2016 fall 〈Freshman Seminar〉

"New materials to open the future"

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1. High Entropy Alloy

* Search for new and advanced materials

: addition of alloying elements, microstructural modification and by subjecting the materials to thermal, mechanical, or thermo-mechanical processing methods

→ Completely new materials
" Stronger, Stiffer, Lighter and Hotter…"

: Nanocrystalline Materials, High Temperature Superconductors,
Metallic Glass (1960), Quasi-crystal (1984), Gum Metal (2003), High Entropy Alloy (2004)

Representative FCC high entropy alloy: $Fe_{20}Cr_{20}Mn_{20}Ni_{20}Co_{20}$

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MATERIALS SCIENCE & ENGINEERING A
www.elsevier.com/locate/msea

Microstructural development in equiatomic multicomponent alloys

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Abstract

Multicomponent alloys containing several components in equal atomic proportions have been manufactured by casting and melt spinning, and their microstructures and properties have been investigated by a combination of optical microscopy, scanning electron microscopy, electron probe microanalysis, X-ray diffractrometry and microhardness measurements. Alloys containing 16 and 20 components in equal proportions are multiphase, crystalline and brittle both as-cast and after melt spinning. A five component $Fe_{20}Cr_{20}Mn_{20}Ni_{20}Co_{20}$ alloy forms a single fcc solid solution which solidifies dendritically. A wide range of other six to nine component late transition metal rich multicomponent alloys exhibit the same majority fcc primary dendritic phase, which can dissolve substantial amounts of other transition metals such as Nb, Ti and V. More electronegative elements such as Cu and Ge are less stable in the fcc dendrites and are rejected into the interdendritic regions. The total number of phases is always well below the maximum equilibrium number allowed by the Gibbs phase rule, and even further below the maximum number allowed under non-equilibrium solidification conditions. Glassy structures are not formed by casting or melt spinning of late transition metal rich multicomponent alloys, indicating that the confusion principle does not apply, and other factors are more important in promoting glass formation.

Keywords: Multicomponent alloys; Equiatomic; Casting

* Development strategy of completely new materials

a. Alloyed pleasures: Multi-metallic cocktails

b. Synthesize metastable phases

Equilibrium conditions → Non-equilibrium conditions

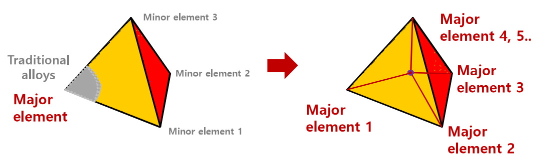
: non-equilibrium processing = "energize and quench" a material

TABLE 1.1

Departure from Equilibrium Achieved in Different Nonequilibrium Processing Methods

Technique	Effective Quench Rate (K s⁻¹), Ref. [25]	Maximum Departure from Equilibrium (kJ mol⁻¹) Ref. [28]	Refs. [29,30]
Solid-state quench	10^3	—	16
Rapid solidification processing	10^5–10^8	2–3	24
Mechanical alloying	—	30	30
Mechanical cold work	—	—	1
Irradiation/ion implantation	10^{12}	—	30
Condensation from vapor	10^{12}	—	160

Basic concepts of high entropy alloy (HEA)



Conventional alloy system
Ex) 304 steel - $Fe_{74}Cr_{18}Ni_8$

High entropy alloy system
Ex) $Al_{20}Co_{20}Cr_{20}Fe_{20}Ni_{20}$

- Equimolar: AlCoCrCuFeNi
- Nonequimolar: AlCo0.5CrCuFe1.5Ni1.2
- Minor addition: AlCo0.5CrCuFe1.5Ni1.2B0.1C0.15

→ Any 13 metal elements will produce 7099 equimolar HEAs!!

Basic concepts of high entropy alloy (HEA)

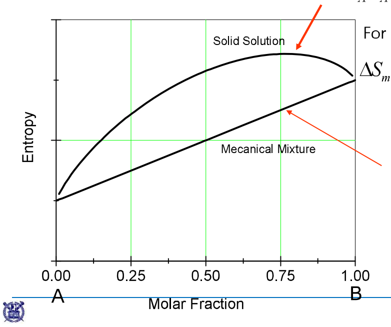
* **Thermodynamic approach**: Solid solution has higher entropy than the mechanical mixture does.

$$S = X_A S_A + X_B S_B + \Delta S_{mix}$$

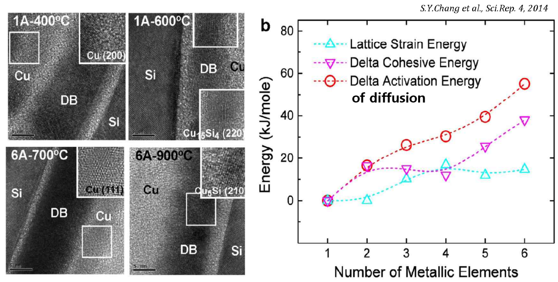
For the regular solution:

$$\Delta S_{mix} = -R(X_A Ln X_A + X_B Ln X_B)$$

$$S = X_A S_A + X_B S_B$$



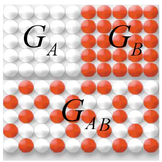
a. Sluggish diffusion of high entropy alloy



Comparison of diffusion barrier effect from Ti(1A) to TiTaCrZrAlRu(6A)

→ Muticomponent system (HEA) may induce "Sluggish diffusion ".

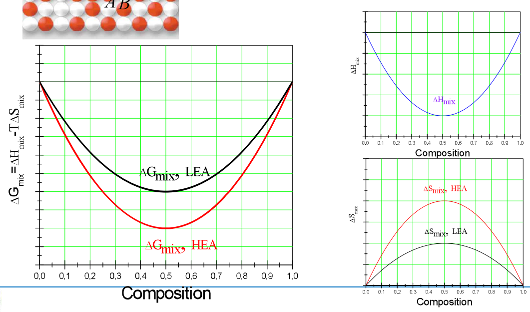
Basic concepts of high entropy alloy (HEA)



Gibbs Free Energy

$$\Delta G_{mix} = G_{AB} - (X_A G_A + X_B G_B)$$

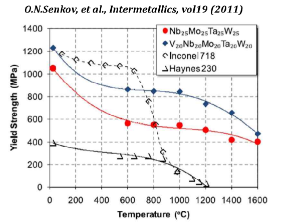
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

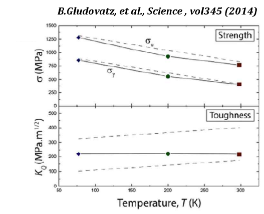


b. Thermal stability of high entropy alloy

"HEA = Structural material with good thermal stability"

High temperature strength in BCC HEA | **Low temperature toughness in FCC HEA**

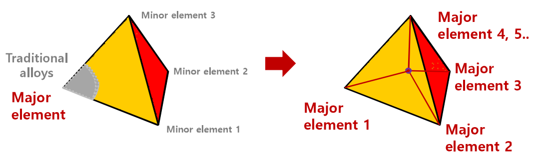




$V_{20}Nb_{20}Mo_{20}Ta_{20}W_{20}$ HEA has higher strength than $Nb_{25}Mo_{25}Ta_{25}W_{25}$, which means significant solid solution hardening effect in high temperature.

The toughness of the HEA remains unchanged, and by some measures actually increases at lower temp due to change of deformation mechanism.

Basic concepts of high entropy alloy (HEA)



Conventional alloy system | High entropy alloy system

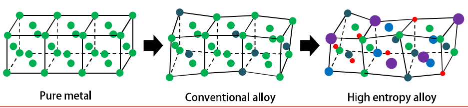
Ex) 304 steel - $Fe_{74}Cr_{18}Ni_8$ | Ex) $Al_{20}Co_{20}Cr_{20}Fe_{20}Ni_{20}$

(1) Thermodynamic : high entropy effect

(2) Kinetics : sluggish diffusion effect

(3) Structure : severe lattice distortion effect

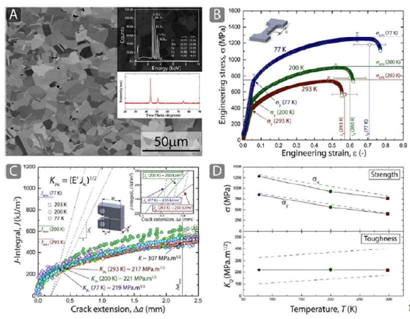
(4) Property : cocktail effect



Severe lattice distortion → Sluggish diffusion & Thermal stability

b. Thermal stability of high entropy alloy

A Fracture resistant high-entropy alloy for cryogenic applications

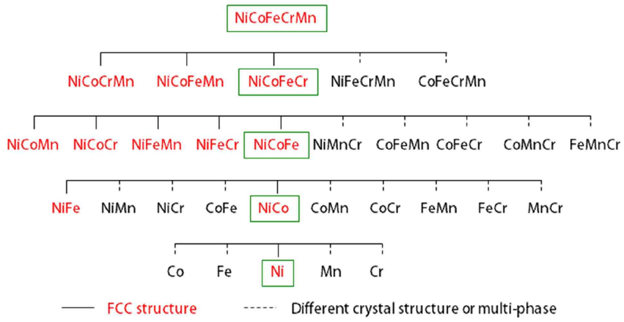


in *Science*, July 2014

Microstructure and mechanical properties of the CrMnFeCoNi HEA

Similar to austenitic stainless steels or cryogenic Ni steels, the strength of the HEA increases with decreasing temp. ; however, while the toughness of the other materials decreases with decreasing temp.. the toughness of the HEA remains unchanged, and by some measures actually increases at lower temp.

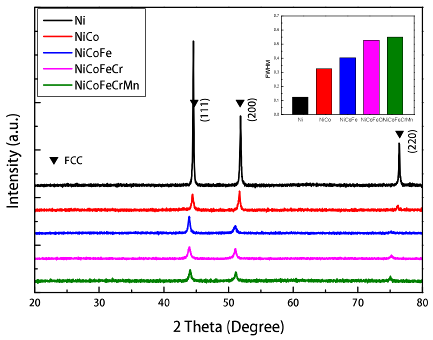
Singe-phase FCC solid solution: Ni → Ni-Co-Fe-Cr-Mn HEA



Single-phase FCC solid solutions after homogenization are written in RED.
The five alloys chosen in this study are marked by square.

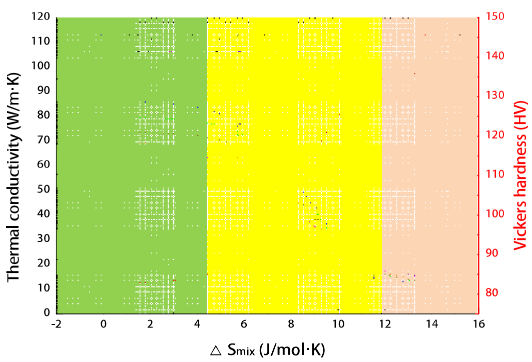
Singe-phase FCC solid solution: Ni → Ni-Co-Fe-Cr-Mn HEA

XRD patterns of NiCoFeCrMn HEA and its sub-alloys after homogenization



The inset shows full width at half maximum values of the alloys.

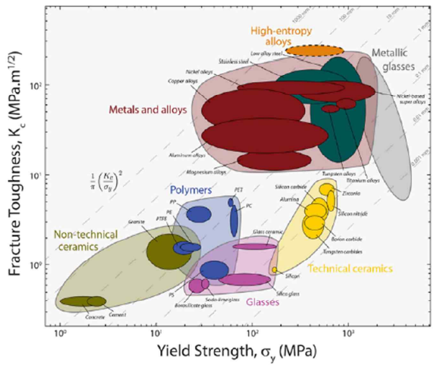
Singe-phase FCC solid solution: Ni → Ni-Co-Fe-Cr-Mn HEA



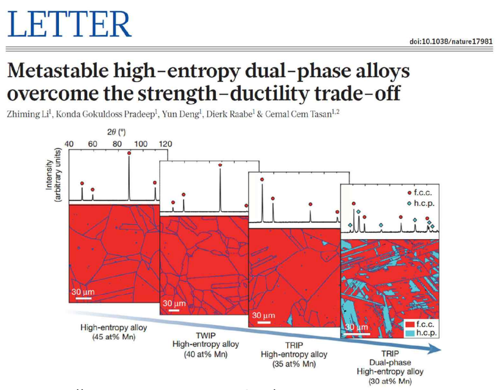
Micro-hardness and thermal conductivity at various temperatures of
Ni → Ni-Co-Fe-Cr-Mn HEA as a function of configurational entropy of mixing

HEA conclusion

"HEA = new menu of engineering materials"



HEA conclusion



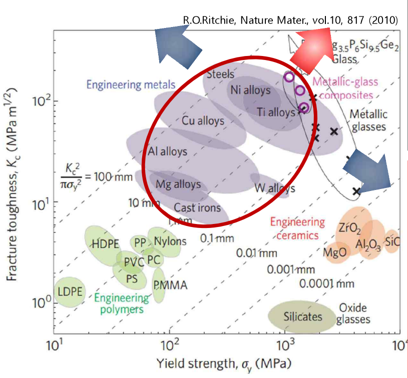
High entropy alloy
Solid solution strengthening

➕

Steel
Hardening due to decreased phase stability

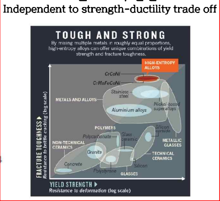
HEA conclusion

* 칵테일 효과: 강도/연성의 동시 증가 가능



기존의 합금
Intrinsic strength-ductility trade off

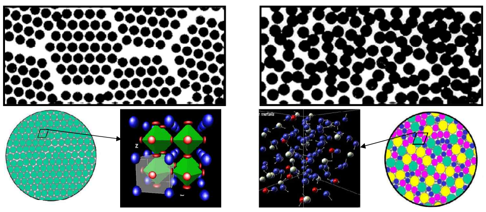
고엔트로피 합금
Independent to strength-ductility trade off



2. Bulk Metallic Glass

Structure of crystals, liquids and glasses

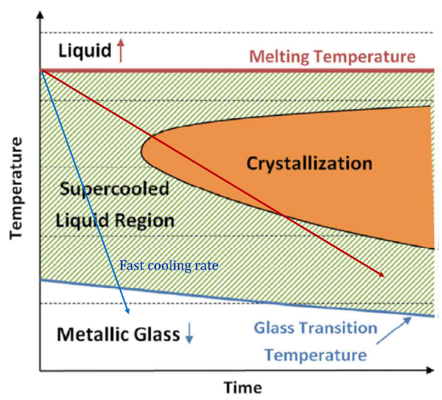
Crystals | **Liquids, glasses**



- periodic
- grain boundaries

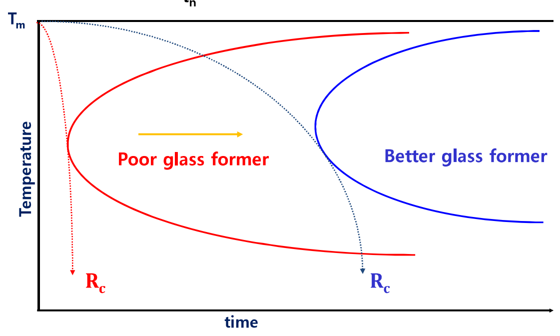
- amorphous = non-periodic
- no grain boundaries

Glass formation : (1) Fast Cooling



Glass formation : (2) Better Glass Former

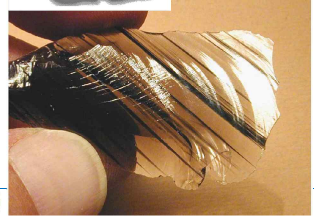
GFA $R_c = \frac{\Delta T}{t_n}$ undercooled liquid → crystalline



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

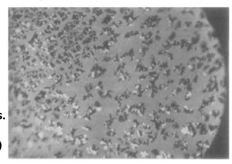
Über nichtleitende Metallmodifikationen [1])

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)



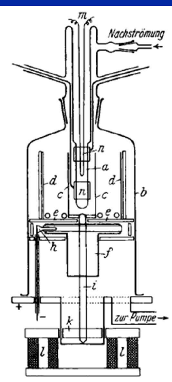
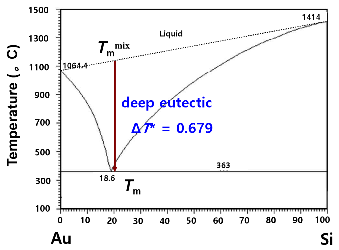


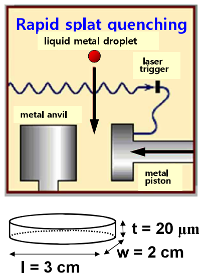
Fig. 1. Zerstäubungsapparatur

Glass formation : stabilizing the liquid phase

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

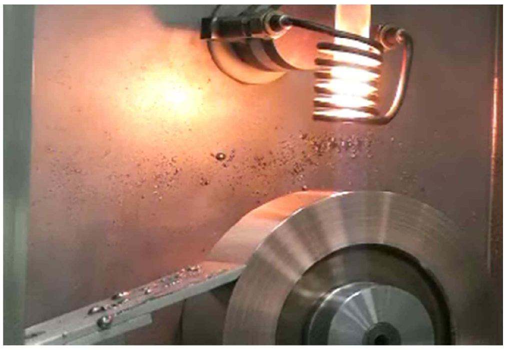


W. Klement, R.H. Willens, P. Duwez, Nature 1960; **187**: 869.



Glass formation : rapid quenching of liquid phase

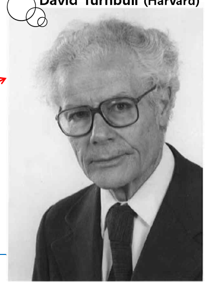
- 1969 Ribbon type with long length using melt spinner : FePC, FeNiPB alloy



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.

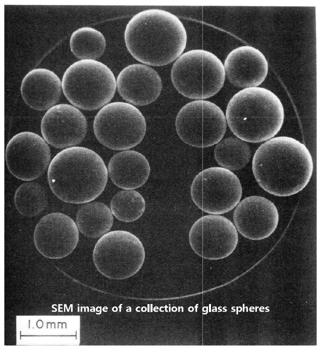
David Turnbull (Harvard)

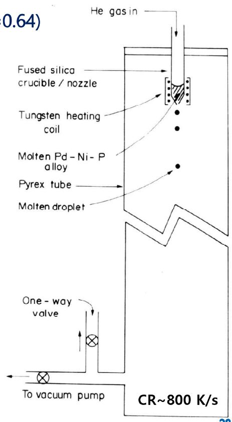


Bulk formation of metallic glass

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

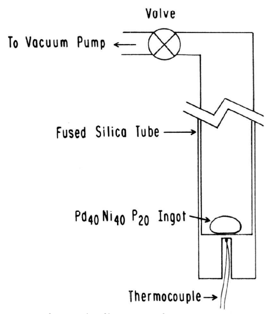
By droplet quenching (CR~800 K/s)





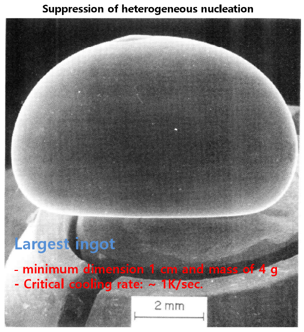
Bulk formation of metallic glass

- 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)

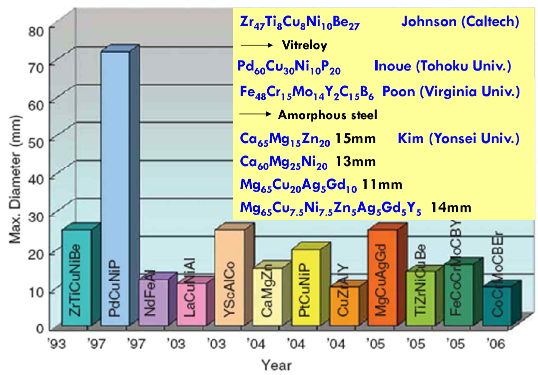


<Schematic diagram of apparatus>

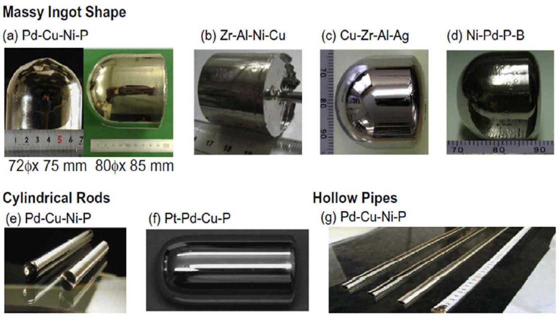
Suppression of heterogeneous nucleation



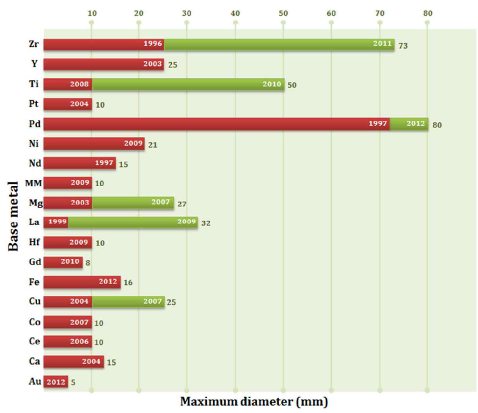
Recent BMGs with critical size ≥ 10 mm



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

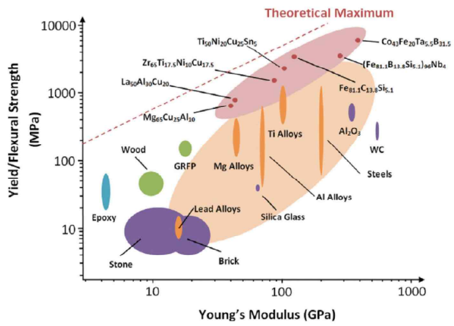


Recent BMGs with critical size ≥ 10 mm



Are amorphous metals useful?

1. High strength of BMGs

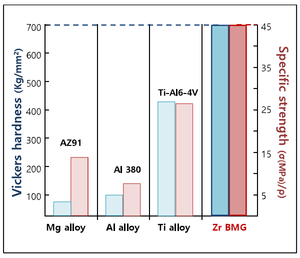


High fracture strength over 5 GPa in Fe-based BMGs

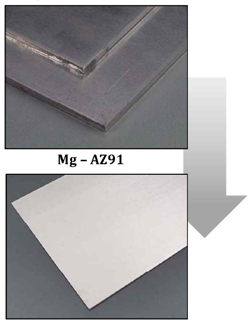
A.L. Greer, E. Ma, MRS Bulletin, 2007; 32: 612.

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**



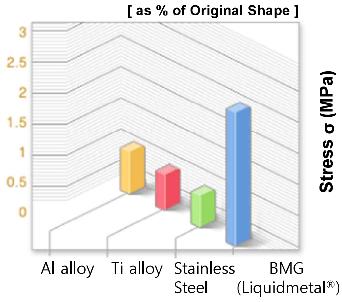
Comparison of specific strength among Zr based BMG and conventional light alloys

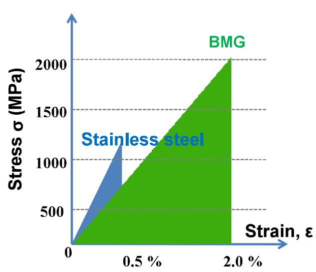


Mg – AZ91

Thinner plate: BMG

2. Large elastic strain limit of BMGs





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.

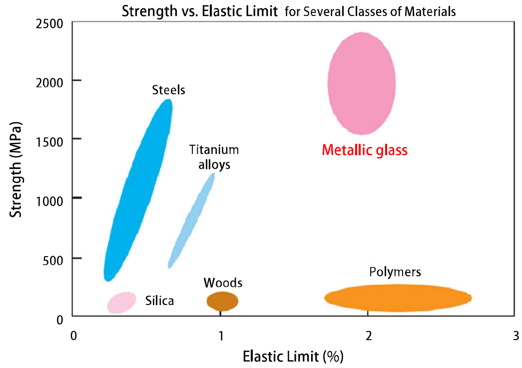
the modulus of resilience, U,

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

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.)

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



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

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

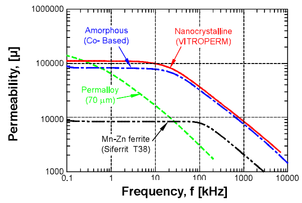
* Sporting Goods : Striking face plate in golf clubs/ Frame in tennis rackets / Baseball and softball bats/ Skis and snowboards / Bicycle parts / Fishing equipment/ Marine applications

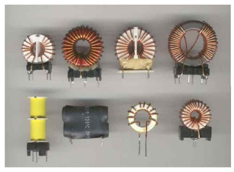
(a)

(b)

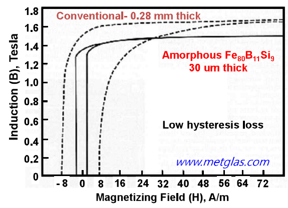
FIGURE 10.3
(a) Baseball bat and (b) tennis racket made of Liquidmetal (BMG) alloys.

3. Old uses: soft magnet





Magnetic cores

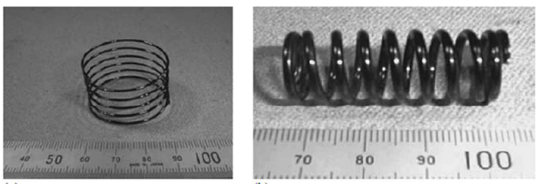


Transformers

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, the overall weight of the engine will come down by 4 kg (about 10 lb).

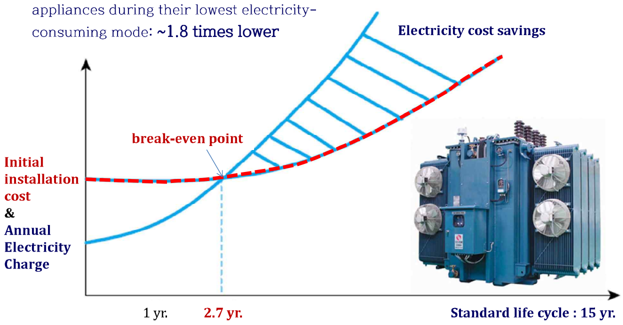


(a) (b)

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.)

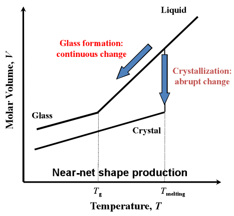
< Energy savings of amorphous transformers>

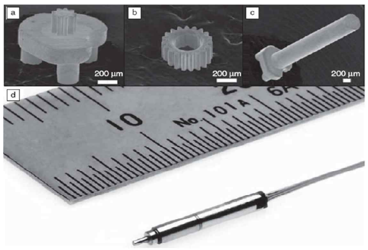
- Initial installation cost : ~ 1.5 times expensive
- Standby power, which is the power consumed by appliances during their lowest electricity-consuming mode: ~1.8 times lower

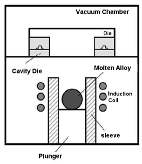


4. Processing metals as efficiently as plastics

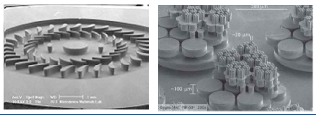
1) Micro-casting & forming







Precision Gears for Micro-motors

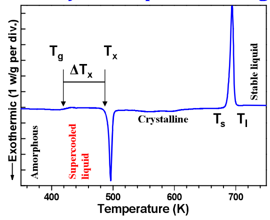


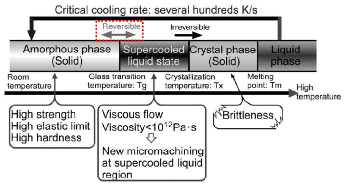
Precision die casting

MRS BULLETIN ***32*** *(2007)654.*

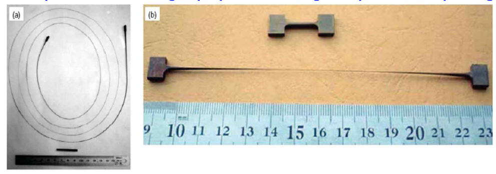
4. Processing metals as efficiently as plastics

2) Thermoplastic forming





Tensile specimens following superplastic forming in supercooled liquid region



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

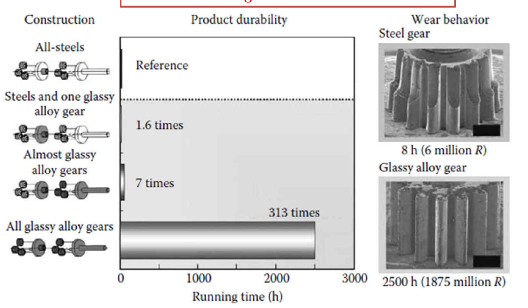
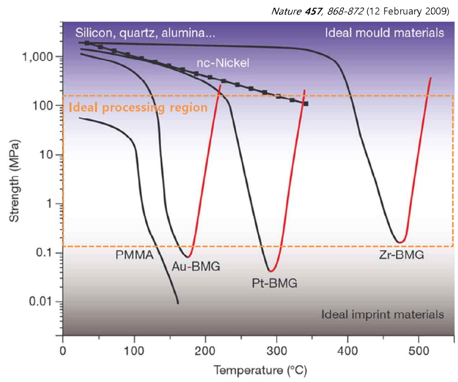


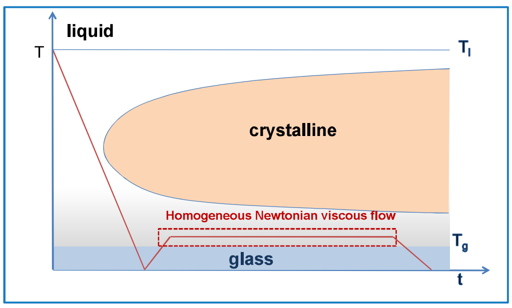
FIGURE 10.7
Comparative wear resistance behavior of gears made with different materials in a 2.4 mm diameter geared motor. (Reprinted from Inoue, A. et al., *Mater. Sci. Eng. A*, 441, 18, 2006. With permission.)

High processibility of metallic glass according to temperature

Nature 457, 868-872 (12 February 2009)



Thermoplastic forming (TPF) in SCLR

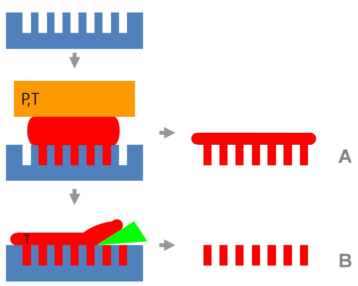


Metallic glass can be processed like plastics by homogeneous Newtonian viscous flow in supercooled liquid region (SCLR).

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

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**

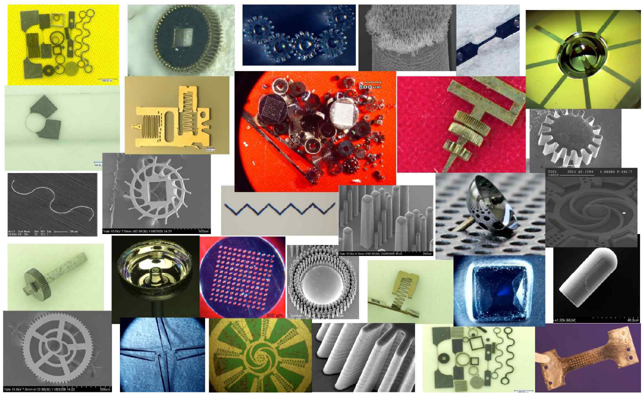


J. Schroers, Q. Pham and A. Desai, J. MEMS, 16, 240 (2007).

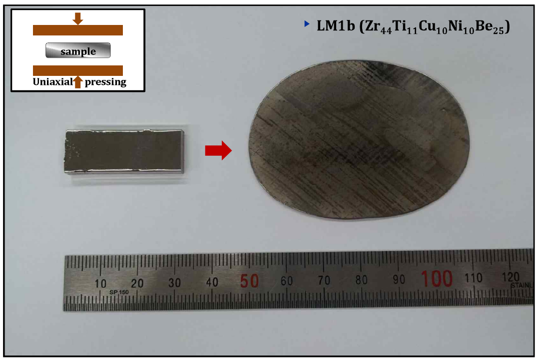
Materials Views www.MaterialsViews.com ADVANCED MATERIALS www.advmat.de

Processing of Bulk Metallic Glass

Adv. Mater. 2009, 21, 1–32

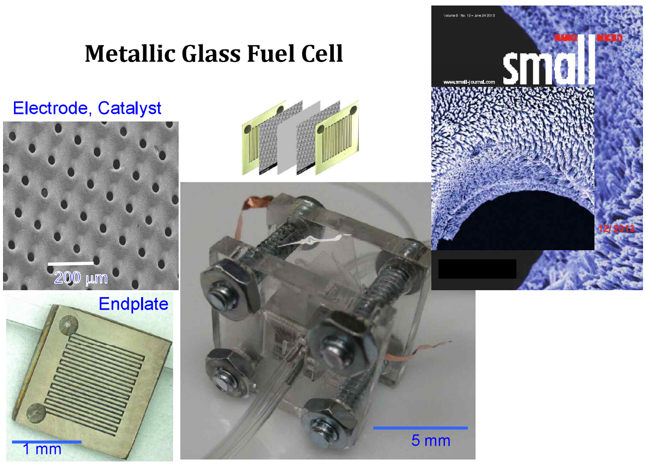


b. Thermoplastic forming (TPF) - Fabrication of BMG plate!



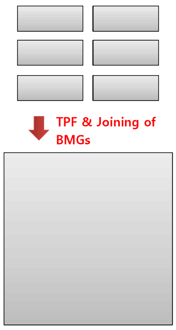
(ESPark Group)

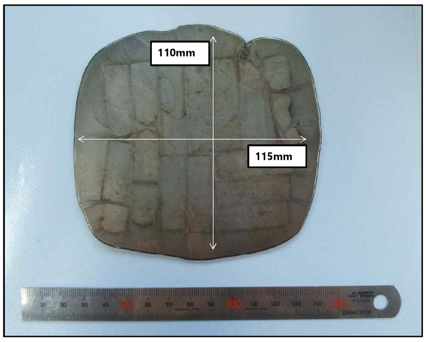
Metallic Glass Fuel Cell



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

c. Thermoplastic forming & joining– No size limitation!

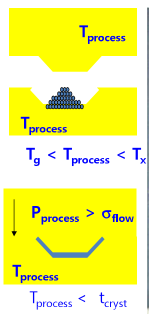




(ESPark Group)

MG Hologram in air by thermoplastic forming

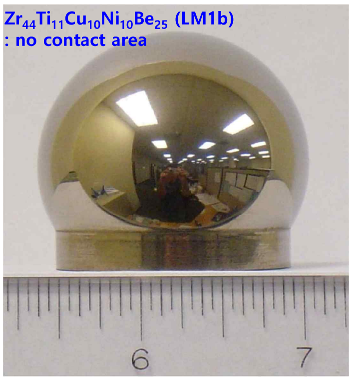
d. TPF-based Compression Molding : No size limitation!

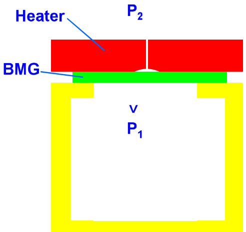


J. Schroers, JOM, 57, 34 (2005)

e. BLOW-MOLDING: easy forming!

$Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ (LM1b)
: no contact area





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)

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

"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."

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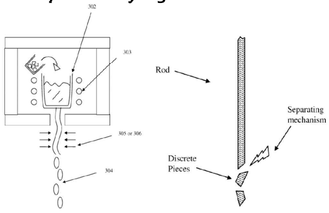
4,157,327	A	6/1979	Martin et al.
4,478,918	A	10/1984	Ueno et al.
4,623,387	A	11/1986	Masumoto et al.
4,648,609	A	3/1987	Deike
4,721,154	A	1/1988	Christ et al.
4,743,513	A	5/1988	Scruggs

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 A1

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

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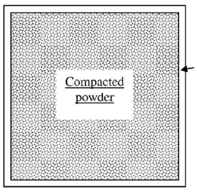
C22C 45/00 (2006.01)
B22F 3/20 (2006.01)
B22F 3/02 (2006.01)
B22F 3/105 (2006.01)
B22F 3/14 (2006.01)
C22C 1/04 (2006.01)
C22C 33/00 (2006.01)

(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.

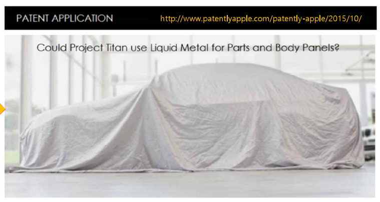


Apple continuing work on Liquidmetal "casting techniques"...

October 29, 2015

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

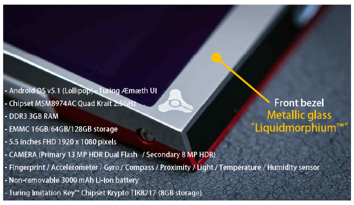
Liquidmetal™ in NEXT iPhone?



Apple's patents cover the use of liquid metal in every imaginable Apple product 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™"

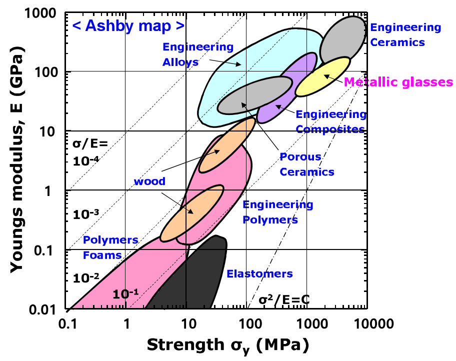


"Unhackable"
"Waterproof"
+
"Unbreakable"

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.

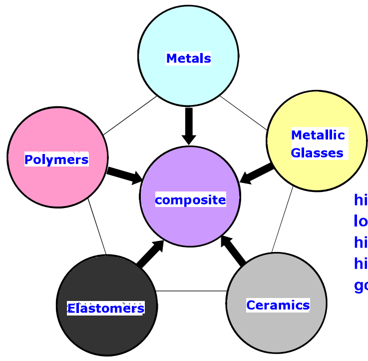
from https://www.turingphone.com/

At the Cutting Edge of Metals Research: Bulk Metallic Glasses



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

"BMG = new menu of engineering materials"



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High plasticity

higher strength
lower Young's modulus
high hardness
high corrosion resistance
good deformability
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the effectiveness of
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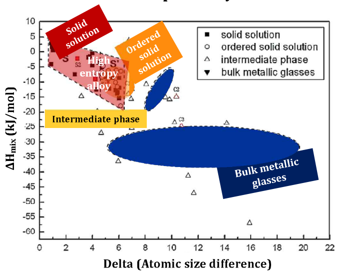
Multi-component system



Bulk metallic glass (BMG)

- multi-component systems consisting of more than three elements
- Significant difference in atomic size ratios above about 12% among the three constituent elements
- Negative heats of mixing among the three main constituent elements

High entropy alloy (HEA)

- Multi-component systems consisting of more than five elements
- Small difference of atomic size ratio under 12%
- Almost zero value of heats of mixing among the three main constituent elements

➡ **By linking the BMGs and HEAs, we can understand more about multi-component alloy systems.**