2018 Spring

"Advanced Physical Metallurgy"

- Bulk Metallic Glasses-

03.07.2018

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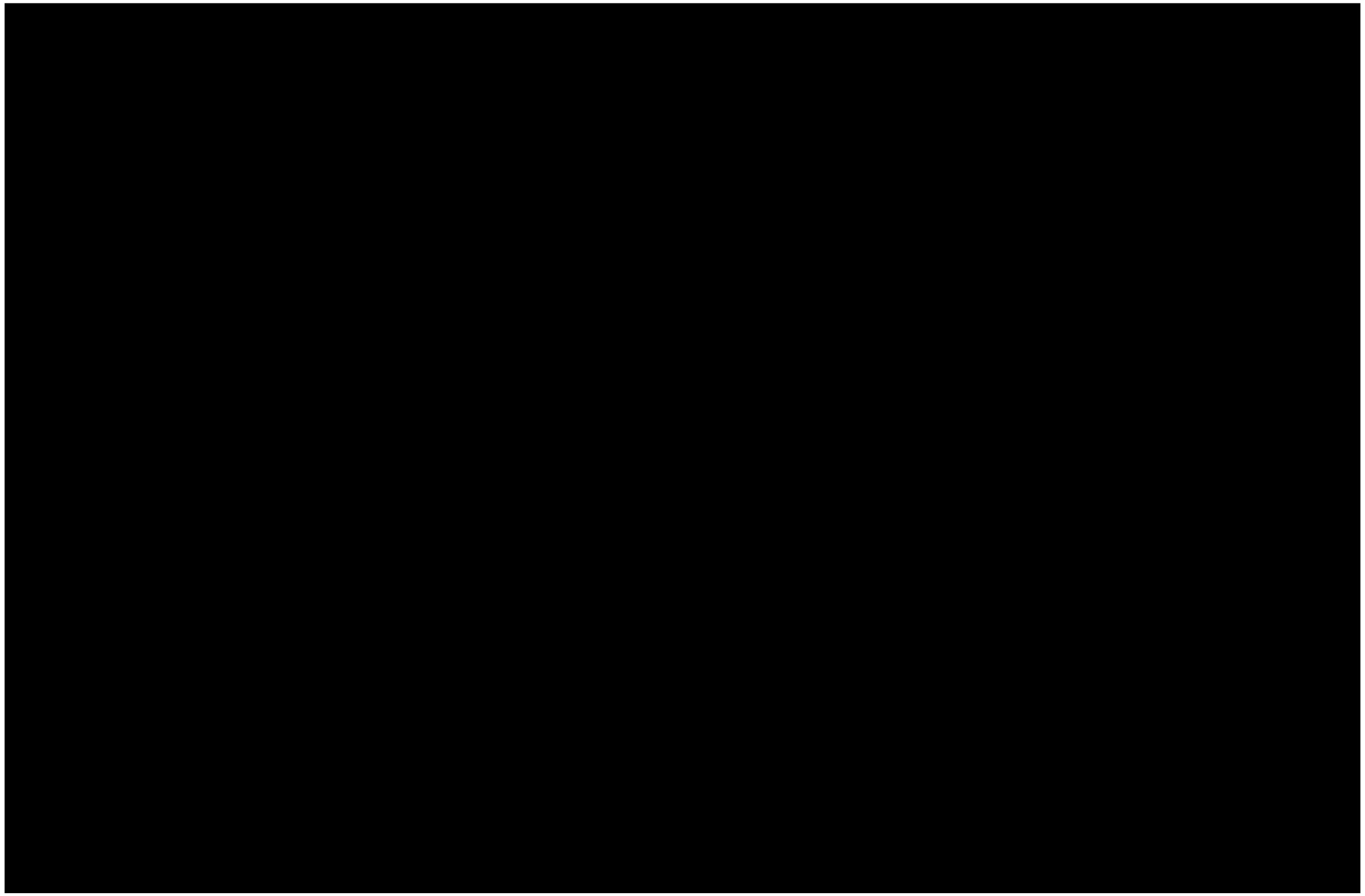
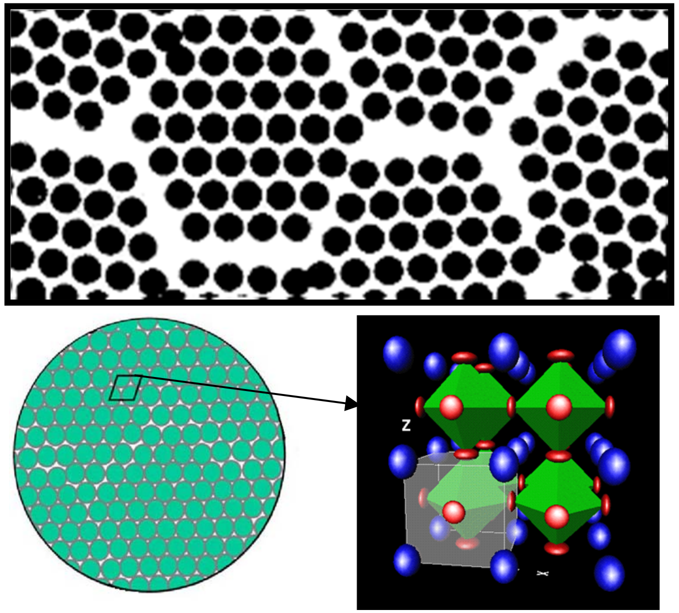
Bulk Metallic Glass: the 3rd Revolution in Materials?



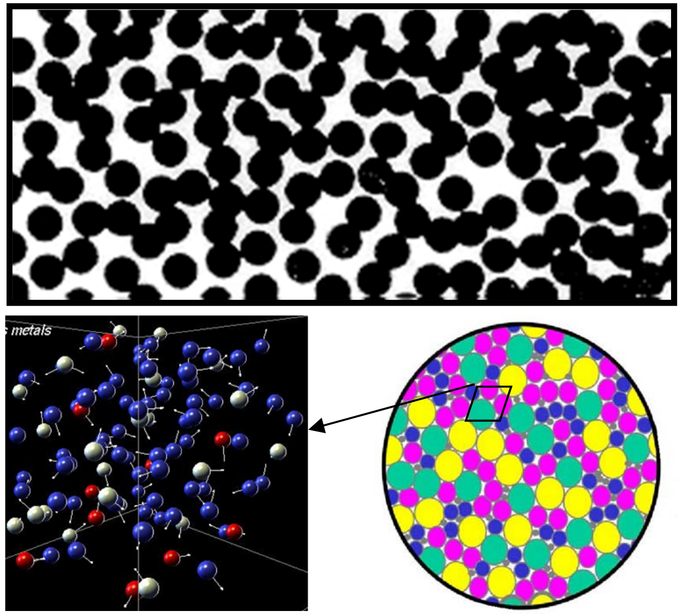
Structure of crystals, liquids and glasses

Crystals



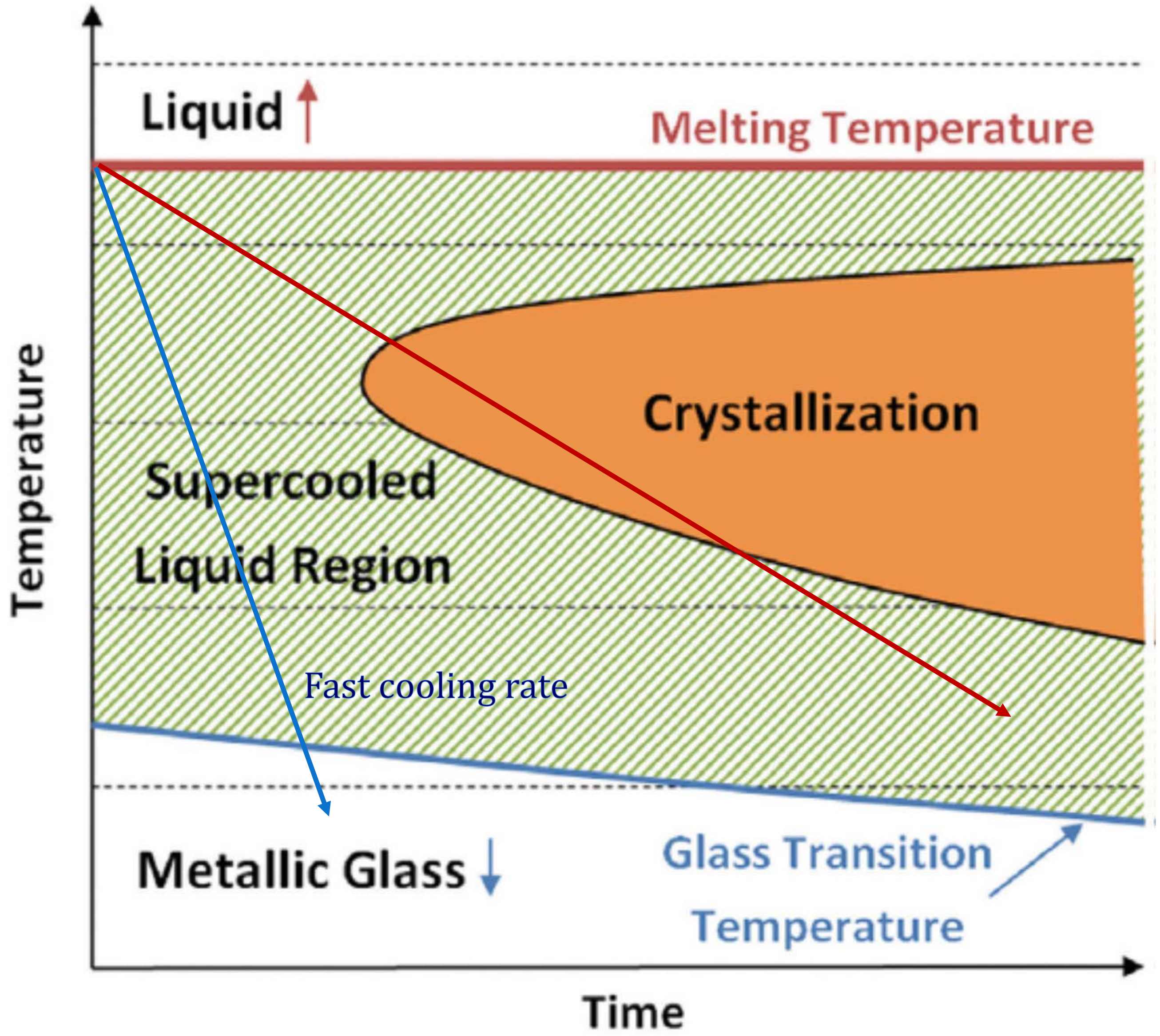
• periodic
• grain boundaries

Liquids, glasses



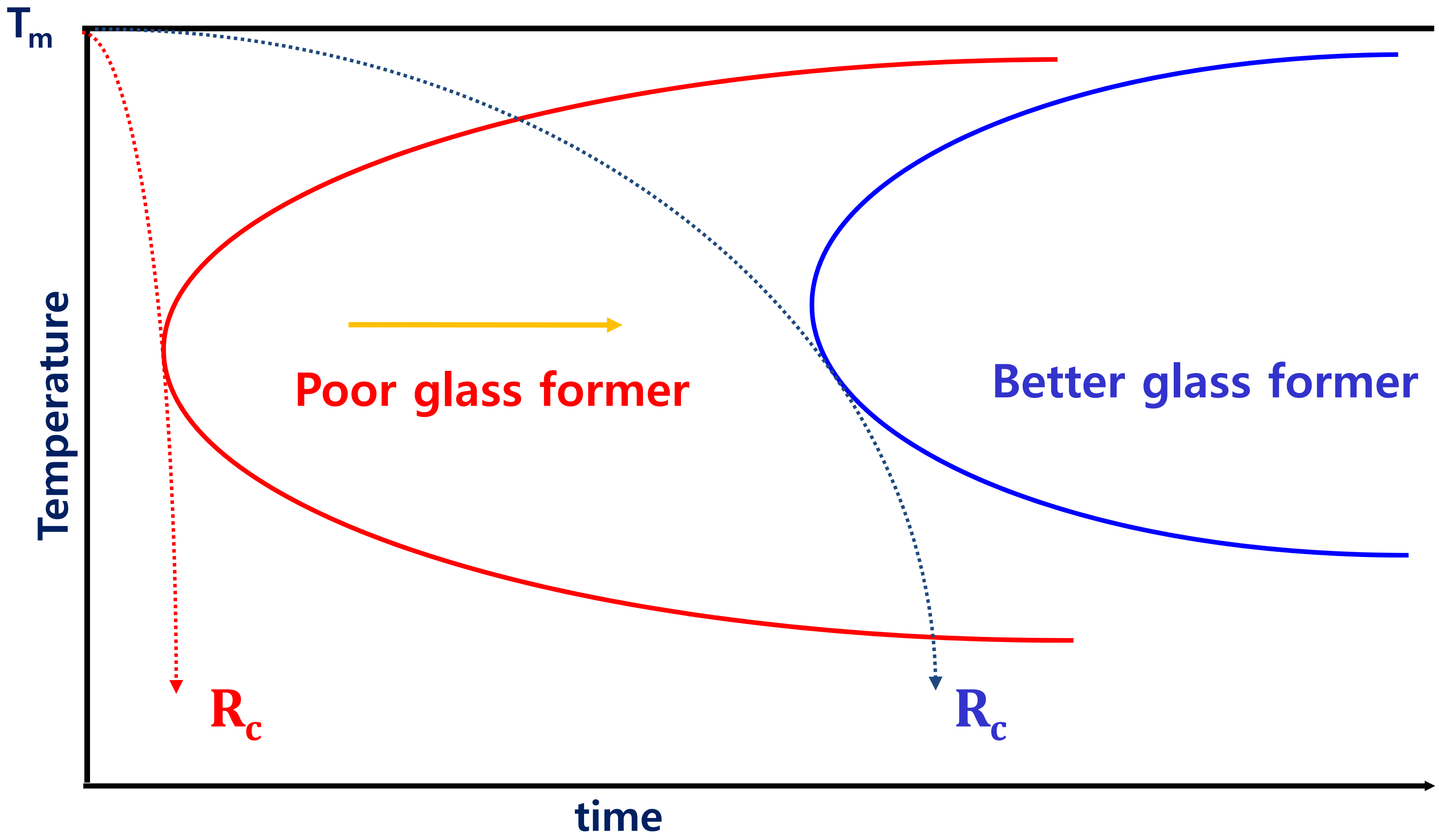
• amorphous = non-periodic
• no grain boundaries

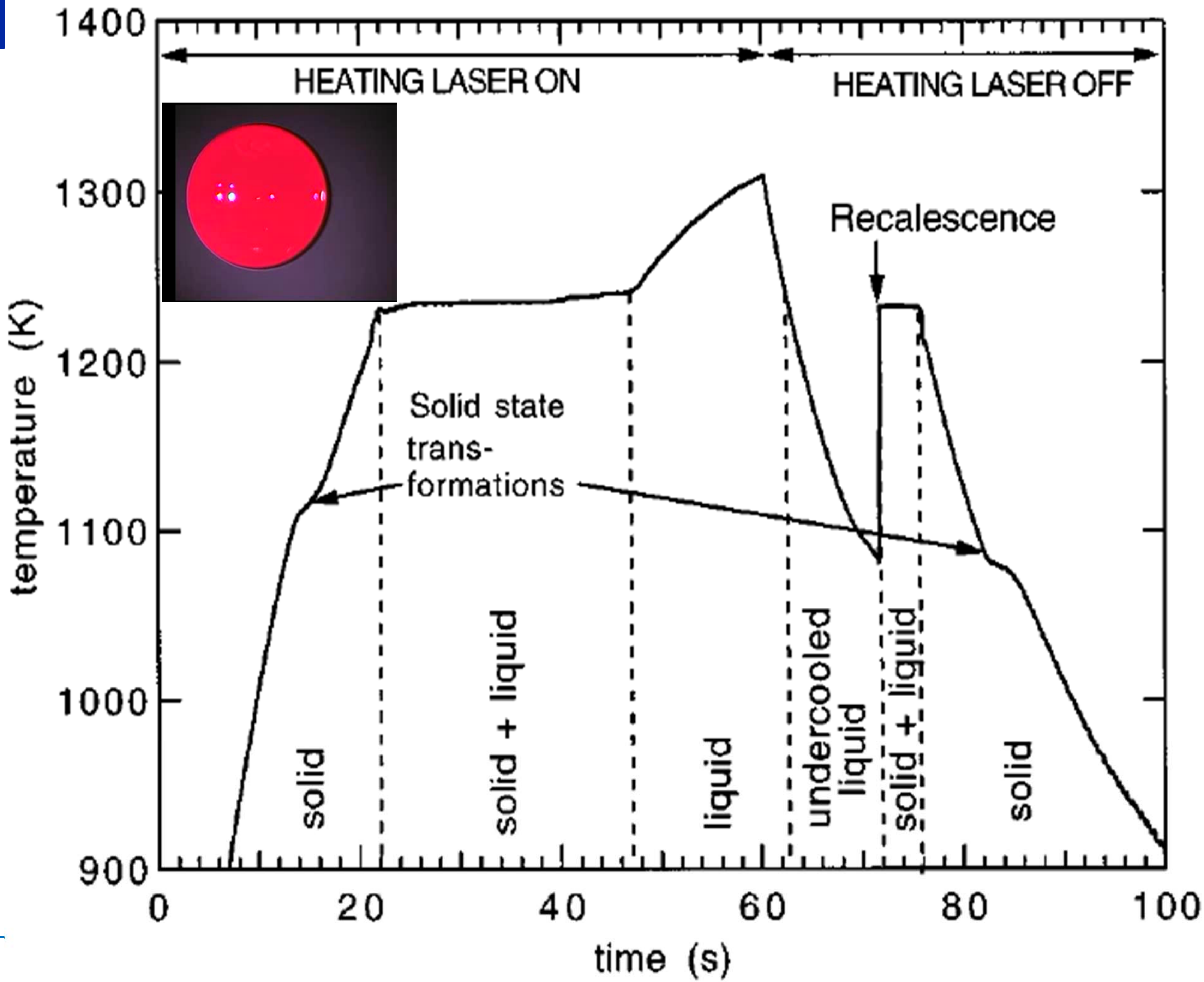
Glass formation : (1) Fast Cooling



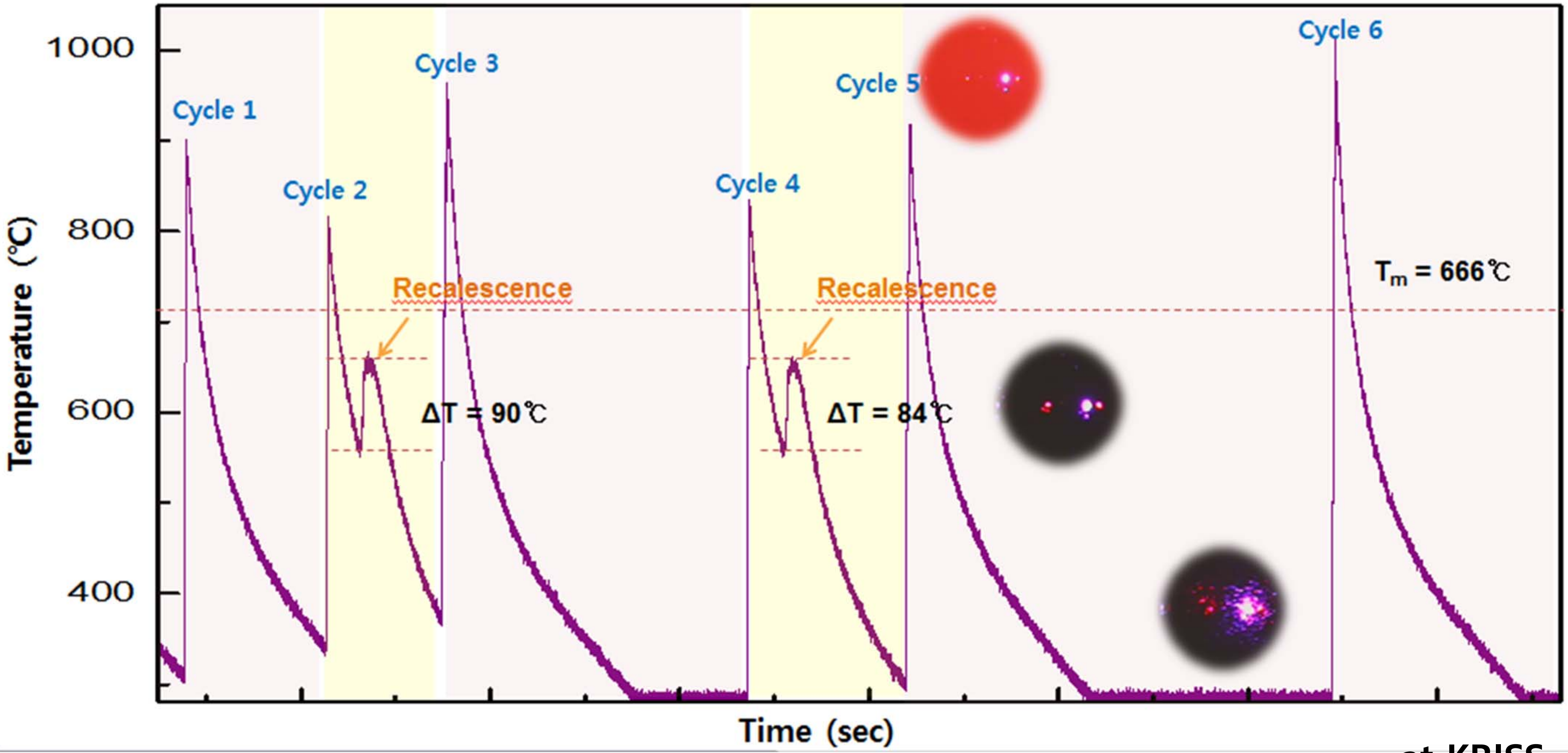
Glass formation : (2) Better Glass Former

GFA $$R_c = \frac{\Delta T}{t_n}$$ undercooled liquid → crystalline




HEATING LASER ON
HEATING LASER OFF
Recalescence
Solid state trans- formations
temperature (K)
time (s)
solid
solid + liquid
liquid
undercooled liquid
solid + liquid
solid
1400
1300
1200
1100
1000
900
0
20
40
60
80
100

Electrostatic Levitation: cooling curve of Vitreloy 1 system



at KRISS

Amorphous Materials

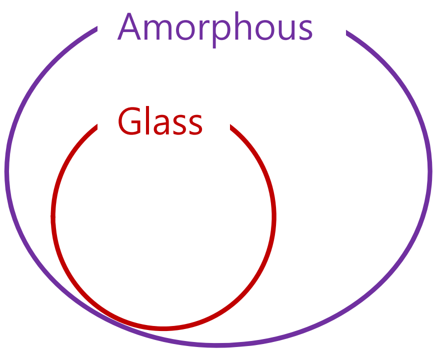
• Amorphous materials

a wide diversity of materials can be rendered amorphous indeed almost all materials can.

- **metal, ceramic, polymer**

- **glassy/non-crystalline material**

cf) amorphous vs glass
- random atomic structure (short range order)
- showing glass transition.

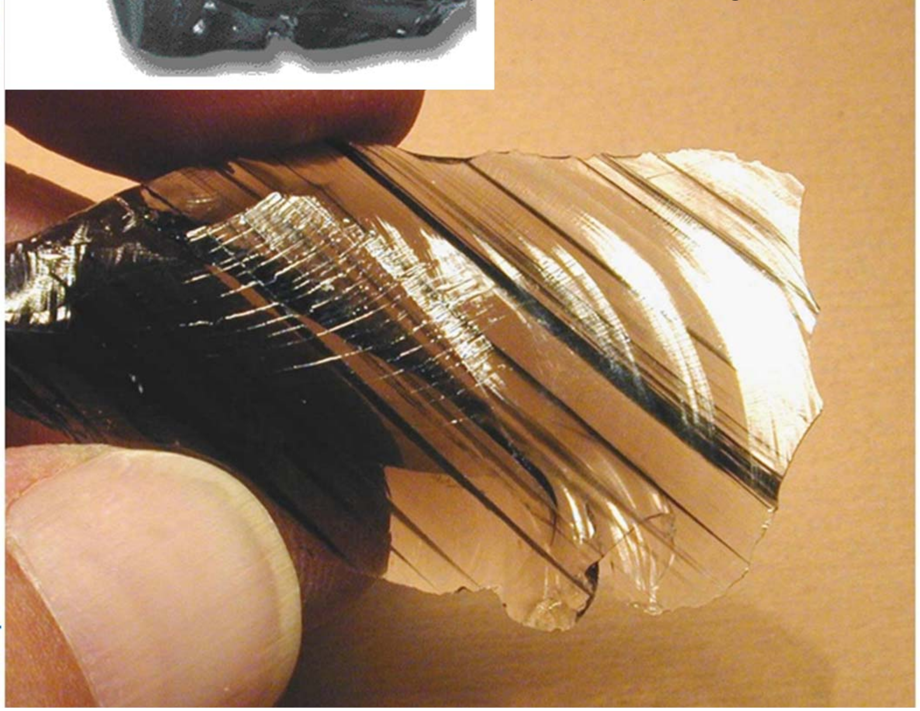


- retain liquid structure
- rapid solidification from liquid state

Glassmaking by humans can be traced back to 3500 BCE in Mesopotamia (current Iraq).

Obsidian is a naturally occurring volcanic glass formed as an extrusive igneous rock. It is produced when felsic lava extruded from a volcano cools rapidly with minimum crystal growth. Obsidian is commonly found within the margins of rhyolitic lava flows known as **obsidian flows**, where the chemical composition (high silica content) induces a high viscosity and polymerization degree of the lava. The inhibition of atomic diffusion through this highly viscous and polymerized lava explains the lack of crystal growth. Because of this lack of crystal structure, sharp obsidian blade edges can reach almost molecular thinness, leading to its ancient use as projectile points and cutting and piercing tools, and its modern use as surgical scalpel blades.

http://en.wikipedia.org/wiki/Obsidian



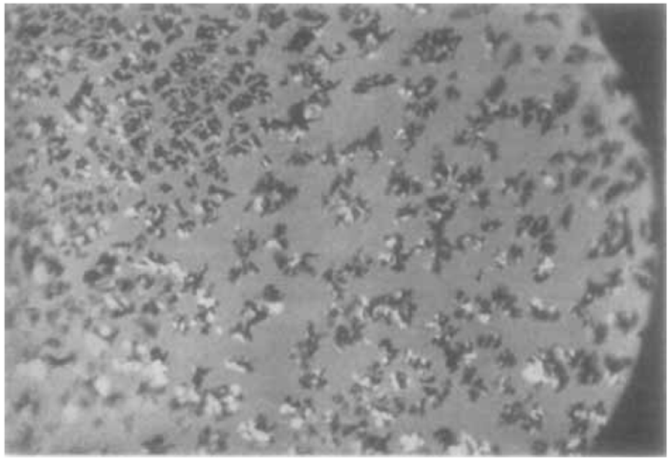
First Amorphous Metals: evaporation method

Über nichtleitende Metallmodifikationen[1])

Von Johannes Kramer

(Mit 8 Figuren)

Das metallische Leitvermögen wird bekanntlich auf das Vorhandensein freibeweglicher Elektronen und damit auch ortsgebundener positiver Ionen zurückgeführt. Da nun ein nichtionisierter Metalldampf ein vollkommener Nichtleiter ist, so liegt die Vermutung nahe, daß es bei Kondensation eines solchen Dampfes gelingen müßte, nichtleitende Schichten zu erhalten, wenn Wechselwirkungen zwischen den regellos aufeinandergepackten Atomen vermieden werden könnten. Man hätte es dann mit einem Gebilde zu tun, das als völlig amorph anzusehen wäre und in seiner Konstitution am ehesten einem hochkomprimierten Gase entspräche.



J. Kramer
Nonconducting modifications of metals. Ann. Physik (Berlin, Germany) 19, 37 (1934)

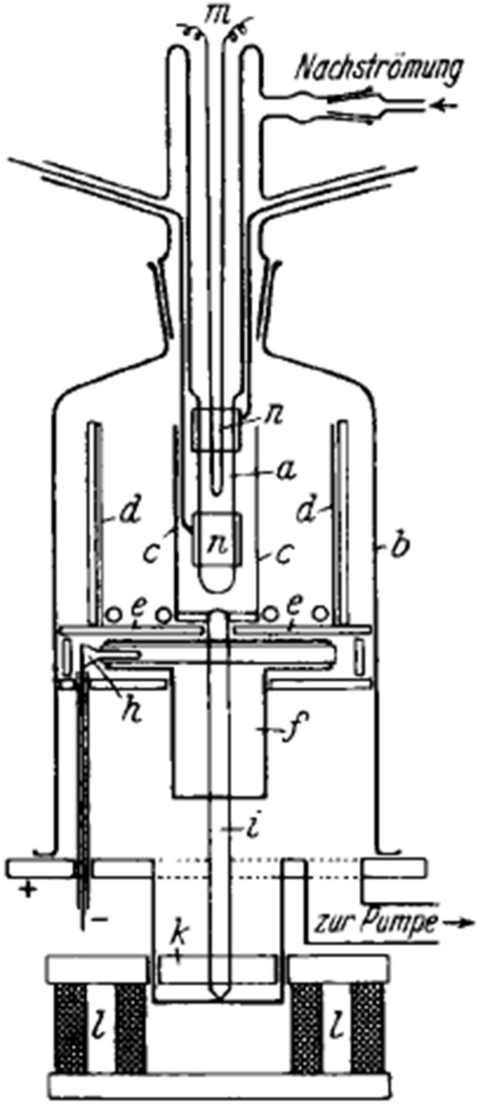
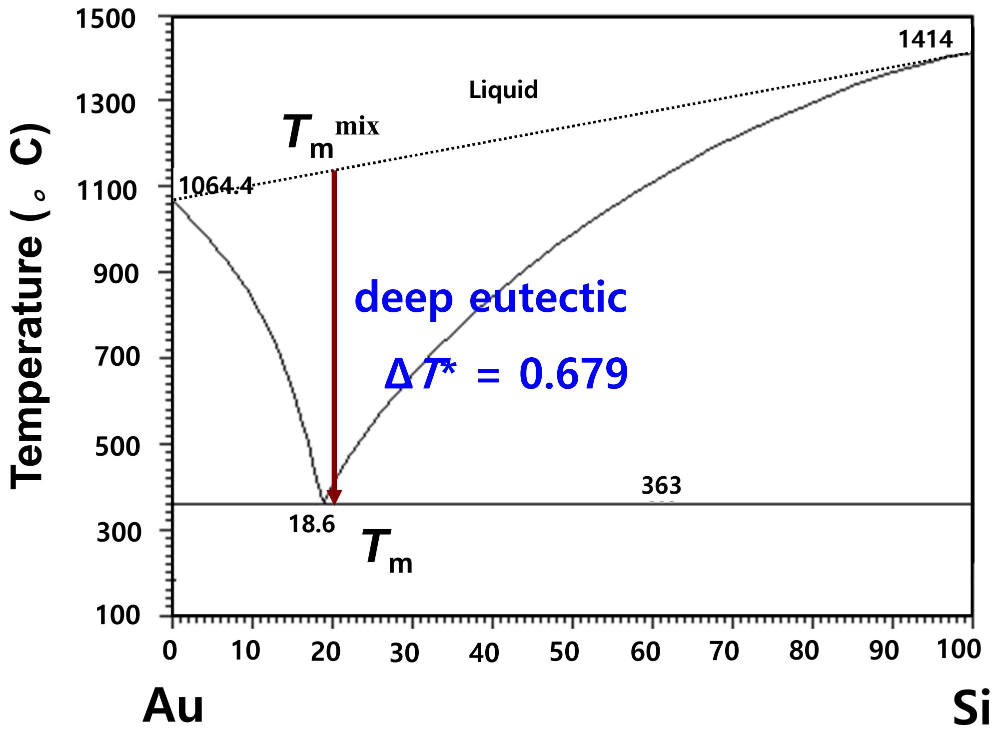


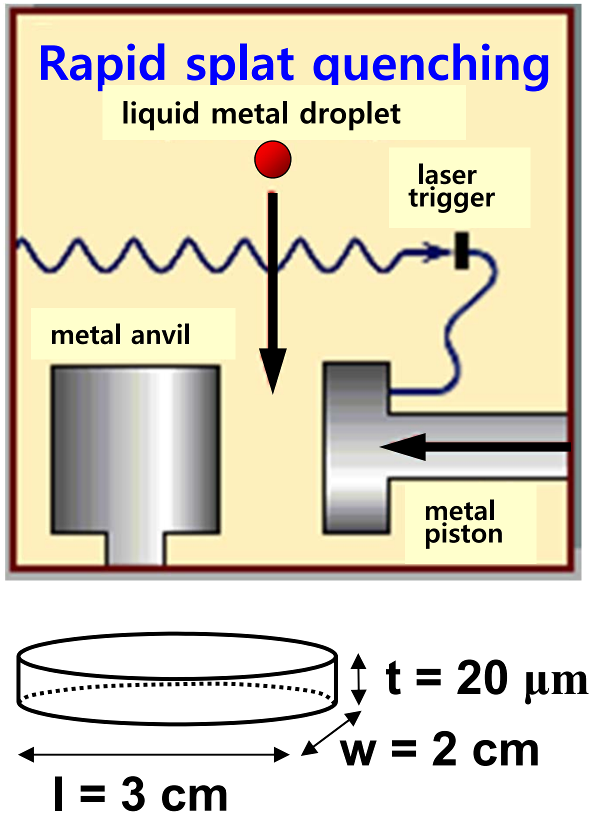
Fig. 1.
Zerstäubungsapparatur

Glass formation : stabilizing the liquid phase

- First metallic glass ($Au_{80}Si_{20}$) produced by splat quenching at Caltech by Pol Duwez in 1960.

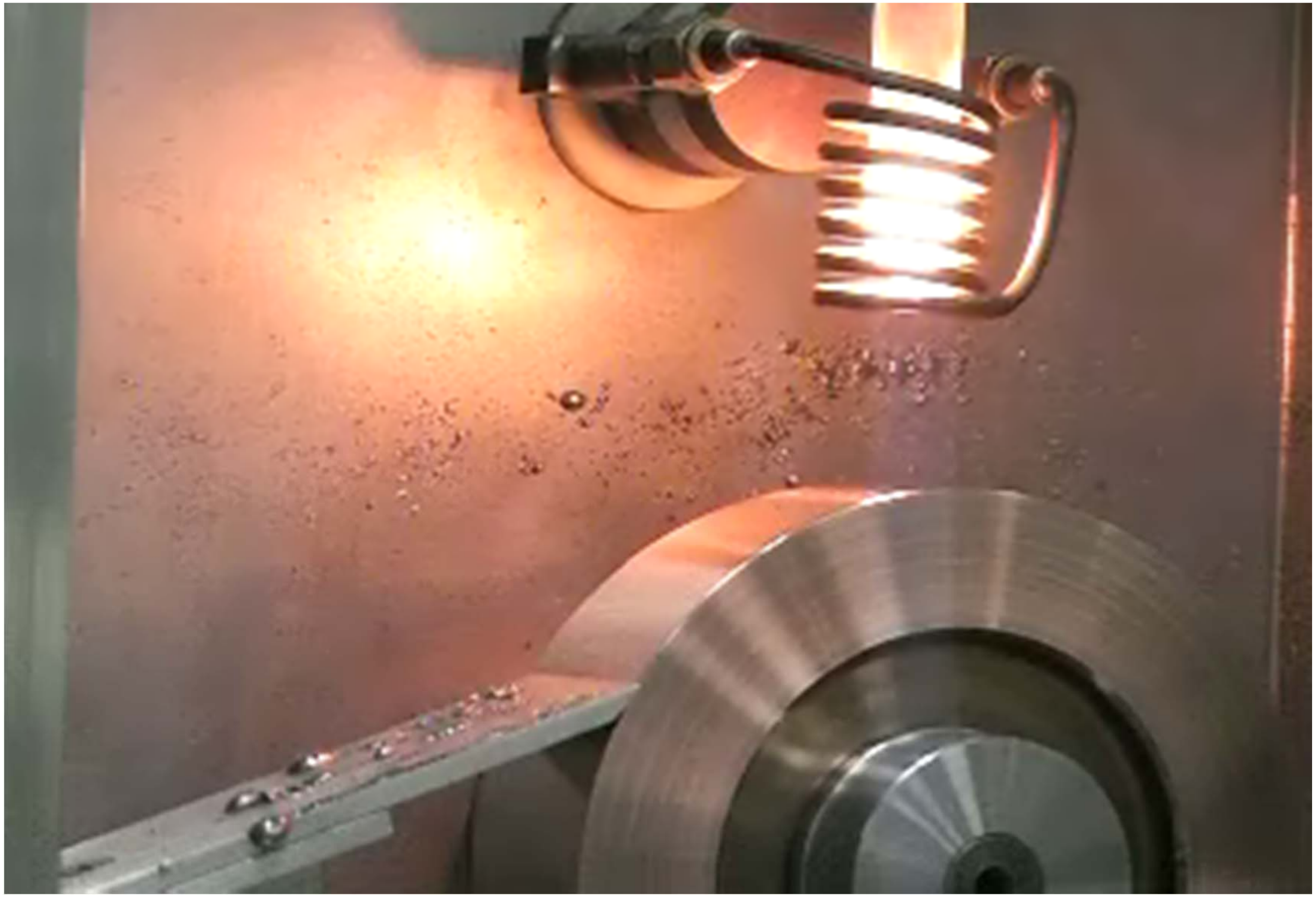


W. Klement, R.H. Willens, P. Duwez, Nature 1960; ***187****: 869.*



Glass formation : rapid quenching of liquid phase

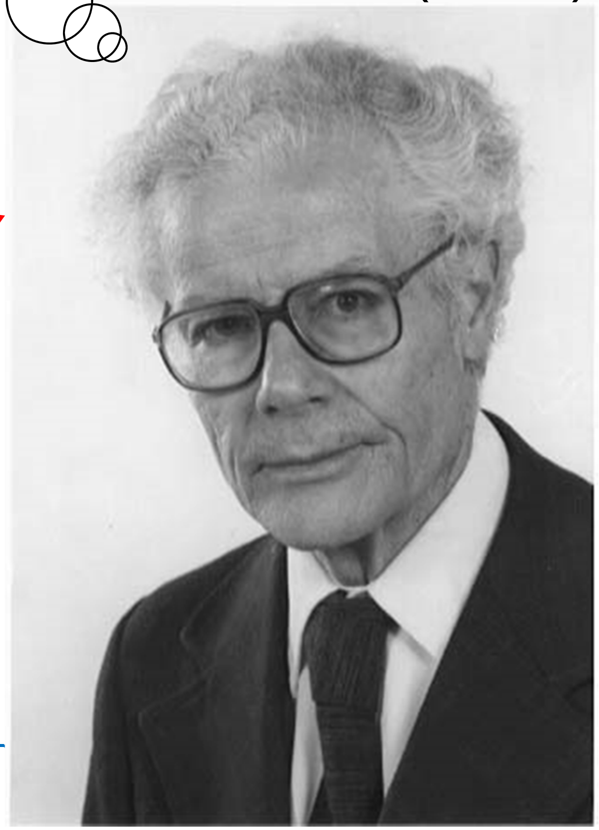
- 1969 Ribbon type with long length using melt spinner : FePC, FeNiPB alloy



Bulk formation of metallic glass

By eliminating or reducing
the effectiveness of
heterogeneous nucleation sites,
it should be possible to form
bulk metallic glasses
with virtually unlimited dimensions.

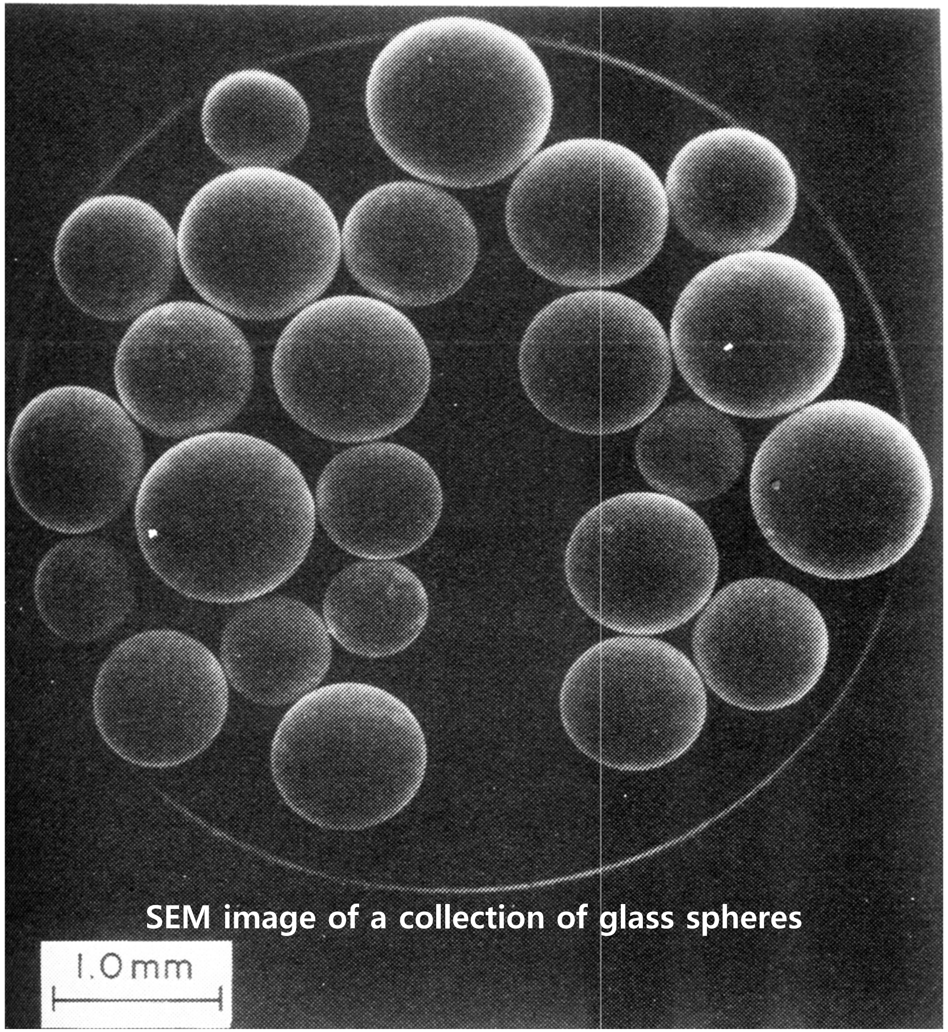
David Turnbull (Harvard)



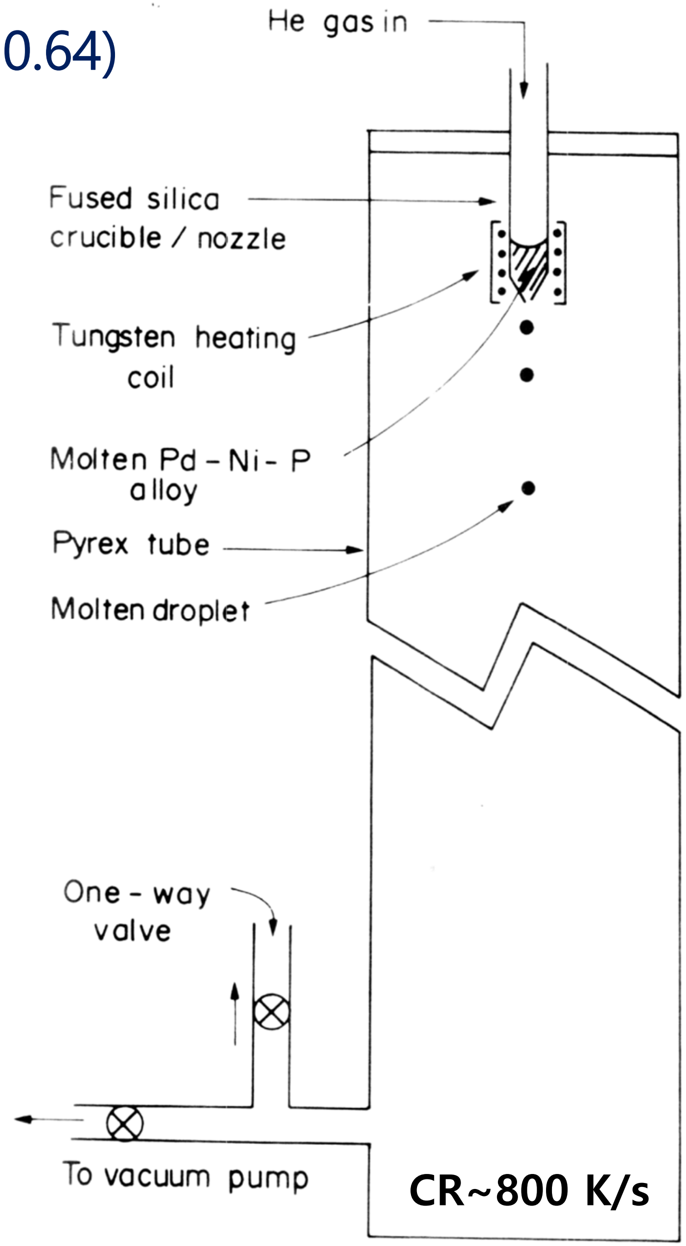
Bulk formation of metallic glass

- First bulk metallic glass: $Pd_{77.5}Cu_6Si_{16.5}$ (T_{rg}=0.64)

By droplet quenching (CR~800 K/s)



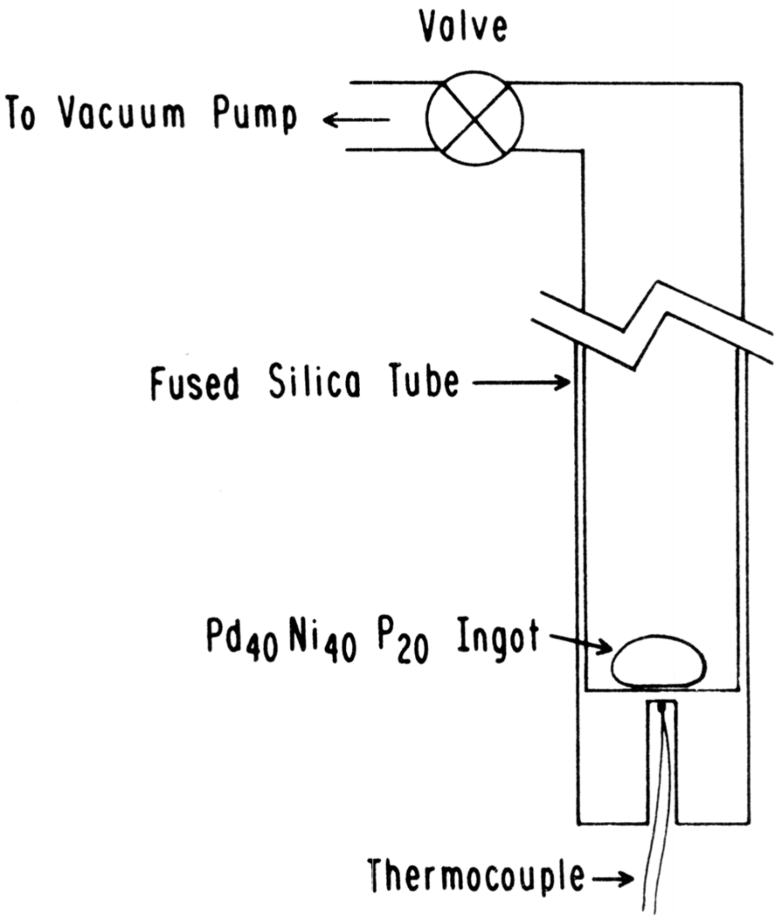
SEM image of a collection of glass spheres



Bulk formation of metallic glass

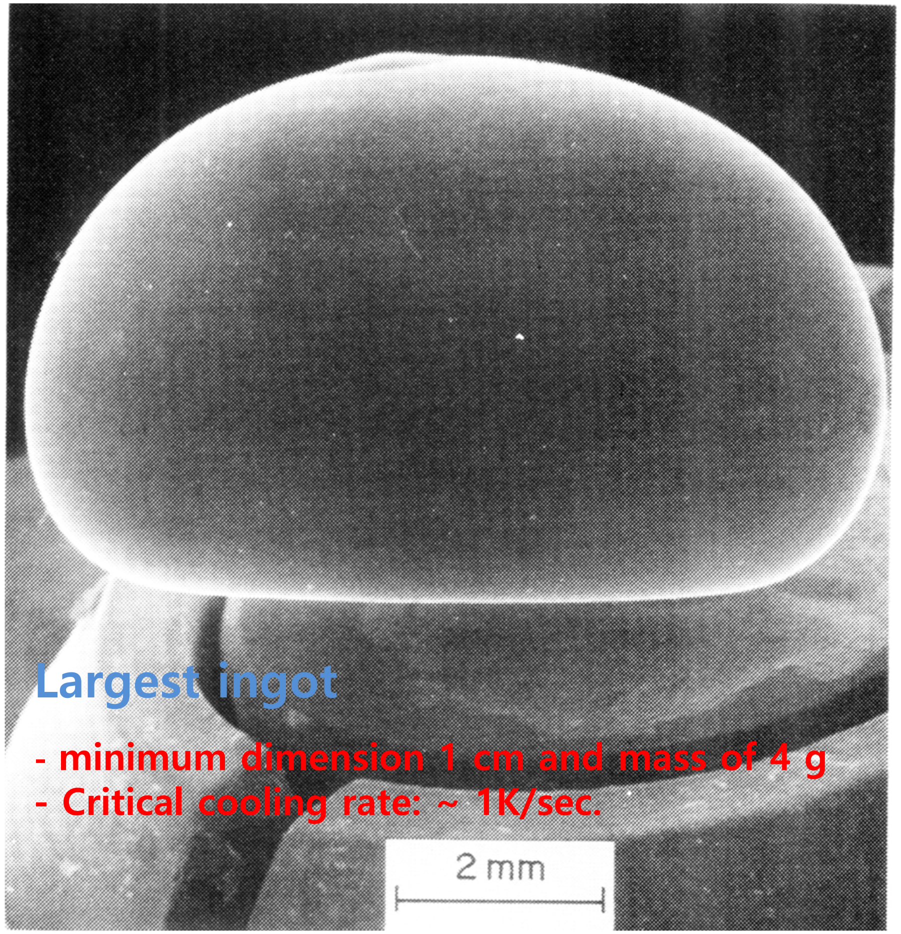
- First bulk metallic glass
  $Pd_{77.5}Cu_6Si_{16.5}$ (T_{rg}=0.64)

- Alloy Selection: consideration of T_{rg}
  $Pd_{40}Ni_{40}P_{20}$ (T_{rg}=0.67)

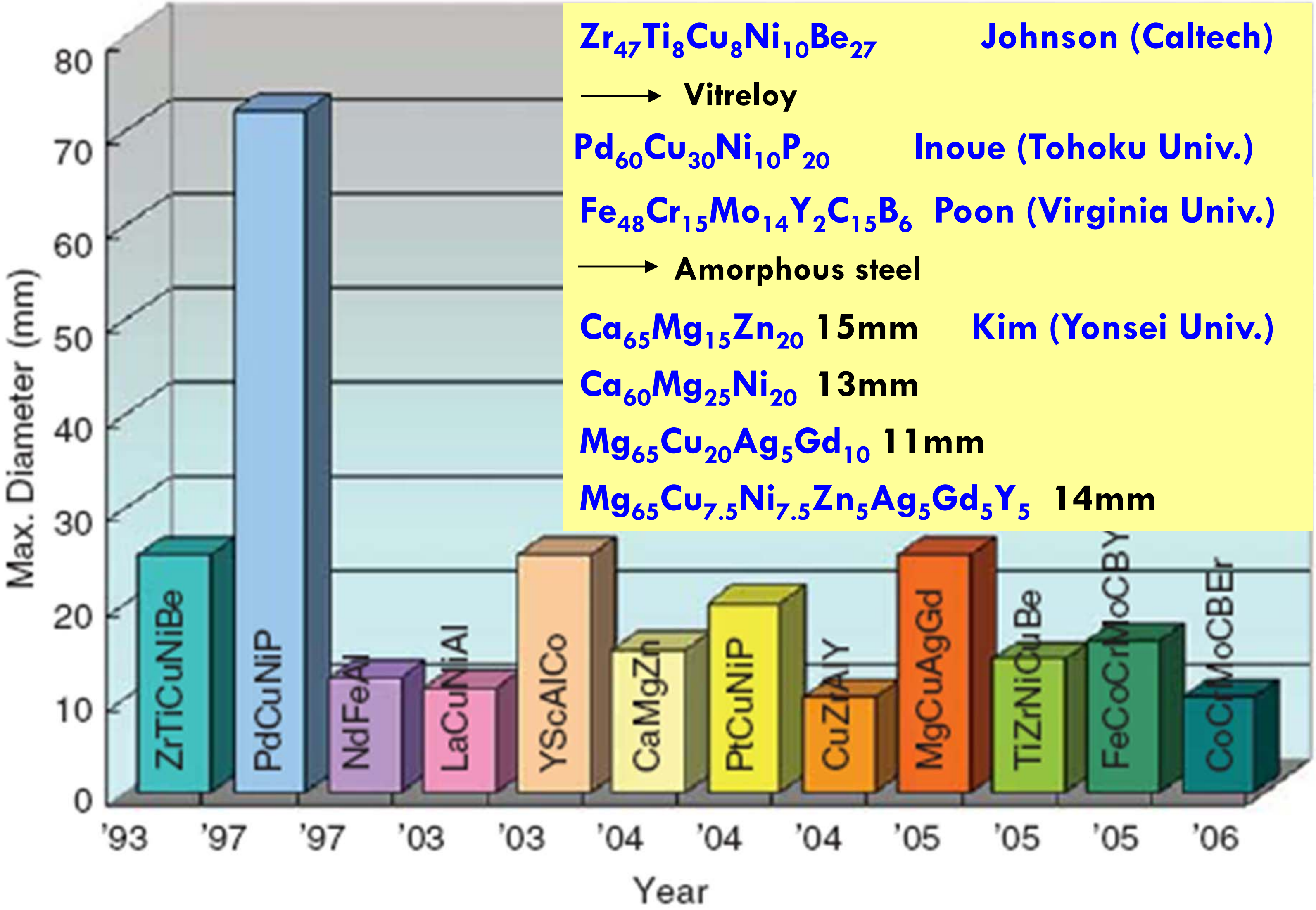


<Schematic diagram of apparatus>

Suppression of heterogeneous nucleation



Recent BMGs with critical size ≥ 10 mm



$Zr_{47}Ti_8Cu_8Ni_{10}Be_{27}$ Johnson (Caltech)

→ Vitreloy

$Pd_{60}Cu_{30}Ni_{10}P_{20}$ Inoue (Tohoku Univ.)

$Fe_{48}Cr_{15}Mo_{14}Y_2C_{15}B_6$ Poon (Virginia Univ.)

→ Amorphous steel

$Ca_{65}Mg_{15}Zn_{20}$ 15mm Kim (Yonsei Univ.)

$Ca_{60}Mg_{25}Ni_{20}$ 13mm

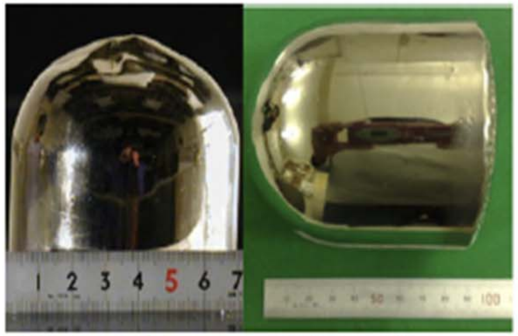
$Mg_{65}Cu_{20}Ag_5Gd_{10}$ 11mm

$Mg_{65}Cu_{7.5}Ni_{7.5}Zn_5Ag_5Gd_5Y_5$ 14mm

Bulk glass formation in the Pd-/Ni-/Cu-/Zr- element system

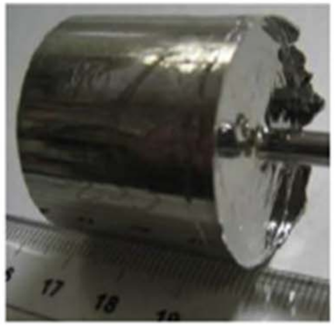
Massy Ingot Shape

(a) Pd-Cu-Ni-P



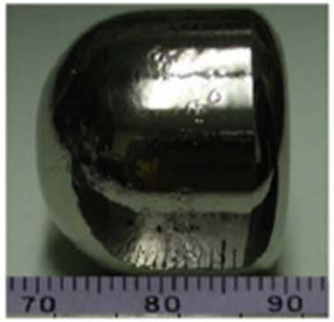
72ϕx 75 mm 80ϕx 85 mm

(b) Zr-Al-Ni-Cu



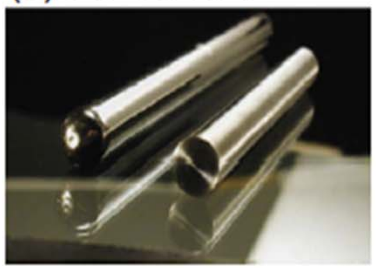
(c) Cu-Zr-Al-Ag

(d) Ni-Pd-P-B

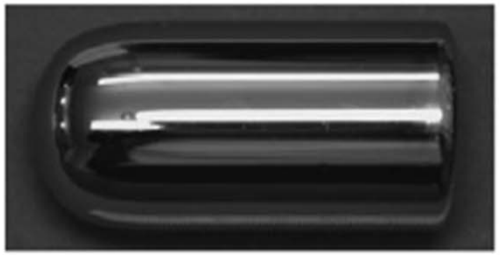


Cylindrical Rods

(e) Pd-Cu-Ni-P

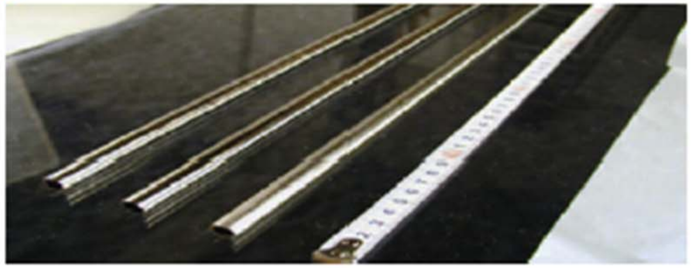


(f) Pt-Pd-Cu-P

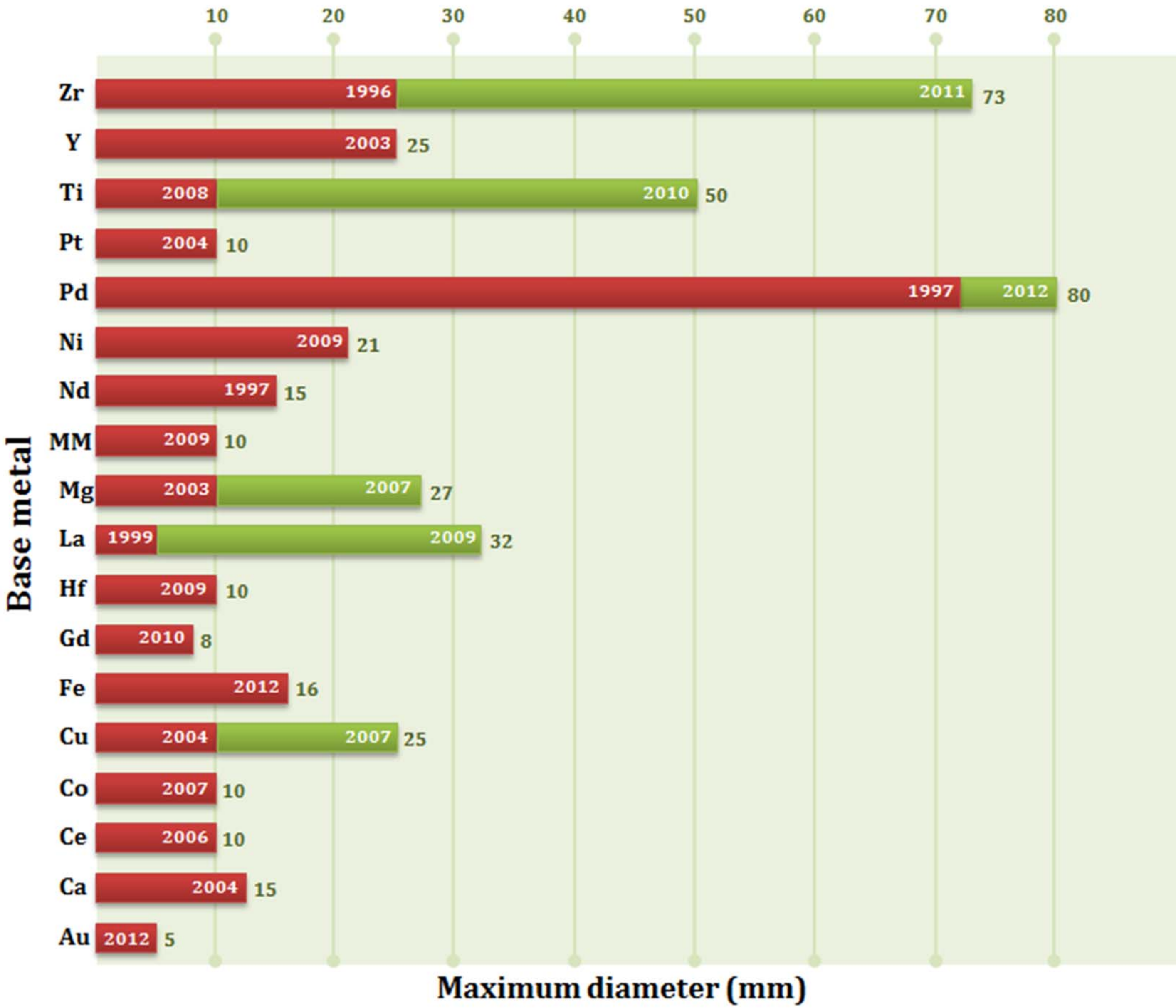


Hollow Pipes

(g) Pd-Cu-Ni-P

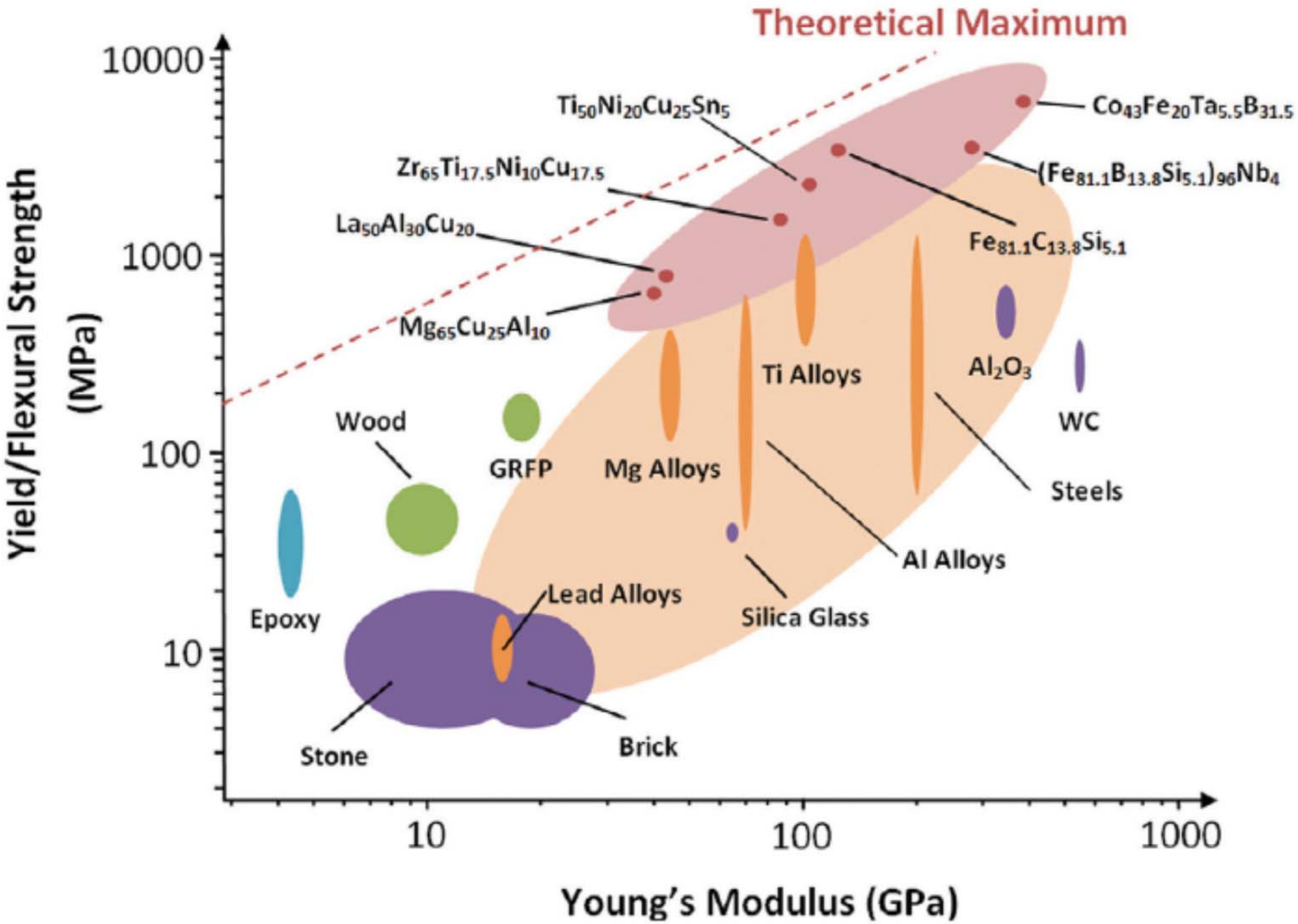


Recent BMGs with critical size ≥ 10 mm



Are amorphous metals useful?

1. High strength of BMGs



High fracture strength over 5 GPa in Fe-based BMGs

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

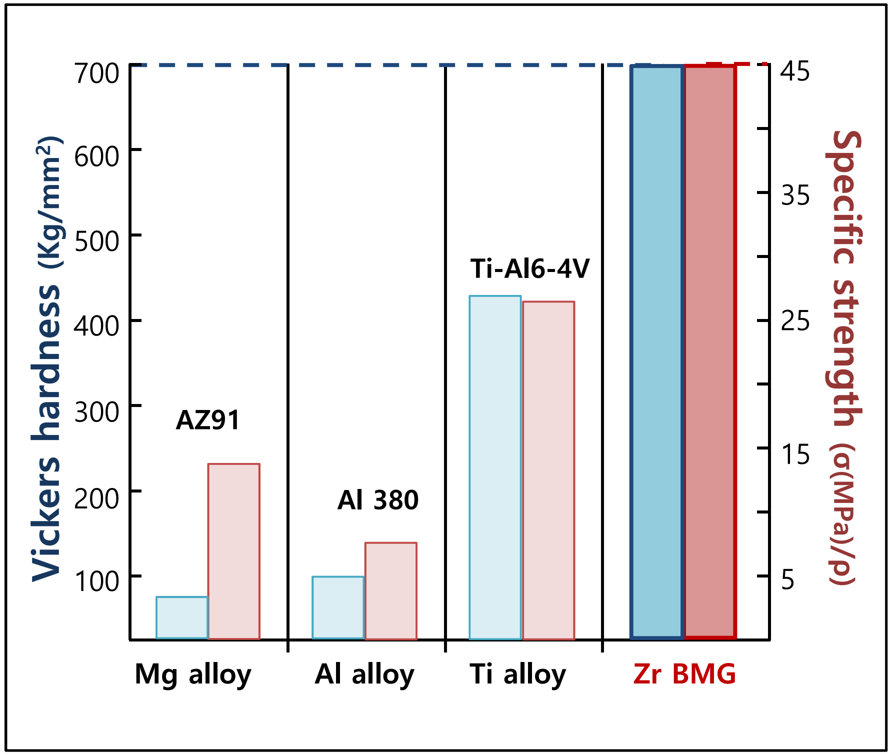
1. High strength of BMGs

Bulk metallic glasses with high strength

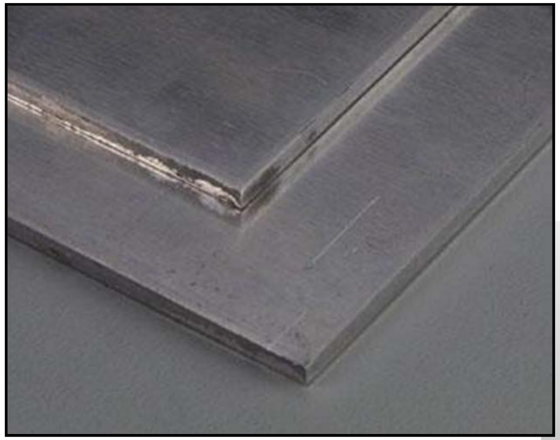
- **"High specific strength"** → Ultra-thin product with reasonable strength

  : Possible to reduce more thickness with same standard strength than conventional light alloys due to superior specific strength

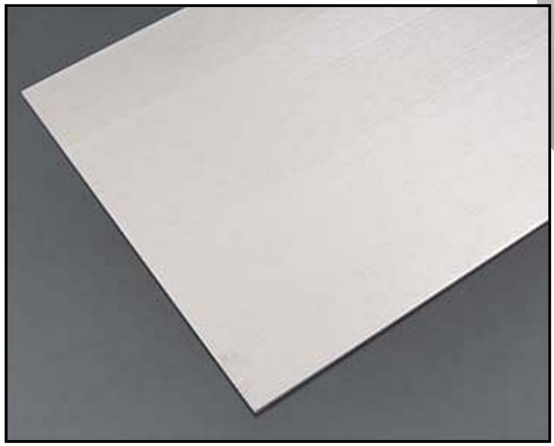
  → **Flexible / Wearable electronics**



Comparison of specific strength among Zr based BMG and conventional light alloys

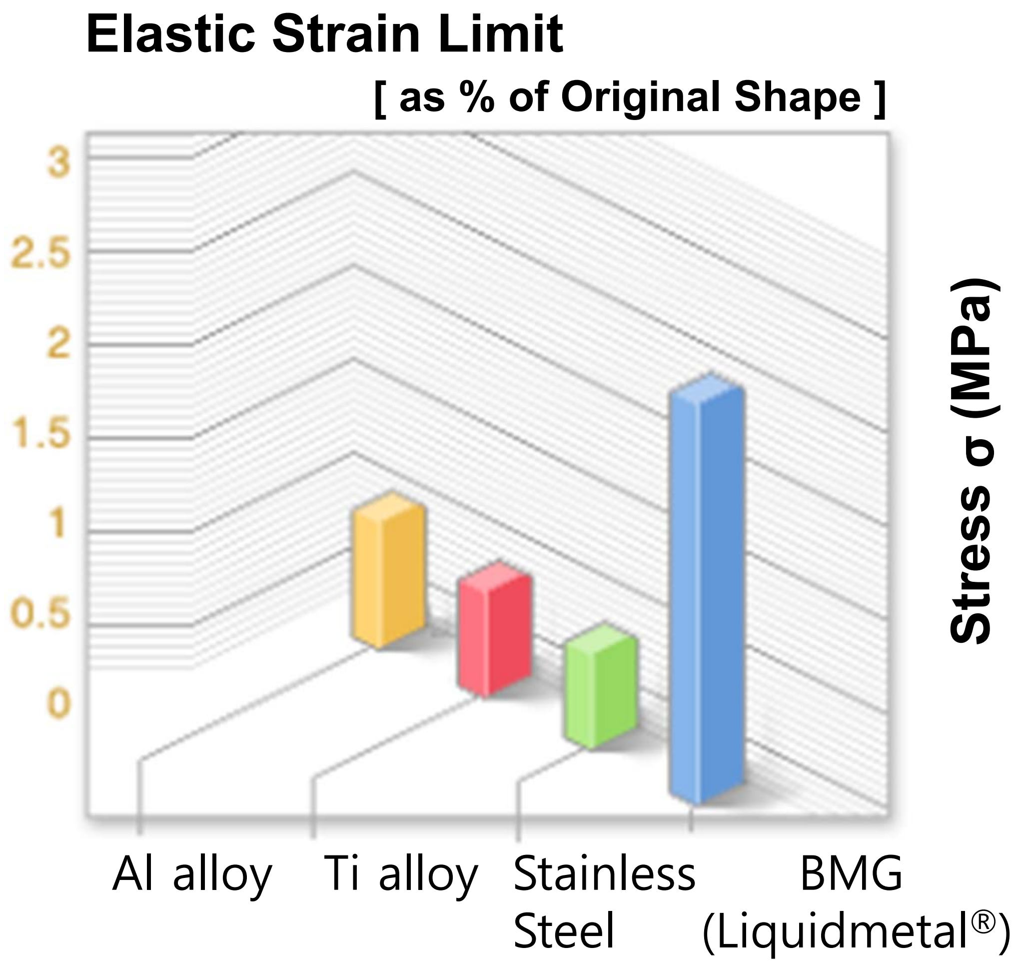


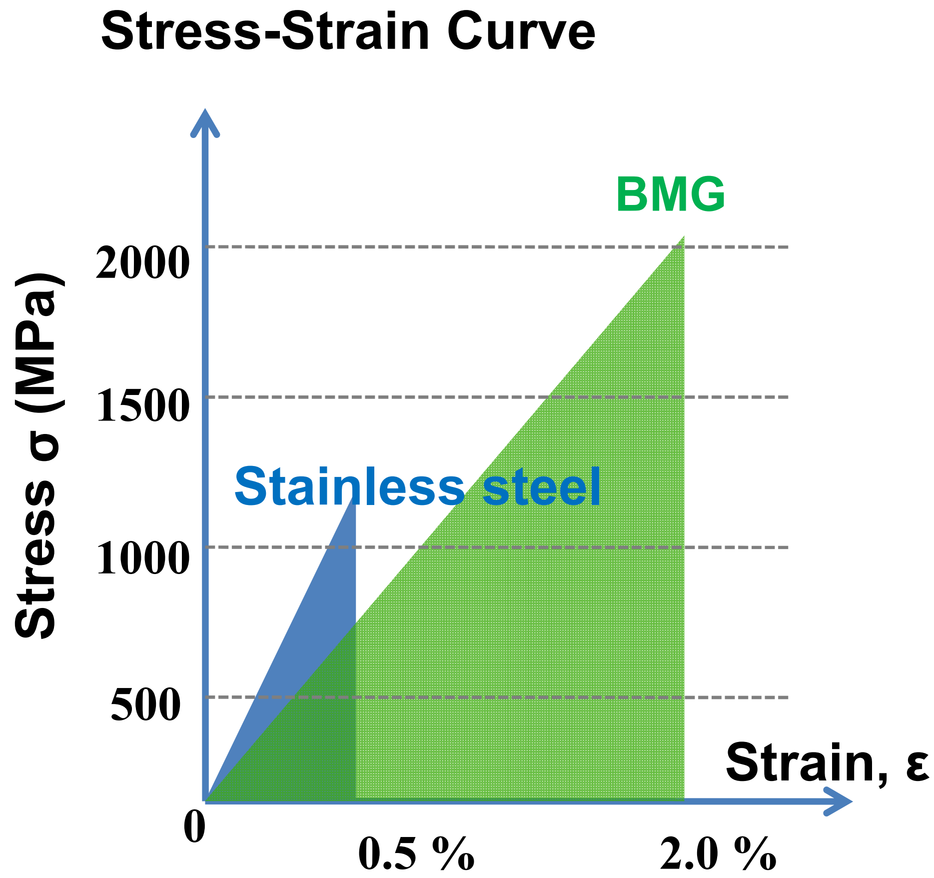
Mg – AZ91



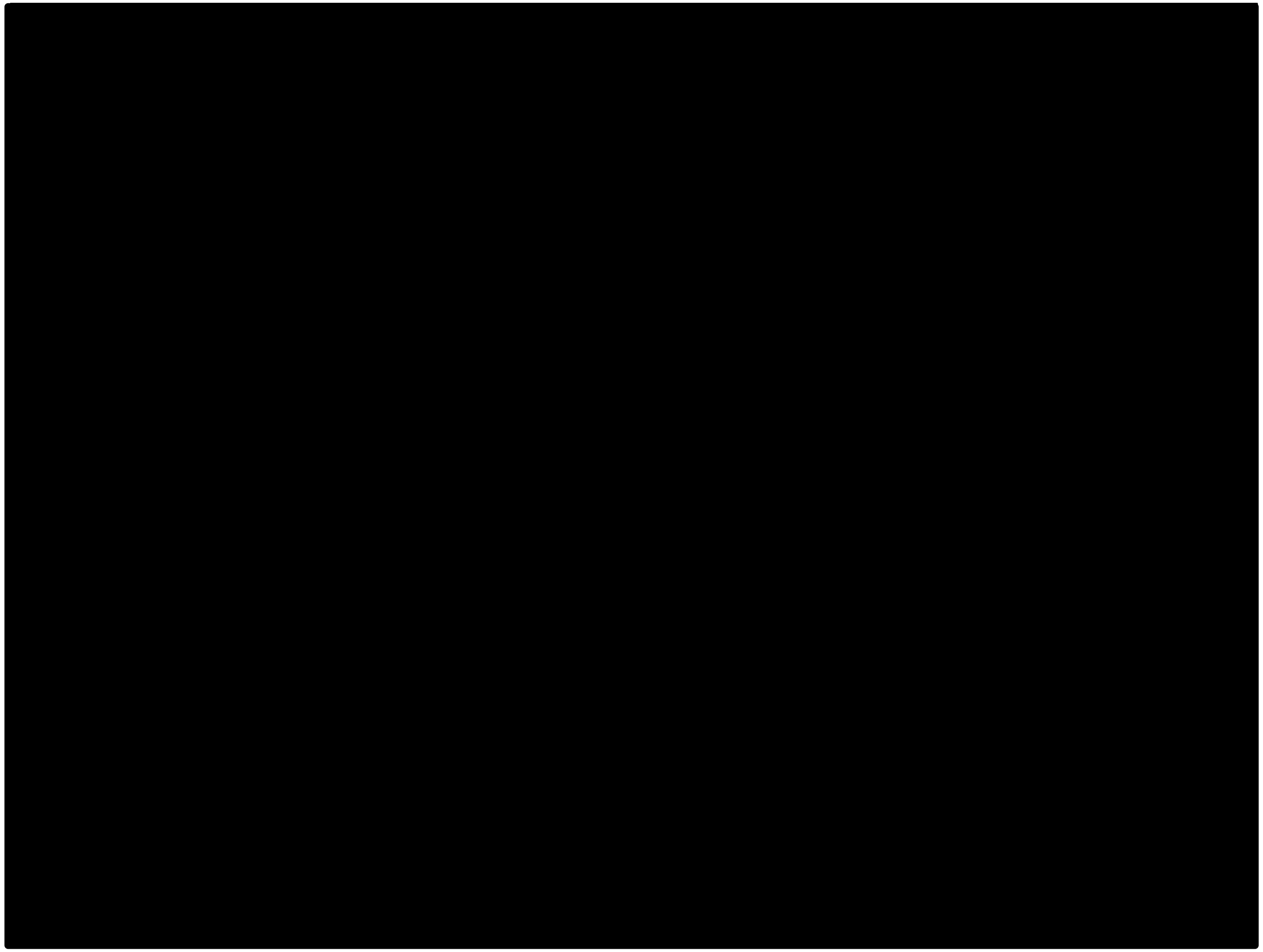
Thinner plate: BMG

2. Large elastic strain limit of BMGs





2. Large elastic strain limit of BMGs



Structural Applications: high yield (or fracture) strength, low Young's modulus large elastic strain limit, and easy formability in the SCLR

* Sporting Goods : Golf club

The repulsive efficiency (defined as the ratio of ball velocity/club head velocity) was found to 1.43 for the BMG alloy face, whereas it is only 1.405 for the Ti-alloy face. The overall flying distance was 225 m for the BMG alloy face, whereas it is only 213 m for the Ti-alloy face.

the modulus of resilience, U,

$$U = \frac{1}{2}\sigma_y \cdot \varepsilon_y = \frac{1}{2}E\varepsilon_y^2$$

where

σ_y and ε_y are the yield stress and elastic strain limit, respectively
E is the Young's modulus

FIGURE 10.2
Outer shapes of commercial golf club heads in wood-, iron-, and putter-type forms where the face materials are made of Zr-based BMG alloy. (Reprinted from Kakiuchi, H. et al., *Mater. Trans.*, 42, 678, 2001. With permission.)

Structural Applications: high yield (or fracture) strength, low Young's modulus, large elastic strain limit, and easy formability in the SCLR

*** Sporting Goods** : **Striking face plate in golf clubs/ Frame in tennis rackets / Baseball and softball bats/ Skis and snowboards / Bicycle parts / Fishing equipment/ Marine applications**

(a)

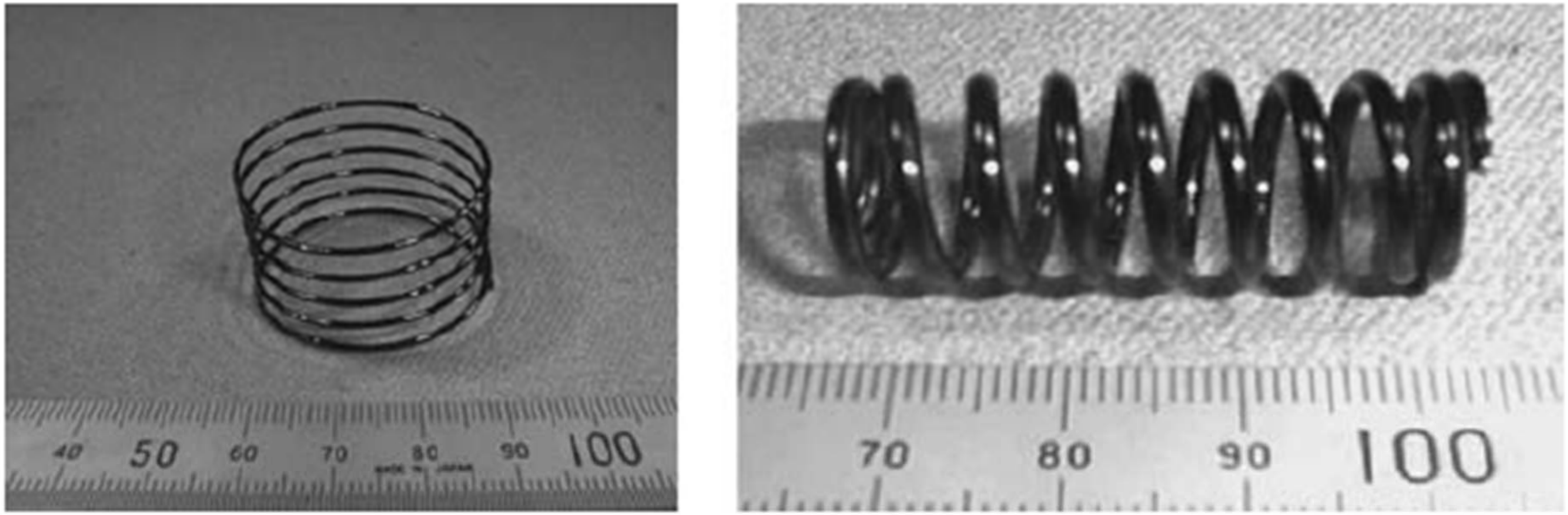
(b)

FIGURE 10.3
(a) Baseball bat and (b) tennis racket made of Liquidmetal (BMG) alloys.

Structural Applications: high yield (or fracture) strength, low Young's modulus, large elastic strain limit, and easy formability in the SCLR

* Automobile Valve Springs

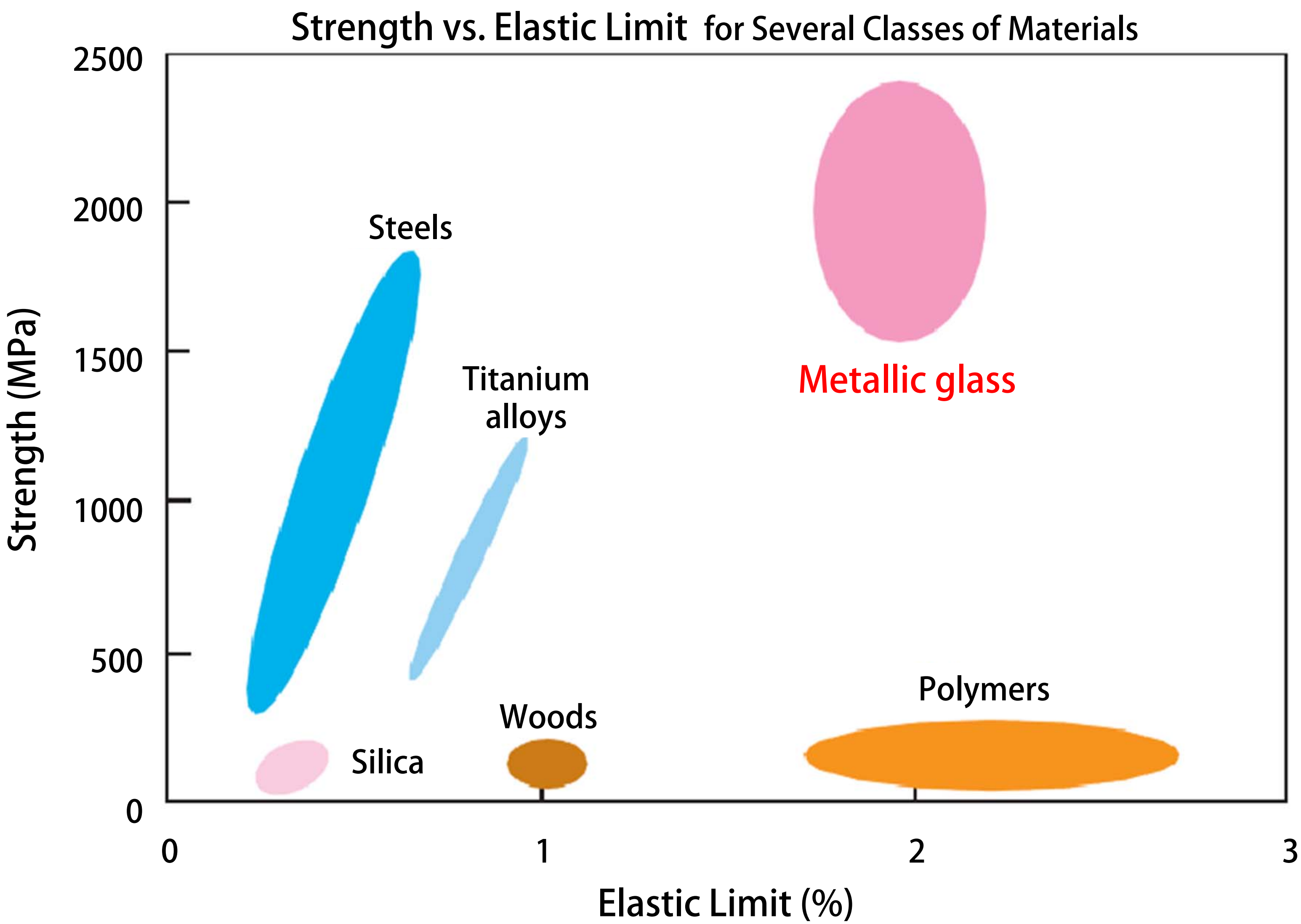
: It was estimated that if the conventional valve springs made of oil-tempered and shot peened Si-Cr steel are replaced with Zr- or Ti-based BMGs, <u>the overall weight of the engine will come down by 4 kg (about 10 lb).</u>



(a) (b)

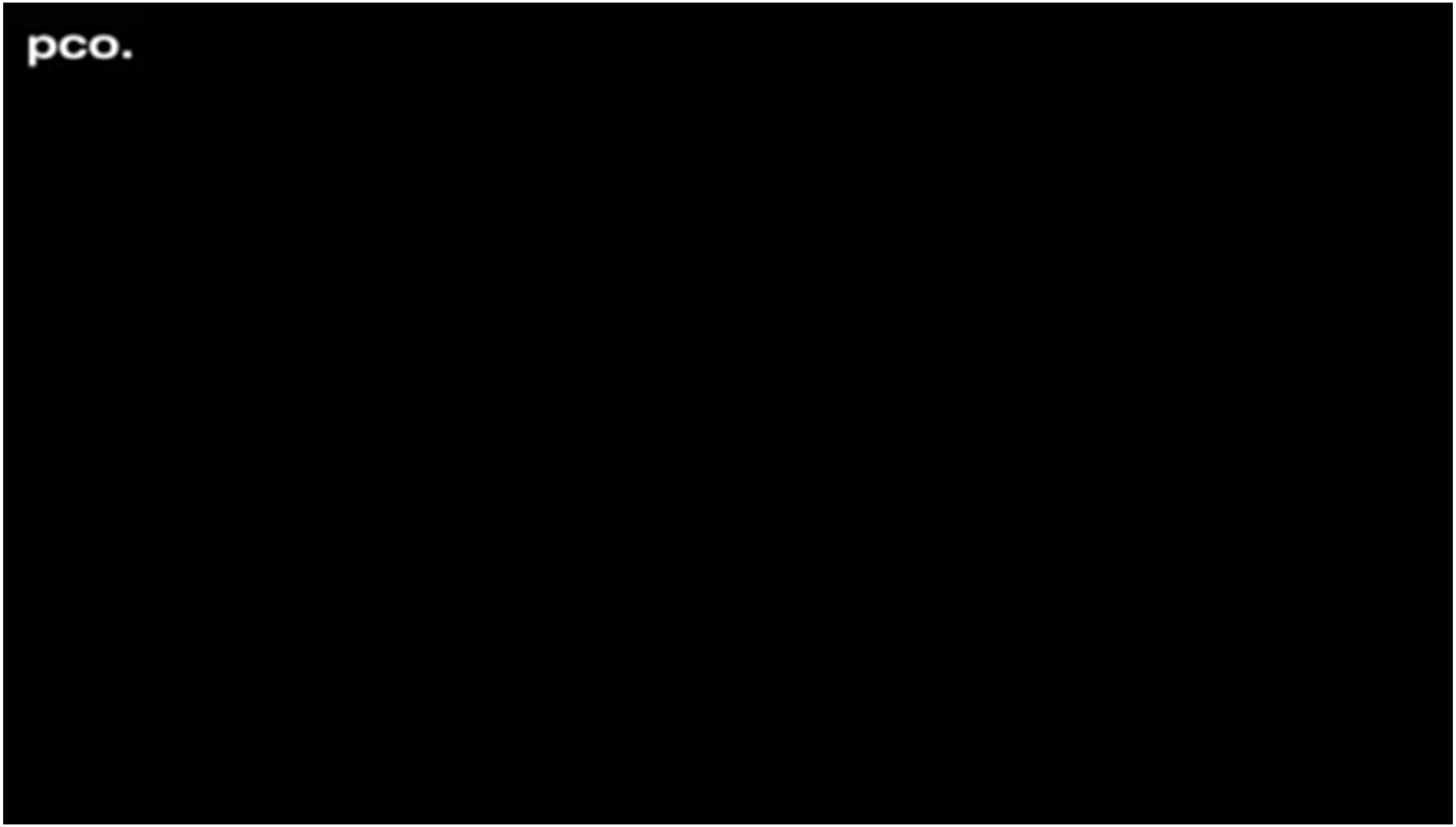
FIGURE 10.10
Helical springs of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG alloy produced by the coiling of wires of (a) 1 mm and (b) 2 mm in diameter. (Reprinted from Son, K. et al., *Mater. Sci. Eng. A*, 449–451, 248, 2007. With permission.)

I. Bulk metallic glasses with high strength & high elastic limit



: Metallic Glasses Offer a Unique Combination of High Strength and High Elastic Limit

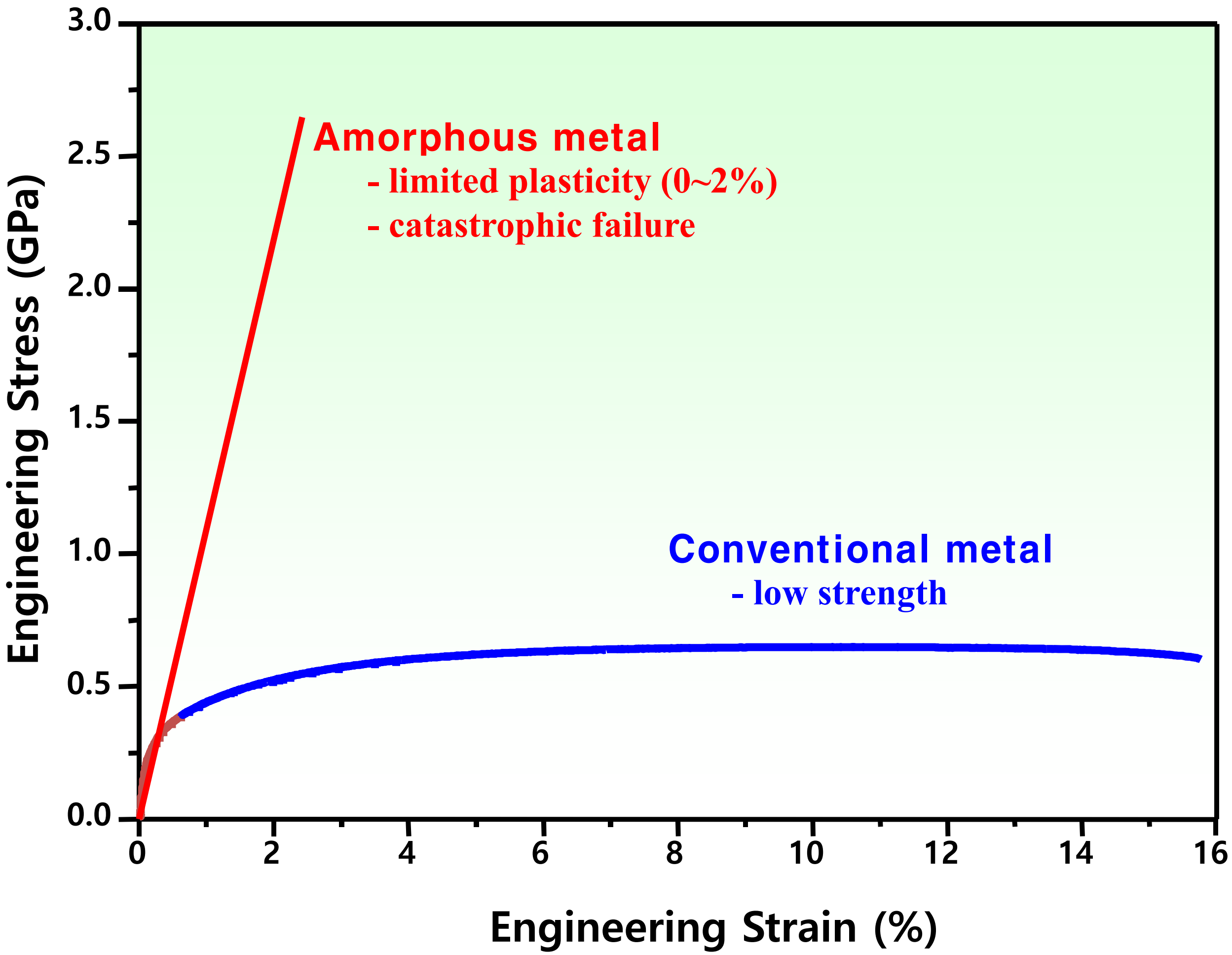
“Drawback” of BMGs as a Structural Material

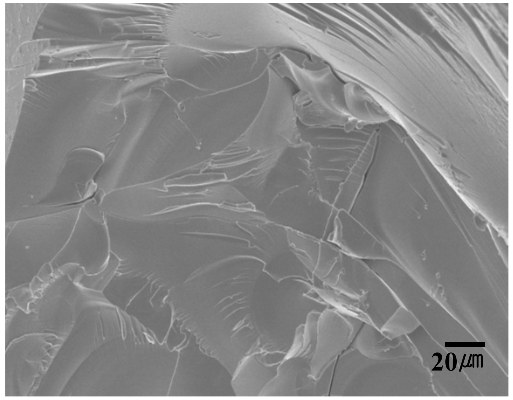


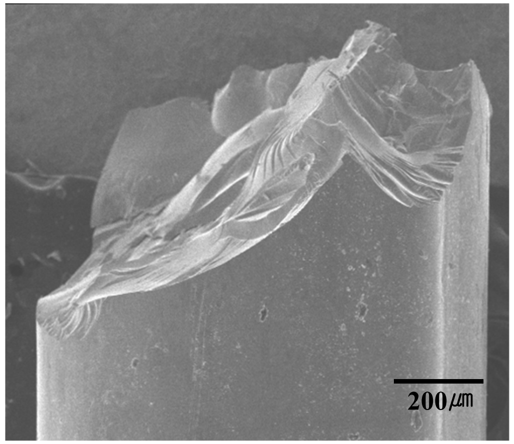
Limited Plasticity by shear softening and shear band

- Microscopically brittle fracture

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

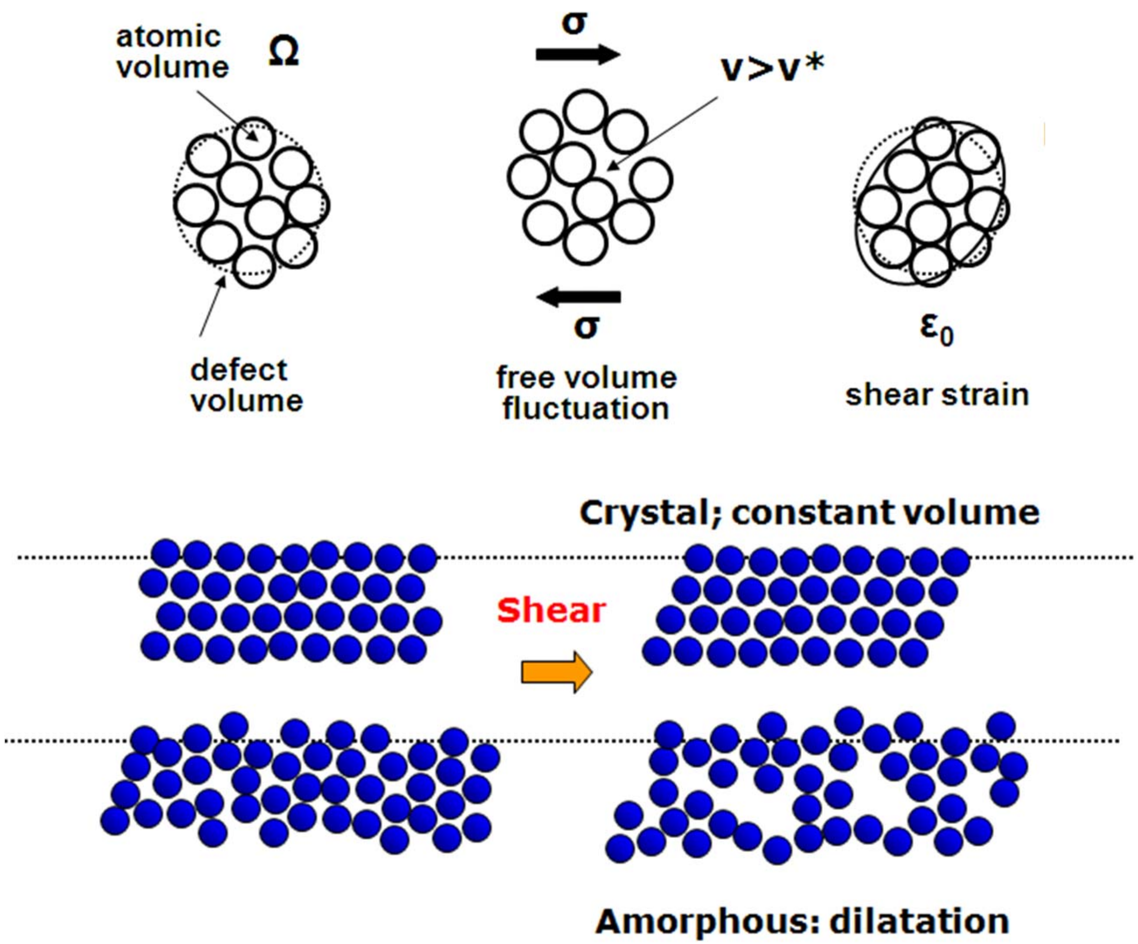






(ESPark Group)

Deformation of metallic glass : Viscous flow →"Shear bands"



Water quickly disappears underneath footprints in sand.

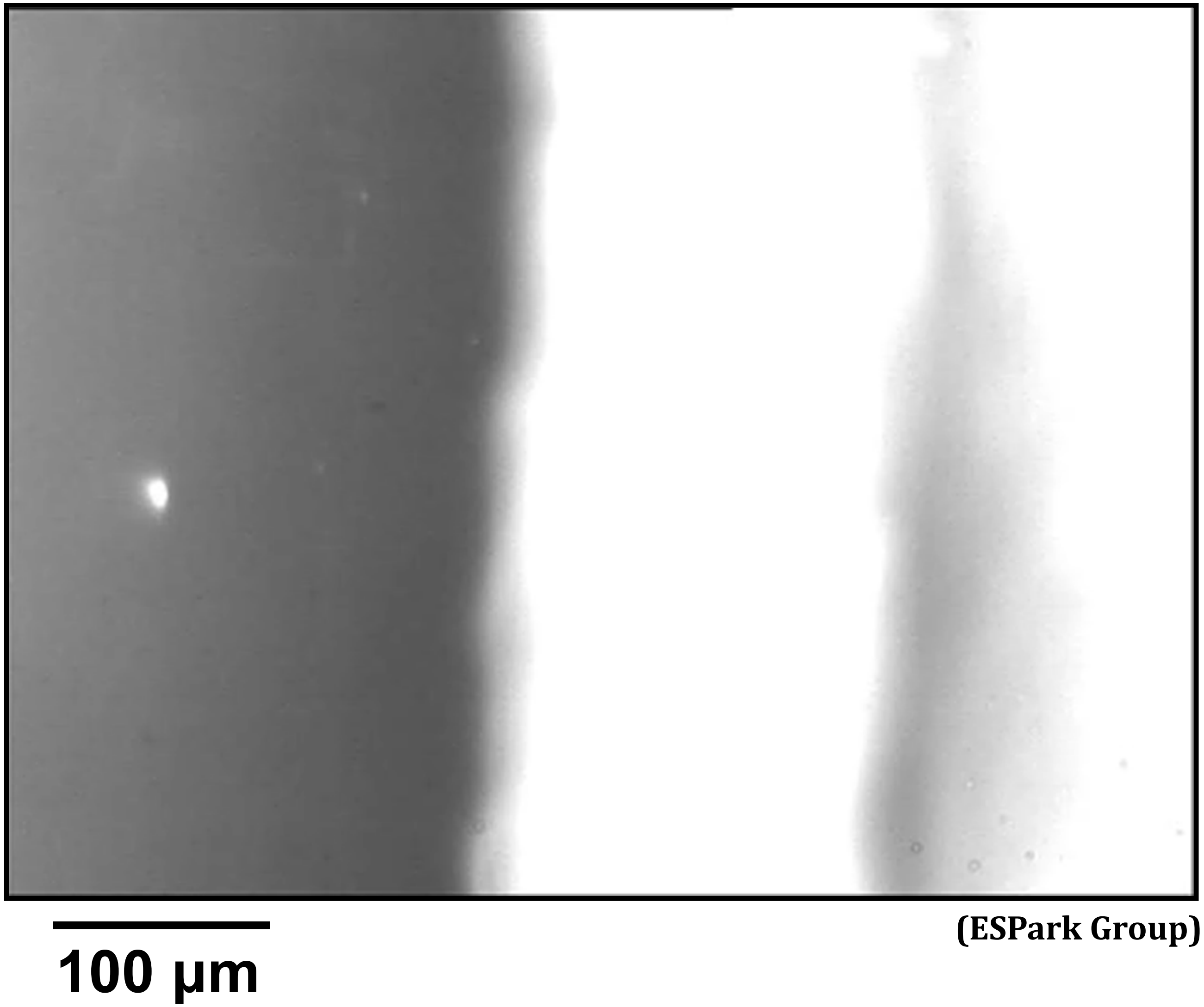
Shear bands form by accumulation of defects during deformation.

nature materials | VOL 5 | JANUARY 2006 | www.nature.com/naturematerials

Effect of local favored structure on SB nucleation

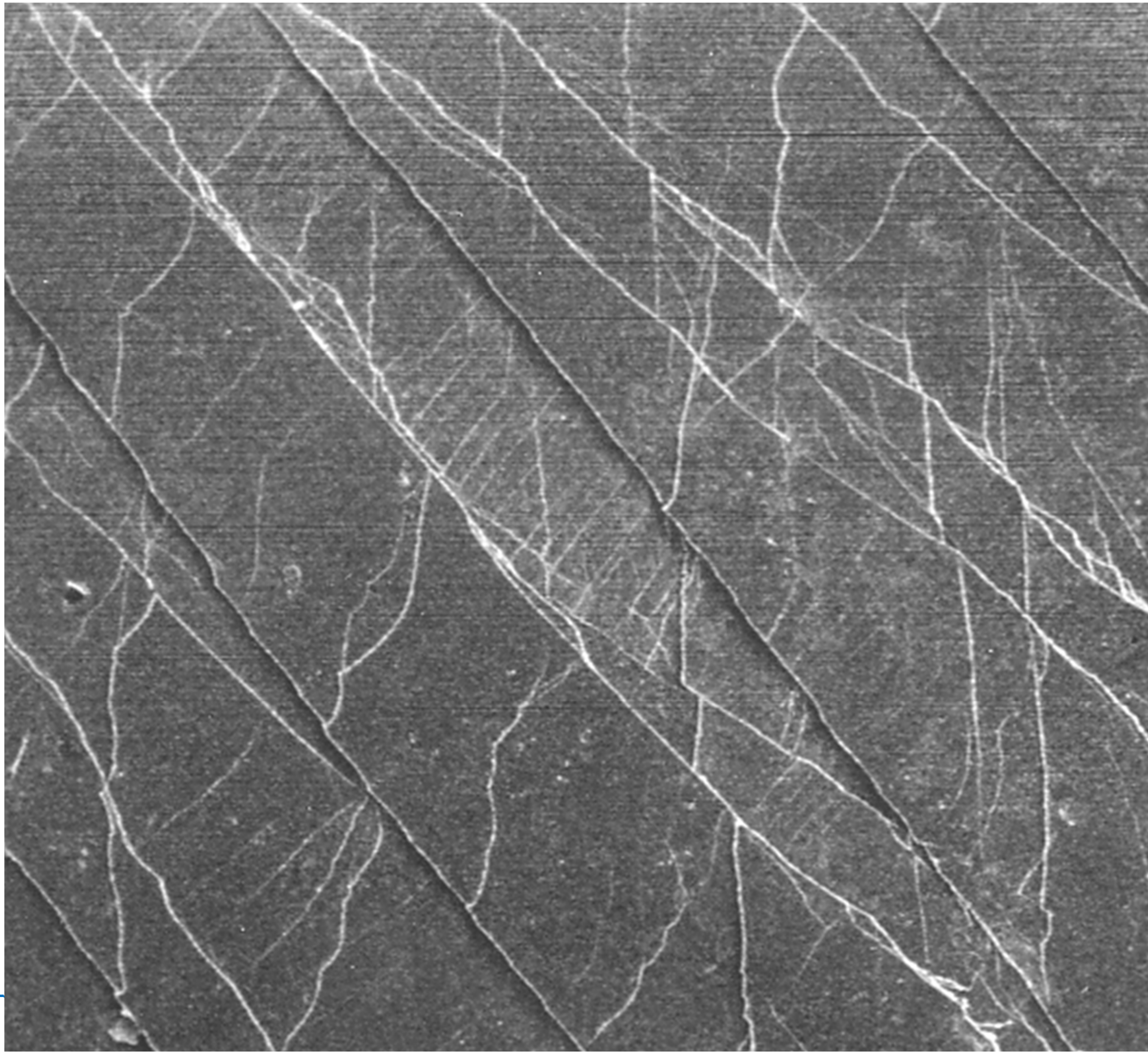
- $Ni_{60}Nb_{40}$: fully amorphous phase

S=0.016 mm/sec

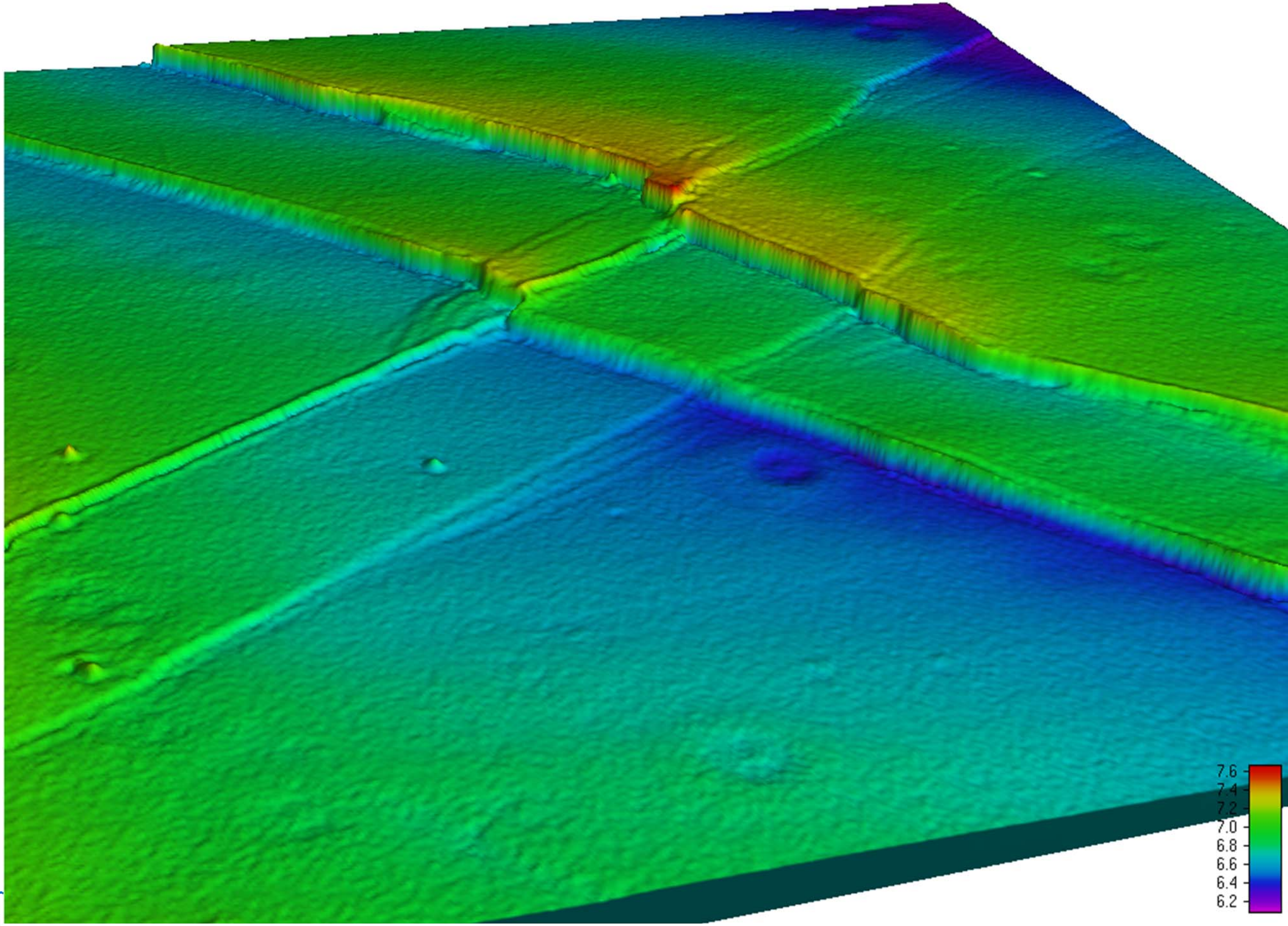


(ESPark Group)

Formation of multiple shear bands during deformation

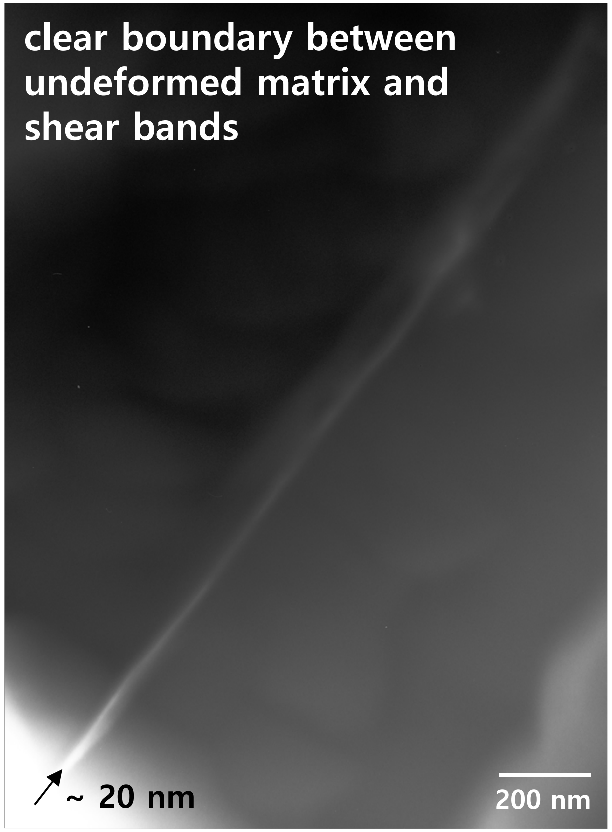


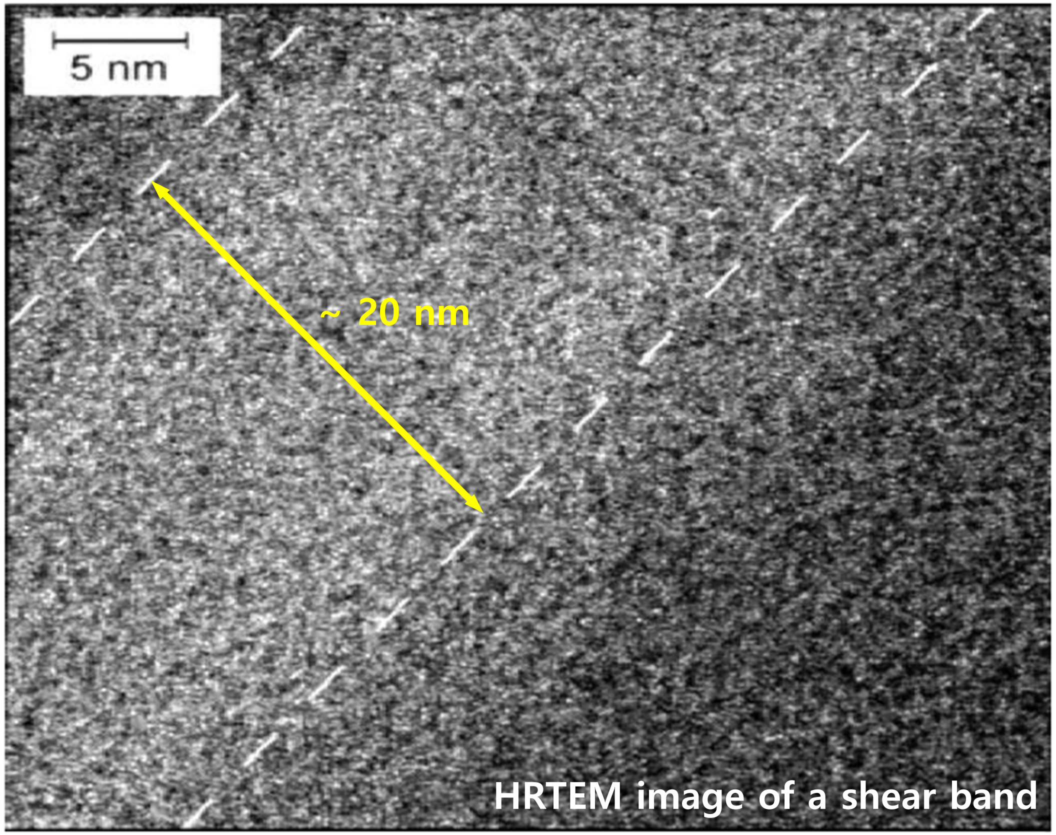
Multiple shear bands = Multiple shear planes



Formation of shear bands : variation of free volume

Shear bands form by accumulation of defects during deformation.





Shear deformed areas with the same composition & different density of free volume

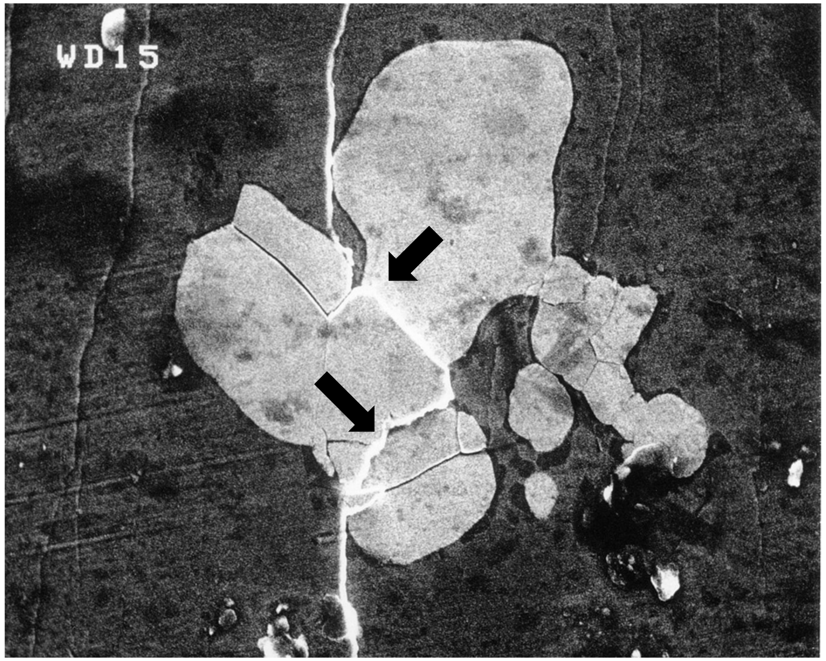
Plastic deformation in metallic glasses: Manipulation of SBs!

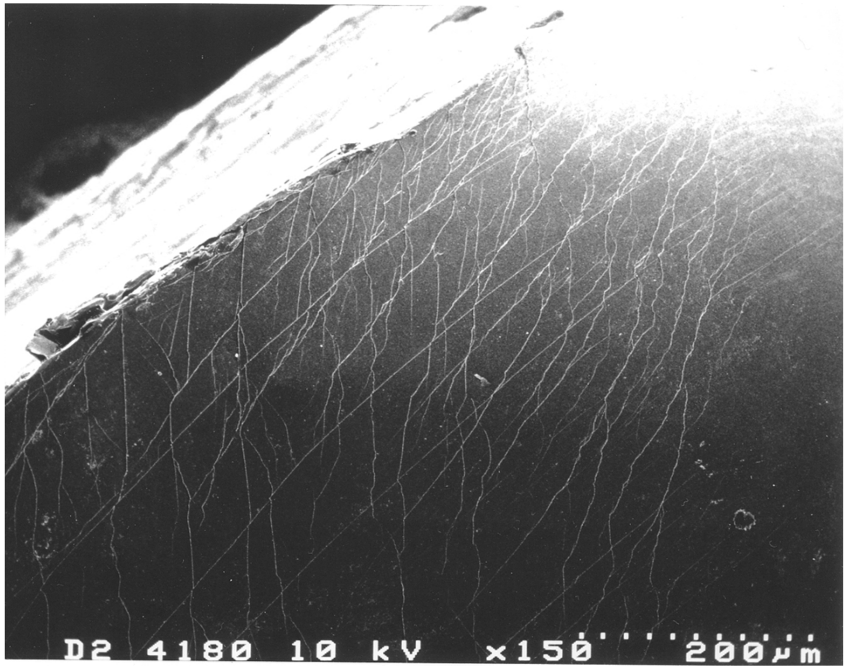
BMGs : No dislocation or slip system

Inhomogeneous deformation in shear bands → brittle fracture

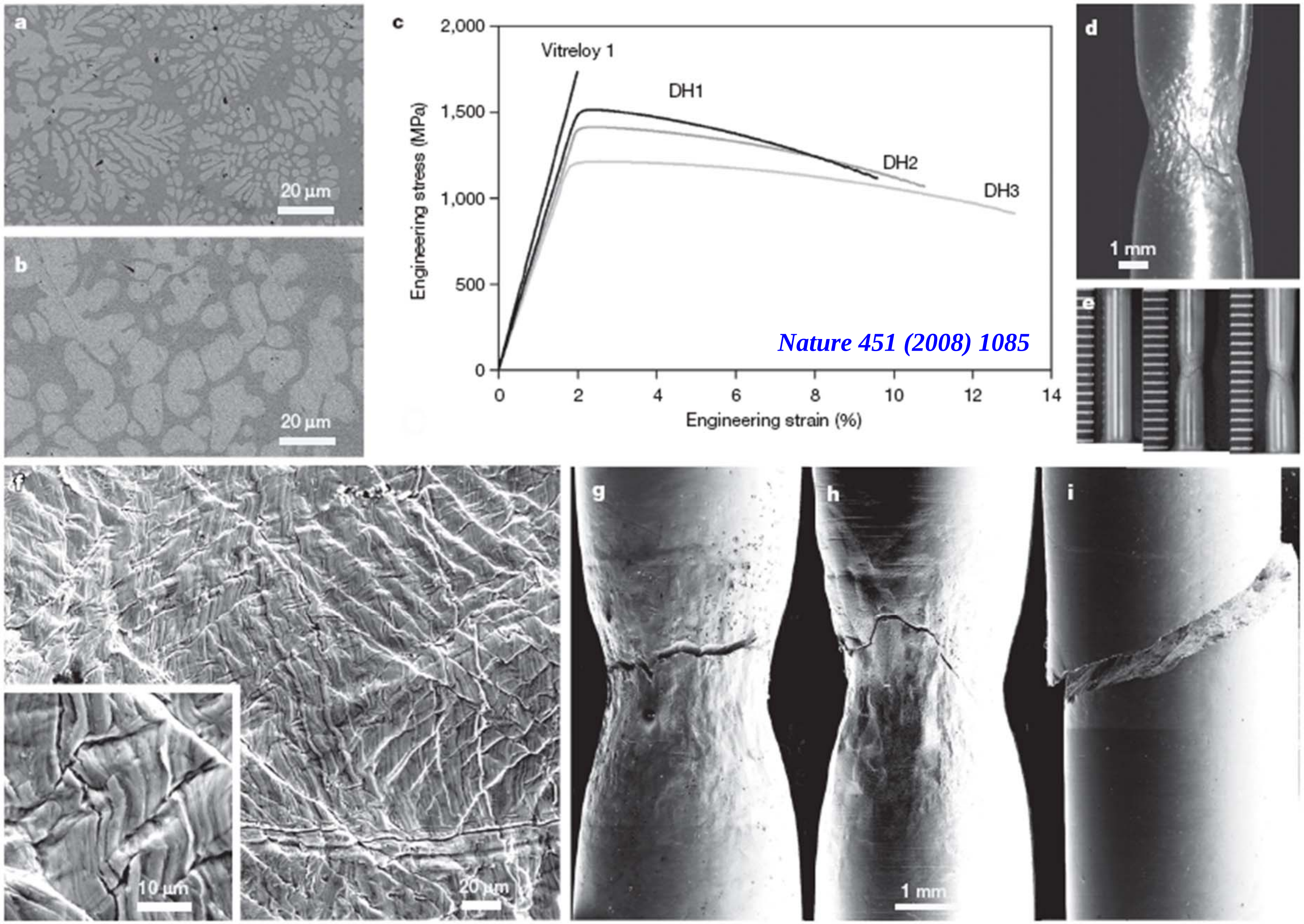
To improve plasticity in BMGs,

- Interruption of shear band propagation ⇨ **BMG matrix composites**
- Formation of multiple shear bands





In-situ BMG matrix composites with tensile ductility



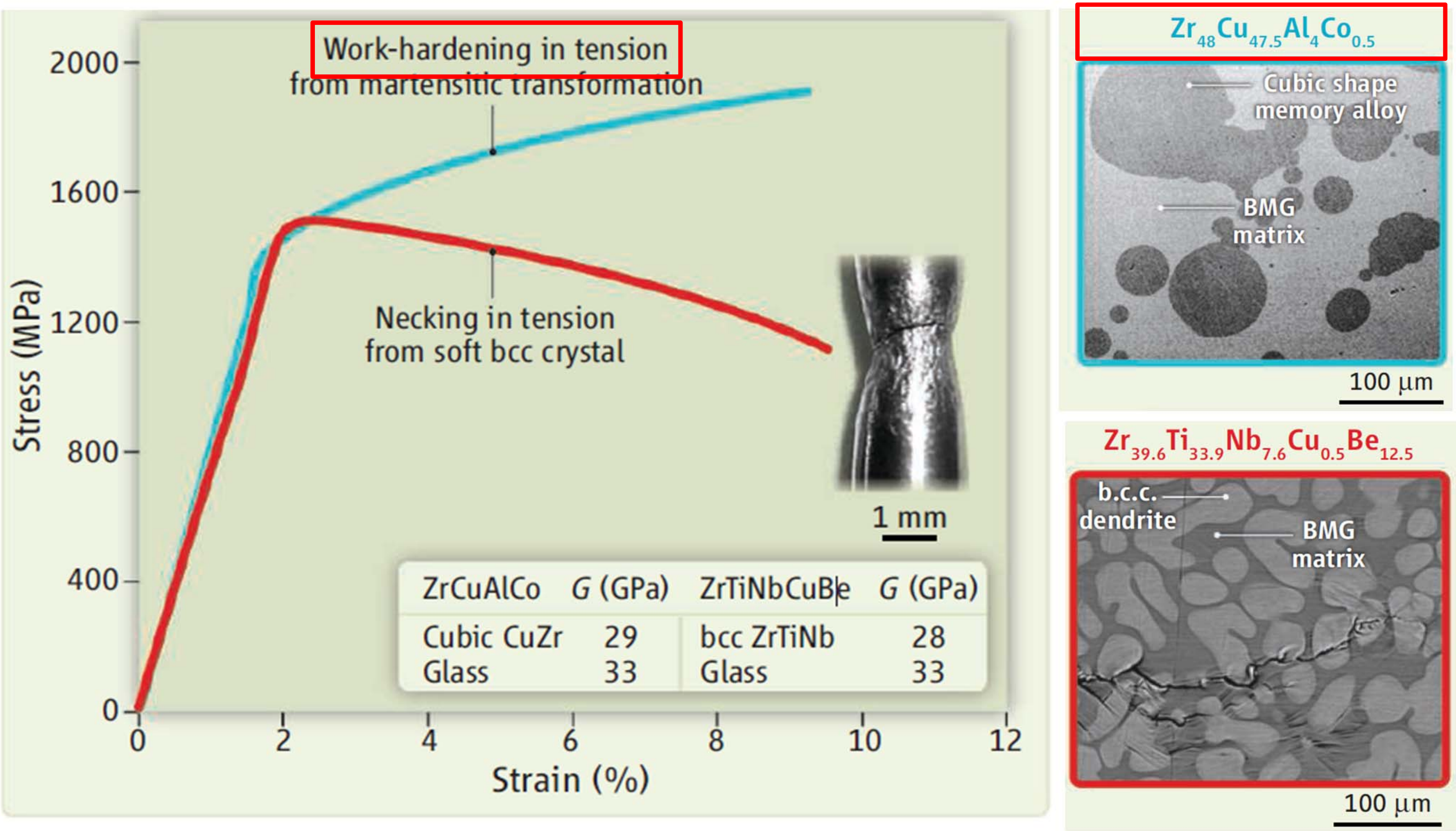
High fracture toughness: > 10 % plastic strain in tensile test

MATERIALS SCIENCE

Shape Memory Bulk Metallic Glass Composites

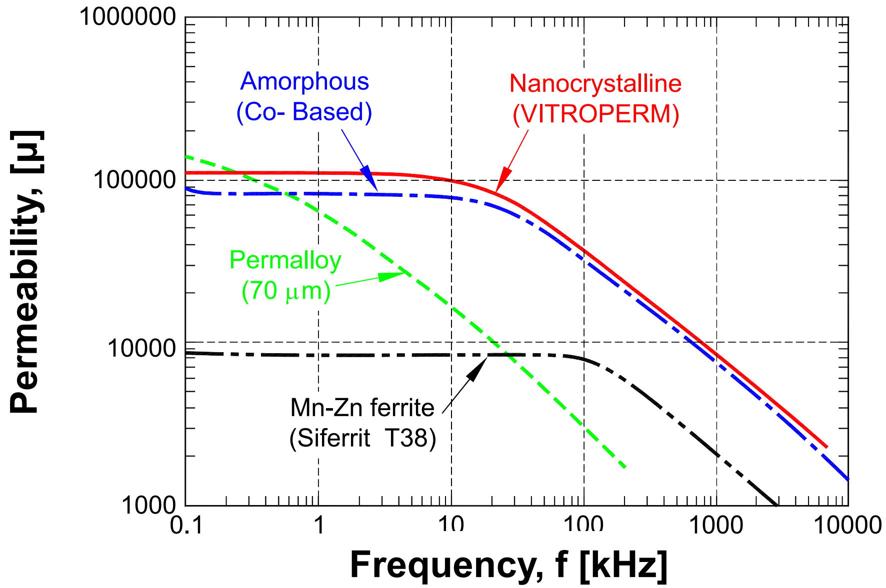
Glass-forming and shape memory metals may provide a route to fabricating materials with enhanced mechanical properties.

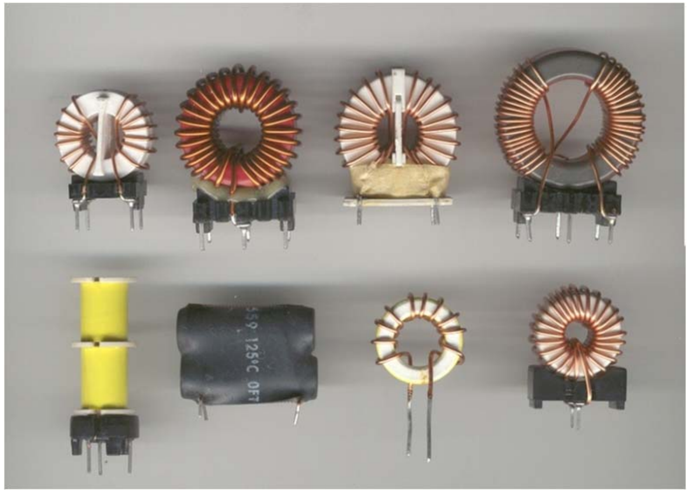
Douglas C. Hofmann



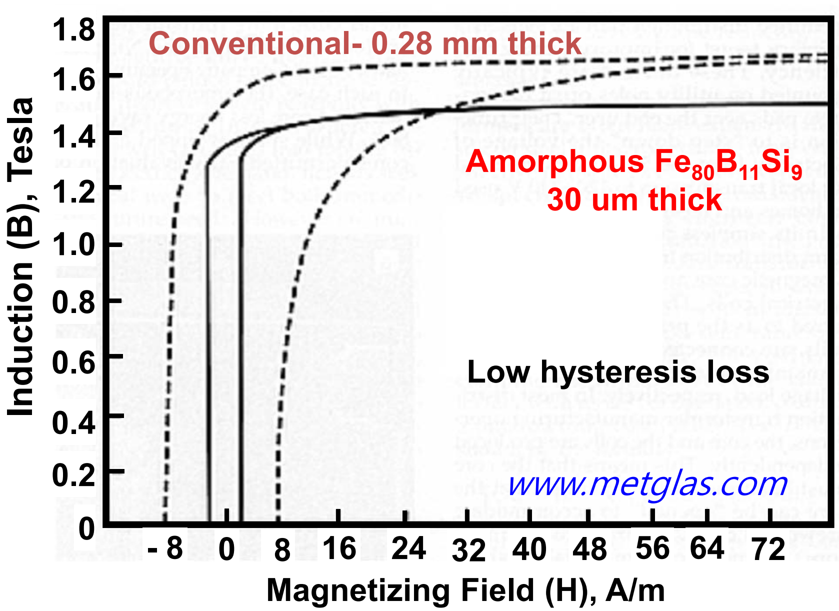
ZrCuAlCo	*G* (GPa)	ZrTiNbCuBe	*G* (GPa)
Cubic CuZr	29	bcc ZrTiNb	28
Glass	33	Glass	33

3. Old uses: soft magnet





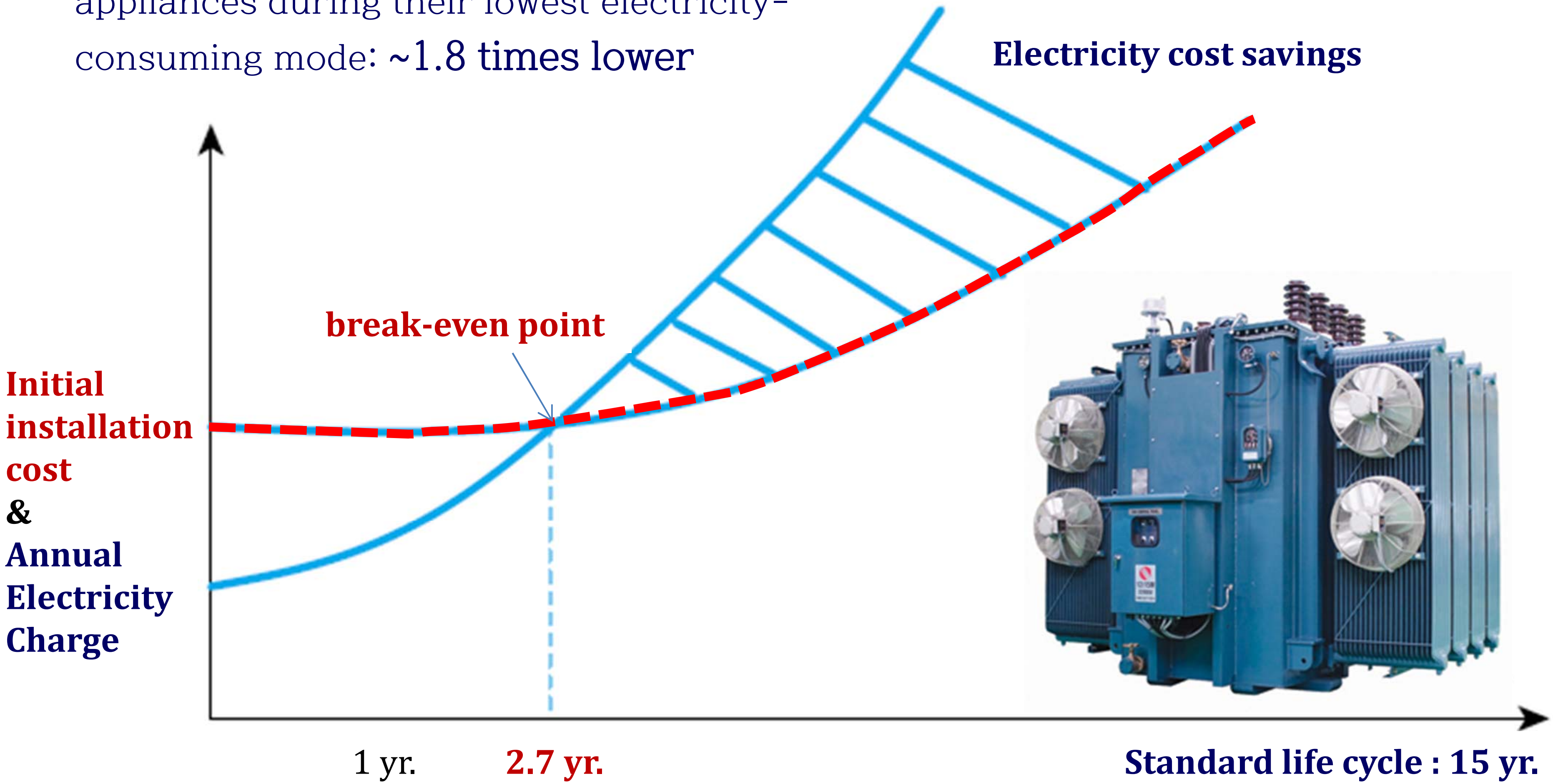
Magnetic cores



Transformers

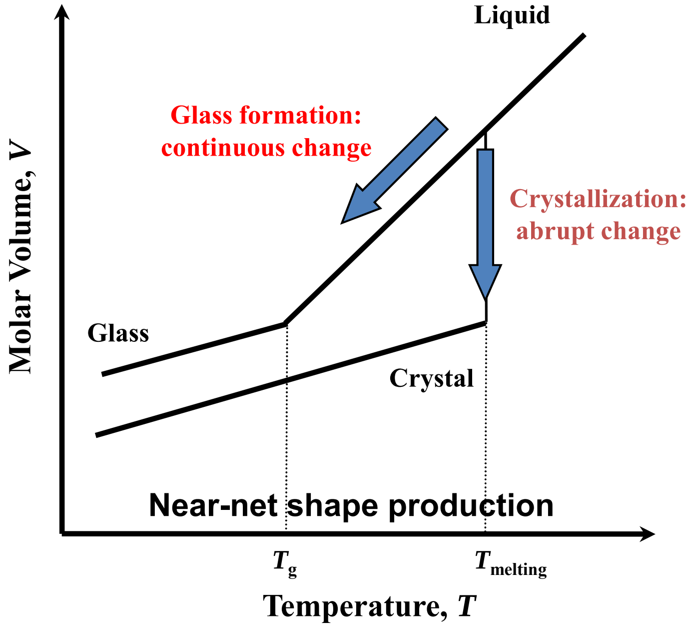
< Energy savings of amorphous transformers>

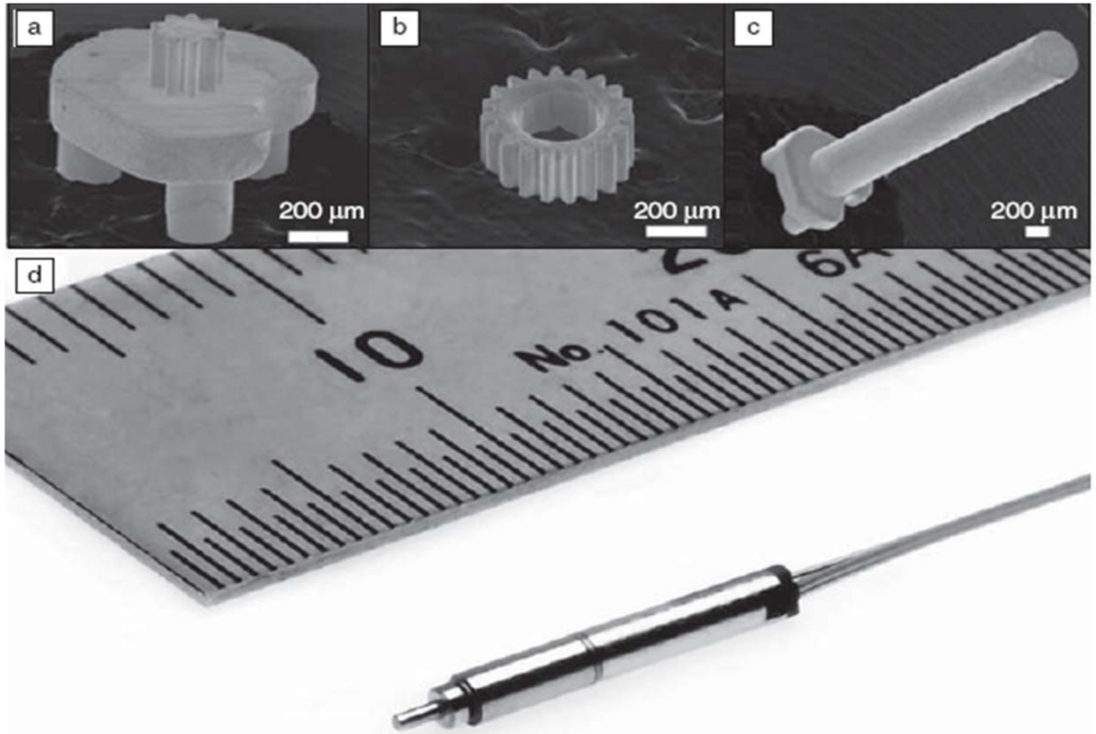
- **Initial installation cost** : ~ 1.5 times expensive
- ⟺ **Standby power**, which is the power consumed by appliances during their lowest electricity-consuming mode: ~1.8 times lower

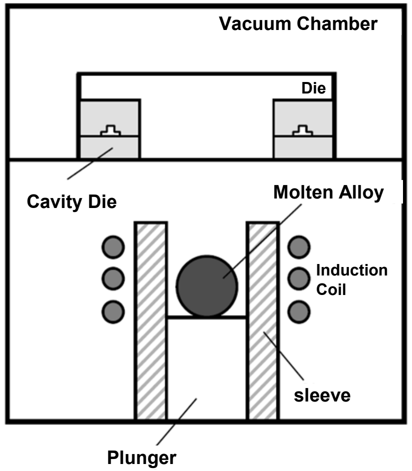


4. Processing metals as efficiently as plastics

1) Micro-casting & forming

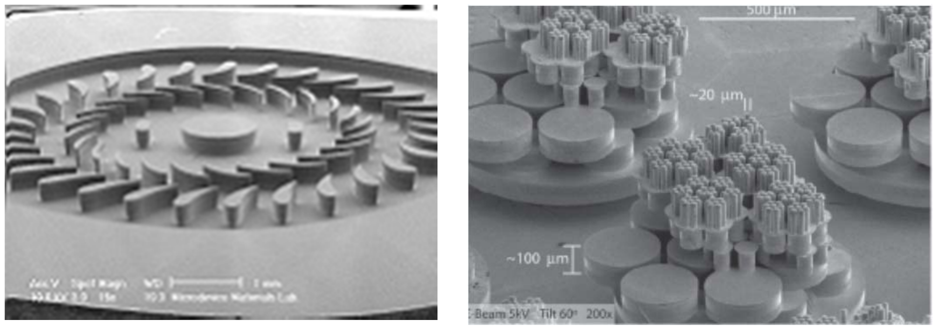






Precision die casting

Precision Gears for Micro-motors



Structural Applications: high yield (or fracture) strength, low Young's modulus, large elastic strain limit, and easy formability in the SCLR

* Micro-Motors

- Higher dimensional accuracy
- 313 times longer than conventional motor

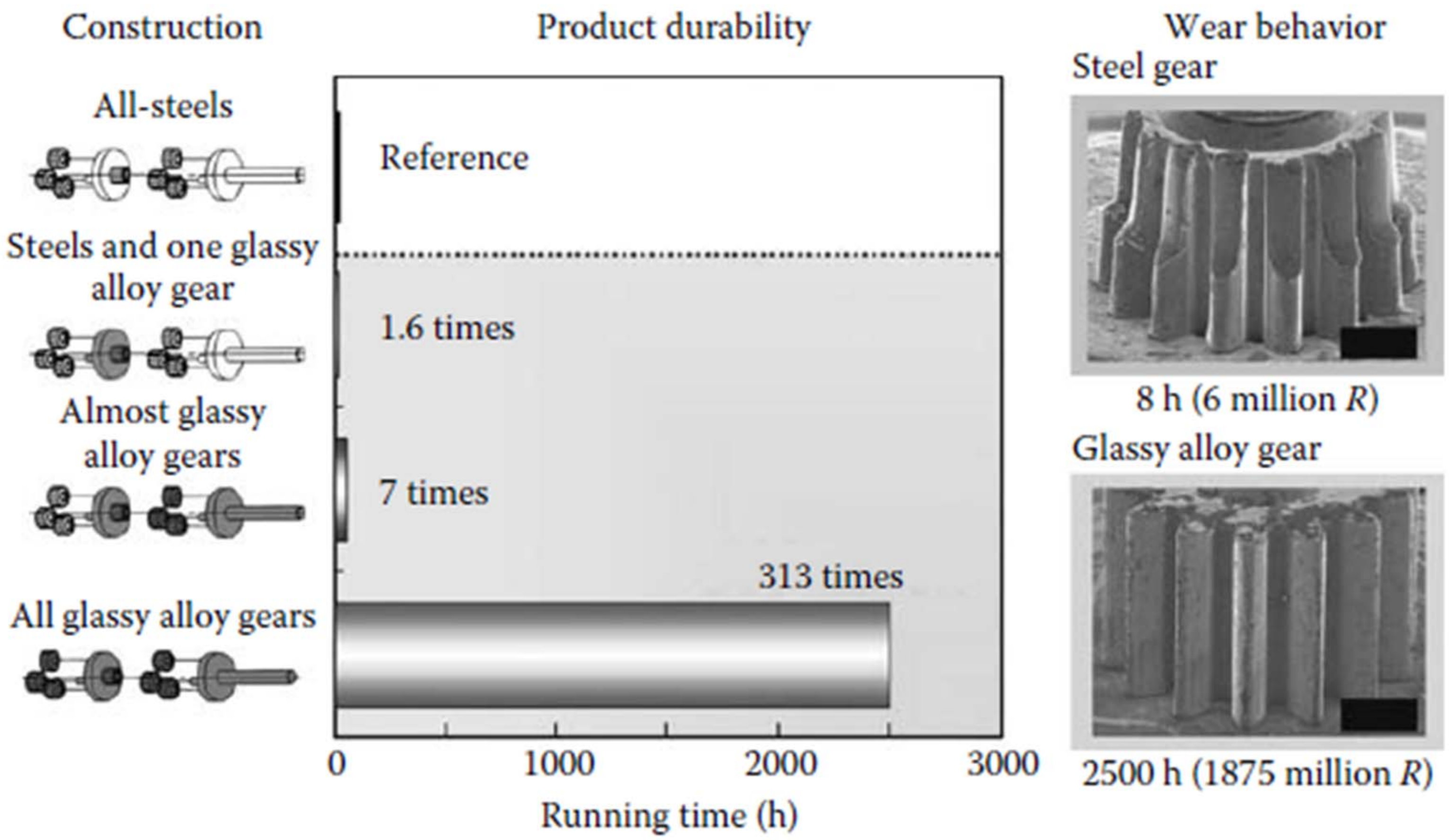
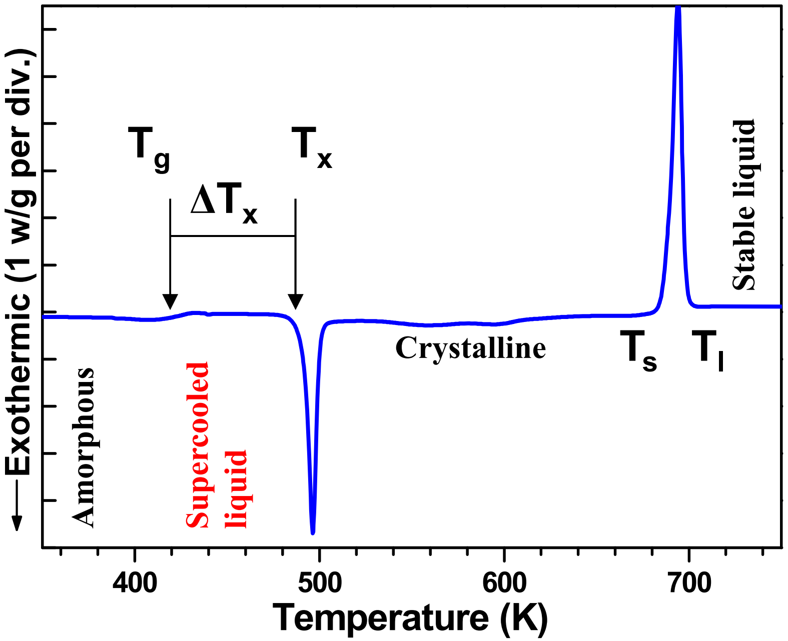
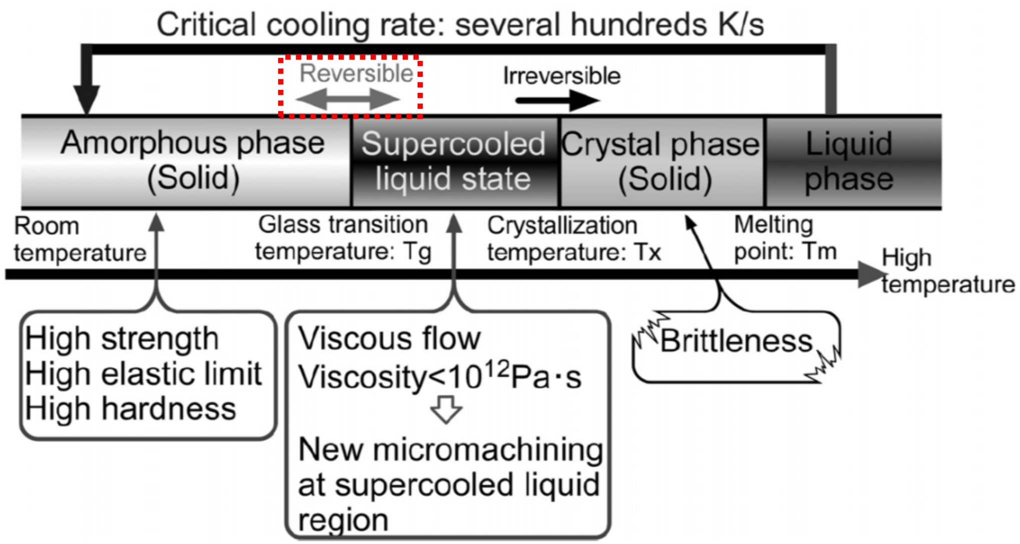


FIGURE 10.7
Comparative wear resistance behavior of gears made with different materials in a 2.4 mm diameter geared motor. (Reprinted from Inoue, A. et al., *Mater. Sci. Eng. A*, 441, 18, 2006. With permission.)

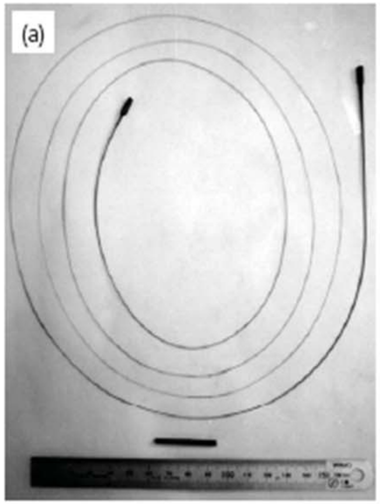
4. Processing metals as efficiently as plastics

2) Thermoplastic forming

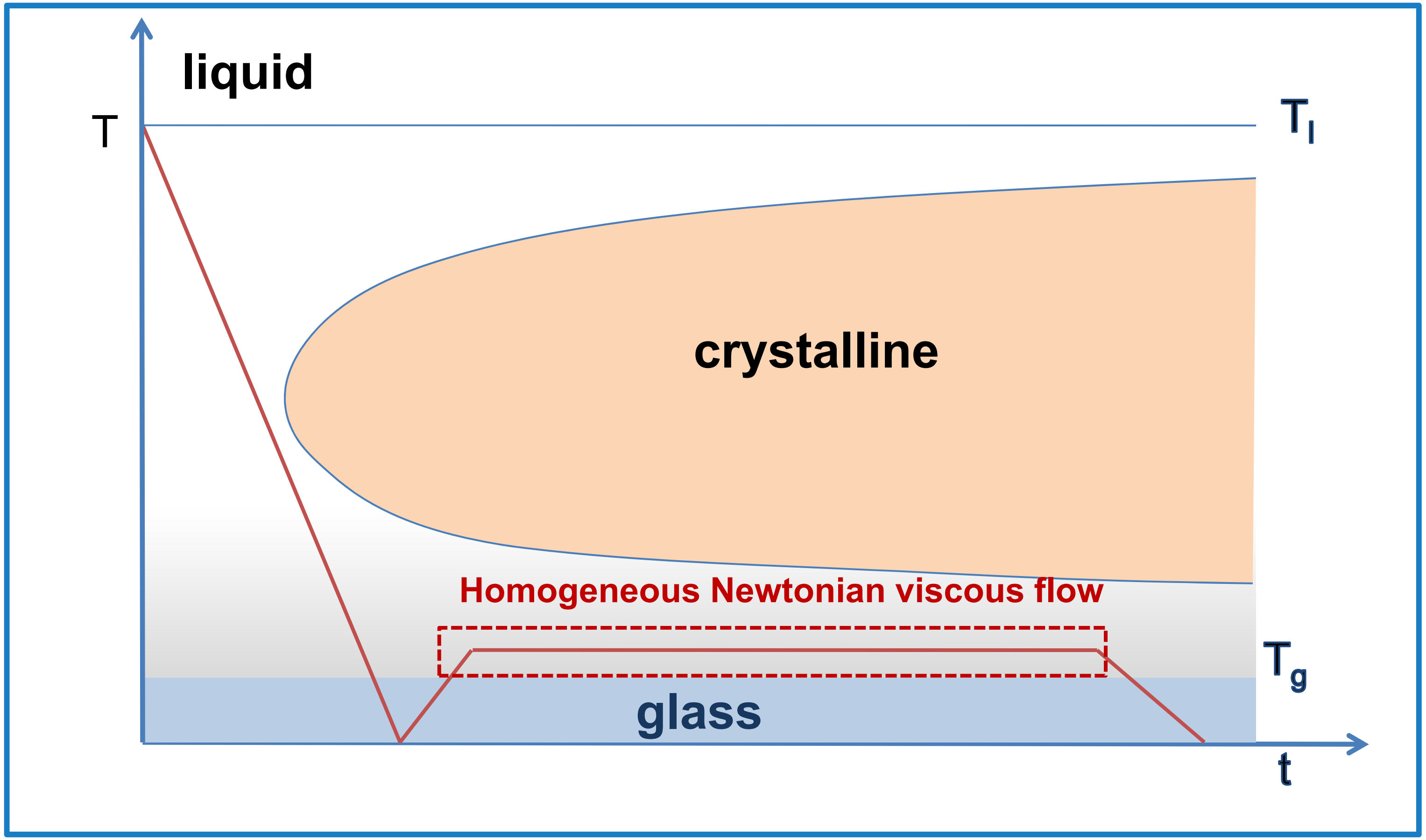




Tensile specimens following superplastic forming in supercooled liquid region



Thermoplastic forming (TPF) in SCLR

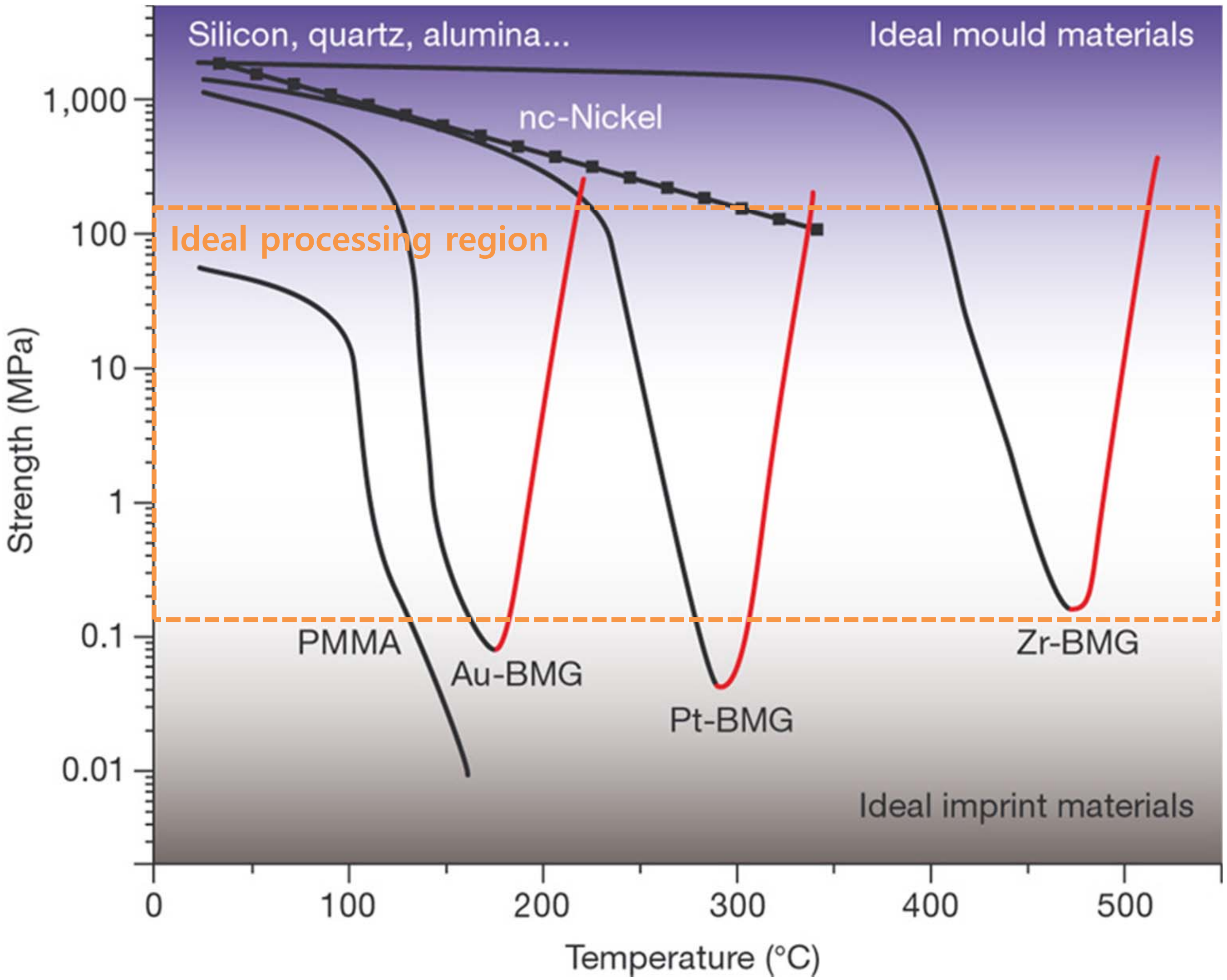


Metallic glass can be processed like plastics by homogeneous Newtonian viscous flow in supercooled liquid region (SCLR).

➡ **Possible to deform thin and uniform MG**

High processibility of metallic glass according to temperature

Nature ***457****, 868-872* (12 February 2009)



Thermoplastic forming in supercooled liquid region

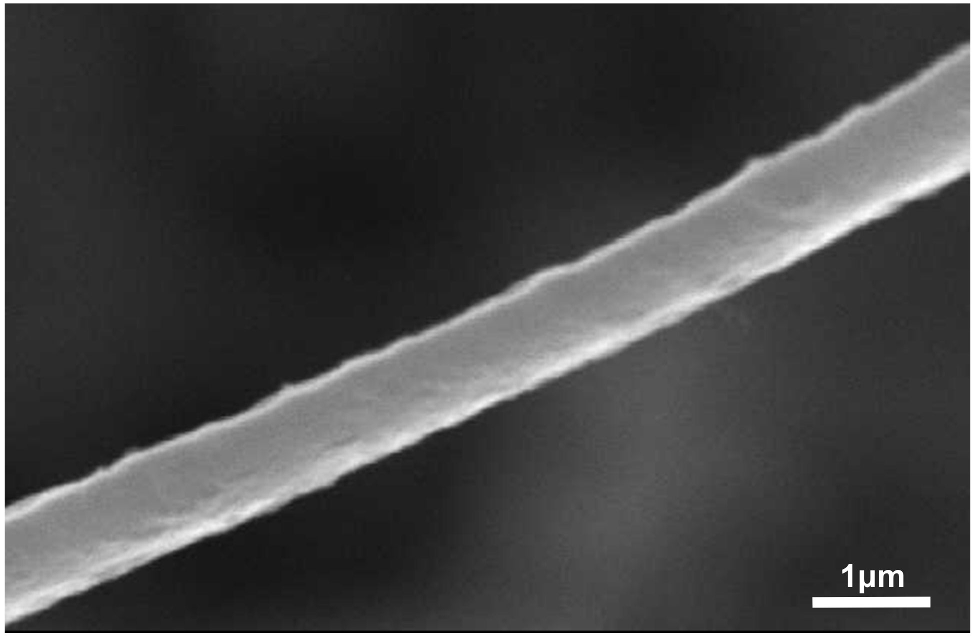
$Mg_{65}Cu_{25}Gd_{10}$ metallic glass ribbon

- Drawing sample at 220°C ➡ Elongation over 1100%

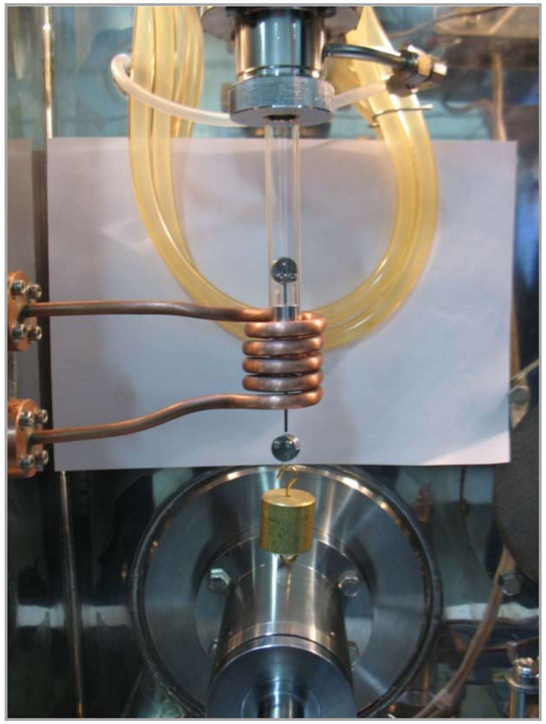
Thermoplastic forming - Fabrication of nanowire

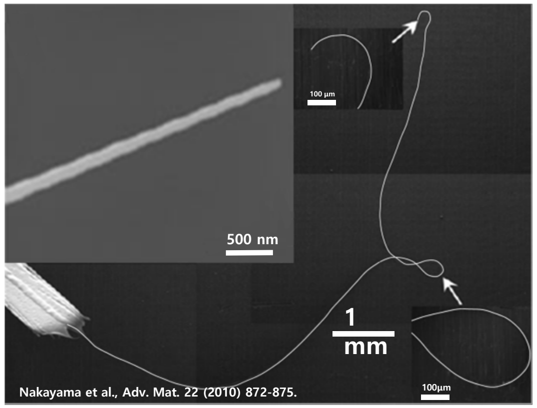
Homogeneous Newtonian viscous flow

mm ribbon → (drawing; low temp. SLR) → μm wire ⇢ (drawing; Control of strain rate & temp.) ⇢ nm wire



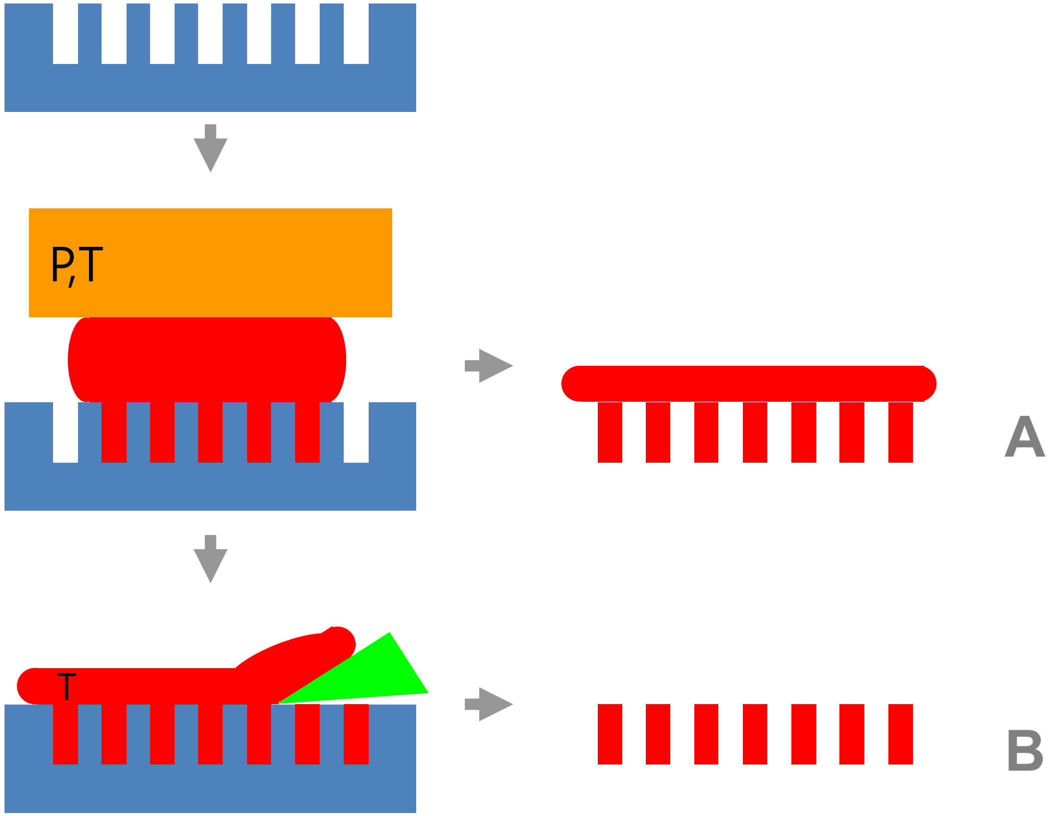
SEM image of nanometer scale metallic glass wire formed by drawing micrometer scale wire on hotplate





a. TPF-based miniature molding– down to nanoscale!

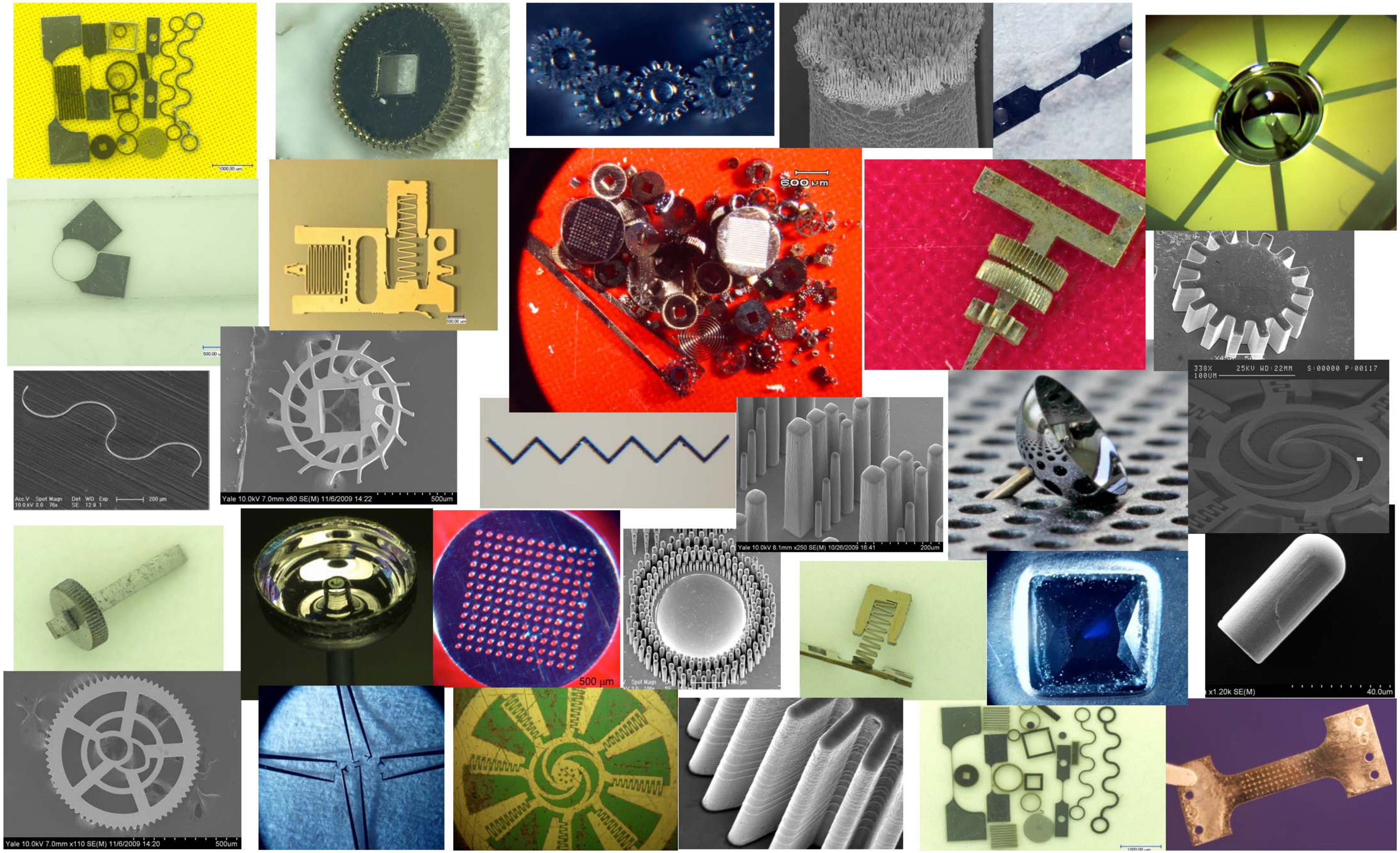
- BMGs have no intrinsic size limitation
- Competition weak (silicon, electroplated metals, polymers)
- BMGs properties become more attractive on the small scale



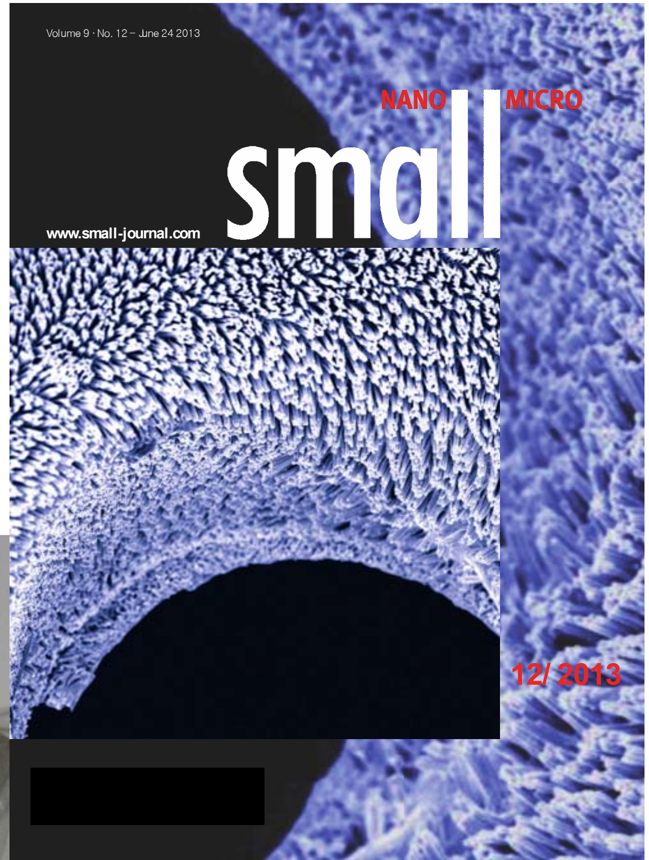
J. Schroers, Q. Pham and A. Desai, J. MEMS, 16, 240 (2007).

Processing of Bulk Metallic Glass

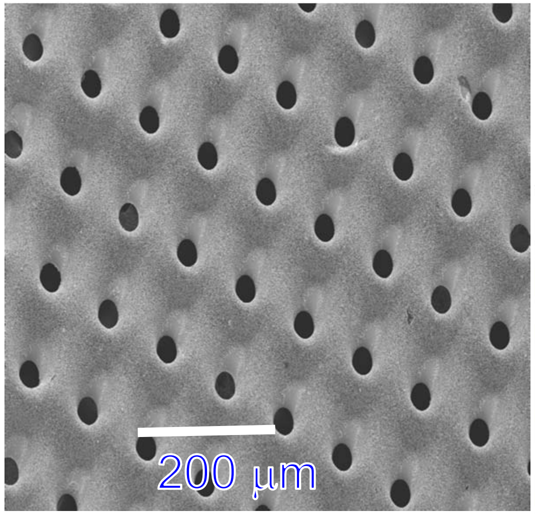
Adv. Mater. **2009**, *21*, 1–32

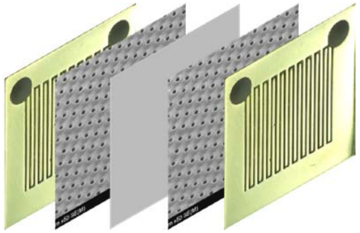


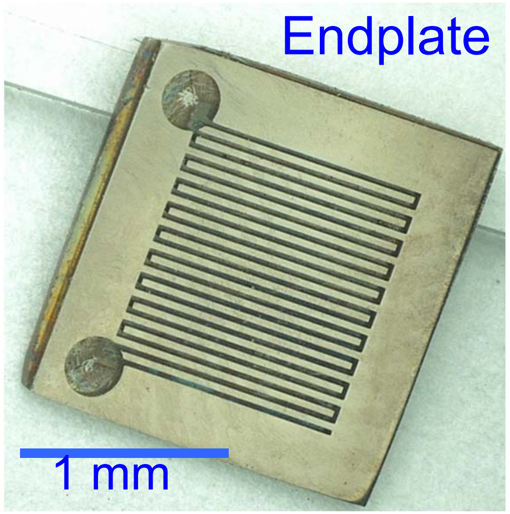
Metallic Glass Fuel Cell

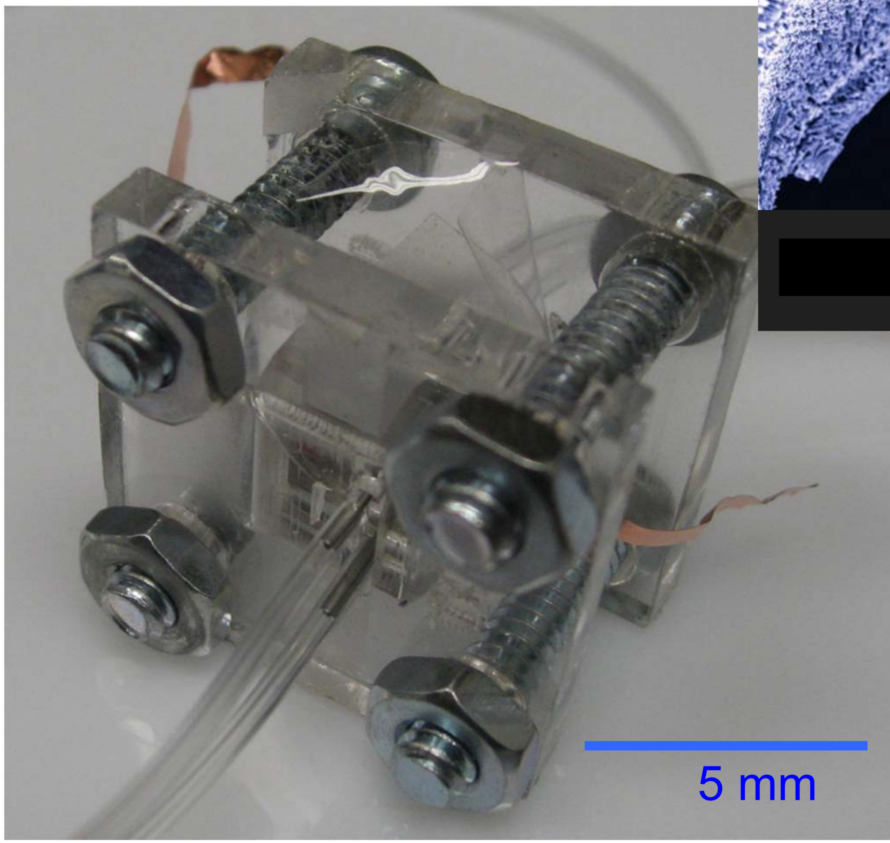


Electrode, Catalyst

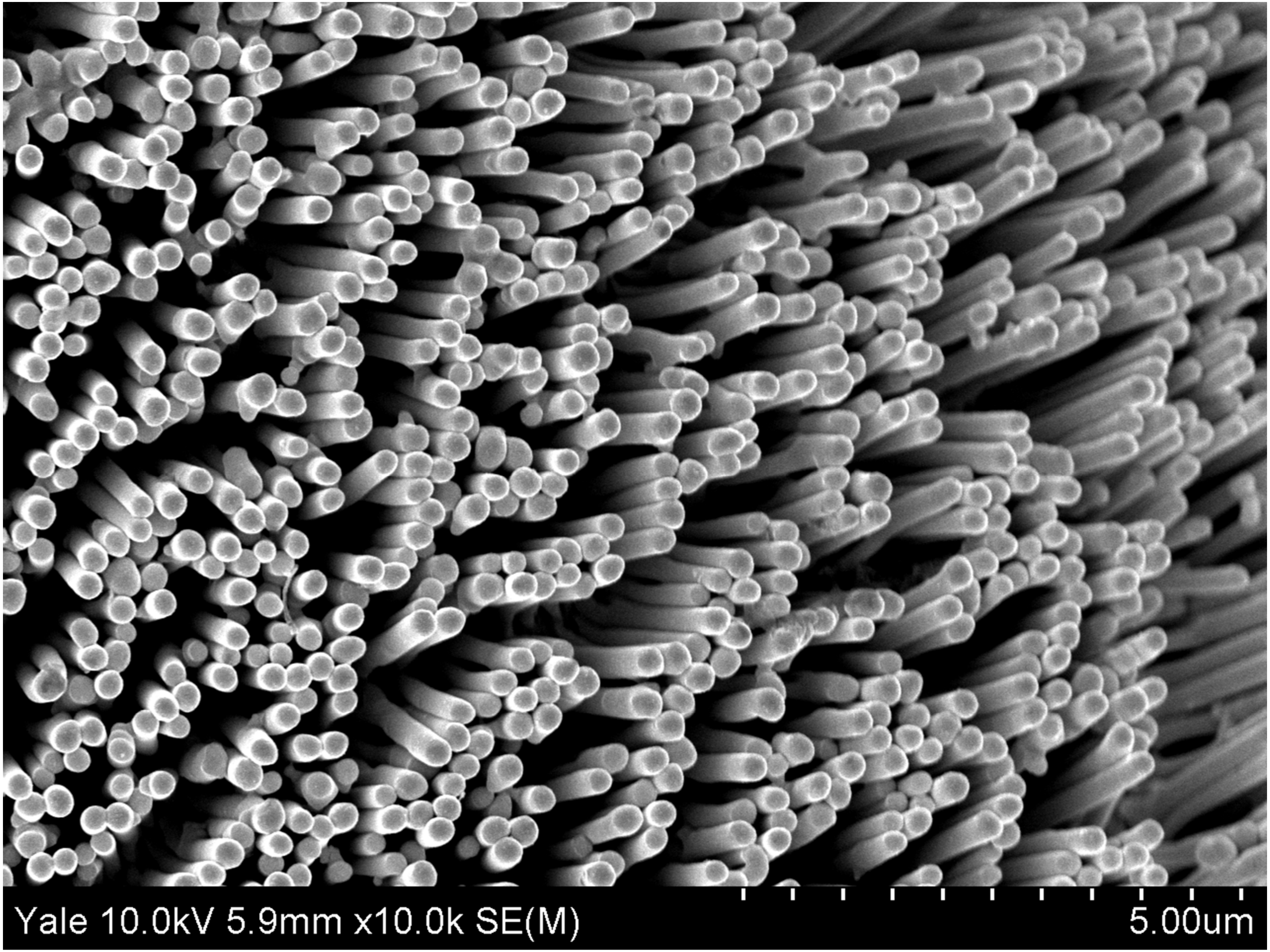








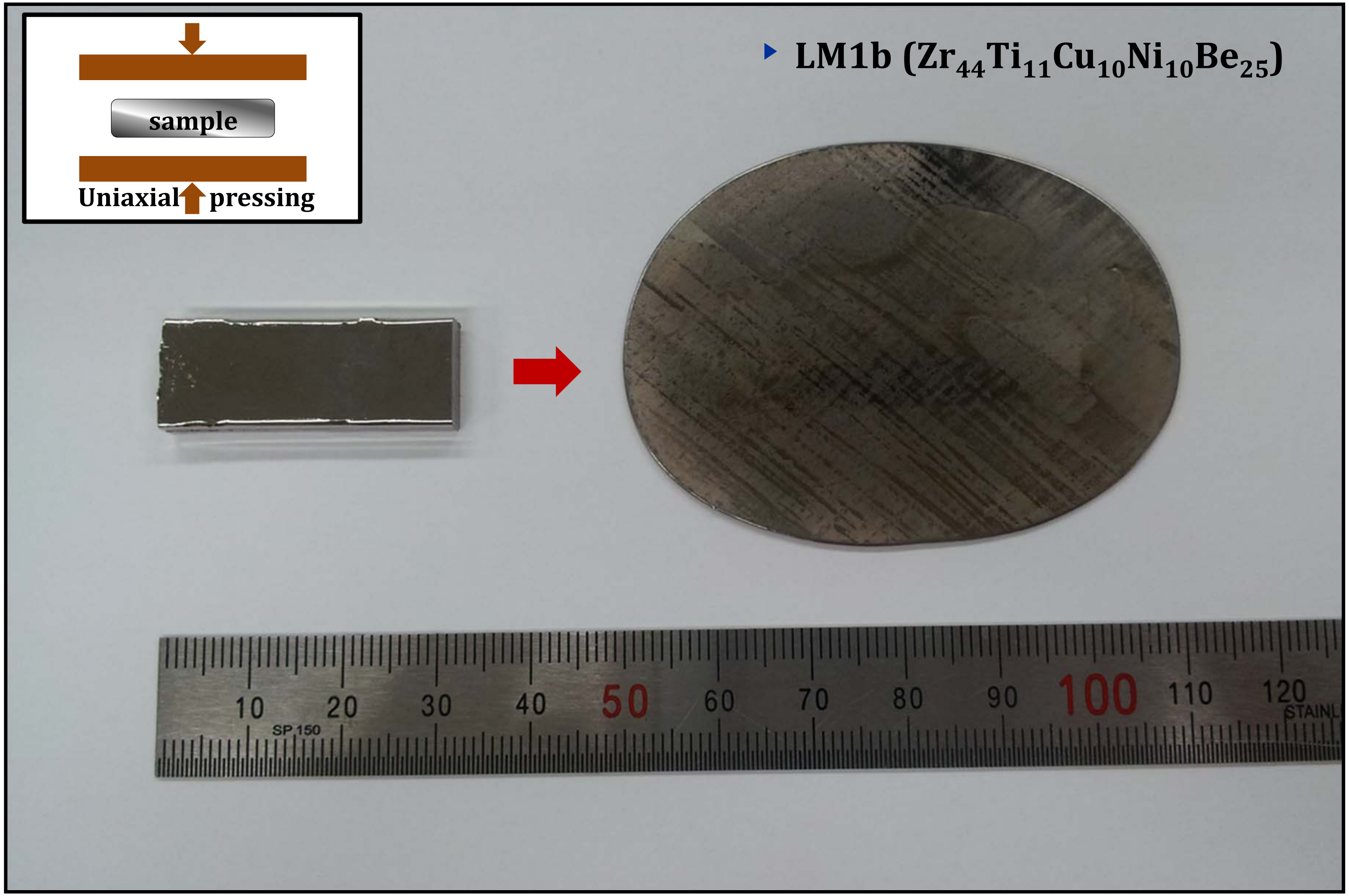
R. C. Sekol, M. Carmo, G. Kumar, J. Schroers, and A. D. Taylor, Small 9, 2081 (2013)


Yale 10.0kV 5.9mm x10.0k SE(M)
5.00um

Jan Schroers, Adv. Mater., 2010, hologram pattern

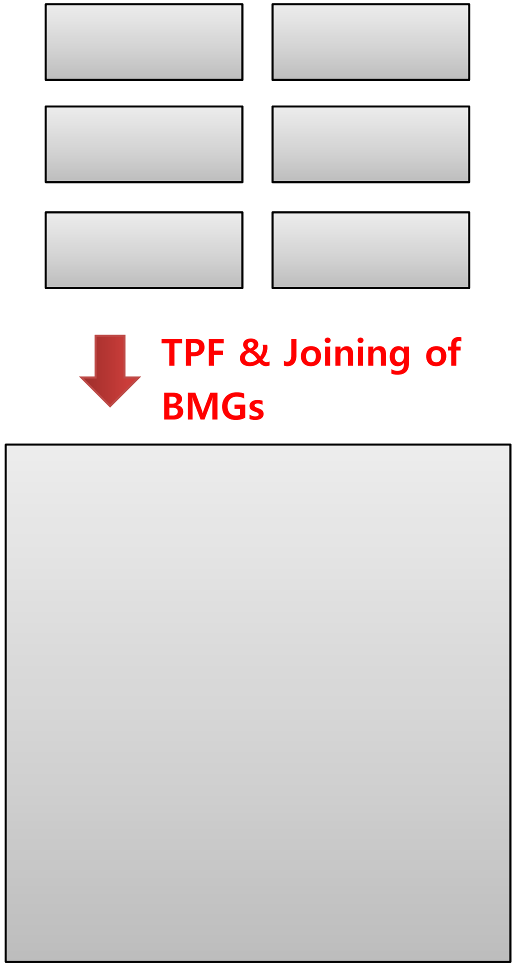

OPTICAL

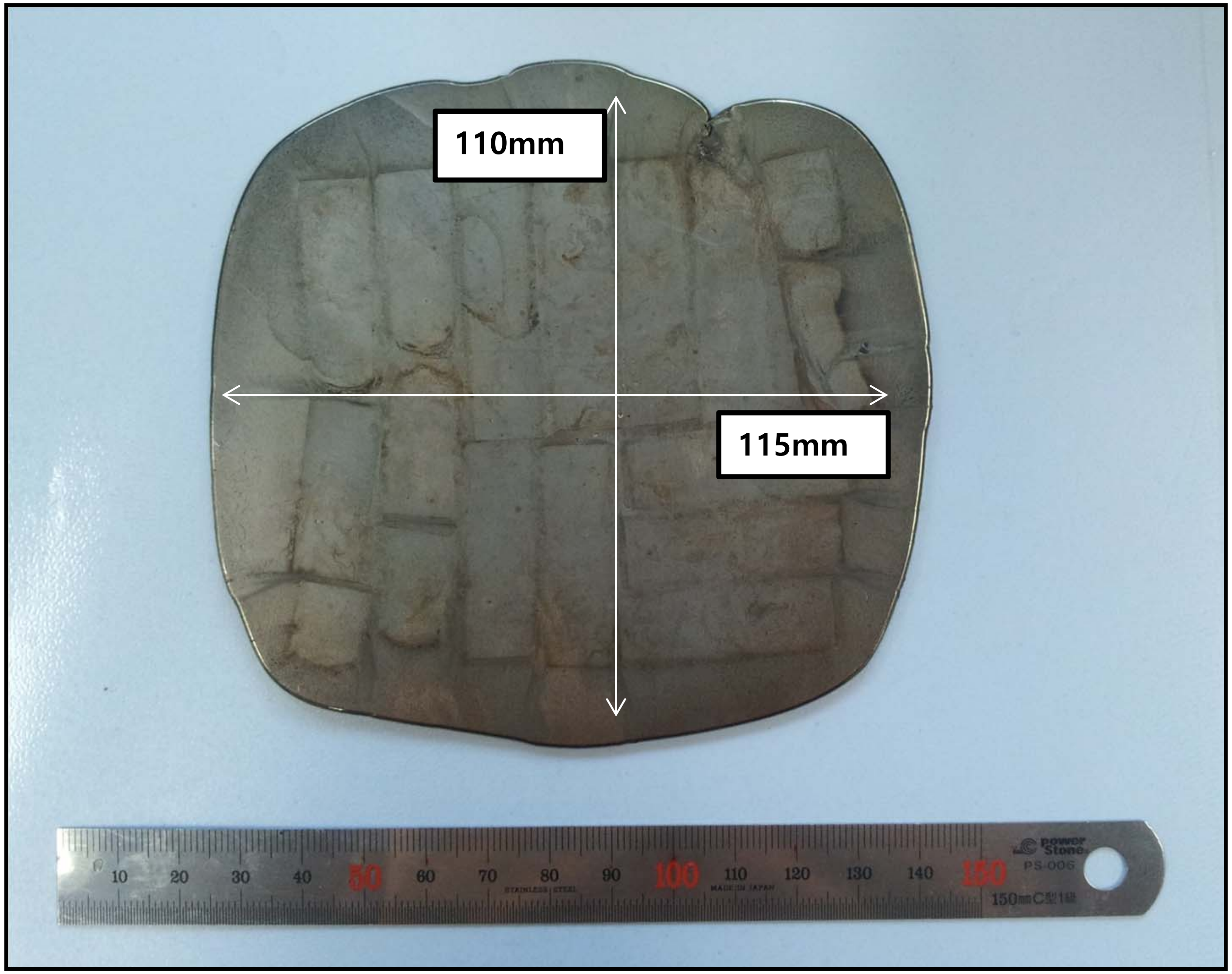
b. Thermoplastic forming (TPF) - Fabrication of BMG plate!



(ESPark Group)

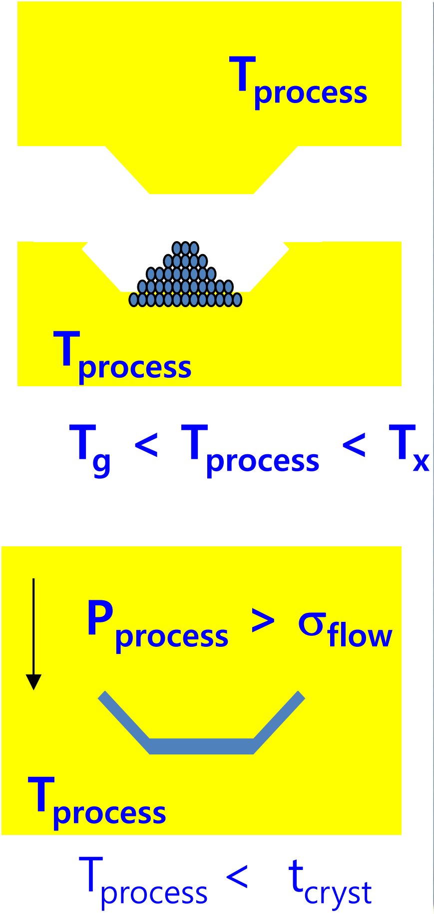
c. Thermoplastic forming & joining– No size limitation!





(ESPark Group)

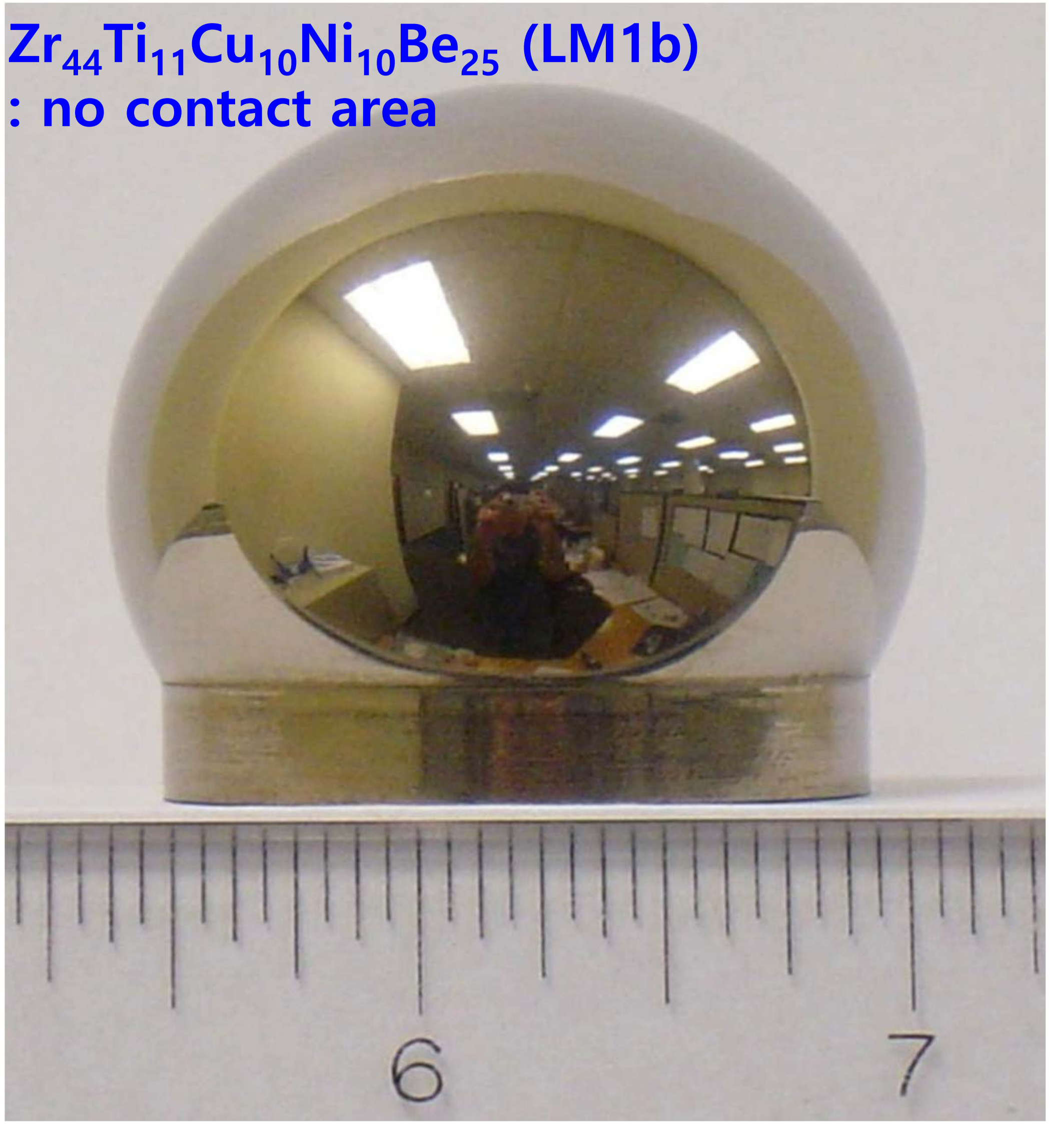
d. TPF-based Compression Molding : No size limitation!

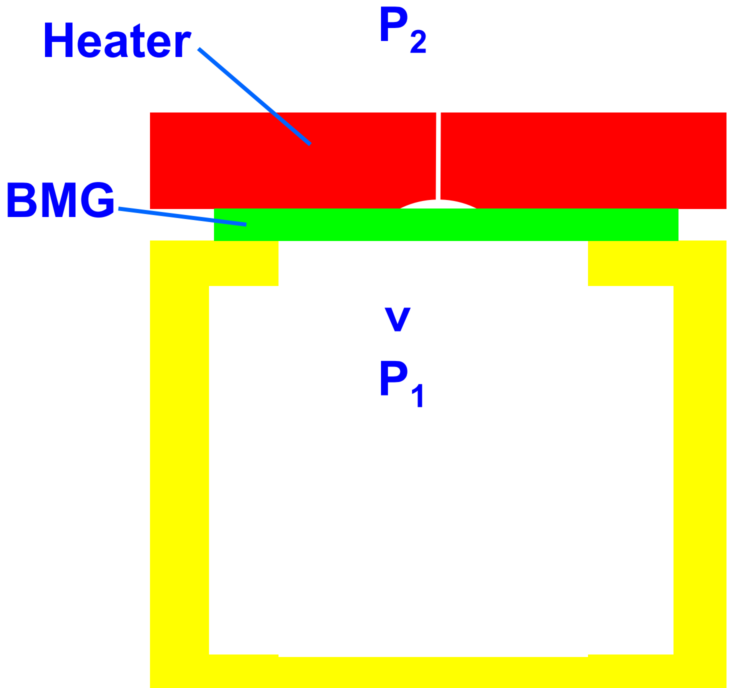


J. Schroers, JOM, 57, 34 (2005)

Glassblowers in the US in 1908

e. BLOW-MOLDING: easy forming!





10^5 Pa, 400% strain

T=460° C, t =40 sec

J. Schroers, T. Nguyen, A. Peker, N. Paton, R. V. Curtis, Scripta Materialia, 57, 341 (2007)


SCHROERS LAB
YALE SCHOOL OF
ENGINEERING &
APPLIED SCIENCE
N°5
CHANEL
PARIS
EAU DE PARFUM


SuperCool
shaping technologies

"Yale professor makes the case for Supercool Metals"

According to Yale researcher Jan Schroers, This material is 50 times harder than plastic, nearly 10 times harder than aluminum and almost three times the hardness of steel."

II. Processing metals as efficiently as plastics: net-shape forming!

Seamaster Planet Ocean Liquidmetal® Limited Edition

- Superior thermo-plastic formability

  : possible to fabricate complex structure without joints

  ↳ Multistep processing can be solved by simple casting

  ↳ Ideal for small expensive IT equipment manufacturing

Apple buys exclusive right for Liquidmetal

Apple is using Liquidmetal for…

USIM ejector (iphone 4)

Enclosure / Antenna

Apple continuing work on Liquidmetal…

Apple is Granted Its First Liquidmetal Patent

Apple's new patent "amorphous alloy" collector plates for fuel cells (2011)

US007862957B2

(12) **United States Patent**
Wende

(10) **Patent No.:** **US 7,862,957 B2**
(45) **Date of Patent:** **Jan. 4, 2011**

(54) **CURRENT COLLECTOR PLATES OF BULK-SOLIDIFYING AMORPHOUS ALLOYS**

(75) Inventor: **Trevor Wende**, Boston, MA (US)

(73) Assignee: **Apple Inc.**, Cupertino, CA (US)

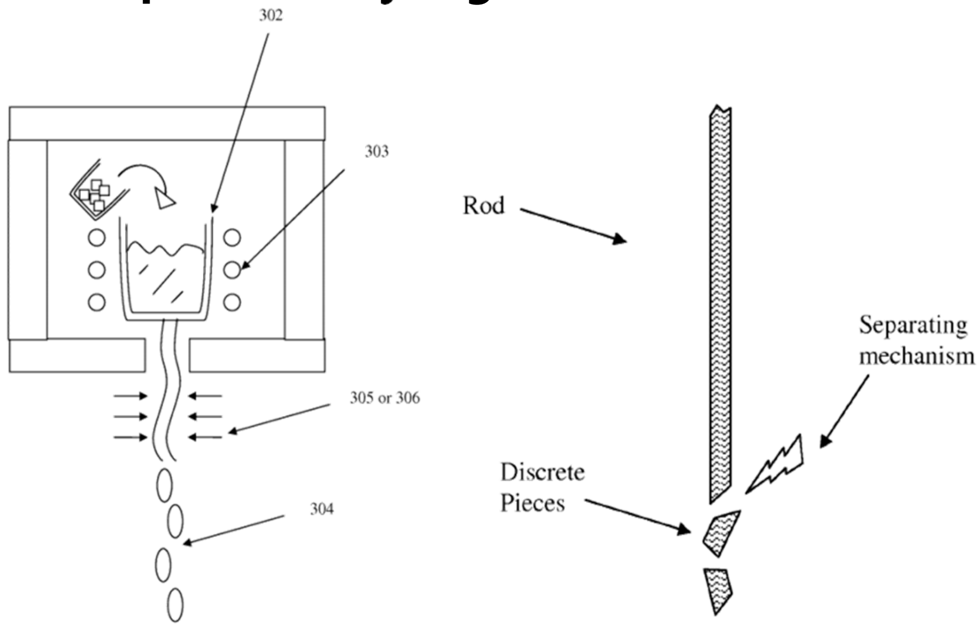
(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 1071 days.

4,126,449	A	11/1978	Tanner et al.
4,135,924	A	1/1979	Tanner et al.
4,148,669	A	4/1979	Tanner et al.
4,157,327	A	6/1979	Martin et al.
4,478,918	A	10/1984	Ueno et al.
4,623,387	A	11/1986	Masumoto et al.
4,648,609	A	3/1987	Deike
4,721,154	A	1/1988	Christ et al.
4,743,513	A	5/1988	Scruggs

Apple continuing work on Liquidmetal "casting techniques"…

Apple's new patent (2013)

"Continuous moldless fabrication of amorphous alloy ingots"



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

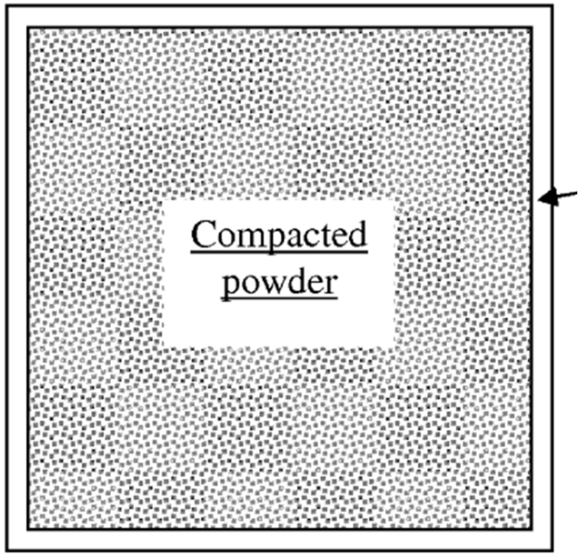
(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 September 2013 (26.09.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/141879 Al

Apple continuing work on Liquidmetal “casting techniques”...



Apple’s new patent (2015)

“Amorphous Alloy Powder Feedstock Processing”

US 20150307967A1

(19) **United States**

(12) **Patent Application Publication**

Prest et al.

(10) **Pub. No.: US 2015/0307967 A1**

(43) **Pub. Date: Oct. 29, 2015**

(54) **AMORPHOUS ALLOY POWDER FEEDSTOCK PROCESSING**

(75) Inventors: **Christopher D. Prest**, San Francisco, CA (US); **Joseph C. Poole**, San Francisco, CA (US); **Joseph Stevick**, Olympia, WA (US); **Theodore A. Waniuk**, Lake Forest, CA (US); **Quoc Tran Pham**, Anaheim, CA (US)

(73) Assignee: **Apple Inc.**, Cupertino, CA (US)

(21) Appl. No.: **14/387,023**

(22) PCT Filed: **Mar. 23, 2012**

(86) PCT No.: **PCT/US2012/030389**

§ 371 (c)(1), (2), (4) Date: **Jun. 17, 2015**

Publication Classification

(51) **Int. Cl.**

C22C 1/00	(2006.01)
C22C 45/00	(2006.01)
B22F 3/20	(2006.01)
B22F 3/02	(2006.01)
B22F 3/105	(2006.01)
B22F 3/14	(2006.01)
C22C 1/04	(2006.01)
C22C 33/00	(2006.01)

(52) **U.S. Cl.**

CPC . ***C22C 1/002*** (2013.01); ***C22C 1/04*** (2013.01); ***C22C 45/00*** (2013.01); ***C22C 33/003*** (2013.01); ***B22F 3/02*** (2013.01); ***B22F 3/105*** (2013.01); ***B22F 3/14*** (2013.01); ***B22F 3/20*** (2013.01); *B22F 2003/1051* (2013.01)

(57) **ABSTRACT**

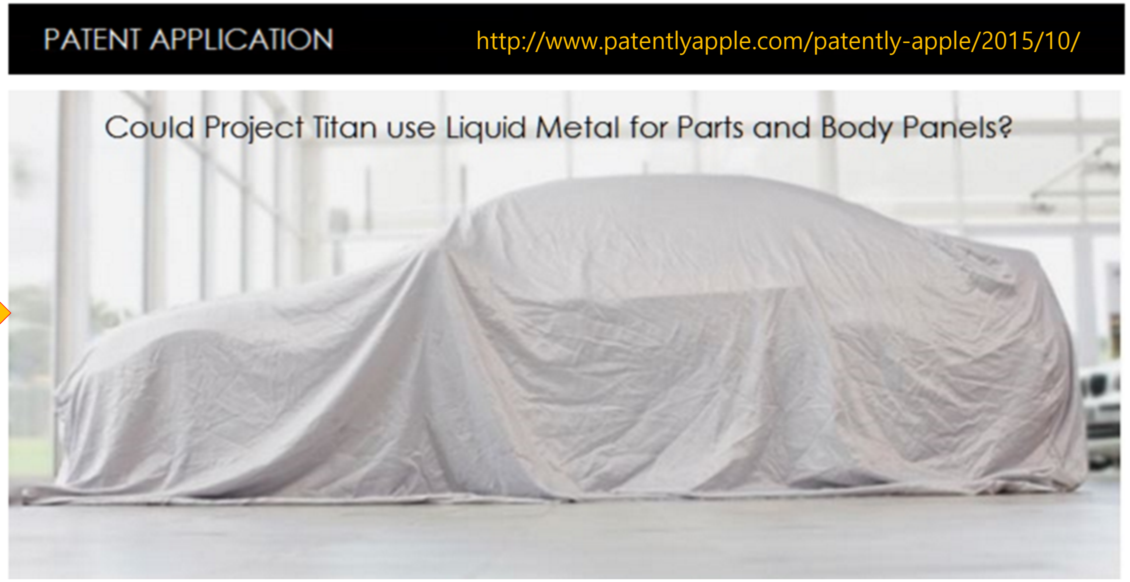
Described herein is a method of producing a feedstock comprising a BMG. A powder is compacted to for the feed-stock. The powder has elements of the BMG and the elements in the powder have a same weight percentage as in the BMG. Described herein is a method of producing a feedstock comprising a BMG. A powder is compacted into a sheath to for the feedstock. The powder and the sheath together have elements of the BMG and the elements in the powder have a same weight percentage as in the BMG.

Apple continuing work on Liquidmetal "casting techniques"...

October 29, 2015

Two New Liquid Metal Inventions Published Today Cover Every Current Apple Product and even Complete Car Panels

Liquidmetal™ in NEXT iPhone?



Apple's patents cover the use of liquid metal in <u>every imaginable Apple product</u> and even hints that the process described in these inventions could produce complete car panels. That makes you wonder if Apple's Project Titan will be able to take advantage of the liquid metal process for car parts and beyond.

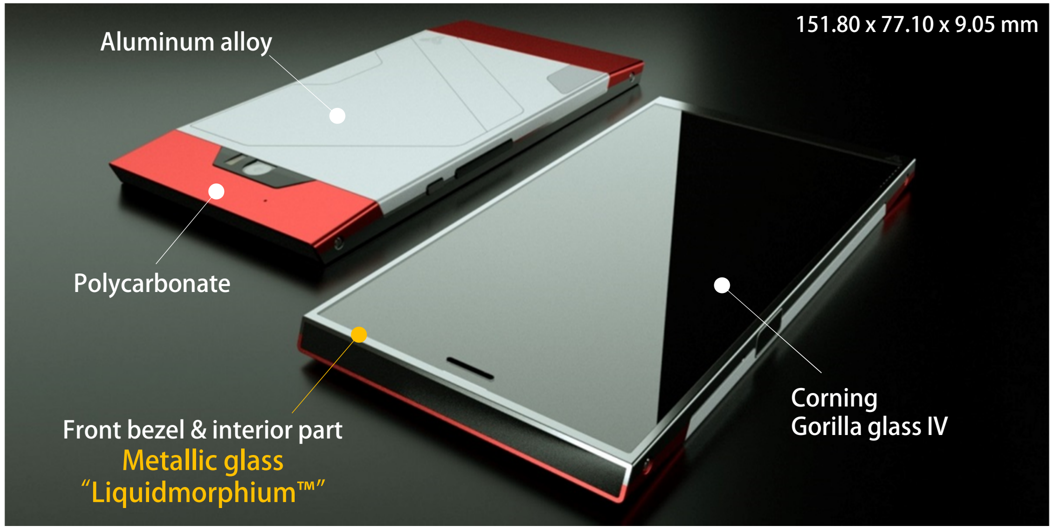
World-first Smart Phone with BMG exterior (2015)

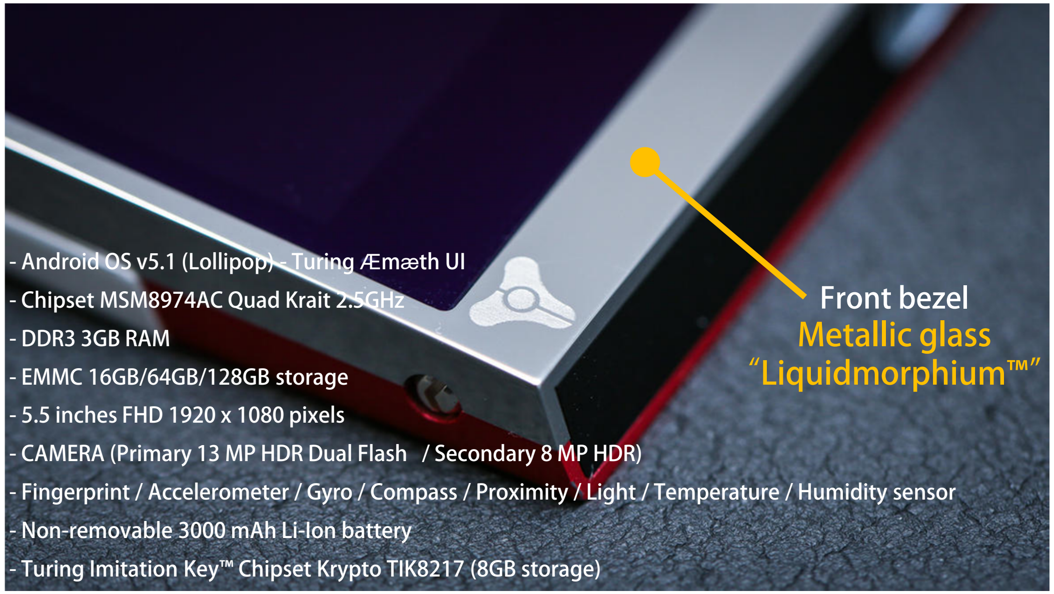
Turing phone

by Turing Robotics Industries (UK)

with

Metallic glass
“Liquidmorphium™”



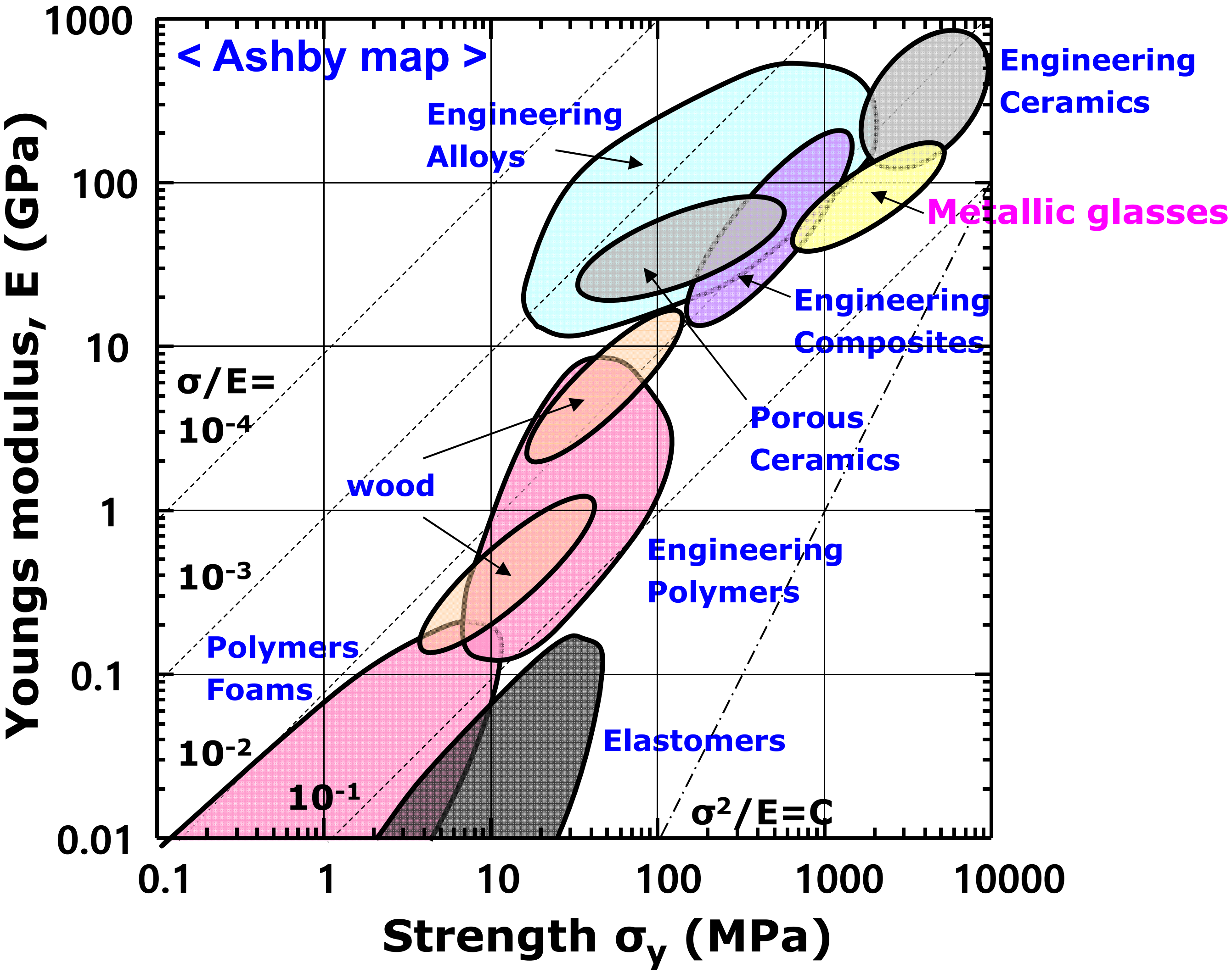


“Unhackable”
“Waterproof”
+
“Unbreakable”

The Turing Phone is built with a pioneering material called **Liquidmorphium™**, an amorphous “liquid metal” alloy tougher than either titanium or steel - so what’s in your hand is as strong as your privacy protection.

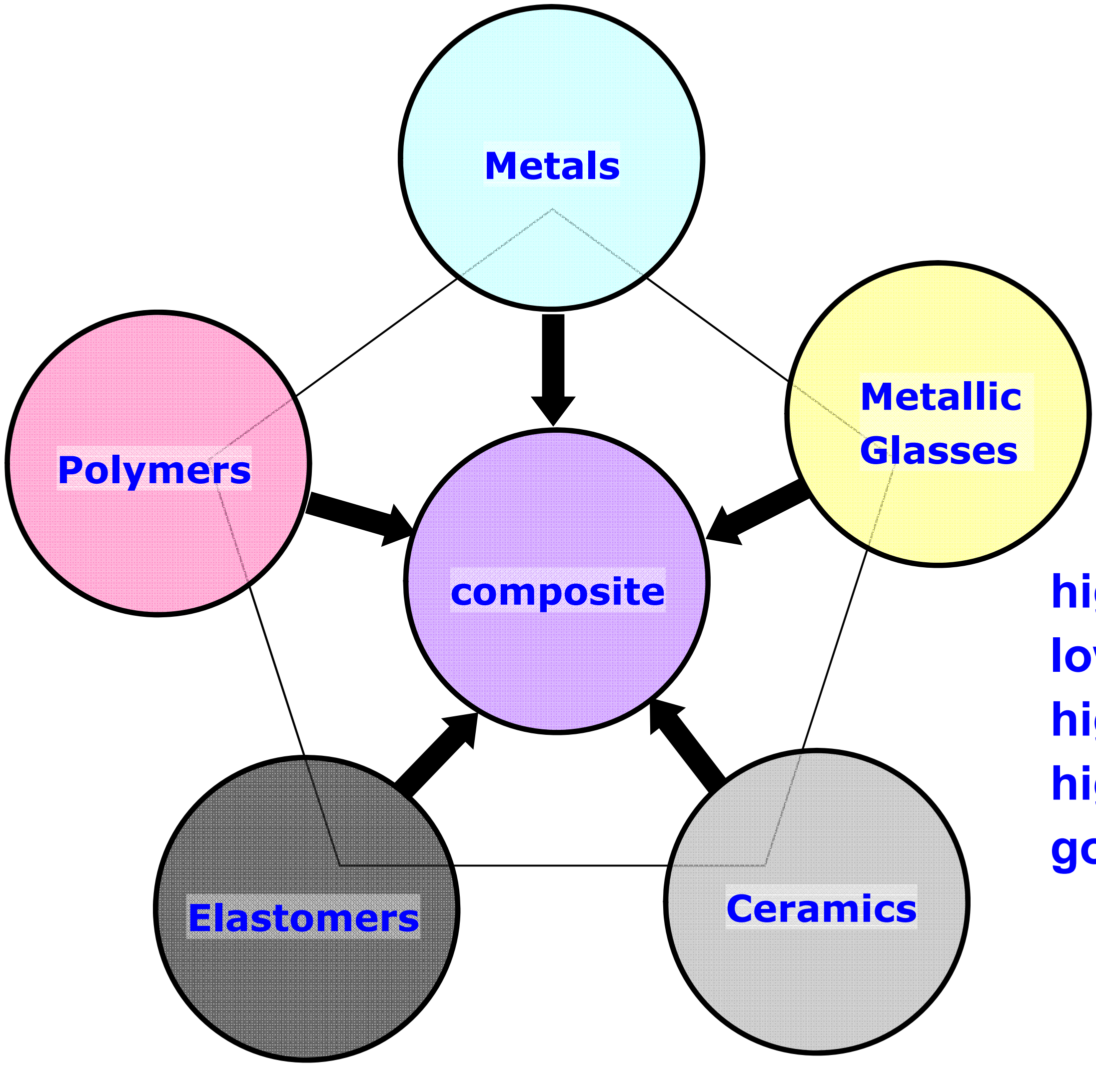
from https://www.turingphone.com/

At the Cutting Edge of Metals Research: Bulk Metallic Glasses



Bulk Metallic Glass: the 3rd Revolution in Materials!!

"BMG = new menu of engineering materials"



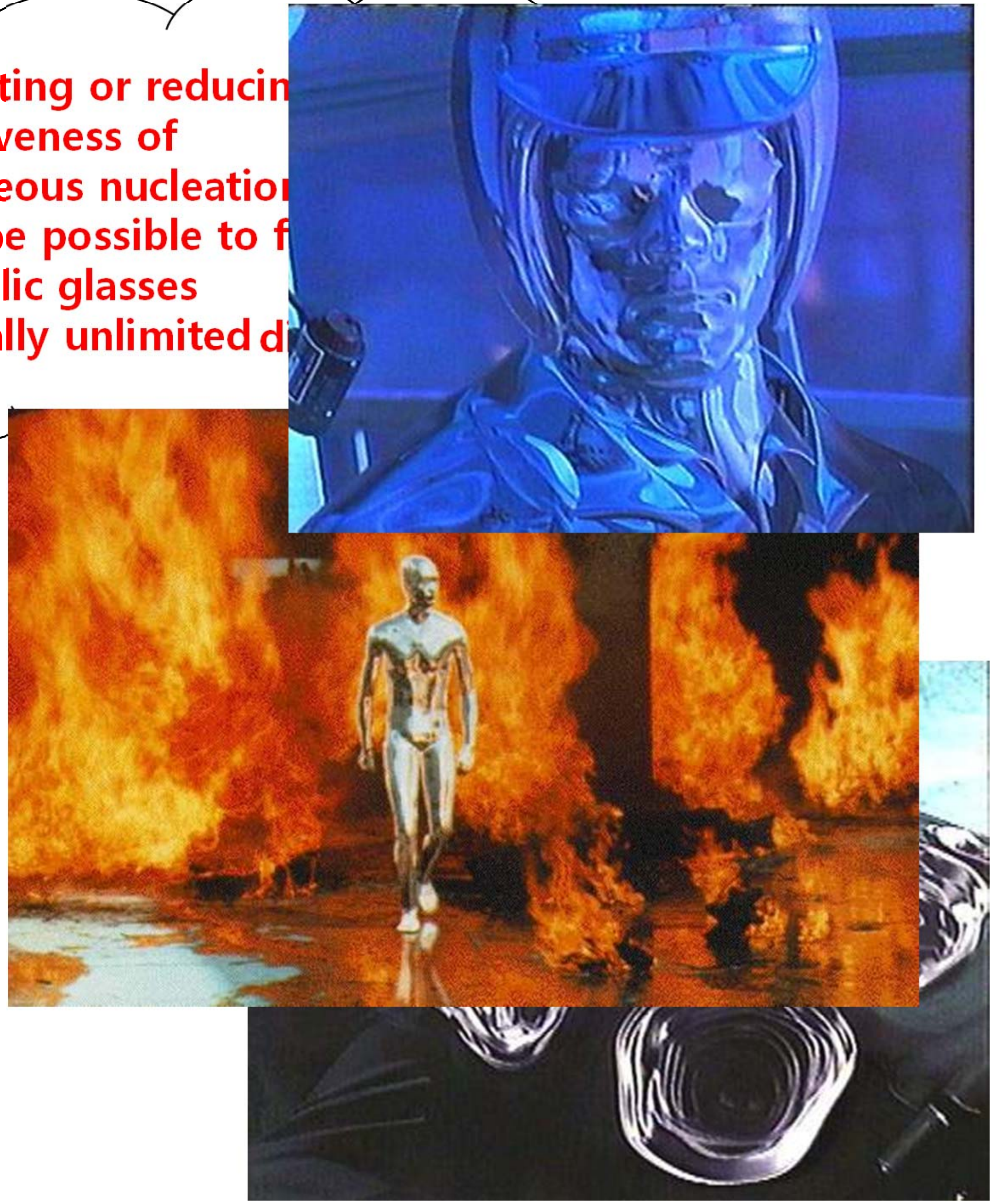
High GFA

High plasticity

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

Bulk Metallic Glass: the 3rd Revolution in Materials!!

By eliminating or reducin
the effectiveness of
heterogeneous nucleatio
it should be possible to f
bulk metallic glasses
with virtually unlimited d



“**Revolution in materials** starts
at the limitation of technological development.”

Schedule

week 1 Introduction to Amorphous materials

week 2 Classification of Solids

week 3 Definition of Amorphous Materials

week 4 Preparation of Amorphous Materials

week 5 Phase Transition: glass transition

week 6 Measurement of Glass Transition Temperature

week 7 Theories for the Glass Transition I: thermodynamic / entropy

week 8 Theories for the Glass Transition II: relaxation behavior / viscosity

week 9 Structural Approach to Glass Formation

week 10 Kinetic Approach to Glass Formation

week 11 Ease of Glass Transition: glass-forming ability

week 12 Glass Forming Ability Parameters

week 13 Formation of Bulk Metallic Glasses

week 14 Mechanical Properties of Bulk Metallic Glasses and Their Composites

week 15 Unique Properties of of Bulk Metallic Glasses

week 16 Potential Applications of Bulk Metallic Glasses

Please read Chapter 1 (Introduction) of the textbook and reference papers before next class!

Reminder "Homework 1":

Please find one of the advanced metallic materials and make a summary of the material within 3 pages ppt.

Submission due date: March 16, 2018

You may have a chance to discuss the materials in class on March 19, 2018.