FS 2024/25

MSE-422 – Advanced Metallurgy

9-High Entropy Alloys and Bulk Metallic Glasses

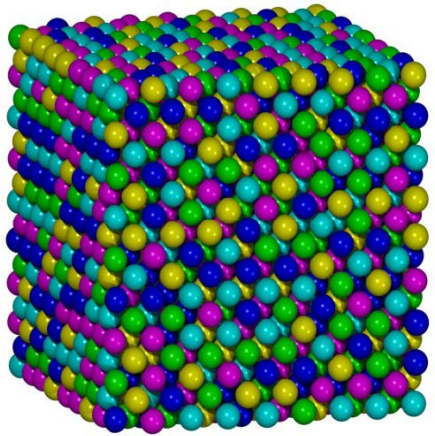
Christian Leinenbach

Multicomponent alloying strategies

- Traditional alloy limitations
  - Conventional alloys rely on a single dominant element (e.g., Fe in steel, Al in aluminum alloys) with minor additions to improve specific properties
  - This approach limits enhancements in strength, corrosion resistance, and thermal stability, as adding more elements often causes phase separation or brittleness
- Inspiration for multicomponent alloy development
  - Researchers began exploring multi-element systems to achieve unique properties through interactions among multiple elements
  - Advances in thermodynamic/kinetic and atomistic modeling and simulation in the 1980s and 90s revealed that multicomponent alloys could form stable solution phases under certain conditions
  - Discovery of bulk metallic glasses (e.g., Zr-Ti-Cu-Ni-Be), which avoid crystallization due to high complexity and sluggish crystallization kinetics, paving the way for high-performance materials

Some basic facts about Medium/High Entropy Alloys

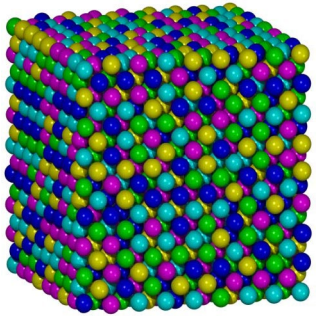
- **Terminology:** High/Medium Entropy Alloys (HEA, MEA); Multiple Principal Element Alloys (MPEAs) or Complex Concentrated Alloys (CCAs)
- **Characteristics:** alloys with 3-4 (MEAs) or 5 or more (HEAs) elements in near-equimolar ratios, without a primary or matrix element
- **Research timeline:** HEAs were theorized in the 1980s, but major research began post-2004 with initial successful syntheses
- **Unexpected phase behavior:** although Gibbs' phase rule suggests multiple phases, M/HEAs typically form single solid-solution phases instead of intermetallics
- **Solid-solution characteristics:** in classical metallurgy, a solid solution has a main solvent element and minor solutes. In M/HEAs, near-equimolar compositions make it difficult to distinguish solvent from solute



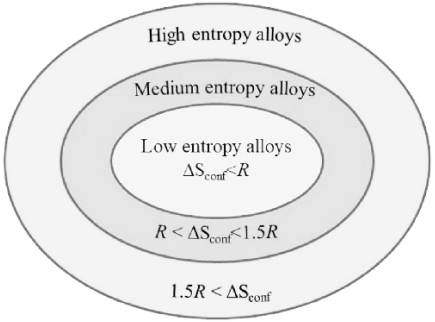
/S. Wang, Entropy 15(12) (2013) 5536–5548/

Medium/High Entropy Alloys - definitions

- Composition-based definition
  - HEAs: n ≥ 5 components in near-equimolar ratios or each element between 5-35 at.%
  - MEAs: 3-4 principal elements in significant, often near-equimolar ratios
- Entropy-based definition
  - HEAs: molar entropy of mixing > 1.5R ($R = N_a k = 8.314\ J \cdot K^{-1} \cdot mol^{-1}$)
  - MEAs: intermediate configurational entropy, typically between 1R and 1.5R
- Microstructure-based definition
  - HEAs: typically form single-phase solid solutions with high-symmetry structures (bcc, fcc, or hcp)
  - MEAs: may form single-phase solid solutions (fcc, bcc, (hcp)) but can also exhibit more complex phases due to simpler composition



/S. Wang, Entropy 15(12) (2013) 5536–5548/



Basic thermodynamic considerations for HEAs

Entropy and enthalpy in multi-component alloys

- Ideal mixing: $\Delta G^{mix} = \Delta H^{mix} - T\Delta S^{mix}$
- The entropy of mixing of an ideal mixture given by

$$\Delta S^{mix} = -R \sum x_i ln x_i$$

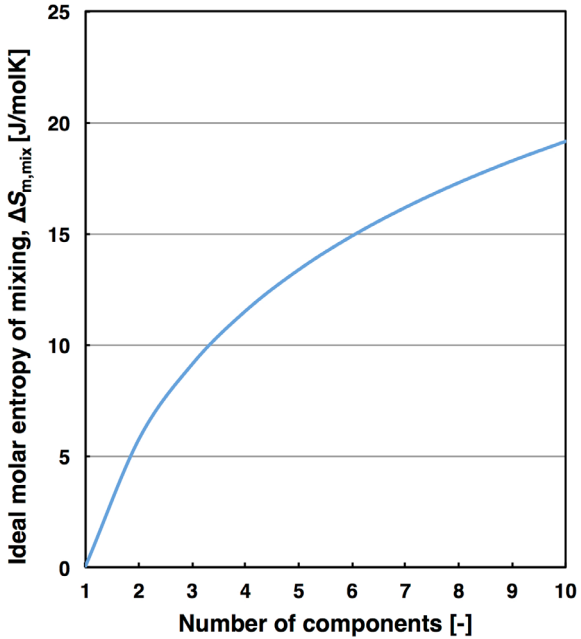
- For the sake of simplicity, consider an alloy with N components in equimolar concentration ($x_1 = x_2 = \ldots = x_N$)

$$\sum_{i=1}^{N} x_i = x_1 + x_2 + \cdots + x_N = 1 \rightarrow x_i = \frac{1}{N}$$

- The molar entropy of mixing is:

$$\Delta S^{mix} = -RN\left(\frac{1}{N} ln \frac{1}{N}\right) = -RN \frac{1}{N} lnN = -RlnN$$

- For combinations with concentrations for each component between 5 and 35 at.-pct. (i.e. the wide definition) the entropy of mixing is slightly less



Basic thermodynamic considerations for HEAs

Entropy and enthalpy in multi-component alloys

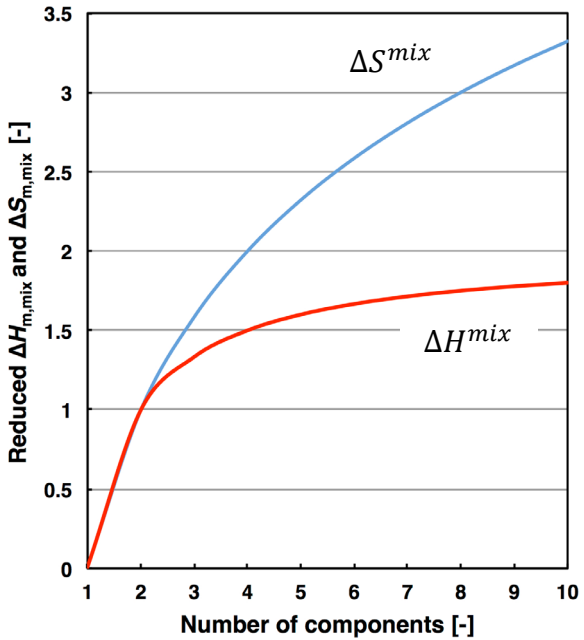
- The molar enthalpy of mixing of the same equiatomic alloy is given in the framework of the regular solution model as

$$\Delta H^{mix} = \sum_{i=1}^{N-1} \sum_{j>1}^{N} x_i x_j \Omega_{ij} = \sum_{i=1}^{N-1} \sum_{j>1}^{N} \frac{1}{N^2} \Omega_{ij}$$

- Consider $\Omega_{ij} = const. = \Omega$; then ΔH^{mix} can be written as

$$\Delta H^{mix} = \Omega \frac{N(N-1)}{2N^2} = \frac{1}{2}\Omega\left(1 - \frac{1}{N}\right)$$

- For equimolar compositions and $N \to \infty$, ΔH^{mix} roughly doubles, while the increase in ΔS^{mix} is much more pronounced (with regard to the values of a binary alloy)



Normalization is done with regard to the values of a binary system.

Stability criteria for HEAs

- Not all 4+ or 5+ element alloys with (near-)equiatomic compositions can form M/HEAs
- Based on an empirical study, the following stability criteria for HEAs were proposed
  1) **Entropy of mixing** (ΔS^{mix}) must be maximized
  2) **Enthalpy of mixing** (ΔH^{mix}) between -10 and 5 kJ/mol
  3) **Valence Electron Concentration** (VEC)
     >8 for fcc and <6.87 for bcc
  4) **Size mismatch** of the atomic radii δ ≤ 6.6%

$$\delta[\%] = 100\sqrt{\sum_i c_i(1-\frac{r_i}{\bar{r}})^2} \text{ with } \bar{r} = \sum_i c_i r_i$$

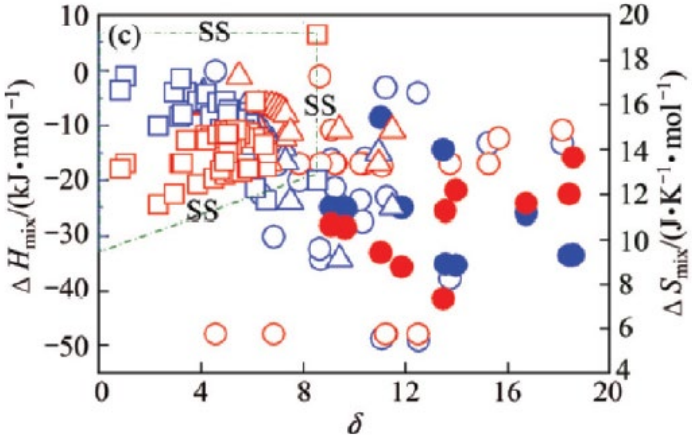
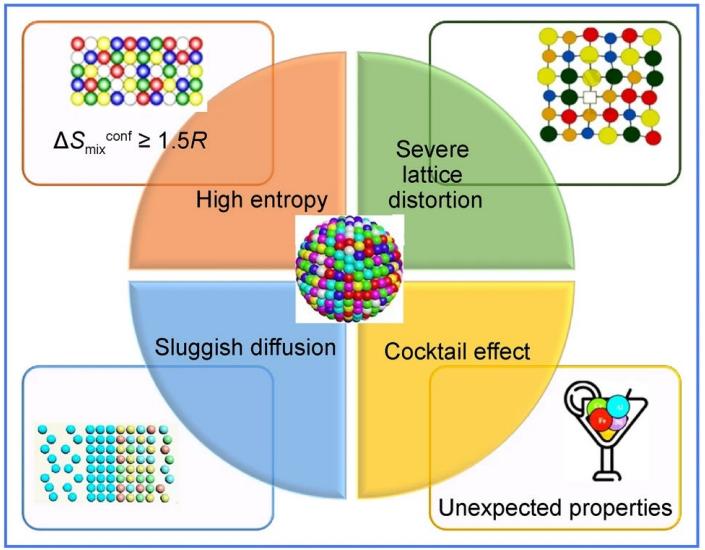


Fig. 2 Superimposed effect of ΔH_{mix} and δ (a), ΔS_{mix} and δ (b), and all three parameters ΔH_{mix}, δ and ΔS_{mix} (c) on phase stability in equiatomic multi-component alloys and BMGs. The symbol ○ represents equiatomic amorphous phase forming alloys; ● represents non-equiatomic amorphous phase forming alloys; □ represents solid solution phases and △ represents intermetallic phases. The region delineated by the dash-dotted lines in (c) indicates the requirements for solid solution phases to form.

/S. Guo, C.T. Liu, Prog. Natur. Sci. Mater Int. 21 (2011) /

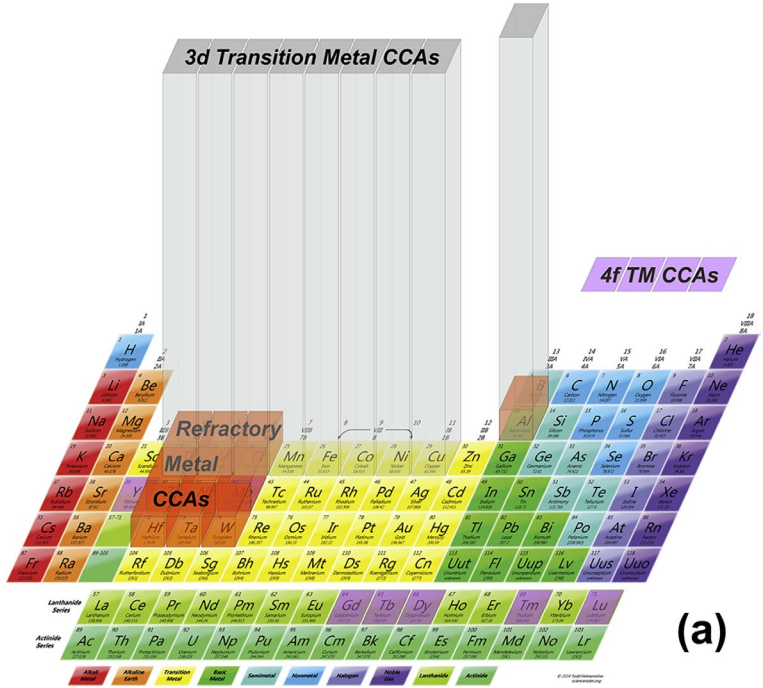
Main high entropy effects

- **Thermodynamics:** High entropy favors solid-solution phases over ordered intermetallics, which have low or zero configurational entropy
- **Kinetics:** HEAs show sluggish diffusion due to an inhomogeneous bonding energy landscape, with varying bond strengths that increase activation energy for atomic movement, enhancing high-temperature stability
- **Structures:** Severe lattice distortion occurs as elements occupy lattice sites randomly, causing lattice strain due to differences in atomic radii and enhancing mechanical strength
- **Properties:** The “cocktail effect” leads to unique properties in HEAs, such as improved hardness, corrosion resistance, and thermal stability, often unattainable in single-element materials



Classes of HEAs

- Various classes of HEAs have been identified, with six main classes studied so far
  1) 3d transition metal-based HEAs with fcc structure: typically include metals like Co, Cu, Fe, Ni, Mn, and Cr, with additions of elements like Al, Mo, or Ti.
  2) Refractory HEAs with bcc structure: composed of early transition metals from the first, second, and third long periods (Ti, V, Zr, Nb, Mo, Hf, Ta, W).
  3) Rare earth HEAs with hcp structure: based on elements like Gd, Tb, Dy, Tm, and Lu.



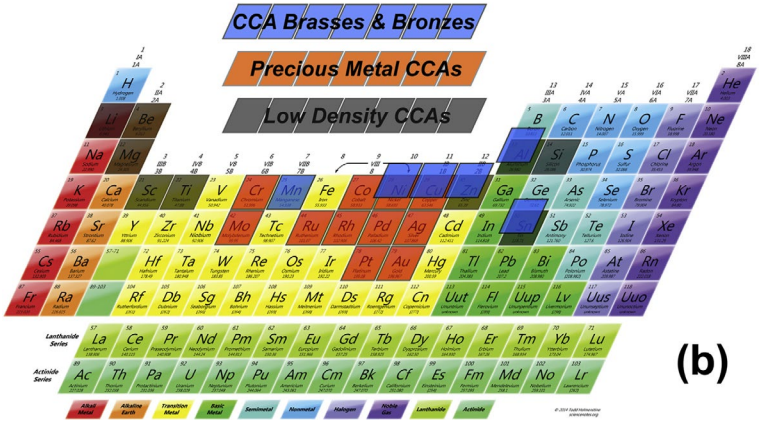
/Miracle & Senkov, Acta Materialia 122 (2017) 448-511/

Classes of HEAs

4) Light metal-based HEAs:
alloys like LiBeMgScTiAl, but challenging to process due to high reactivity with oxygen.

5) Copper alloy HEAs:
based on existing Cu alloys (bronzes and brasses) by creating a Cu, Ni, Mn solid solution.

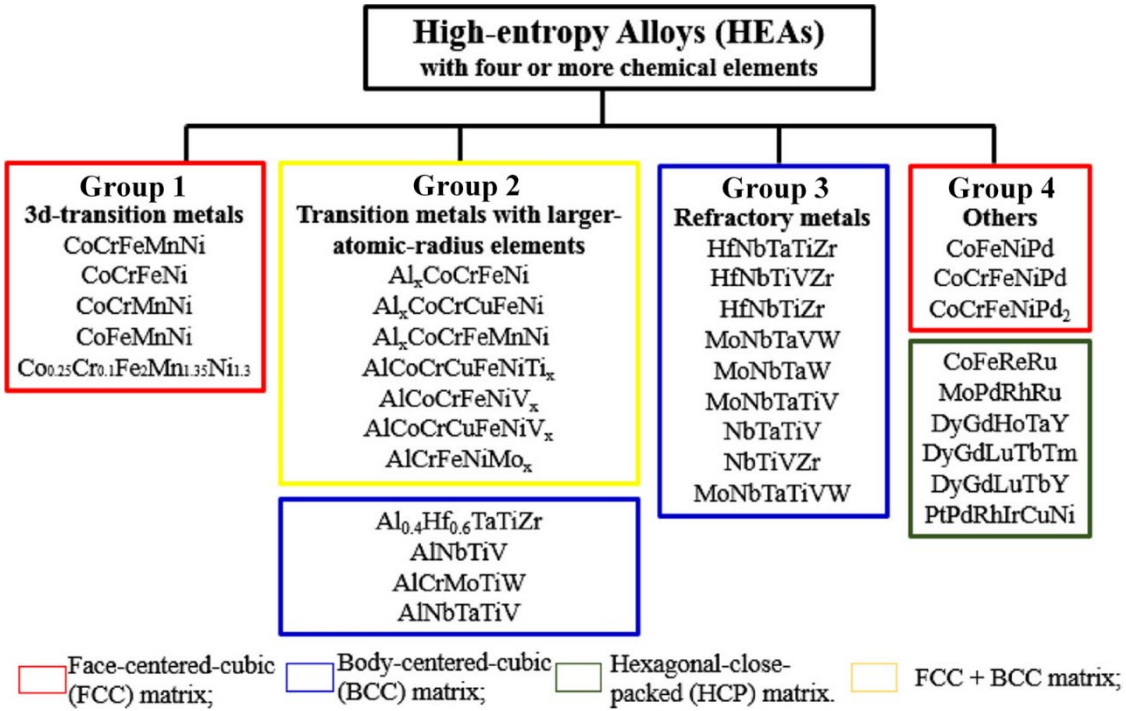
6) Precious metal HEAs:
alloys of RhPdAgPtAu, sometimes with Cr or Mo, typically forming an fcc lattice



(b)

/Miracle & Senkov, Acta Materialia 122 (2017) 448-511/

Classes of HEAs

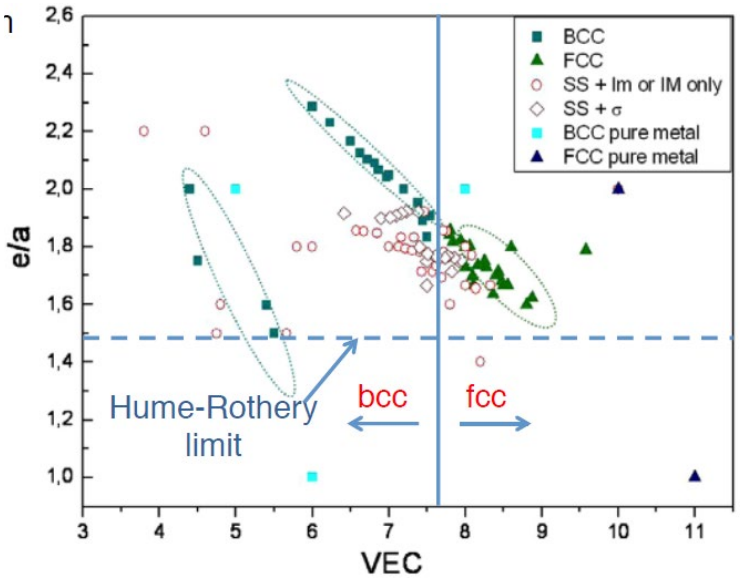


/H.Y. Diao et al., Curr. Opin. Solid State Mater. Sci. 2017/

HEAs with fcc structure

Influence of electron concentration on HEAs

- Composition and Tuning:
  - HEAs based on CoCuFeNiCr + Al are studied for their unique properties.
  - Al addition reduces VEC and raises conduction electron concentration (e/a), affecting structure and properties.
- Phase Transition with Al Content:
  - Low Al (high VEC): FCC structure, offering higher ductility.
  - High Al (low VEC): Transitions to BCC, enhancing strength but reducing ductility.
- Critical VEC for Transition:
  - FCC to BCC transition occurs around VEC ≈ 7.5, similar to pure metals' phase shifts.

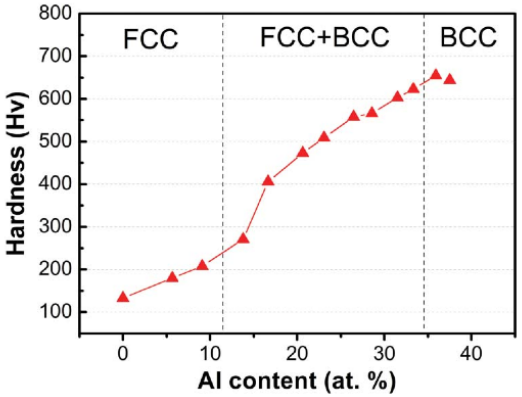


/M.G. Poletti, L. Battezzati / Acta Materialia 75 (2014) 297–306/

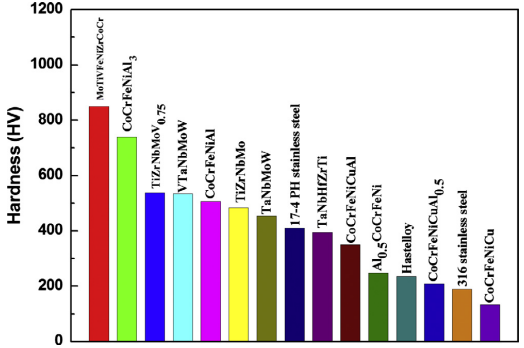
HEAs with fcc structure

Influence of crystal structure on hardness

- Hardness significantly increases when transitioning from the fcc to the bcc phase
- In TM-HEAs (transition metal HEAs like Cr, Fe, Co, Ni, Cu, Mn), the fcc phase resembles austenite in stainless steel, providing softness and ductility
- The bcc structure has fewer slip systems, resulting in higher hardness compared to the fcc phase
- HEA hardness varies widely based on composition and crystal structure, enabling tailored properties for specific applications



/M.H. Tsai and J.W. Yeh, Mater. Res. Lett. 2 (2014) 107-123/

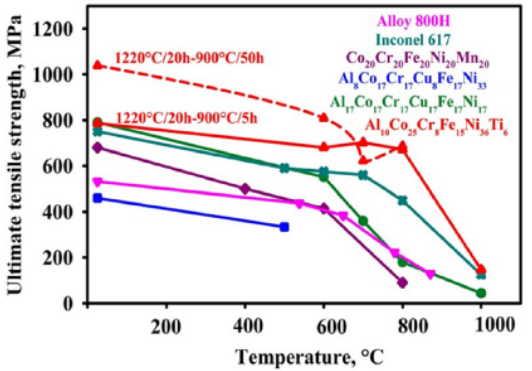


/Y. Zhang et al., Prog. Mater. Sci 61 (2014) 1–93/

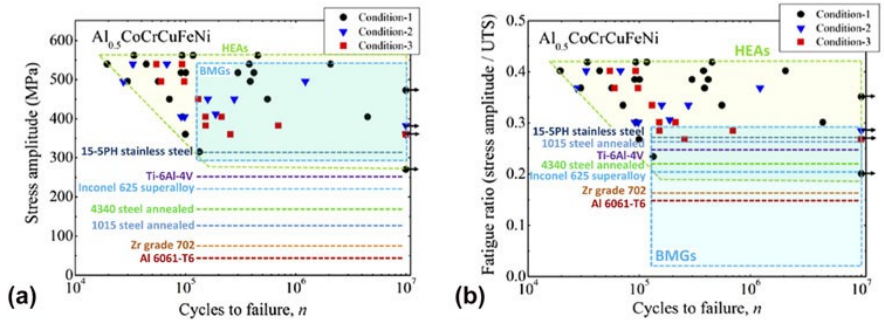
HEAs with fcc structure

Mechanical properties of HEAs

- Very good temperature stability:
  - HEAs maintain high strength across a wide temperature range, often outperforming conventional alloys in high-temperature applications
- High fatigue resistance:
  - HEAs demonstrate superior resistance to cyclic loading
- Balanced strength and ductility:
  - HEAs provide a unique combination of high strength and good ductility
- Tunable properties for specific applications:
  - Different HEA compositions can be optimized for targeted performance, from wear resistance to fatigue life, through ongoing R&D.



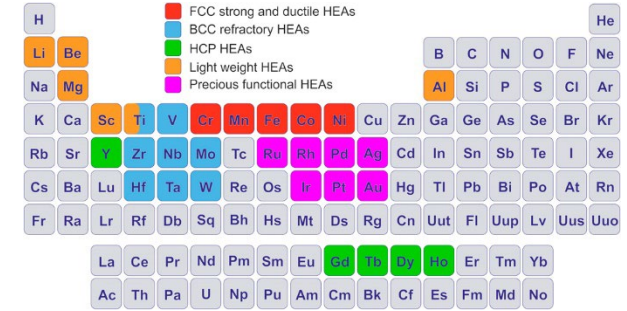
O. Senkov et al. Intermetallics 18 (2010) 1758-1765

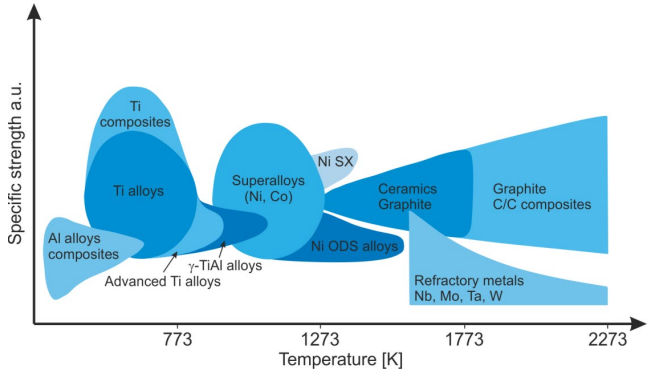


/W. Li et al. J. Mater. Res. 33(19) (2018) 3011-3034/

Refractory HEAs with bcc structure

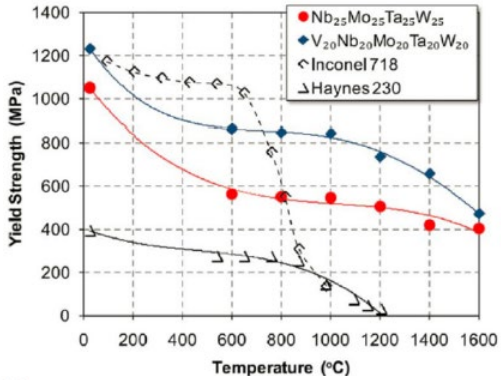
- Around 2010, HEA research shifted toward refractory elements (Nb, Ta, Mo, W, Hf) for their high melting points and thermal stability
- Early alloys such as MoNbTaW and HfNbTaTiZr showed promising high-temperature performance
- Driven by aerospace and nuclear needs, refractory HEAs became a key topic, focusing on strength, oxidation resistance, and phase stability at elevated temperatures

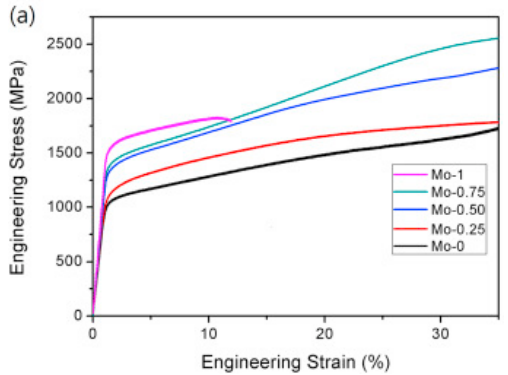




Refractory HEAs with bcc structure

- R-HEAs can exhibit exceptional strength at high temperatures, ideal for extreme environments
- Unlike many bcc metals and alloys, R-HEAs are both strong and reasonably ductile
- MoNbTaW and HfNbMoTaTi R-HEAs are currently widely investigated because of their balanced properties
- Increasing Mo increases strength but reduces ductility, allowing tailored properties
- Maintaining stable protective oxide layers is crucial for high-temperature oxidation resistance
- Efforts focus on reducing heavy elements (W, Ta) to lower density, aiming to make R-HEAs competitive with Ni-based superalloys in aerospace

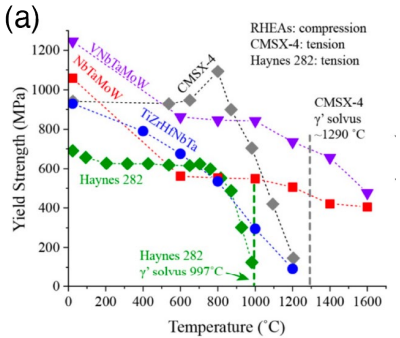




O. Senkov et al. Intermetallics 18 (2010) 1758-1765

Refractory HEAs with bcc structure

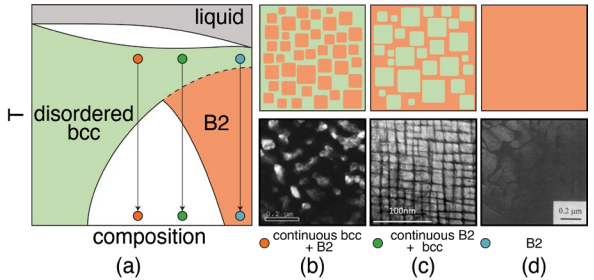
- Single-phase refractory HEAs still underperform compared to two-phase Ni-based superalloys (e.g., CMSX-4)
- There is a strength-ductility trade-off:
  - Ductile alloys (e.g., TiZrHfNbTa) lack sufficient strength
  - Stronger alloys (e.g., VNbTaMoW) are too brittle for practical use
- Single-phase disordered alloys show poor creep resistance at high temperature
  - Example: TiZrHfNbTa creeps >100× faster than CMSX-4 under similar conditions and even faster than the CMSX-4 matrix alone
- To enable high-temperature applications, creep strength of the matrix must be improved and strengthening precipitates introduced (analogous to Ni-superalloys)



Current research trends for HEAs

Two-phase HEAs

- Adding Ru to RMPEAs can form stable B2 intermetallics with Ti, Zr, and Hf inside a disordered BCC matrix
- Similar ordered phases can also be formed by adding Al or Re via decomposition from a high-temperature disordered phase
- The target microstructure is a continuous BCC matrix with a dense, fine, coherent B2 precipitate distribution
- Microstructure depends on cooling path:
  - Fine B2 precipitates in a BCC matrix (desired strengthening)
  - Inverse structure (BCC inclusions in B2 – too brittle)
  - Fully ordered single-phase B2
- Achieving and stabilizing this microstructure through alloy design and processing is a key step toward replacing Ni-based superalloys at high temperatures

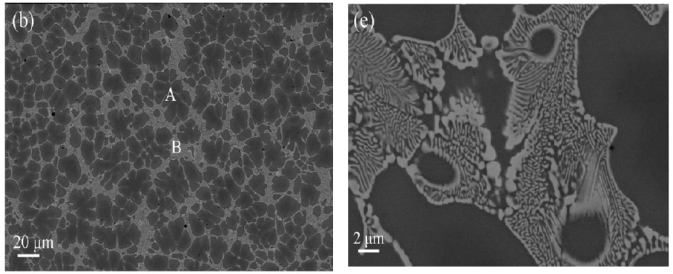


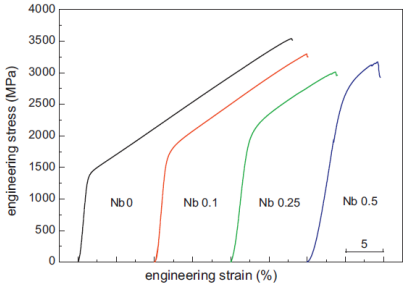
Current research trends for HEAs

Two-phase HEAs

- Development of fcc HEAs with secondary phases for further strengthening
- Development of fcc HEAs with low stacking fault energy and TRIP/TWIP effect

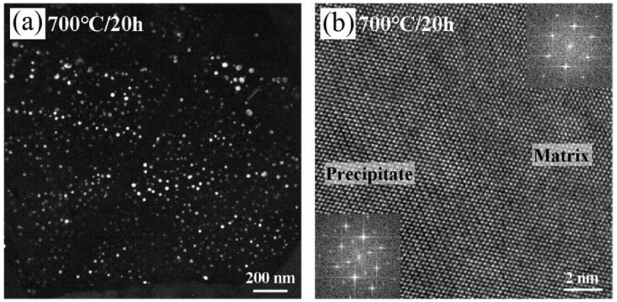
Two-phase eutectic in a $AlCoCrFeNb_xNi$ HEA

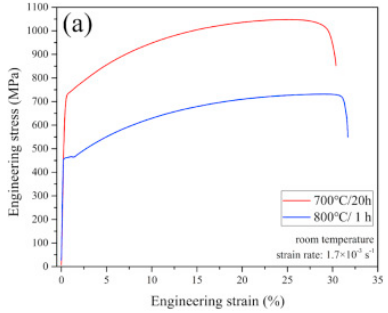




/S.G. Ma, Y. Zhang et al., MSEA A 532 (2012) 480–486/

Coherent precipitates in a $Al_{0.2}CrFeCoNi_2Cu_{0.2}$ HEA



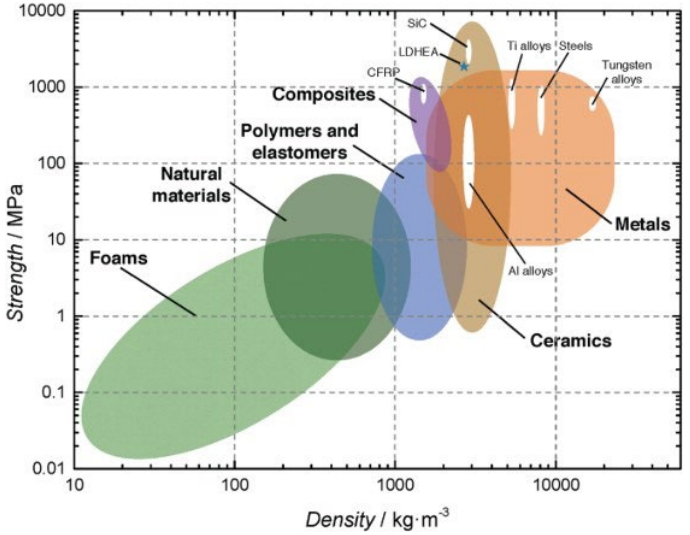


/Y. Zhang et al., Prog. Mater. Sci 61 (2014) 1–93/

Current research trends for HEAs

High-strength low-density HEAs

- Extremely high strength has been obtained in a low-density HEA with the composition $Al_{20}Li_{20}Mg_{10}Sc_{20}Ti_{30}$
- Due to the large difference in melting temperature of the constituents, such HEAs have been so far produced by powder metallurgy
- A problem is its high affinity to oxygen of these elements, that leads to significant oxygen pick-up during processing
- The alloys are typically also not single phase, but tend to be mixtures of solid solutions and intermetallics

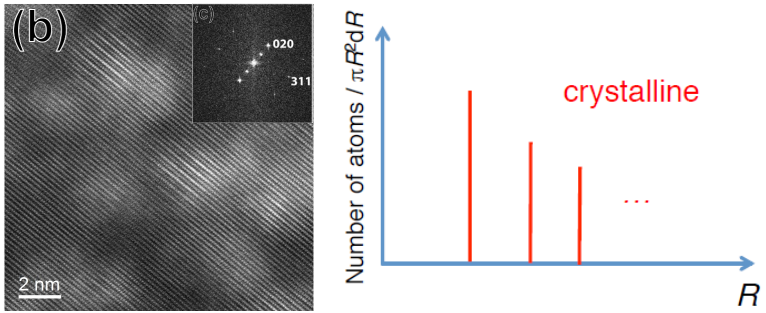


/K.M. Youssef et al. Mat. Res. Letters 3 (2015) 95-99/

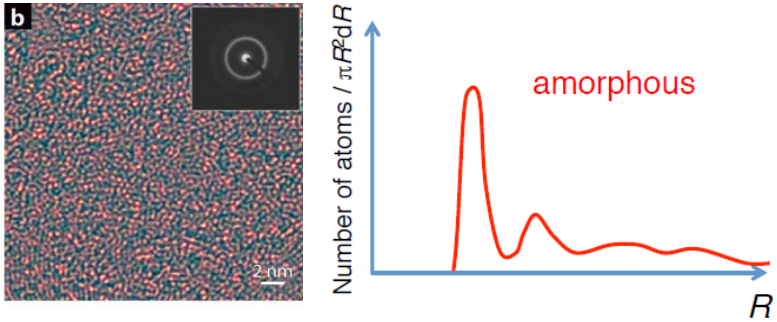
Crystalline vs. amorphous alloys

- As metals cool from high temperatures to 0K, they transition from gas to liquid to solid, decreasing entropy and increasing bonding energy (enthalpy decreases)
  - Condensation (Gas to Liquid): Shortens interatomic distances with variable atomic coordination
  - Solidification (Liquid to Solid): Creates a crystalline structure with long-range translational order and defined atomic coordination
  - Rapid Cooling: If cooling is too fast, atoms lack time to arrange into a crystal, resulting in a disordered or amorphous solid

Crystalline Al-Mg-Zr alloy

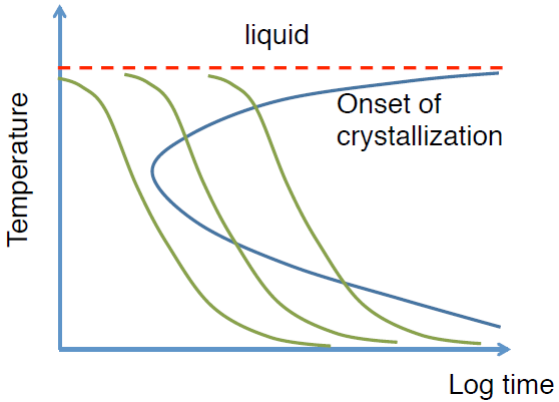


Amorphous metal



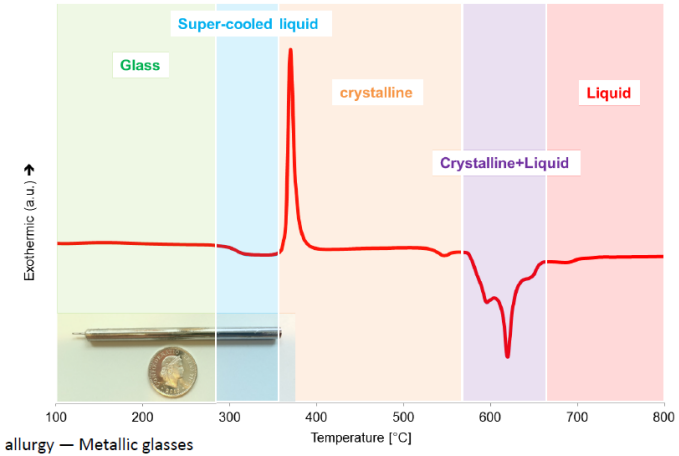
How to prevent crystallization?

- Upon cooling, nucleation and growth rates reach a maximum
  - Above the maximum: Nucleation limits crystallization due to low driving force
  - Below the maximum: Growth slows as atomic diffusion decreases
- To form a fully amorphous solid, the cooling rate must avoid crossing the “onset of crystallization” curve
- Factors influencing the “onset of crystallization curve”:
  - Free energy gain from crystallization
  - Interface energy between the nucleus and liquid
  - Atomic mobility (viscosity)
- Goal in metallic glass development: shift the “onset of crystallization” curve to the upper right, allowing more stable amorphous formation over a wider range of conditions



Amorphous metal vs. metallic glasses

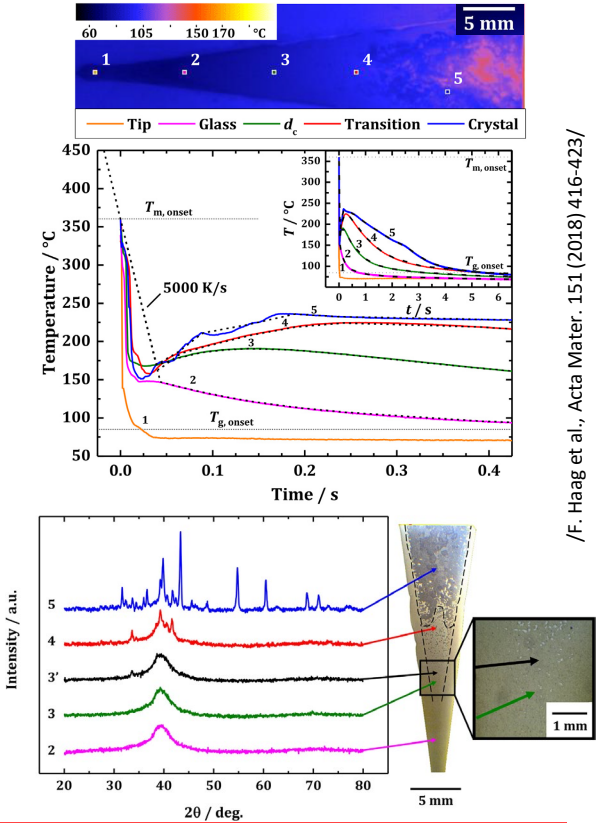
- Glassy solids are a type of amorphous solid. Upon heating, an amorphous solid crystallizes directly, while a glassy solid first undergoes a **glass transition** before crystallizing at a higher temperature.
- **Glass Transition Temperature (Tg)**: Defined where viscosity is 1013 Paxs Above Tg, viscosity decreases; below Tg, it increases.
- **Glassy Structures** are **thermodynamically metastable**, forming because crystalline kinetics are too slow during cooling from the melting temperature (Tm) to Tg.
- In **oxide glasses** and **polymers**, crystallization can take seconds to days due to structural hindrance. In **metals**, crystallization is much faster because of the isotropic metallic bonds



allurgy — Metallic glasses

Metallic glass vs. bulk metallic glass

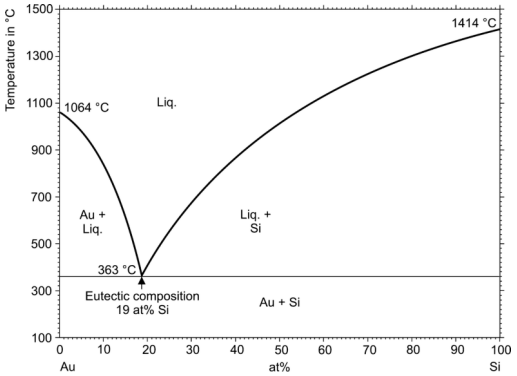
- Cooling depends on the heat transfer coefficient at the surface (h) and the thermal diffusivity (α_{th}) within the liquid.
- When h is high, the distance (x) from the surface where a certain temperature is reached follows $\sqrt{\alpha t}$.
- There is a critical thickness (d_{crit}) beyond which thermal diffusivity limits the cooling rate, affecting glass formation.
- If d_{crit} > 1 mm, the material is termed a bulk amorphous metal; if not, it is an amorphous metal.
- A bulk amorphous metal with a defined glass transition temperature is classified as a bulk metallic glass (BMG).



/F. Haag et al., Acta Mater. 151 (2018) 416-423/

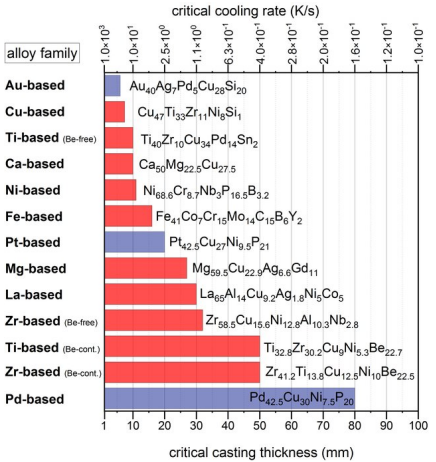
«Rules» for finding BMGs

- **High cooling rate:** rapid cooling prevents crystallization, though alloys with good glass-forming ability (GFA) can tolerate slower rates
- **Confusion principle:** requires at least three elements capable of forming different crystalline structures to enhance disorder
- **High entropy:** using multiple principal elements increases configurational entropy, discouraging crystallization
- **Eutectic composition:** alloys near eutectic points have a higher tendency to form amorphous structures
- **Negative enthalpy of mixing:** strongly negative heat of mixing between each pair of main elements reduces crystallization likelihood
- **Atomic size difference:** significant atomic size difference (more than 12%) among main constituents improves glass formation
- **T_g/T_m ratio:** a value of T_g/T_m around 0.66 stabilizes the liquid phase, aiding in glass formation (Turnbull criterion)



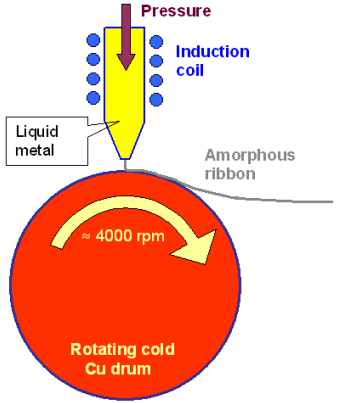
Development of BMGs

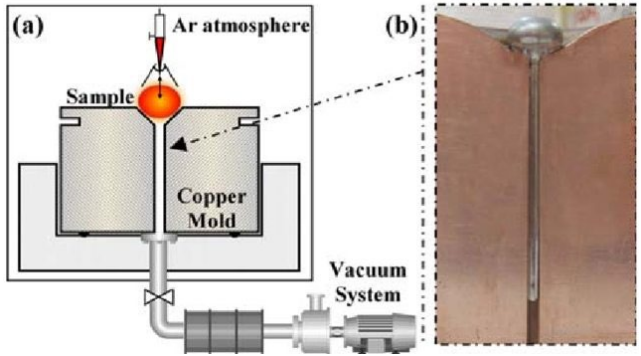
- Metallic glasses have first been studied in 1960 by Duvez at Caltech in the system Au-Si
- Bulk metallic glasses have entered the scene in the 1980's
- To date there are thousands of different alloys known to be able to be solidified as glass with $d_{crit} > 1$ mm
- The largest metallic glasses known can be solidified in more than 10 cm diameter.

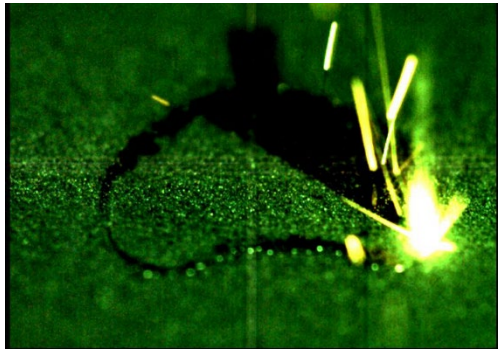


Fabrication of BMGs

- (Bulk) metallic glasses are fabricated from the melt using methods like melt spinning, splat quenching, suction copper mold casting, and laser-based additive manufacturing.
- BMGs must be produced in clean atmospheres (e.g., high-purity argon or vacuum) as they contain elements prone to react with oxygen. Oxide formation could act as crystallization sites, compromising the amorphous structure.
- Sometimes BMGs are annealed below their glass transition temperature to relieve internal stresses or modify properties. This is done carefully to avoid any risk of crystallization.



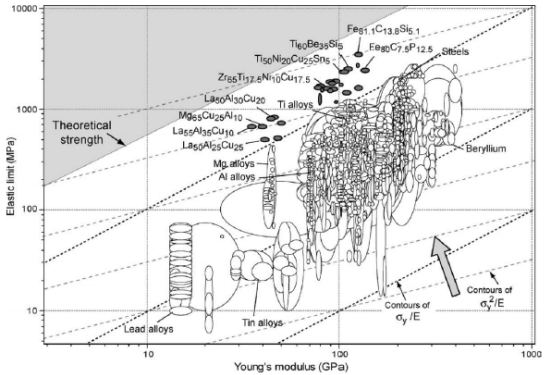


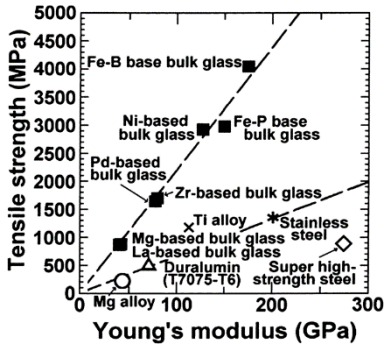


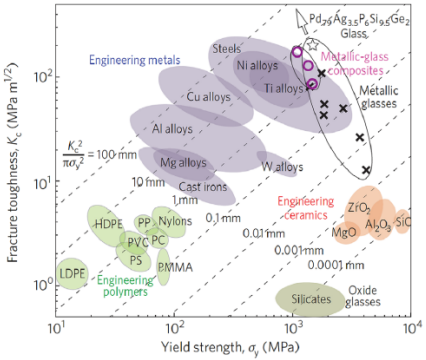
/Z.O. Yazici et al, Met. Mater. Int. 22(1) (2016) 50-57/

Properties of BMGs

- Due to the lack of crystalline periodicity and the absence of lattice defects such as dislocations, metallic glasses typically exhibit relatively high strengths
- Furthermore metallic glasses are homogenous and isotropic with no discontinuity such as grain boundaries
- Mechanical properties
  - Young's modulus is typically smaller than the one of corresponding crystalline material.
  - Higher yield stress than for the crystalline material (important exception metallic glasses containing metalloids)
  - Elastic strain that is much larger than for crystalline material allowing large reversible deformation
  - High elastic energy storage

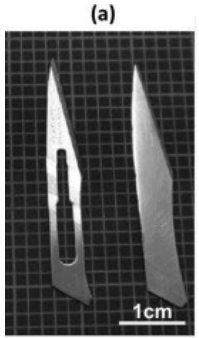


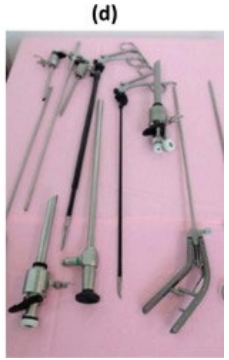




Properties of BMGs

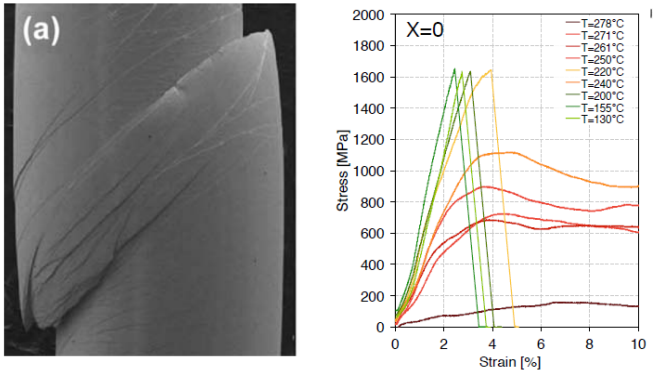
- BMGs show several other interesting properties
  - Better resistance to wear and corrosion than crystalline materials
  - Very low thermal and electrical conductivity
  - Very low magnetic losses
  - Ability to form metallic sheet of complicated alloys (e.g. foils for brazing)
  - Ability to be deformed in the supercooled liquid region
- Despite the promising properties, there are only a few commercial products on the market so far



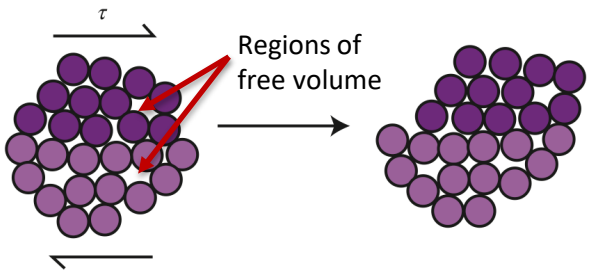


Plastic deformation of BMGs

- Plastic deformation mechanisms in bulk metallic glasses (BMGs) below the glass transition temperature depend on temperature and strain rate
  - **High temperature / low stress**: At higher temperatures and lower stresses, BMGs deform through **homogeneous flow**, allowing more uniform deformation.
  - **Low temperature**: Well below the glass transition, BMGs deform via **localized shear bands**, where plastic deformation is confined to narrow regions.
  - **Shear Transformation Zones (STZs)**: Without dislocations, BMGs accommodate plasticity through **localized, irreversible atomic rearrangements** (STZs), involving tens of atoms shifting in response to stress.
  - **Free volume accumulation**: STZs require free volume, and shear band formation generates additional free volume, facilitating further deformation but limiting ductility in BMGs.

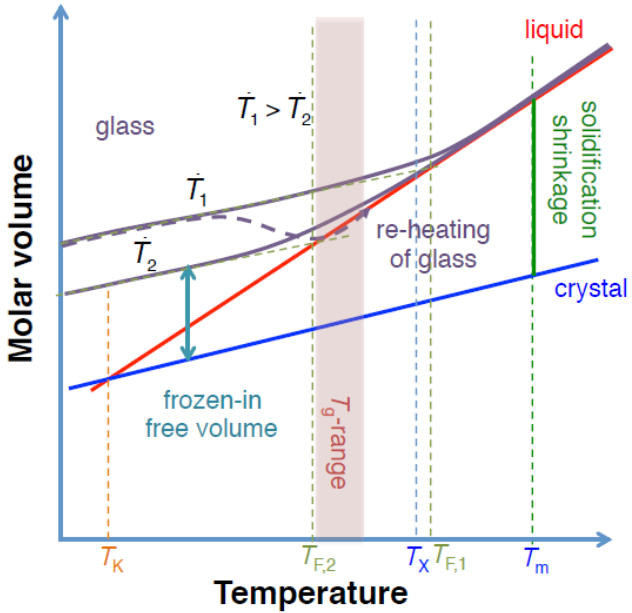


/D.V. Louzguine-Luzgin et al., Metals 3(1) (2013) 1-22/



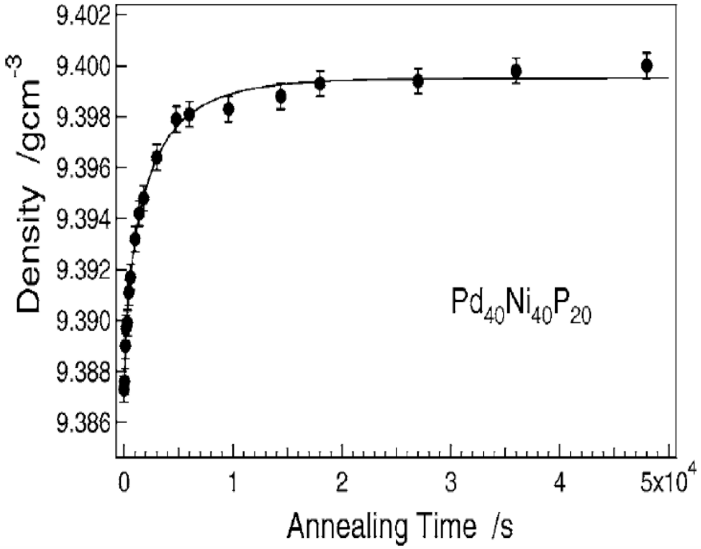
The «frozen-in» free volume

- **Crystallization vs. glass formation:** in crystallization, most free volume is eliminated. In BMGs, some free volume remains “frozen-in”
- **Free volume reduction:** upon cooling, atomic rearrangements reduce free volume gradually in BMGs, depending on cooling rate
- **Frozen-in free volume:** difference between the crystalline and glass molar volumes. Extrapolating glass volume to higher temperatures intersects with liquid volume at the fictive temperature (T_F)
- **T_F is dependent on cooling rate**; higher T_F leads to more ductile glass
- **Impact on T_g:** The amount of frozen-in free volume slightly affects T_g, resulting in a T_g range



Relaxation and rejuvenation of BMGs

- The reduction of free volume upon reheating a glass is known as “relaxation”. This can be observed by exposing a glass to a temperature near its Tg and measuring its density over time.
- The opposite process, “rejuvenation”, involves increasing free volume through methods like ion bombardment or plastic deformation near T_g.
- Due to its link to ductility, which depends partly on free volume, rejuvenation methods are a current focus of research to improve the mechanical properties of glasses.



Learning objectives

- High Entropy Alloys (HEAs)
  - Understand HE alloying concepts: understand multicomponent alloying strategies
  - Thermodynamics: understand high entropy effects, sluggish diffusion.
  - HEA classes and structures: fcc, bcc and hcp HEA types
  - Mechanical properties: mechanical properties of HEAs, including high-temperature strength and fatigue resistance.
  - Application potential: recognize HEAs' uses in extreme environments like aerospace and nuclear.
- Bulk Metallic Glasses (BMGs)
  - Formation mechanisms: understand critical cooling rates, free volume, and the importance of the fictive temperature.
  - Properties and challenges: basic BMG properties, including high strength, ductility limitations, and resistance to wear and corrosion.
  - Plastic deformation mechanisms: shear bands, shear transformation zones (STZs), and free volume accumulation.
  - Fabrication techniques: review methods like melt spinning, splat quenching, and additive manufacturing.