2014 Spring

“Advanced Physical Metallurgy”

- Bulk Metallic Glasses -

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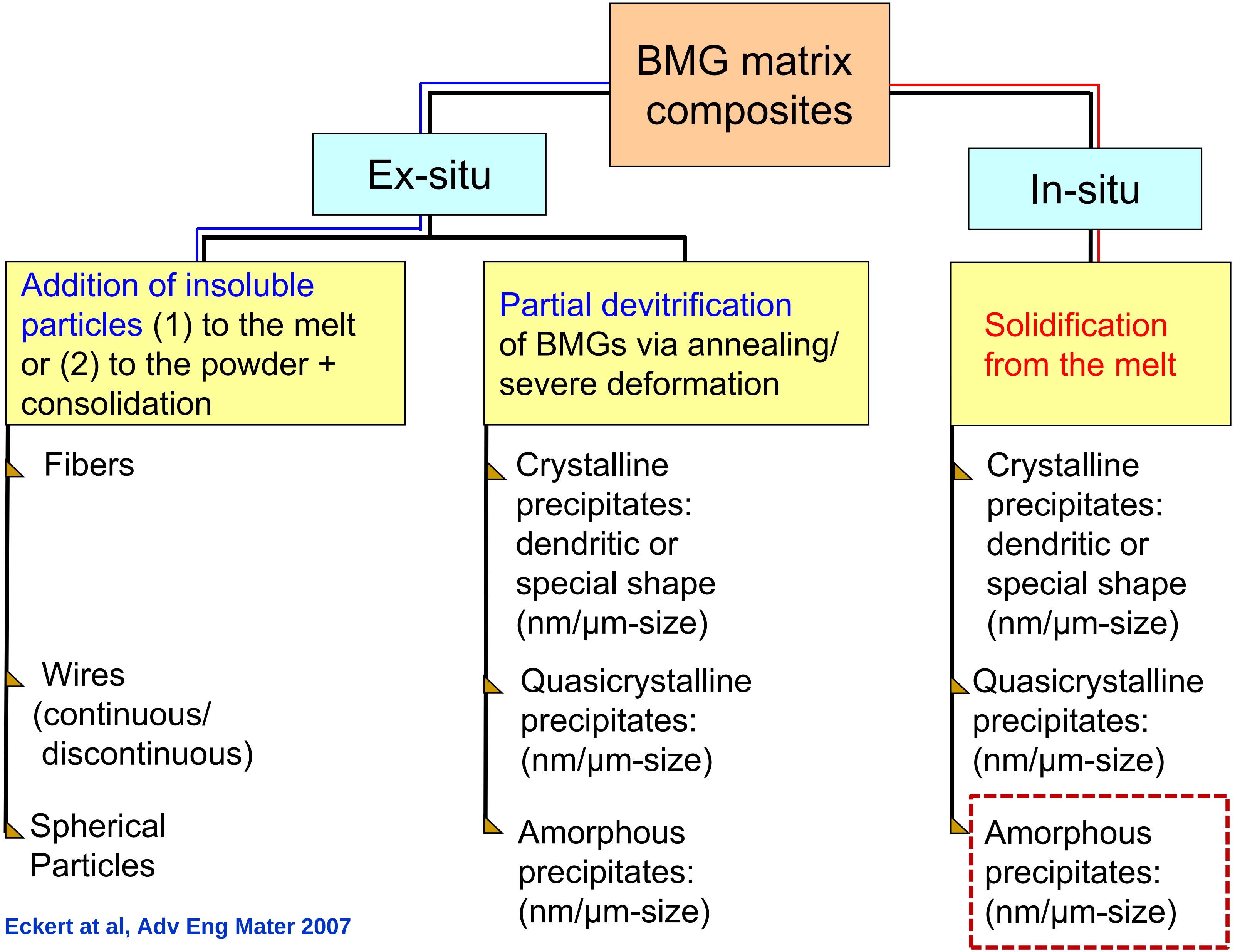
Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by appointment

4.7 Bulk Metallic Glass Composites

: exhibit much better mechanical properties → detail later in Chapter 8



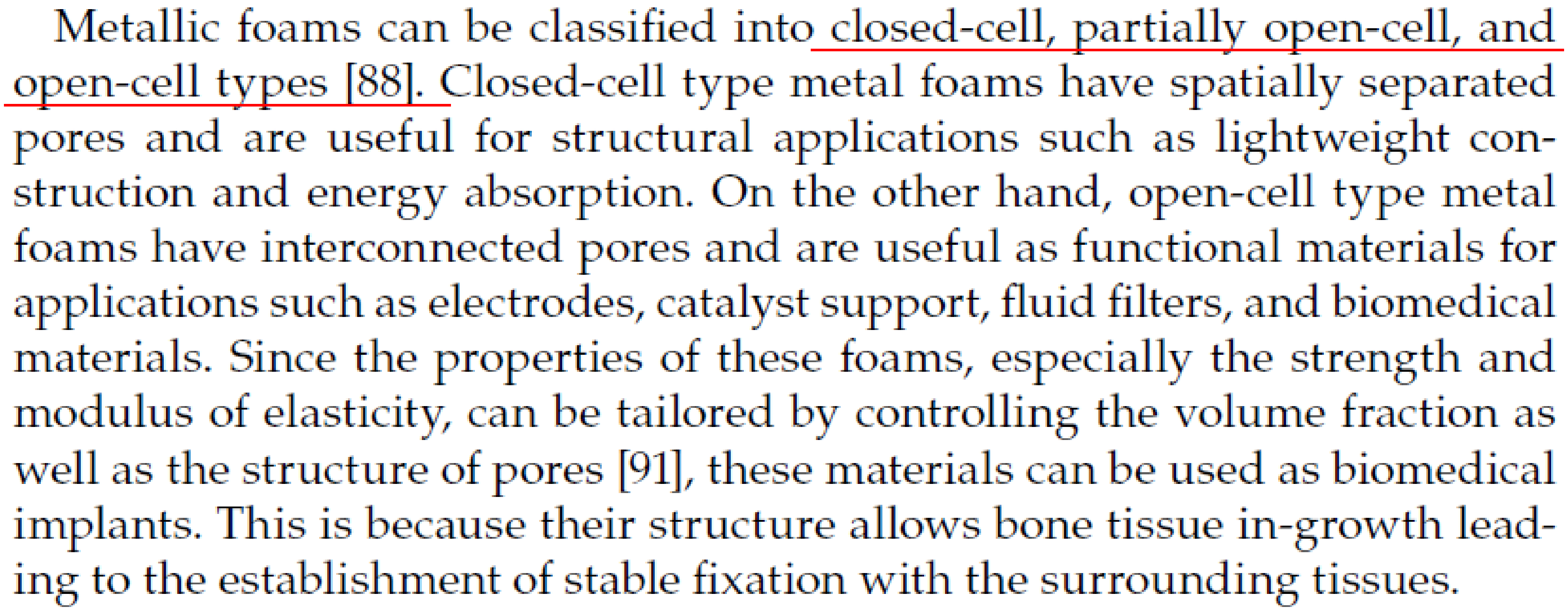
BMG matrix composites

- Ex-situ
  - Addition of insoluble particles (1) to the melt or (2) to the powder + consolidation
    - Fibers
    - Wires (continuous/ discontinuous)
    - Spherical Particles
  - Partial devitrification of BMGs via annealing/ severe deformation
    - Crystalline precipitates: dendritic or special shape (nm/μm-size)
    - Quasicrystalline precipitates: (nm/μm-size)
    - Amorphous precipitates: (nm/μm-size)
- In-situ
  - Solidification from the melt
    - Crystalline precipitates: dendritic or special shape (nm/μm-size)
    - Quasicrystalline precipitates: (nm/μm-size)
    - Amorphous precipitates: (nm/μm-size)

Eckert at al, Adv Eng Mater 2007

4.9 Bulk Metallic Glass Foams

: have interesting combination of properties such as high stiffness in conjunction with very low specific weight, high gas permeability combined with high thermal conductivity, high mechanical energy absorption, and good acoustic damping.



Metallic foams can be classified into closed-cell, partially open-cell, and open-cell types [88]. Closed-cell type metal foams have spatially separated pores and are useful for structural applications such as lightweight construction and energy absorption. On the other hand, open-cell type metal foams have interconnected pores and are useful as functional materials for applications such as electrodes, catalyst support, fluid filters, and biomedical materials. Since the properties of these foams, especially the strength and modulus of elasticity, can be tailored by controlling the volume fraction as well as the structure of pores [91], these materials can be used as biomedical implants. This is because their structure allows bone tissue in-growth leading to the establishment of stable fixation with the surrounding tissues.

→ By producing BMGs as foams, their ductility could be increased without sacrificing the strength

Pore sizes ranging from the sub-micrometer to the millimeter scale and porosities ranging from 2% to more than 85%

Images of several representative porous amorphous metals, produced using liquid-state methods, are shown in Figure 1.
These methods demonstrated the possibility of foaming reactive Zr-based alloys of the sort used in most metallic glass applications.

Representative powder-processed porous amorphous metals are shown in Figure 2.

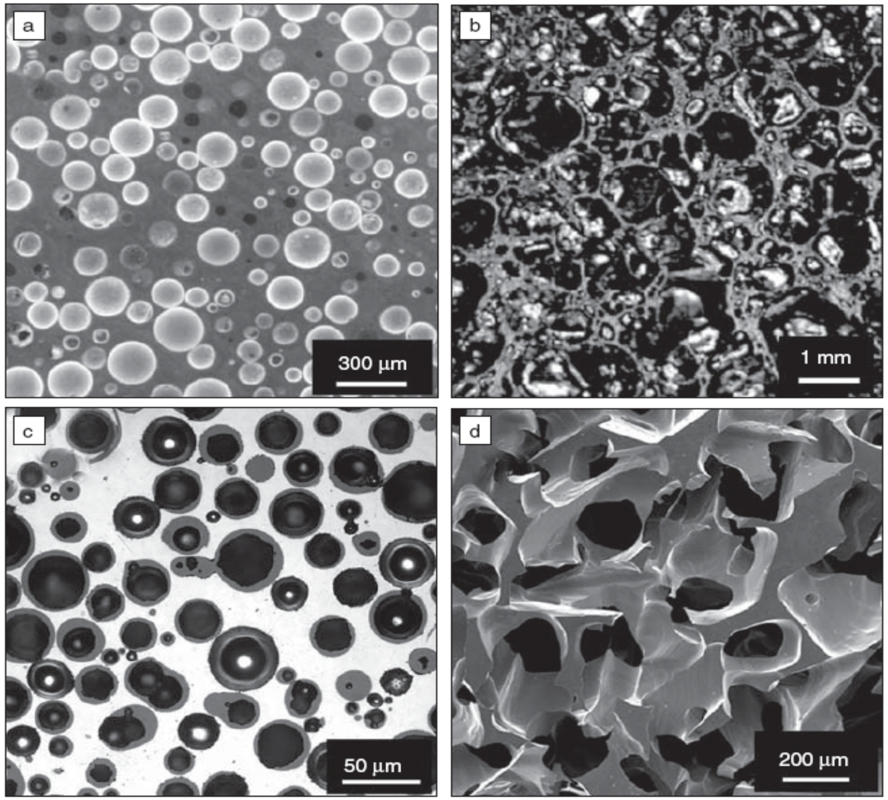


Figure 1. Examples of amorphous metal foams created by liquid-state and supercooled-liquid-state methods. (a) Pd-based foam (porosity $P = 42$–46%) made by precipitation of dissolved hydrogen gas during cooling.[7] (b) Pd-based foam ($P = 85\%$) made by entrapping gas in the melt and then expanding it in the supercooled-liquid state.[5] (c) Zr-based foam made by infiltration of a bed of hollow carbon spheres. Volume fraction of spheres in the foam is 59%.[12] (d) Zr-based foam ($P = 78\%$) made by infiltration of BaF_2 salt particles followed by removal of those particles in an acid bath.[14]

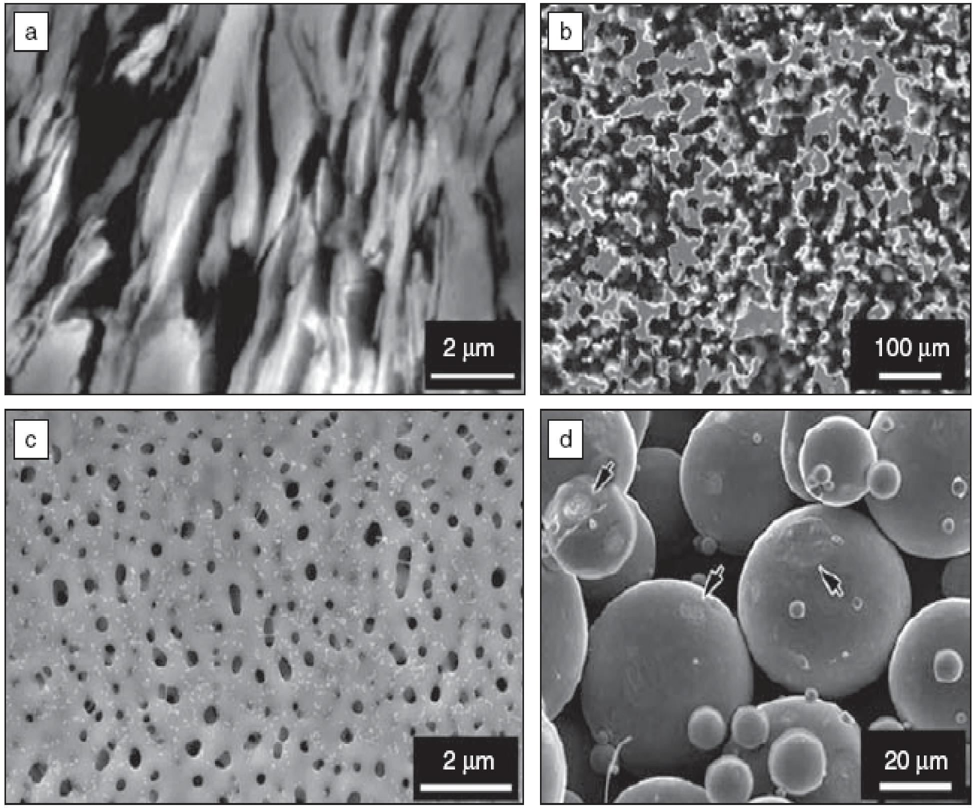
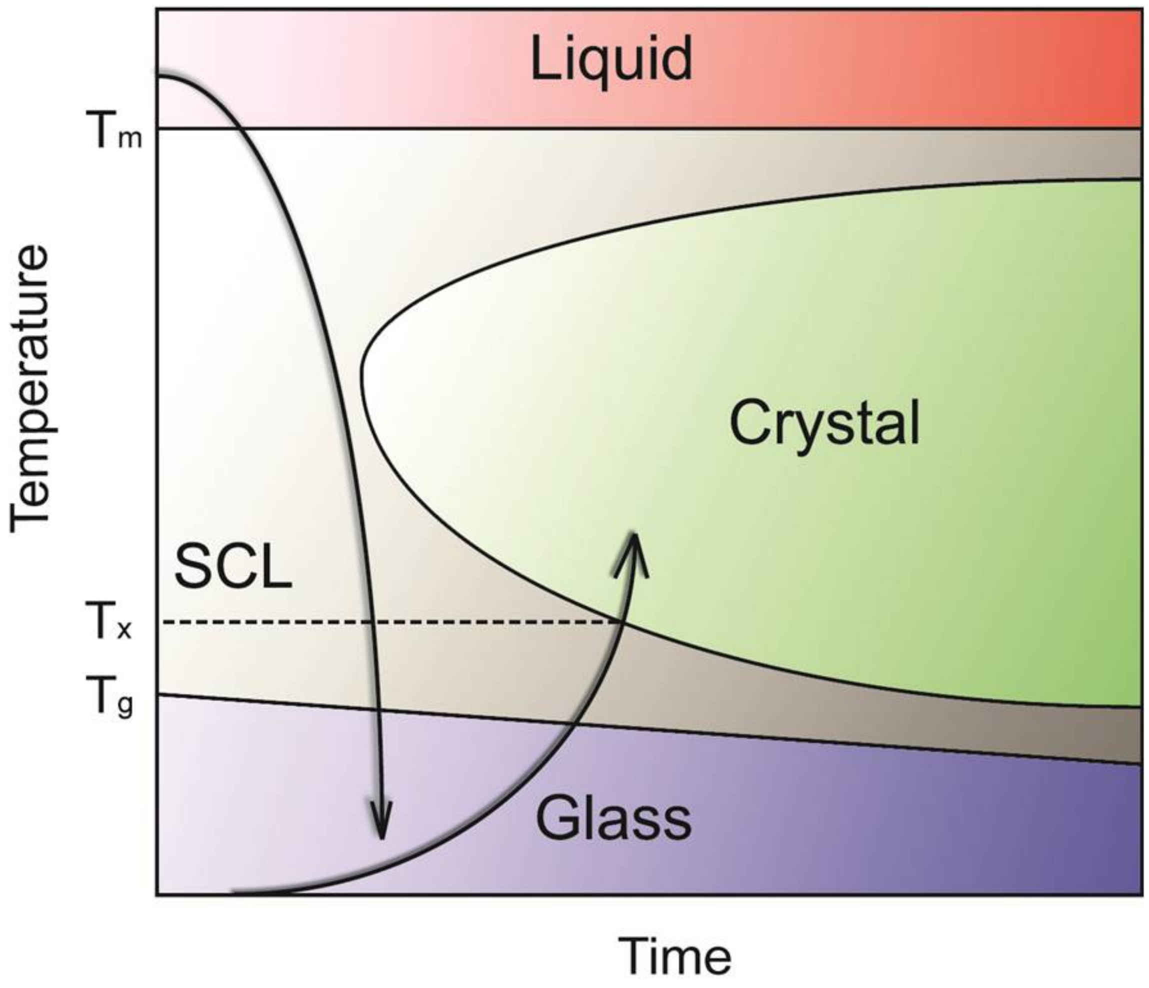


Figure 2. Examples of powder-processed porous amorphous metals and amorphous metal foams created by solid-state methods. (a) Cu-based foam (porosity $P = 75\%$) made by dissolution of crystalline Cu from an extruded composite.[21] (b) Ni-based foam ($P = 42\%$) made by dissolution of brass from an extruded composite.[22] (c) Ti-based porous amorphous metal (P not given) made by selective dissolution of one phase from a two-phase amorphous metal.[19] (d) Zr-based porous compact ($P = 34\%$) made by partial electroconsolidation of amorphous powders.[23]

Crystallization in TTT diagram.



Glass Formation

Retention of liquid phase

↕

Formation of
Crystalline phase

Cooling Process.

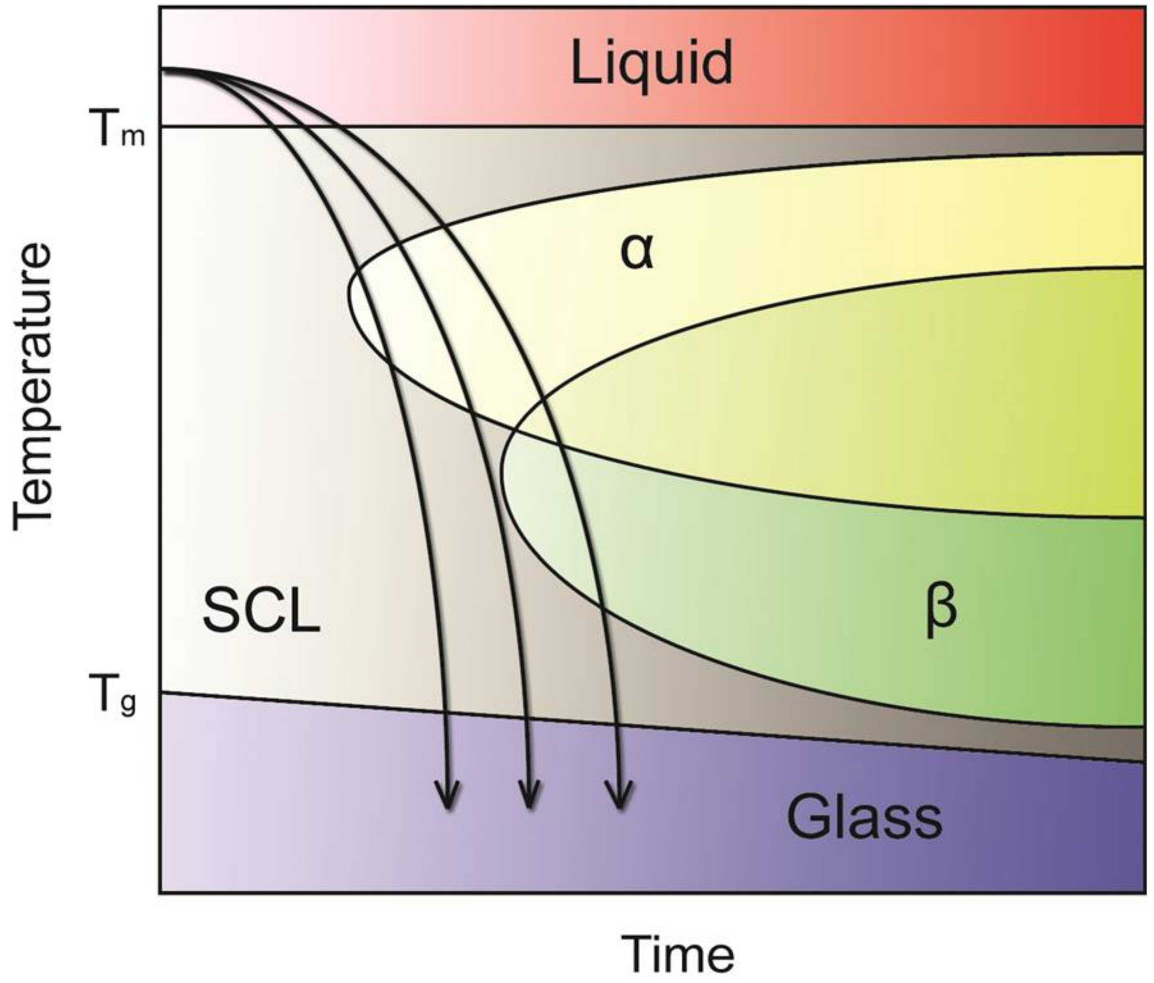
Crystal vs. Glass

→ Thermodynamics

Kinetics

5 *Crystallization Behavior*

Crystallization to Equilibrium or Non-equilibrium Phase.



α : Equilibrium phase

β : Non-Equilibrium phase

Cooling Process.

Only α phase

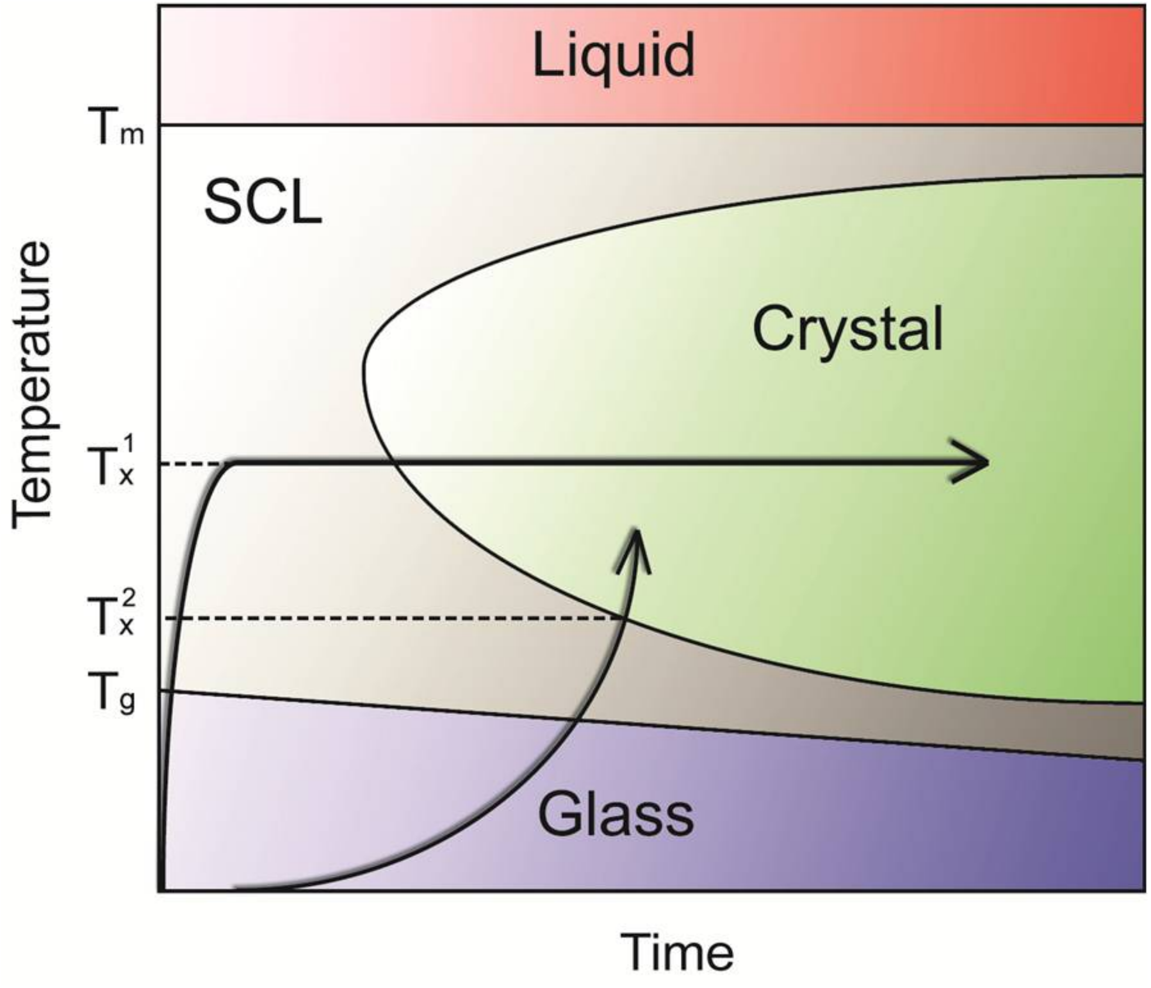
Heating Process.

Low T Crystallize to β

High T Crystallize to α

Crystallization Behavior

Annealing Method.



Heading Process.

Glass ➡ *Crystal*

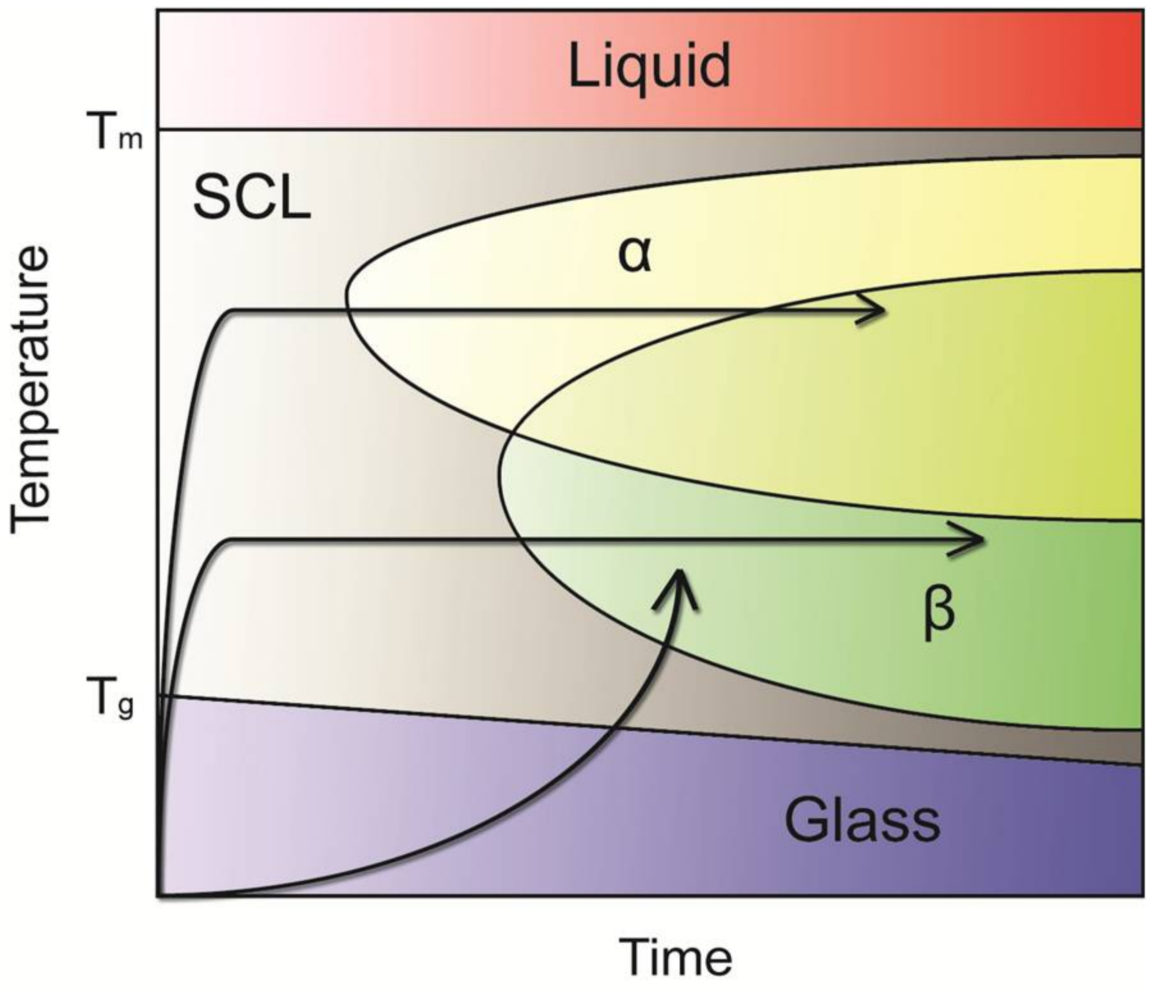
1. Isothermal Heating
2. Continuous Heating

(Annealing temperature has to be higher than T_g)

⬇

Crystallization

Crystallization to Equilibrium or Non-equilibrium Phase.



α : Equilibrium phase

β : Non-Equilibrium phase

Cooling Process.

Only α phase

Heating Process.

Low T Crystallize to β

High T Crystallize to α

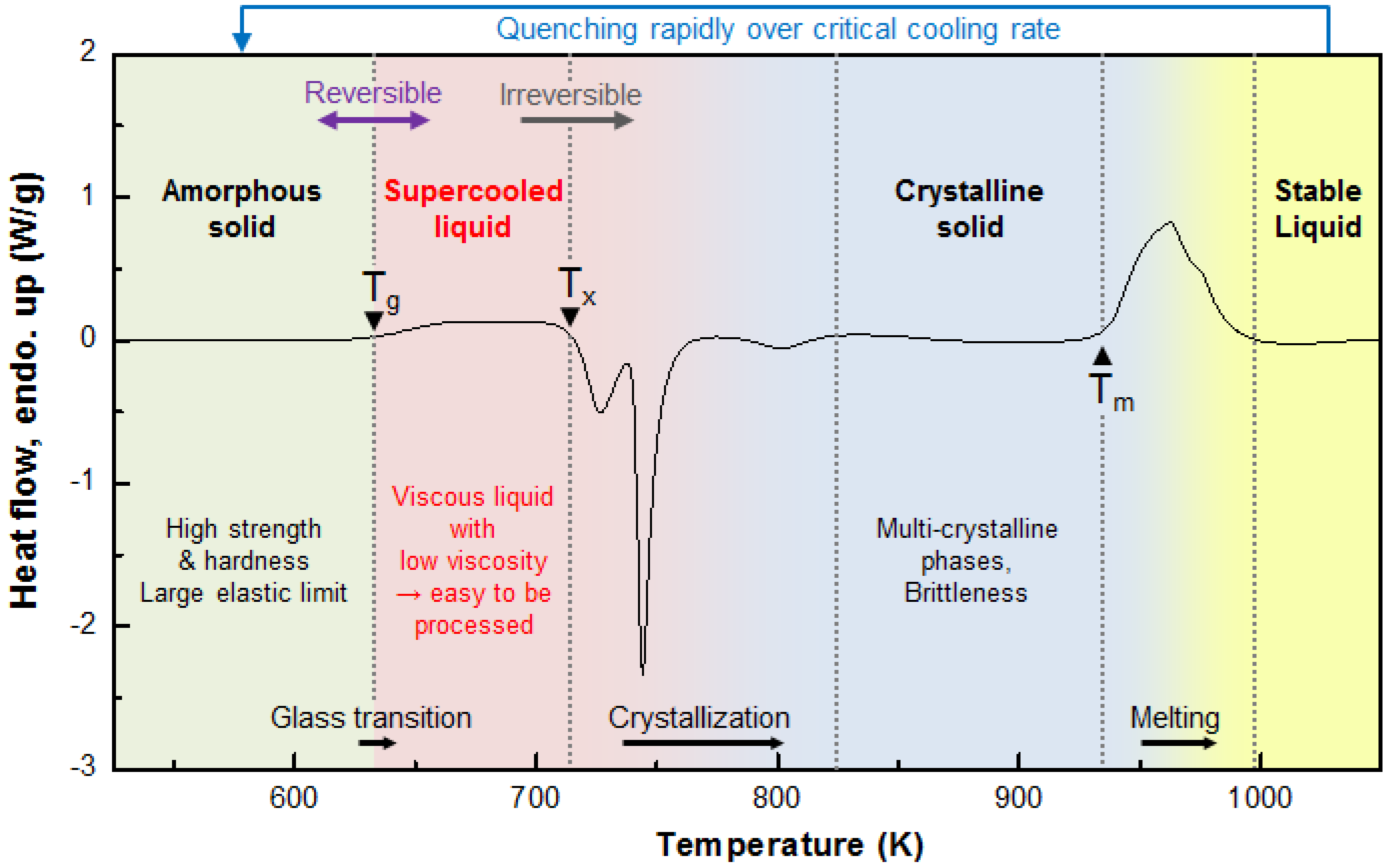
5

Crystallization Behavior

Temp. or Pressure

Amorphous phase $\xrightarrow{\text{Temp. or Pressure}}$ crystal phase
(high E (metastable) state)

Tailor the microstructure to obtain a glass+nanocrystal or an ultrafine-grained composite, or a completely crystalline materials of different grain sizes by controlling the time and temperature of crystallization.



DSC trace of Vitreloy 1 substrate and the temperature regions sectioned according to phase transformations

5

Crystallization Behavior

Temp. or Pressure ↓

Amorphous phase → crystal phase

(high E (metastable) state)

Tailor the microstructure to obtain a glass+nanocrystal or an ultrafine-grained composite, or a completely crystalline materials of different grain sizes by controlling the time and temperature of crystallization.

1) Importance for scientific point of view

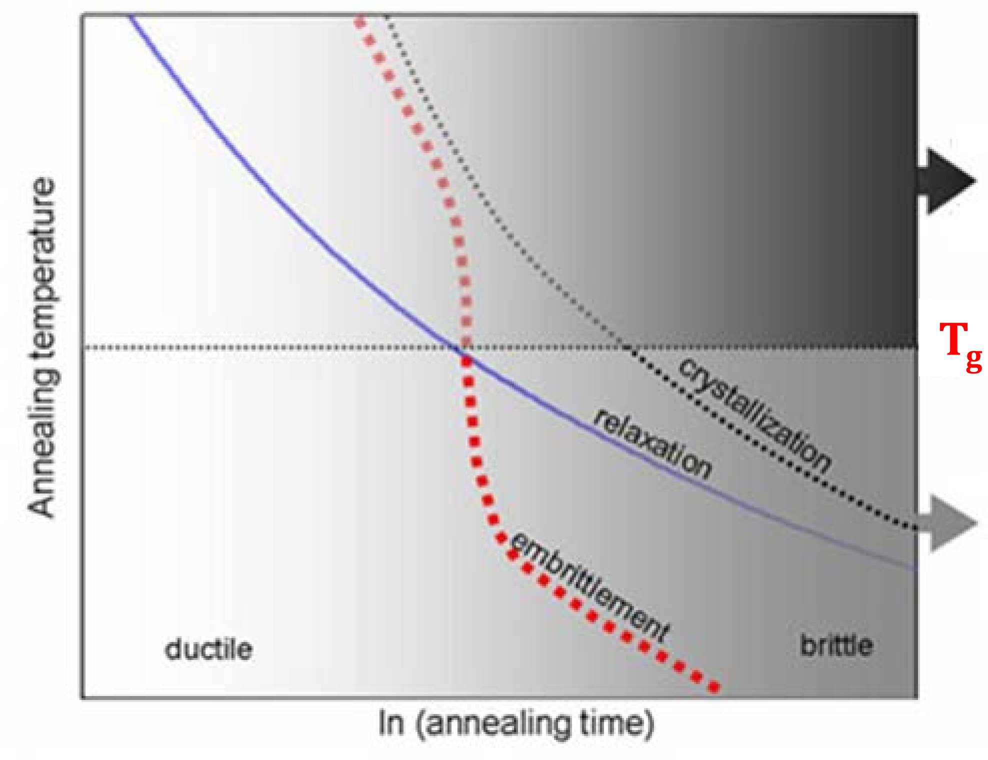
: Crystallization of metallic glasses occurs by a nucleation and growth process, it offers an opportunity to study the growth of crystals into an isotropic medium. Further, this process also offers a chance to test the classical nucleation and growth theories at large undercooling.

2) Importance for technological point of view

: ① The crystallization temperature of metallic glasses provides a real upper limit to the safe use of metallic glasses without losing their interesting combination of properties. The important and interesting properties of metallic glasses are lost as a result of crystallization.

② Metallic glass ribbons were found to lose their bend ductility upon crystallization. But, it should be realized that Tx cannot be taken as an indicator of the safe operating temperature of a metallic glass. For example, even though many Fe-based metallic glasses have Tx in the region of 400℃, their maximum long-term operating temperatures are only of the order of 150℃.

5 *Crystallization Behavior*



Embrittlement due to
Crystallization

Embrittlement due to
Relaxation

5

Crystallization Behavior

Temp. or Pressure

Amorphous phase → crystal phase

(high E (metastable) state)

Tailor the microstructure to obtain a glass+nanocrystal or an ultrafine-grained composite, or a completely crystalline materials of different grain sizes by controlling the time and temperature of crystallization.

- Studies on the crystallization behavior of metallic glasses also provide an opportunity to study the kinetics of crystallization and also the micromechanisms of crystallization. Such results will provide a clear understanding of the way the metallic glass transforms into the crystalline state and offer a means to impede or control the crystallization behavior.

  → the mechanical and other properties could be optimized through a proper understanding of the crystallization behavior of metallic glasses.

- Any property of the material that changes on crystallization of the metallic glass may be used to monitor the crystallization behavior. These include electrical resistivity, saturation magnetization, magnetic coercivity, and elastic modulus, among others. When these properties are followed as a function of temperature during the heating of the metallic glass, there is a sharp and discontinuous change at the crystallization temperature. However, such methods are indirect and therefore caution should be exercised in using them to determine the kinetics of crystallization.

Crystallization → Change of Physical Properties

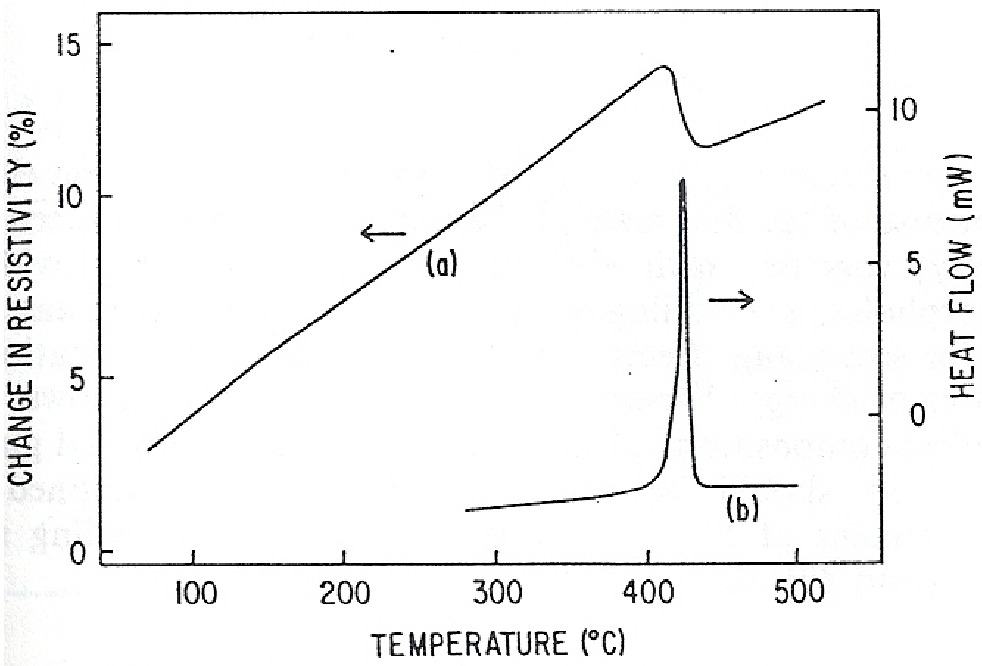


Figure 10.3 (a). Resistivity curve obtained by heating the glass $Fe_{40}Ni_{40}B_{20}$ at 5 K/min from room temperature (courtesy of J. Rout). (b). DSC trace obtained under the same conditions

→ Monitor the crystallization of metallic glass : electrical resistivity – sharp decrease in onset of crystallization

Any of the property changes described above may be used to monitor the crystallization of a metallic glass.

- Electrical Resistivity
- Elastic Modulus
- Magnetic coercivity
- Saturation magnetization

and so on.

5

Crystallization Behavior

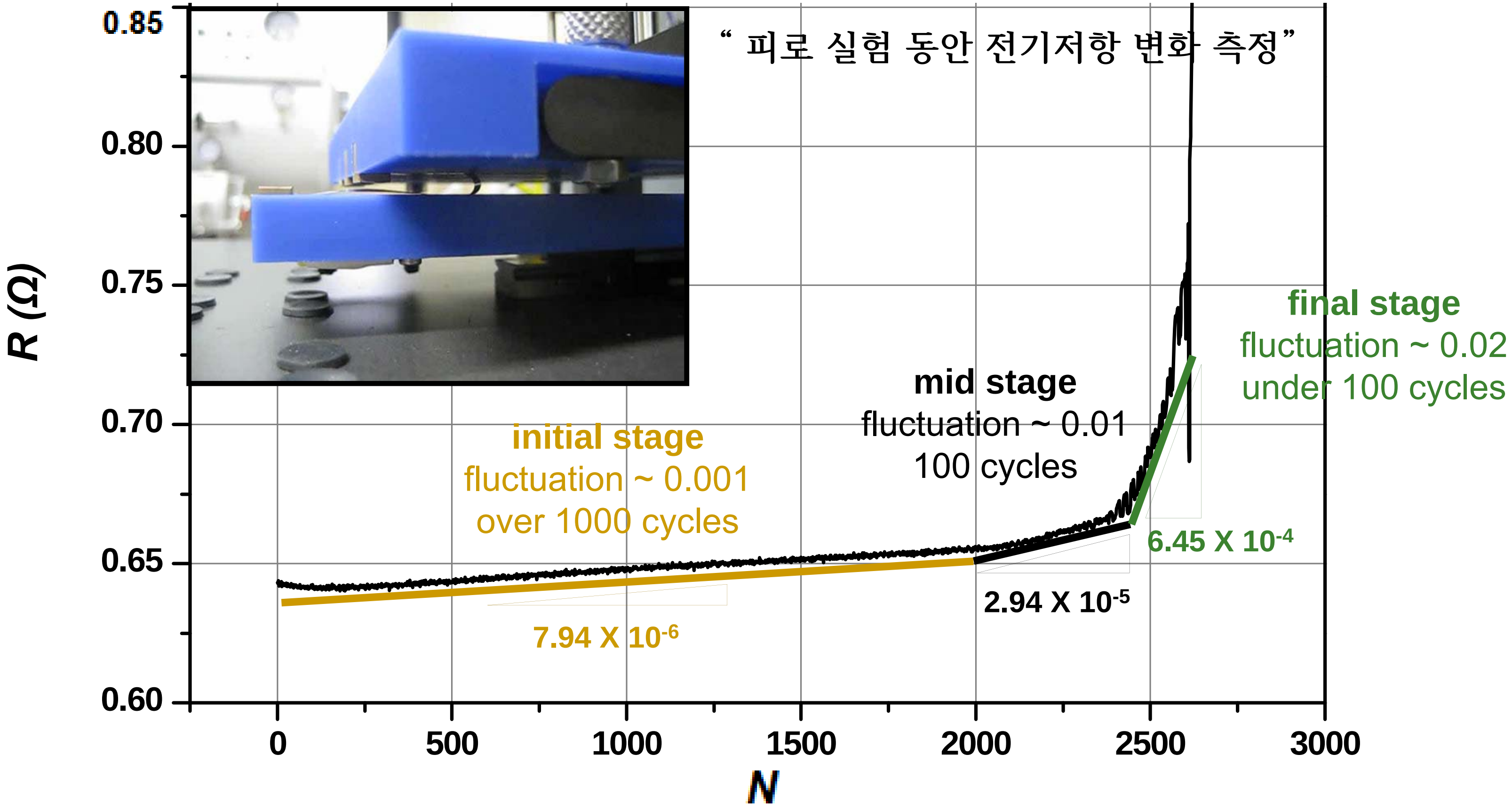
Temp. or Pressure

Amorphous phase → crystal phase

(high E (metastable) state)

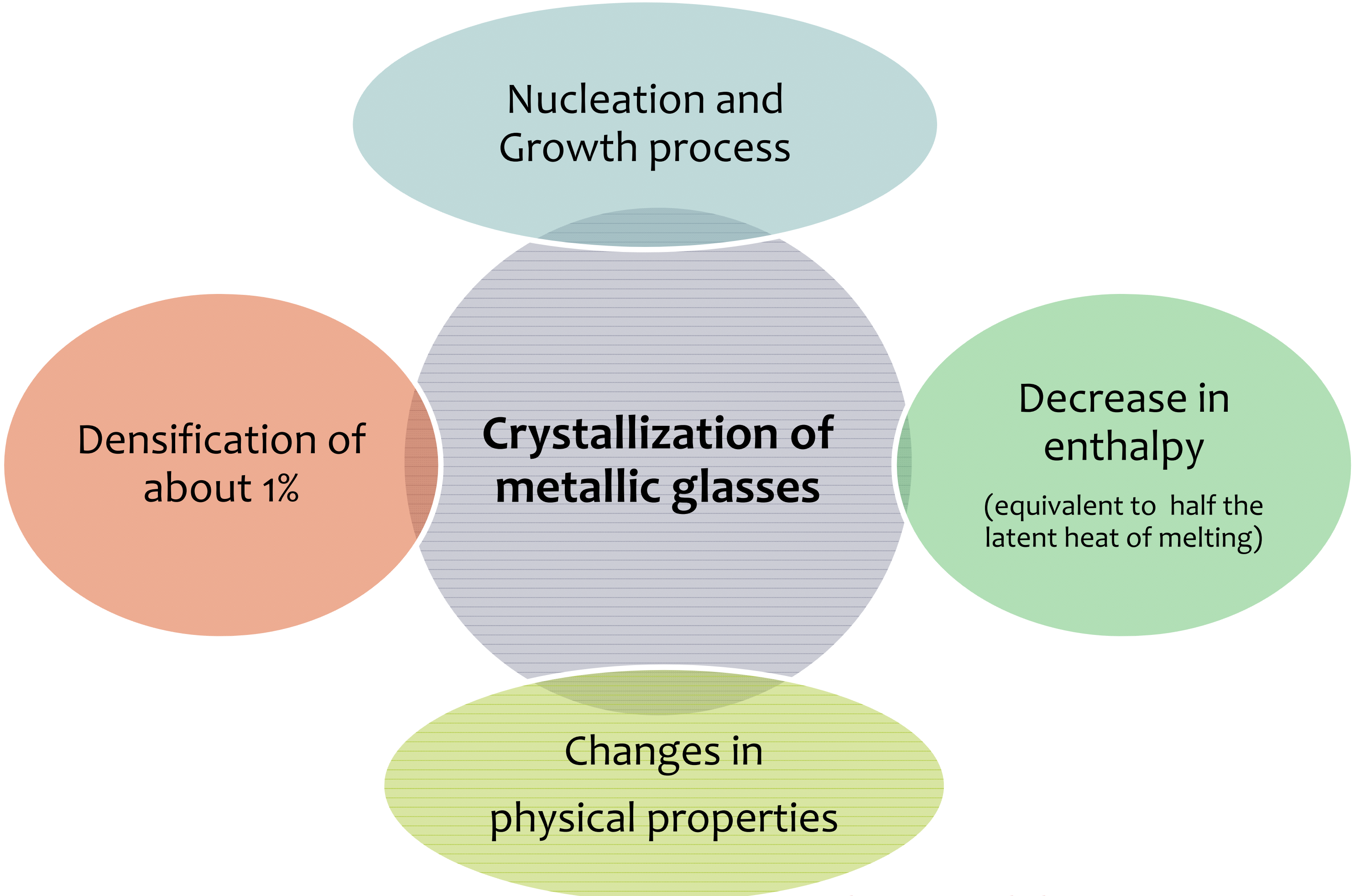

Shear deformed areas

Elastic → Viscoelastic deformed region → Various defects → Cracks → Plastic ↑ ········→ Electrical resistance ↑


“ 피로 실험 동안 전기저항 변화 측정”

균일 반복 피로실험을 통한 비정질 금속의 물성변화 측정

CRYSTALLIZATION



Crystallization of metallic glasses

Nucleation and Growth process

Densification of about 1%

Decrease in enthalpy

(equivalent to half the latent heat of melting)

Changes in physical properties

Elastic modulus, magnetic coercivity

5.2.3 Structural Details

Amorphous vs Nanocrystalline

1) *Microstructural observation*

XRD, (HR)TEM, *EXAFS …*

2) *Thermal analysis*

DSC (Differential Scanning Calorimetry)

: Measure heat absorbed or liberated during heating or cooling

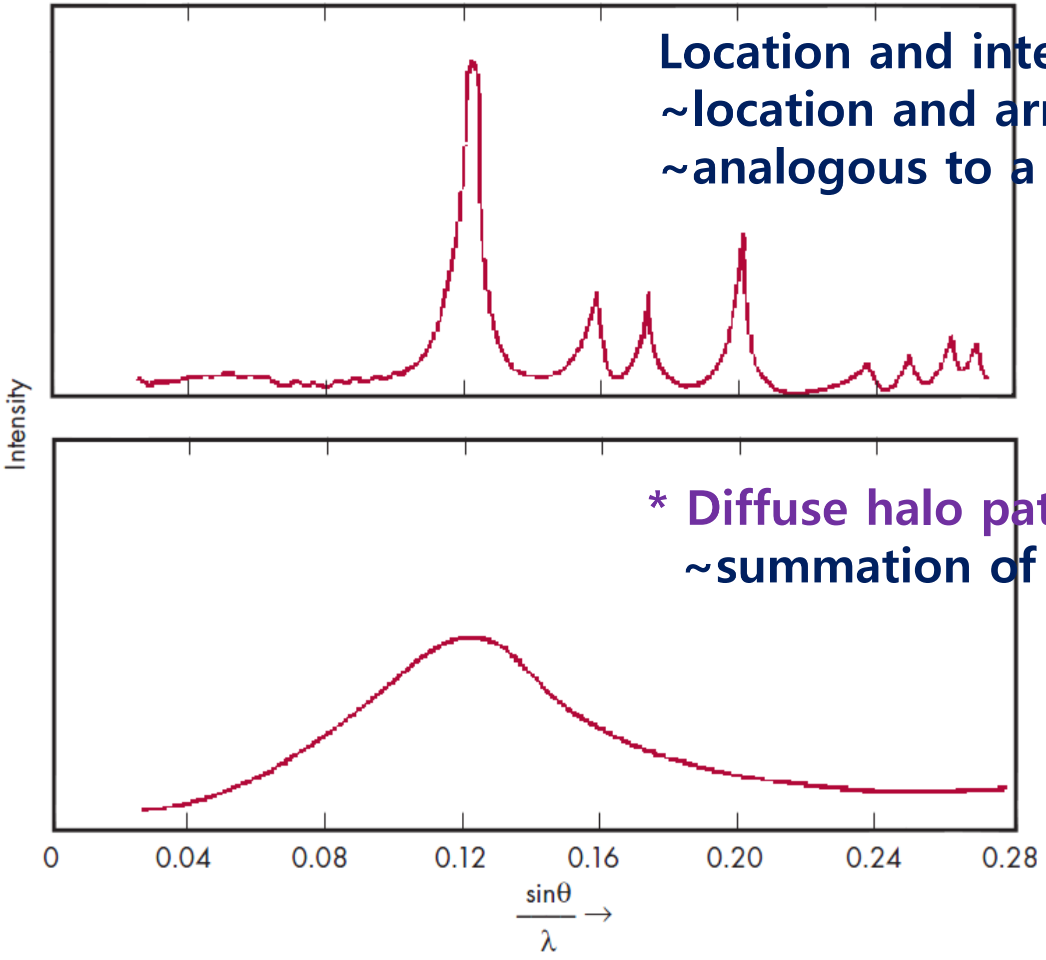
cf) **a)** ***glass*** → ***nucleation & growth***

(perfect random)

b) ***local clustering*****: quenched-in nuclei** → ***only growth***

c) ***Nanocrystalline*** → ***growth***

X-ray or Neutron results



Location and intensity of peaks
~location and arrangement of atoms
~analogous to a fingerprint

* Diffuse halo pattern
~summation of interference

Figure 3. Characteristic Diffraction Patterns from Crystalline Material (Top) and Amorphous Material (Bottom).

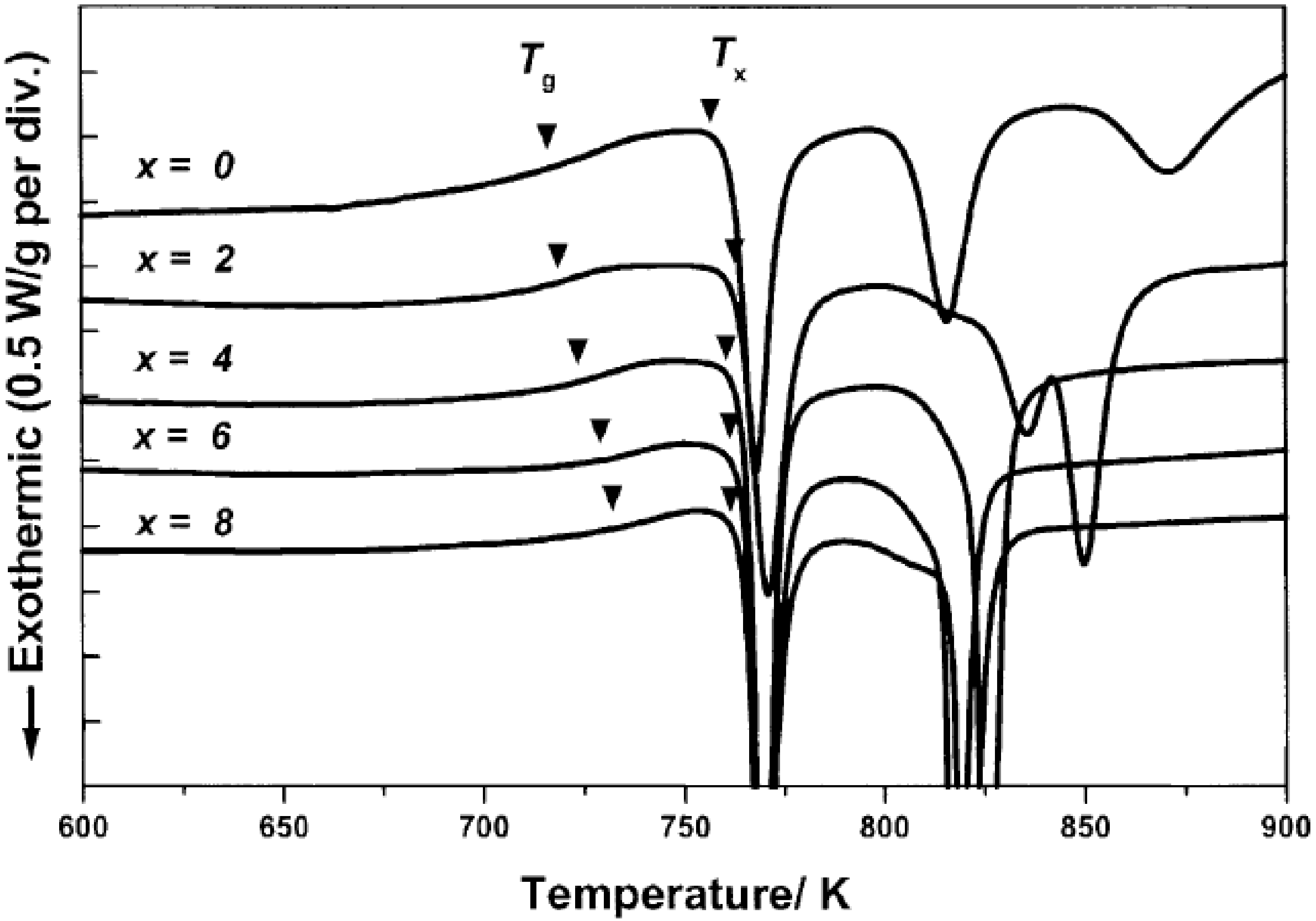
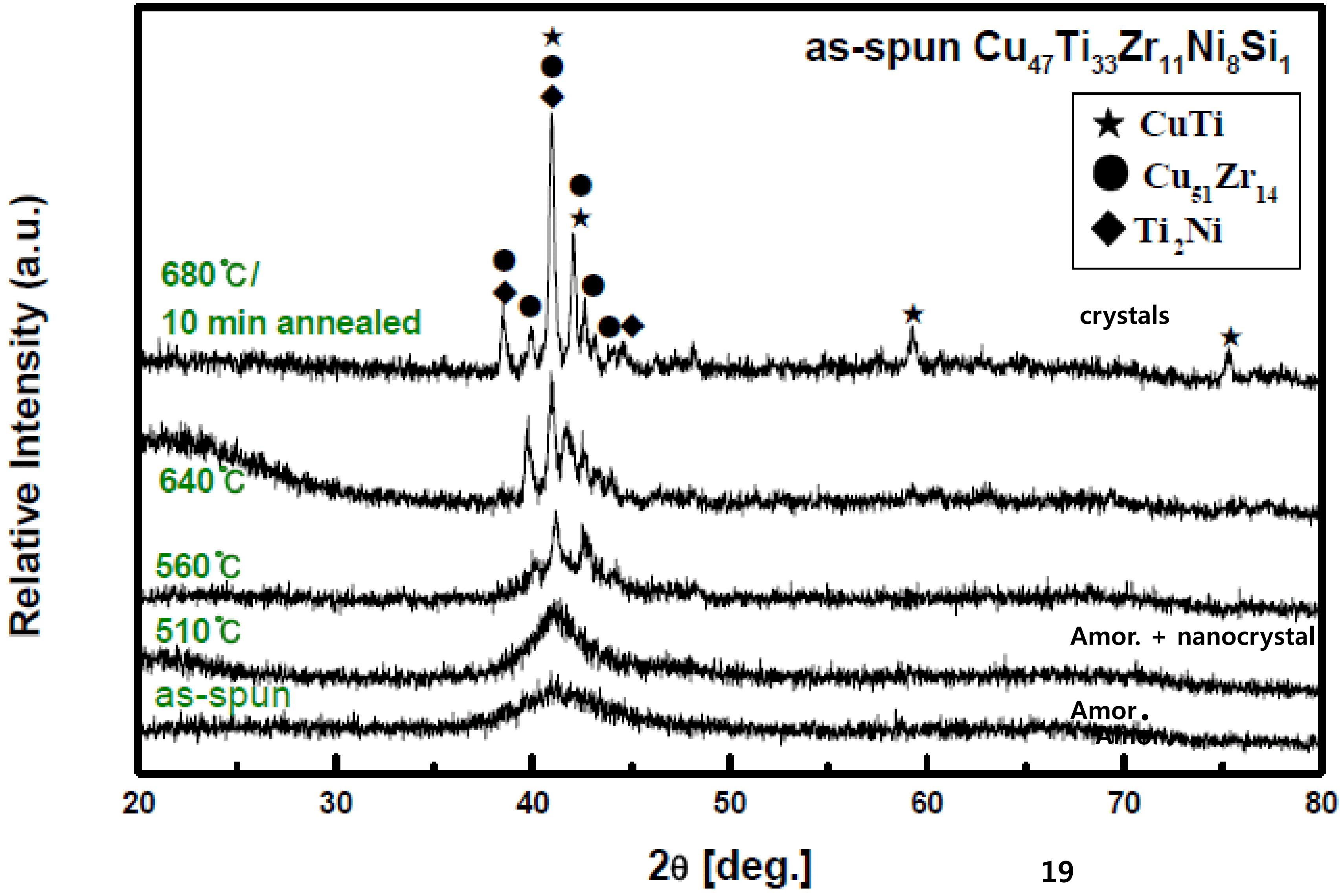


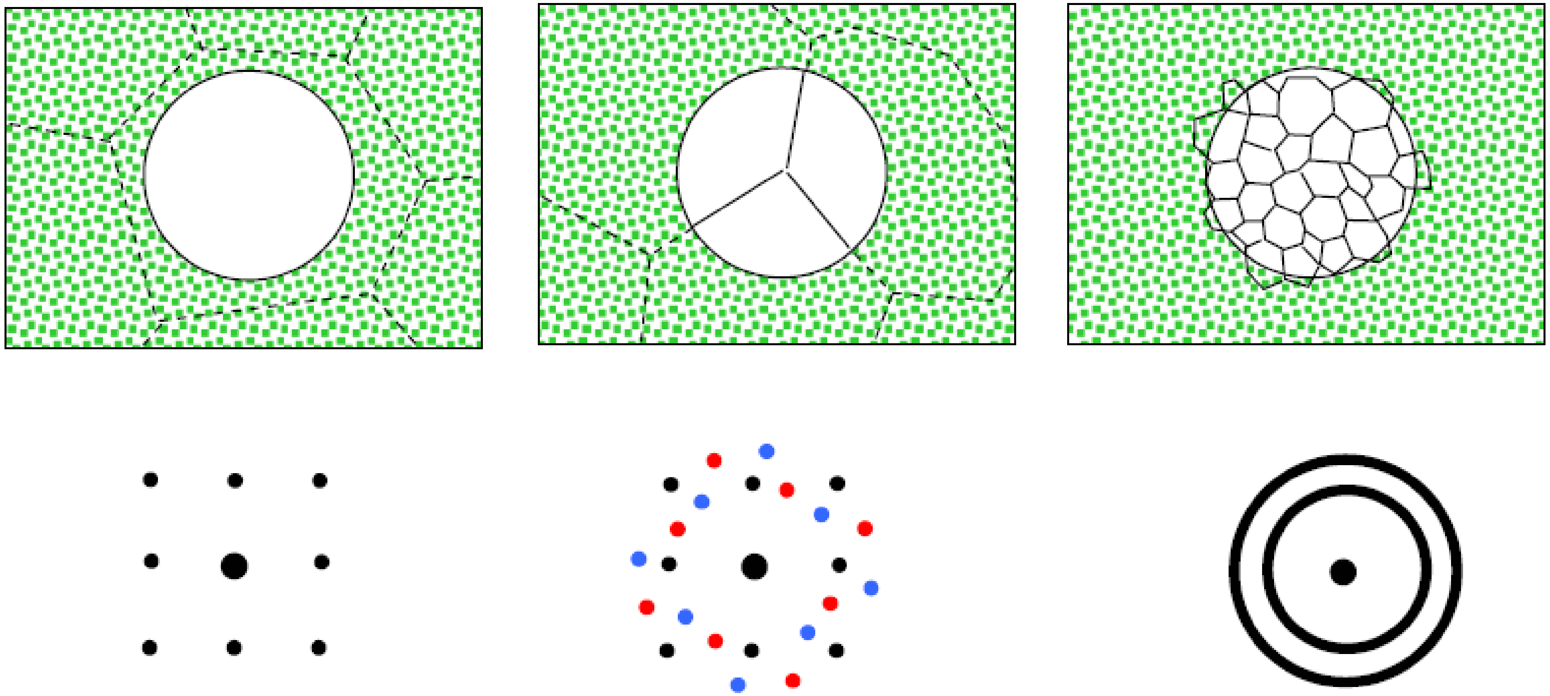
Fig. 1. DSC traces of rapidly solidified $Cu_{47}Ti_{33}Zr_{11}Ni_{8-x}Sn_xSi_1$ ($x = 0, 2, 4, 6, 8$) alloy ribbons obtained during heating with a heating rate 0.667 K/s.

< X-ray diffraction >

Crystallization after annealing



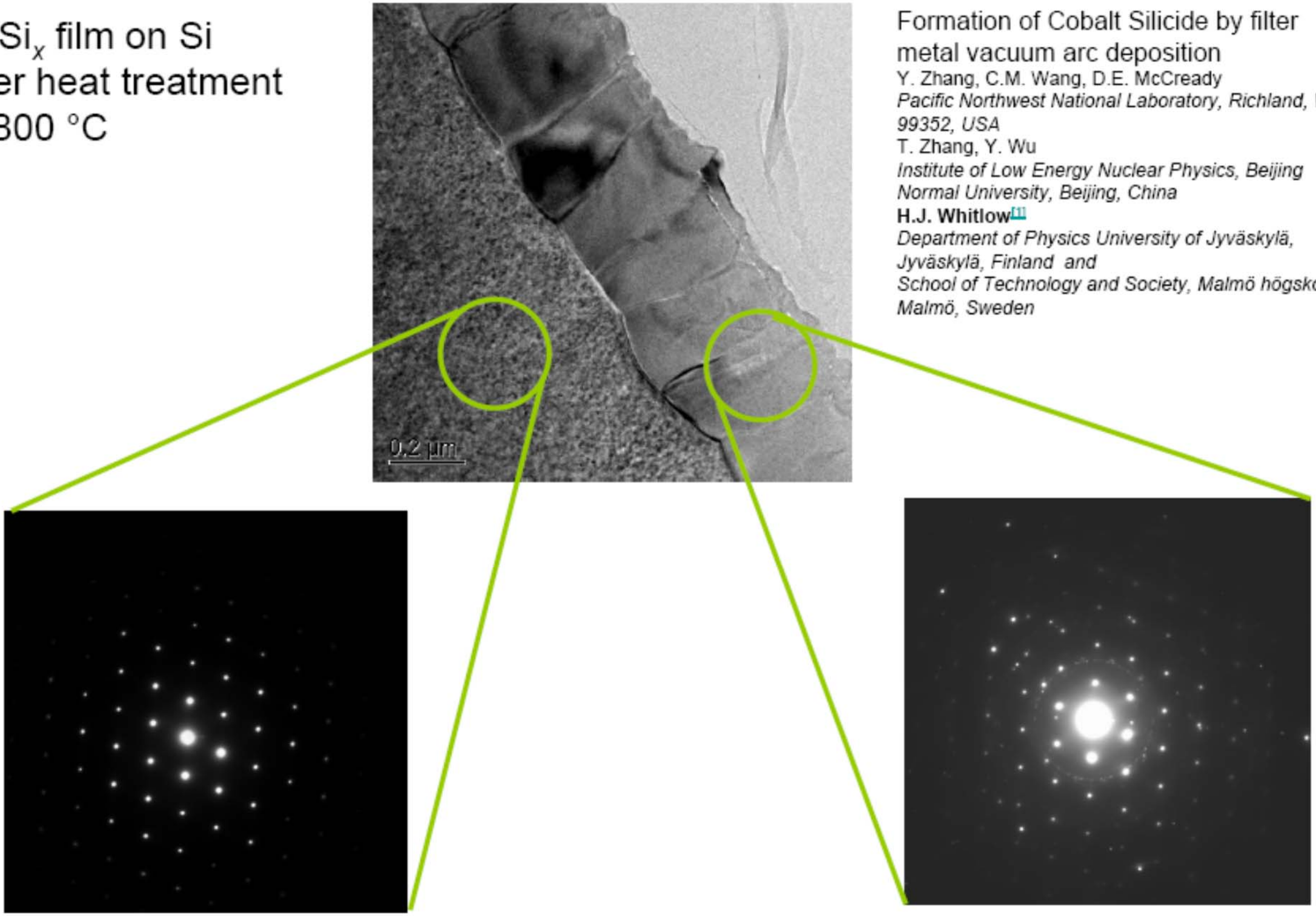
Electron Diffraction Pattern--Spot to Ring



(a) (b) (c)

Selected area diffraction

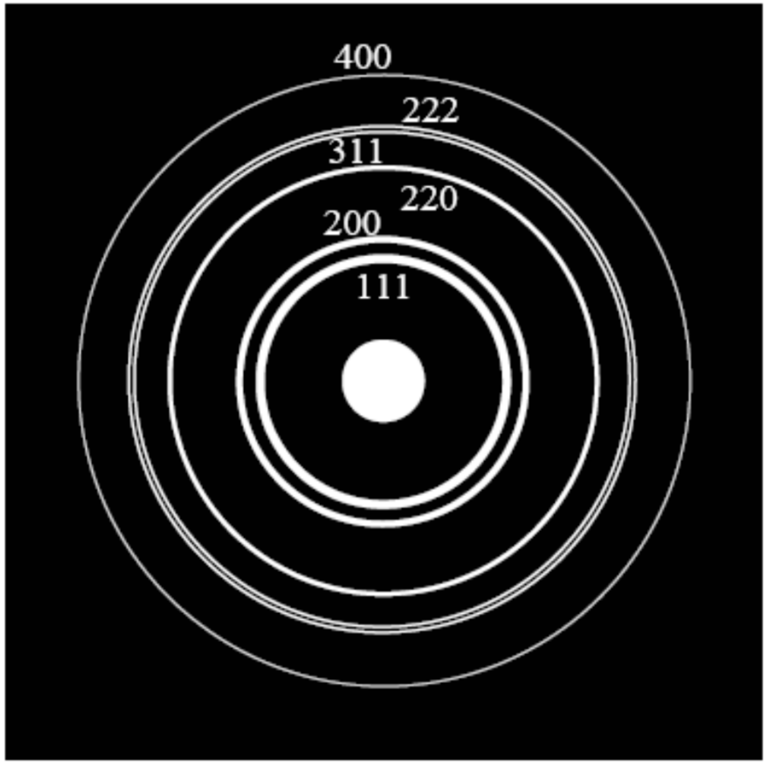
CoSi$_x$ film on Si
after heat treatment
at 800 °C



Formation of Cobalt Silicide by filter metal vacuum arc deposition
Y. Zhang, C.M. Wang, D.E. McCready
Pacific Northwest National Laboratory, Richland, WA 99352, USA
T. Zhang, Y. Wu
Institute of Low Energy Nuclear Physics, Beijing Normal University, Beijing, China
H.J. Whitlow[1]
Department of Physics University of Jyväskylä, Jyväskylä, Finland and
School of Technology and Society, Malmö högskola, Malmö, Sweden

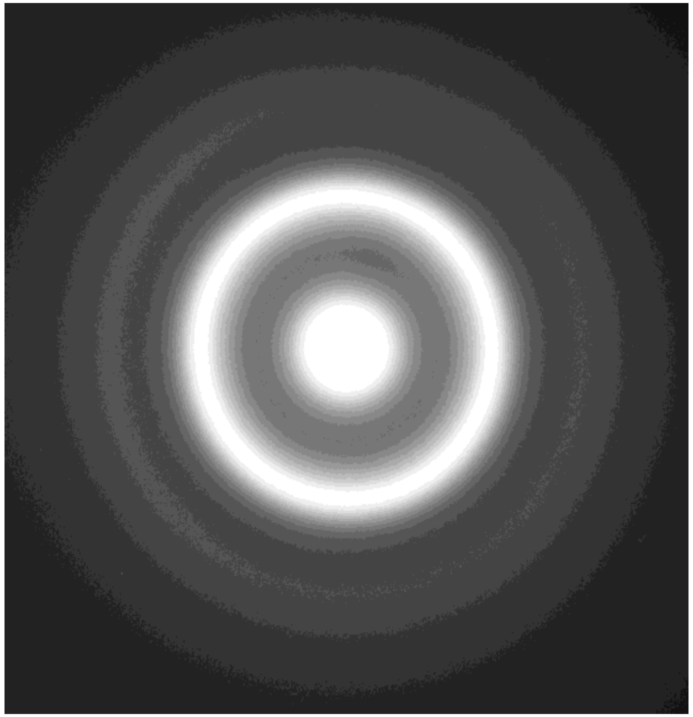
Ring pattern

- Typical polycrystalline Au diffraction pattern

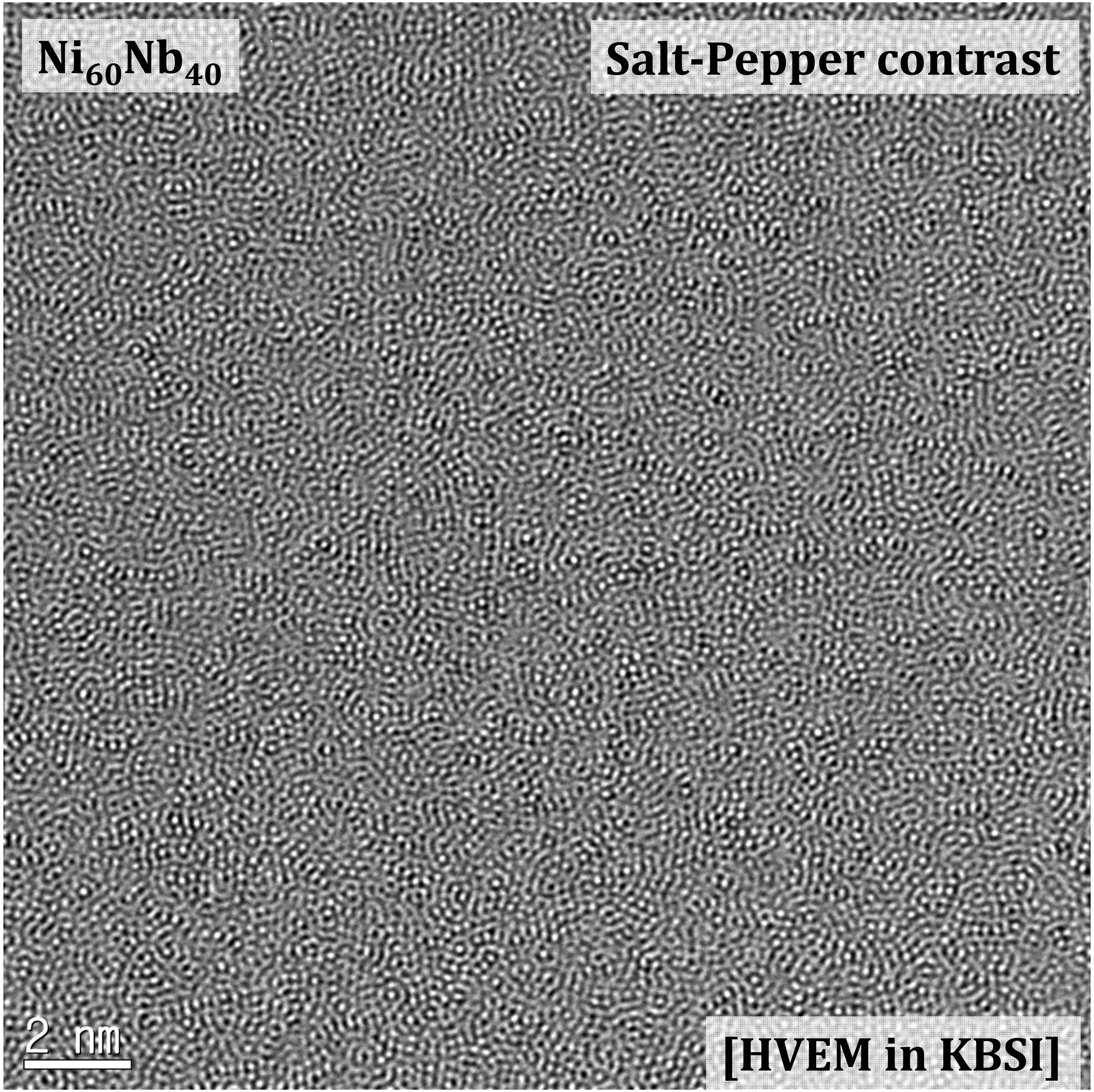


Amorphous materials

- Diffused ring pattern
- Reflecting the short range ordered structure
- Often seen at contamination layer or on carbon support film



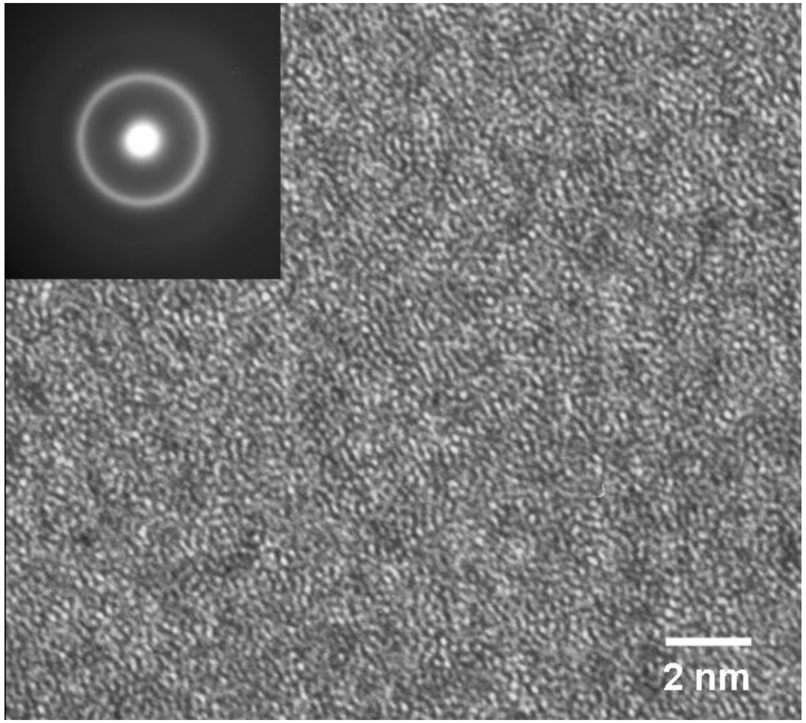
Sample thinning, In-situ heating 시 surface nucleation & diffusion 영향 고려 요망


$Ni_{60}Nb_{40}$
Salt-Pepper contrast
2 nm
[HVEM in KBSI]

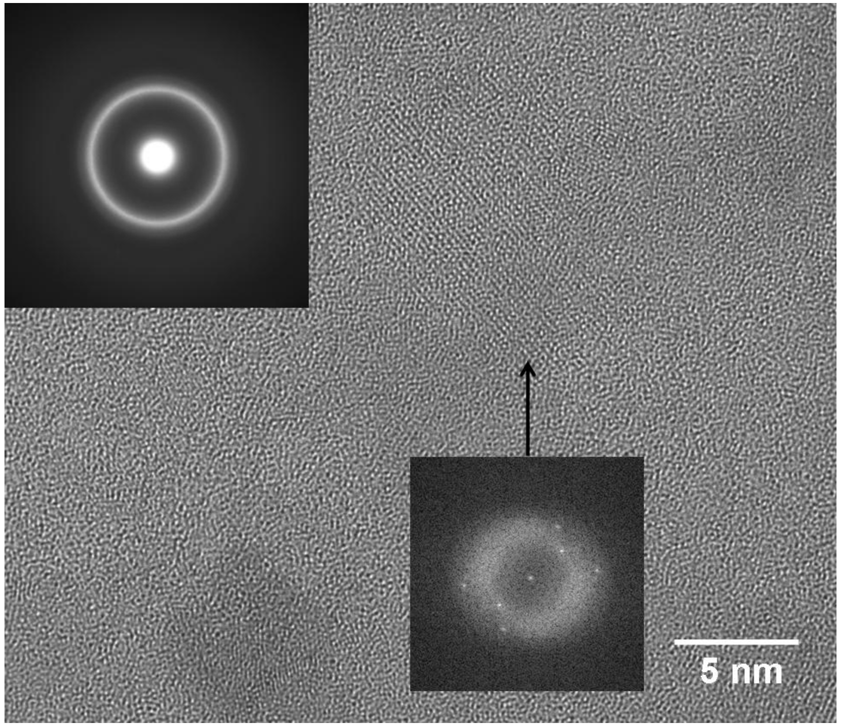
Structural analyses: HRTEM

$Cu_{46}Zr_{42}Al_{7}Y_{5}$

As-melt-spun



Heated up to 480℃



: nanocrystallization of Y rich amorphous phase due to relatively lower GFA

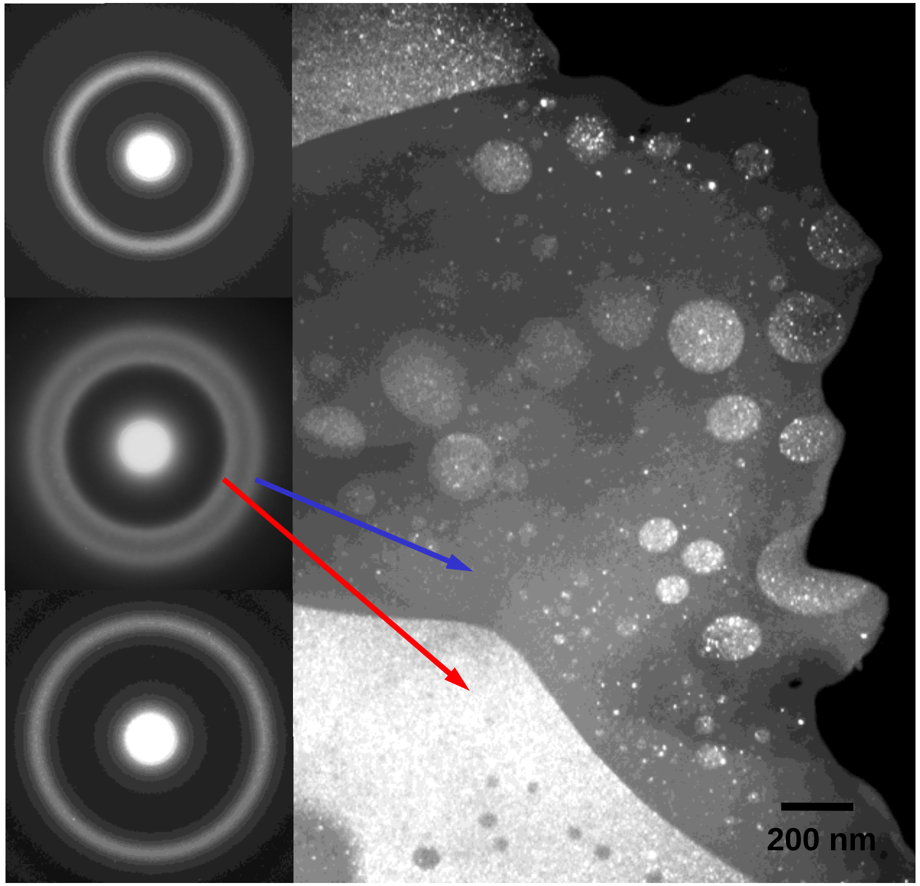
* Acta Materialia, 54, 2597 (2006)

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

Angle range of Small angle scattering

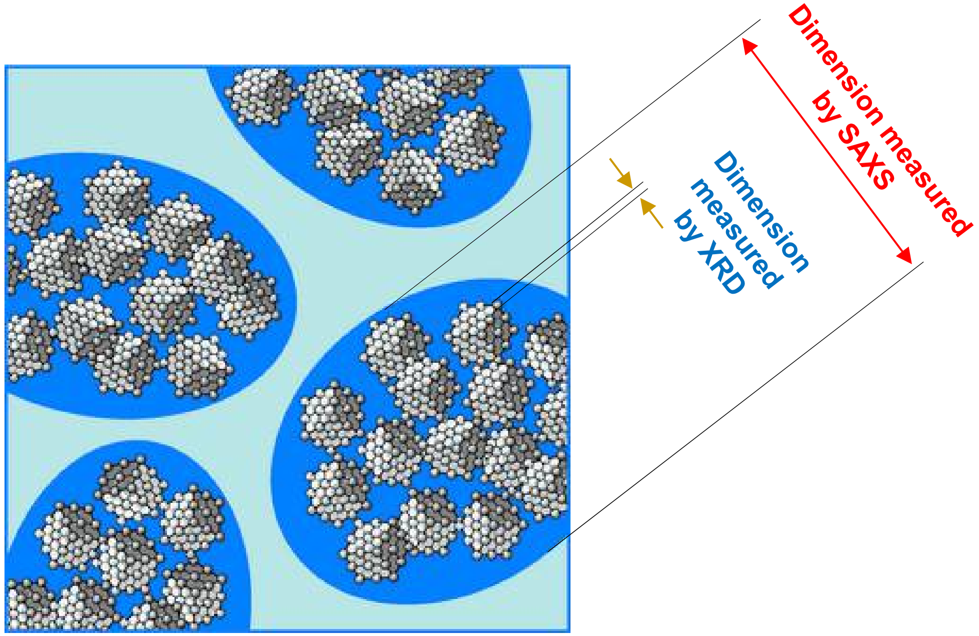
- Length scale of small angle scattering : 1 – 1000 um

- Information on relatively large r is contained in $I(q)$ at relatively small q $(=4\pi\sin\theta/\lambda)$

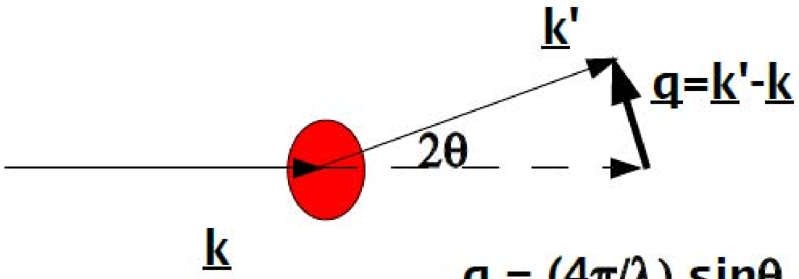
- Bragg's law : $\sin\theta=\lambda/2d$

d = few Å λ = 1 Å 2θ = 20
d = 100 Å λ = 1 Å 2θ = 0.6

- Sample contains a scattering length density inhomogeneity of dimension larger than 1 nm, scattering becomes observable in small angle region (0 ~ 4°)



Diffraction v.s. Small angle scattering

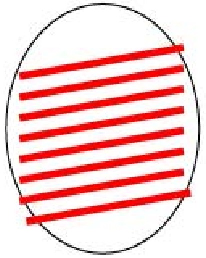


$q = (4\pi/\lambda) \sin\theta$

x-rays scatter from *electrons*

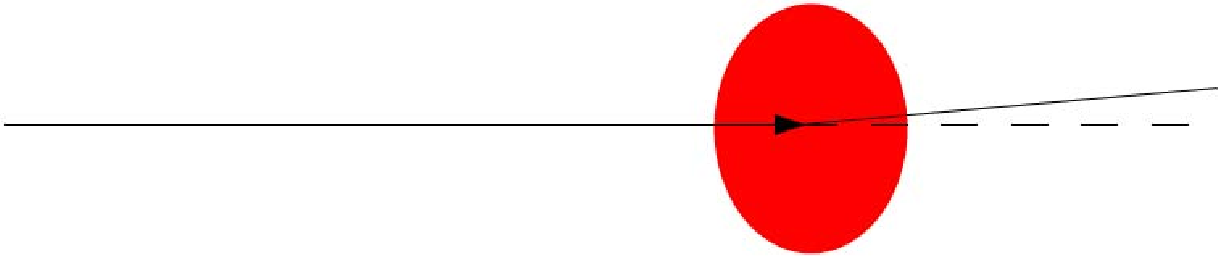
neutrons scatter from *nuclei* and *magnetic moments*

diffraction



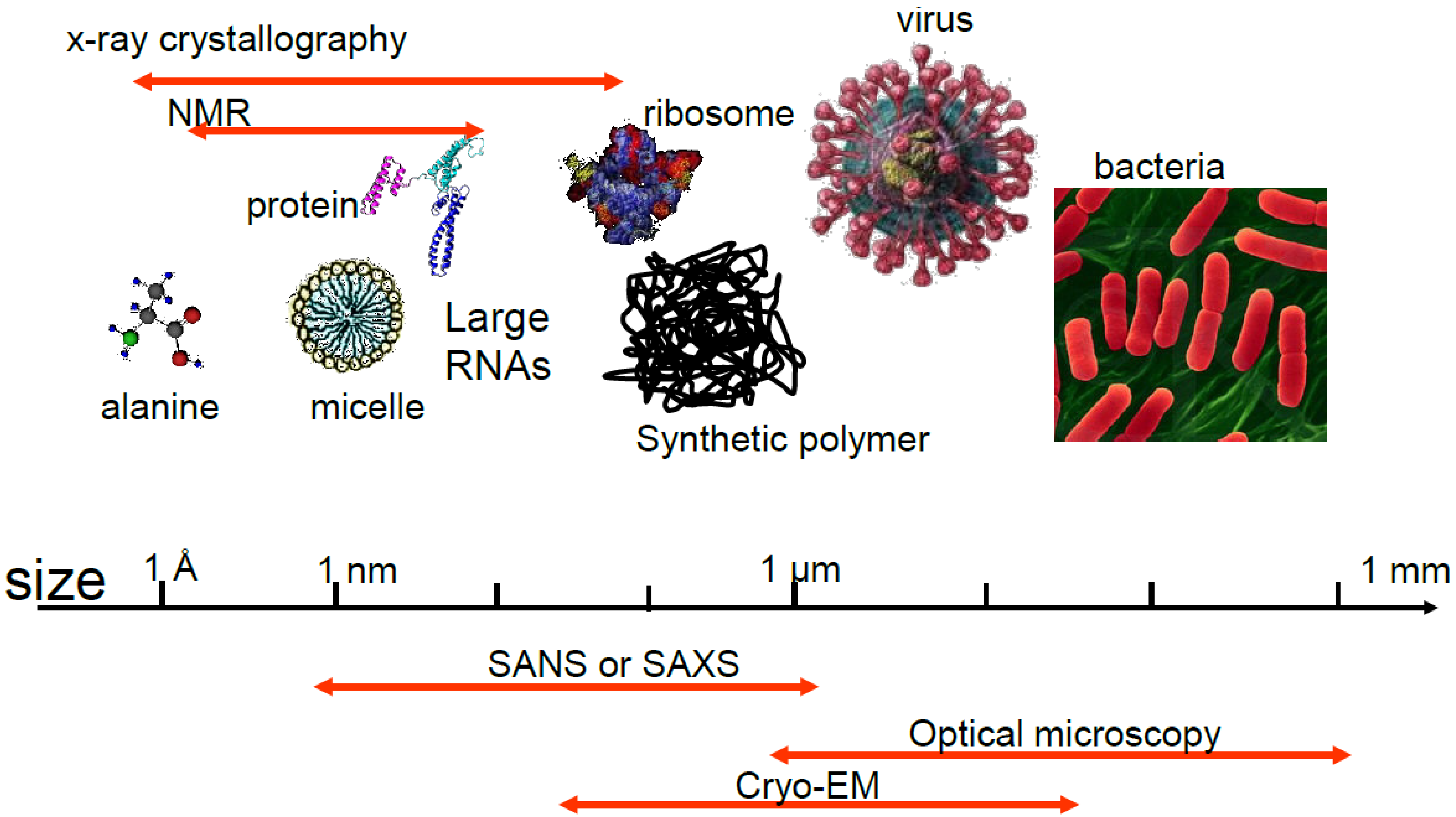
- scattering from *atomic structures*
- size of objects ~ λ
- small length scale -> large angle

small-angle scattering



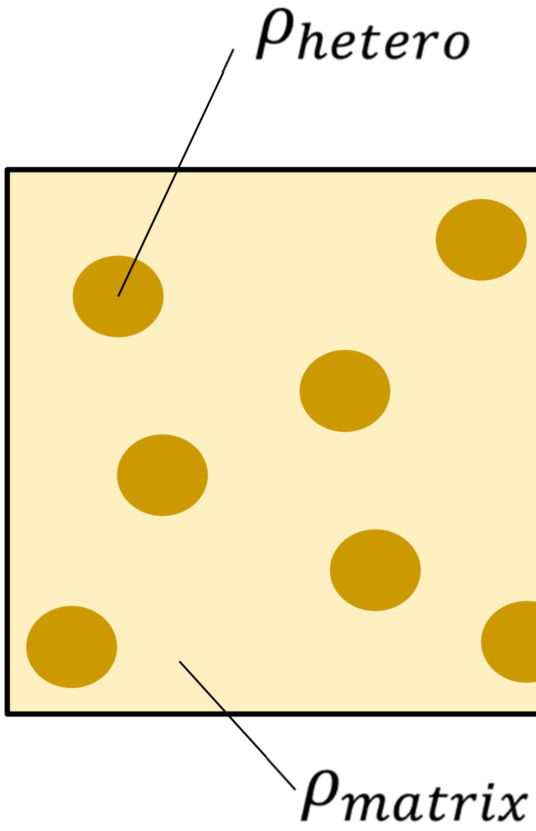
- scattering from *interfaces*
- size of objects >> λ
- large length scale -> small angle

Length scale for small angle scattering



The scope of small angle X-ray scattering in terms of spatial dimension covers ~1nm to ~1µm ranges, perfectly suitable for biomolecular structrual study.

Scattering length density



Scattering length density
(of heterogeneities)

$$\rho = \frac{\sum_j^n b_j}{\bar{V}}$$

b_j : bound coherent scattering length of atom j

$\bar{V}$: Volume containing the n atoms

$$\Delta\rho = \rho_{hetero} - \rho_{matrix}$$

Intensity in small angle scattering

Scattering length density
(of heterogeneities)

$$\rho = \frac{\sum_j^n b_j}{\bar{V}}$$

$$\Delta\rho = \rho_{hetero} - \rho_{matrix}$$

$$\bar{V} = \frac{M_w}{N_A \cdot \rho_{mass}}$$

$$I(q) = \boxed{\Delta\rho^2} d_N \int_0^R N(r)[V(r)F(q,r)]^2 dr$$

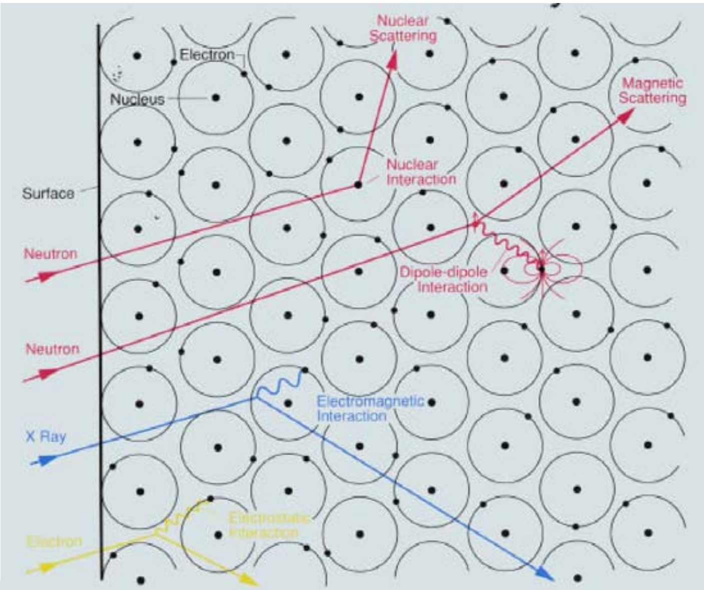
d_N : number density factor
N(r) : normalized size distribution
V(r) : Volume
F(q,r) : Form factor of particles

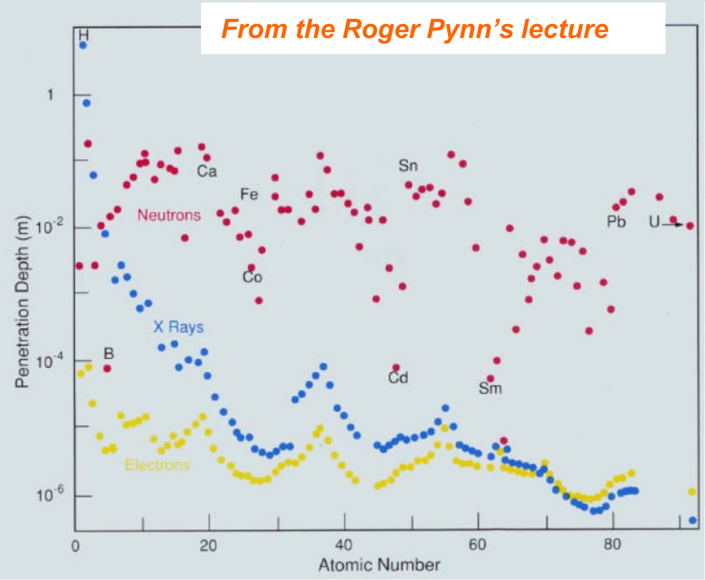
Common factors in both SANS and SAXS

$$\Delta\rho = \rho_{hetero} - \rho_{matri}$$

Coherent and Incoherent Scattering

items	X-ray	neutron
source	collision of electrons with target metals(Cu, Mo, W…) acceleration of charged particles	nuclear reactor spallation neutron source (accelerator)
scattered by	electrons	atomic nuclei, unpaired spins
interaction	EM(electromagnetic)	Nuclear(strong int.) EM
scattering amplitude	linearly depend on Z	nearly indep. on Z
sample amount	μg ~ mg	~g
meas. time	$10^{1\sim2}$min (step scan: ~hr)	$10^{0\sim2}$ hr
hard to see	relatively light elements (H, Li, B, C, O …)	highly abs. nuclei (Gd, Sm, Eu, Cd, B…)

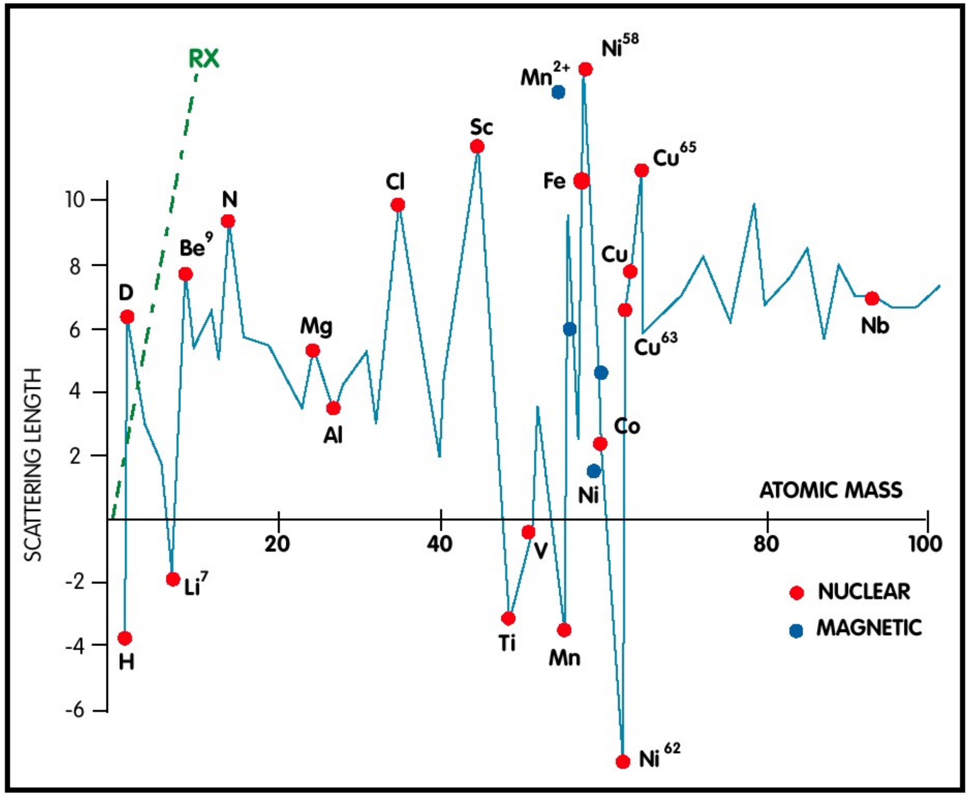




From the Roger Pynn’s lecture

Neutron scattering length

$$\Psi = \psi_{in} + \psi_{scatt} = e^{i\,k\,z} - (b/r)\, e^{i\,k\,r}$$



- **intrinsic property !!!**
- order of 10^{-15}m (fm)
- sometimes negative or imaginary values (resonance scattering)
- independent of the thermal neutron energy
- no correlation with Z or A