Bulk Metallic Glass Foams Applied for Orthopedic Implants

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→ Bulk Metallic Glass Foam (BMGF)

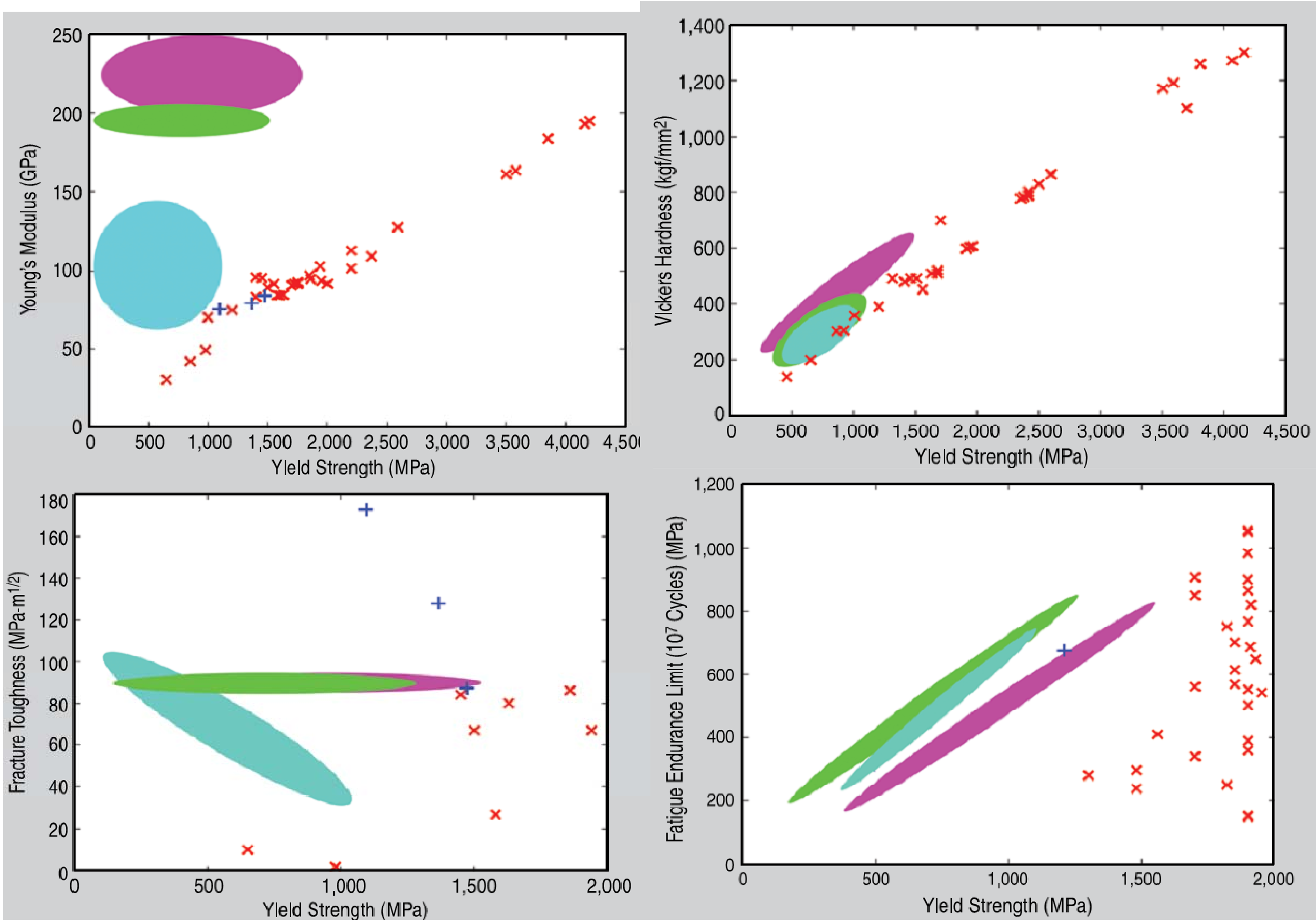
1. Why do the amorphous metals become the attractive candidates for biomedical-implant application?

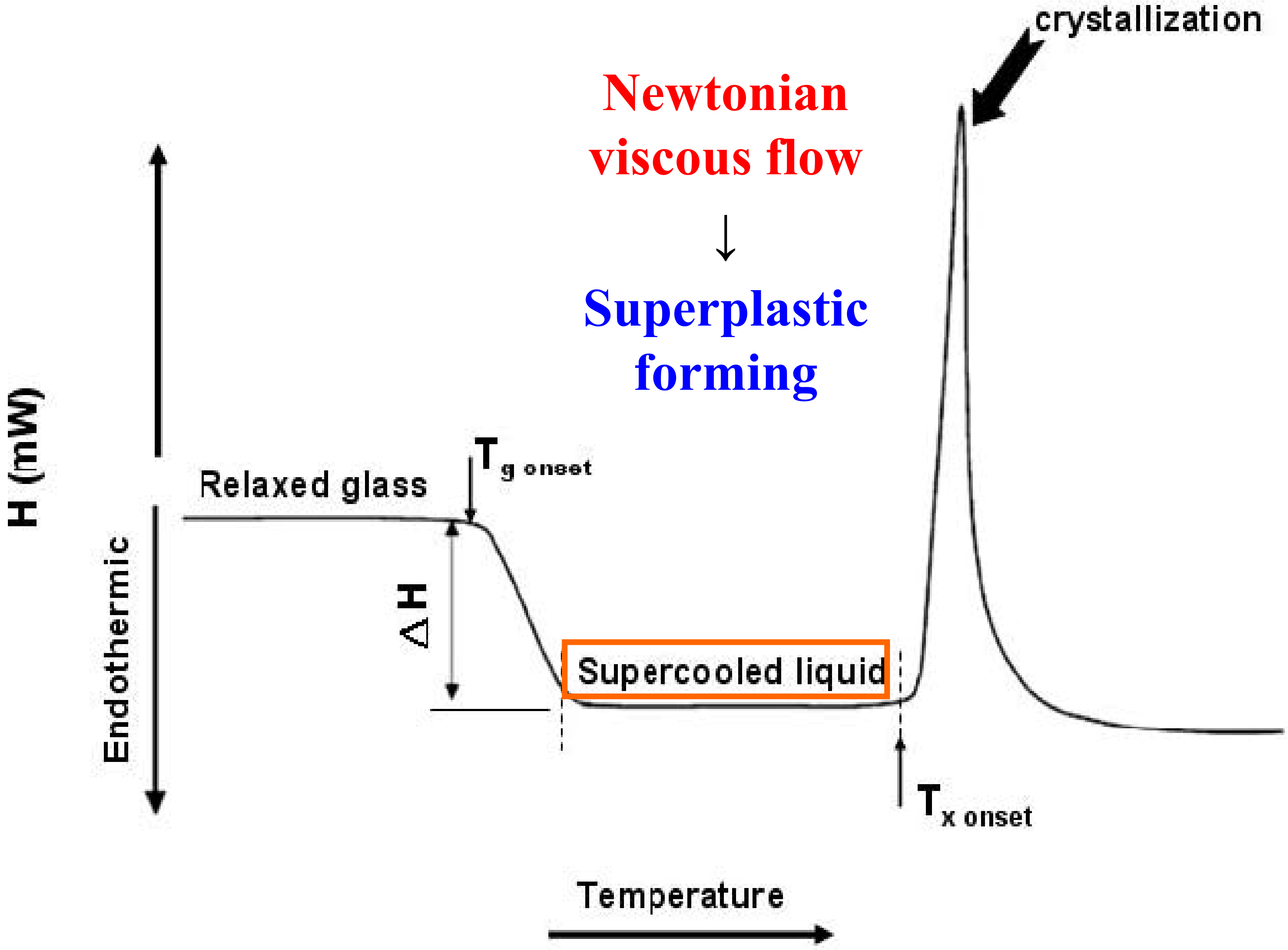
Overall summary

Owing to a unique atomic structure lacking microstructural defects, glassy metals demonstrate certain universal properties that are attractive for load-bearing biomedical-implant applications, such as hard-tissue prosthesis.

1. Mechanically favorable performance
2. Biomedically favorable compatibility

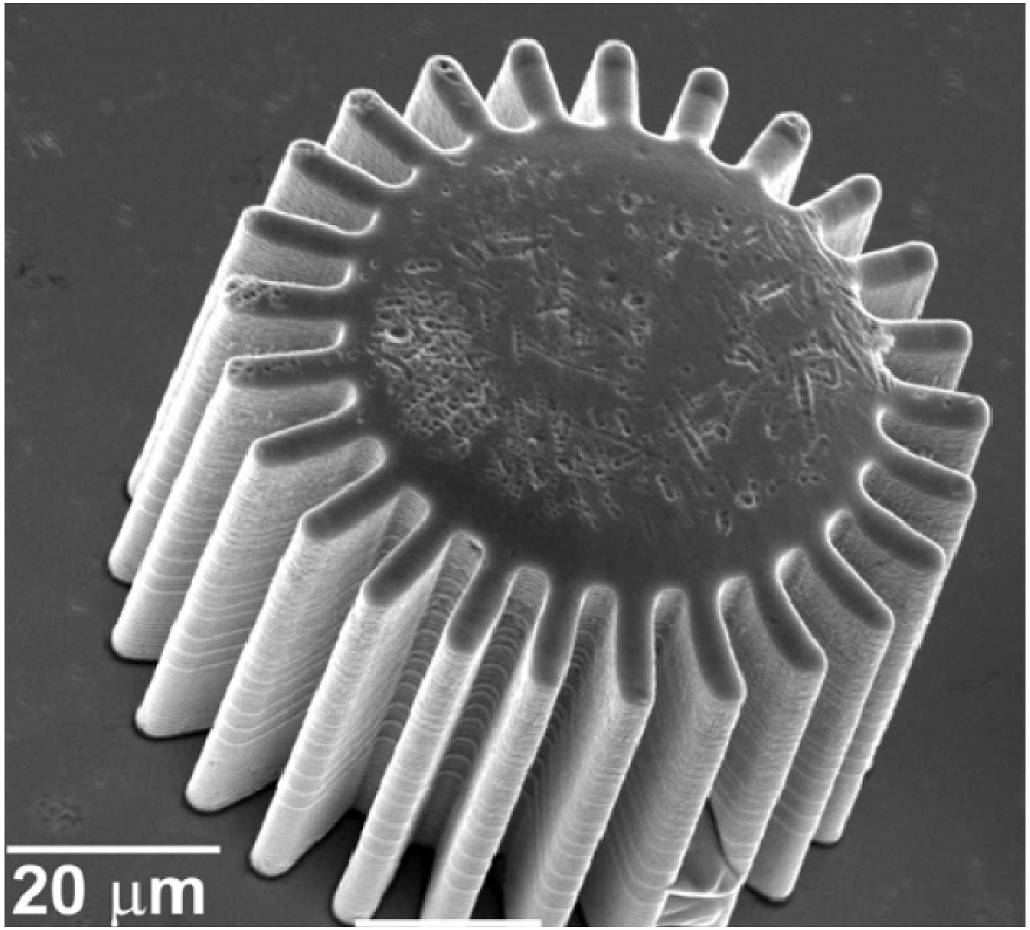
Mechanically favorable performance

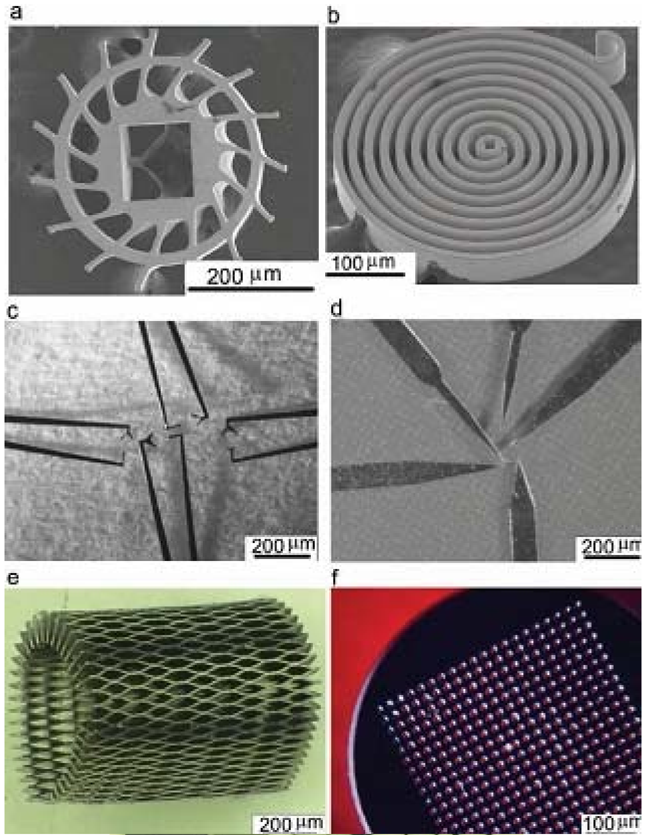


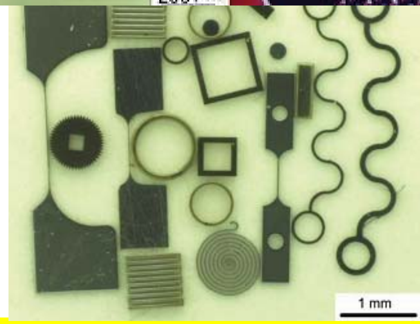


crystallization
Newtonian viscous flow
↓
Superplastic forming
H (mW)
Endothermic
Relaxed glass
Tg onset
ΔH
Supercooled liquid
Tx onset
Temperature

Thermoplastic forming (TPF) based processing



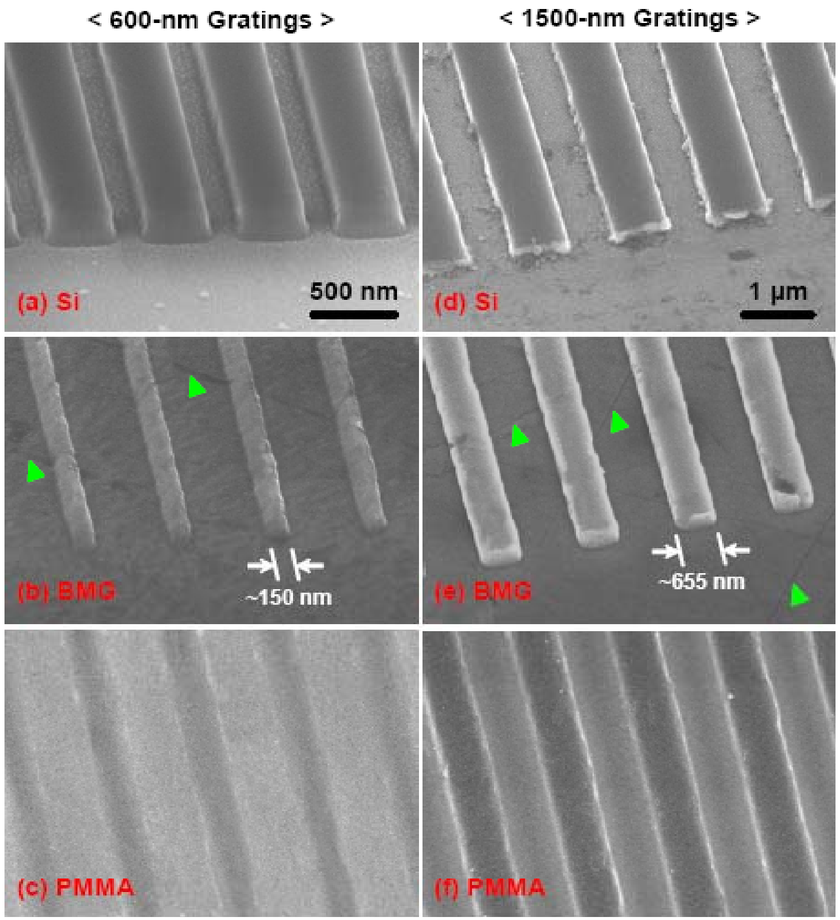


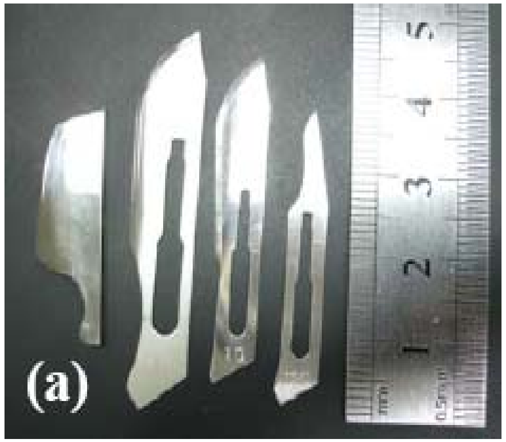


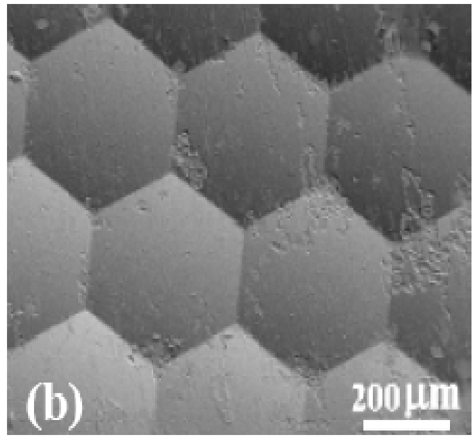
Generic shapes fabricated by TPF-based micro-moding of amorphous metals. Beams, pillars, pipes, square donuts, wavy structure, gears, springs, flexible living hinges and micro-gears and micro-tools.

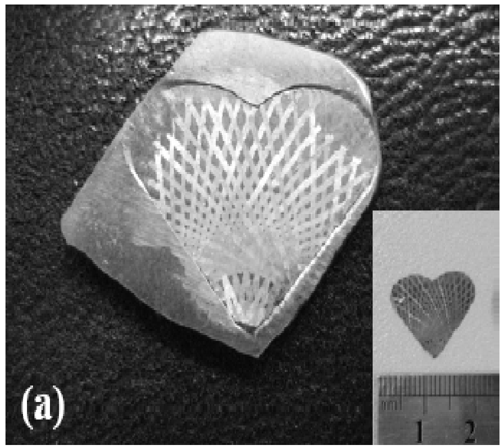
Jan Schroers, Adv. Mater., 2010,22, 1566-1597.
Kumar G et al, Adv. Mater., 2010, XX, 1-16

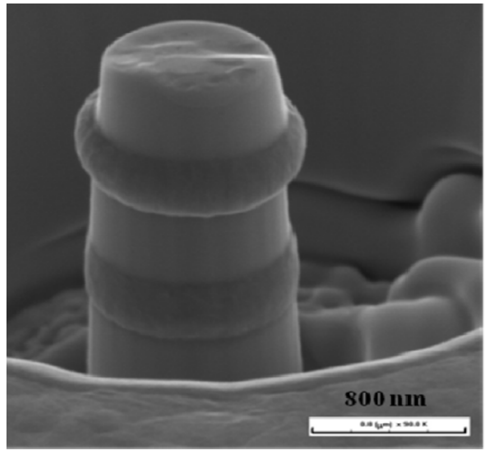
Micro-forming of our groups











Biomedically favorable compatibility

In-vitro **Investigation of one of amorphous metals: Zr-Ti-Co-Be**

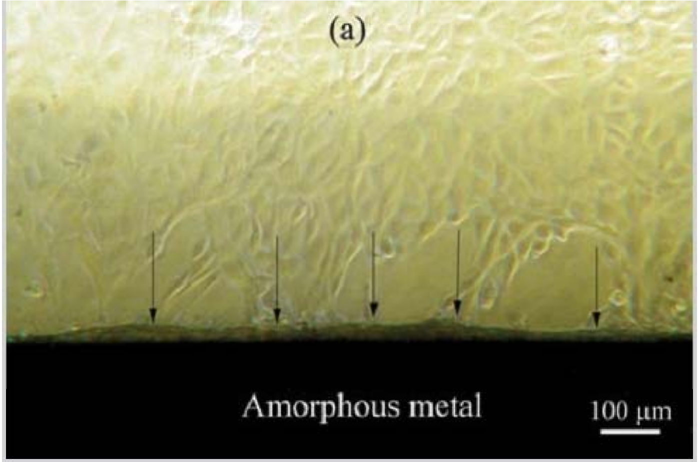
Experiment 1: STANDARD *in-vitro* biocompatibility test (ISO protocol 10993 part 5: Test for cytotoxicity).

Result: No toxicity, no reactivity and no cell lysis.

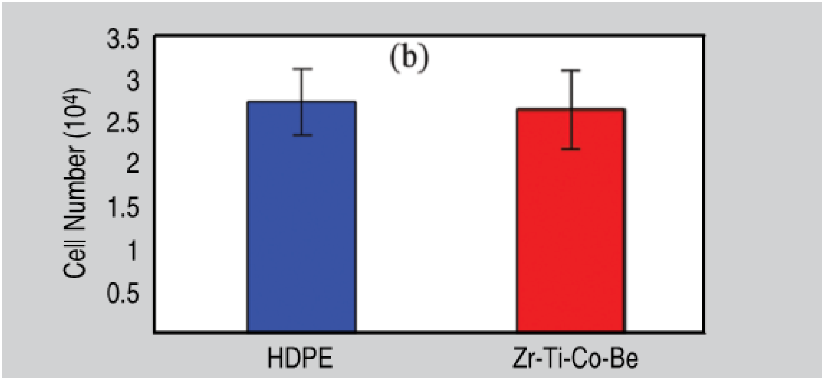
Experiment 2: 7-DAY *in-vitro* cellular adhesion test

Result: cell adherence and proliferation is adequate and compatible.

Many other similar results for other amorphous metals have been reported.



Micrograph of the amorphous metal surface after 7 days, (arrows point to the cell-layer buildup at the interface.)



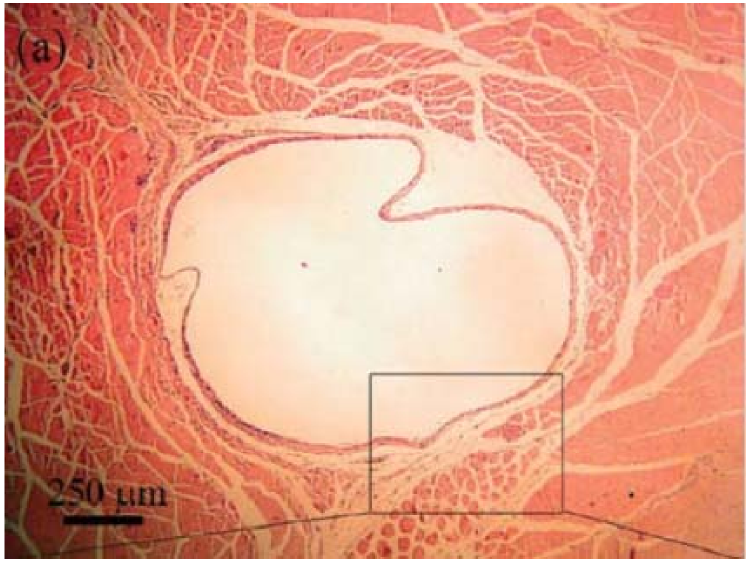
Cell proliferation on the amorphous metal and high-density polyethylene (HDPE) discs.

In-vivo Investigation of one of amorphous metals: Pd-Ag-P-Si

Experiment: STANDARD *in-vivo* biocompatibility test (ISO protocol 10993 part 6: Test for local effects after implantation).

Pd-Ag-P-Si rods implanted subcutaneously in rats for 28 days verified the superb biological performance of this materials, as no tissue reaction was detected.

Most of the researches on other amorphous metals exhibit similar favorable results.



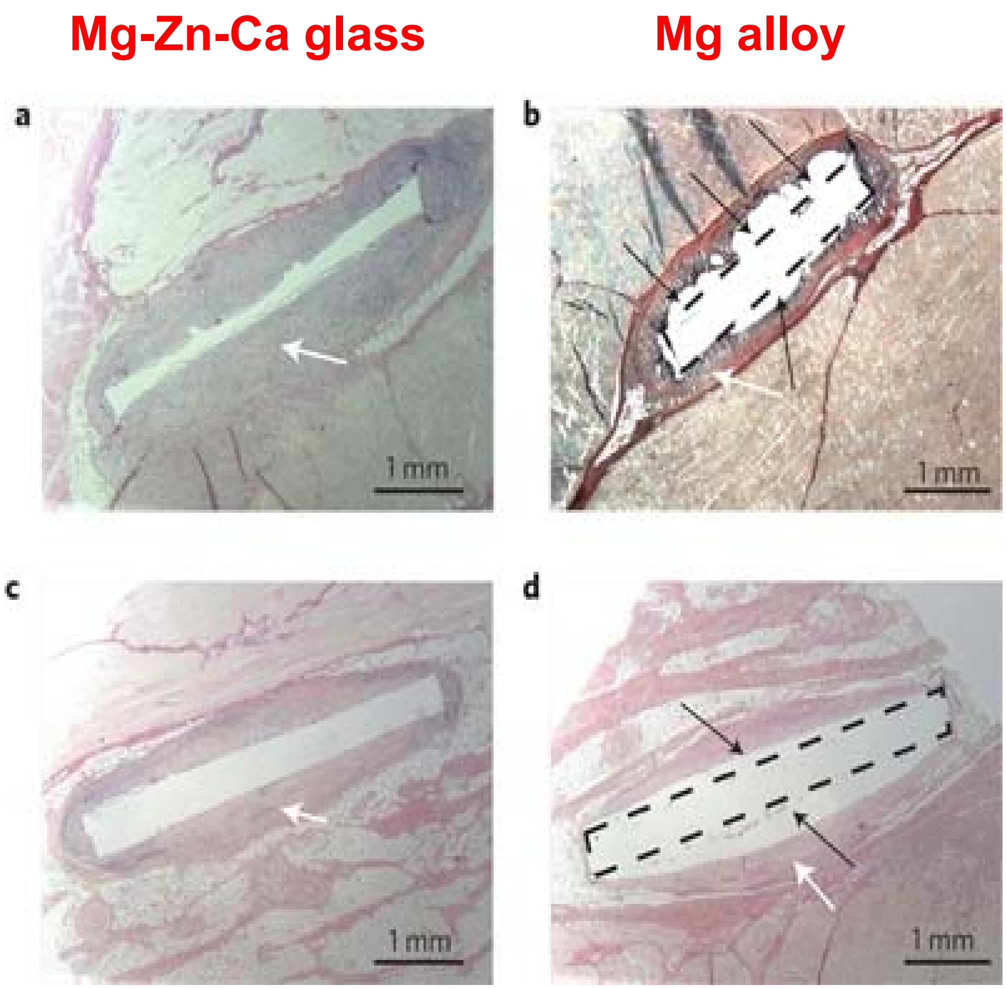
Low magnification

High magnification

A notably biocompatible amorphous metal: biodegradable Mg-Zn-Ca glass without clinically observable hydrogen evolution

Glassy $Mg_{60}Zn_{35}Ca_5$ (a,c) and crystalline Mg alloy (b,d) in two types of porcine abdominal tissue (muscle after 27 days (a,b) and subcutis after 91 days (c,d)).

All samples show a typical fibrous capsule foreign-body reaction (indicated by white arrows), but only the Mg crystalline alloy show pronounced hydrogen evolution.



Bruno Zberg et al, *Nature materials*, 8, 887, 2009.

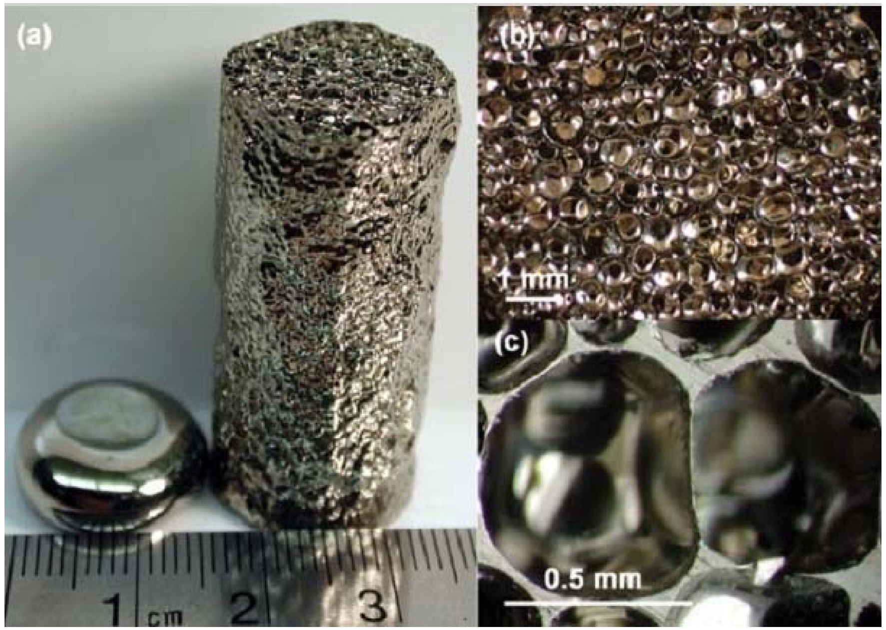
2. Which form of amorphous metals is the most suitable candidate for hard-tissue prosthesis?
→ Bulk Metallic Glass Foam (BMGF)

A current problem to restrain amorphous metals extensive use in the orthopedic industry is the large modulus mismatch (about an order of magnitude) between the Young's modulus of the BMGs implant and that of cortical bone. Fortunately, the modulus of BMGs can be modulated to match bone's modulus if BMGs foams are prepared according to

$$E_{foam} \propto \left(\frac{\rho_{foam}}{\rho_{bulk}} \right)^2$$

where E_{foam} is the Young's modulus of the foam, and ρ_{foam} and ρ_{bulk} are the density of the foam and bulk, respectively.

A Noble Example



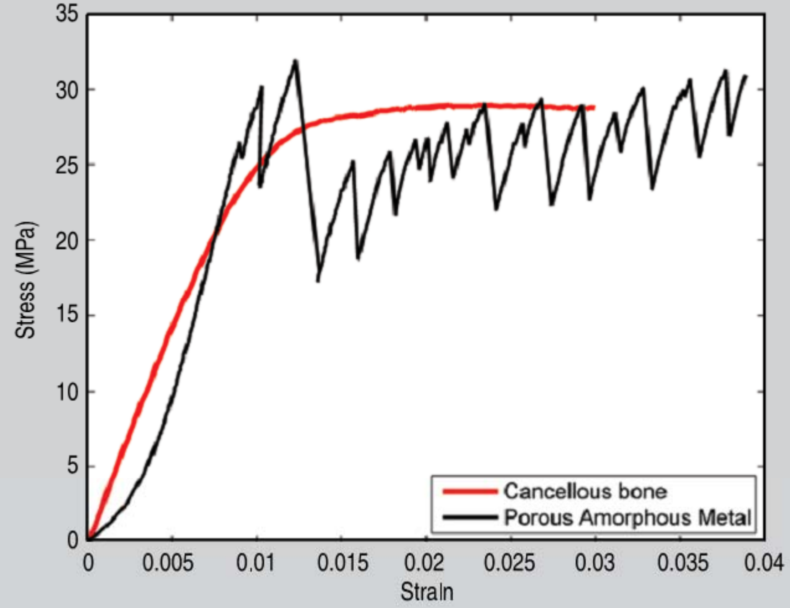


Figure 8. Compressive loading responses of amorphous Pd-Ni-Cu-P foam[51] and cancellous bone.[52]

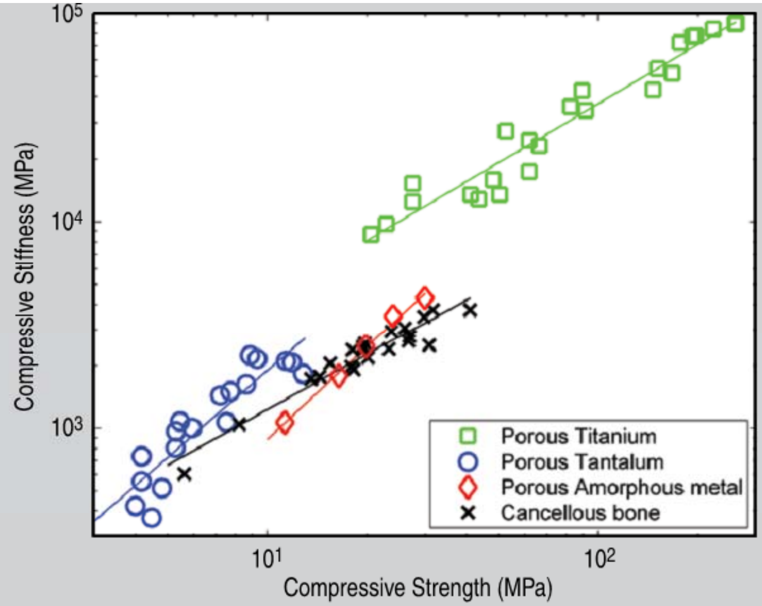


Figure 9. Compressive stiffness vs. strength data for amorphous Pd-Ni-Cu-P foam[51] shown together with data for porous Ti,[53] porous Ta,[54] and cancellous bone.[52]

Amorphous Pd-Ni-Cu-P foam (88% porosity)

Demetriou MD et al

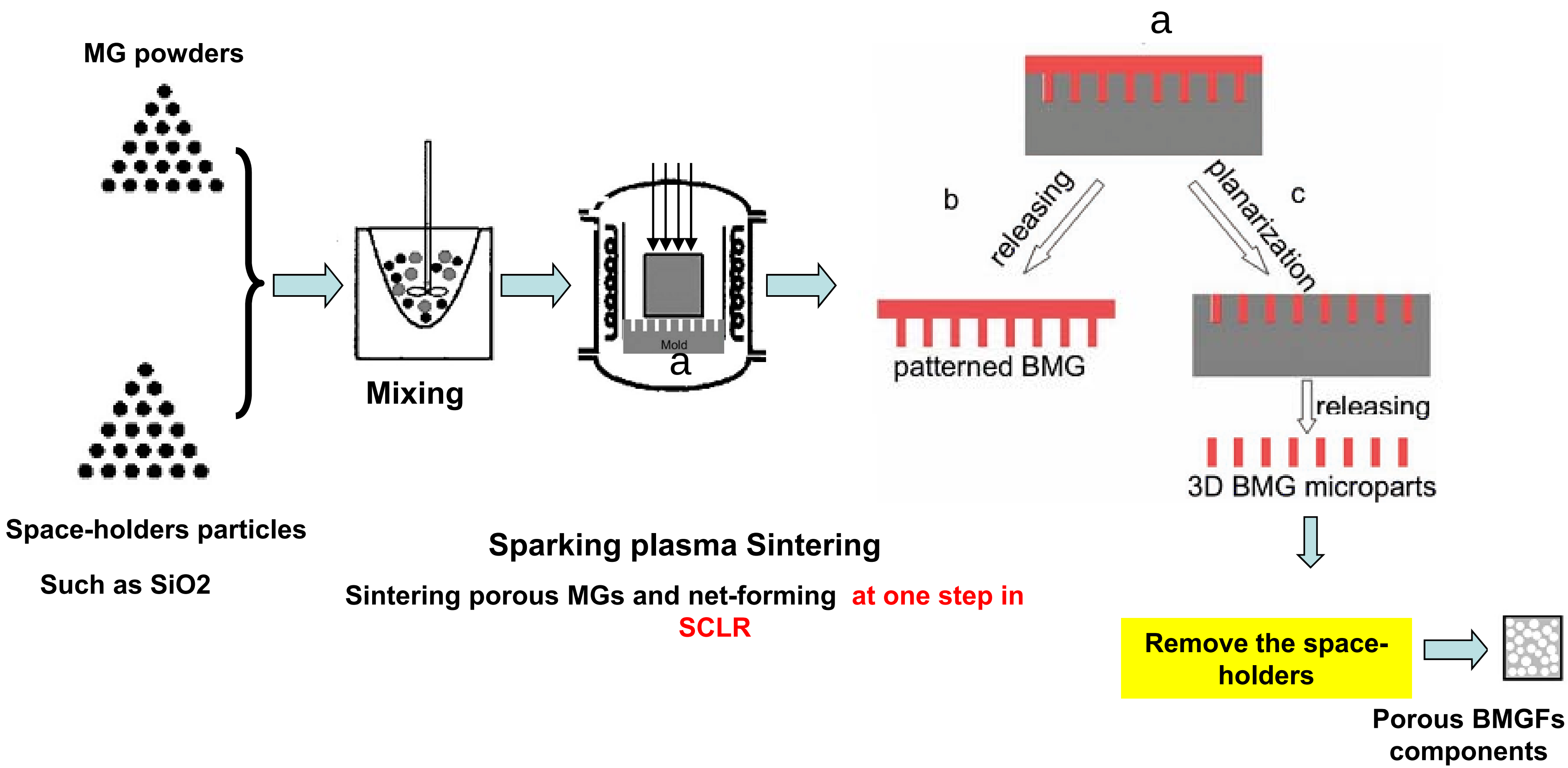
PHYSICAL REVIEW LETTERS, 101, 145702 (2008)

3. What are the problems of the current BMGFs?

1. The most viable method to prepare BMGFs with highly mechanical performance is to quench the mixture of high glass forming ability (GFA) MG forming alloy melts and gas-releasing agents. To achieve high GFA, the addition of Ni, Cu, Al, Co is inevitable for Zr-, Fe- and Noble metal-base BMGs. This action will weaken the BMGs' biocompatibility. In addition, a closed-cell structure is usually fabricated.
2. To fabricate open-cell BMGFS, space-holders with high volume fractions is needed to mix with the melts, and this will reduce the GFA of the alloys by lowering heat conductivity of the melts. Thus, the size of BMGFs samples is limited. The final shape could not be controlled.
3. The existence of pores makes the fabrication the BMGFs to final component more difficult. By pressing way, most of pores will decrease their sizes or even eliminate.

4. How to solve the dilemma?

A newly designed way is proposed in this study.



Tentative trials

$$Zr, Ti + SiO_2 \xrightarrow{SPS} Composite \xrightarrow{Etching} Porous\ BMG$$

$$Mg + Polystyrene \xrightarrow{SPS} Composite \xrightarrow{Etching} Porous\ BMG$$

$$Mg + Ti + Polystyrene \xrightarrow{SPS} Composite \xrightarrow{Etching} Porous\ BMGCF$$

$$Zr, Ti\ alloy\ ingot + NaCl\ (or\ KBr)\ Precursor \xrightarrow{Suction\ (or\ Infiltration)}$$

$$Bulk \xrightarrow{Solution} Porous\ BMG$$

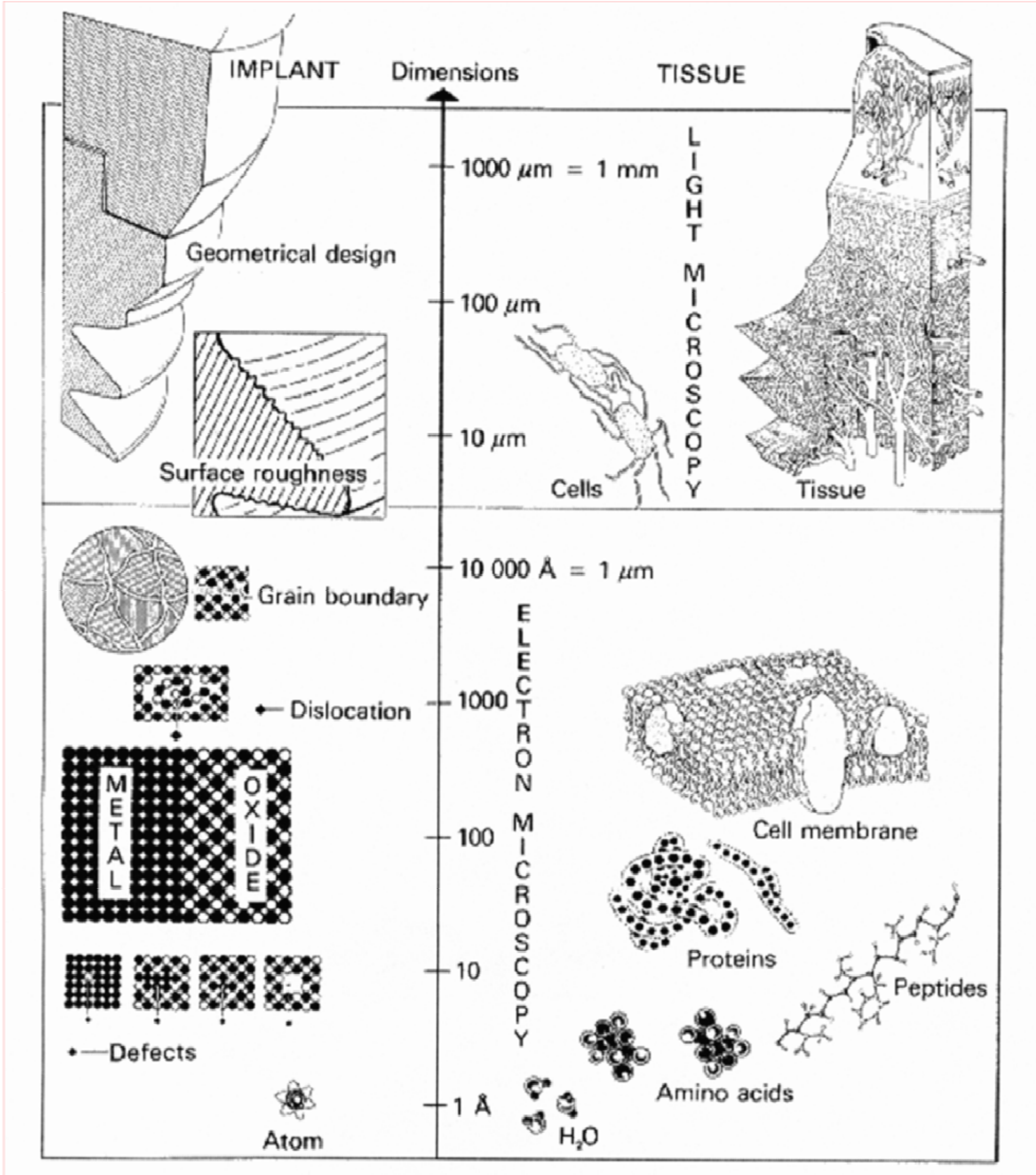
$$Mg + Graphite \xrightarrow{SPS} Composite \xrightarrow{Ultrasound} Porous\ BMG$$

$$MgZnCa\ (+Ceramic) \longrightarrow BMG\ (BMGCF)$$

On the **pore size**

For bio-implant:
1-500 µm

For catalyst support, fluid filters, damping buffer, etc:
10 nm to 10 µm



Metallic glass powders

- **Melt spinning glassy foil → rolled crack amorphous pieces**
- **Spray forming → sprayed amorphous powders**
- **Ball milling → amorphous powders**

Powder size can vary from

50 nm up to 100 μm.

5. The focus of this proposal

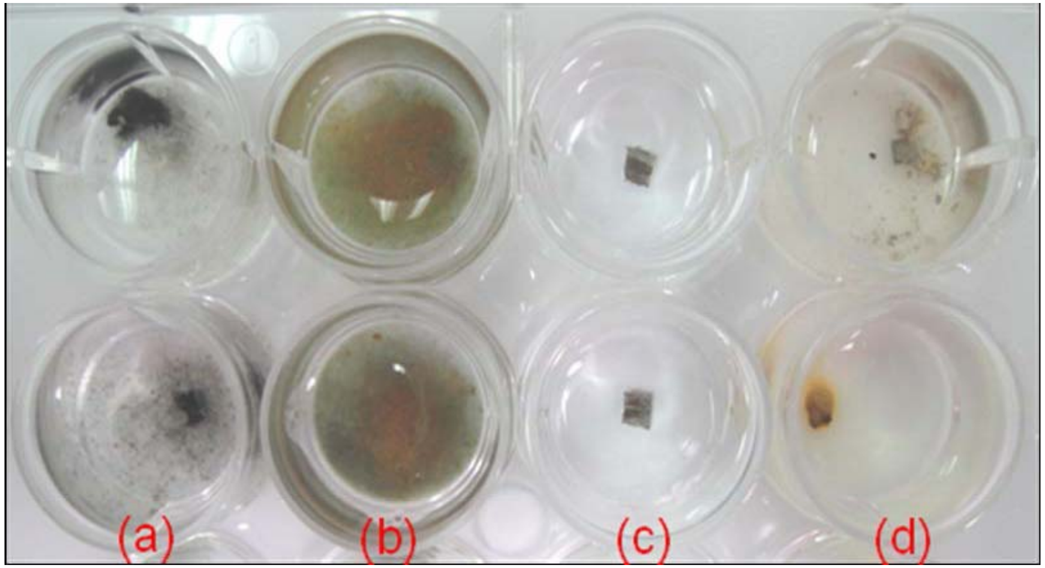
1. To design new amorphous metals with highly biocompatibility. Here, Zr-, Ti-, Mg-, Fe- base BMGFs which are free or minimum of Ni, Cu, Al, Co, Cr, Be elements.
2. To successfully fabricate the high-performance biomedical subject of BMGFs by one route.
3. To evaluate the mechanical properties, such as elasticity, hardness, toughness, etc, and to establish the relationship between the mechanical properties with the porous structure. Here, a mathematic model should be constructed to obtain optimal mechanical properties to match the properties of bones.
4. To study the biological compatibility of the resultant BMGFs, including *in-vitro* and *in-vivo* investigations.

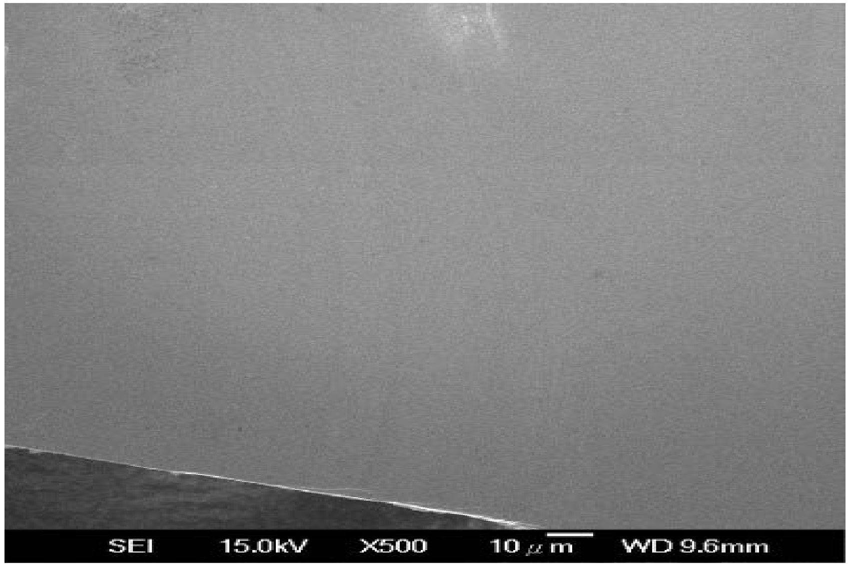
6. Purpose of this research plan and expected results

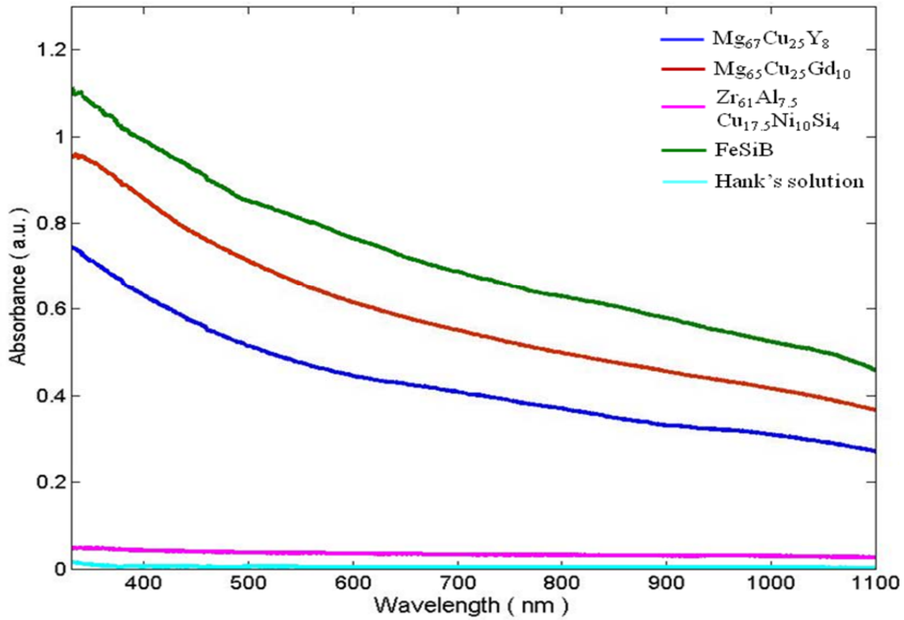
To produce mechanically matched BMGFs biomedical subjects with suitable bone-resembling structures, including high porosity, high interconnectivity and spherical pore shapes.

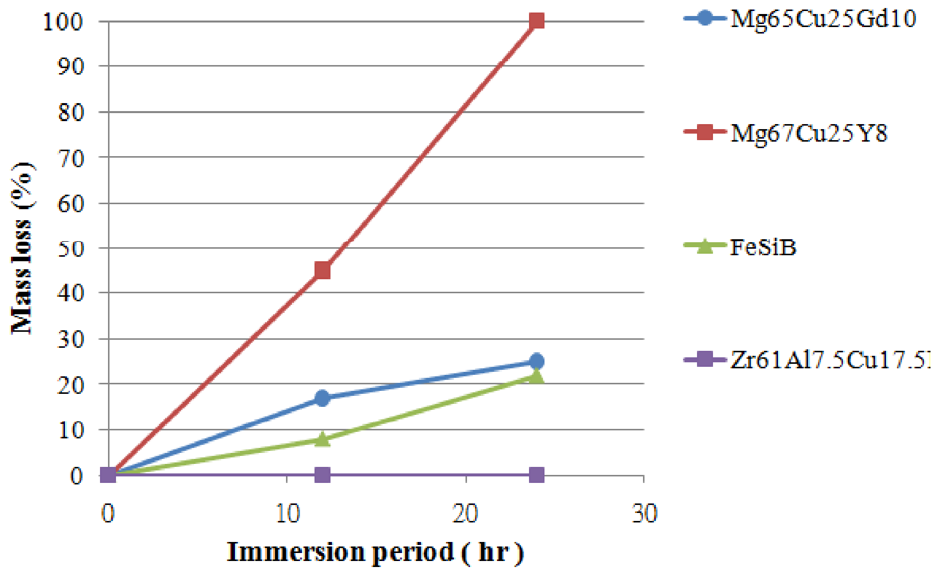
The potential applications of the resultant BMGFs are in the fields of hard-tissue prosthesis, chronic electrode implants, catalyst support, fluid filters, and so on.

Preliminary in vitro test

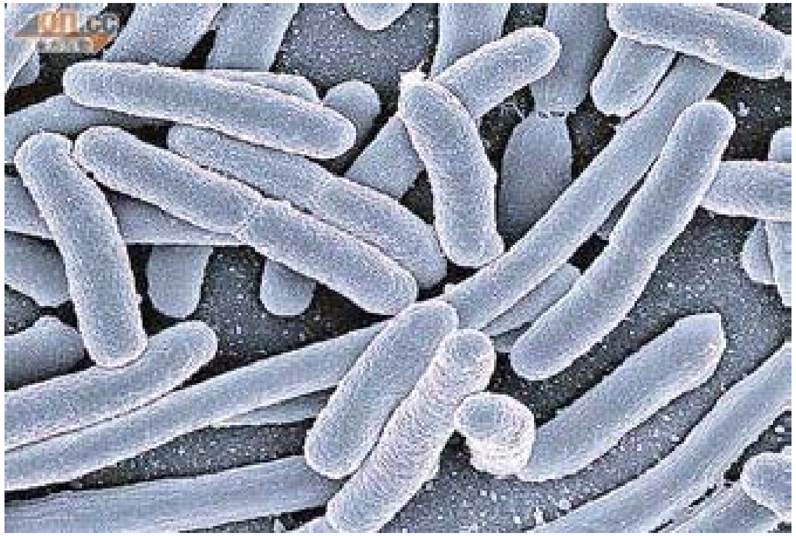


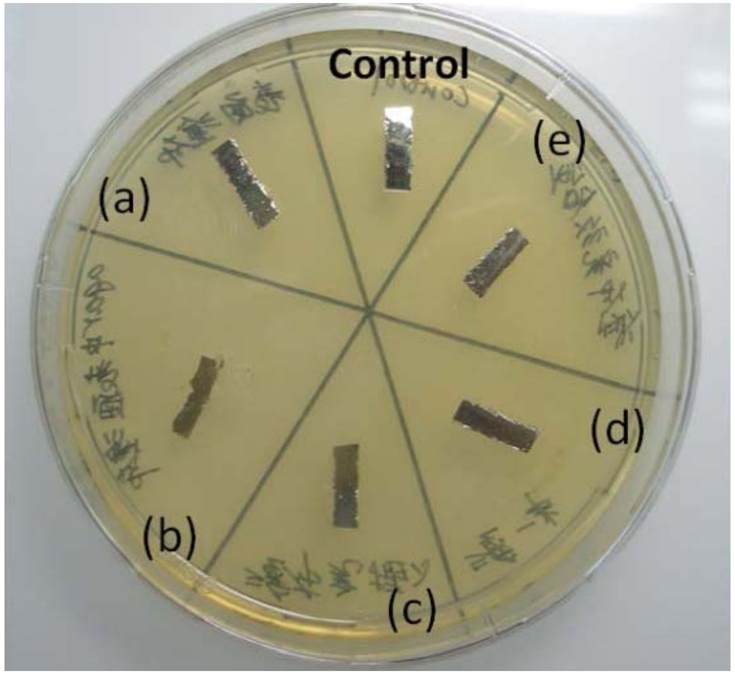


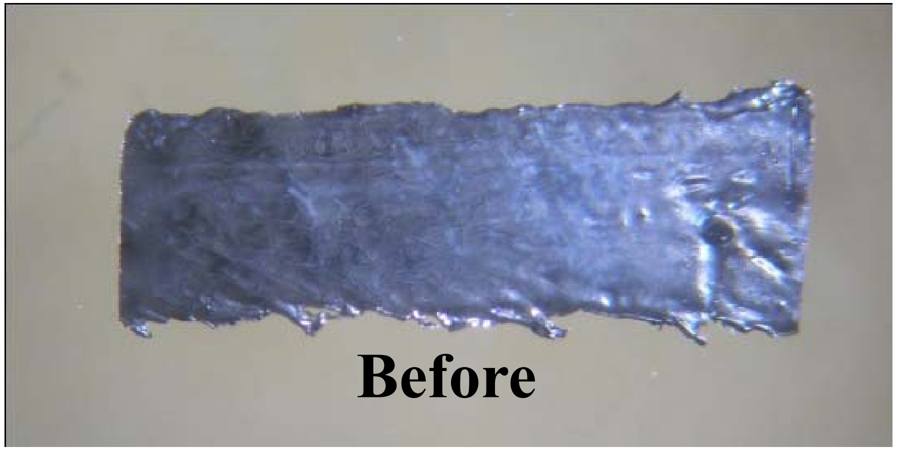


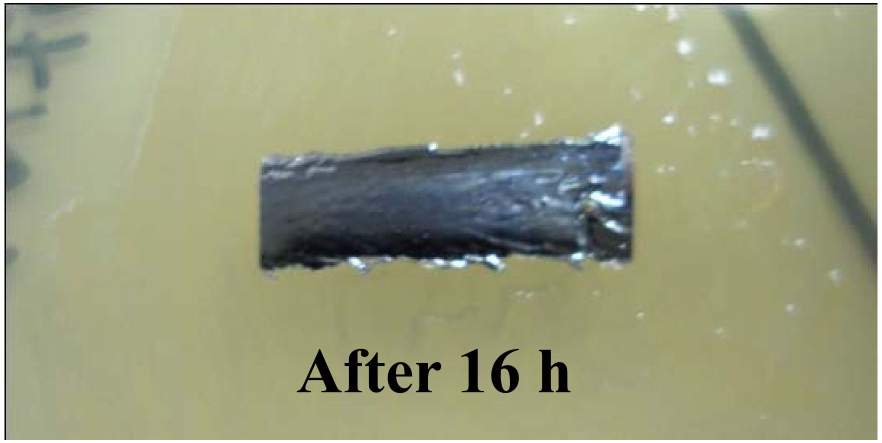


BMG alloy: ZrAlCuNiSi In vitro test (*E.coli*)









MD simulation and Density functional theory, DFT)

- First use DFT on the absorption of protein or related cell molecules on the Mg-Zn-Ca or other metallic glasses
- By force-matching to establish potentials for multiple elements
- MD simulation on biocompatibility