

Development of Al based metallic glasses

Current research issues

Advanced Research of Structural Materials

Opening seminar

2016. 03. 21

W. Kim





- ▶ **Motivation : Al-based MG for Ag paste media**
- ▶ **Al based Metallic glass & Alloy design**
 - **High entropy effect**
- ▶ **Statistical analysis of shear band by nano-indentation**
- ▶ **EXTRA : Phase separation metallic glass (Al-Pb)**

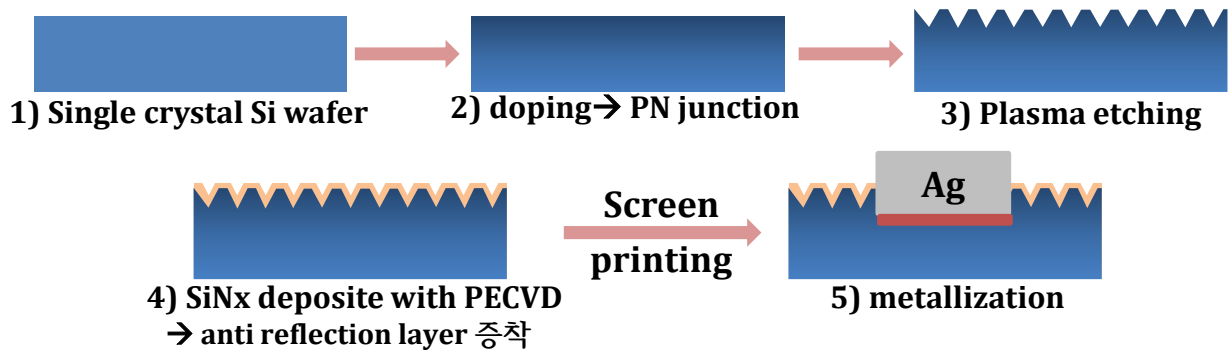
Motivation

Al-based metallic glass frit for Ag paste

Screen printing Si solar cell

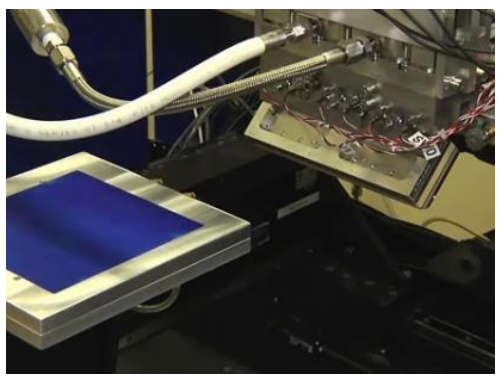
▶ 대면적 실리콘 태양전지 공정

“Screen printing process” 적용해 최대 효율 20%의 태양전지 제조가능

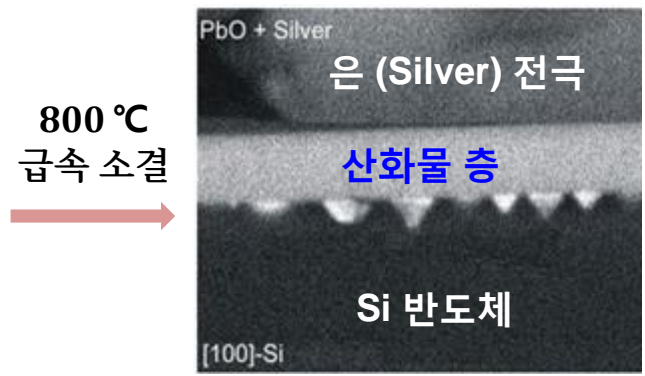


▶ Screen printing process

fine-mesh를 이용하여 Ag paste를 미세 도포 하는 공정법



1) Screen Printing을 통한 Ag paste의 미세 도포



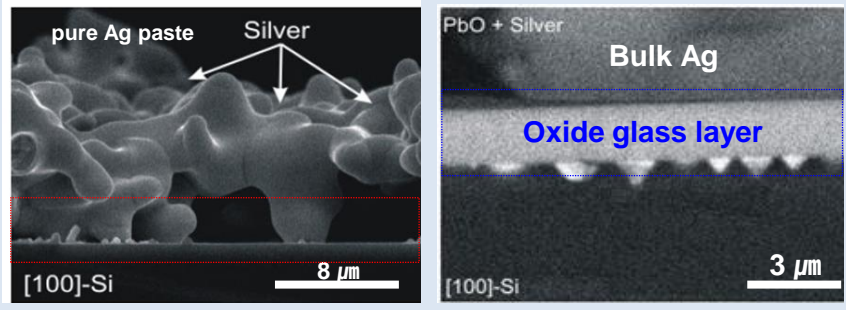
2) 소결을 통한 은 전극/Si 반도체 전기적 접합 가능

- Ag paste : silver + oxide + 유기물
- 1) Screen printing process : Ag paste 미세 도포
- 2) 도포된 Ag paste의 소결 : 은 전극-반도체간 전기적 접합

Role of PbO₂계 Oxide glass

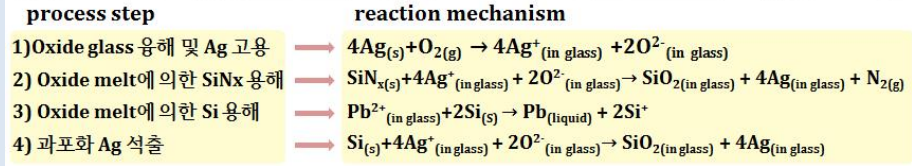
▶ PbO₂계 oxide 적용에 따른 장점 : Ag paste의 소결능 향상 → 전기전도성 증가

1) 소결능 향상 → 접합면적 증가 통한 전도성↑



<Ag 분말 단독 소결: 접합면적 ↓> <Oxide 첨가 소결: 접합면적 ↑>

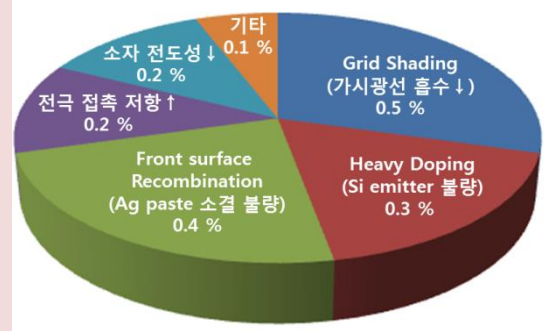
2) SiN_x 건식 에칭 가능 → 실질적인 전극 접합 가능



<Oxide의 건식에칭 메커니즘>

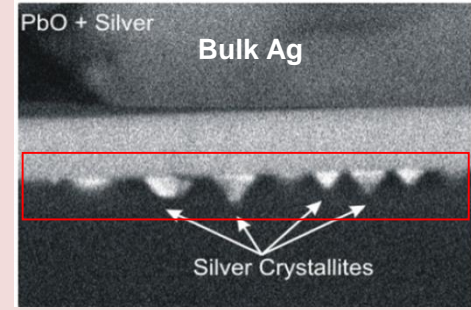
▶ PbO₂계 oxide 적용에 따른 단점 : 전기저항의 증가 → 소자 효율 감소

1) Oxide 적용 따라 최대 2% 효율 저하 발생



<요소별 태양전지 효율 감소율>

2) Ag crystal 석출 따른 전자 산란 발생



Ag 결정상 (최대 크기 1 μm)
 → 전자 산란 유발
 → 전기전도도 감소
 → 소자 효율 감소

<Oxide 의한 silver 결정상의 석출>

태양전지 효율 증가 위해 전기 저항성 높은 Oxide 대체 물질 개발 요구

Metallic glass를 적용한 신개념 Ag paste 개발

Oxide Glass



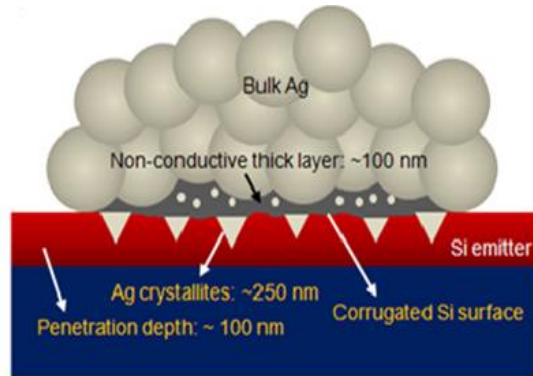
Metallic Glass

Ag powder의 소결 능력 향상

접촉면에 Ag 결정의 고른 분포를 통한 접촉저항 감소

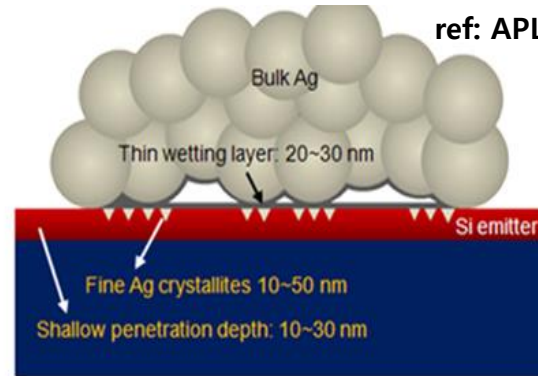
Ag 전극과 Si emitter 층의 두께 감소

스크린 프린팅 태양전지의 에너지 변환 효율을 획기적으로 개선



Ag/OG frit paste

Ag powder + Oxide glass + Organic vehicle



Ag/MG frit paste

Ag powder + Metallic glass + Organic vehicle

ref: APL, 98 (2011) 222112

▶ back plane용 MG/Ag paste에 **Metallic glass** 적용 통한 solar cell 효율 0.1% 개선 가능

↳ Al계 비정질 합금 적용한 front plane용 Ag paste 개발을 목표로 함

우수한 열적 특성 가진 AI 계 비정질 합금 개발

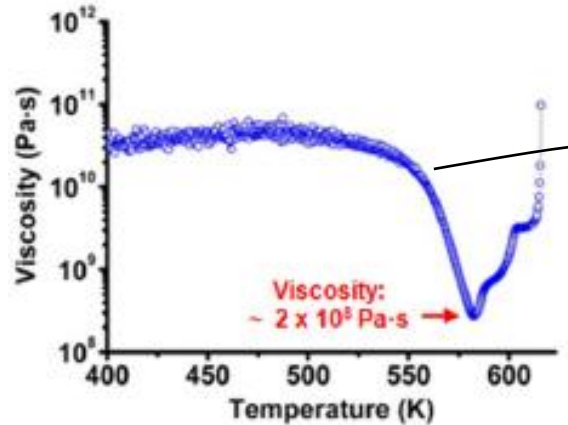
▶ 우수한 열적 특성 ($\Delta T_x \uparrow, T_m \downarrow$) 가진 AI 계 비정질 합금 개발 요구

젖음성 증가 위해 넓은 과냉각 액체영역 가진 합금 설계 요구

$$\frac{24\eta d}{8\gamma \cos\theta} \leq \frac{\Delta T_x}{R_{heat}} = t_{SCL}$$

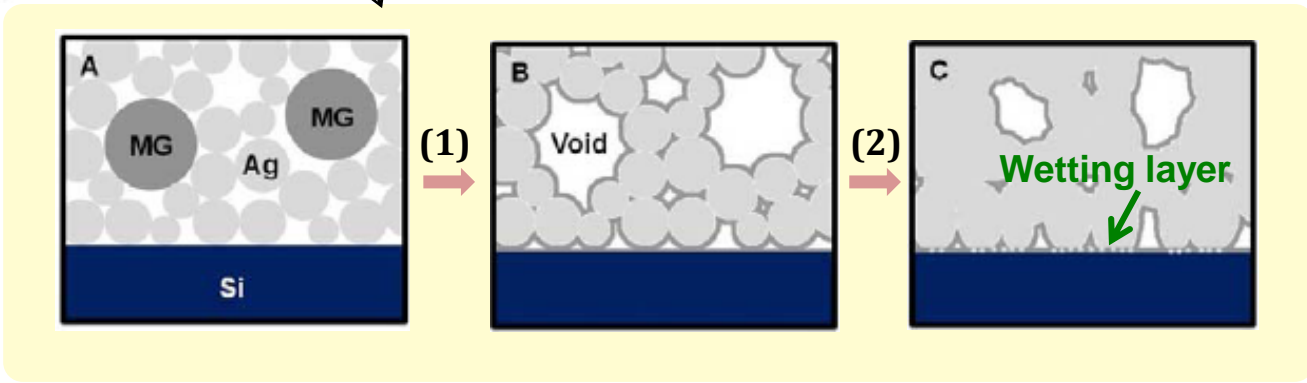
Ref : Scientific reports, 3 2185 (2013)

과냉각액체영역 증가 통해 Cavity filling에 따른 SCLR의 젖음성 증가 ($\theta \downarrow$)



급격한 점성 감소 (super cooled liquid)

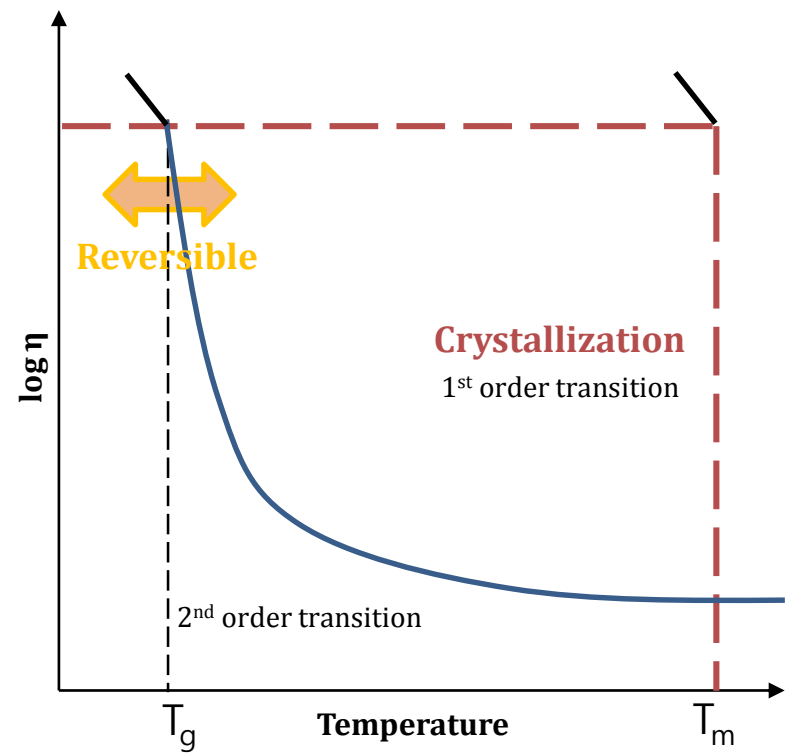
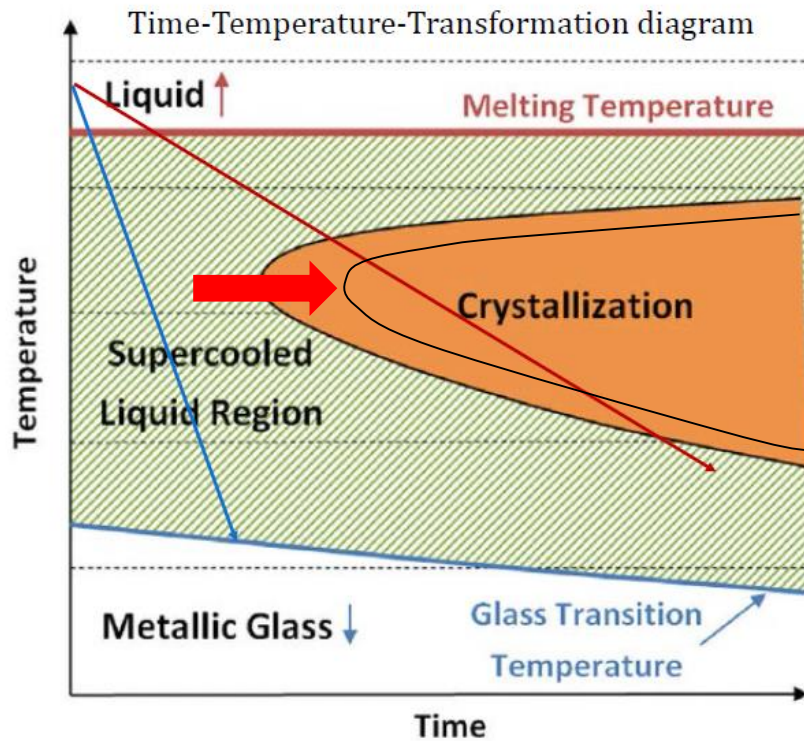
- Ag powder 내부로 모세관 확산
- Ag paste 소결능 및 전극접합성 향상



Metallic glasses



Metallic glasses



Glass forming ability

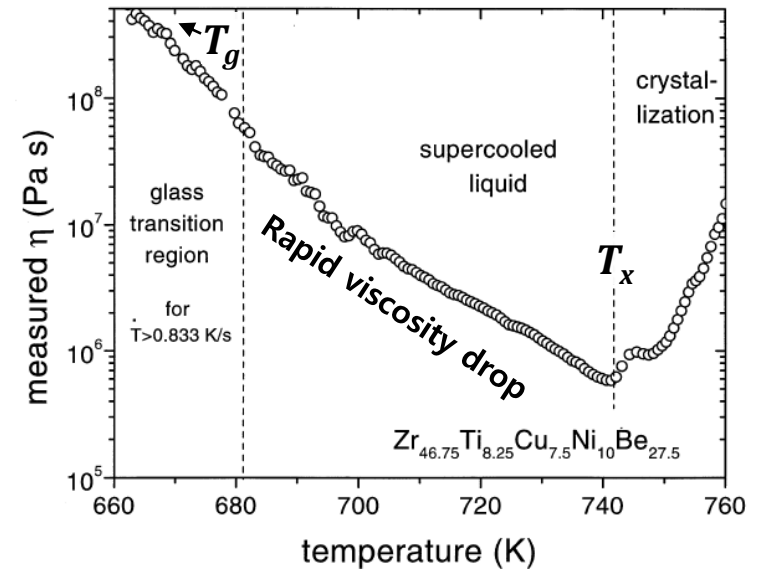
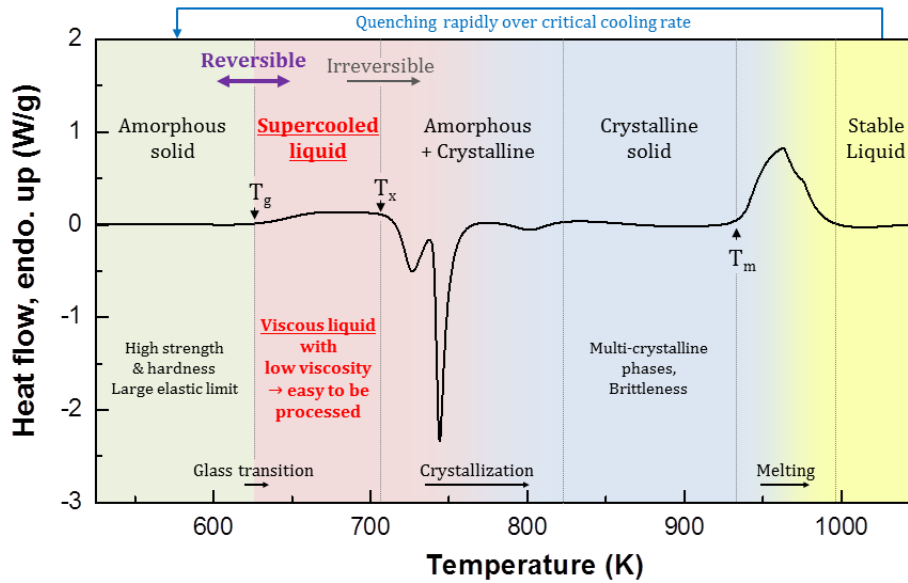
- Activation energy for nucleation ↑
- High initial viscosity of liquid
- High increase rate of viscosity

Glass transition

- Reversible 2nd order transition

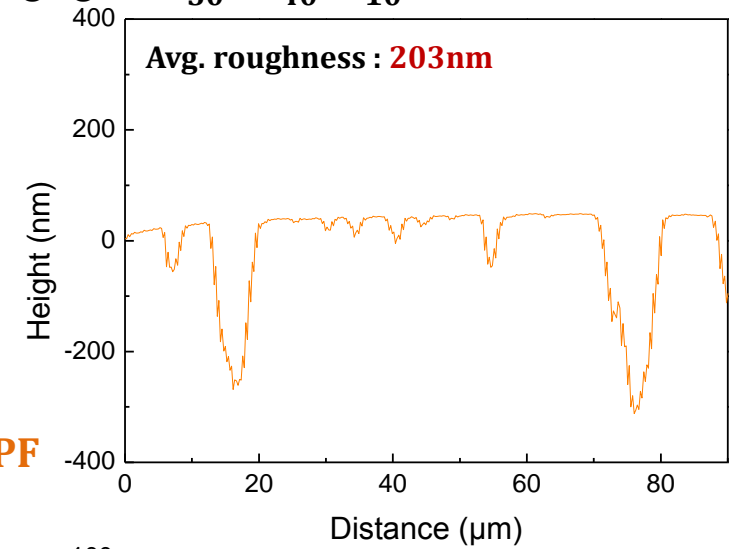
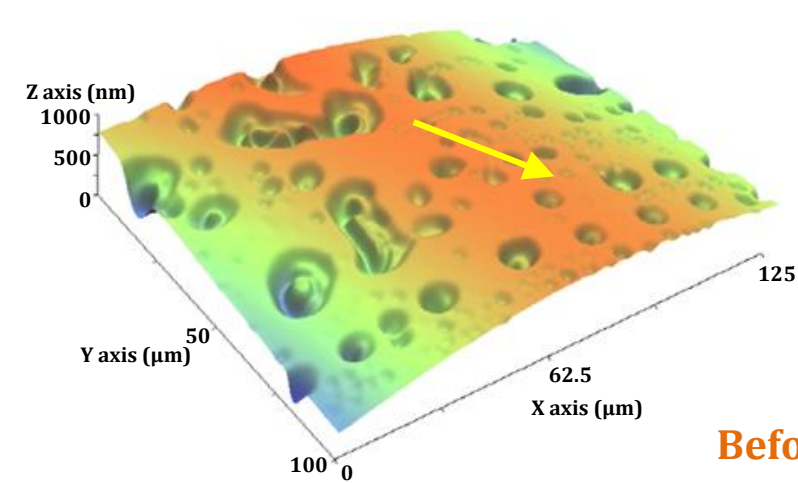
Thermo-plastic deformation

▶ 비정질 합금의 과냉각 액체 영역을 이용한 Thermo-plastic forming (TPF)



Thermo-plastic deformation

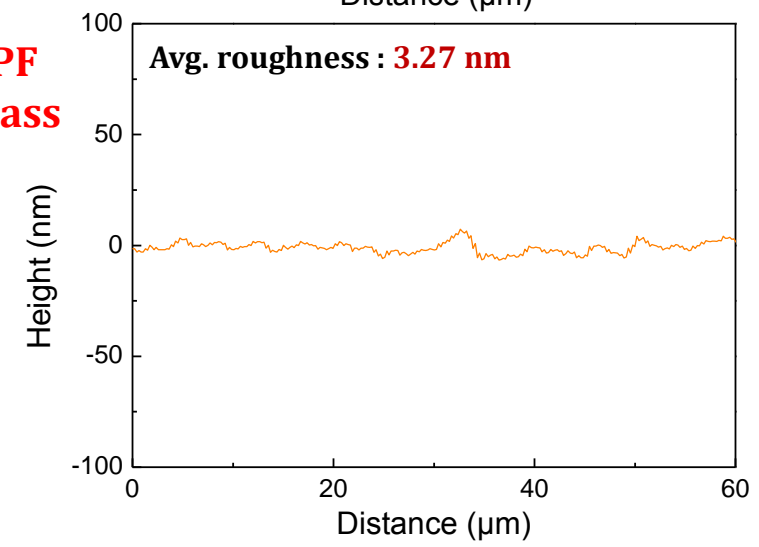
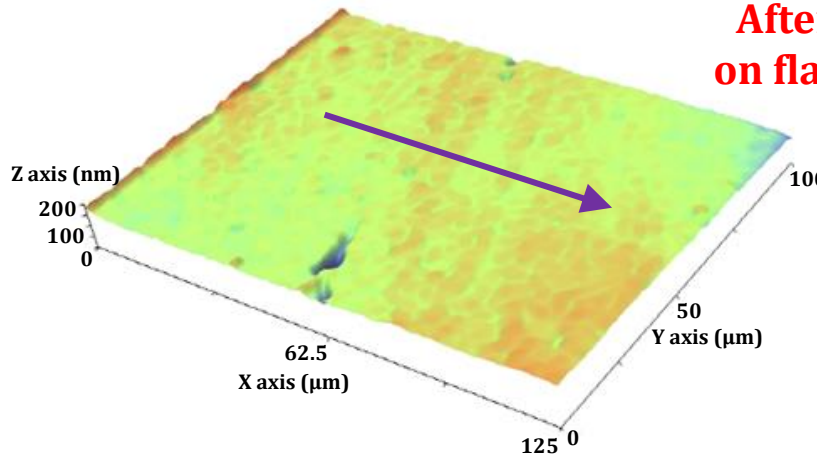
▶ 고온 환경 인장/압축 장치를 이용한 TPF 평탄화 공정 : $Zr_{50}Cu_{40}Al_{10}$ eutectic ribbon



Before TPF



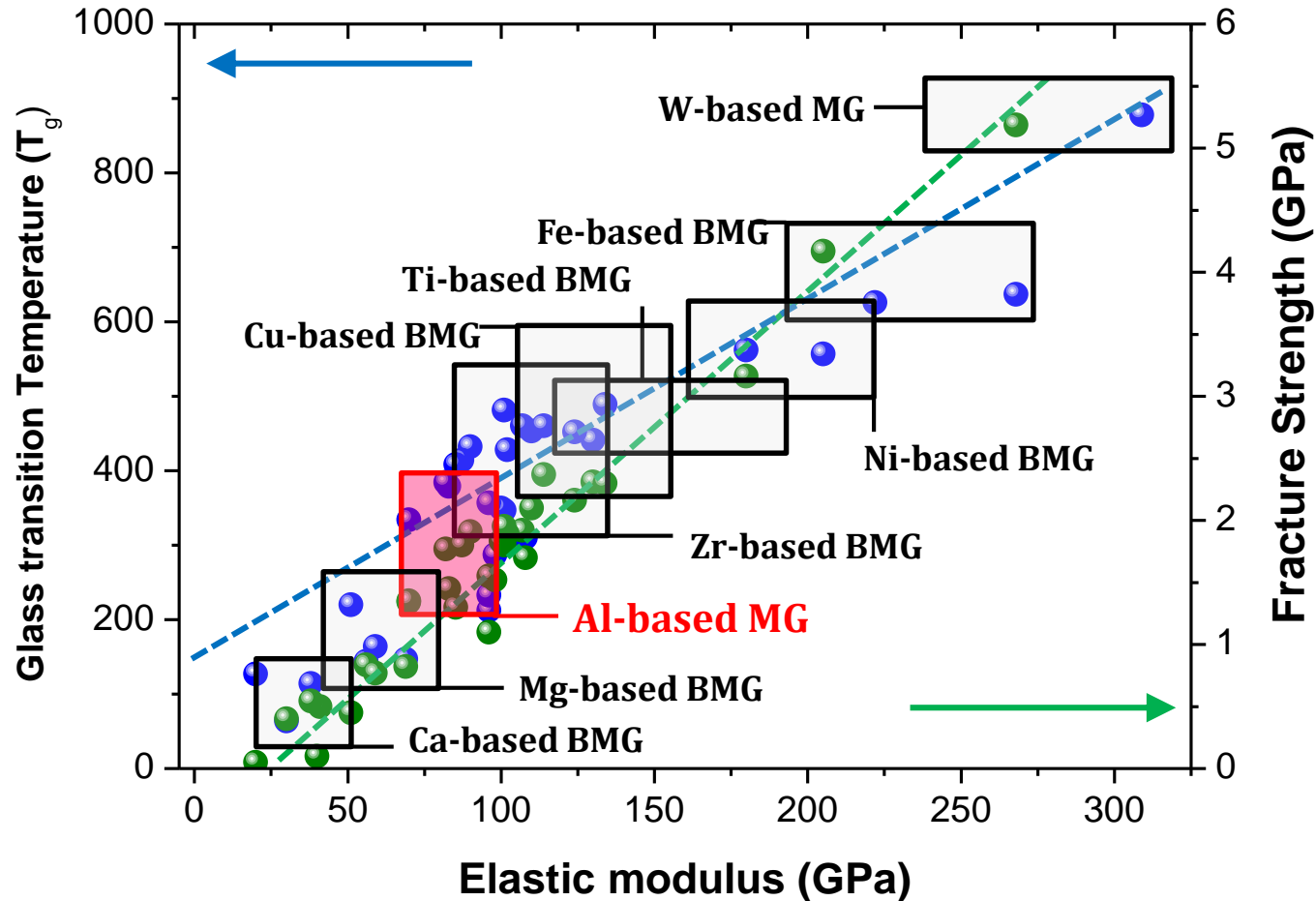
After TPF
on flat glass



200 nm 수준의 리본 표면 roughness → TPF 공정을 통해 수 nm 수준으로 평탄화 구현



Metallic glasses



For the conventional application

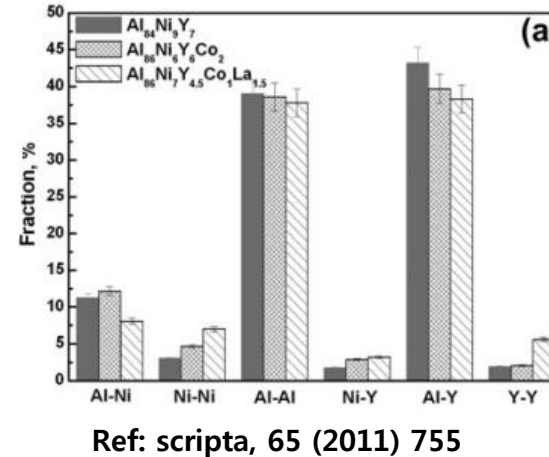
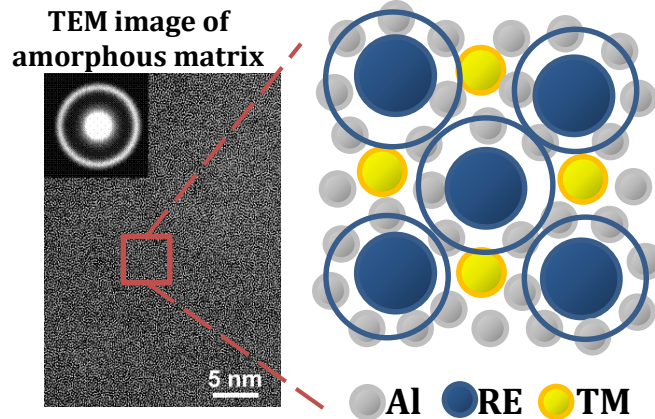
→ relatively low cost elements (Al > 80at%)

→ **Good mechanical properties (Strength > 1GPa)**

**Al-based Metallic glasses
: Development of thermal properties**

New Concept for Al-based MG design

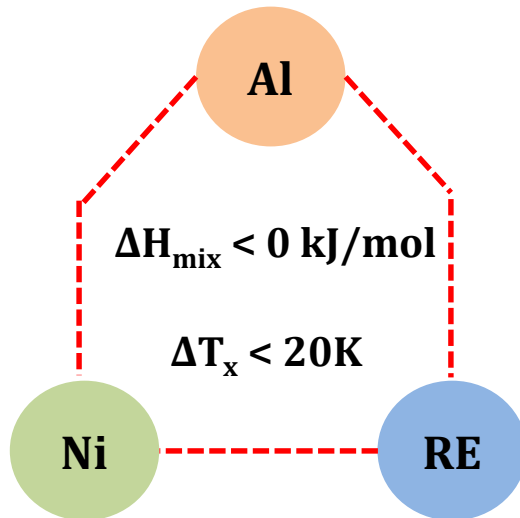
► Bonding nature of Al-based MG



Coordination #
Al-TM : 7~8

Al-RE : 16~18

► Addition of multi-component rare earth elements



ΔH_{mix}	Al	Ni	Ce	La	Nd	Y	Gd	Er
Al	--	-22	-38	-38	-38	-38	-39	-39
Ni	--	--	-28	-27	-30	-31	-31	-31

High entropy effect by multiple RE

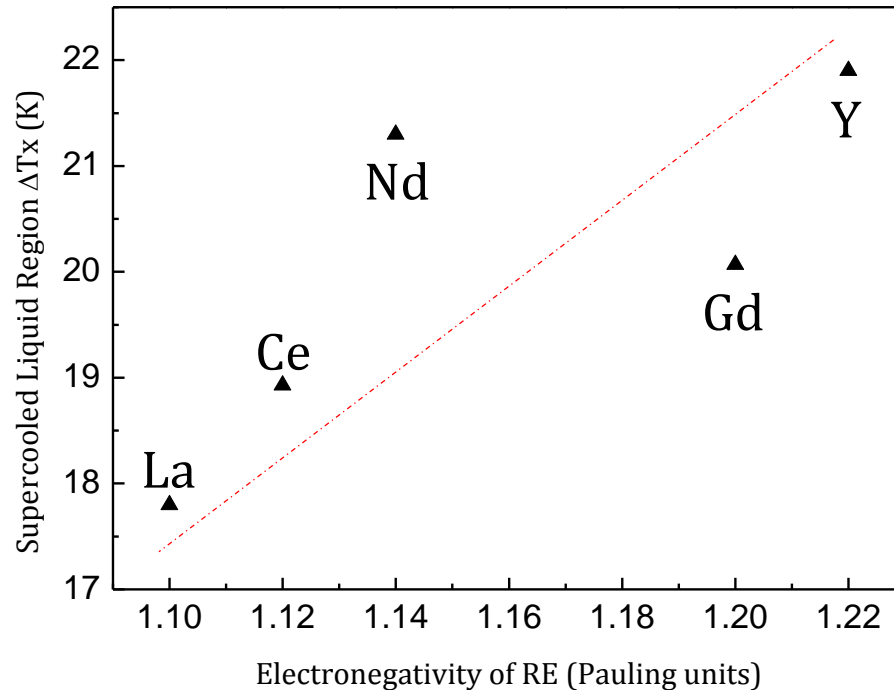
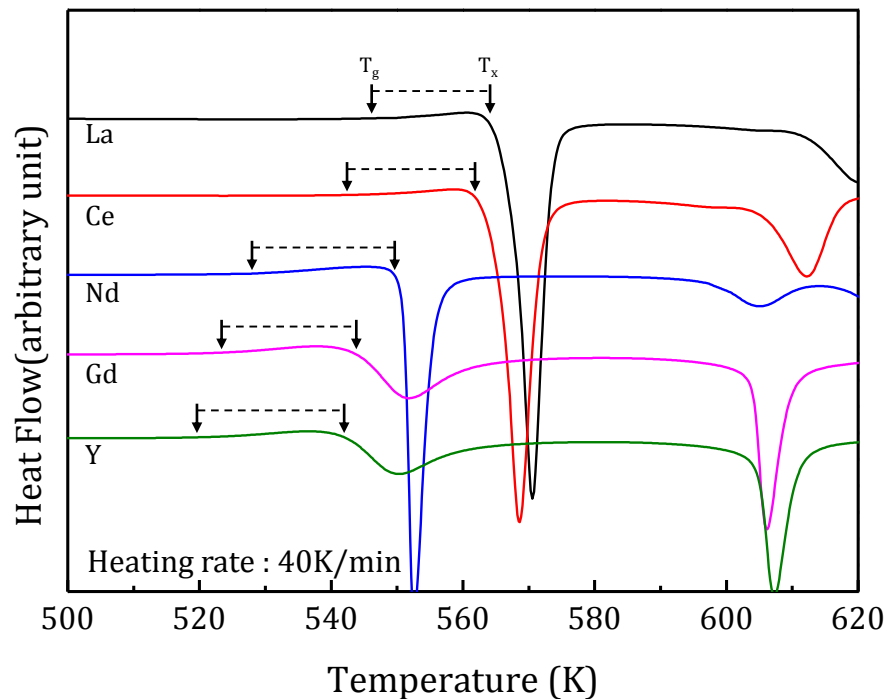
1. complex RE → complex bonding nature

2. liquid stability ↑

3. **Dramatic increase of ΔT_x**

Al-Ni-RE ternary system

▶ $\text{Al}_{84}\text{Ni}_{10}\text{RE}_6$ amorphous alloy system

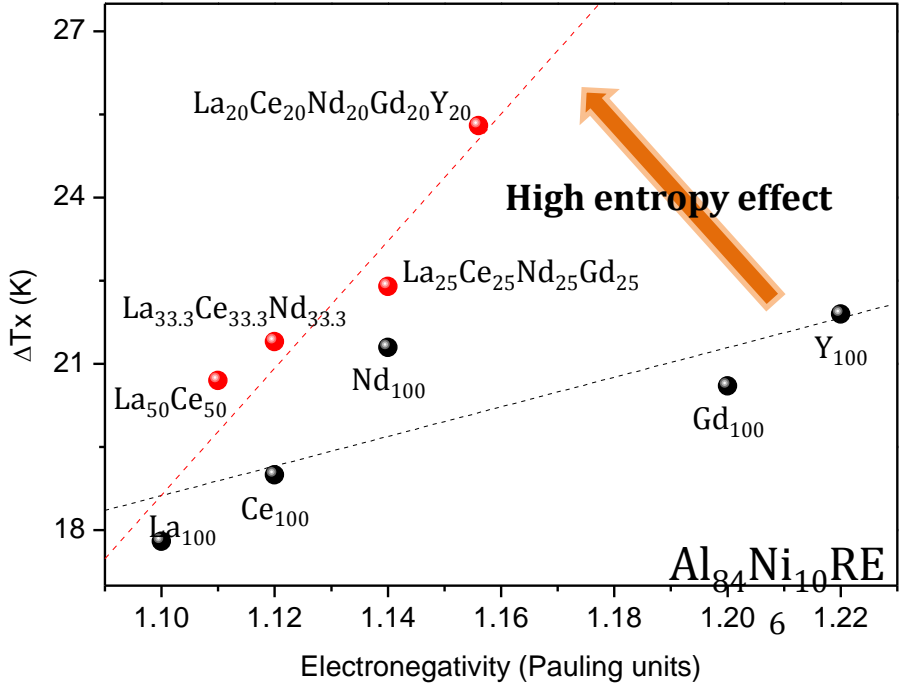
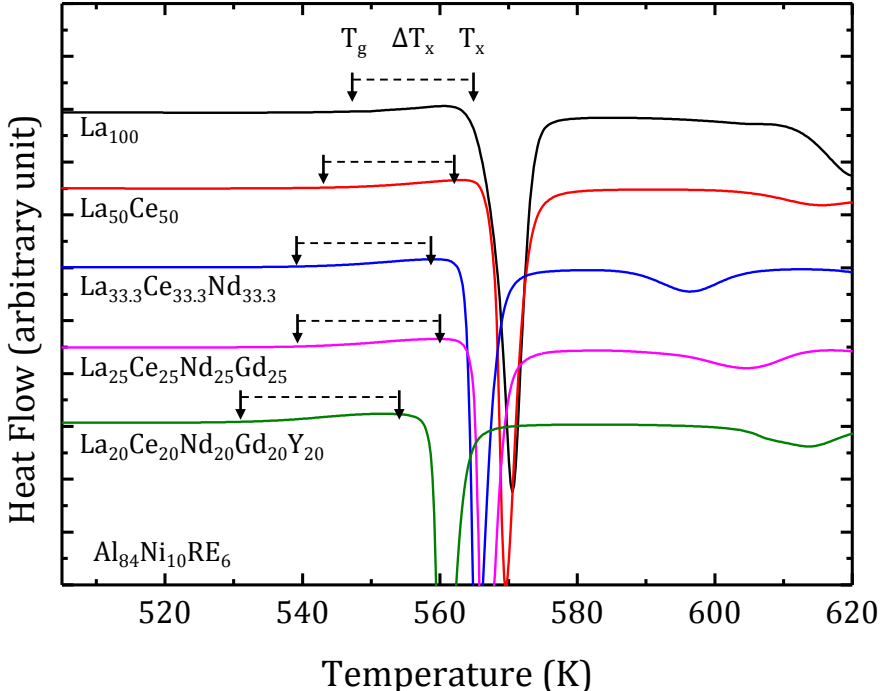


→ ΔT_x has linear relationship with ψ of RE elements.

$$(\text{Al}_{84}\text{Ni}_{10}\text{Y}_6 \Delta T_x = 21.5\text{K})$$

Multicomponent Al-based MG

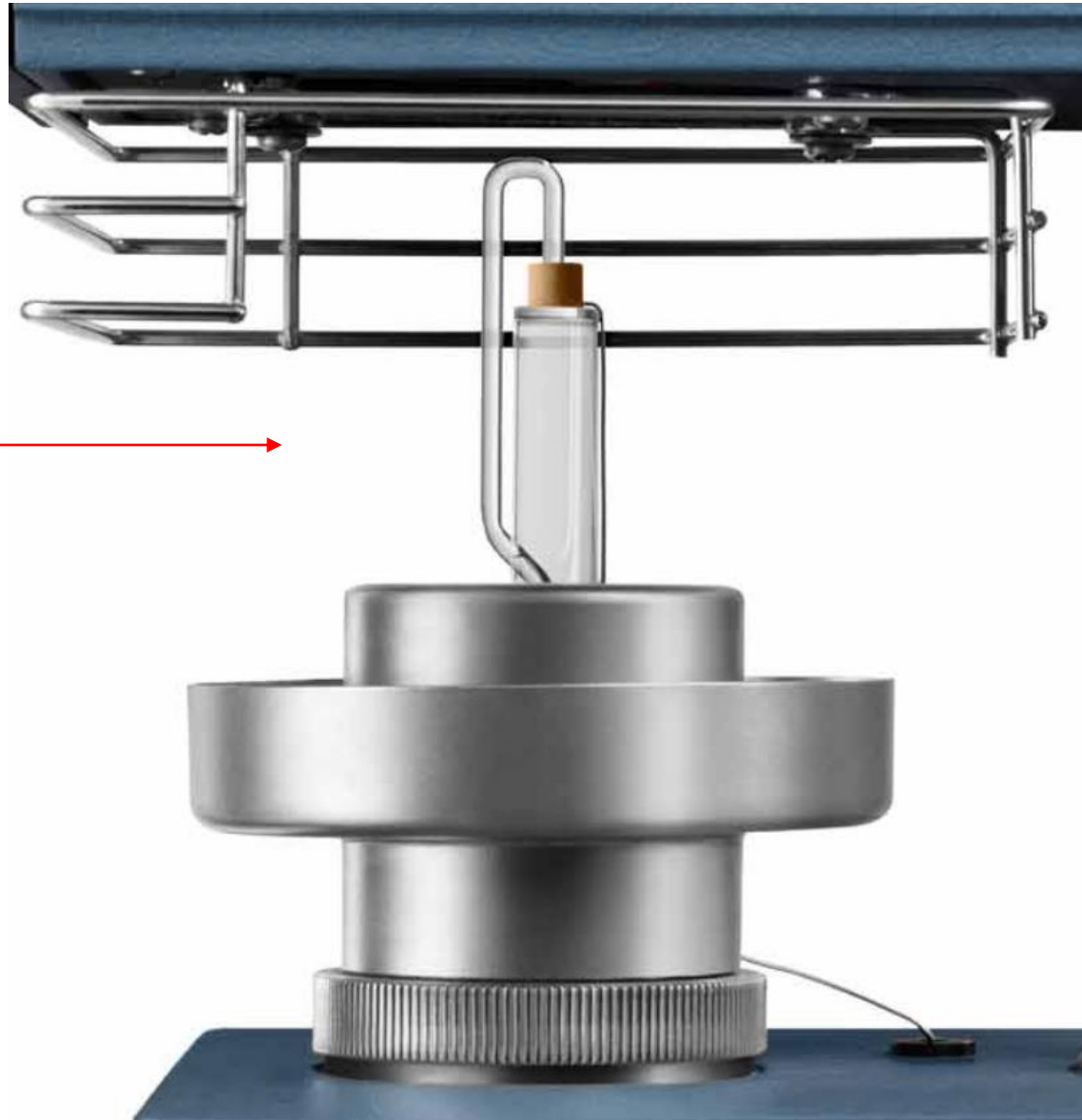
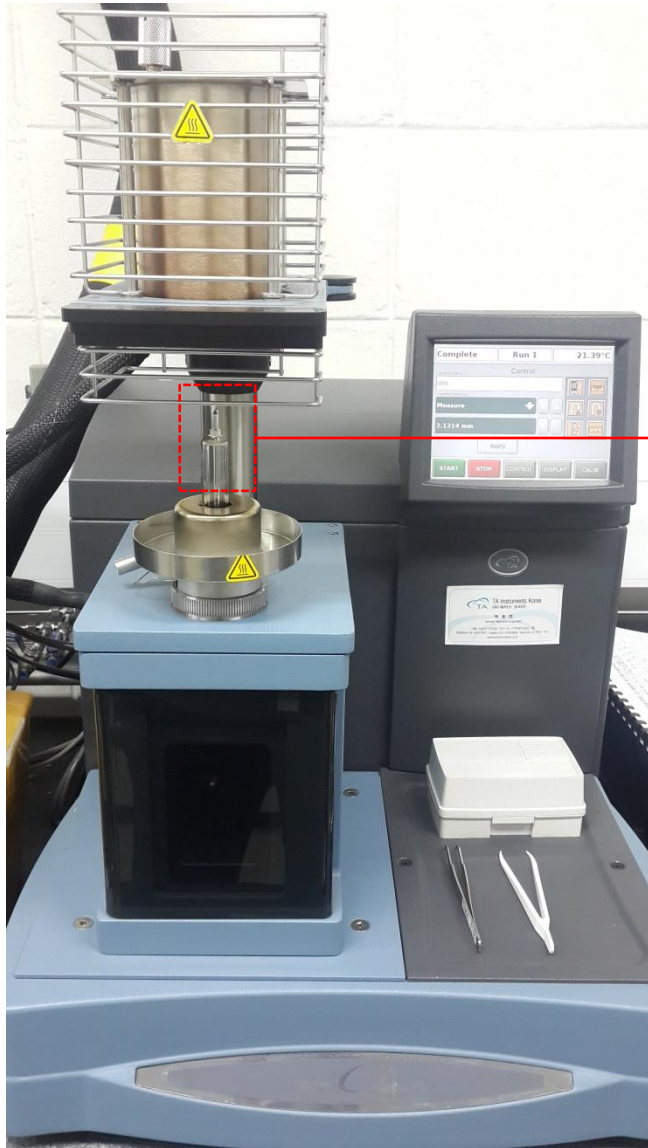
► $\text{Al}_{84}\text{Ni}_{10}\text{RE}_6$ amorphous alloy system

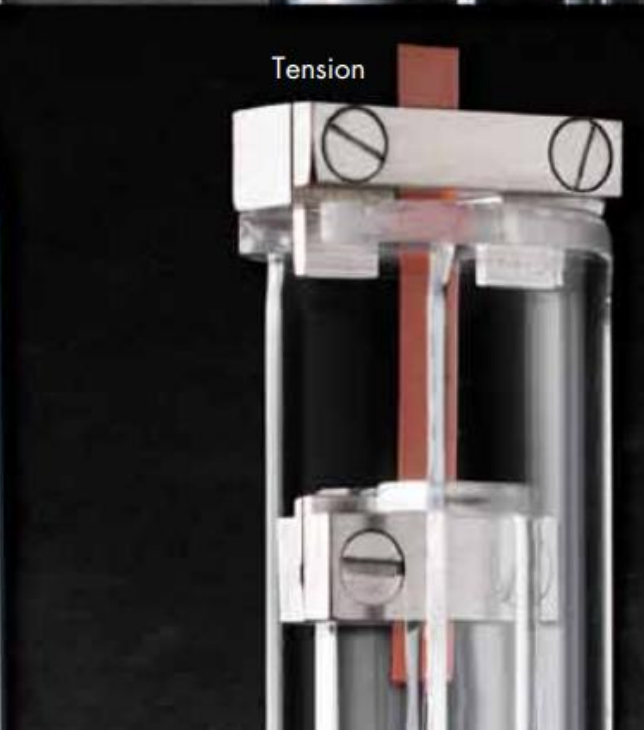
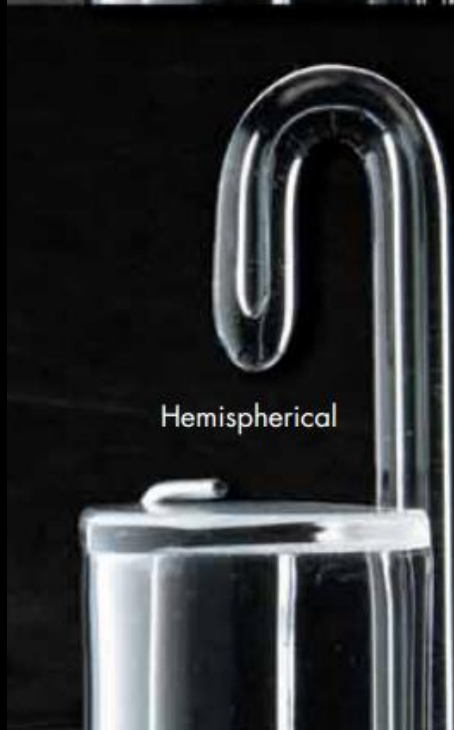


→ ΔT_x increase with number of RE elements
 $(\text{Al}_{84}\text{Ni}_{10}(\text{LaCeNdGdY})_6 \Delta T_x = 25.5\text{K})$

Q: Increase of ΔT_x = Liquid stability & viscosity change?

Thermomechanical analyzer (TMA)

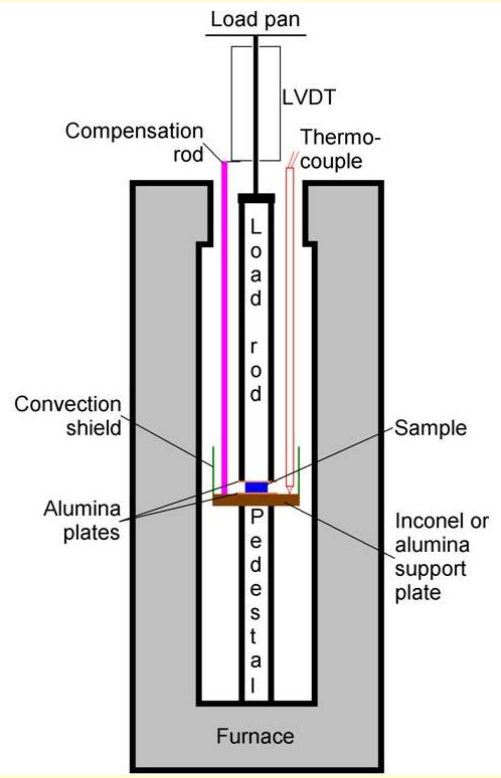




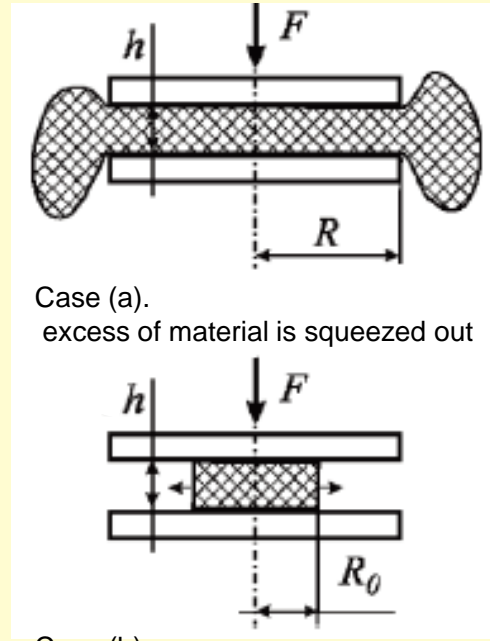


Viscosity in compression : Parallel plate rheometer ($10^5 \sim 10^9 \text{ pa}\cdot\text{s}$)

► Applied Stefan equation



$$\eta = \sigma / 3\dot{\epsilon}$$



Case (a).
excess of material is squeezed out

Case (b).
Squeezing sample of constant volume

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + \eta \nabla^2 \mathbf{v} + \frac{1}{3} \eta \nabla \nabla \cdot \mathbf{v}$$

The general vector eq. of motion of a Newtonian fluid

$\delta v_r / \delta t = 0$ (Steady state flow)
 $R > 10 h$ (Thin plate sample)

$$F = -2\pi \frac{dh}{dt} \frac{3\eta}{h^3} \int_0^R (R^2 - r^2) r dr$$

For case (a), $R = \text{constant}$

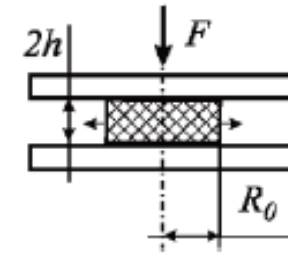
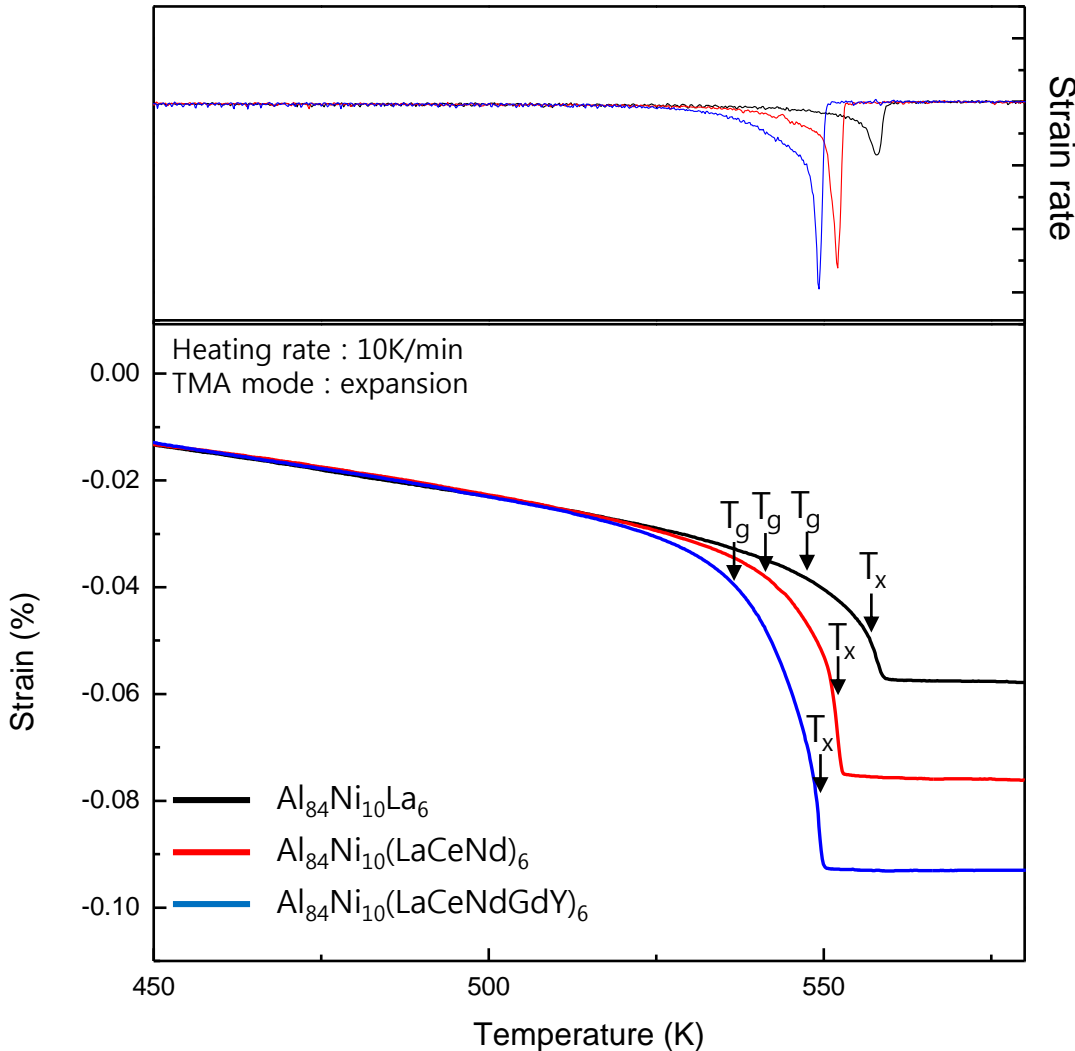
$$F = -\frac{3\pi\eta R^4}{2h^3} \frac{dh}{dt} \quad (\text{Stefan equation})$$

For case (b), R changes with t but $V = \text{constant}$

$$F = -\frac{3\eta V^2}{2\pi h^5} \frac{dh}{dt} \quad (\text{From Dienes and Klemm})$$

Viscous flow of Super cooled liquid

► Strain of Super cooled liquid



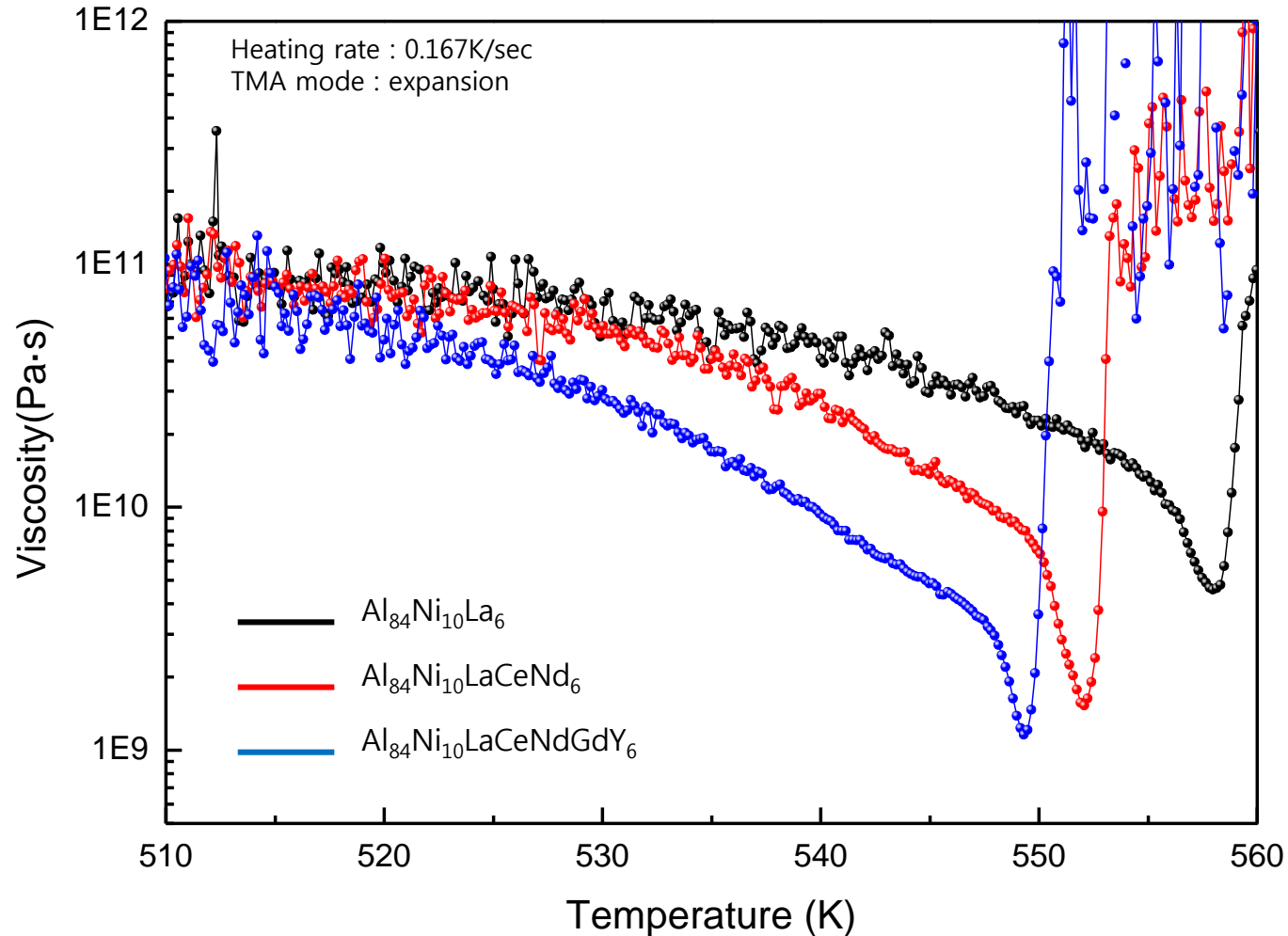
Case (b). Squeezing sample of constant volume

Heating rate 10K/min	T _g . TMA	T _x . TMA
Al ₈₄ Ni ₁₀ La ₆	546.5	557.9K
Al ₈₄ Ni ₁₀ (LaCeNd) ₆	539.9	552.1K
Al ₈₄ Ni ₁₀ (LaCeNdGdY) ₆	538.3	549.3K

NEXT STEP

By applying of Stephan equation
→ Calculation of viscosity

Viscous flow of Super cooled liquid



Increase of $\Delta T_x \rightarrow$ Decrease of viscosity
 \rightarrow Good for TPF & precise fabrication

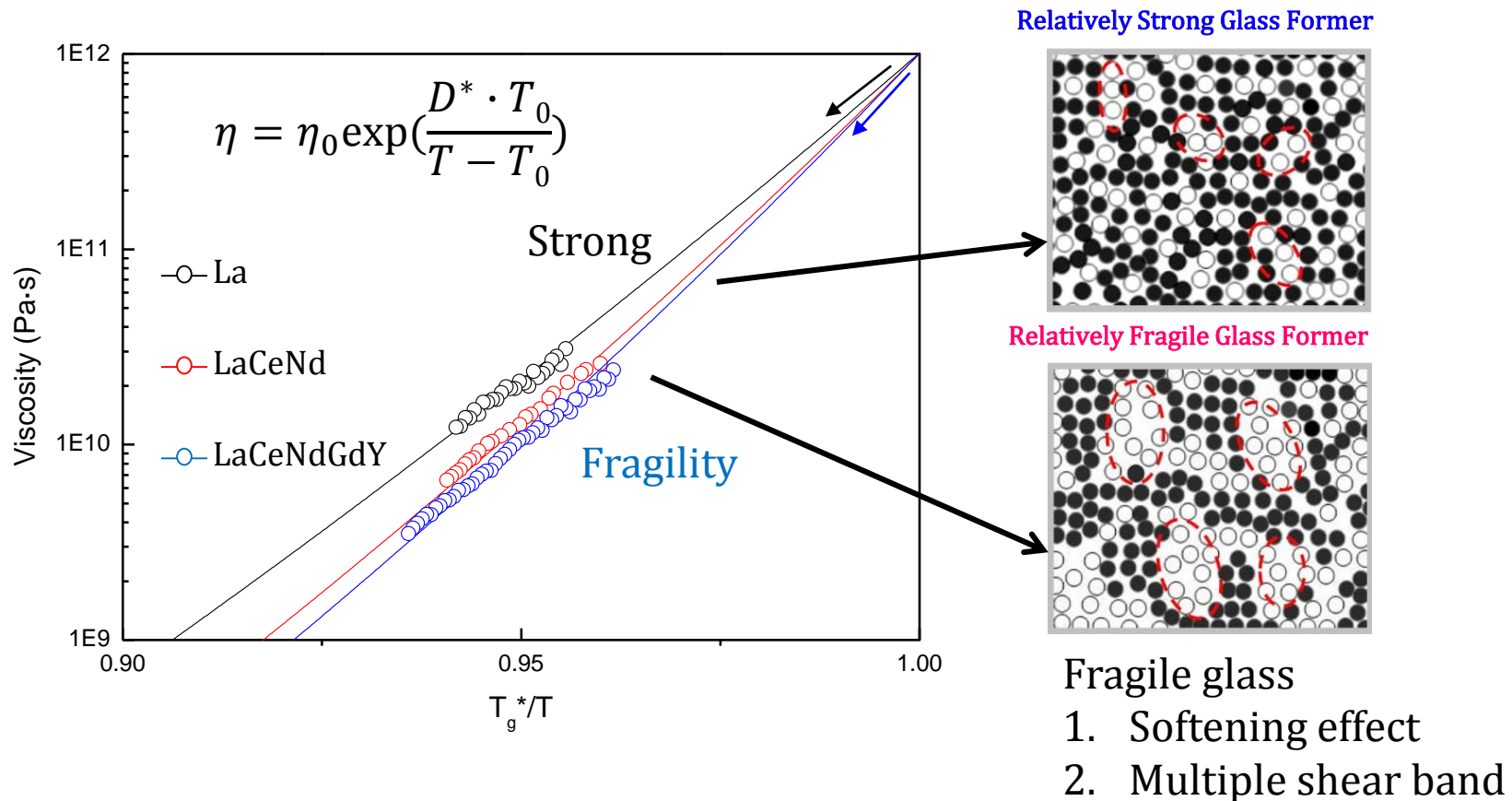
Kinetic fragility

► Strain of Super cooled liquid

Fragility

: liquids are classified as strong glass & fragile glass (by D. Angell)

→ good glass forming alloy : strong liquid with a high viscosity

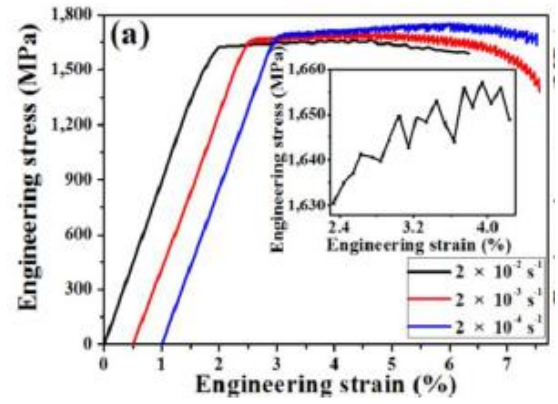
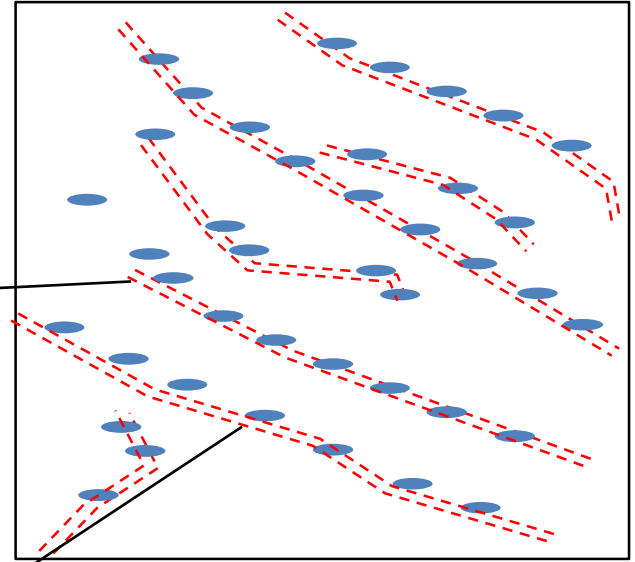
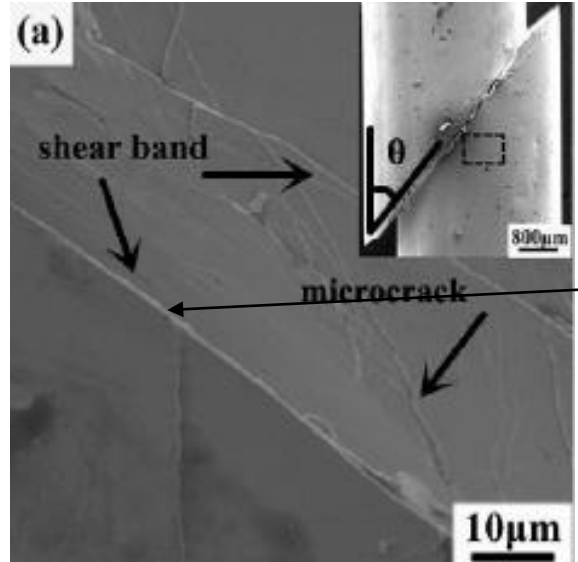


Effect of free volume on mechanical properties

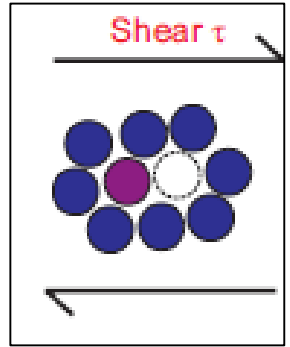
→ Statistical analysis by complexity(SOC)

Plastic deformation of BMG

► Shear bursting : Sum of free volume



<Serration by shear band deformation>



Free volume

Interaction between matrix & Free volume & 2nd phase

→ Control the ductility of metallic glass
: multiple shear band or decrease the cut off size

Self-organization

▶ Self organization

자기조직화 → 무질서 복잡계속의 규칙성

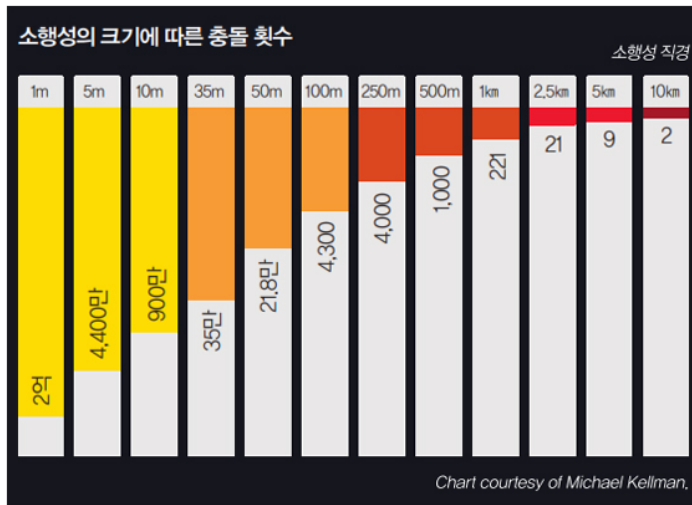


Plan & Design → Organization

Ex) parts + parts + parts + = machine
조직화 하고 난 뒤 조립

Interactions of local parts → Organization

Ex) Cells + Cells + Cells = Organics
만들어지고 나서 조직화



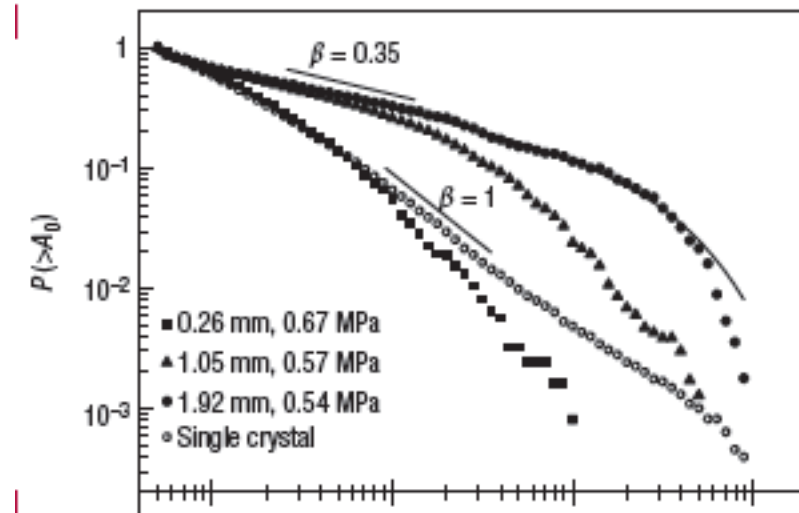
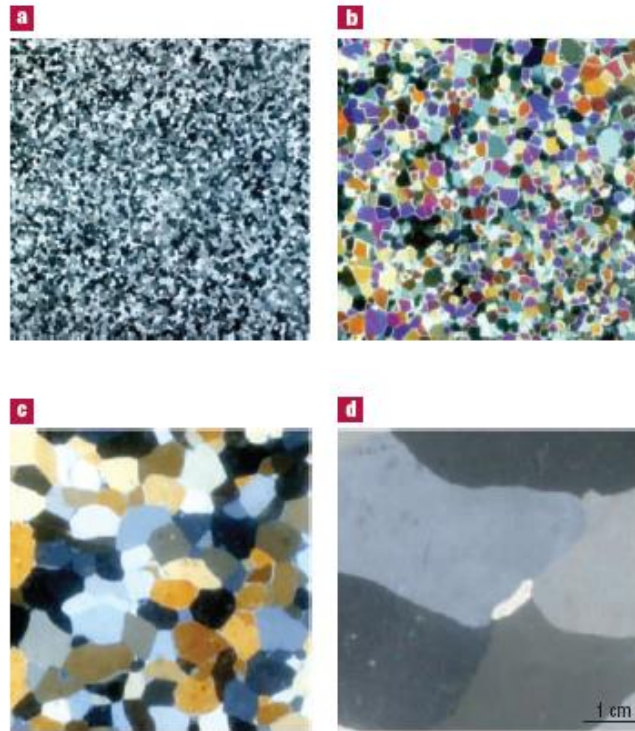
→ 각각의 개발적은 크고 작은 사건
ex) earthquake, Comet impact, car crash,

서로간에 영향은 주지 않으나, 큰 흐름에서 보았을때, 사건발생의 규칙성이 있다.

→ complexity & SOC

Self-organized critical

▶ Grain size effect the dislocation avalanche size



$$P(> S) = AS^{-\beta} \exp\left(\frac{-S}{S_c}\right)$$

Beta : scaling exponent

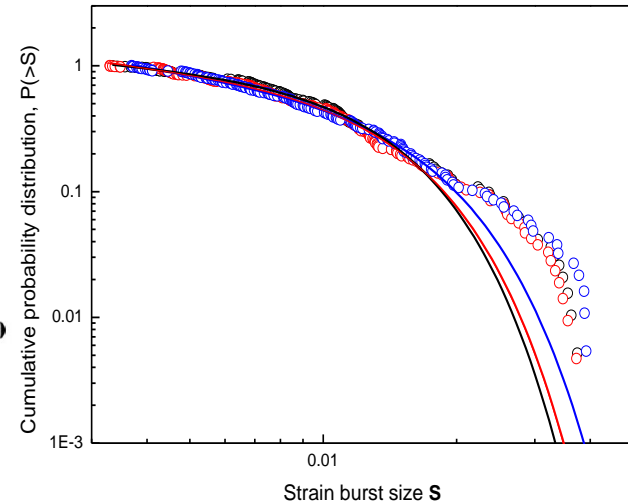
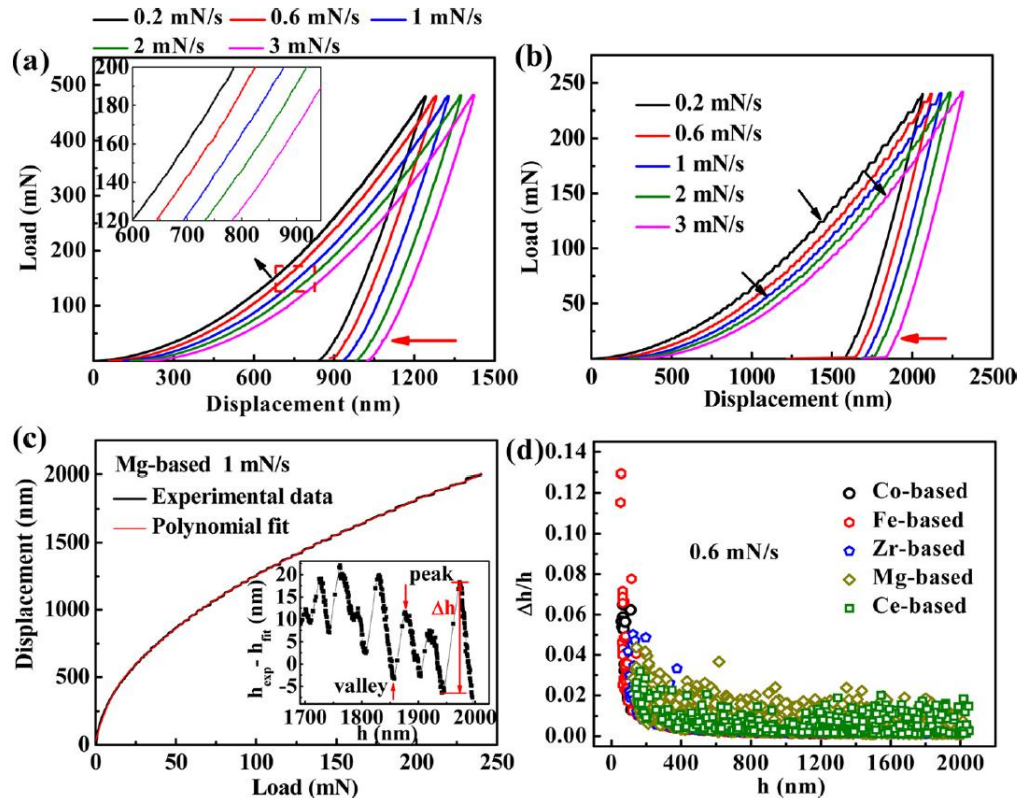
Sc : cut off of strain

Single crystal ($\beta=1$), \gg grain with 1.92($\beta=0.35$)

- High beta value : close to self-organized state
Jamming state : statistically high level of interactions btw disl, matrix
- Low beta value : relatively chaotic state
Unjamming state : low level of interactions

Evaluation SOC in metallic glass

► Pop-in of nano-indentation



$$P(> S) = AS^{-\beta} \exp\left(\frac{-S}{S_c}\right)^2$$

β : scale exponent

→ high β value = SOC state
: Jamming state

→ low β value = Chaotic state
: Unjamming state

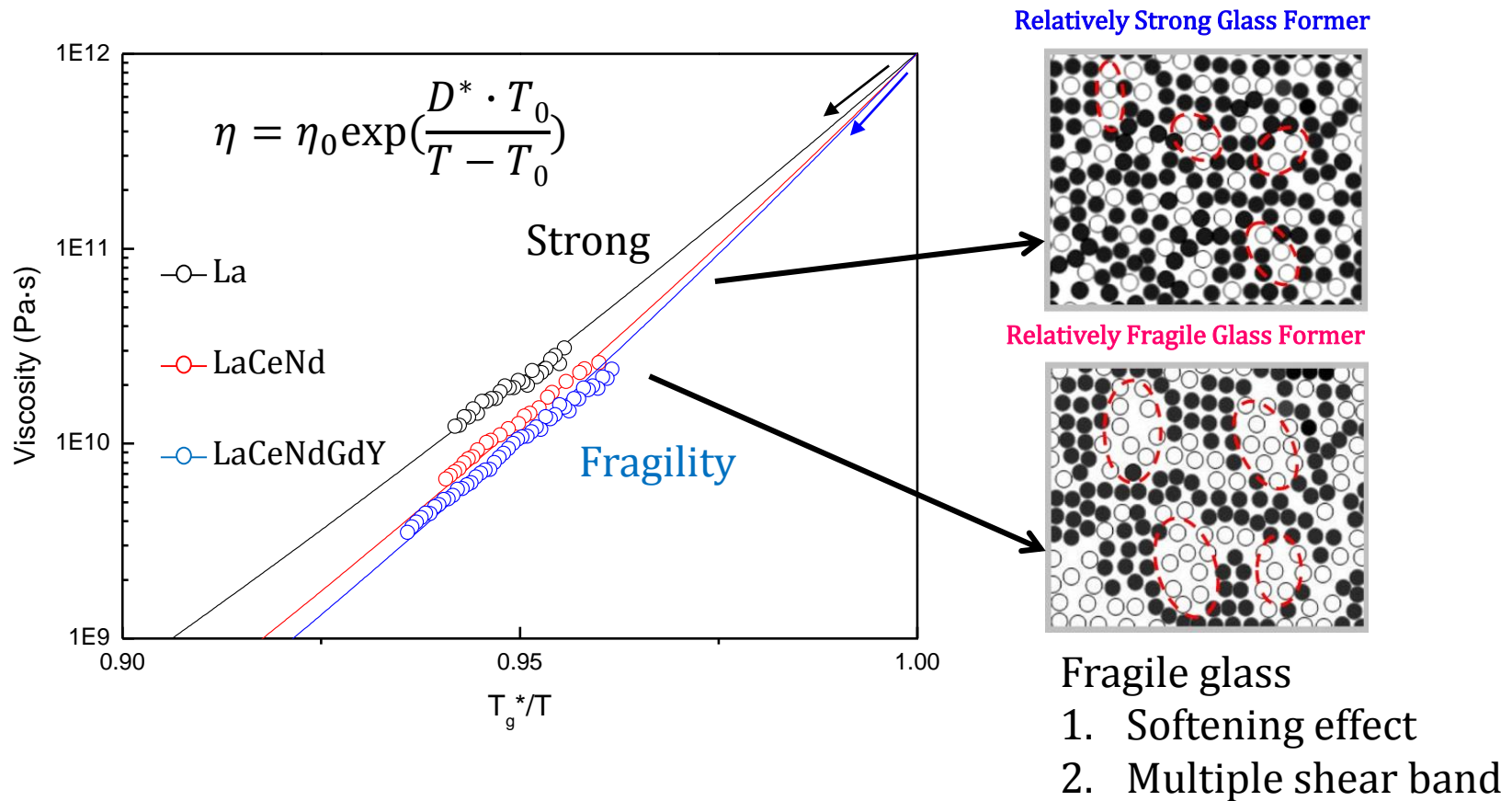
Kinetic fragility

► Strain of Super cooled liquid

Fragility

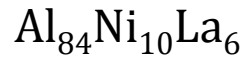
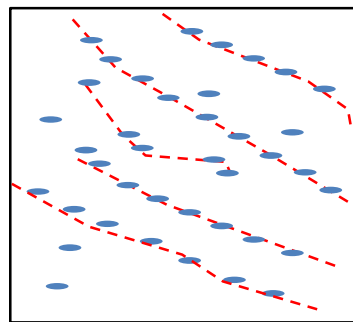
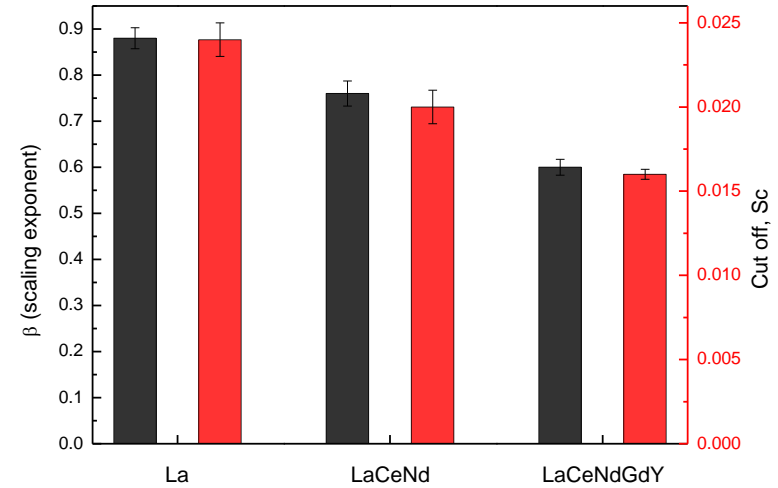
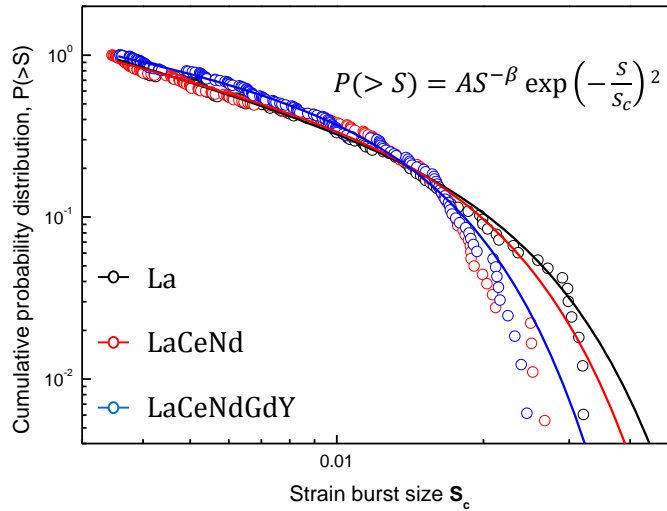
: liquids are classified as strong glass & fragile glass (by D. Angell)

→ good glass forming alloy : strong liquid with a high viscosity



Statistical analysis depending on fragility

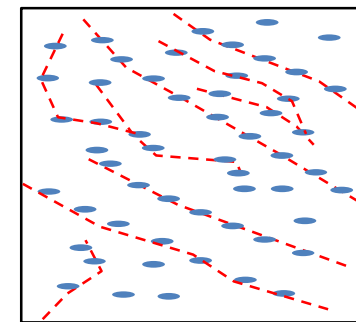
► Effect of free volume on



Fragility \uparrow
Free volume \uparrow
Chaotic deformation



Multicomponent
High entropy effect

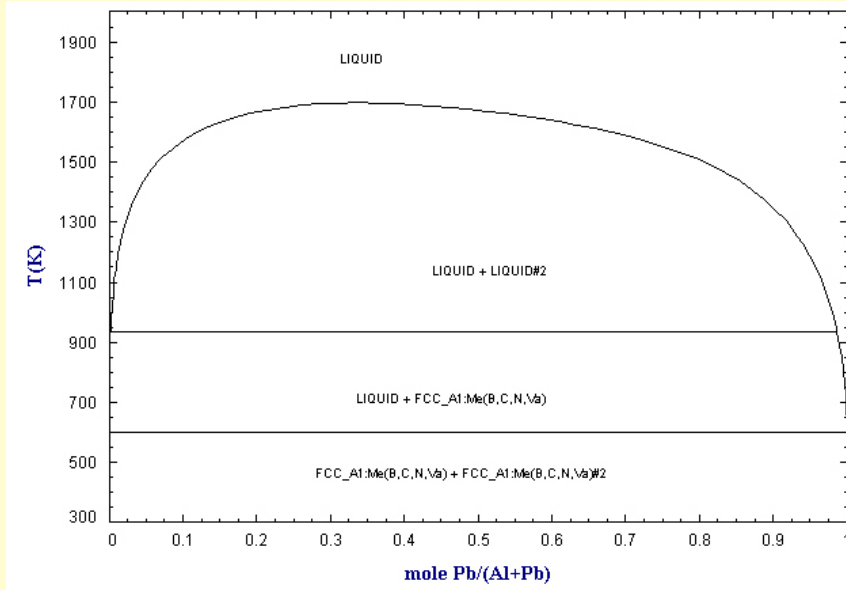


Phase separated Al-based metallic glass

→ Bending & fatigue test

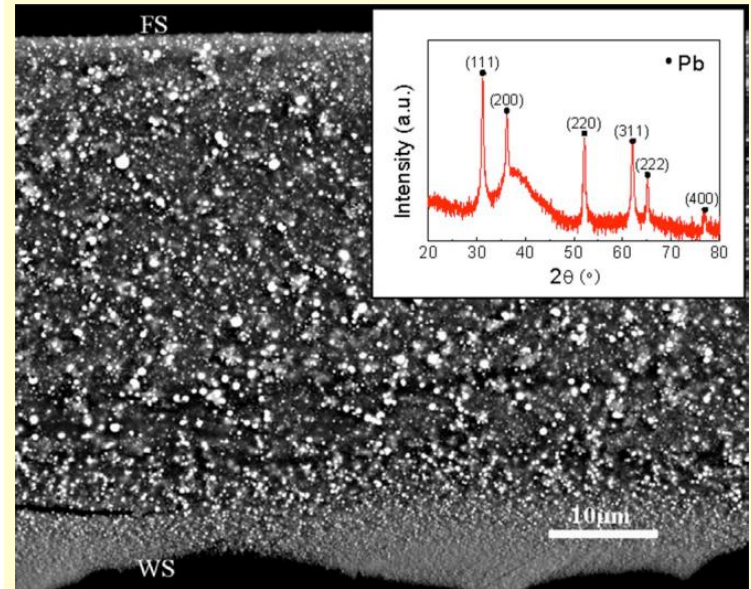
Al-Pb 상분리 합금을 이용한 Ag paste

▶ Al - Pb 상분리 비정질 합금 개발 → 건식 에칭 가능 Al계 비정질 신합금



Al-Pb phase diagram

Ref: APL, 93 (2008) 131907



$\text{Al}_{82.87}\text{Ni}_{4.88}\text{Co}_{1.95}\text{Y}_{7.8}\text{Pb}_{2.5}$
상분리 합금 SEM 이미지

→ Al-Pb 이원계 시스템 전체 조성에서 miscibility gap 보유
: Al-Pb 고용체의 부재로 인한 상분리 현상

→ 상분리 된 Pb-rich phase: SiN_x 건식 에칭 메커니즘 보유 예상

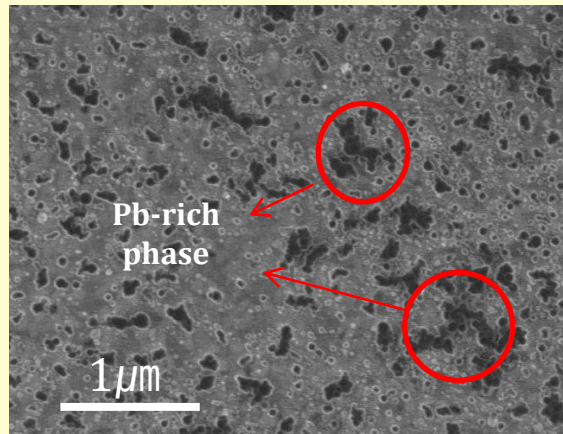
Al-Pb 상분리 합금을 이용한 Ag paste

▶ Al - Pb 상분리 비정질 합금 개발

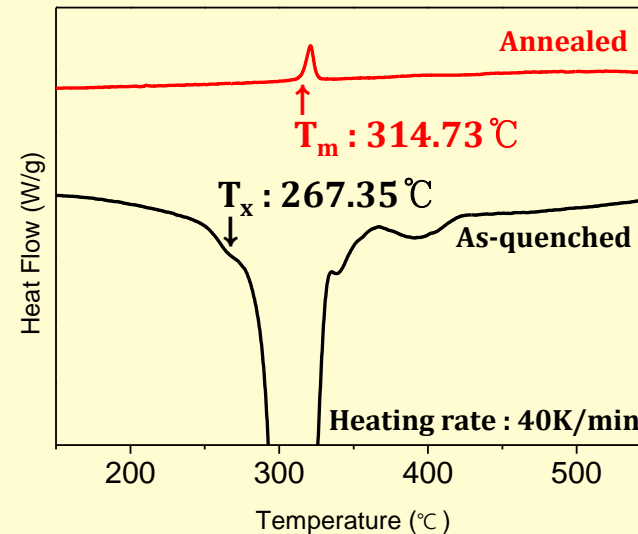
→ AlNiMM 비정질 시스템에 **Pb** 소량 첨가를 통해 **Pb-rich phase 상분리 가능 확인**

→ 300 nm 수준의 Pb-rich phase 다수 석출 : SiN_x 건식 에칭 가능여부 확인 요구

Al-Pb 상분리 합금 SEM 이미지



(Al₈₄Ni₁₀MM₆)₉₇Pb₃ DSC 열분석 결과



▶ 추후 설계 방향 : Pb 절감 친환경 Ag paste 개발

Pb rich Al-Pb 상분리 합금 개발

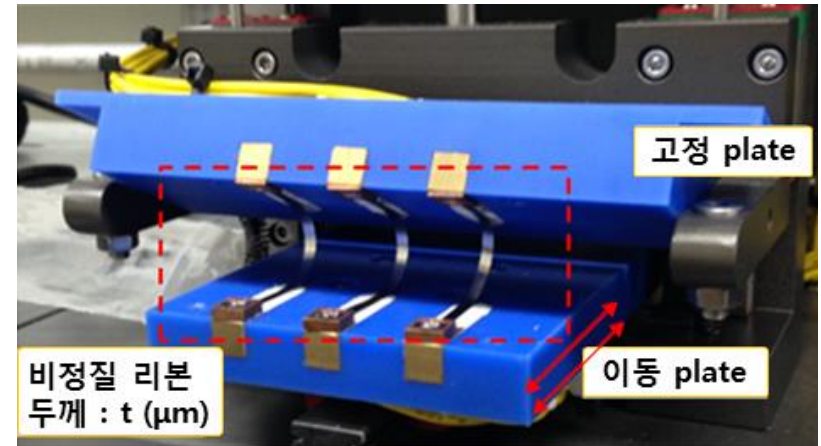
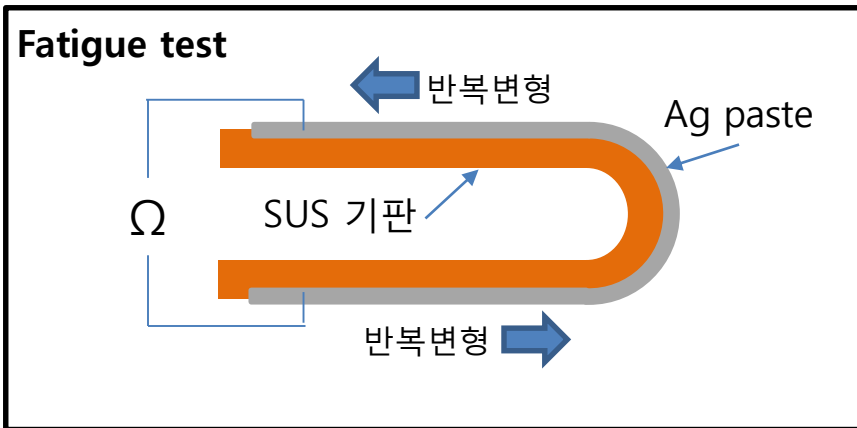
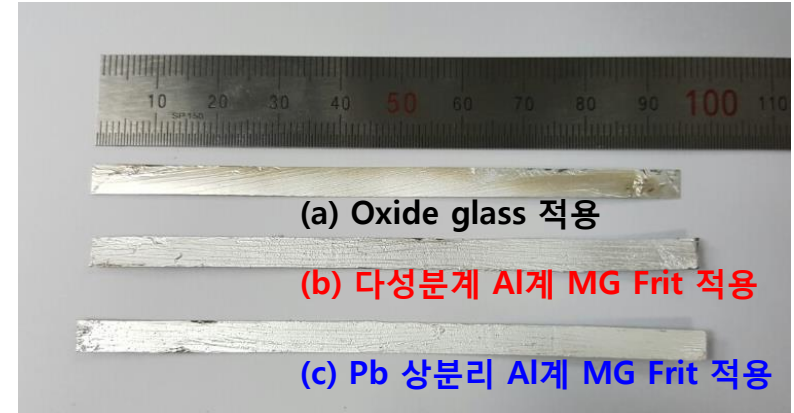
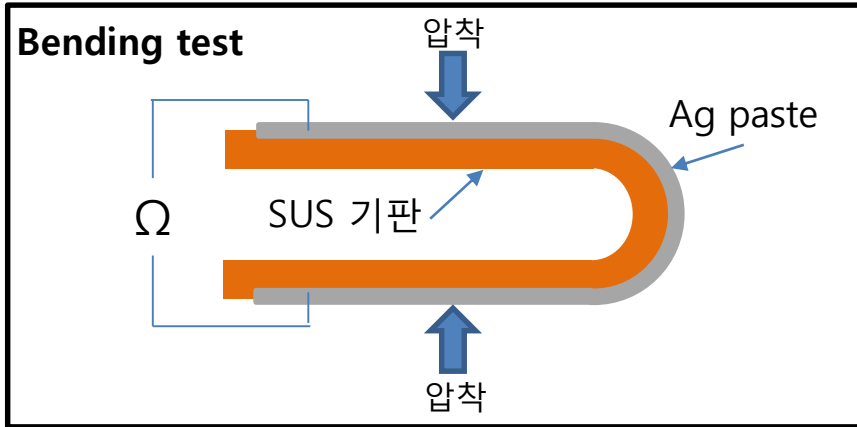
→ Pb rich phase의 용융 통한 SiN_x 건식 에칭 가능

PbO₂ 완전 대체 가능 Al-Pb 상분리 합금 개발

→ 최종 Pb 분율 감소 통한 친환경 Ag paste 개발 가능

Bending / Fatigue test for flexible

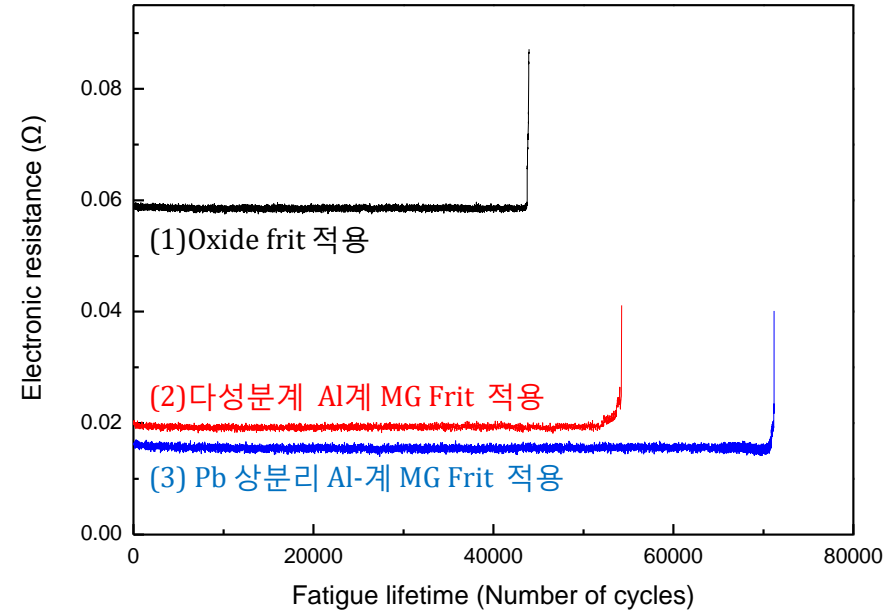
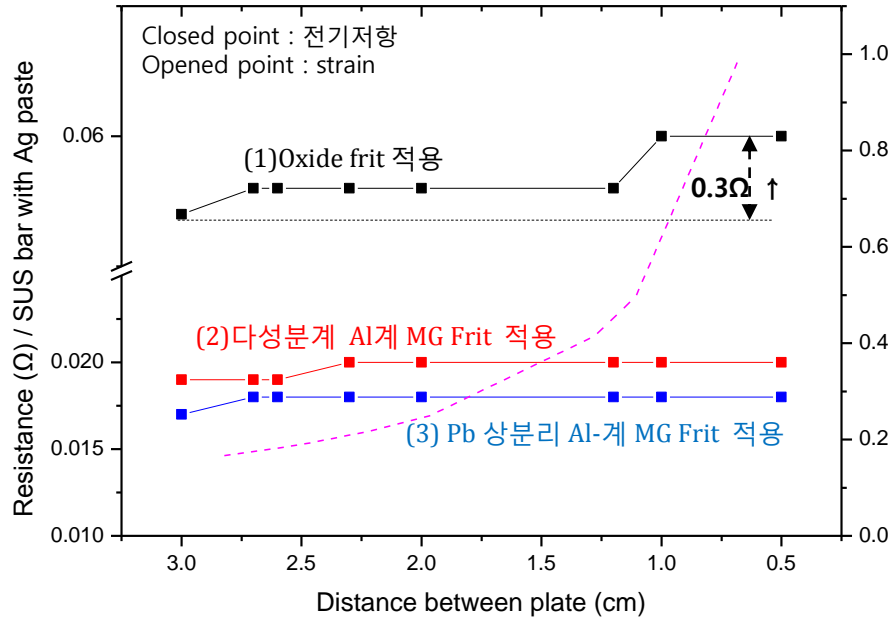
▶ Al - Pb 상분리 비정질 합금 : Flexible Ag paste로써의 가능성



$$\varepsilon(\%) = \frac{t}{(D-t)} \times 100 \quad \rightarrow t : \text{시편 두께} / D : \text{plate간 간격}$$

Bending / Fatigue test for flexible

▶ Bending / fatigue 따른 Ag paste의 전기저항 변화



→ Oxide glass frit 적용

: brittle oxide로 인해 낮은 탄성한계 및 피로저항성

→ Pb 상분리 Al계 비정질 합금

: Pb 상의 낮은 융점으로 인해 젖음성 향상

: 금속개재물에 의한 유연성 증가



상분리 Pb Al-based MG 적용 통해
유연성 높은 Ag paste의 개발 가능

Thanks for your kind attention