2018 Spring

“Advanced Physical Metallurgy”

- Bulk Metallic Glasses-

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Chapter 1. Introduction Development of New Materials

* Search for new and advanced materials

: addition of alloying elements, microstructural modification and by subjecting the materials to thermal, mechanical, or thermo-mechanical processing methods

→ Completely new materials

" Stronger, Stiffer, Lighter and Hotter…"

: Nanocrystalline Materials, High Temperature Superconductors,

Metallic Glass (1960), Shape Memory Alloy (1963), Quasi-crystal (1984), Gum Metal (2003), High Entropy Alloy (2004)

Q1: What kind of new and advanced materials were developed up to now?

The term "superalloy" was first used shortly after World War II to describe a group of alloys developed for use in turbosuperchargers and aircraft turbine engines that required high performance at elevated temperatures.

Superalloys

Definition: A superalloy is a metallic alloy which can be used at high temperatures, often in excess of 0.7 of the absolute melting temperature.
Creep and oxidation resistance are the prime design criteria.

There are three types of superalloys based on the principal constituting element:

1. Nickel based (m.p. of Ni: 1455 ^{o}C)
2. Cobalt based (m.p. of Ni: 1495 ^{o}C)
3. Iron based (m.p. of Ni: 1538 ^{o}C)

Ni-based superalloys are the most complex and widely used among the three types of superalloys due to their high performance capabilities.

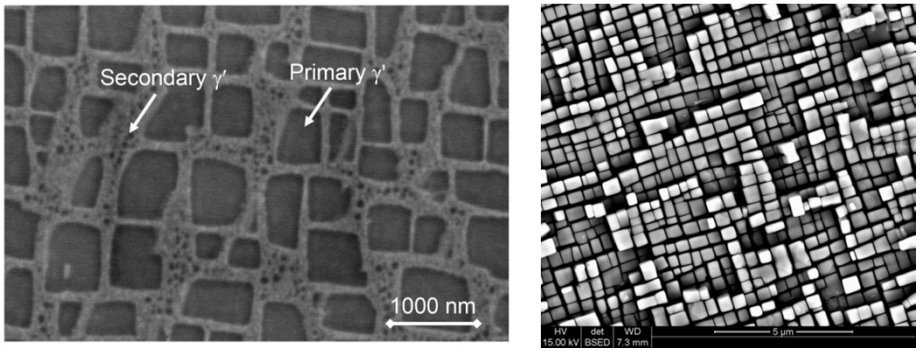
Properties of Superalloys:

- Capable of high temperature application
- Excellent oxidation resistance
- Good corrosion and erosion resistance across wide temperature range
- Strong and ductile at cryogenic temperatures

Microstructure

The superior property at high temperature comes from the optimized microstructure consisting of various phases. The representative phases are listed below:

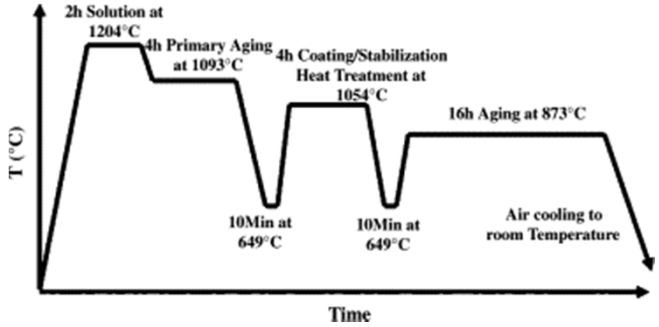
- Gamma (γ) phase: It forms the matrix of the alloy. The volume fraction of γ in certain superalloys maybe as low as 30% due to the precipitates.
- Gamma' (γ') phase: coherent precipitate composed of $Ni_3(Al/Ti)$ strengthen the alloy.
- Carbides: they form at grain boundaries inhibiting grain boundary motion.



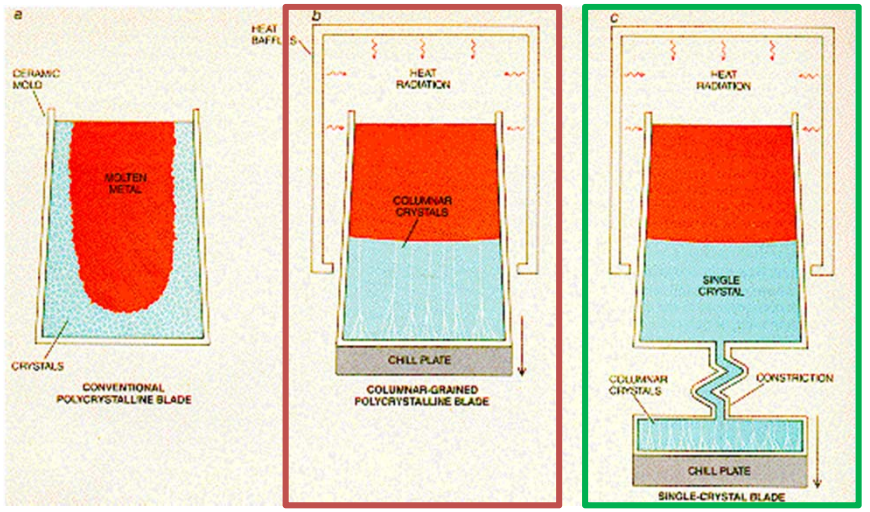
Microstructure of some superalloys exhibiting γ- γ' structure

Processing Techniques

To obtain the desired microstructure, various heat treatments such as variation of cooling rate and one/two step aging processes are employed.



Since grain boundary has great influence on the creep resistance, directionally solidified or single crystal superalloys are fabricated.



Application

- Aircraft gas turbines: disks, combustion chambers, blades, vanes, afterburners, thrust reversers
- Steam turbine power plants: blades, stack gas re-heaters
- Metal processing: hot work tools and dies
- Space vehicles: rocket engine parts, aerodynamically heated skins
- Nuclear power systems: control rod drive mechanisms, springs, valve stems
- Chemical and petrochemical industries: bolts, fans, valves, reaction vessels, piping, pumps
- Coal gasification and liquefaction systems: heat exchangers, re-heaters, piping.

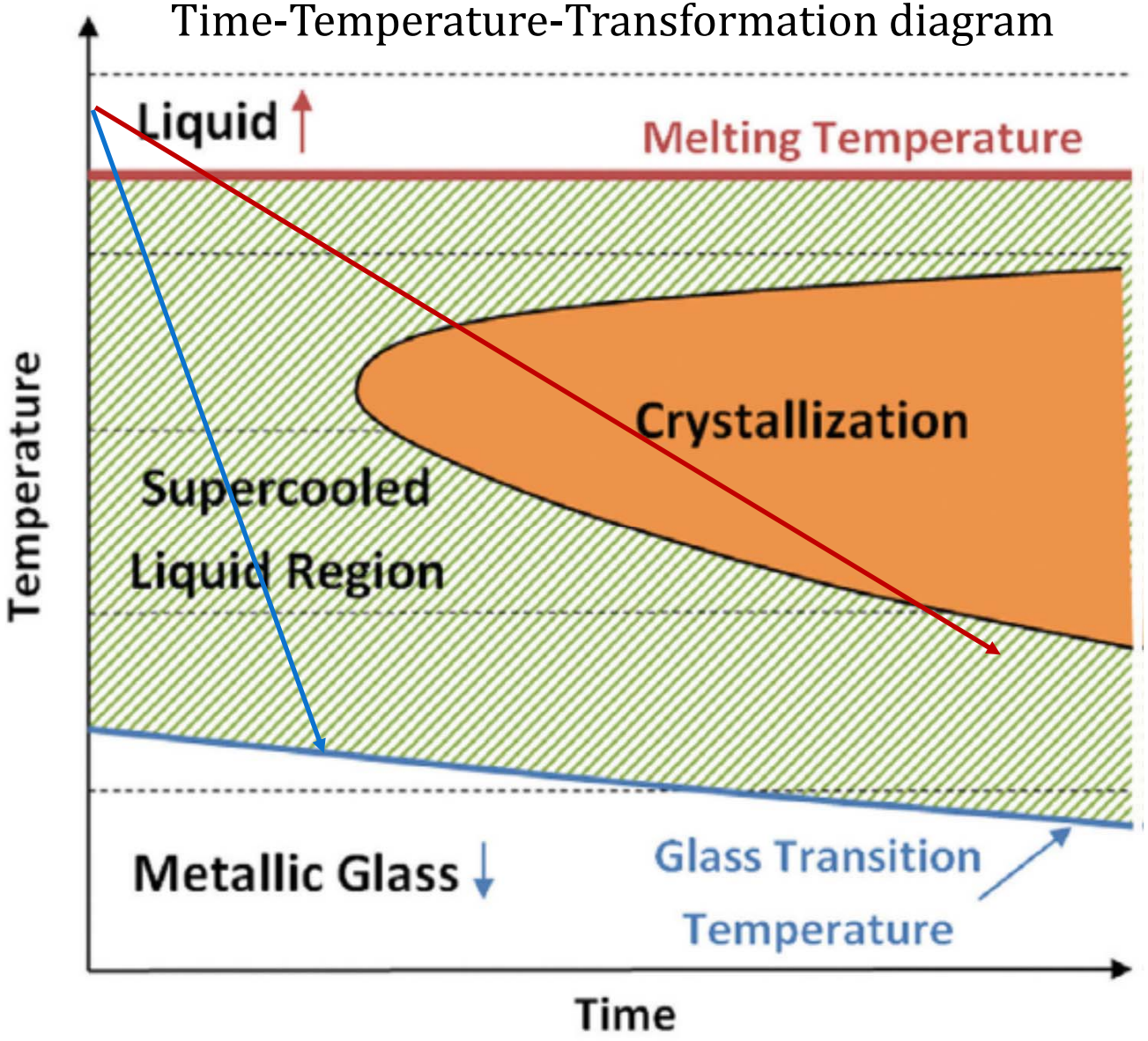
Various machine and engine components made from superalloys

Picture of a turbine blade

A1: Bulk Metallic Glass

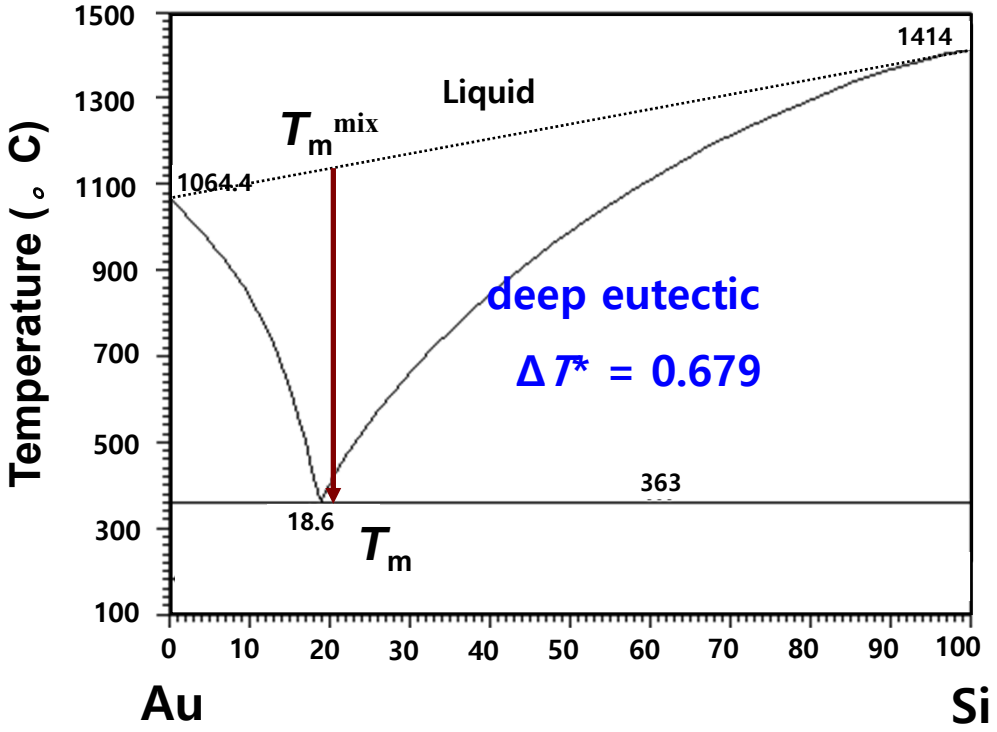
Bulk Metallic Glasses

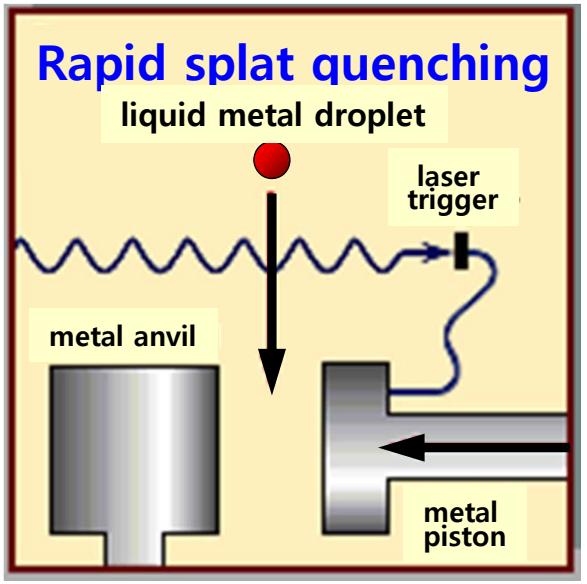
Time-Temperature-Transformation diagram

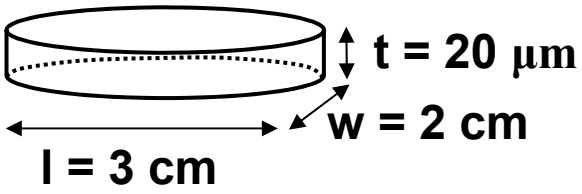


Glass formation : stabilizing the liquid phase & rapid quenching

- First **metallic glass** ($Au_{80}Si_{20}$) produced by splat quenching at Caltech by Pol Duwez in 1960.

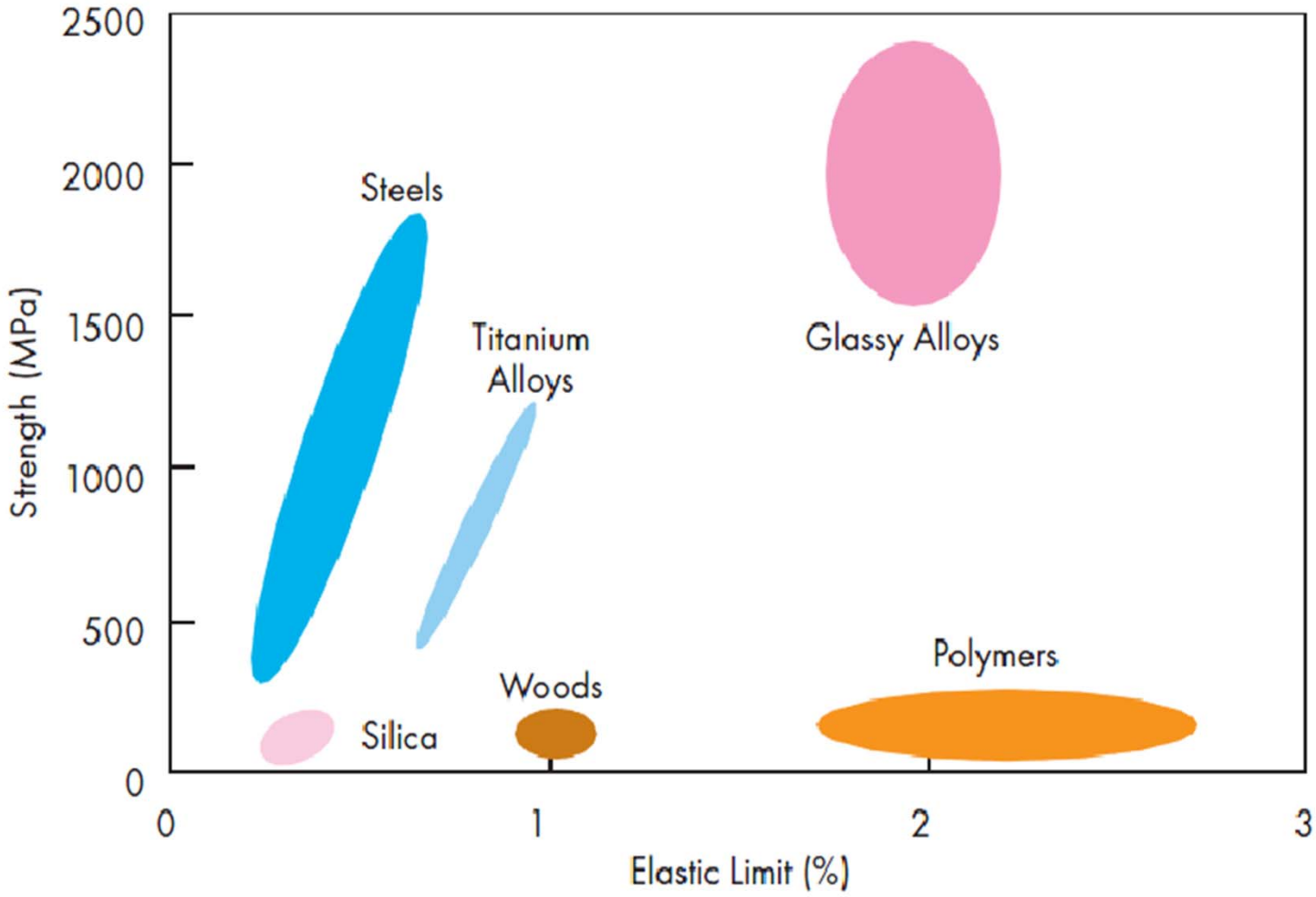






*W. Klement, R.H. Willens, P. Duwez, Nature 1960; **187**: 869.*

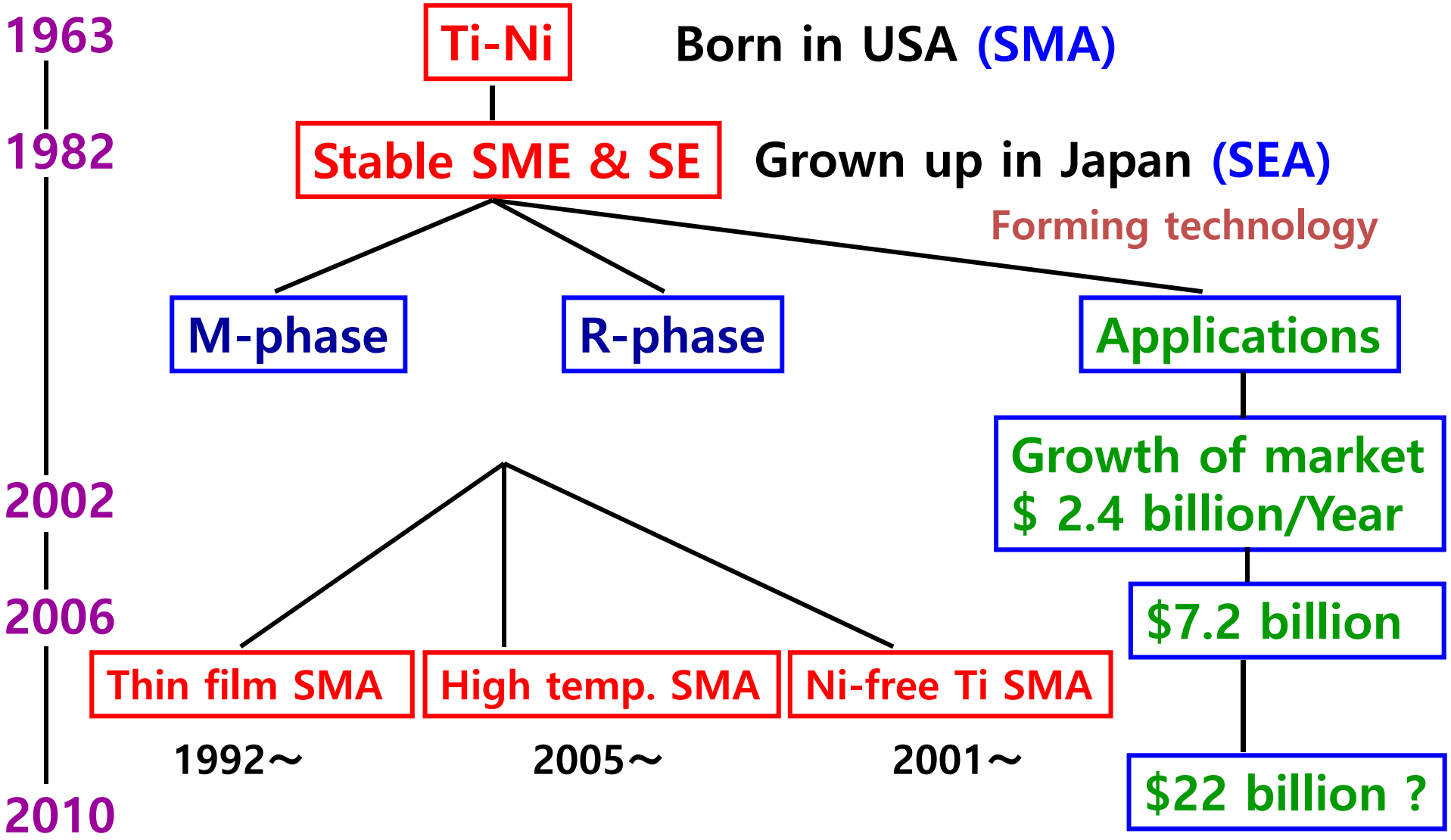
Bulk metallic glasses with high strength & high elastic limit



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

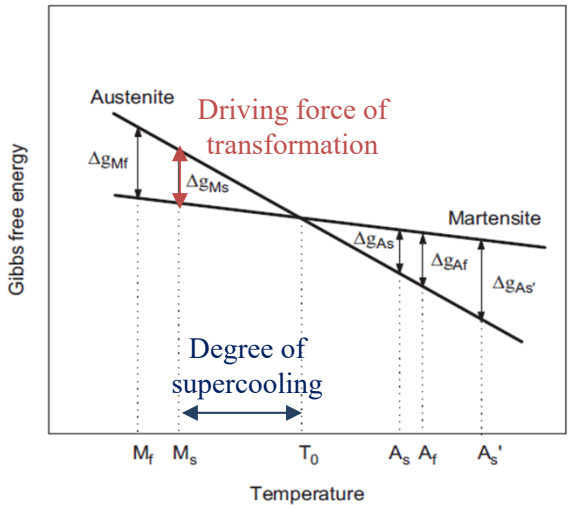
A2: Shape Memory Alloy

History of Shape Memory Alloy



Shape Memory Alloy

Shape memory alloy (SMA) is an alloy that **remember its original shape** through reversible phase transformation from austenite to martensite and vice versa.

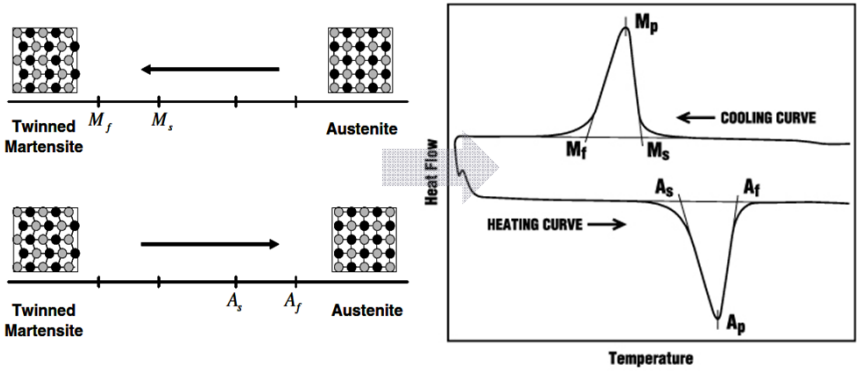


- **Driving force of martensite crystal nucleation**

$$\Delta G = (volume\ of\ martensite) * \Delta g + Interface\ energy\ between\ austenite\ and\ martenstie$$
$$+Elastic\ strain\ energy\ in\ martensite + Plastic\ strain\ energy\ in\ martensite$$
$$= \pi r^2 t \Delta g + 2\pi r^2 \sigma + \pi r t^2 (A + B)$$
$$(r: M\ crystal\ radius, 2t: average\ thickness,$$
$$A: elastic\ strain\ energy\ per\ unit, B: plasic\ strain\ energy\ per\ unit)$$

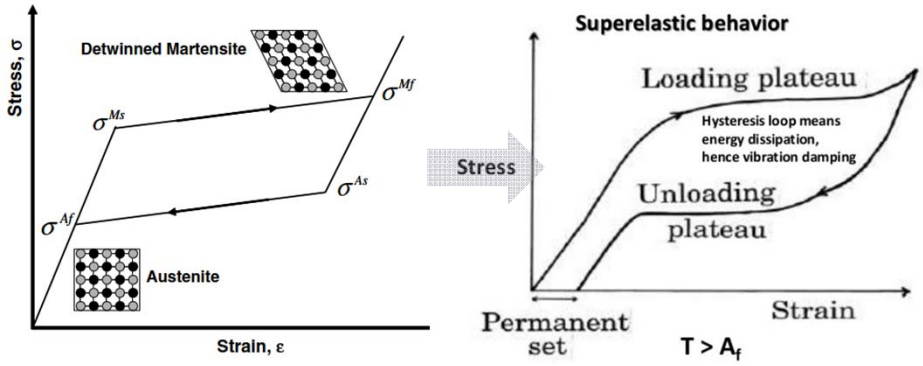
1. Thermally induced martensitic transformation

Upon cooling, the crystal structure changes from austenite to martensite. When the material is heated from the martensitic phase, the crystal structure transforms back to austenite.



2. Stress induced martensitic transformation

Applying a sufficiently high mechanical load to the material can induce phase transformation. And if the temperature is above A_f, a complete shape memory is observed upon unloading, which called *pseudoelastic effect.*

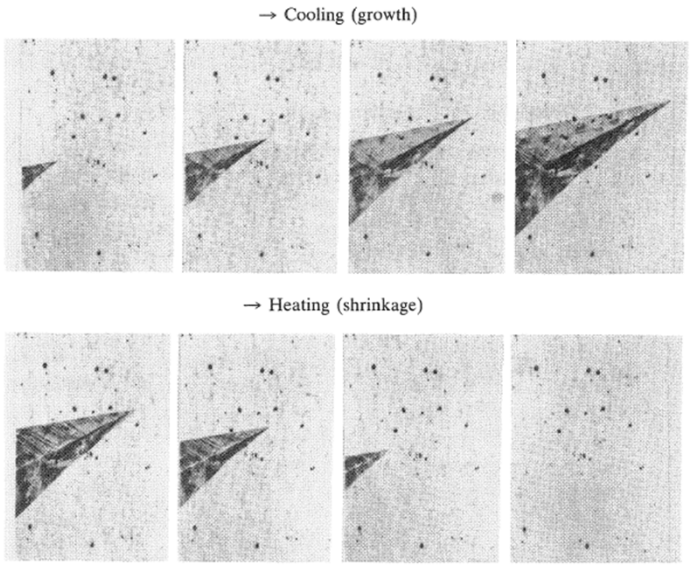


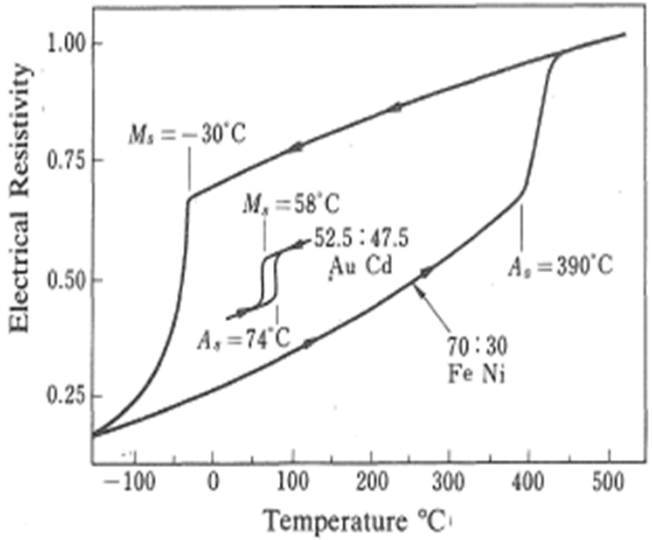
P.K. Kumar and D.C. Lagoudas, "Introduction to shape memory alloys" (2008)

Thermoelastic vs. Non-thermoelastic

* **Thermoelastic Martensitic Transformations**
  - Nucleation E barrier ≈ 0
  - Reversible growth/shrink of M phase
  - Necessary characteristic of SMA

  ex) TiNi, Cu-based alloy





H. Funakubo, Shape memory alloys. *Gordon and Breach Science Publishers.*

non-thermoelastic → thermoelastic

(reducing E barrier…)

Shape memory effect & Superelasticity

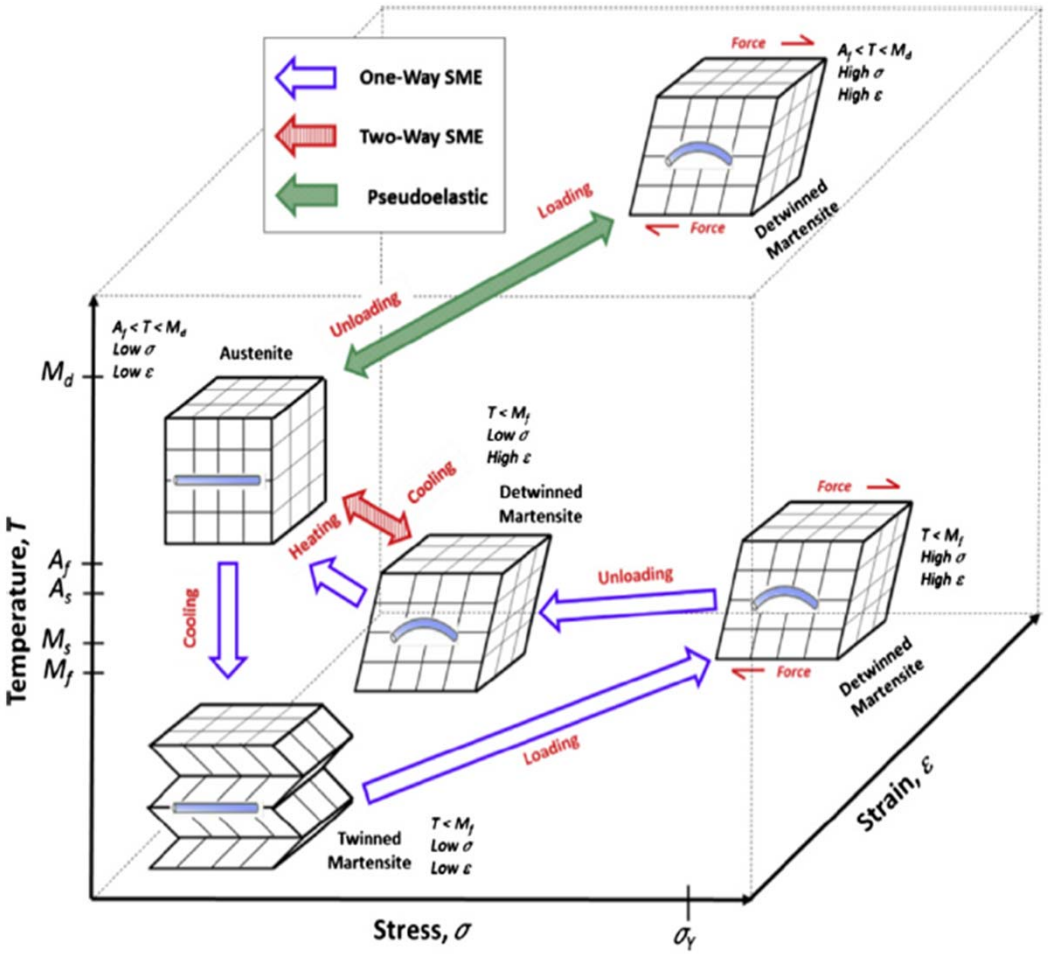
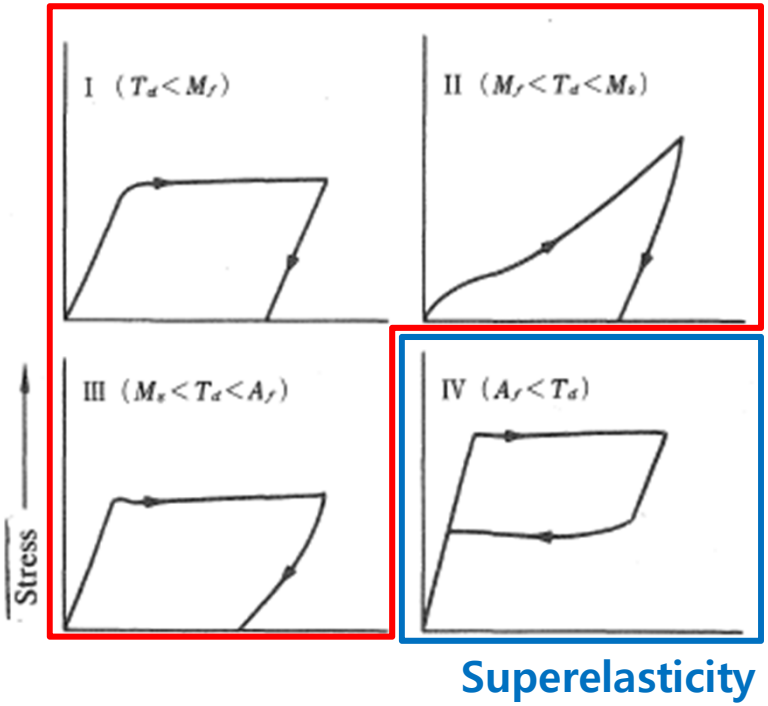


Fig. 1. SMA phases and crystal structures [36–38].

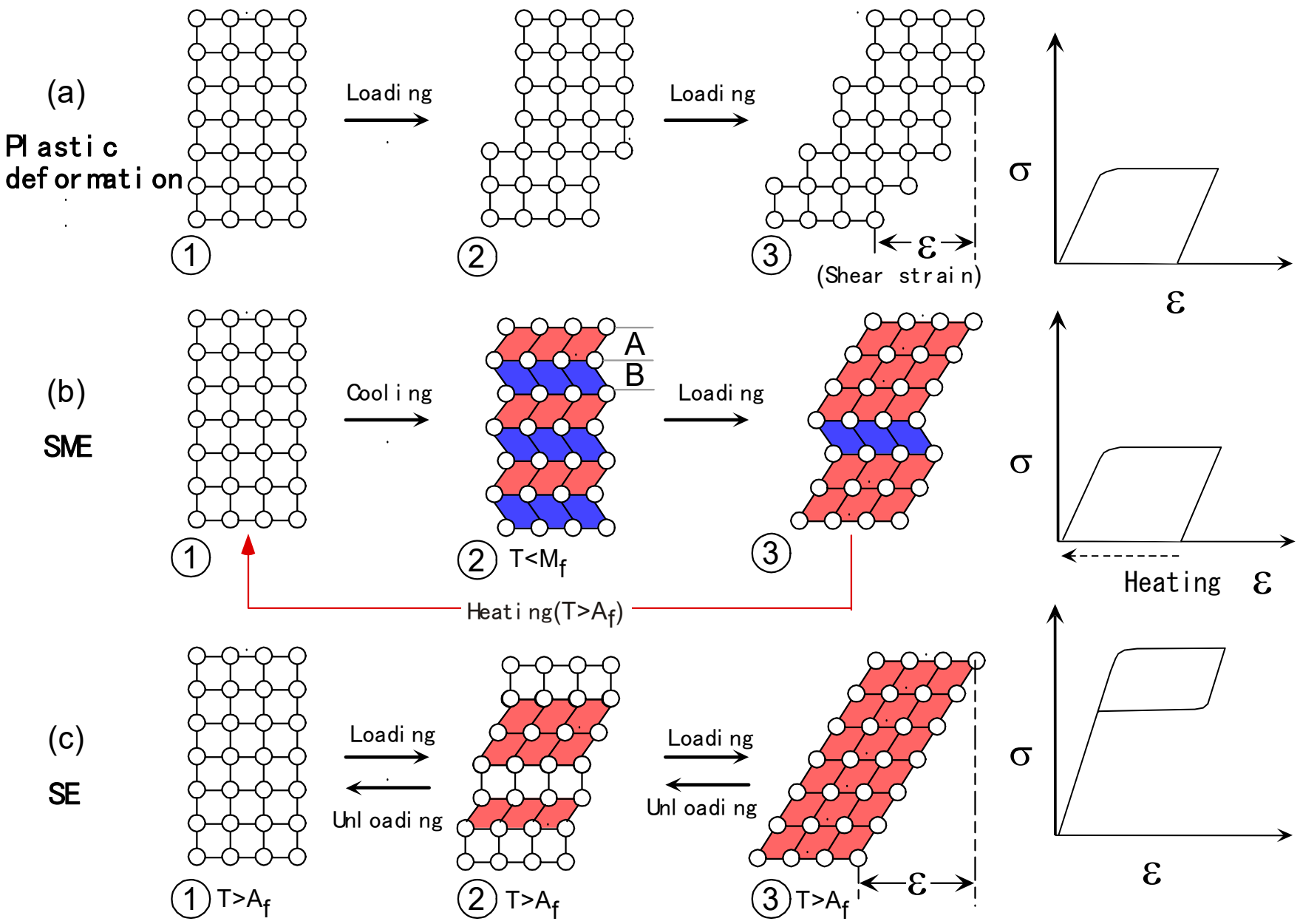
Shape memory effect



Superelasticity

Shape memory effect
(T<Af)
: unloading & heating

Superelasticity
(T>Af)
: unloading


(a)
Plastic deformation
Loading
Loading
1
2
3
ε
(Shear strain)
σ
ε
(b)
SME
Cooling
Loading
A
B
1
2 T<Mf
3
Heating(T>Af)
σ
Heating
ε
(c)
SE
Loading
Unloading
Loading
Unloading
1 T>Af
2 T>Af
3 T>Af
ε
σ
ε

A3: Quasicrystals

Quasicrystals (Impossible Crystals)

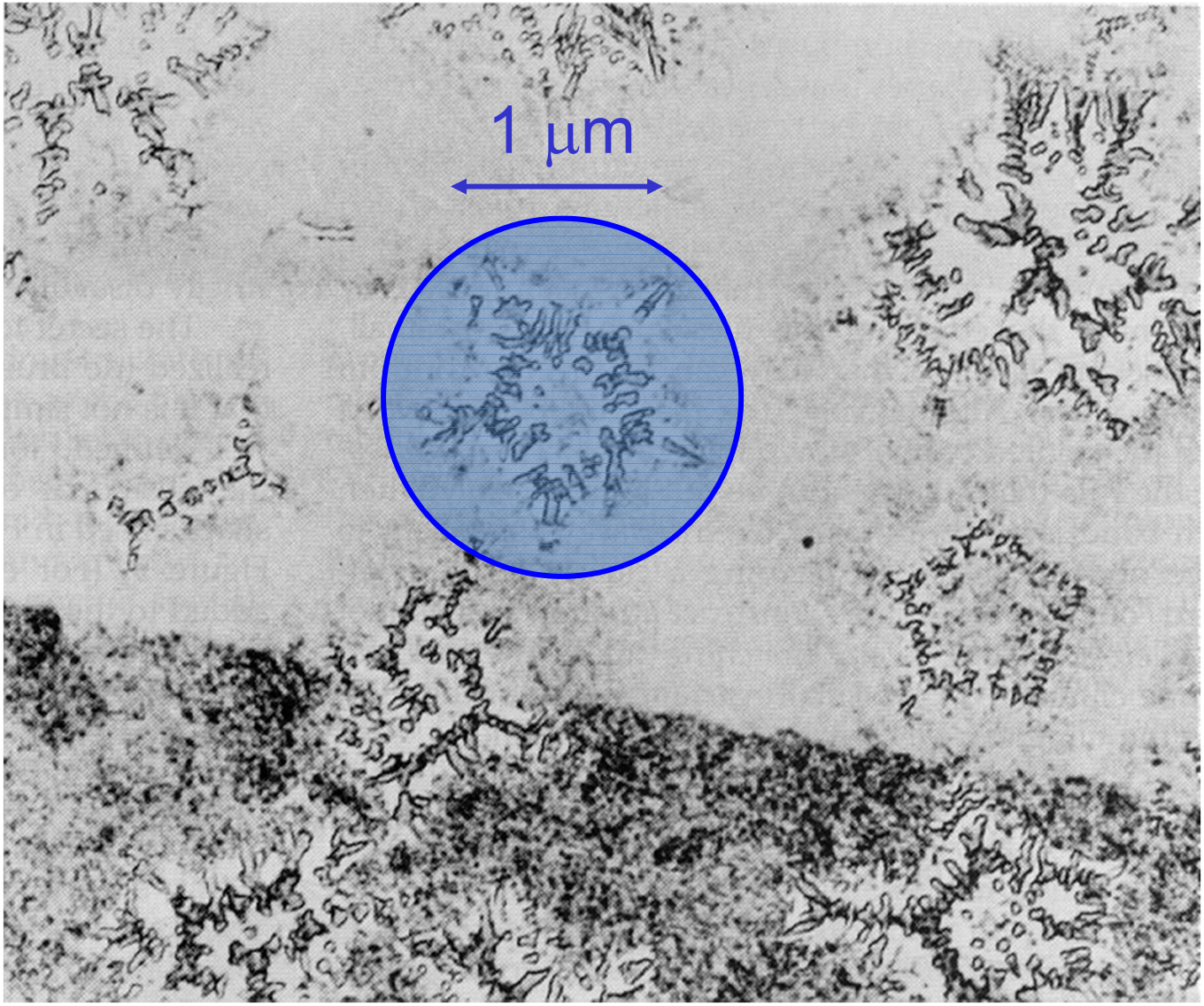
were first discovered in the laboratory by

Daniel Shechtman, Ilan Blech, Denis Gratias and John Cahn

in a beautiful study of an alloy of Al and Mn (1984)

D. Shechtman, I. Blech, D. Gratias, J.W. Cahn (1984)

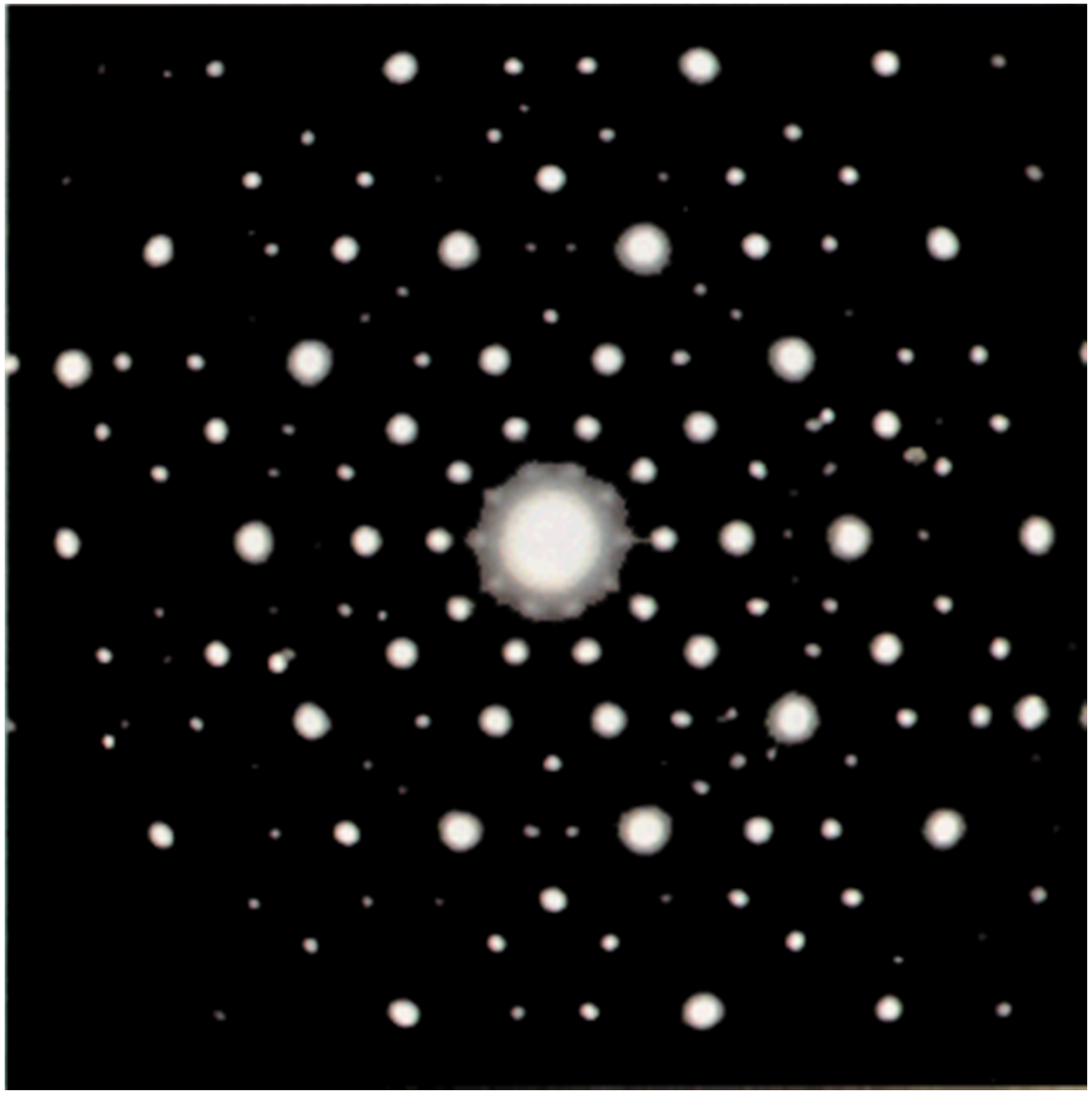
Al_6Mn



Their surprising claim:

"Diffracts electrons like a crystal . . .
But with a symmetry strictly forbidden for crystals"

Al_6Mn

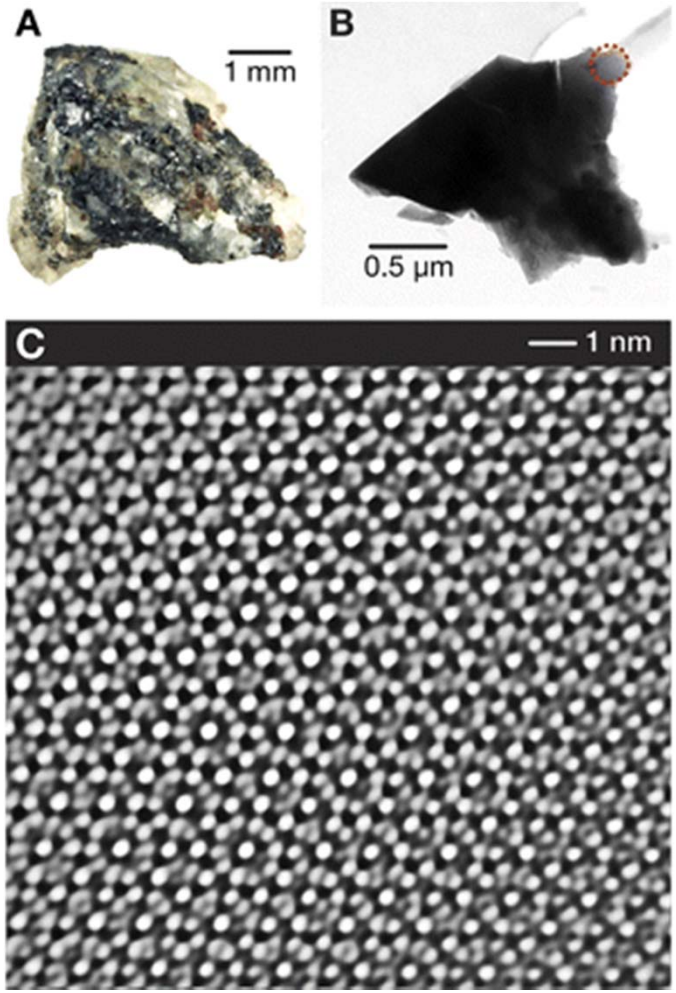


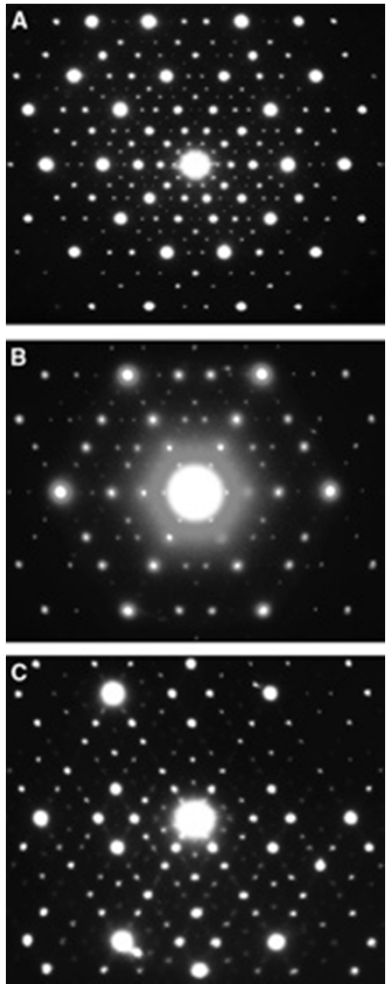
2011 Nobel Prize in Chemistry: Quasicrystal

A new ordered phase showing the apparent fivefold symmetry was observed by Sastry et al. [Mater. Res. Bull. 13: 1065-1070] in 1978 in a rapidly solidified Al-Pd alloy, but was interpreted to arise from a microstructure Consisting of a series of fine twins. This was later shown to be a two-dimensional (or decagonal) qasicrystal.

Discovery of a Natural Quasicrystal

L Bindi, P. Steinhardt, N. Yao and P. Lu
Science 324, 1306 (2009)





LEFT: Fig. 1 (A) The original khatyrkite-bearing sample used in the study. The lighter-colored material on the exterior contains a mixture of spinel, augite, and olivine. The dark material consists predominantly of khatyrkite ($CuAl_2$) and cupalite (CuAl) but also includes granules, like the one in (B), with composition $Al_{63}Cu_{24}Fe_{13}$. The diffraction patterns in Fig. 4 were obtained from the thin region of this granule indicated by the red dashed circle, an area 0.1 μm across. (C) The inverted Fourier transform of the HRTEM image taken from a subregion about 15 nm across displays a homogeneous, quasiperiodically ordered, fivefold symmetric, real space pattern characteristic of quasicrystals.

RIGHT: Diffraction patterns obtained from natural quasicrystal grain

Quasicrystals

Crystal with 5 fold symmetry *Mathematically impossible but exist*

1984 $Al_{86}Mn_{14}$ alloy : rapidly solidified ribbon_*Shectman et al.*

: materials whose structure cannot be understood within classical crystallography rules.

"Quasiperiodic lattices", with long-range order but without periodic translations in three dimensions

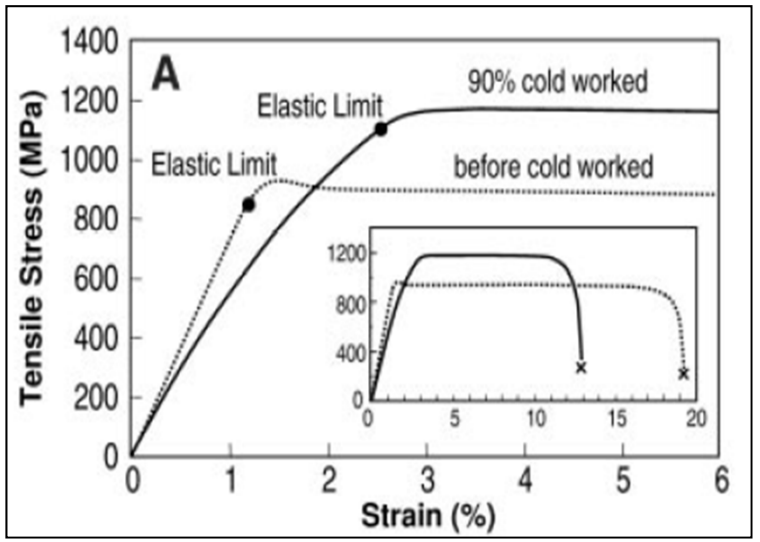
- long range order: quasiperiodic
- no 3-D translational symmetry
- sharp diffraction patterns

http://www.youtube.com/watch?v=k_VSpBI5EGM

A4: GUM Metal

Gum metal – Toyota Central R&D Labs (2003)

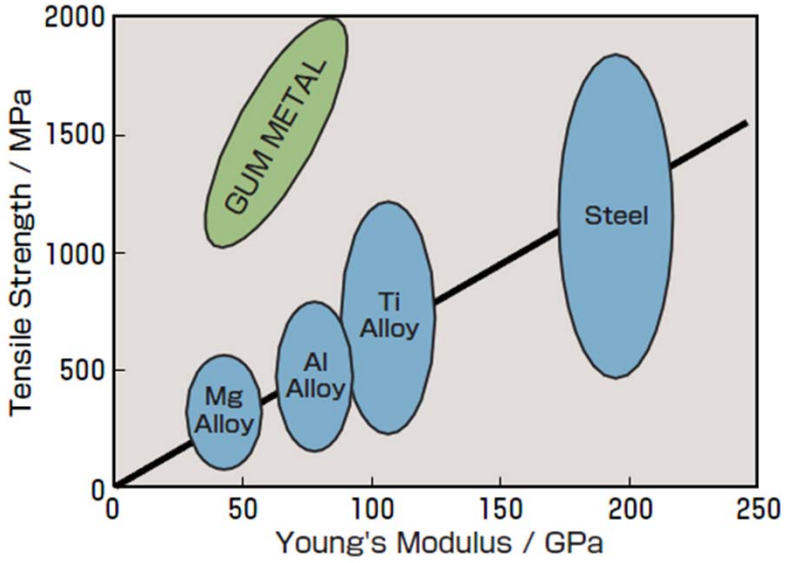
Metastable Beta-Ti alloy, for example,
Ti-12Ta-9Nb-3V-6Zr-O, Ti-23Nb-0.7Ta-2Zr-O



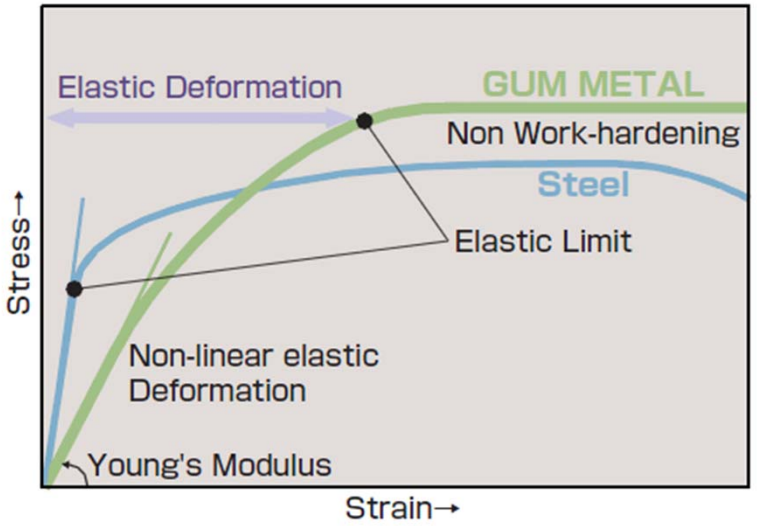
- Large elastic limit (2.5 %)
- High yield stress (1~2 GPa)
- Low young's modulus (50~70 GPa)
- Large plasticity
- Super-elasticity (≥1 %)

- Non-linear elastic deformation
- Non-work hardening
- No dislocation, No twinning, but large plasticity by giant fault (similar to shear band)

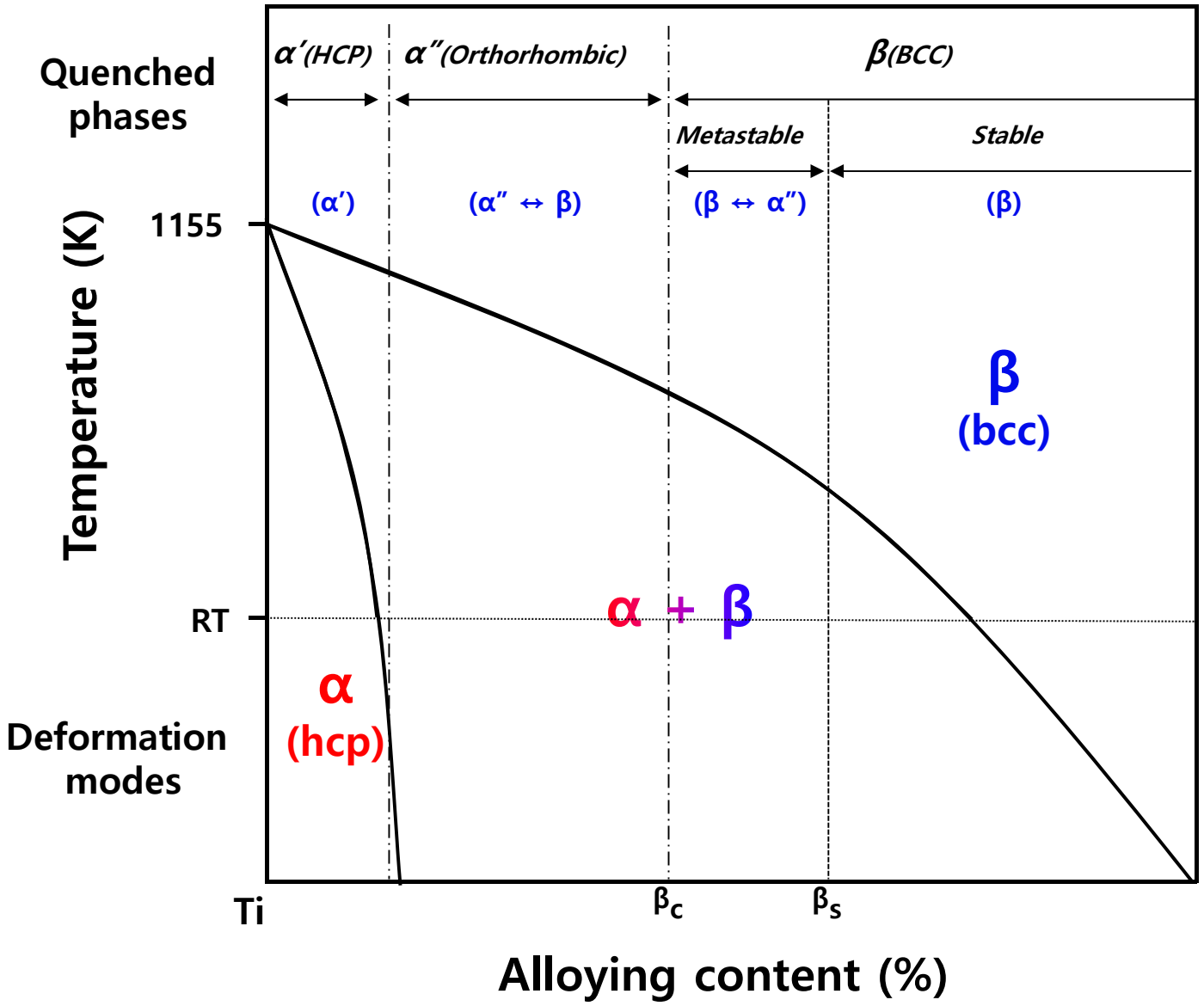
【Fig.1】Position of Young's Modulus and Strength of GUM METAL



【Fig.2】Stress-Strain Curve of GUM METAL



Ti-based alloys



Gum metal - Science (2003)

Science
AAAS

Multifunctional Alloys Obtained via a Dislocation-Free Plastic Deformation Mechanism
Takashi Saito *et al.*
Science **300**, 464 (2003);
DOI: 10.1126/science.1081957

Multifunctional Alloys Obtained via a Dislocation-Free Plastic Deformation Mechanism

Takashi Saito,[1]* Tadahiko Furuta,[1] Jung-Hwan Hwang,[1] Shigeru Kuramoto,[1] Kazuaki Nishino,[1] Nobuaki Suzuki,[1] Rong Chen,[1] Akira Yamada,[1] Kazuhiko Ito,[1] Yoshiki Seno,[1] Takamasa Nonaka,[1] Hideaki Ikehata,[1] Naoyuki Nagasako,[1] Chihiro Iwamoto,[2] Yuuichi Ikuhara,[2] Taketo Sakuma[3]

We describe a group of alloys that exhibit "super" properties, such as ultralow elastic modulus, ultrahigh strength, super elasticity, and super plasticity, at room temperature and that show Elinvar and Invar behavior. These "super" properties are attributable to a dislocation-free plastic deformation mechanism. In cold-worked alloys, this mechanism forms elastic strain fields of hierarchical structure that range in size from the nanometer scale to several tens of micrometers. The resultant elastic strain energy leads to a number of enhanced material properties.

Gum metal - elastic property

- Normal β-Ti alloy: Super-elasticity by Martensitic transformation (β ↔ α")

  ↔ Gum metal: "true super-elasticity" as an intrinsic property
  without martensitic transformation (β → α")

- Conformation of non-linear elastic limit by in-situ XRD

In-situ XRD
- confirm elastic limit

S. Kuramoto et al. / Materials Science and Engineering A 442 (2006) 454–457

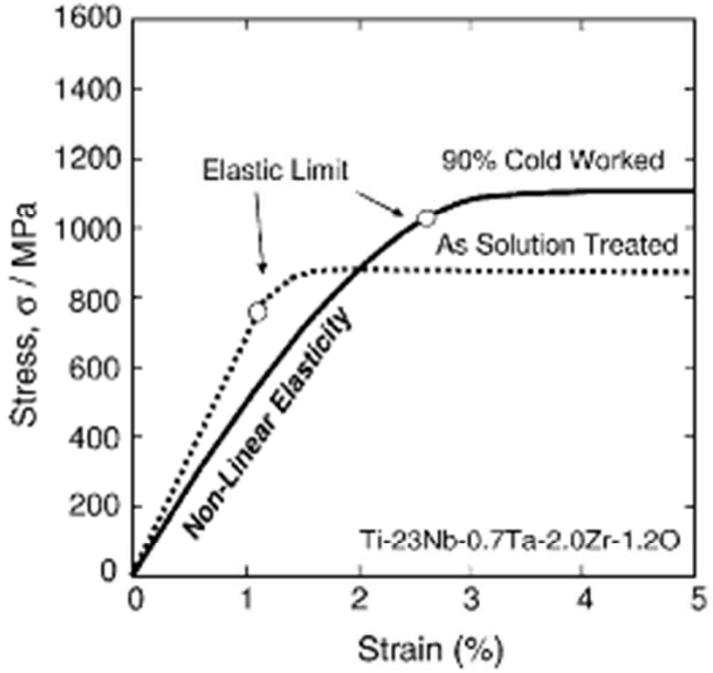


Fig. 1. Change in tensile stress-strain curve of specimen at room temperature both before and after cold working with a 90% reduction in area.

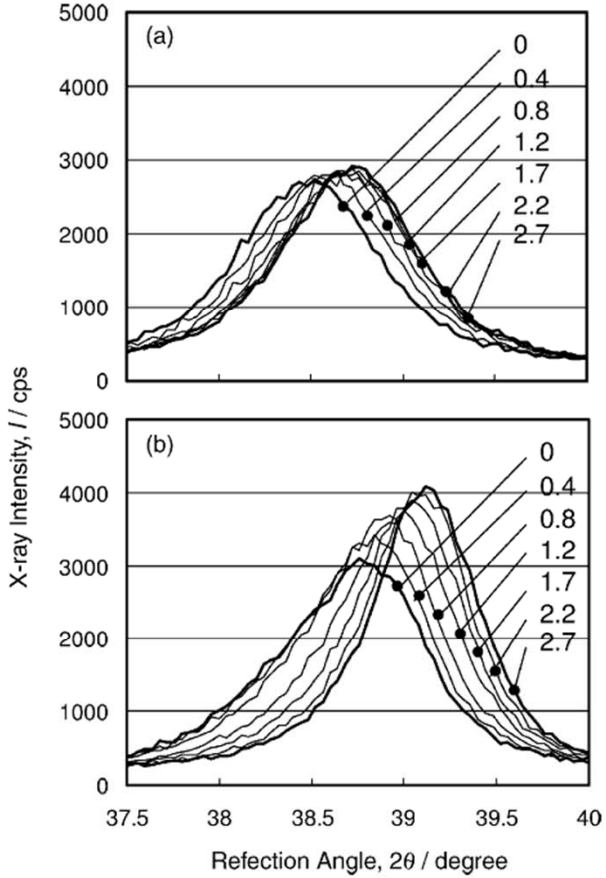
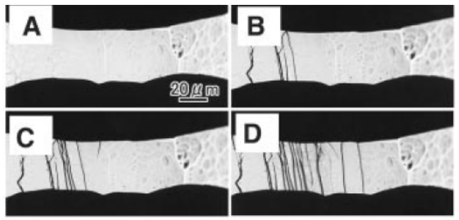


Fig. 4. Changes in X-ray profile during tensile deformation. Amounts of tensile strain (%) are indicated in the figure: (a) solution treated and (b) cold worked.

Gum metal - plastic property

- Deformation mechanism: No Dislocation / twin →
  shear band like giant fault → Unique Marble-like structure



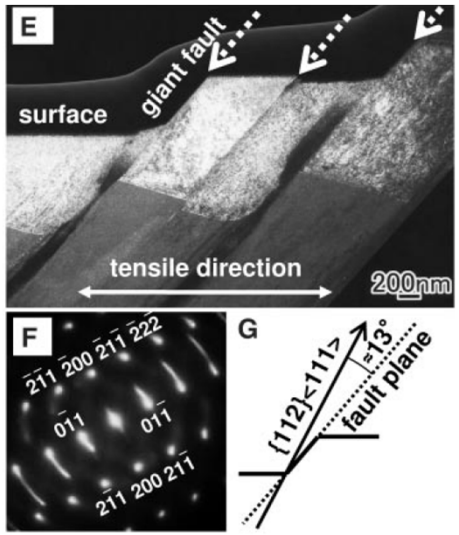
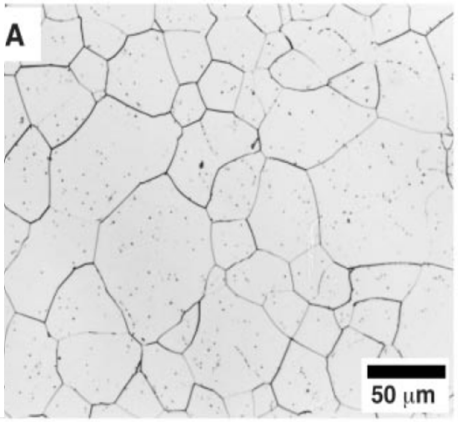


Fig. 3. (**A** to **D**) Changes in surface morphology of a tensile specimen of annealed Ti-23Nb-0.7Ta-2Zr-1.2O alloy. The amounts of deformation are (A) 0, (B) 4.3%, (C) 6.1%, and (D) 10.3%. (**E**) A TEM image near the surface of the specimen and (**F**) the corresponding electron diffraction pattern, which indicates crystal rotation near the giant fault. The foil was prepared perpendicular to the surface. (**G**) A schematic diagram showing orientation near the giant fault. The {112}<111> direction is one of the slip systems for dislocation glide and also a major orientation of twinning in bcc crystals.

Unique microstructure after cold working



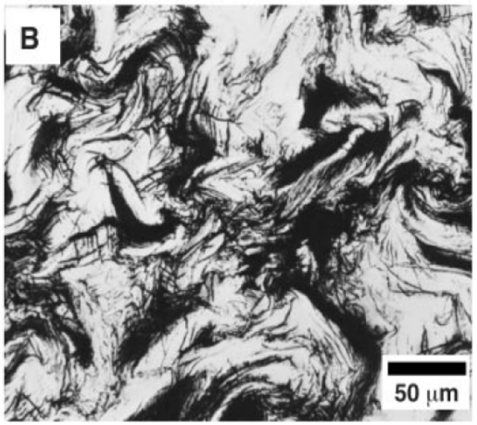


Fig. 2. Comparison of optical microstructure of Ti-23Nb-0.7Ta-2Zr-1.2O alloy (**A**) annealed at 1273 K and (**B**) cold-worked by 90% reduction in area.

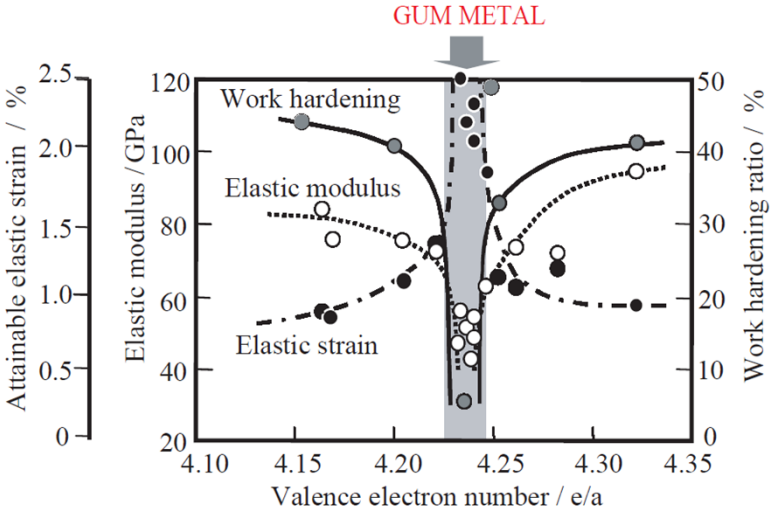
- Marble-like structure

: storage of elastic strain energy near giant faults
→ plastic deformation by elastic mechanism

Gum metal - Science (2003) (Optimum fabrication condition of Gum metal)

(i) a compositional average valence electron number [electron/atom (e/a) ratio] of about 4.24
(ii) a bond order (B_o value) of about 2.87 based on the DV-X cluster method, which represents the bonding strength
(iii) a "d" electron-orbital energy level (M_d value) of about 2.45 eV, representing electronegativity

Magic number 4.24



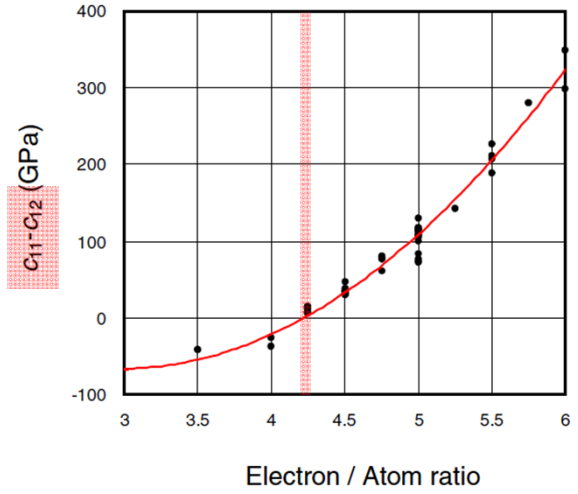


Fig. 3 Anomaly in properties of Ti-Nb-Ta-Zr-O alloys.

$$\tau_{max} = 0.11 G_{111} = 0.11 \frac{3C_{44}(C_{11} - C_{12})}{(C_{11} - C_{12}) + 4C_{44}} \quad (1)$$

where G_{111} is the shear modulus along $< 111 >$ on $\{011\}$, $\{112\}$ or $\{123\}$.

➡ **Alloy satisfied with magic number → simple BCC (A2) structure → cold work**

ex) Ti-12Ta-9Nb-3V-6Zr-O/ Ti-23Nb-0.7Ta-2Zr-O (O: 0.7~3 mol%)

Gum metal - Science (2003)

- Why Oxygen and Zirconium are added together to fabricate a GUM metal?

→ Cluster formation by Oxygen disturb activation of dislocation near Zr.

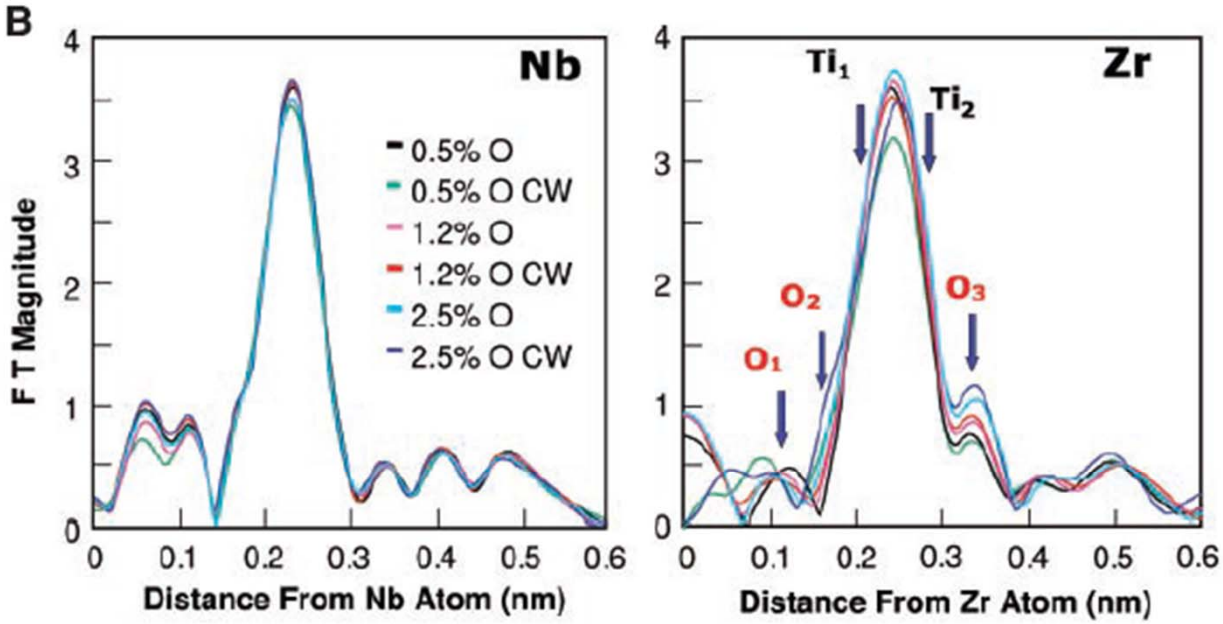


Fig. 4. (A) A distribution of alloying elements in the 90% cold-worked Ti-23Nb-0.7Ta-2Zr-1.2O alloy by EELS using a 200-kV TEM and a TEM image of the same magnification. (B) Comparison of the Fourier transferred spectra calculated from the K-edge EXAFS spectra for niobium and zirconium atoms using 8-GeV synchrotron radiation beam obtained for six sample types. Specimens of three oxygen levels of 0.5, 1.2, and 2.5 mol % were examined before and after 90% cold swaging. Ti_n and O_n represent positions of neighboring titanium and interstitial oxygen atoms, respectively. Strong dependences on both oxygen concentration and cold working are seen only for zirconium atoms, whereas the spectra around niobium atoms (same for tantalum atoms) are almost overlapping for all specimens.

Gum metal - β-Ti alloy with improved phase stability

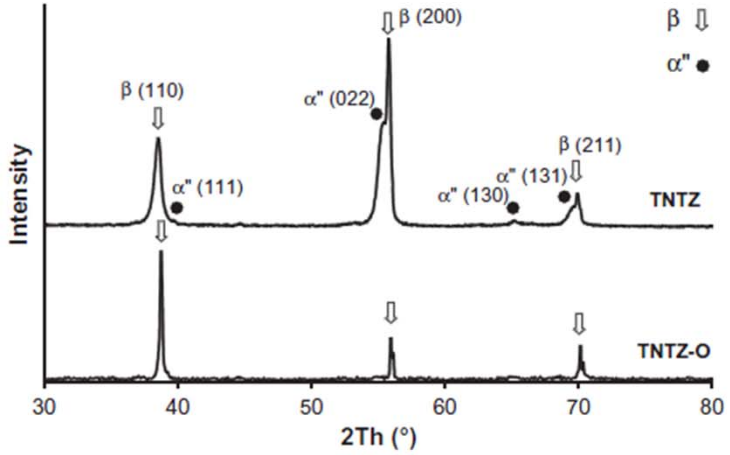


Fig. 2. XRD from the TNTZ and TNTZ-O alloys in the recrystallized/ quenched state.

M. Besse et al. / Acta Materialia 59 (2011) 5982–5988

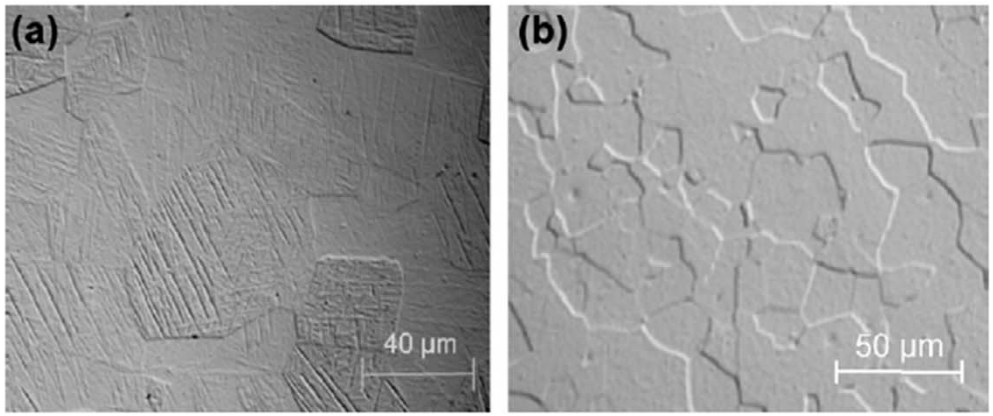
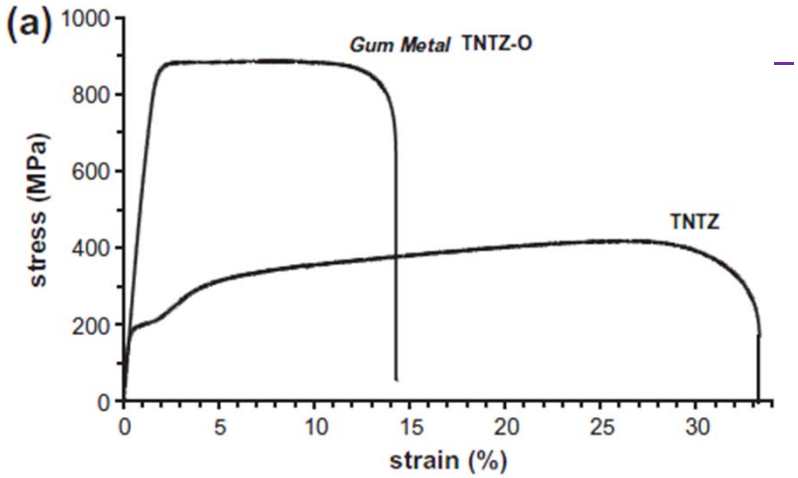


Fig. 1. Microstructures of the TNTZ (a) and TNTZ-O (b) alloys observed by optical microscopy.



- Strengthening by oxygen
- Strengthening by suppress of phase transformation

➡ Similar to deformation mechanism of **β-Ti** alloy but unique phenomena by oxygen clustering

A5: High Entropy Alloy

Representative FCC high entropy alloy: $Fe_{20}Cr_{20}Mn_{20}Ni_{20}Co_{20}$

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Materials Science and Engineering A 375–377 (2004) 213–218

MATERIALS SCIENCE & ENGINEERING A

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Microstructural development in equiatomic multicomponent alloys

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School of Metallurgy and Materials, Birmingham University, Birmingham B15 2TT, UK

Abstract

Multicomponent alloys containing several components in equal atomic proportions have been manufactured by casting and melt spinning, and their microstructures and properties have been investigated by a combination of optical microscopy, scanning electron microscopy, electron probe microanalysis, X-ray diffractrometry and microhardness measurements. Alloys containing 16 and 20 components in equal proportions are multiphase, crystalline and brittle both as-cast and after melt spinning. A five component $Fe_{20}Cr_{20}Mn_{20}Ni_{20}Co_{20}$ alloy forms a single fcc solid solution which solidifies dendritically. A wide range of other six to nine component late transition metal rich multicomponent alloys exhibit the same majority fcc primary dendritic phase, which can dissolve substantial amounts of other transition metals such as Nb, Ti and V. More electronegative elements such as Cu and Ge are less stable in the fcc dendrites and are rejected into the interdendritic regions. The total number of phases is always well below the maximum equilibrium number allowed by the Gibbs phase rule, and even further below the maximum number allowed under non-equilibrium solidification conditions. Glassy structures are not formed by casting or melt spinning of late transition metal rich multicomponent alloys, indicating that the confusion principle does not apply, and other factors are more important in promoting glass formation.
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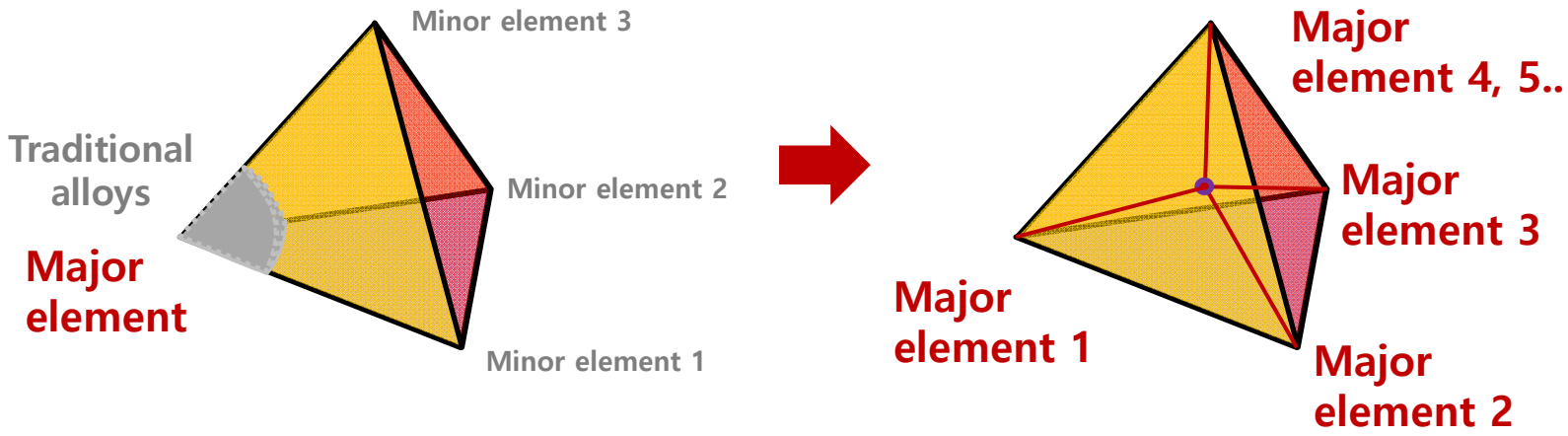
Keywords: Multicomponent alloys; Equiatomic; Casting

Basic concepts of high entropy alloy (HEA)



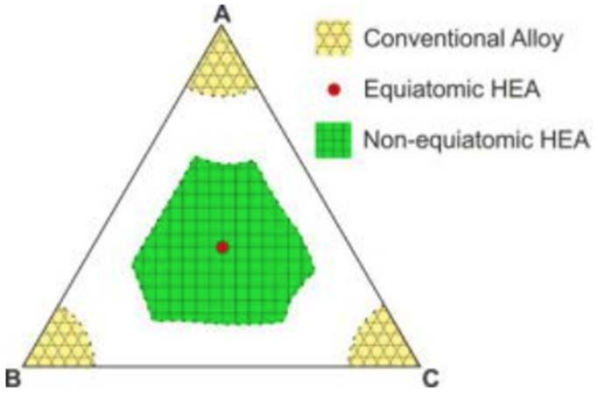
Conventional alloy system

Ex) 304 steel - $Fe_{74}Cr_{18}Ni_8$

High entropy alloy system

Ex) $Al_{20}Co_{20}Cr_{20}Fe_{20}Ni_{20}$

- Equimolar: AlCoCrCuFeNi
- Nonequimolar: AlCo0.5CrCuFe1.5Ni1.2
- Minor addition: AlCo0.5CrCuFe1.5Ni1.2B0.1C0.15

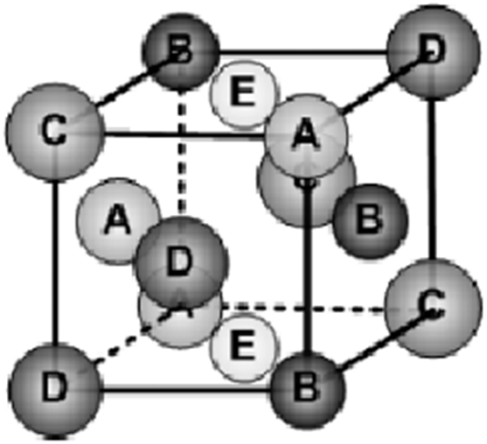


→ Any 13 metal elements will produce 7099 equimolar HEAs!!

Basic concepts of high entropy alloy (HEA)

HEAs=A+B+C+D+E; 15%<A₩B₩C₩D₩E<35%

FCC: 5 principal elements



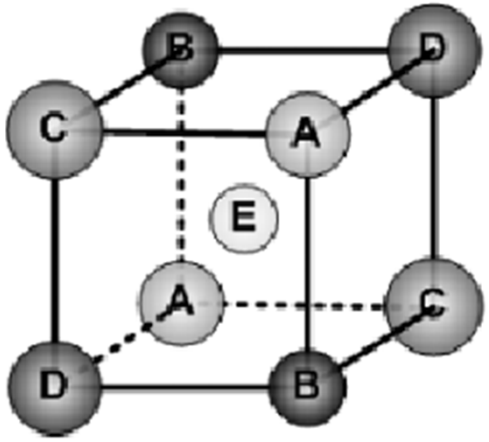
FCC type HEA Solid Solution

CoCrCuFeNi=HEA,

Yeh, MMTA, 2004;

BCC type HEA Solid Solution

BCC: 5 principal elements



AlCoCrFeNi=HEA ,

Zhou, APL, 2007

$Al_{20}[TiVMnHEA]_{80}$,

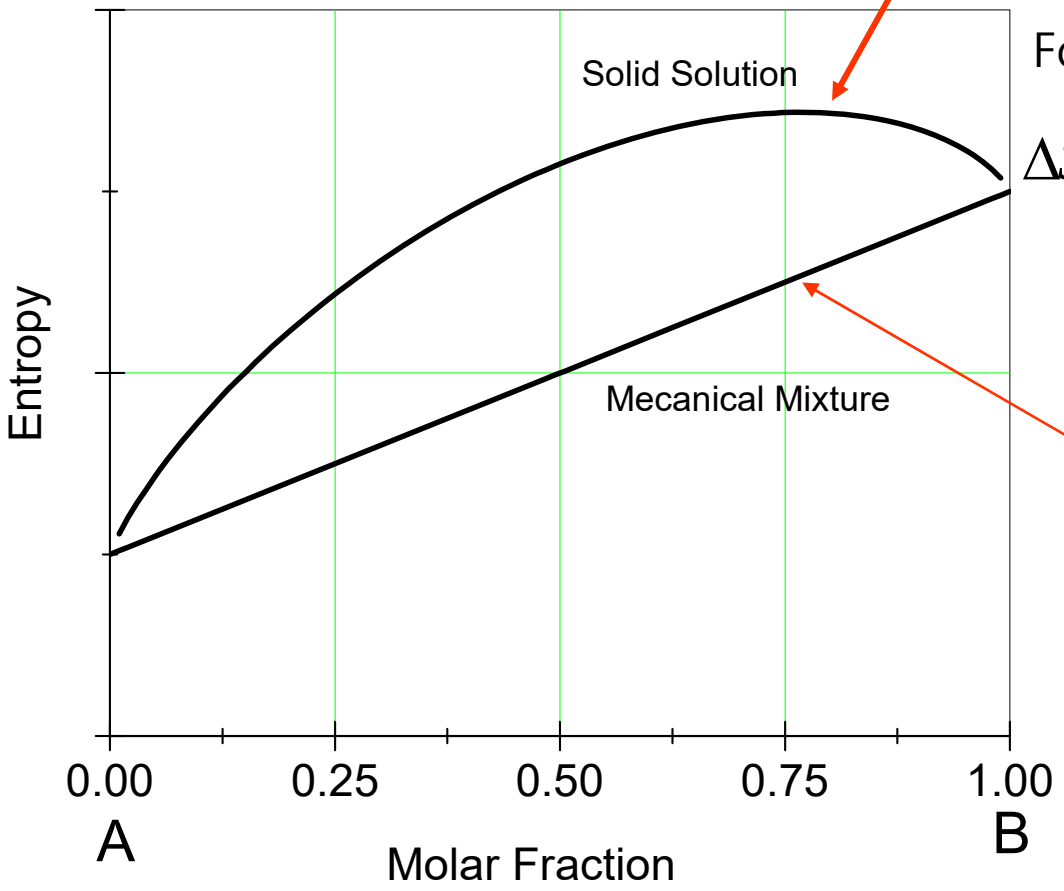
Zhou, MSEA, 2007

Basic concepts of high entropy alloy (HEA)

* **Thermodynamic approach**: Solid solution has higher entropy than the mechanical mixture does.

Entropy of mixing > 1.5 R

$$S = X_A S_A + X_B S_B + \Delta S_{mix}$$

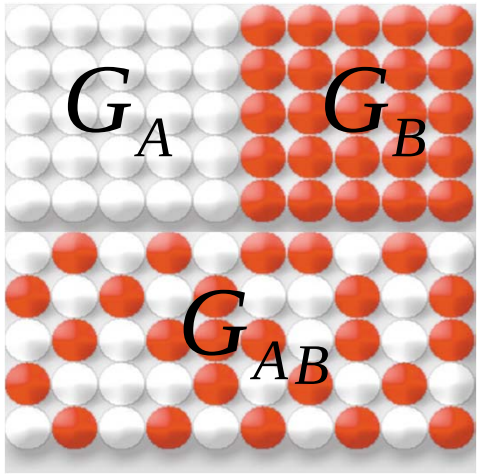


For the regular solution:

$$\Delta S_{mix} = -R(X_A Ln X_A + X_B Ln X_B)$$

$$S = X_A S_A + X_B S_B$$

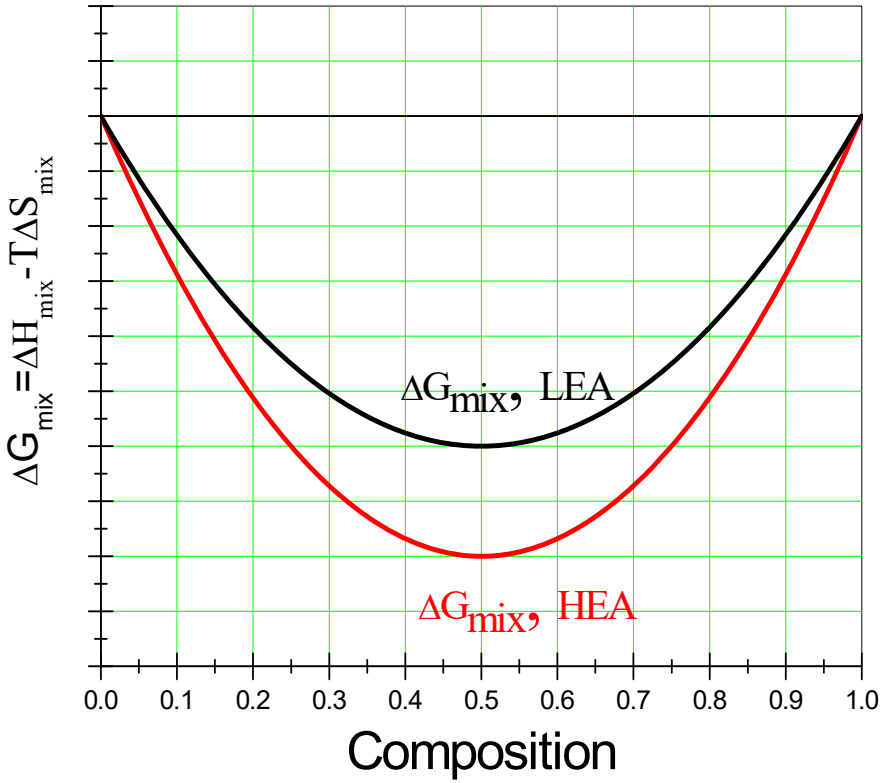
Basic concepts of high entropy alloy (HEA)

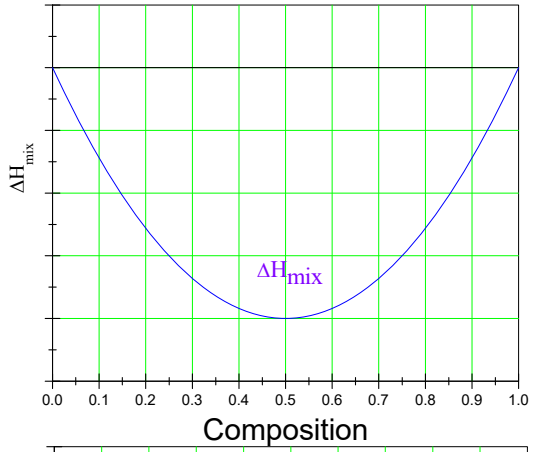


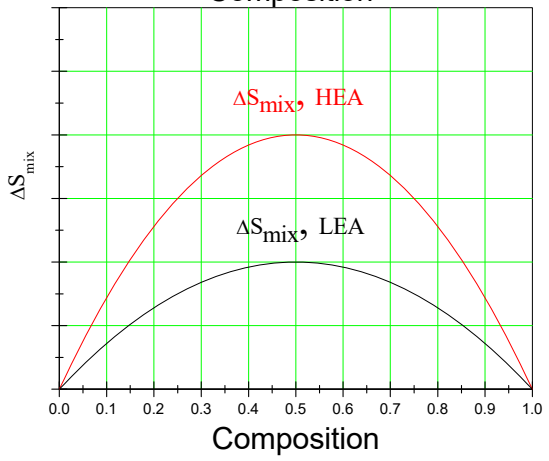
Gibbs Free Energy

$$\Delta G_{mix} = G_{AB} - (X_A G_A + X_B G_B)$$

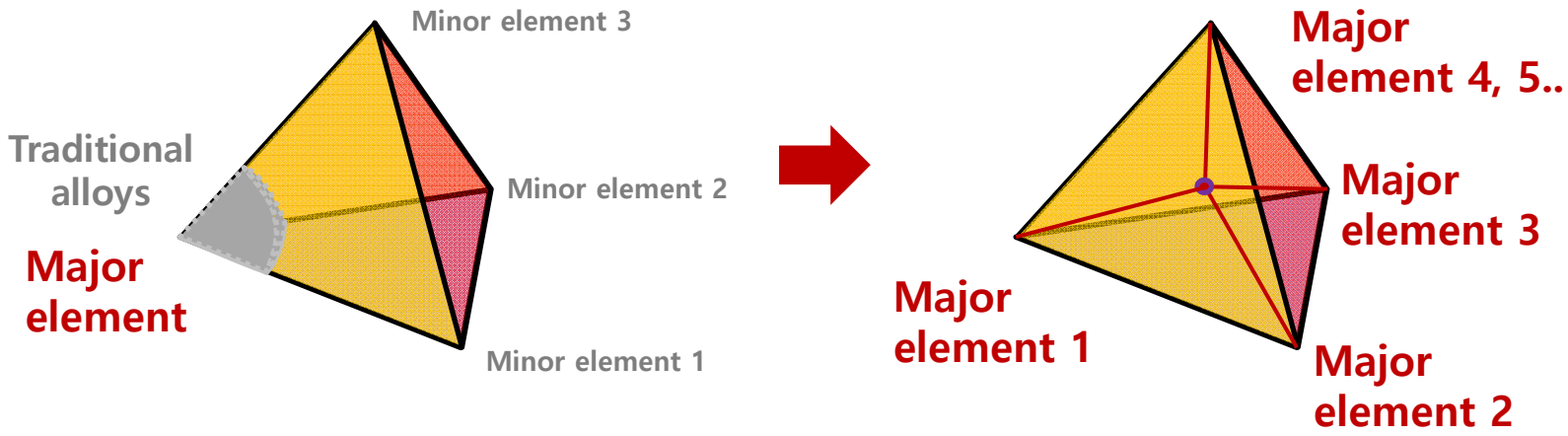
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$







Basic concepts of high entropy alloy (HEA)



Conventional alloy system

Ex) 304 steel - $Fe_{74}Cr_{18}Ni_8$

High entropy alloy system

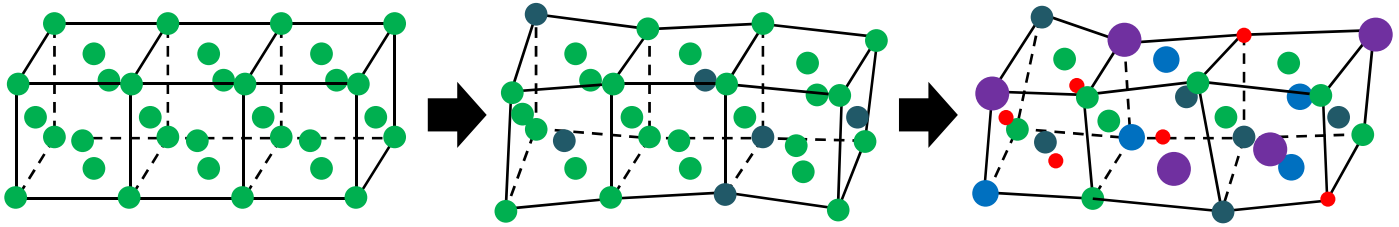
Ex) $Al_{20}Co_{20}Cr_{20}Fe_{20}Ni_{20}$

(1) Thermodynamic : high entropy effect

(2) Kinetics : sluggish diffusion effect

(3) Structure : severe lattice distortion effect

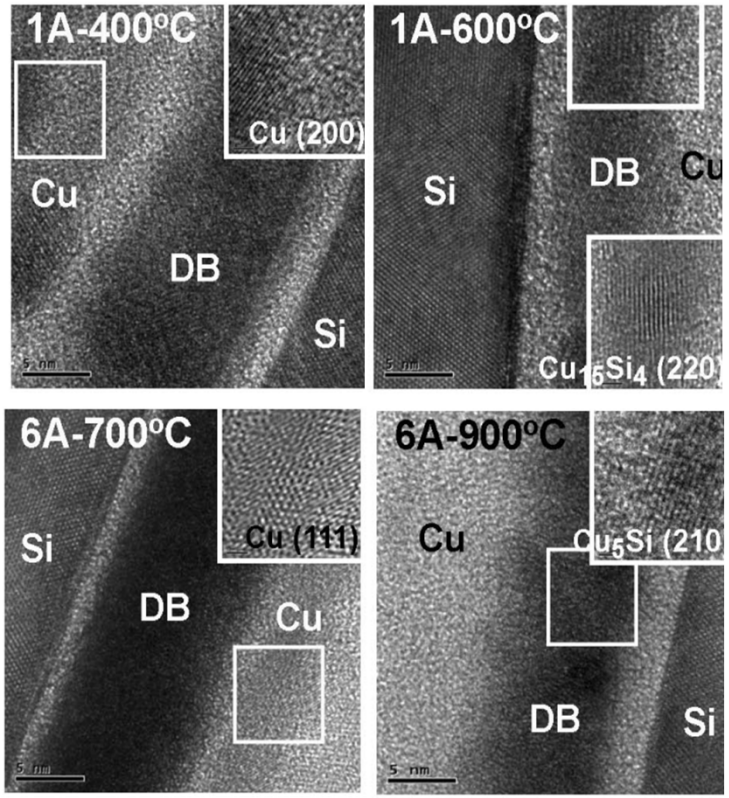
(4) Property : cocktail effect



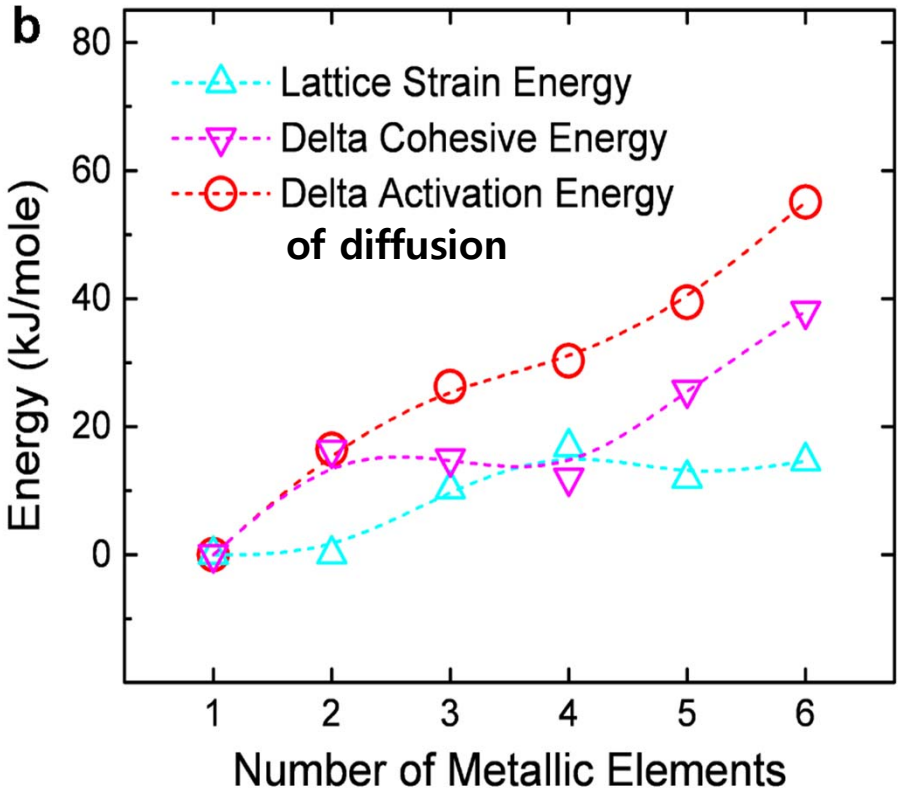
Pure metal | Conventional alloy | High entropy alloy

Severe lattice distortion → Sluggish diffusion & Thermal stability

a. Sluggish diffusion of high entropy alloy



S.Y.Chang et al., Sci.Rep. 4, 2014



Comparison of diffusion barrier effect from Ti(1A) to TiTaCrZrAlRu(6A)

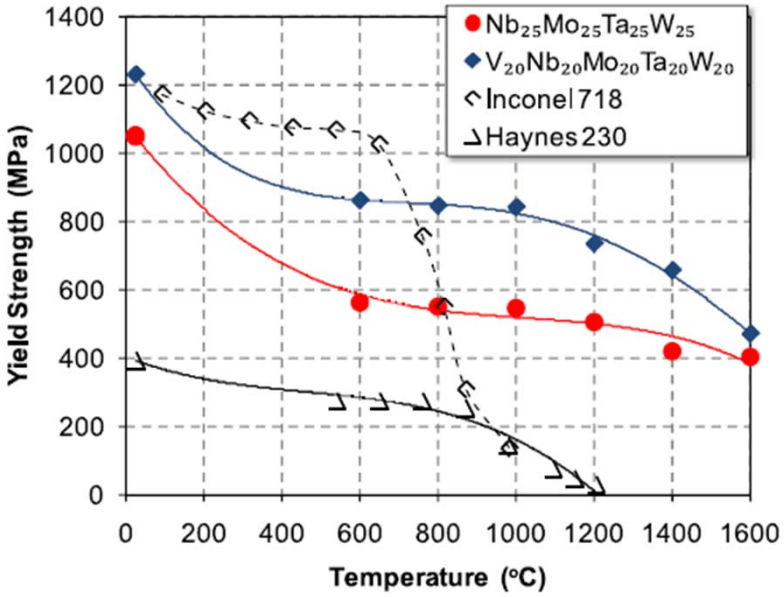
→ Muticomponent system (HEA) may induce "Sluggish diffusion ".

b. Thermal stability of high entropy alloy

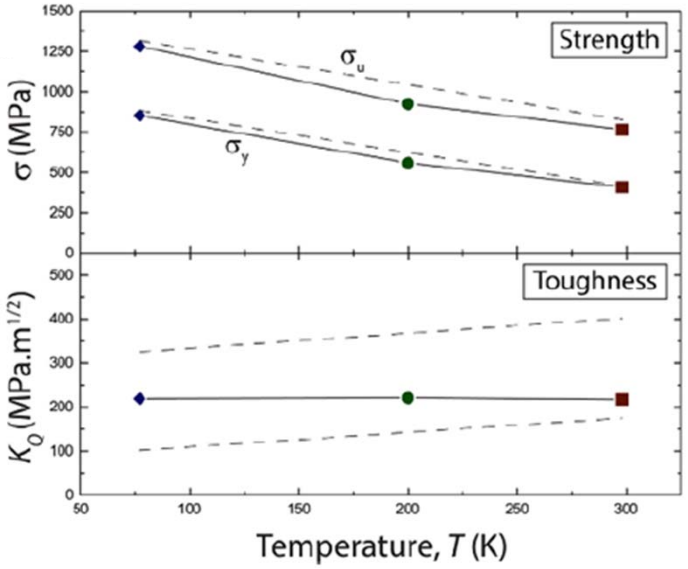
"HEA = Structural material with good thermal stability"

High temperature strength in BCC HEA **Low temperature toughness in FCC HEA**

O.N.Senkov, et al., Intermetallics, vol19 (2011)



B.Gludovatz, et al., Science , vol345 (2014)

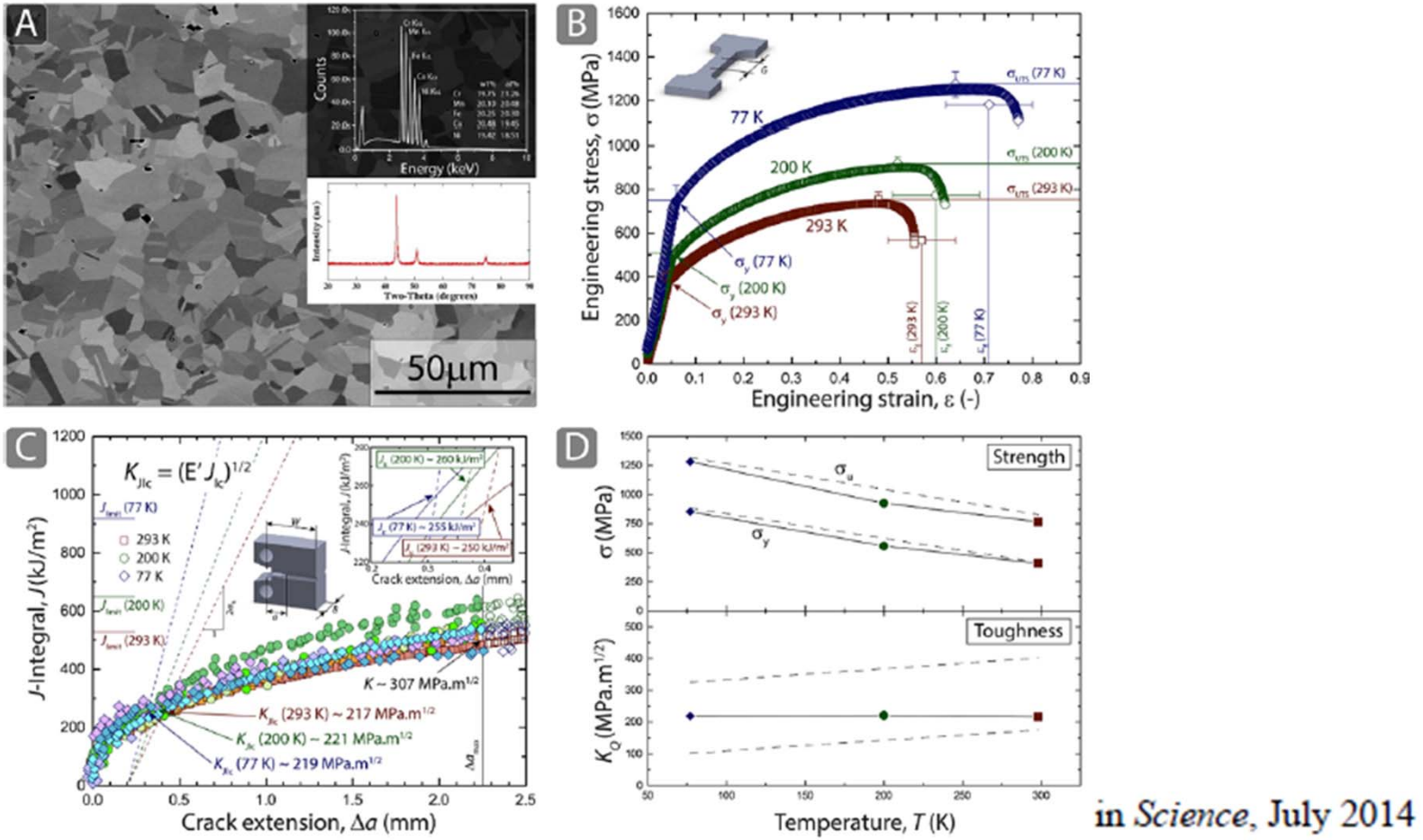


$V_{20}Nb_{20}Mo_{20}Ta_{20}W_{20}$ HEA has higher strength than $Nb_{25}Mo_{25}Ta_{25}W_{25}$, which means significant solid solution hardening effect in high temperature.

The toughness of the HEA remains unchanged, and by some measures actually increases at lower temp due to change of deformation mechanism.

b. Thermal stability of high entropy alloy

A Fracture resistant high-entropy alloy for cryogenic applications

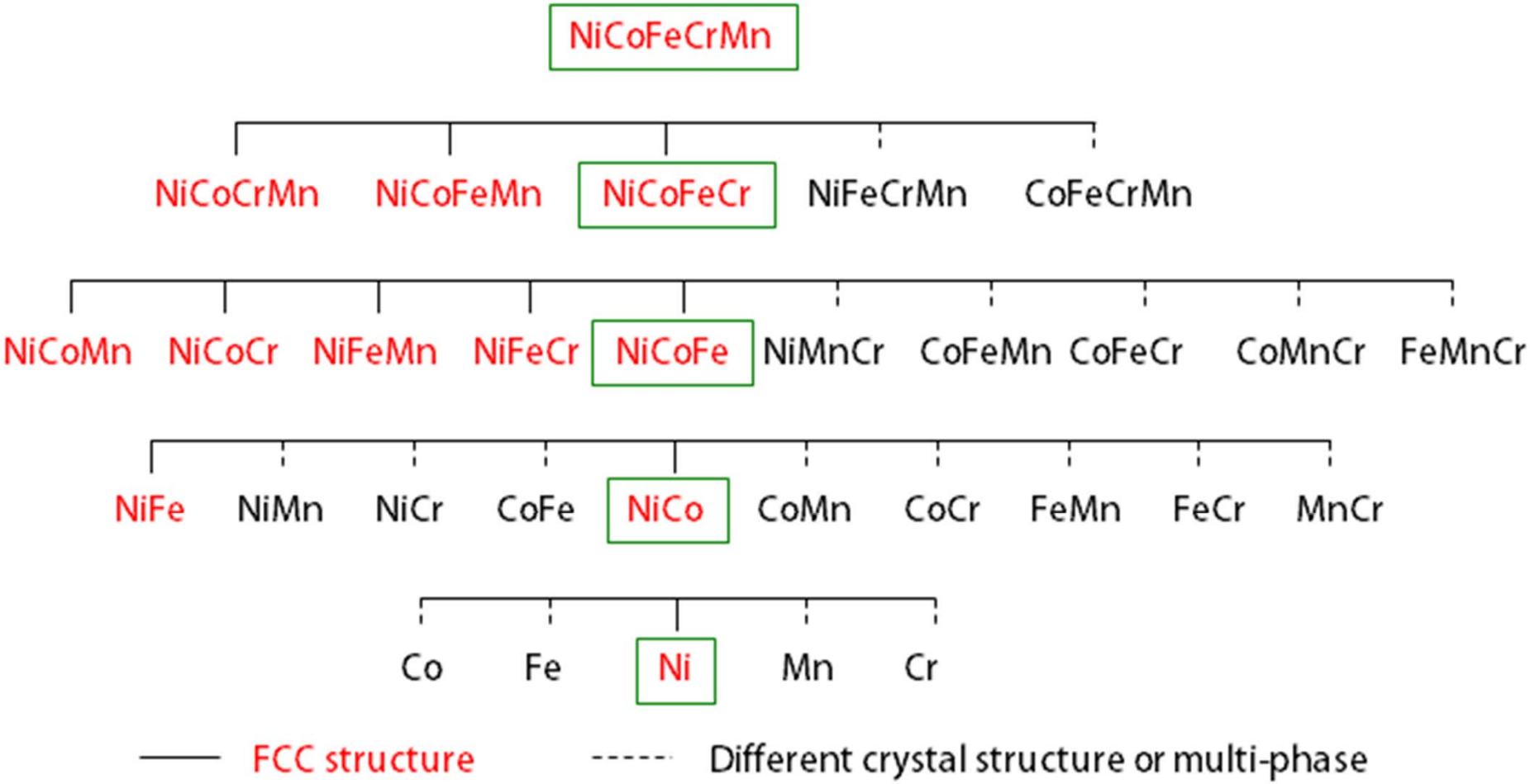


in *Science*, July 2014

Microstructure and mechanical properties of the CrMnFeCoNi HEA

Similar to austenitic stainless steels or cryogenic Ni steels, the strength of the HEA increases with decreasing temp. ; however, while the toughness of the other materials decreases with decreasing temp.. the toughness of the HEA remains unchanged, and by some measures actually increases at lower temp.

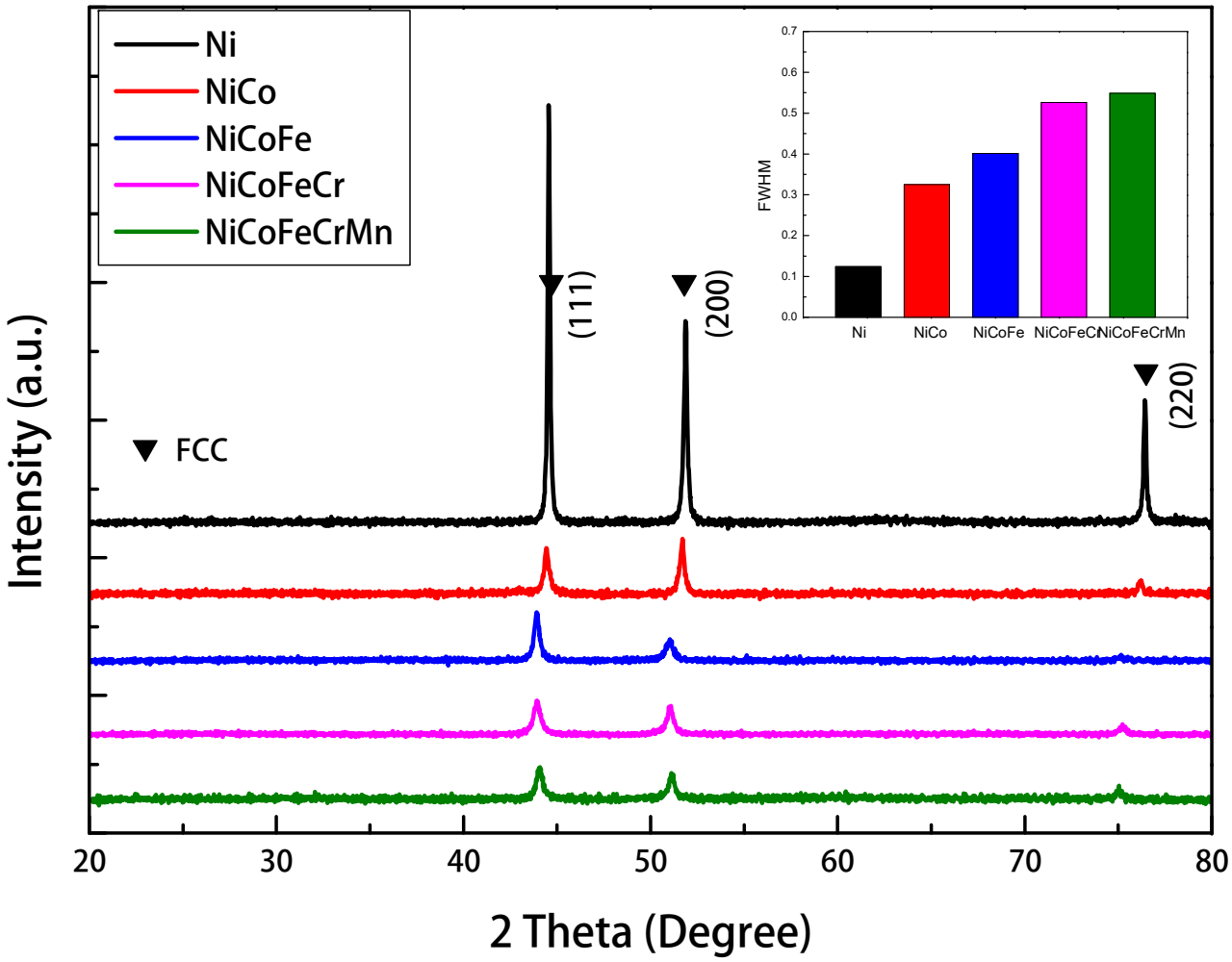
Singe-phase FCC solid solution: Ni → Ni-Co-Fe-Cr-Mn HEA



Single-phase FCC solid solutions after homogenization are written in RED.
The five alloys chosen in this study are marked by square.

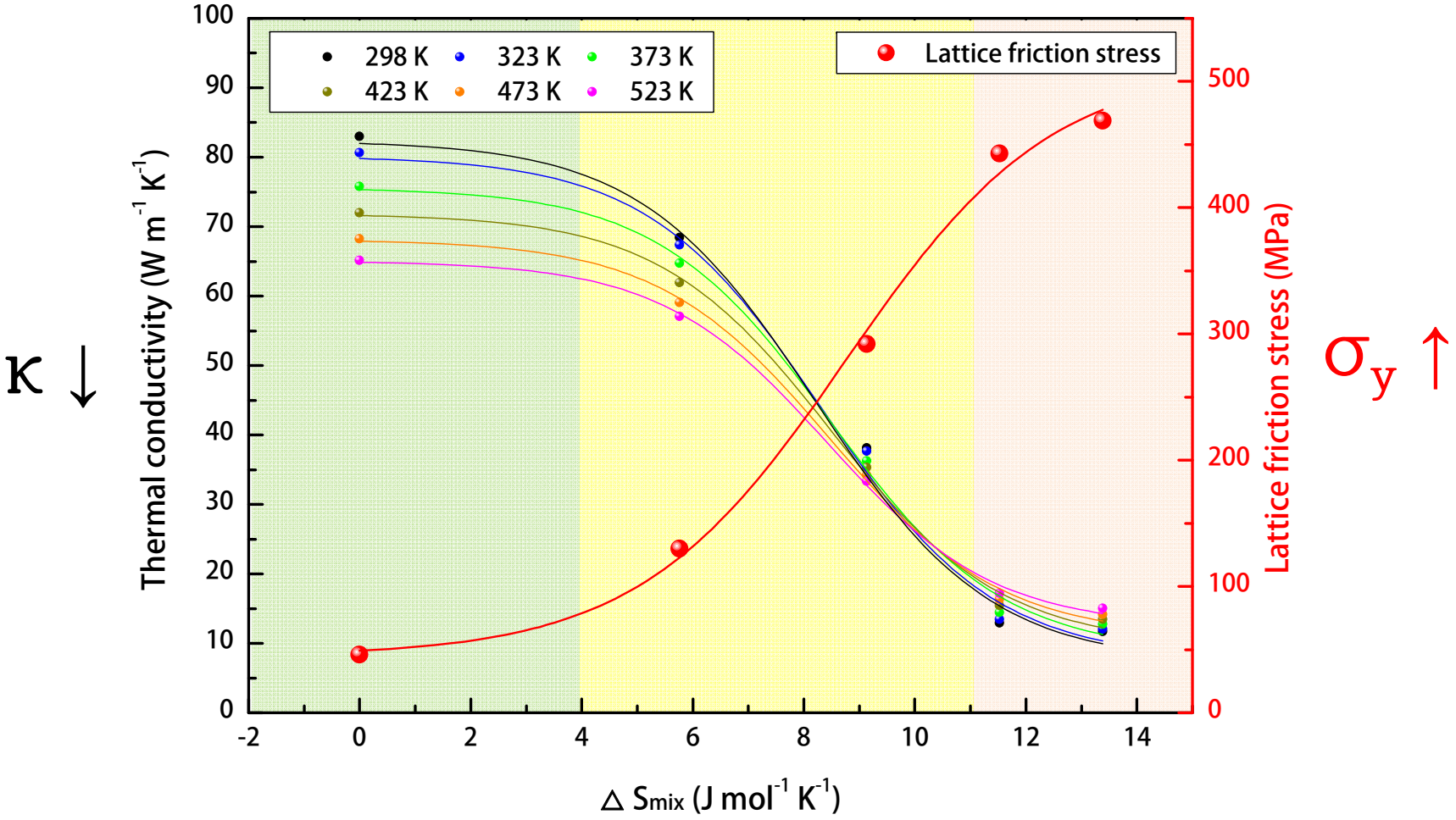
Singe-phase FCC solid solution: Ni → Ni-Co-Fe-Cr-Mn HEA

XRD patterns of NiCoFeCrMn HEA and its sub-alloys after homogenization



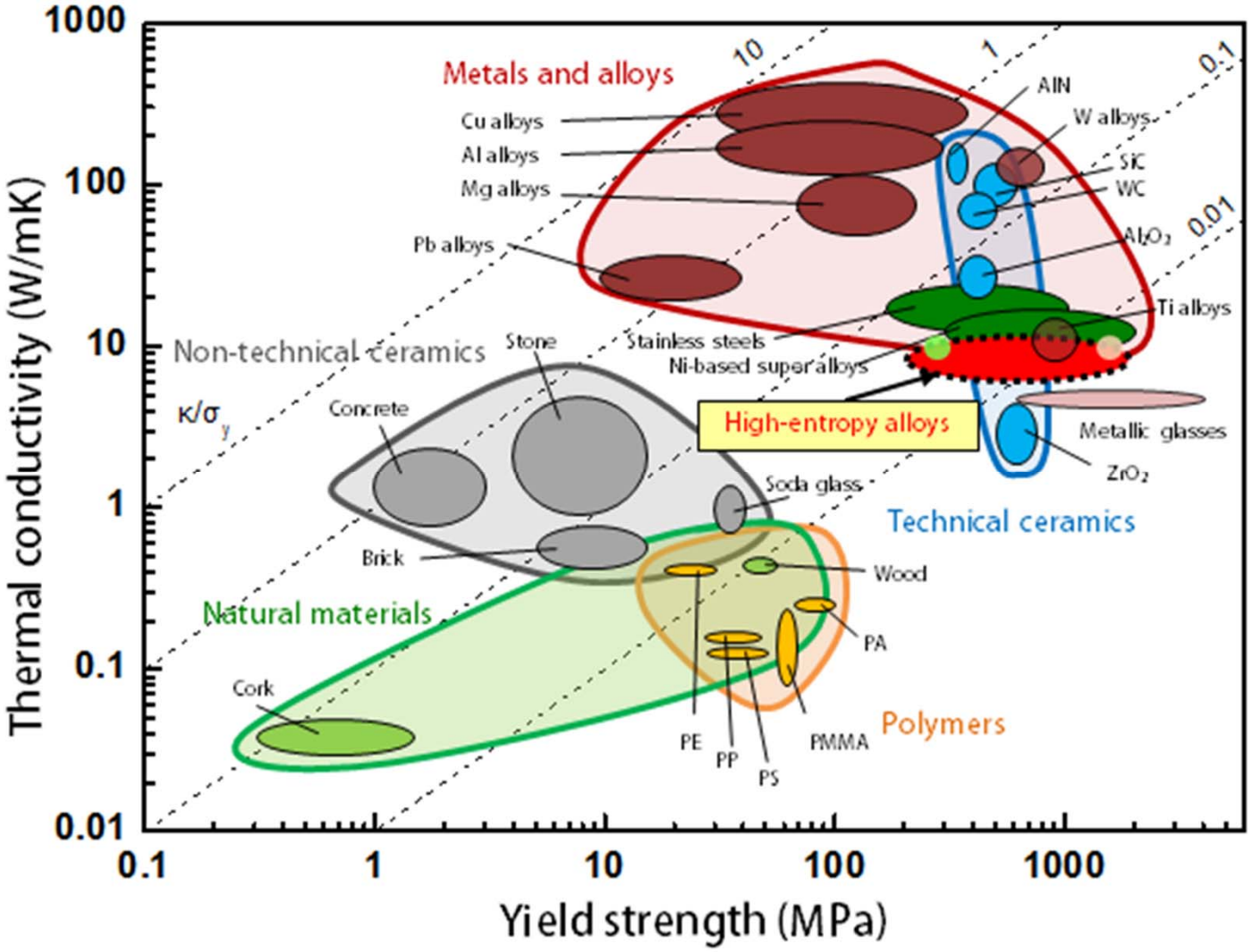
The inset shows full width at half maximum values of the alloys.

Singe-phase FCC solid solution: Ni → Ni-Co-Fe-Cr-Mn HEA



Micro-hardness and thermal conductivity at various temperatures of Ni → Ni-Co-Fe-Cr-Mn HEA as a function of configurational entropy of mixing

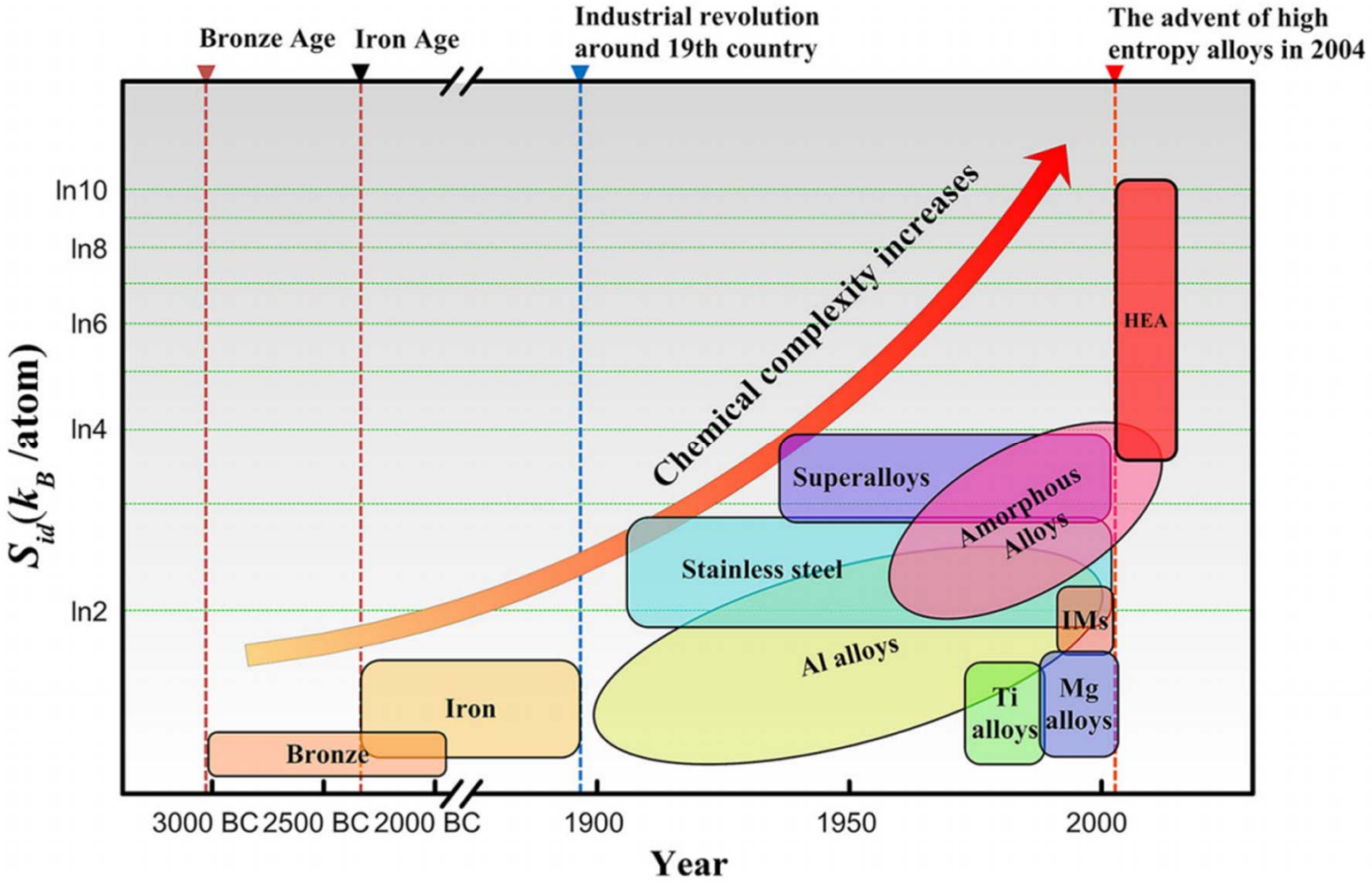
Ashby map showing thermal conductivity vs yield strength



METAL MIXOLOGY

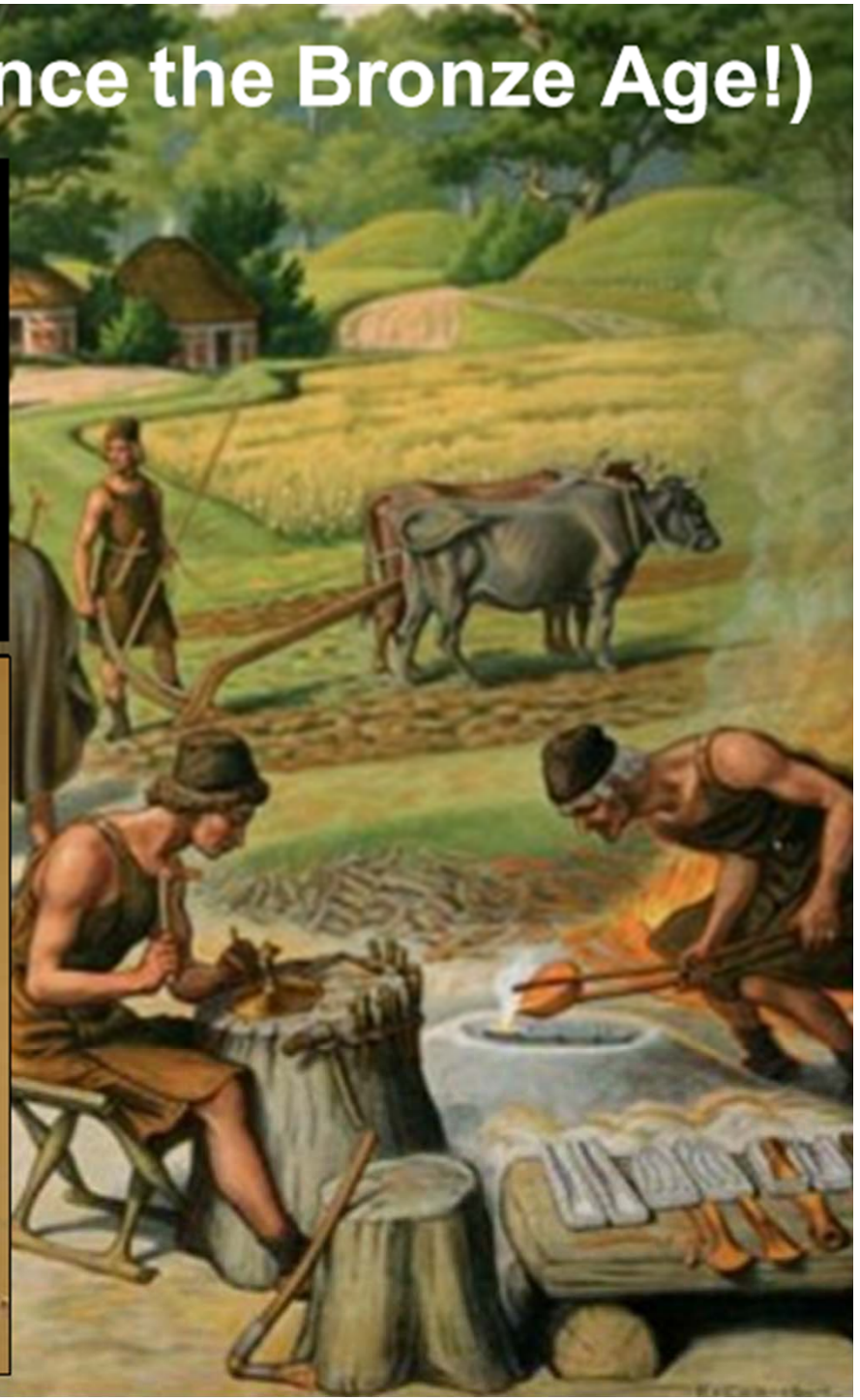
* Development strategy of completely new materials

a. Alloyed pleasures: Multi-metallic cocktails

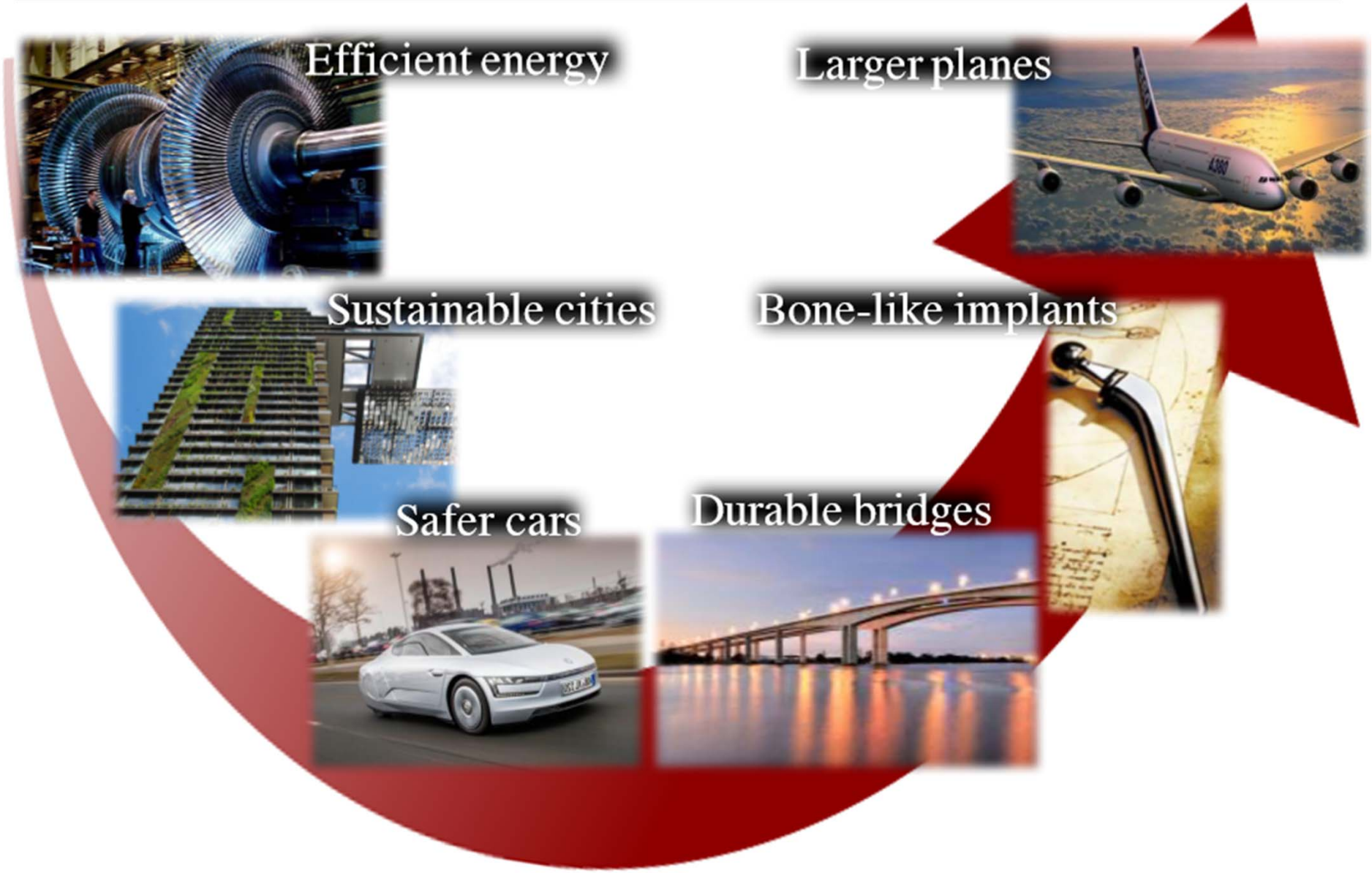


Rising trend of alloy chemical complexity versus time. Note that "IMs" stands for intermetallics or metallic compounds and "HEA" for high-entropy alloy.

Design-for-properties (since the Bronze Age!)



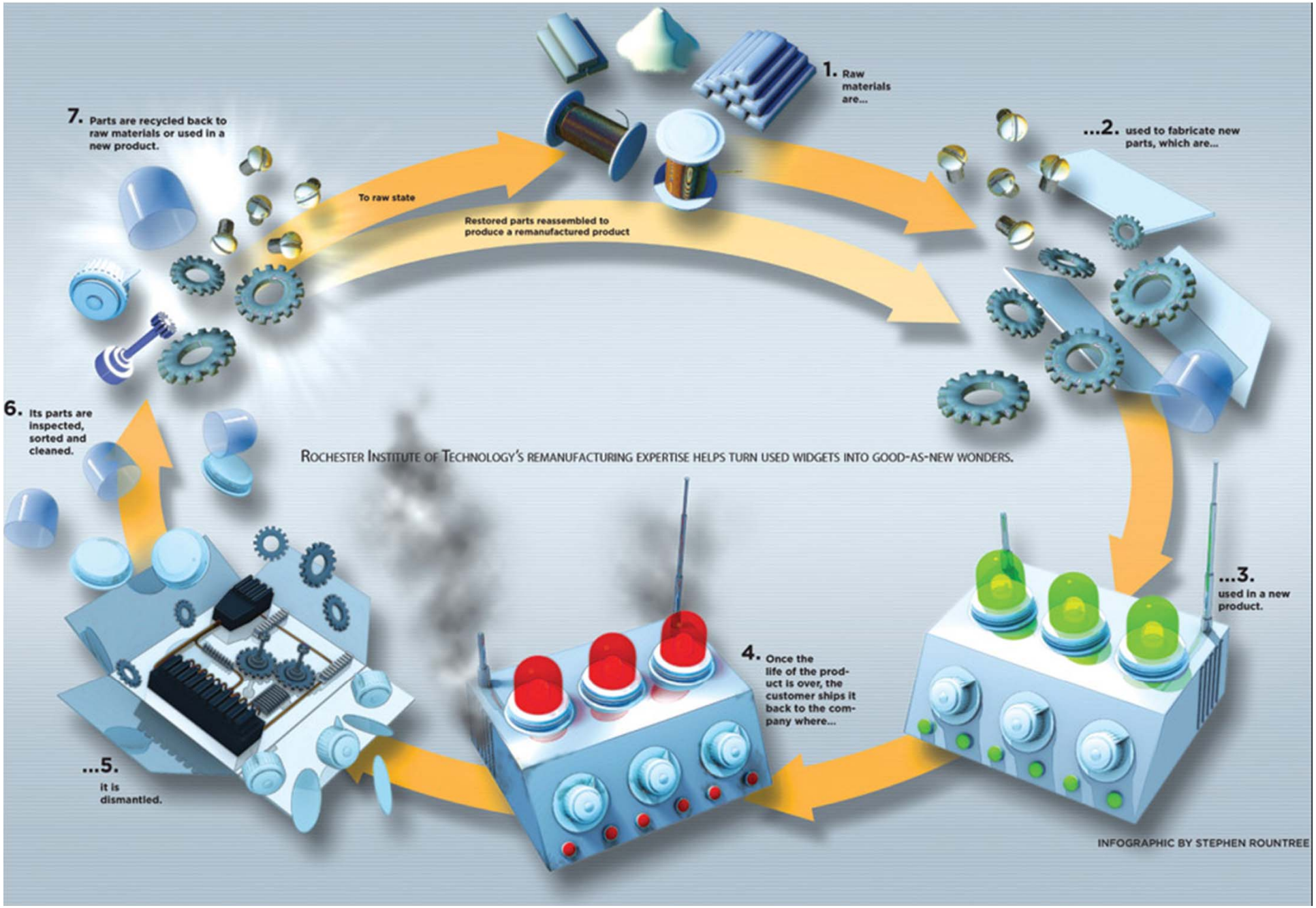
Still design-for-properties, to enable new technologies



New challenges for materials design

"Less use", "Extend Lifetime", "Reuse"!

Remanufacturing: Machine design for reuse



Materials design for reuse

Damage process is incremental, and often local → repair opportunity

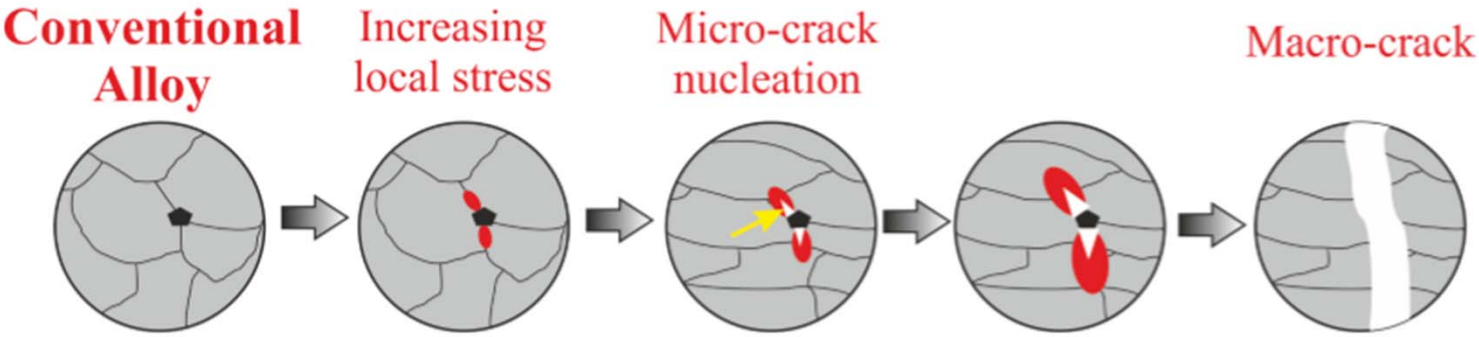
Two damage repair options possible:

- The metal autonomously repair damage → ***Self-healing***

- Damage is repaired by an external treatment → ***Resetting***

Self-healing metals vs Resettable alloys

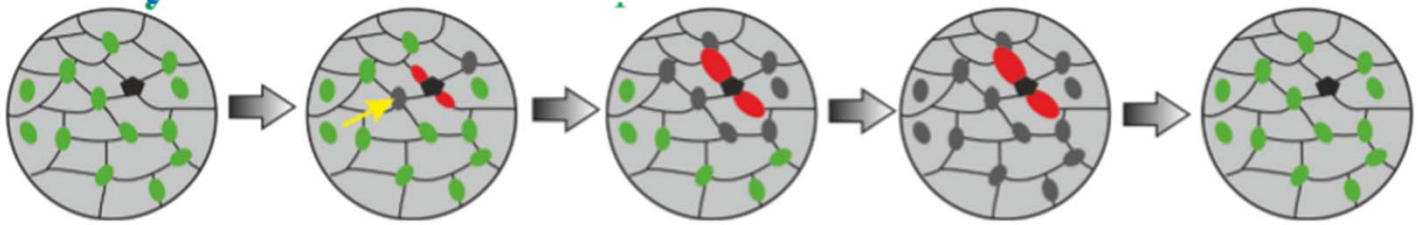
- self-healing: "*autonomic closure of micro-cracks*"
- resetting: "*non-autonomic retrieval of crack-arresting ability*"



Resettable Alloy

In-situ monitoring &
Smart sensing for micro-crack

Resetting treatment : before critical level of "damage" & feasible



: revert to the original microsturcture

Different failure mechanisms require different resetting strategies

Urgent need for mission change:

Materials design-for-“properties” & “reuse”