2010 Spring

“Amorphous Materials”

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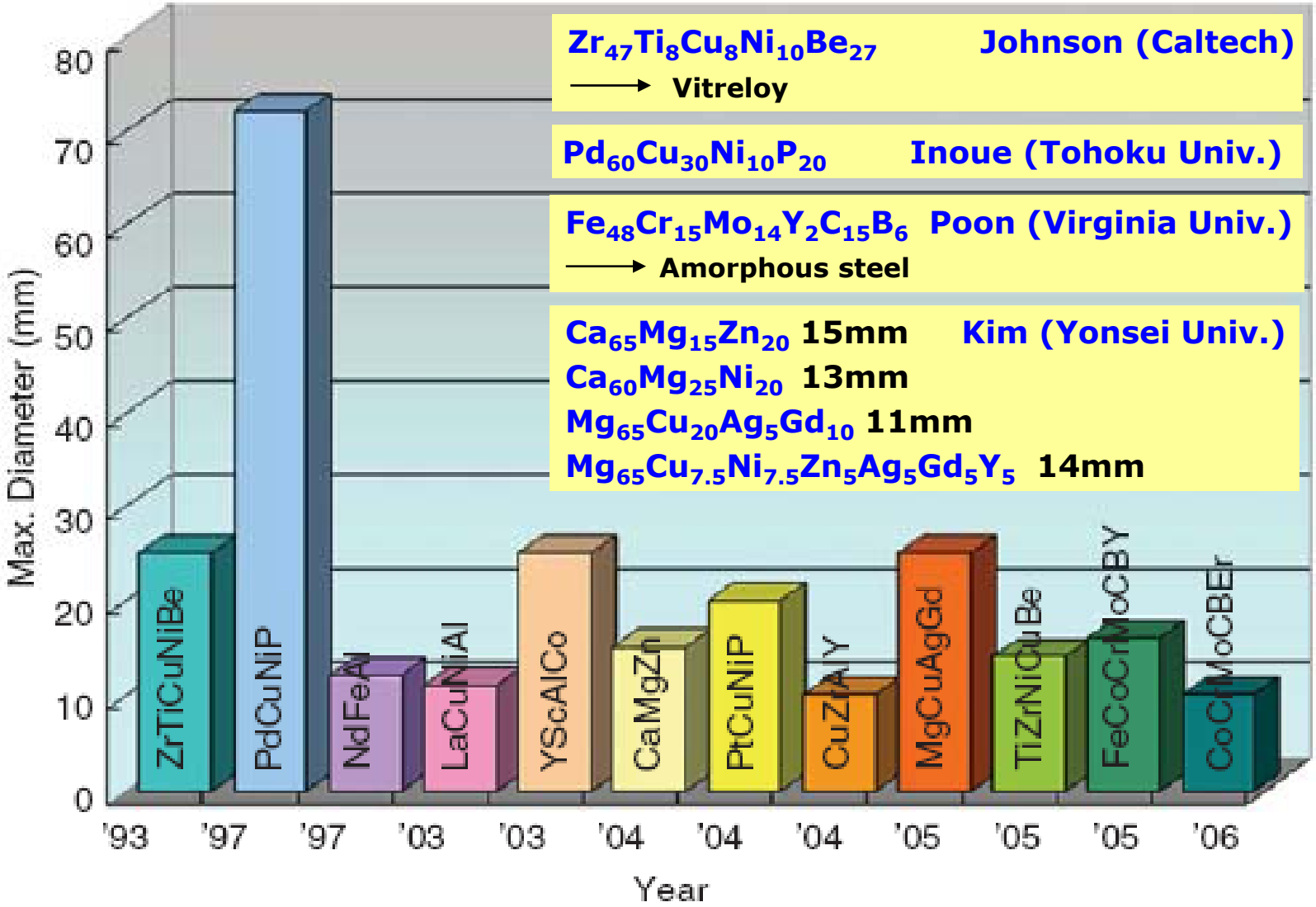
Recent BMGs with critical size ≥ 10 mm

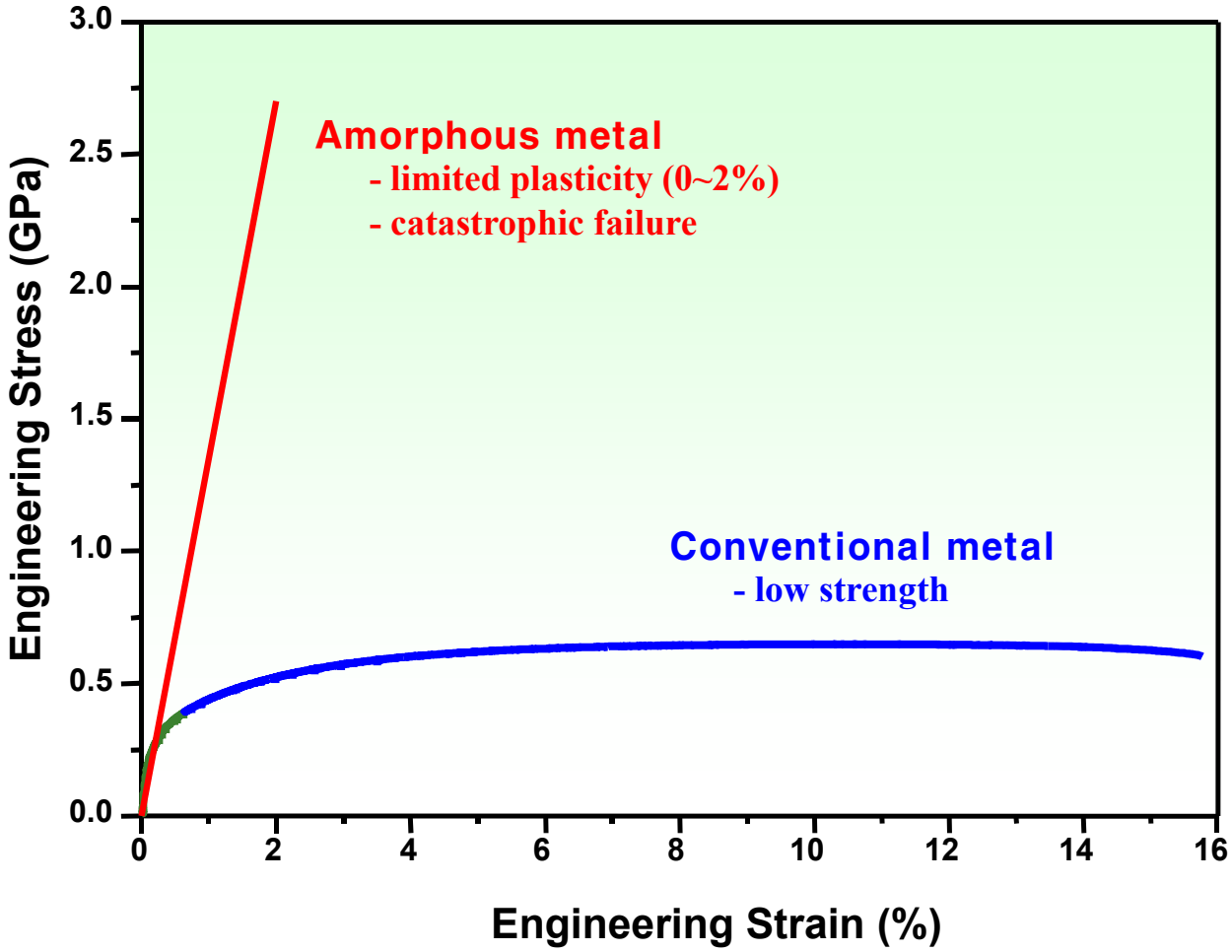


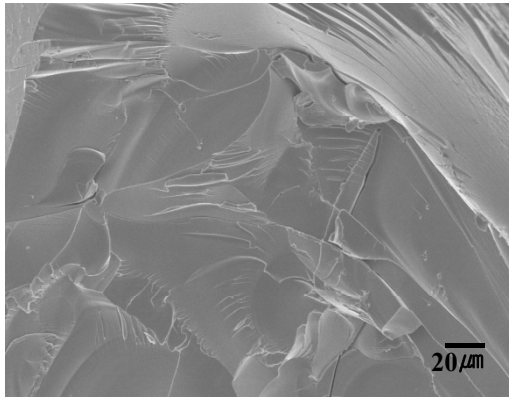
A.L. Greer, E. Ma, MRS Bulletin, 2007; 32: 612.

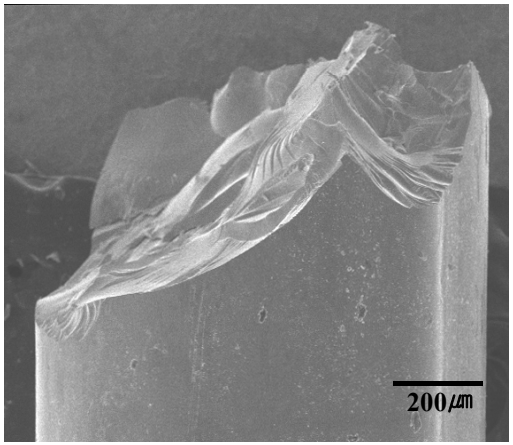
Limited Plasticity by shear softening and shear band

- **Microscopically brittle fracture**

  ➡ **Death of a material for structural applications**







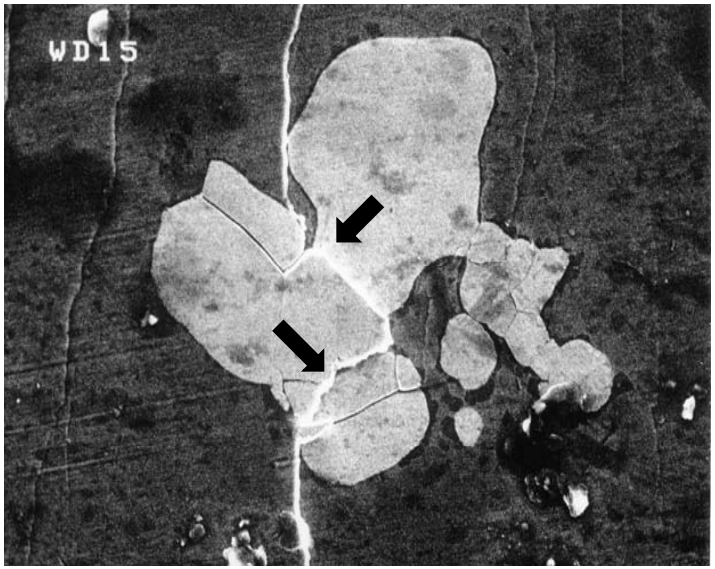
Plastic deformation in metallic glasses

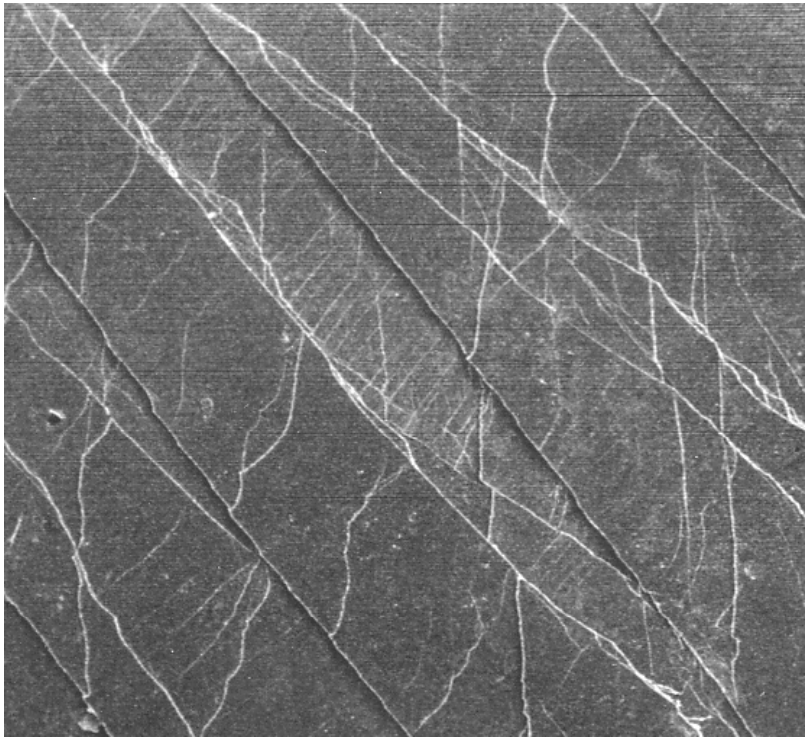
Plastic deformation in metallic glass

- *No* dislocation / *No* slip plane
- Inhomogeneously localized plastic flow in the shear band

interrupt the localization of stress and deformation

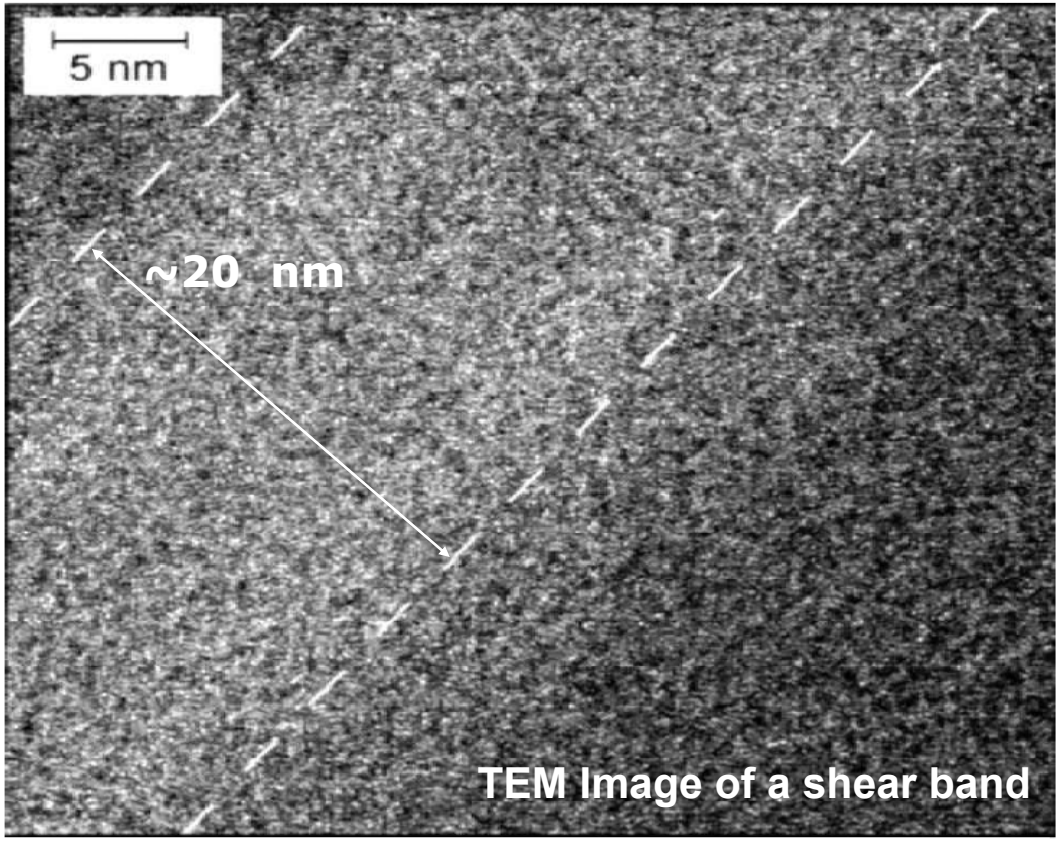
- Prevent propagation of single shear band → BMG matrix composites
- Multiple shear band formation





Size of heterogeneity

Shear bands are ~20 nm in width



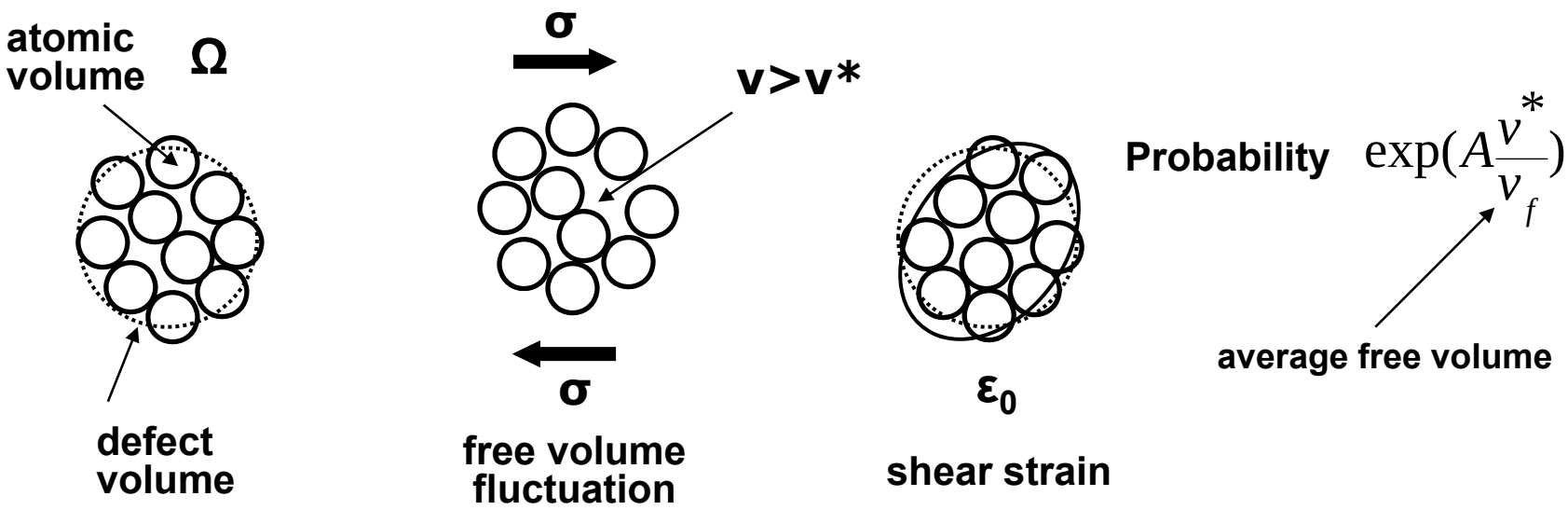
- **Prevent propagation of single shear band**

➡ **Micro- or nanometer scale heterogeneity**

: In-situ & Ex-situ composite

Size of heterogeneity

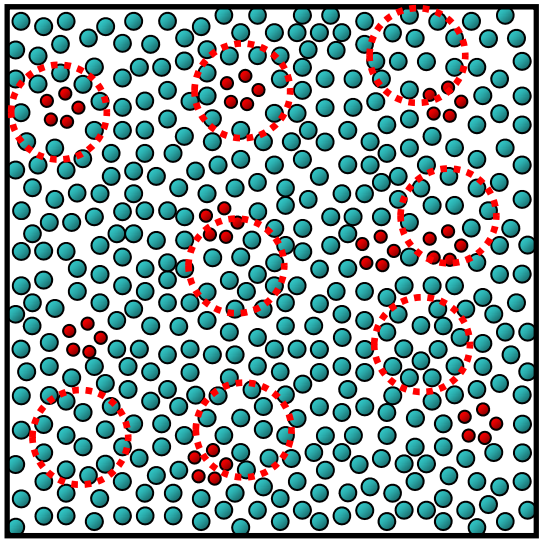
- Elementary flow event in an metallic glasses



Flow governed by localized defect (~10 atoms) and creates defects

atomic scale heterogeneity

$$\eta = \eta_0 \exp\left\{ A \frac{V_0}{V_f} \right\}$$



Viscosity measurement /
Fragility index calculation

Enhancement plasticity in BMGs with atomic scale heterogeneity

a) Effect of quenched-in quasicrystal nuclei

b) Effect of element with positive enthalpy of mixing among constituent elements

c) Effect of element with significantly different enthalpy of mixing among constituent elements

- Atomic scale heterogeneity

⇨ SB nucleation sites ⇨ Formation of multiple SB

- **Tailoring of structural inheterogeneity**

Alloy design + **Process control**

atomic scale inhomogeneity generation — Solidification under appropriate condition

Phase separation in metallic glasses

- A New class of BMG composites -

[1] Phase separation in solid state

- Pd-Si-Ag alloy / two amorphous phase formation after heating just above T_g

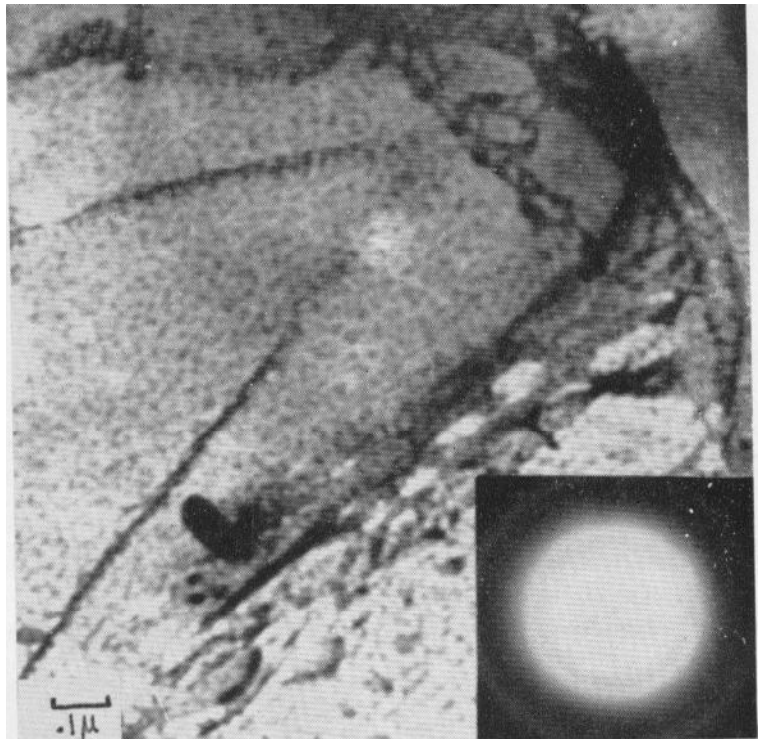
Chen and Turnbull, Acta Metall., 17, 1021 (1969)

- Zr-Ti-Cu-Ni-Be BMG / small angle neutron scattering

Schneider et al, Appl. Phys. Lett., 68, 493 (1996)

- Local composition change due to partitioning of alloying elements

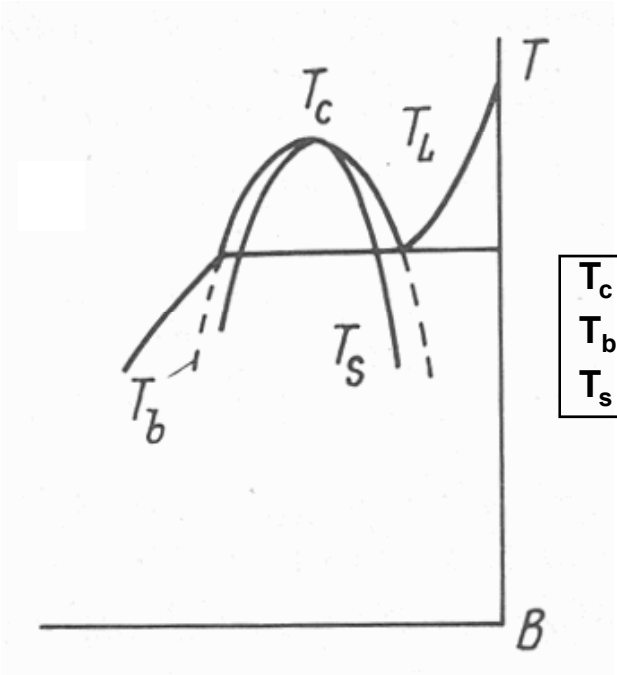
Martin et al., Acta Mater., 52, 4427 (2004)



- After heating just above T_g, two amorphous separation occurs, but crystallization occurs simultaneously.

[2] Phase separation in liquid state

- **Stable immiscibility**

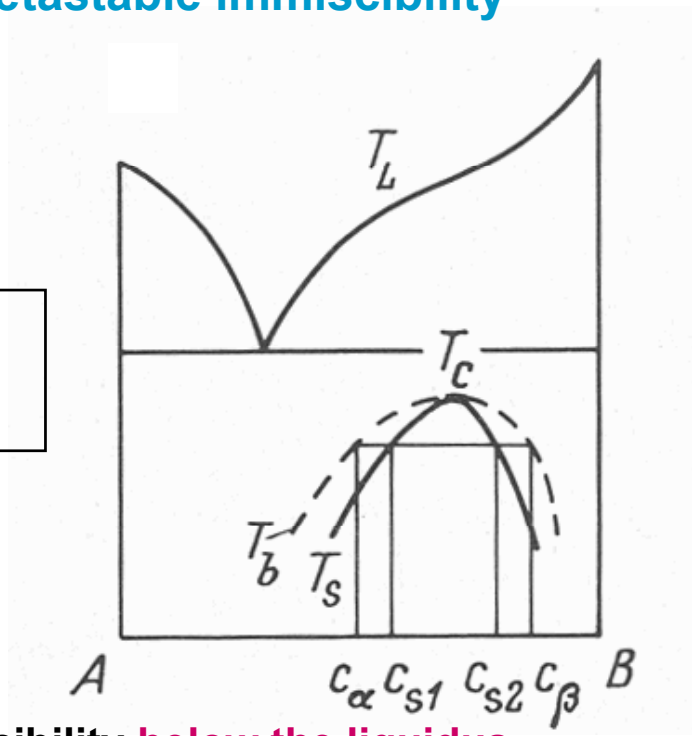


immiscibility above the liquidus

⇒ decomposition into stable liquid

T_c : critical temperature
T_b : binodal curve
T_s : spinodal curve

- **Metastable immiscibility**

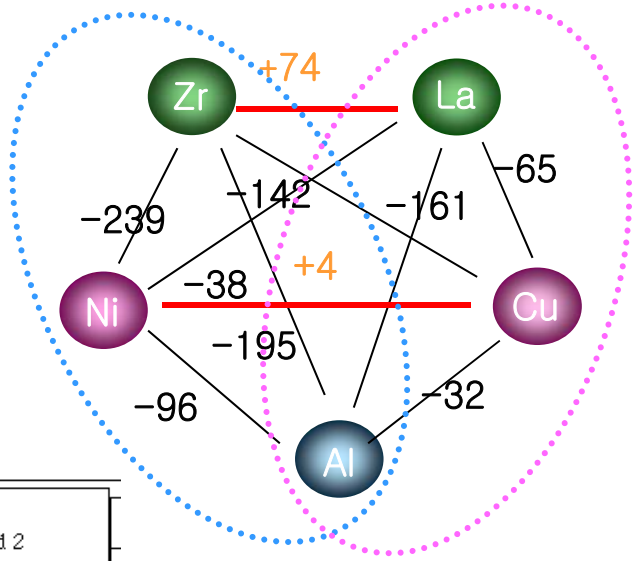


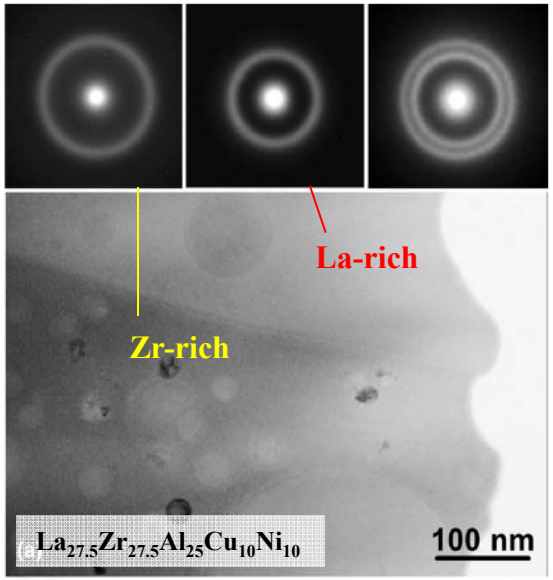
immiscibility below the liquidus

⇒ decomposition into metastable liquid

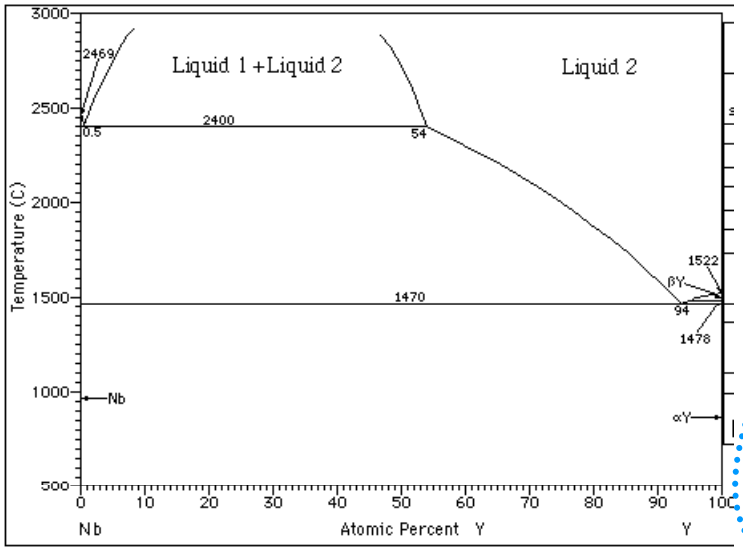
"Phase separation in glass" ed. by Mazurin and Porai-Koshits (1984)

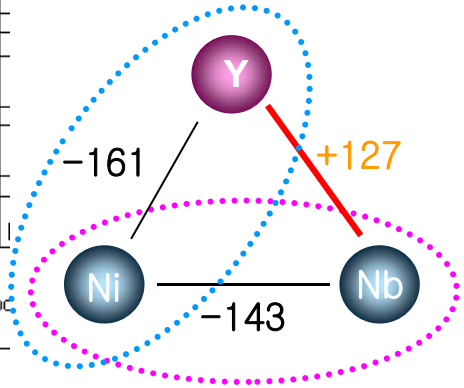
- **Previous studies**

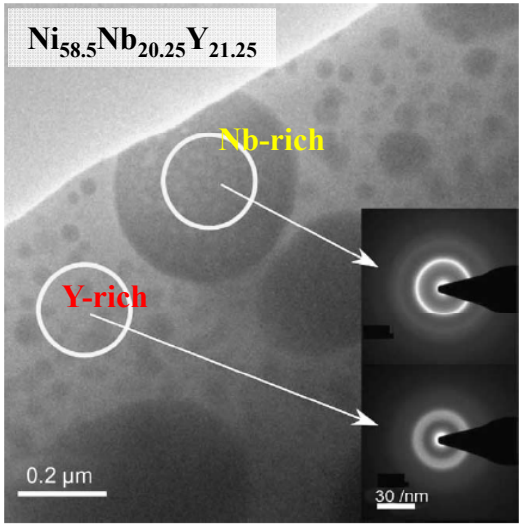




-Kundig et al. , Acta Mater., 52, 2441 (2004)





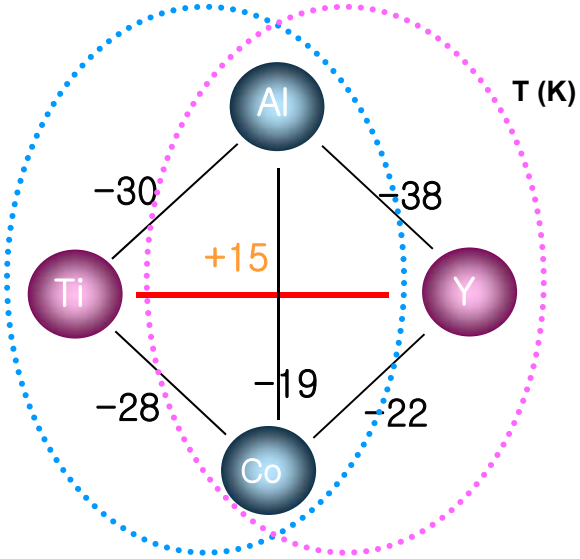


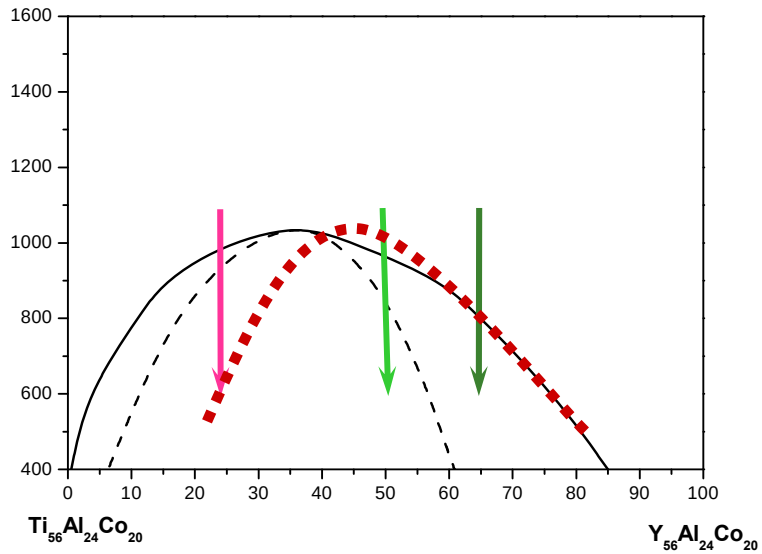
- N. Mattern et al. Scripta Mat. 53, (2005) 271

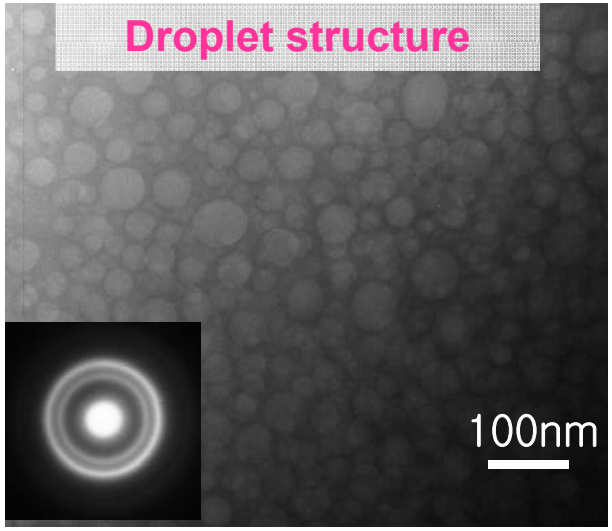
- **Two liquids at high temperature (liquid decomposition)**

  ⇒ **droplet structure**

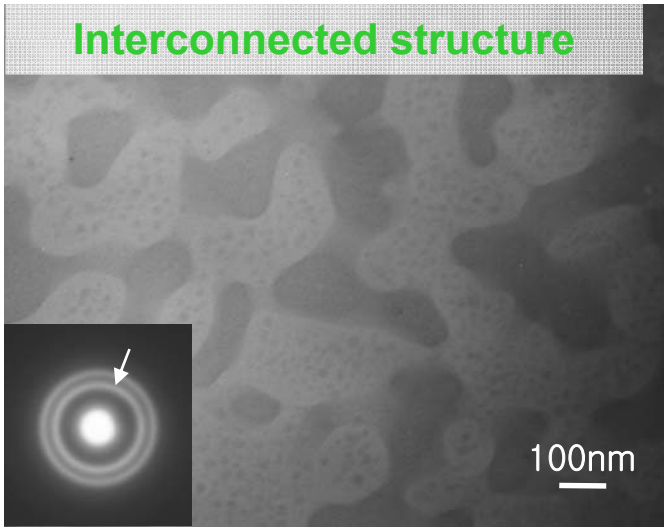
- **Previous studies**



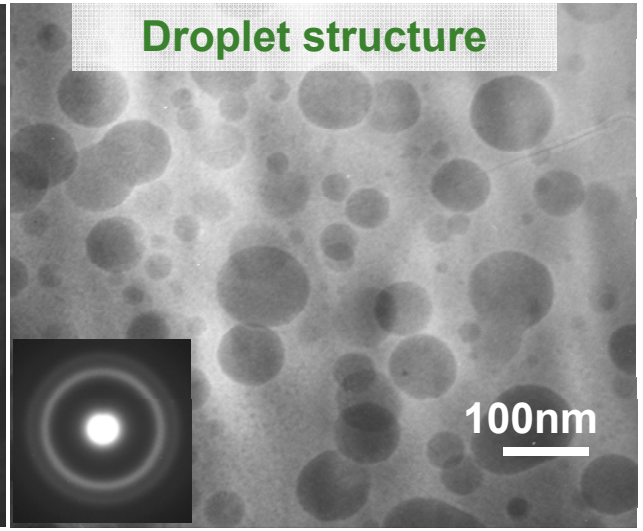




$(Y_{56}Al_{24}Co_{20})_{25}(Ti_{56}Al_{24}Co_{20})_{75}$



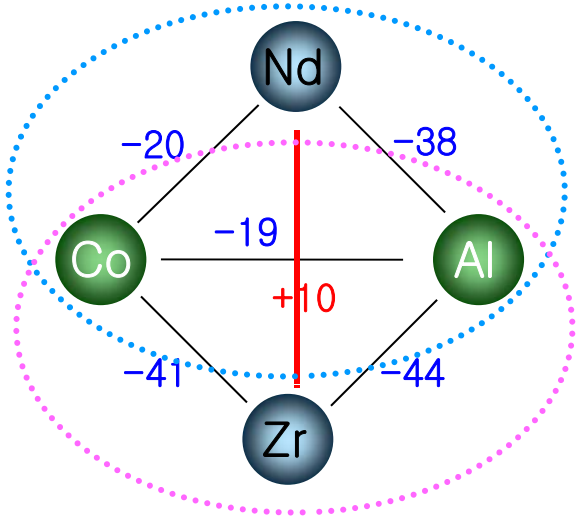
$(Y_{56}Al_{24}Co_{20})_{50}(Ti_{56}Al_{24}Co_{20})_{50}$



$(Y_{56}Al_{24}Co_{20})_{65}(Ti_{56}Al_{24}Co_{20})_{35}$

Phase separation by adding elements having PEM

*** Substitution of Nd with Zr in Nd-Co-Al system**



$Nd_{60}Al_{10}Co_{30}$ - 5mm

$Zr_{55}Al_{20}Co_{25}$ - 3mm

Possibility of two phase !!!

→ Nd-Co-Al, Zr-Co-Al

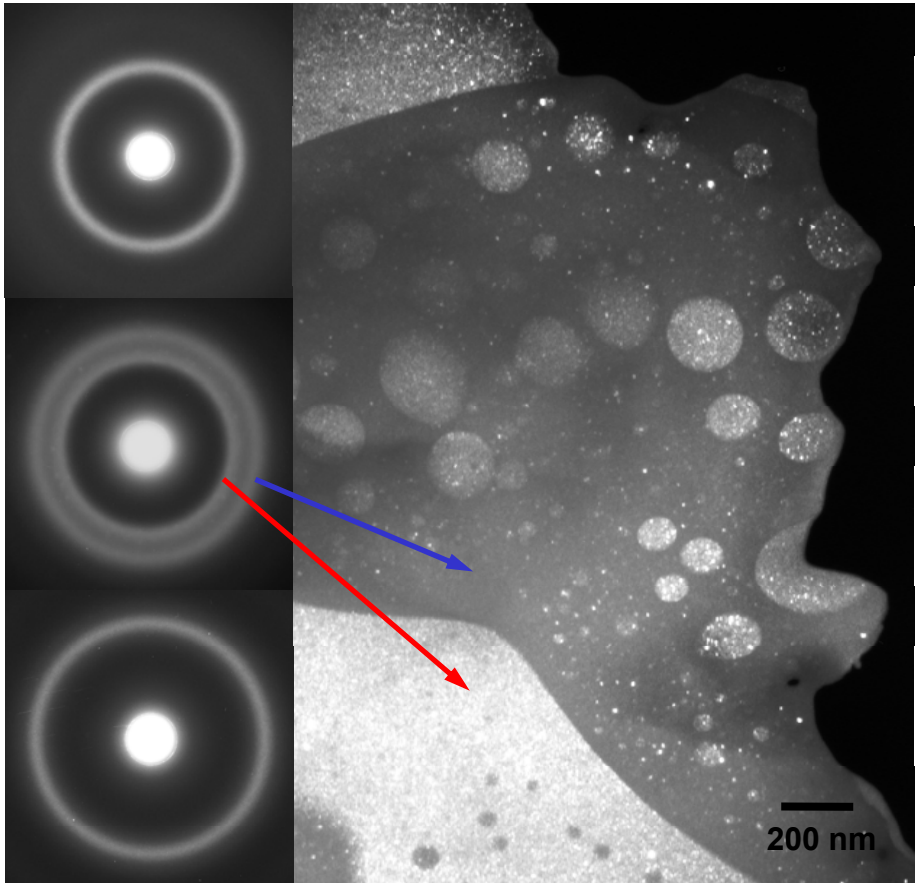
• Sripta Mater. 56, 197 (2007)

TEM results for $Nd_{30}Zr_{30}Al_{10}Co_{30}$ alloy

$Nd_{60}Al_{10}Co_{30}$
2.91 Å

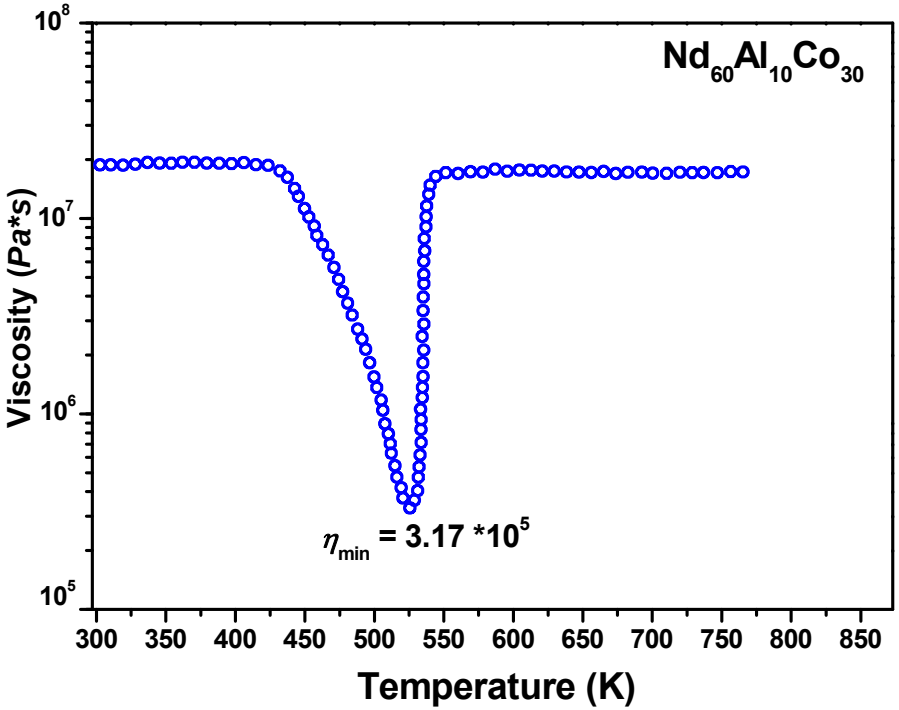
$Nd_{30}Zr_{30}Al_{10}Co_{30}$
2.37 Å, 2.99 Å

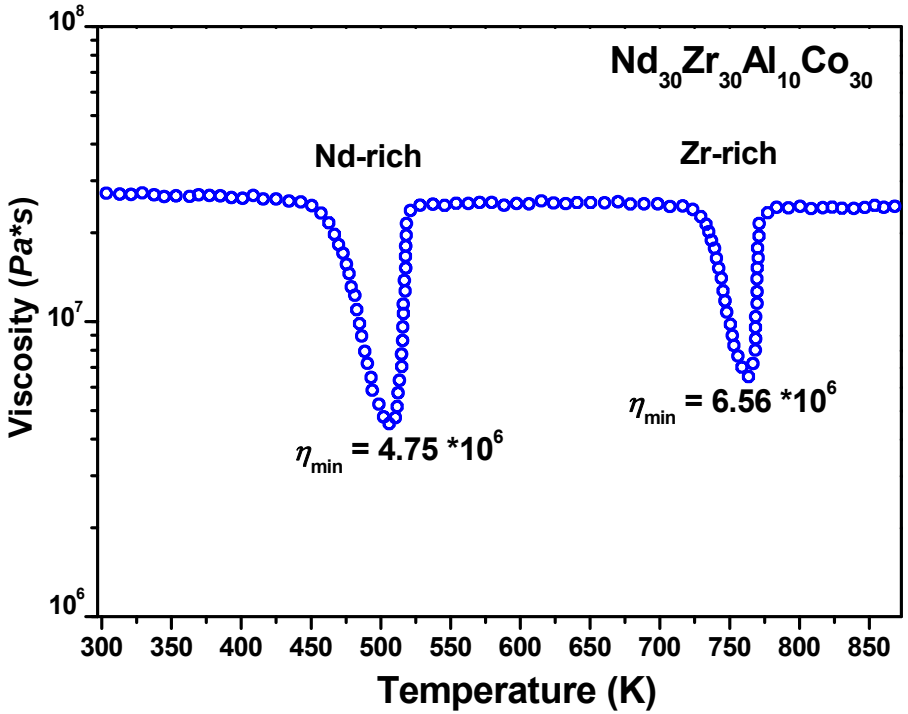
$Zr_{60}Al_{10}Co_{30}$
2.40 Å



SADP and Dark-field TEM image

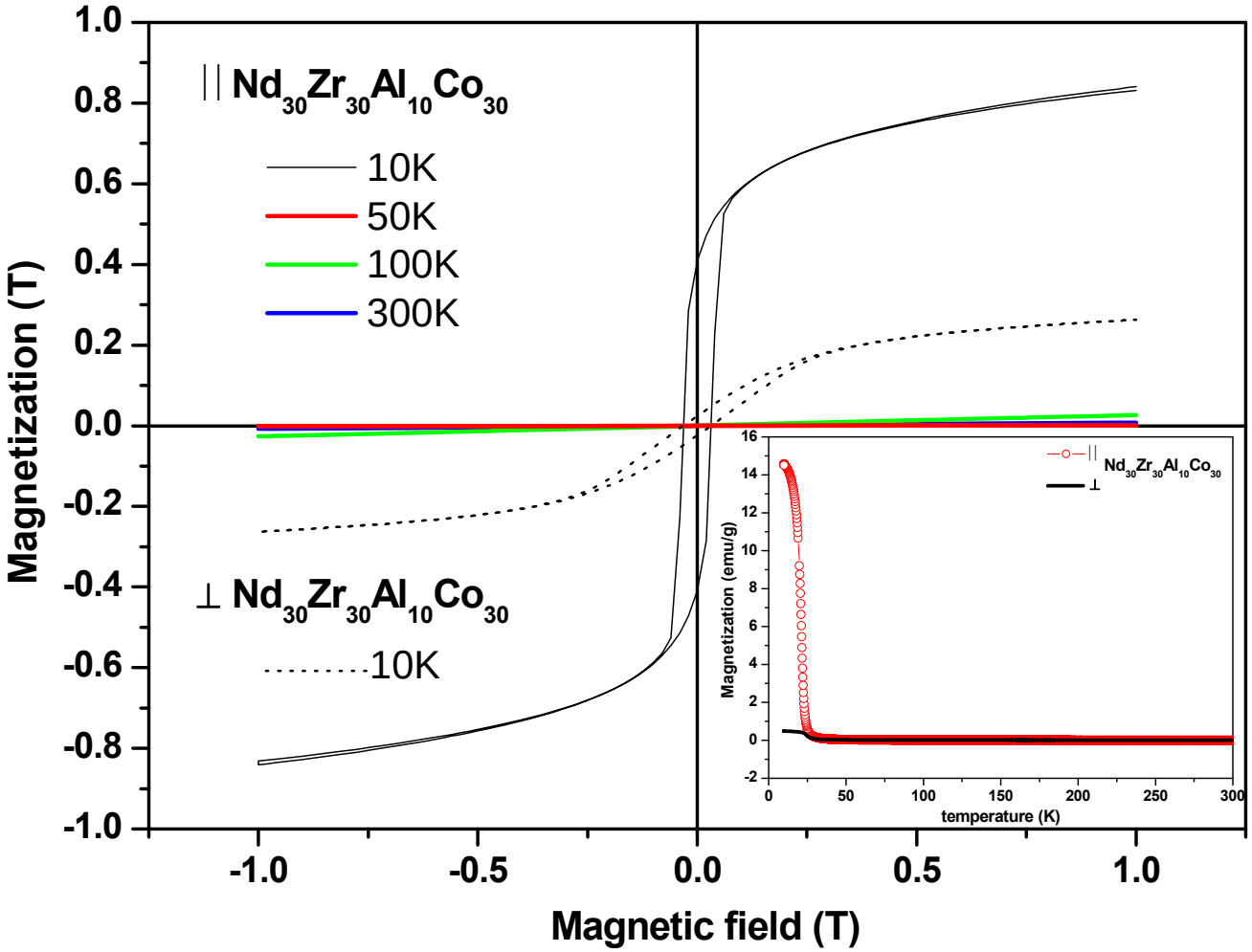
Measurement of viscosity using TMA





Selective partial devitrification (first SLR), followed by easy deformation of the amorphous/ crystalline composite structure (second SLR) is possible for this alloy system.

Measurement of magnetic property using VSM

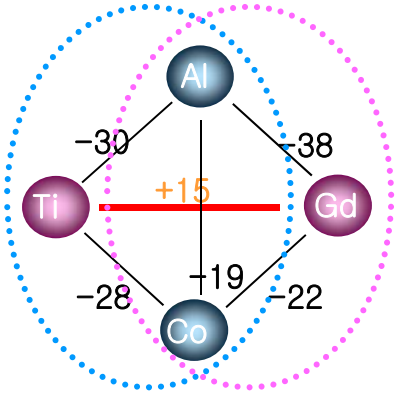


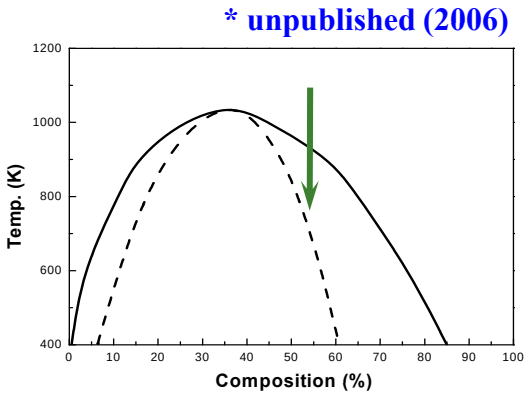
Directional changes of magnetic property in two-phase metallic glass

Phase separation

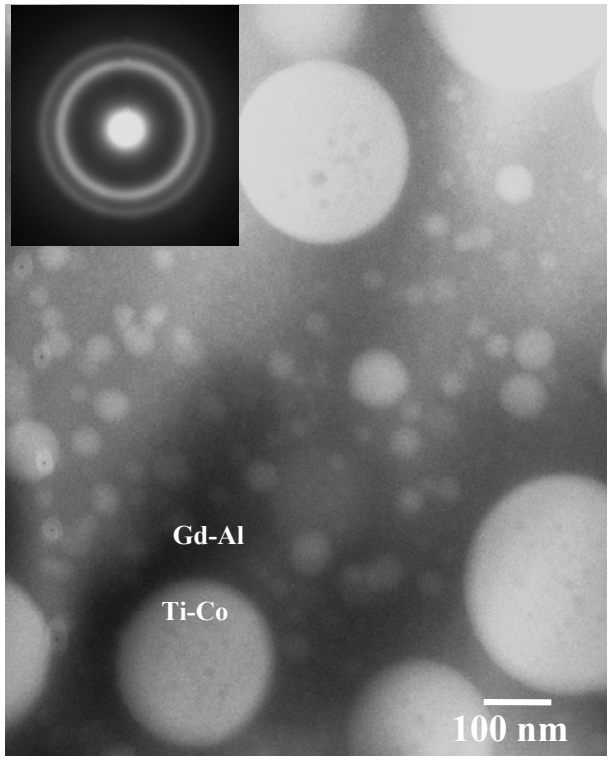
1) Droplet structure

in Gd-Ti-Al-(Co, Ni, Cu) alloy system

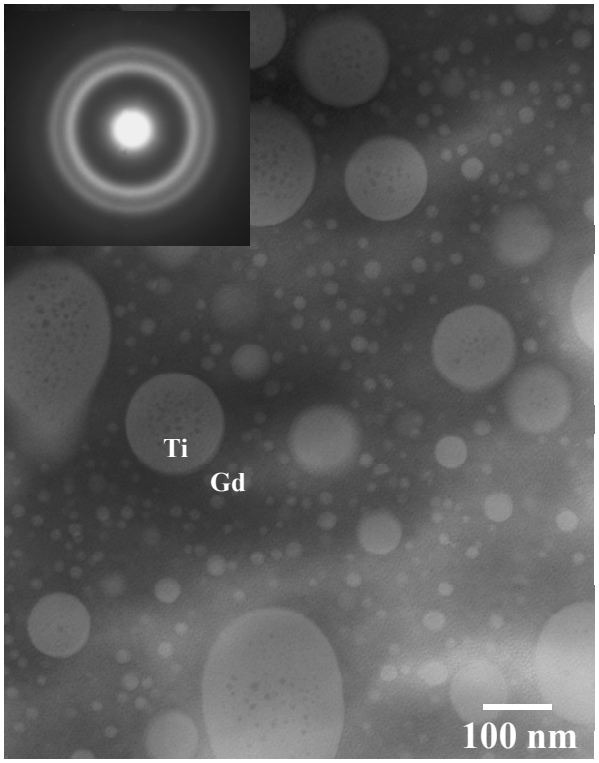




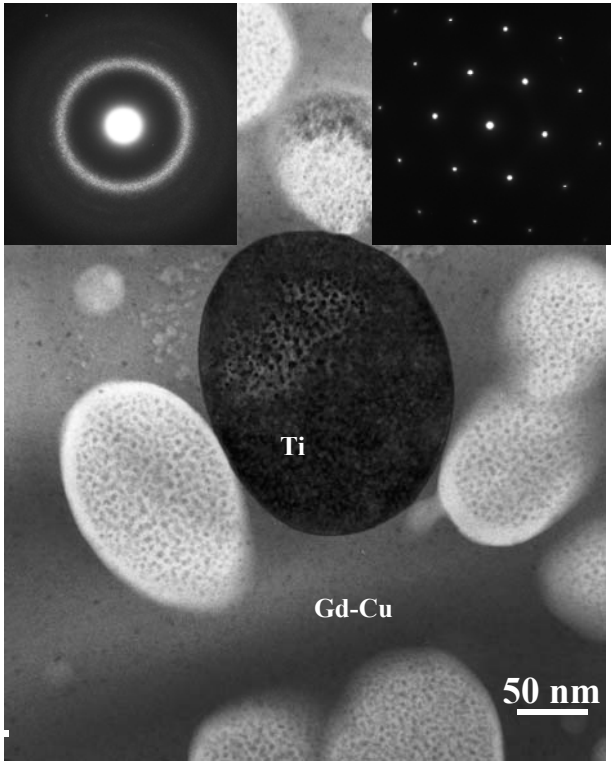
$Gd_{30}Ti_{25}Al_{25}Co_{20}$



$Gd_{30}Ti_{25}Al_{25}Ni_{20}$



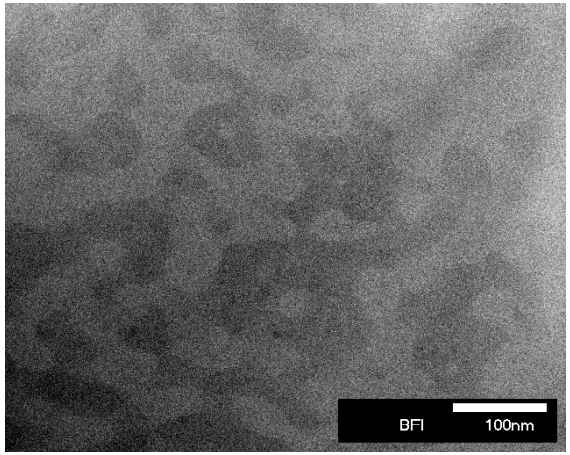
$Gd_{30}Ti_{25}Al_{25}Cu_{20}$

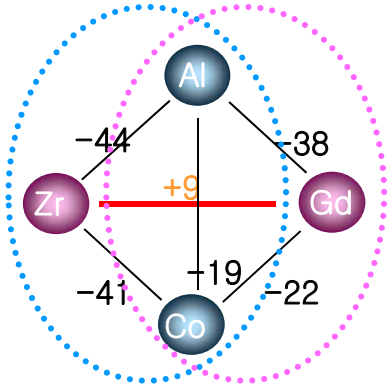


Phase separation

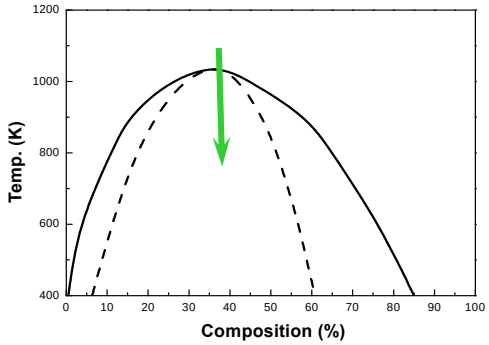
2) Interconnected structure

in Gd-Zr-Al-(Co, Ni, Cu) alloy system

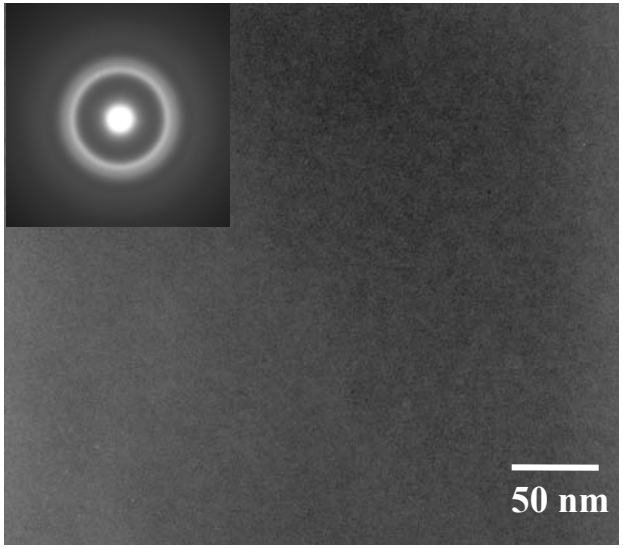




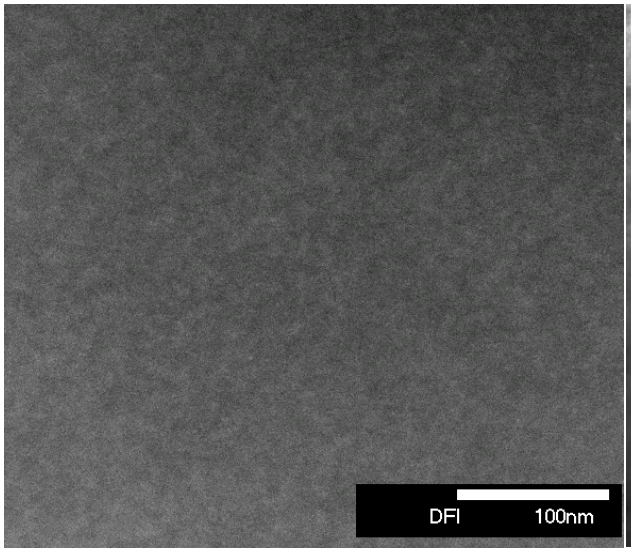
* unpublished (2006)



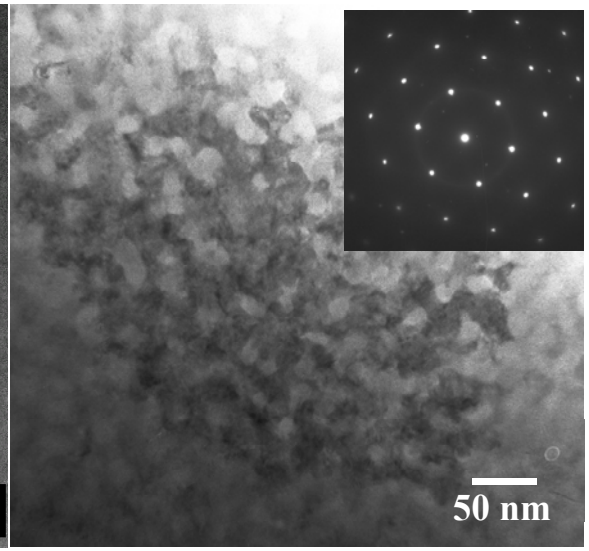
$Gd_{30}Zr_{25}Al_{25}Co_{20}$



$Gd_{30}Zr_{25}Al_{25}Ni_{20}$



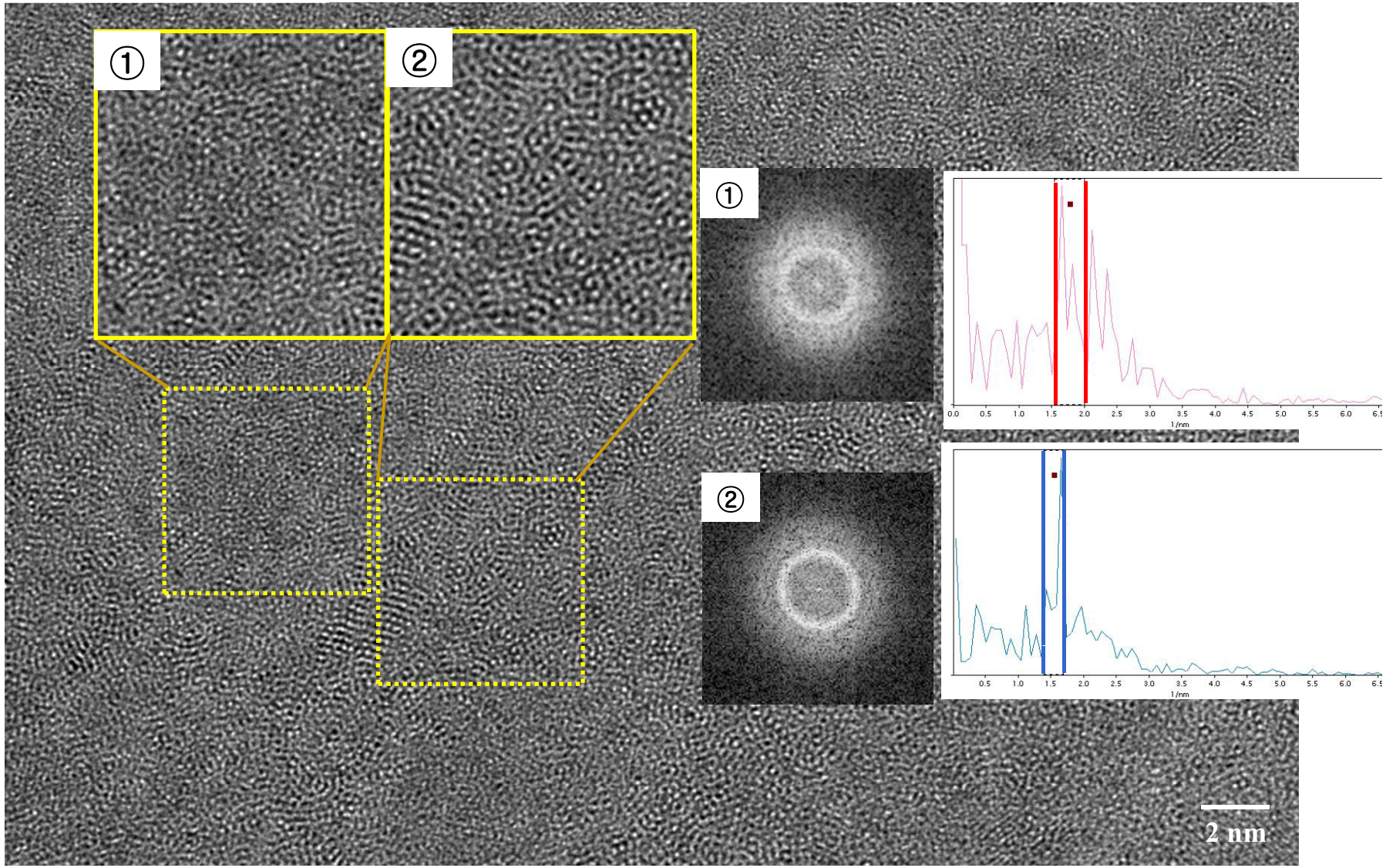
$Gd_{30}Zr_{25}Al_{25}Cu_{20}$

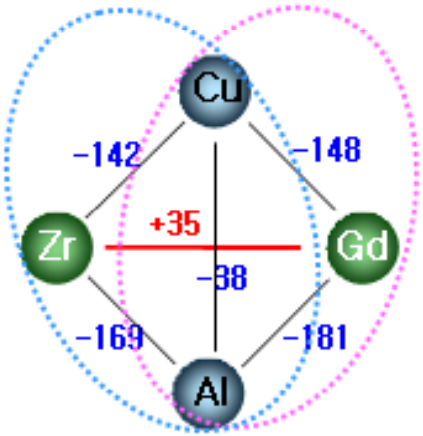


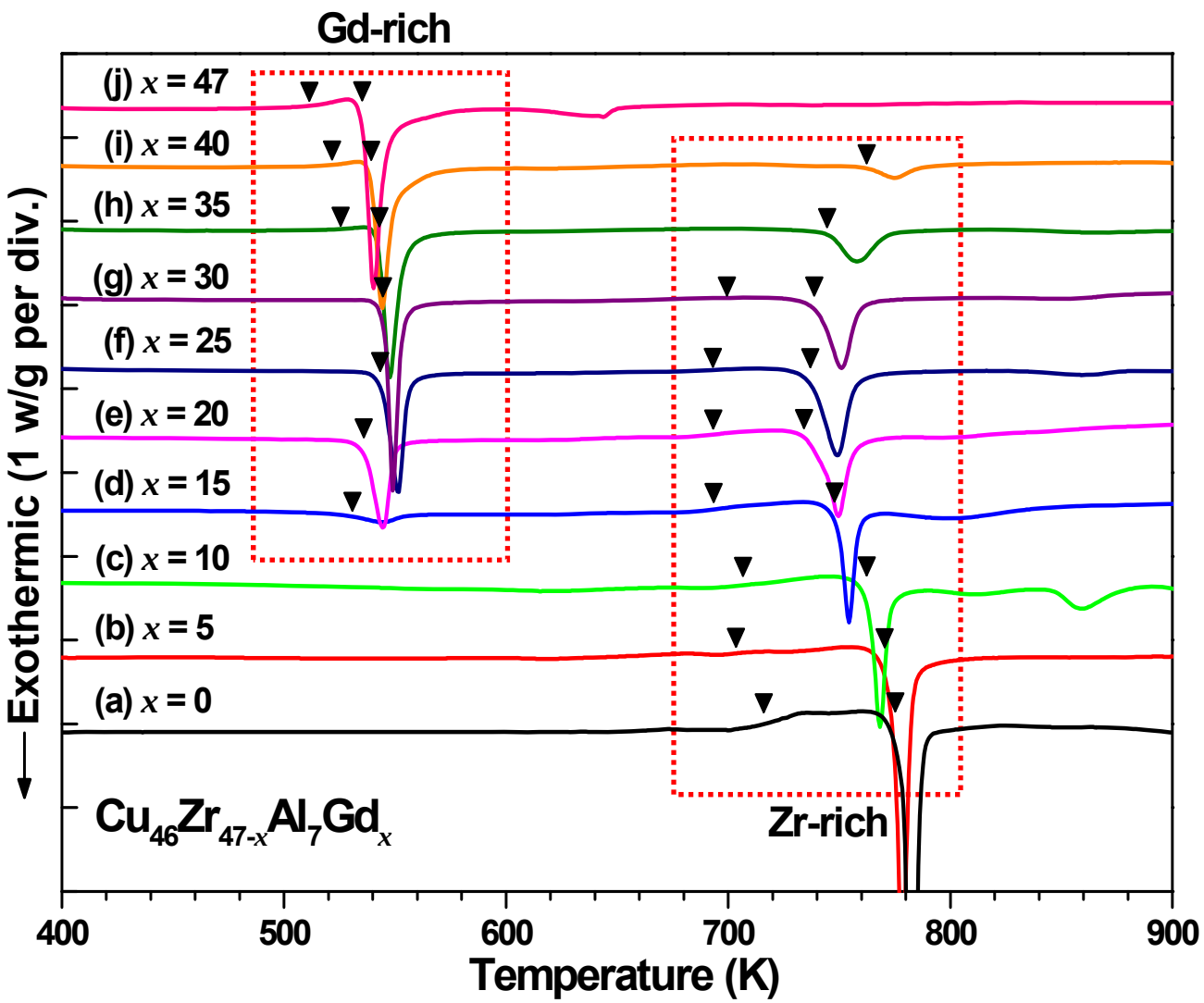
Nano scale (<3 mm) interconnected Phase separation

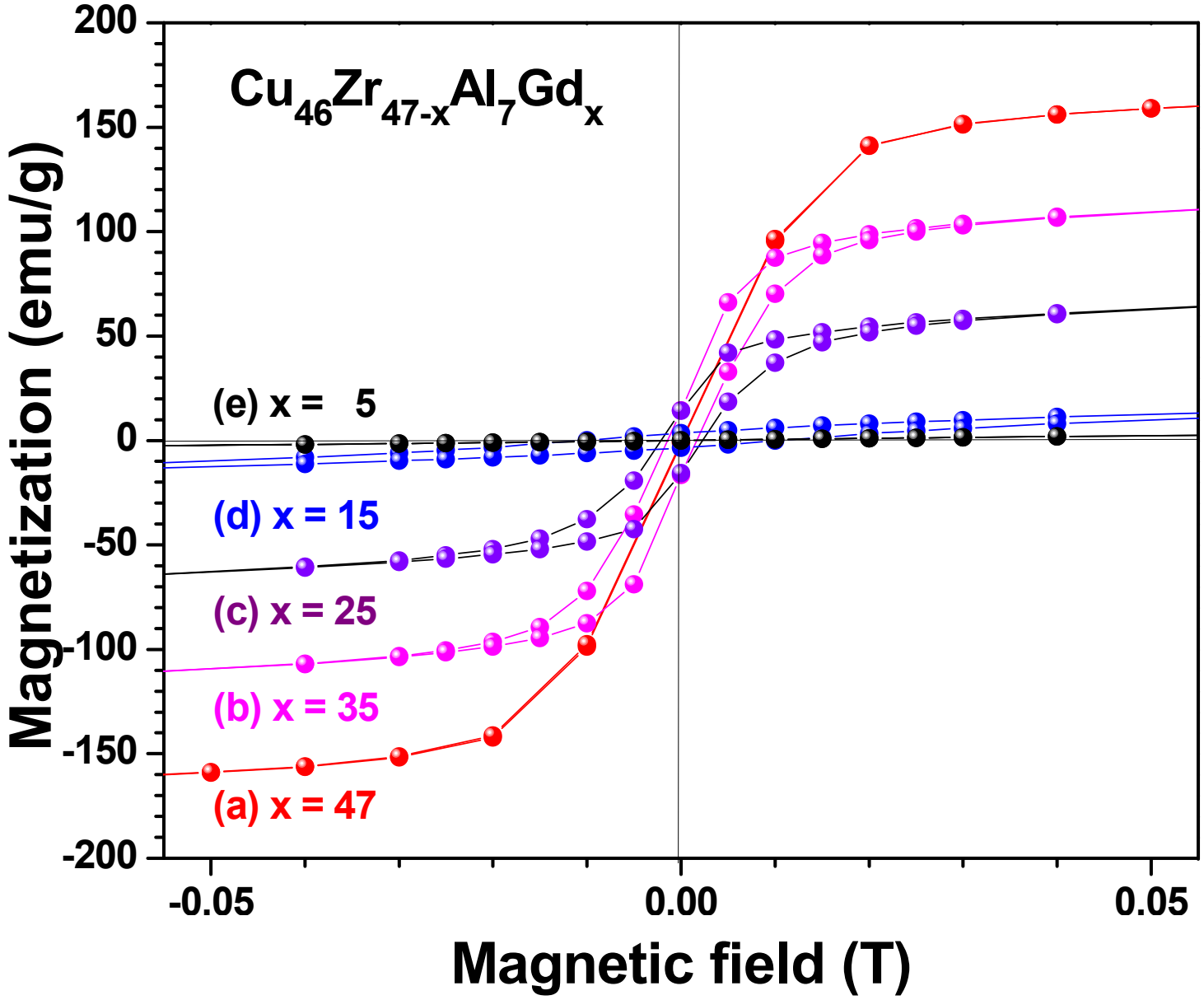
$Gd_{30}Zr_{25}Al_{25}Co_{20}$

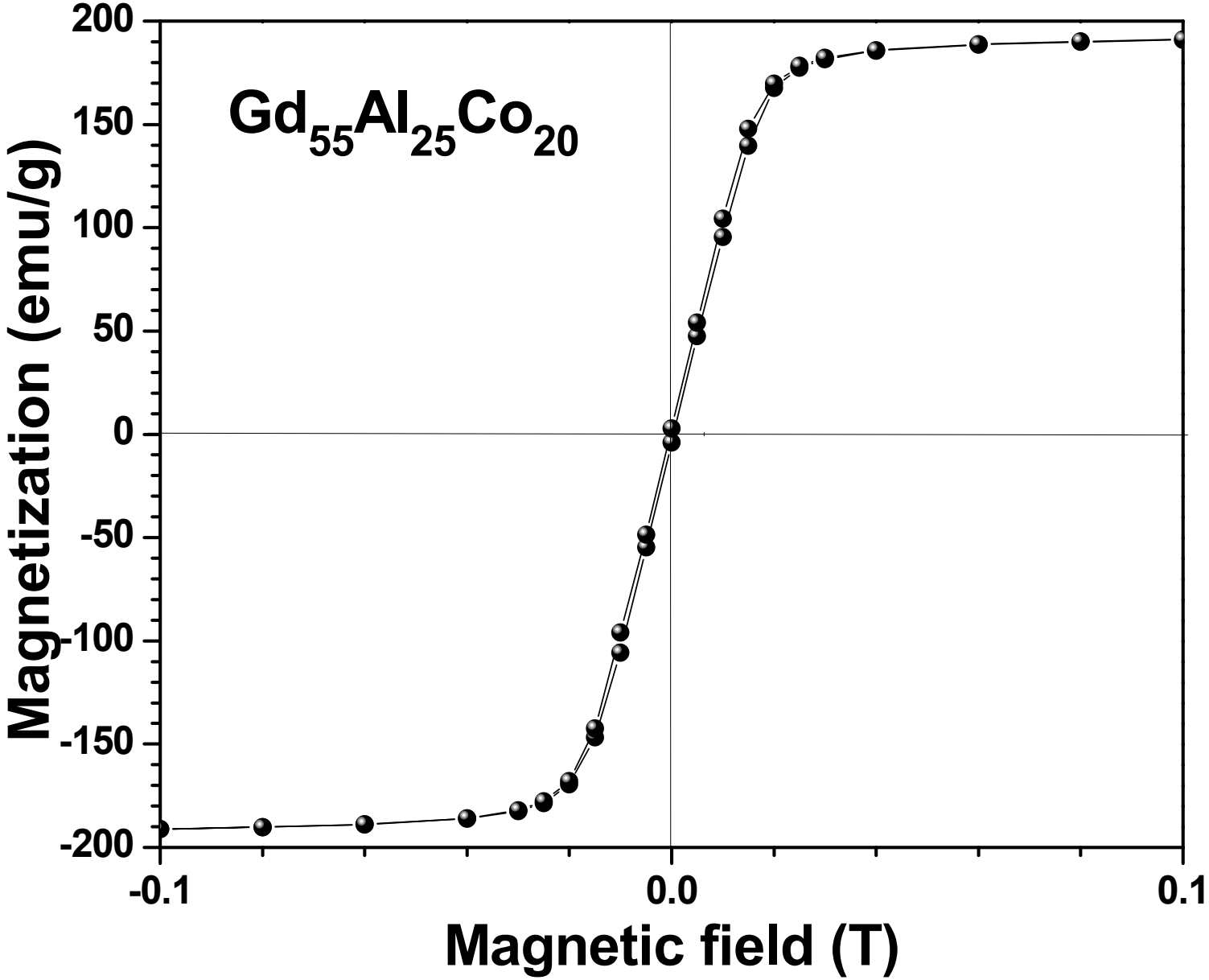
* unpublished (2008)

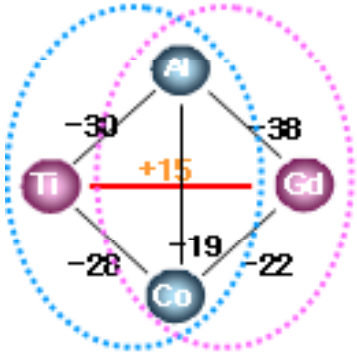



Cu
Zr
Gd
Al
−142
−148
+35
−38
−169
−181


Gd-rich
Zr-rich
(j) x = 47
(i) x = 40
(h) x = 35
(g) x = 30
(f) x = 25
(e) x = 20
(d) x = 15
(c) x = 10
(b) x = 5
(a) x = 0
Cu46Zr47-xAl7Gdx
Exothermic (1 w/g per div.)
400
500
600
700
800
900
Temperature (K)


Cu46Zr47-xAl7Gdx
(e) x = 5
(d) x = 15
(c) x = 25
(b) x = 35
(a) x = 47
Magnetization (emu/g)
Magnetic field (T)
200
150
100
50
0
-50
-100
-150
-200
-0.05
0.00
0.05

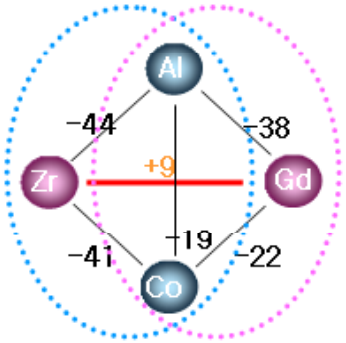

Gd55Al25Co20
Magnetization (emu/g)
Magnetic field (T)
200
150
100
50
0
-50
-100
-150
-200
-0.1
0.0
0.1



$Gd_{55}Al_{25}Co_{20}$

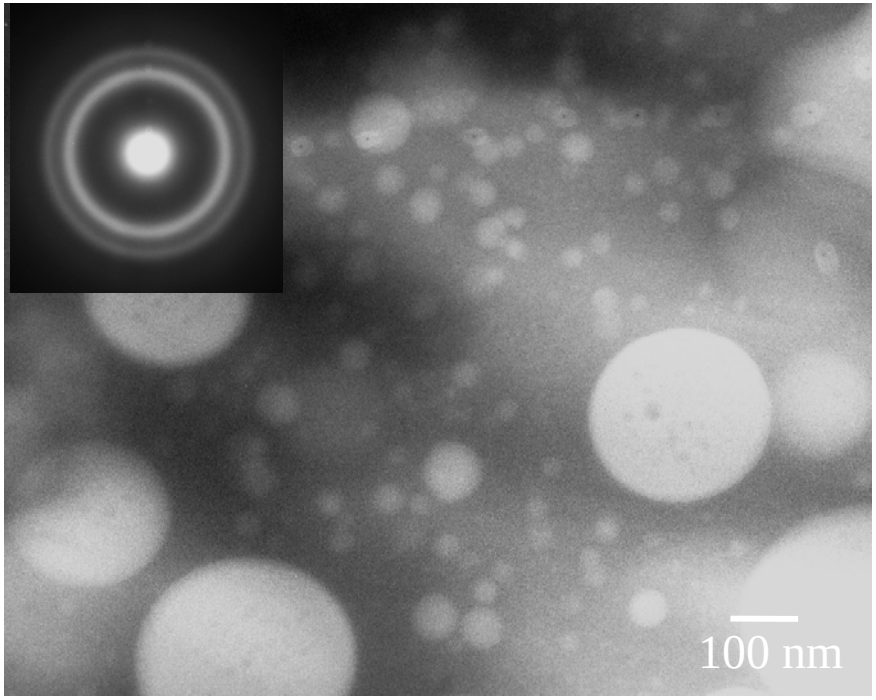
Ti

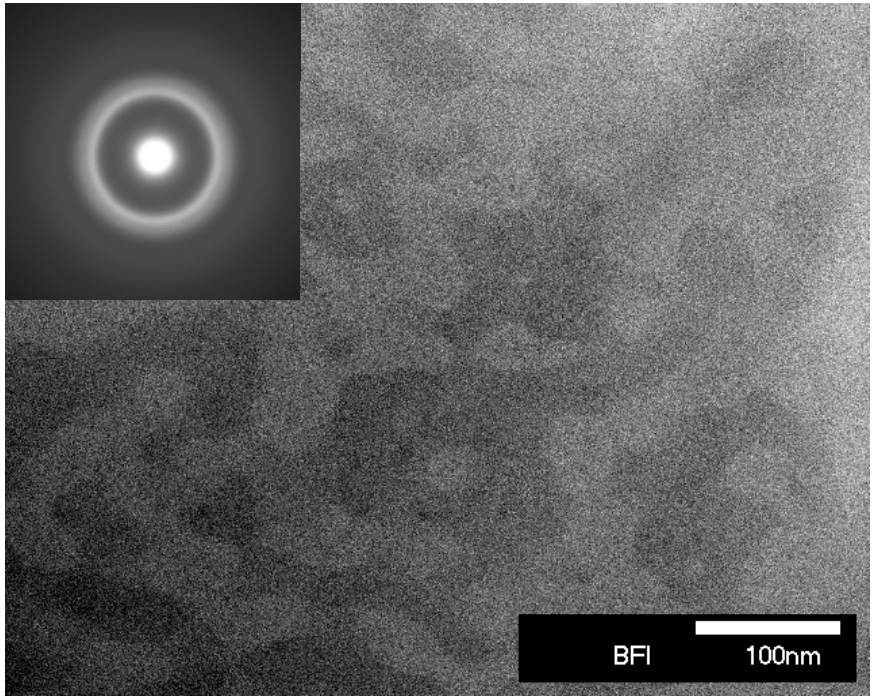
Zr



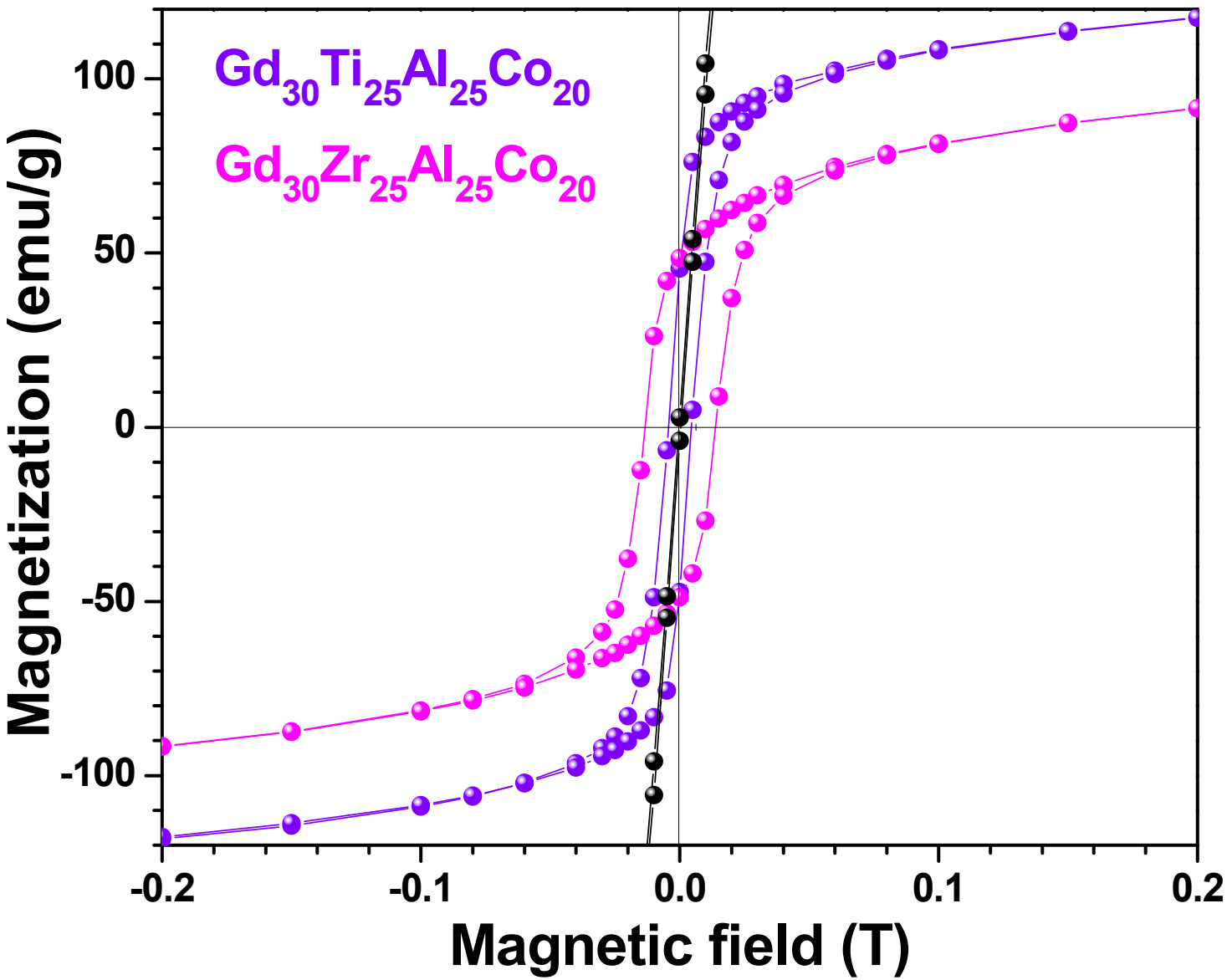
$Gd_{30}Ti_{25}Al_{25}Co_{20}$

$Gd_{30}Zr_{25}Al_{25}Co_{20}$



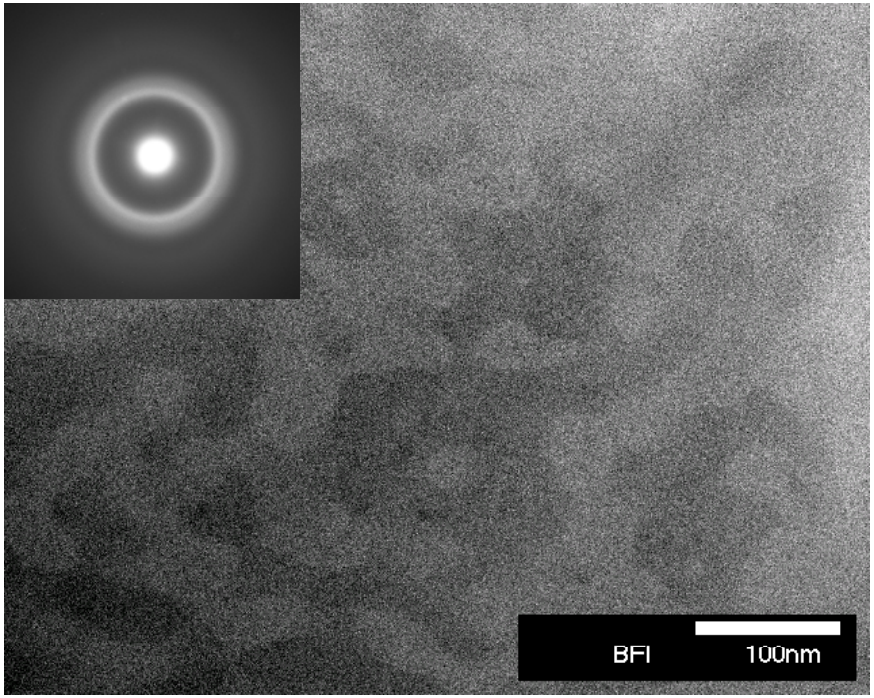


Droplet structure ⟷ Interconnected structure


$Gd_{30}Ti_{25}Al_{25}Co_{20}$
$Gd_{30}Zr_{25}Al_{25}Co_{20}$
Magnetization (emu/g)
100
50
0
-50
-100
-0.2
-0.1
0.0
0.1
0.2
Magnetic field (T)

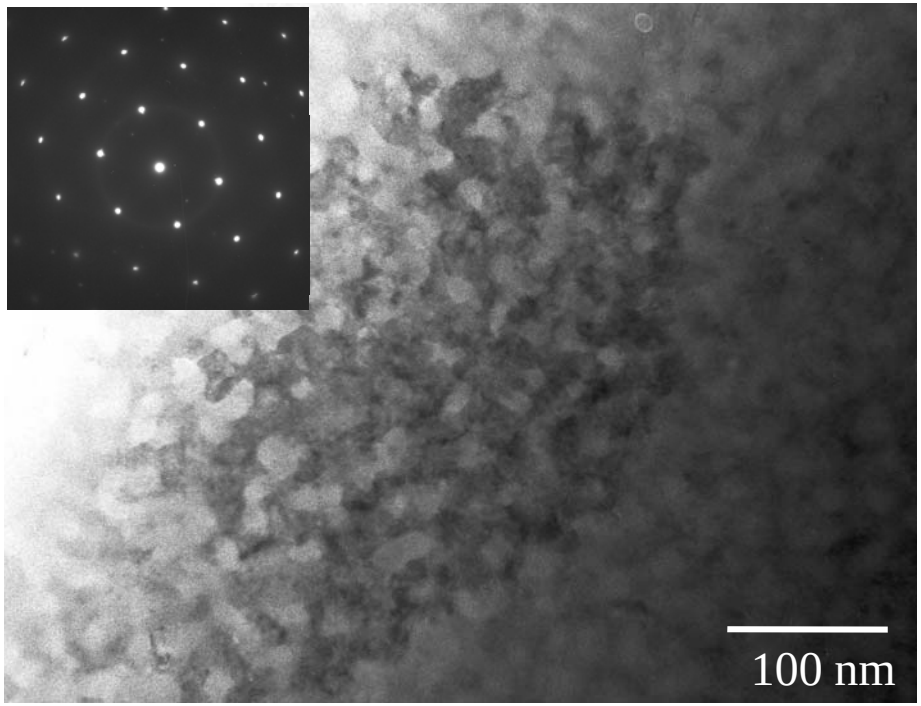
Interconnected structure

$Gd_{30}Zr_{25}Al_{25}Co_{20}$

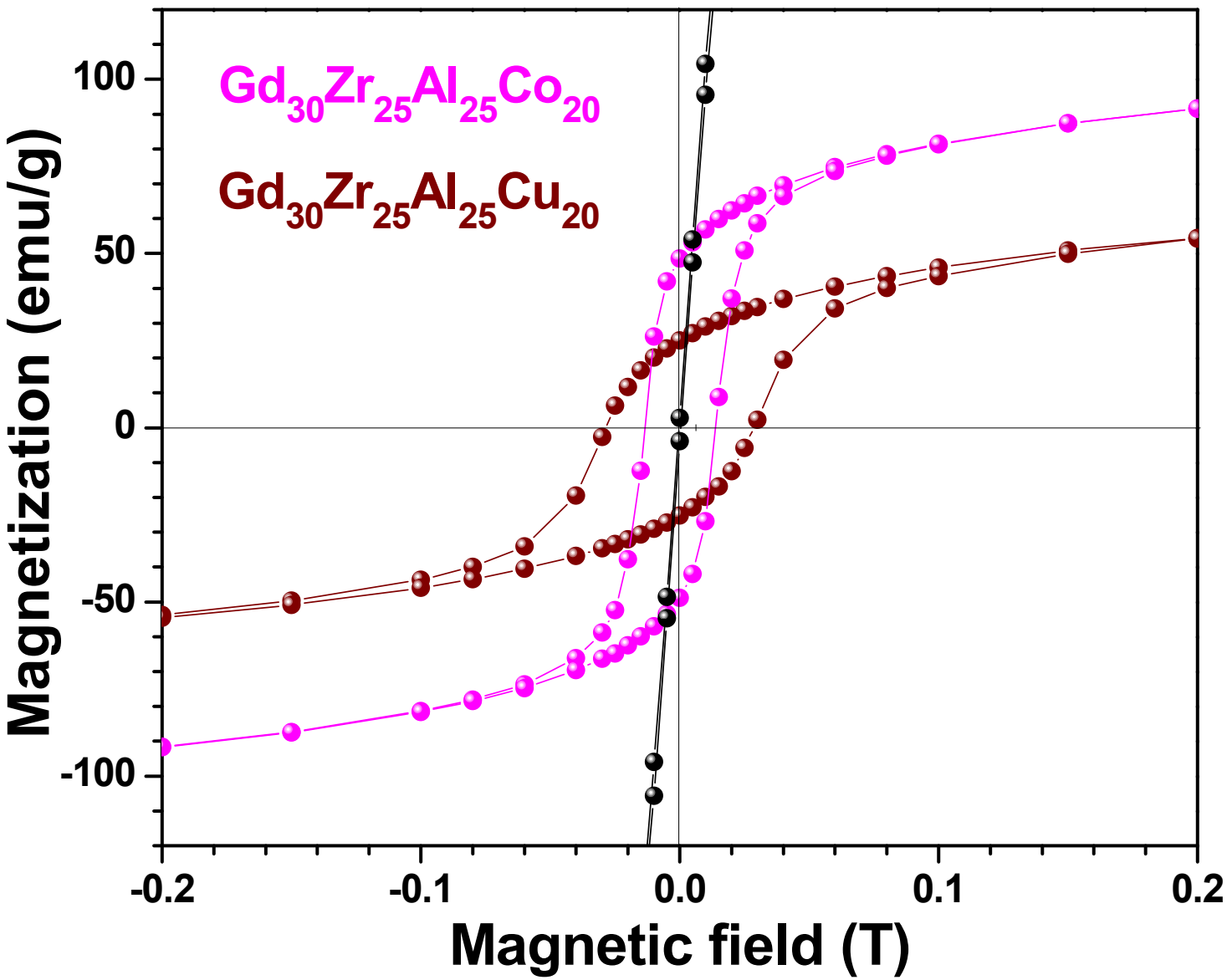


Amorphous + Amorphous

$Gd_{30}Zr_{25}Al_{25}Cu_{20}$

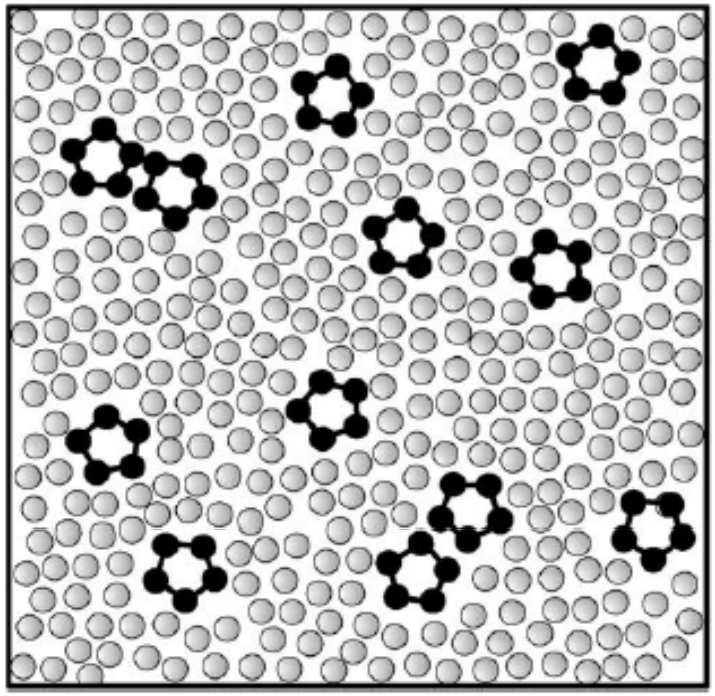


Amorphous + Crystals


Gd30Zr25Al25Co20
Gd30Zr25Al25Cu20
Magnetization (emu/g)
Magnetic field (T)
100
50
0
-50
-100
-0.2
-0.1
0.0
0.1
0.2

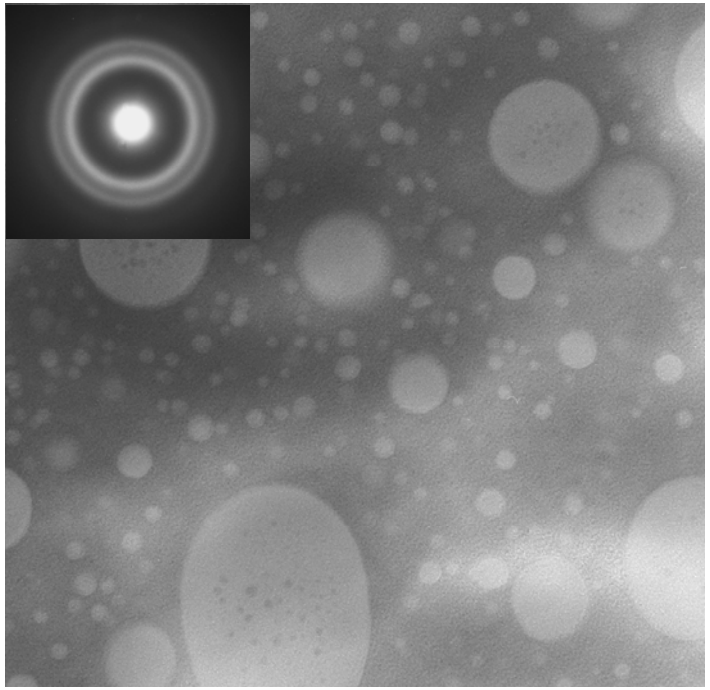
Enhancement of plasticity in BMG with atomic scale heterogeneity

atomic scale heterogeneity



Enhancement of plasticity in BMGs

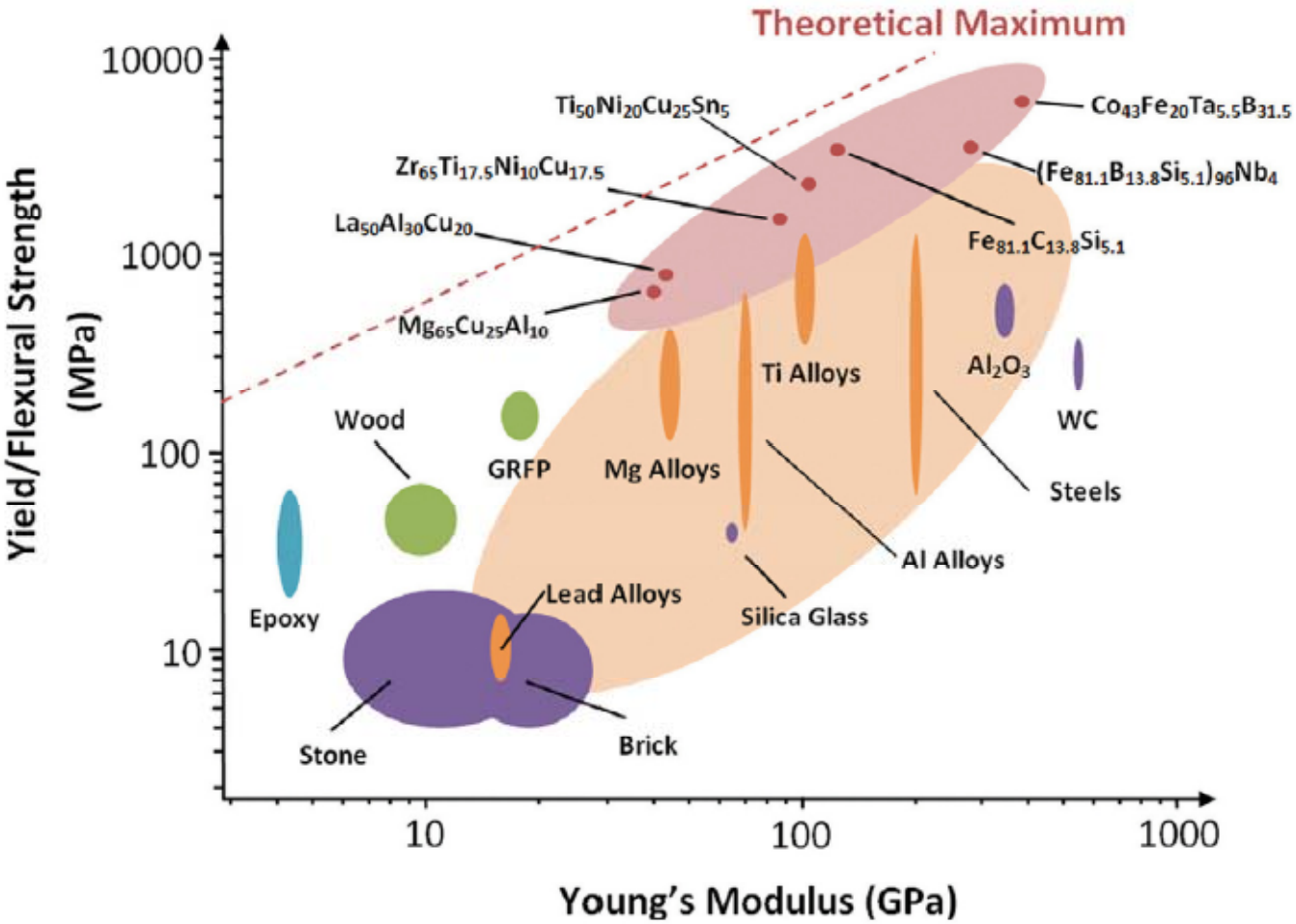
Phase separating metallic glasses



Unique properties

Are amorphous metals useful?

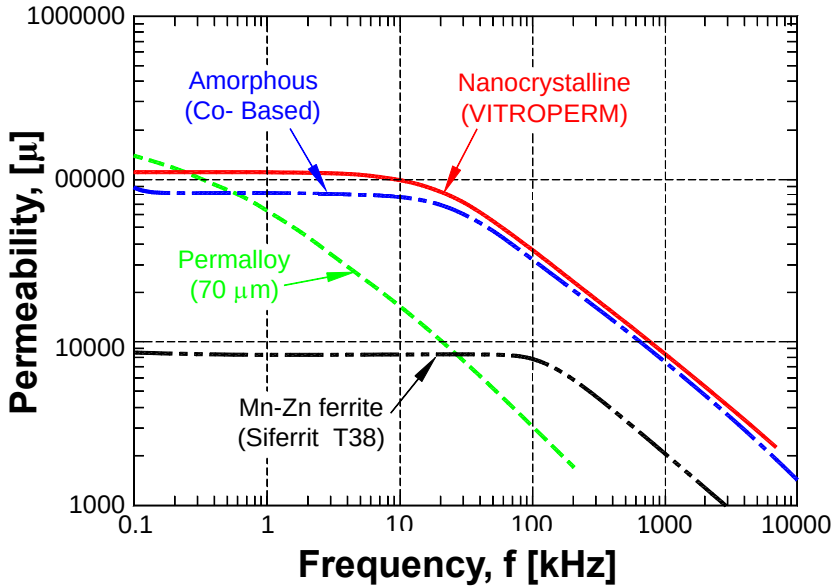
High strength of BMGs

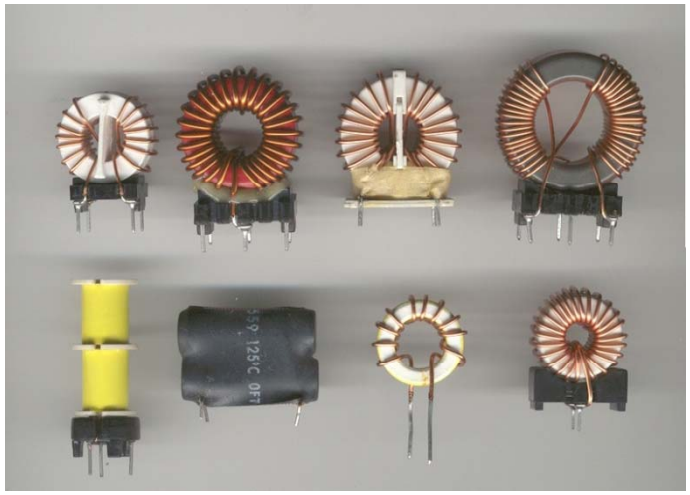


High fracture strength over 5 GPa in Fe-based BMGs

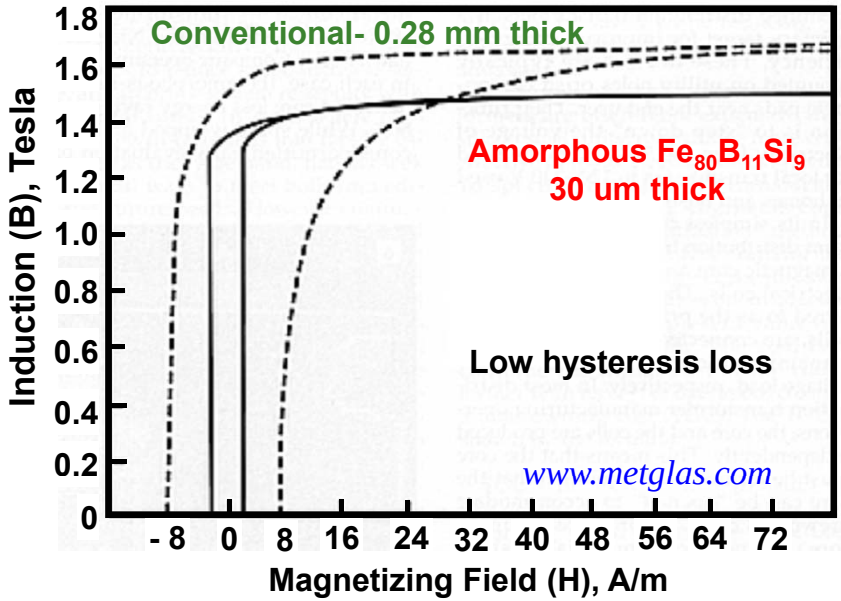
A.L. Greer, E. Ma, MRS Bulletin, 2007; 32: 612.

Old uses: soft magnet





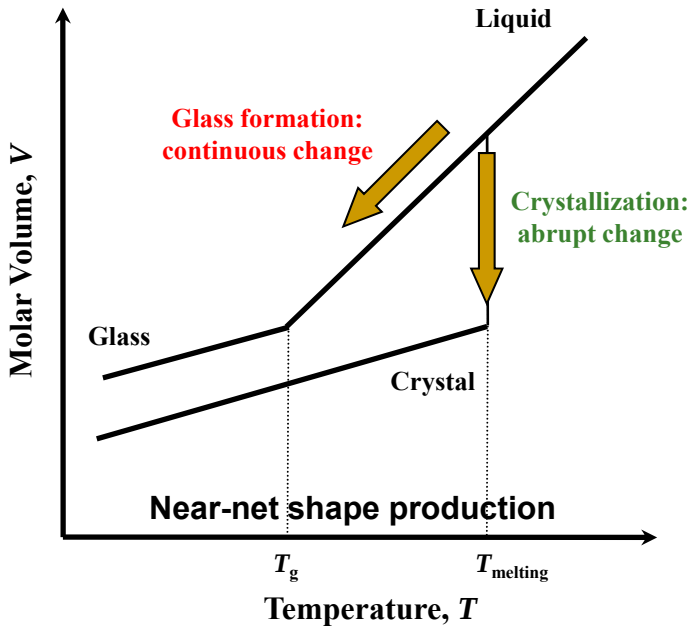
Magnetic cores

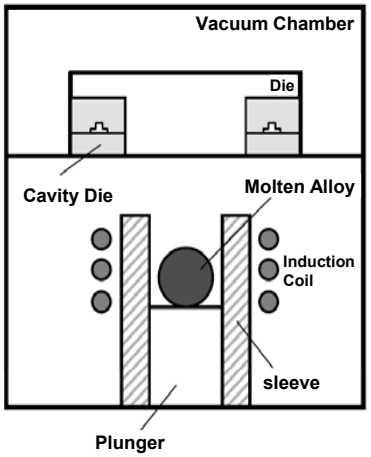


Transformers

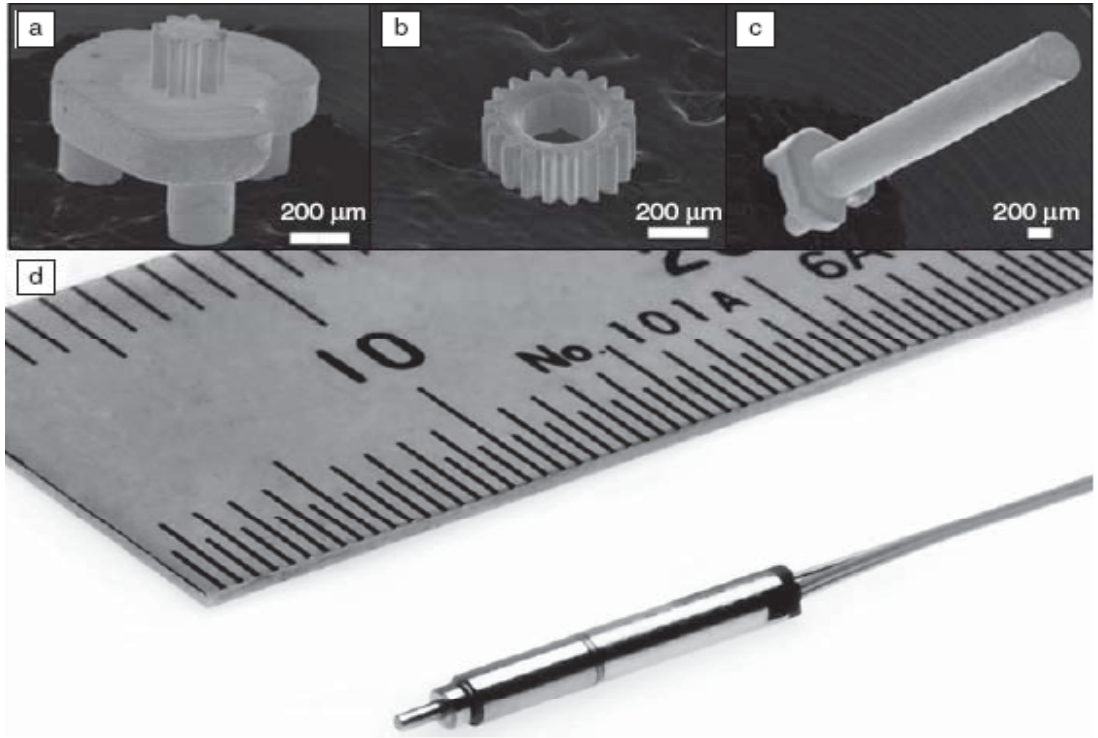
Recently: processing metals as efficiently as plastics

1) Micro-casting

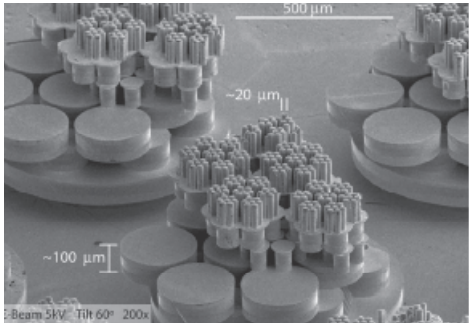




Precision die casting



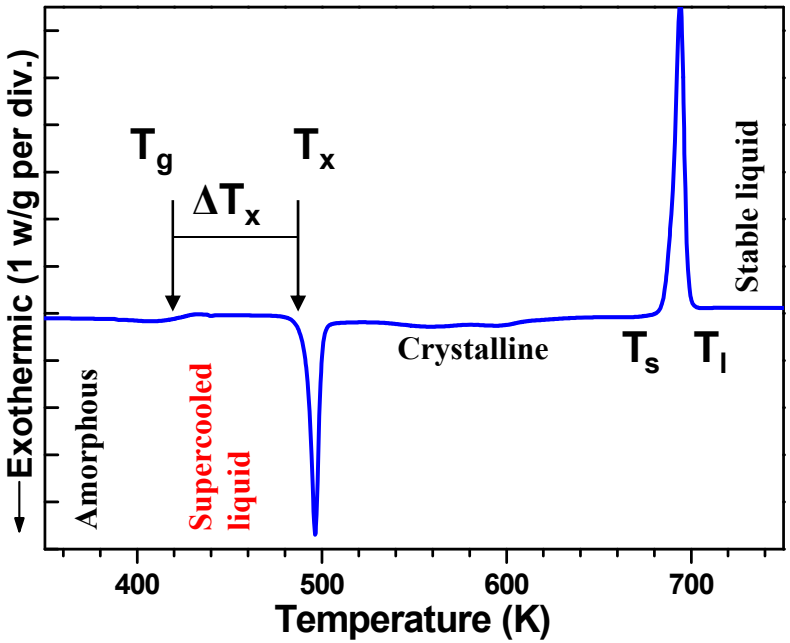
Precision Gears for Micro-motors



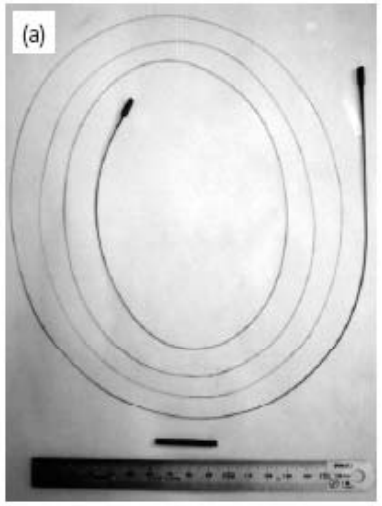
MRS BULLETIN ***32*** *(2007)654.*

Recently: processing metals as efficiently as plastics

2) Superplastic forming



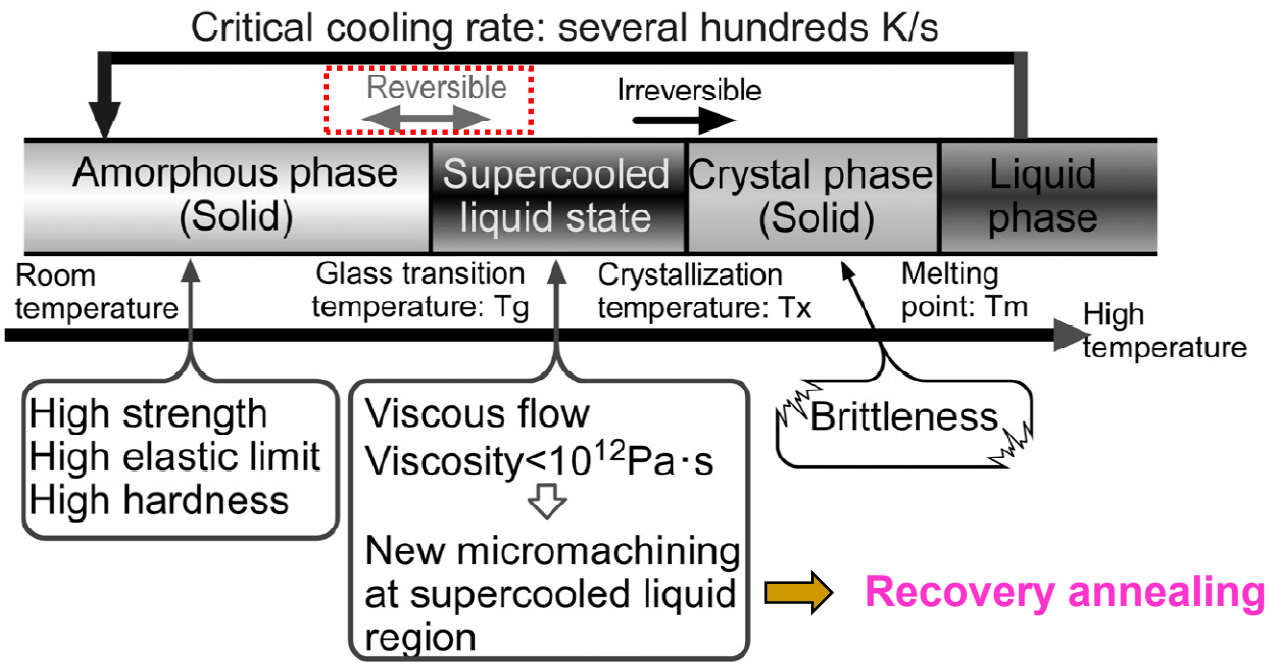
Tensile specimens following superplastic forming in supercooled liquid region



Synthesis of metallic glass nanowire

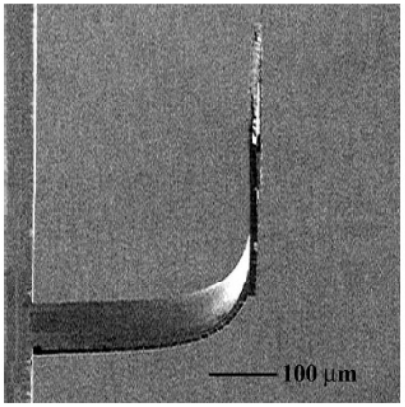
Recently: processing metals as efficiently as plastics

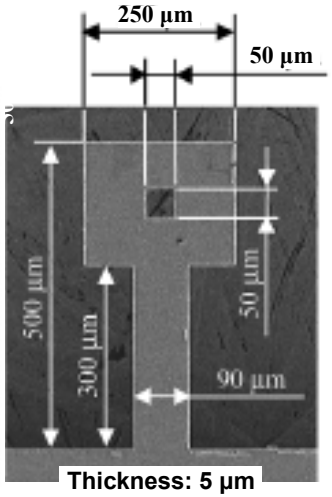
3) Micro-forming



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

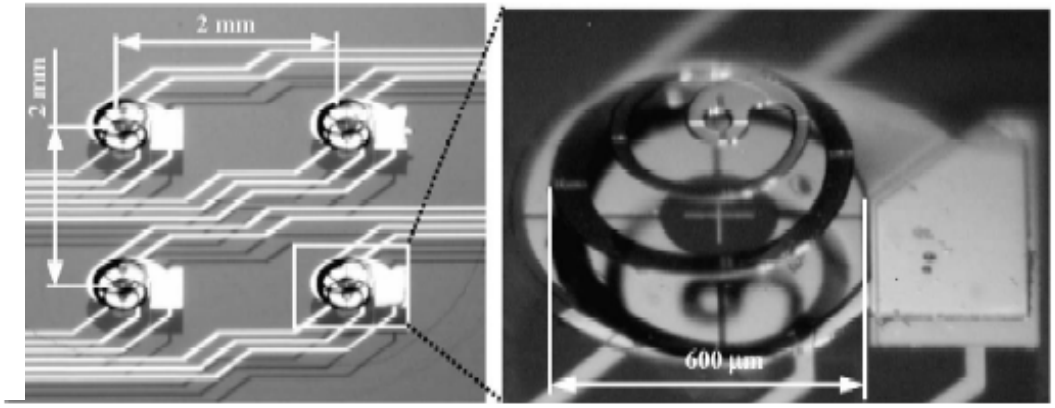
Micro-cantilever





Thickness: 5 µm

Integrated conical spring linear actuator



Commercialization of BMG products

Sporting Goods

Electronic Casings

Medical Devices

Industrial Coating

Drill pipe, container etc.

Fine jewelry

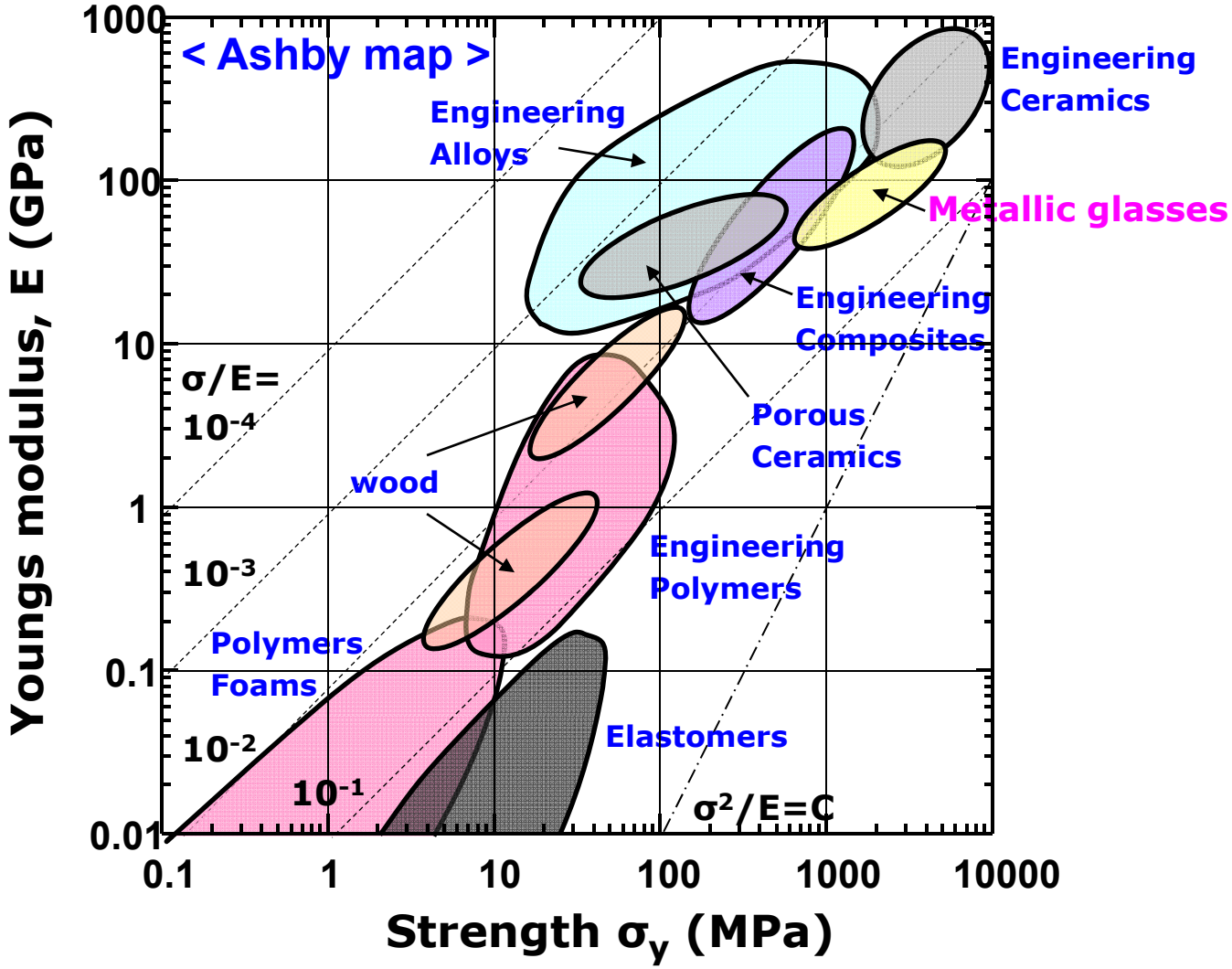
www.liquidmetal.com

Defense Applications

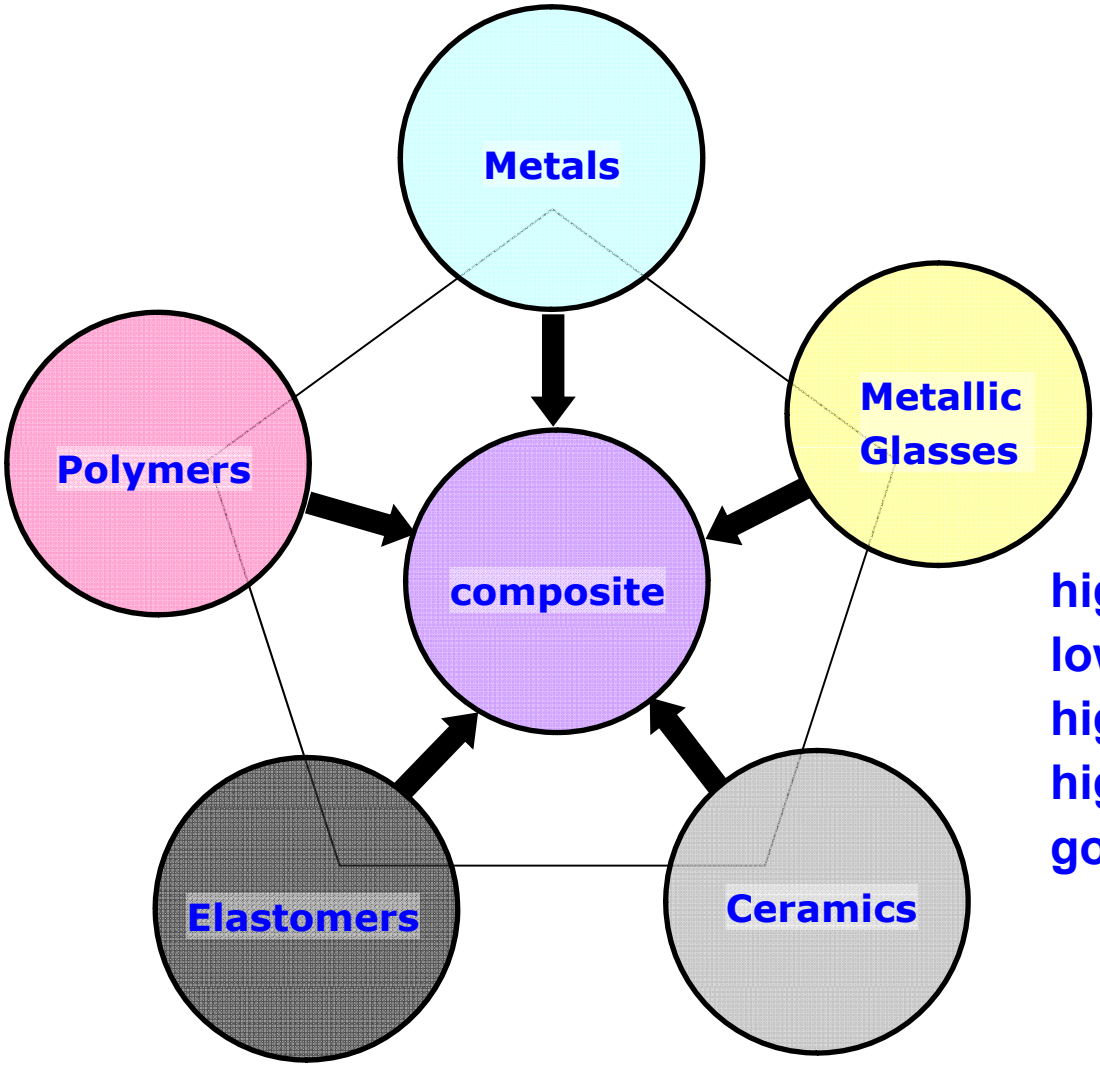
W-loaded composite BMGs

Tailormade material design

Ashby map


< Ashby map >
Engineering Alloys
Engineering Ceramics
Metallic glasses
Engineering Composites
Porous Ceramics
wood
Engineering Polymers
Polymers Foams
Elastomers
σ/E=
10-4
10-3
10-2
10-1
σ2/E=C
Youngs modulus, E (GPa)
Strength σy (MPa)
1000
100
10
1
0.1
0.01
0.1
1
10
100
1000
10000

Menu of engineering materials



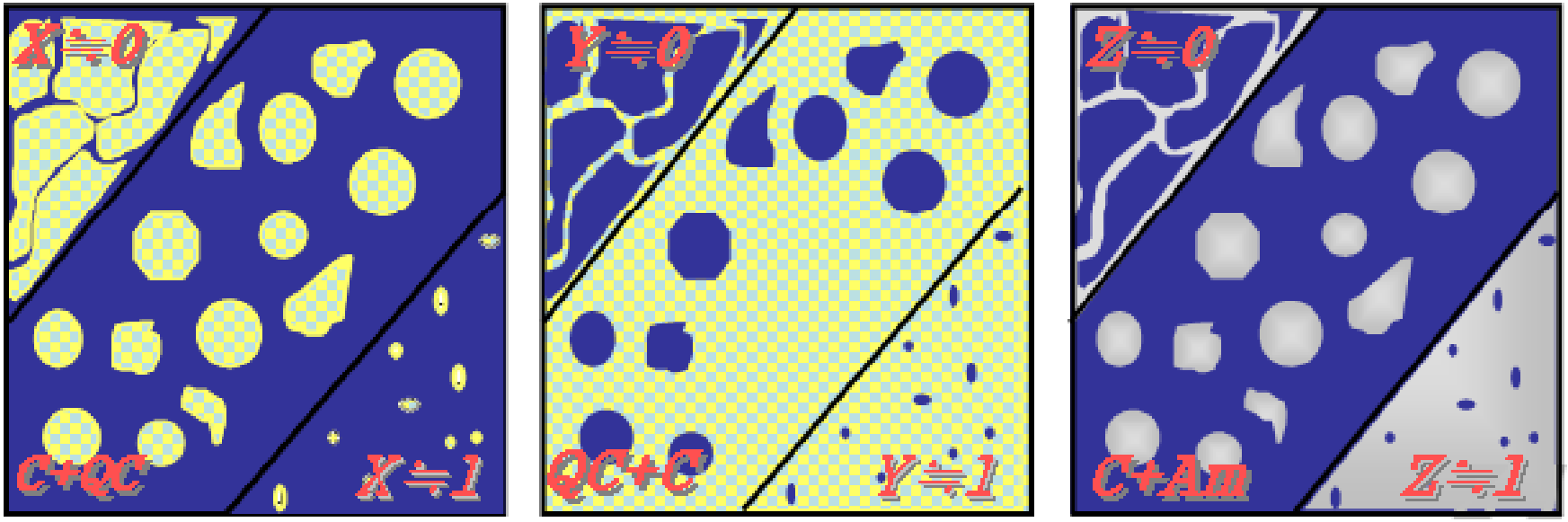
High GFA

High plasticity

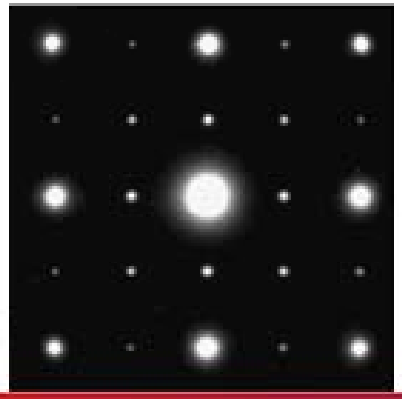
higher strength
lower Young's modulus
high hardness
high corrosion resistance
good deformability
⋮

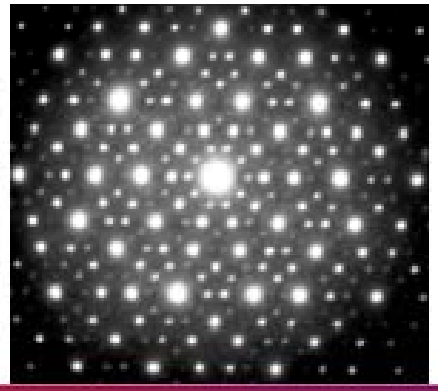
Tailor made material design

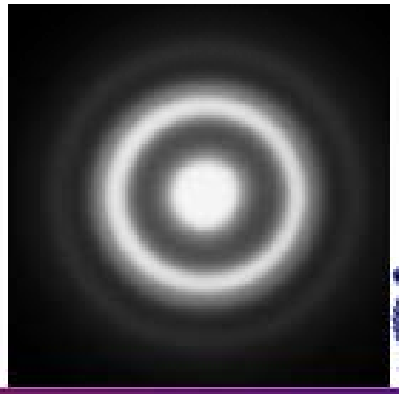
Design of composites with quasicrystalline and amorphous structure



X%[crystalline phase] Y%[quasicrystalline phase] Z%[amorphous phase]







Schedule

week 1 Introduction to Amorphous materials
week 2 Classification of Solids
week 3 Definition of Amorphous Materials
week 4 Preparation of Amorphous Materials
week 5 Phase Transition: glass transition
week 6 Measurement of Glass Transition Temperature
week 7 Theories for the Glass Transition I: thermodynamic / entropy
week 8 Theories for the Glass Transition II: relaxation behavior / viscosity
week 9 Structural Approach to Glass Formation
week 10 Kinetic Approach to Glass Formation
week 11 Ease of Glass Transition: glass forming ability
week 12 Glass Forming Ability Parameters
week 13 Formation of Bulk Metallic Glasses
week 14 Mechanical Properties of Bulk Metallic Glasses and Their Composites
week 15 Unique Properties of of Bulk Metallic Glasses
week 16 Potential Applications of Bulk Metallic Glasses

Final Presentation : summary and brief review