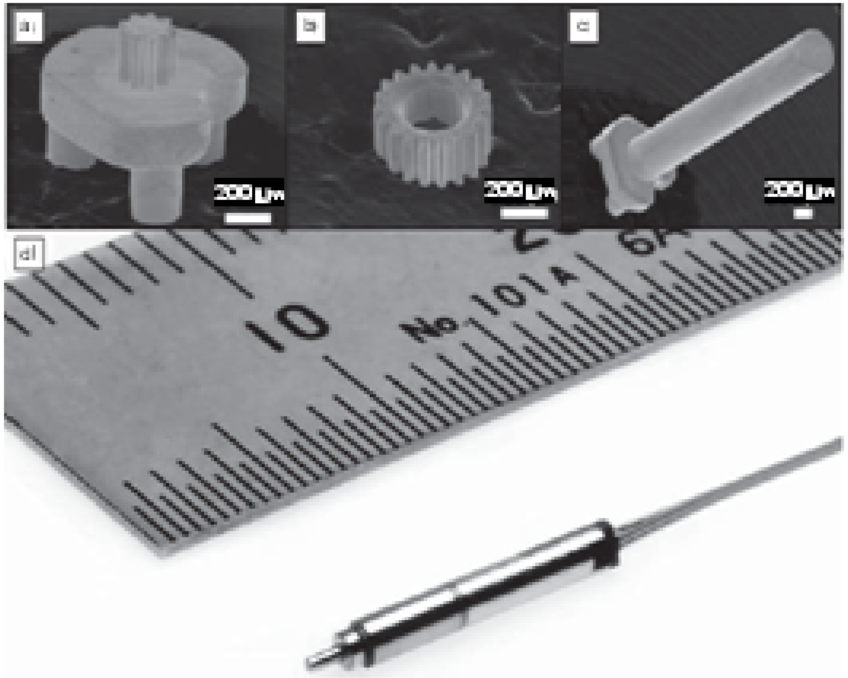


processing metals as efficiently as plastics

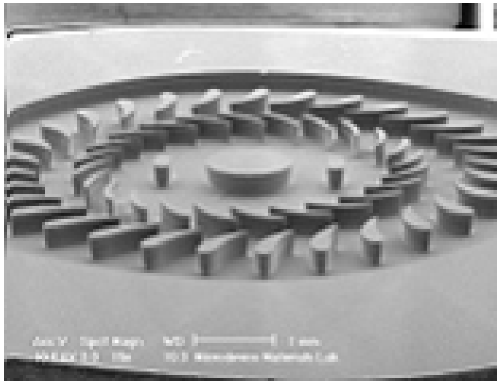
Micro-casting

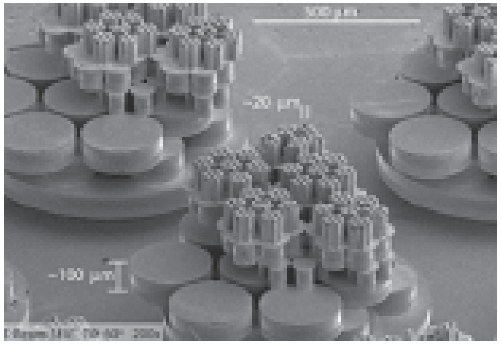


Precision die casting



Precision Gears for Micro-motors





MRS BULLETIN 32 (2007) 654.

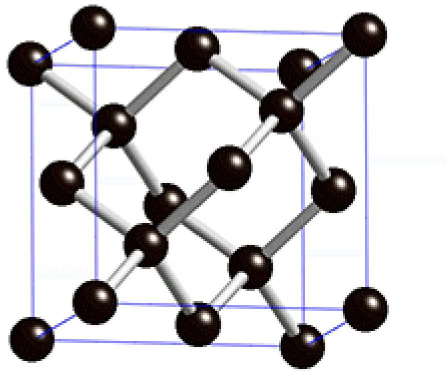
Introduction_Amorphous Materials

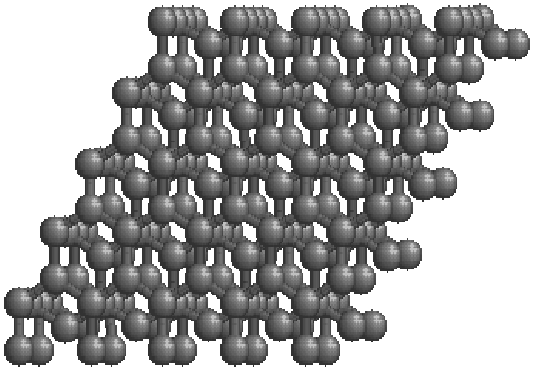
- ***Unique Properties*:**

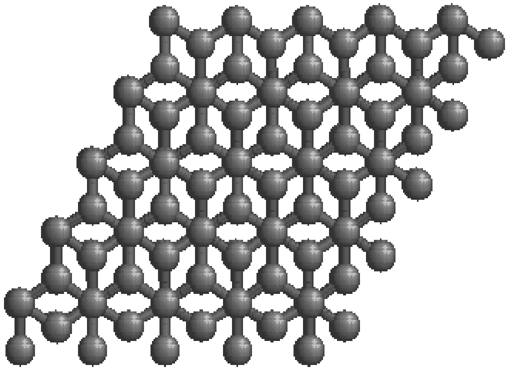
  - not shared by crystalline solids at all

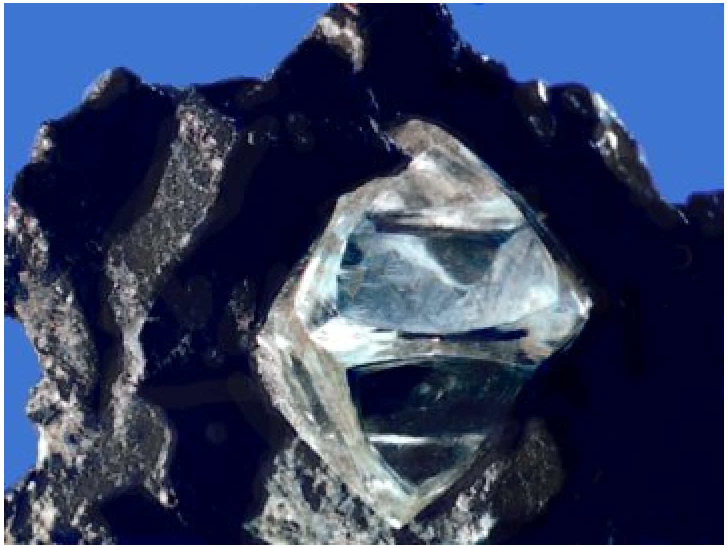
5) electrical resistivity

Allotropes of carbon









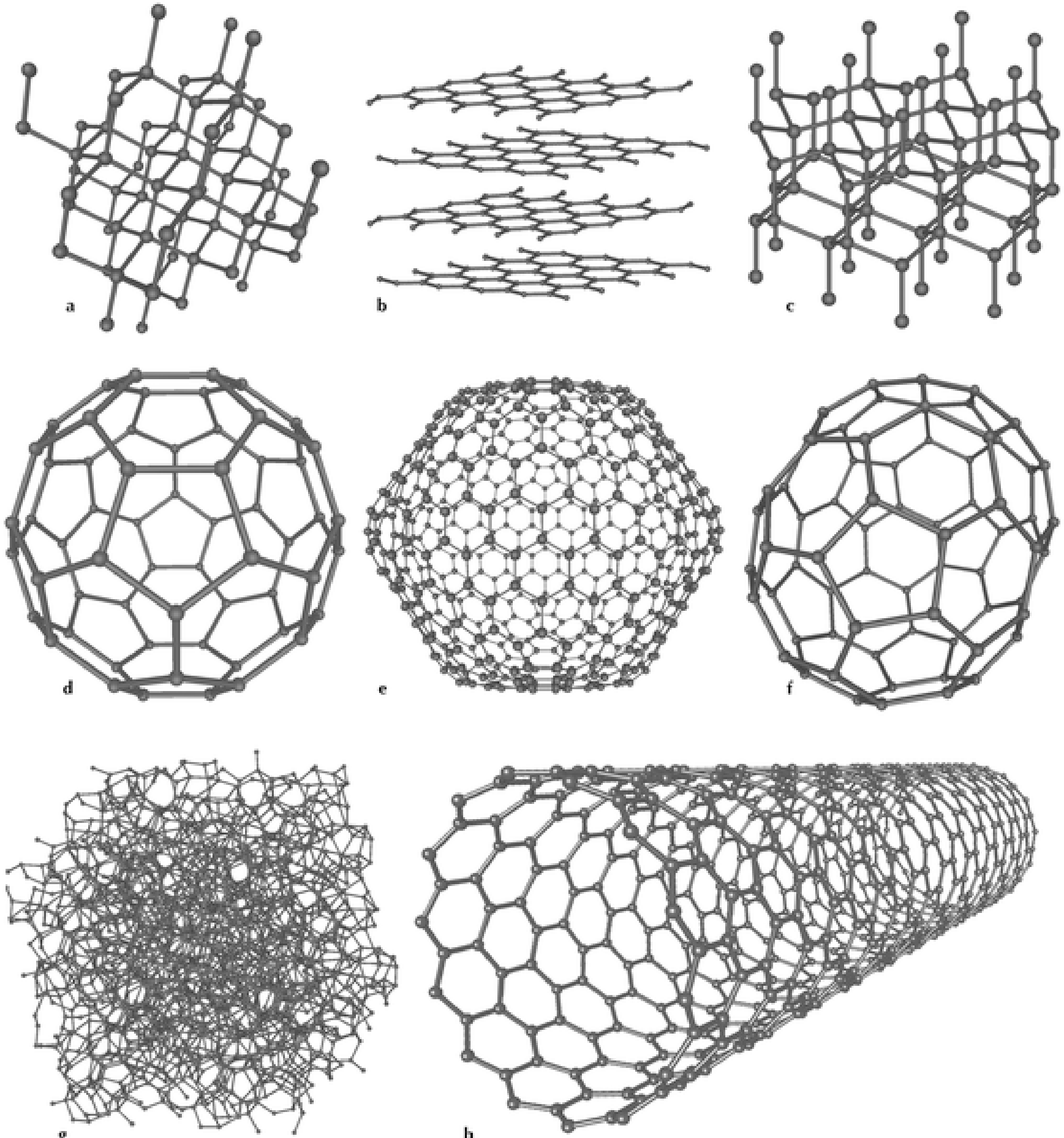
ex) diamond

ex) carbon

Allotropes of carbon

Eight allotropes of carbon: diamond, graphite, lonsdaleite, C60, C540, C70, amorphous carbon and a carbon nanotube.

http://en.wikipedia.org/wiki/Allotropes_of_carbon

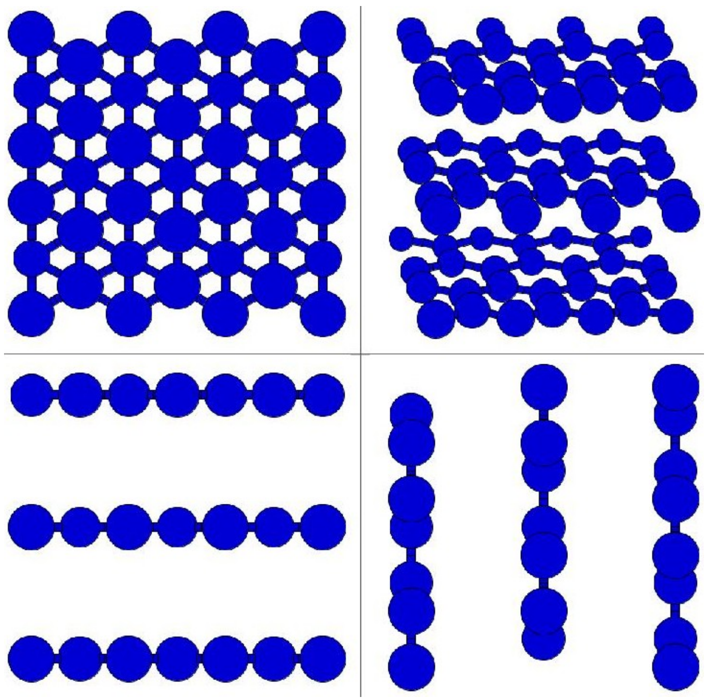


Introduction_Amorphous Materials

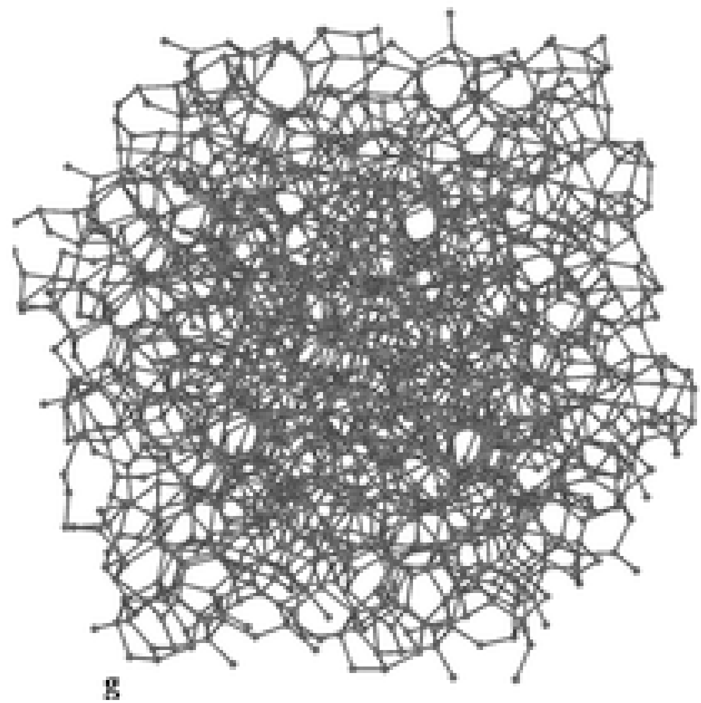
- ***Unique Properties*:**

  - not shared by crystalline solids at all

5) electrical resistivity ***3~4 times higher than crystalline alloy***



Crystalline carbon (graphite)



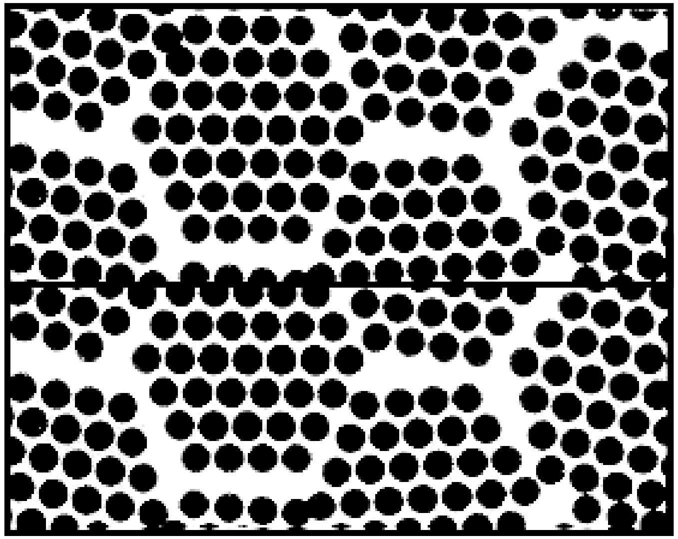
Amorphous carbon

Introduction_Amorphous Materials

- ***Unique Properties*:**

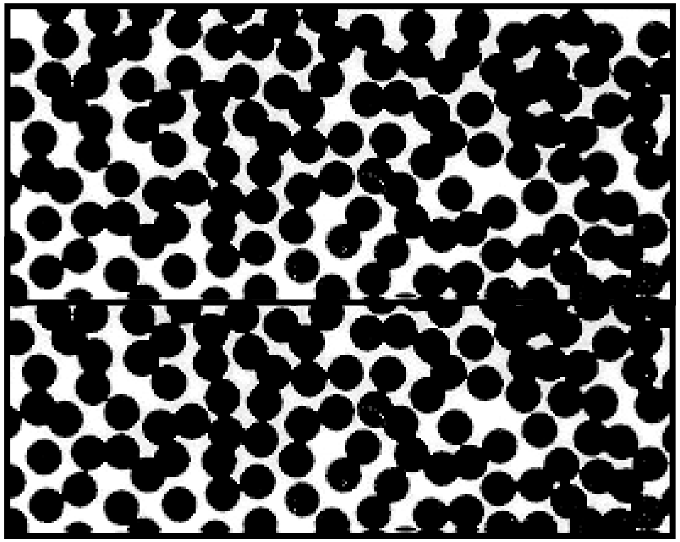
  - not shared by crystalline solids at all

6) corrosion resistance



Crystals

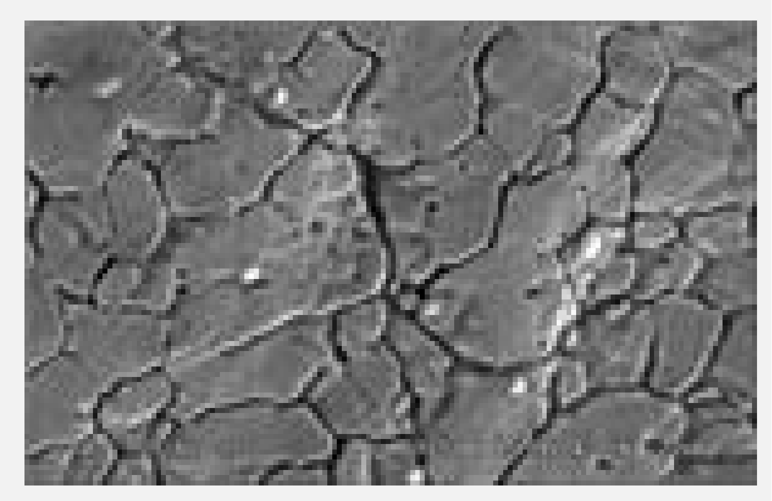
• grain boundaries



Liquids, glasses

• no grain boundaries

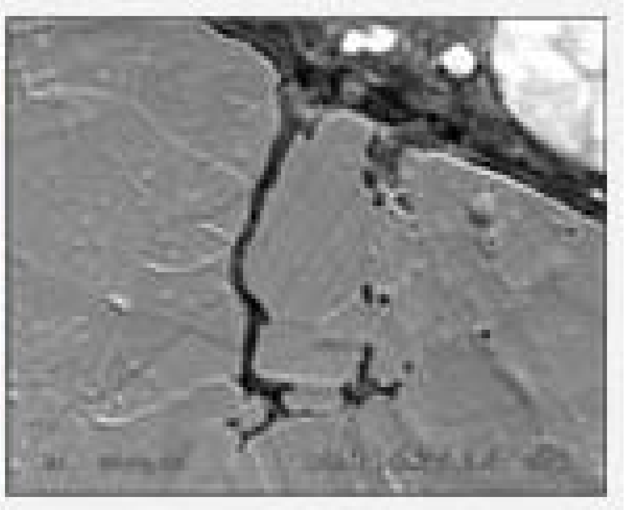
- Grain boundary corrosion



SEM micrograph

showing severe grain boundary corrosion

The sensitized structure lends itself to intergranular corrosion as shown below.



(Left) Optical micrograph showing intergranular corrosion from the outer diameter to sub-surface.

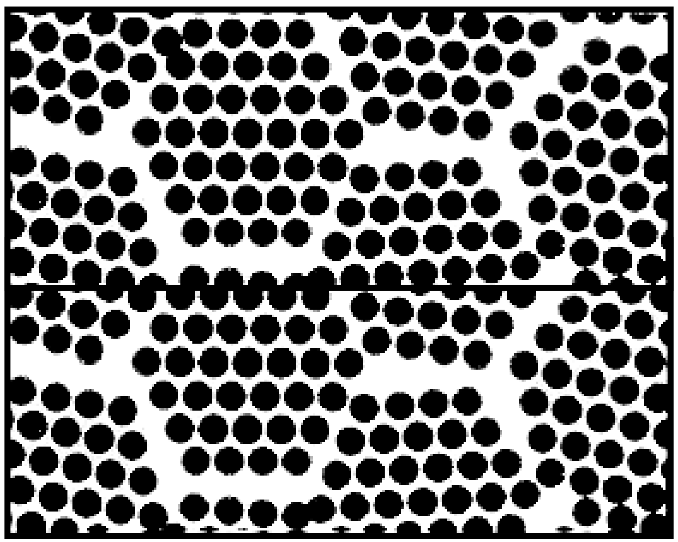
(Right) SEM micrograph of the same region.

Introduction_Amorphous Materials

- ***Unique Properties*:**

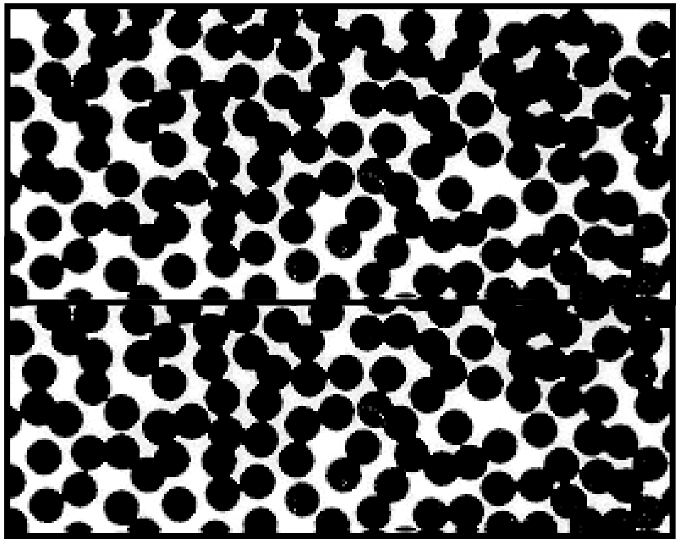
  - not shared by crystalline solids at all

6) exceptionally high corrosion resistance



Crystals

• **grain boundaries**



Liquids, glasses

• **no grain boundaries**

Introduction_Amorphous Materials

- ***Unique Properties*:**

- not shared by crystalline solids at all

1) very soft magnetic material

- low magnetic loss

2) very hard, high strength

very brittle

3) large elastic strain limit

4) thermal expansion coeff.: ~ zero

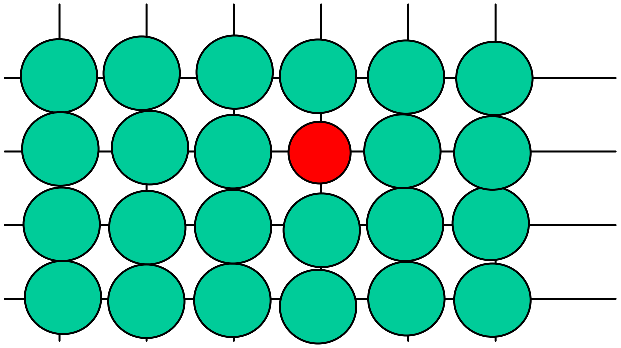
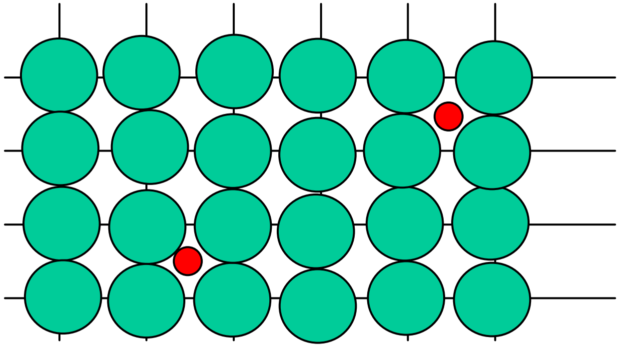
5) electrical resistivity

3~4 times higher than crystalline alloy

6) exceptionally high corrosion resistance

Alloying: atoms mixed on a lattice
Solid Solutions and Ordered Compounds

Two Possibilities for Solid Solutions: B atoms in A atoms

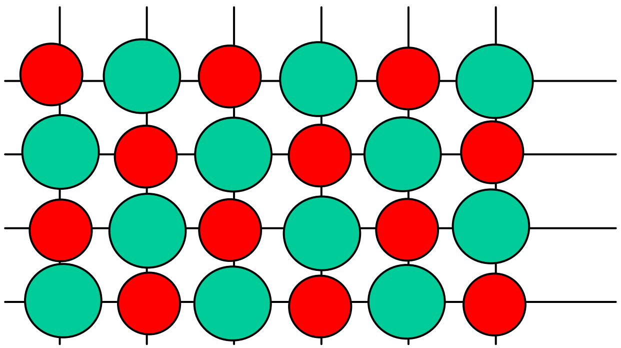
Substitutional	**Interstitials**
'new element replaces host atoms'	**'new element goes in holes'**
	
e.g. Ni in Cu, steels	e.g. semiconductor devices: doped-Si C in Fe

Can we roughly estimate what atoms will form solid solutions?

Alloying: atoms mixed on a lattice
Solid Solutions and Ordered Compounds

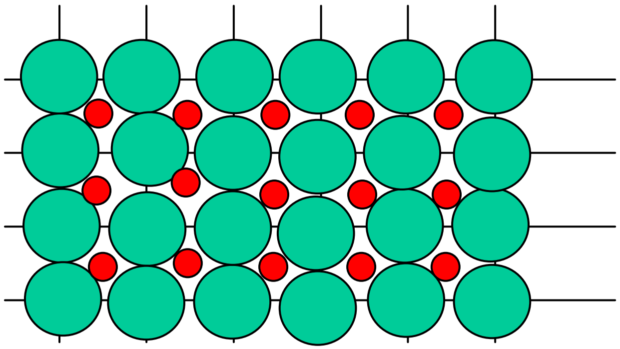
Ordered Substitutional and Interstitititials Compounds

Substitutional
element replaces host atoms in an orderly arrangement



e.g., Ni_3Al (hi-T yield strength), $Al_3(Li,Zr)$ (strengthening)

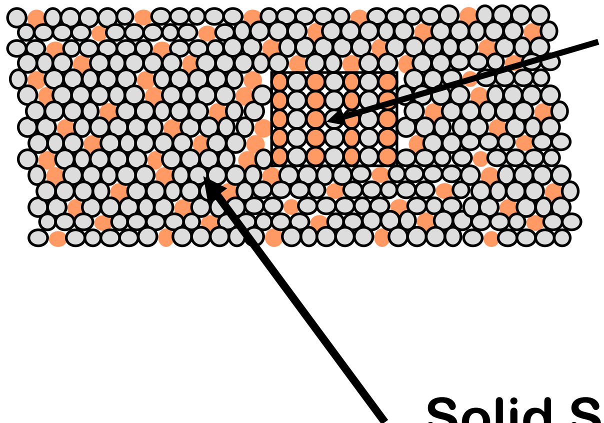
Interstitial
element goes into holes in an orderly arrangement



e.g., small impurities, clays ionic crystals, ceramics.

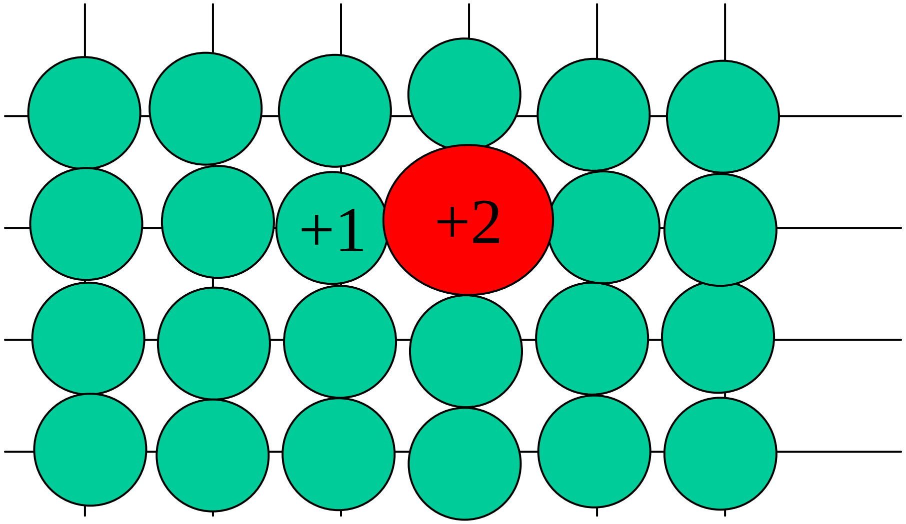
Particles of New Phase in Solid-Solution Alloys

- **Solid solution of B in A plus particles of a new phase (usually for a larger amount of B)**



Hume-Rothery Rules for Alloys (atoms mixing on a lattice)

Will mixing 2 (or more) different types of atoms lead to a solid-solution phase?



Empirical observations have identified 4 major contributors through :

Atomic Size Factor , Crystal Structure, Electronegativity, Valences

Hume-Rothery Rules for Mixing

Empirical rules for substitutional solid-solution formation were identified from experiment that are not exact, but give an expectation of formation. Briefly,

1) Atomic Size Factor **The 15% Rule**

If "size difference" of elements are greater than ±15%, the lattice distortions (i.e. local lattice strain) are too big and solid-solution will not be favored.

$$\text{DR\%}= \frac{r_{solute} - r_{solvent}}{r_{solvent}} \text{x}100\%$$

< ±15% will <u>not disallow</u> formation.

2) Crystal Structure **Like elemental crystal structures are better**

For appreciable solubility, the crystal structure for metals must be the same.

3) Electronegativity **DE ~ 0 favors solid-solution.**

The more electropositive one element and the more electronegative the other, then "intermetallic compounds" (order alloys) are more likely.

4) Valences **Higher in lower alright. Lower in higher, it's a fight.**

A metal will dissolve another metal of higher valency more than one of lower valency.

Hume-Rothery Empirical Rules In Action

Is solid-solution favorable, or not?

- **Cu-Ni Alloys**

Rule 1: r_{Cu} = 0.128 nm and r_{Ni}= 0.125 nm.

DR%= $\dfrac{r_{solute} - r_{solvent}}{r_{solvent}} x100\%$ = 2.3% **favorable √**

Rule 2: Ni and Cu have the FCC crystal structure. **favorable √**

Rule 3: E_{Cu} = 1.90 and E_{Ni}= 1.80. Thus, DE%= -5.2% **favorable √**

Rule 4: Valency of Ni and Cu are both +2. **favorable √**

Expect Ni and Cu forms S.S. over wide composition range.

At high T, it does (helpful processing info), but actually phase separates at low T due to energetics (quantum mechanics).

Hume-Rothery Empirical Rules In Action

Is solid-solution favorable, or not?

- **Cu-Ag Alloys**

Rule 1: r_{Cu} = 0.128 nm and r_{Ag}= 0.144 nm.

DR%= $\frac{r_{solute} - r_{solvent}}{r_{solvent}} x100\%$ = 9.4% **favorable √**

Rule 2: Ag and Cu have the FCC crystal structure. **favorable √**

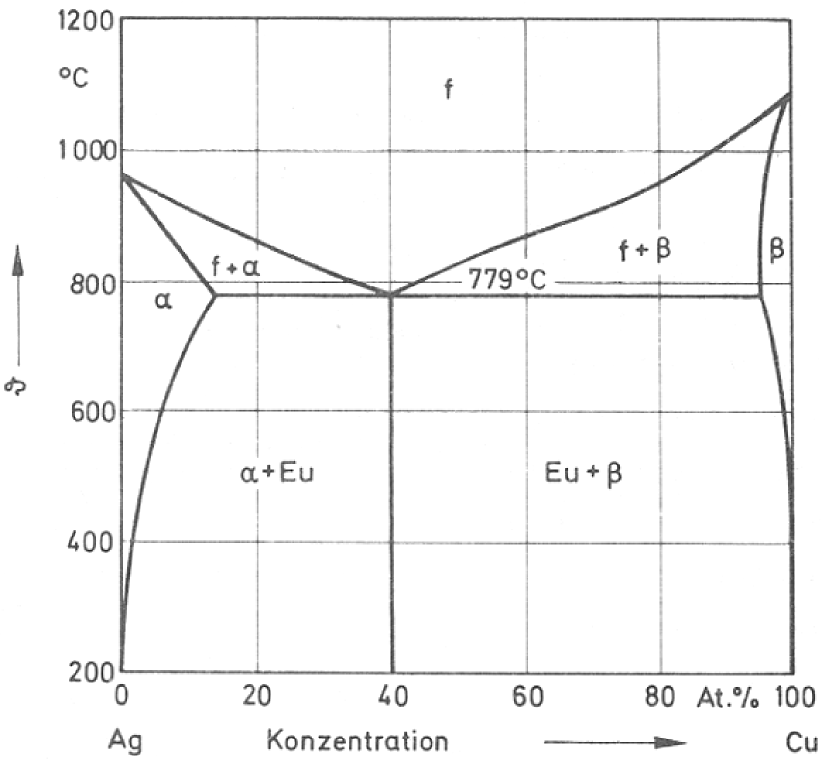
Rule 3: E_{Cu} = 1.90 and E_{Ni}= 1.80. Thus, DE%= -5.2% **favorable √**

Rule 4: Valency of Cu is +2 and Ag is +1. **NOT favorable**

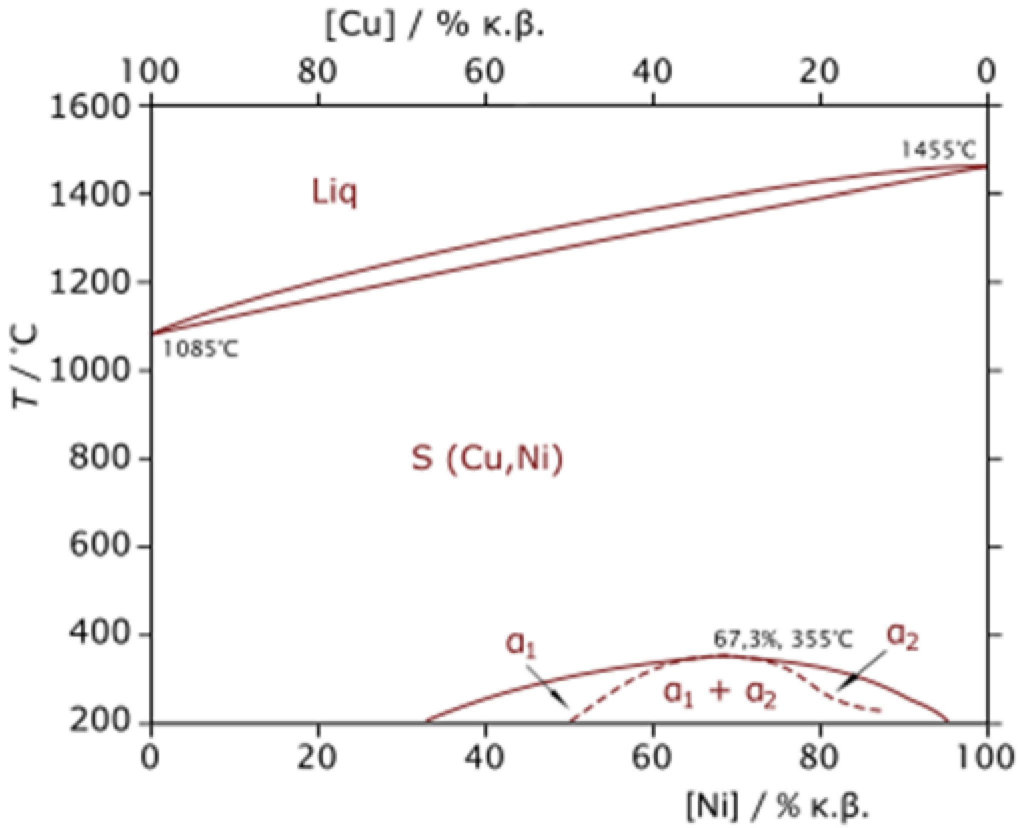
Expect Ag and Cu have limited solubility.

In fact, the Cu-Ag phase diagram (T vs. c) shows that a solubility of only 18% Ag can be achieved at high T in the Cu-rich alloys.

Cu-Ag Alloys



Cu-Ni Alloys



Introduction_Amorphous Materials

Ex) Application of amorphous alloy systems

1) Magnetic amorphous alloy (ribbon)

- transition metal-metalloid (TM-M) alloys rapid quenching
- RE-TM alloys sputtering
- TM-Zr(Hf) alloys rapid quenching

⋮

role of metalloid element (ex. B) : lower melting point

2) Amorphous alloy as brazing filler (ribbon)

ex) Ni-based amorphous alloy

- for almost all metal without binder