Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden

Institut für Komplexe Materialien (IKM)

Neue Entwicklungen im Bereich der metallischen Massivgläser

Mihai Stoica

Leibniz-Institut
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Dresden

Leibniz-Institute for Solid State and Materials Research Dresden

Institute for Complex Materials (ICM)

New achievements in the area of Bulk Metallic Glasses (BMGs)

Mihai Stoica

Organization

Executive board

Scientific Director	**Administrative Director**
Prof. Dr. L. Schultz	Dr. h.c. R. Pfrengle

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Institute for Solid State Research	**Institute for Metallic Materials**	**Institute for Complex Materials**	**Institute for Integrative Nanosciences**	**Institute for Theoretical Solid State Physics**
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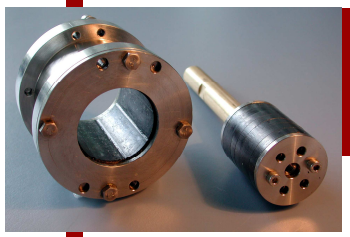
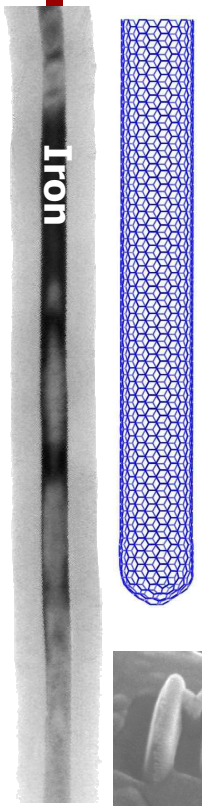
Research Technology	**Administration**
Dr. D. Lindackers	Dipl.-Kffr. F. Jaeger

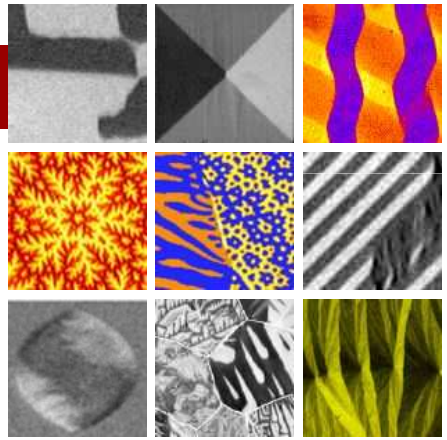
Research Areas



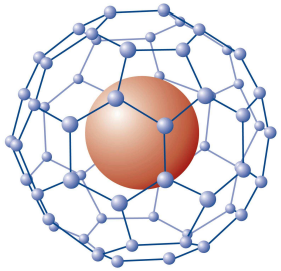
Superconductivity and superconductors

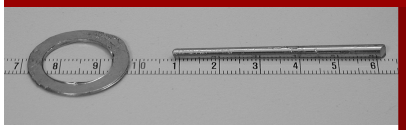
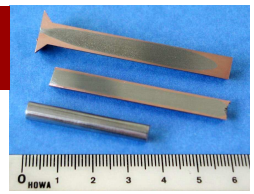
Magnetism and magnetic materials

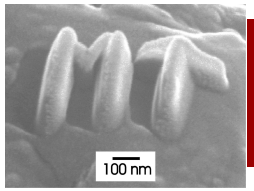


Molecular magnets and molecular solids

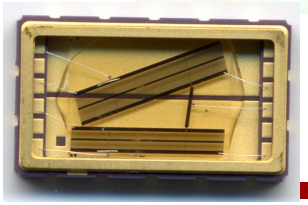


Metastable alloys

Stress-driven architectures and phenomena




Preparation, properties and applications of BMGs

- **Metallic Glasses**
  - Theoretical basis
  - Preparation
  - Properties and interesting alloy systems
  - Applications
- **Glass Matrix Composites**

Theoretical basis: historical development

Silicate glass (window glass)

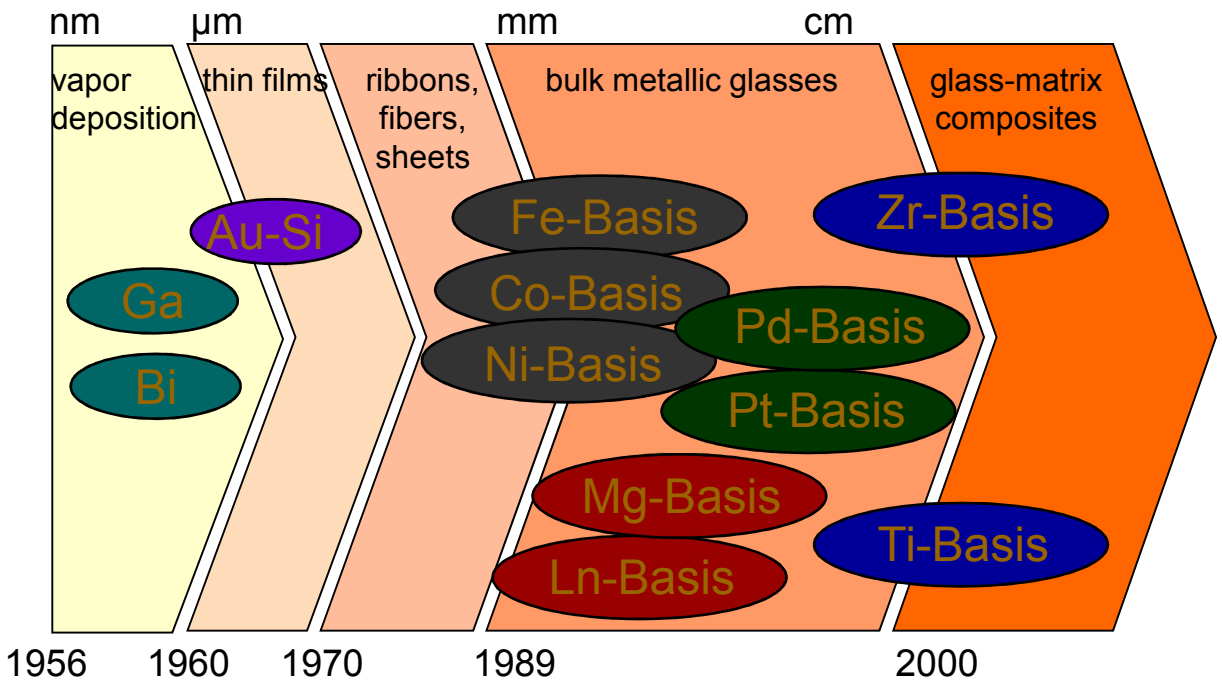
- the oldest from 7000 B.C.
- transparent
- hard and brittle

Metallic glass

- massive first time in 1989
- metallic luster
- not transparent
- very hard
- good elasticity, partially deformable

but: different atomic structure! amorphous = not ordered

Theoretical basis: historical development



Theoretical basis: historical development

Nonferrous alloy systems

Mg-Ln-M (lanthanide metal; M: Ni,Cu,Zn	1988
Ln-Al-TM (TM: Fe,Co,Ni,Cu)	1989
Ln-Ga-TM	1989
Zr-Al-TM	1990
Ti-Zr-TM	1993
Zr-Ti-TM-Be	1993
Zr-(Ti,Nb,Pd)-Al-TM	1995
Pd-Cu-Ni-P	1996
Pd-Ni-Fe-P	1996
Pd-Cu-B-Si	1997
Ti-Ni-Cu-Sn	1998
Cu-(Zr,Hf)-Ti	2001
Cu-(Zr,Hf)-Ti-(Y,Be)	2001
Cu-(Zr,Hf)-Ti-(Fe,Co,Ni)	2002

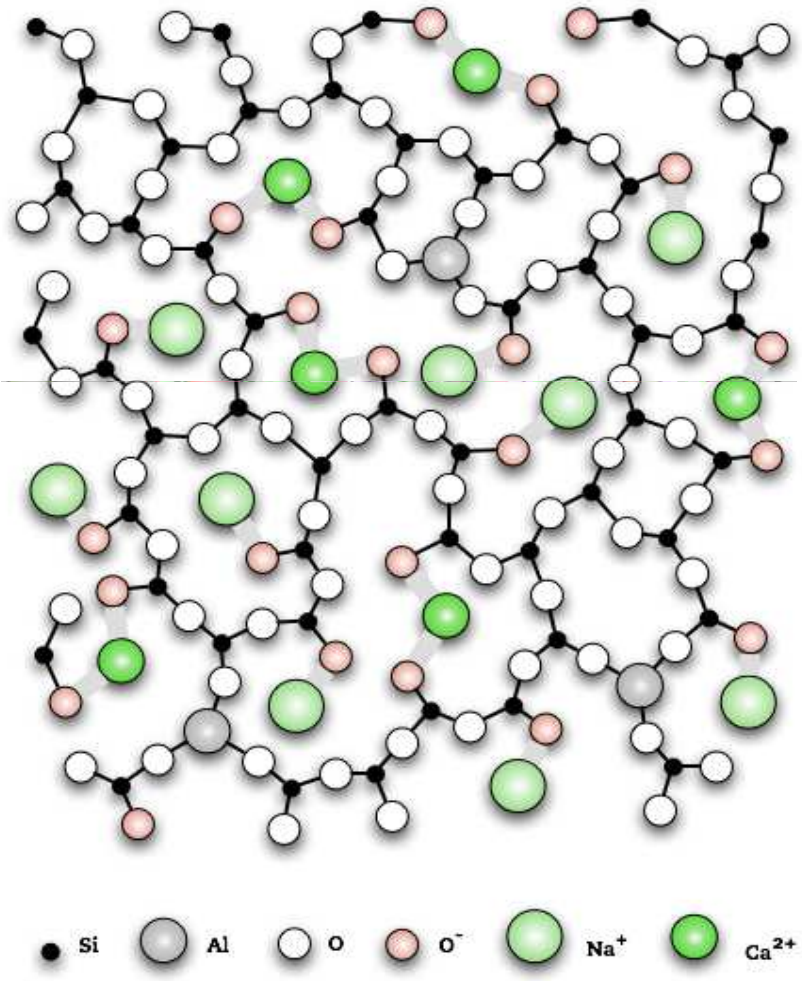
Ferrous alloy systems

Fe-(Al,Ga)-(P,C,B,Si,Ge)	1995
Fe-(Nb,Mo)-(Al,Ga)-(P,B,Si)	1995
Co-(Al,Ga)-(P,B,Si)	1996
Fe-(Zr,Hf,Nb)-B	1996
Co-(Zr,Hf,Nb)-B	1996
Ni-(Zr,Hf,Nb)-B	1996
Fe-Co-Ln-B	1998
Fe-Ga-(Cr,Mo)-(P,C,B)	1998
Fe-(Nb,Cr,Mo)-(C,B)	1999
Ni-(Nb,Cr,Mo)-(P,B)	1999
Co-Ta-B	1999
Fe-Ga-(P,B)	2000
Ni-Zr-Ti-Sn-Si	2001
Ni-(Nb,Ta)-Zr-Ti	2002
Fe-Si-B-Nb	2002
Co-Fe-Si-B-Nb	2002
Ni-Si-B-Ta	2002

Inoue et al.: Acta Mater.52 (2004)

Theoretical basis: glassy state

1. No translational symmetry → Random atomic distribution



Prefered neighbour links

short range order

Type of atoms

chemical short-range order

Amount of, distances, angle relations:

physical short-range order

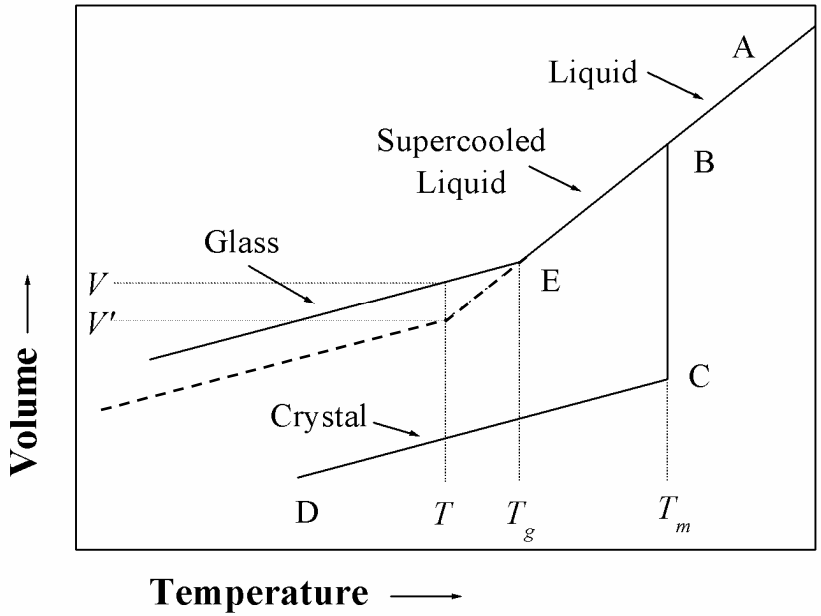
Theoretical basis: glassy state

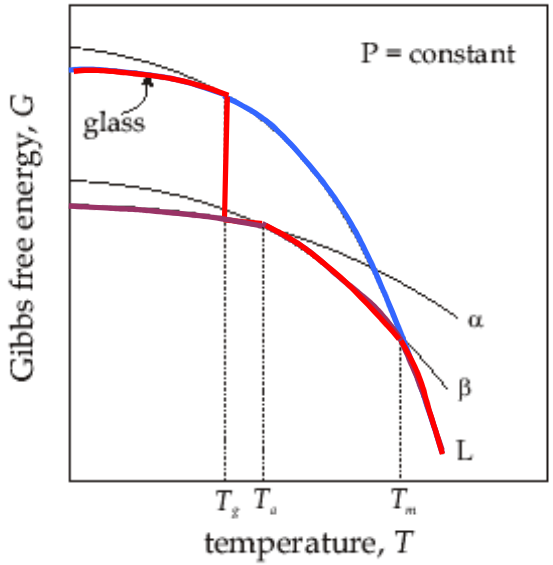
2. Glass transition

- seen by cooling the melt / heating the glass
- changes of the thermodynamic properties
  (volume *V*, entropy *S*, specific heat c_p)
- continuous transformation of the **undercooled** melt in glassy solid (kinetic freezing)

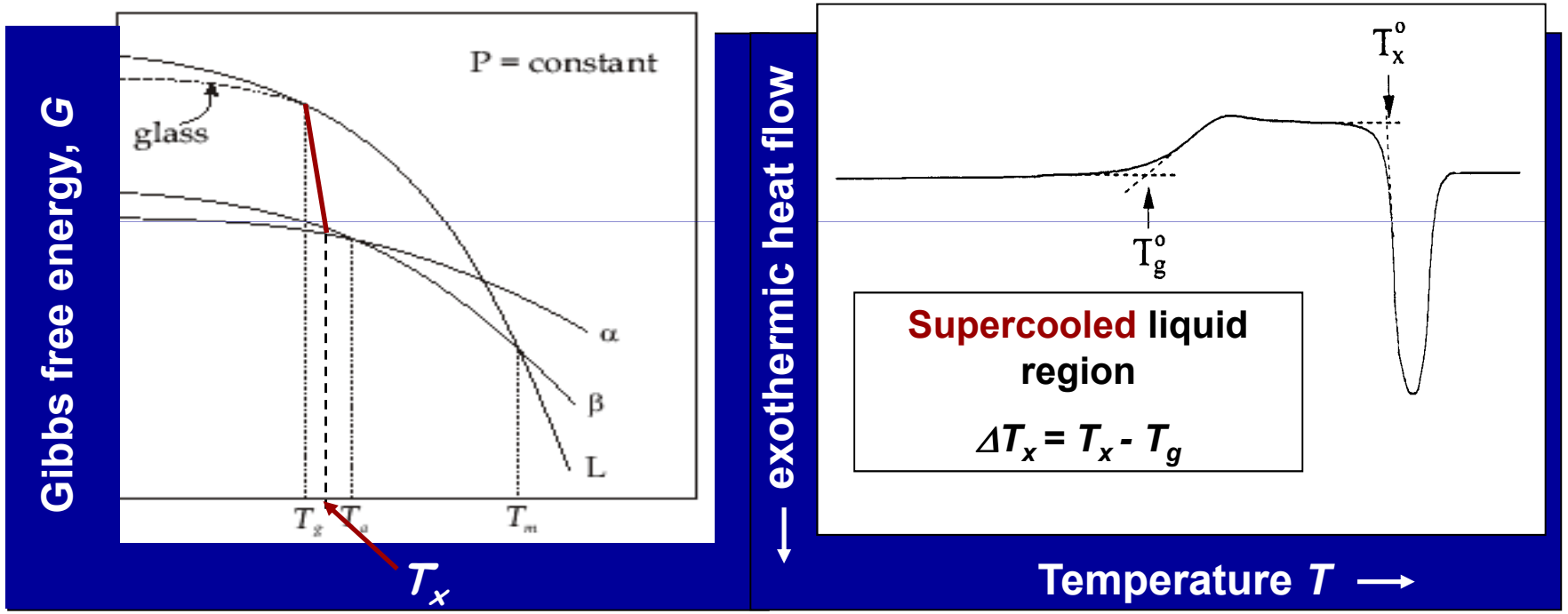
Glass transition temperature T_g :

- cannot be defined precisely → temperature interval
- heating / Cooling rate dependent (thermal history)





Theoretical basis: glassy state



Theoretical basis: thermodynamic and kinetic influences on glass forming ability

Multicomponent systems consisting of more than three elements* with *difference in atomic size ratio (> 12%)* and *negative heats of mixing

↓

Dense random packed structure

↓

Liquid with new atomic configurations and multicomponent interactions

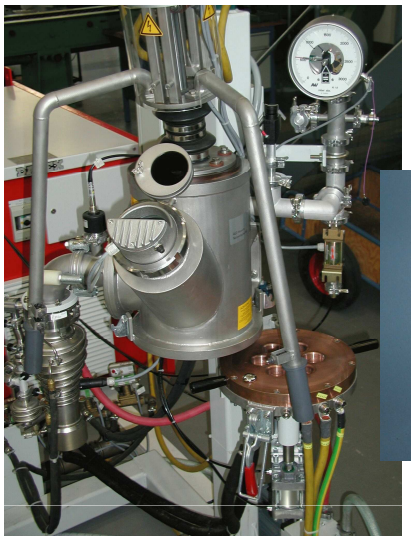
Increase of solid/liquid interfacial energy	Difficulty of atomic rearrangement (decrease of atomic diffusivity, increase of viscosity)	Necessity of atomic rearrangement on a long-range scale for crystallization
↓	↓	↓
Suppression of nucleation of a crystalline phase	Increase of T_g	Suppression of growth of a crystalline phase

↓

Deep eutectic with low T_m, increased T_g / T_m and ΔT_x

Inoue et al.: Acta Mater.48 (2000)

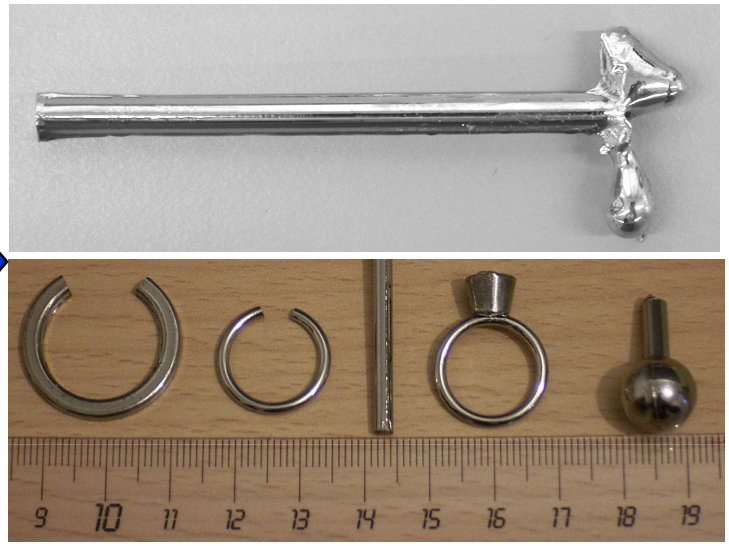
Preparation of BMGs: inexpensive casting



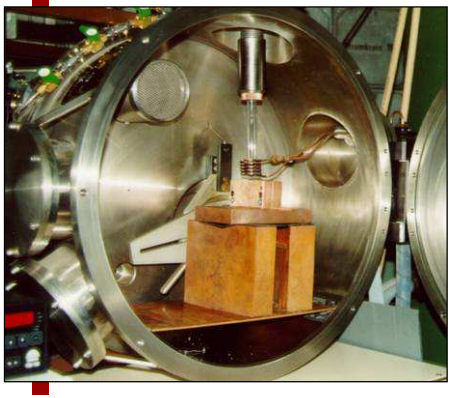
Master alloy by
arc melting

mold casting

l = 50 mm, d = 3 mm

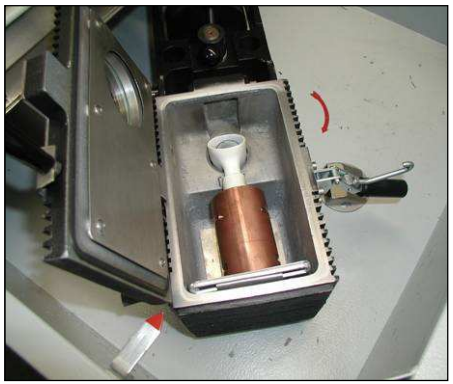


injection



∅ 3-6 mm × 50 mm

centrifugal

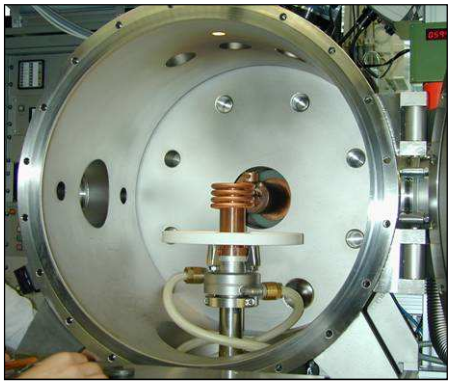


∅ 3-6 mm × 75 mm

suction

∅ 3-6 mm × 75 mm

cold crucible



∅ 10 mm × 180 mm

Preparation of BMGs: powder metallurgy

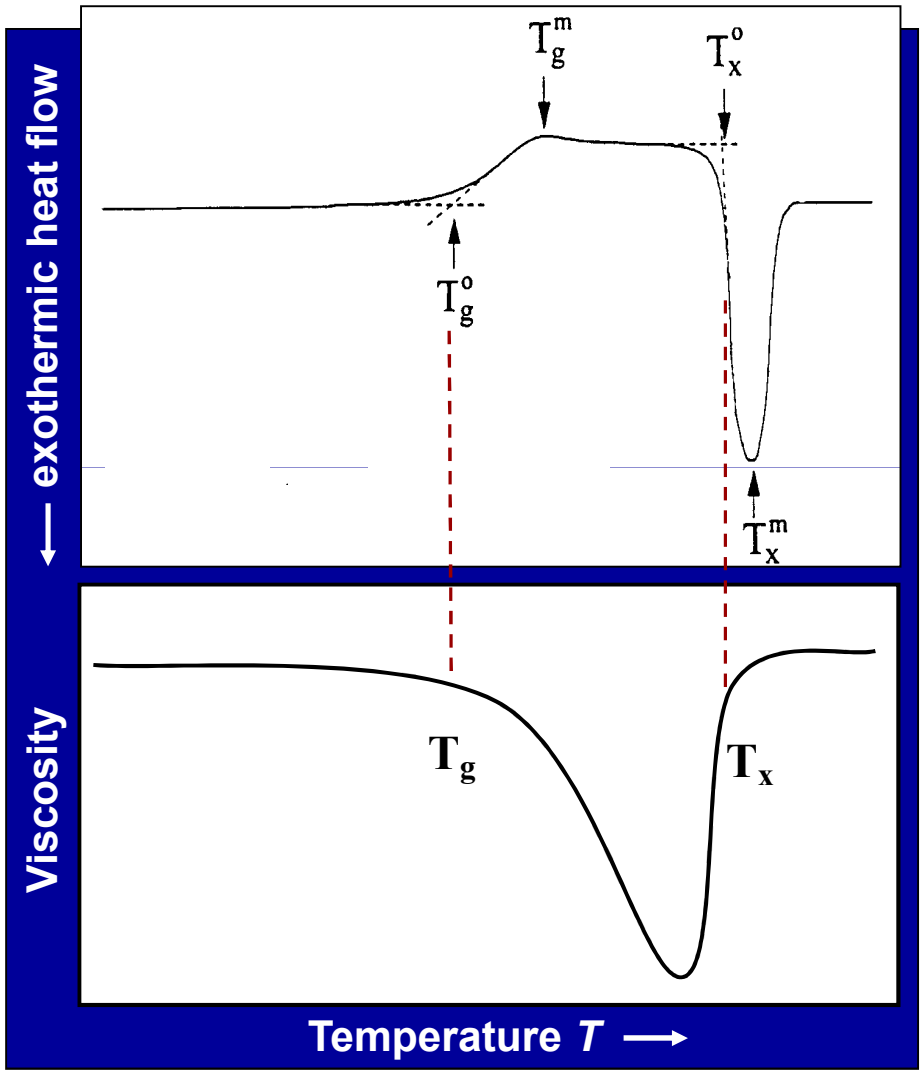
mechanical alloying / milling

planetary mill

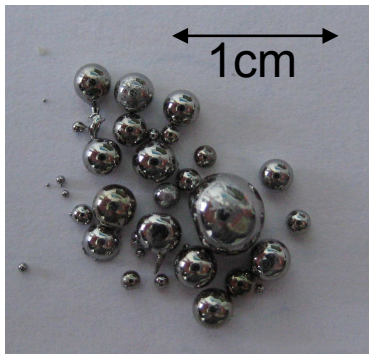
compaction

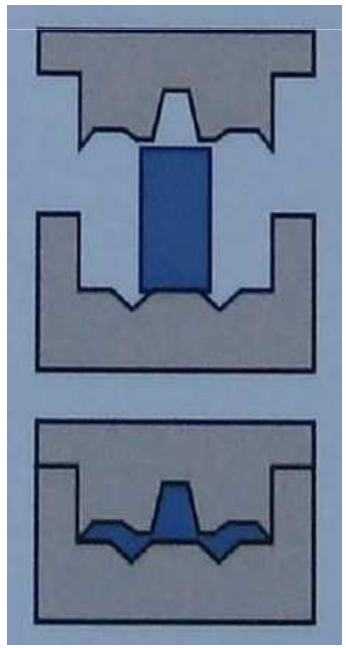
hot press

Preparation of BMGs: thermoplastic deformation



- amorphous granules or semifinal product
- plastic deformation above T_g



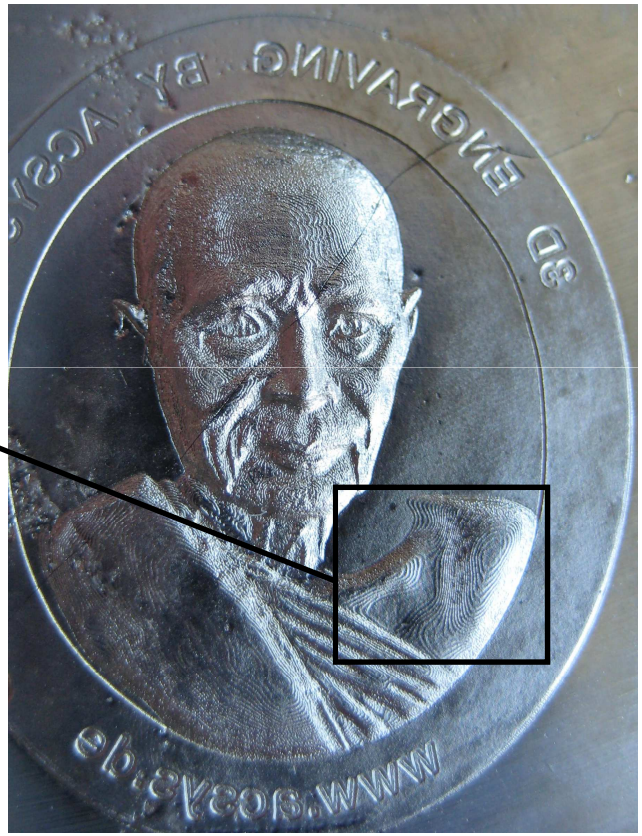


Preparation of BMGs: thermoplastic deformation

$Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$

J. Schroers et al.: The Superplastic Forming of Bulk Metallic Glasses; APL 87, 061912, 2005

Preparation of BMGs: thermoplastic deformation

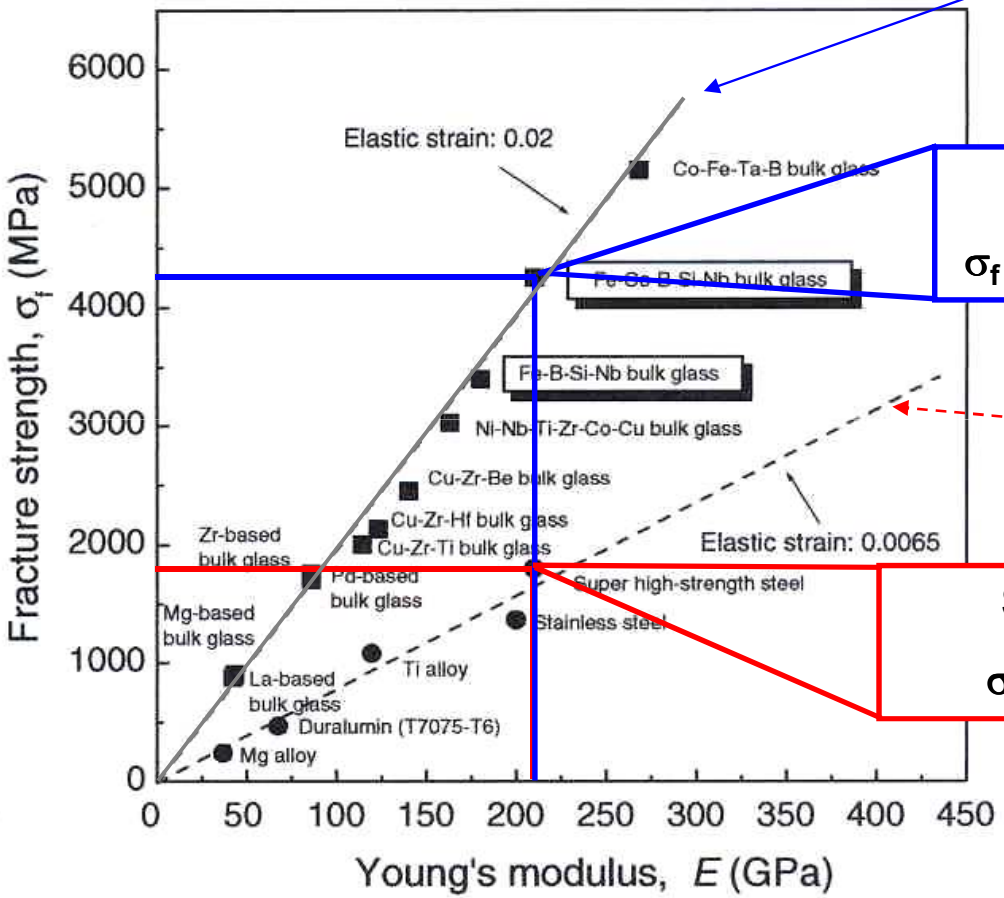


Preparation of BMGs: powder injection molding

Processing steps may be reduced from 8 to 4 (**50 %**)
by using metallic glasses as starting materials !!

No shrinkage !!

Mechanical properties (static)



glass

Fe-Co-B-Si-Nb

$\sigma_f \approx 4250$ MPa; $E \approx 210$ GPa

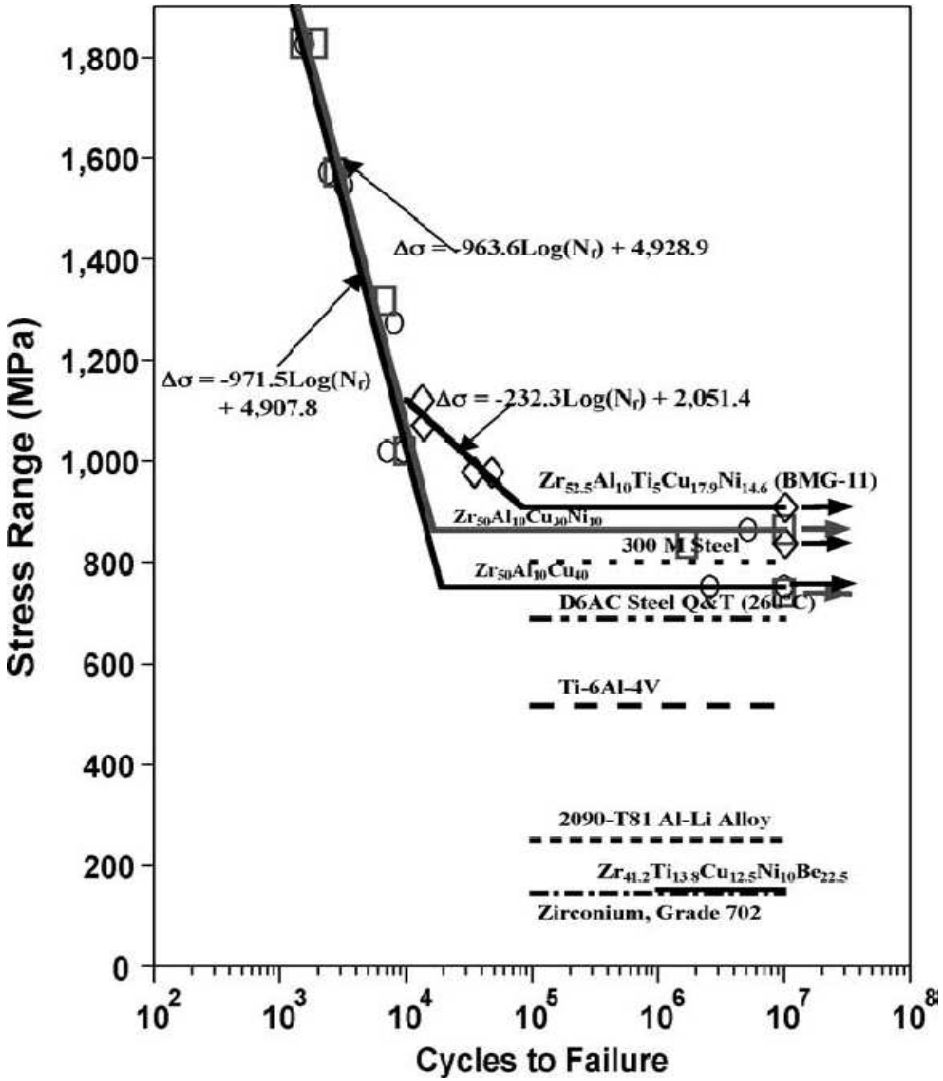
crystalline

Super high-strength steel

$\sigma_f \approx 1800$ MPa; $E \approx 210$ GPa

A. Inoue et al.: Acta Mater. ***52*** *(2004)*

Mechanical properties (dynamic)

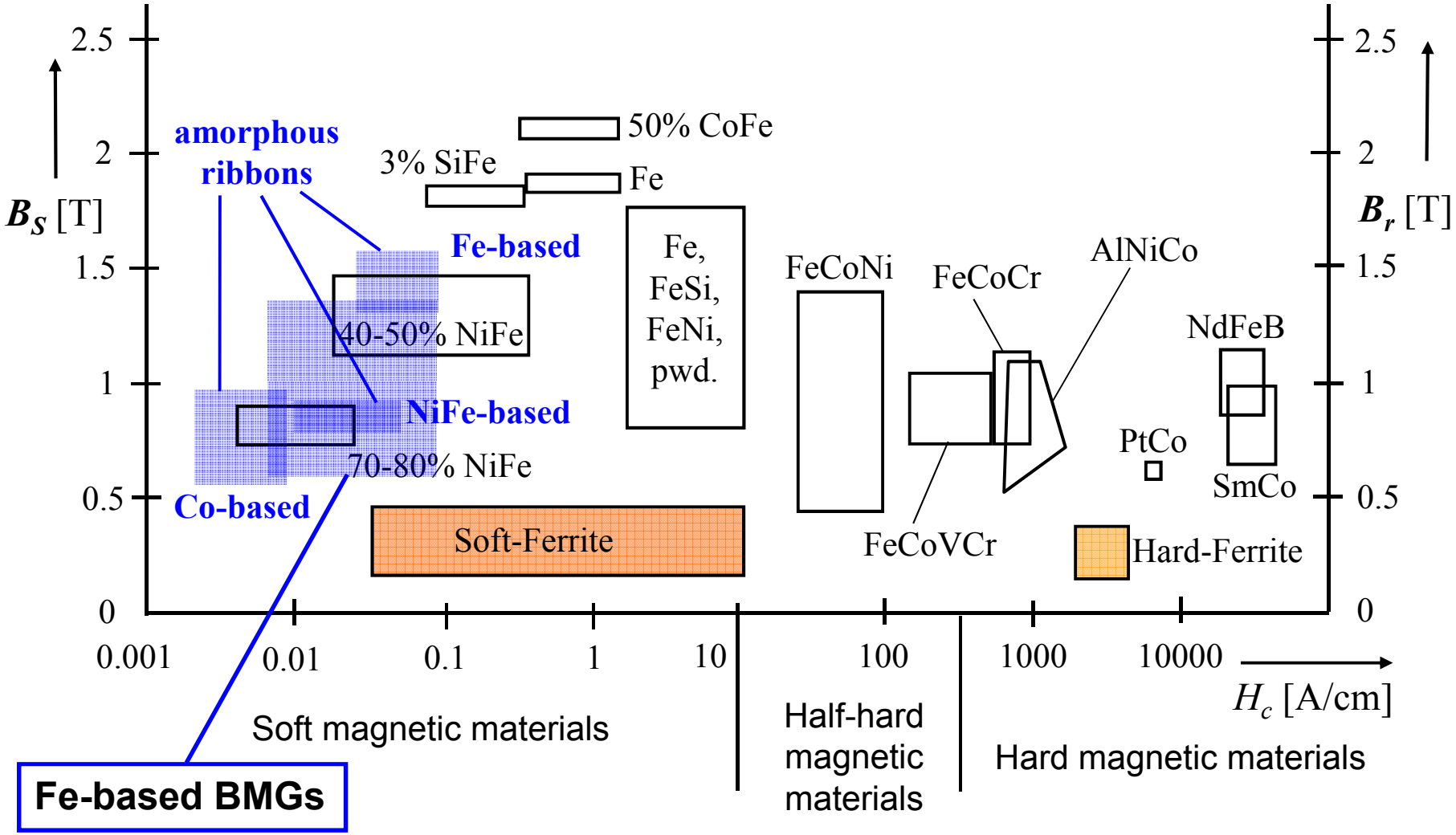


Glass

Crystalline

*G.Y. Wang et al.: Intermetallics **12** (2004)*

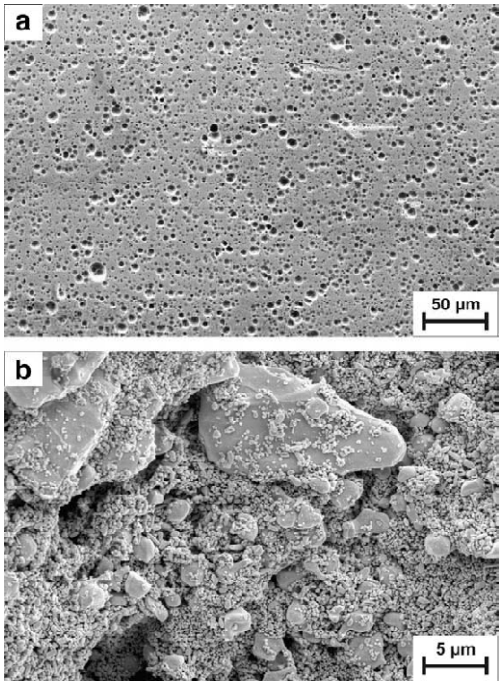
Magnetic properties (DC)



R. Boll: Weichmagnetische Werkstoffe, VAC GmbH, Ed. Siemens AG (1990)

Electrochemical properties- corrosion resistance

0.5 M H_2SO_4

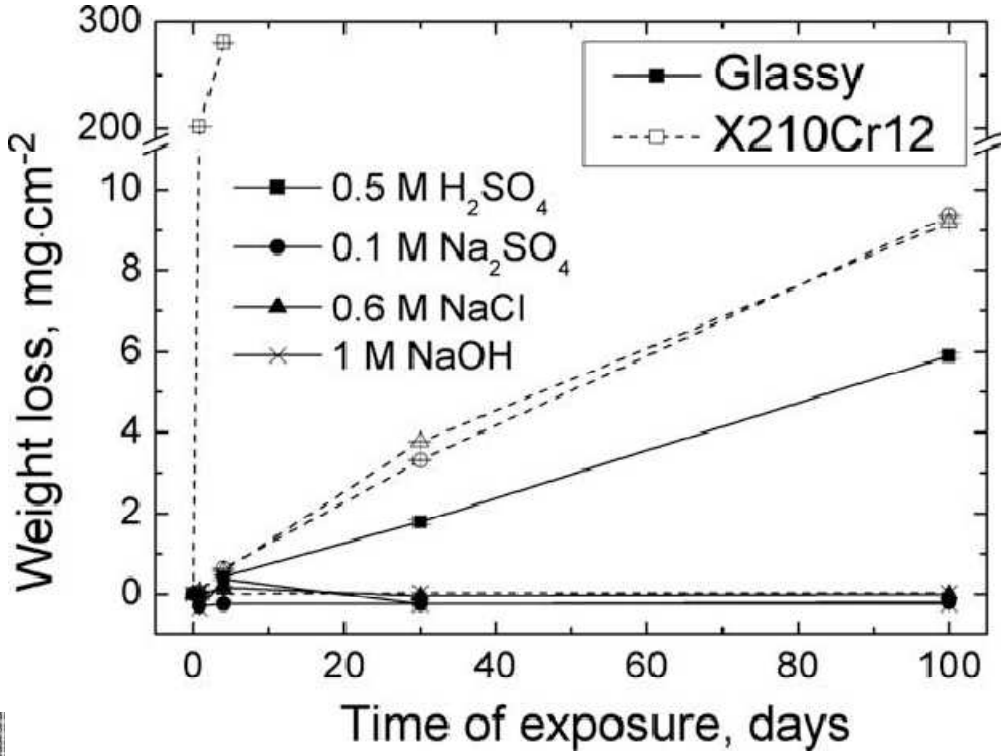


After 20 hours

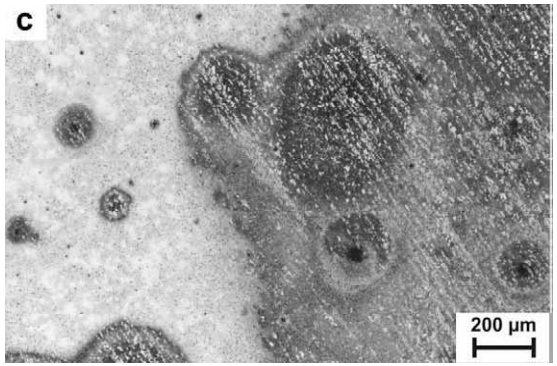
conventional steel X210Cr12

After 100 days (2400 hours)

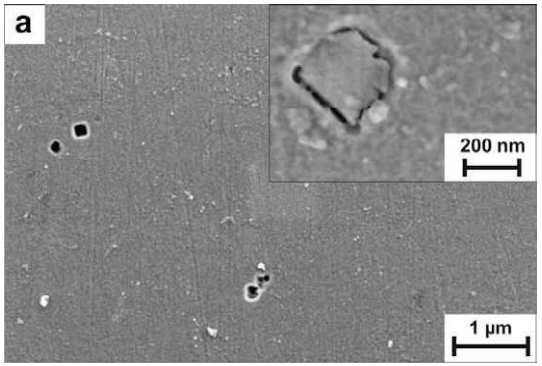
$(Fe_{44.3}Cr_5Co_5Mo_{12.8}Mn_{11.2}C_{15.8}B_{5.9})_{98.5}Y_{1.5}$ BMG



Pitting in 0.01 M NaCl



P.F. Gostin, Corr. Science (2010)



Pitting in 0.6 M NaCl

Interesting alloys

Alloy	amorphous up to	E [GPa]	σ_f [MPa]	ε_y [%]
$Mg_{65}Cu_{7.5}Ni_{7.5}Zn_5Ag_5Y_{10}$	9 mm ∅	39	490-650	1.7
$Cu_{54}Zr_{27}Ti_9Be_{10}$	5 mm ∅	146	2500	2.0
$Ti_{50}Cu_{20}Ni_{24}Sn_3B_1Si_2$	4 mm ∅	110	2100	2.0
$Zr_{52.5}Ti_5Cu_{17,5}Ni_{14,6}Al_{10}$	5 mm ∅	70-90	1700-1800	**2.0-2.7**
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	**few cm**			
$Ni_{53}Nb_{20}Ti_{10}Zr_8Co_6Cu_3$	3 mm ∅	140	3010	2.4
$Co_{43}Fe_{20}Ta_{5,5}B_{31,5}$	2 mm ∅	268	**5185**	< 2
$(Fe_{44.3}Cr_5Co_5Mo_{12.8}Mn_{11.2}C_{15.8}B_{5.9})_{98.5}Y_{1.5}$	12 mm ∅	257	3000	< 2

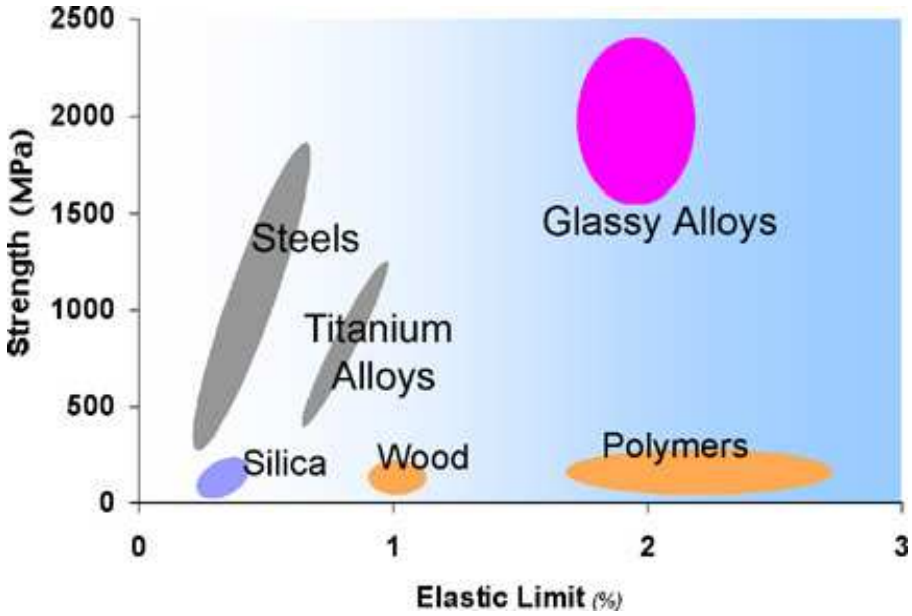
l = 50 mm
∅ = 10 mm

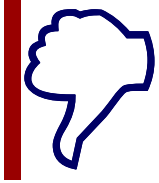
high mechanical tensions

Pro & cons, possible applications

- high strength, high elasticity
- excellent soft magnetic properties
- increased corrosion resistance
- thermoplastic deformable
  (no shrinkage, good formability)
- extremely smooth surfaces

M. Telford, Materials Today (2004)





- reduced reproducibility (purity of the elements, preparation parameters)
- relatively high price
- very brittle in tension

Applications- possible fields

Jewelry

Sensing units

Mechanical tools

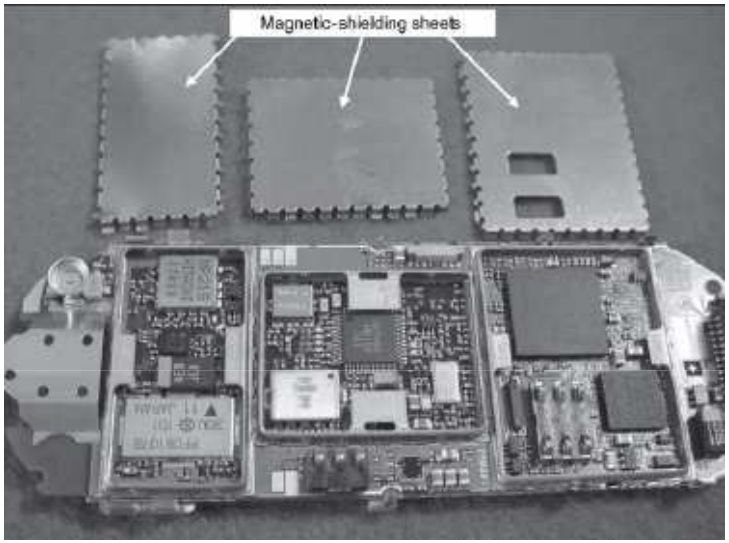
Fine mechanic

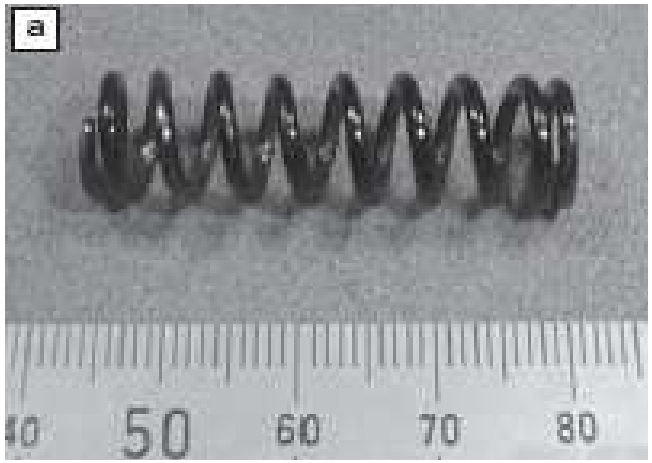
Medical tools

Magnetic parts

Applications- examples

LIQUIDMETAL TECHNOLOGIES





taken from:

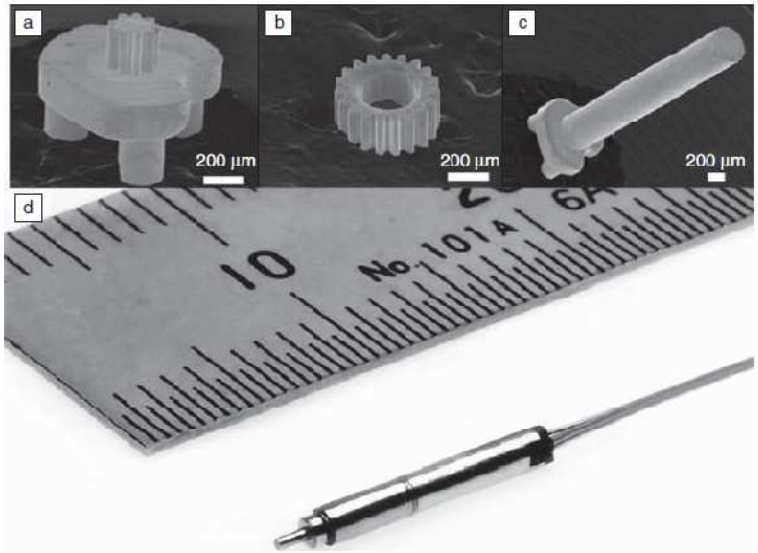
A. Inoue, N. Nishiyama,

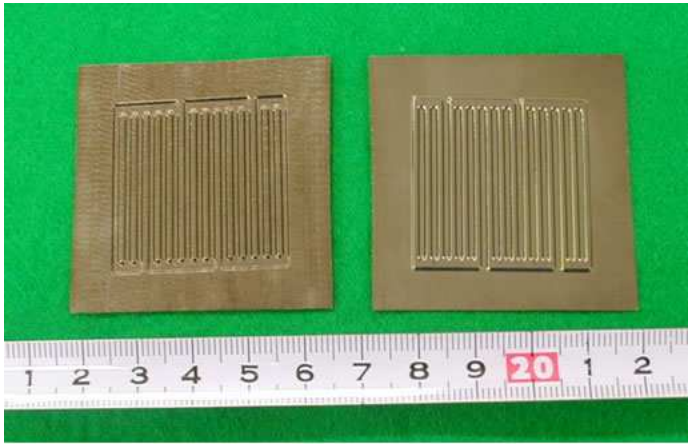
MRS Bulletin 32 (2007);

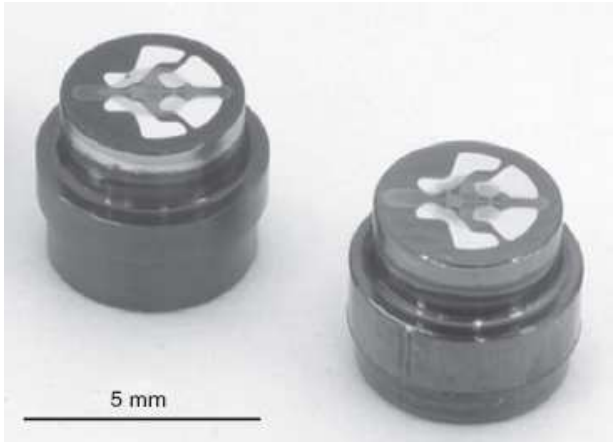
www.liquidmetal.com

www.arcmg.imr.tohoku.ac.jp

Applications- examples







taken from:

A. Inoue, N. Nishiyama,

MRS Bulletin 32 (2007);

www.liquidmetal.com

www.arcmg.imr.tohoku.ac.jp

Monolithic BMGs- future?

Technology development

amorphous semi-finite materials, amorphous granules

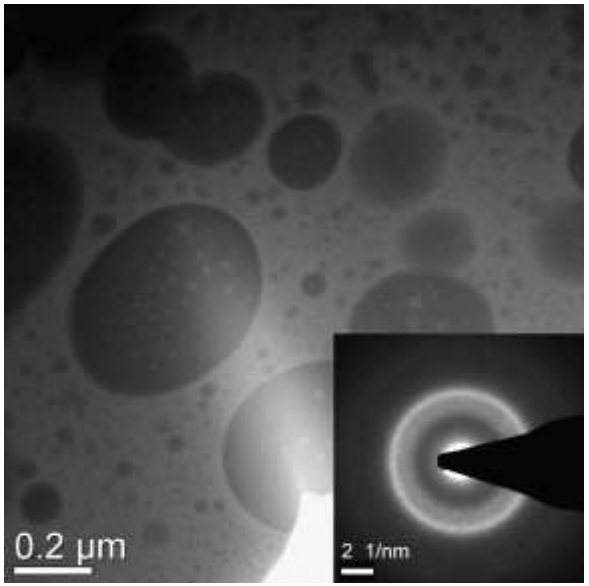
thermoplastic forming, injection molding

Fabrication of small, complicated parts for high demands

Expanding the applications field: composites

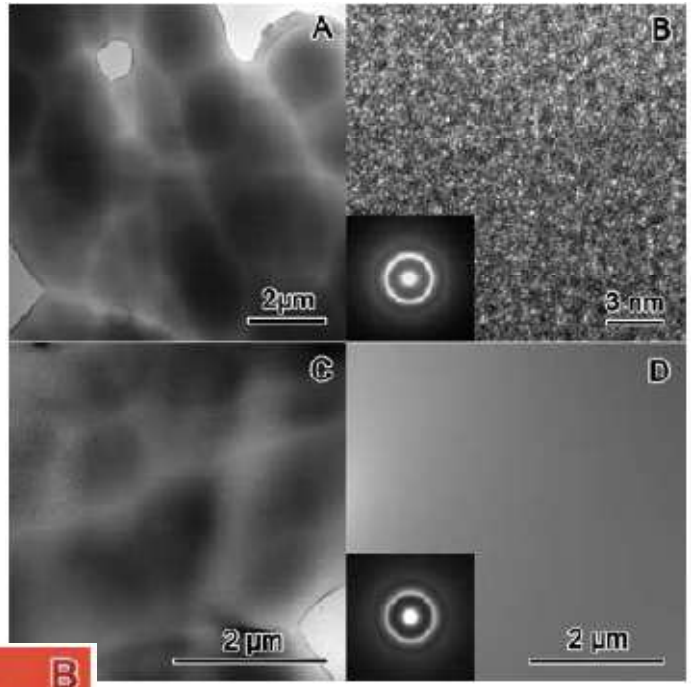
- **Phase separation in BMGs**
- **Amorphous matrix plus metallic crystalline particles (ductile)**
  - in-situ
  - ex-situ
- **Metal matrix (ductile) + glass particle (hard, high strength)**
  - ex-situ

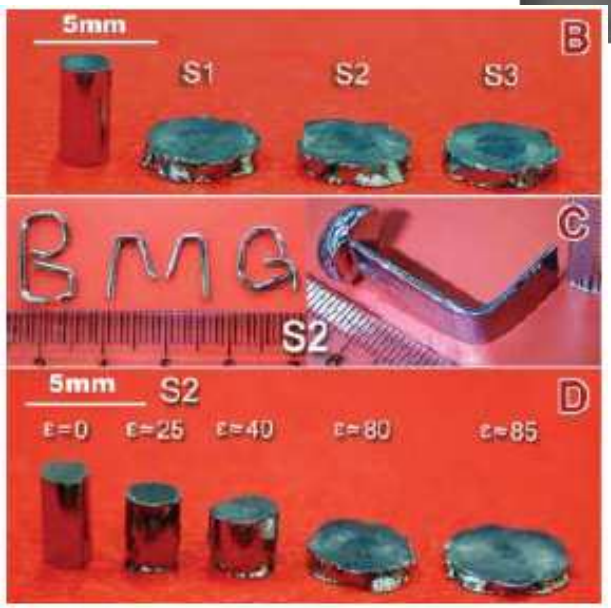
BMG phase separation



$Ni_{54}Nb_{23}Y_{23}$

N. Mattern: Scripta Mater. (2007)



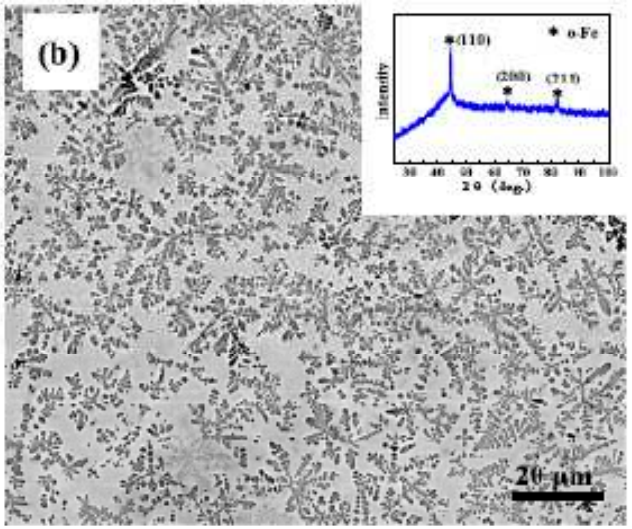


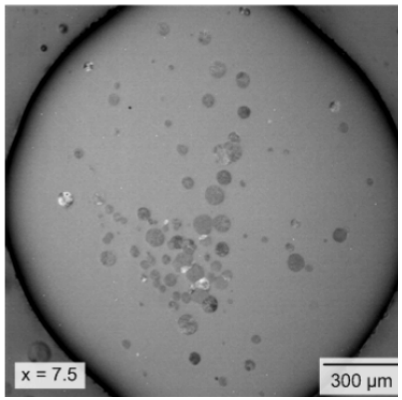
$Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10}$

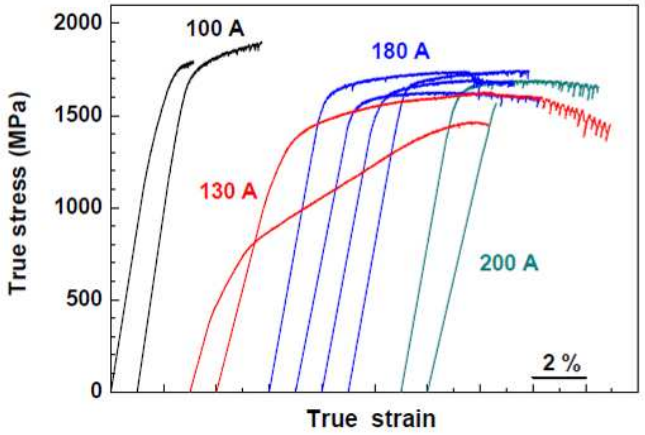
Science (2007)

W.H. Wang's group

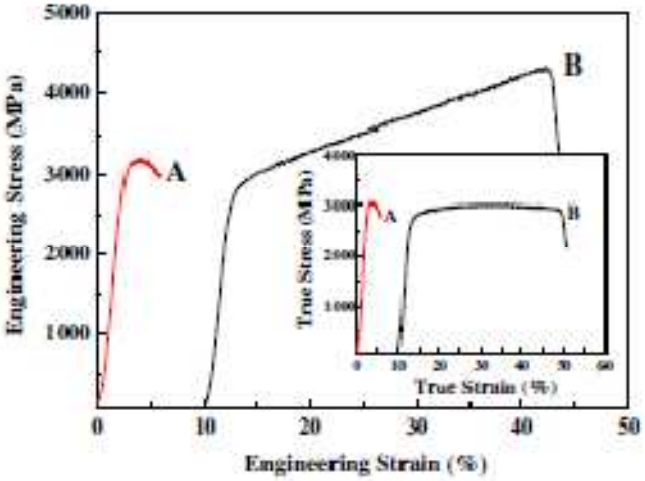
Amorphous matrix composites: in-situ





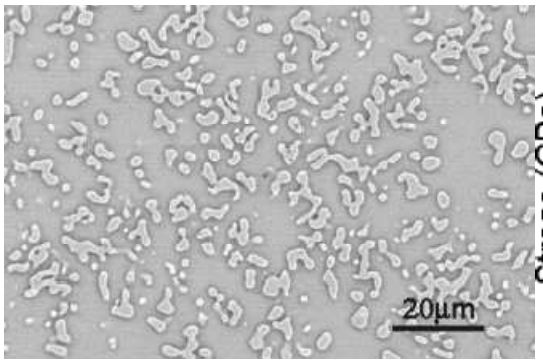


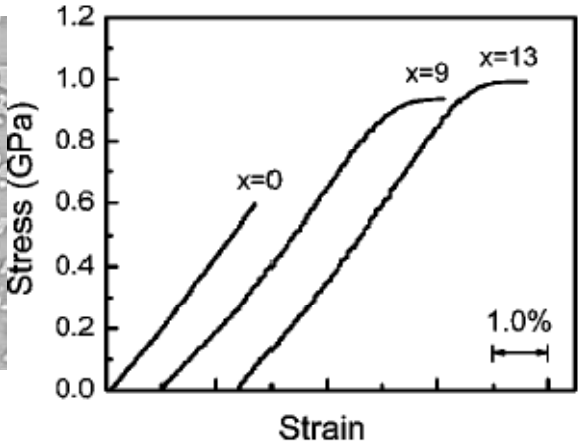
$(Cu_{50}Zr_{50})_{100-x-y}Ti_xAl_y$; S. Pauly, PhD thesis (2010)



$Fe_{77}Mo_5P_9C_{7.5}B_{1.5}$

S.F. Guo, Scripta Mater. (2010)

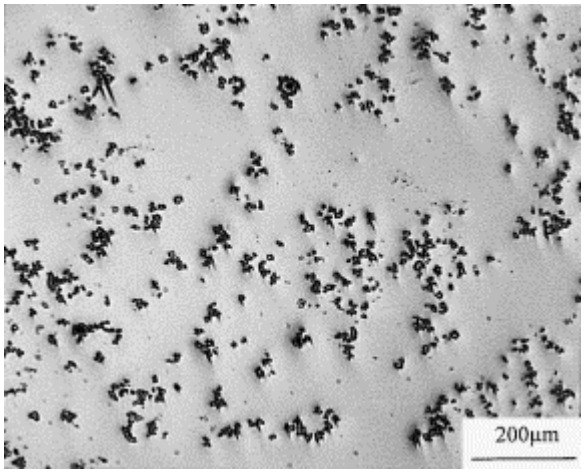


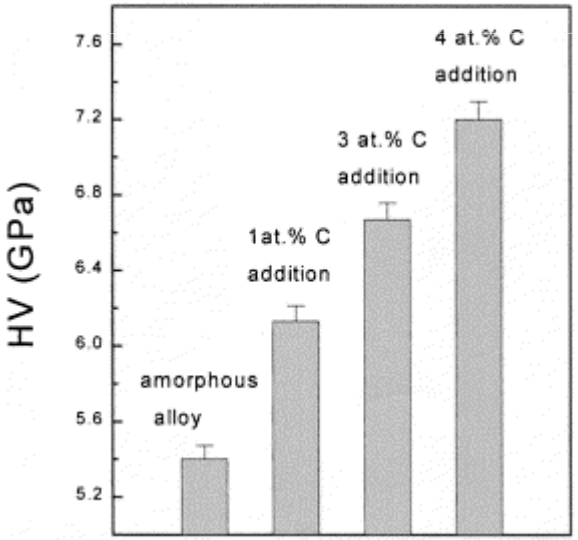


$(Mg_{0.65}Cu_{0.075}Ni_{0.075}Zn_{0.05}Ag_{0.05}Y_{0.1})_{100-x}Fe_x$

H. Ma, APL (2003)

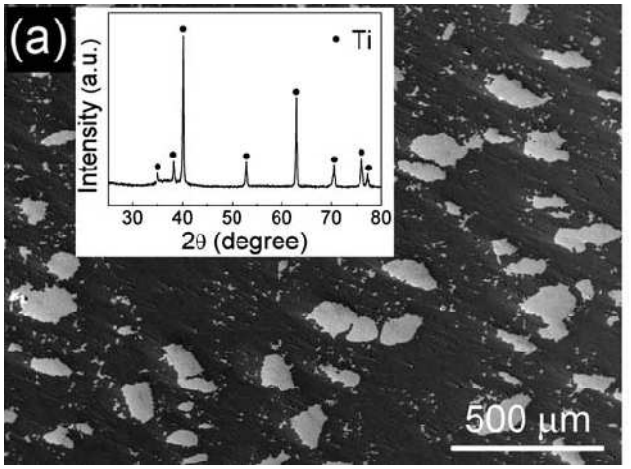
Amorphous matrix composites: ex-situ

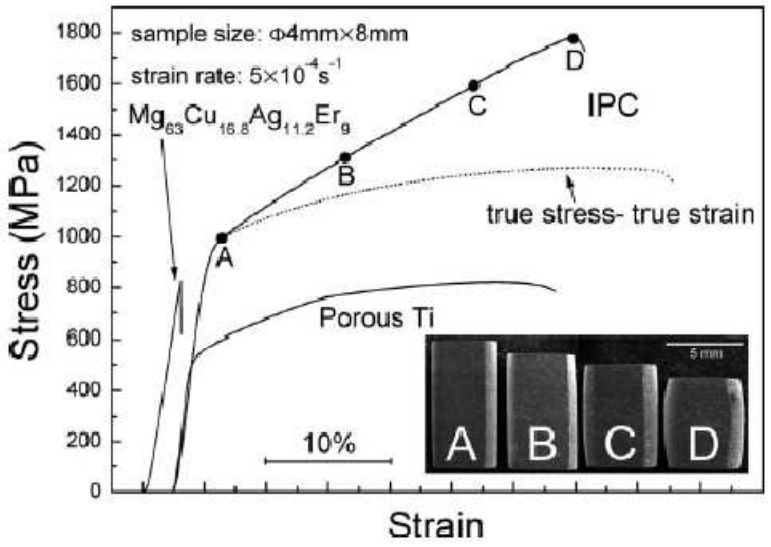




$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ + C

W.H. Wang, Mater. Letters (2000)





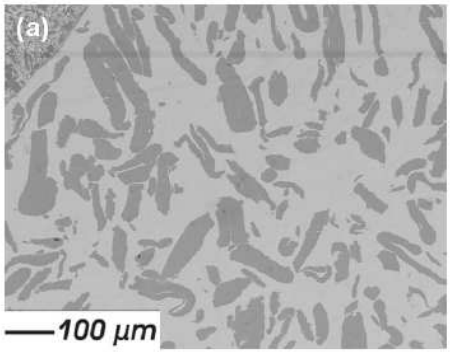
$Mg_{63}Cu_{16.8}Ag_{11.2}Er_9$ + Ti

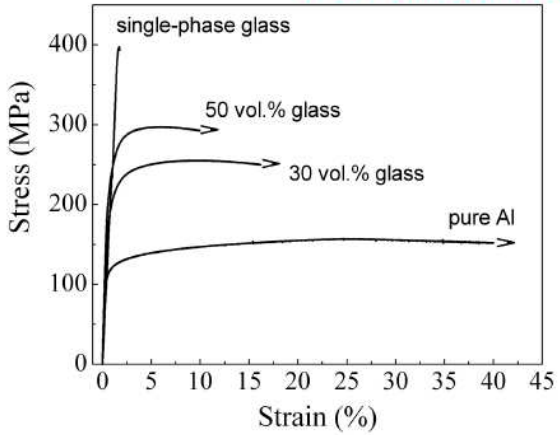
Y. Sun, APL (2009)

Metal matrix composites

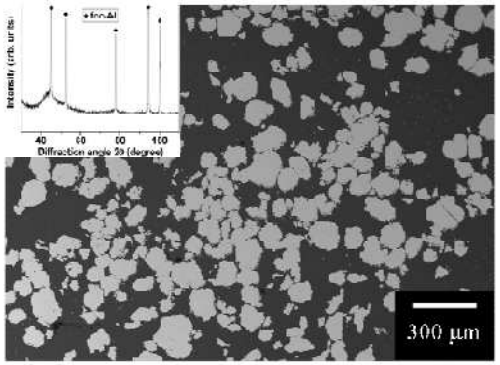
Pure Al + BM $Al_{85}Y_8Ni_5Co_2$ glassy ribbons (30 and 50 vol.%)

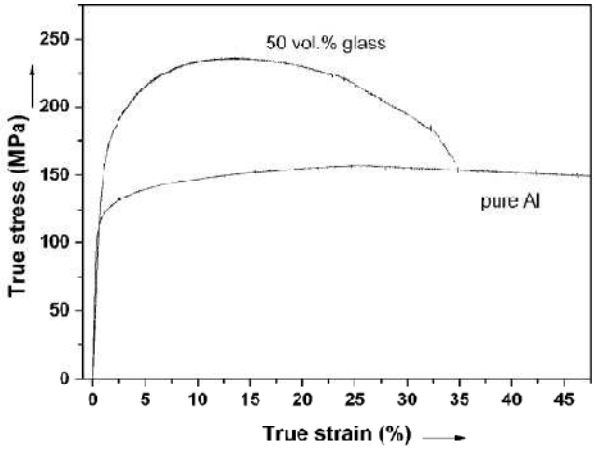
RT compression tests





Pure Al + BM $Zr_{65}Ag_5Cu_{12.5}Ni_{10}Al_{7.5}$ glassy powders





S. Scudino, several works 2006-2010

PSS-RRL, Scripta mater., etc.

Acknowledgments

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M. Frey, H.-J. Klauß, S. Donath, B. Bartusch, H. Schulze …..

A.L. Greer, A.R. Yavari, G. He, U. Köster, D.J. Sordelet, L.Q. Xing, Z.F. Zhang, W.L. Johnson, A. Inoue, M.D. Baro, Y. Li, K. Lu, E. Ma, T.G. Nieh, S.K. Roy W.H. Wang, ...

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