2014 Spring

"Advanced Physical Metallurgy"

- Bulk Metallic Glasses -

06.17.2014

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Are amorphous metals useful?

10

Applications



1) Bulk formation: cast into large section thickness

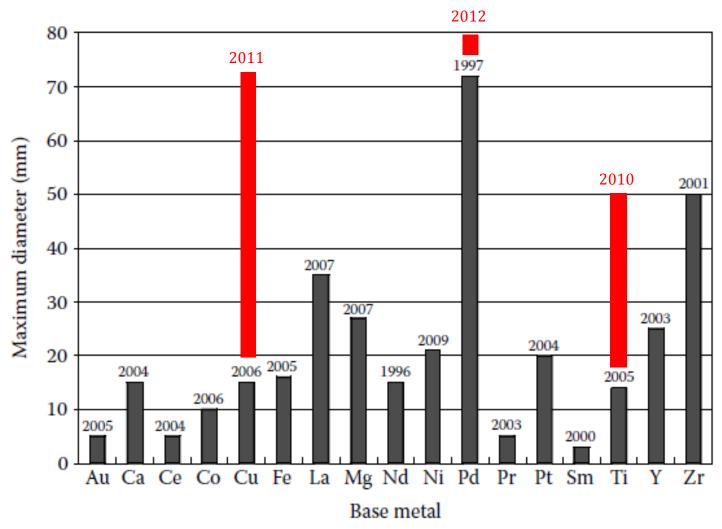
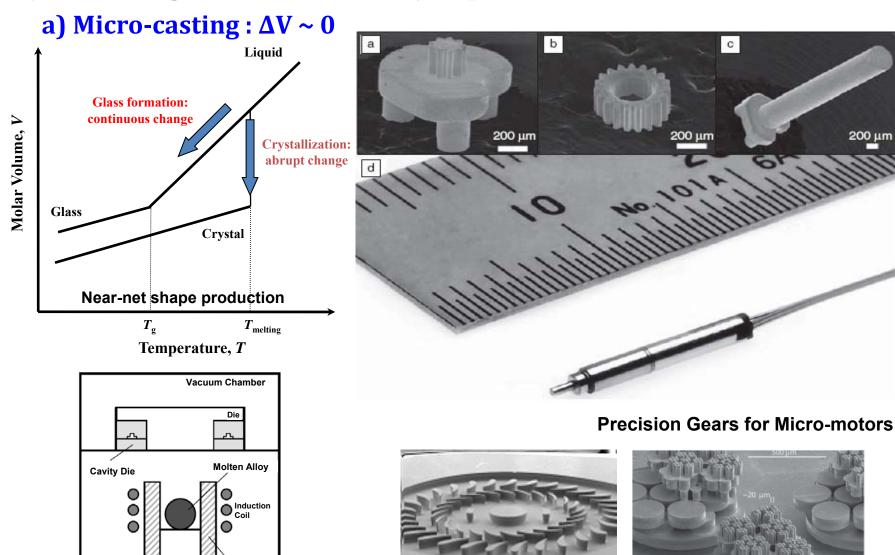


FIGURE 2.7

Maximum diameters of the BMG rods achieved in different alloy systems and the years in which they were discovered.

2) Processing metals as efficiently as plastics



Precision die casting

Plunger

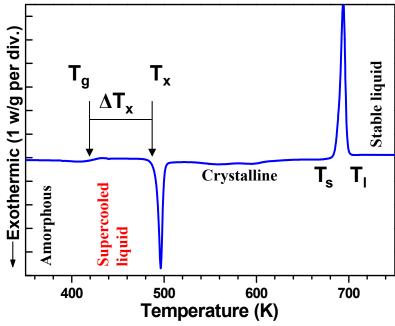
sleeve

MRS BULLETIN 32 (2007)654.

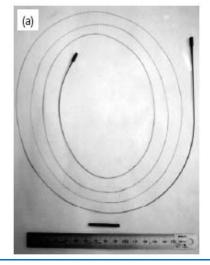
200 µm

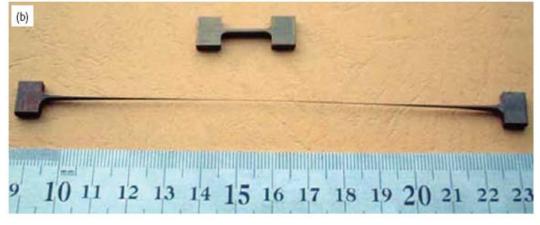
2) Processing metals as efficiently as plastics

- b) Thermoplastic forming
- : Large supercooled liquid region



Tensile specimens following superplastic forming in supercooled liquid region

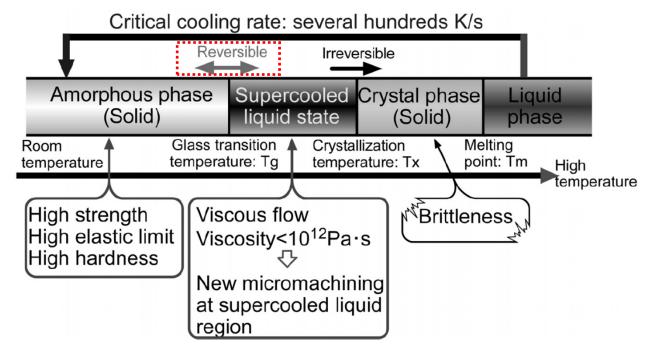




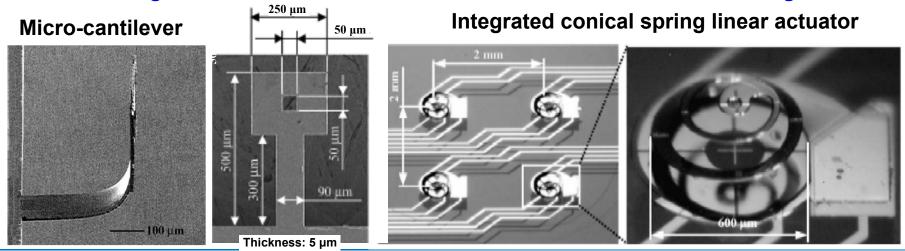


2) Processing metals as efficiently as plastics

c) Micro-forming

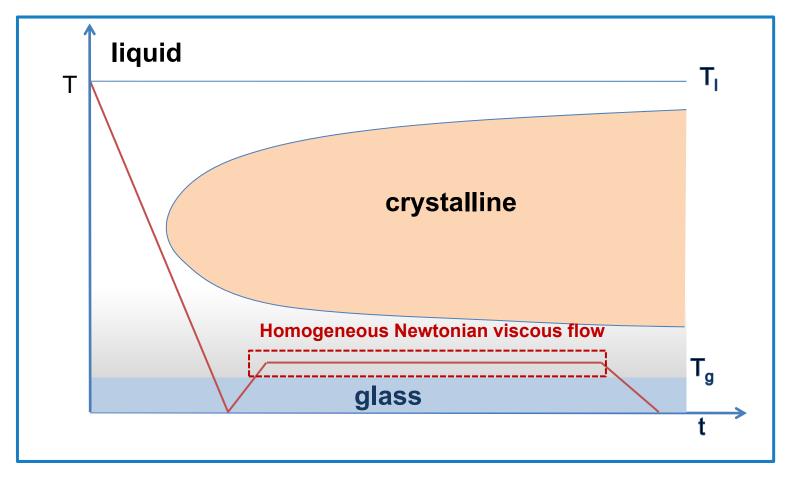


Micro-forming of three-dimensional microstructures from thin-film metallic glass





Thermoplastic forming in SCLR

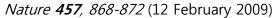


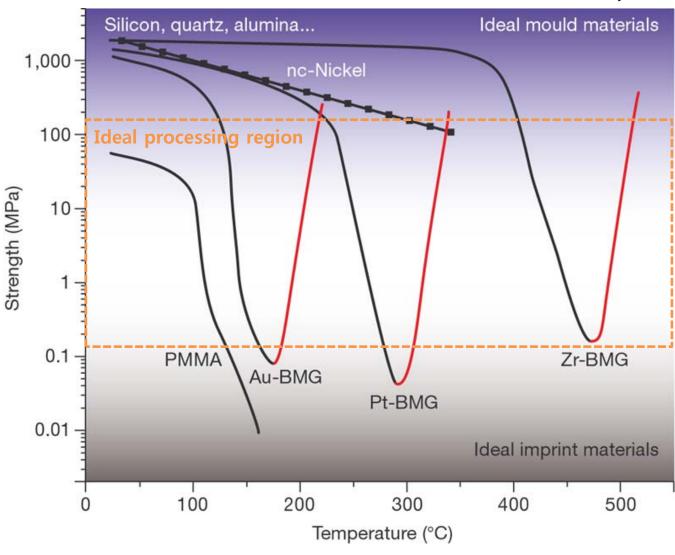
Metallic glass can be processed like plastics by homogeneous Newtonian viscous flow in supercooled liquid region (SCLR).

Possible to deform thin and uniform MG



High processibility of metallic glass according to temperature





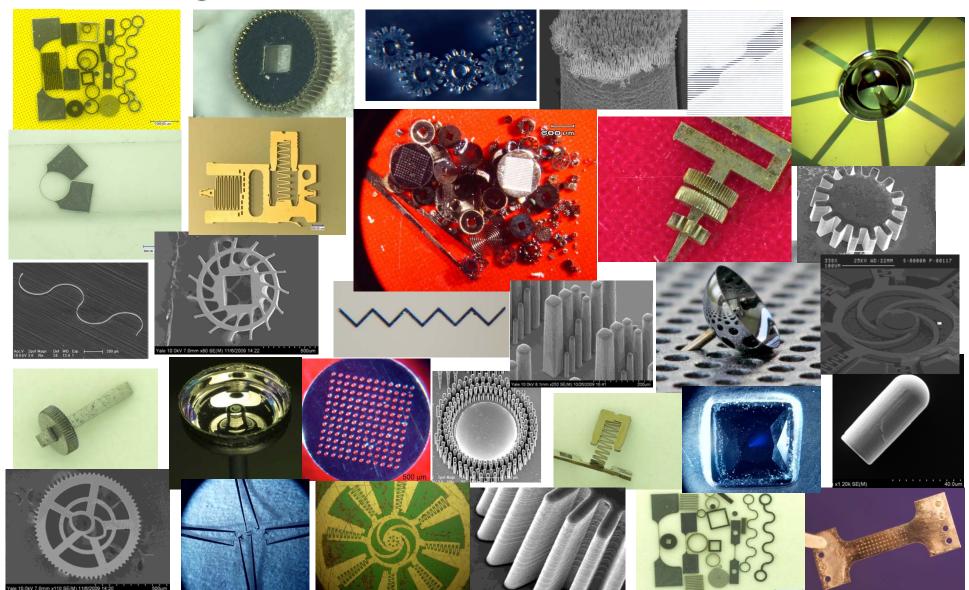


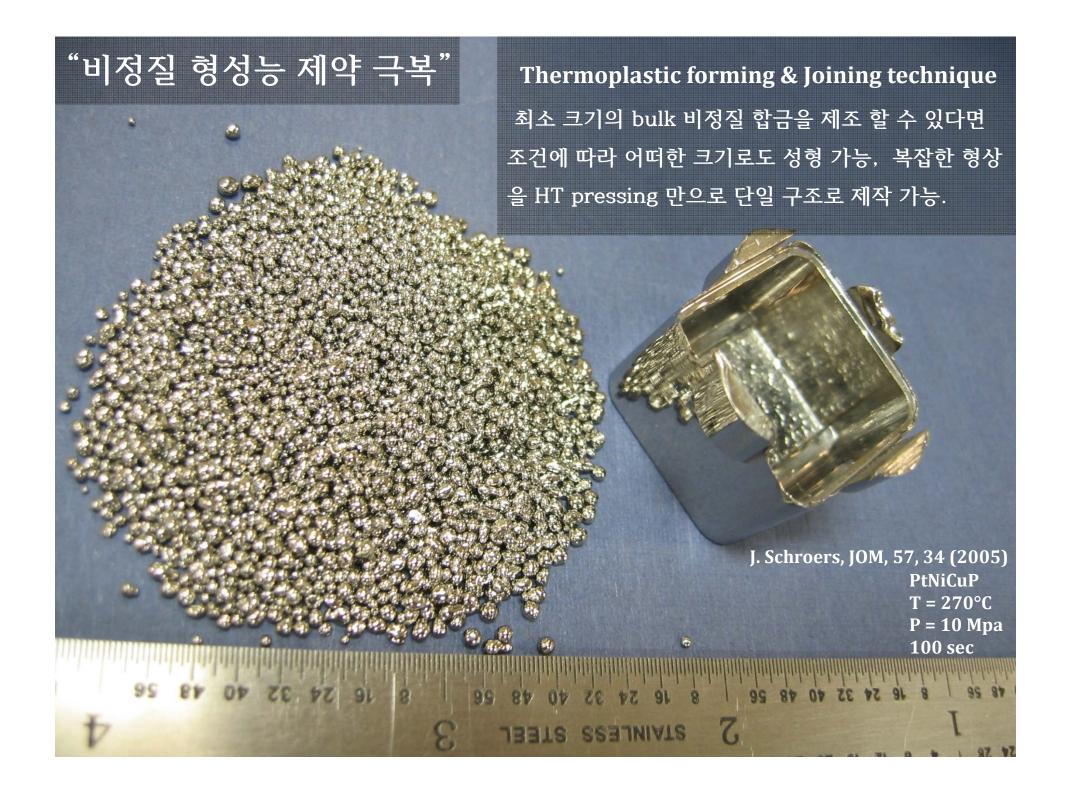




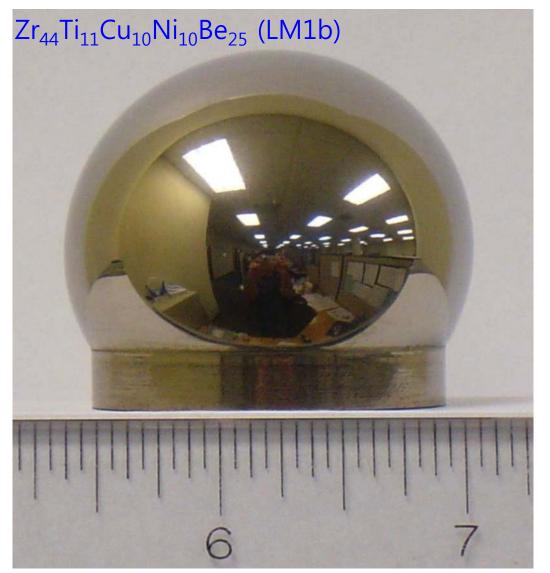
Processing of Bulk Metallic Glass

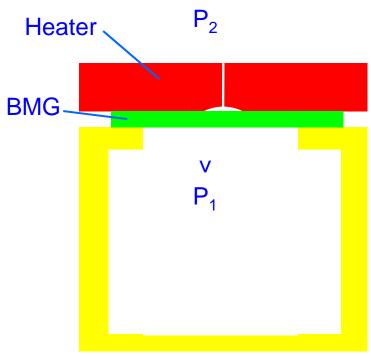
Adv. Mater. **2009**, 21, 1–32





Blow Molding - No Contact Area





10⁵ Pa, 400% strain

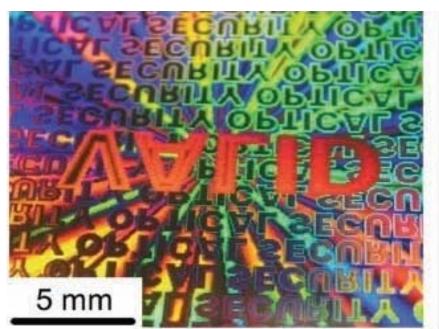
 $T=460^{\circ} C$, t =40 sec

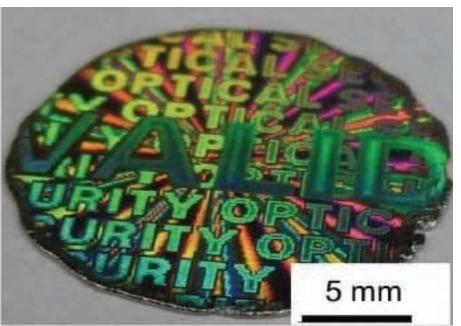
J. Schroers, T. Nguyen, A. Peker, N. Paton, R. V. Curtis, Scripta Materialia, 57, 341 (2007)



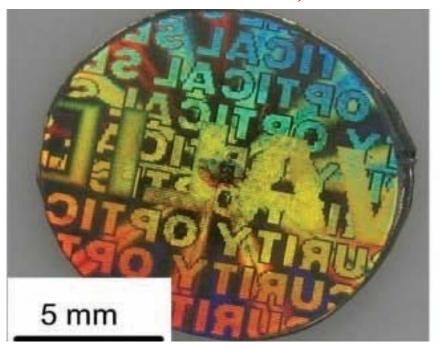


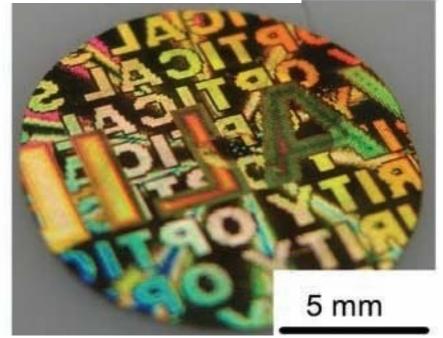


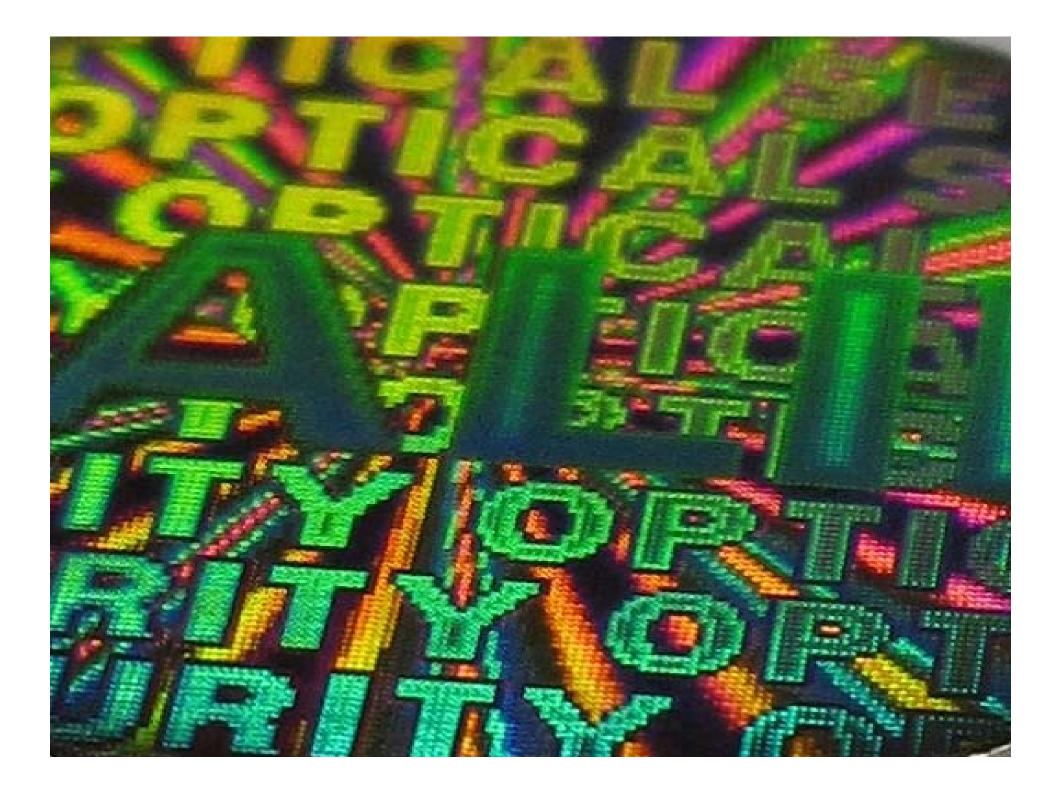




Jan Schroers, Adv. Mater., 2010, hologram pattern







Processing metals as efficiently as plastics



Seamaster Planet Ocean Liquidmetal® Limited Edition

- ▶ 우수한 고온 성형성 (Superplastic Forming)
 - : 복잡한 형태도 단일 구조로 제조, 접합부 없이 성형 가능
 - ▶ 다단계의 공정을 casting단계 만으로 해결 가능
 - ▶ 고가의 소형 IT기기 제조에 적합





Apple buys exclusive right for Liquidmetal





USIM ejector (iphone 4)

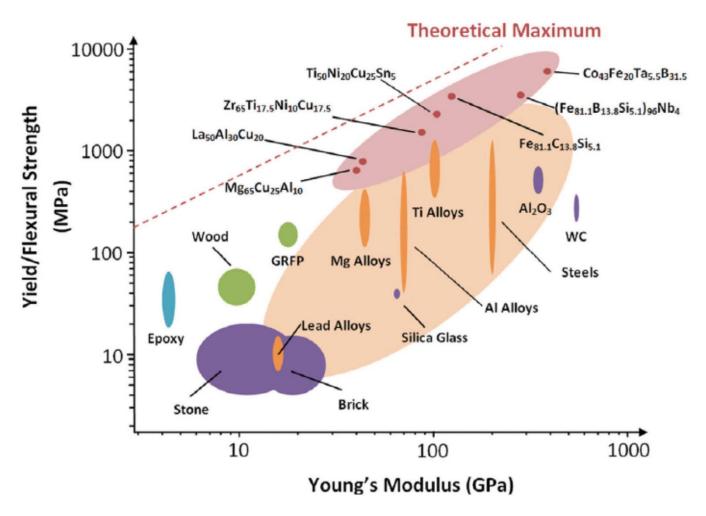




Enclosure / Antenna

High performance Liquidmetal® alloy

3) High yield (or fracture) strength and hardness



High fracture strength over 5 GPa in Fe-based BMGs

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



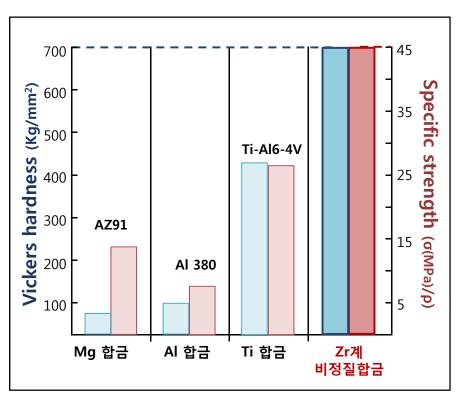
3) High yield (or fracture) strength and hardness



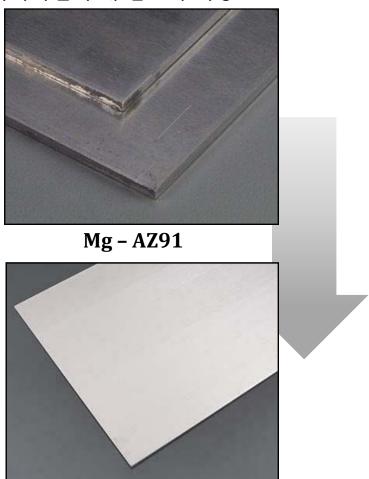


Bulk metallic glasses with high strength

- ▶ 고비강도 및 고경도 (강도)
- ▶ 초경량화 및 초경박화에 적합기존 상용 경량합금에 비하여 월등한 비강도로 재료의 획기적인 두께 감소가 가능



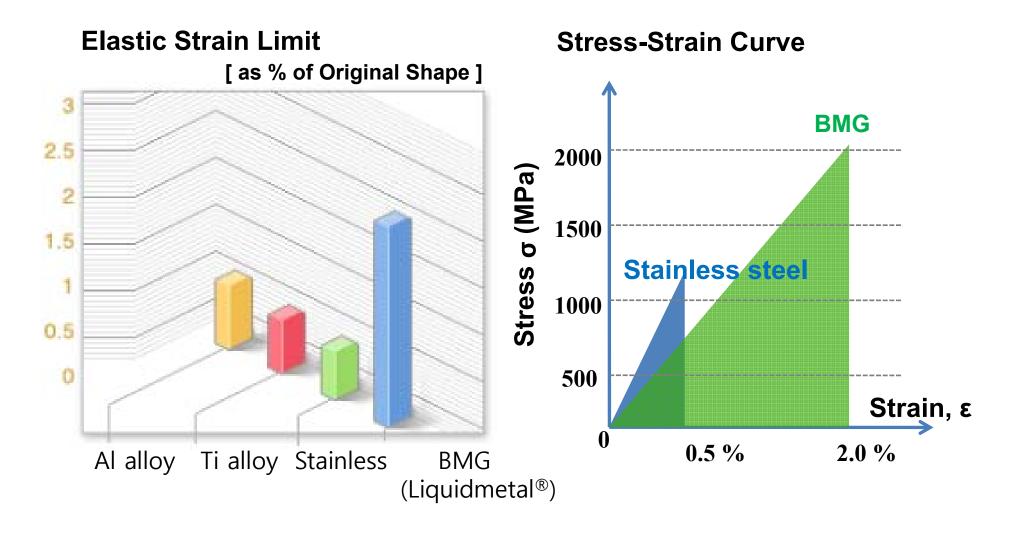
Zr계벌크 비정질 합금과 타 경량 합금의 경도와 비강도





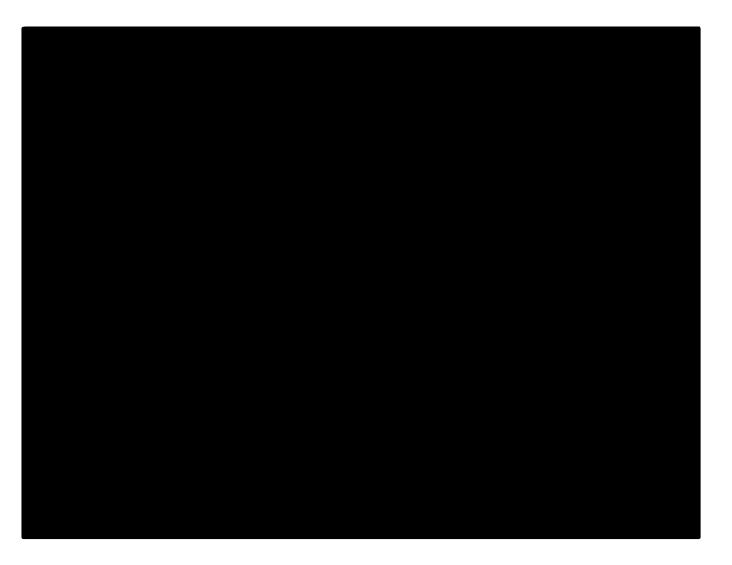


4) Large elastic strain limit of about 2 % at room temperature



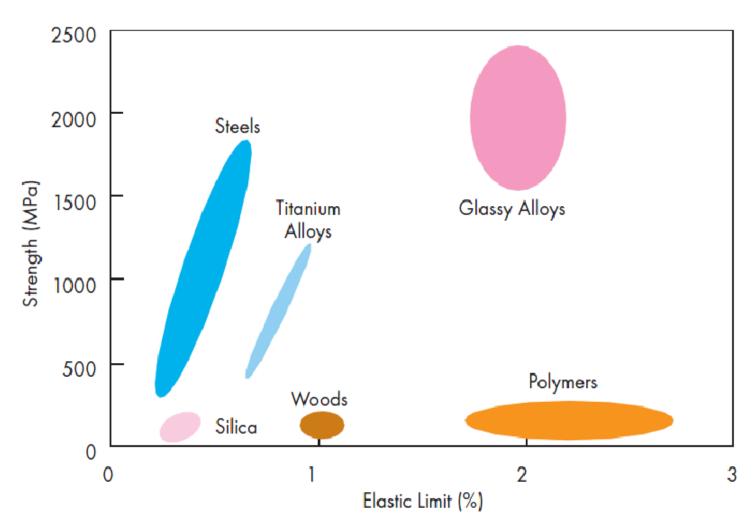


4) Large elastic strain limit of about 2 % at room temperature





Bulk metallic glasses with high strength & high elastic limit

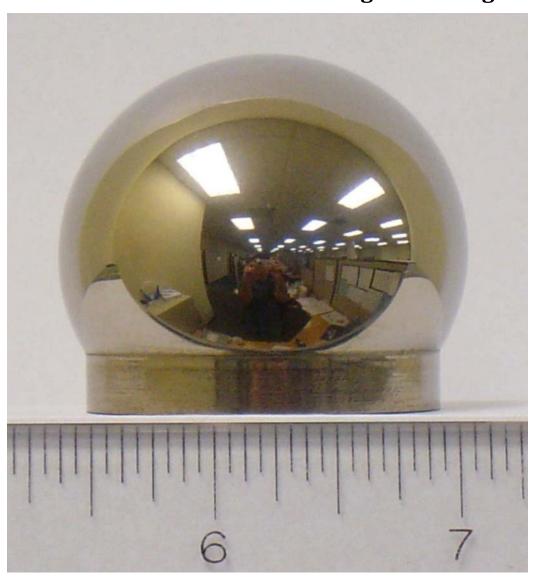


: Metallic Glasses Offer a Unique Combination of High Strength and High Elastic Limit



5) Ability to achieve a very high surface finish

: do not have microstructural features such as grains and grain boundaries



* Different forms of the glassy materials: rods, sheets, plates, spheres, pipes, etc.

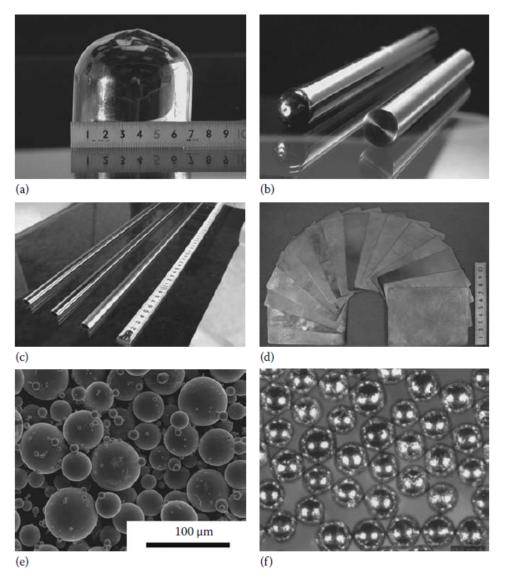


FIGURE 10.1

Different forms in which BMGs have been produced. (a) Cast cylinder, (b) rods, (c) pipes, (d) sheets, (e) powder, and (f) spheres.

10. 3. 1 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 mm for the BMG alloy face, whereas it is only 213 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.)

- 10.3 Structural Applications: high yield (or fracture) strength, low Young's modulus, large elastic strain limit, and easy formability in the SCLR
- 10. 3. 1 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

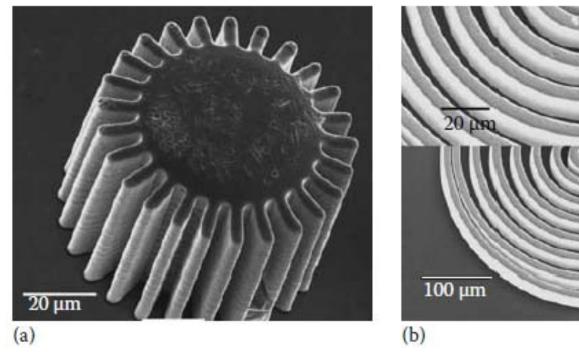


FIGURE 10.3

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

10. 3. 2. Precision Gears

- No shrinkage during solidification
- No grain boundary High flatness
- High strength



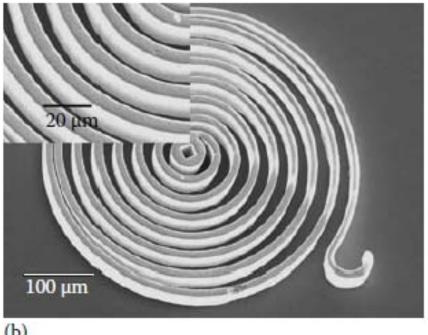


FIGURE 10.5

(a) A complex micro gear and (b) coil shape spring made from a Zr₄₄Ti₁₁Cu₁₀Ni₁₀Be₂₅ BMG alloy. (Reprinted from Schroers, J. et al., *Mater. Sci. Eng. A*, 449–451, 898, 2007. With permission.)

10. 3. 2. Precision Gears

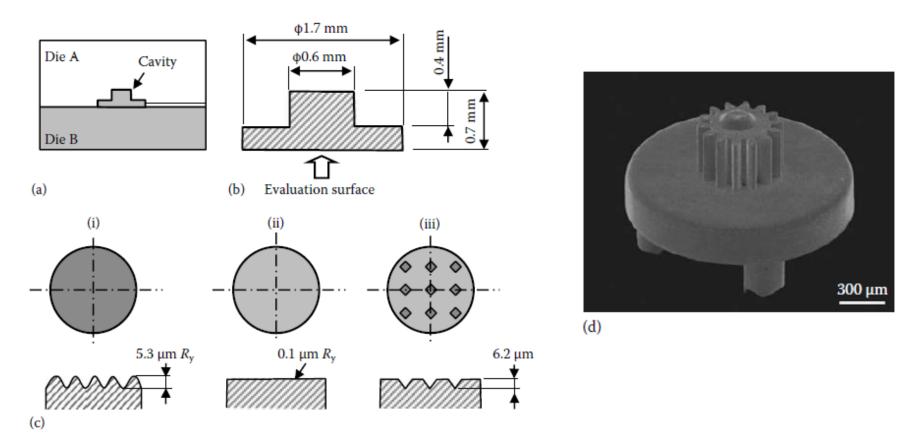
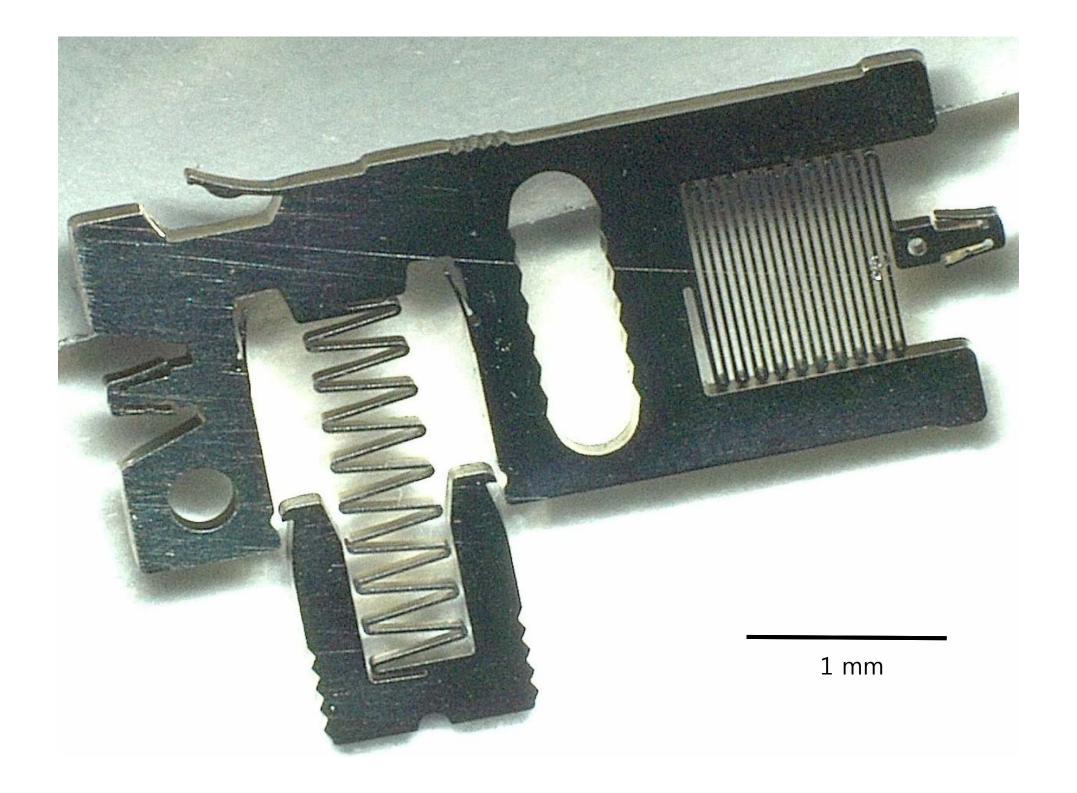
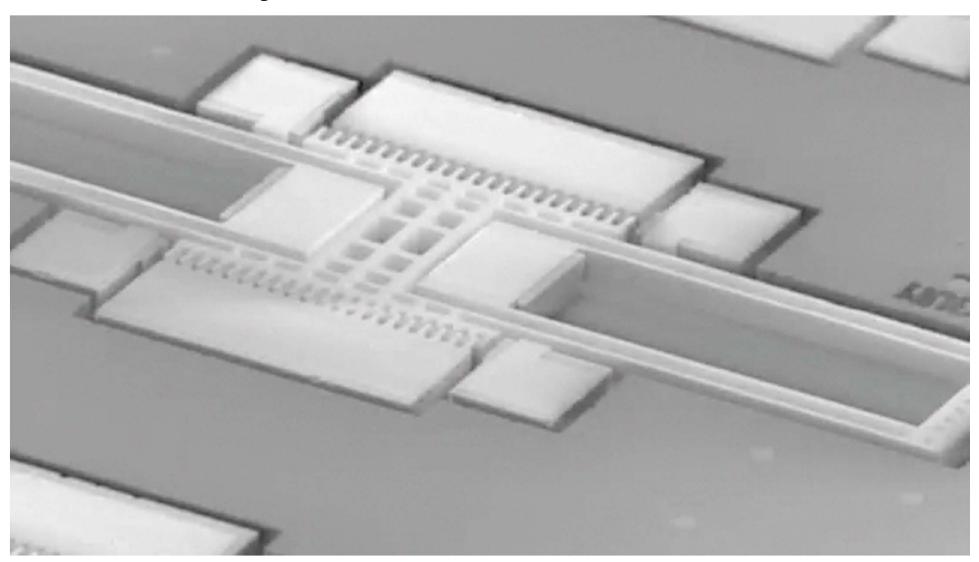


FIGURE 10.4

(a) Schematic illustration of the die assembly. (b) Schematic of the specimen with the dimensions indicated. (c) Schematic illustrations of the top surface of Die B prepared by (i) electro-discharge machining, (ii) polishing, and (iii) Vickers indentation. (d) External appearance of the Ni-based BMG sun-carrier fabricated by the precision die casting technique from an electro-discharge machined mold. (Reprinted from Ishida, M. et al., *Mater. Trans.*, 45, 1239, 2004. With permission.)



Fully functional MEMS device



10. 3. 3 Motors

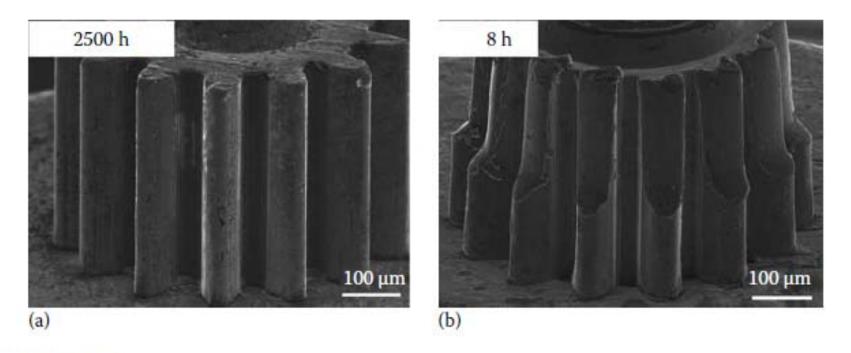


FIGURE 10.6

SEM images of the gears after the durability tests. (a) The gear made out of the Ni-based BMG alloy after 2500 h of use (1875 million revolutions) and (b) the carbon steel gear after 8 h of use (6 million revolutions). Notice the serious damage in the carbon steel gear even after just 8 h of use, while the BMG gear is intact even after 2500 h of use. (Reprinted from Ishida, M. et al., Mater. Sci. Eng. A, 449–451, 149, 2007. With permission.)

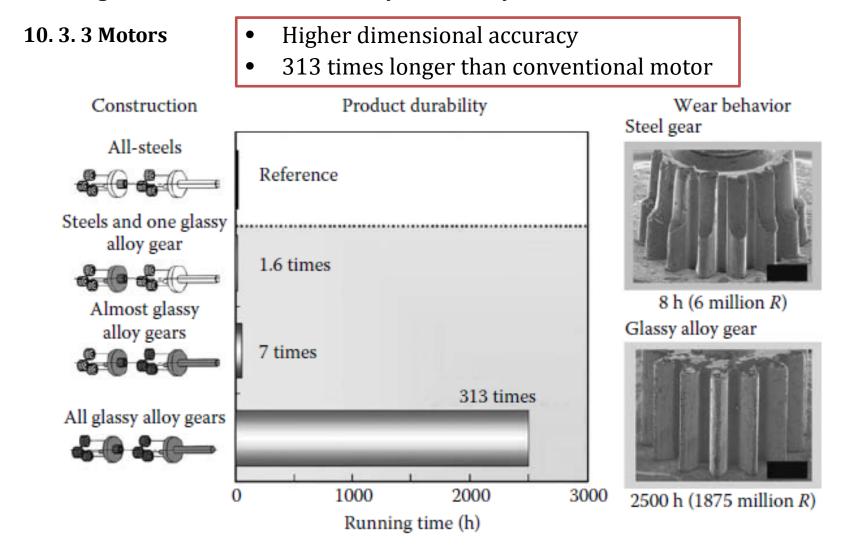


FIGURE 10.7

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.)

10.3.3 Motors

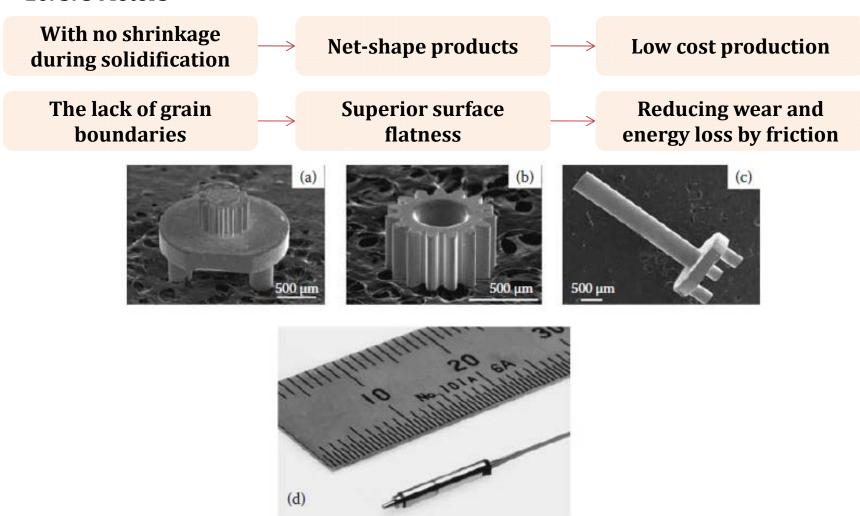


FIGURE 10.8

Precision microgear parts produced by injection casting of an Ni₅₃Nb₂₀Zr₈Ti₁₀Co₆Cu₃ BMG alloy: (a) sun-carrier, (b) planetary gear, and (c) an output shaft. (d) Micro-geared motor with a diameter of 1.5 mm and a length of 9.4 mm fabricated from the Ni₅₃Nb₂₀Zr₈Ti₁₀Co₆Cu₃ BMG alloy.

10.3.3 Motors

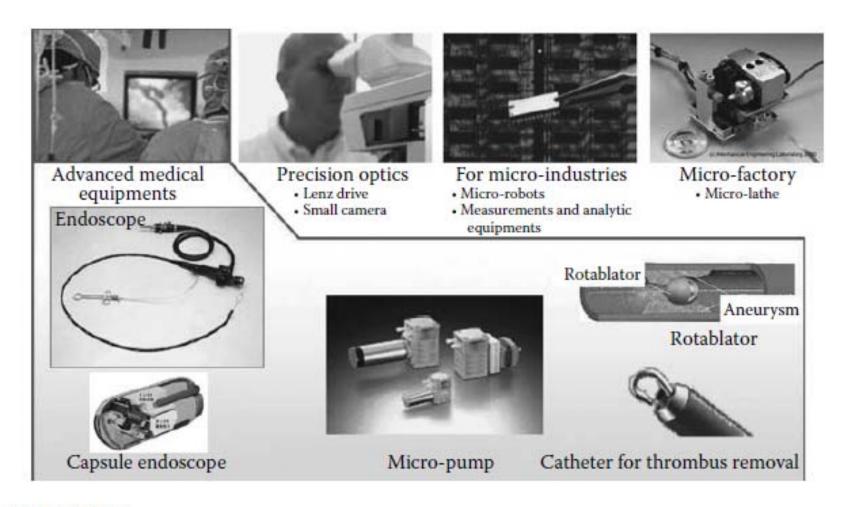
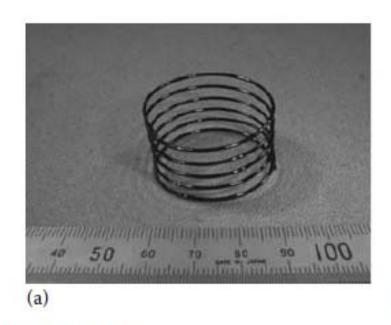


FIGURE 10.9

Projected application areas where micro-geared motors will find application.

10. 3. 4 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).



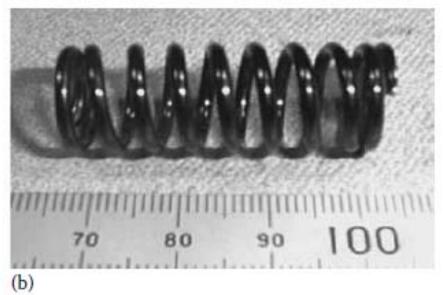


FIGURE 10.10

Helical springs of Zr₅₅Cu₃₀Al₁₀Ni₅ 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.)

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

10. 3. 5 Diaphragms for Pressure Sensors

Requiring	material property
Miniaturized and high sensitivity	lower Young's modulus and higher strength
mass production a low-cost production and commercialization	Possible to net shaping

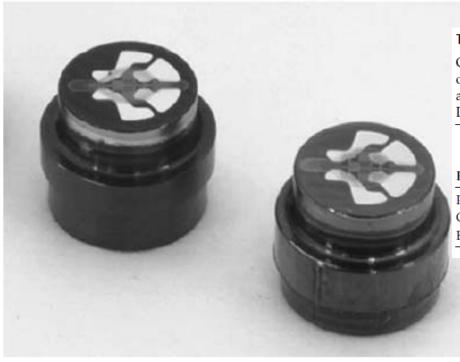


TABLE 10.1

Output Voltage for Pressure Sensors at a Testing Pressure of 20 MPa Using Commercial Stainless Steel (SUS 630) and Zr-Based $Zr_{55}Cu_{30}Al_{10}Ni_{5}$ BMG with Strain Gauges Deposited under Identical Conditions

	Output Voltage (mV) Using				
Process	Stainless Steel (SUS 630)	Zr-Based Zr ₅₅ Cu ₃₀ Al ₁₀ Ni ₅ BMG			
Plasma CVD	60	_			
Cat-CVD	50	100			
Excimer laser annealing	110	230			

Sensitivity is 3.8 times greater than a conventional diaphragm

FIGURE 10.11

Zr-based BMG diaphragm with a strain gauge deposited at low temperatures. (Reprinted from Nishiyama, N. et al., *Mater. Sci. Eng. A*, 449–451, 79, 2007. With permission.)

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

10. 3. 5 Diaphragms for Pressure Sensors

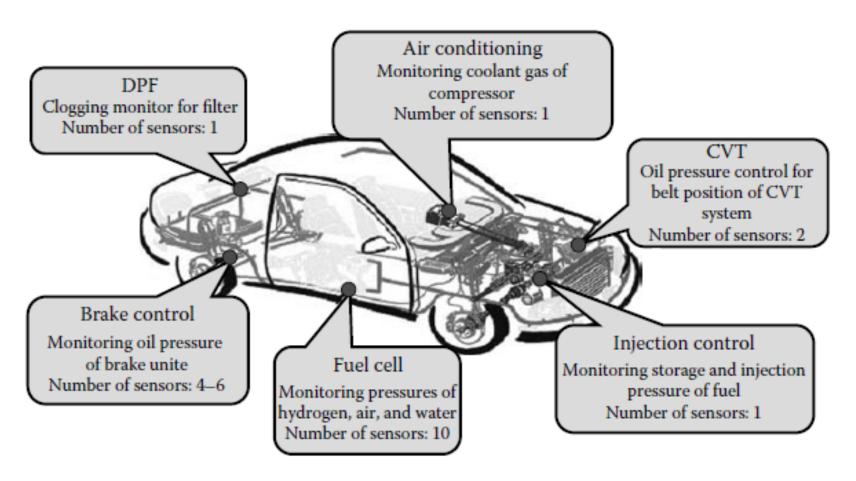


FIGURE 10.12

Expected market for pressure sensors to be used in different parts of an automobile.

10. 3. 6 Pipes for a Coriolis Mass Flow meter

: CFM determined by the density, Young's modulus, and strength of the materials used in the measurement pipe

: Young's modulus $\downarrow \rightarrow$ elastic deformation \uparrow for the same applied force

→ measurement of super-small liquid flow







FIGURE 10.13

Ti-based BMG pipes with outer diameters of (a) 6 and (b) 2 mm. (Reprinted from Nishiyama, N. et al., J. Non-Cryst. Solids, 353, 3615, 2007. With permission.)

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

10. 3. 6 Pipes for a Coriolis Mass Flow meter

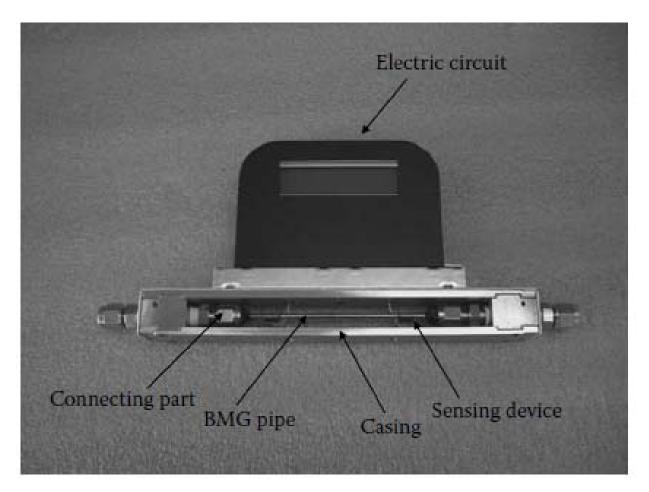


FIGURE 10.14
CMF developed using the Ti-based BMG pipes.

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

10. 3. 6 Pipes for a Coriolis Mass Flow meter

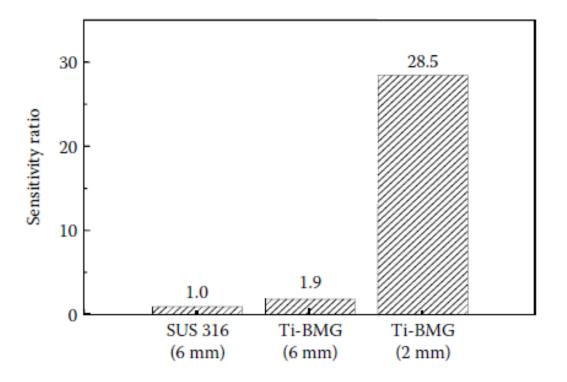


FIGURE 10.15
Sensitivity obtained by the CMF using the Ti-based BMG with diameters of 2 and 6 mm. Their sensitivity is compared with that of commercial stainless steel (SUS 316L) pipe with a diameter of 6 mm. (Reprinted from Ma, C.L. et al., *Mater. Sci. Eng. A*, 407, 201, 2005. With permission.)

10. 3. 7 Optical Mirror Devices: Optical coating

- Ideal isotropic material have no grain boundary (Polymer and oxide glass)
- Have Metallic luster Reflective parts of optical device, Optical Mirror









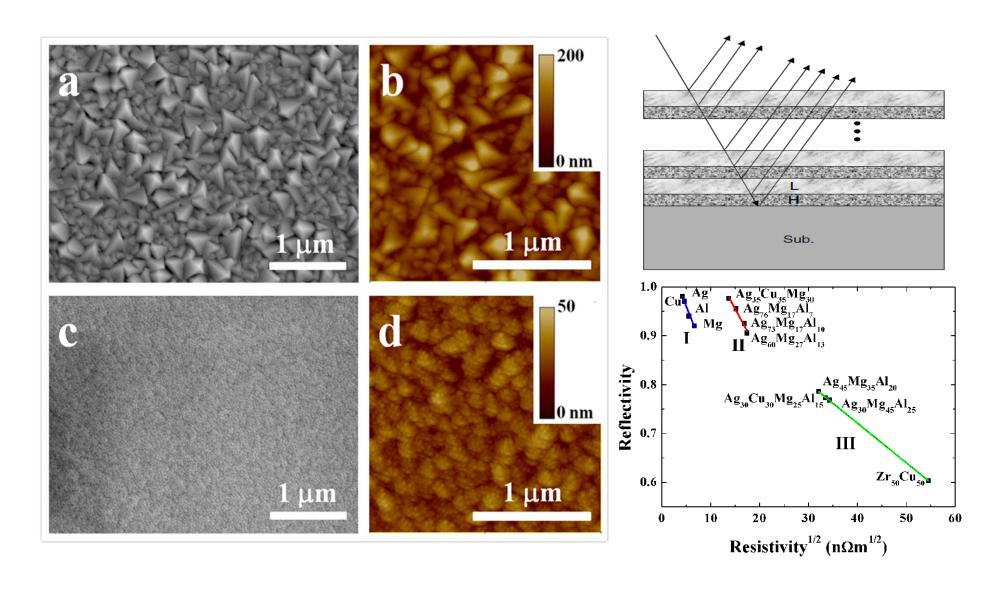
- •LED display
- •Solar cell, ligh t collector
- •3C enclosure
- •Lighting, high refection
- Tool coating



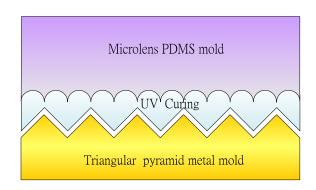


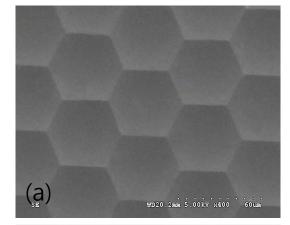


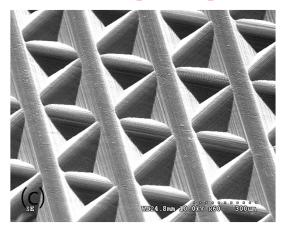
High light reflection TFMG coating

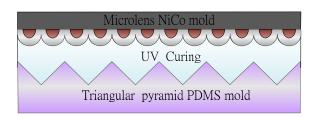


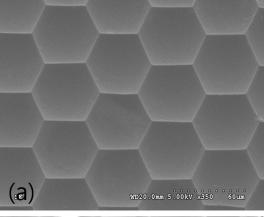
Optical lens for light con/diverging

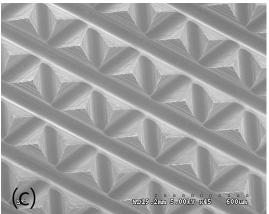


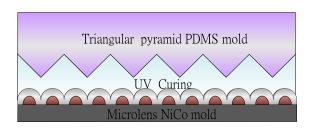


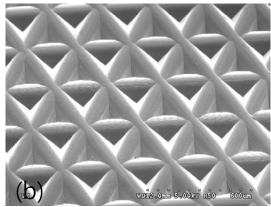


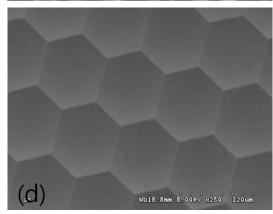




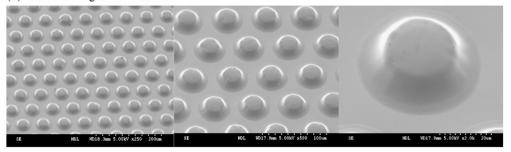




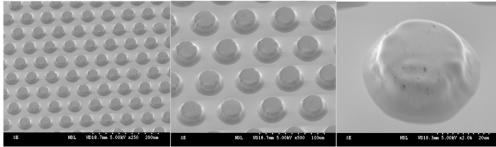




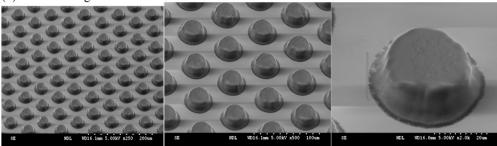
(a) Oven 200 degree C - 30min



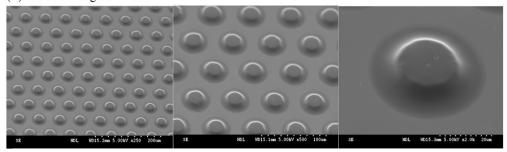
(b) Oven 230 degree C - 1hr

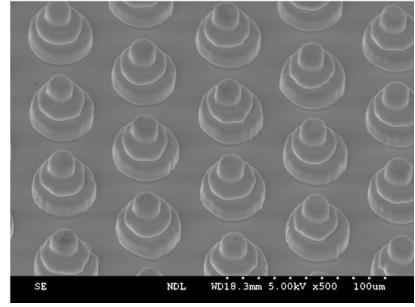


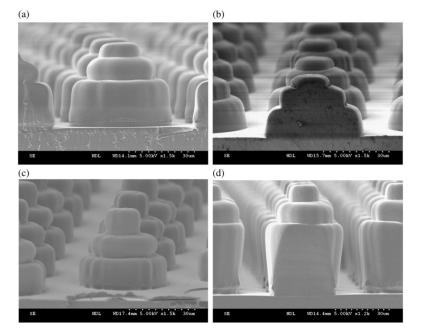
(c) Oven 260 degree C - 1hr



(d) Oven 280 degree C - 1hr







10. 3. 8 Structural Parts for Aircraft: slat-track over surrounding a set of guide rails at the front of the wings_high formability and corrosion resistance (exposure to ambient atmosphere moistened by rain or seawater)

high strength and low Young's modulus

engines may be lightened by miniaturizing cylinder heads

spring wires to be slimmer springs themselves to be shorter

increasing the revolution limit of engines by reducing their inertial mass

possible to improve fuel consumption

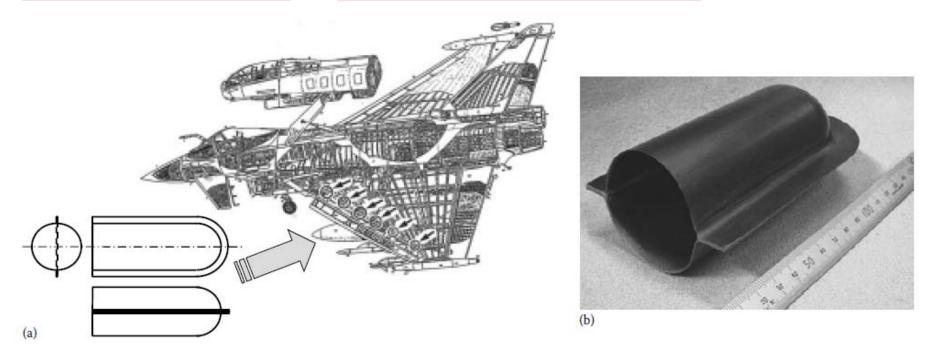


FIGURE 10.16

(a) Some areas (see small arrows) of an aircraft in which BMGs could be exploited. (b) Slat track cover fabricated by joining two identical parts obtained by viscous flow forming of a $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG plate.

- 10.3 Structural Applications: high yield (or fracture) strength, low Young's modulus, large elastic strain limit, and easy formability in the SCLR
- 10. 3. 9 Shot Peeing Balls: high strength, good ductility, high endurance against cyclic bombadment load, and high corrosion resistance

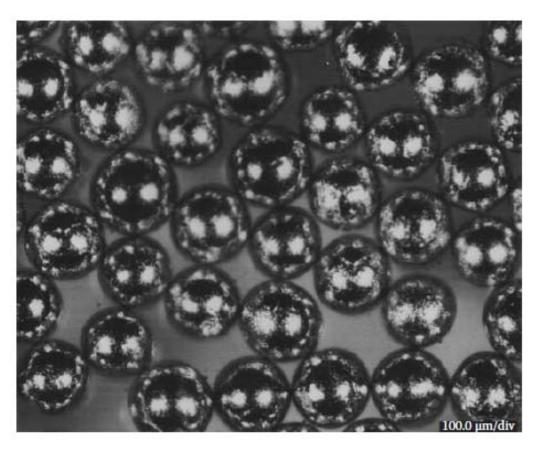


FIGURE 10.17 Size and surface finish of commercial $Fe_{44}Co_5Ni_{24}Mo_2B_{17}Si_8$ glassy alloy shots of $80\,\mu m$ diameter produced by water atomization. (Reprinted from Inoue, A. et al., *Mater. Trans.*, 44, 2391, 2003. With permission.)

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

10. 3. 9 Shot Peeing Balls: high strength, good ductility, high endurance against cyclic bombadment load, and high corrosion resistance

Mechanical Properties of the Fe-Based BMG and Two Other Cast Steel Shots Used in the Investigation

Property	Fe-Based BMG Fe ₄₄ Co ₅ Ni ₂₄ Mo ₂ B ₁₇ Si ₈	High-Speed Steel Fe-1.15C-4Cr-5Mo- 2.5V-6.5W-8Co (wt.%)	Cast Steel Fe-1C-0.9Si- 0.7Mn (wt.%)
Young's modulus (GPa)	80	215	210
Fracture strength (MPa)	3200	2100	1100
Vickers hardness	930	815	810
Density (g cm ⁻³)	7.4	7.7	7.55

TABLE 10.3

Effects of Bombardment with Fe-Based BMG
Alloy Shots and Cast Steel Shots for 40s on
Two Commercial Steel Sheets

Attribute	Fe-Based BMG	Cast Steel
Crater size (µm)	20	7
Average crater height (µm)	15	5
Depth of affected region (µm)	100	45
Surface Vickers hardness	510	480
Maximum compressive stress on the surface (MPa)	1600	1470
Depth (µm) of the region at which the compressive stress was 500 MPa	27	18
Endurance time needed to final rupture of the peening shots (h)	28	_

Chemical Applications

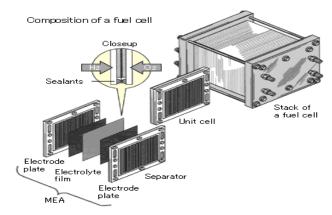
Very hard, high strength High corrosion resistance

Viscous deformability

Chemical Applications

1) Fuel cell separator

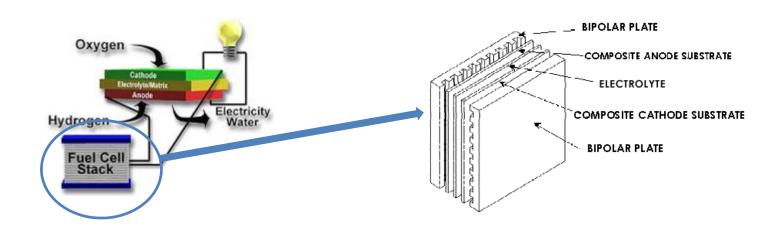
Lower interfacial contact resistances higher corrosion resistance high strength



2) hydrogen-permeable membrane

Defect-free film growth High strength and ductility Corrosion resistance Good H2 solubility repeated cycling
Withstanding high temperature
high pressure

Compositional flexibility and homogeneity High catalytic surface activities for H2 interactions



10. 4 Chemical Applications: a) Fuel cell separators_high strength, superior corrosion resistance, and excellent formability in SCLR

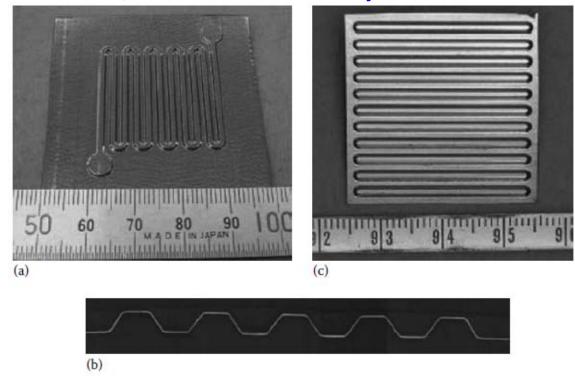


FIGURE 10.18

(a) Prototype fuel cell separator using a Ni-based BMG sheet, (b) cross-sectional morphology of the groove-formed specimen, and (c) appearance of the BMG separator after power generation for 350 h. (Reprinted from Inoue, A. et al., *Mater. Trans.*, 46, 1706, 2005. With permission.)

b) Hydrogen separating membrane:

Good hydrogen permeability + melt-spun

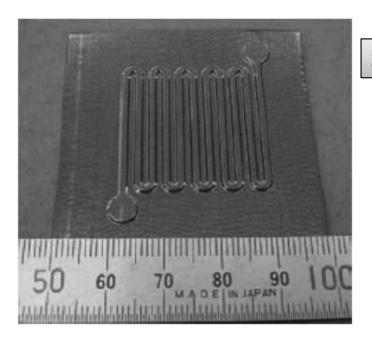
→ Possible to <u>mass-production</u> technique by using amorphous hydrogen permeable membranes



10. 4 Chemical Applications: Fuel cell separators_high strength, superior corrosion resistance, and excellent formability in SCLR

BMG

- High strength
- Superior corrosion resistance
- Viscous deformability



Stainless steel

drastic drop of output voltage

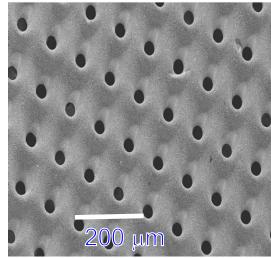


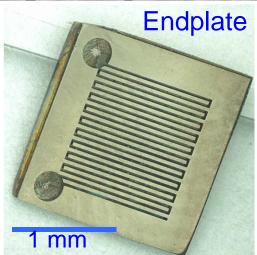
BMG

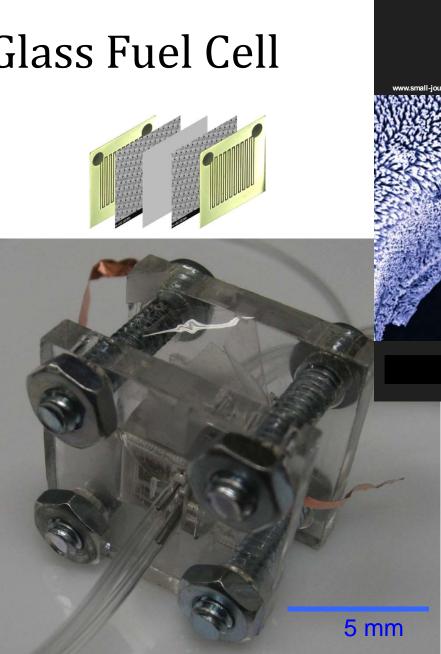
System smaller
lighter
low product cost
High voltage output
Slow degradation

Metallic Glass Fuel Cell

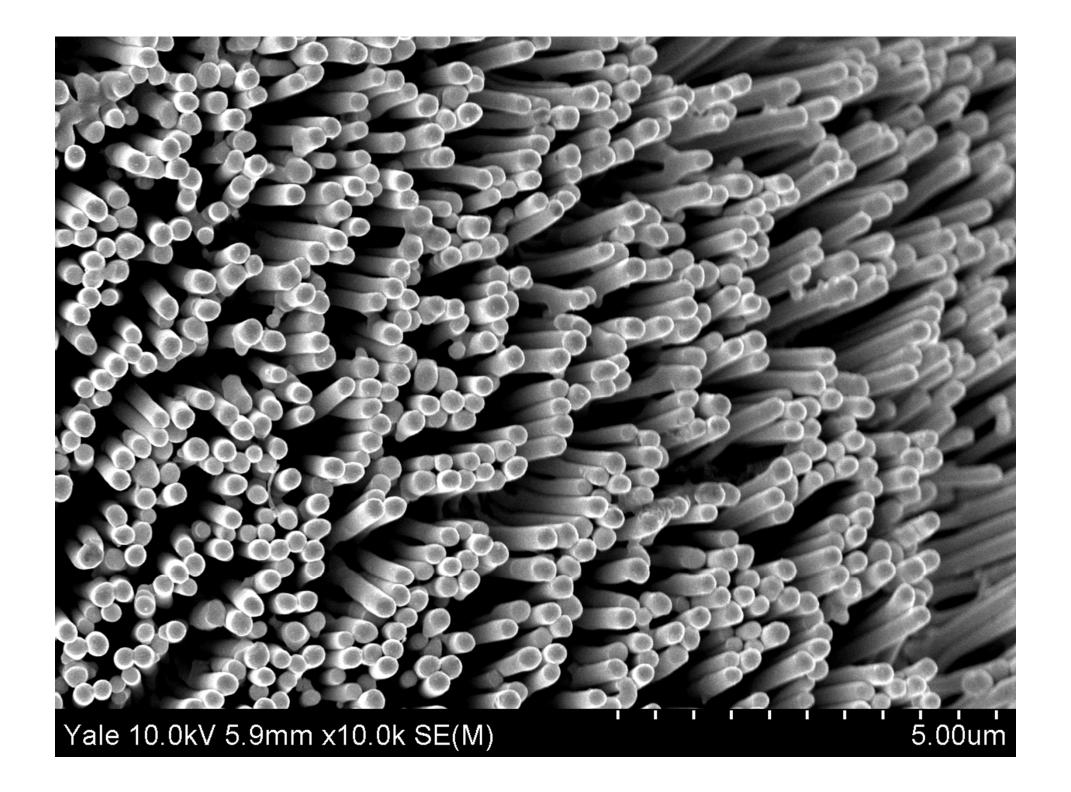
Electrode, Catalyst







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



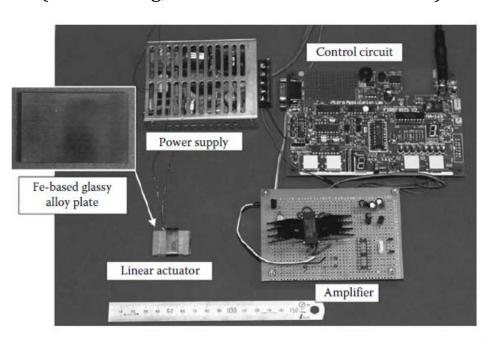
10. 5. Magnetic Applications:

BMG

High permeability Low coercivity

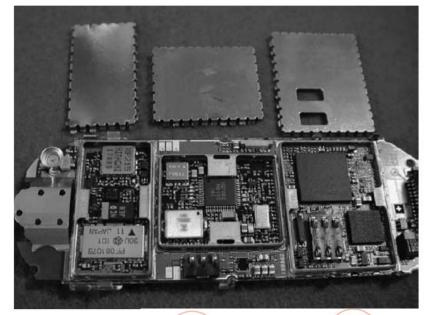


* $Fe_{73}Ga_4P_{11}C_5B_4Si_3$ BMG plates (30 mm long, 20 mm wide and 1 mm thick)

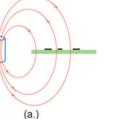


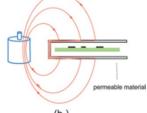
 $\label{eq:FIGURE 10.19} FIGURE \ 10.19$ Magnetic yoke made of an Fe $_{73}$ Ga $_4$ P $_{11}$ C $_5$ B $_4$ Si $_3$ BMG plate for a prototype linear actuator.

* Fe-Ga-Al-P-C BMG : Low core loss 610 kW/m³ at 100kHz (High freq.)



IGURE 10.20 MG magnetic shielding sheets





Magnetic Applications

Very soft magnetic material

High electrical resistivity

Magnetic Applications

1) Sensor

• Sensitivity ferrite < <u>amorphous alloy</u> < superconductor

• Operating temp. <u>amorphous alloy</u> > ferrite , superconductor

• Compactness <u>amorphous alloy</u>, ferrite > superconductor

• Reliability <u>amorphous alloy, ferrite>>ferrite>superconductor</u>

Shape	Dimension	Fabrication	Applications	compositions
Ribbon	15~30 μmt 0.1~200mm W	Melt spinning (single roll technique)	Magnetic hand Cartridge Torque sensor Data tablet Magnetic-field sensor Current sensor	CoFeSiB FeSiB
Wire	90~160μm φ	In-rotating water Melt quenching	Magnetic-field sensor Current sensor Security sensor Rotation sensor Displacement sensor	CoFeMSiB
Thin film	500~400Å t	Sputtering	Pressure sensor Magnetic head	FeB CoFeMSiB
Composite	10∼30µm t	Laser-quenching	Torque sensor	FeBsi

Magnetic Applications

Very soft magnetic material

High electrical resistivity

Magnetic Applications

1) Sensor

• Sensitivity ferrite < <u>amorphous alloy</u> < superconductor

• Operating temp. <u>amorphous alloy</u> > ferrite , superconductor

• Compactness <u>amorphous alloy</u>, ferrite > superconductor

• Reliability <u>amorphous alloy, ferrite>>ferrite>superconductor</u>

Zero- magnetostrictive alloy	Magnetic head sensor			
	Data tablet(Matteucci effect)			
	Magnetic cartridge			
	Magnetic-field sensor	Magnetometer , Current sensor, Direction sensor Displacement sensor, Card reader, Security sensor Motor-flux sensor, Eddy-current sensor →proximity sensor		
High- magnetostrictive alloy	Stress-magnetic effect	Torque sensor, pressure sensor, shock sensor		
	Magnetoelastic wave propagation effect	Data tablet, frost sensor Distance sensor, touch sensor		
	Large Barkhausen effect	Security sensor, rotation speed sensor, distance sensor		
	Matteucci effect	degitizer		

10. 6. 1 Jewelry

TABLE 10.4
Selected Properties of Au-Based and Pt-Based BMGs and Their Approximate Crystalline Counterparts

	Density	Yield Strength	Elastic Elongation		
Material	(g cm ⁻³)	(MPa)	(%)	Hardness	$S = \Delta T_{\rm x}/(T_\ell - T_{\rm g})$
Au ₄₉ Ag _{5.5} Pd _{2.3} Cu _{26.9} Si _{16.3} (LM18kAu)	11	1200	1.5	360	0.24
Au-Ag-Cu (18k)	15.4	350	< 0.5	150	_
Pt _{57.5} Cu _{14.7} Ni _{5.3} P _{22.5} (LM850Plat)	15.3	1400	1.3	402	0.34
Pt/Ir850/150	21.5	420	<0.5	160	_

10. 6. 1 Jewelry

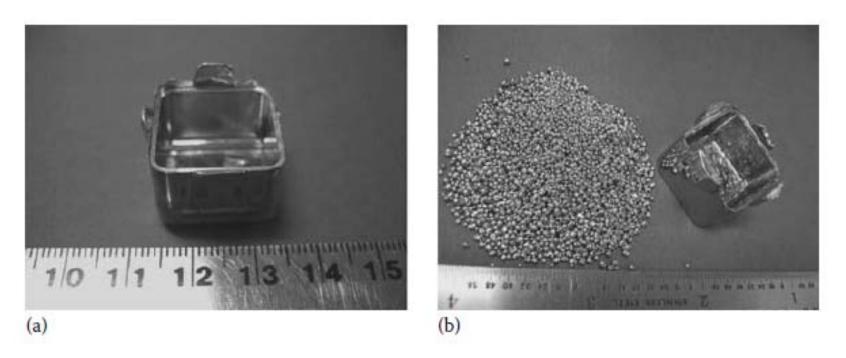


FIGURE 10.21

Net shape formability using Au-based and Pt-based BMG alloys. (a) The Au-based alloy was formed at 150°C for 200s under a pressure of 100 MPa. (b) The Pt-based alloy formed at 270°C for 100s under a pressure of 28 MPa using pellets as feedstock material. (Reprinted from Schroers, J. et al., Mater. Sci. Eng. A, 449–451, 235, 2007. With permission.)

10. 6. 2. Biomedical Applications

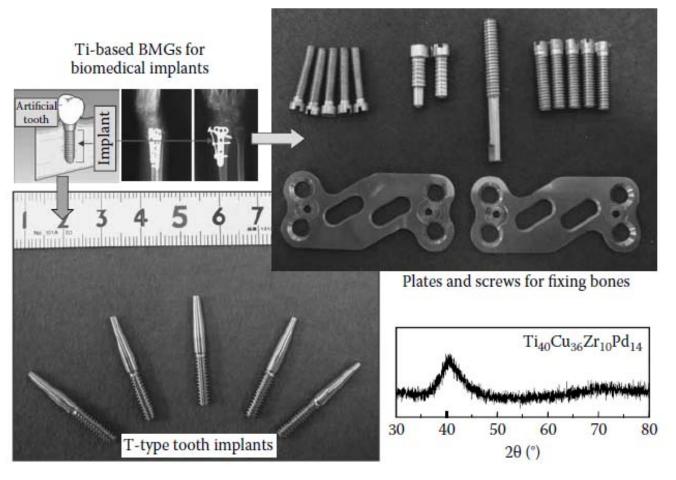
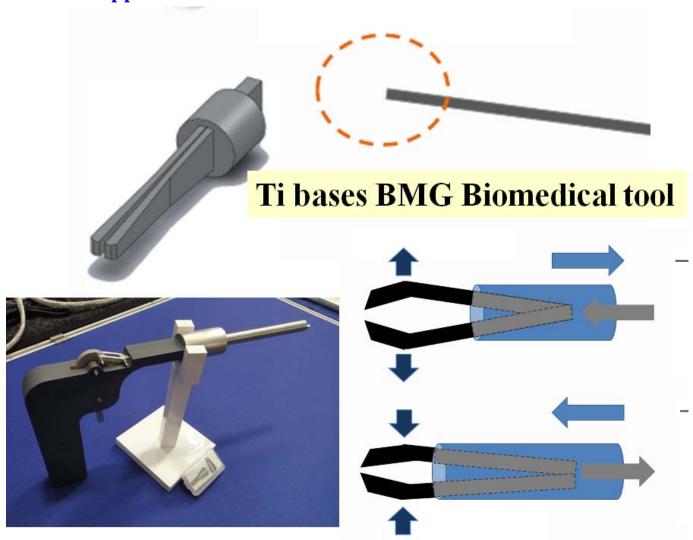


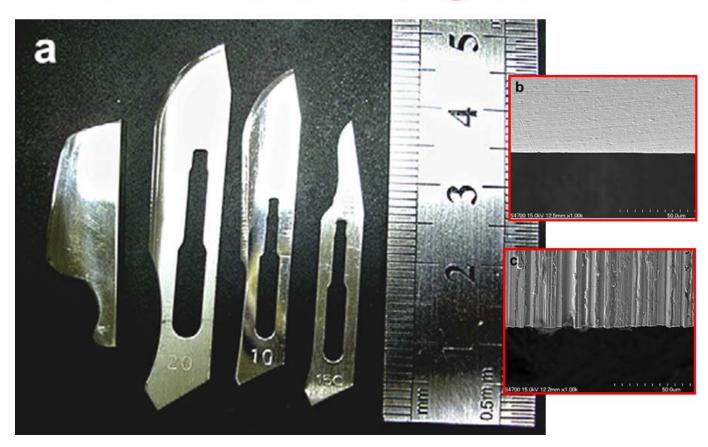
FIGURE 10.22 $Ti_{40}Zr_{10}Cu_{36}Pd_{14} \ BMG \ alloy \ implants \ for \ T-type \ teeth \ and \ plates \ and \ screws \ for \ fixing \ bones.$

10. 6. 2. Biomedical Applications



10. 6. 3. Medical Devices

Anti-microbial surgical tools



Zr-based alloy

Catching solar wind

As part of NASA's Discovery Program, August 2001 saw the launch of the \$200 million Genesis spacecraft(Fig. a) with the aim of collecting samples of solar wind22. Orbiting the Lagrange point, Genesis is expected to capture 10-20 μ g of solar wind particles and ions using five, 1 m diameter circular passive collector arrays.

Zr-Nb-Cu-Ni-Al

10cm

 $X 55 \rightarrow Circular passive collector array$

Absorbing and retaining noble gases He and Ne

Bring collectors to Earth and acid etching

Captured higher ions

[higher-energy ions] differ in composition from the solar wind

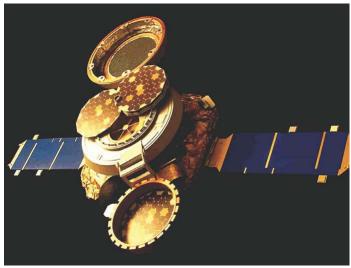


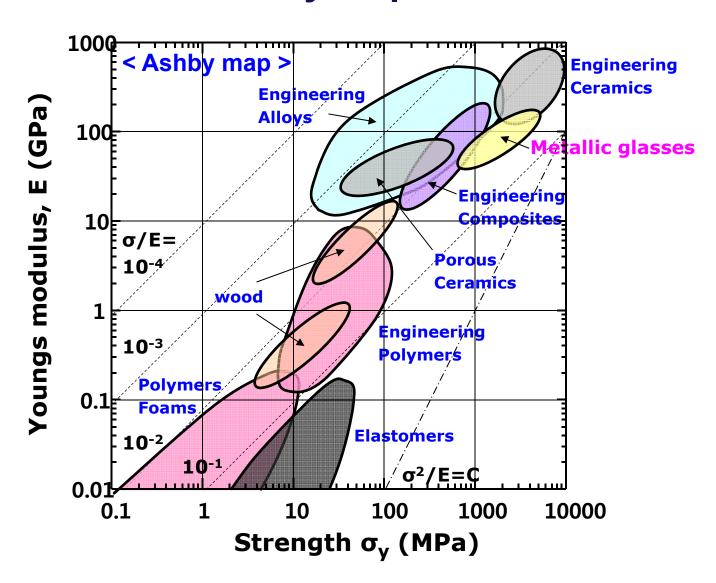


Fig. (a) Artist's impression of the Genesis spacecraft in collection mode, opened up to collect and store samples of solar wind particles. The cover of the canister contains one collector array and the body of a stack of four arrays that can be rotated out when the spacecraft begins its orbit. (b) Genesis' array, held by Andy Stone of the Jet Propulsion Laboratory, showing the collector materials. [(a) courtesy of JPL; (b) courtesy of NASA Johnson Space Center.]

The beginning of a new era in metallic materials

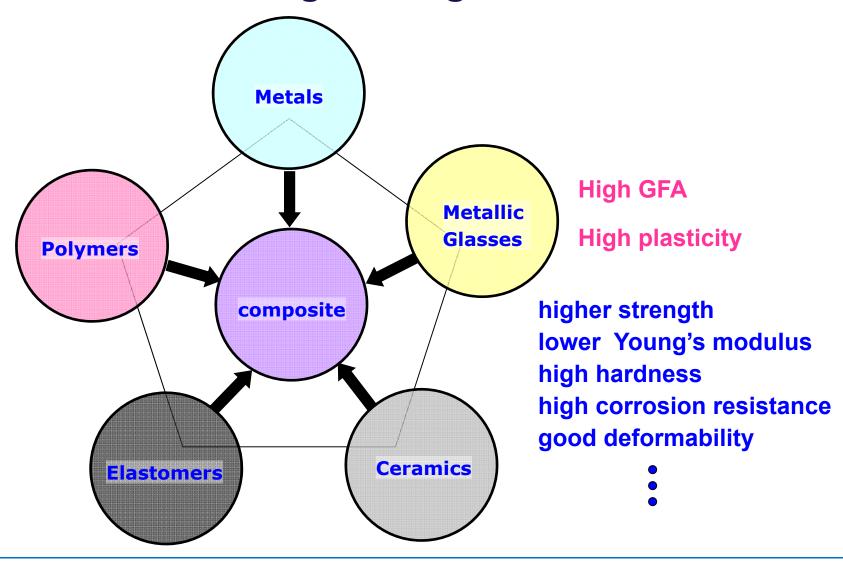
At the Cutting Edge of Metals Research: Bulk Metallic Glasses

Ashby map



At the Cutting Edge of Metals Research: Bulk Metallic Glasses

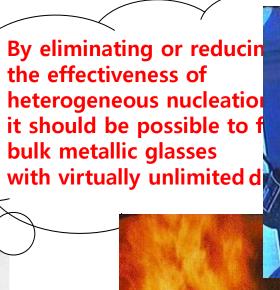
Menu of engineering materials

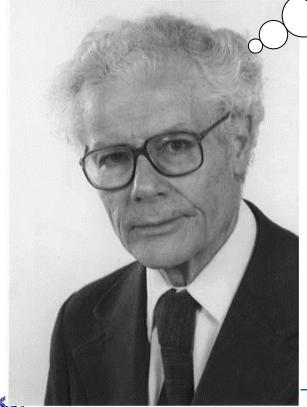


ESPark Research Group



At the Cutting Edge of Metals Research: Bulk Metallic Glasses







"기술개발이 한계를 만날 때 신소재의 혁신은 시작된다."



Schedule

- week 1 Ch1. Introduction to amorphous materials
- week 2 Ch2. Metallic Glasses_Glass formation
- week 3 Ch2. Metallic Glasses_Thermodynamics of glass formation
- week 4 Ch2. Metallic Glasses_Kinetics of glass formation
- week 5 Ch2. Metallic Glasses_Methods to synthesize metallic glasses
- week 6 Ch3. Glass-Forming Ability of Alloys _ Glass-forming ability
- week 7 Ch3. Glass-Forming Ability of Alloys _ GFA parameters
- week 8 Ch3. Glass-Forming Ability of Alloys _ Development of GFA parameters
- week 9 Ch4. Synthesis of Bulk Metallic Glasses
- week 10 Ch4. Synthesis of Bulk Metallic Glasses
- week 11 Ch4. Synthesis of Bulk Metallic Glasses_BMG composites
- week 12 Ch5. Crystallization Behavior_Crystallization modes
- week 13 Ch5. Crystallization Behavior_Annealing of BMGs
- week 14 Ch. 8 Mechanical Behavior_Deformation maps
- week 15 Ch. 8 Mechanical Behavior_Improvement of Plasticity in BMGs
- week 16 Ch 10. Potential Applications of BMGs