Nanoimprinting with amorphous metals

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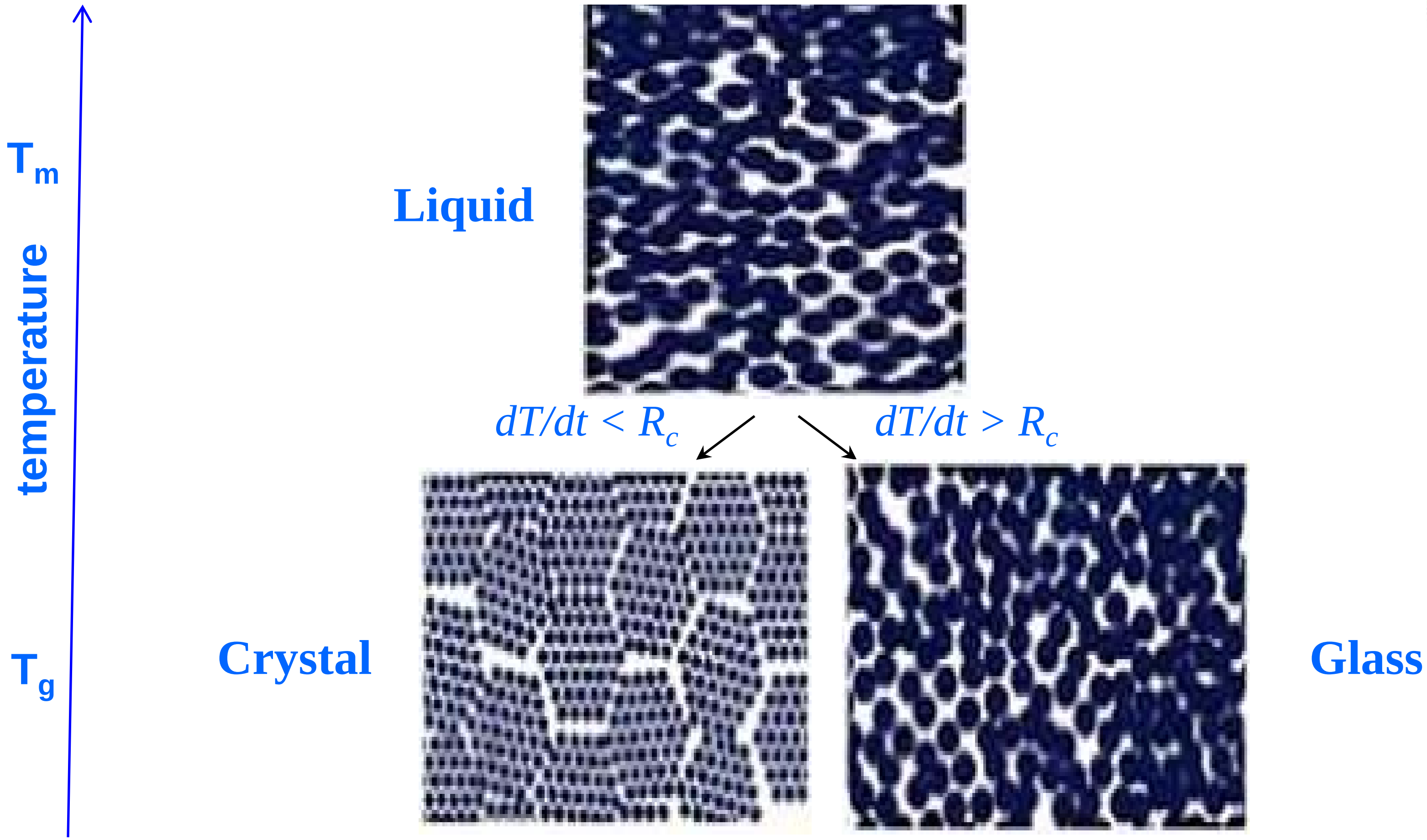
Overview

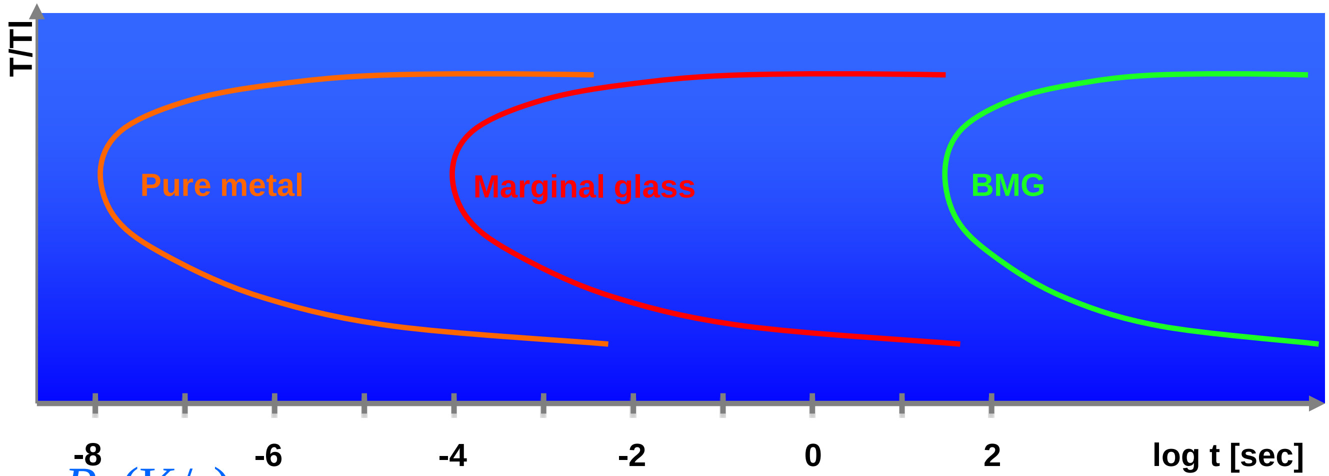
- Amorphous metal (metallic glasses) (Bulk metallic glasses)
  - -synthesis (glass formation)
  - -properties
- Processing of BMGs
- Thermoplastic forming of BMGs
- Stuck above 100 nm
- Nanoforming of BMGs
- How can it be utilized in nanoimprinting
- Nanoimprinting on non-planar surfaces

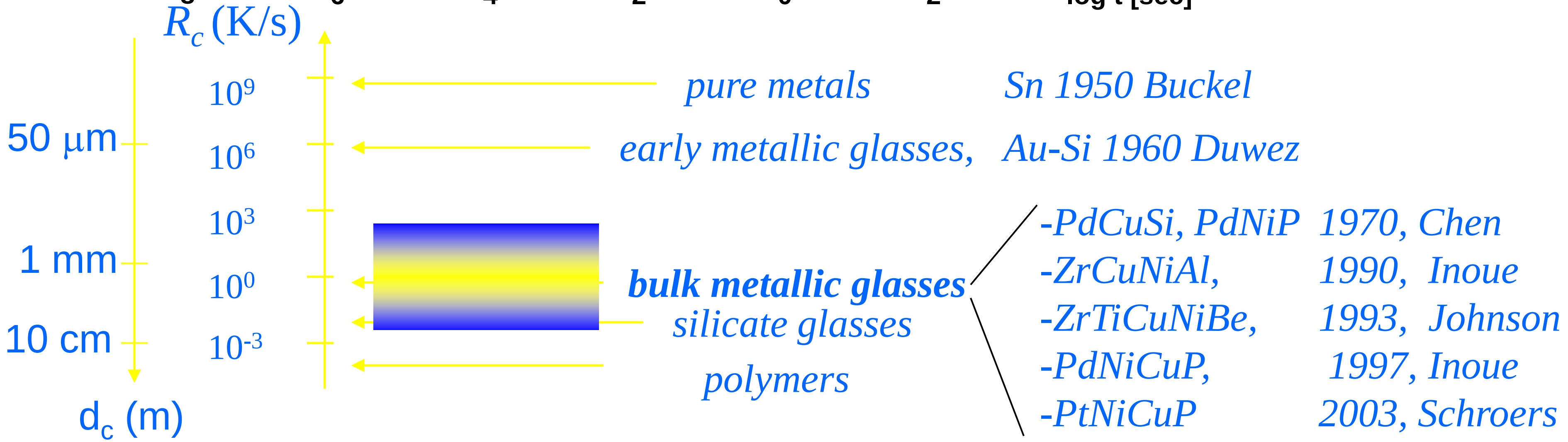
Amorphous Metals-Glass Formation



Any metal can be vitrified but requires different rates

Bulk Metallic Glass formers





BMGs: Zr, Ti, Ni, Cu, Fe, Hf, Mg, Al, Y, La, Pd, Ce, Au, Pt

CHARACTERISTICS OF BMG FORMERS

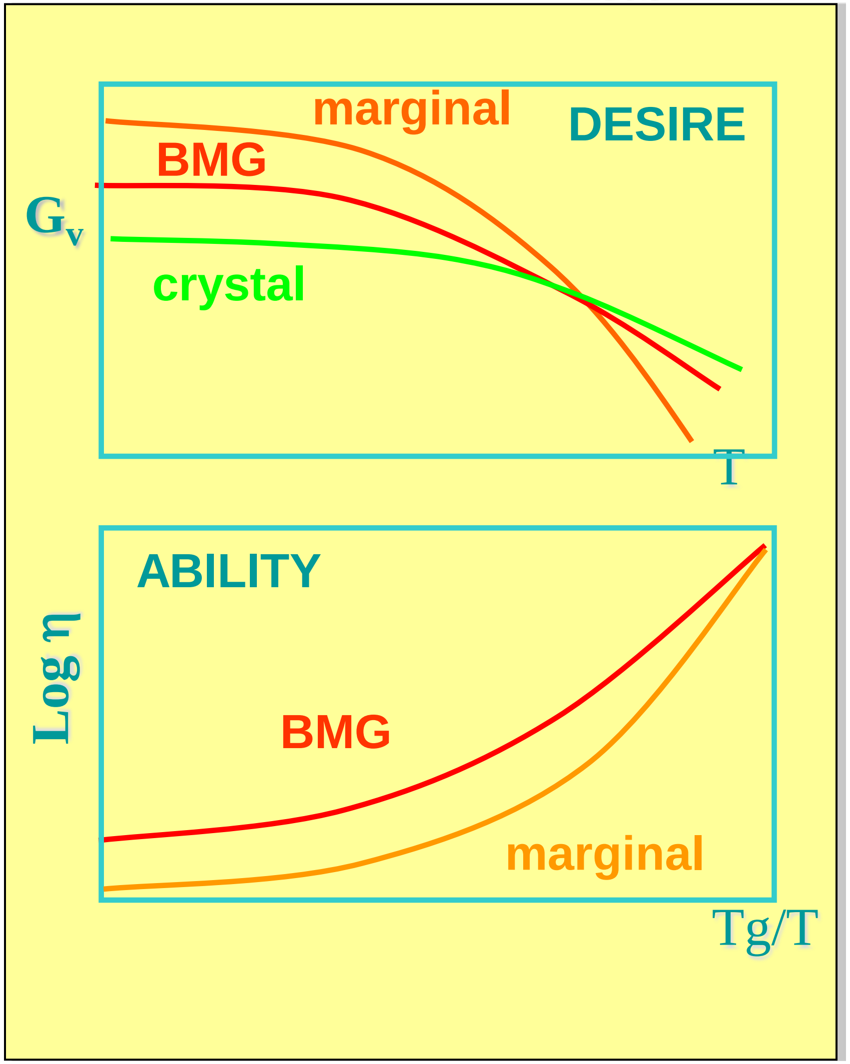
- *Desire*, Thermodynamic: small ΔG
- *Ability*, Kinetic: strong liquid behavior

Accomplished by (Inoue 1993):

- More than three elements
- Large size difference at least 25 %
- Large negative heat of mixing among at least two elements, deep eutectics

Viscosity strongest influence on glass forming ability

⇒ BMG forming liquids are densely packed (highly (short range) ordered) liquids



S. Mukherjee, J. Schroers, W. L. Johnson, and W. K. Rhim, Physical Review Letters 52, (2005)

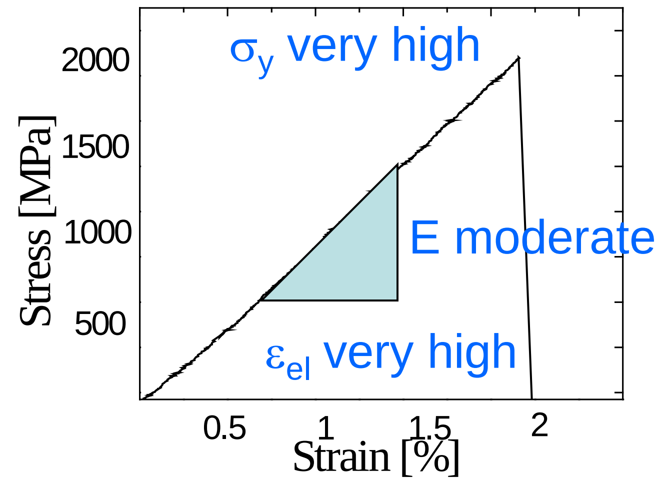
Bulk Metallic Glass Properties

- The amorphous structure in BMGs results in:

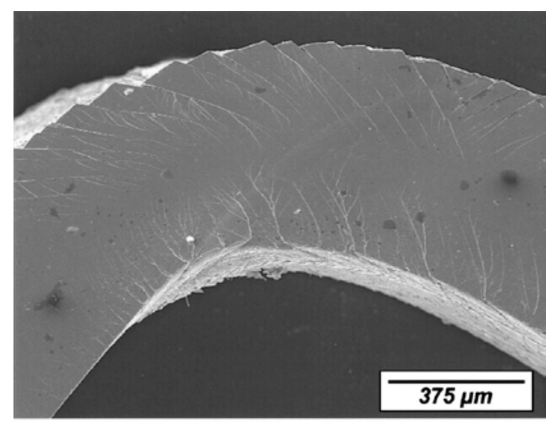
-high strength, 2000 MPa vs. 700 MPa steel,
-high elasticity, 2% vs. 0.3% steel,
-high fracture energy, 4 J/m^2 Si, 5x10^4 J/m^2 BMGs

- Plasticity when 1D is <1 mm

- homogeneous structure down to atomic length scale (crystalline metals 100 nm to 100 microns, polymers up to 100 nm)



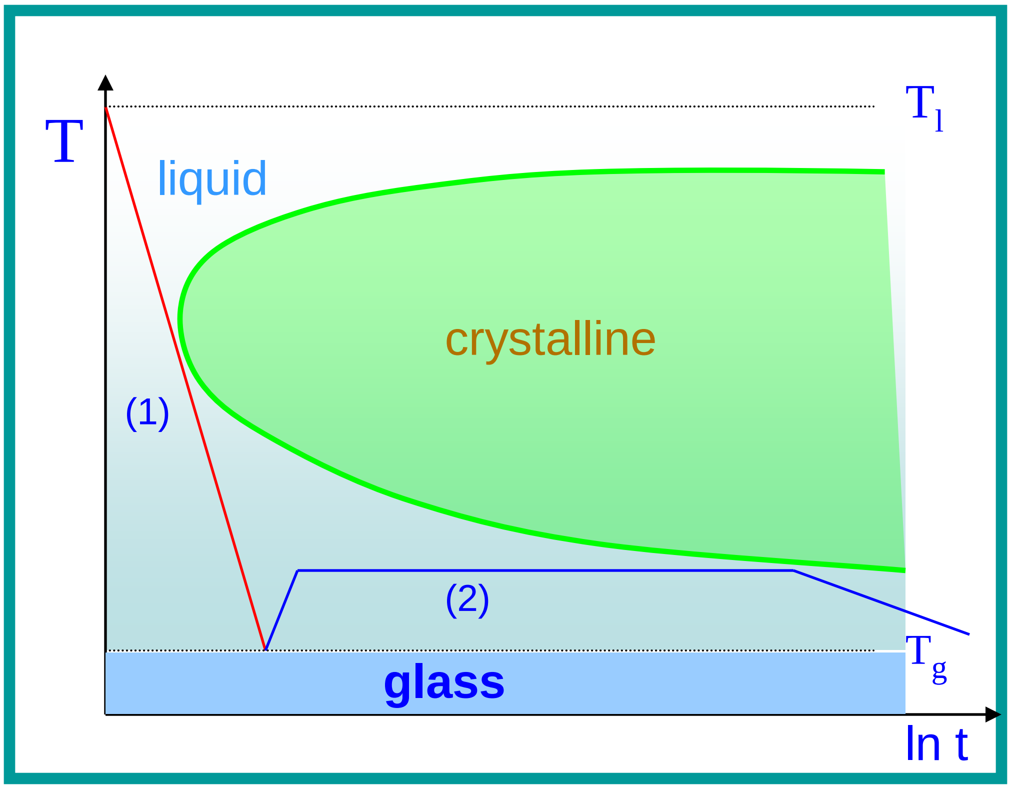
=> Promising properties for top-down nanomaterial



R.D. Conner, W.L. Johnson, N.E. Paton, and W.D. Nix, *Journal of Applied Physics, 2003. 94(2): p. 904-911.*

PROCESSING OF BMG

Processing Challenge: avoid crystallization



1: direct: casting,
cooling and forming simultaneously

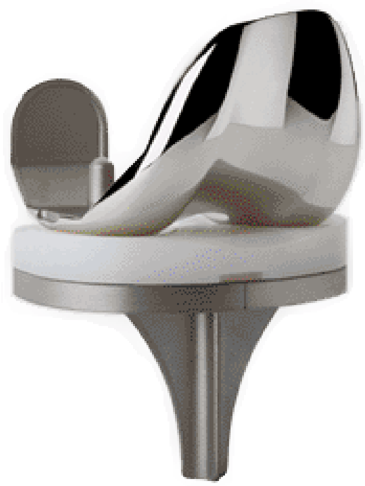
2: indirect: Thermo Plastic Forming (TPF)
decouples forming and cooling

TPF processing parameters:
Temperature: 160° C, 270° C, 430° C
Pressure: 0.1 – 200 MPa
time: 0.5 - 4 min

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

Commercial Applications

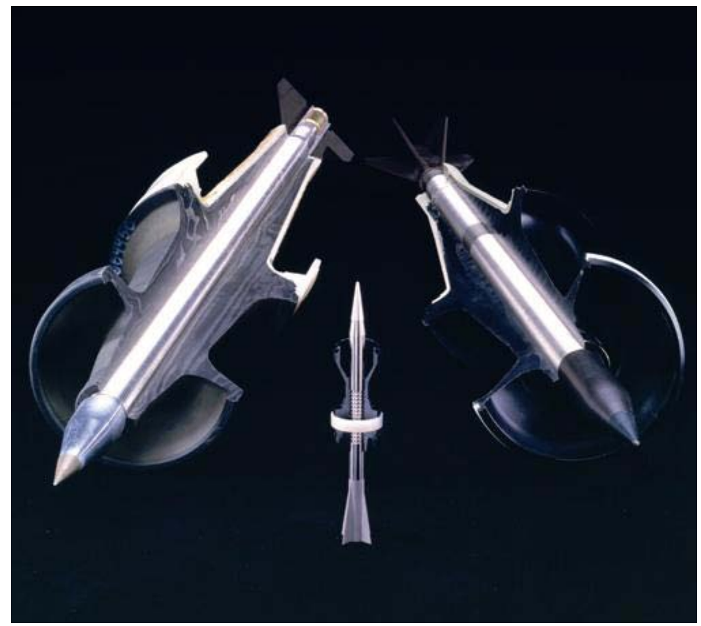
Commercial Applications



- Biocompatible
- wear

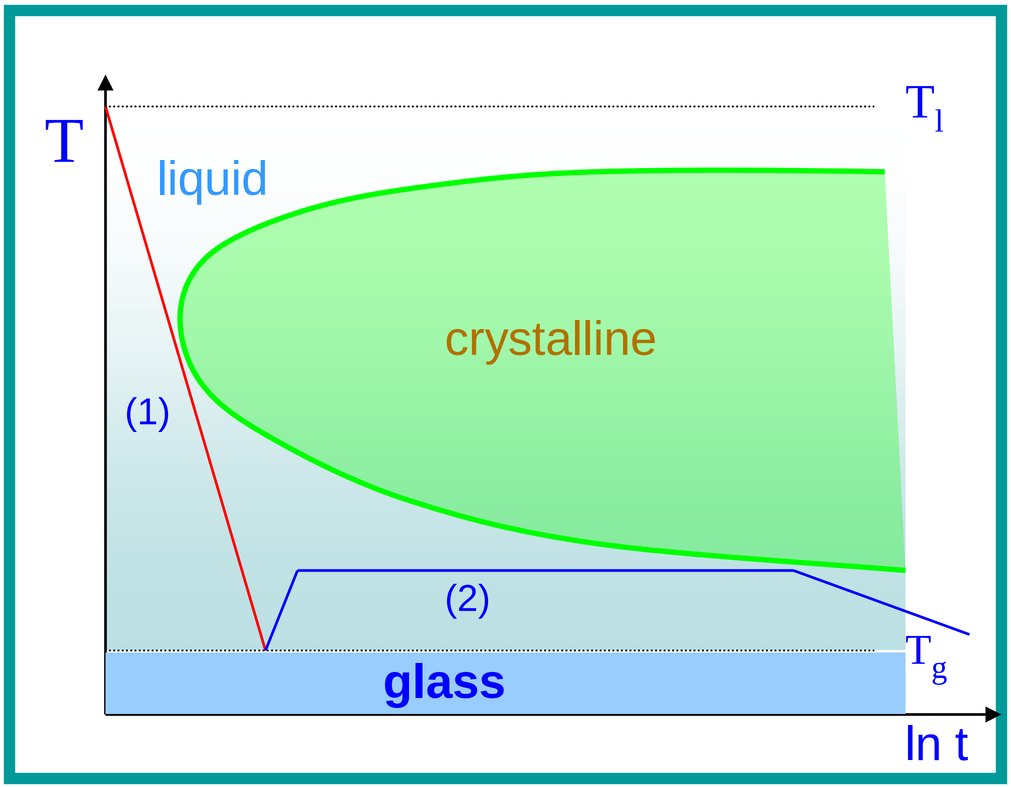
- Self sharpening

- hardness



PROCESSING OF BMG

Processing Challenge: avoid crystallization



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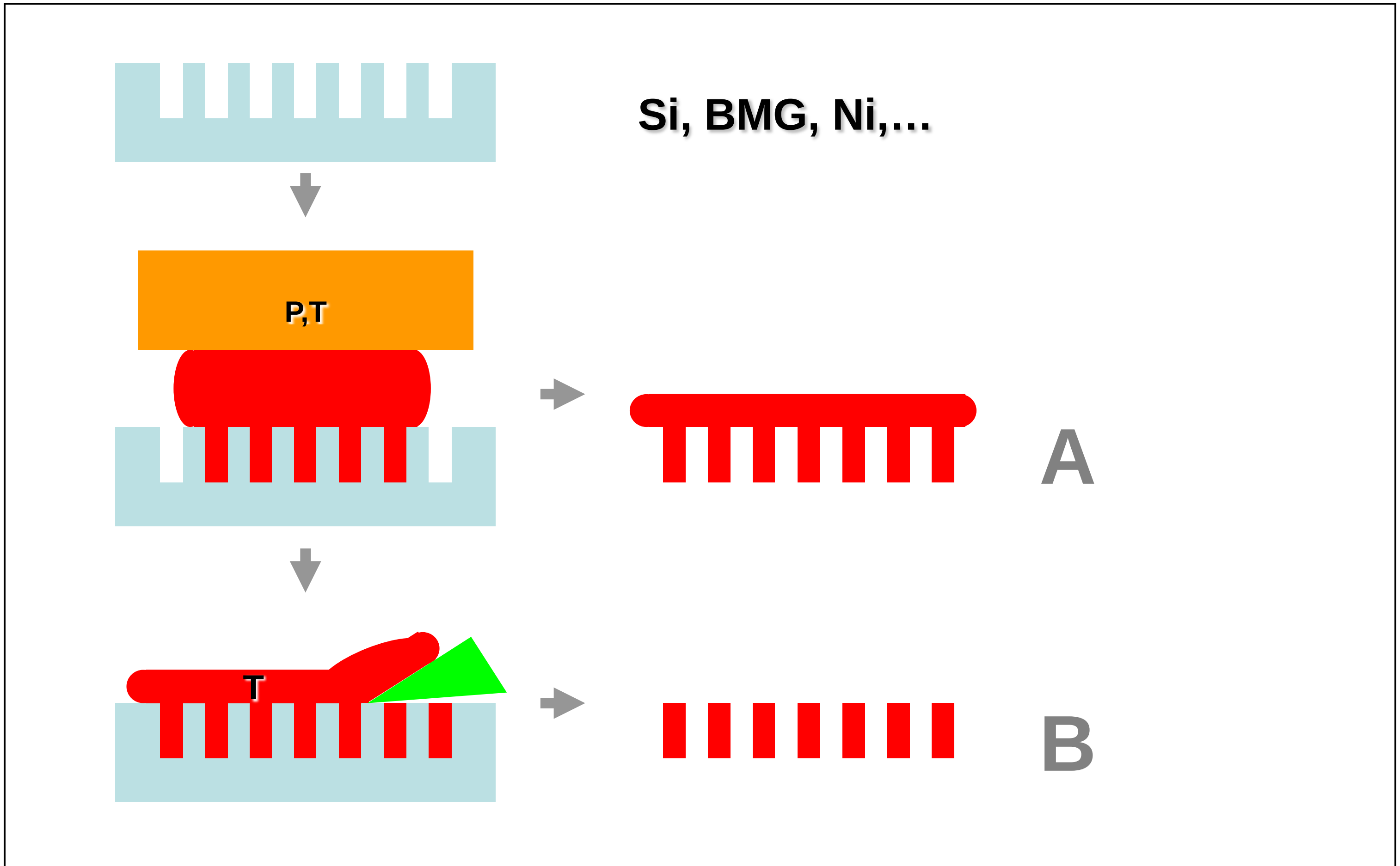
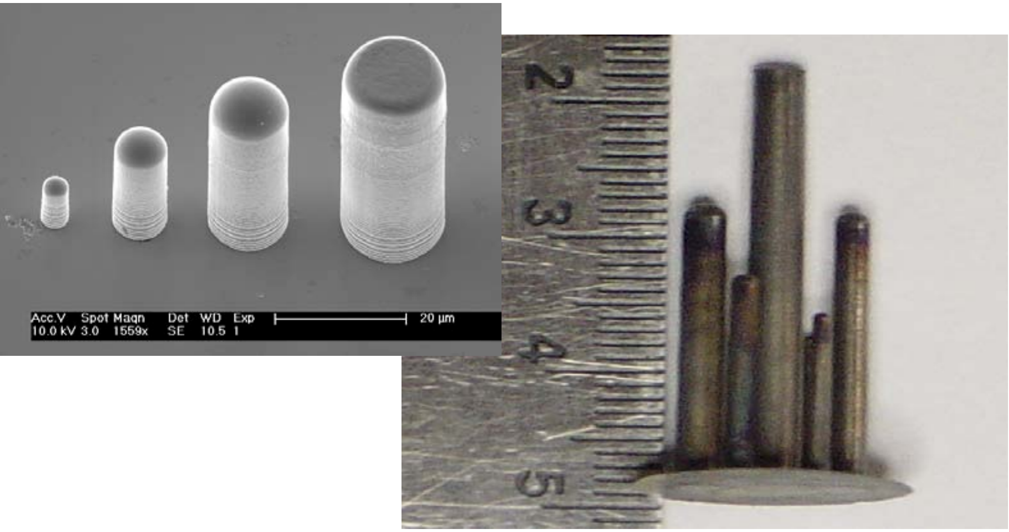
J. Schroers, JOM, 57, 34 (2005)

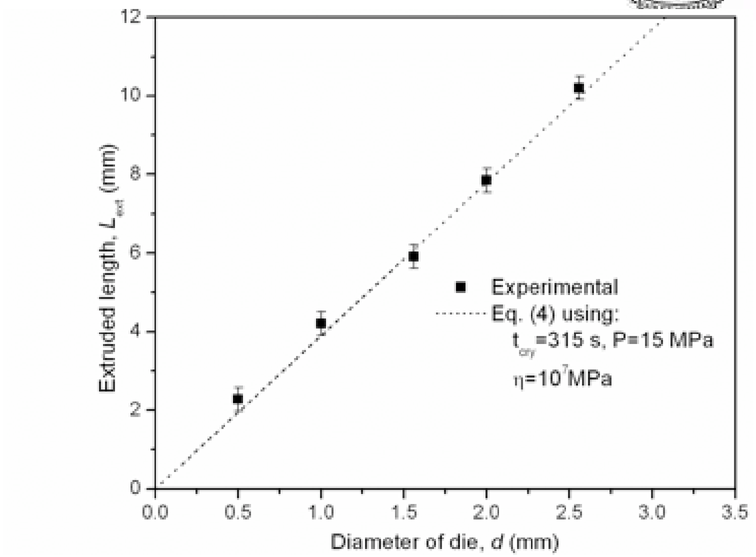
Schematics of miniature forming



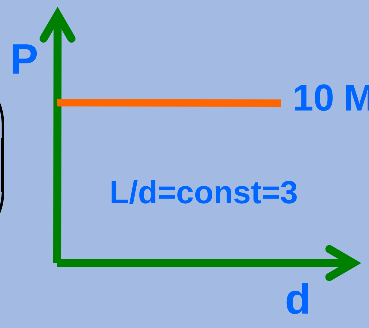
J. Schroers, Q. Pham, A. Desai, J. MEMS, 37, 83 (2007)

Millimeter-Micron Forming





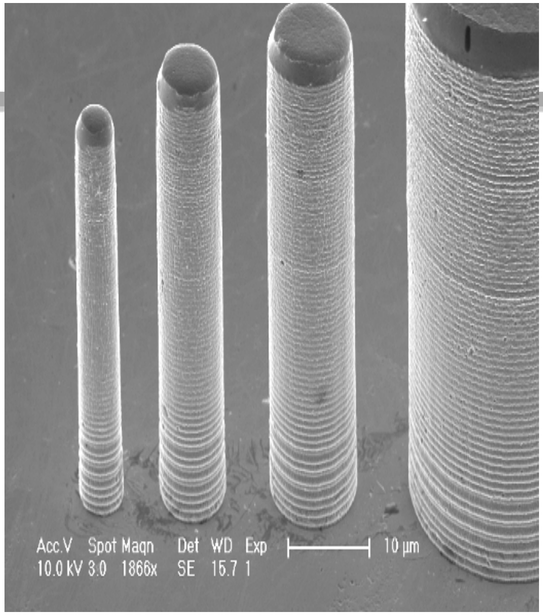
$$P = \frac{1}{t}\left(32\eta\frac{L^2}{d^2}\right)$$

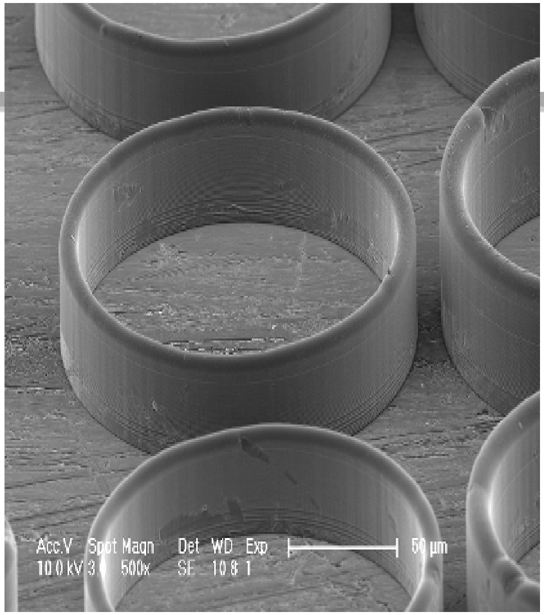


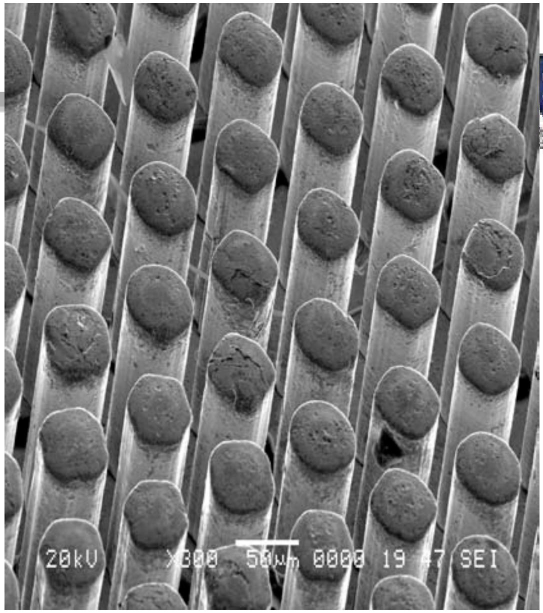
- obeys creep flow (stick conditions, Re≈0)
- Forming pressure is constant when scaling down, L/d=constant
- Suggest smallest features are possible
- **Viscosity** and forming time defines the absolute value of P

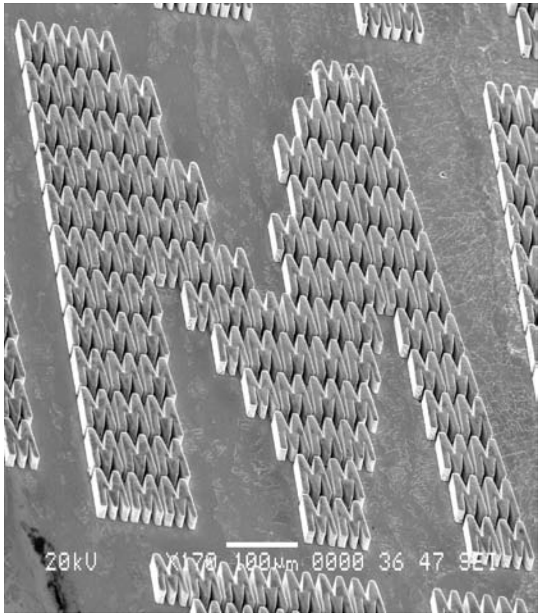
J. Schroers, JOM, 57, 34 (2005), H-M Chiu, G. Kumar, J. Blawzdziewicz, J. Schroers, Scripta Mat. 61, 28 (2009)

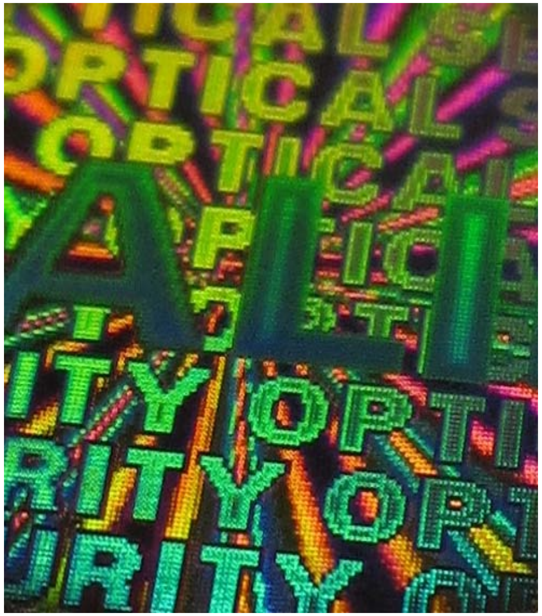
SURFACE REPLICATION WITH BMGs

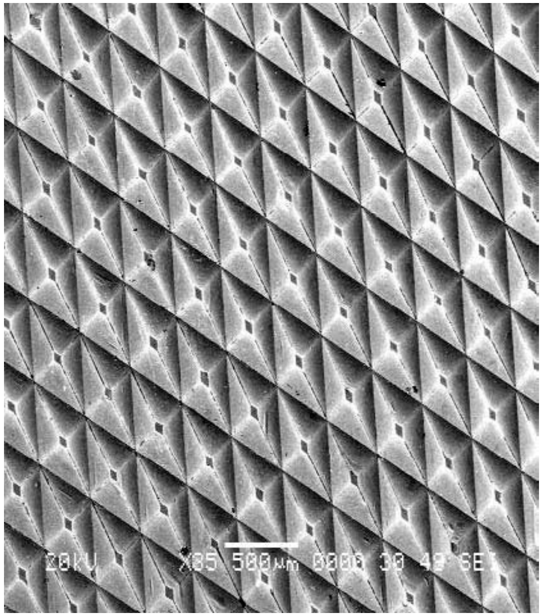






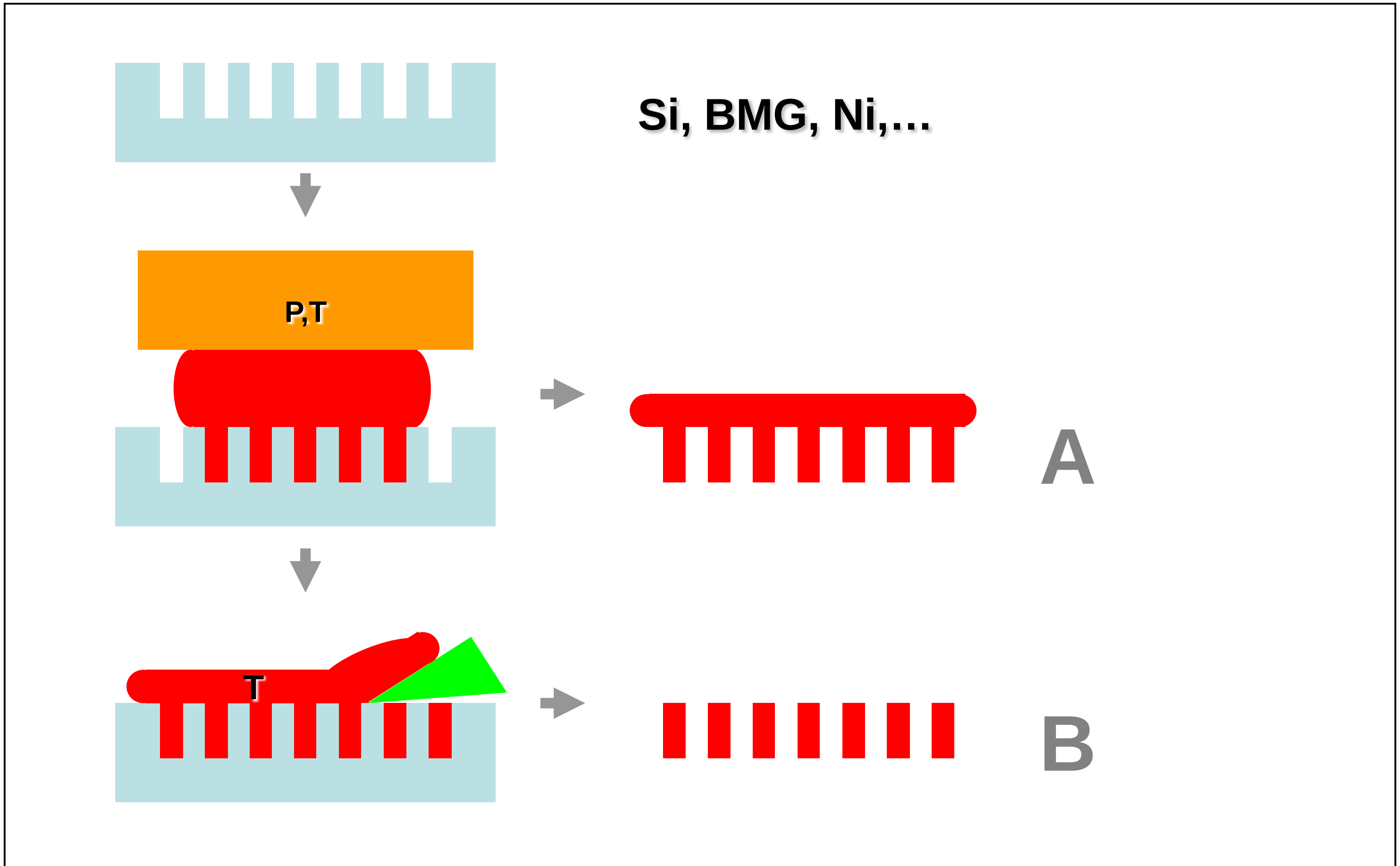






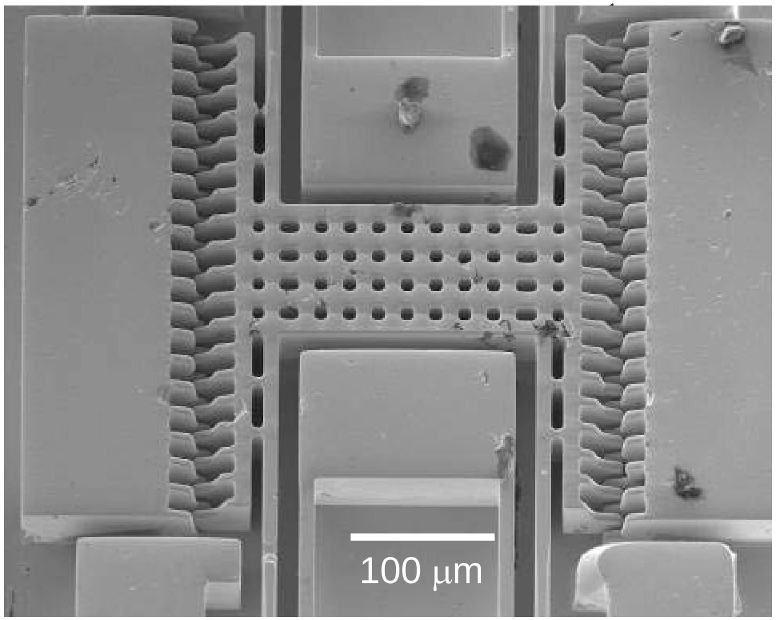
J. Schroers, Advanced Materials, 21 (2010)

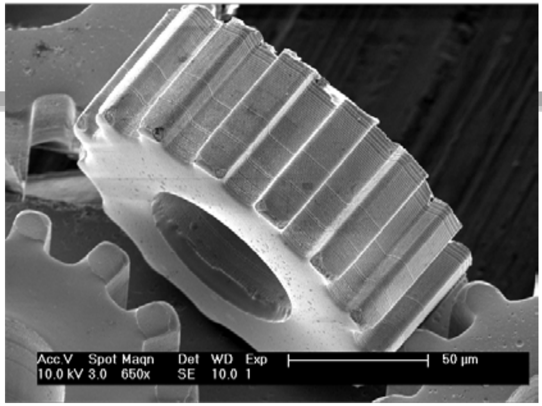
Schematics of miniature forming

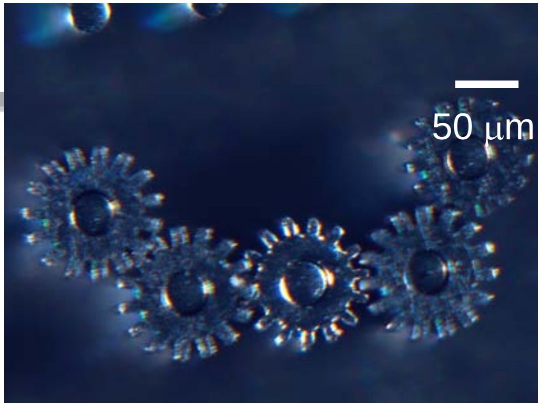


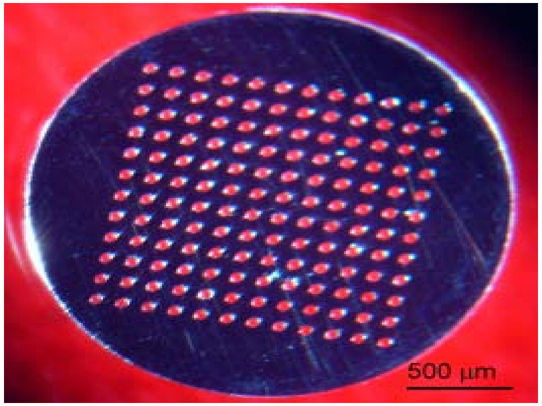
J. Schroers, Q. Pham, A. Desai, J. MEMS, 37, 83 (2007)

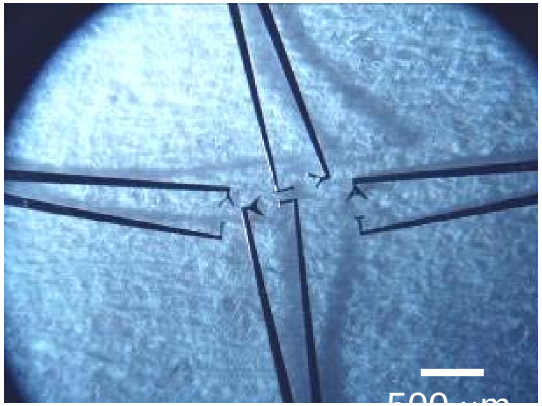
Hot Cutting Of BMGs- 3D Miniature Parts

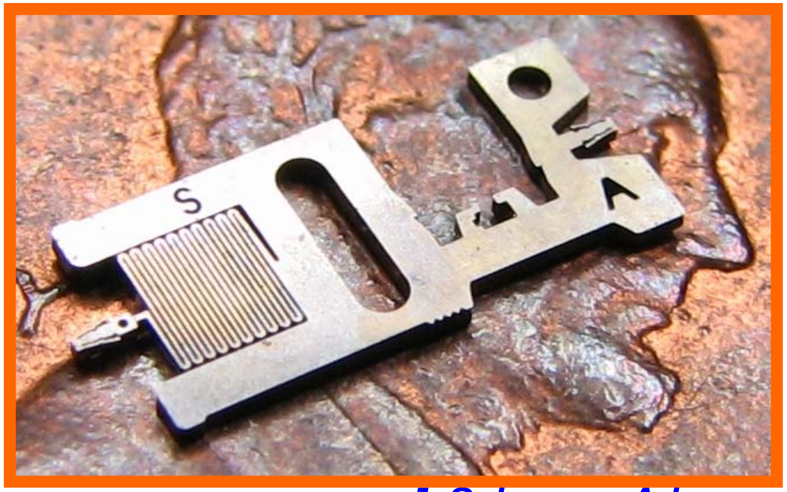


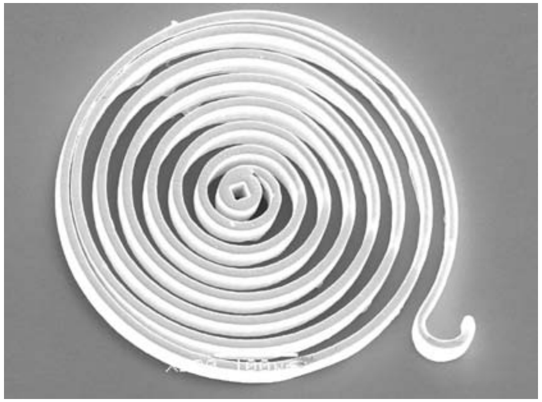


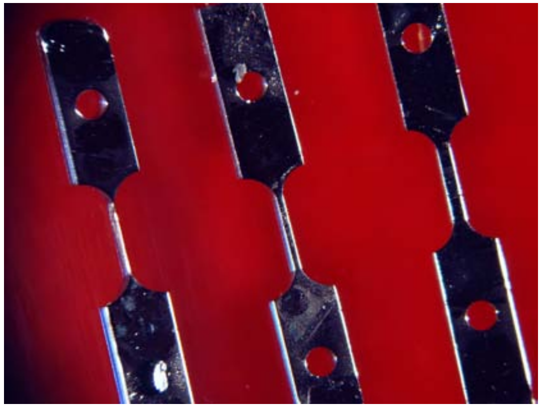








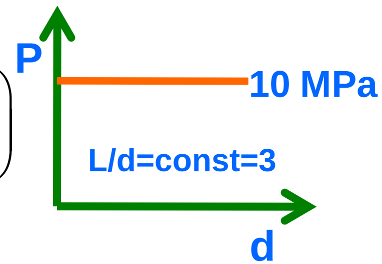




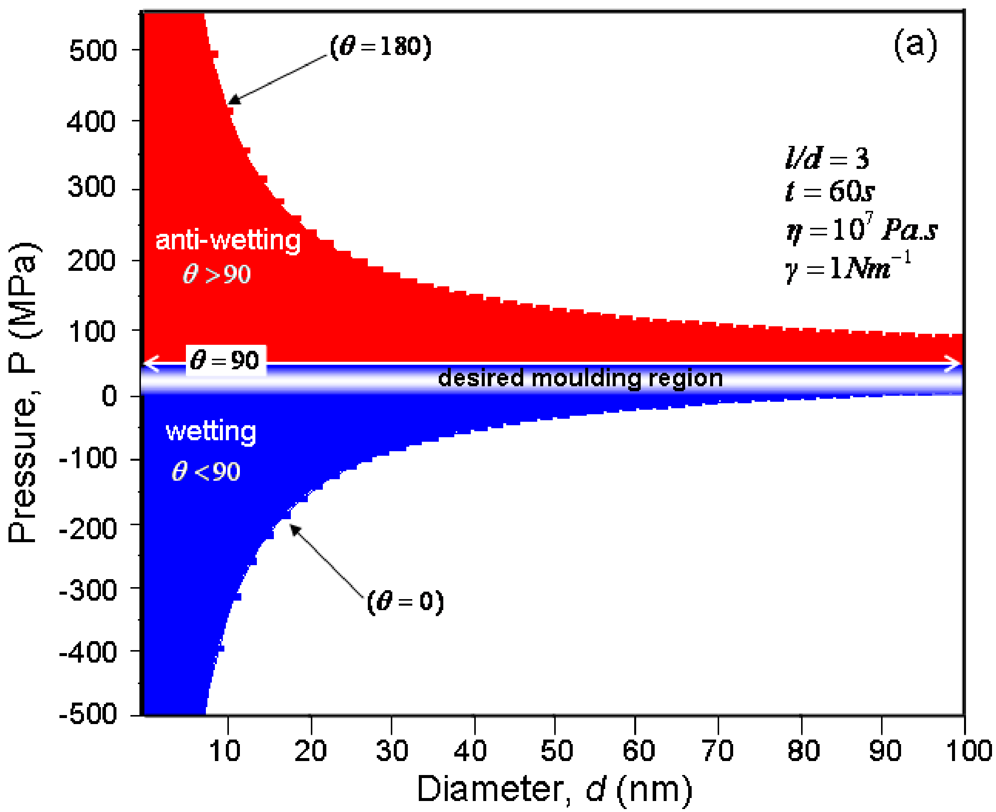
J. Schroers, Advanced Materials, 21 2009

TPF OF BMG-How small can you go?

$$P = \frac{1}{t}\left(32\eta\frac{L^2}{d^2}\right)$$



•Contradicts experiments for d < 100 nm



$$P = \frac{1}{t}\left[32\eta\frac{L^2}{d^2}\right] - \frac{4\gamma}{d}\cos(\theta)$$

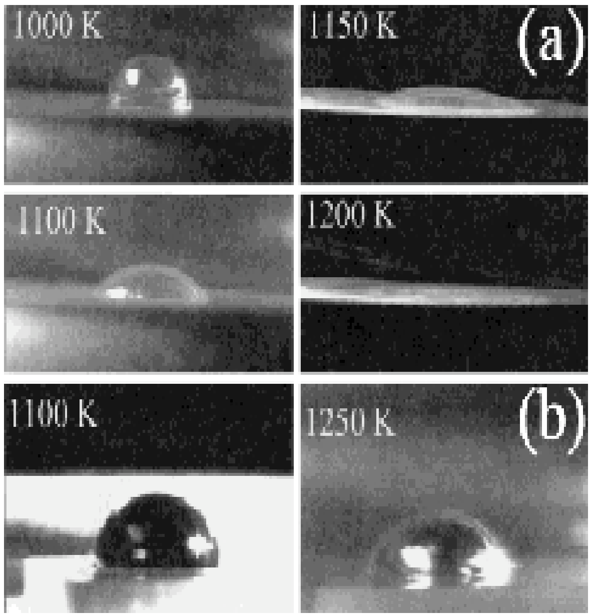
•On the small scale wetting between mold and BMG dominates the filling characteristics

•Transition from viscous controlled forming to capillary force controlled forming @~100 nm

G. Kumar, H. Tang, and J. Schroers, Nature 457, 828 (2009)

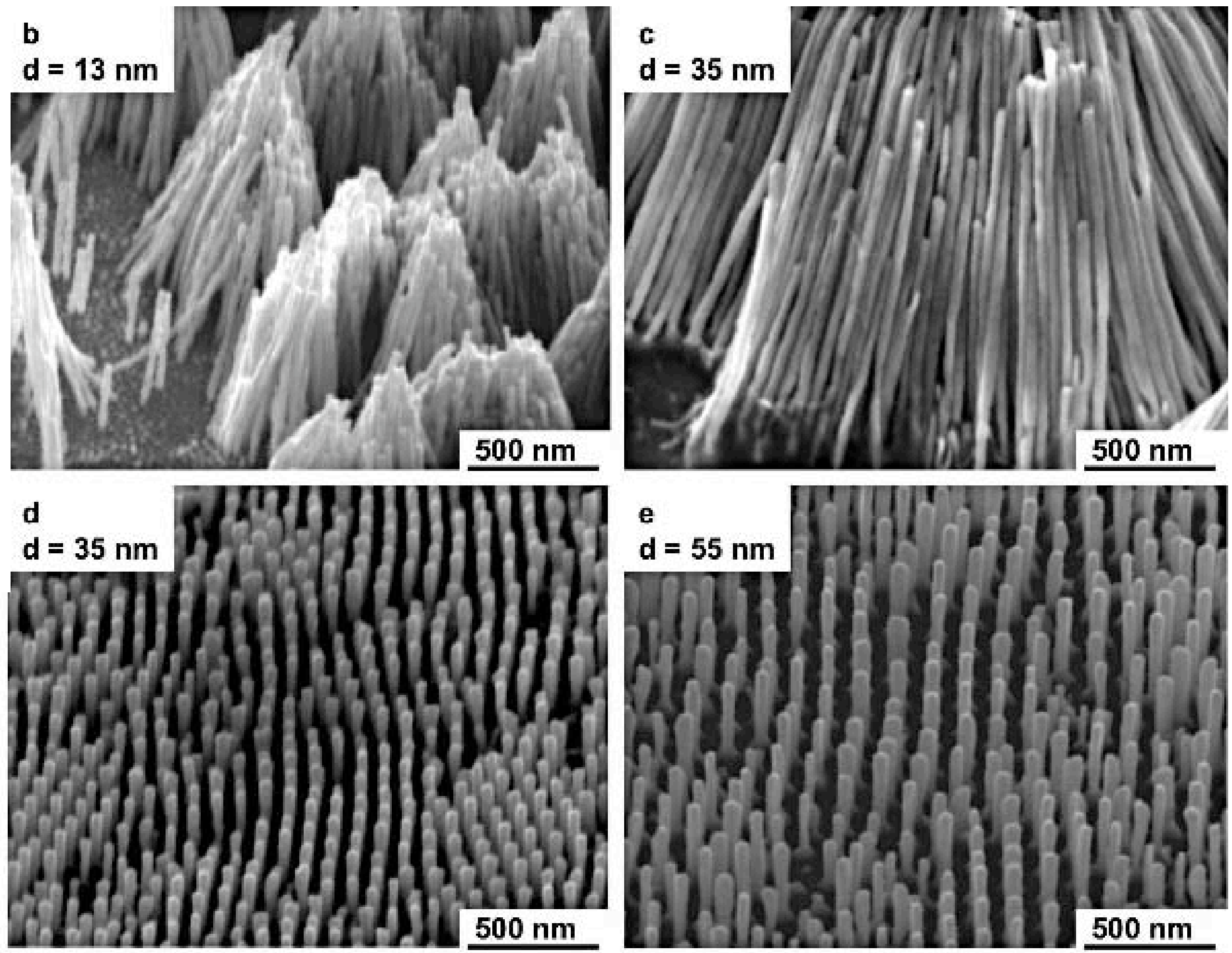
TPF OF BMG-How small can you go?

ZrTiNiCuBe on C (a) AlN (b)

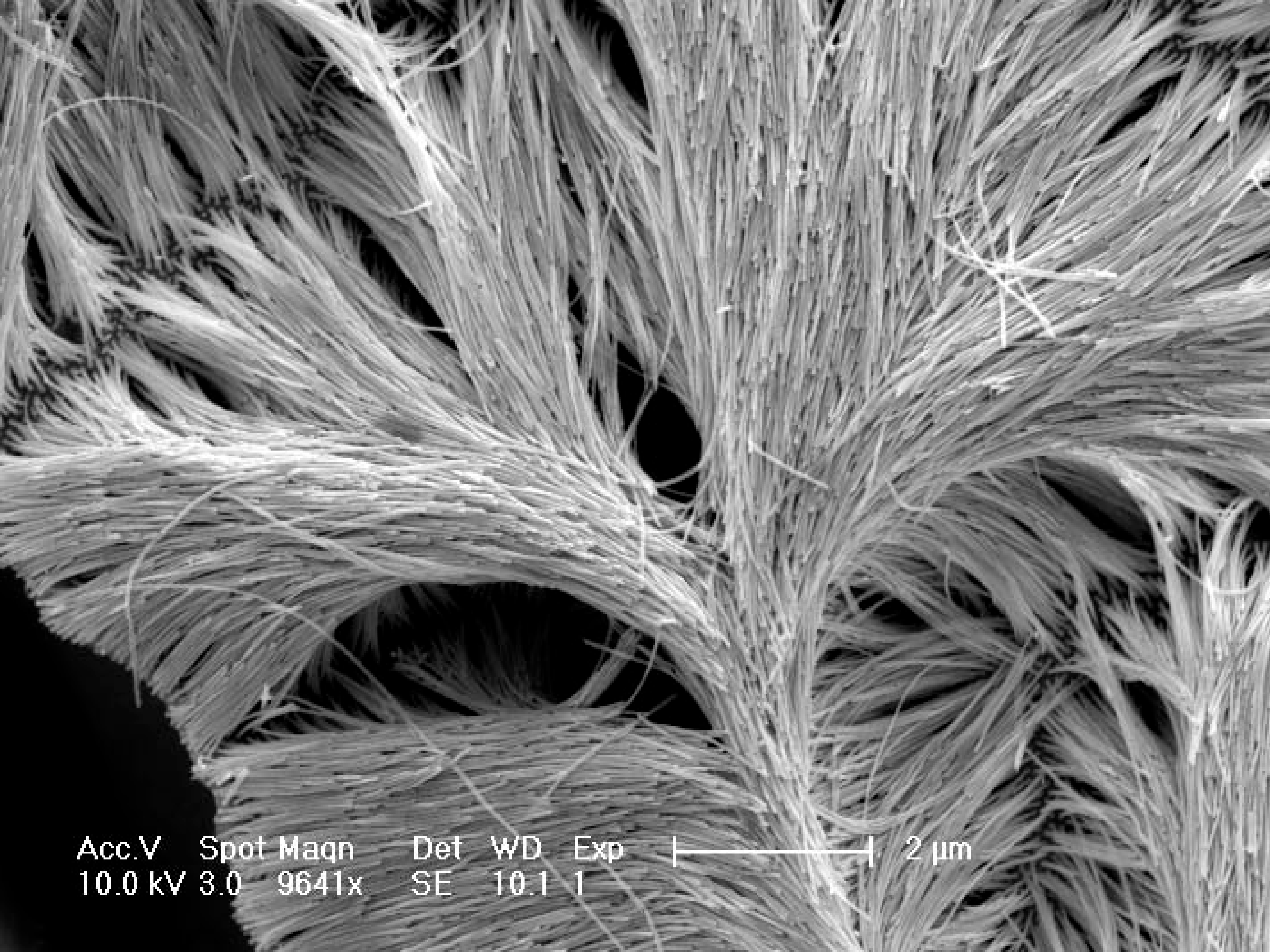


J. Schroers, K. Samwer, F. Szuecs, W.L. Johnson, JMR, 15, 1617 (2000)

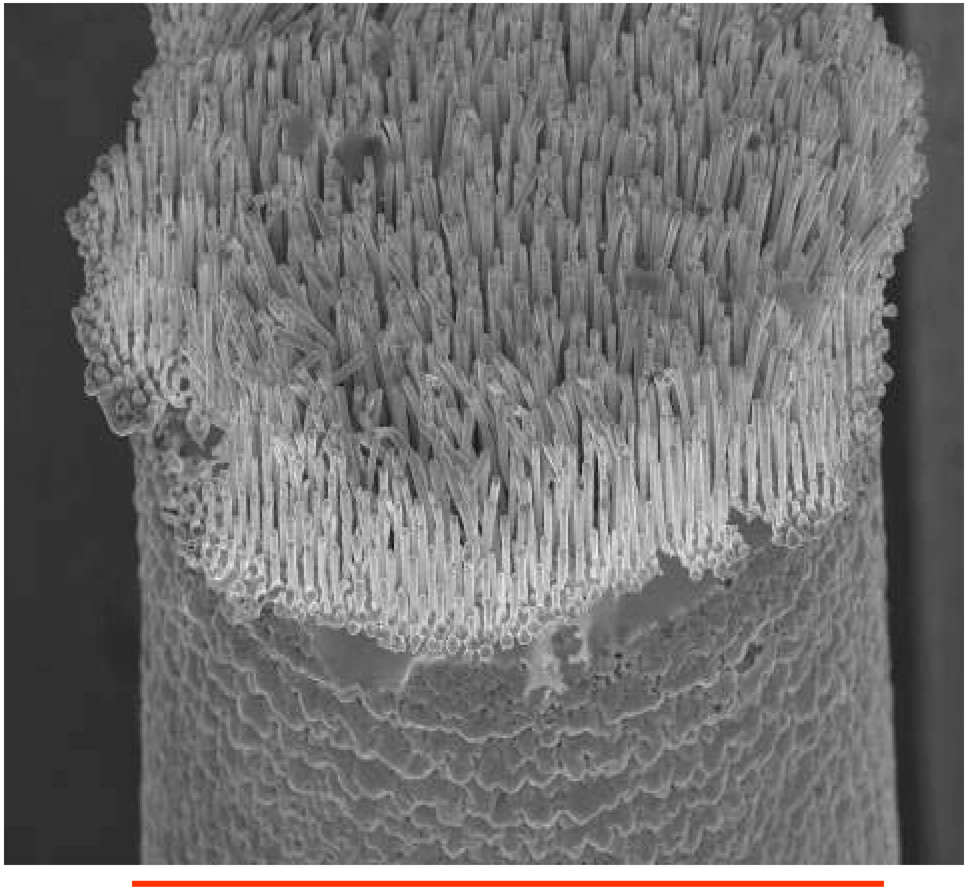
PtNiCuP into porous Al_2O_3



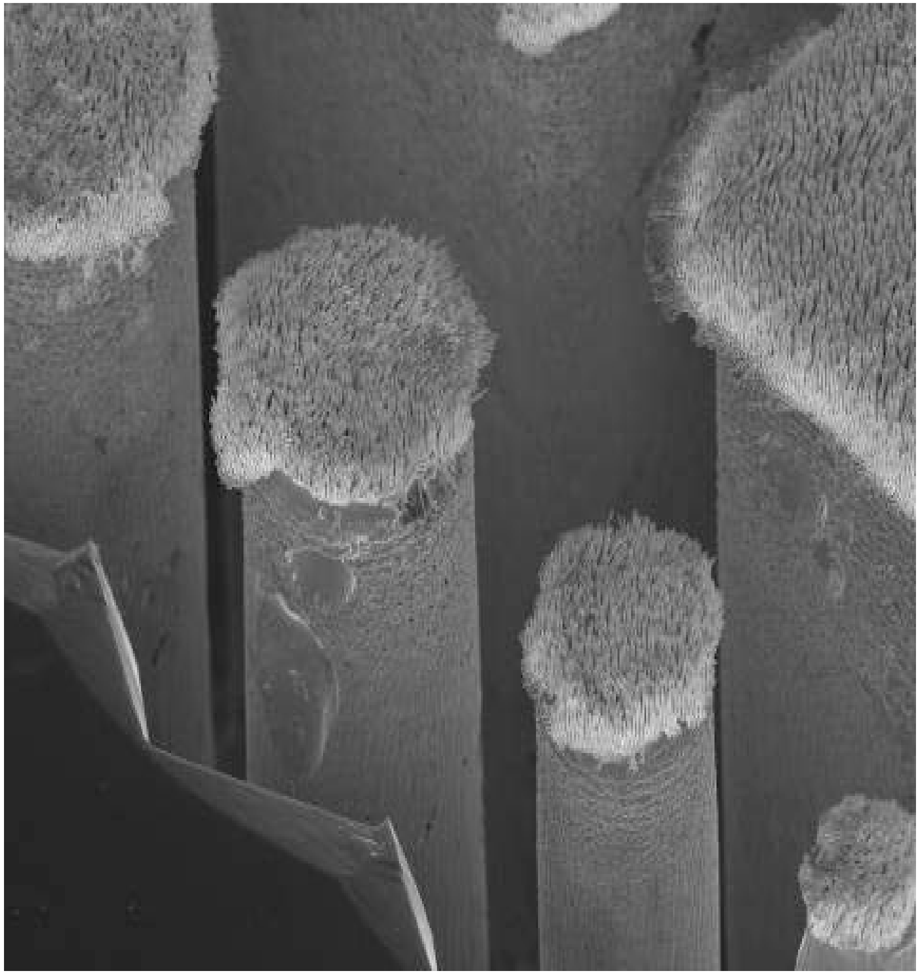
G. Kumar, H. Tang, and J. Schroers, Nature 457, 868 (2009)


Acc.V Spot Magn Det WD Exp
10.0 kV 3.0 9641x SE 10.1 1
2 µm

Patterning on multiple length scales

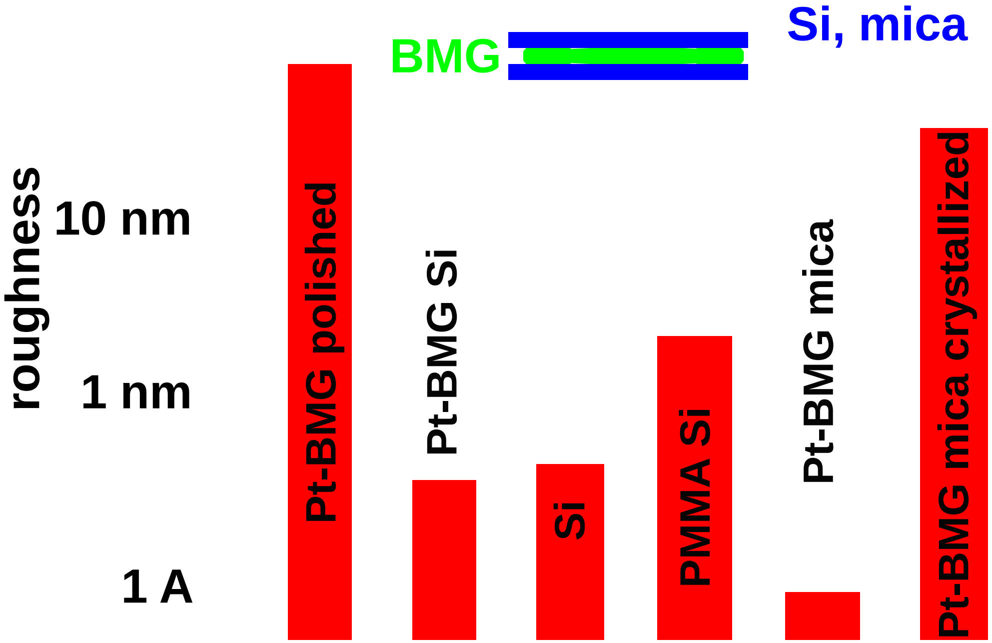


10 μm

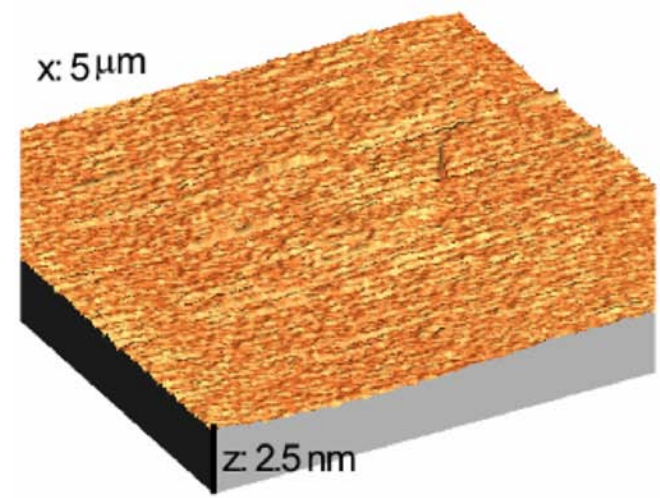


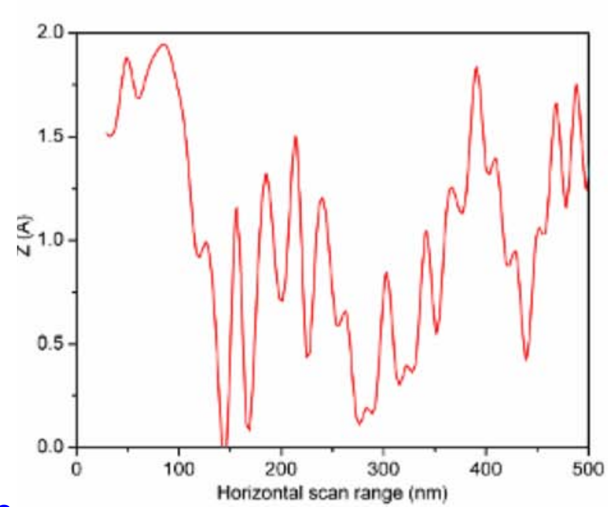
How is this technology useful for nanoimprinting?

TPF of BMG Surface Roughness



d: Pt-BMG formed on mica



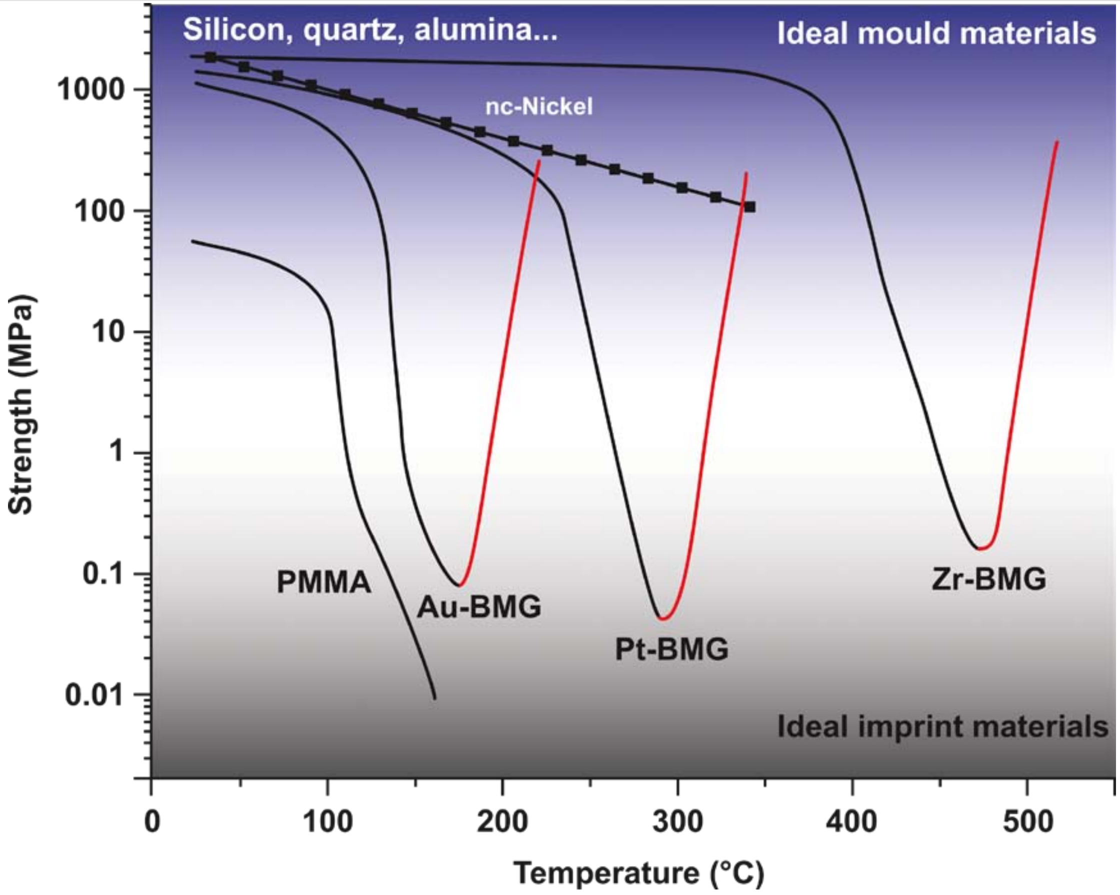


- Forming process smoothens the surface
- Replicates roughness of mold (sub nanometer)
- Significant smoother than PMMA
- Amorphous structure required

=> as-formed surface smoother than polished!

G. Kumar, P. Staffier, U. Schwarz, J. Schroers, J. Blawzdziewicz submitted (20

BMGs as template and imprint material for nanoimprinting

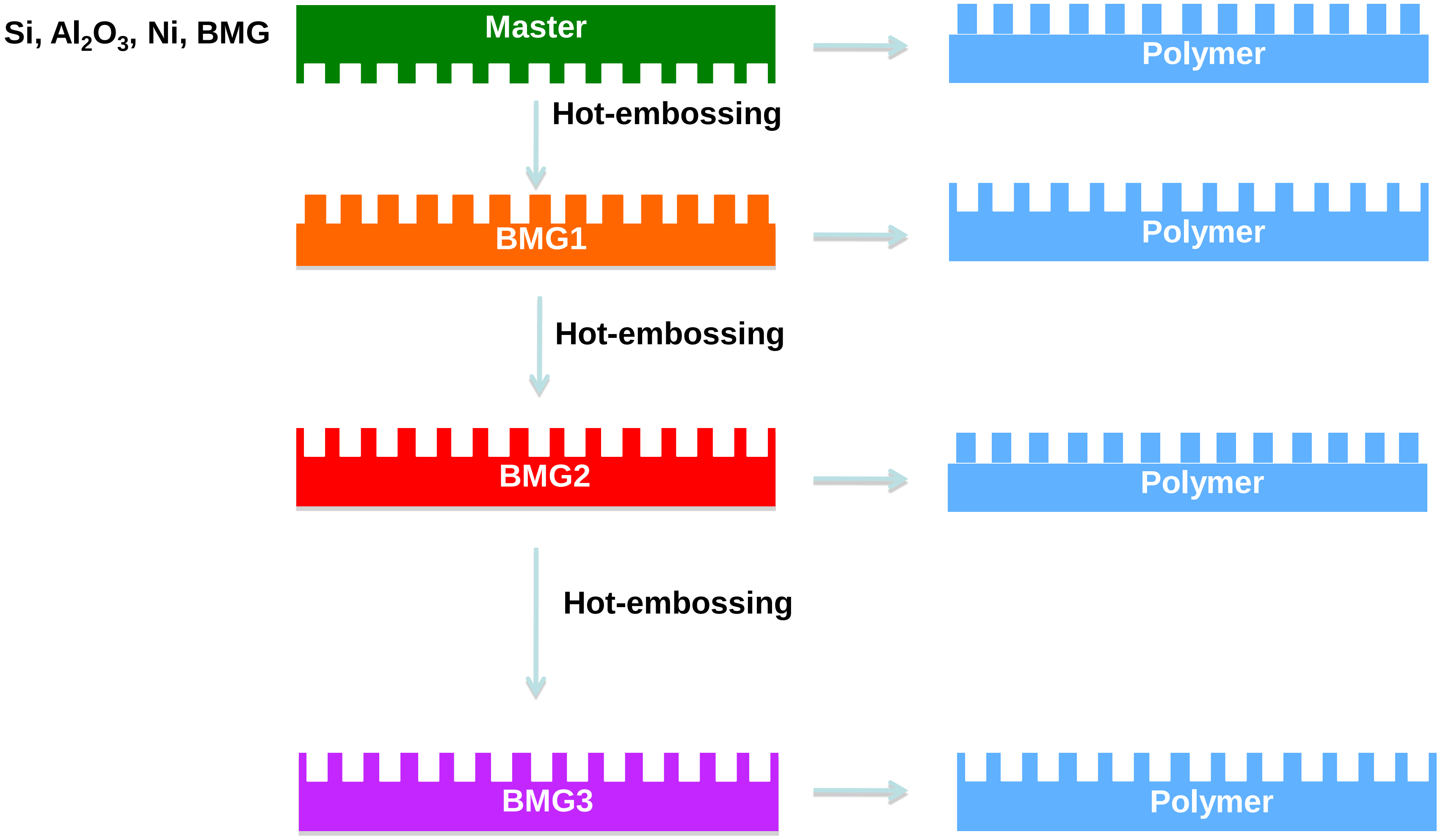


$T_{process}$ [°C]	BMG
80	$Ce_{70}Al_{10}Cu_{20}$
150	$Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$
270	$Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$
350	$Pd_{43}Ni_{10}Cu_{27}P_{20}$
430	$Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$

BMGs are high strength metal that can be processed like a plastic
=>Ideal template and imprint material
=> Provides unique and versatile toolbox for nanoimprinting

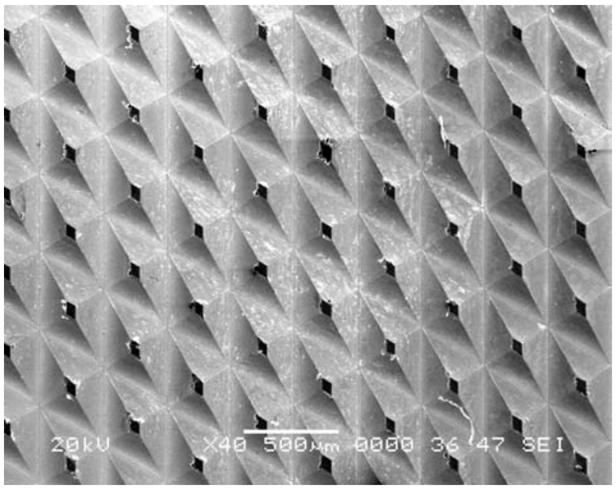
J. Schroers and N. Paton, Advanced Materials Processes 1, 61, 2006

IMPRINT TOOLBOX

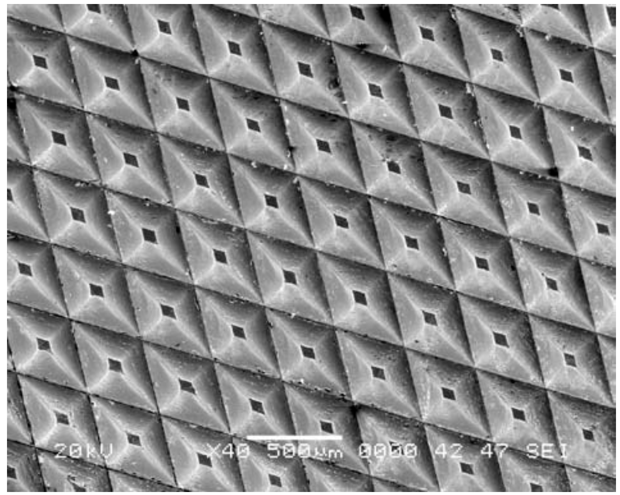


Imprint toolbox

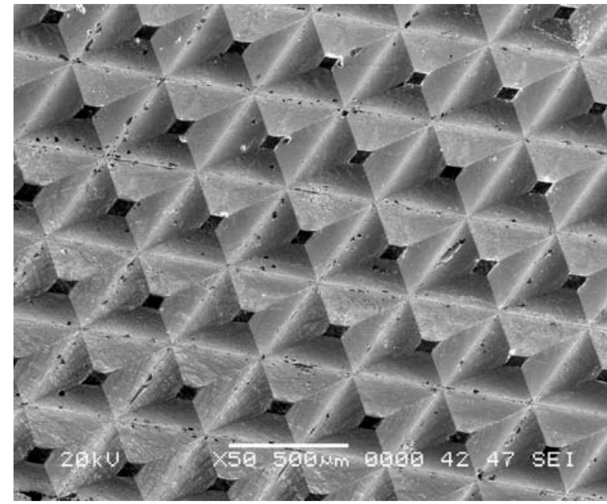
MASTER



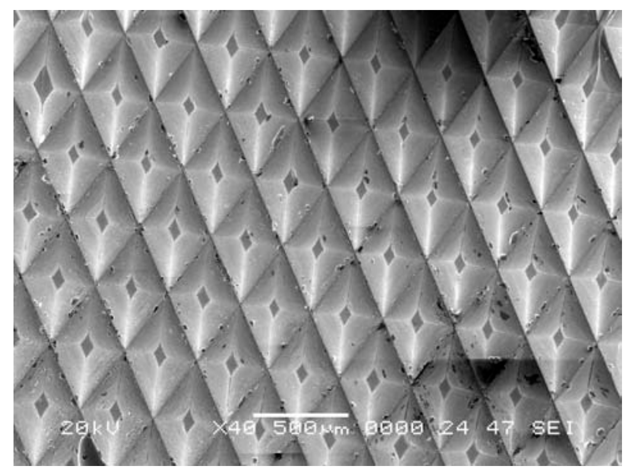
Zr-based BMG
Tg = 350° C,Tpro = 450° C



Pt-based BMG
Tg = 230° C,Tpro = 280° C



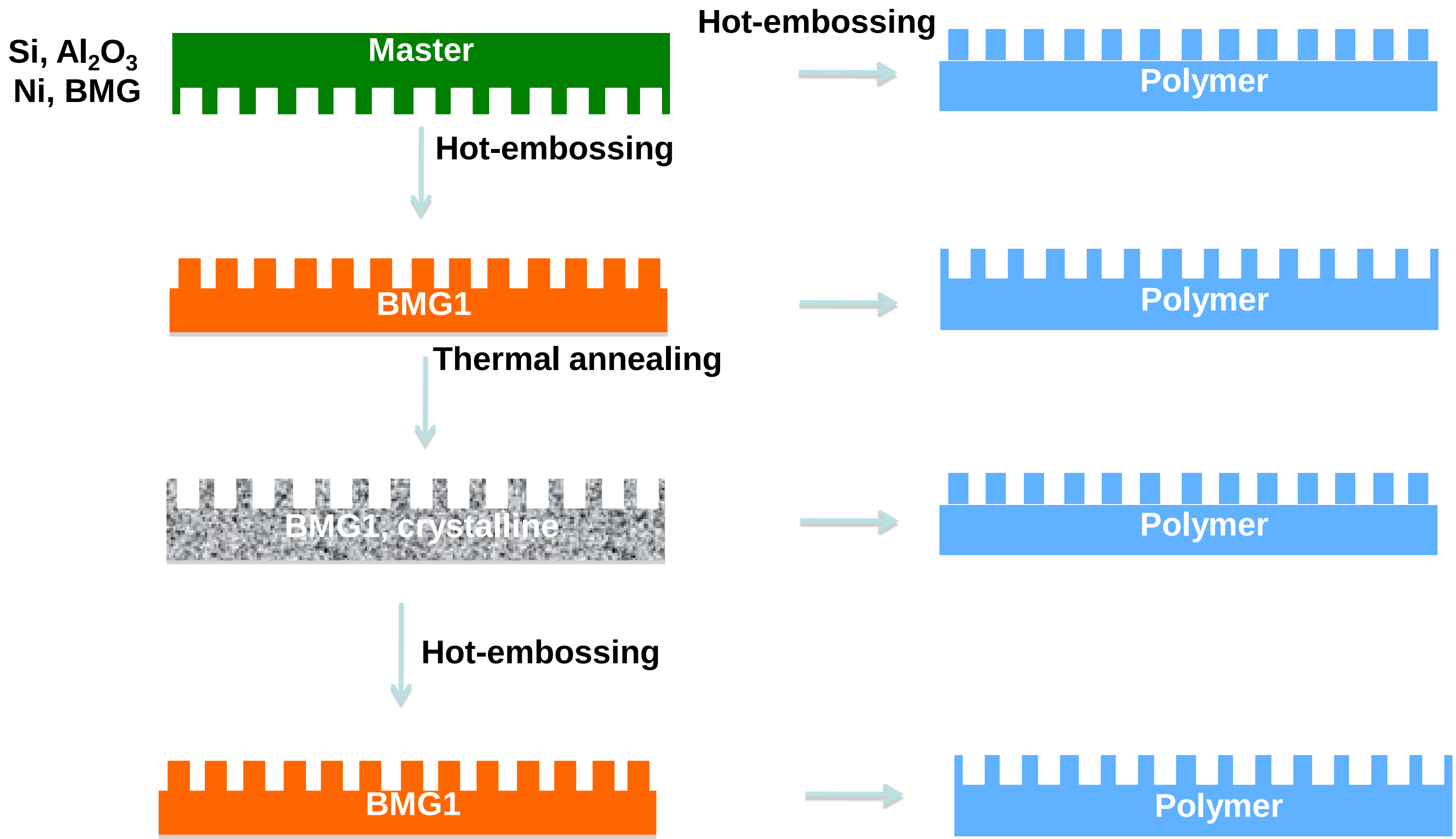
Au-based BMG Tg = 130° C



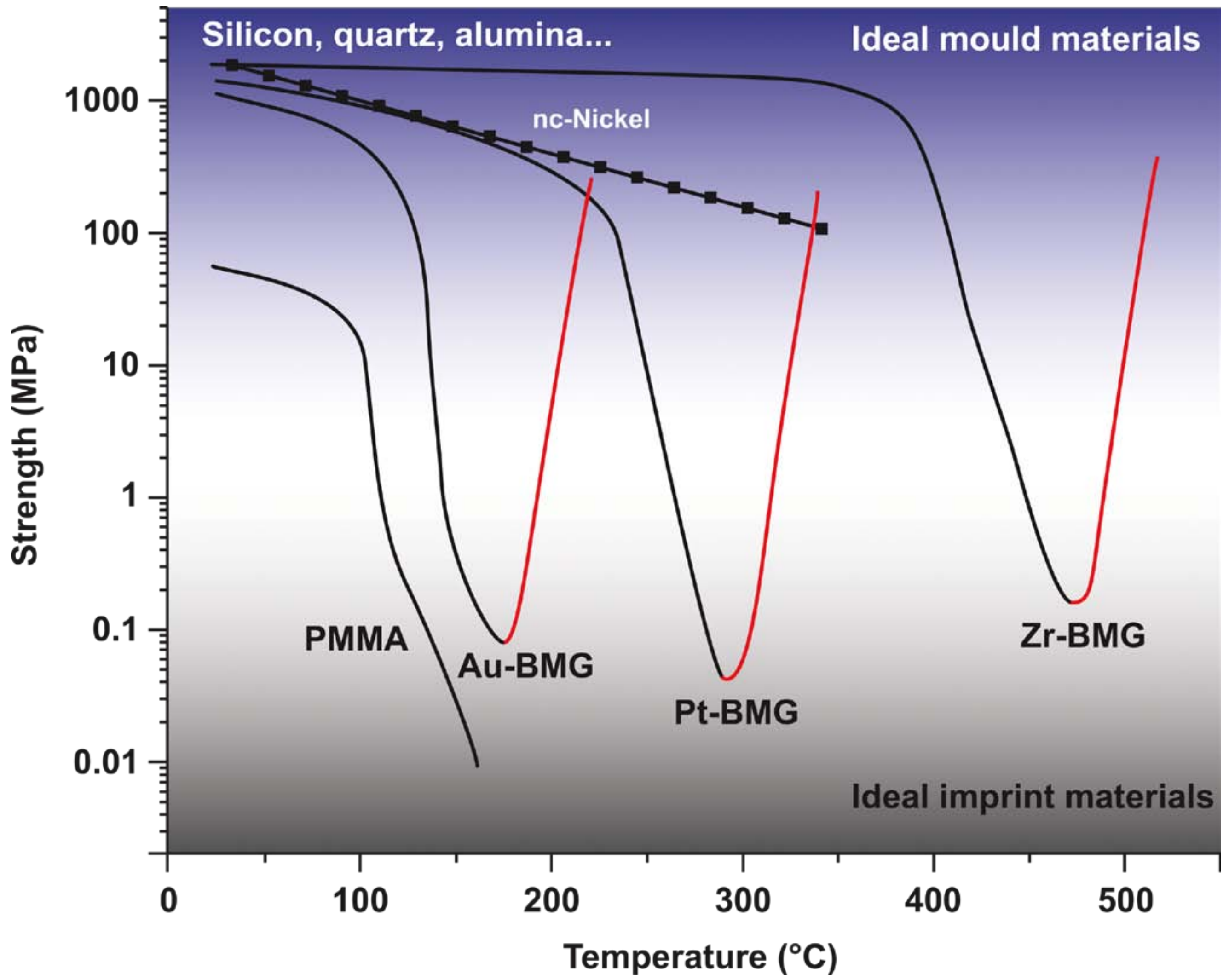
- BMG can be both imprinted material and mold
- mass production (master-daughter-granddaughter mold)
- particularly interested when grey scale or *e*-beam Lithography is required
- no disposable molds necessary
- LIGA alternative

J. Schroers, T. Nguyen, A. Desai, J. MEMS, 37, 83 (2007)

IMPRINT TOOLBOX

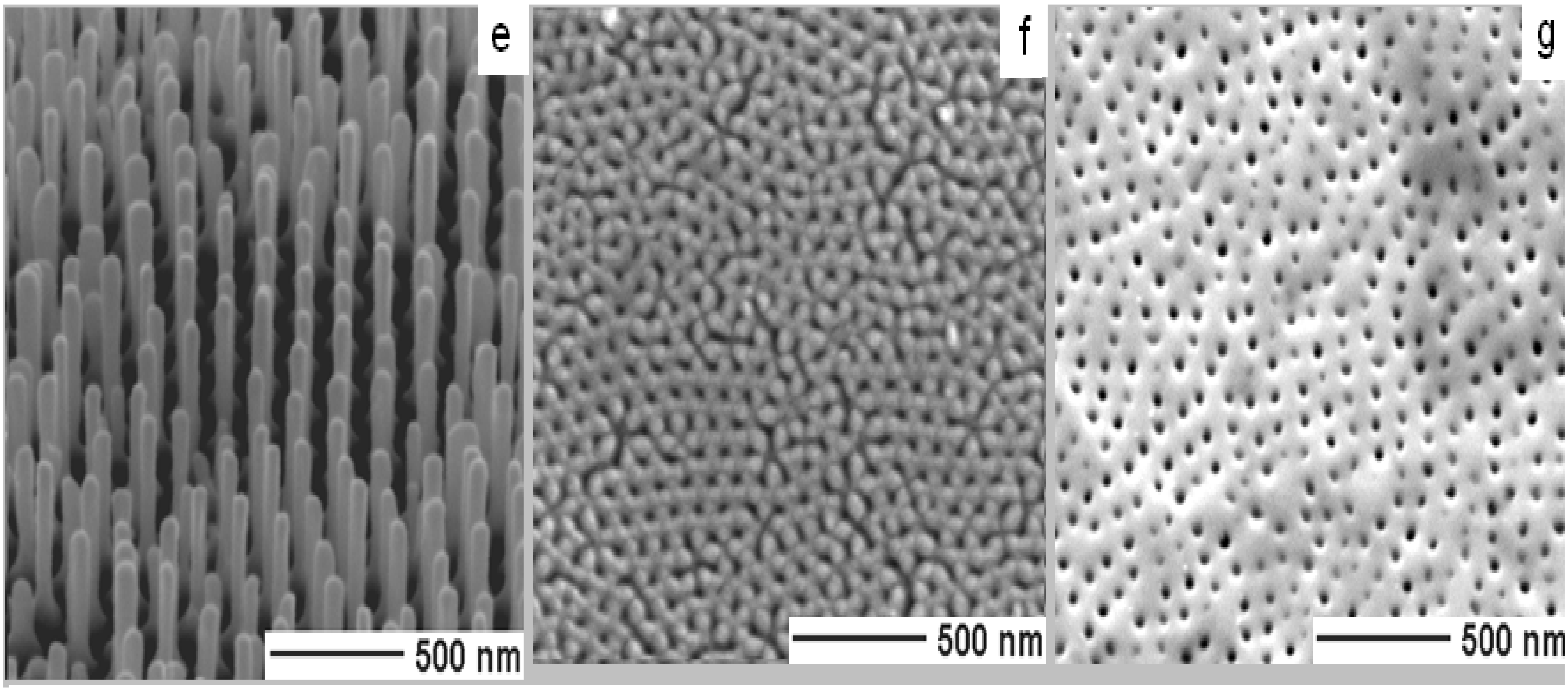


BMGs as template and imprint material for nanoimprinting



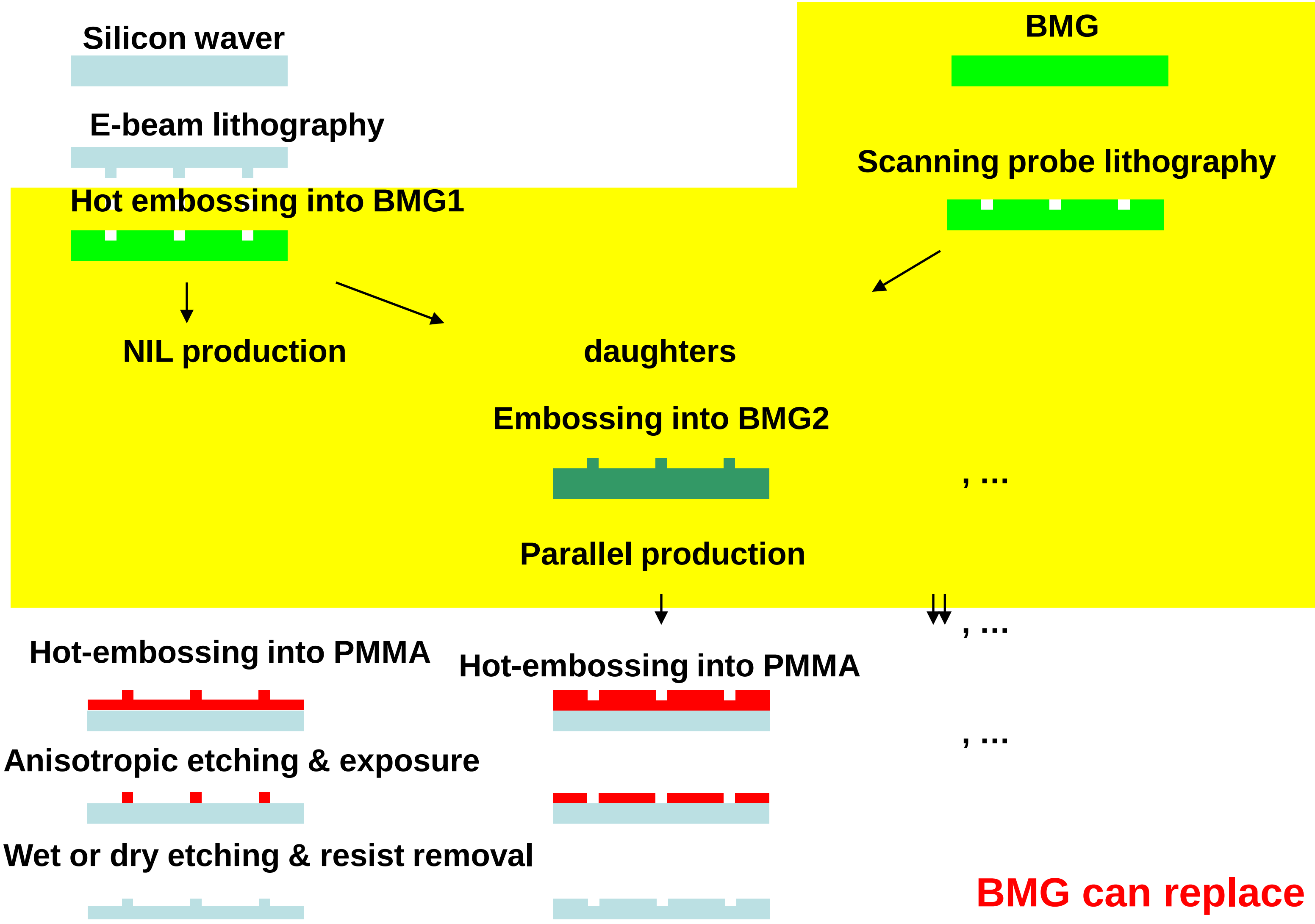
Imprint toolbox

BMG1 | BMG1 -> PMMA | BMG1 crystalline -> BMG1



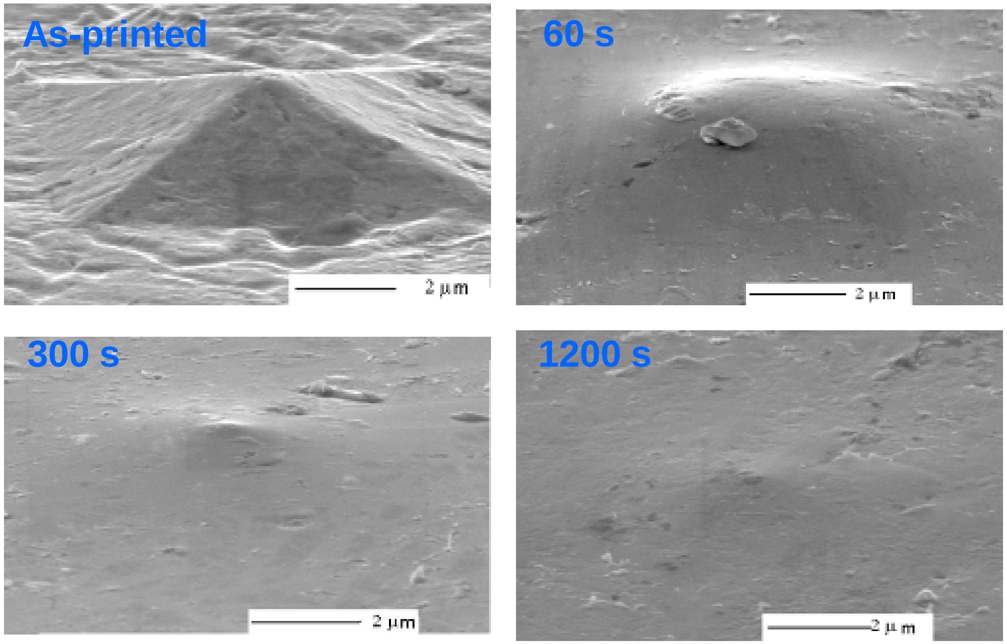
G. Kumar, H. Tang, and J. Schroers, Nature 457, 868 (2009)

BMG use in Nanoimprinting-Nanoimprint Lithography



BMG can replace fragile Si in the imprinting process

Write and Erase –High density data storage



Capillary force is sufficient to significantly deform BMG in its SCLR

Erasing time

$$t_e = \frac{9\eta h_0}{\gamma}$$

t_e = 1.3 sec for 13 nm features
t_e = 1000 sec for 6 µm features

- Write and erase process
  (900 times for PtNiCuP, 13 nm)

Can be used for high density rewritable data storage (sequential and parallel)

G. Kumar, J. Schroers, Applied Physics Letters, 92, 031901 (2008)

Nanopatterning complex surfaces

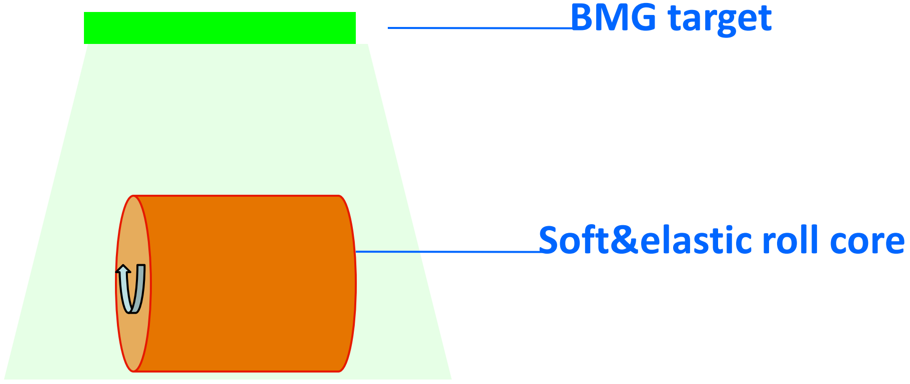
Increasing demand for non-planar nano-patterned surfaces

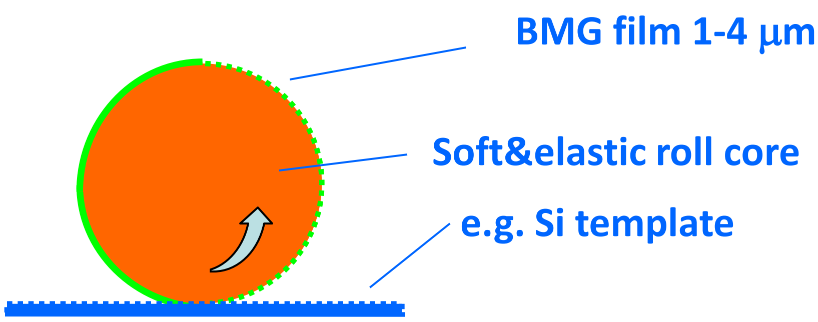
•Biomedical (program desired cellular response)

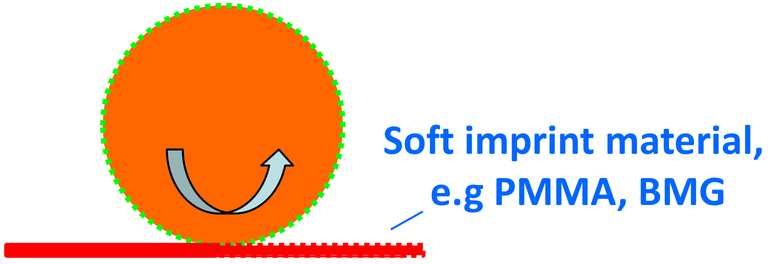
•Functionialization low symmetry surfaces

•Imprinting (high symmetry) (roller imprint system for continuous processing)

BMG nano patterned rolls







BLOW-MOLDING with BMGs

$Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ (LM1b)

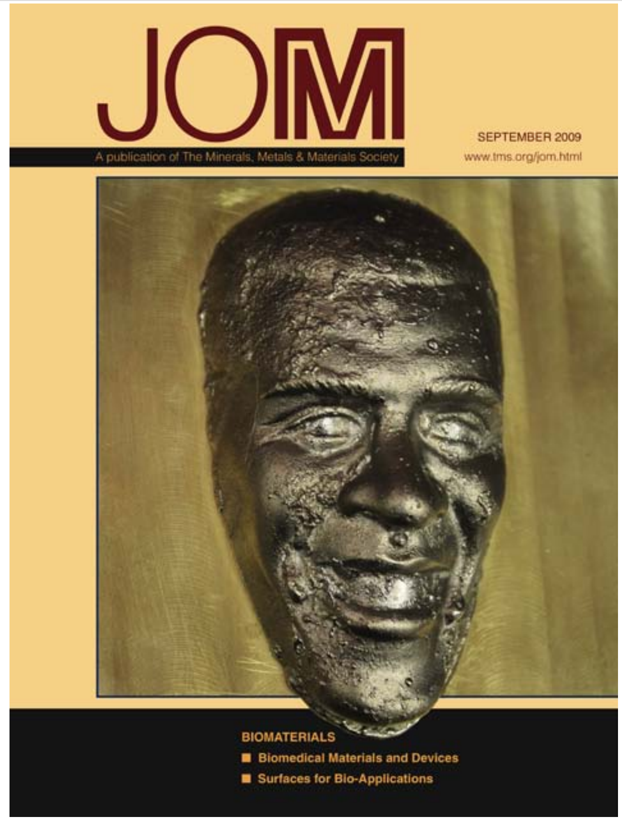
T=460° C, t =40 sec

10^5 Pa, 400% strain

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

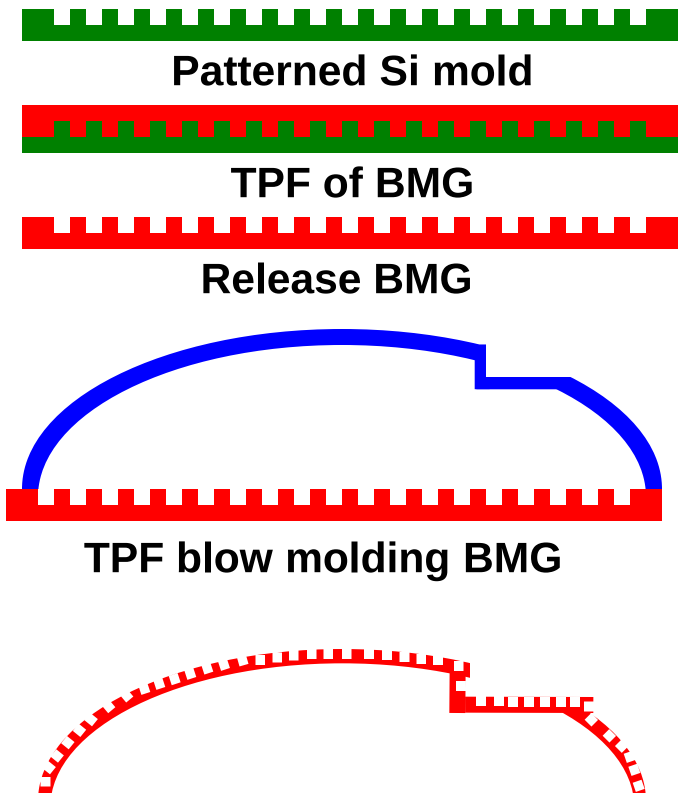
Unachievable shapes for metals

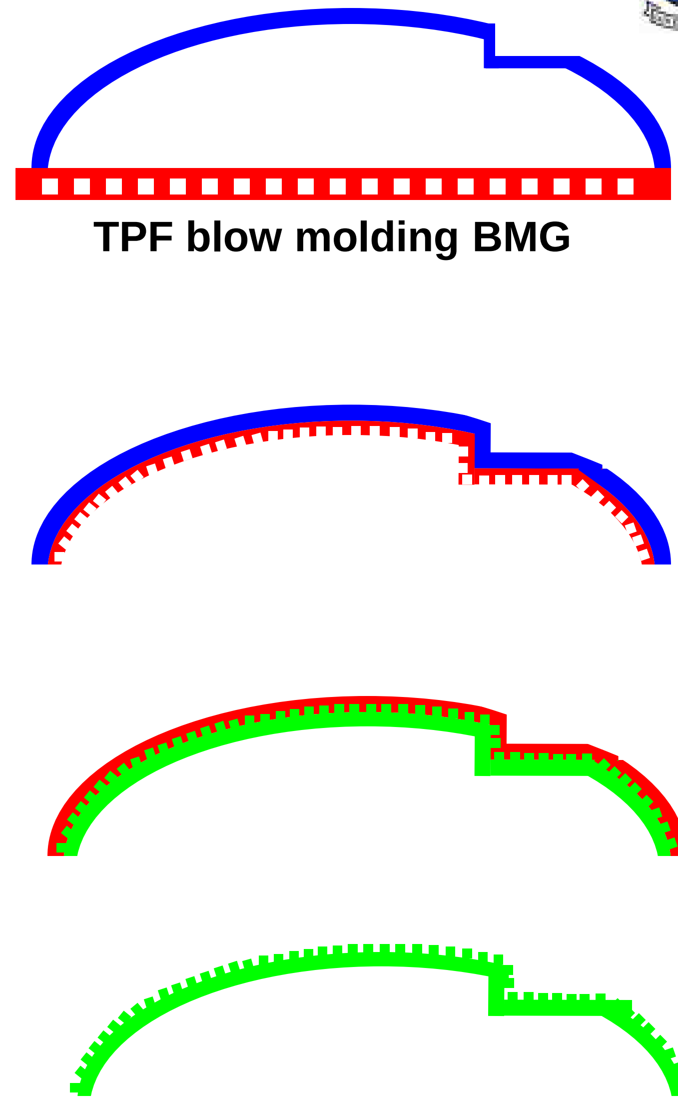
Hollow, thin, seamless, complex parts



J. Schroers, Advanced Materials, 21 (2010)

Nanopatterning irregular surfaces: Fabrication processes





$$\sigma = \Delta p \frac{L}{2t}$$

J.Schroers, G. Kumar, T.M. Hodges, US Patent #US0884905

Multi Length Scale, Multi Dimension Patterning

Yale

Conclusions

•BMG have promising properties for top down nanofabrication (homogeneous and superior mechanical properties)

•Shown that features ~10 nm can be directly imprinted (much smaller possible) under low forming pressure

•BMGs can be used as both hard mold and soft imprint material
⇒BMG provides a versatile toolbox for nanoimprinting
⇒Improves/commercially enable currently identified nanoimprint applications
e.g., provides technology to replicate fragile and expensive Si templates

Future:
-Non planar imprint processes
-combine with forming process
-combine with other length scale patterning
=>enable us to program desirable properties into surfaces of complex shaped metals

THANK YOU!