Current Status of Structural Materials

Deformation behavior of metallic glasses with inhomogeneous structure in atomic scale

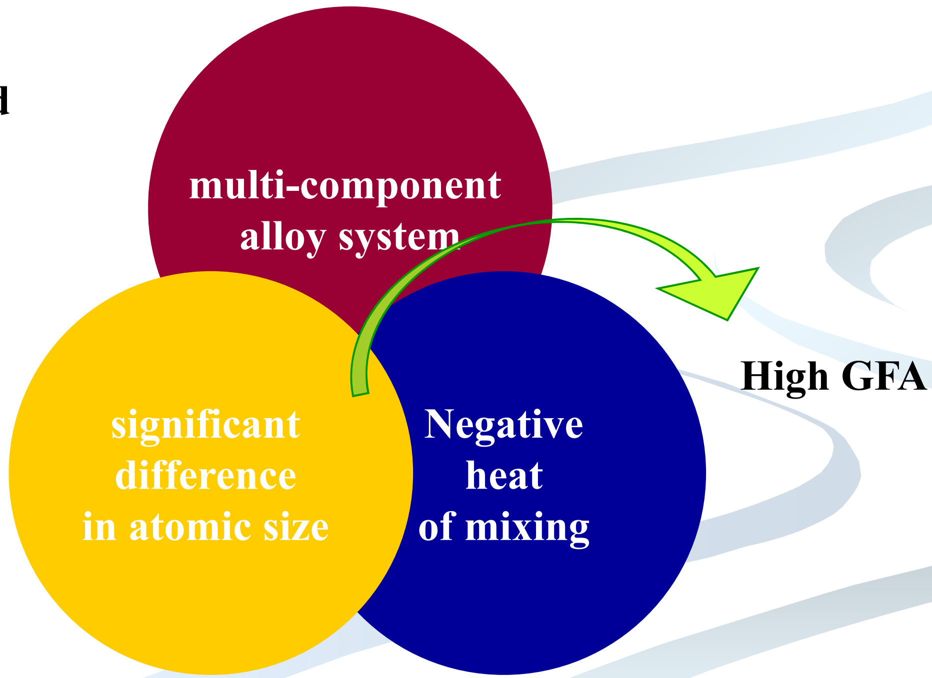
Research background

Metallic glass alloy composition search & bulk up

- **The first metallic glass (MG): $Au_{75}Si_{25}$** *(by Duwez in 1960)*
- **The first bulk metallic glass (BMG) : Pd-Cu-Si alloy** *(by Chen in 1974)*
- **Main direction of research on metallic glass since the first report of MG**
  - Search for wide composition range of high glass forming ability (GFA)

3 empirical rules for BMG

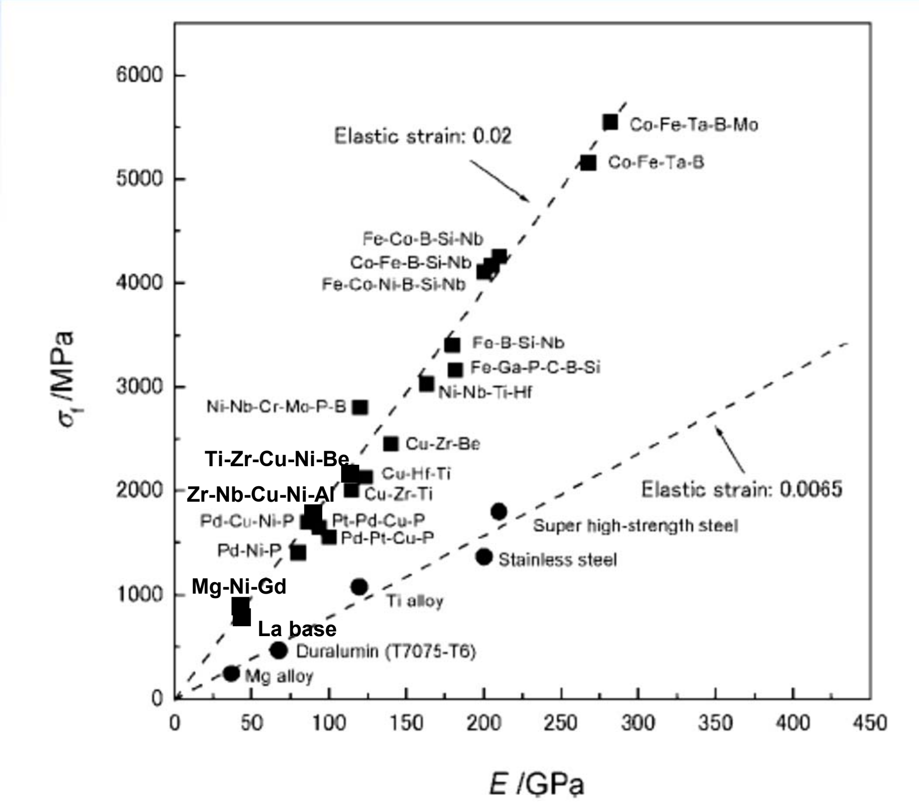
- **Suppression of nucleation and growth of crystalline phase during solidification**



- A. Inoue et al.

Research background

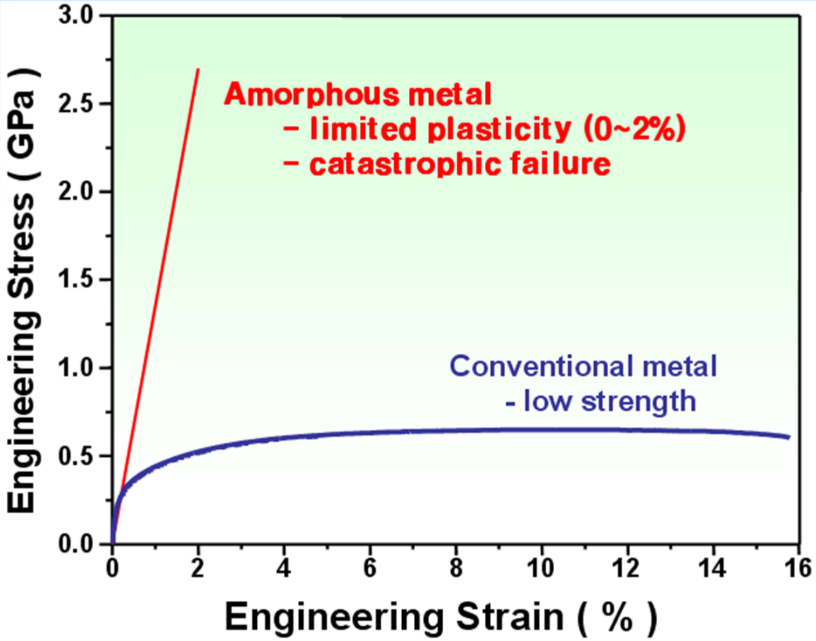
Potential of BMG as structural materials



- **Higher strength compared to conventional metallic alloys**
- **Large elastic strain ≈ 2 %**

Research background

Critical issue in BMG



- **Overcome brittleness of BMG for practical application as structural materials**

- **Provision of plastic deformation**
  - **Prevention of stress concentration and localization of deformation**
  - **Formation of multiple shear bands**

☞ **Provision of inhomogeneity in MG matrix**

Research background

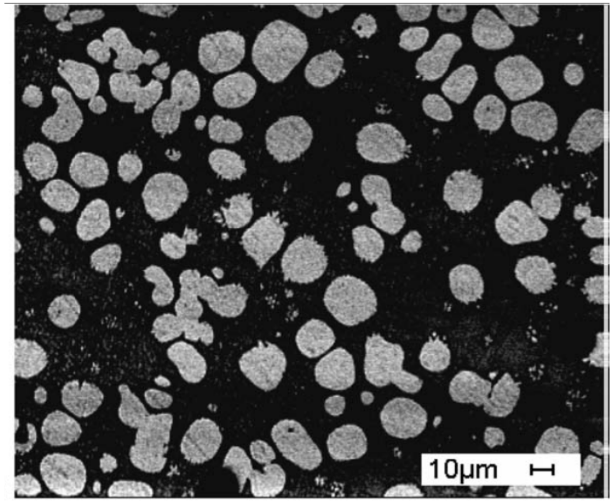
Enhancement of plasticity: previous report

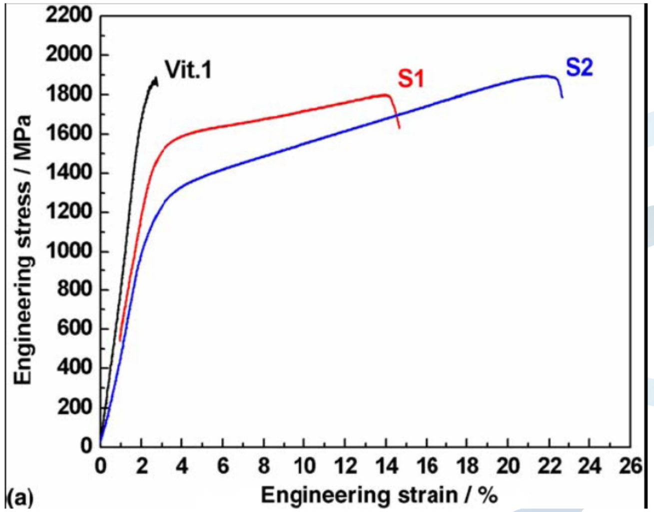
[1] Metallic glass matrix composite (MGMC)

- *μm* scale imhomogeneity

- **In-situ composite**

- Formation of primary ductile phase during solidification

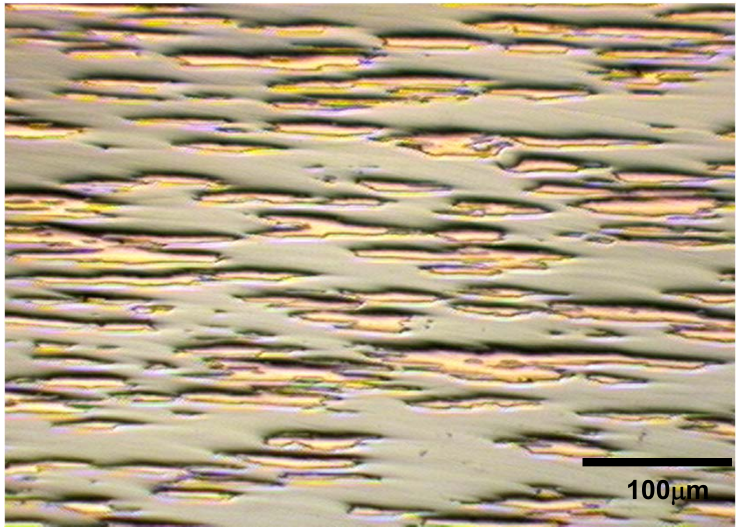


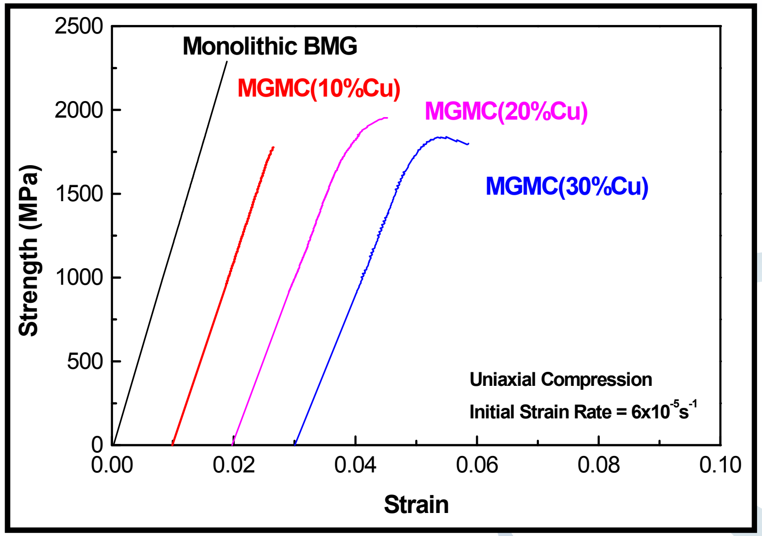


Research background

Enhancement of plasticity: previous report

- **Ex-situ composite**
  - **- Powder metallurgy method, casting method**





-M. H. Lee et al., JMR., 18 (9) (2003) 2101

Research background

Enhancement of plasticity: previous report

[2] monolithic BMG

- sub-nm scale inhomogeneity

Composition	Max. dia. (mm)	Compressive Global Strain (%)	Heat of mixing	Reference
$Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$		≈ 3.8	Ta-Zr (+13 kJ/mol)	Xing et al., Phys. Rev. B (2001)
$Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$		≈ 9		
$Ni_{60}Nb_{40}$	1	2	Nb-Ti (+9 kJ/mol)	W. Zhang et al., Mater. Trans. 43 (2002) 2342
$Ni_{60}Nb_{25}Ti_{15}$	1.5	3.8		
$Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$	3	4.1	Nb-Zr (+17KJ/mol),	J. Y. Lee et al., J. Mater. Res. 18 (2005) 2101
$Ni_{59}Zr_{16}Nb_7Ti_{13}Si_3Sn_2$	5	8.4	Nb-Ti (+9 kJ/mol),	
$Cu_{50}Zr_{43}Al_7$	3	≈ 6	Cu-Ag (+5 kJ/mol)	D. S. Sung et al., Metal. Mater. Int. 10 (2004) 575
$Cu_{43}Zr_{43}Al_7Ag_7$	8	≈ 9		
$Cu_{47}Ti_{33}Zr_{11}Ni_8Si_1$	4	3.5	Nb-Ti (+9 kJ/mol),	E. S. Park et al., J. of Non-Cryst. Sol. 351 (2005) 1232
$Cu_{47}Ti_{33}Zr_7Nb_4Ni_8Si_1$	5	6.05	Nb-Zr (+17 kJ/mol)	
$Cu_{50}Zr_{43}Al_7$		3.2	Zr-Y (+35 kJ/mol)	E. S. Park et al. Acta. Mater., 54 (2006) 2597
$Cu_{48}Zr_{43}Al_7Y_2$		5.2		
$Mg_{85}Cu_{25}Gd_{10}$	8	1.8	Cu-Ag (+5 kJ/mol)	E. S. Park et al., J. Mater. Res., 20 (2005) 2379
$Mg_{85}Cu_{20}Ag_5Gd_{10}$	11	2.3		

- Increased plastic strain with addition of elements having (+) positive heat of mixing with constituent elements

Mechanism for plastic deformation

Plastic deformation

- "A permanent deformation without recovery when the load is removed"

Plastic deformation in metallic glass

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

Shear band (determined in crystalline materials)

- Narrow bands with intense plastic shear strain
- develops after large plastic deformations.
- usually precursors of ductile fracture

Adiabatic shear band

- Shear bands which is formed in dynamic process and related to rapid and local heating effects

Nanocrystallization in the shear band in MGs ?
Adiabatic heating ?

Research Motivation / objective

Unsolved issues

- Understanding the mechanism of plasticity enhancement in monolithic BMG
- Formation of multiple shear band during deformation
- Argue on the structural change in the shear band

Research originality (1)

[1] Understanding the mechanism providing plasticity

· Provision of inhomogeneity in the amorphous phase: ternary system

- inhomogeneous chemical ordering
- inhomogeneous distribution of free volume

1. Addition of element which has (+) heat of mixing with constituent elements

2. quenched-in icosahedral nuclei

· Structural characterization to identify the origin of plasticity

TEM
nm scale analysis

EXAFS
atomic scale chemical analysis
→ coordination number (C.N.)
→ bonding length

· Enhancement of plasticity by controlling microstructure of BMG

⇒ Tailor-made BMGs with enhanced plastic elongation

Research originality (2)

[2] Observation of deformation behavior in BMG

· Shear band formation after compression & tension test

: Comparison of shear band between alloys which show enhanced / no plastic elongation

· Structural change in the shear band

: alloy composition (with change of T_x)

: test mode

After compression	After tension	In situ tension

· Mechanism of fracture and deformation in BMG

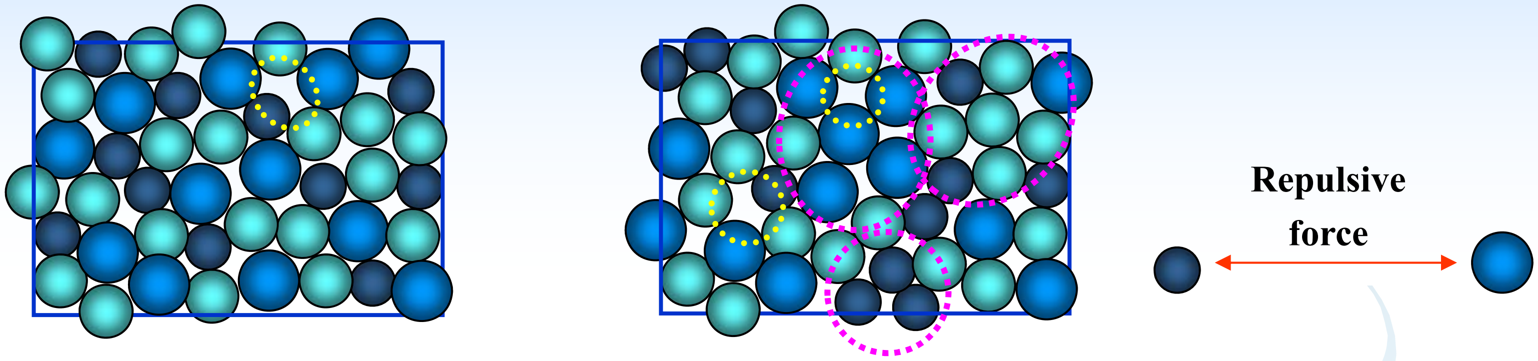
: observation of fracture by in situ tensile test

⇒ **Understanding deformation mechanism of BMGs**

Approach 1.

Enhancement of plasticity

- Provide inhomogeneous amorphous structure



(+) heat of mixing with constituent elements

· Monolithic BMG

: inhomogeneous amorphous structure

: atomic structure analysis by EXAFS (Extended X-ray Absorption Fine Structure)

· Metallic glass matrix composite

: second phase (ductile crystalline/quasicrystalline phase) in the metallic glass matrix

· Phase separation

: two amorphous phases

Quenched-in icosahedral nuclei

: embedded quenched-in icosahedral nuclei in the amorphous matrix during cooling

Approach 2.

Deformation behavior

- **Comparison of shear band formation**
  - **: monolithic BMG**
  - **: phase separation**
  - **: MGM composite**

- **Structural change in the shear band**
  - **: alloy composition (with change of T_x)**
  - **: test mode**

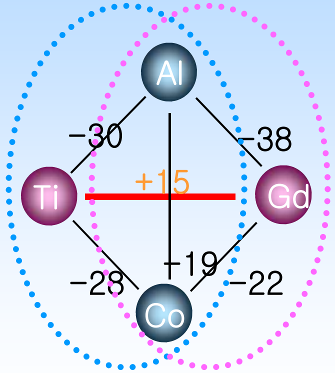
	After compression	After tension	In situ tension
Monolithic BMG	$Ti_{40}Zr_{29}Cu_9Ni_8Be_{14}$ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ $Zr_{57}Ti_8Nb_{2.5}Cu_{13.9}Ni_{11.1}Al_{7.5}$ (2mm)	$Ti_{40}Zr_{29}Cu_9Ni_8Be_{14}$	$Ti_{40}Zr_{29}Cu_9Ni_8Be_{14}$ $Ni_{60}Nb_{40}$ $Al_{83}Ni_7Gd_6$
MGMC	$Mg_{80}Cu_{15}Gd_5$ $Zr_{57}Ti_8Nb_{2.5}Cu_{13.9}Ni_{11.1}Al_{7.5}$ (3mm)		
Phase separation	$Gd_{30}Ti_{25}Al_{25}Cu_{20}$ $Gd_{30}Zr_{25}Al_{25}Cu_{20}$	$Gd_{30}Ti_{25}Al_{25}Co_{20}$ $Gd_{30}Zr_{30}Al_{20}Co_{20}$	

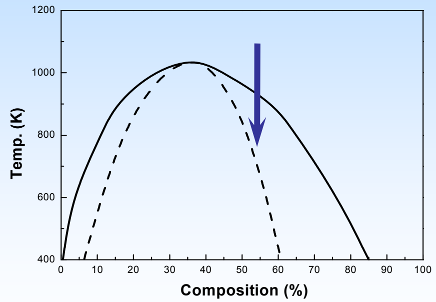
(1) Enhancement of plasticity

Preliminary study

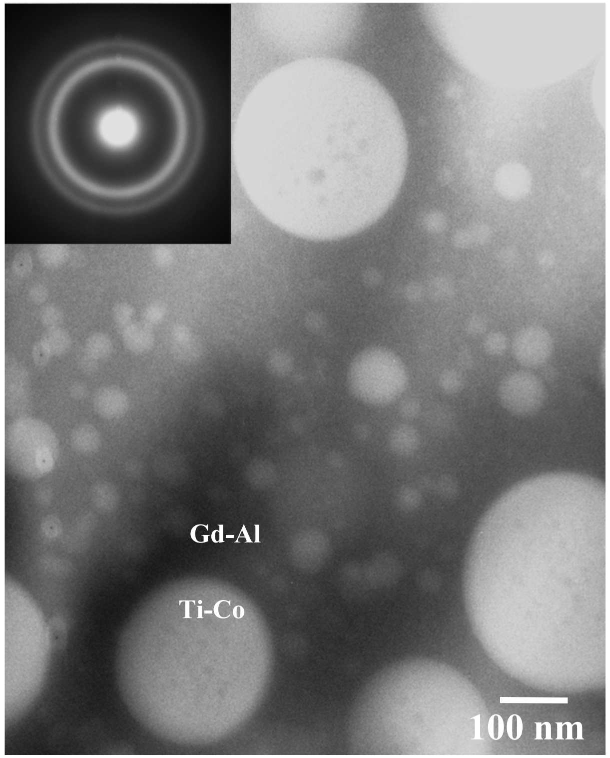
Phase separation

- **Droplet structure**

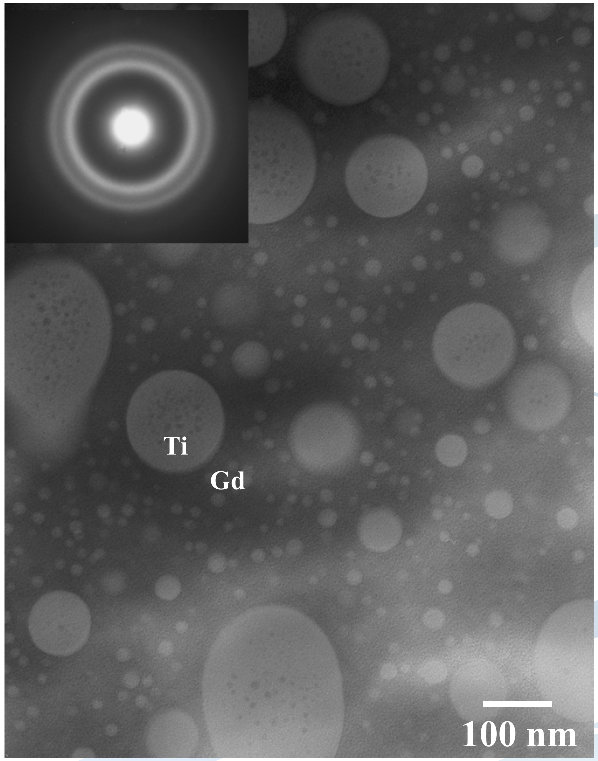




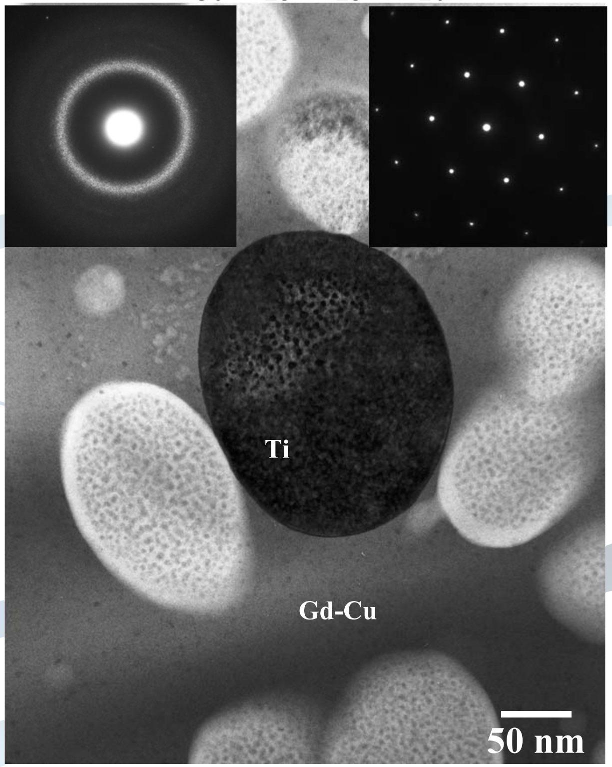
$Gd_{30}Ti_{25}Al_{25}Co_{20}$



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



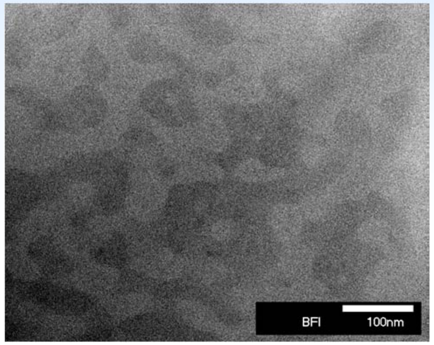
$Gd_{30}Ti_{25}Al_{25}Cu_{20}$

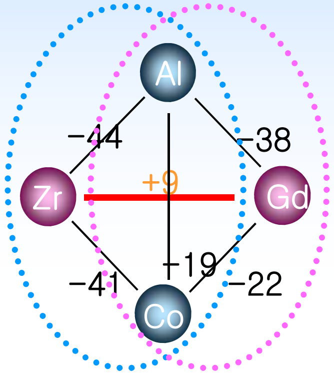


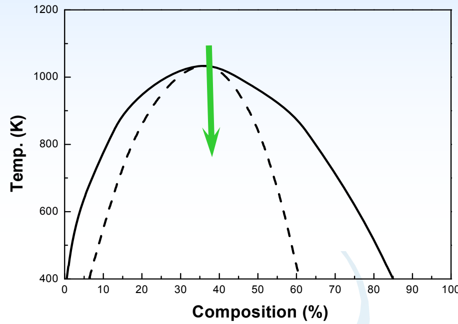
Preliminary study

Phase separation

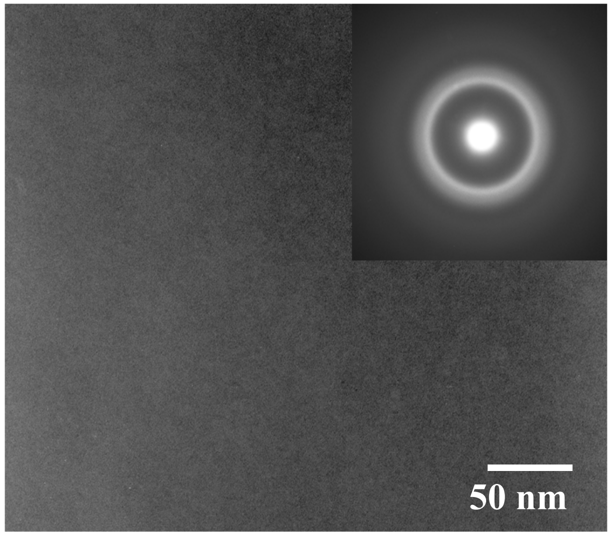
Interconnected structure



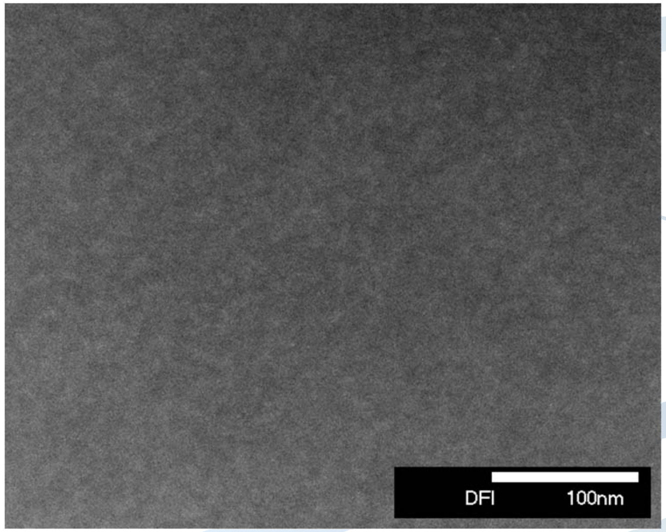




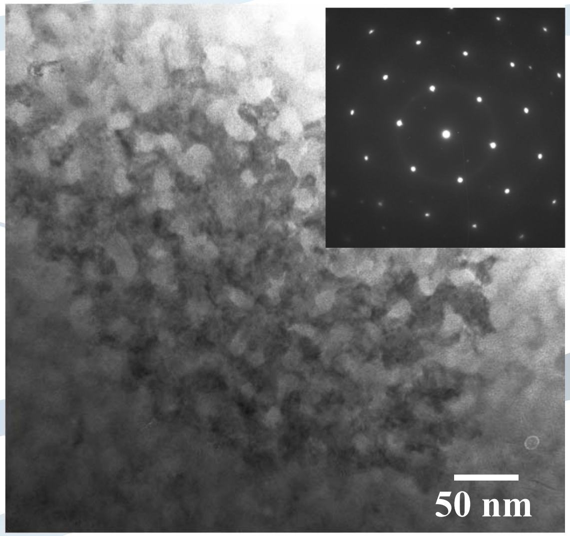
$Gd_{30}Zr_{25}Al_{25}Co_{20}$



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

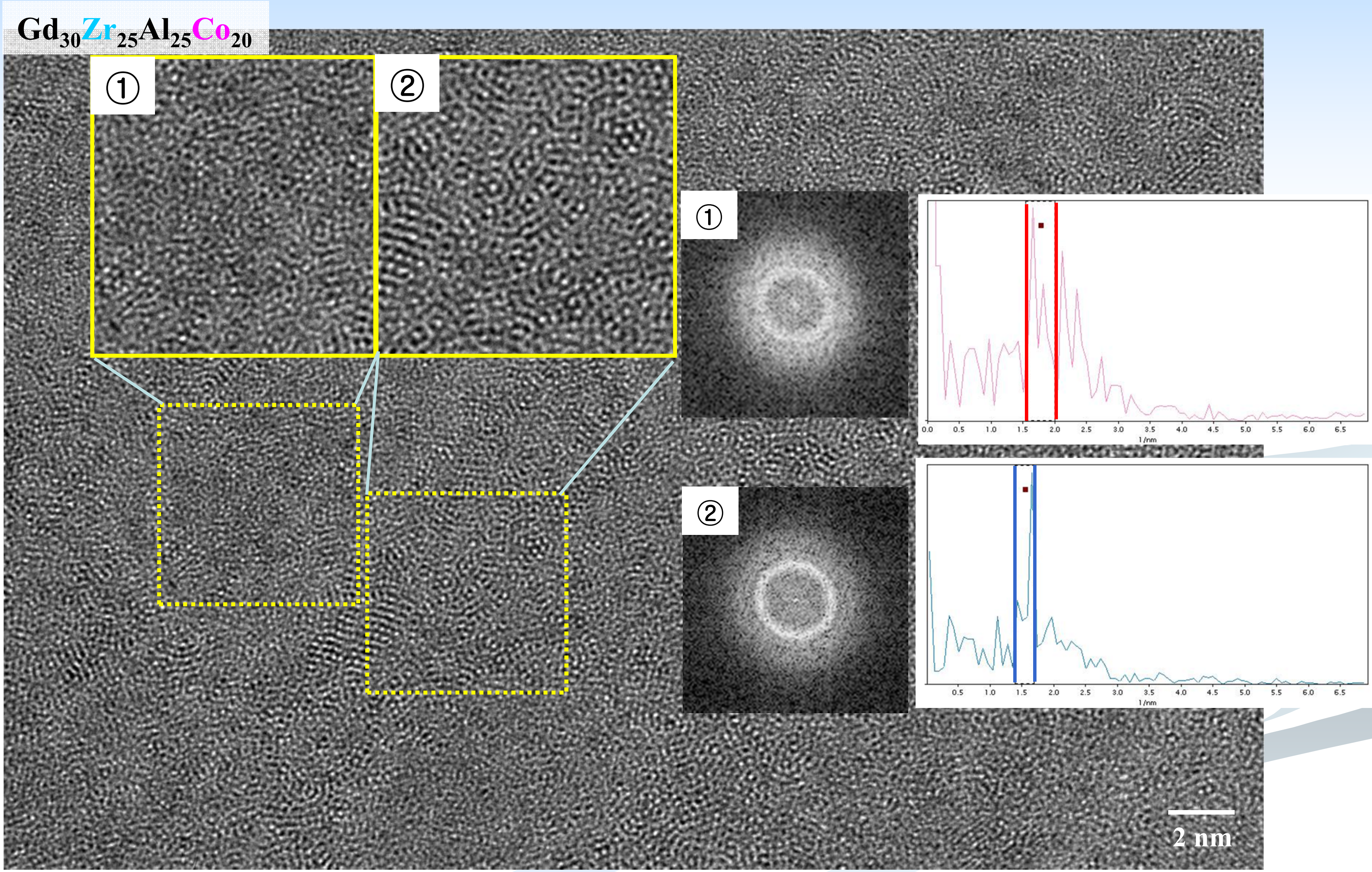


$Gd_{30}Zr_{25}Al_{25}Cu_{20}$



Preliminary study

- **Nano scale (<3 nm) interconnected phase separation**



Preliminary study

Alloy design

(+) heat of mixing with constituent elements

- Well known simple bulk metallic alloy systems : Cu-Zr, Ni-Nb
- Systematic addition of elements having (+) heat of mixing with constituent elements

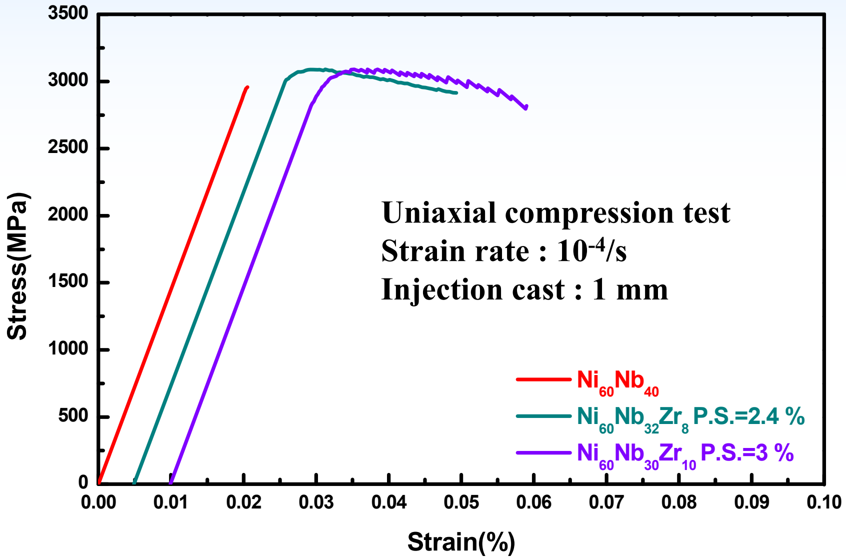
	Nb	Ta	Zr	Y, Gd
Ni	-143	-133	-167	-161
Nb		0	+15	+127

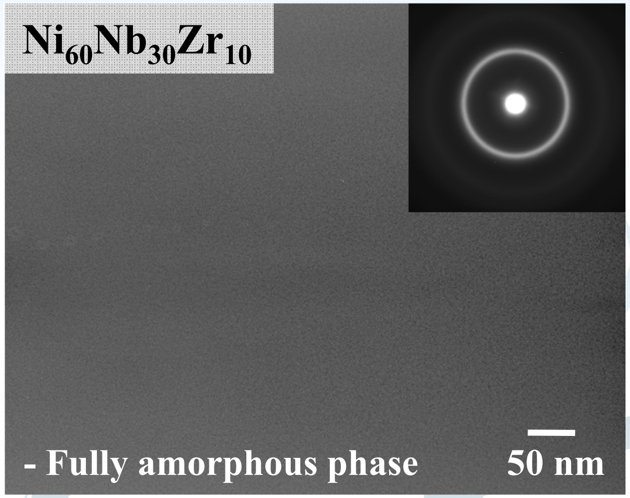
	Zr	Al	Be	Ag
Cu	-142	-38	-4	+5
Zr		-169	-53	-112

Reference : A. R. Miedema et al.

Preliminary study

Enhanced plasticity in monolithic Ni-Nb-Zr alloy





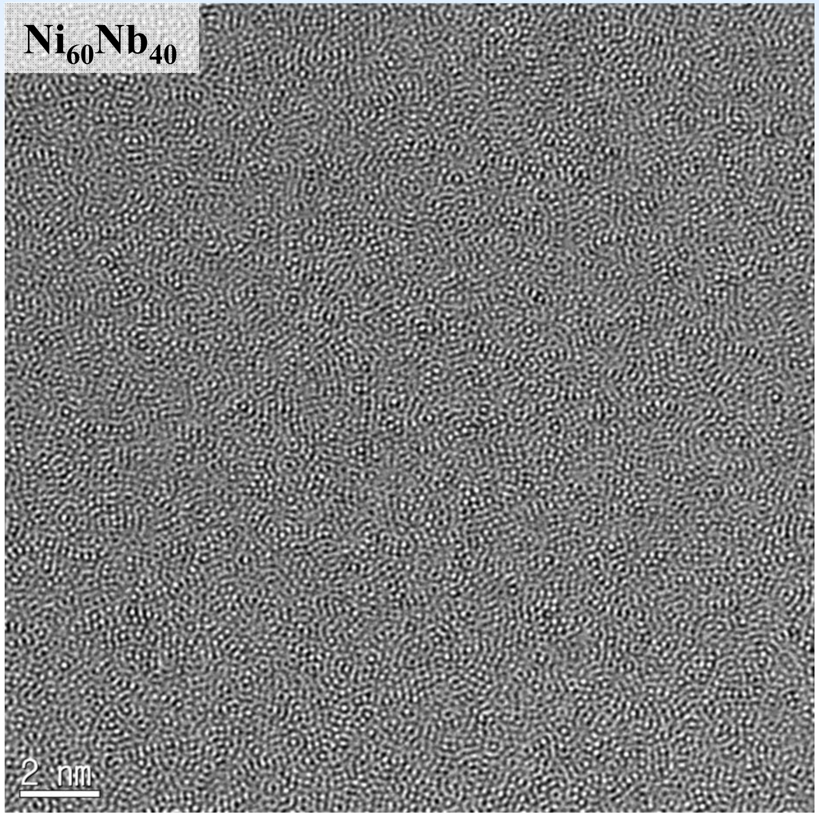
<TEM BF and SADP obtained from the fractured sample after compression test>

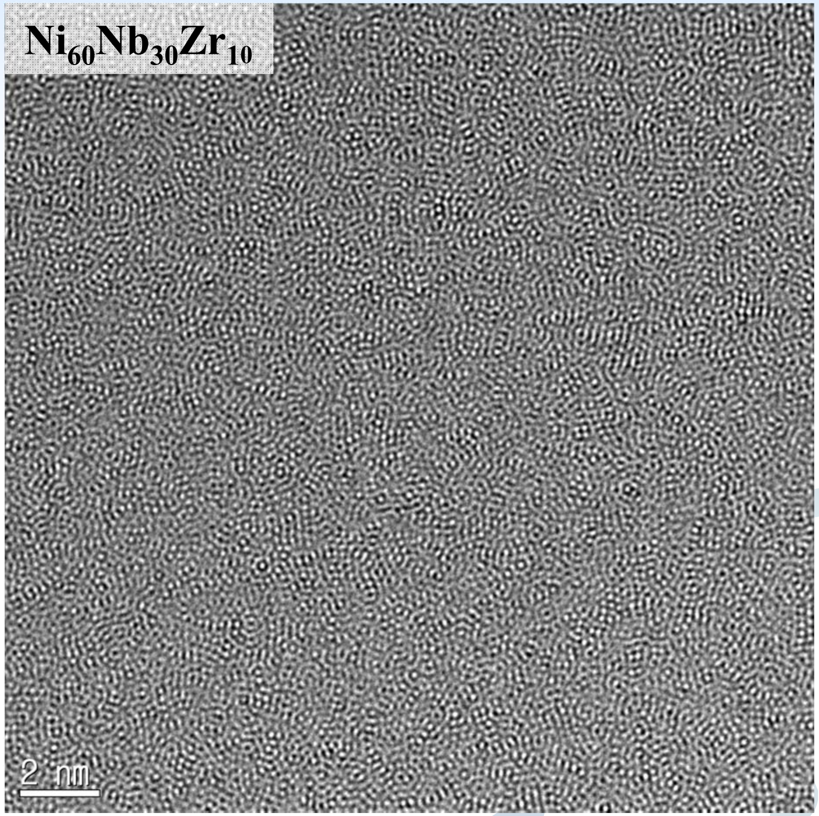
- Enhanced plasticity in $Ni_{60}Nb_{30}Zr_8$ & $Ni_{60}Nb_{30}Zr_{10}$ alloy (σ_{max} : 3.2 GPa, ε_p : 3 %)

  ➡ Contribution of atomic scale inhomogeneity with addition of Zr

Preliminary study

Limit of amorphous structural analysis by TEM





[HVEM in KBSI]

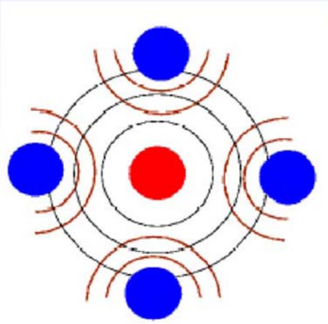
- **Typical HREM image of MG**

  → **No detectable topological change by TEM**

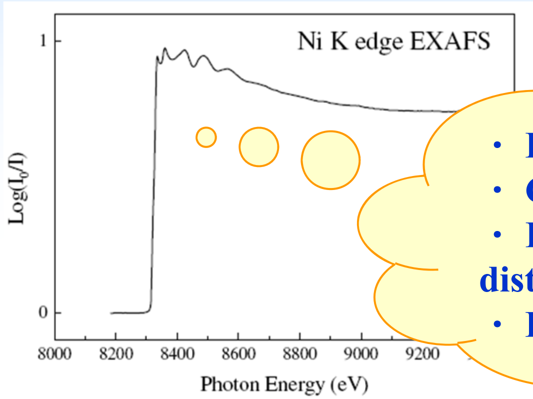
Preliminary study

EXAFS (Extended X-ray Absorption Fine Structure)

What is EXAFS ?



The photoelectron propagates as a spherical wave and scatters off the surrounding atoms.



Absorption spectrum

- Bond lengths
- Coordination number
- Partial pair distributions
- RMS displacements about bond lengths

EXAFS condition

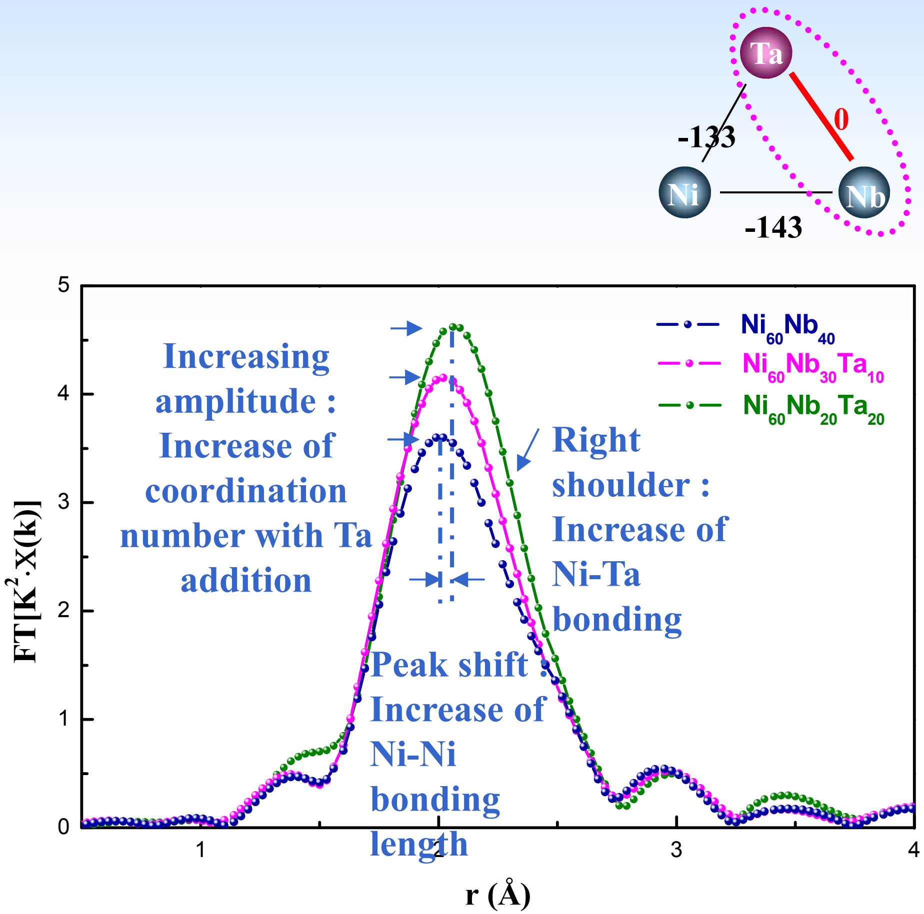
- Performed at PAL (Pohang Accelerator Laboratory) 7C BL.
- Sample - Ribbon : 30 ㎛ (in thickness), 6 mm (in width)
- Fluorescence mode

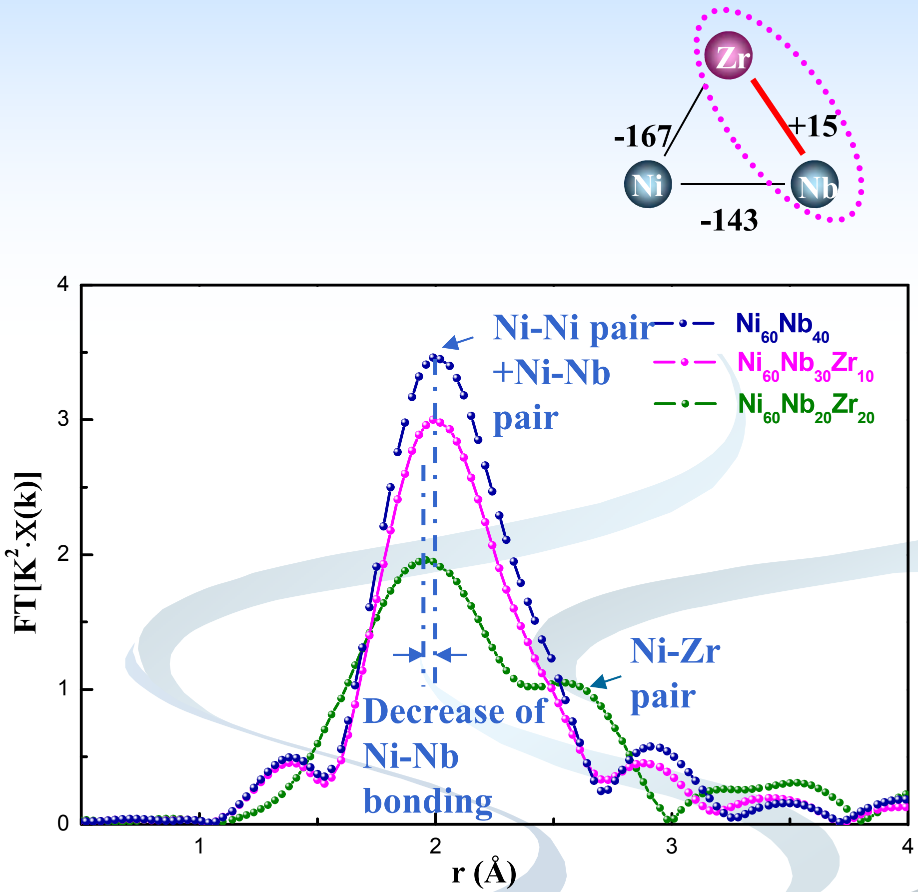
$$\mu(E) \propto I_f / I_0$$

- window : Hanning function ($\cos^2$)
- k- range : $2 < k < 11.5$ (Å-1)
- k weight : 3
- Normalization → Background → Fitting

Preliminary study

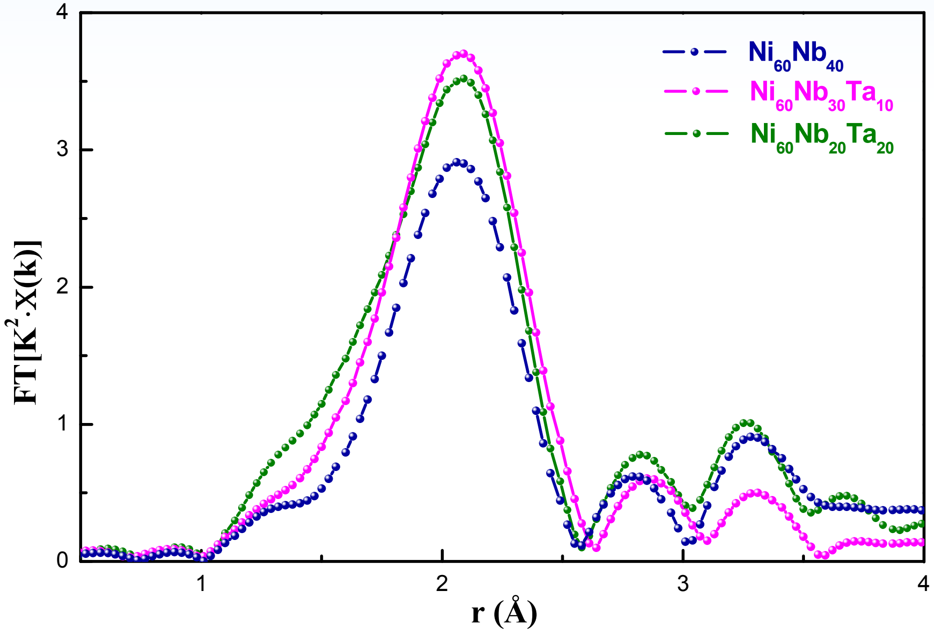
Ni environment

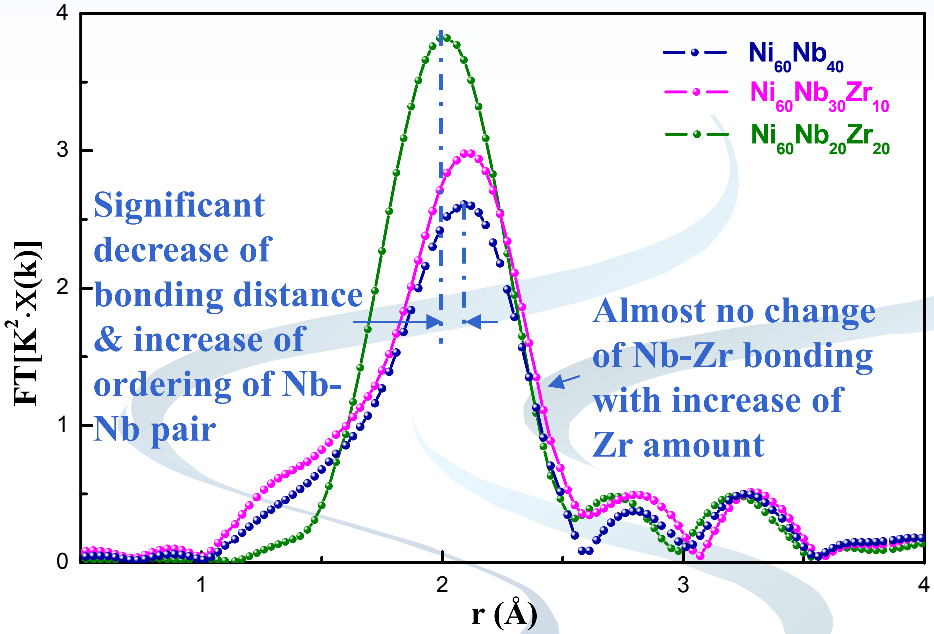




Preliminary study

Nb environment





Preliminary study

Fitting results

[S_0^2(Ni)=0.85934, S_0^2(Nb)=0.985], σ^2 : Debye Waller factor (disordered parameter)

Composition	Ni-Ni			Ni-Nb			Nb-Ni			Nb-Nb			Ni-X (Ta or Zr)			Nb-X (Ta or Zr)		
	r(Å)	C.N.	σ^2	r(Å)	C.N.	σ^2	r(Å)	C.N.	σ^2	r(Å)	C.N.	σ^2	r(Å)	C.N.	σ^2	r(Å)	C.N.	σ^2
$Ni_{60}Nb_{40}$	2.4124	1.62	0.0087	2.6589	1.63	0.0240	2.624	3.94	0.0180	2.707	0.84	0.0088						
$Ni_{60}Nb_{40}Ta_{10}$	2.4244	1.96	0.0092	2.6447	0.87	0.0180	2.6425	5.61	0.0180	2.6948	1.97	0.0067	2.631	0.35	0.0067	2.677	0.35	0.0015
$Ni_{60}Nb_{40}Ta_{20}$	2.4496	2.35	0.0104	2.6965	0.51	0.0120	2.635	6.34	0.0190	2.6758	1.65	0.0068	2.667	2.75	0.0192	2.669	0.37	0.0014
$Ni_{60}Nb_{40}Zr_{10}$	2.4355	1.73	0.0111	2.6978	2.19	0.0220	2.628	3.97	0.0160	2.687	1.413	0.0109	2.863	0.59	0.0086	2.835	0.44	0.0073
$Ni_{60}Nb_{40}Zr_{20}$	2.4424	1.18	0.0085	2.6187	4.31	0.0250	2.619	5.43	0.0163	2.666	2.575	0.0078	2.785	0.98	0.0196	2.853	0.34	0.0074

- When third elements are added, the total coordination number increases making more densely packed amorphous structure. → Enhancement of GFA
- (+) heat of mixing ↑, percent of additional elements ↑

  ☞ inhomogeneous distribution of chemical ordering ↑, local disordering ↓

  Ex) 20 % of Zr addition : C.N. of Ni-Nb (or Nb-Ni) increase significantly, C.N. of Nb-Nb increases and disordering decreases, C.N. of Ni-X increase. But, C.N. of Nb-X remains almost same.

Preliminary study

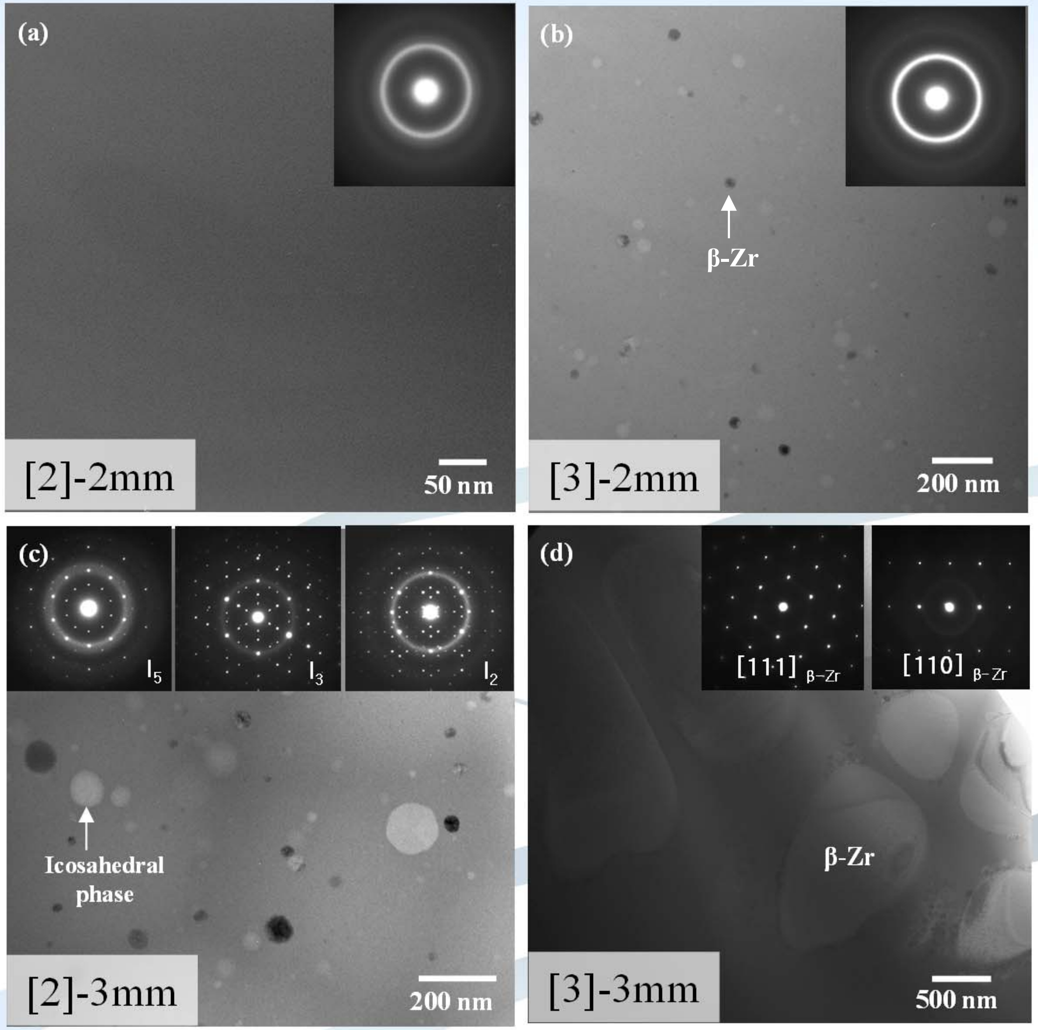
Cooling rate effect

Alloy design (at.%)

	Zr	Ti	Cu	Ni	Al	Nb
[1]	54.5	7.5	20	8	10	-
[2]	57	8	13.9	11.1	7.5	2.5
[3]	63	5	15.8	6.3	7.9	2
[4]	66.4	-	10.5	8.7	8	6.4

Φ= 2 mm

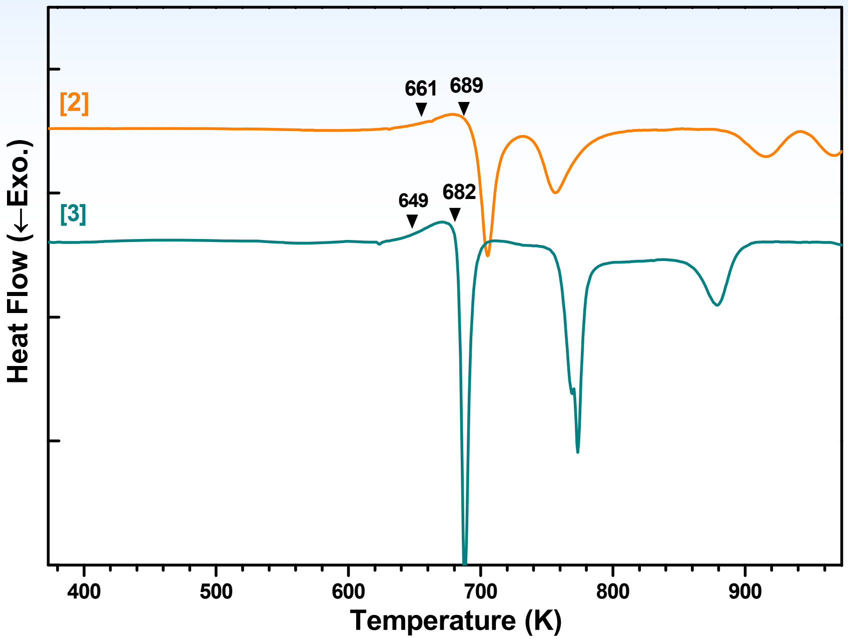
Φ= 3 mm

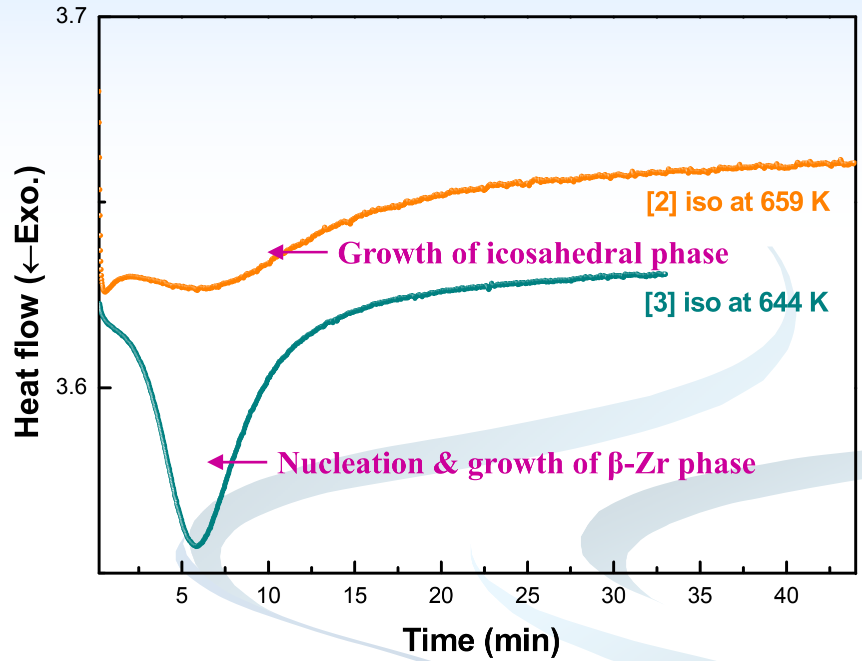


Preliminary study

Quenched-in icosahedral nuclei/composite

Isotherm in DSC





- Symmetric exothermic pick in [3] alloy ☞ Nucleation & growth reaction.
- Asymmetric exothermic pick in [2] alloy ☞ No nucleation reaction
  - ☞ Quenched-in icosahedral nuclei in amorphous matrix
  - ☞ Enhanced plasticity of monolithic BMG

(2) Deformation Mechanism

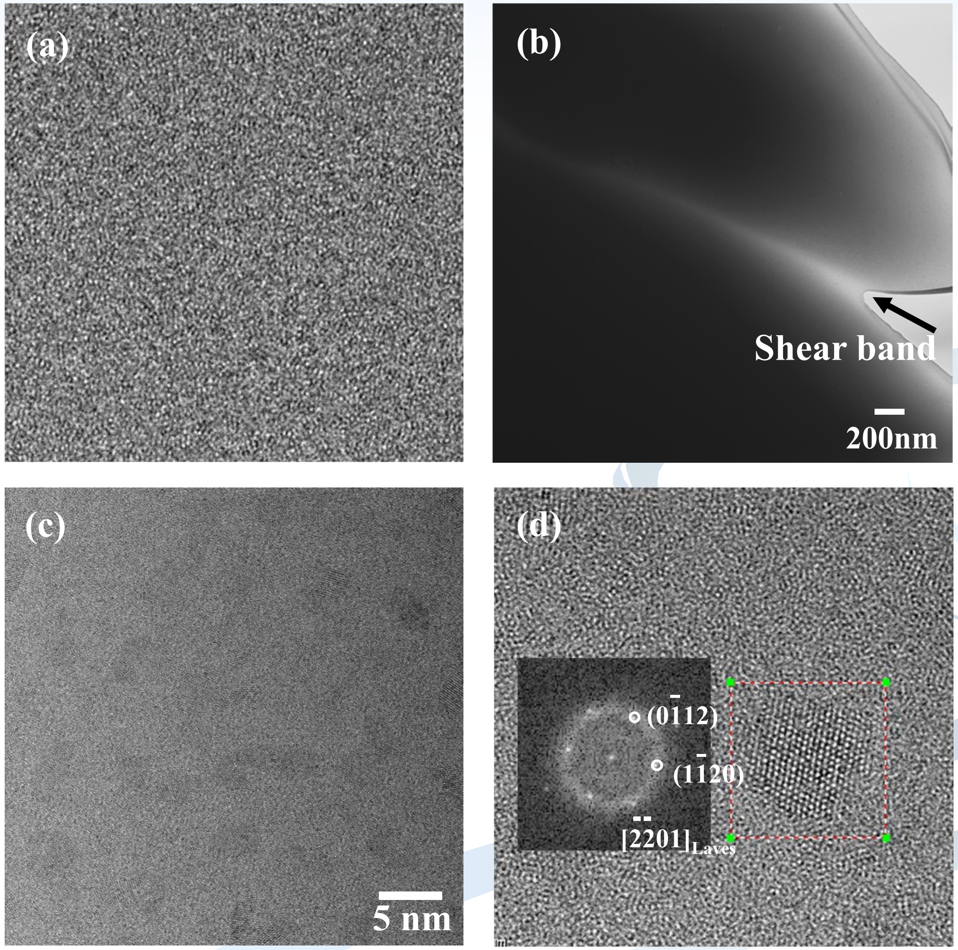
Preliminary study

Deformation behavior

After compression test

-Crystallization in the shear band

- Precipitation of Laves phase that is stable at high temperature



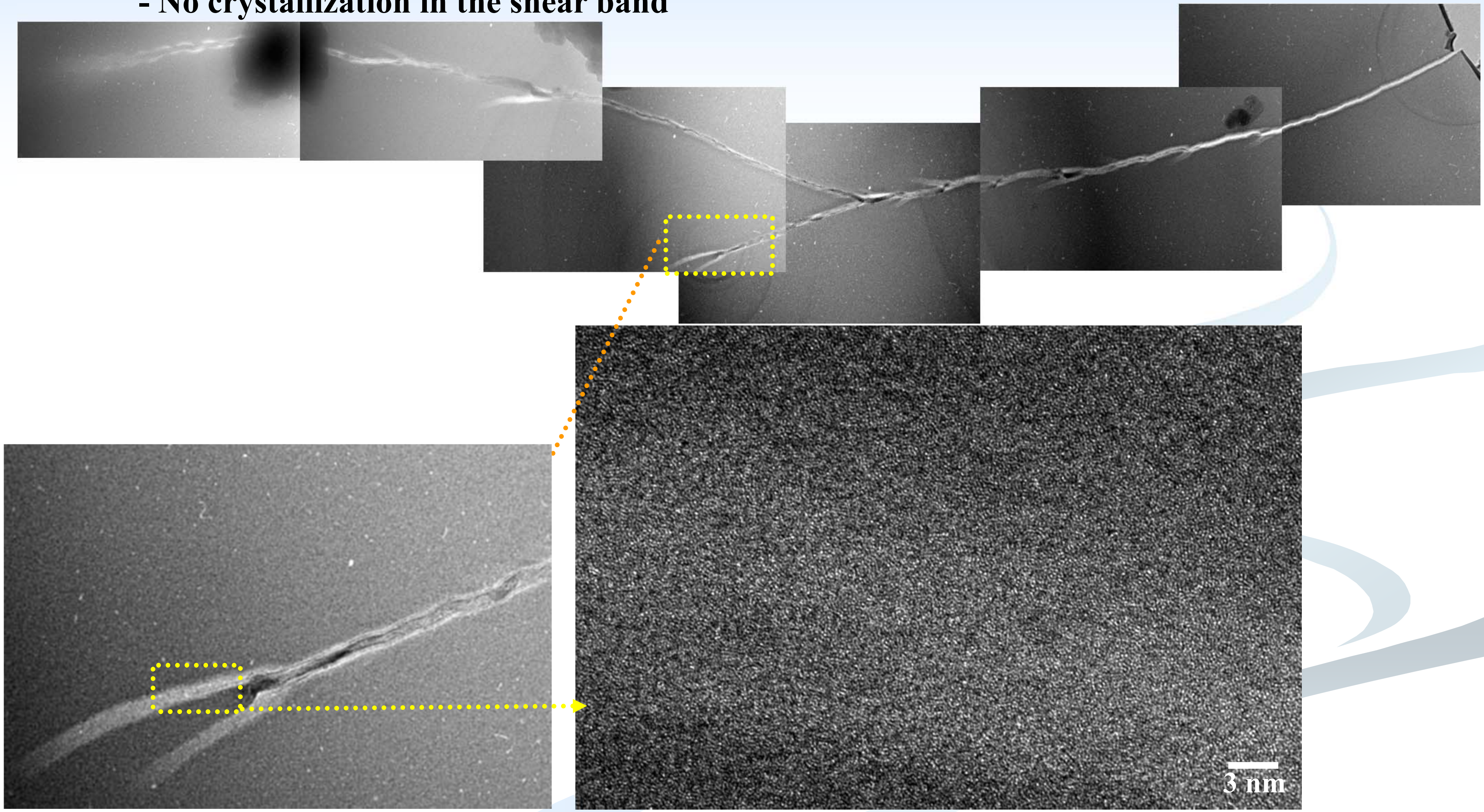
[H. J. Chang et al. Scripta Materialia 55 (2006) 509–512]

Preliminary study

Deformation behavior

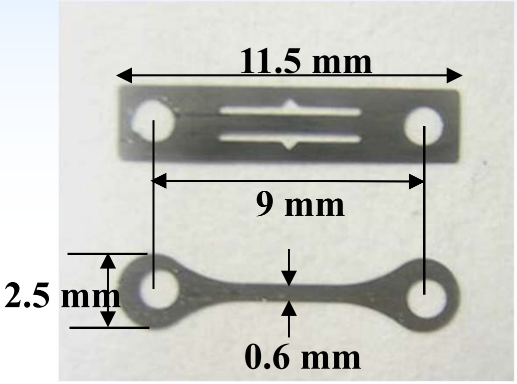
After tension test

- No crystallization in the shear band



Preliminary study

In situ strain in TEM



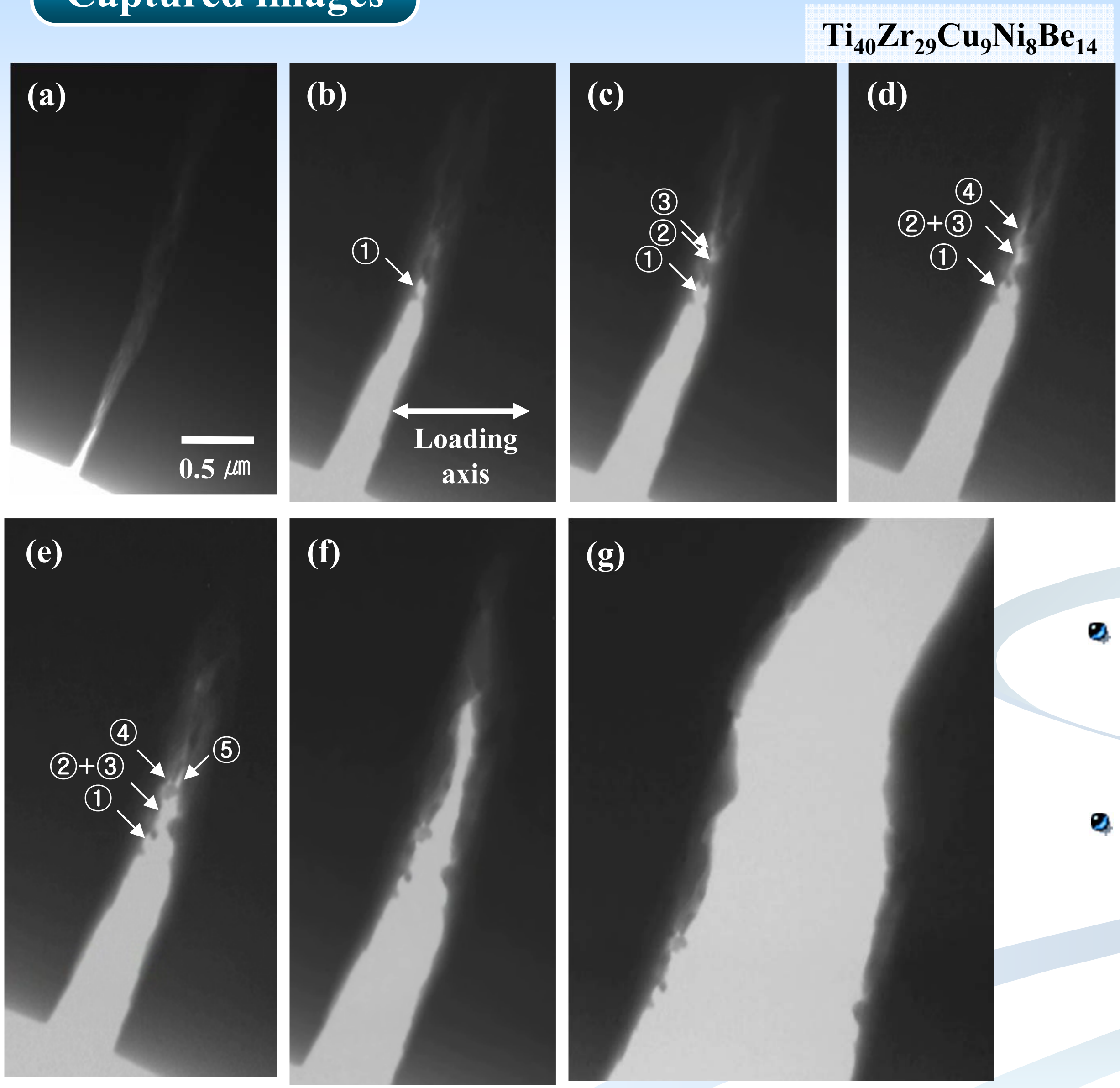
$Ti_{40}Zr_{29}Cu_9Ni_8Be_{14}$

- **Thinning method** : Jet polishing (No ion-milling)
- **Strain interval** = 1.0 ㎛/s ~ 0.01 ㎛/s

Sample composition (at.%)	$Ti_{40}Zr_{29}Cu_9Ni_8Be_{14}$	$Ni_{60}Nb_{40}$	$Al_{83}Ni_7Gd_6$
Sample thickness (㎛)	60	40	20
T_x (℃)	350	651	195
Compressive strength (MPa)	1978	2940	-
Plastic strain (%)	6.7	0	-

Preliminary study

Captured images

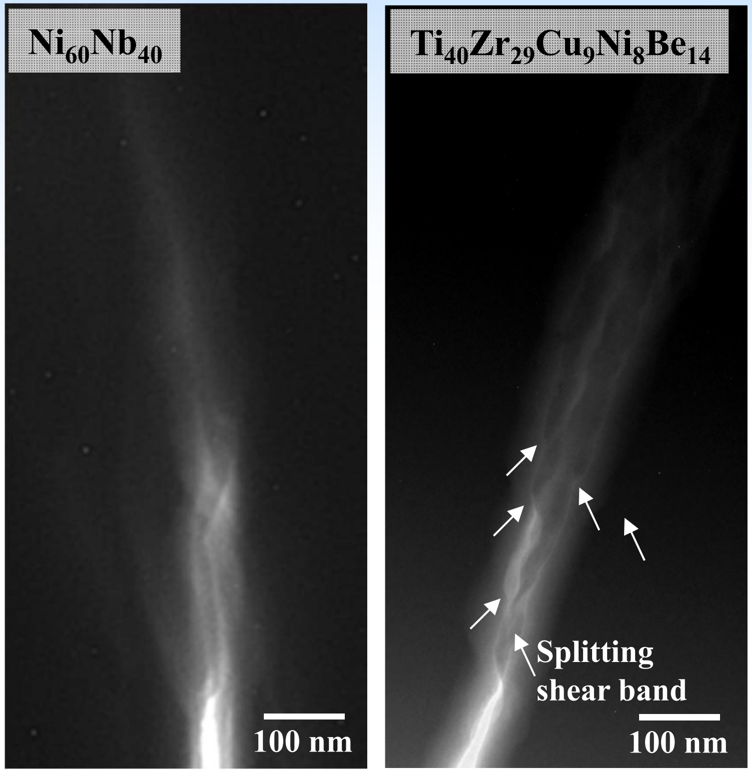


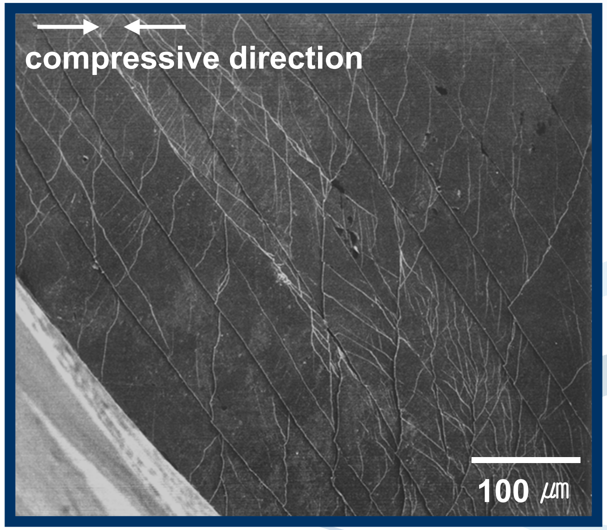
- Initiation of discontinuous nano cracks ahead of the main crack tip
- Linkage of nano cracks leading propagation of cracks.

☞ Not perfectly brittle fracture

Preliminary study

Multiple shear bands

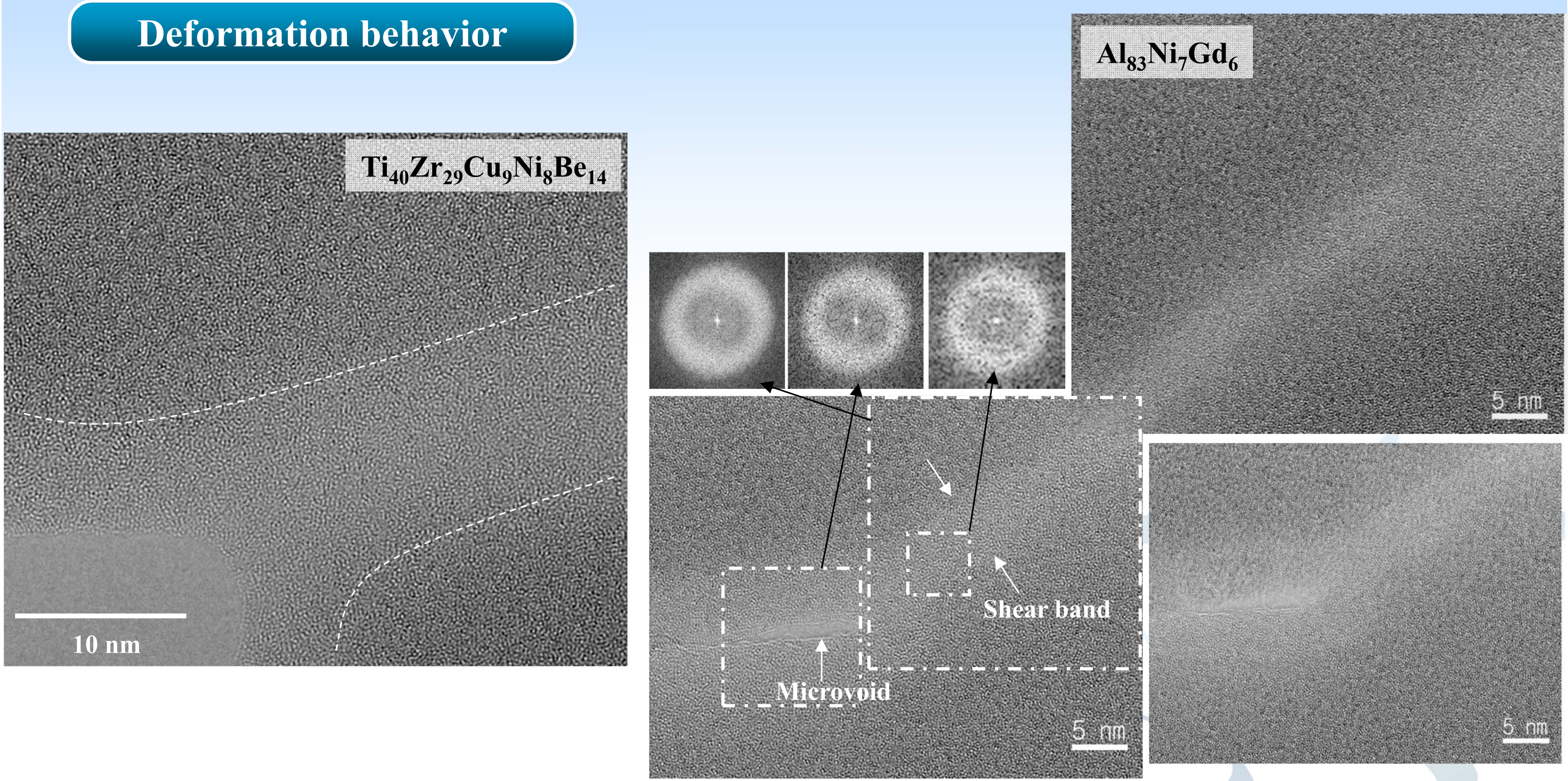




- $Ti_{40}Zr_{29}Cu_9Ni_8Be_{14}$ alloy having **higher plastic strain** (6.7 %) than $Ni_{60}Nb_{40}$ alloy (0 %) under compressive mode shows **multiple shear bands** during in situ straining.
- The branching of shear bands will delocalize the plastic deformation of BMG, thus prevents catastrophic failure.
- It is not clear yet where the shear band splits.

Preliminary study

Deformation behavior



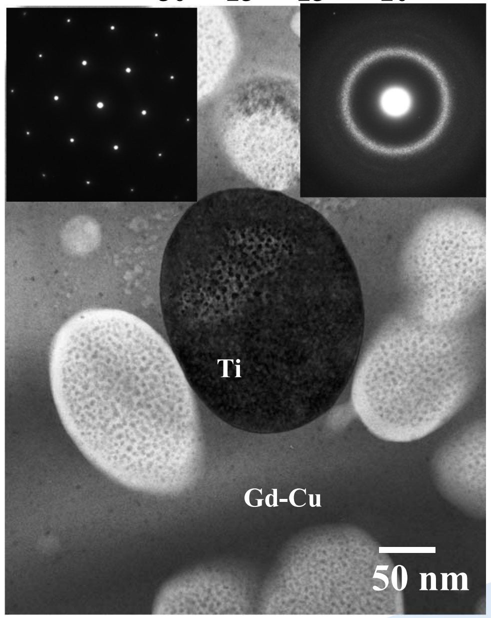
- **In situ straining shows no crystallization in the shear band in $Ti_{40}Zr_{29}Cu_9Ni_8Be_{14}$ alloy and $Al_{83}Ni_7Gd_6$ ($(T_x) = 195^oC$).**
  ⇒ No severe temperature increase during tensile test

Future works

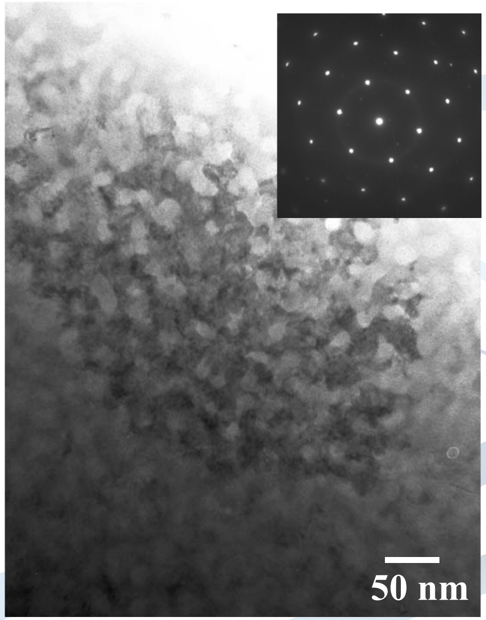
Mechanical property of phase separated composites

- Gd-Ti(Zr)-Al-Co alloy system
- 1 amorphous phase + 1 crystalline phase
- Droplet structure / interconnected structure

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



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

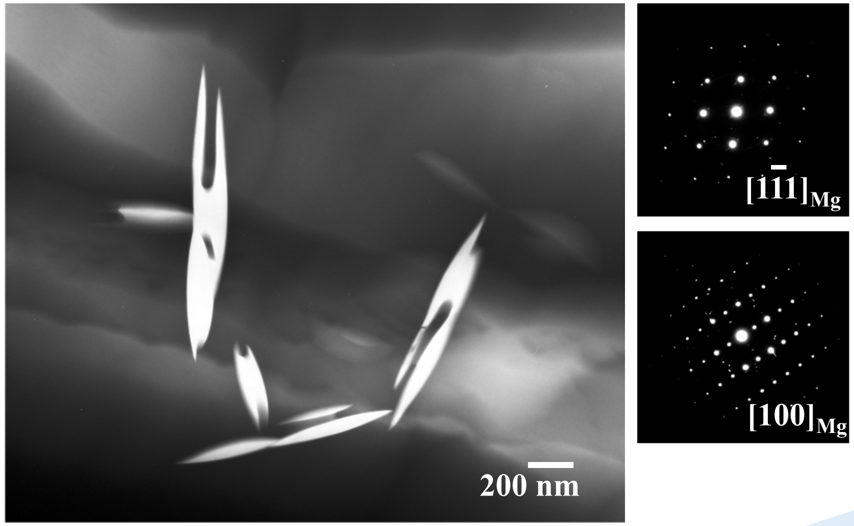


Future works

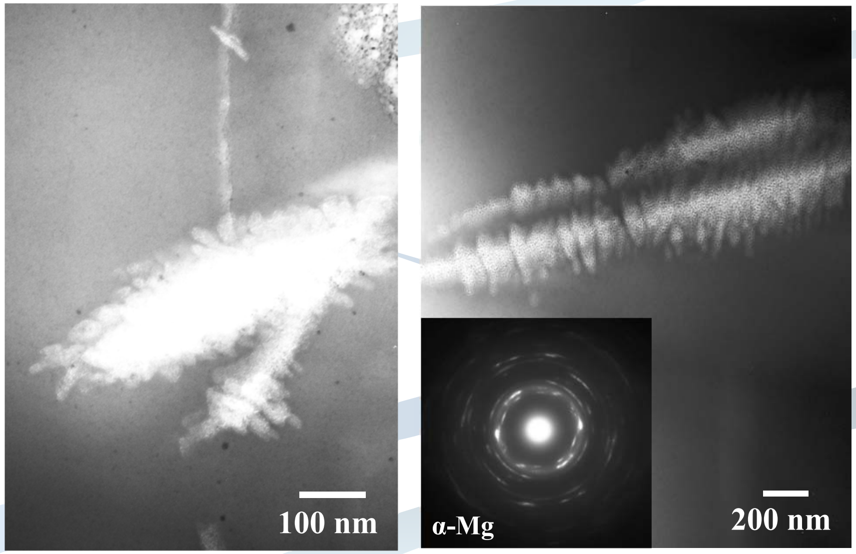
Deformation in Mg-based MGMC

- $Mg_{80}Cu_{15}Gd_5$
- Outstanding plasticity in Mg-based MGMC (ε_p = 3.5 %)
- Low temp. of crystallization at about 100 ℃ ☞ low thermal stability

Before compression test



After compression test



Future works

Size of plastic deformation zone in BMG

- Comparison in size of plastic deformed zone in several MG alloys
- Plasticity

☞ Quantitative correlation between size of plastic deformation zone and plasticity

Pure shear band excluding the effect of history

- Different effects of history on compression & tension mode test
- Frictional heating, fracture, sample geometry etc.
- Observation of shear band in interrupted compressive mode test

☞ Crystallization (adiabatic heating) in the shear band ?

Structural change in shear band

EELS (electron energy loss spectrum)
SADP (selected area diffraction pattern)

→

ELNES (energy loss near edge structure)
EXELFS (extended electron energy loss fine structure)
RDF (reduced density function)

→

Local coordination geometry
Density of free volume
Charge transfer

VEELS (valence electron energy loss spectroscopy) → Elastic property, Cohesive energy

☞ Amorphous structure of shear band / undeformed matrix using advanced TEM technique

- *Thank you* -