

2018 Spring

**“Advanced Physical Metallurgy”
- Bulk Metallic Glasses -**

06.18.2018

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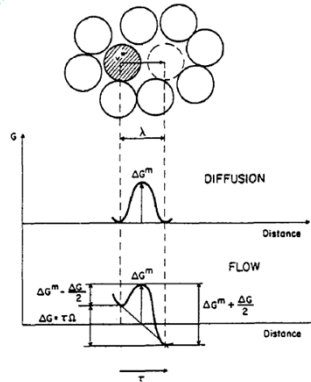
Deformation modes

Plastic deformation

(γ , τ , T)

F. Spaepen : Free volume theory

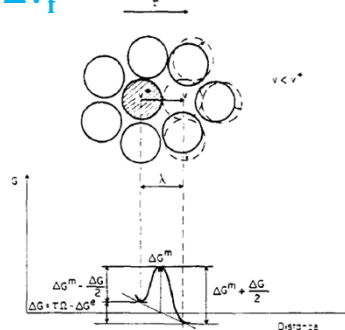
Homogeneous flow @ steady state



Inhomogeneous flow @ steady state

Competition of shear-induced disordering and a diffusion controlled reordering;
creation of FV vs. relaxation

$$\Delta v_f^+ = \Delta v_f^-$$



A. S. Argon / C. A. Schuh: STZ model

Homogeneous plastic flow

Viscous flow of a SCL

Steady-state flow

Structural disordering과 ordering,
즉 free volume creation과 annihilation 사이의 균형.

$$\Delta v_f^+ = \Delta v_f^-$$

Local diffusive jump 또는 STZ operation이 stress를 분산시키고, dilatation을 통해 free volume을 만들지만 동시에 relaxation이 진행되어 free volume을 없앤다.

Structural maintenance

Non-steady-state flow

Structural transience가 일어남.

균형이 이루어지지 않아 net gain / loss of free volume이 일어날 수 있다.

“overshoot” “undershoot”

Inhomogeneous plastic flow

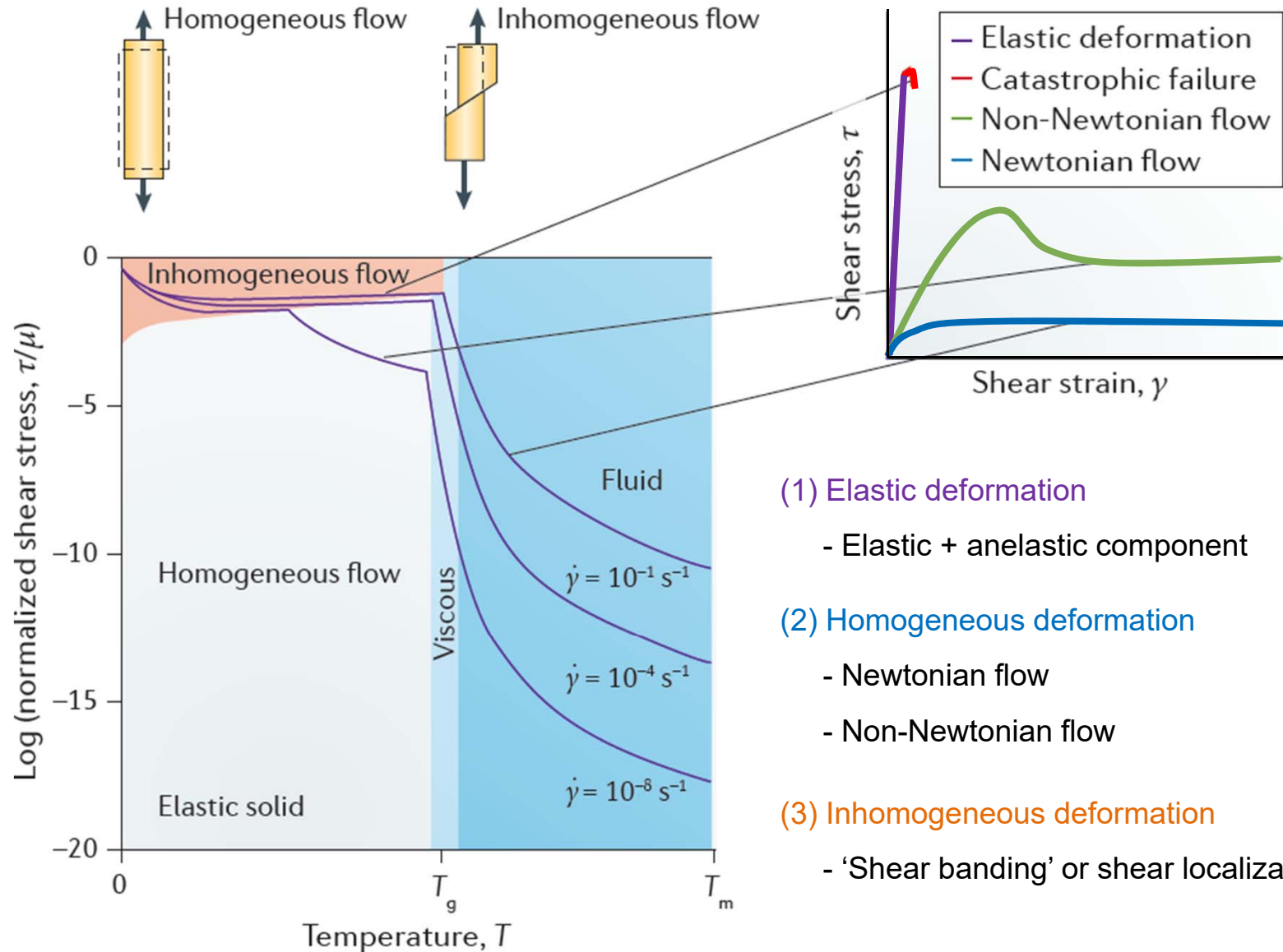
Localization → Shear band formation

local production of FV (dilatation)

local evolution of structural order due to STZ operation

redistribution of internal stresses

Deformation mode of bulk metallic glasses



(1) Elastic deformation

- Elastic + anelastic component

(2) Homogeneous deformation

- Newtonian flow
- Non-Newtonian flow

(3) Inhomogeneous deformation

- 'Shear banding' or shear localization

Deformation behavior of nanoscale metallic glass

Bulk metallic glass

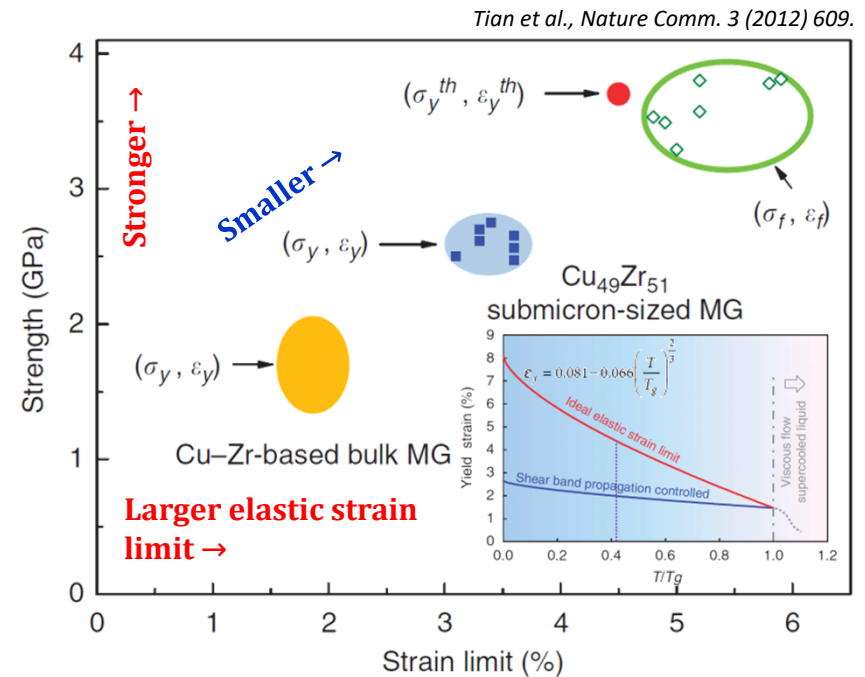
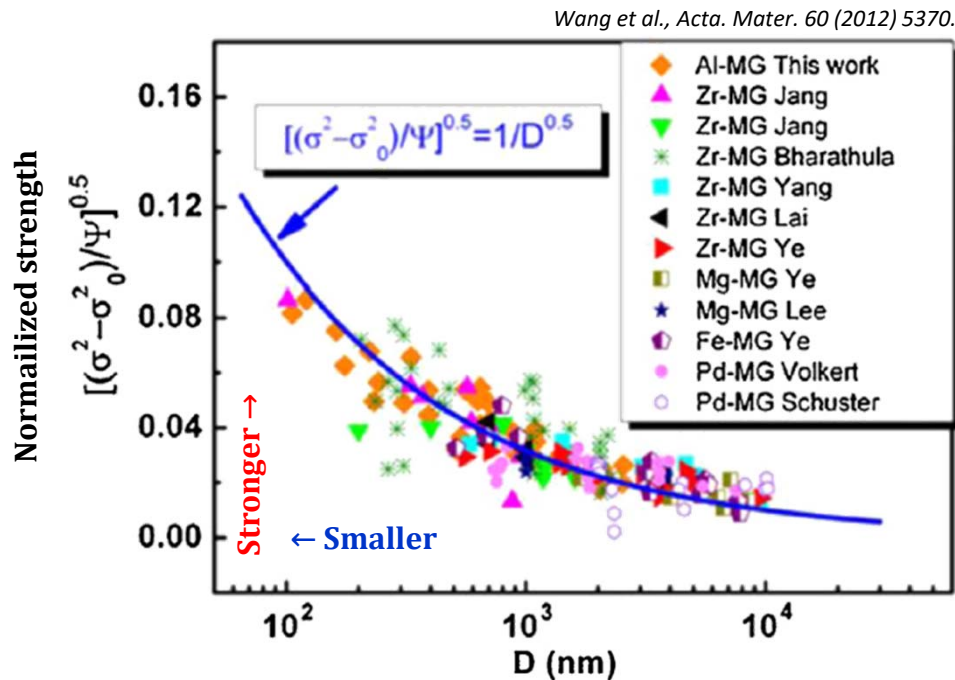
(Brittleness, Strength $\sim 0.02E$)



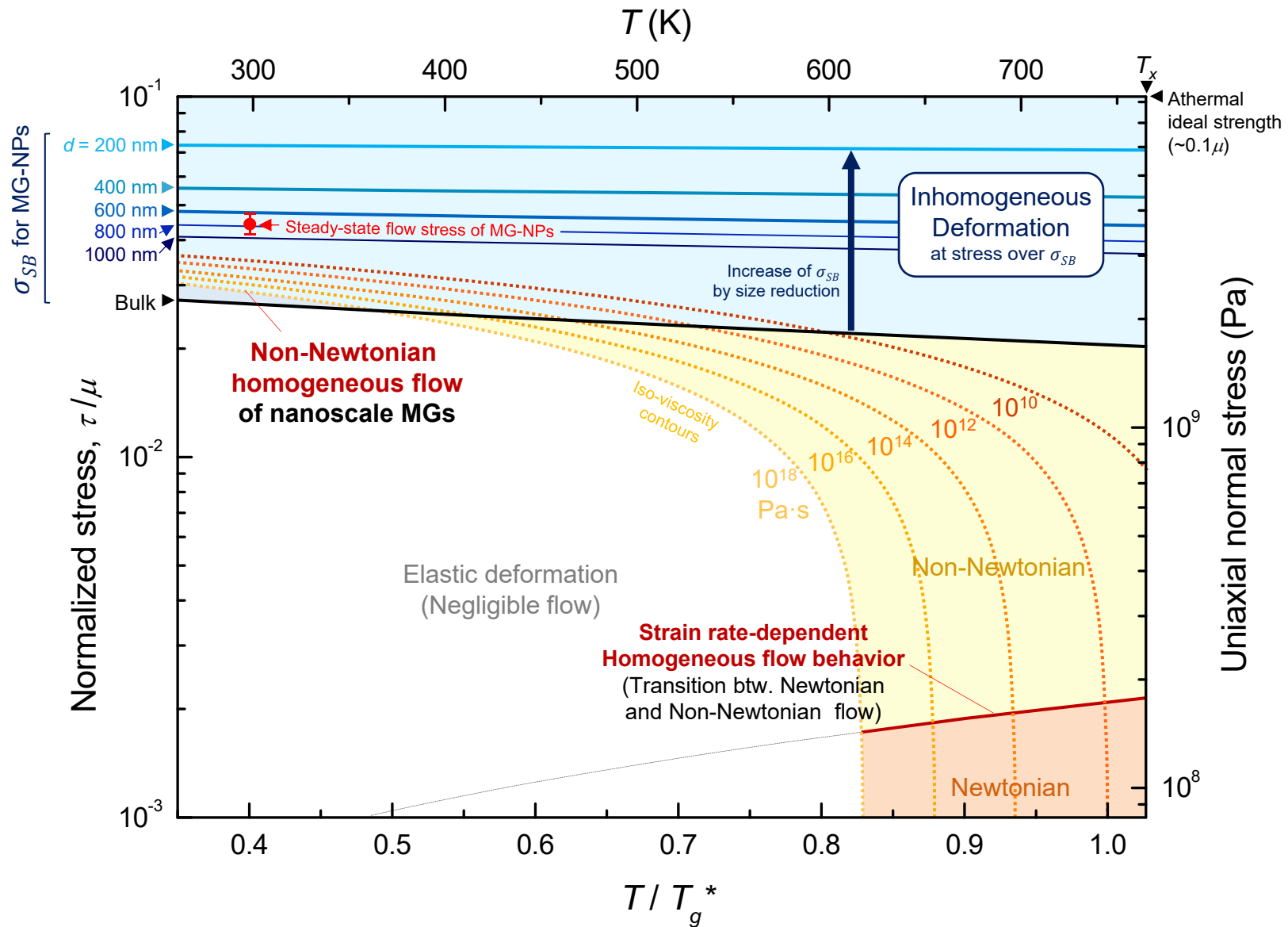
Nanoscale metallic glass

(The smaller is the stronger,
and be also more ductile!)

▶ Sample size effect on the strength and elastic limit of metallic glasses



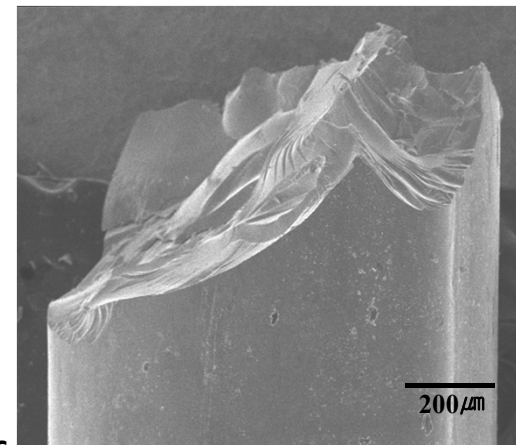
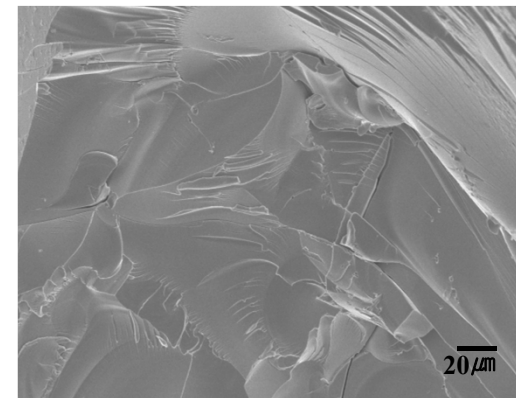
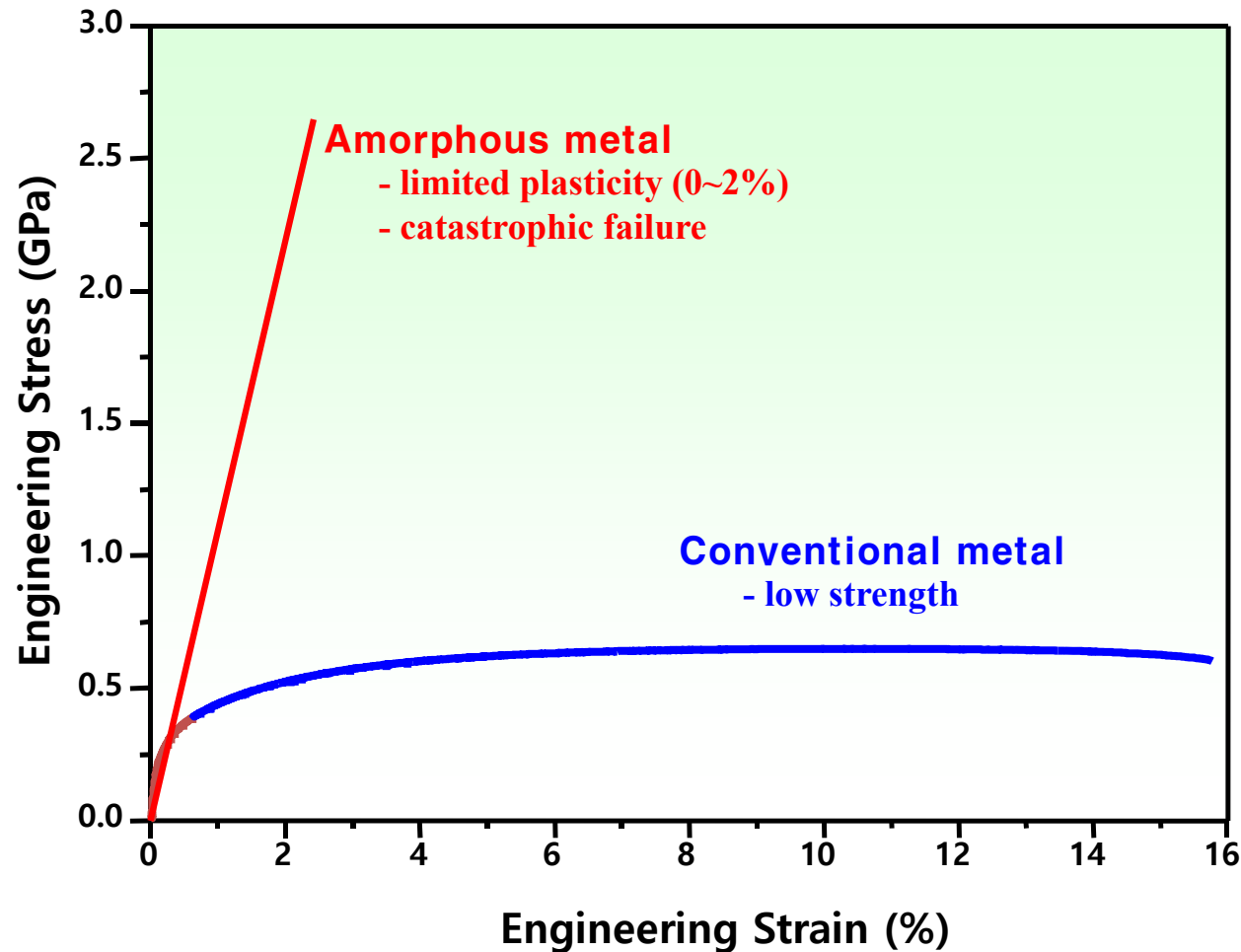
III. Construction of deformation map of nanoscale metallic glasses

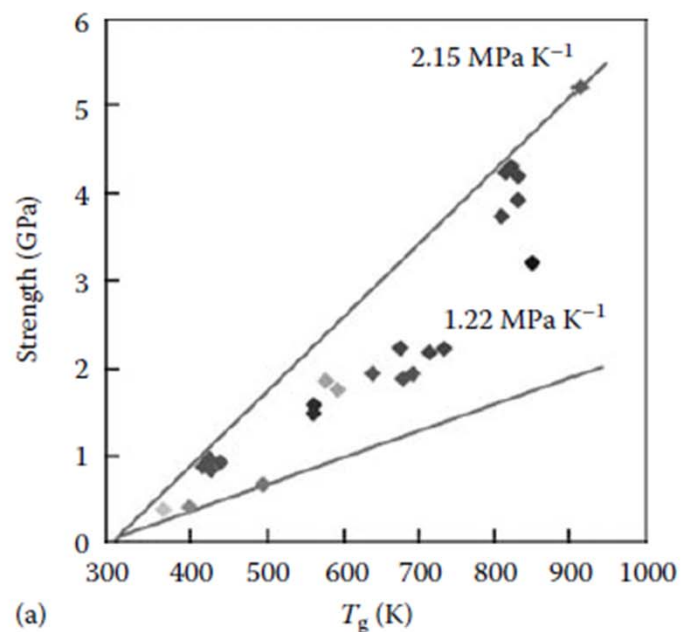


Limited Plasticity by shear softening and shear band

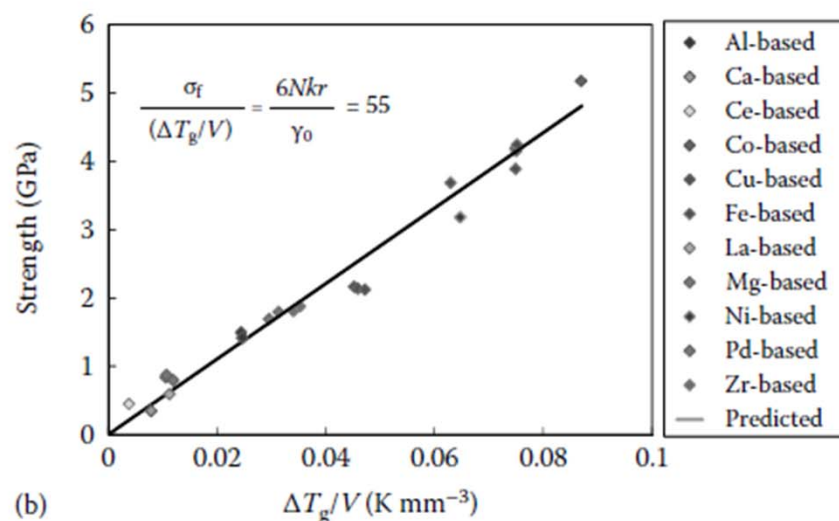
- Microscopically brittle fracture

➔ Death of a material for structural applications





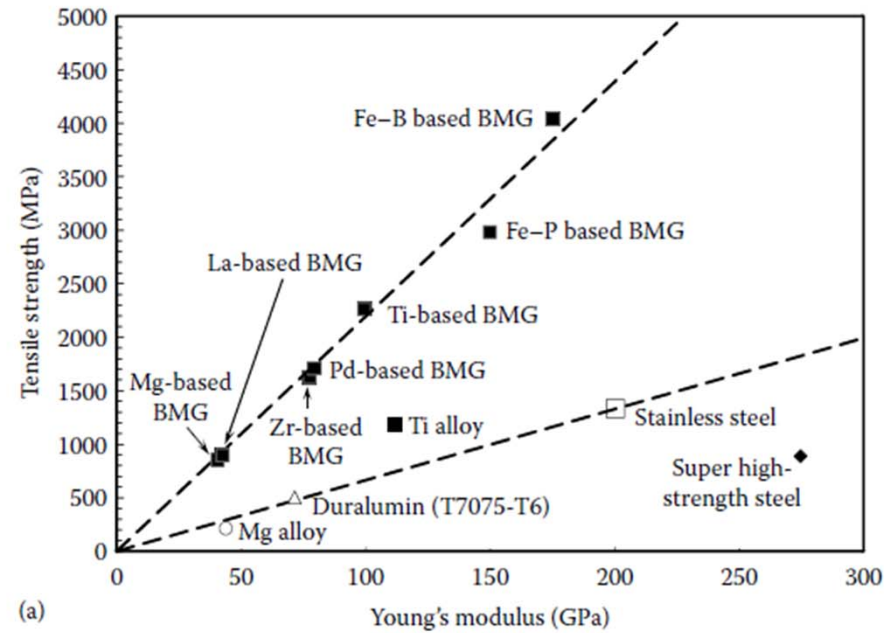
(a)



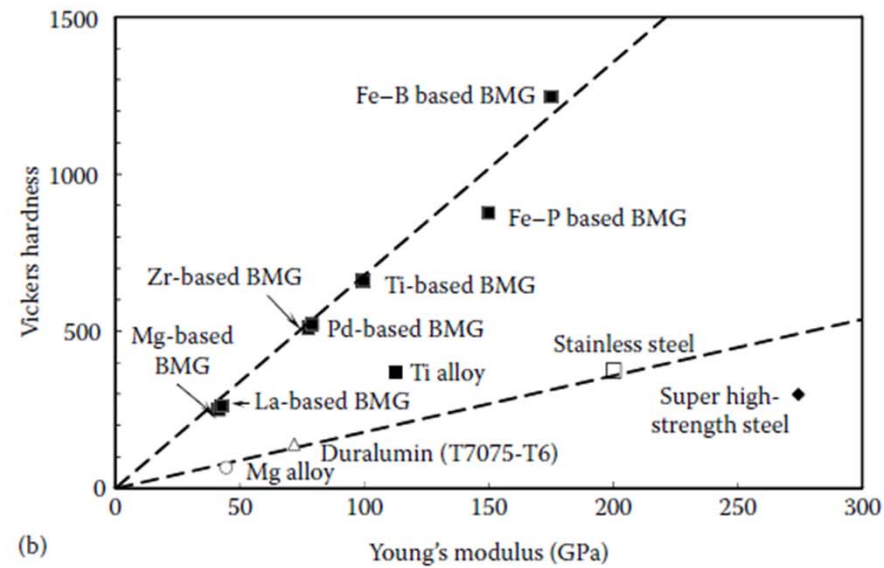
(b)

FIGURE 8.11

(a) Variation of strength with glass transition temperature, T_g for a number of BMGs. (b) Relationship between the calculated fracture strength from a free-volume model and the ratio of $\Delta T_g/V$ for a variety of BMGs. (Reprinted from Yang, B. et al., *Appl. Phys. Lett.*, 88, 221911-1, 2006. With permission.)



(a)



(b)

FIGURE 8.13

Relationship between (a) tensile strength and Young's modulus and (b) Vickers hardness and Young's modulus for some typical BMGs. The data for crystalline alloys are also shown for comparison. (Reprinted from Inoue, A., *Acta Mater.*, 48, 279, 2000. With permission.)

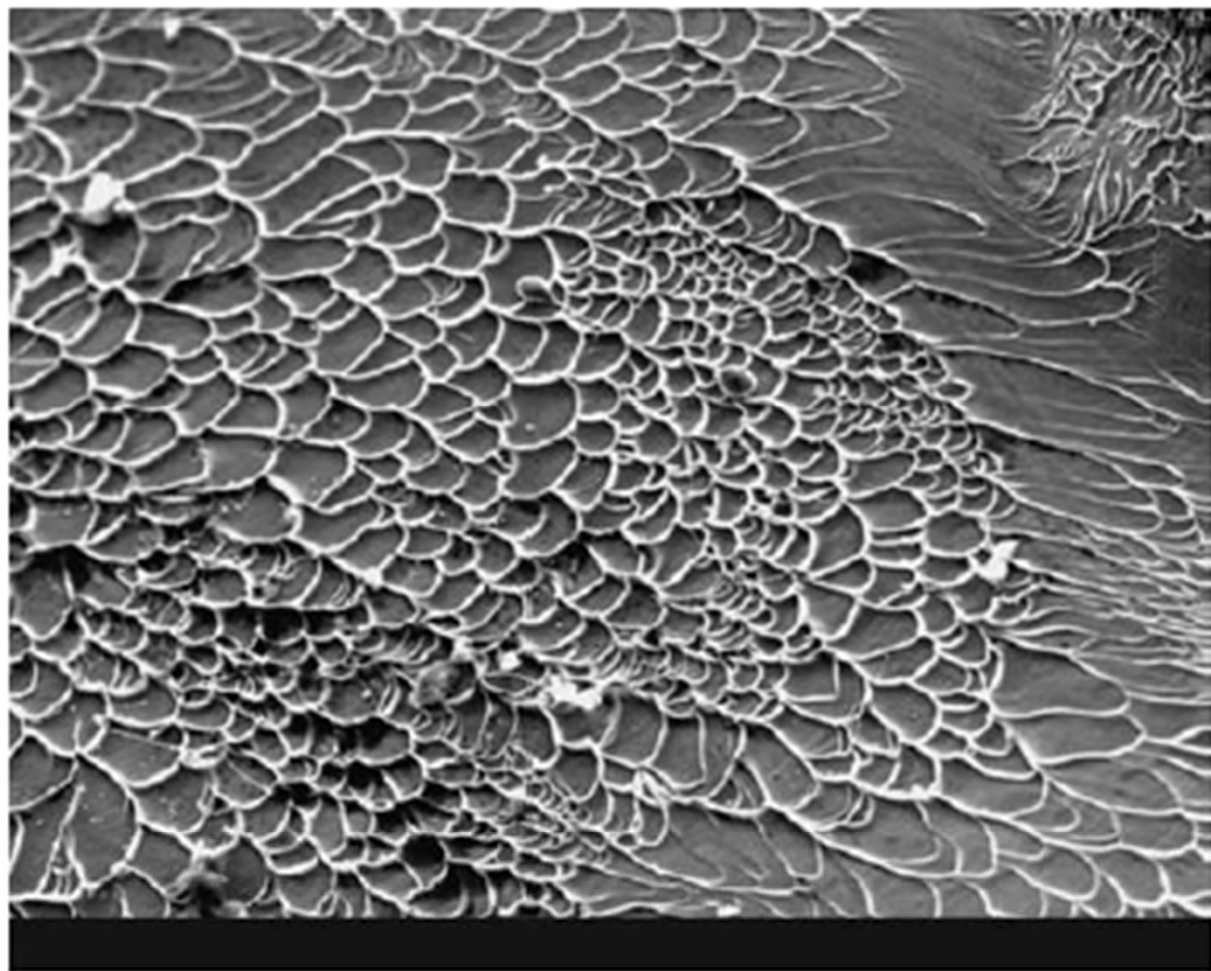


FIGURE 8.27

Scanning electron micrograph of the fractured surface of a bulk metallic glass alloy specimen. Note the vein pattern, which is typical of many metallic glasses that fracture along a shear band. Such microstructures are obtained both in tension and compression.

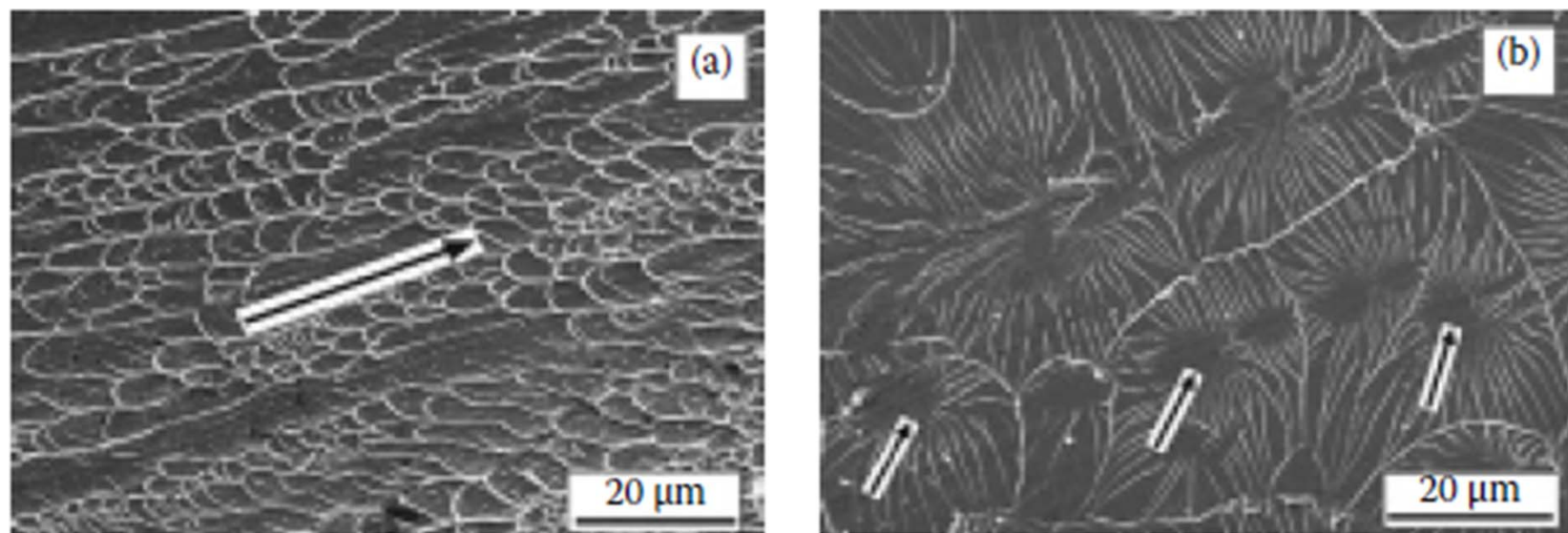


FIGURE 8.28

Comparison of the fracture surfaces of $Zr_{59}Cu_{20}Al_{10}Ni_8Ti_3$ BMG alloy that has failed under (a) compressive loading and (b) tensile loading. Notice that the specimen that has failed under compressive loading exhibits vein-like pattern while the specimen that had failed in tension shows round cores with vein-like features radiating outward from their centers. The arrow in (a) shows the shear direction, while the arrows in (b) indicate the location of the round cores. (Reprinted from Zhang, Z.F. et al., *Acta Mater.*, 51, 1167, 2003. With permission.)

What governs plasticity in metallic glasses?

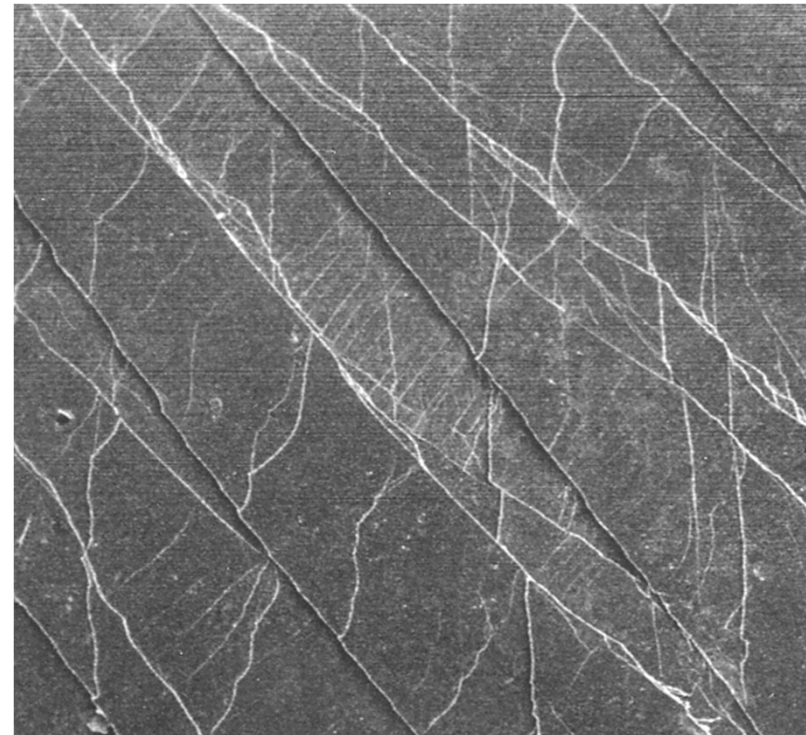
Plastic deformation in metallic glasses

Plastic deformation in metallic glass

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

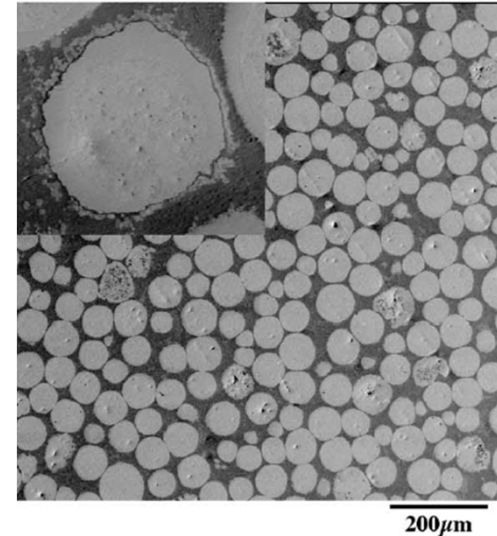
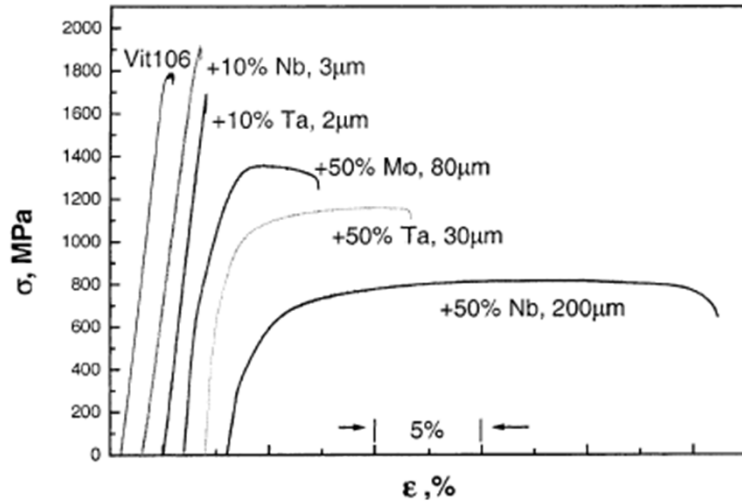
interrupt the localization of stress and deformation

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



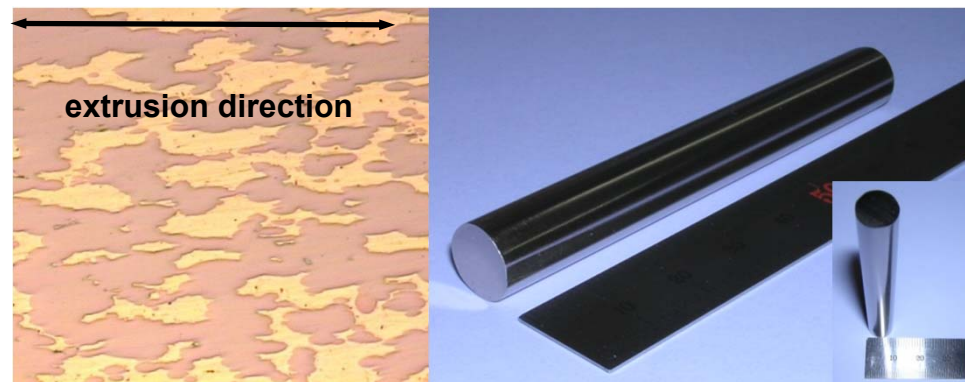
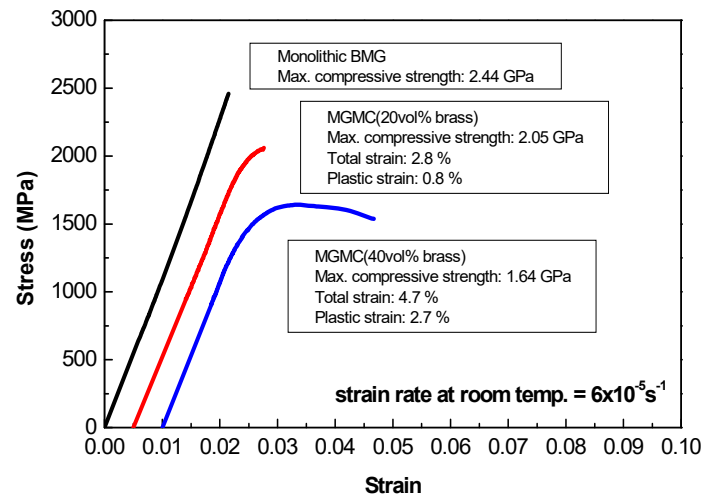
Ex-situ BMG matrix composites

1) Casting : hard/ductile particle



(Johnson et al., Acta Mater., 1999)

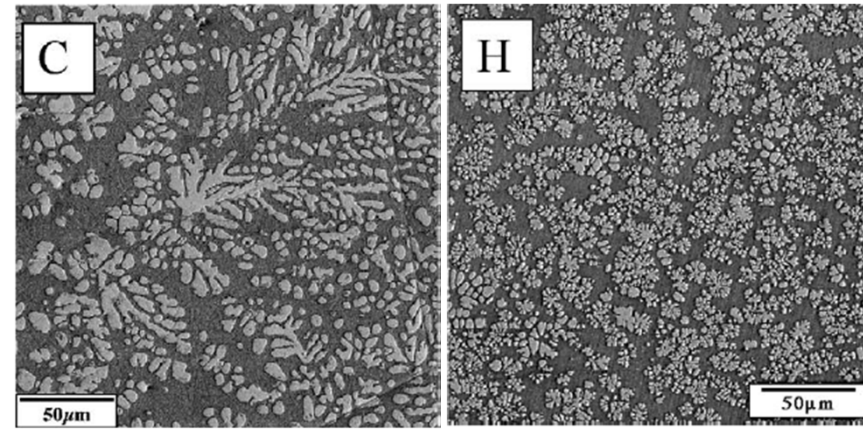
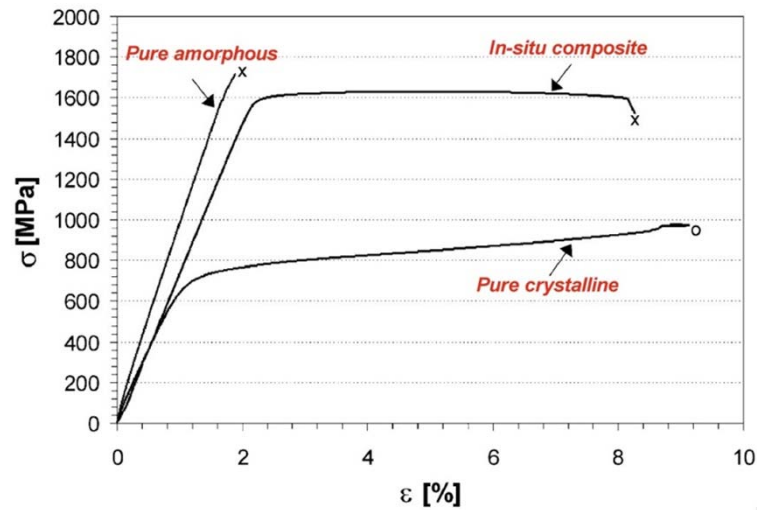
2) Extrusion : ductile powder



(Kim et al., J. Non-cryst. Solids, 2002)

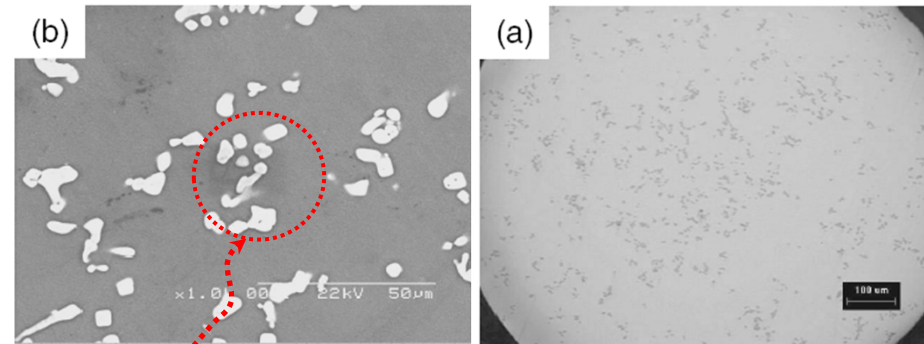
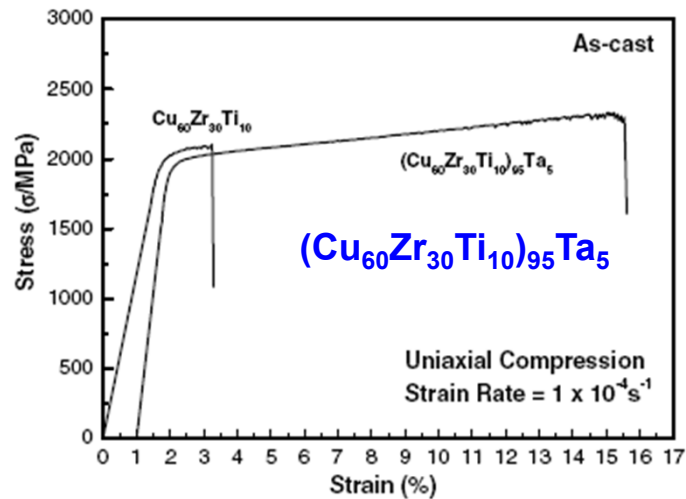
In-situ BMG matrix composites

1) Solidification : formation of primary ductile phase



(Johnson et al., Acta Mater., 2001)

2) Solidification : precipitation of ductile phase

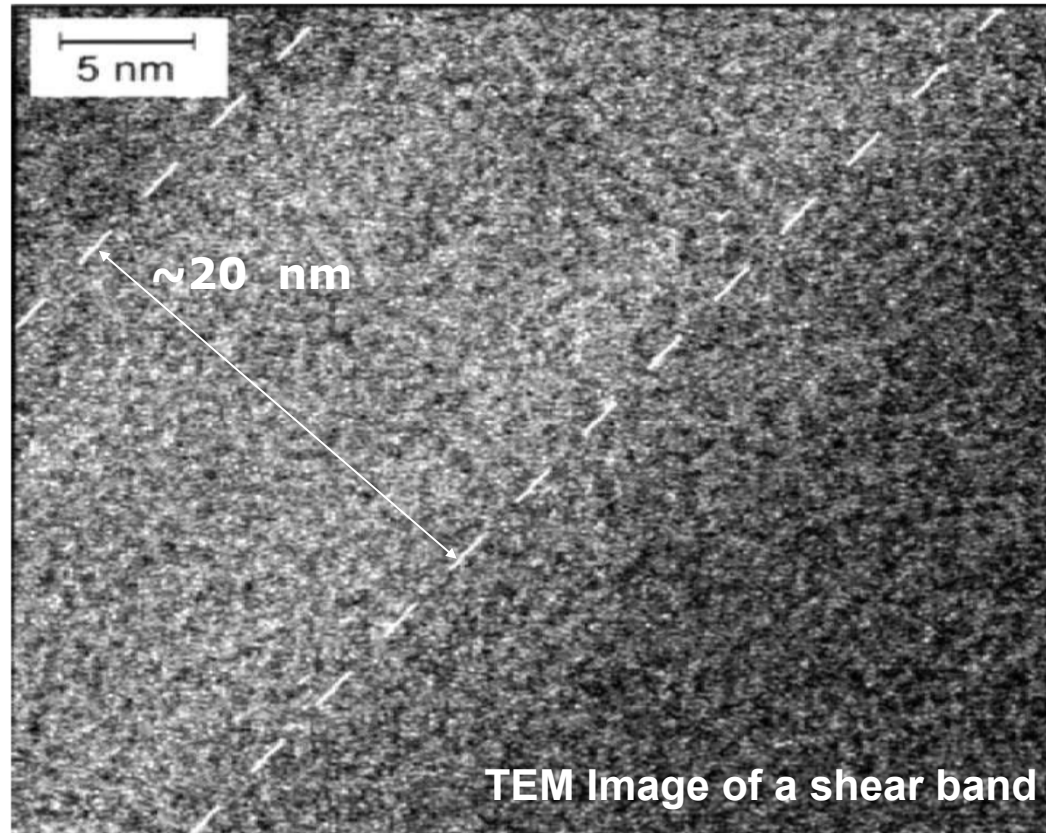


Ta rich particle

(Johnson et al., Acta Mater., 2001)

Size of heterogeneity

Shear bands are ~20 nm in width

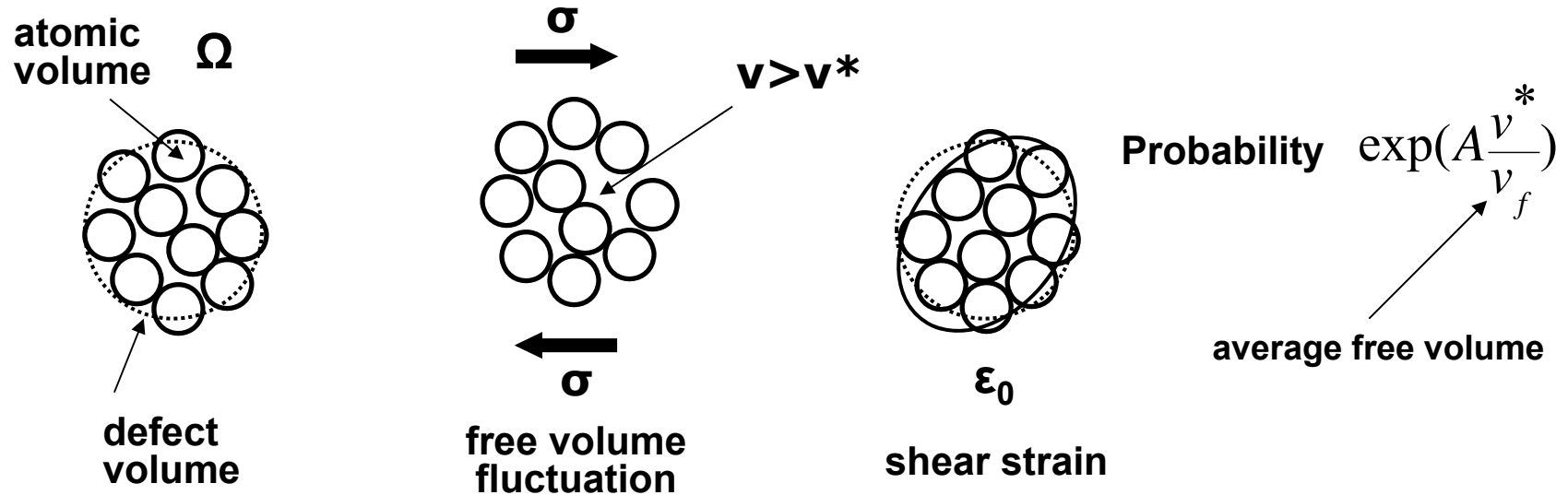


- Prevent propagation of single shear band

➔ **Micro- or nanometer scale heterogeneity**

Size of heterogeneity

- Elementary flow event in an metallic glasses

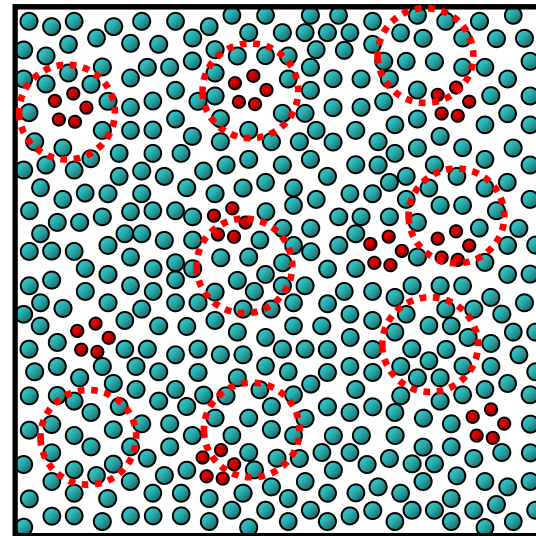


Flow governed by localized defect (~10 atoms) and creates defects

atomic scale heterogeneity

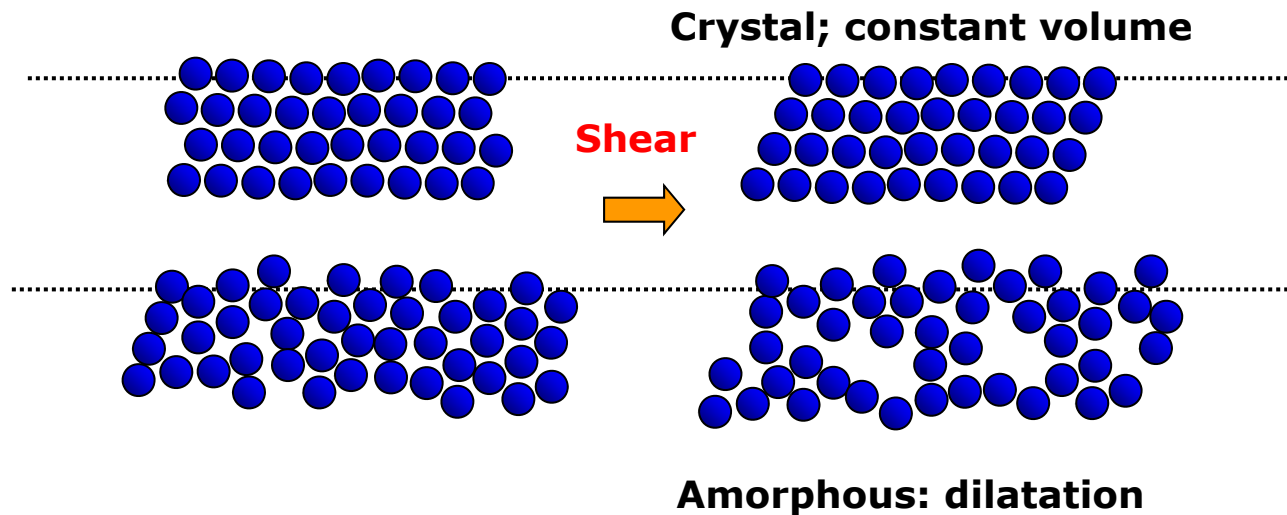


$$\eta = \eta_0 \exp\left\{A \frac{V_0}{V_f}\right\}$$



Plastic deformation in metallic glasses

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



- Shear bands form by accumulation of defects



Understanding how shear bands form and propagate in metallic glasses

Fragility

- Fragility ~ extensively use to figure out liquid dynamics and glass properties corresponding to “frozen” liquid state

< Classification of glass >

Strong network glass : Arrhenius behavior



$$\eta = \eta_0 \exp\left[\frac{E_a}{RT}\right]$$

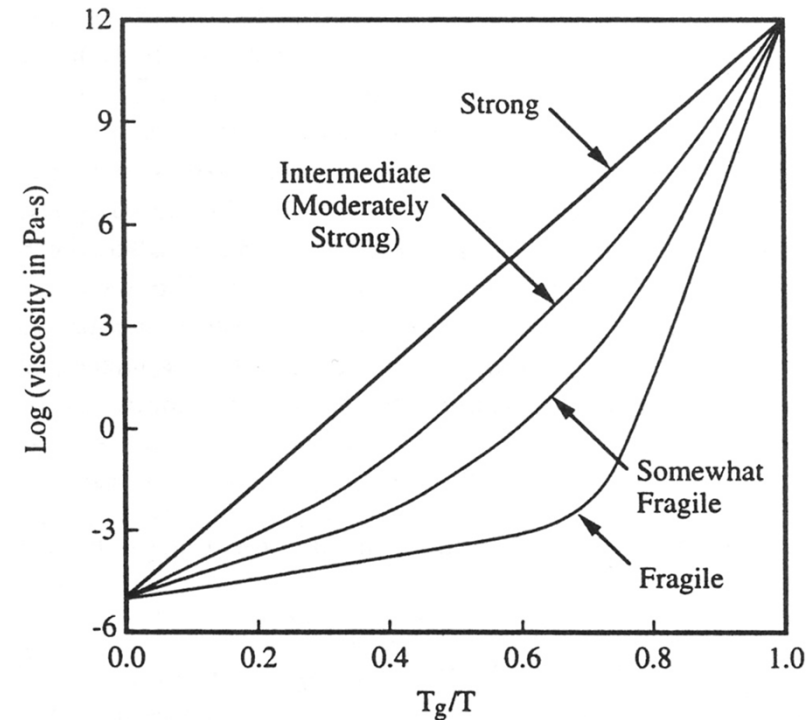
Fragile network glass : Vogel-Fulcher relation

$$\eta = \eta_0 \exp\left[\frac{B}{T - T_0}\right]$$

< Quantification of Fragility >

$$m = \left. \frac{d \log \eta(T)}{d(T_{g,n} / T)} \right|_{T=T_{g,n}} = \left. \frac{d \log \tau(T)}{d(T_g / T)} \right|_{T=T_g}$$

Slope of the logarithm of viscosity, η (or structural relaxation time, τ) at T_g

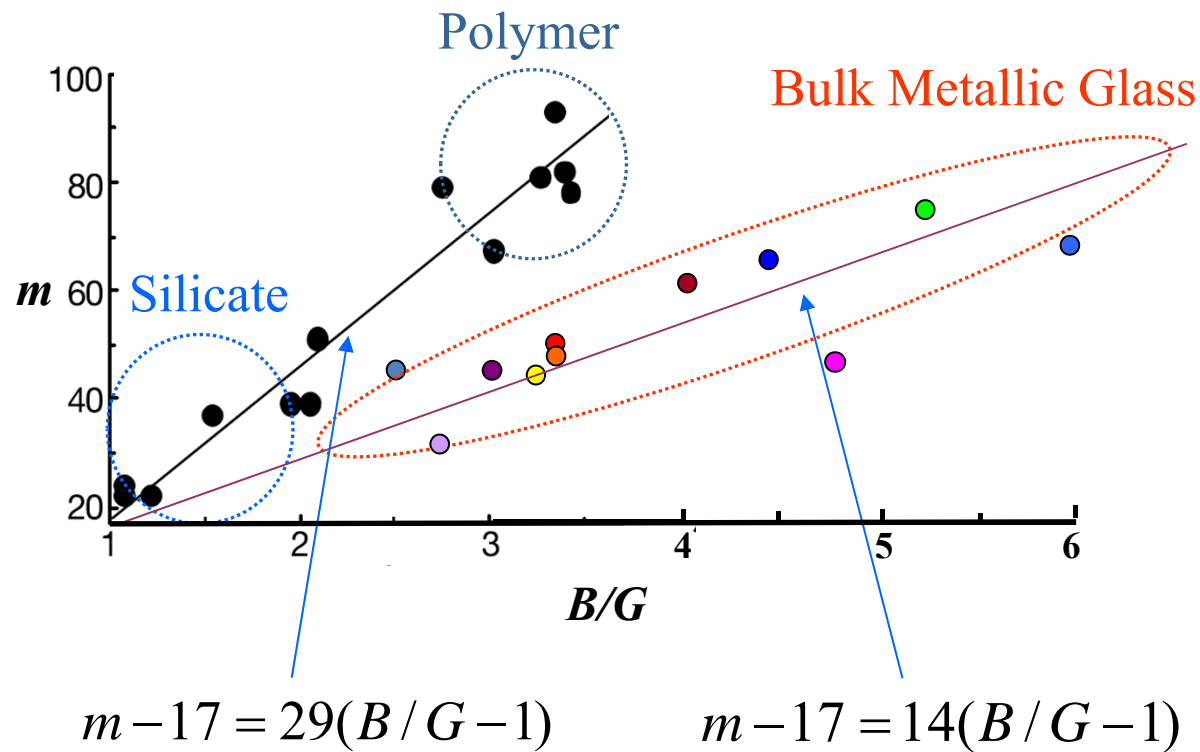


Correlation between fragility and plasticity

- Correlation between elastic constants and plasticity



Jan Schroers et al., Phys. Rev. Lett. 93, 255506 (2004).



** J. Mater. Res. 23, 523 (2008)*

Correlation between fragility and plasticity

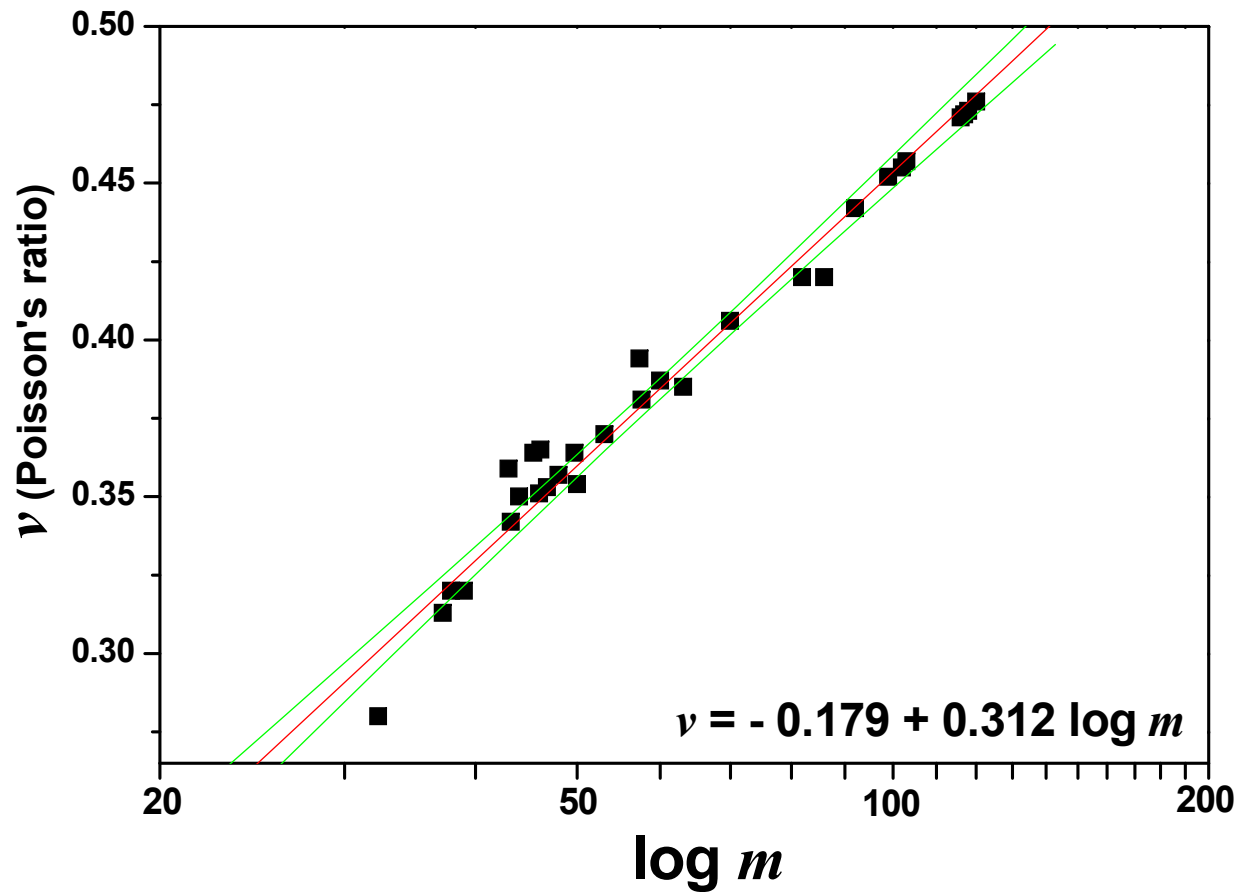
*Low G/B
High ν*



*High m
(fragility index)*



*Large Plasticity
(multiple shear band)*



* Appl. Phys. Lett., 91, 031907.

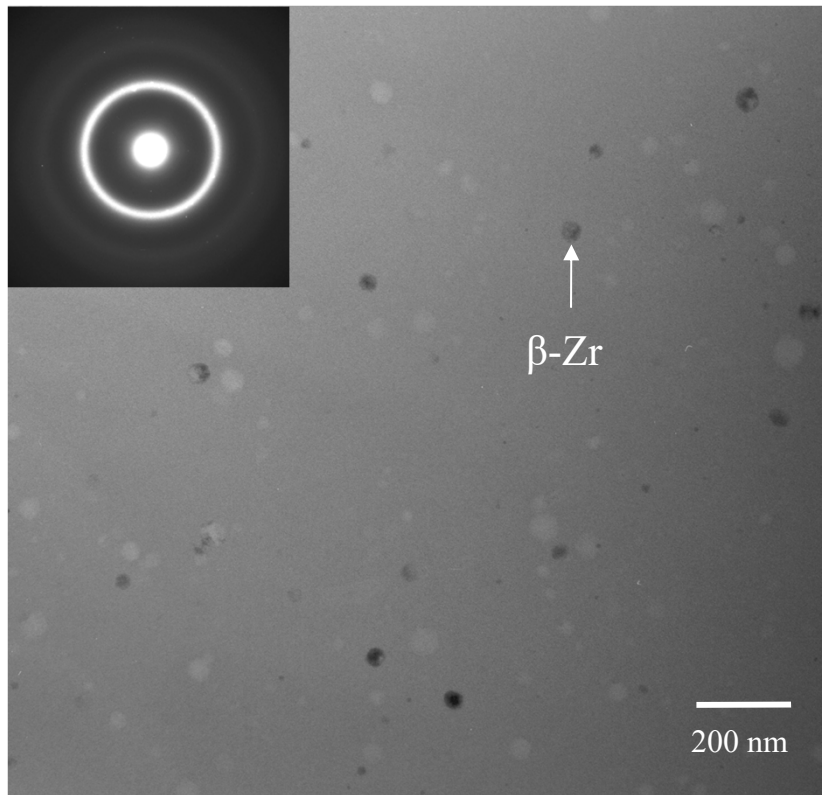
Enhancement plasticity in BMGs with atomic scale heterogeneity

a) Effect of quenched-in quasicrystal nuclei

Effect of quenched-in quasicrystal nuclei

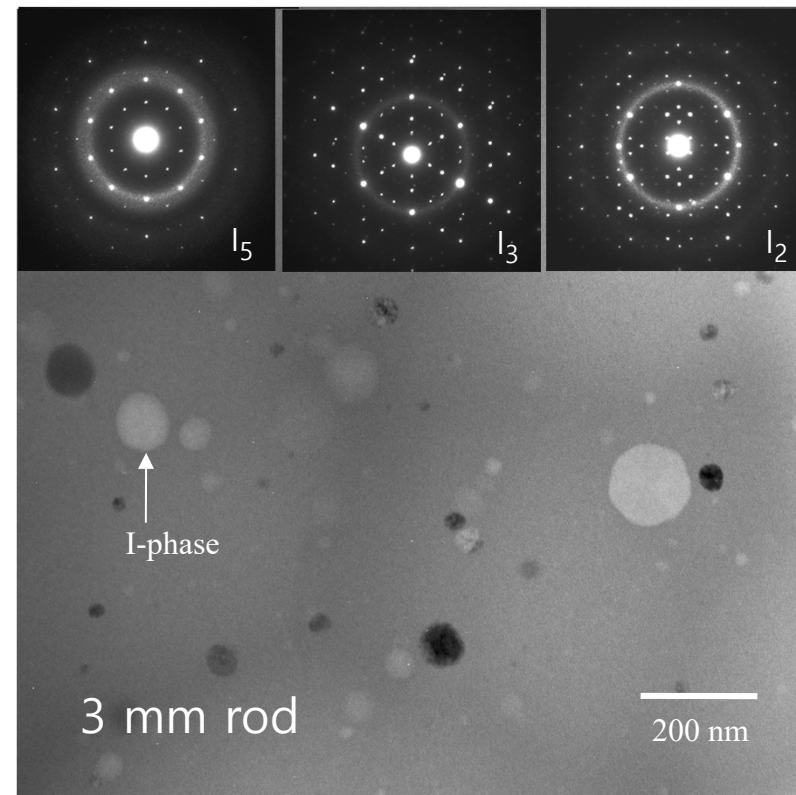
2 mm rod

(a) $\text{Zr}_{63}\text{Ti}_5\text{Nb}_2\text{Cu}_{15.8}\text{Ni}_{6.3}\text{Al}_{7.9}$



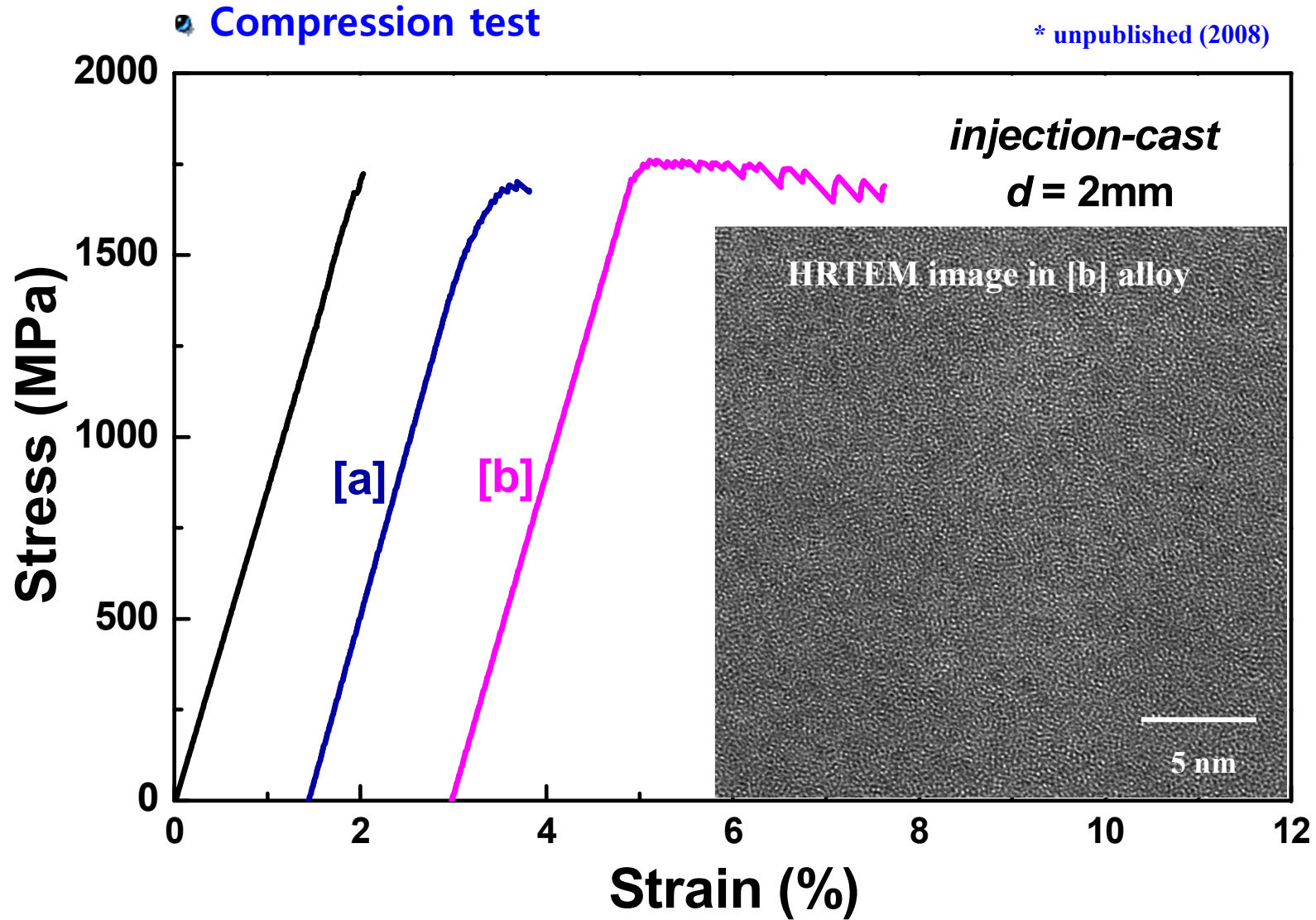
β -Zr particle (~70 nm) in amorphous matrix

(b) $\text{Zr}_{57}\text{Ti}_8\text{Nb}_{2.5}\text{Cu}_{13.9}\text{Ni}_{11.1}\text{Al}_{7.5}$



I-phase particle in amorphous matrix

Effect of quenched-in quasicrystal nuclei



Enhancement plasticity in BMGs with atomic scale heterogeneity

a) Effect of element having positive enthalpy of mixing among constituent elements

Improvement of plasticity in monolithic BMGs

* Enhancement of plasticity in monolithic BMGs

➡ No clear explanations so far.

* Reports for enhancement of plasticity in monolithic BMGs

	Compressive plastic strain, ϵ_p (%)
$Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ ¹	~ 6.1
$Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$	~ 1.1
$Ni_{59}Zr_{16}Nb_7Ti_{13}Si_3Sn_2$ ²	~ 6.2
$Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$	~ 2.1
$Cu_{47}Ti_{33}Zr_7Nb_4Ni_8Si_1$ ³	~ 4.1
$Cu_{47}Ti_{33}Zr_{11}Ni_8Si_1$	~ 1.5
$Cu_{43}Ag_7Zr_{43}Al_7$ ⁴	~ 4.1
$Cu_{50}Zr_{43}Al_7$	~ 1.5

¹ Xing et al., Phys. Rev. B (2001)

² Lee et al., Intermetallics (2004), BMG III

³ Park et al., J. Non-cryst. Sol. (2005)

⁴ Sung et al., Met. Mater. –Int (2004) and
Oh et al., Scripta Mater. (2005)

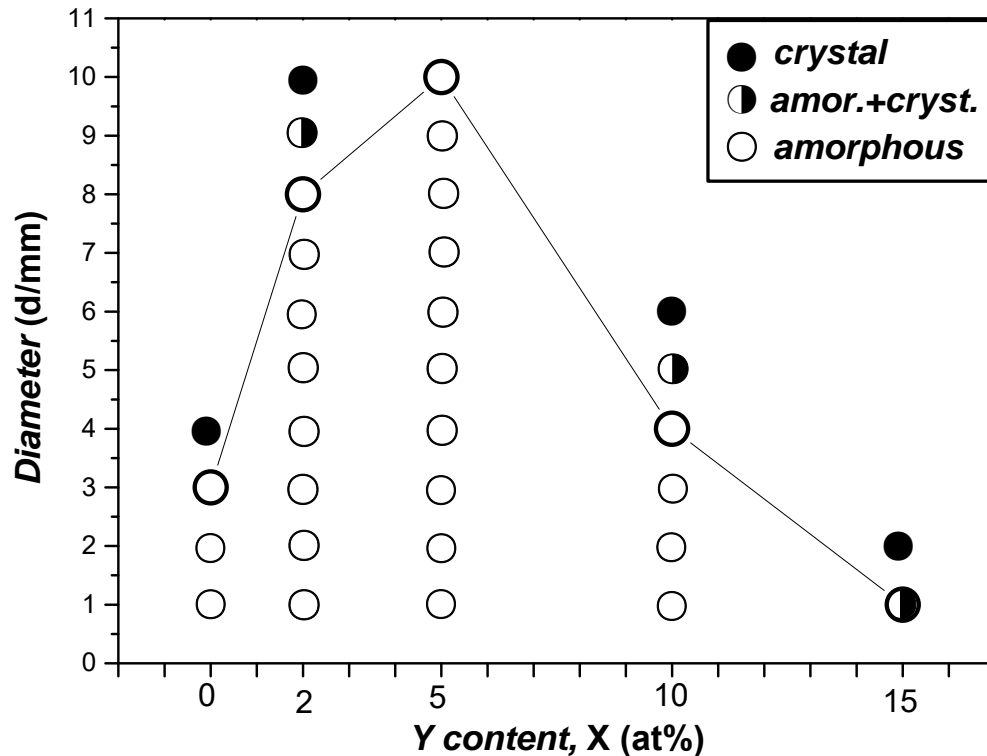
(Ta-Zr: +13KJ/mol, Nb-Zr: +17KJ/mol, Nb-Ti: +9KJ/mol, Cu-Ag: +5 KJ/mol)

- Previous results on the effect of micro-alloying on plasticity

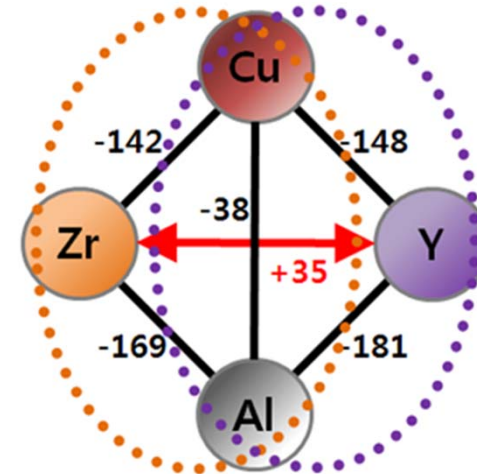
: Effect of elements having positive heat of mixing

Alloy design

* Substitution of Zr with Y in Cu-Zr-Al system



D. Xu, G. Duan and W.L. Johnson, Phys. Rev. Lett. 92, 245504 (2004)



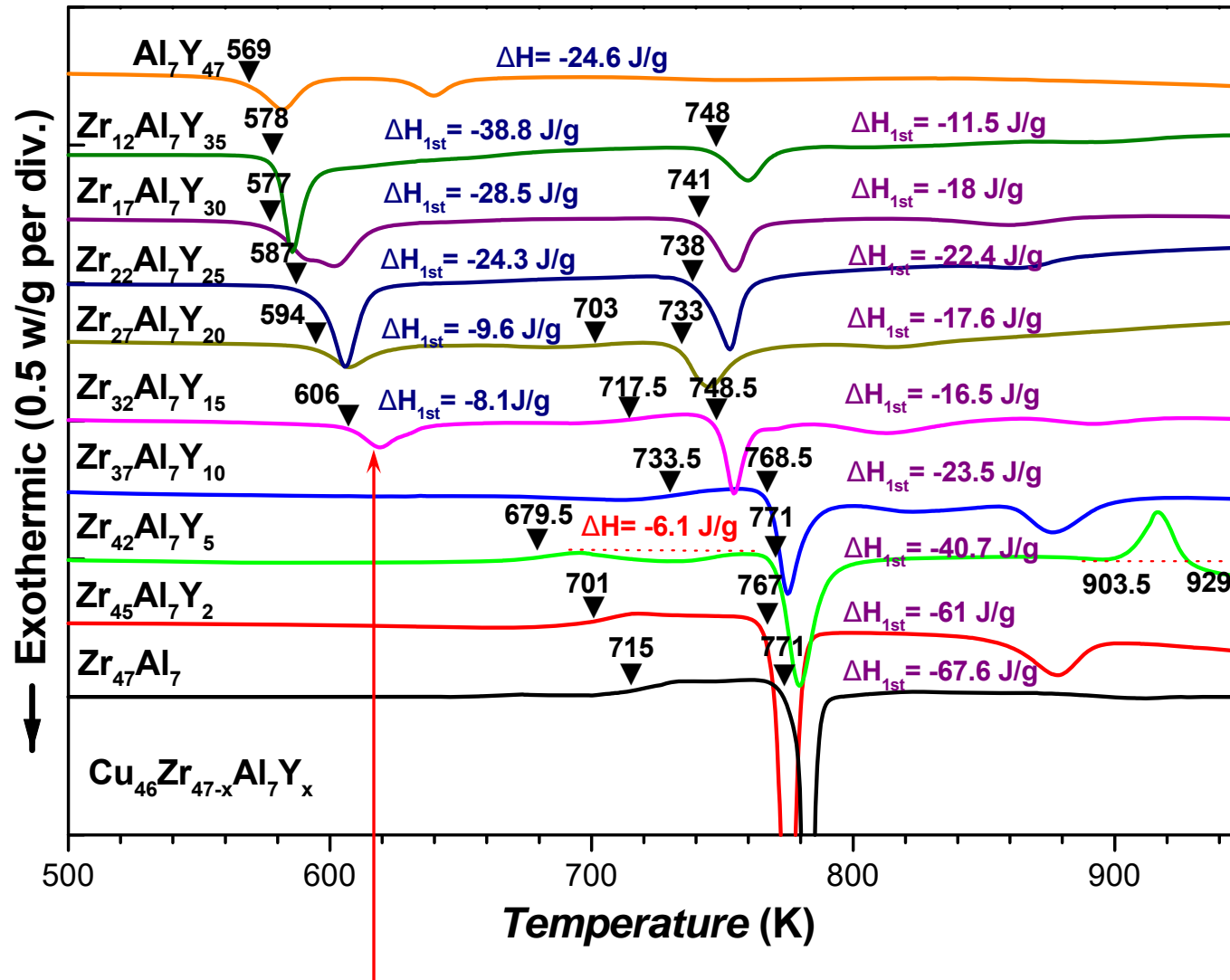
Possibility of two phase !!!

➔ Cu-Zr-Al , Cu-Y-Al

Indirect evidence of inhomogeneity = Phase separation

* Acta Materialia, 54, 2597 (2006)

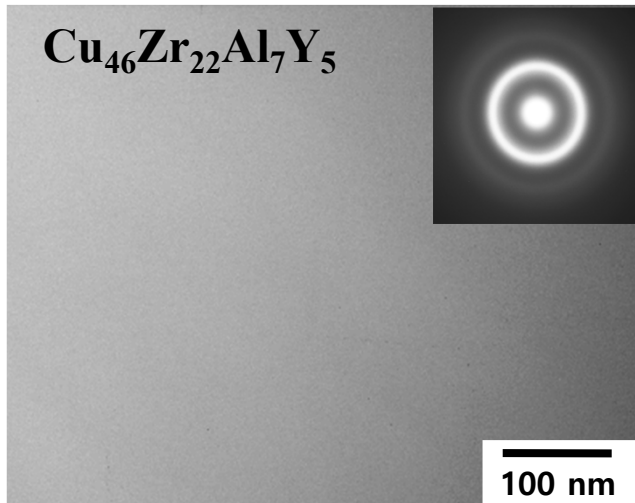
Thermal analysis : DSC results



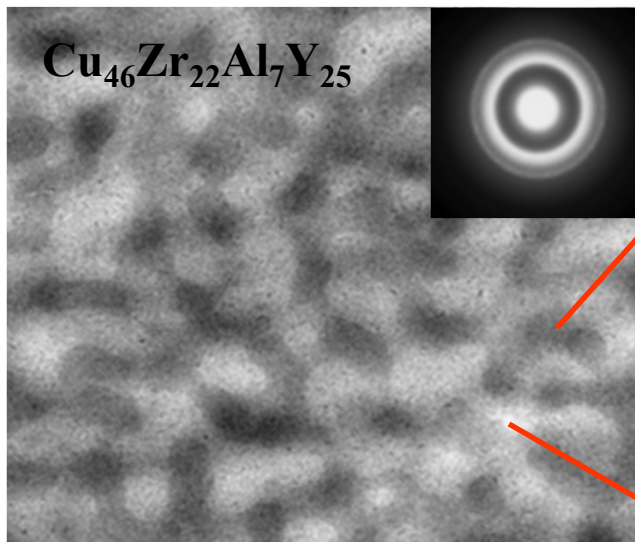
Exothermic peak which exhibit that Y rich amorphous phase crystallize

Structural analyses : TEM results

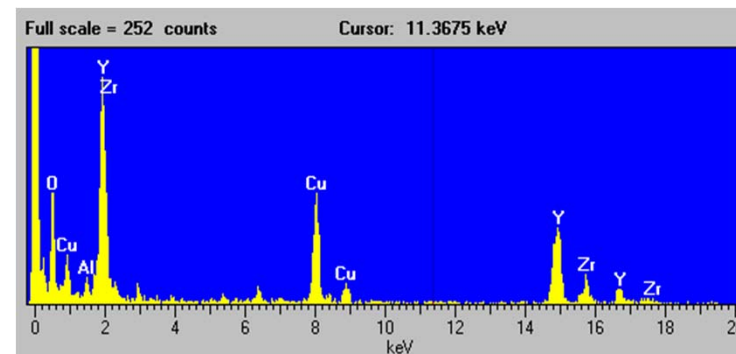
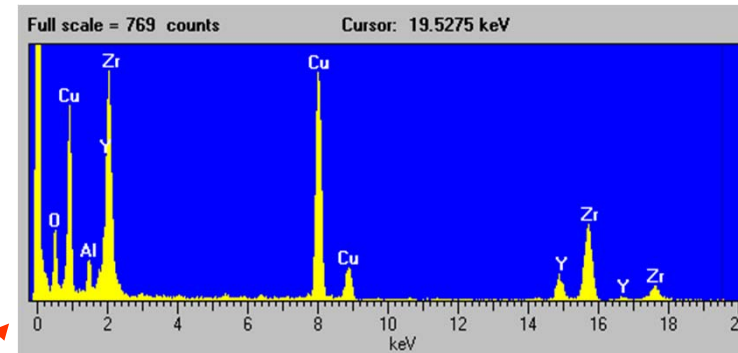
As-melt-spun



- With increasing Y content,
Compositional inhomogeneity → Phase separation

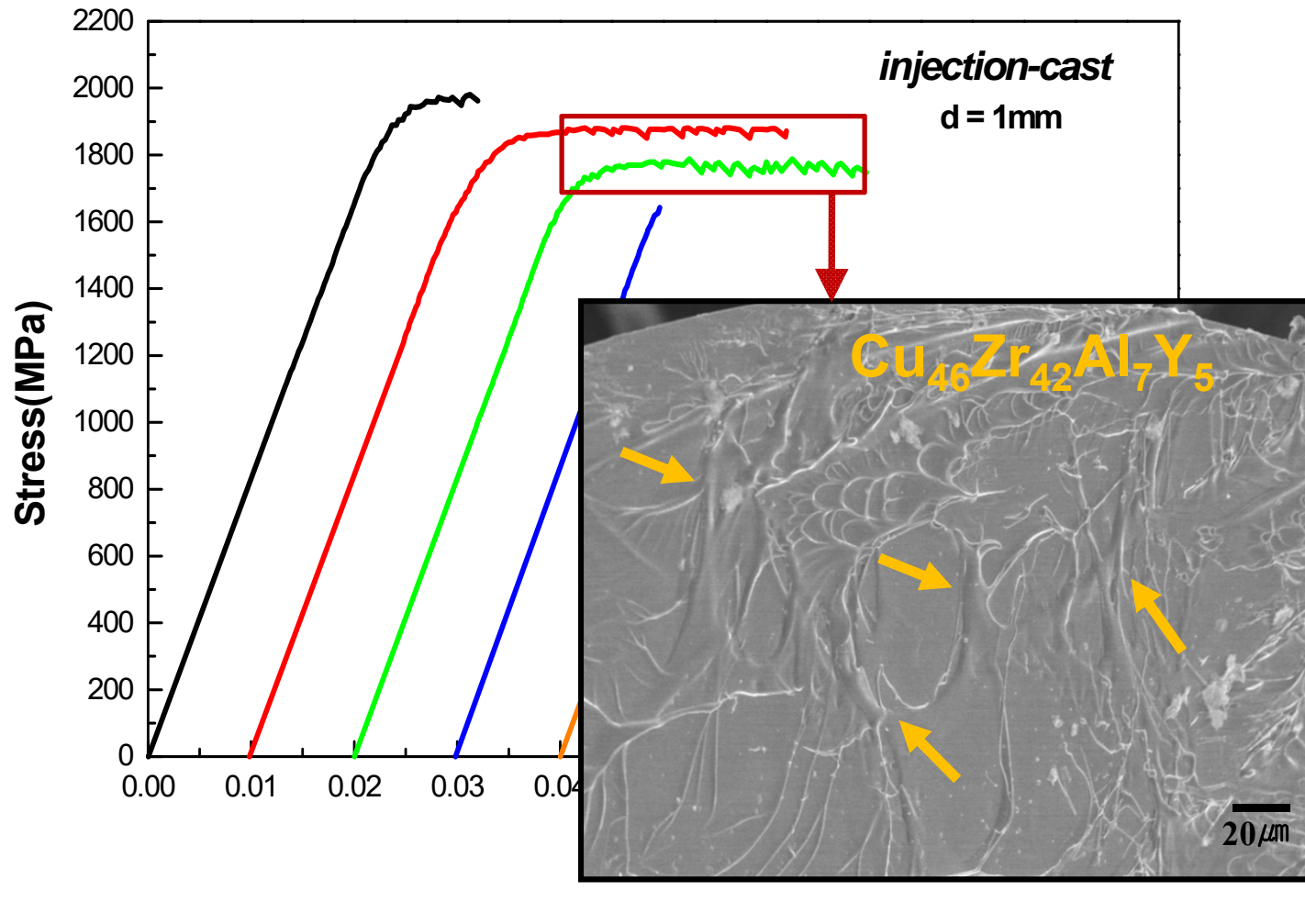


$\text{Cu}_{53.4}\text{Zr}_{31.8}\text{Y}_{8.3}\text{Al}_{6.5}$ (CuZr-rich)



$\text{Cu}_{35.7}\text{Zr}_{12.8}\text{Y}_{44.3}\text{Al}_{7.2}$ (CuY-rich)

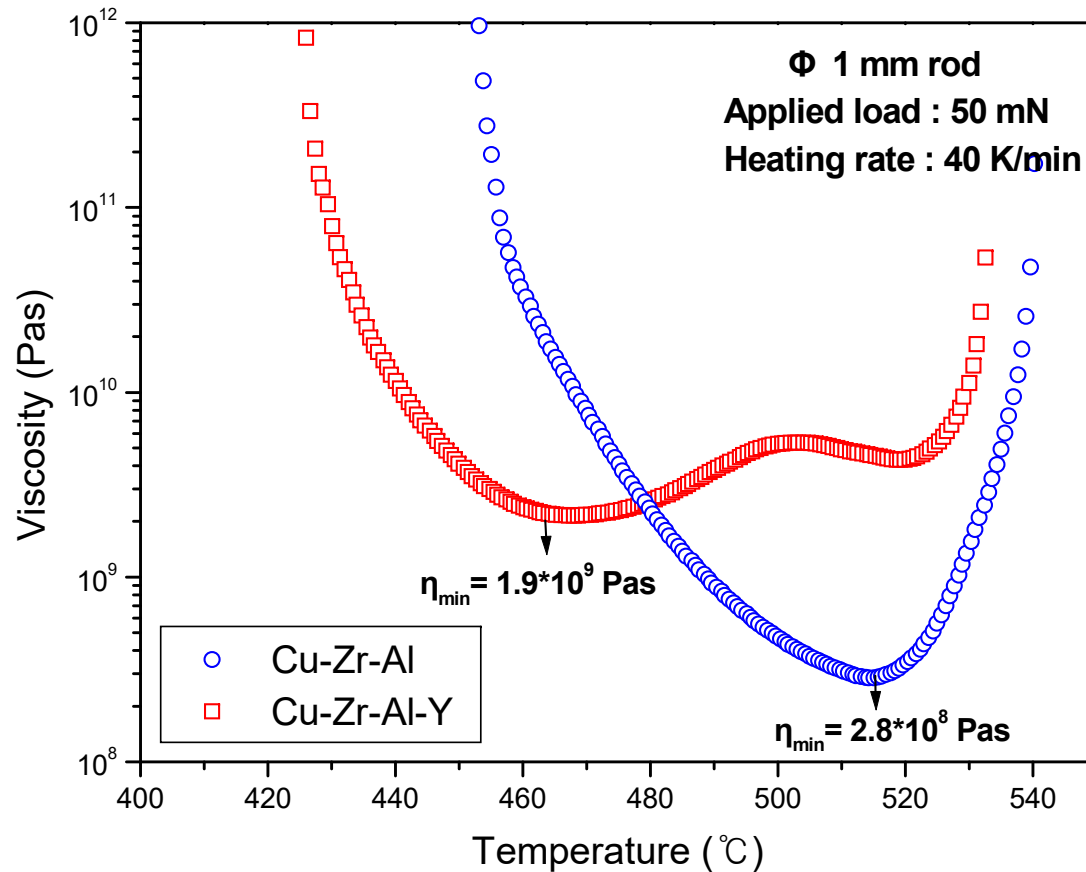
Compression test in Cu-Zr-Al-Y alloy system



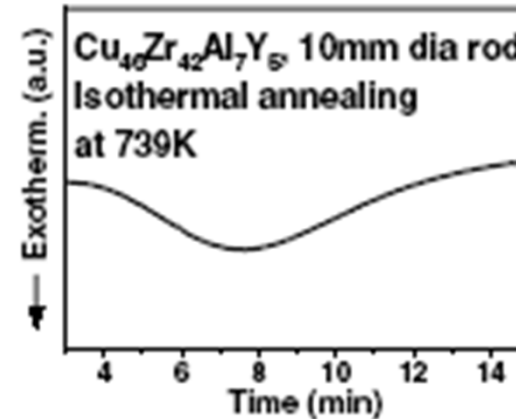
► A larger amount of strain along the shear band led to **localized melting** before fracture

Measurement of viscosity using TMA

<Supercooled liquid region>



<1st Crystallization behavior>



: nucleation and growth

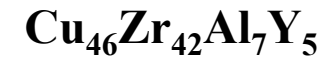
Cu₄₆Zr₄₇Al₇
 $\eta_{\min} = 2.8 \cdot 10^8$ pas

<

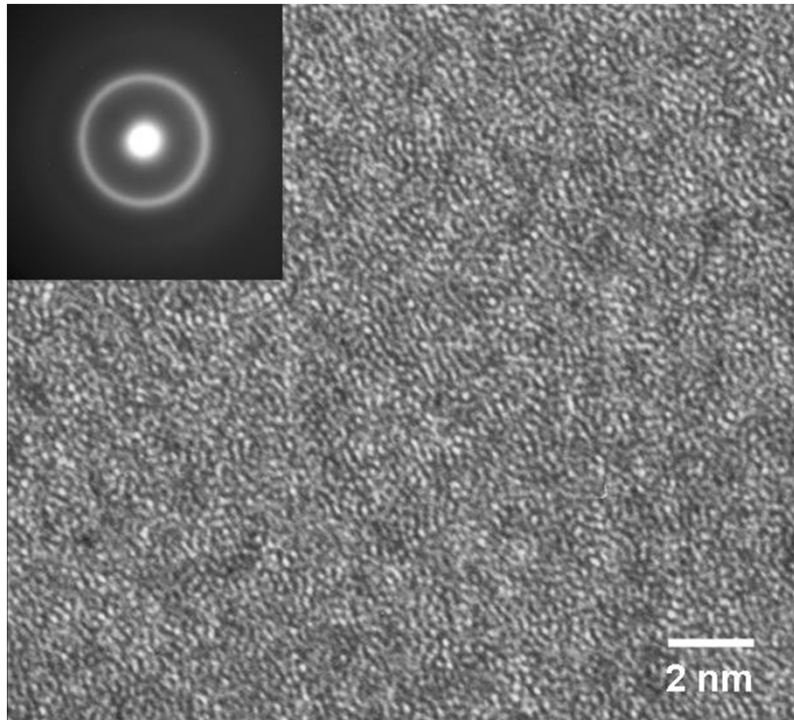
Cu₄₆Zr₄₂Al₇Y₅
 $\eta_{\min} = 1.9 \cdot 10^9$ pas

Relatively easy crystallization

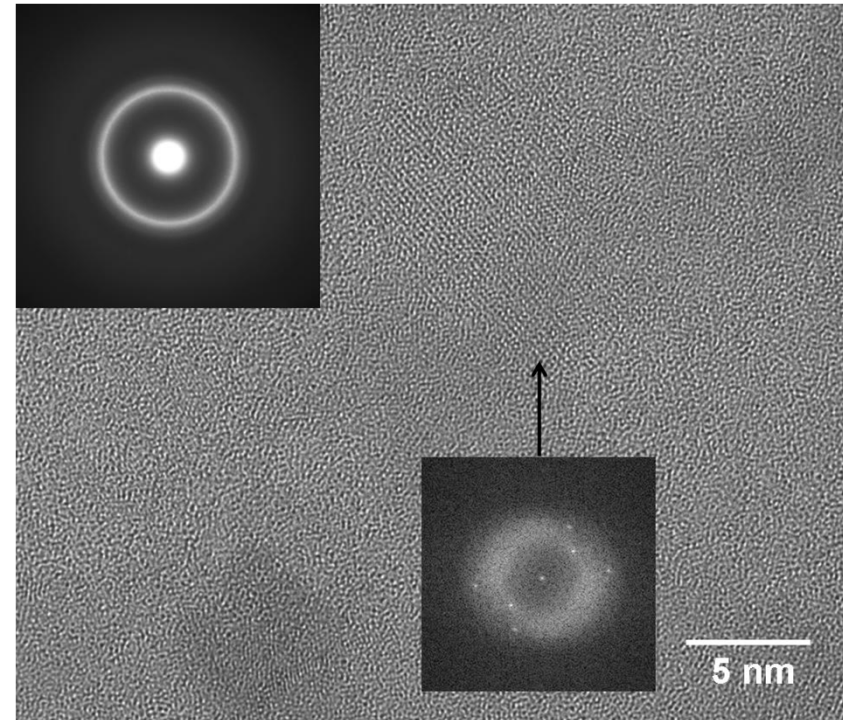
Structural analyses: HRTEM



As-melt-spun



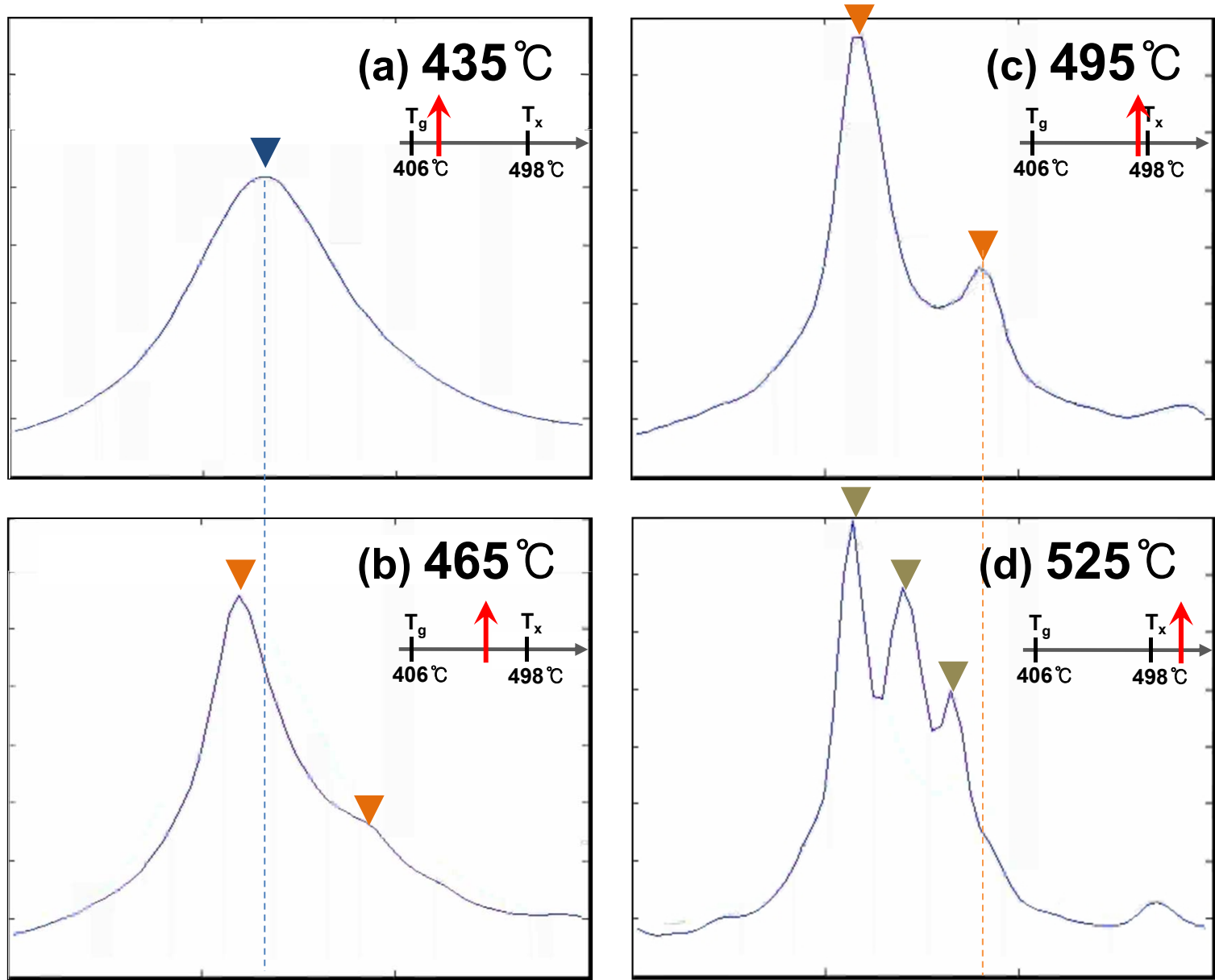
Heated up to 480 °C



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

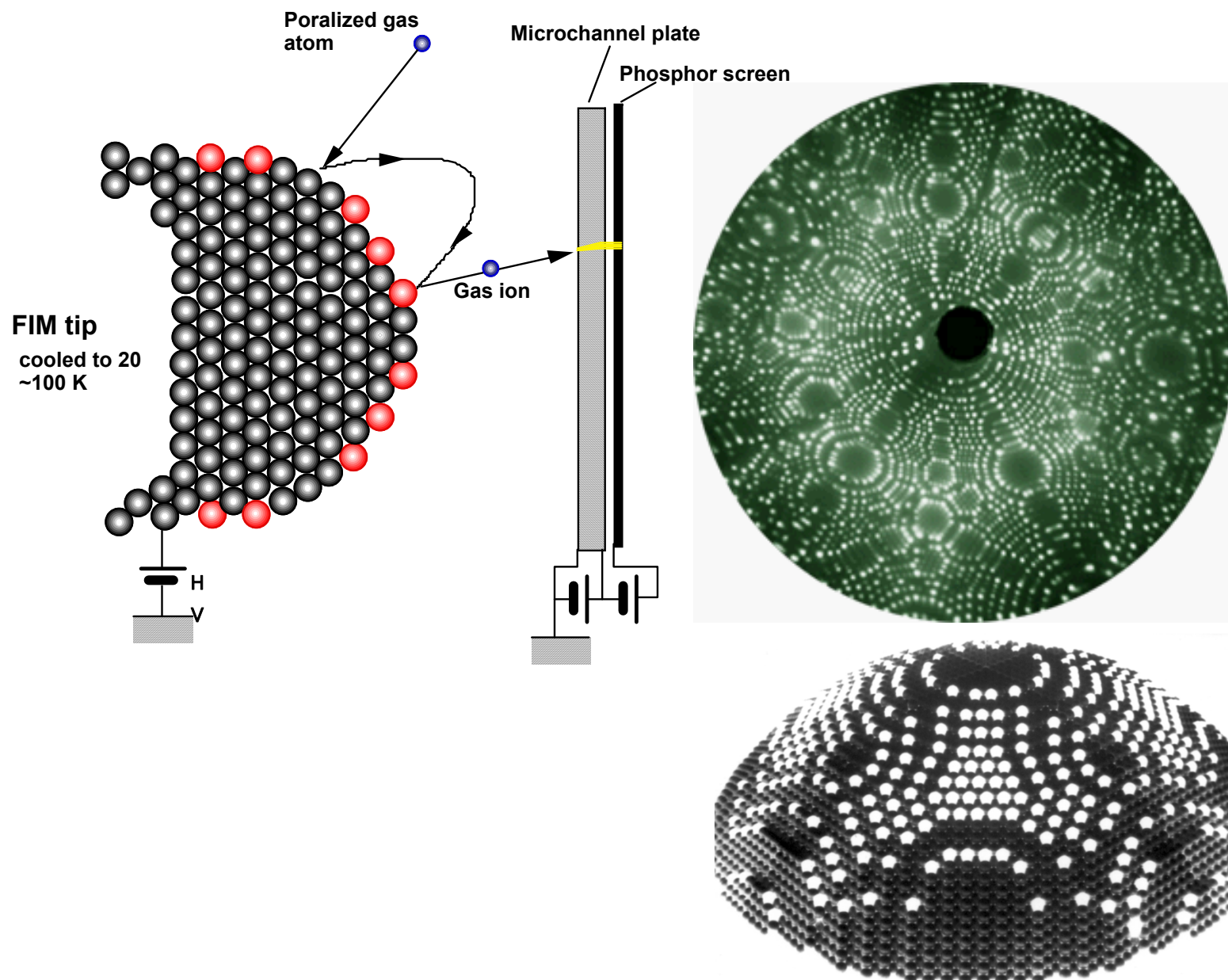
* Acta Materialia, 54, 2597 (2006)

In-situ WAXS analysis of $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ during heating

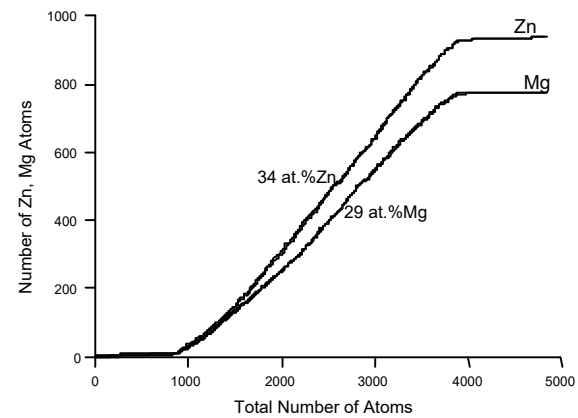
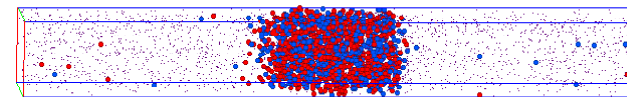
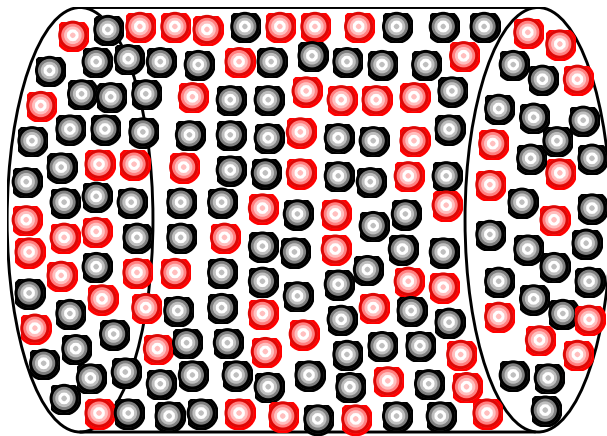
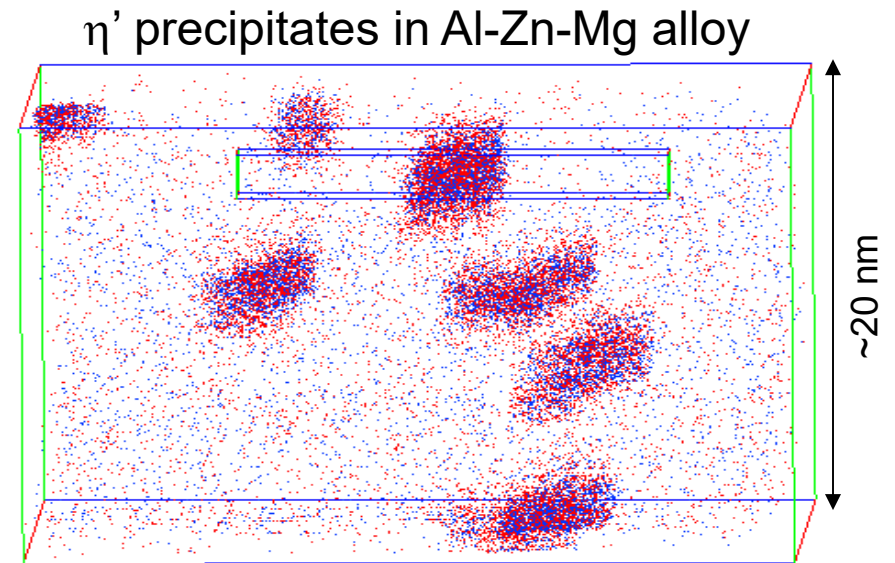
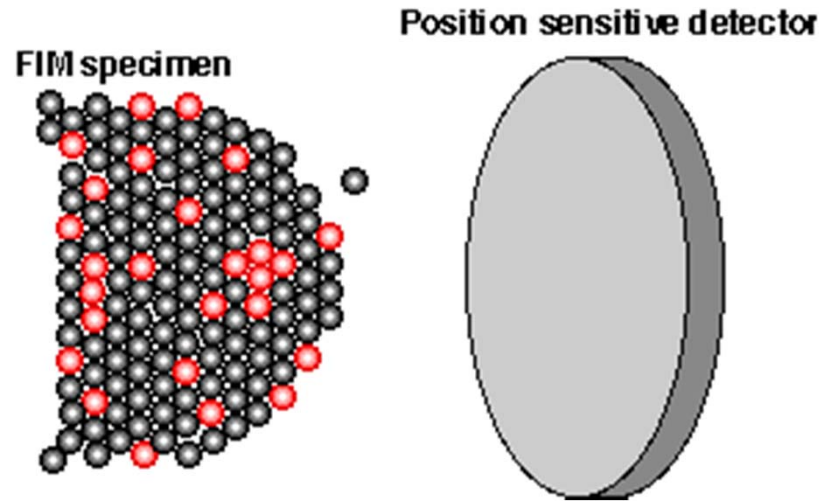


Obtained from Argon National Lab.

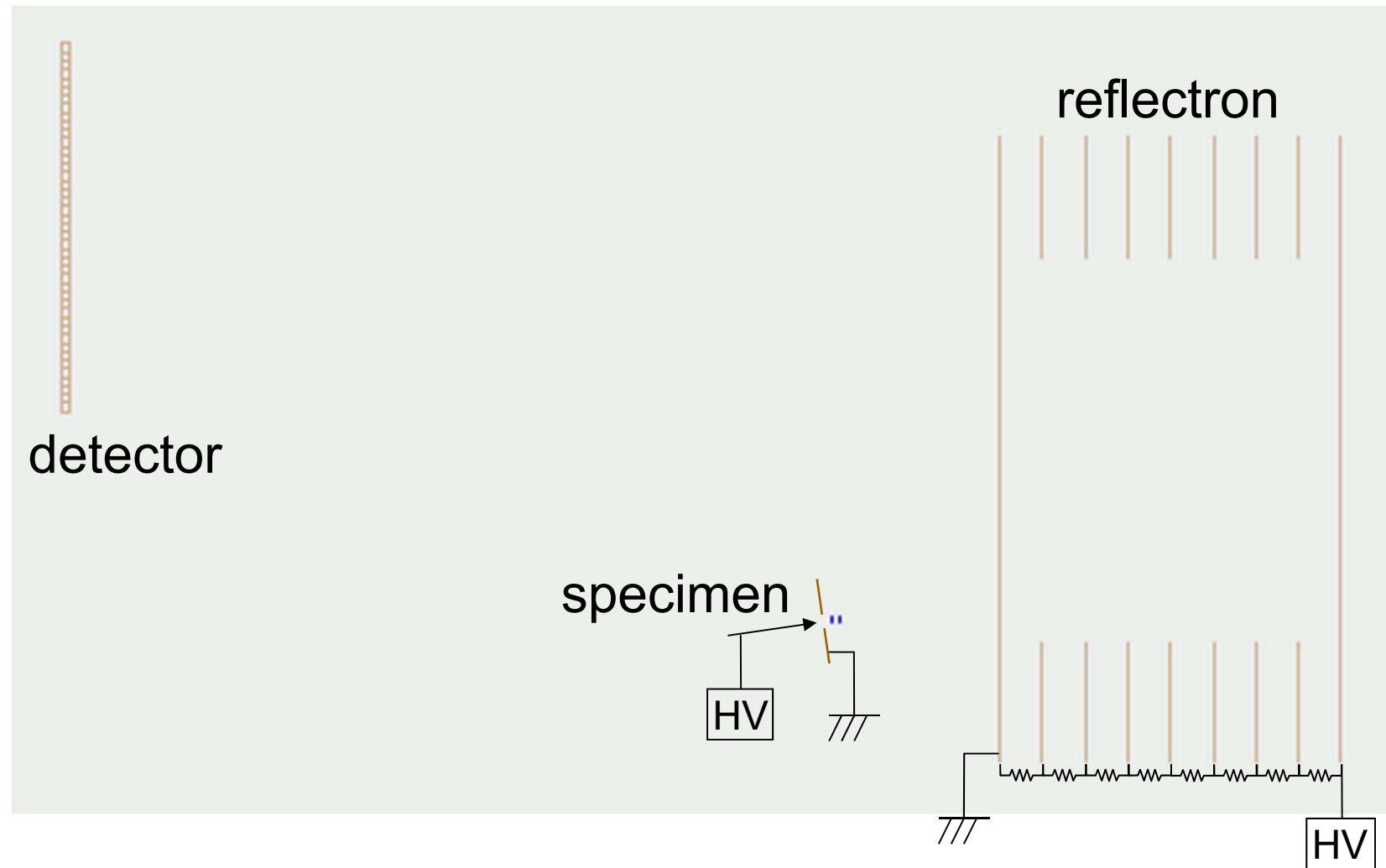
Visualization of Atoms by FIM



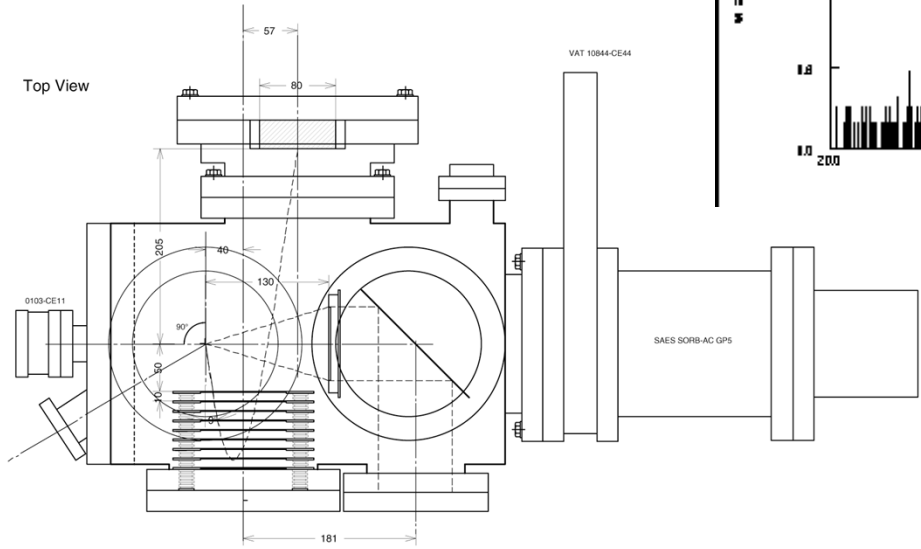
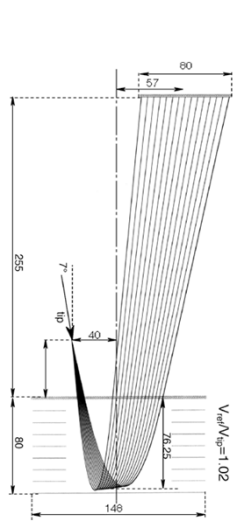
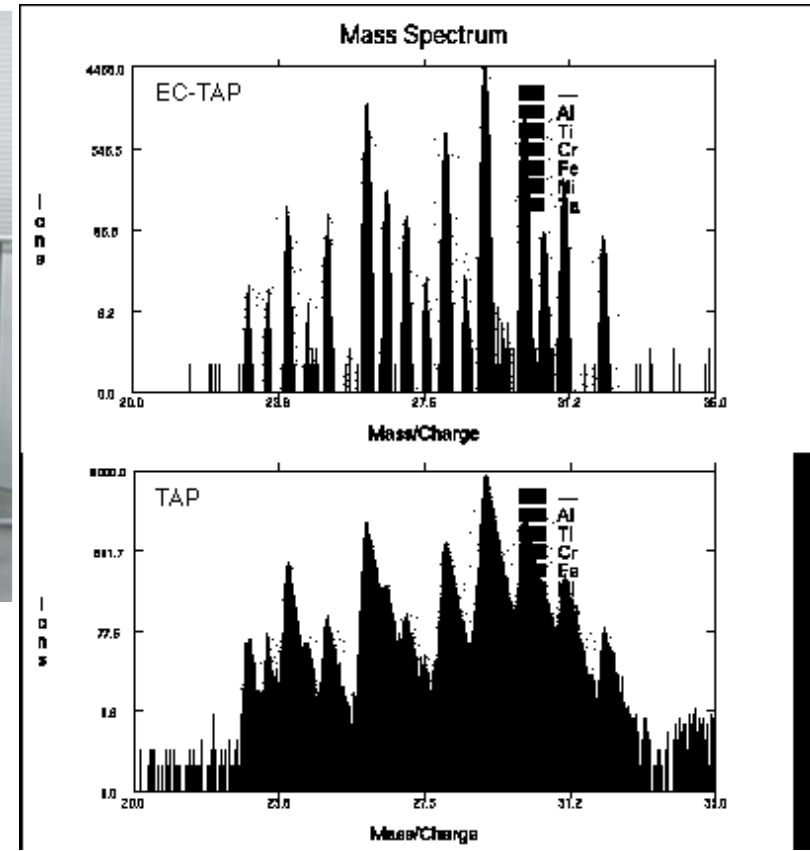
Analysis of atoms by 3DAP



Energy-compensating reflectron

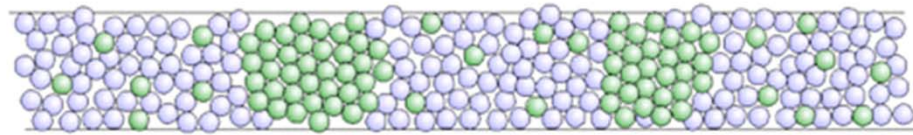
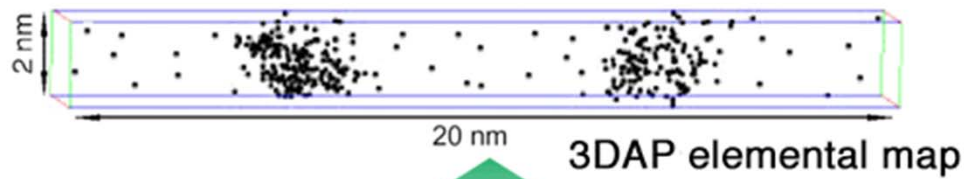


NIMS 3DAP

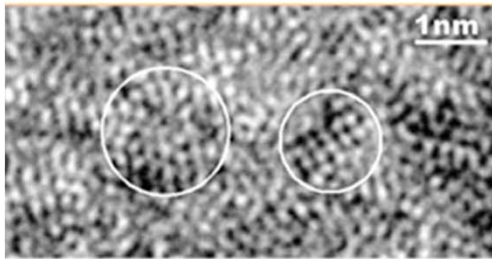


Complementary structural analysis

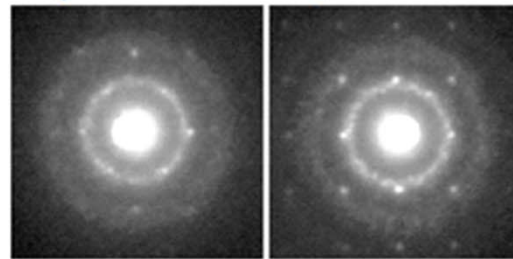
Local Chemical Composition



HREM image

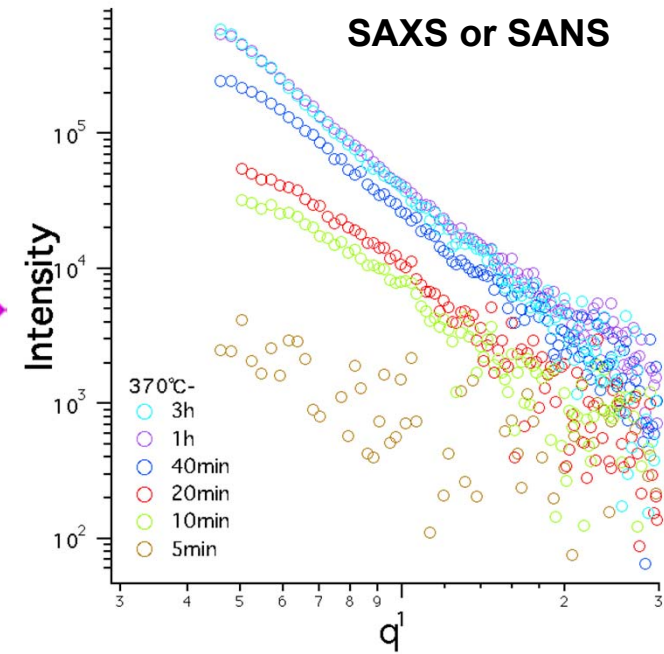


Nanobeam diffraction



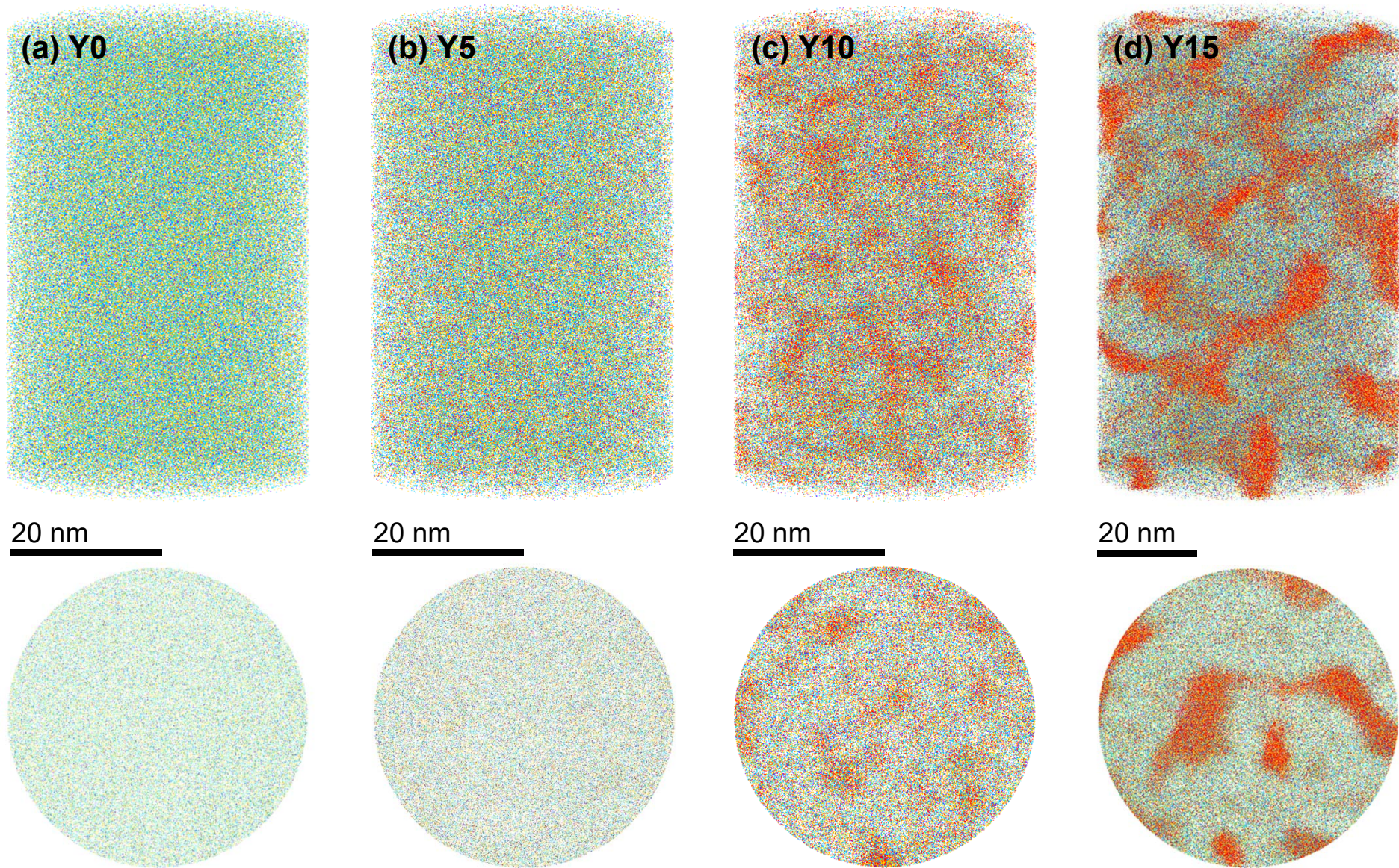
Local Structure

SAXS or SANS



Average Scale

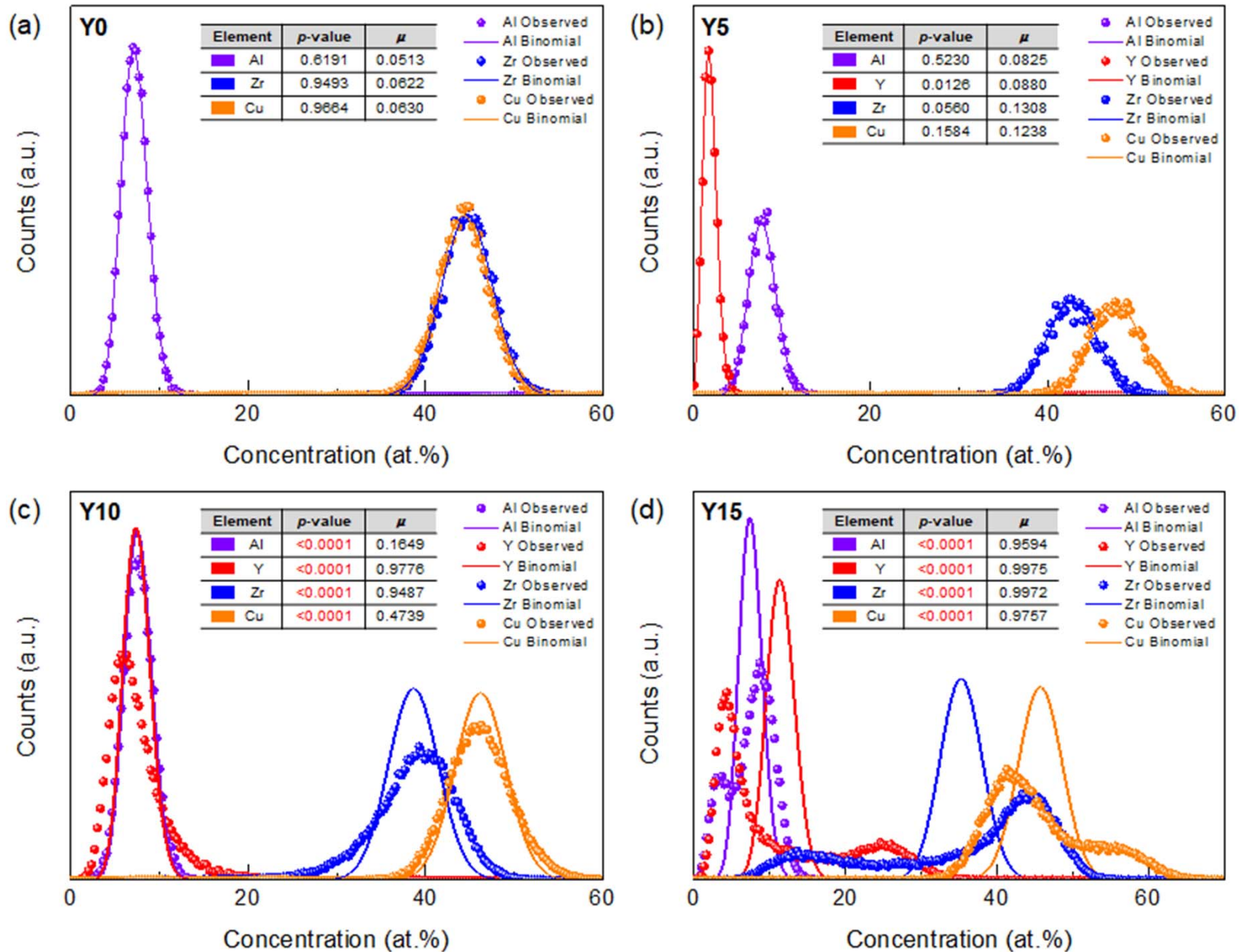
APT results of $\text{Cu}_{46}\text{Zr}_{47-x}\text{Al}_7\text{Y}_x$ ($x = 0, 5, 10, 15$) ribbons



APT reconstructions showing the distribution of the alloy metallic elements (Cu-Yellow; Zr-blue; Al-purple; Y-red). The upper images are three-dimensional views for cylindrical regions, and the lower images are 2 nm-thick virtual slices of the respective reconstructions.

Statistical binomial frequency distribution analysis

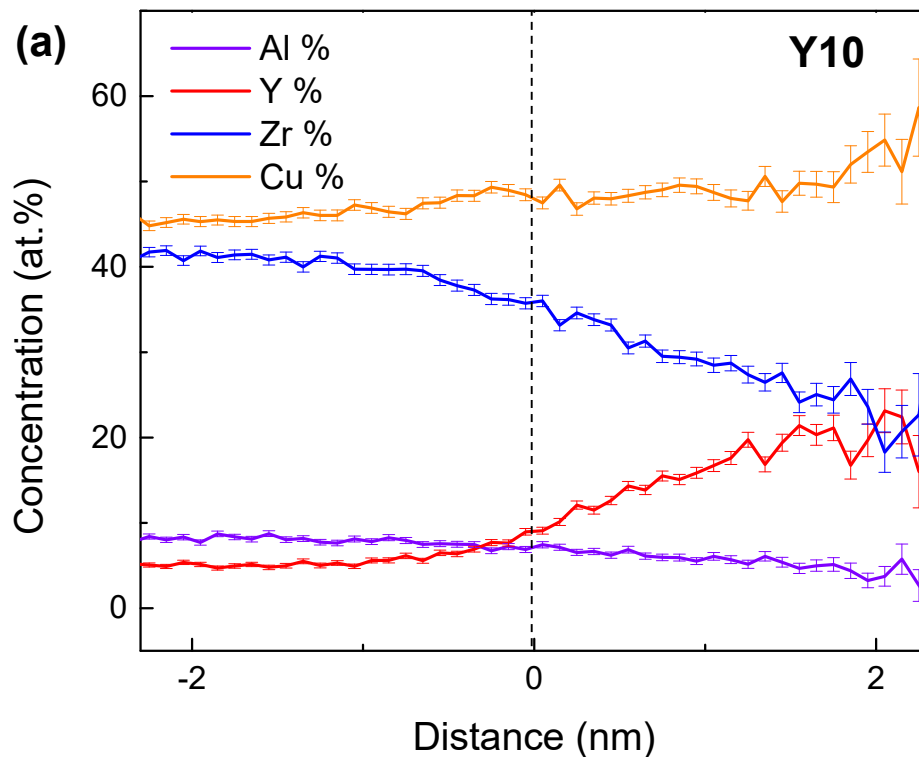
The quality of the binomial fit was quantified using p -value and μ parameters, as listed in the inset tables.



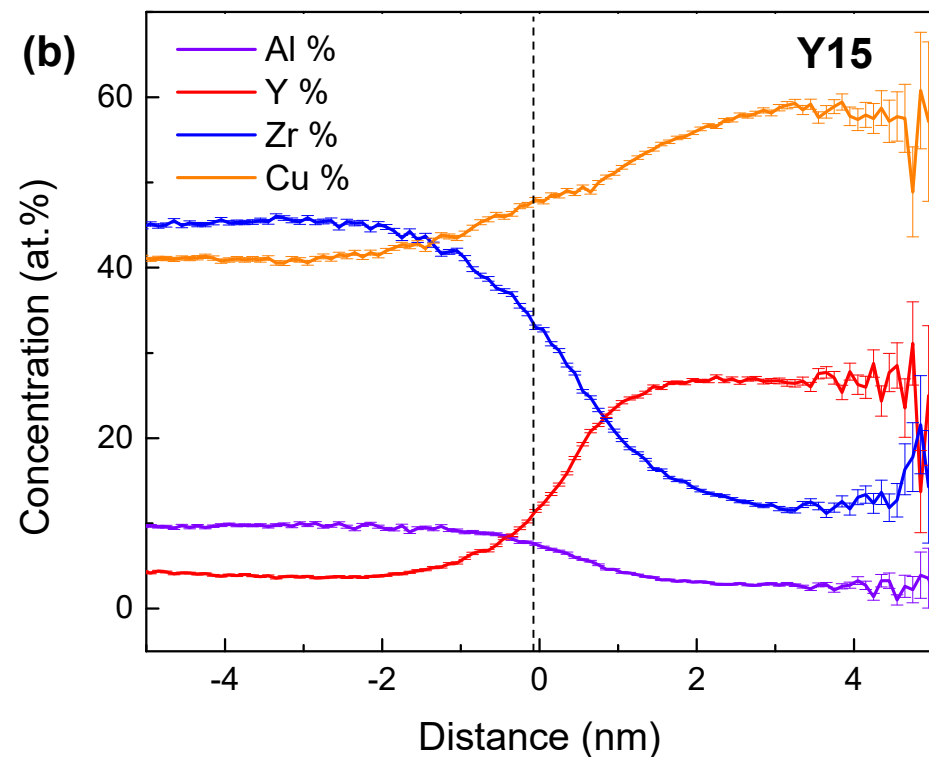
Proxigrams with respect to interfaces btw Zr- and Y-rich region

calculated with a bin size of 0.3 nm

Compositional heterogeneity with nanoscale network



Phase separation with interconnected structure

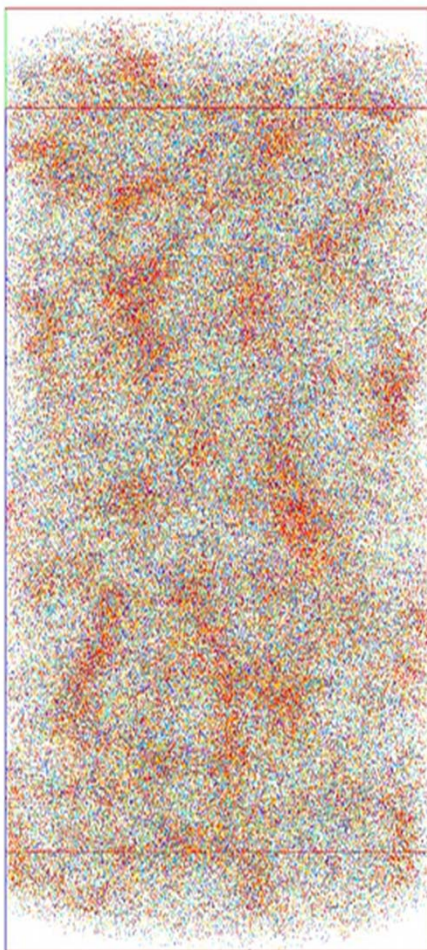


The interfaces (distance=0) in (a) and (b) are estimated from the frequency distribution analysis results to be the positions with Y composition of 10 at. % and 16 at.%, respectively.

APT results of $\text{Cu}_{46}\text{Zr}_{37}\text{Al}_7\text{Y}_{10}$ vs $\text{Cu}_{46}\text{Zr}_{32}\text{Al}_7\text{Y}_{15}$ ribbons

Compositional heterogeneity
with nanoscale network

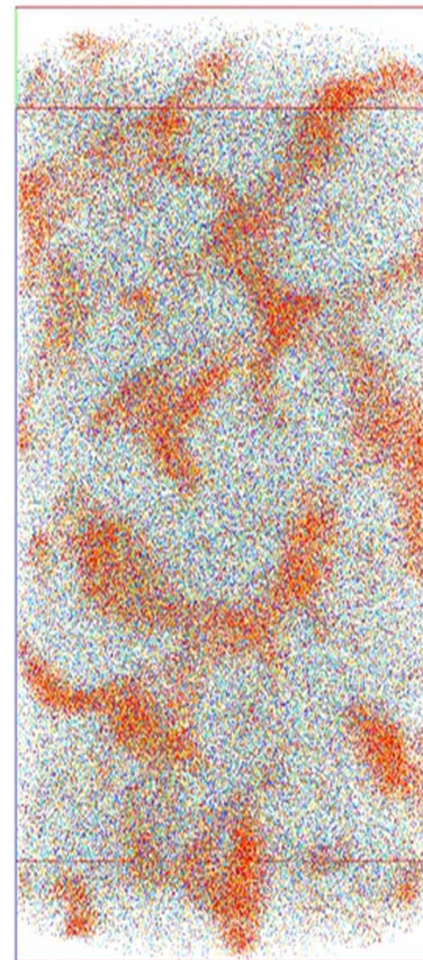
Y10



20 nm

Phase separation
with interconnected structure

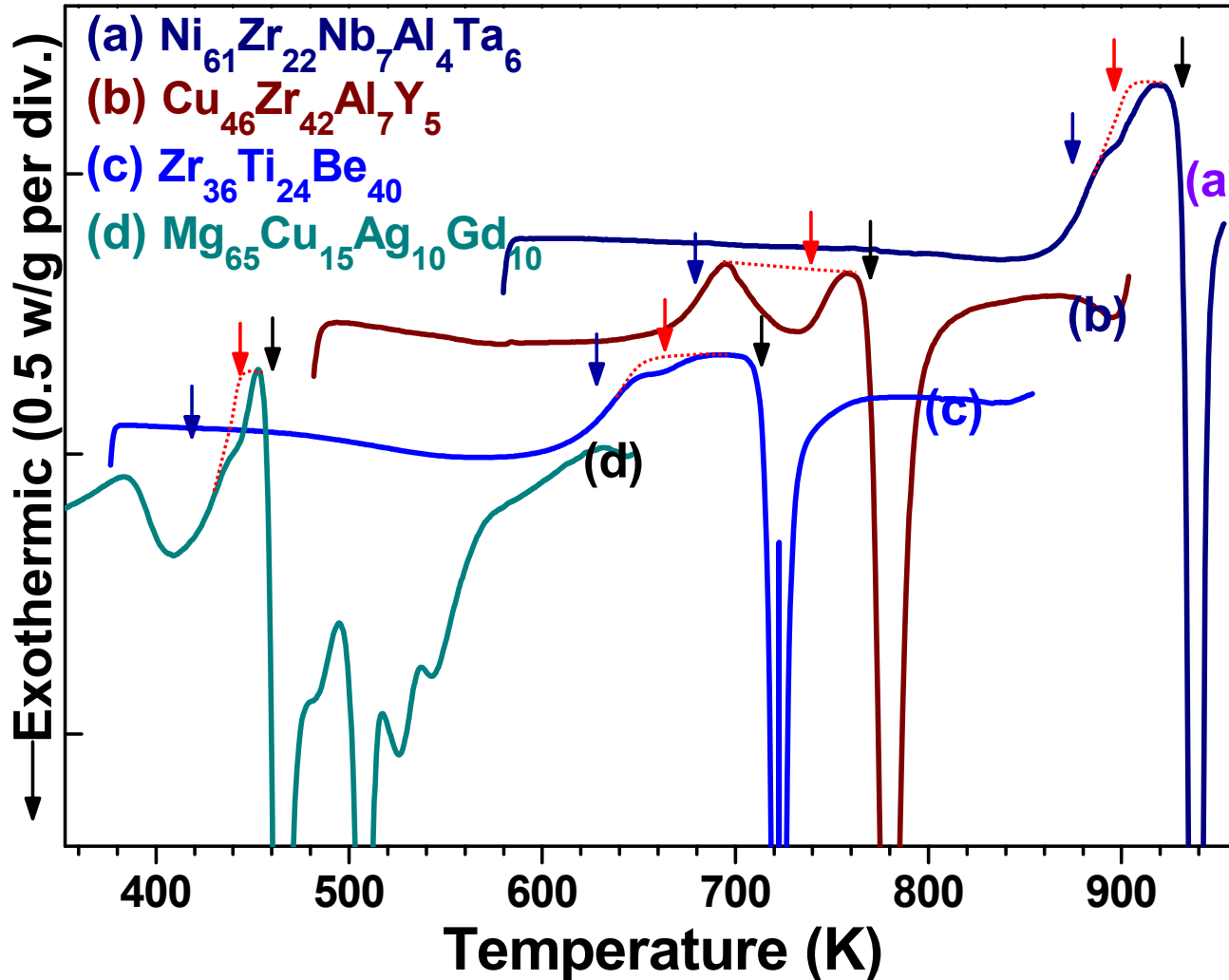
Y15



20 nm

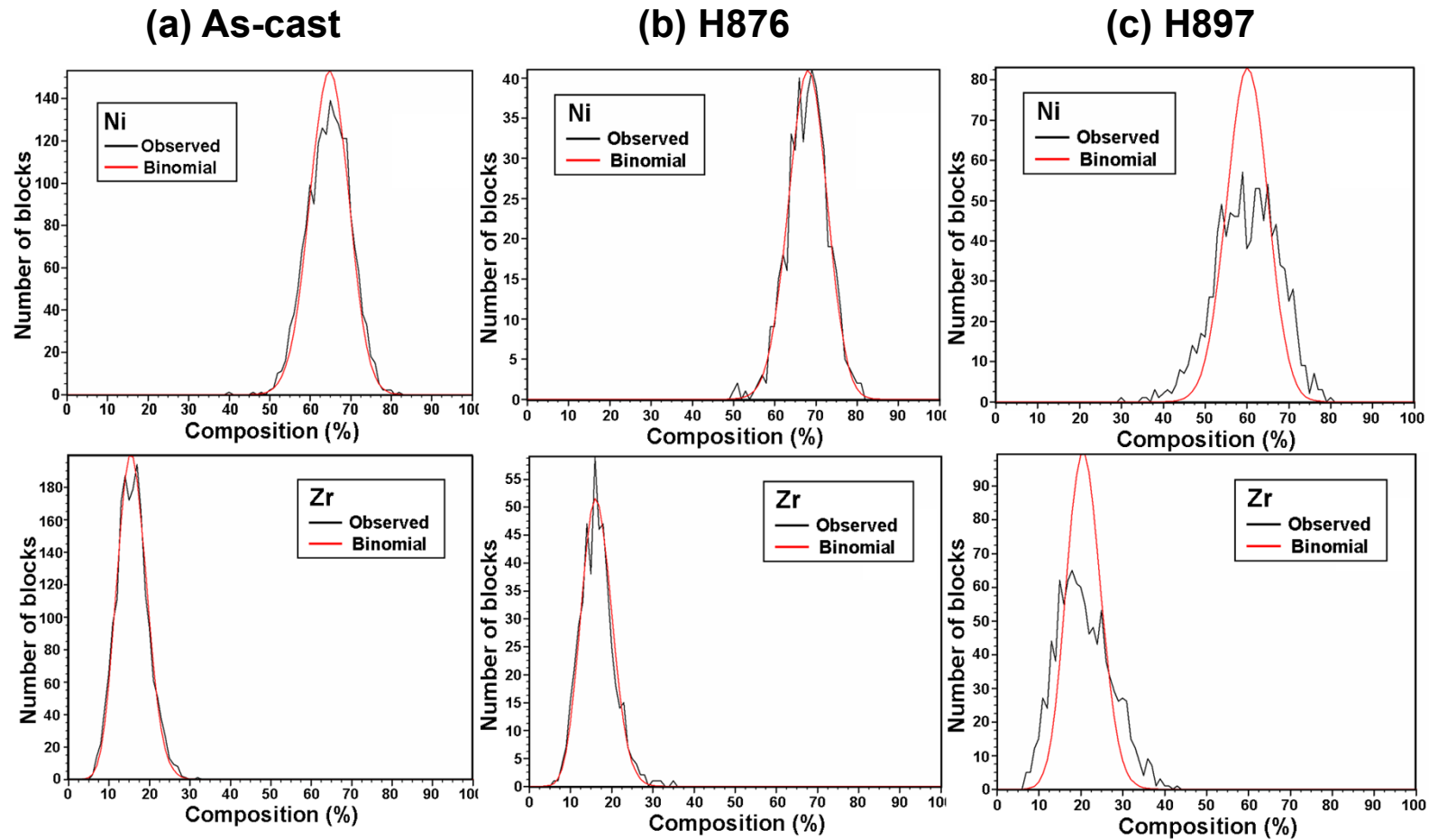
Effect of element having positive enthalpy of mixing

- Abnormal behavior of supercooled liquid region



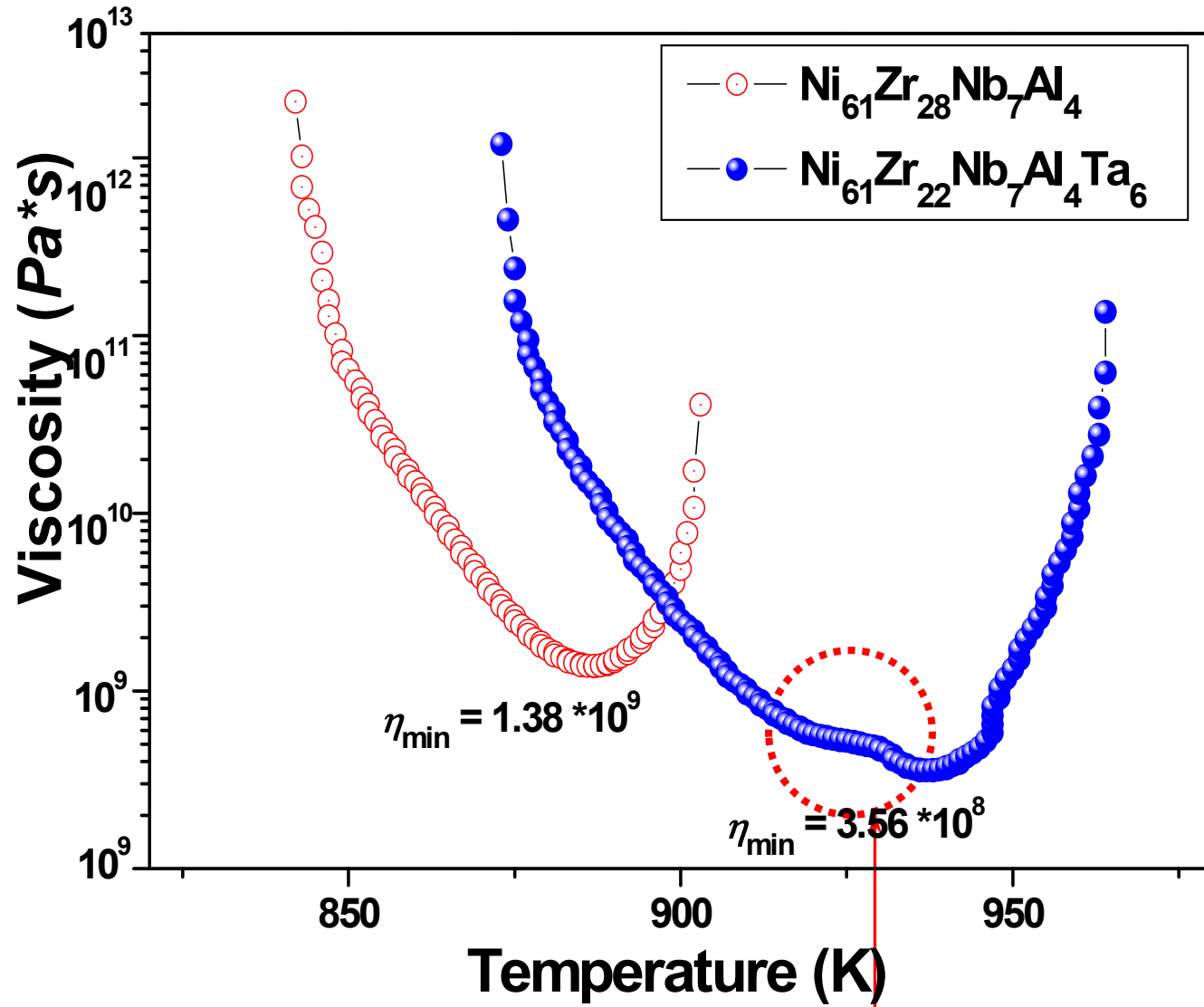
Effect of element having positive enthalpy of mixing

Atom probe concentration depth profiles in $\text{Ni}_{61}\text{Zr}_{22}\text{Nb}_7\text{Al}_4\text{Ta}_6$



easy crystallization

Effect of element having positive enthalpy of mixing



Ordering in supercooled liquid region

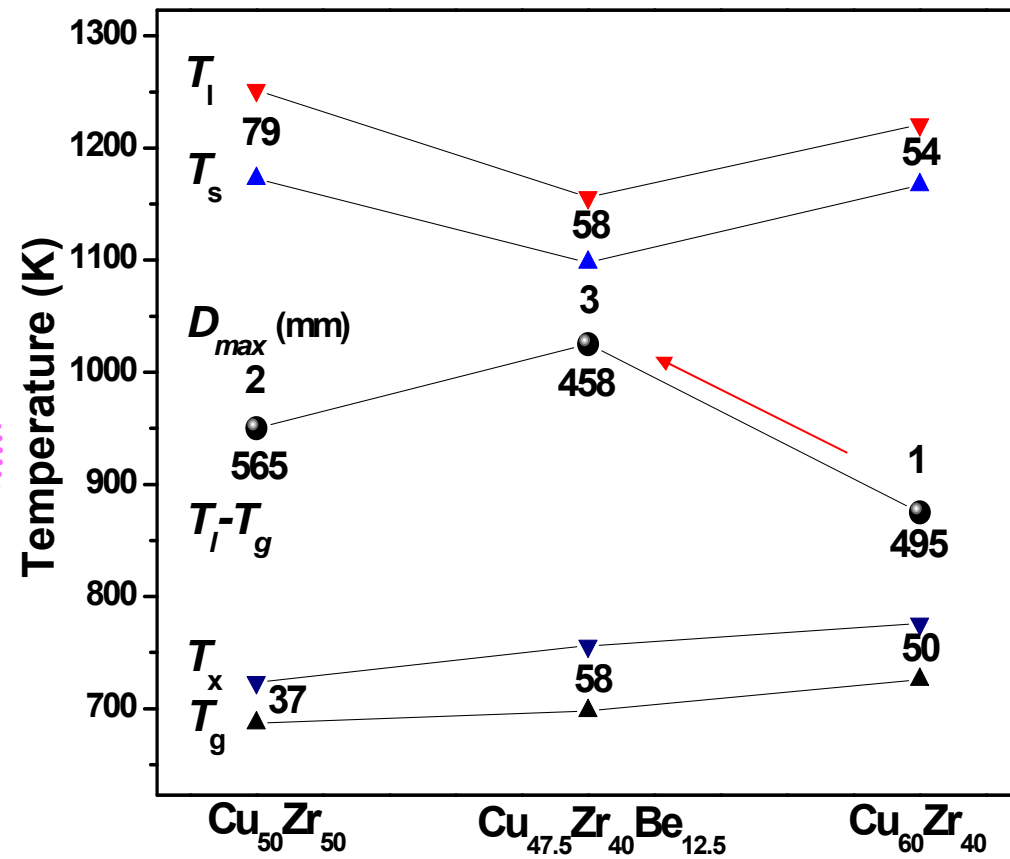
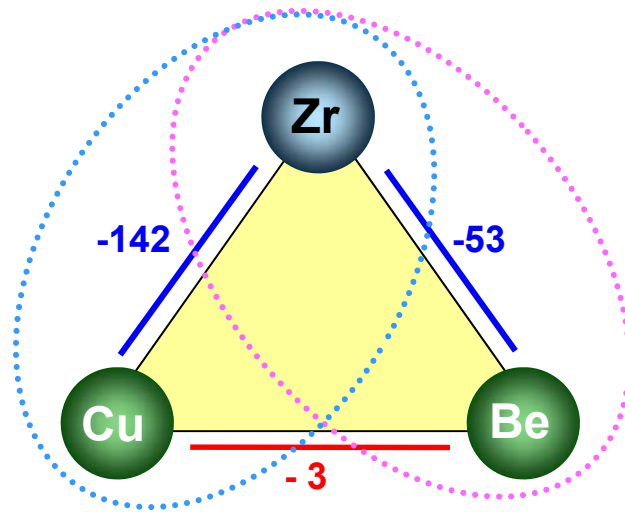
Enhancement plasticity in BMGs with atomic scale heterogeneity

- b) Effect of element having significantly different enthalpy of mixing among constituent elements

Effect of element having large different enthalpy of mixing

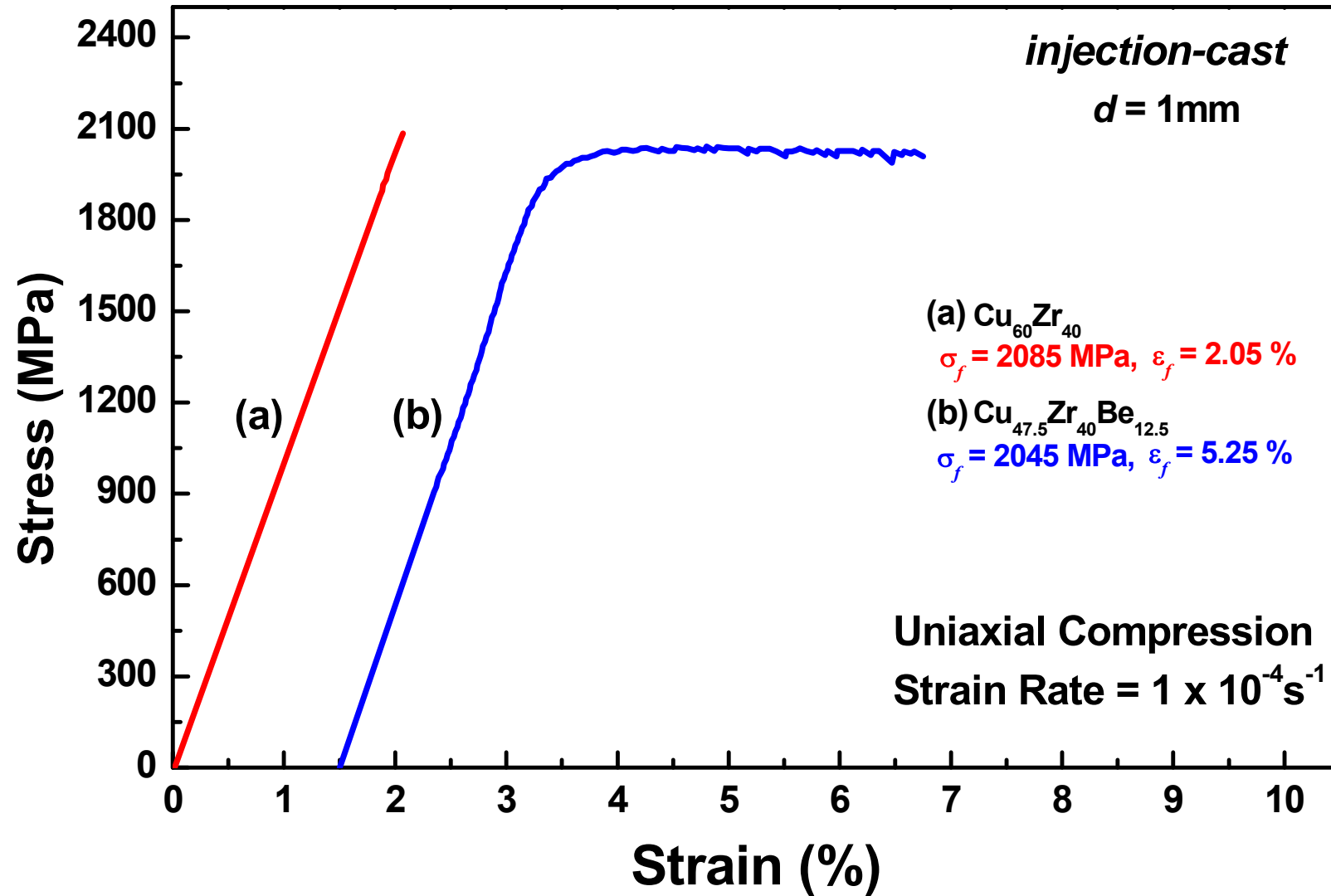
Cu-Zr-Be ternary alloy system

* Acta Materialia, 56 3120 (2008)



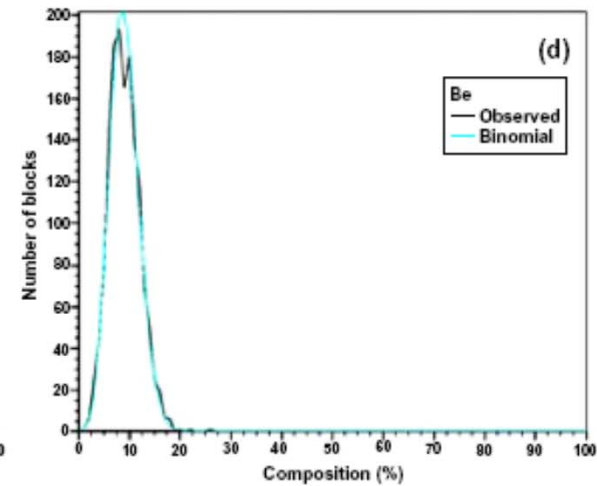
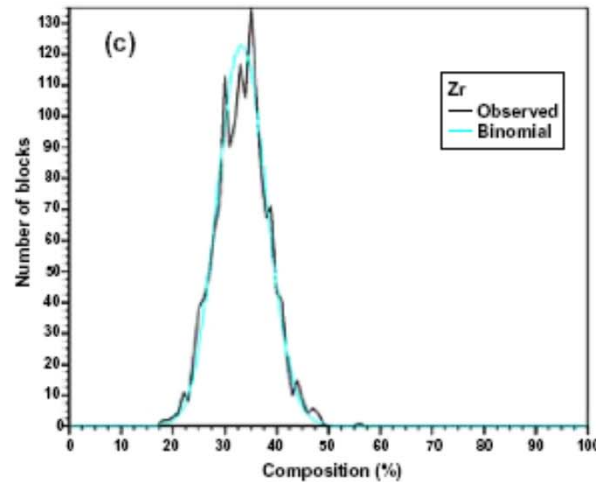
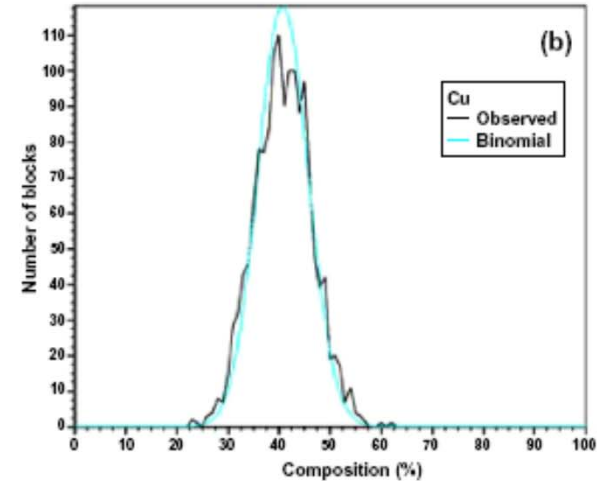
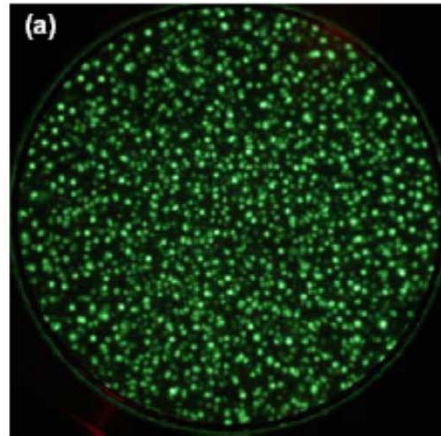
Effect of element having large different enthalpy of mixing

• Compression test



Effect of element having large different enthalpy of mixing

3DAP-FIM results



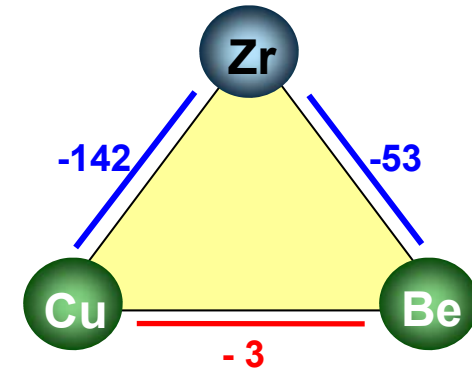
(a) FIM image and (b)-(d) composition depth profile of the as-spun $\text{Cu}_{47.5}\text{Zr}_{40}\text{Be}_{12.5}$ ribbon sample

Effect of element having large different enthalpy of mixing

* Acta Materialia, 56 3120 (2008)

EXAFS analysis

	r (Å)		N		Total N	σ^2	
	Cu-Cu	Cu-Zr	Cu-Cu	Cu-Zr		Cu-Cu	Cu-Zr
$\text{Cu}_{60}\text{Zr}_{40}$	2.49	2.69	3.0	3.7	6.7	0.0116	0.0233
$\text{Cu}_{47.5}\text{Zr}_{40}\text{Be}_{12.5}$	2.51	2.70	2.5	4.8	7.3	0.0107	0.0227
	Zr-Zr	Zr-Cu	Zr-Zr	Zr-Cu		Zr-Zr	Zr-Cu
$\text{Cu}_{60}\text{Zr}_{40}$	3.10	2.68	6.9	4.4	11.3	0.0263	0.0124
$\text{Cu}_{47.5}\text{Zr}_{40}\text{Be}_{12.5}$	3.12	2.69	6.2	3.5	9.7	0.0257	0.0130



Atomic diameter in Å: Cu-Cu = 2.56, Cu-Zr = 2.88, Zr-Zr = 3.20.

Cargill-Spaepen short-range order parameters, η

	Z_{AB}	$\langle Z \rangle$	Z^*_{AB}	Z^{**}_{AB}	η
$\text{Cu}_{60}\text{Zr}_{40}$	3.7	8.540	3.416	3.546	0.043
$\text{Cu}_{47.5}\text{Zr}_{40}\text{Be}_{12.5}$	4.8	7.348	2.939	3.855	0.245

Cargill-Spaepen SRO parameter

$$\eta = Z_{AB} / Z_{AB}^{**} - 1$$

$$Z_{AB}^{**} = x_B Z_B Z_A / \langle Z \rangle$$

$$\eta > 0$$

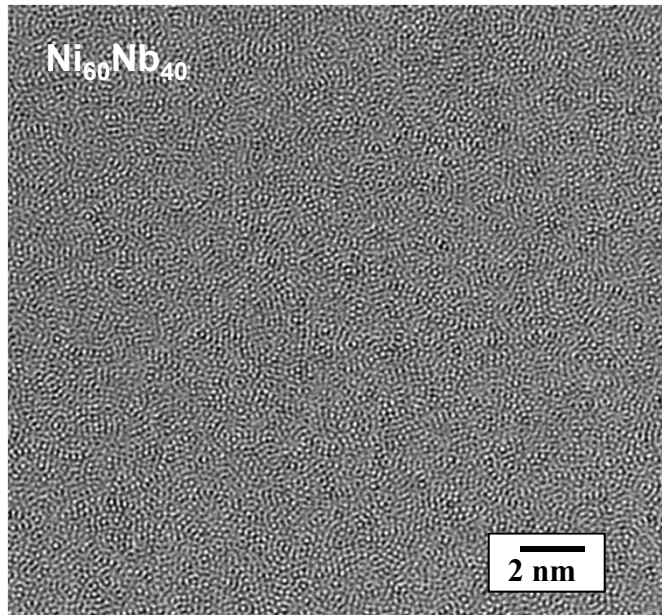
chemical ordering between AB nearest-neighbor pairs

Enhancement plasticity in BMGs with atomic scale heterogeneity
c) Effect of atomic scale heterogeneity on SB nucleation

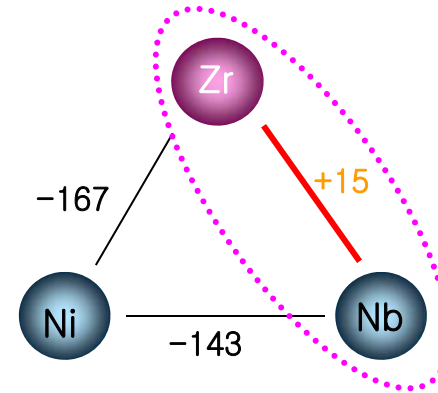
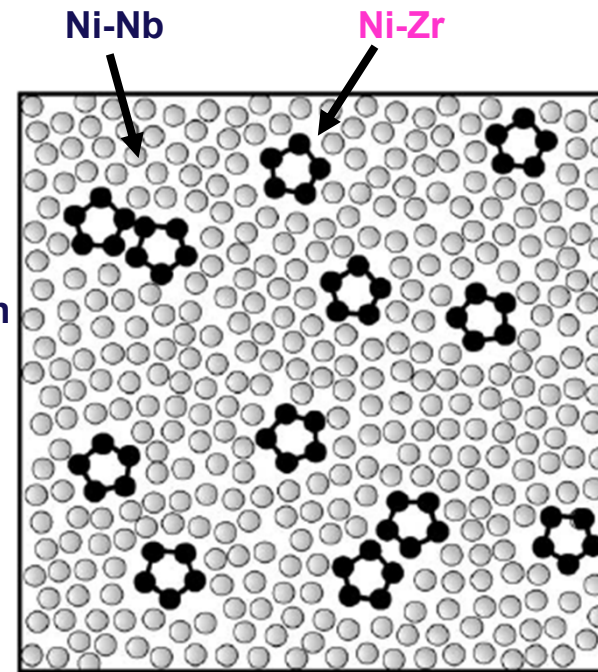
Effect of alloy composition on SB nucleation

*Ni-Nb-Zr ternary alloy system

$\text{Ni}_{60}\text{Nb}_{40}$ and $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ alloys

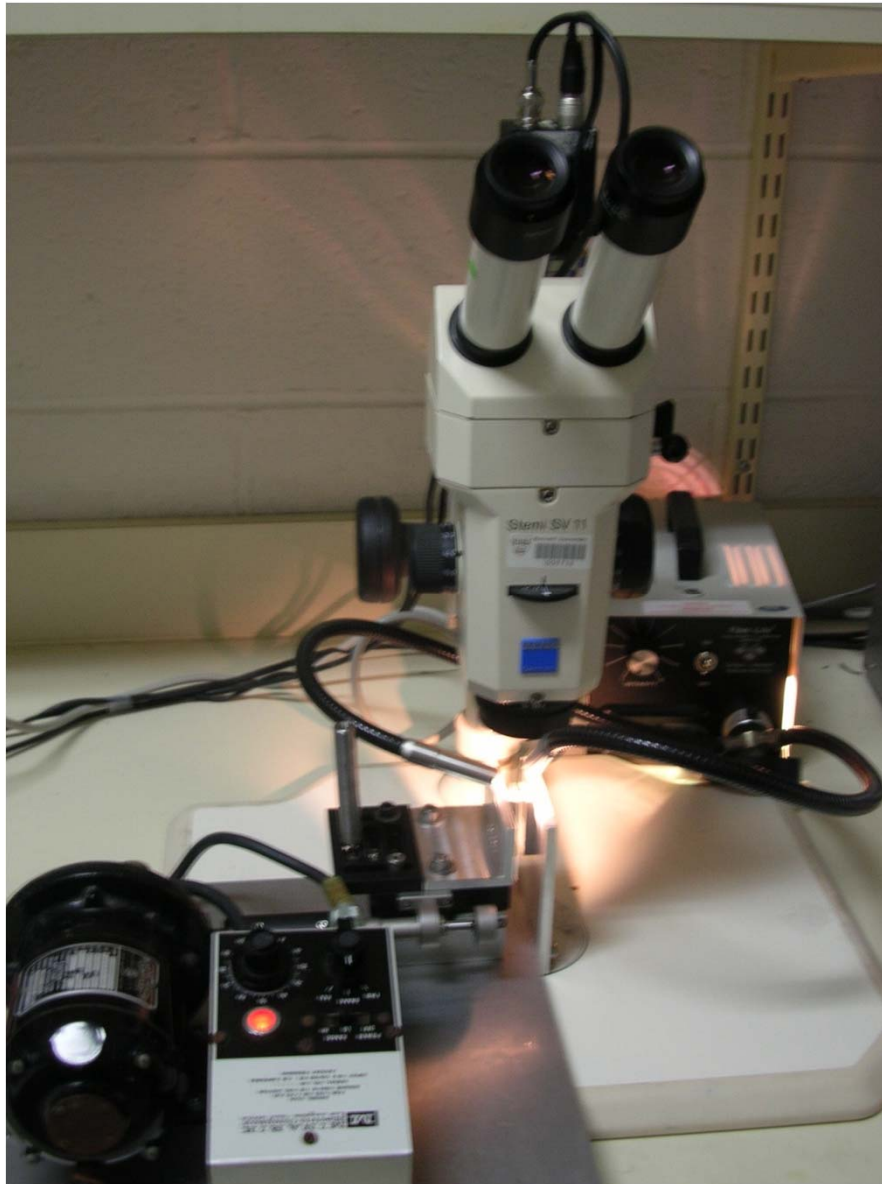


Zr addition

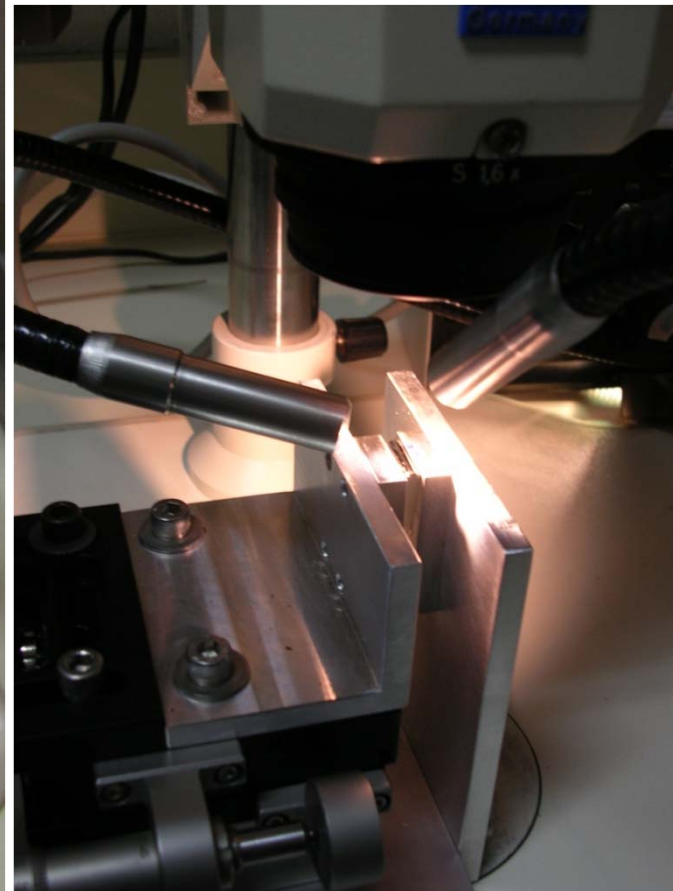


Compositional inhomogeneity
(conformed by EXAFS)

Experimental equipment



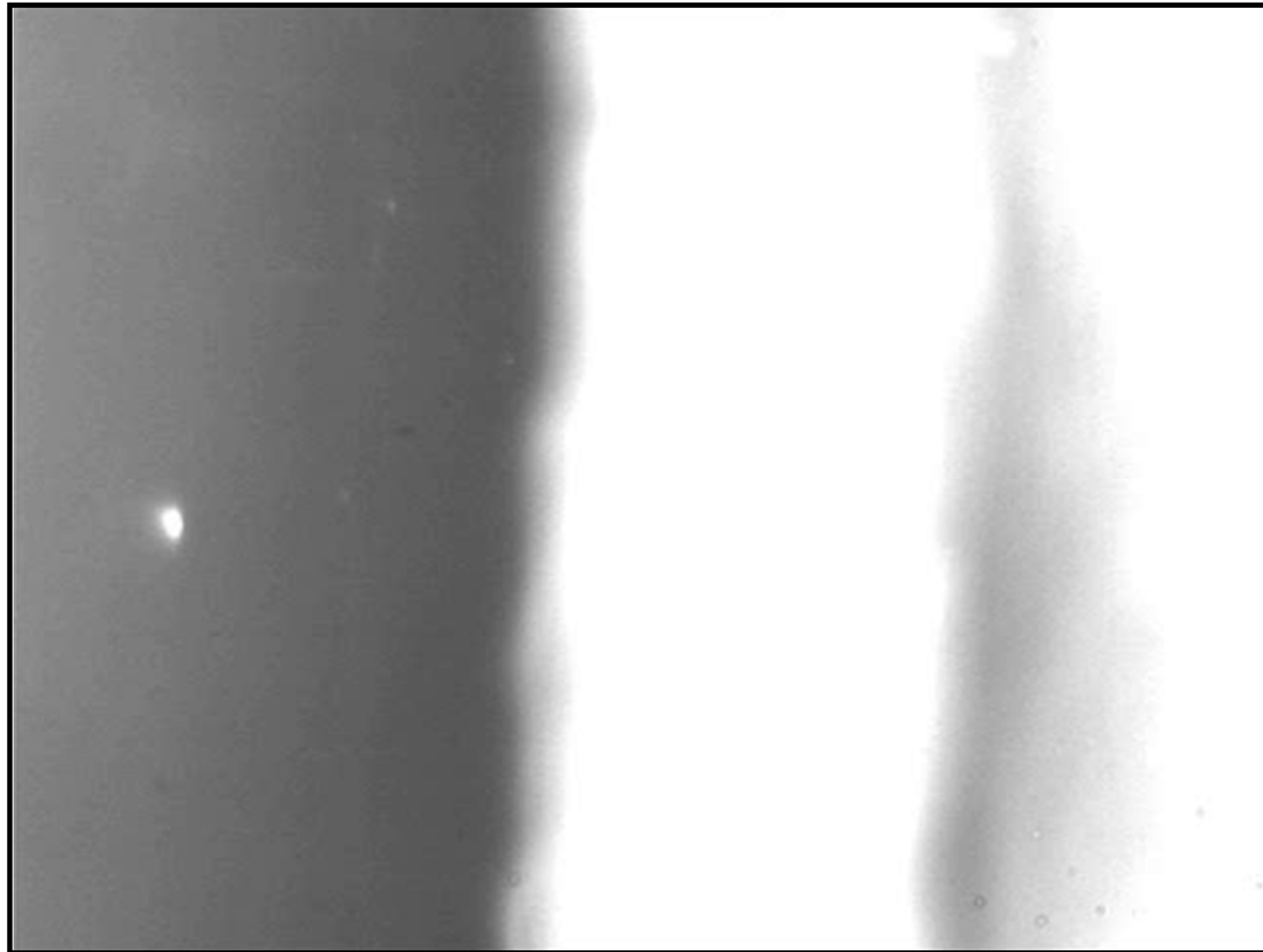
Normal camera
25 frames per sec
Interval : 0.04 sec



Effect of local favored structure on SB nucleation

• $\text{Ni}_{60}\text{Nb}_{40}$: fully amorphous phase

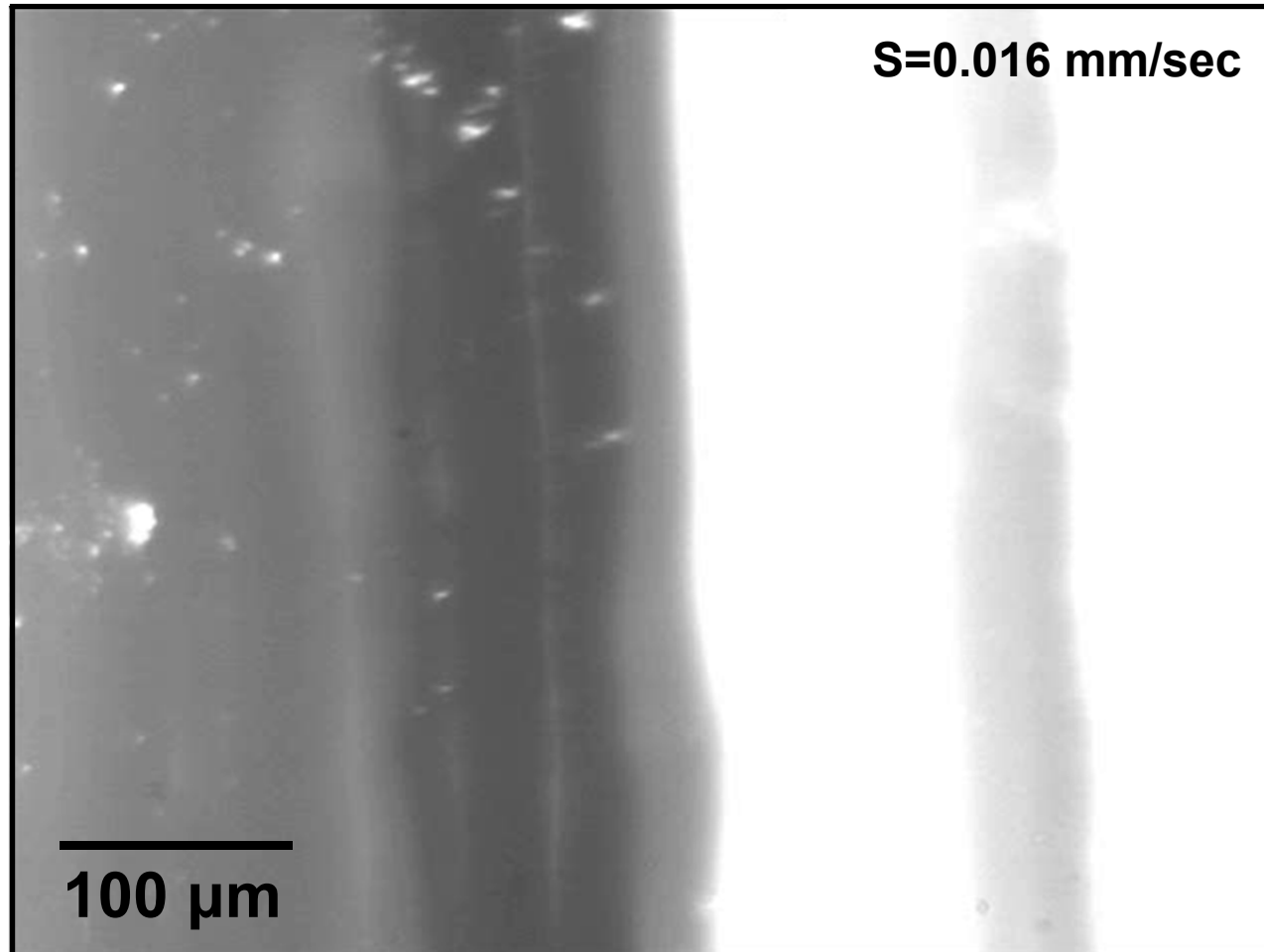
$S=0.016$ mm/sec



100 μm

Effect of local favored structure on SB nucleation

• $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$: amorphous phase with local favored structure



- Increased nucleation sites of shear bands
; evaluate the local heterogeneity in amorphous phase

Tailoring of structural inheterogeneity



Alloy design

+

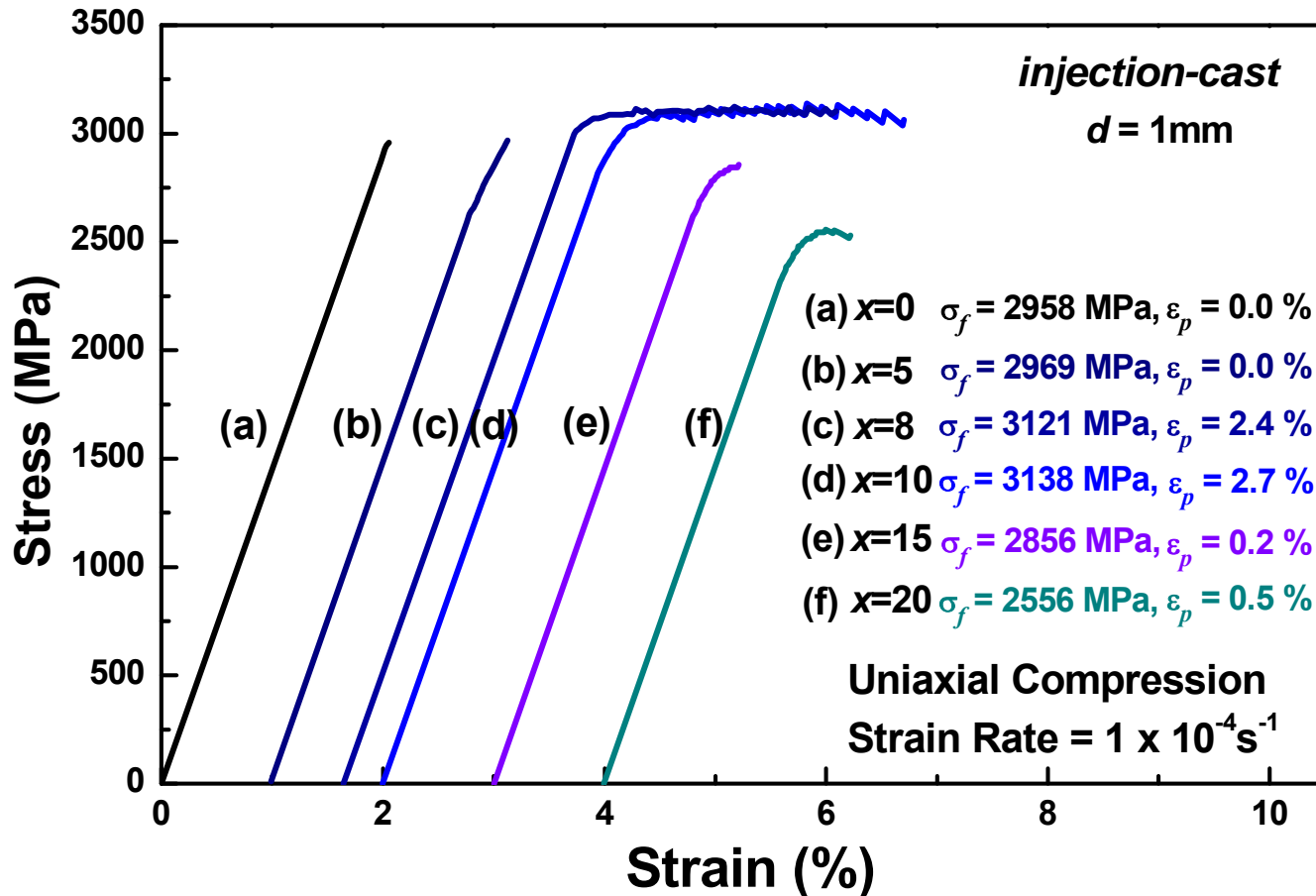
Process control

atomic scale inhomogeneity generation

Solidification under appropriate conditions

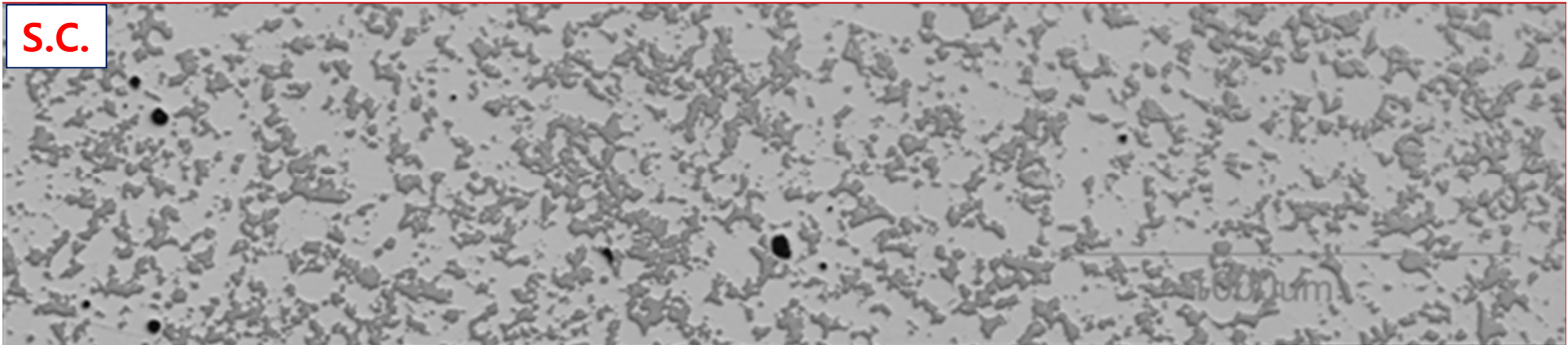


Enhanced plasticity in $\text{Ni}_{60}\text{Nb}_{32}\text{Zr}_8$, $\text{Ni}_{60}\text{Nb}_{30}\text{Zr}_{10}$ BMGs (σ_{max} : 3.2 GPa, ε_p : 2.5 %)

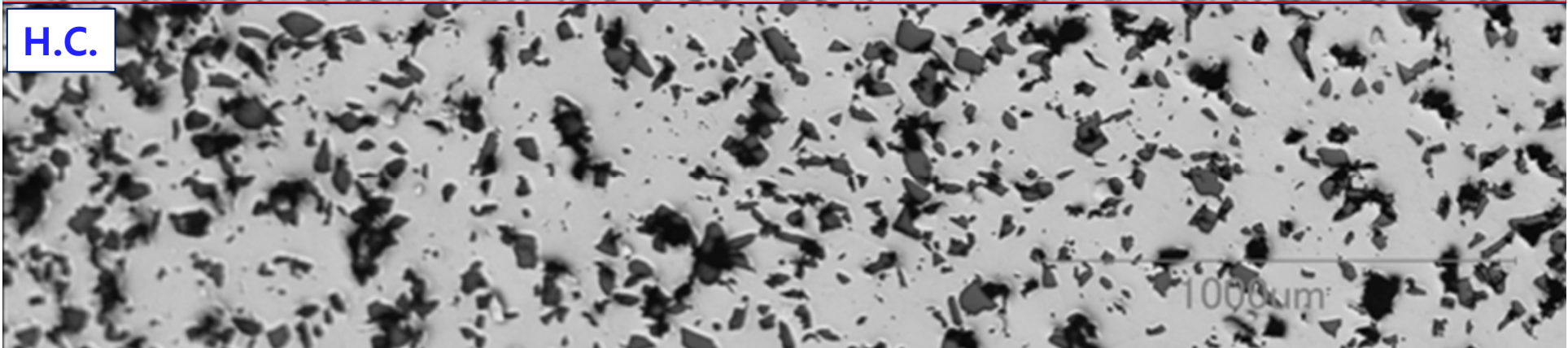


Comparison of Work-hardenability depending on 2nd Phases

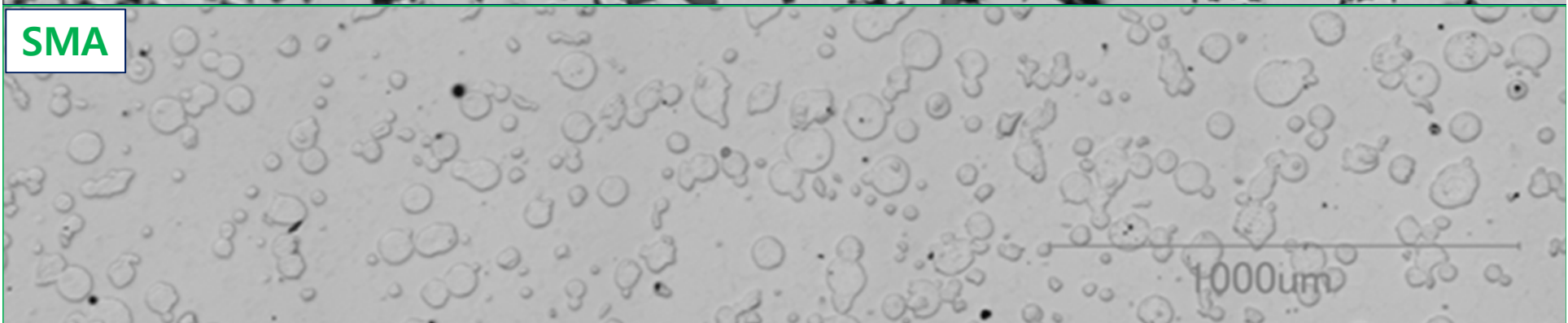
S.C.



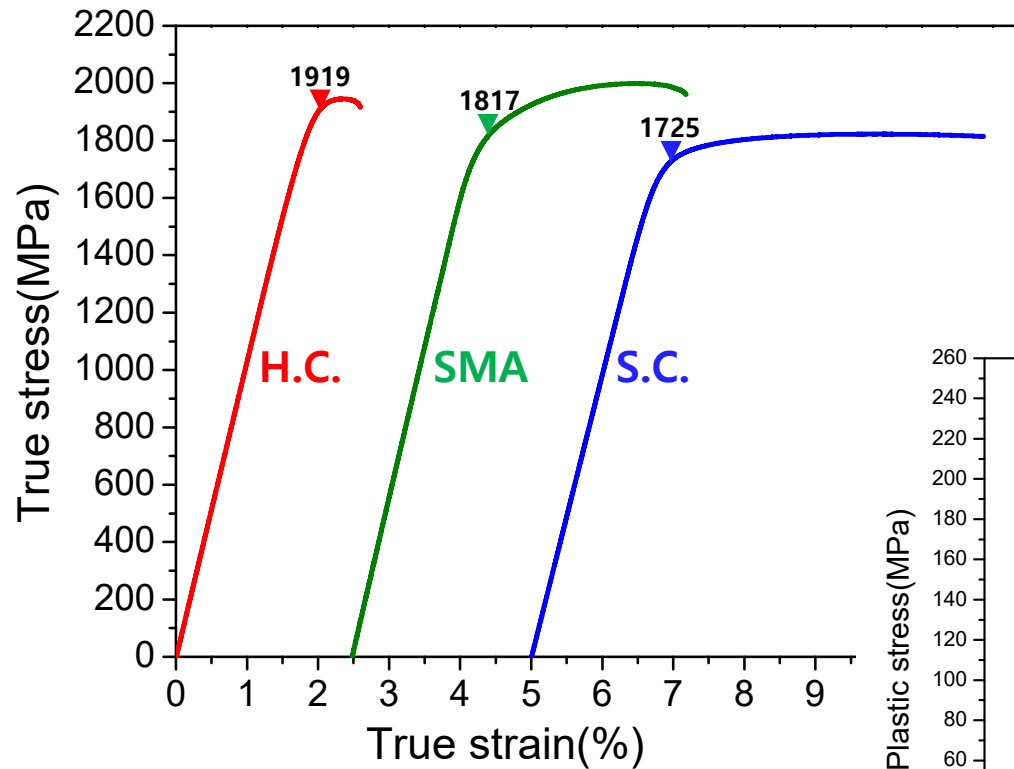
H.C.



SMA

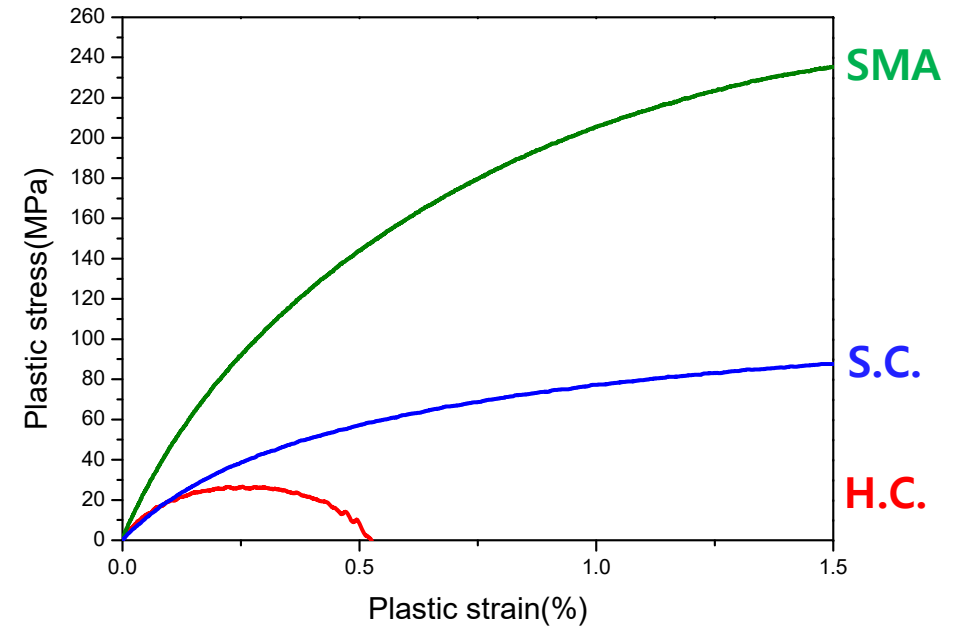


Comparison of Work-hardenability depending on 2nd Phases



$$\sigma_p = \sigma - \sigma_y$$

$$\varepsilon_p = \varepsilon - \varepsilon_y - \frac{\sigma_p}{E}$$



- SMA : Strain hardening
- H.C., S.C. : Strain softening

Higher strain hardening of SMA, then larger work hardenability of BMGMCs

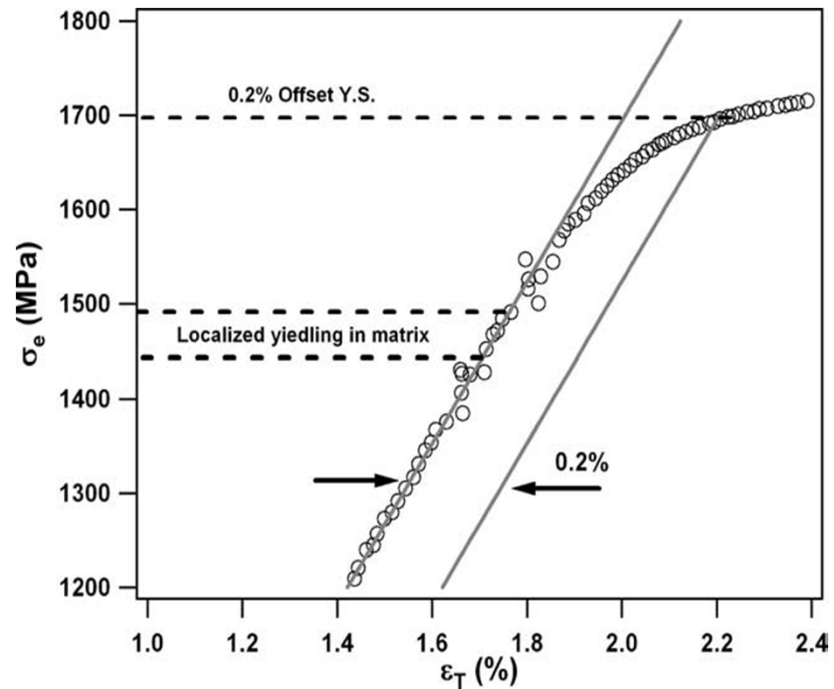
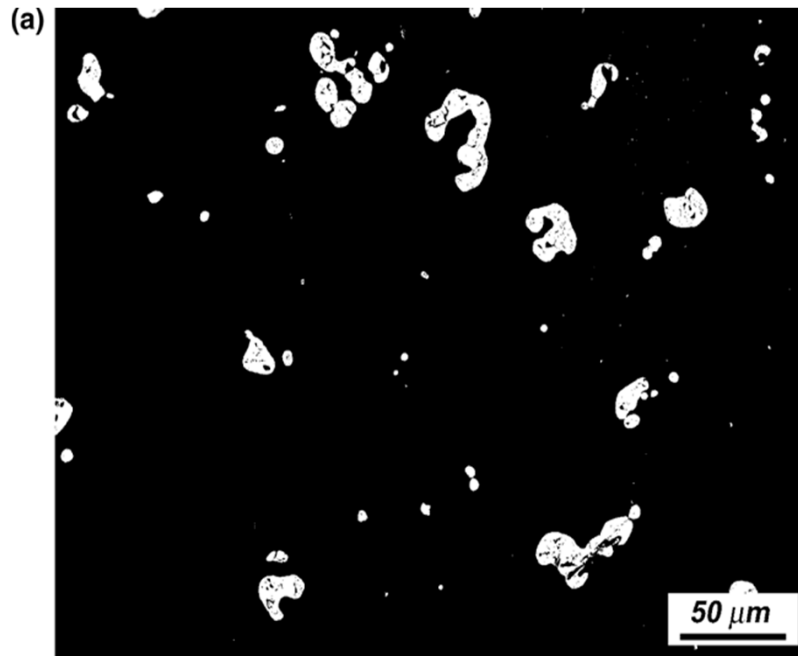
Strain hardening(2nd) → Work hardening

(SMA > S.C. > H.C.)

(SMA > S.C. > H.C.)

Investigation of deformation of BMGC with “soft” phases

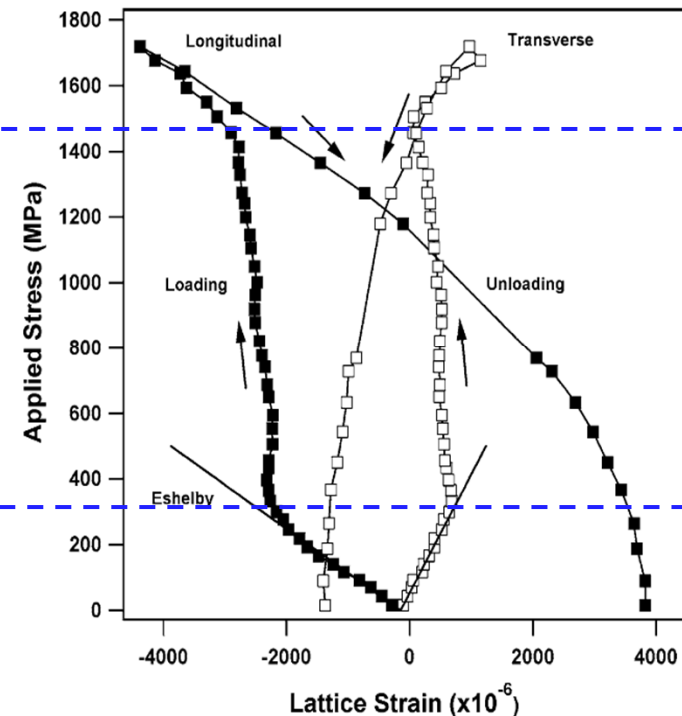
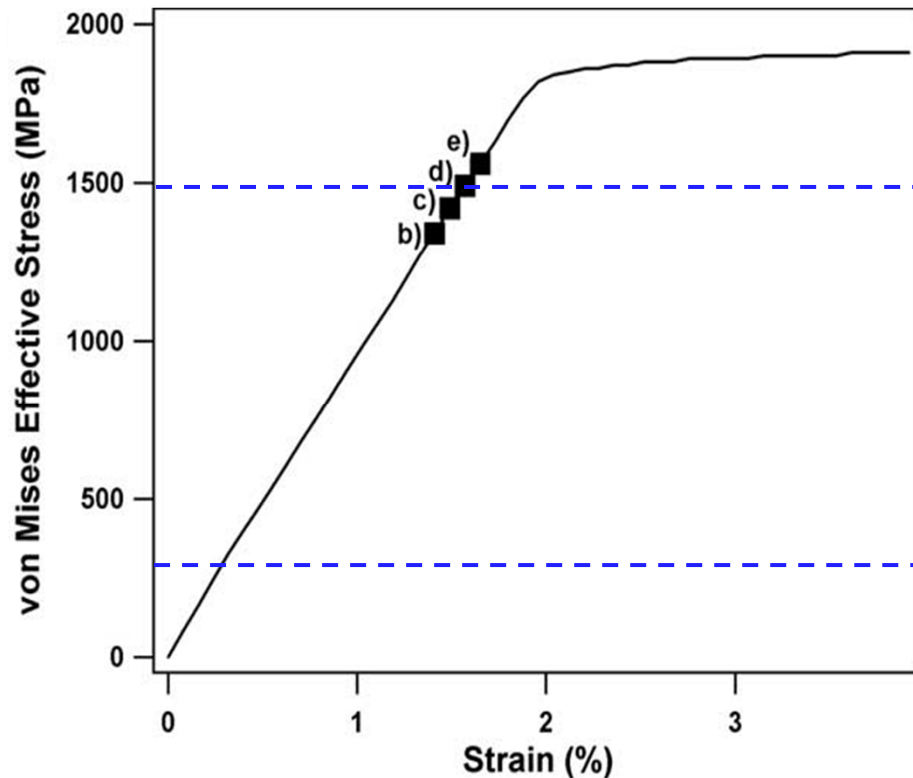
* BMGCs with soft crystalline 2nd phases



- Zr based metallic glass + 8% Ta
- Compression test with in-situ X-ray synchrotron diffraction
(Beamline 1-ID beamline of the Advanced Photon Source at Argonne National Laboratory)

Investigation of deformation of BMGC with “soft” phases

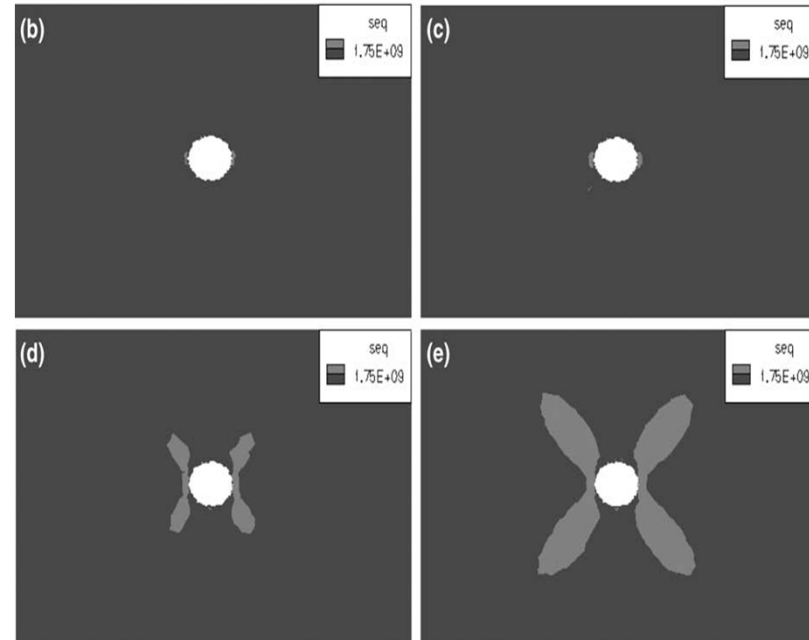
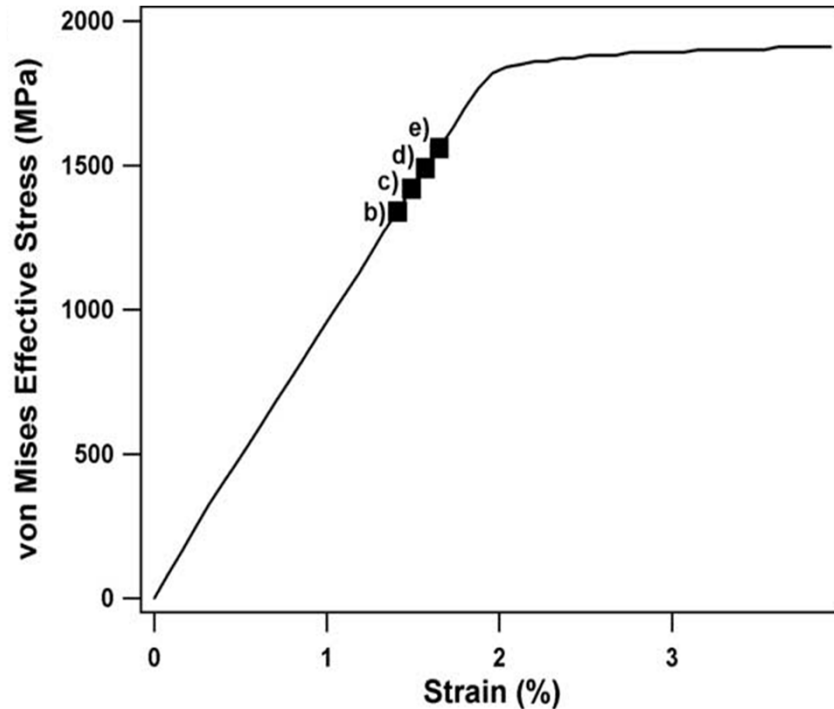
* BMGCs with soft crystalline 2nd phases



- At approximately 325 MPa applied stress, the particles yield, which are constrained by amorphous matrix causing plastic misfit stress near the particles.
- **At an applied stress of 1450 MPa (just below yield stress), the lattice stress-strain curve changes slope again for both the longitudinal and transverse directions, indicating an increase in the fraction of the load being transferred to Ta particles.**

Investigation of deformation of BMGC with “soft” phases

* BMGCs with soft crystalline 2nd phases

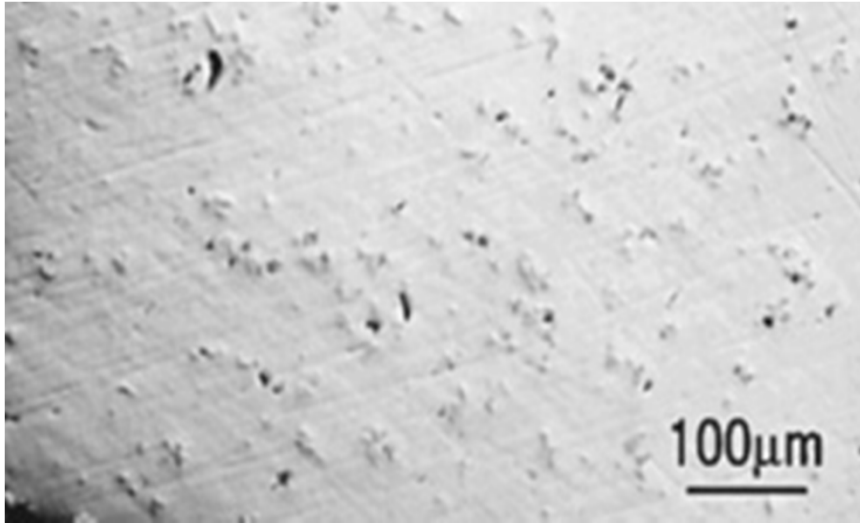


- Plastic misfit strain creates a significant stress concentration around the particles.
- **Shear bands** initiates near the particles due to the localized stress concentration.
- If a shear band initiates at the particle and propagates away, it will quickly encounter a region where the yield criterion is not satisfied and the shear stress is insufficient to sustain shear band propagation.

Principle of multiple shear band initiations & blocking shear bands propagation

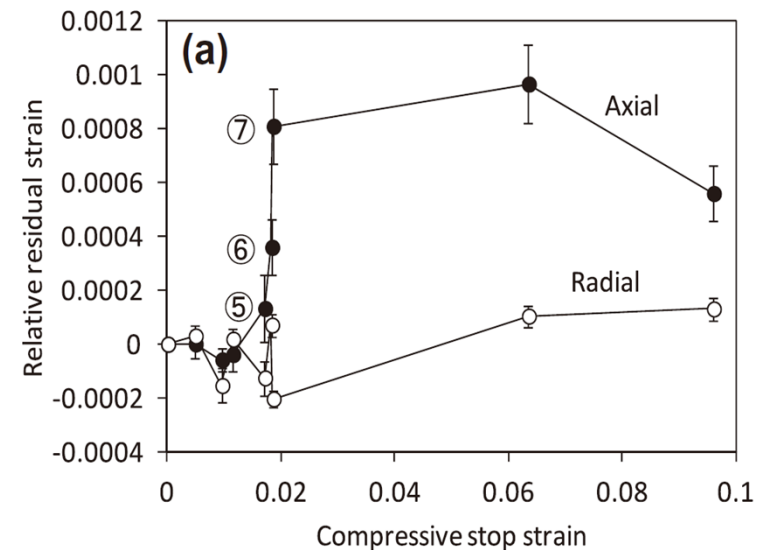
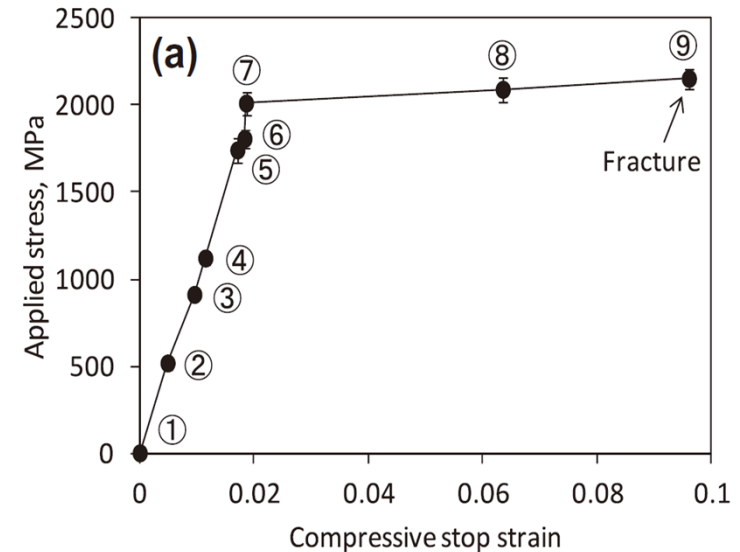
Investigation of deformation of BMGC with “hard” phases

* BMGCs with hard ceramic 2nd phase



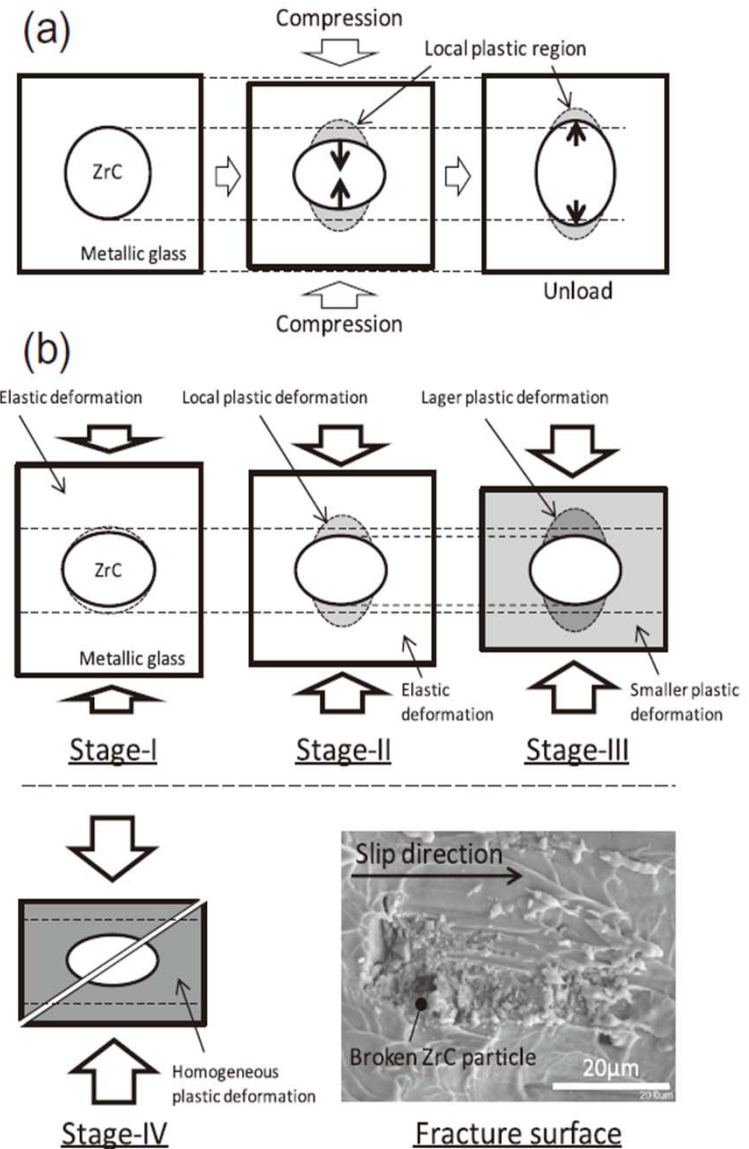
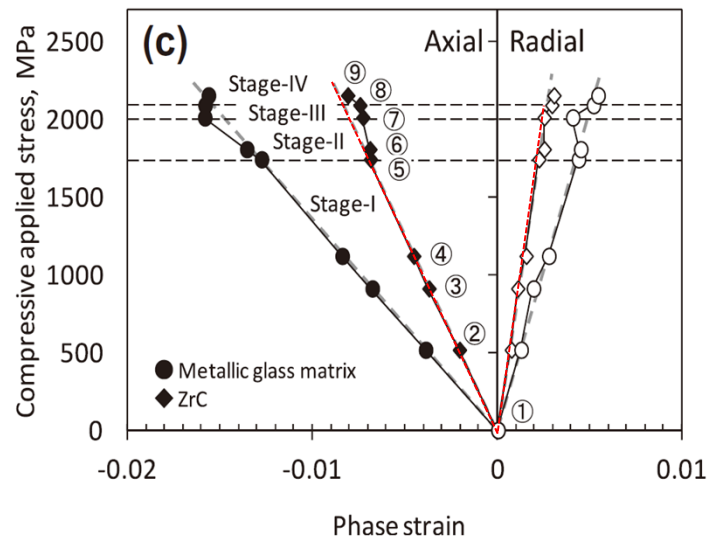
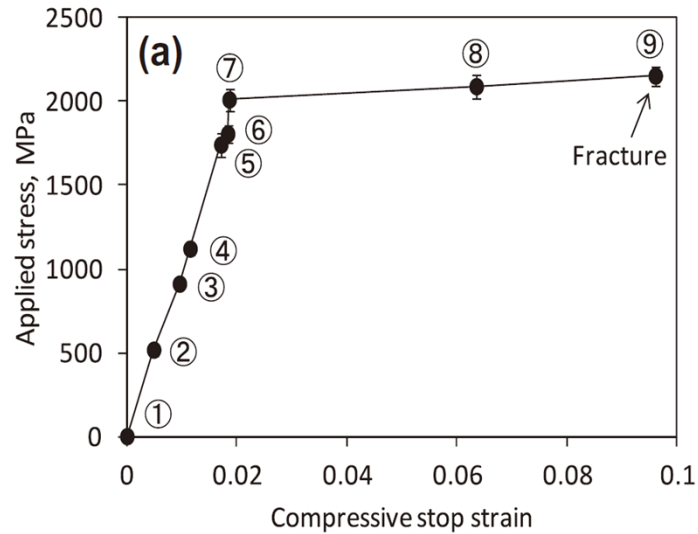
- Residual strain were measured by neutron diffraction.
- Each phase strain in the ZrC-BMG during compressive loading was estimated from the **residual strains** in each specimen according to following equations:

$$\varepsilon_A = \frac{\sigma_{\text{appl.}}}{E} + \varepsilon_{\text{res}_A} \quad \varepsilon_R = \varepsilon_{\text{res}_R} - \frac{\nu\sigma_{\text{appl.}}}{E}$$



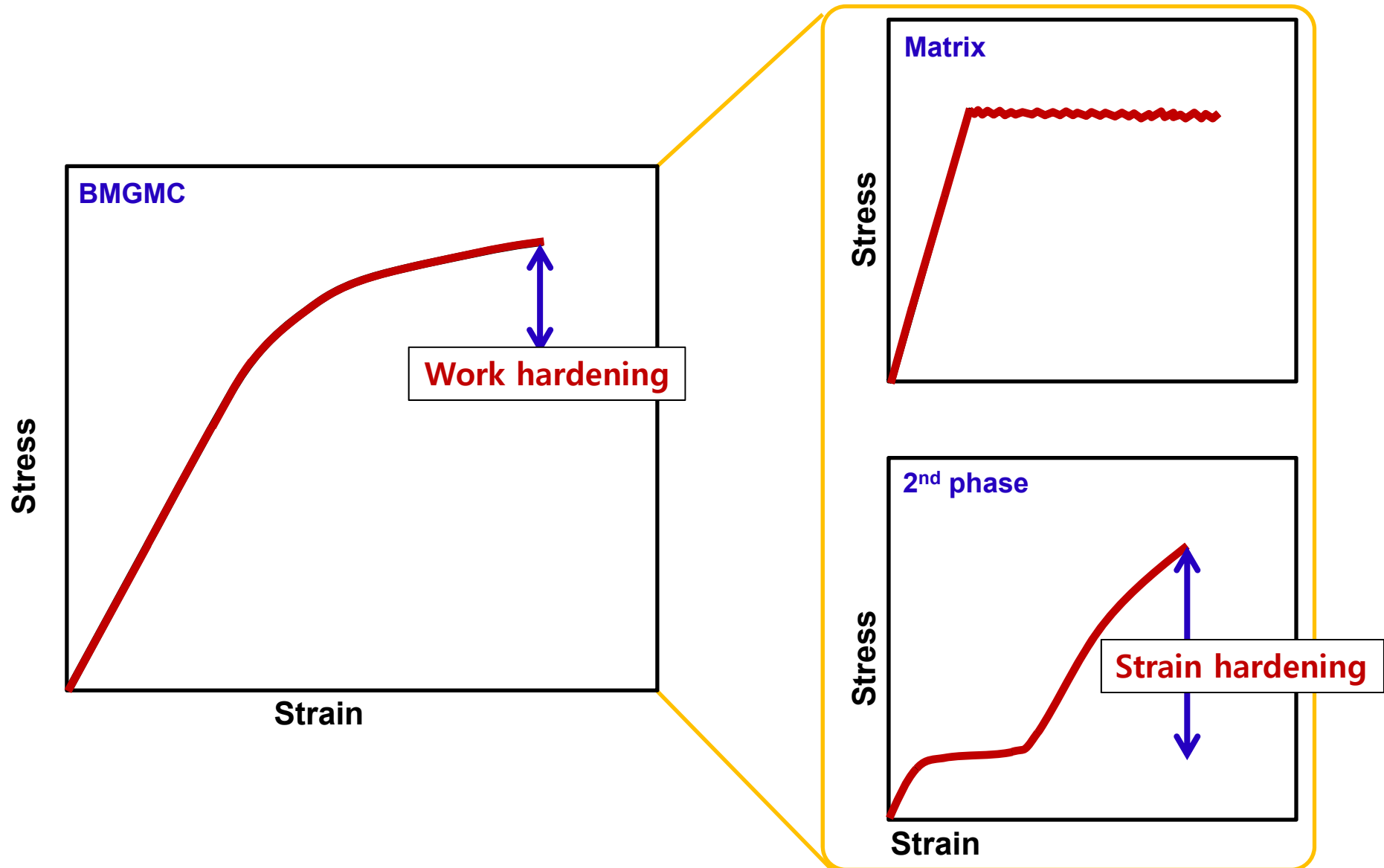
Investigation of deformation of BMGC with "hard" phases

* BMGCs with hard ceramic 2nd phases



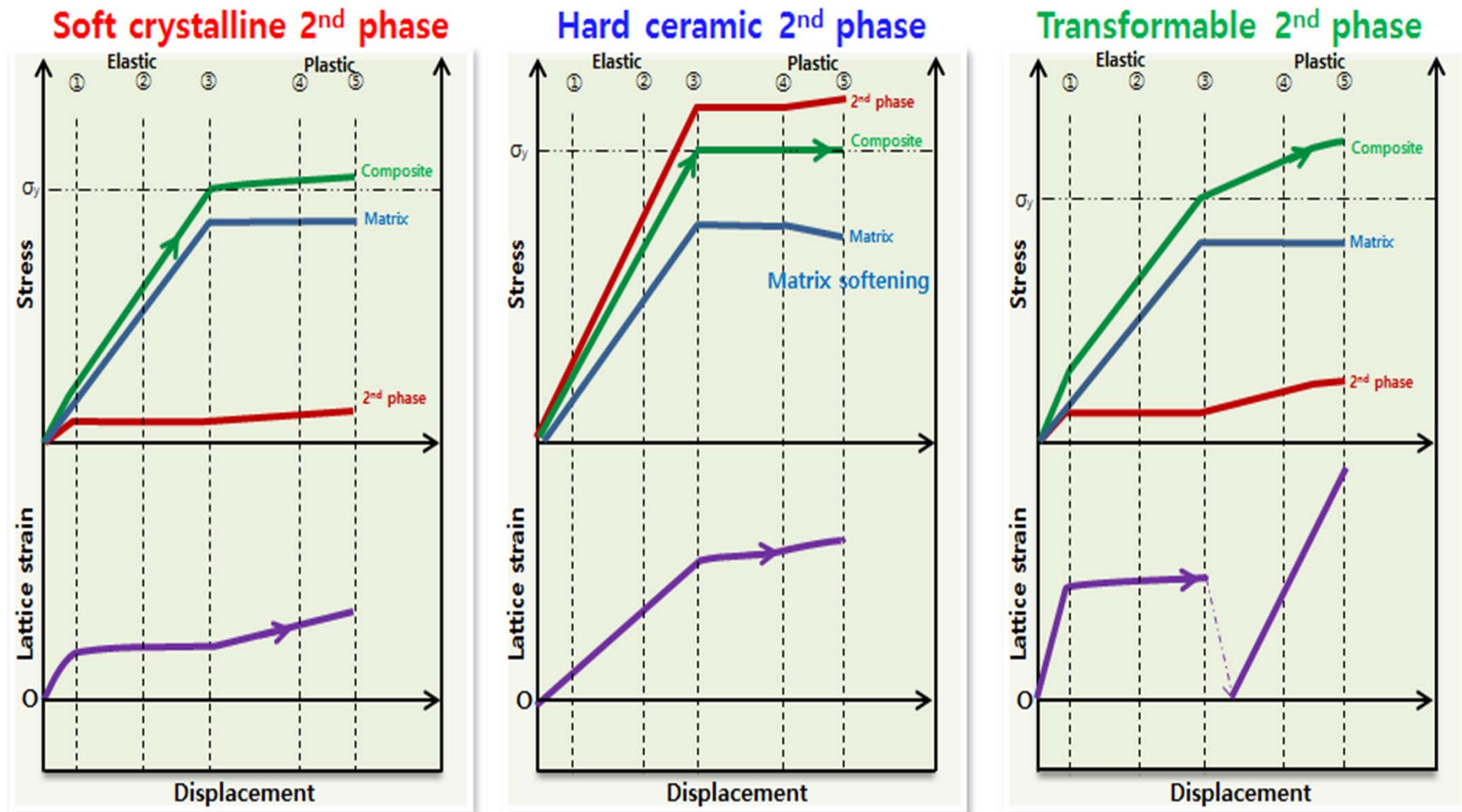
Mechanism of Work-hardening in BMGC with transformable 2nd phase

“Strain hardening of 2nd phase contributes to work hardening behavior of BMGC.”



Deformation behaviors of BMGC depending on 2nd phase

< Compression >



BMGMCs

Strain hardening(2nd)



Work hardening

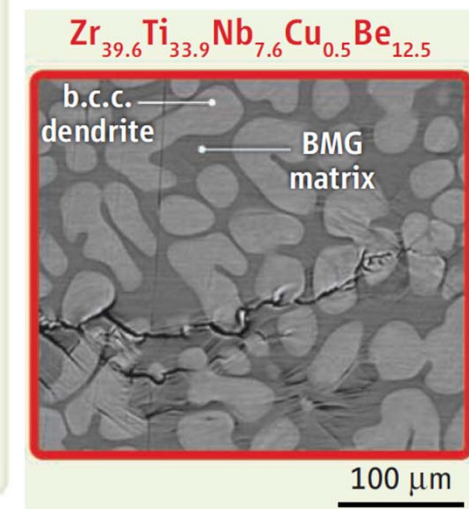
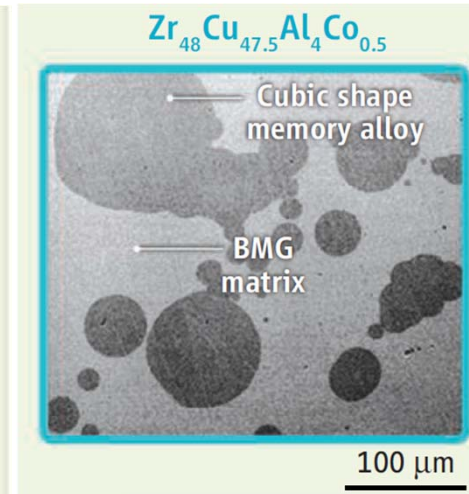
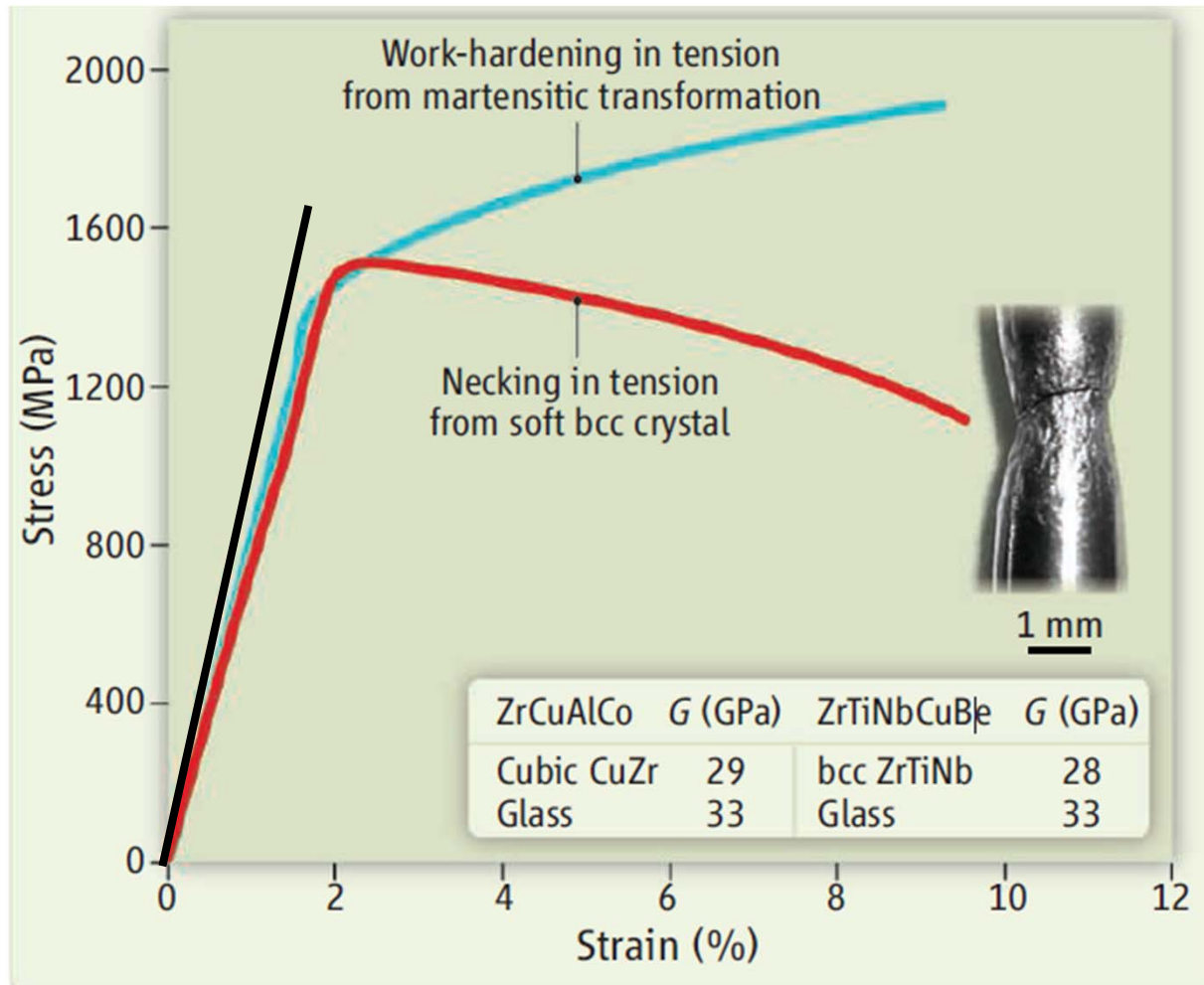
(SMA > S.C. > H.C.)

(SMA > S.C. > H.C.)

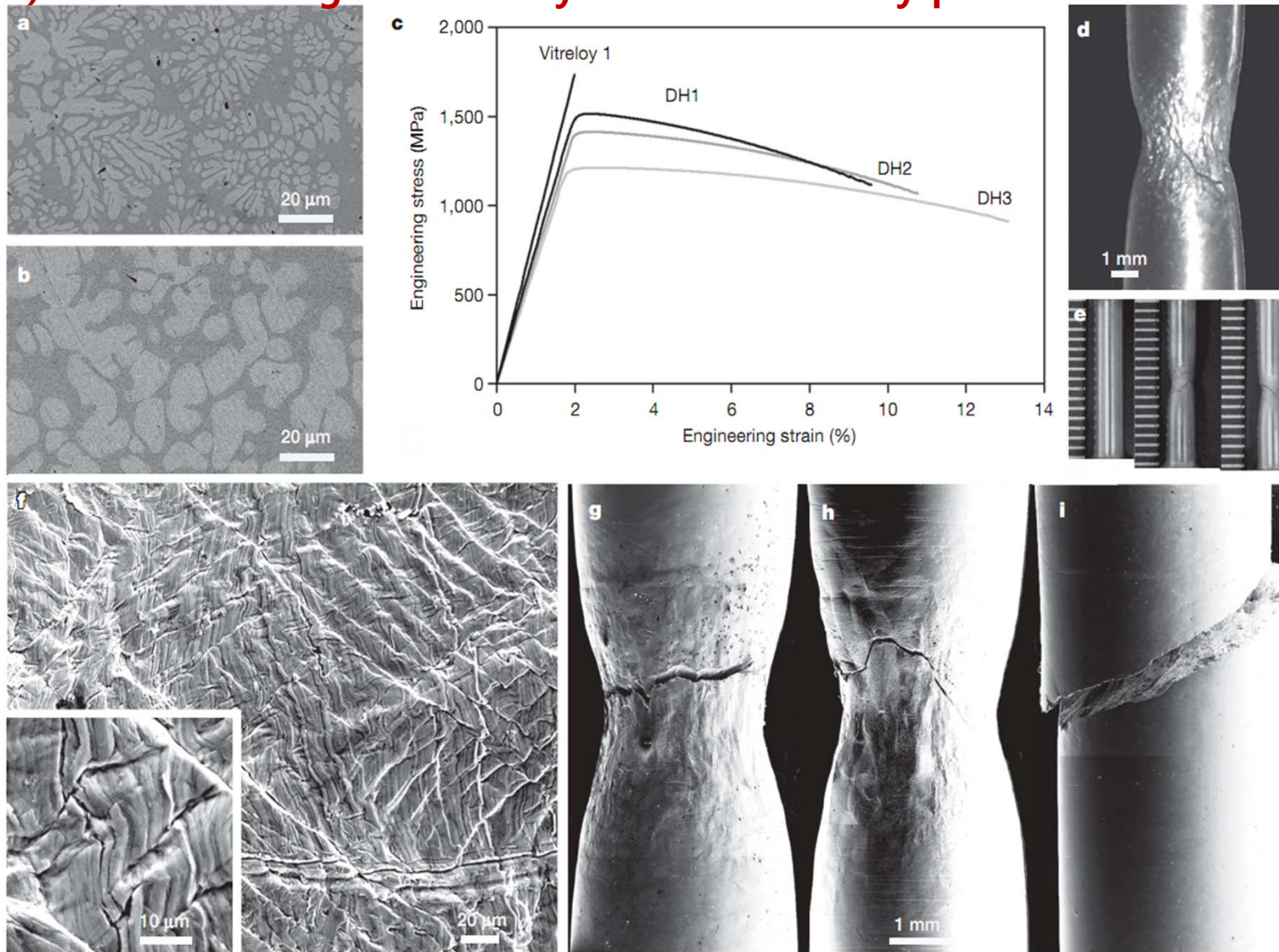
Shape Memory Bulk Metallic Glass Composites

Douglas C. Hofmann

Glass-forming and shape memory metals may provide a route to fabricating materials with enhanced mechanical properties.



1) Work softening behavior by ductile secondary phase



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

Transformation-mediated ductility in CuZr-based bulk metallic glasses

S. Pauly, S. Gorantla, G. Wang, U. Kühn & J. Eckert

[Affiliations](#) | [Contributions](#) | [Corresponding author](#)

Nature Materials 9, 473–477 (2010) | doi:10.1038/nmat2767

Received 17 November 2009 | Accepted 09 April 2010 | Published online 16 May 2010

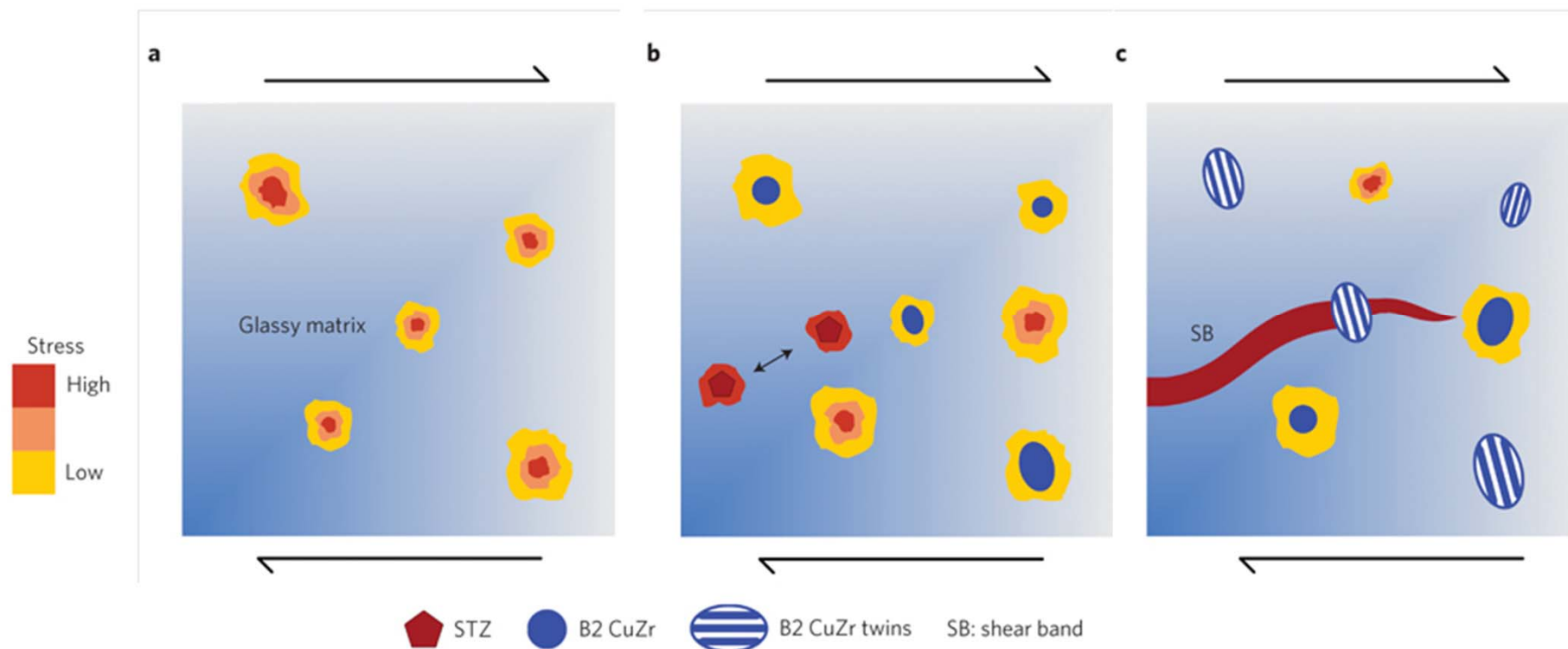
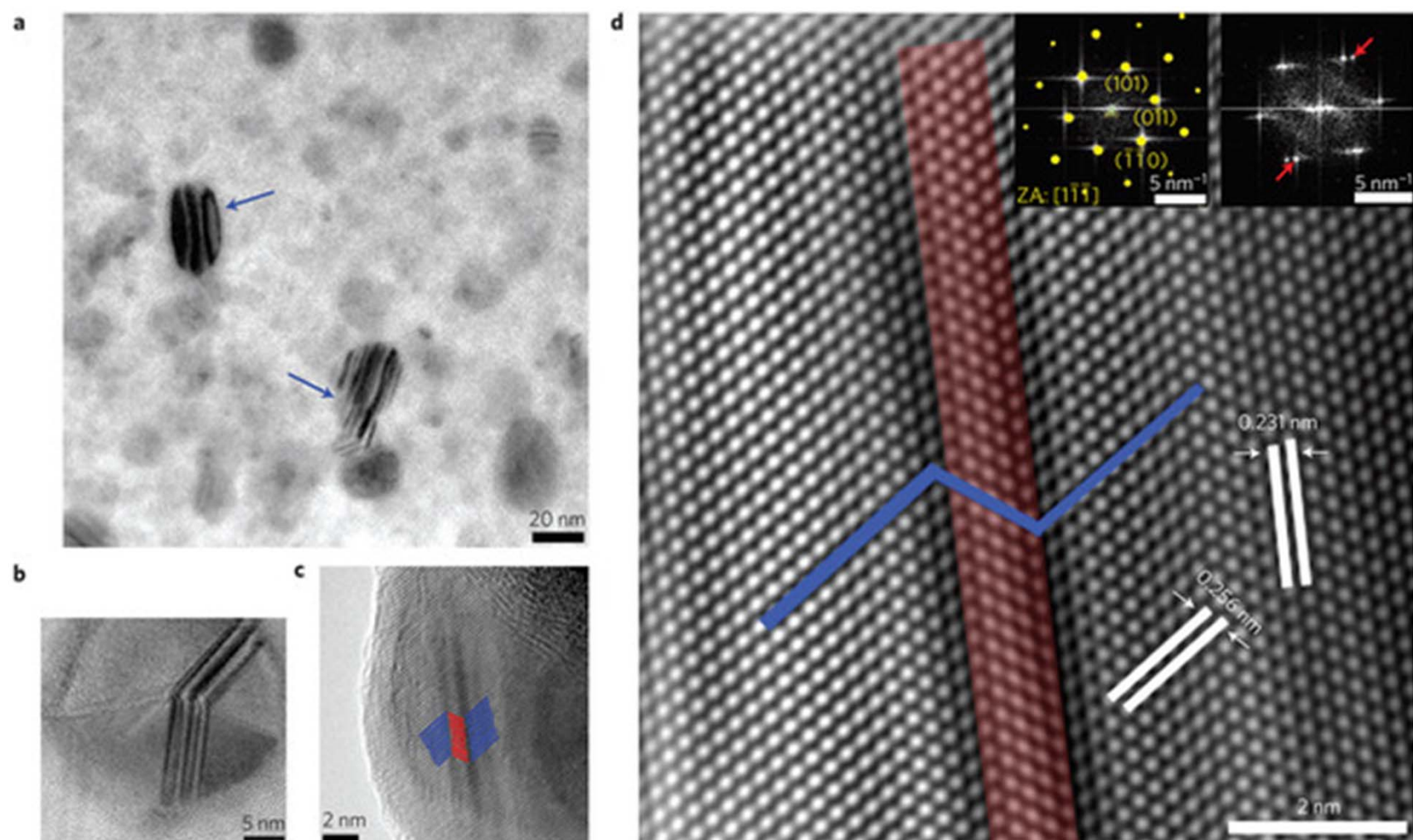


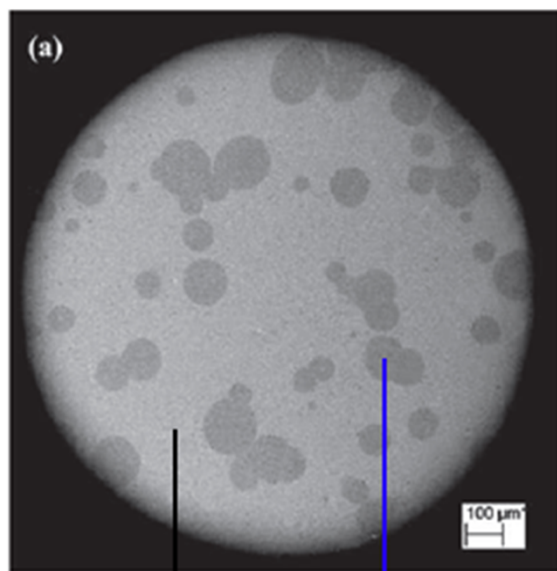
Figure 3: Microstructure of a $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ specimen deformed to fracture.



Work-hardening behavior of BMGCs in tension

Materials Views

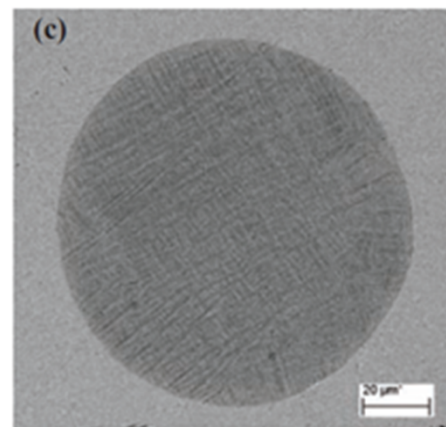
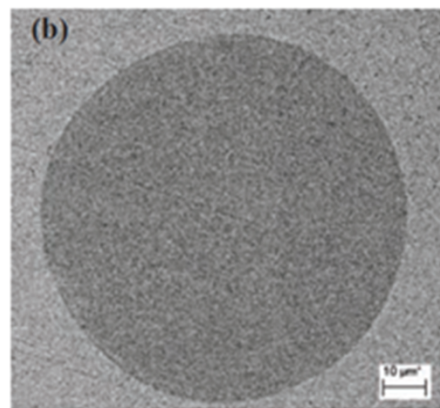
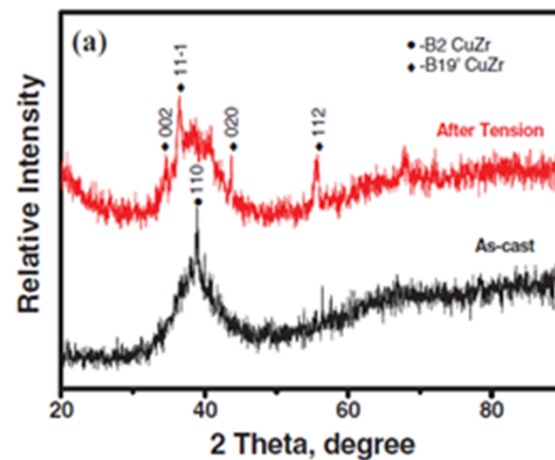
www.MaterialsViews.com



BMG matrix CuZr B2
Transformation media
metastable phase at RT

Yuan Wu, et al. Adv. Mater. 2010, 22, 2770–2773

B2 $\xleftrightarrow[\text{stress}]{\text{temperature}}$ B19'



[XRD pattern & Morphology of secondary phase before / after tensile test]

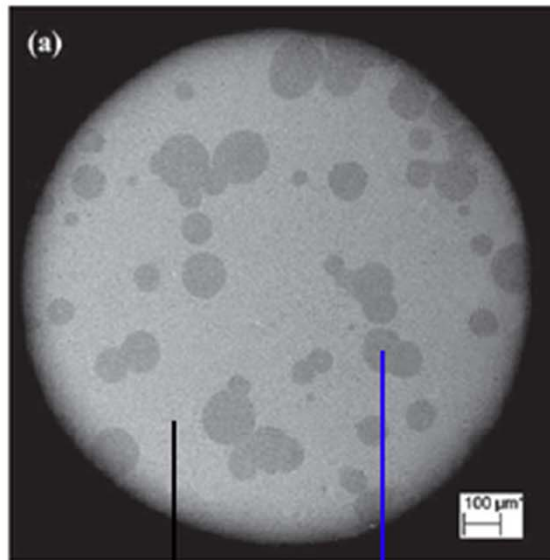
Work-hardening behavior of BMGCs in tension

Materials Views

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ADVANCED MATERIALS

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BMG matrix

CuZr B2
Transformation media
metastable phase at RT

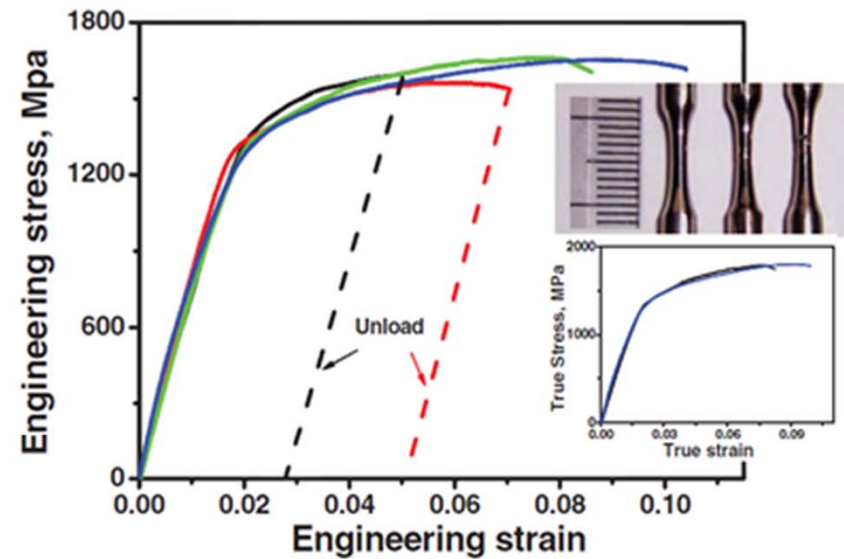


Figure 2. Engineering tensile stress–strain curves of the BMG composites. Dashed lines indicate the unloading process. Top inset shows the outer appearance of the tensile samples pre-strained at the different stages and the lower inset shows the true tensile stress–strain curves, indicating a significant strain-hardening behavior.

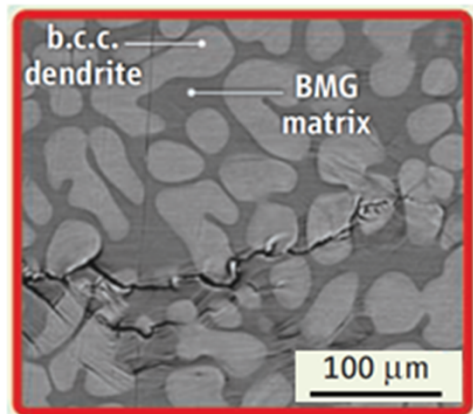
COMMUNICATION

Yuan Wu, et al. Adv. Mater. 2010, 22, 2770–2773

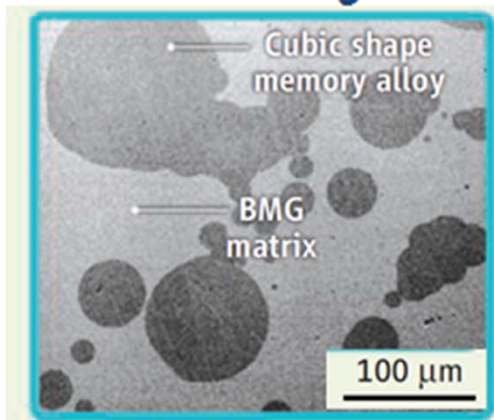
➔ Cu-Zr-Al system

Two different deformation behaviors of BMGC depending on 2nd phase

- 1) Ductile phase $Zr_{39.6}Ti_{33.9}Nb_{7.6}Cu_{0.5}Be_{12.5}$
 → **Work softening**

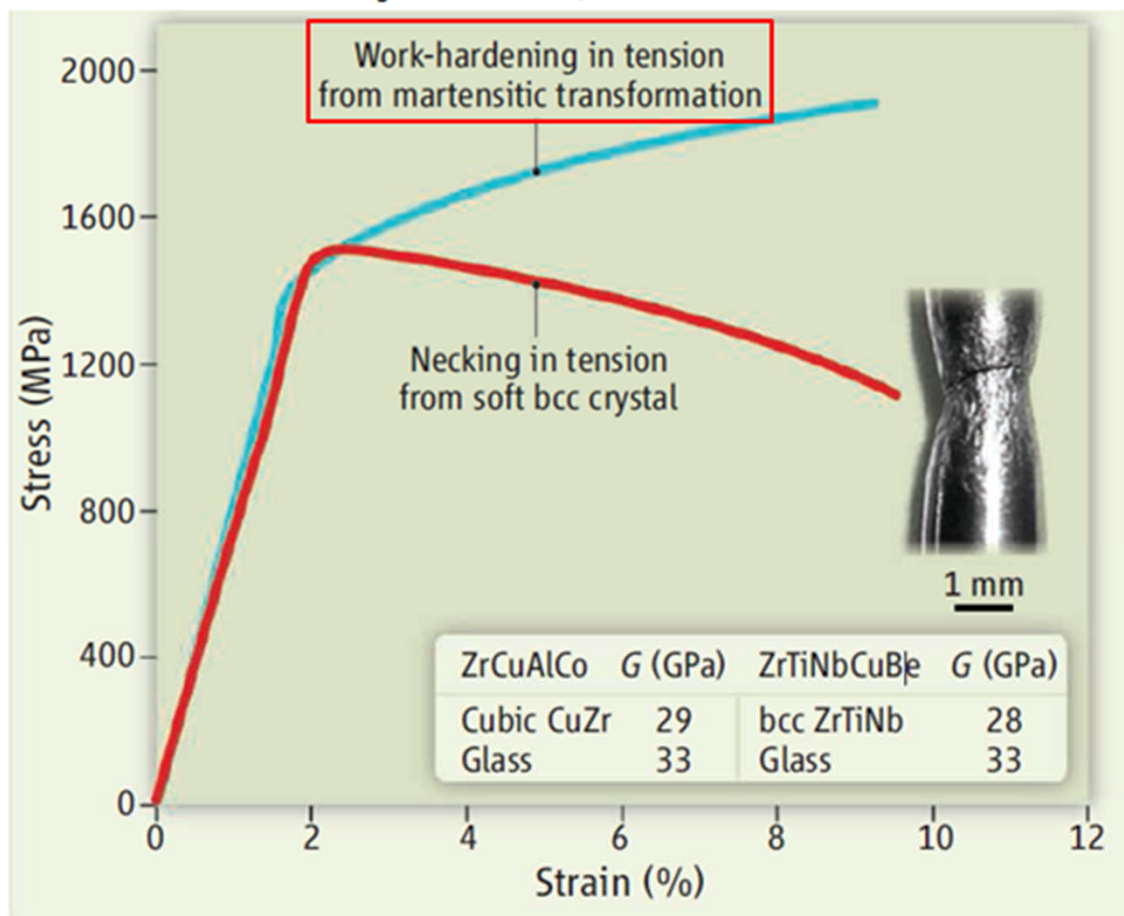


- 2) Transformation media $Zr_{48}Cu_{47.5}Al_4Co_{0.5}$
 → **Work hardening**



< Tension >

Douglas C. Hofmann, SCIENCE VOL 329 10 SEPTEMBER 2010



Development of a **New Ti-based BMGC** with High Work-hardenability

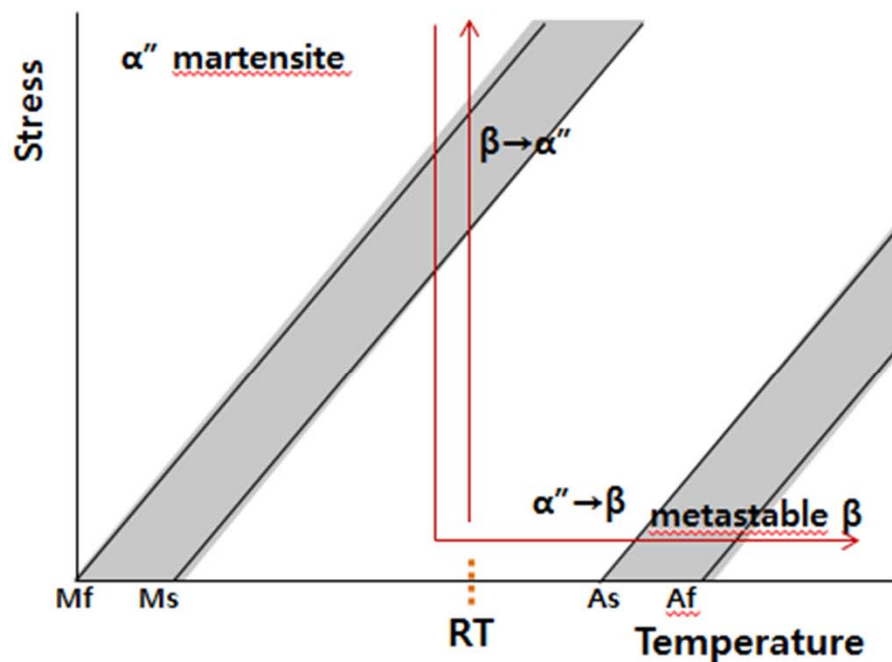
▶ Alloy system **Cu-Zr-Al system**
Secondary phase **CuZr**
Metastable B2 phase at RT
"Shape Memory Behavior"



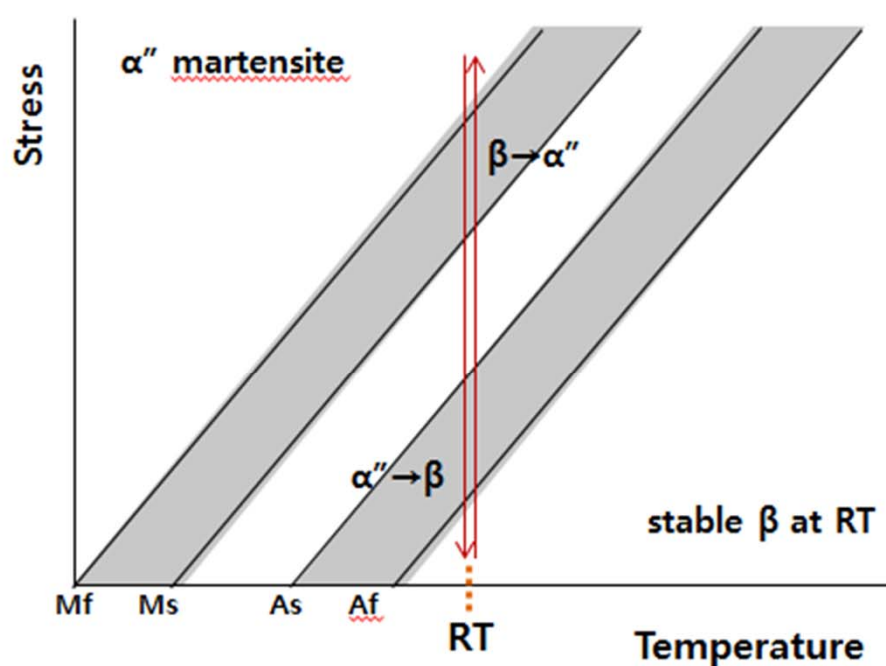
Ti-Cu-Ni system

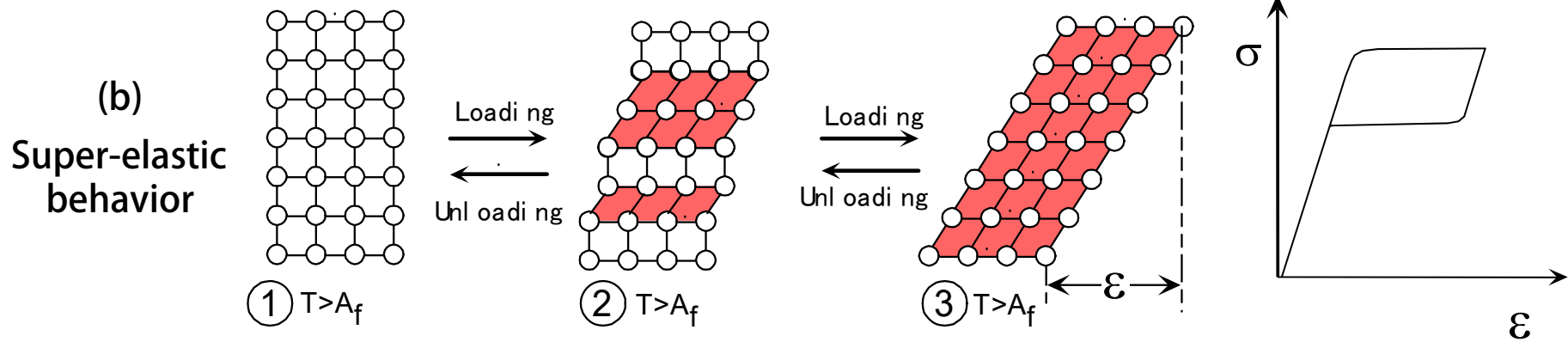
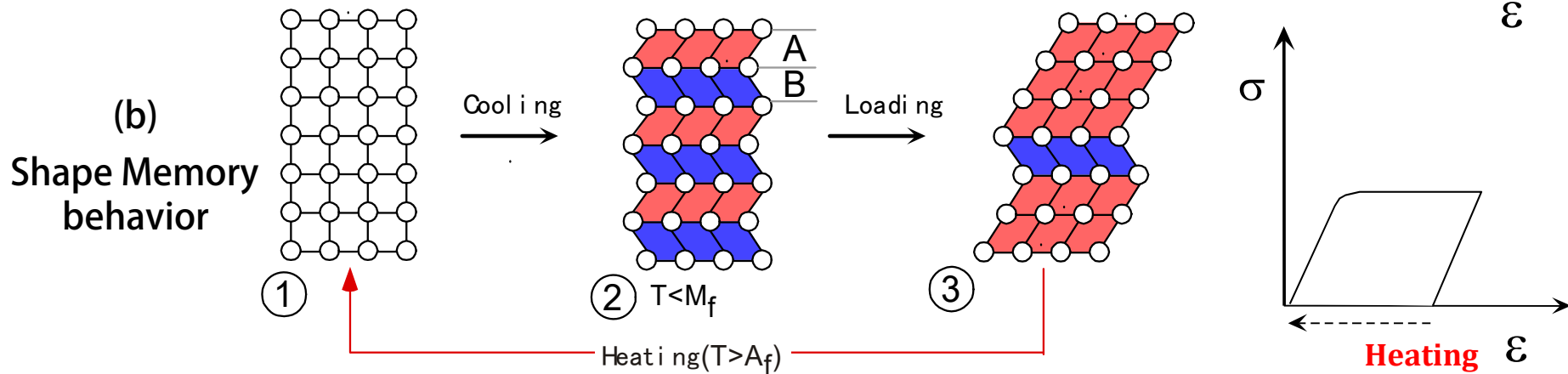
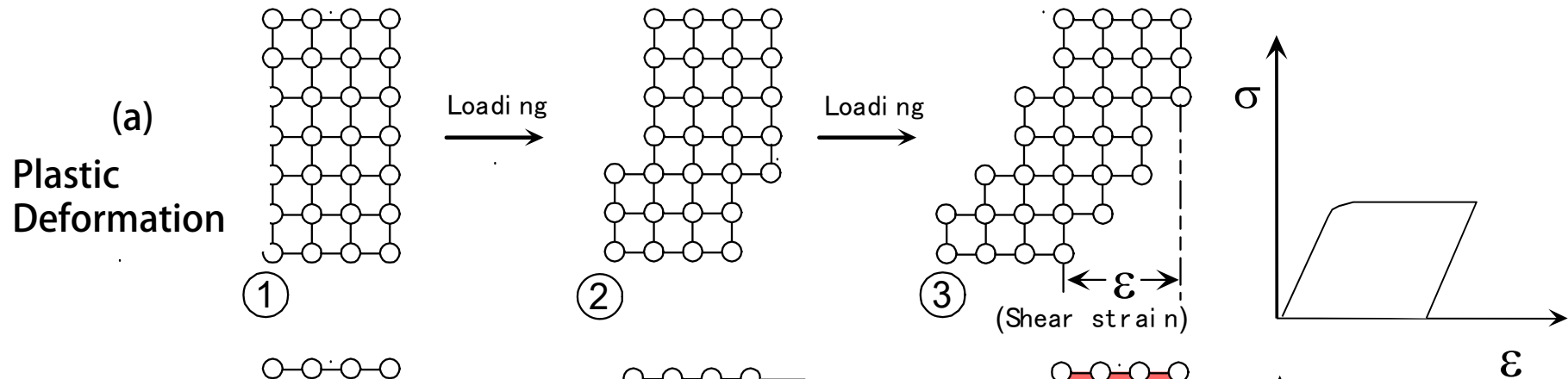
Ti-X
Stable B2 phase at RT
"Super-elastic Behavior"

Shape Memory Alloy (SMA)



Super-Elastic Alloy (SE alloy)





Development of a **New Ti-based BMGC** with High Work-hardenability

▶ Alloy system **Cu-Zr-Al system**

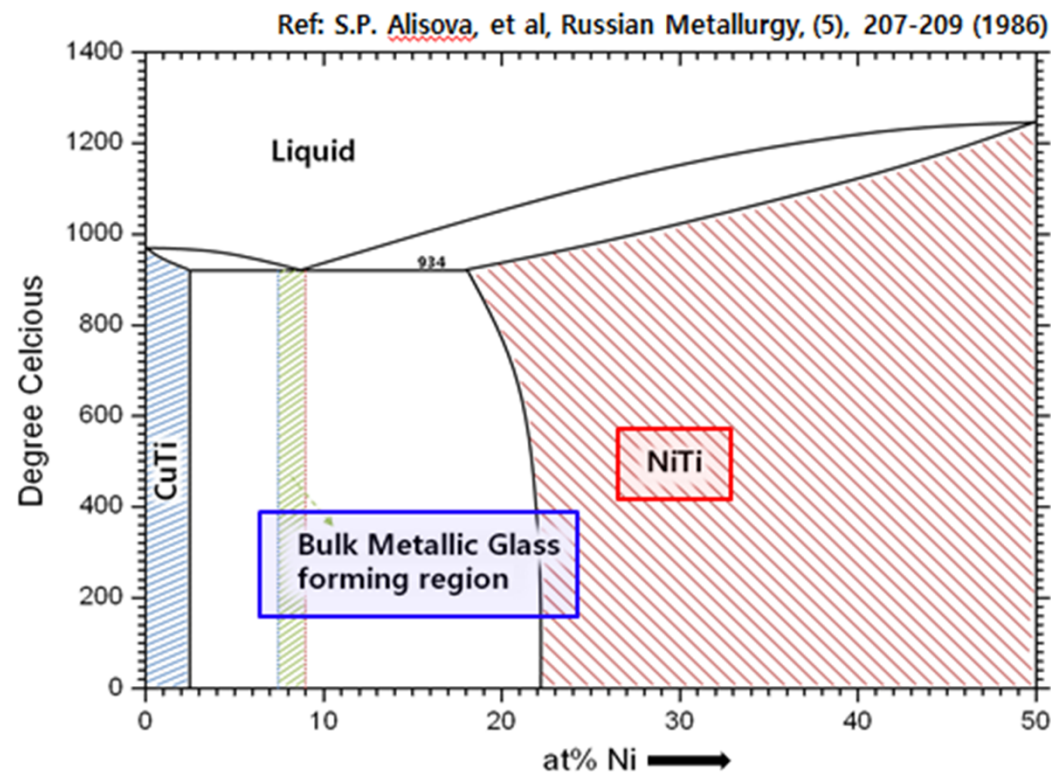
Secondary phase

CuZr
Metastable B2 phase at RT
"Shape Memory Behavior"



Ti-Cu-Ni system

Ti-X
Stable B2 phase at RT
"Super-elastic Behavior"



▶ **TiCu-NiTi pseudo-binary eutectic**

High glass forming ability $\sim 1.5\phi$

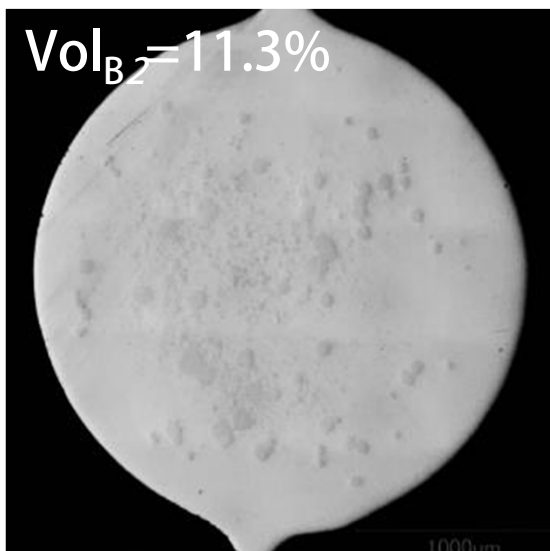
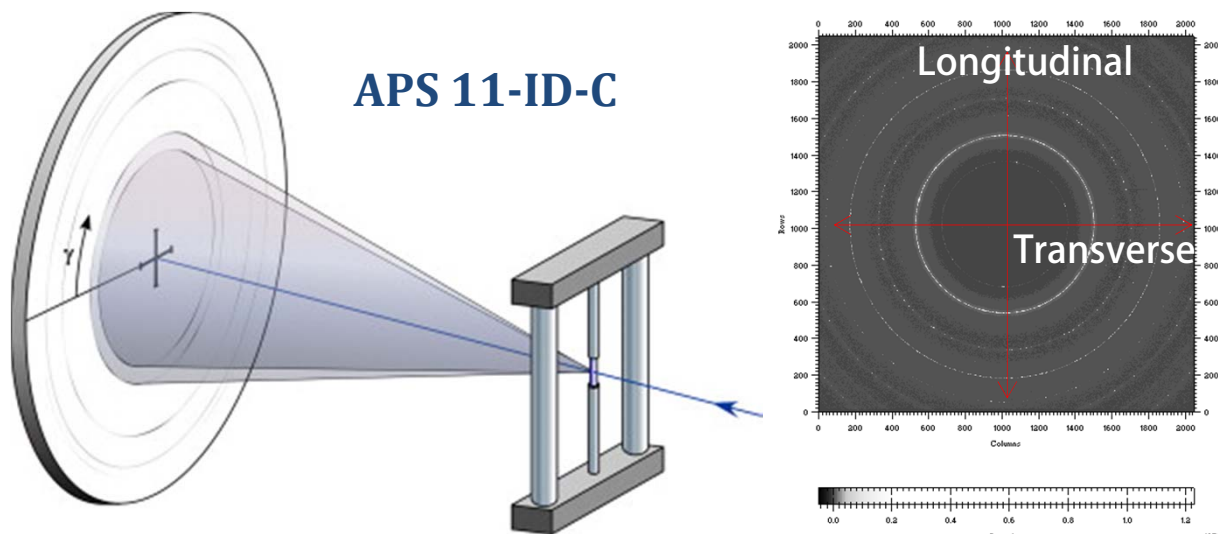


NiTi \sim representative SMA

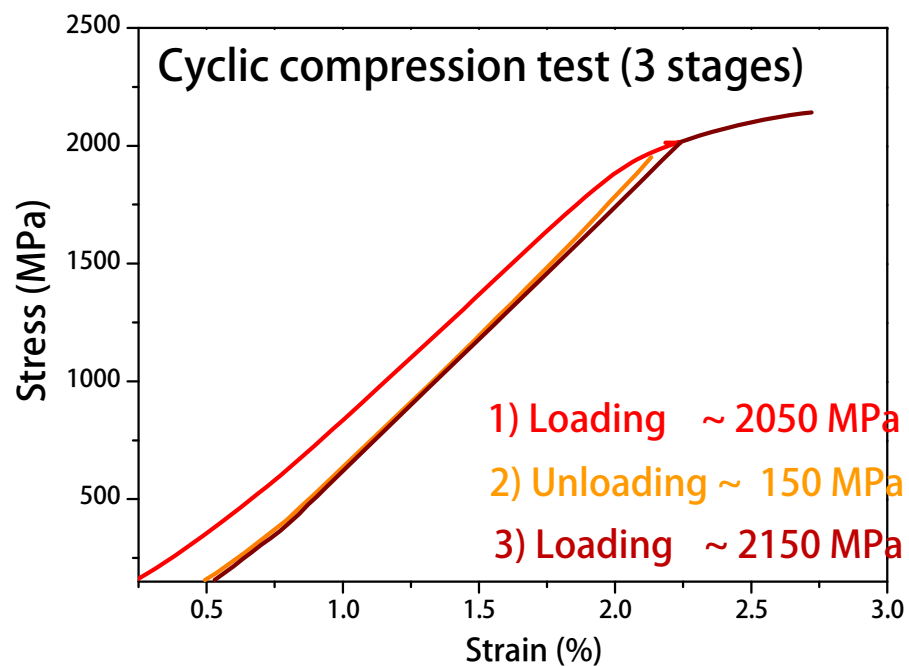
or

Ti-X \sim Superelastic alloy by phase transformable B2 phase

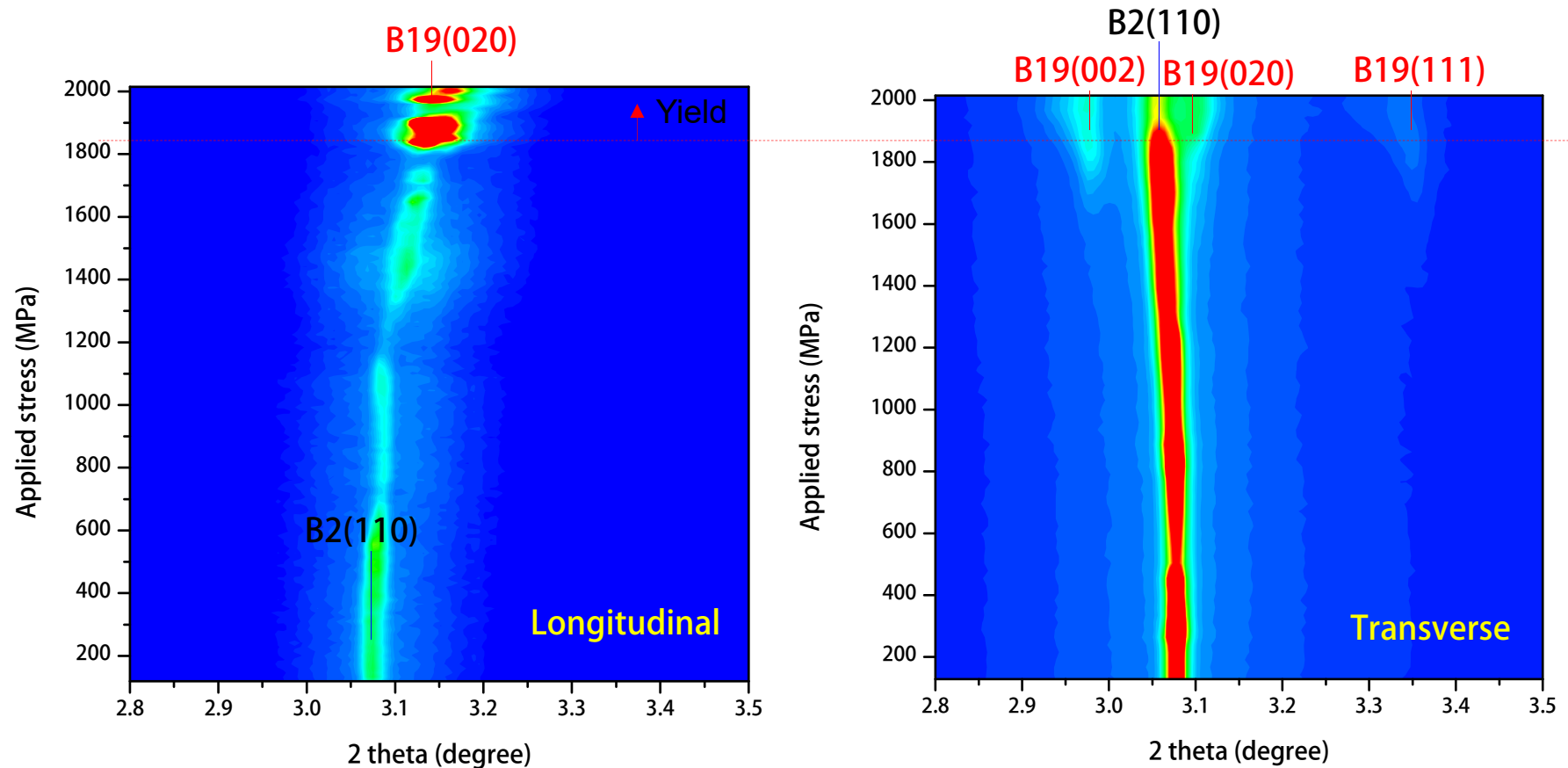
In-situ high energy X-ray diffraction under compression (APS 11-ID-C)



PT stress of 2nd phase ~ 850 MPa

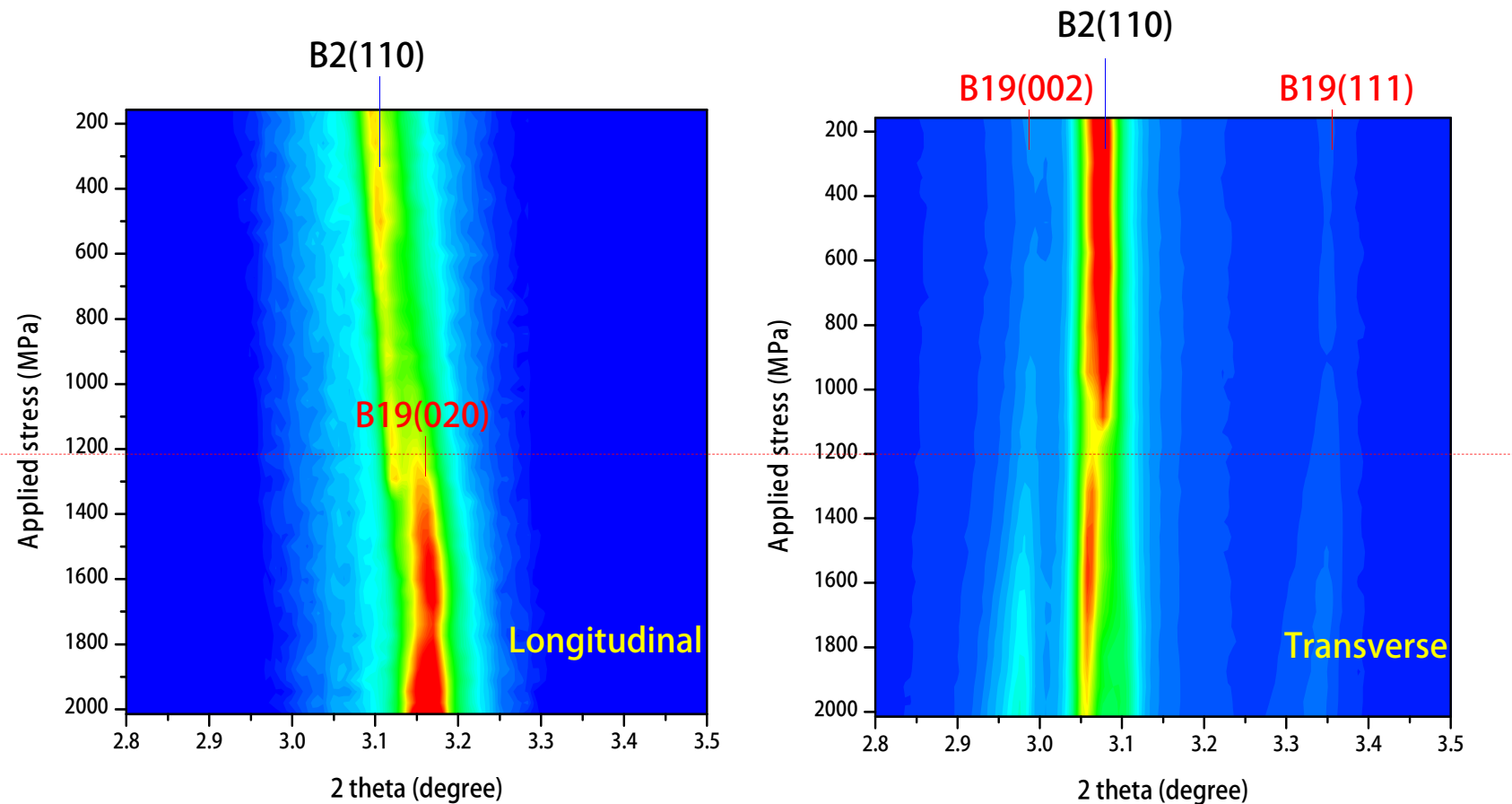


In-situ diffraction under compression: 1st loading ~ 2050 MPa



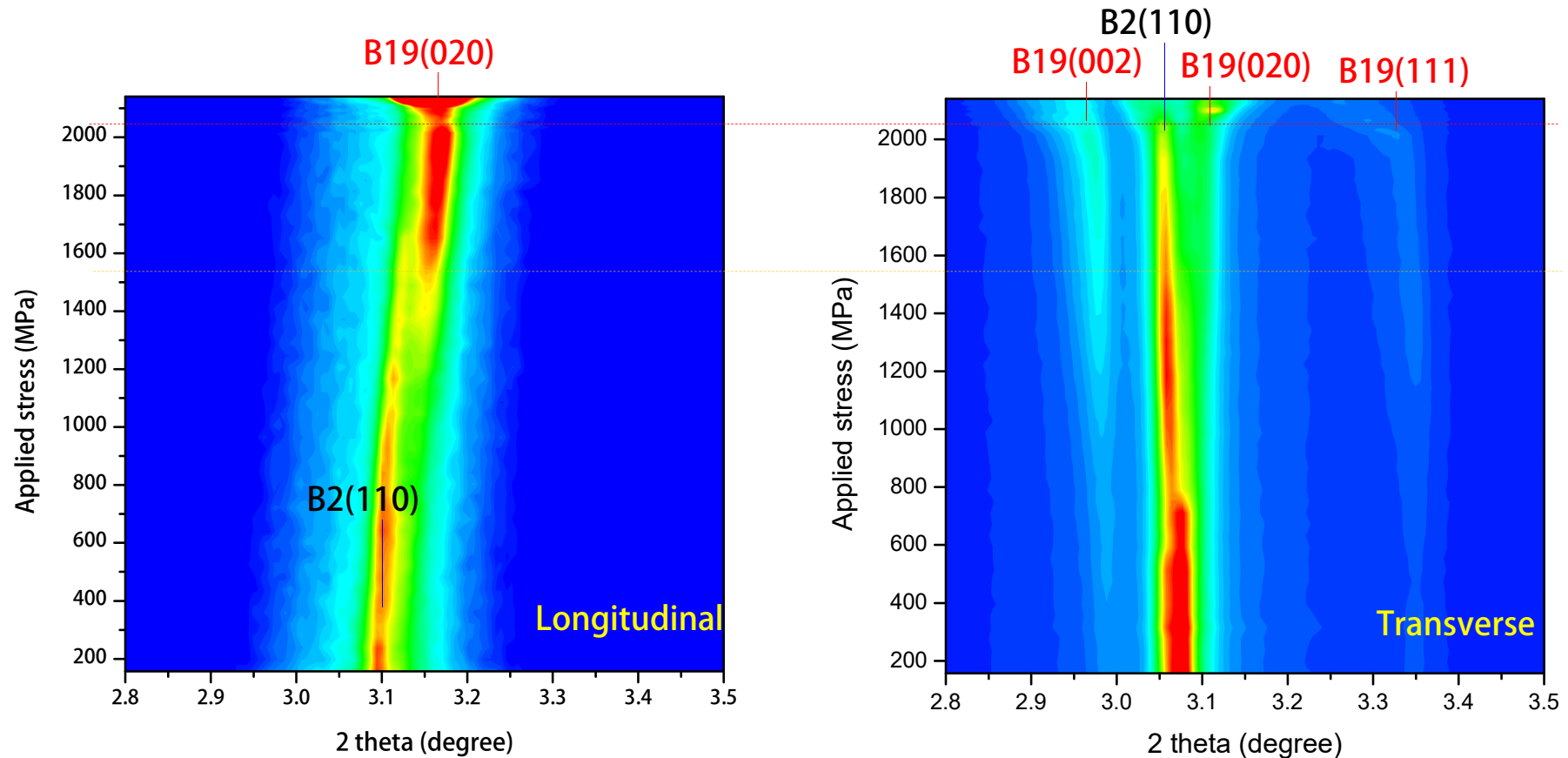
- M.T. is constrained by horizontal frame of MG matrix because of the imbalance of Poisson's ratio during M.T. (~0.5) with elastic loading of MG matrix (~0.33).
- Preferred orientation before deformation = B2 (110), Preferred orientation after deformation for Longitudinal direction = B19 (020) and for Transverse direction = B19(002), B19(020), B19 (111)

In-situ diffraction under compression: Unloading ~ 150 MPa



- After unloading down to ~150MPa, most of B19 reverse transformed to B2, but small fraction of B19(002) & (111) remained.
- Preferred orientation before deformation = B19 (020) / after deformation = B2(110)

In-situ diffraction under compression: 2nd loading ~ 2150 MPa



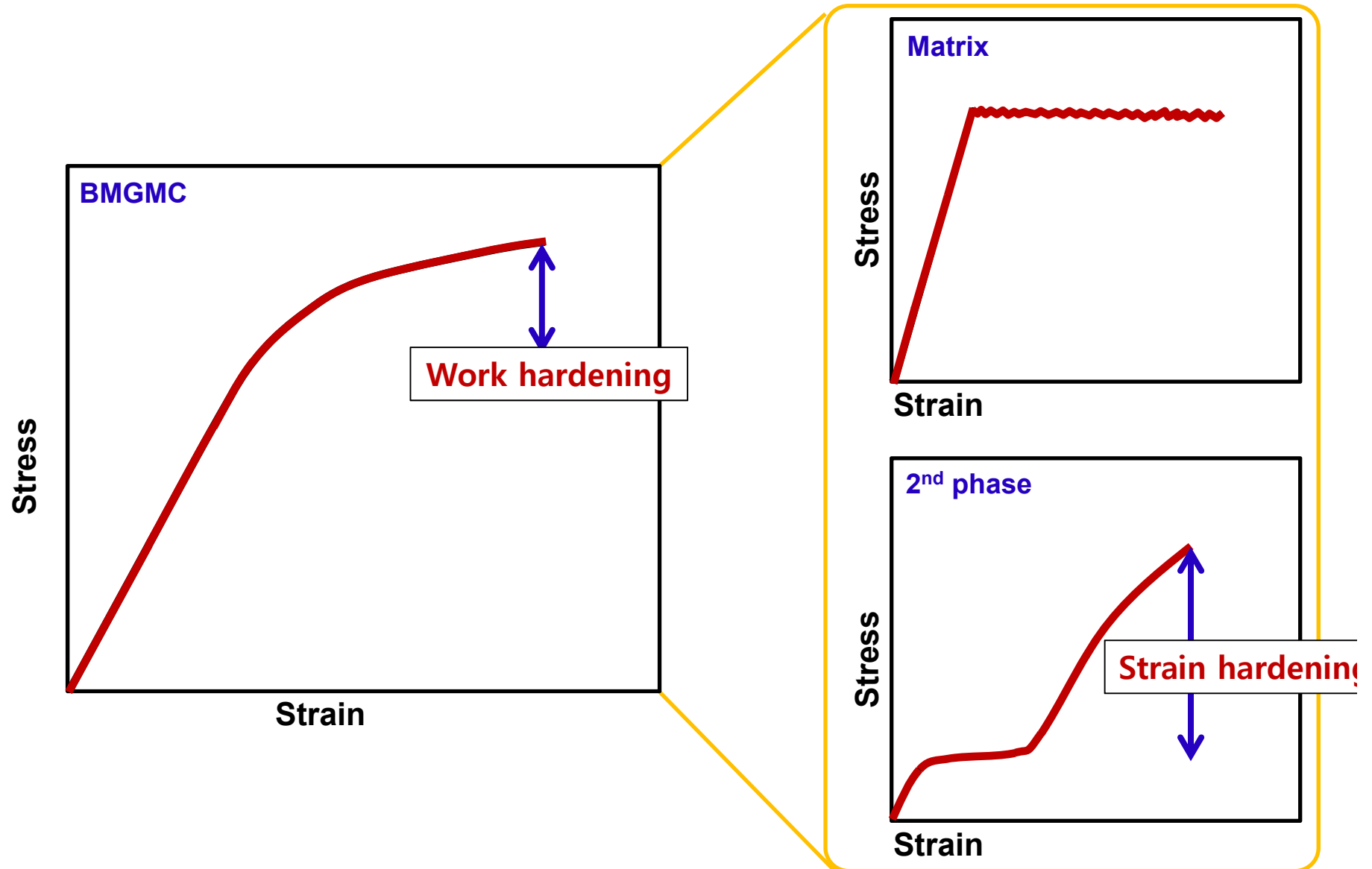
- M.T. is constrained by horizontal frame of MG matrix because of the imbalance of Poisson's ratio during M.T. (~0.5) with elastic loading of MG matrix (~0.33).
- Preferred orientation before deformation = B2 (110), Preferred orientation after deformation for Longitudinal direction = B19 (020) and for Transverse direction = B19(002), B19(020), B19 (111)



The observed work hardening in the CuZr based BMG composites cannot be solely attributed to the **1) intrinsic strain hardening of the B2 phases**, but also arises from **2) a constraining effect of the glassy matrix on the martensitic transformation and the subsequent deformation of the transformed phases.** In theory, this constraint effect, also called *Eshelby back stress effect*, increases the elastic energy stored in the whole composite system, which leads to an increase in the applied stress and thus manifests as strain hardening in the BMG composite

Origin for Improved work-hardenability in TRIP BMGC by SE 2nd phase

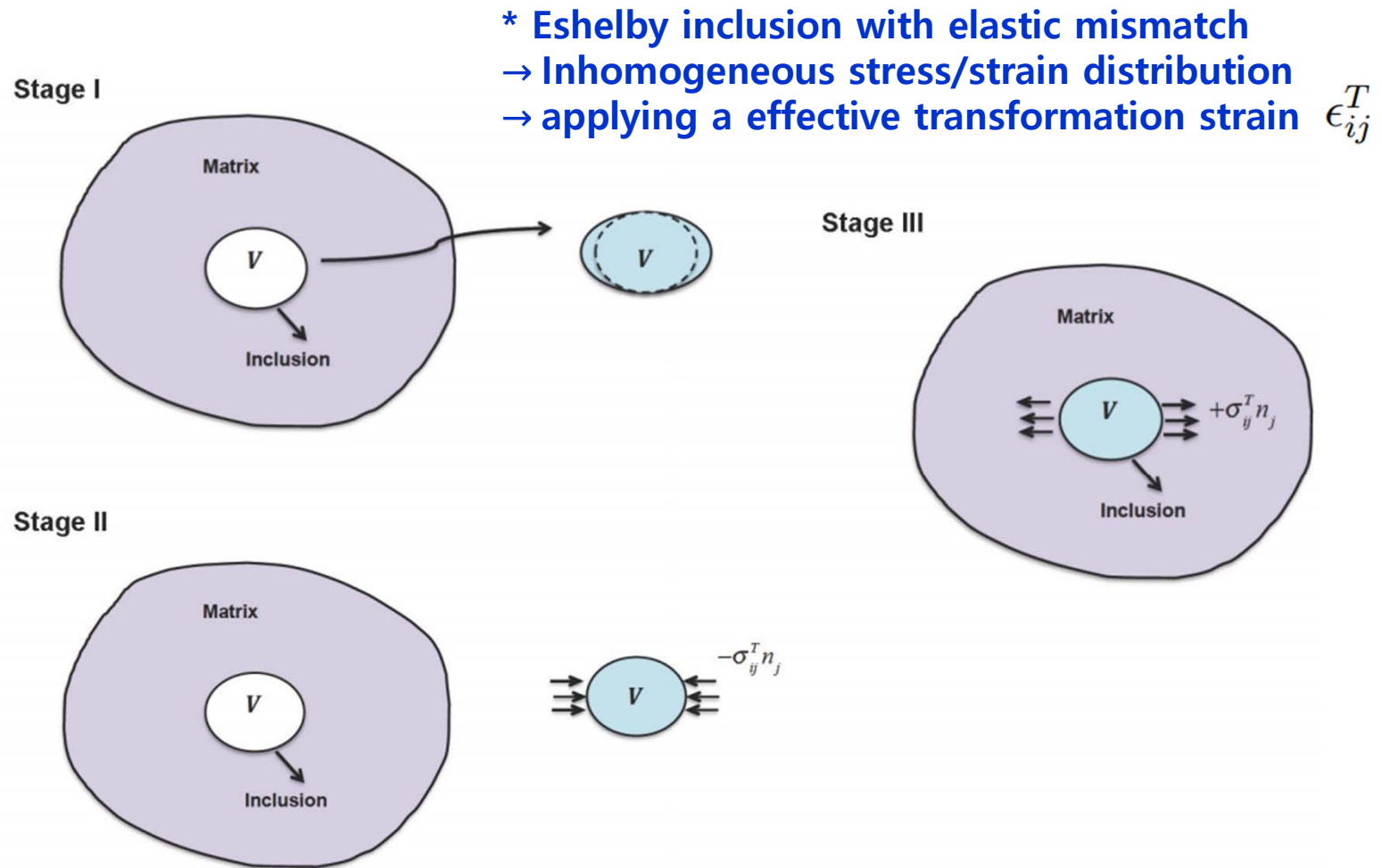
1) "Strain hardening of transformable 2nd phase"



The observed work hardening in the CuZr based BMG composites cannot be solely attributed to the **1) intrinsic strain hardening of the B2 phases**, but also arises from **2) a constraining effect of the glassy matrix on the martensitic transformation and the subsequent deformation of the transformed phases**. In theory, this constraint effect, also called *Eshelby back stress effect*, increases the elastic energy stored in the whole composite system, which leads to an increase in the applied stress and thus manifests as strain hardening in the BMG composite

Origin for Improved work-hardenability in TRIP BMGC by SE 2nd phase

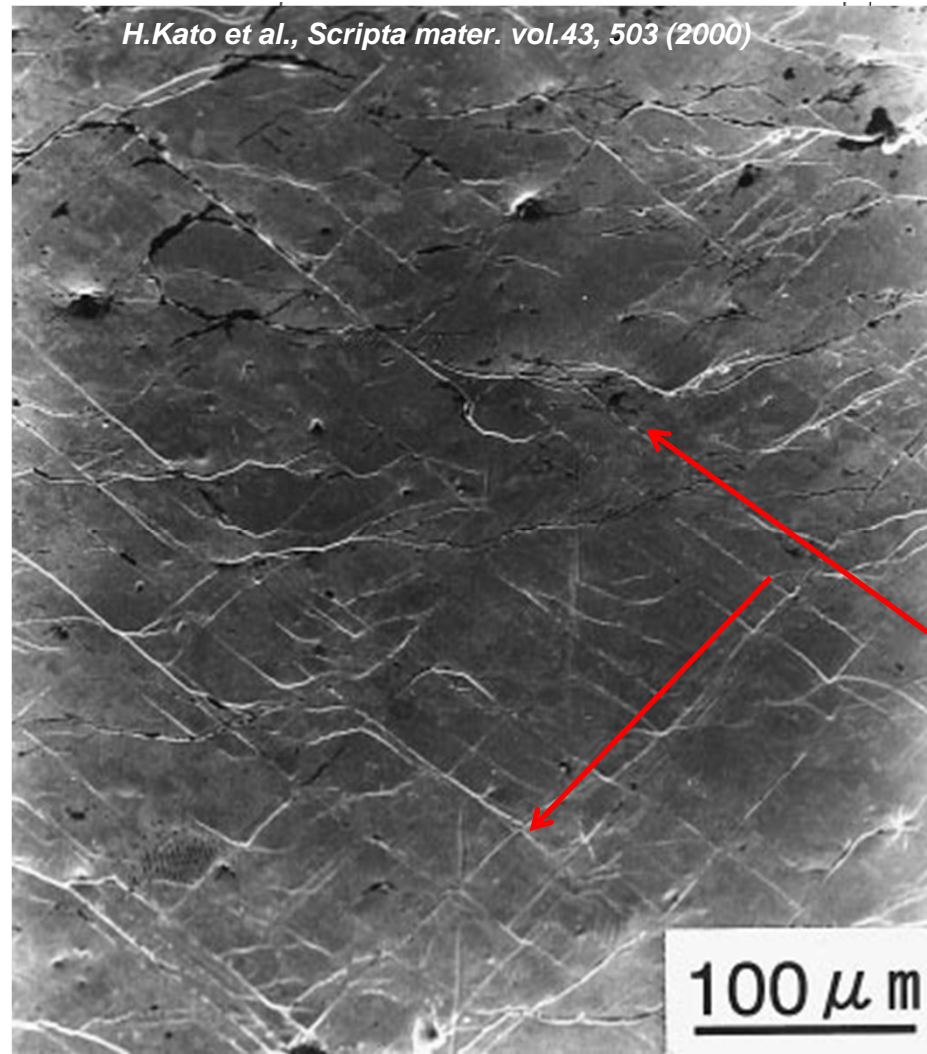
2) “Strong Eshelby back stress effect of transformable 2nd phase”



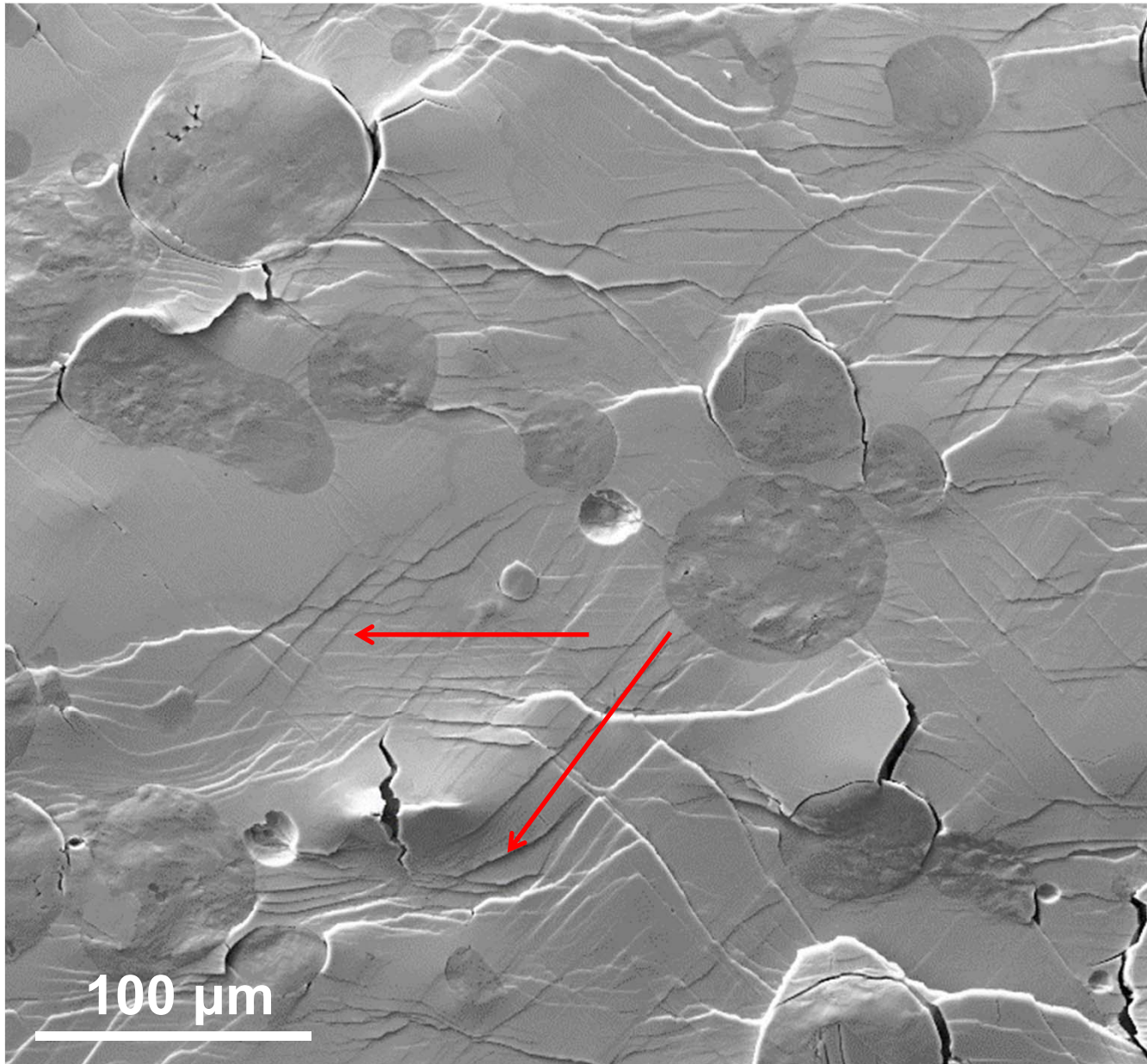
The schematic illustration of the three stages of Eshelby approach for solving the stress and strain fields due to the deformation of an inclusion in the matrix.

Origin for Improved work-hardenability in TRIP BMGC by SE 2nd phase

BMG composite with ceramic ZrC

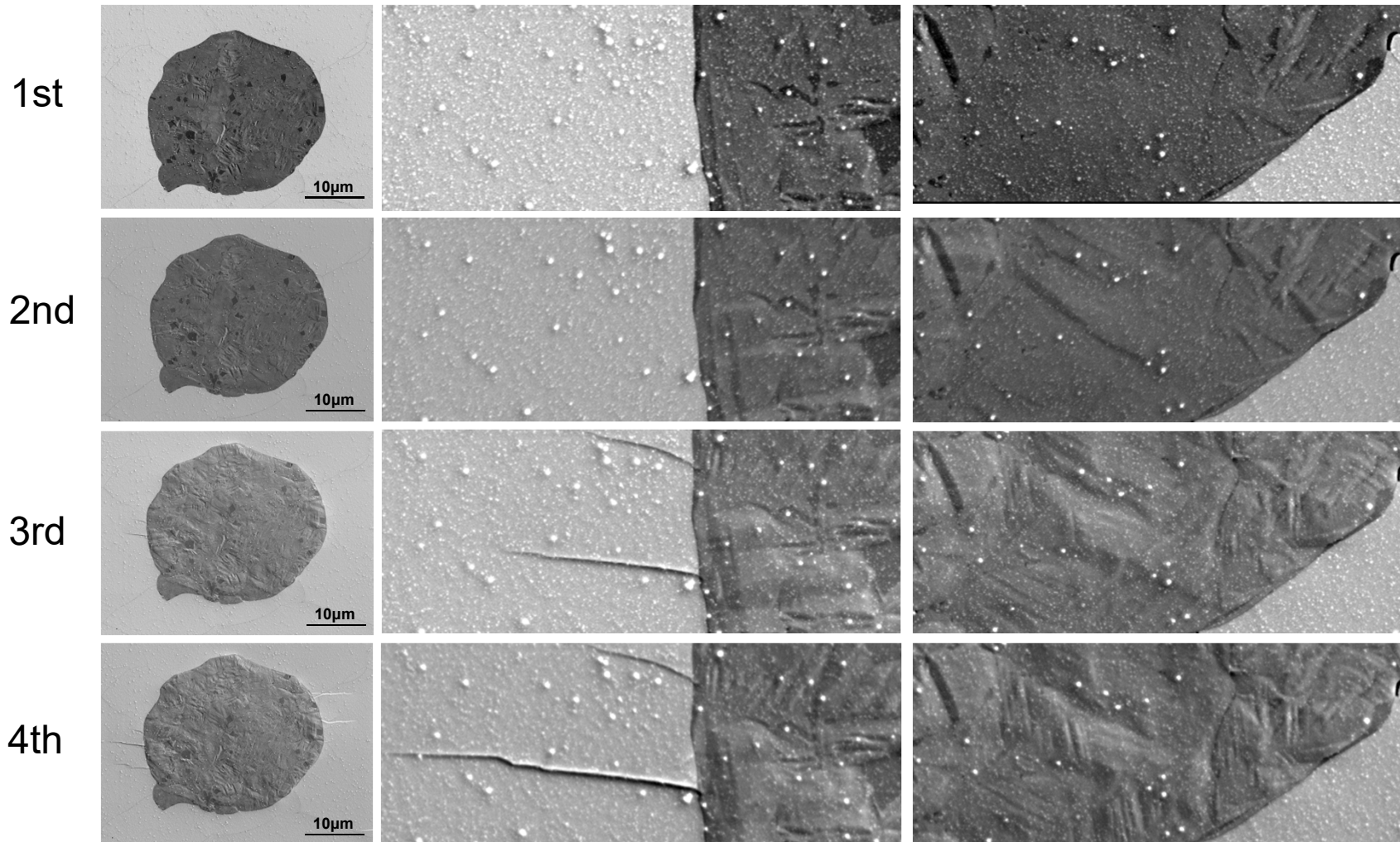


Origin for Improved work-hardenability in TRIP BMGC by SE 2nd phase



Origin for Improved work-hardenability in TRIP BMGC by SE 2nd phase

In-situ SEM test

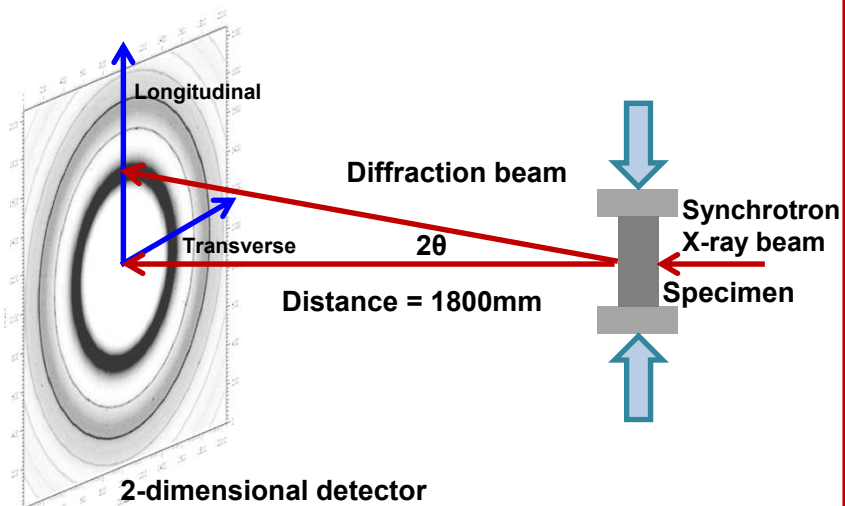


Martensitic transformation occurred during compressive deformation.

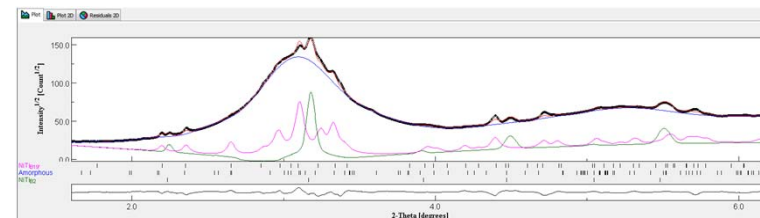
Direction of shear bands : perpendicular to the loading direction

In-situ synchrotron radiation _Advanced Photon Source (APS) 11-ID-C

In-situ compression

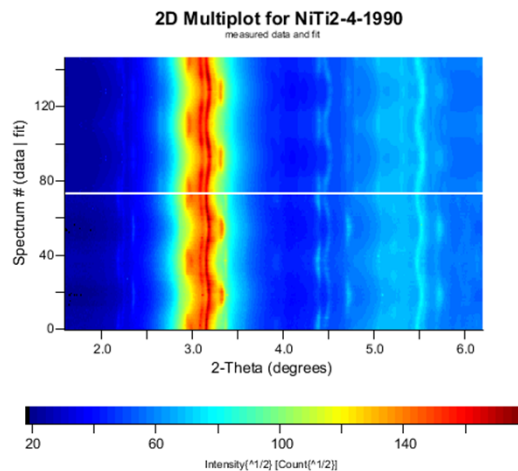


Rietveld refinement



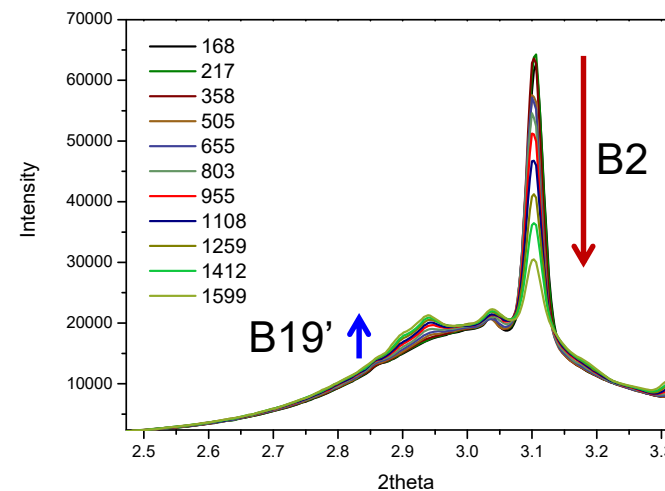
- Fitting at single azimuth angle
Rwp : 5.81% (<10% is good fitting)
- Amorphous : Cu₃Zr, orthorhombic, Pnma – Paracrystalline
(small crystallite, large residual stress,
Ref. M.Baricco, et al., J.Allo.Comp. 495, 377 (2010))
- NiTi_B2, NiTi_B19'

Fitting through whole azimuth angle

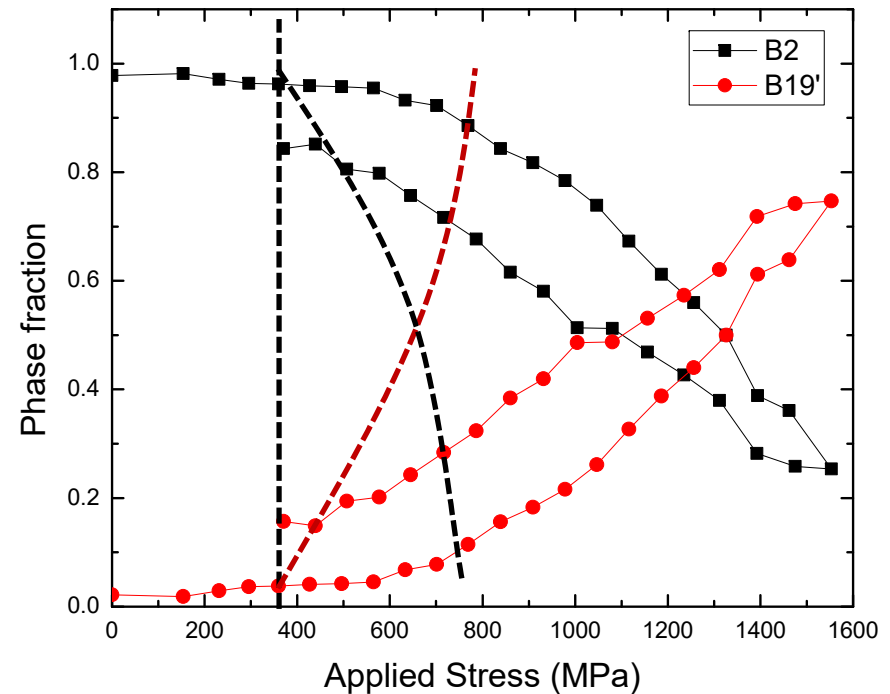
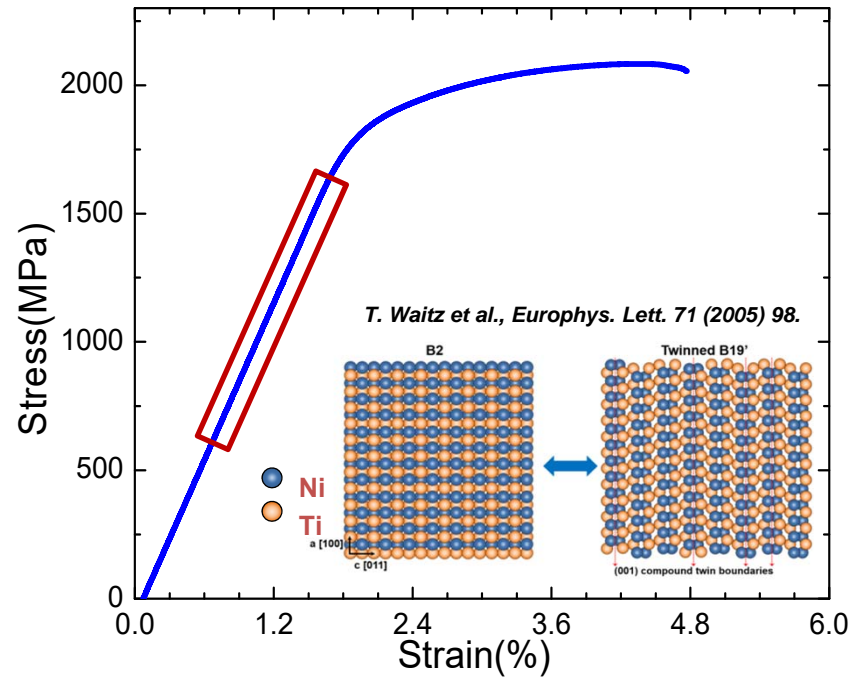


Lattice information, Phase fraction, Texture

Fitting through whole stress level

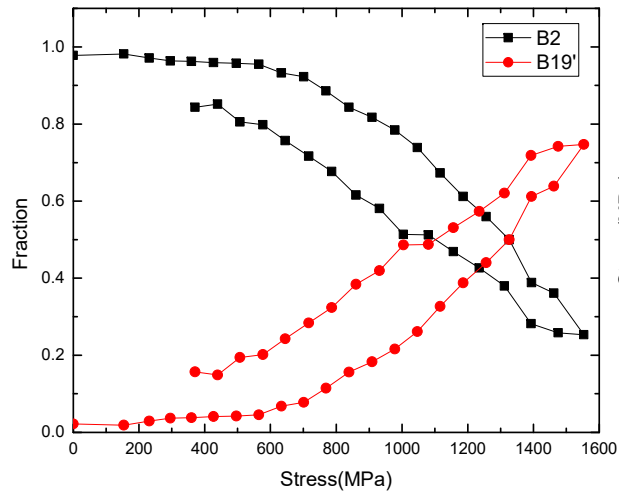


The fraction of martensitic transformation in elastic region

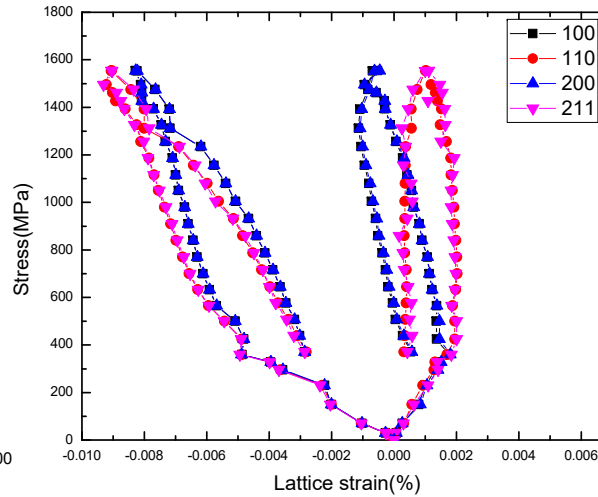


- Martensitic transformation occurred gradually.
- Martensitic transformation is delayed by the interaction between 2nd phase and metallic glass matrix. ($\Delta\text{modulus}$ btw matrix & 2nd phase > 30GPa)

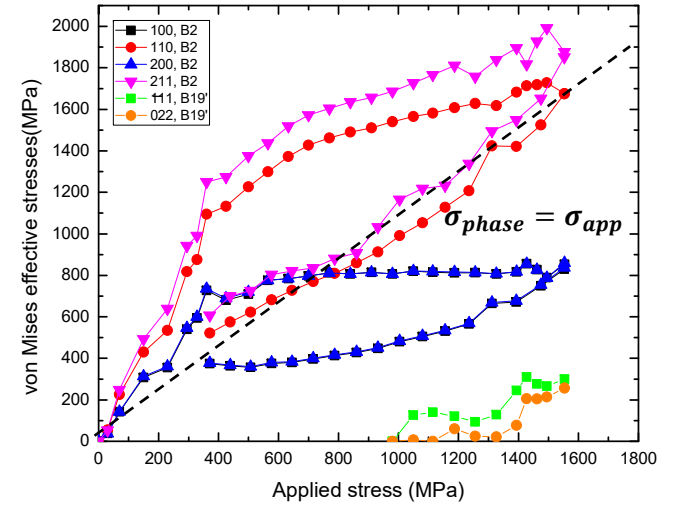
Phase fraction



Lattice strain

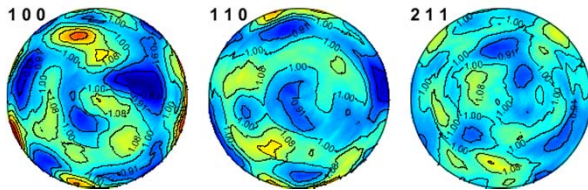


Effective stress

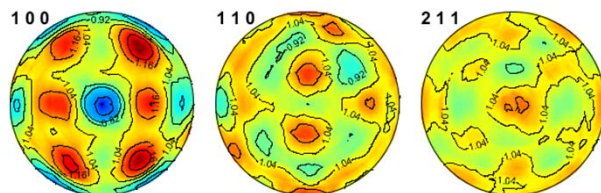


Texture of B2

Before load



Maximum load



E100 = 143GPa
E110 = 216GPa
E211 = 240GPa

$$\sigma_1 = \sigma_3 = \frac{E}{1+\nu} \varepsilon_1 + \frac{\nu E}{(1+\nu)(1-2\nu)} (\varepsilon_1 + \varepsilon_2 + \varepsilon_3),$$

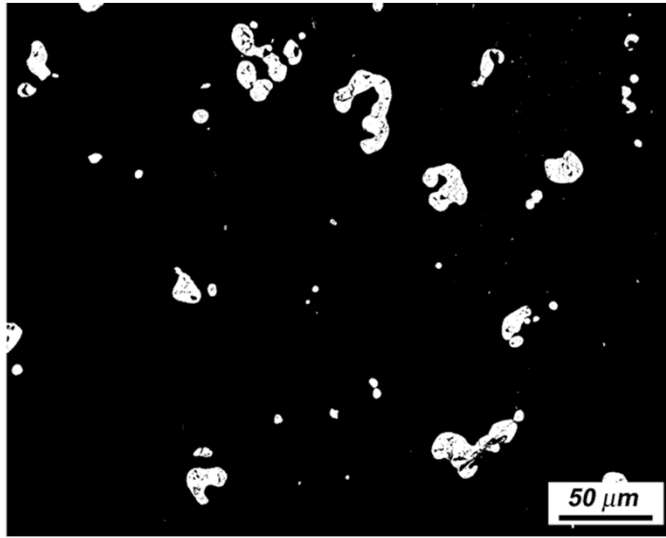
$$\sigma_2 = \frac{E}{1+\nu} \varepsilon_2 + \frac{\nu E}{(1+\nu)(1-2\nu)} (\varepsilon_1 + \varepsilon_2 + \varepsilon_3),$$

$$\sigma_{\text{eff}} = \frac{1}{\sqrt{2}} \left[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 \right]^{1/2}$$

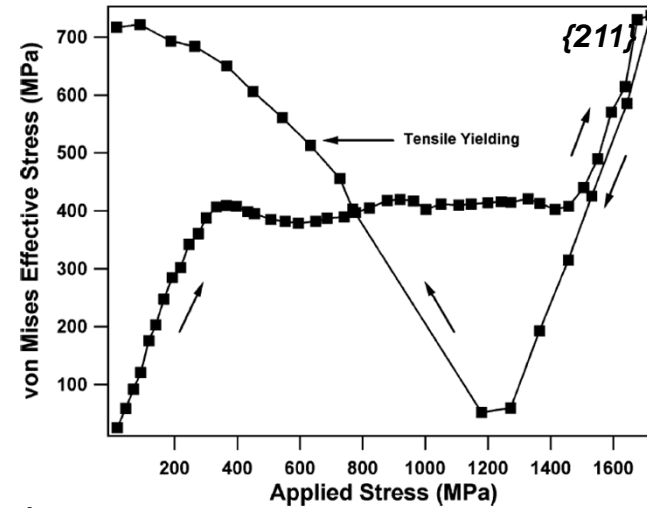
1. Martensitic transformation occurred at $\langle 100 \rangle$ B2 crystallites.

Compare with soft crystalline 2nd phase

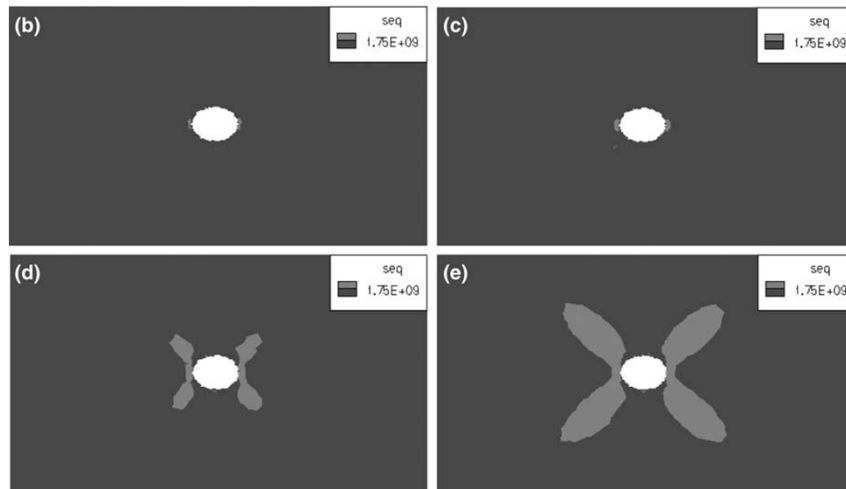
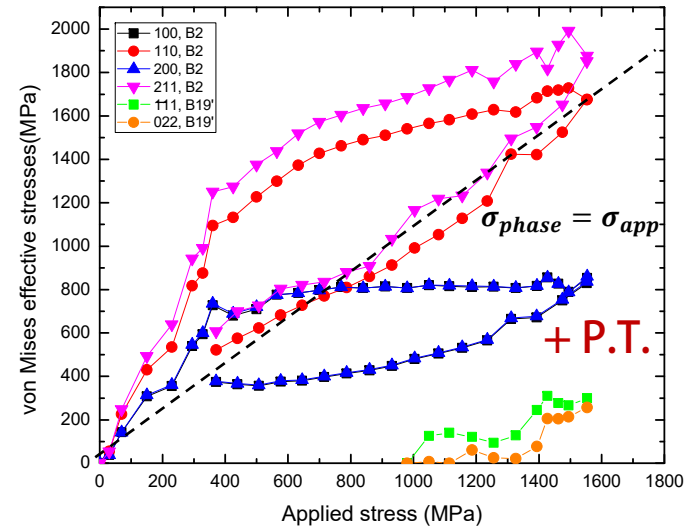
BMG composite with 10% Ta



R.T. Ott et al., Acta Mater. vol. 53, 1883 (2005)



Shape memory

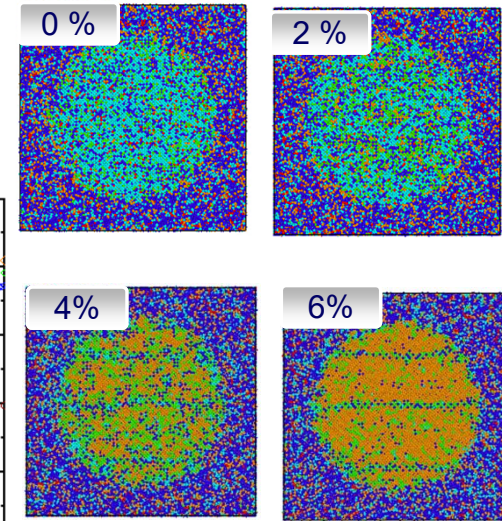
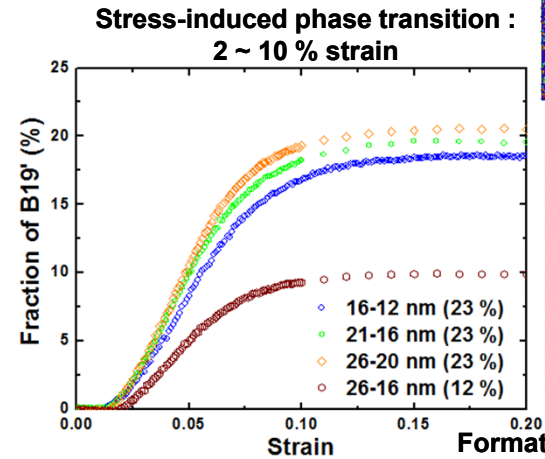
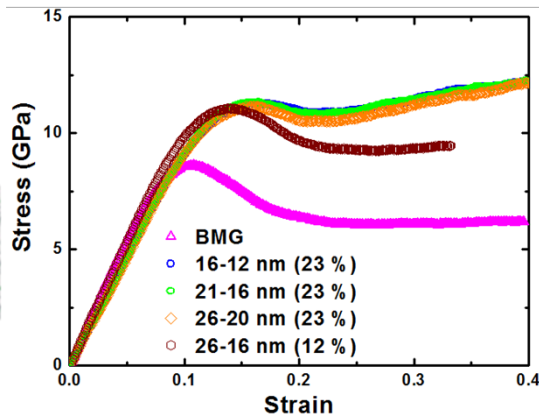
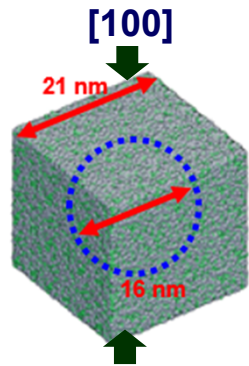


2. Misfit stress between matrix and 2nd phase become less pronounced by martensitic transformation of 2nd phase.

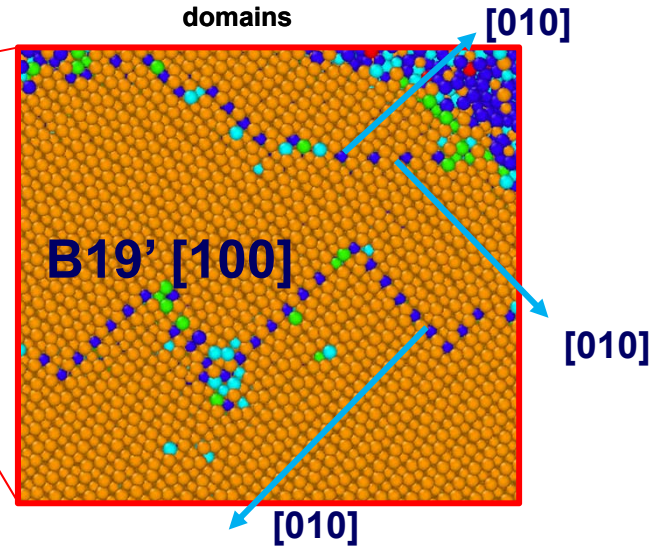
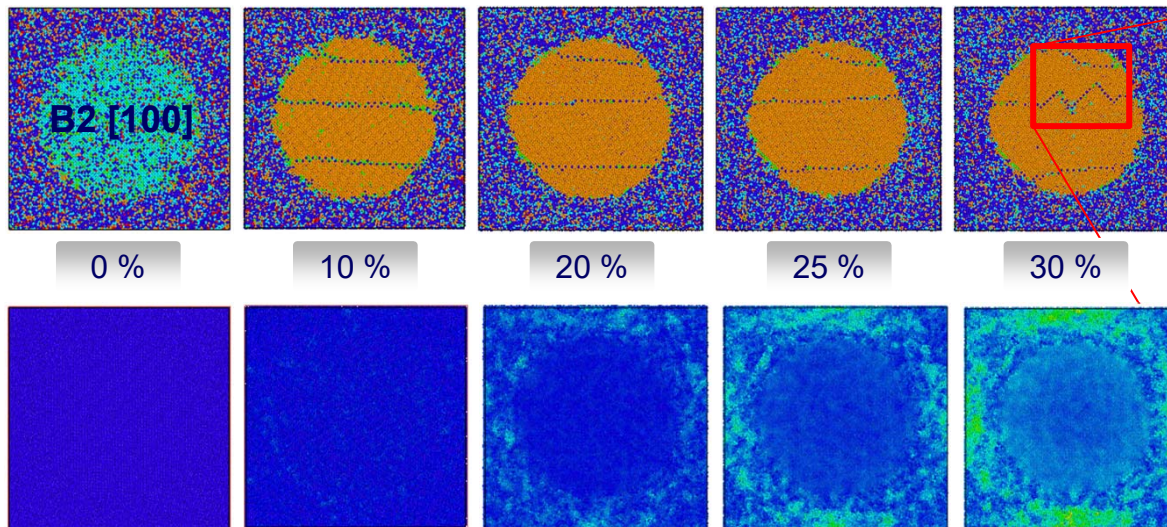
DFT-based MD simulation

Stress-induced phase transformation of NiTi in BMGC

Potential based MD simulation



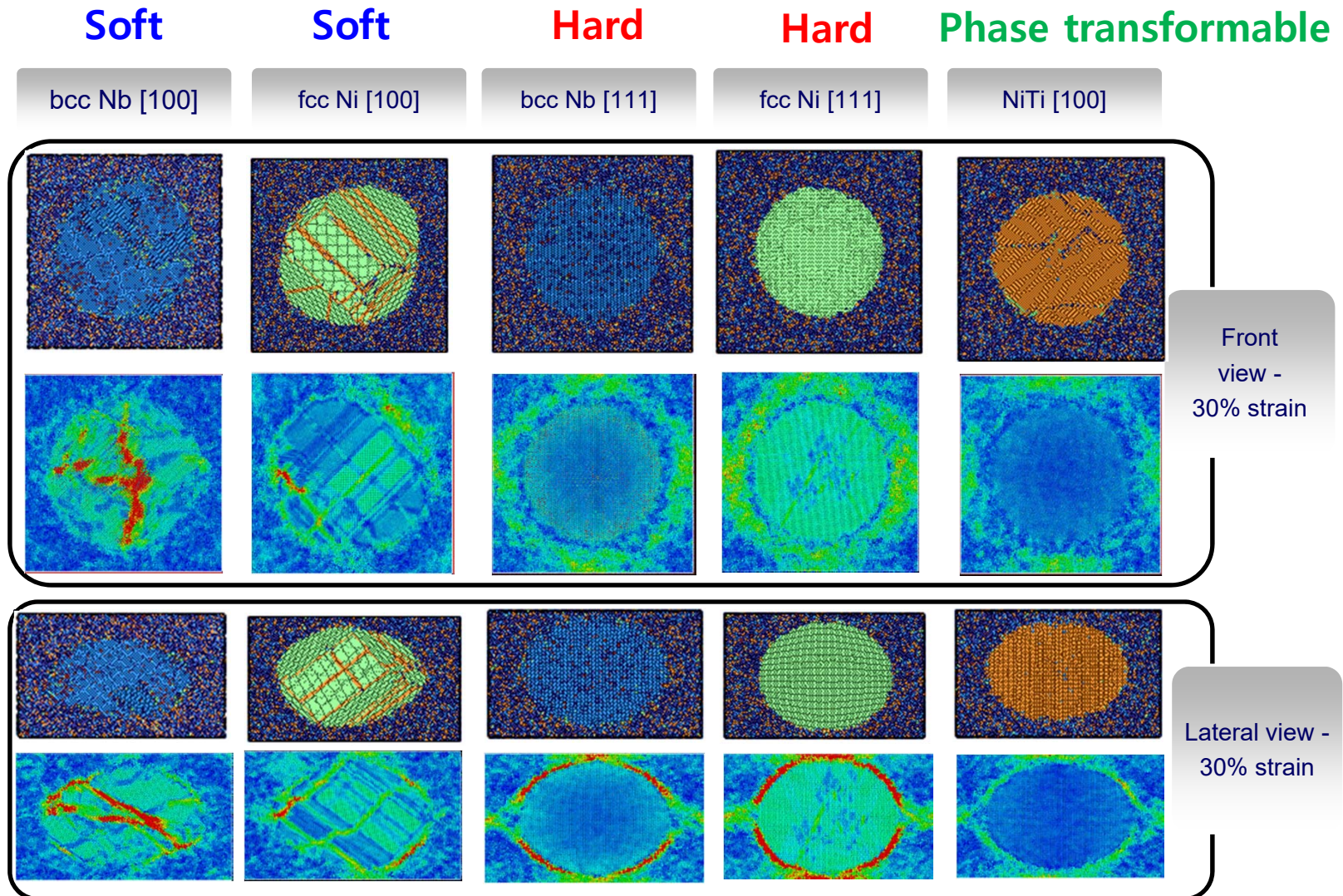
* Visualized based on the common neighbor analysis



* Visualized based on the atomic strain analysis (min=0, max=0.9)

Formation of shear band along lateral directions

DFT-based MD simulation



* Visualized based on the atomic strain analysis (min=0, max=0.9)

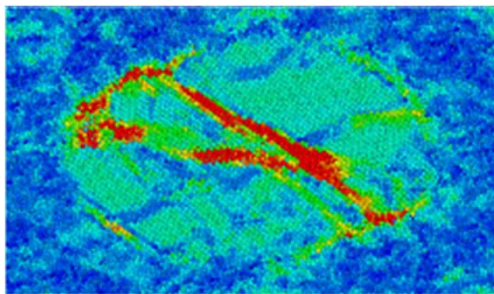
Strain localization of NiTi containing cell is less pronounced than other cases

Origin for Improved work-hardenability in TRIP BMGC by SE 2nd phase

Contribution to mechanical properties		Mono lithic	Soft	Hard	Transformable
Character of 2 nd phase		no	elastic+ plastic	elastic	elastic+ plastic+ TRIP
1. Eshelby backstress effect		-	depends	weak	Strong
2. Damage management	Blocking shear band propagation	no	middle	middle	Superior (reusable for SE phase)
	Stress/strain localization	-	localized	localized	Delocalized

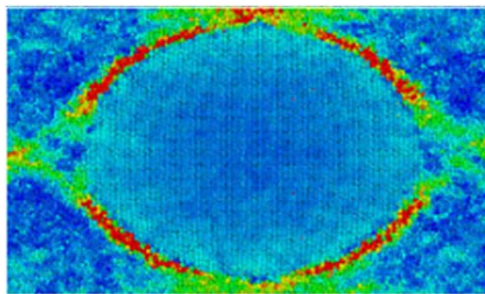
Soft crystalline

bcc Nb [100]



Hard ceramic

bcc Nb [111]



Transformable

NiTi [100]

