2016 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)

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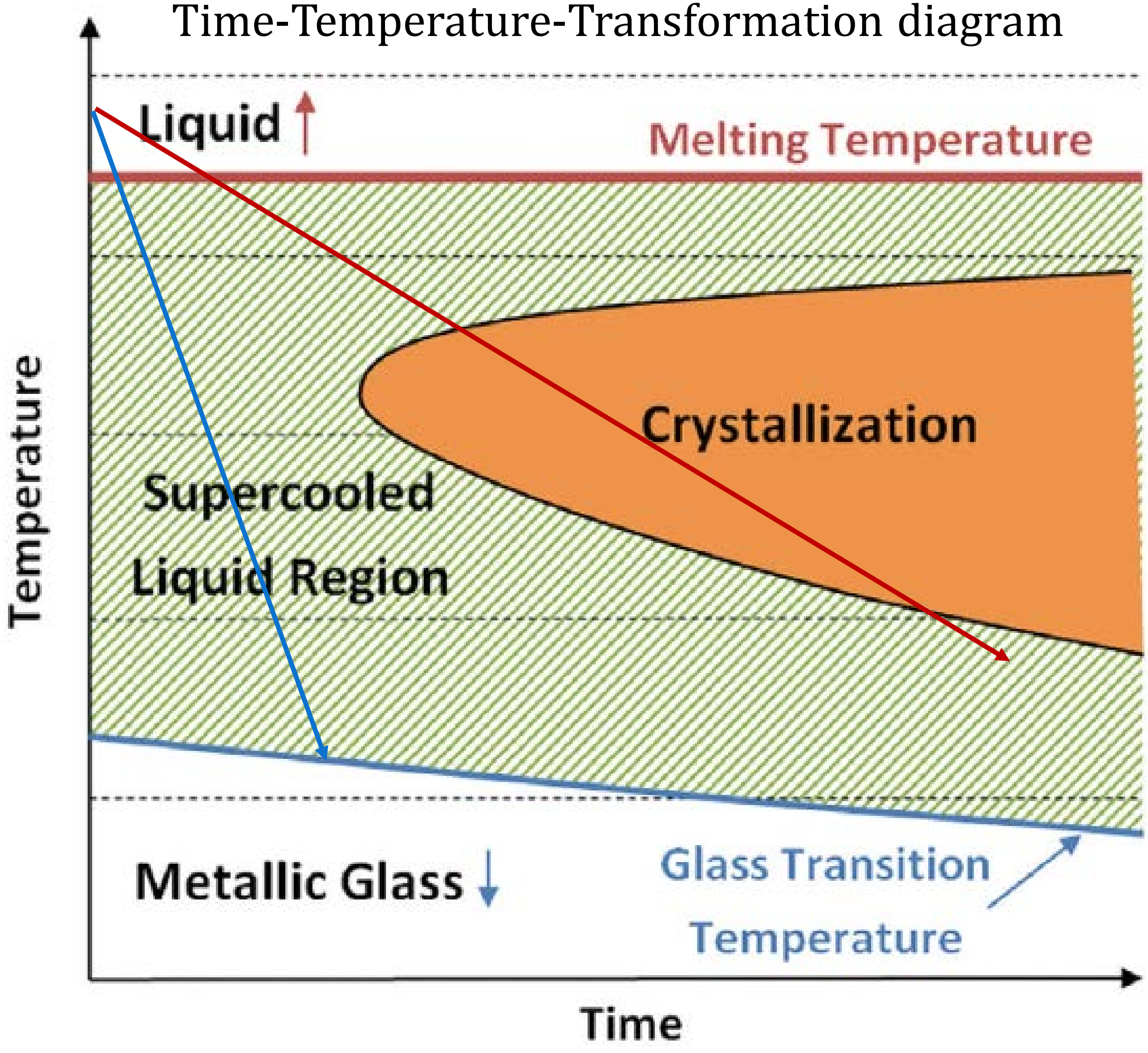
Q1: What kind of new and advanced materials were developed up to now?

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.

A1: Bulk Metallic Glass

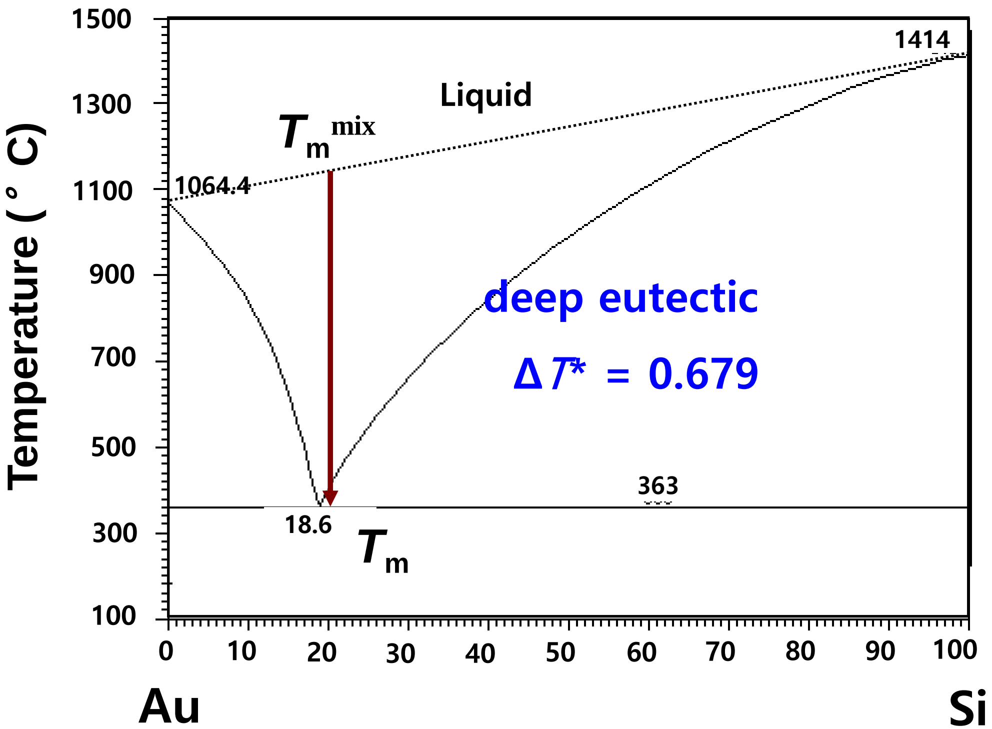
Bulk Metallic Glasses

Time-Temperature-Transformation diagram

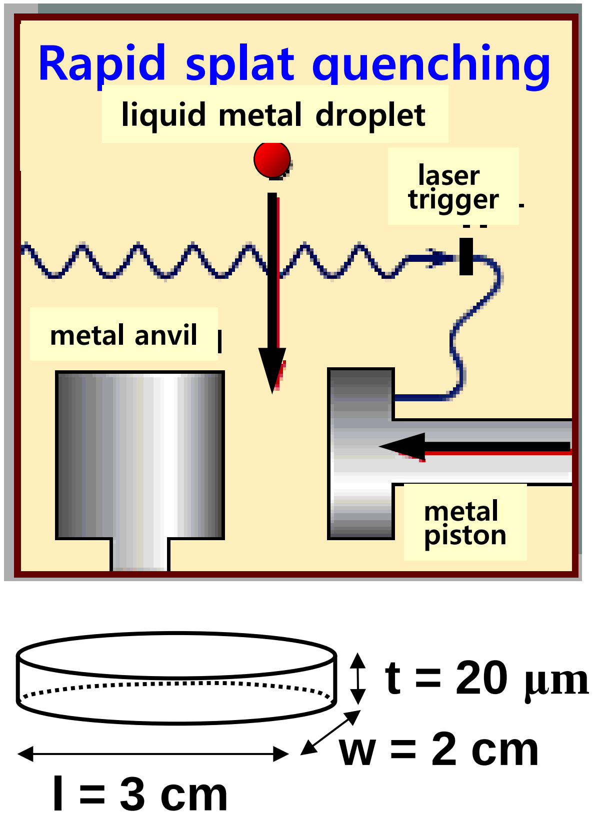


Glass formation : stabilizing the liquid phase & rapid quenching

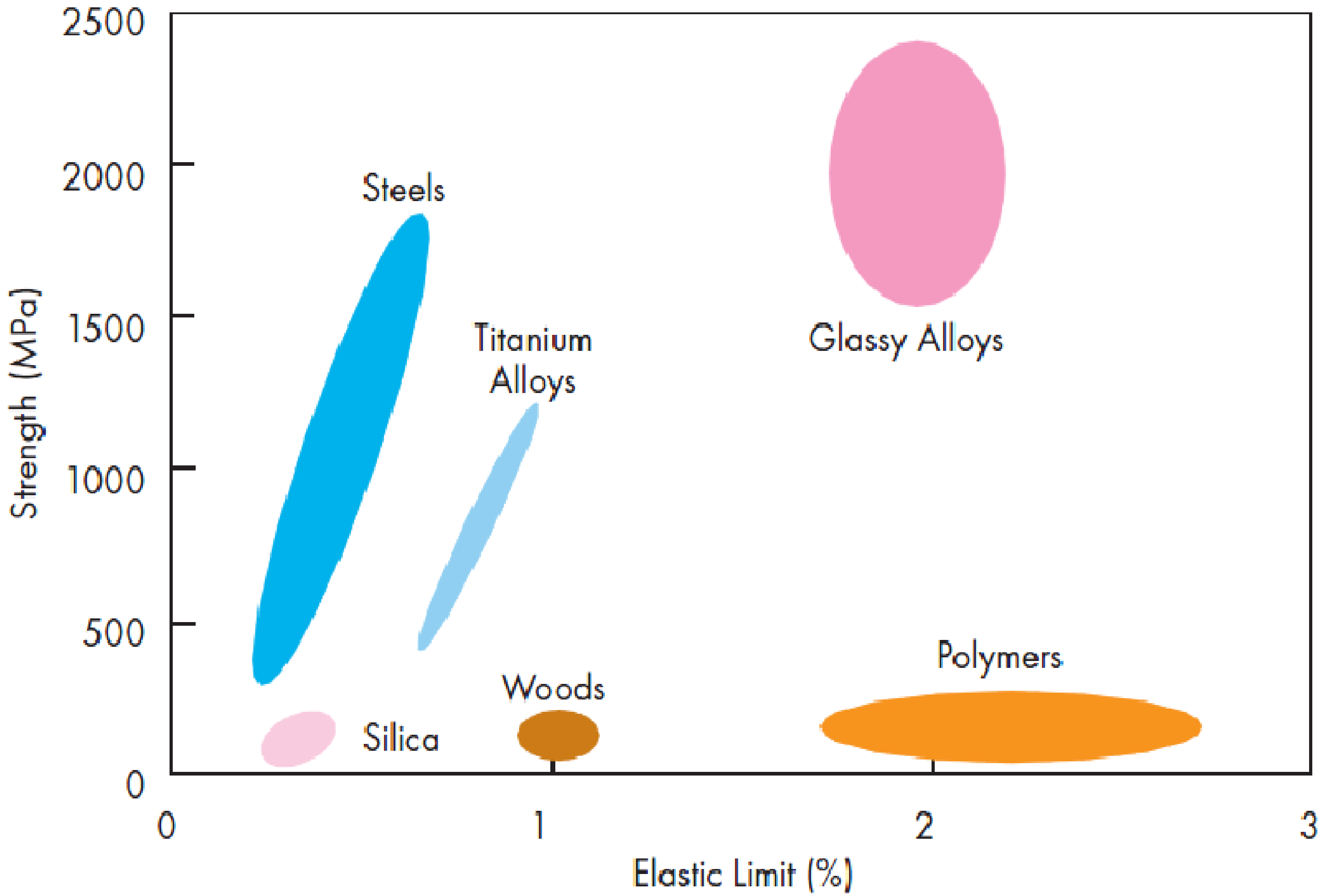
- First **metallic glass** ($Au_{80}Si_{20}$) produced by splat quenching at Caltech by Pol Duwez in 1960.



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



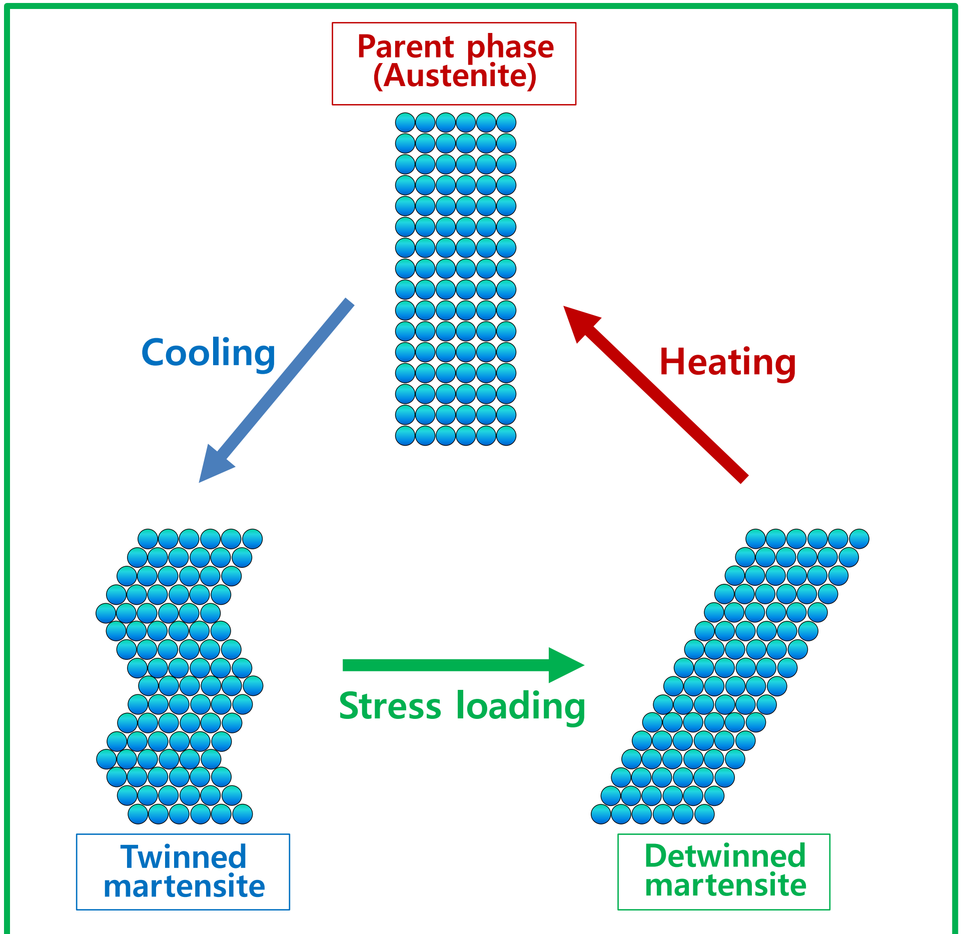
Bulk metallic glasses with high strength & high elastic limit



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

A2 : Shape Memory Alloy

Principles - Shape memory process



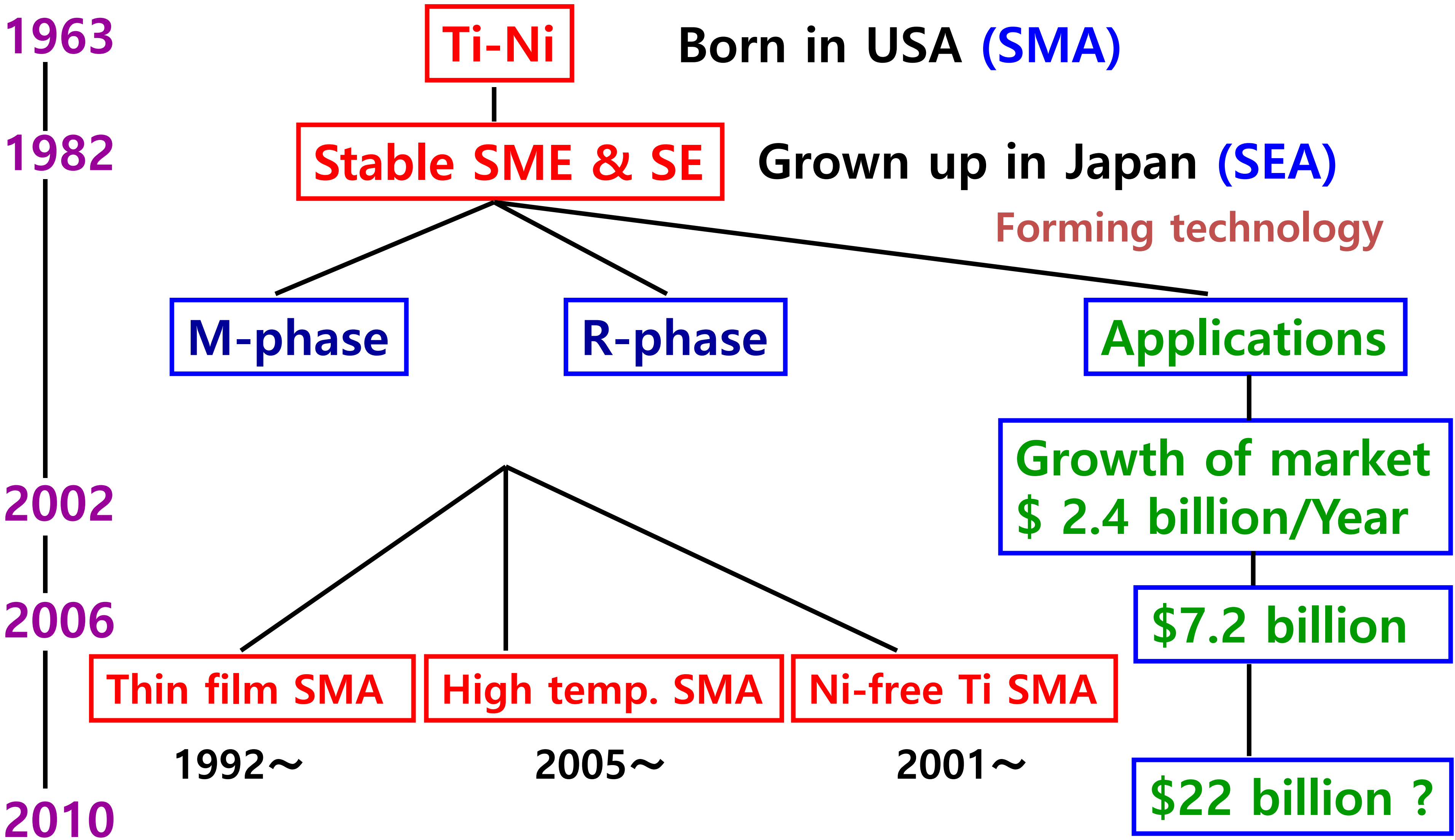
1. A_f 이상의 온도로 열처리를 통해 Austenite 상에서 형상 기억

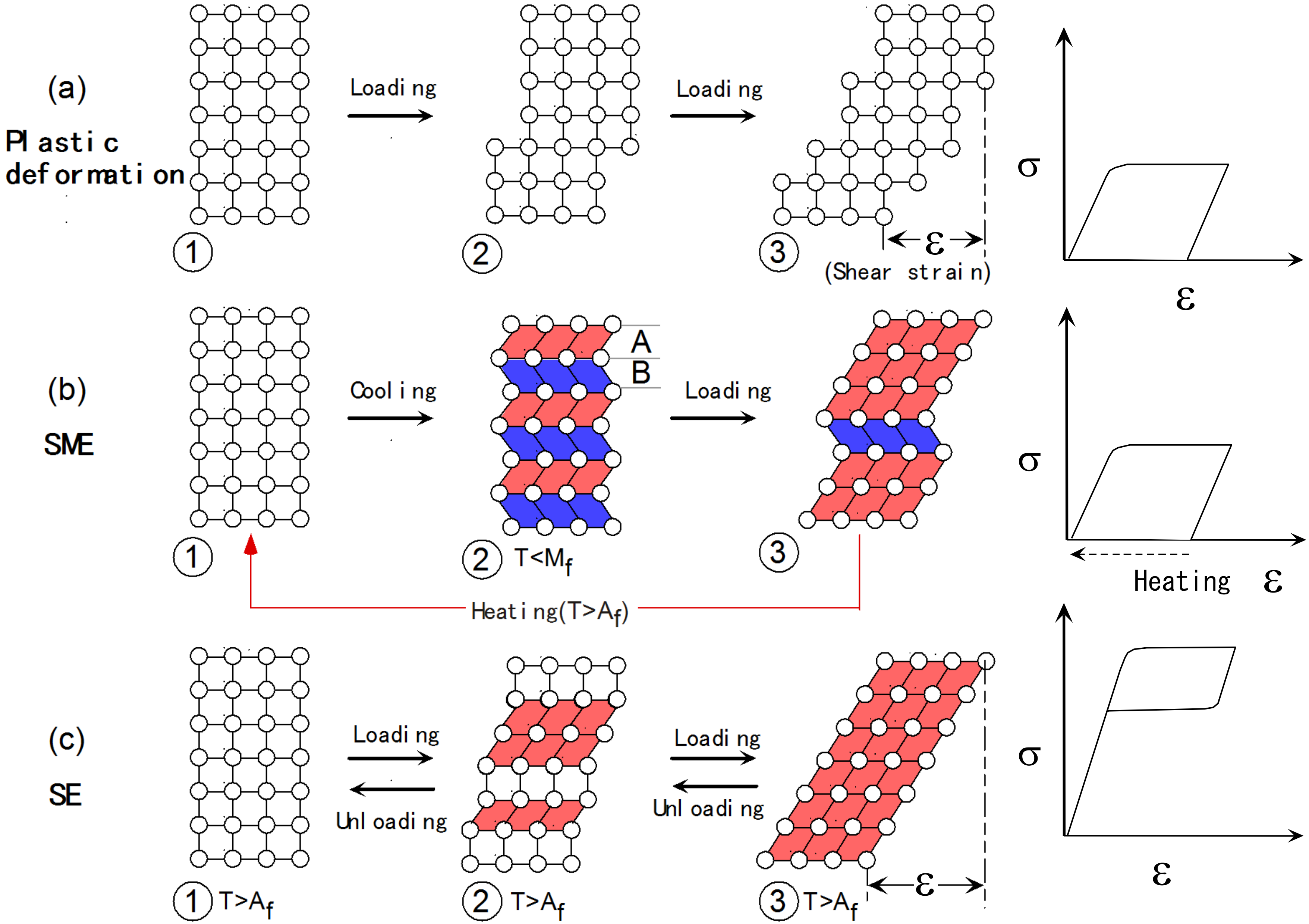
2. M_s 이하의 온도로 냉각시 Twinned martensite 생성

3. 항복강도 이상의 응력을 가하면 Twin boundary의 이동에 의한 소성 변형

4. A_f 이상으로 가열해주면 martensite에서 다시 Austenite로 변태
   ➡ 기억된 형상으로 회복

History of Shape Memory Alloy





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

A3: Quasicrystals

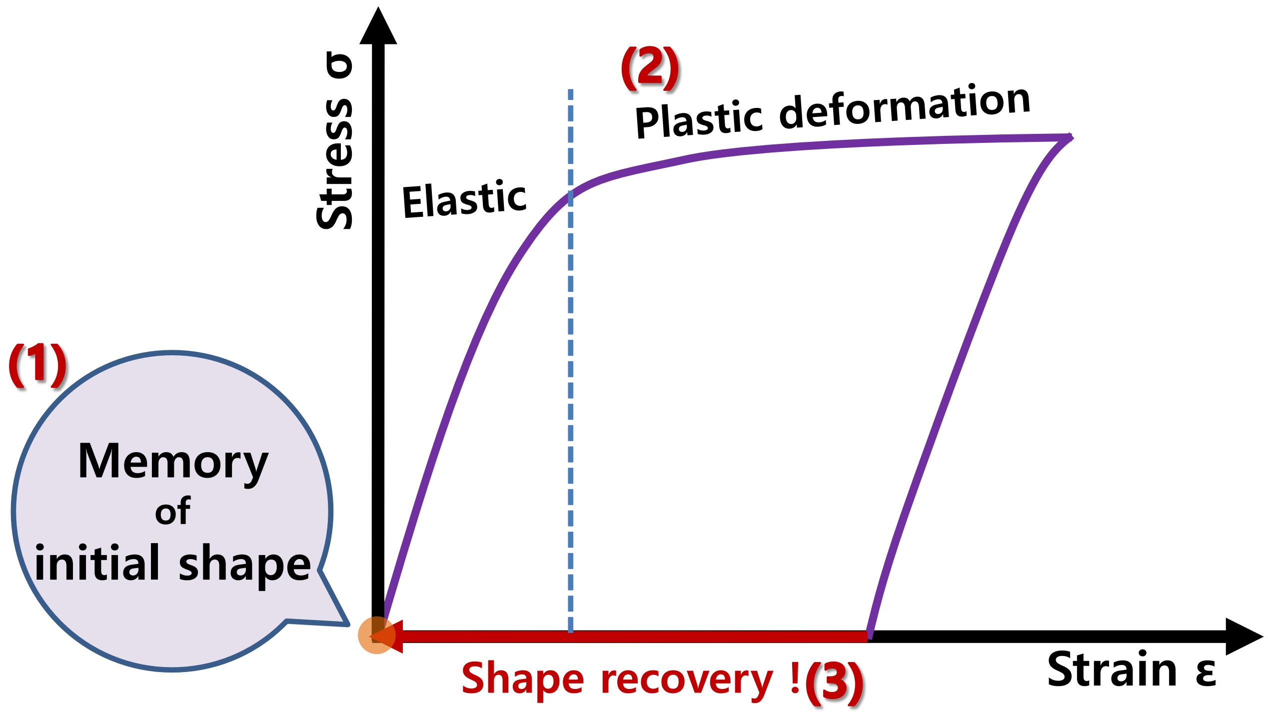
Quasicrystals (Impossible Crystals)

were first discovered in the laboratory by

Daniel Shechtman, Ilan Blech, Denis Gratias and John Cahn

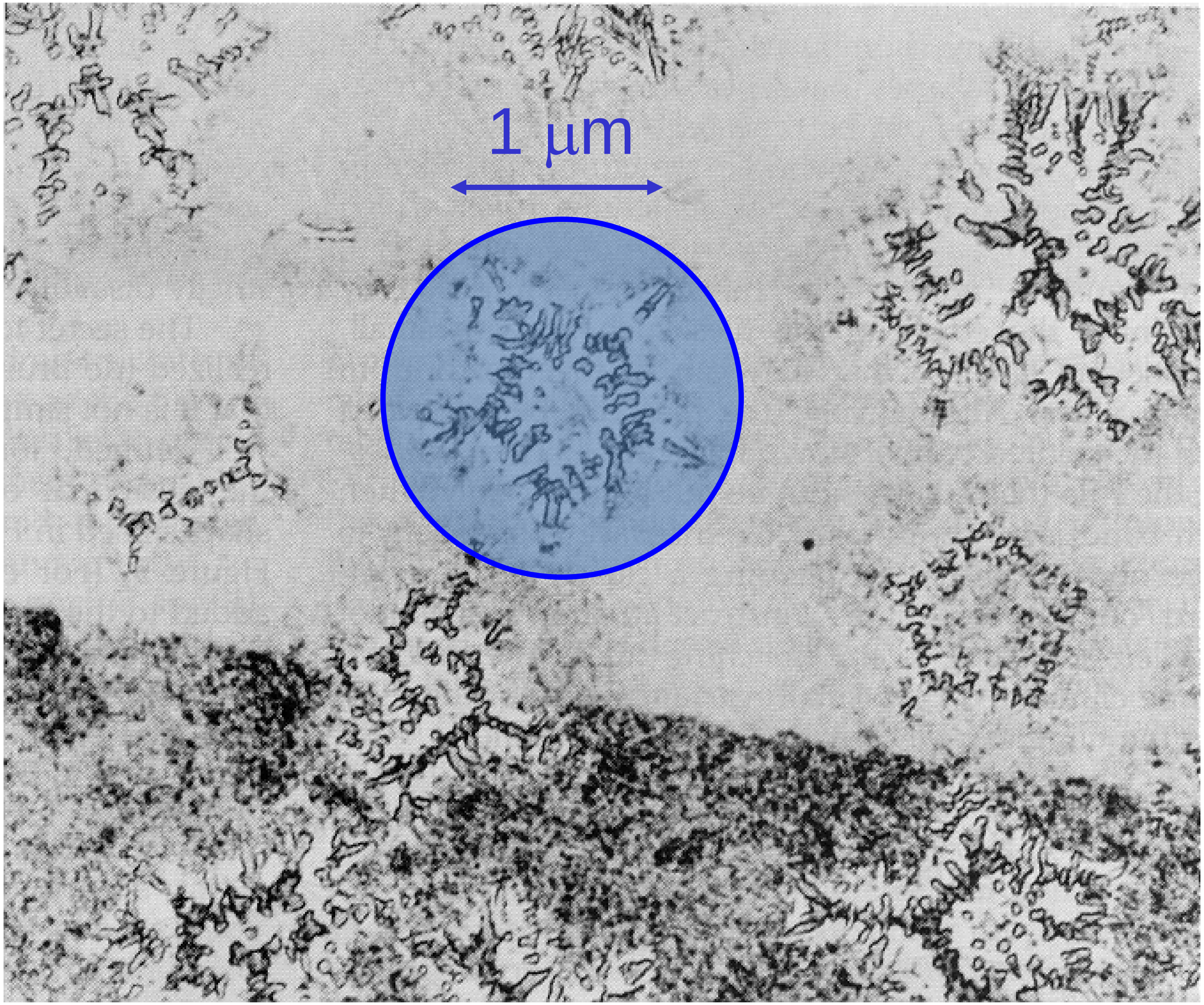
in a beautiful study of an alloy of Al and Mn (1984)

Introduction - Stress-Strain cycle
Shape memory effect



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

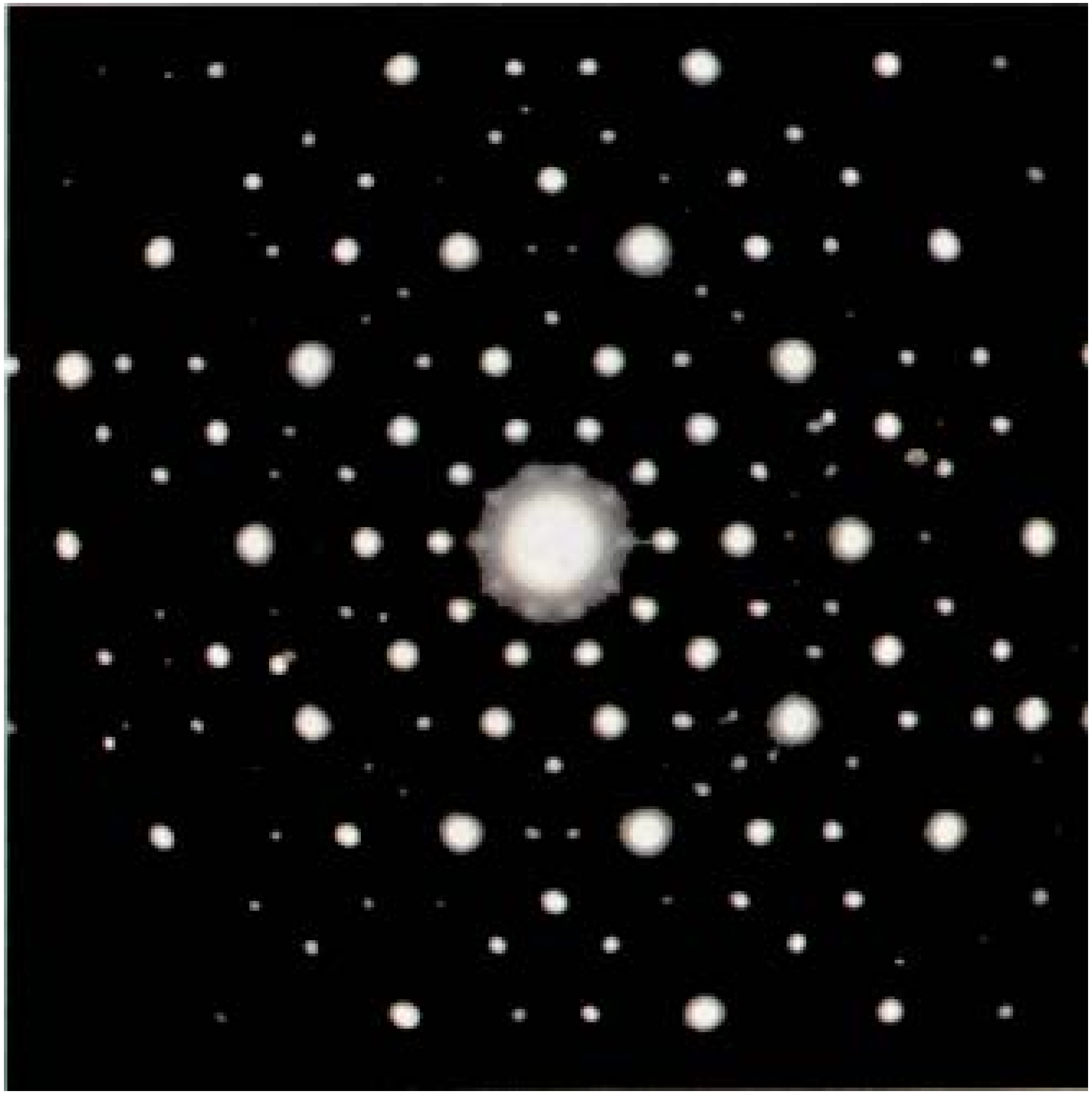
Al_6Mn



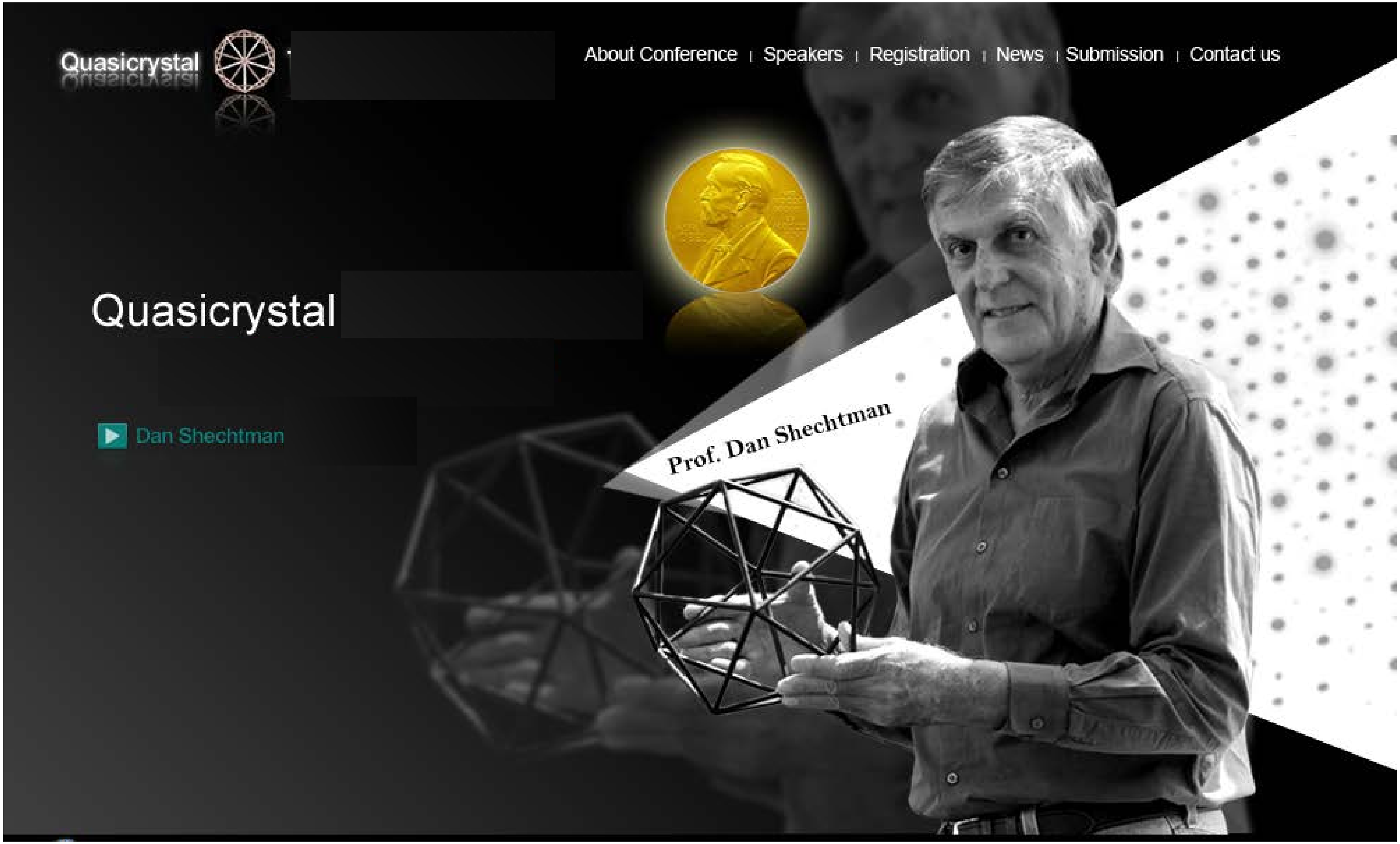
Their surprising claim:

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

Al_6Mn



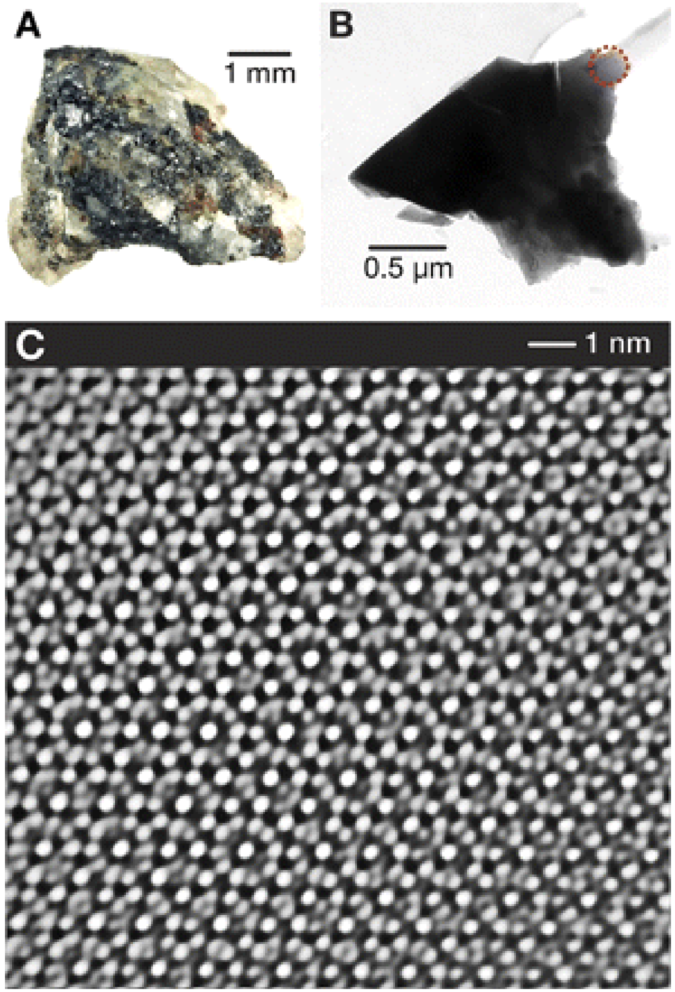
2011 Nobel Prize in Chemistry: Quasicrystal

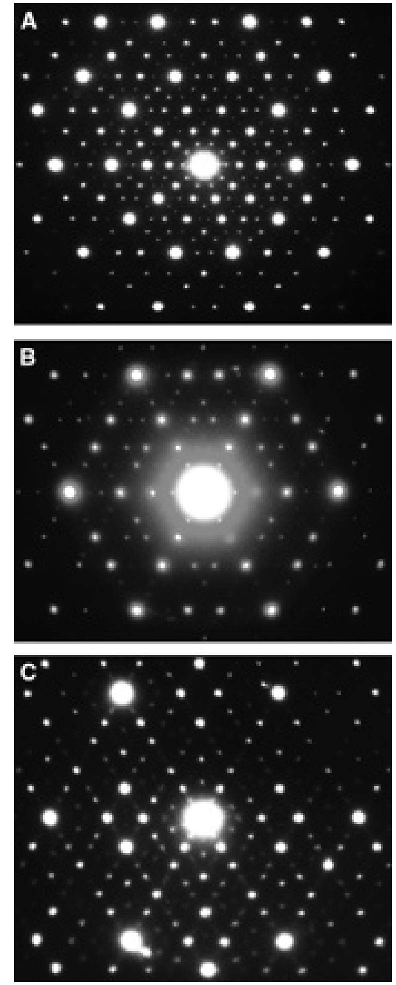


A new ordered phase showing the apparent fivefold symmetry was observed by Sastry et al. [Mater. Res. Bull. 13: 1065-1070] in 1978 in a rapidly solidified Al-Pd alloy, but was interpreted to arise from a microstructure Consisting of a series of fine twins. This was later shown to be a two-dimensional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

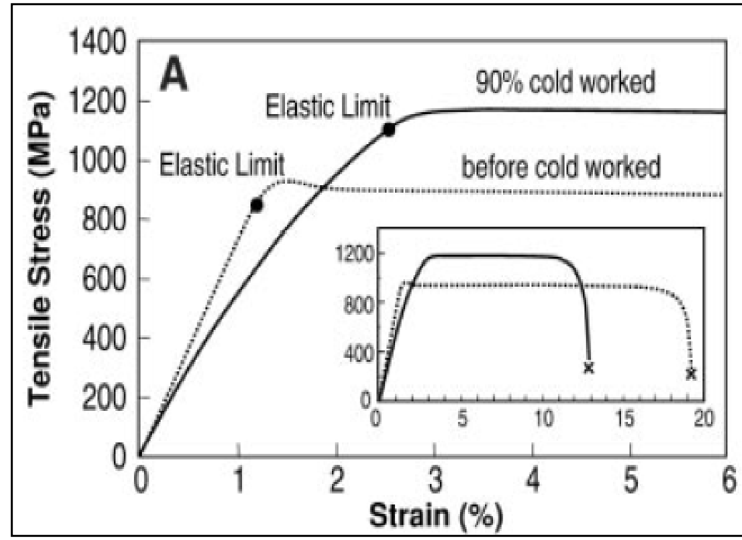
http://www.youtube.com/watch?v=k_VSpBI5EGM

A4: GUM Metal

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

Metastable Beta-Ti alloy, for example,

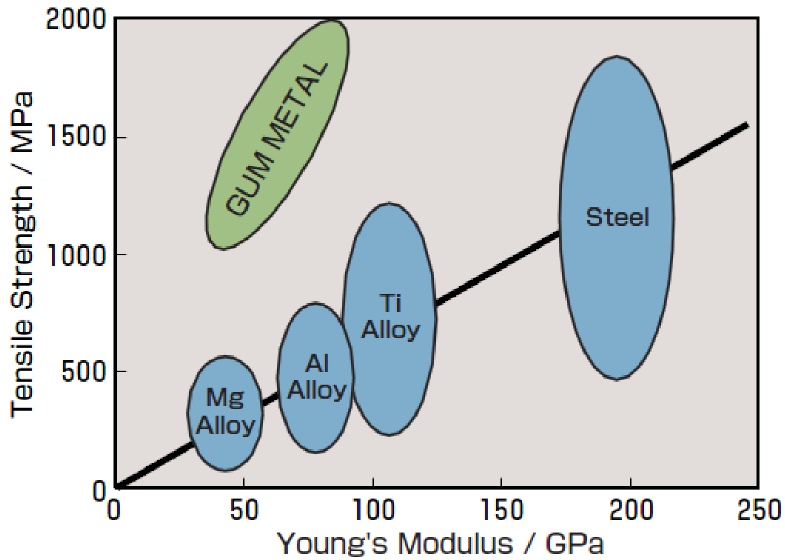
Ti-12Ta-9Nb-3V-6Zr-O, Ti-23Nb-0.7Ta-2Zr-O



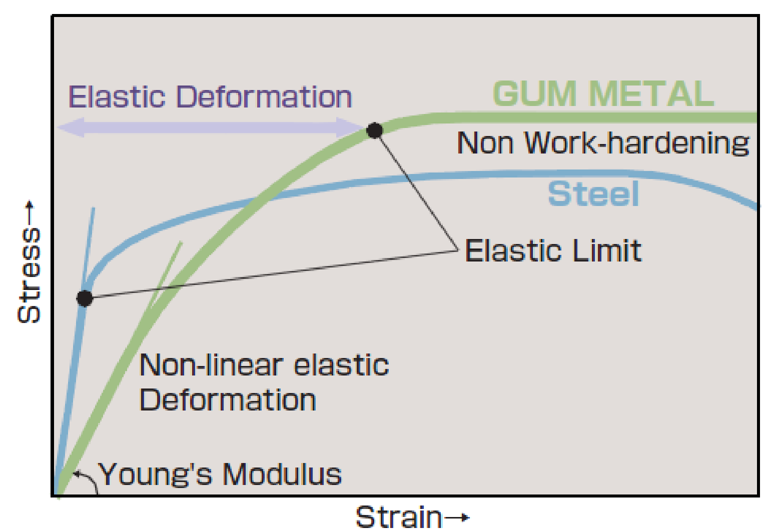
- Large elastic limit (2.5%)
- High yield stress (1~2GPa)
- Low young's modulus (50~70GPa)
- Large plasticity
- Super-elasticity (≥1%)

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

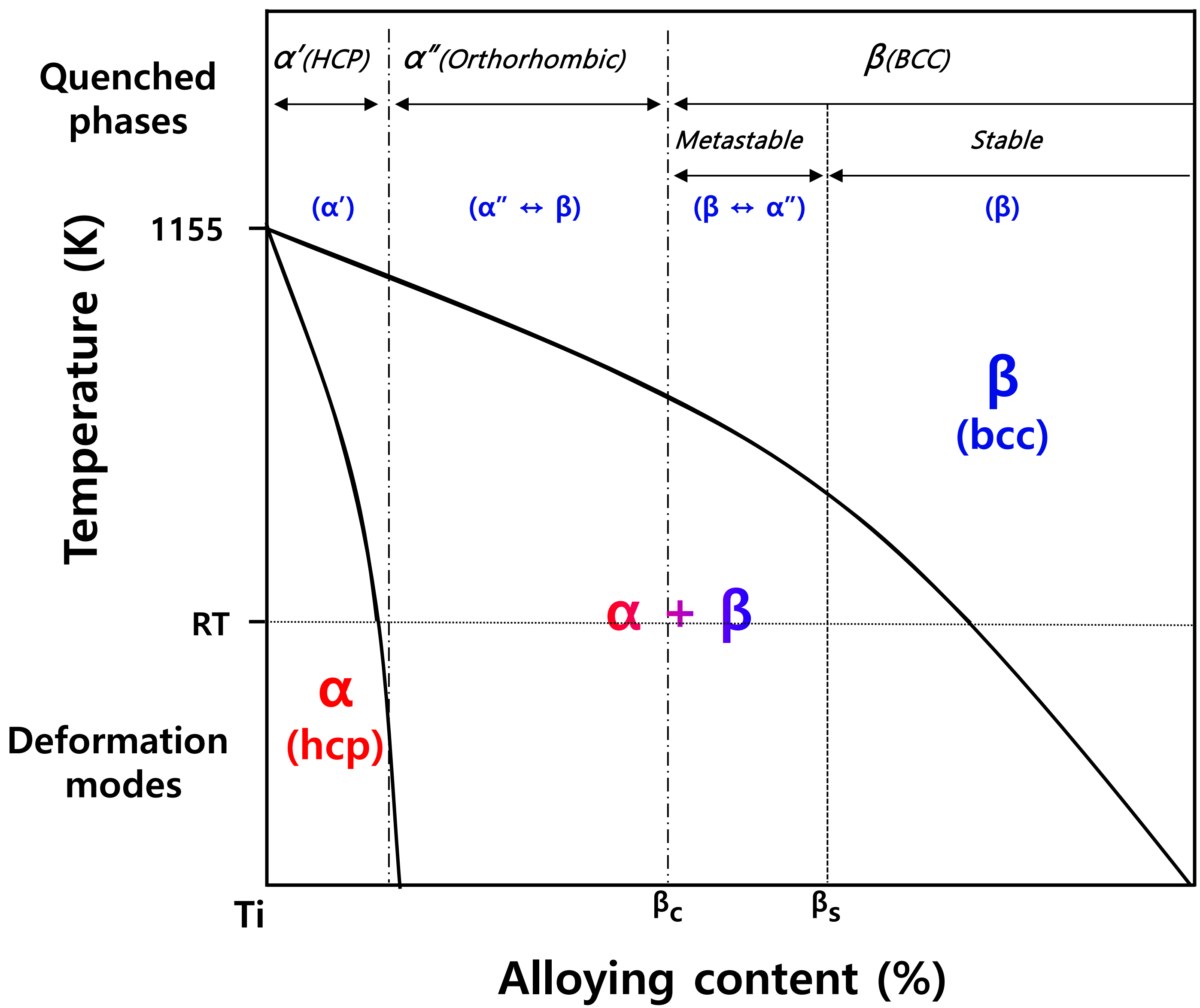
【Fig.1】Position of Young's Modulus and Strength of GUM METAL



【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

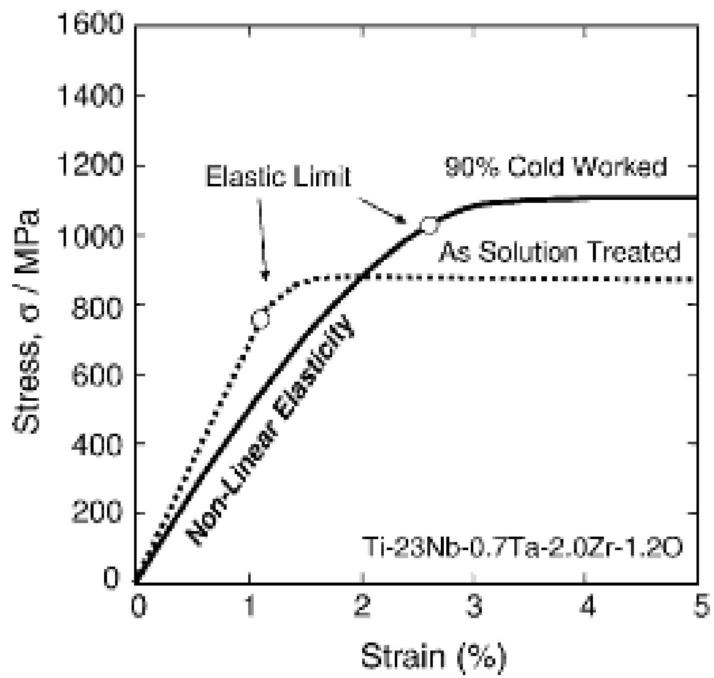


Fig. 1. Change in tensile stress-strain curve of specimen at room temperature both before and after cold working with a 90% reduction in area.

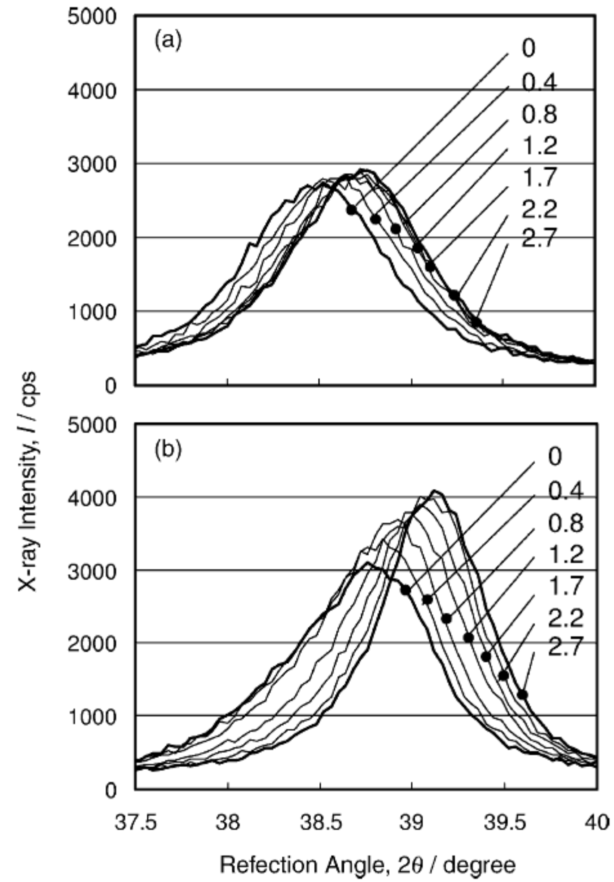
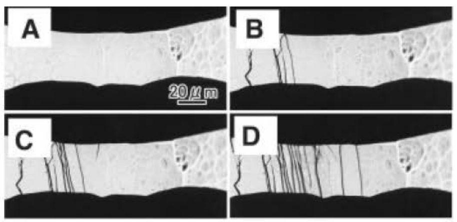


Fig. 4. Changes in X-ray profile during tensile deformation. Amounts of tensile strain (%) are indicated in the figure: (a) solution treated and (b) cold worked.

Gum metal - plastic property

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



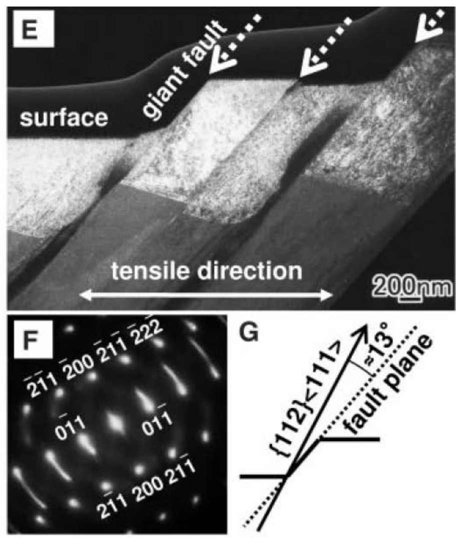
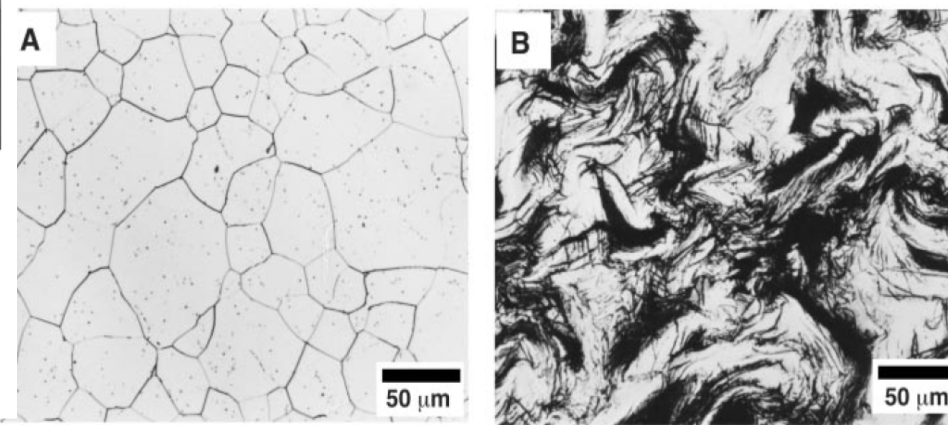


Fig. 3. (**A** to **D**) Changes in surface morphology of a tensile specimen of annealed Ti-23Nb-0.7Ta-2Zr-1.2O alloy. The amounts of deformation are (A) 0, (B) 4.3%, (C) 6.1%, and (D) 10.3%. (**E**) A TEM image near the surface of the specimen and (**F**) the corresponding electron diffraction pattern, 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 (Bo value) of about 2.87 based on the DV-X cluster method, which represents the bonding strength

(iii) a "d" electron-orbital energy level (Md value) of about 2.45 eV, representing electronegativity.

Magic number 4.24

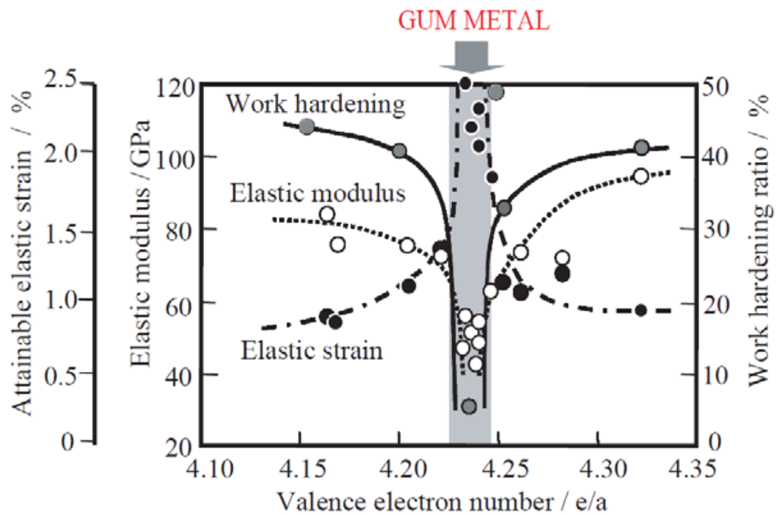
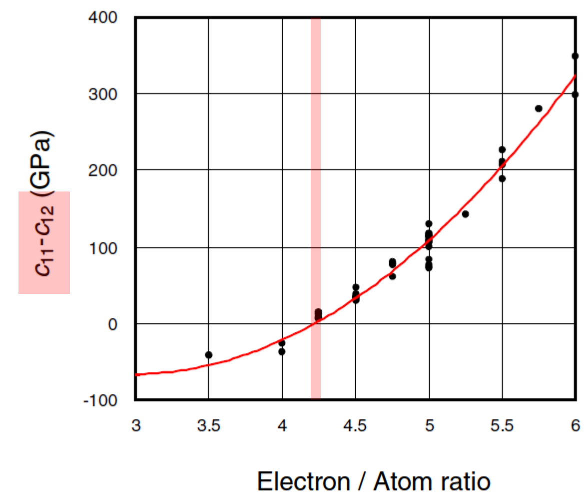


Fig. 3 Anomaly in properties of Ti-Nb-Ta-Zr-O alloys.



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

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.

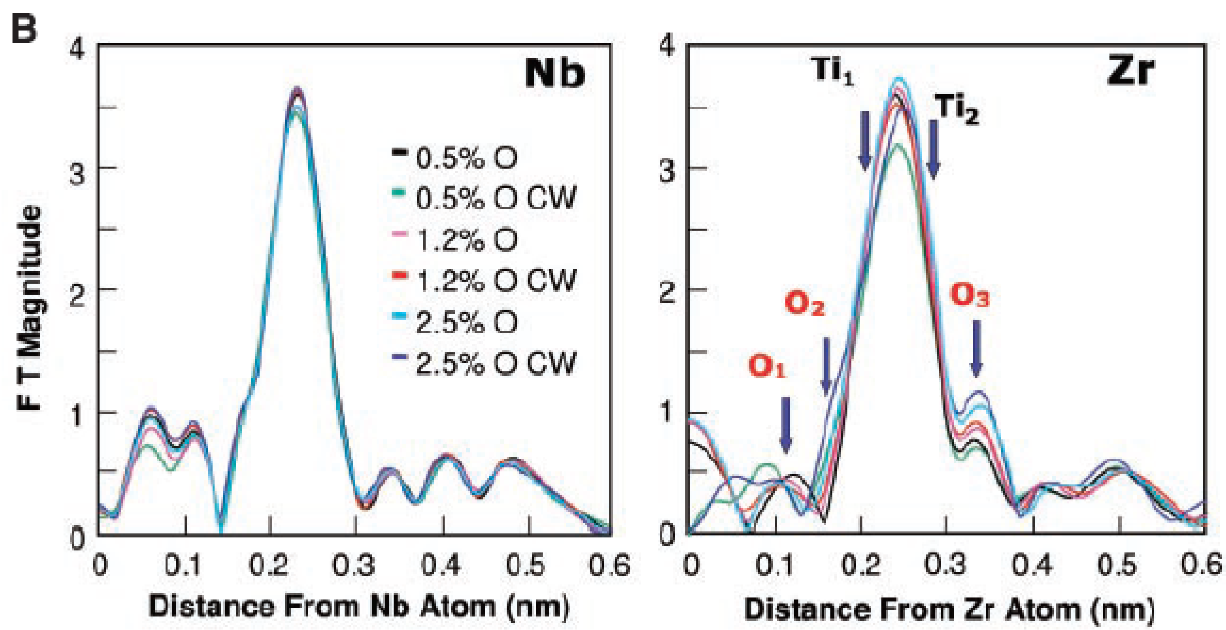


Fig. 4. (A) A distribution of alloying elements in the 90% cold-worked Ti-23Nb-0.7Ta-2Zr-1.2O alloy by EELS using a 200-kV TEM and a TEM image of the same magnification. (B) Comparison of the Fourier transferred spectra calculated from the K-edge EXAFS spectra for niobium and zirconium atoms using 8-GeV 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

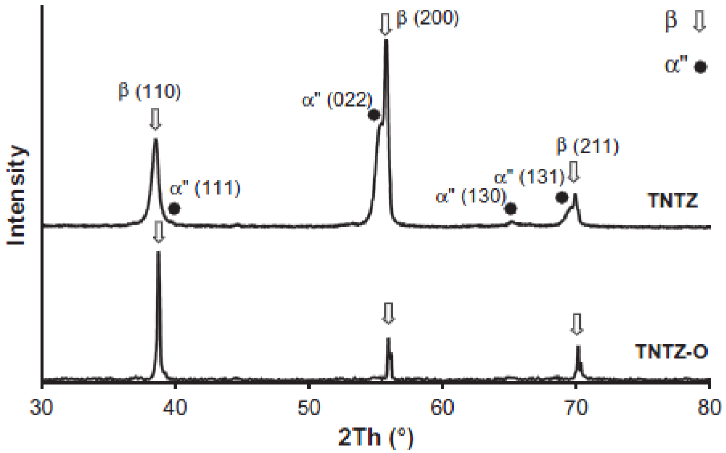


Fig. 2. XRD from the TNTZ and TNTZ-O alloys in the recrystallized/quenched state.

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

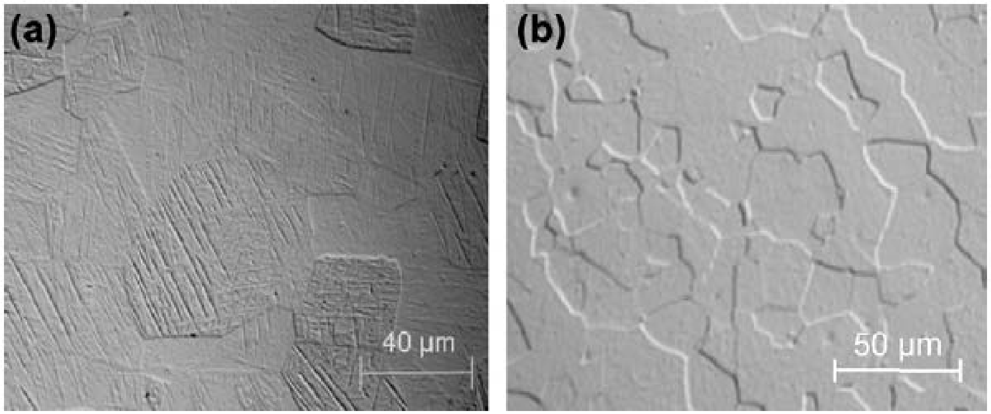
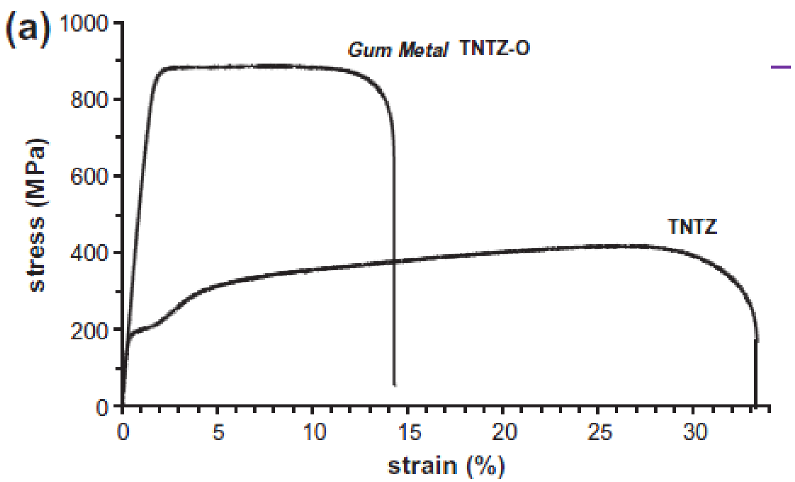


Fig. 1. Microstructures of the TNTZ (a) and TNTZ-O (b) alloys observed by optical microscopy.



- 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: $Fe_{20}Cr_{20}Mn_{20}Ni_{20}Co_{20}$

ELSEVIER

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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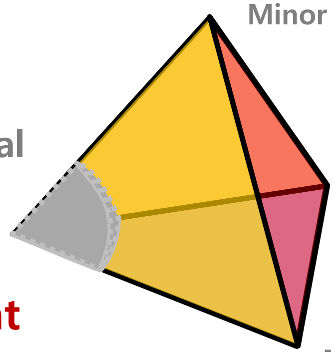
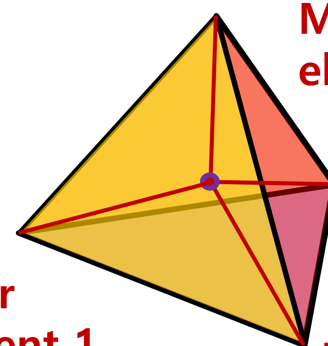
Abstract

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.

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

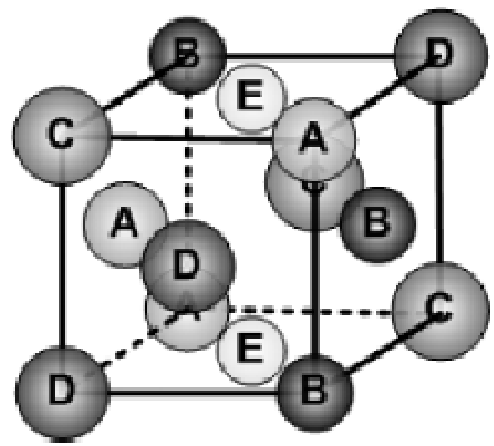
- Equimolar: AlCoCrCuFeNi
- Nonequimolar: AlCo0.5CrCuFe1.5Ni1.2
- Minor addition: AlCo0.5CrCuFe1.5Ni1.2B0.1C0.15

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

Basic concepts of high entropy alloy (HEA)

HEAs=A+B+C+D+E; 50%<A₩B₩C₩D₩E>15%

FCC: 5 principal elements

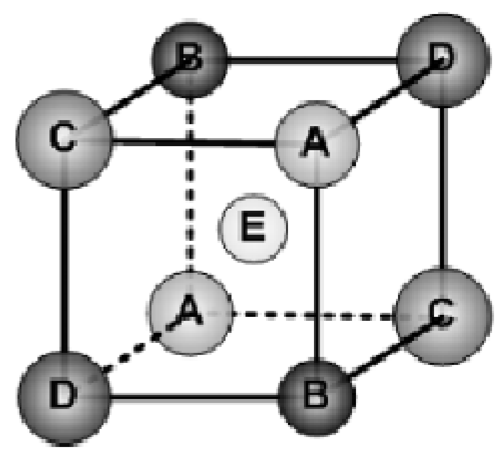


FCC type HEA Solid Solution

CoCrCuFeNi=HEA,

Yeh, MMTA, 2004;

BCC: 5 principal elements



BCC type HEA Solid Solution

AlCoCrFeNi=HEA ,

Zhou, APL, 2007

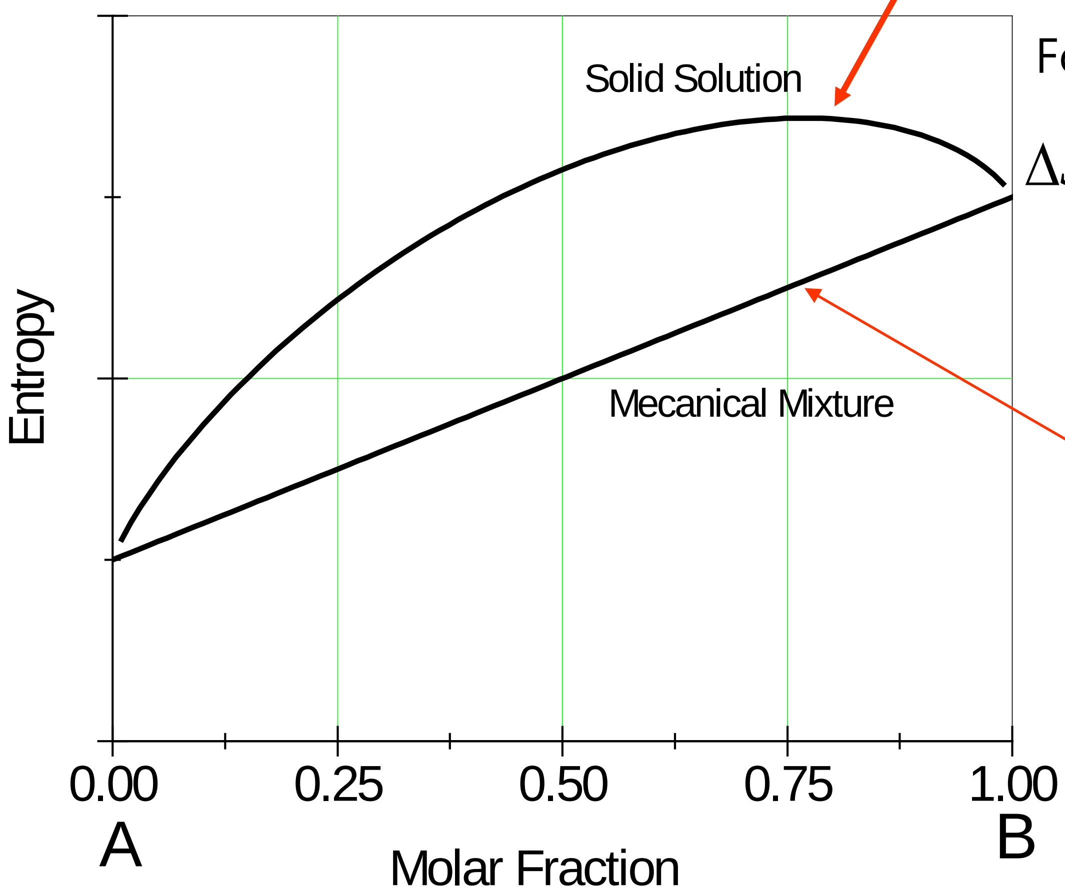
Al_{20}[TiVMnHEA]$_{80}$,

Zhou, MSEA, 2007

Basic concepts of high entropy alloy (HEA)

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

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

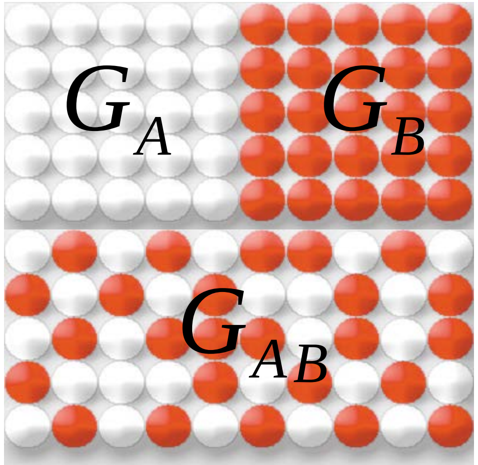


For the regular solution:

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

$$S = X_A S_A + X_B S_B$$

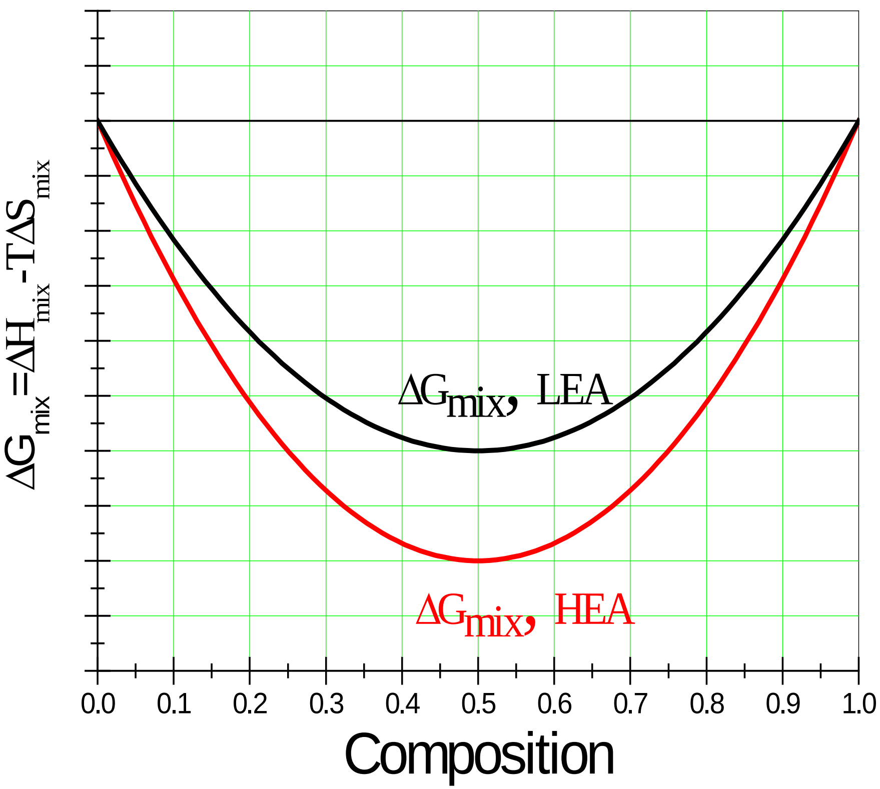
Basic concepts of high entropy alloy (HEA)

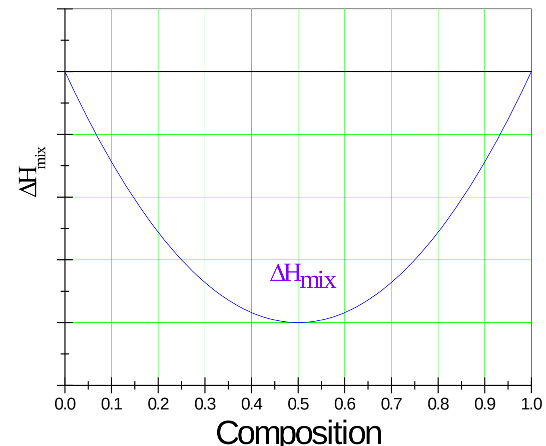


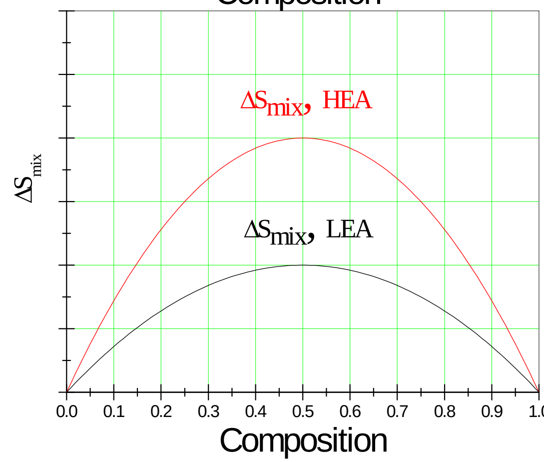
Gibbs Free Energy

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

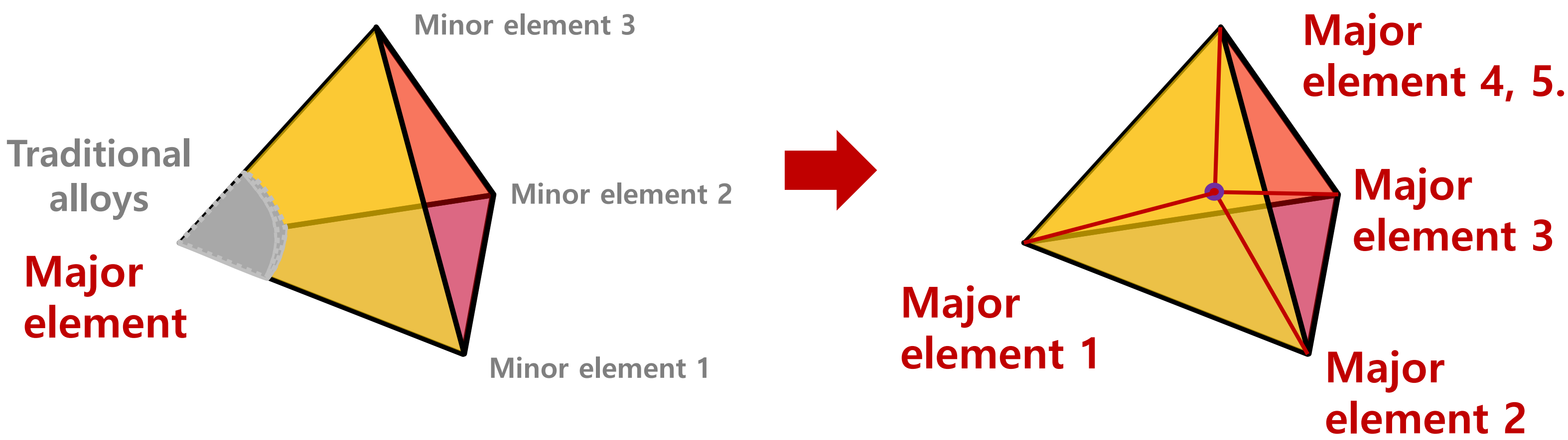
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$







Basic concepts of high entropy alloy (HEA)



Conventional alloy system

Ex) 304 steel - $Fe_{74}Cr_{18}Ni_{8}$

High entropy alloy system

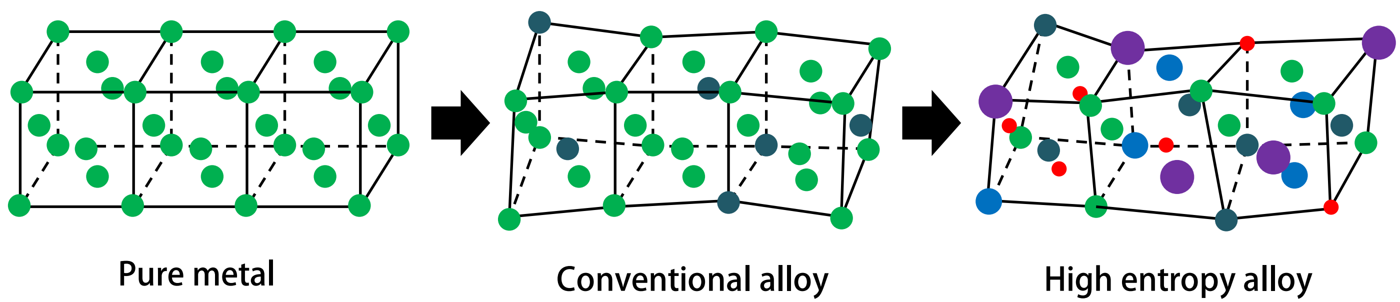
Ex) $Al_{20}Co_{20}Cr_{20}Fe_{20}Ni_{20}$

(1) Thermodynamic : high entropy effect

(2) Kinetics : sluggish diffusion effect

(3) Structure : severe lattice distortion effect

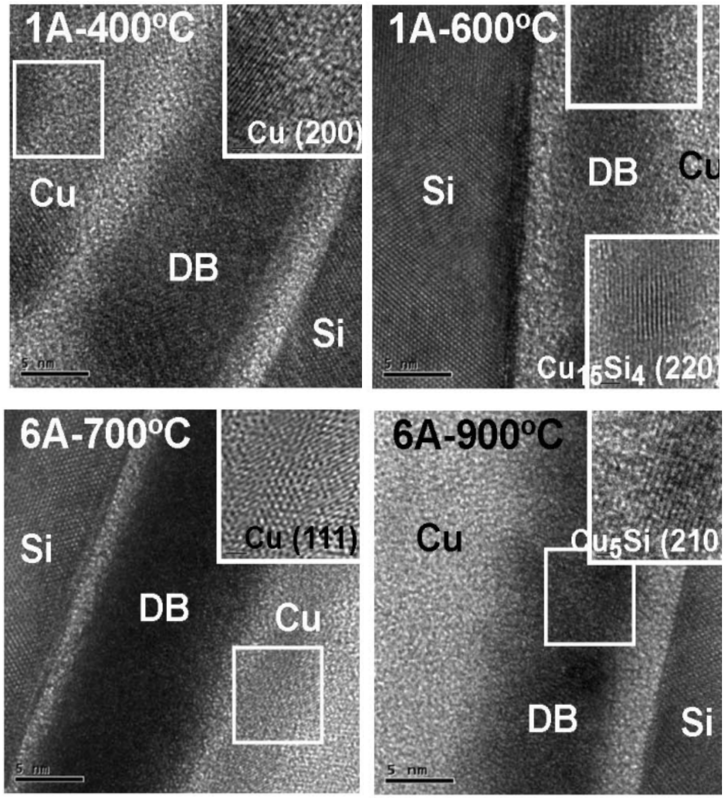
(4) Property : cocktail effect

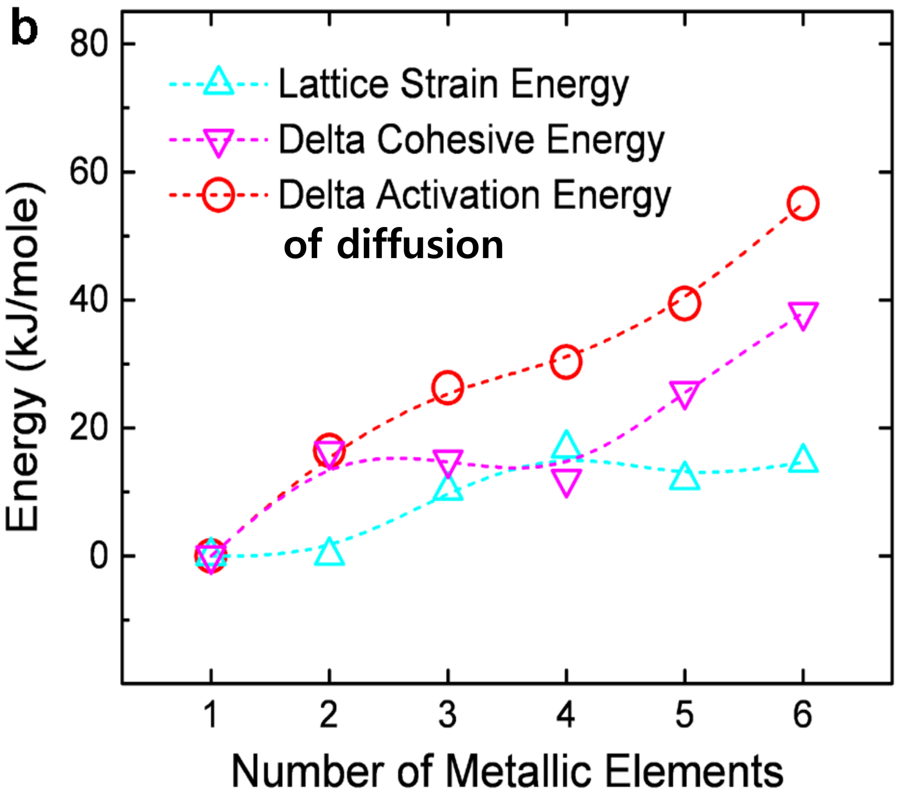


Severe lattice distortion → Sluggish diffusion & Thermal stability

a. Sluggish diffusion of high entropy alloy

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





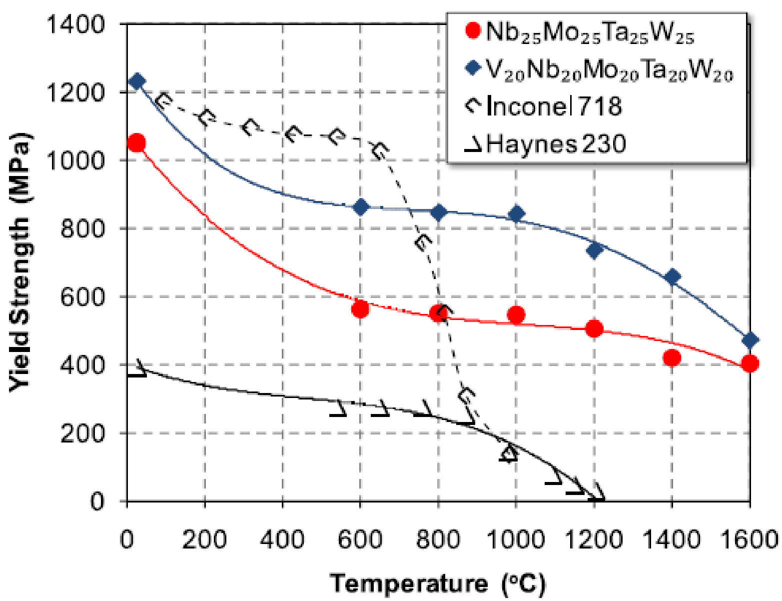
Comparison of diffusion barrier effect from Ti(1A) to TiTaCrZrAlRu(6A)

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

"HEA = Structural material with good thermal stability"

High temperature strength in BCC HEA

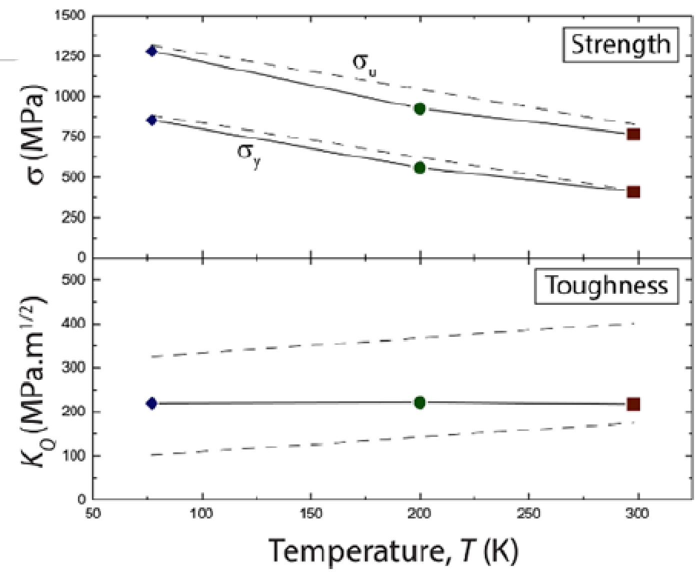
O.N.Senkov, et al., Intermetallics, vol19 (2011)



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

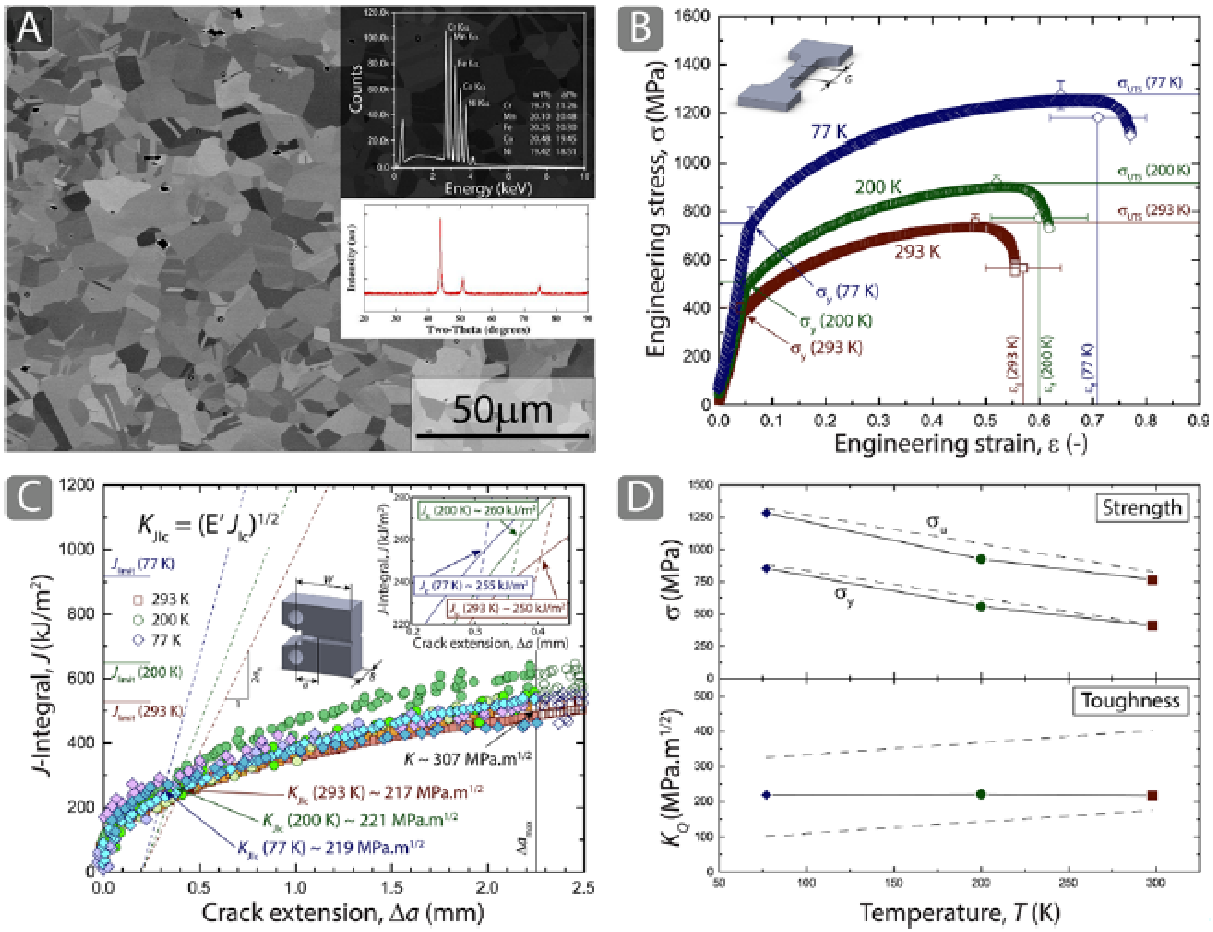
Low temperature toughness in FCC HEA

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



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

A Fracture resistant high-entropy alloy for cryogenic applications

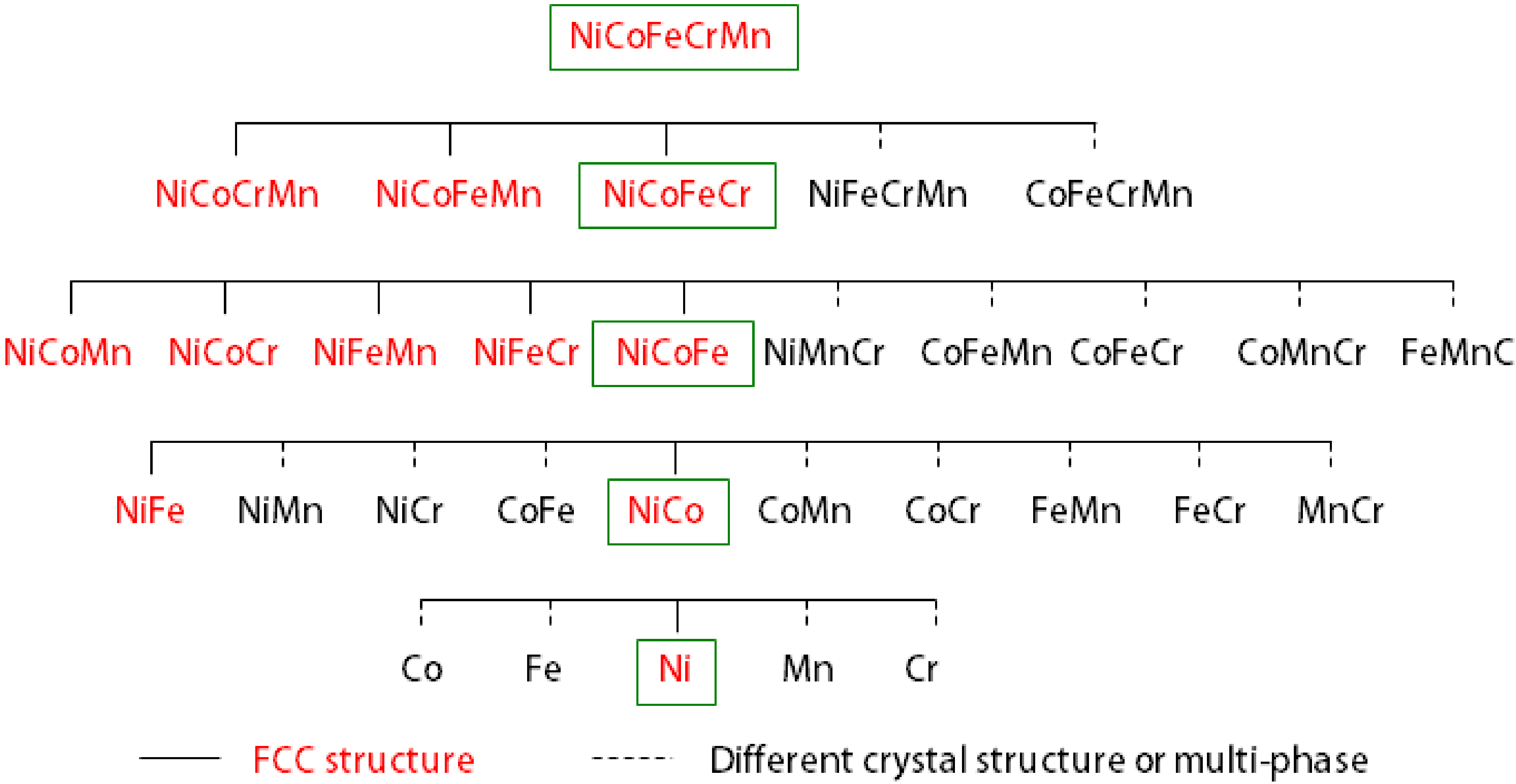


in *Science*, July 2014

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.

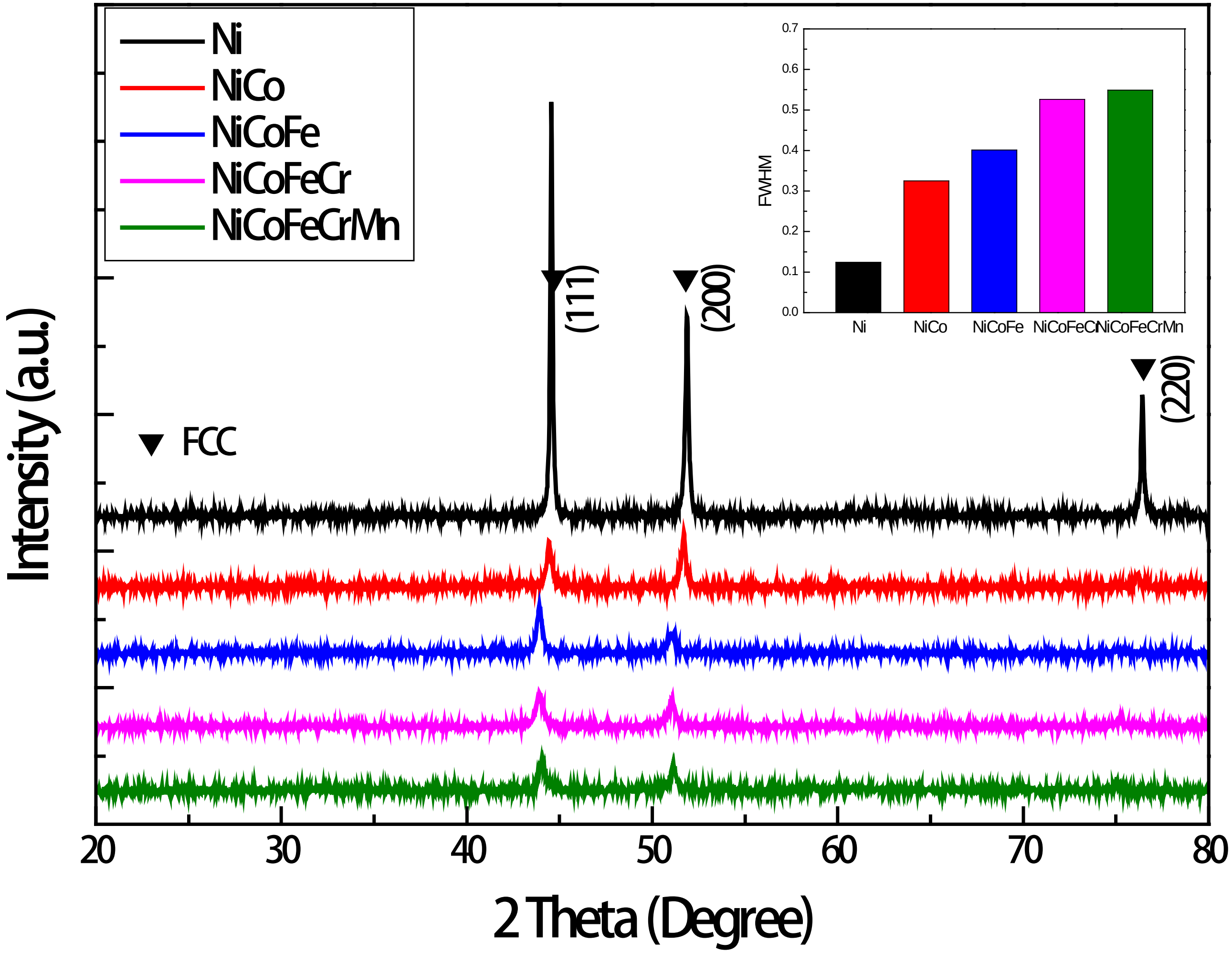
Singe-phase FCC solid solution: Ni → Ni-Co-Fe-Cr-Mn HEA



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

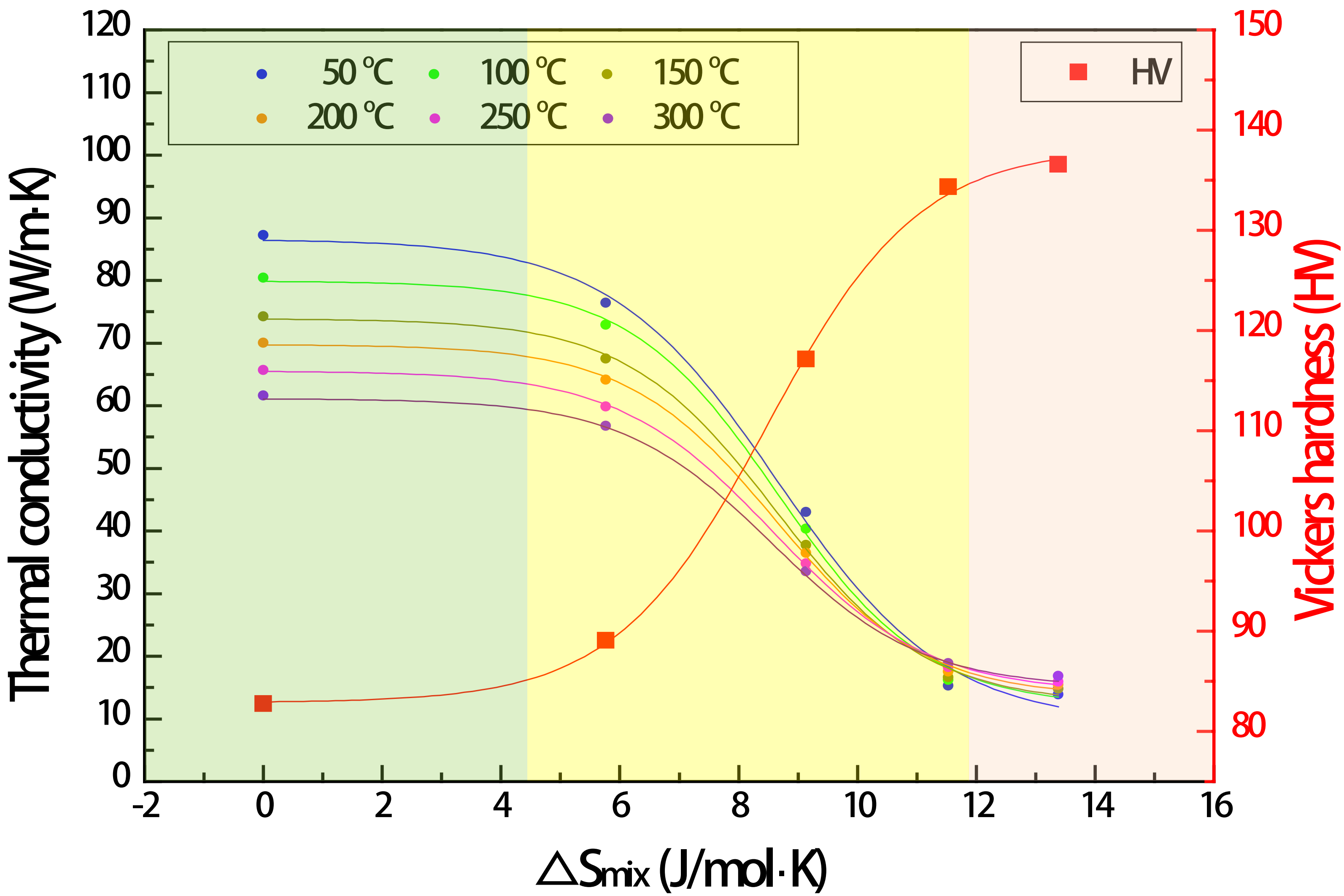
Singe-phase FCC solid solution: Ni → Ni-Co-Fe-Cr-Mn HEA

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



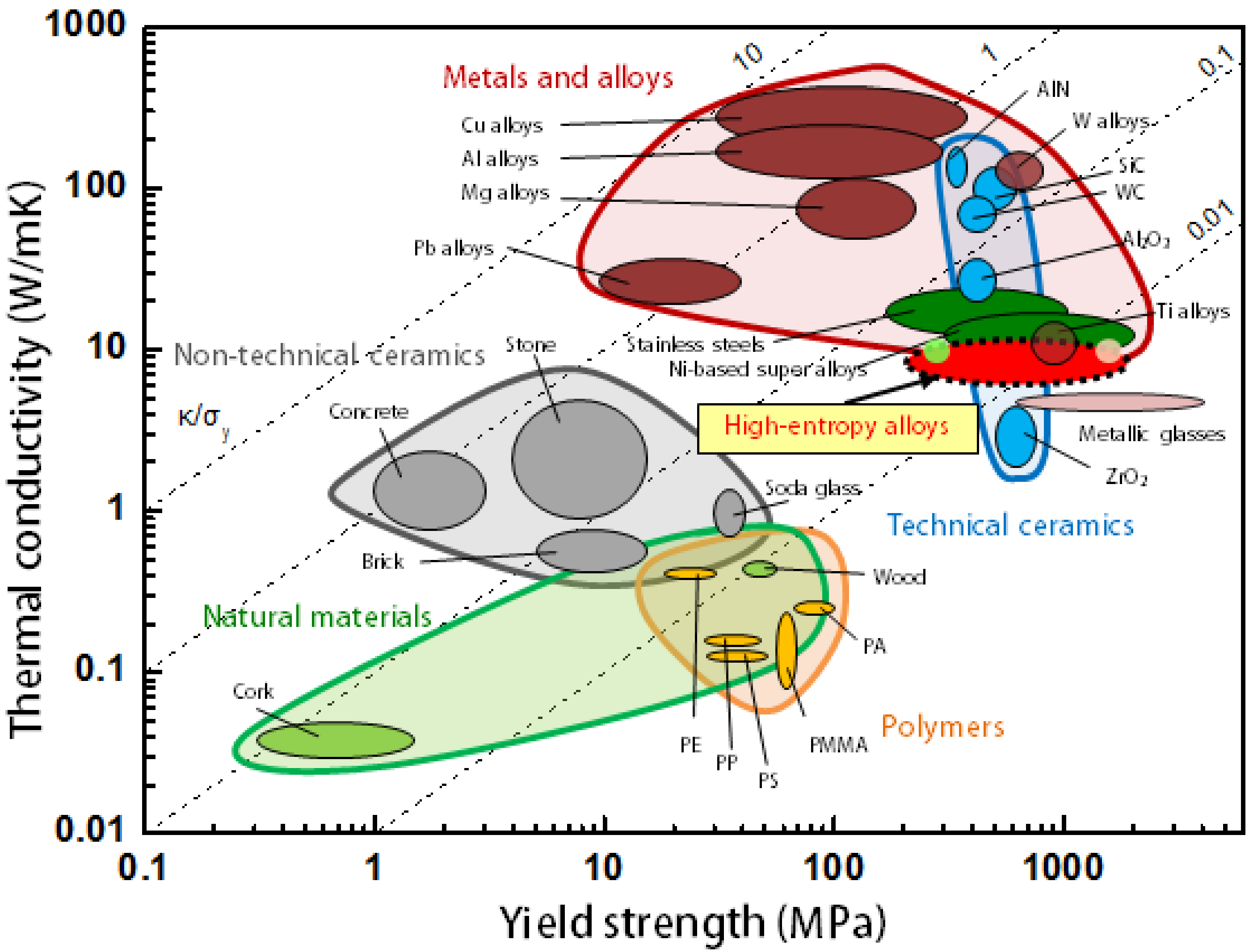
The inset shows full width at half maximum values of the alloys.

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



Q2: What is the development strategy of completely new materials?

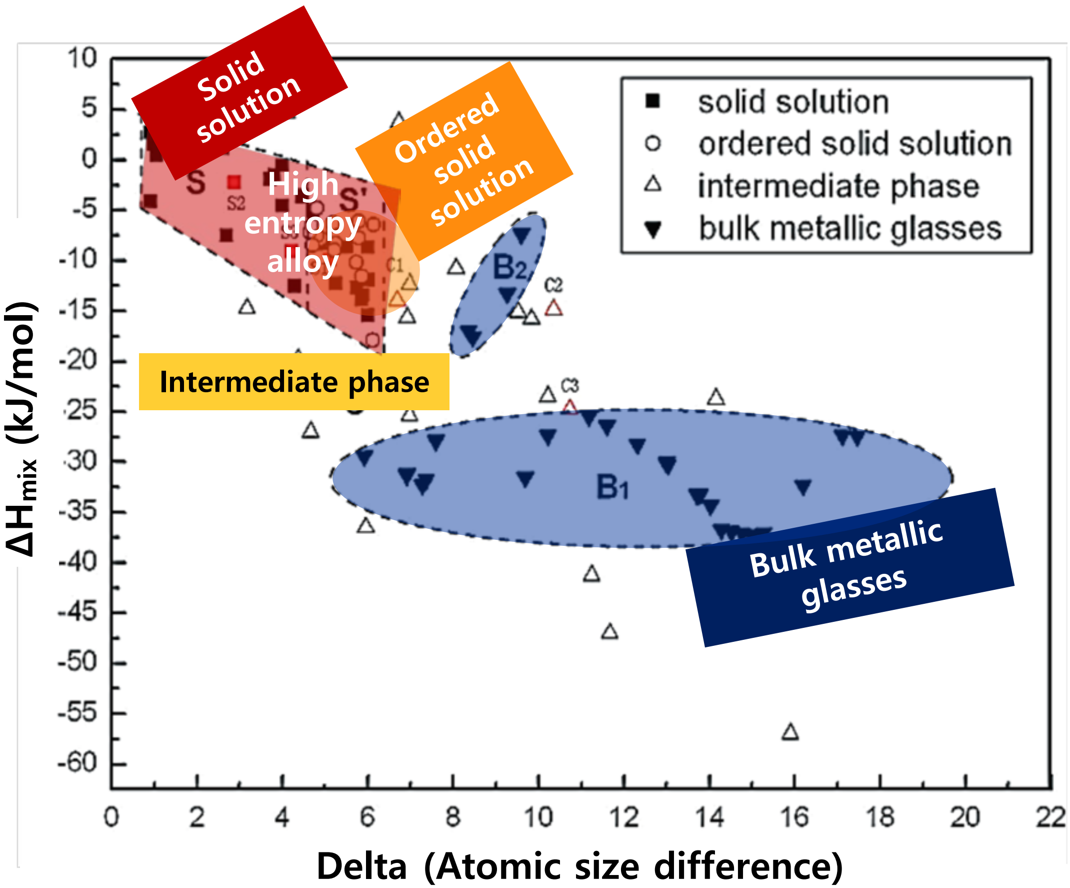
a. Alloyed pleasures: Multi-metallic cocktails

b. Synthesize metastable phases

* Development strategy of completely new materials

a. Alloyed pleasures: Multi-metallic cocktails

Multi-component system



High entropy alloy (HEA)

- Multi-component systems consisting of more than five elements
- Small difference of atomic size ratio under 12%
- Almost zero value of heats of mixing among the three main constituent elements

Bulk metallic glass (BMG)

- multi-component systems consisting of more than three elements
- Significant difference in atomic size ratios above about 12% among the three constituent elements
- Negative heats of mixing among the three main constituent elements

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Equilibrium conditions → Non-equilibrium conditions

: non-equilibrium processing = "energize and quench" a material

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Condensation from vapor	10^{12}	—	160

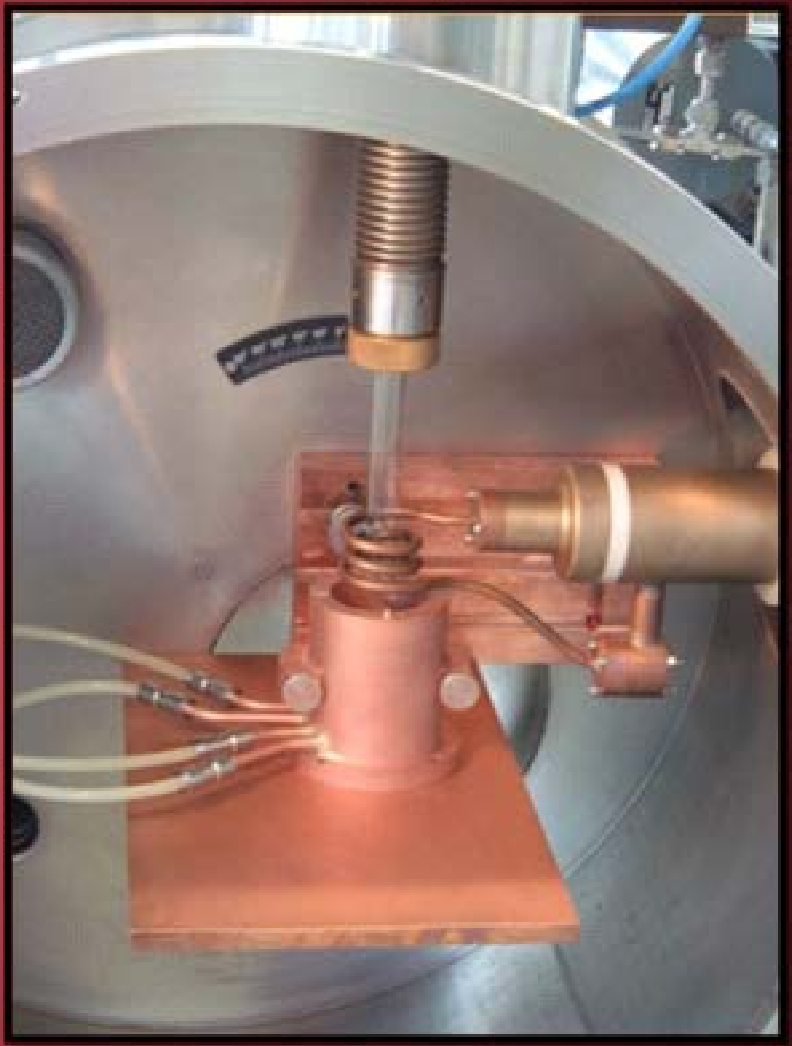
Bulk sample: rod

Injection casting

- Simple casting method for preparing bulk samples

- Cooling medium :
  Cu mold with water cooling

- Max. cooling rate for rod sample with
  D=5mm : ~10 K/s
  D=3mm : ~10^2 K/s



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1.3 Rapid Solidification Processing (RSP)

1. *Droplet methods*: In this group of methods, a molten metal is atomized into small droplets, and these are allowed to solidify either in the form of splats (on good thermally conducting substrates, e.g., as in "gun" quenching) or by impinging a cold stream of air or an inert gas against the molten droplets (as, for example, in atomization solidification).
2. *Jet methods*: In these methods, a flowing molten stream of metal is stabilized so that it solidifies as a continuous filament, ribbon, or sheet in contact with a moving chill surface (e.g., chill block melt spinning and its variants).

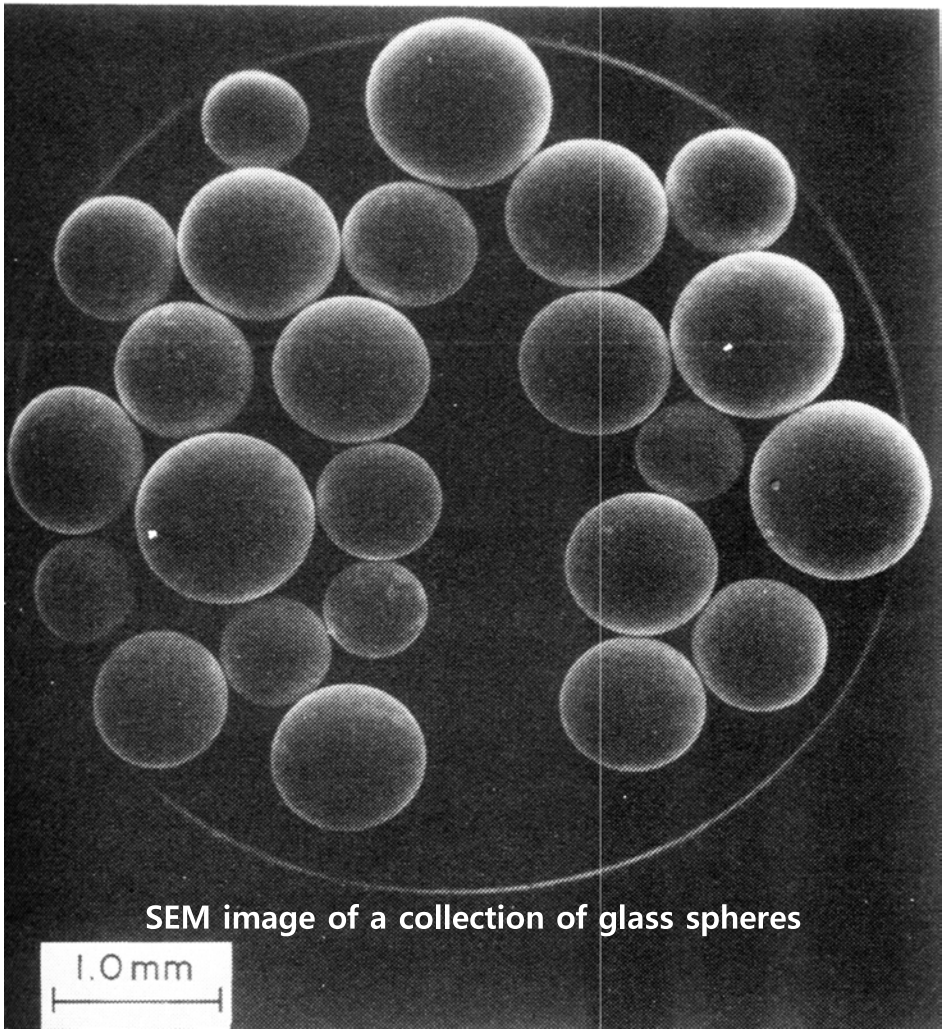
   A typical solidification rate for a foil of 50 um thickness is about 10^6 K/s.

3. *Surface melting technologies*: These methods involve rapid melting at the surface of a bulk metal followed by high rates of solidification achieved through rapid heat extraction into the unmelted block (laser surface treatments).

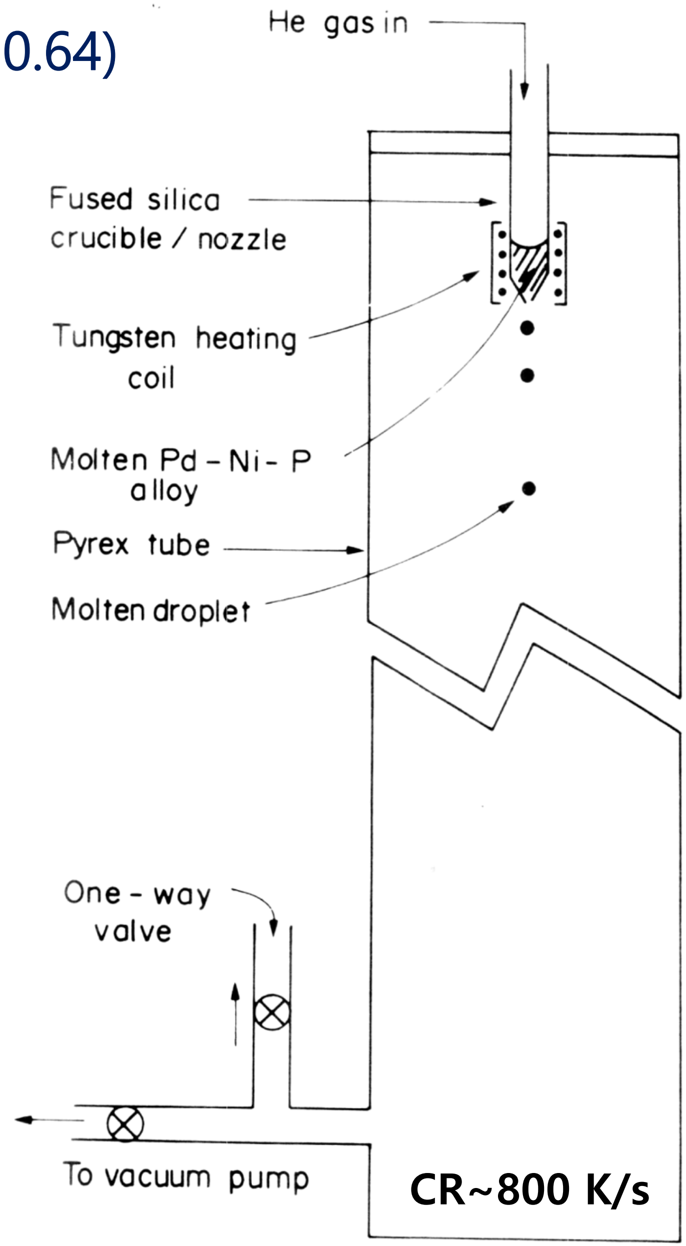
Bulk formation of metallic glass

- First bulk metallic glass: $Pd_{77.5}Cu_6Si_{16.5}$ (T_{rg}=0.64)

By droplet quenching (CR~800 K/s)

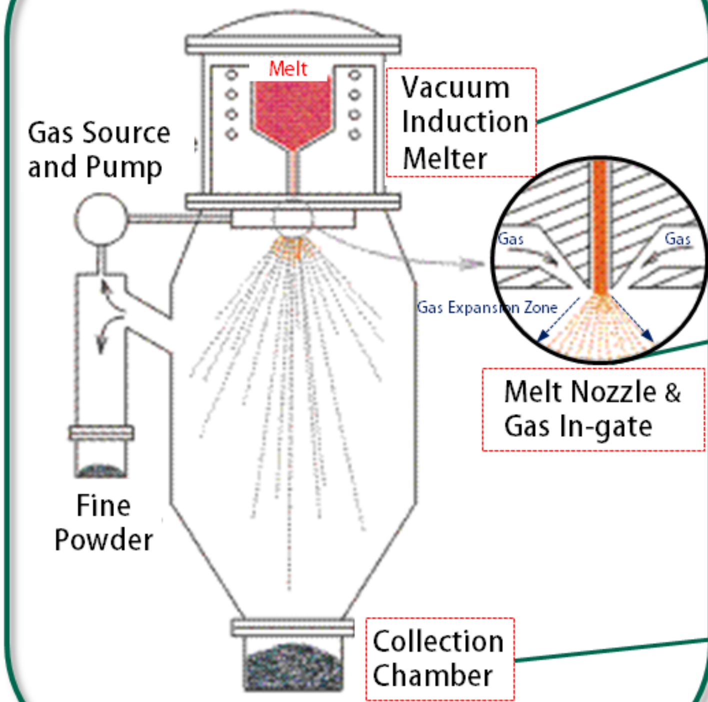


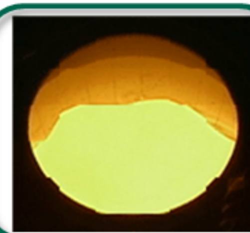
SEM image of a collection of glass spheres



CR~800 K/s

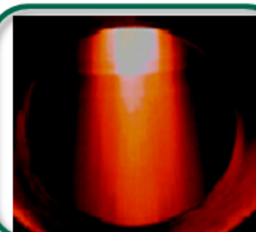
Gas Atomization





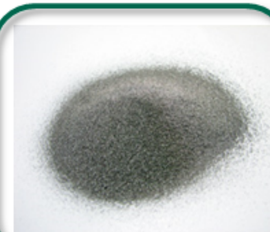
- **Melting Furnace Facility**

  Melting of Metal or Ceramics



- **Melt Nozzle and Gas In-gate**

  A rapidly expanding gas breaks up the liquid stream → thin sheet → ligament → ellipsoid → sphere.



- **Collection Chamber**

  The collection chamber is designed to maximize the yield, minimize contamination, and ease of cleaning.

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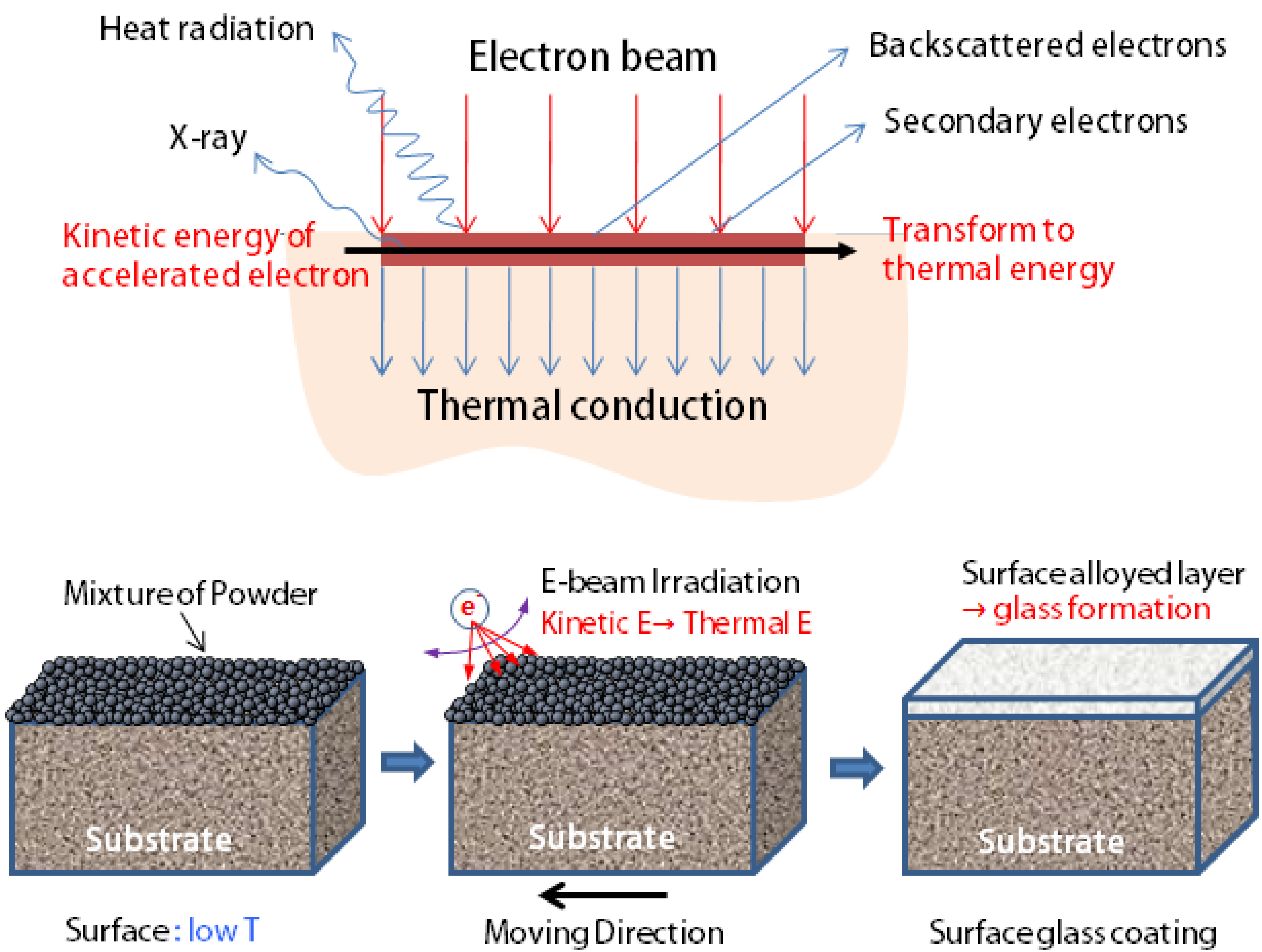
Heat radiation
Electron beam
Backscattered electrons
X-ray
Secondary electrons
Kinetic energy of
accelerated electron
Transform to
thermal energy
Thermal conduction
Mixture of Powder
E-beam Irradiation
e
Kinetic E→ Thermal E
Surface alloyed layer
→ glass formation
Substrate
Substrate
Substrate
Surface : low T
Moving Direction
Surface glass coating

Glass formation : Rapid quenching of liquid phase

- 1969 Ribbon type with long length using melt spinner : FePC, FeNiPB alloy

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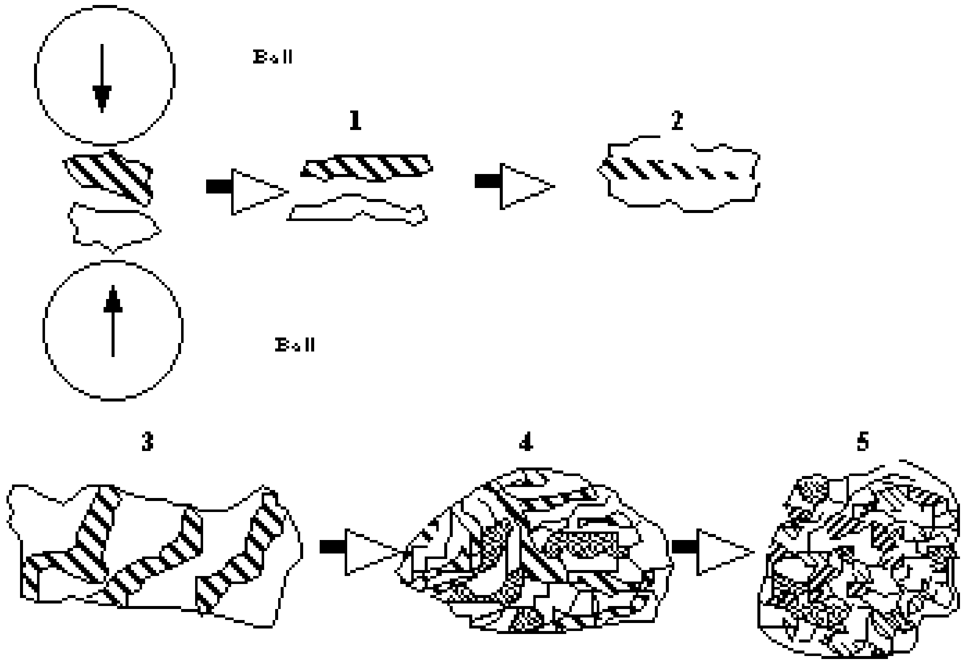
1.4 Mechanical Alloying

Mechanical alloying takes place via repeated plastic deformation, fracturing, and cold welding of powder particles in a high-energy ball mill.

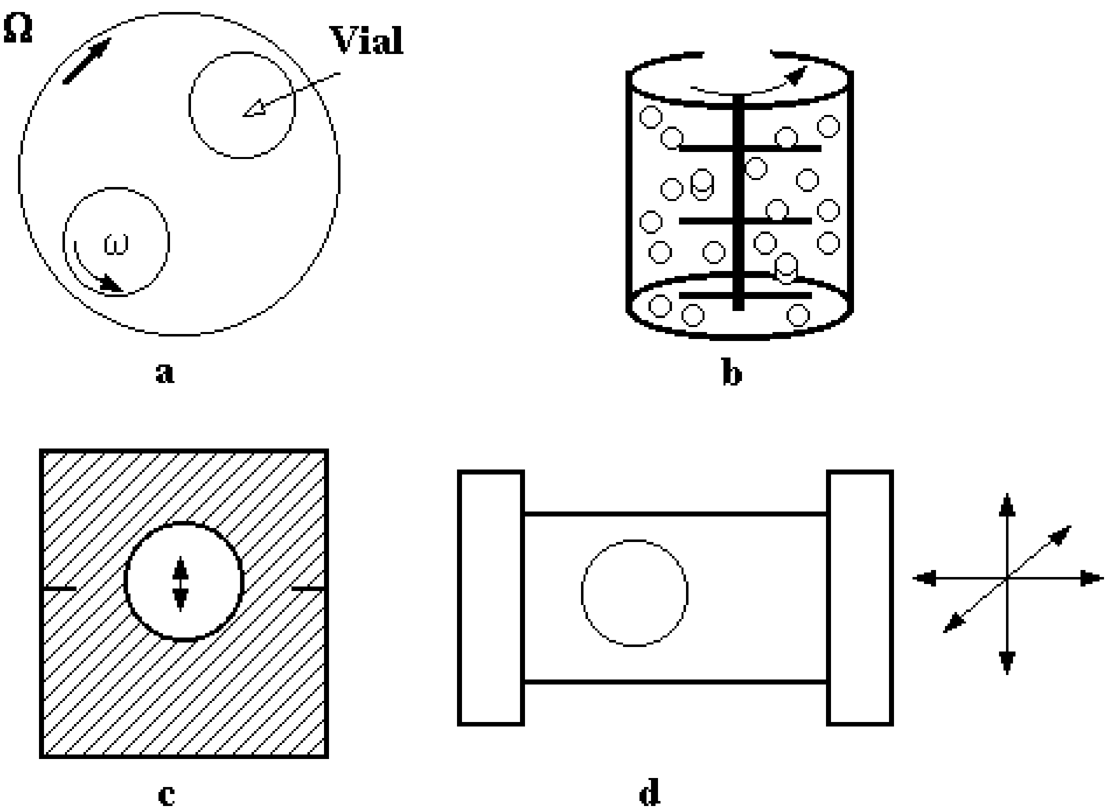
It is a method that can produce extremely small grain size (to below 10 nm), metastable phases (both crystalline and amorphous), and high concentration of lattice defects.

The figure below is a very schematic representation of the process in a mixture of two ductile materials. Notice the formation of layers that get randomized later.



The equipment of mechanical alloying

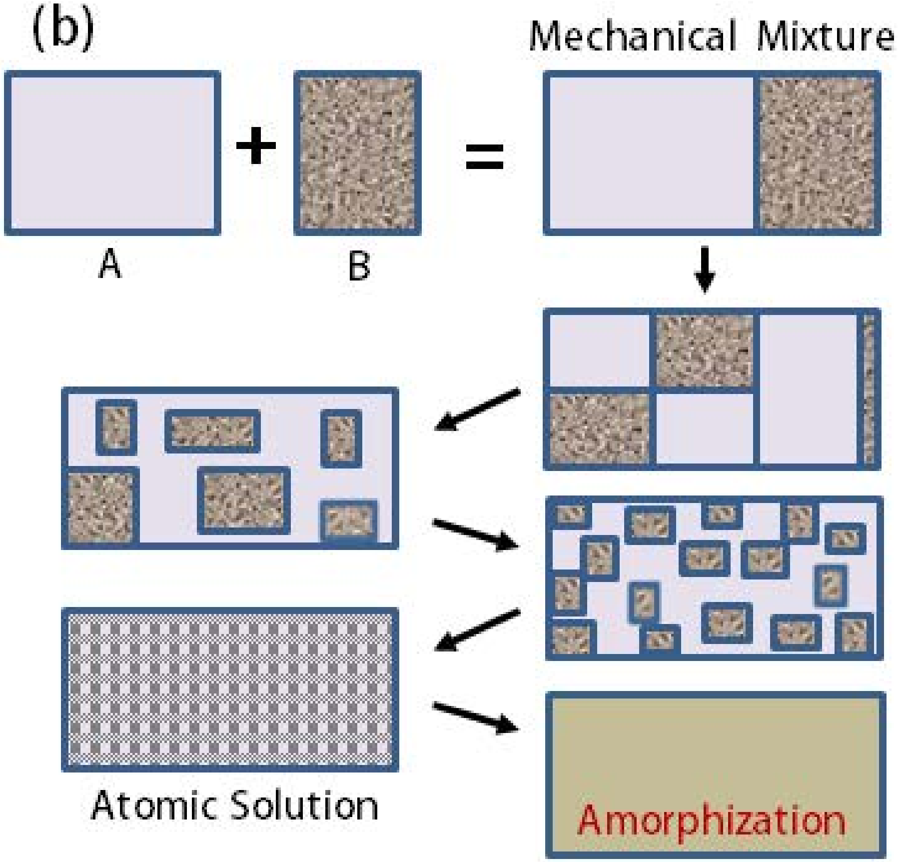
Ball mills produce a mixture of impact and shearing/friction between the balls producing the mixing/alloying needed.



Planetary mills and attritors produce more friction, the dominant form of action in vibratory and shaker mills is impact/ compression.

Available mills range from small laboratory versions to large industrial mills.

Mechanical Alloying/ Milling



* Produce equilibrium alloys & non-equilibrium phase

such as supersaturated solid solution, metastable intermediated phases, quasicrsytalline alloys, nanostructured materials and metallic glasses

starting from blended elemental powders at low temperature

→ Thin lamella + small rise in the temperature

→ increased diffusivity (due to the presence of a high concentration of crystal defects)

→ allows the blended elemental particles to alloy with each other at room or near-room temperature

→ a variety of constitutional and microstructural changes

: In fact, all the nonequlibrium effects achieved by RSP of metallic melts have also been achieved in mechanically alloyed powders.

→ <u>consolidated to full density by conventional or advanced methods</u>

such as vacuum hot pressing, hot extrusion, hot isostatic pressing, or shock consolidation, or combinations of these and <u>obtain bulk samples</u>

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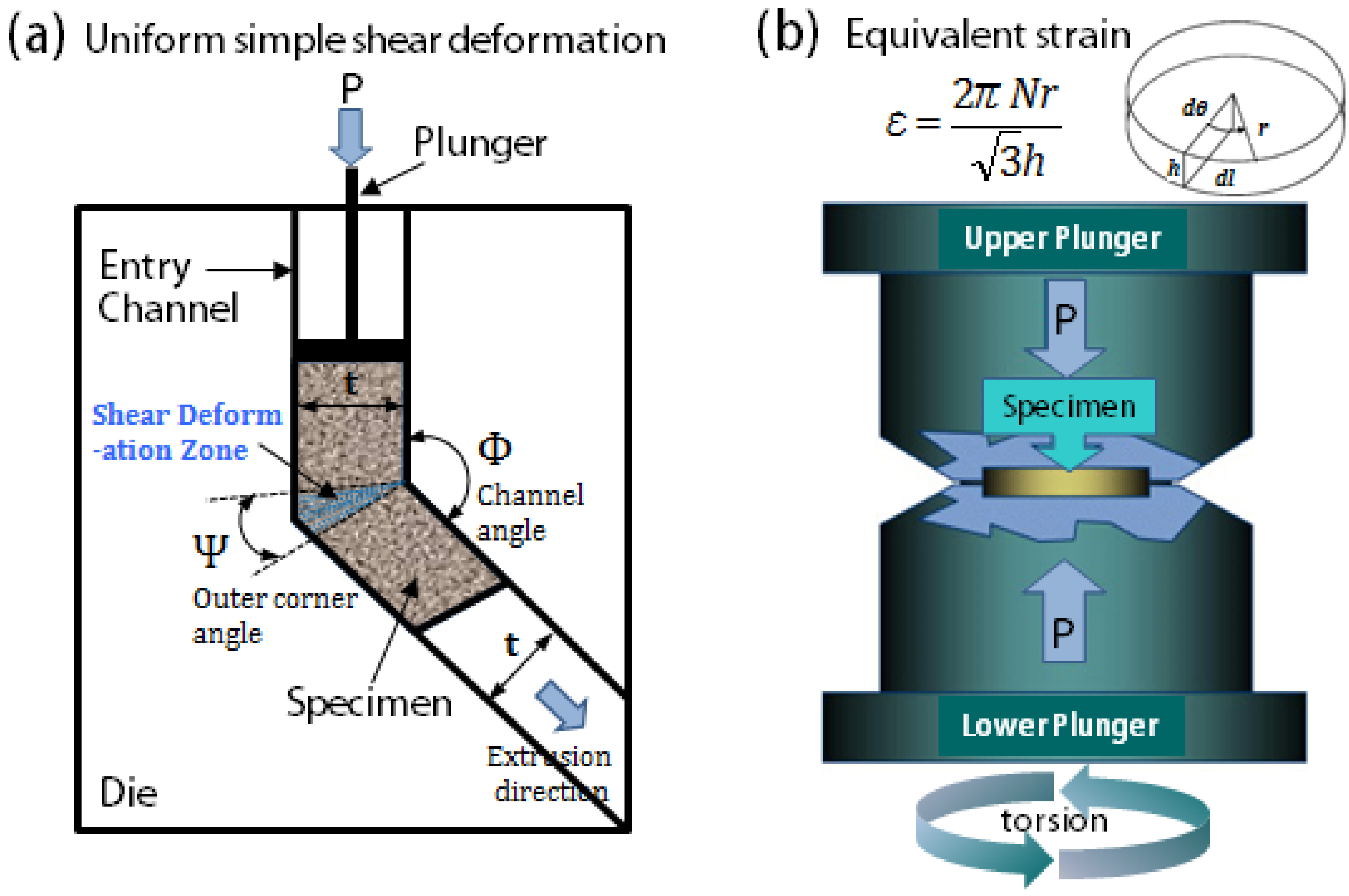
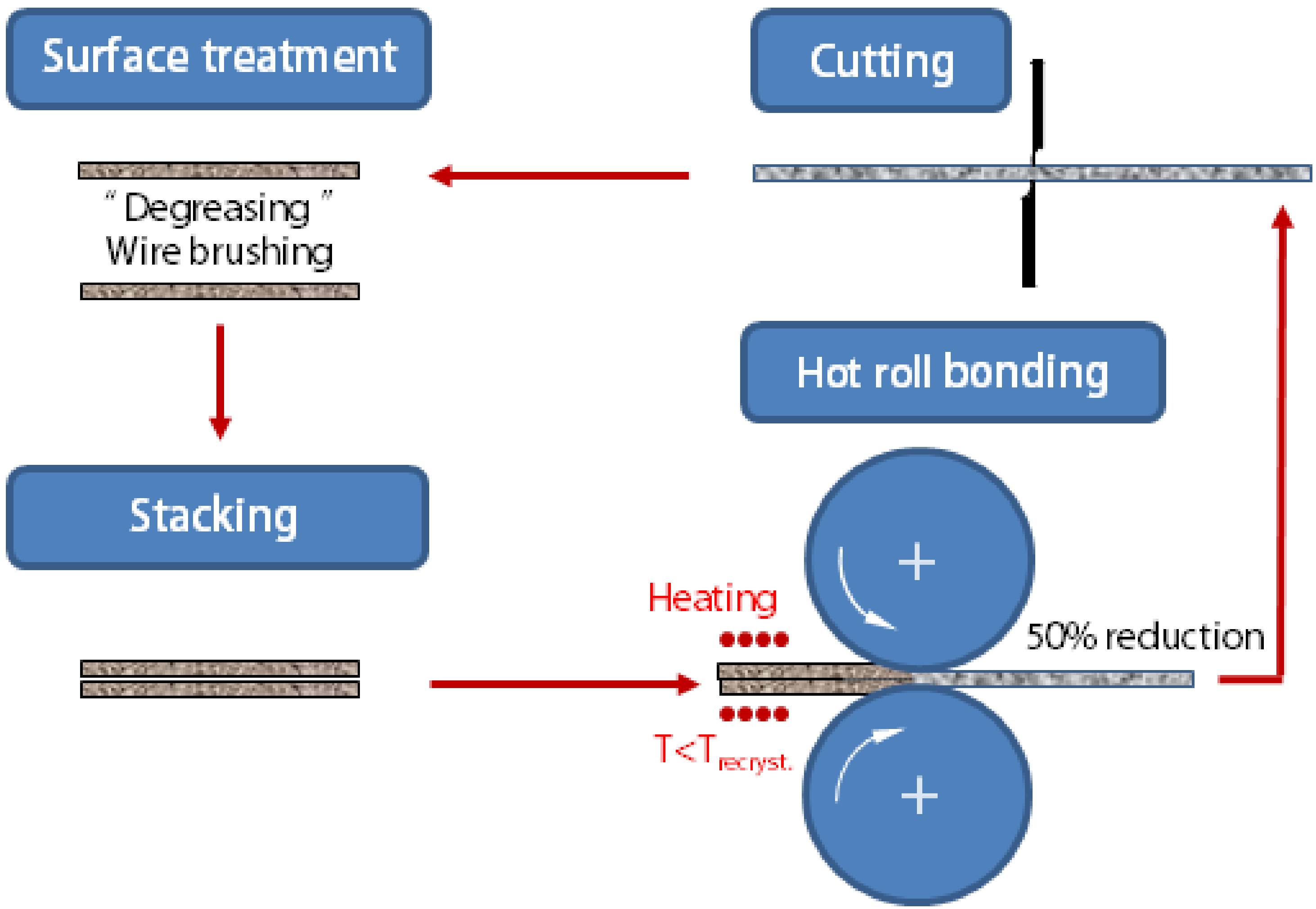
* Severe Plastic Deformation:

Equal channel angular pressing, ECAP **High-pressure torsion**



* Accumulative Rolling Bonding



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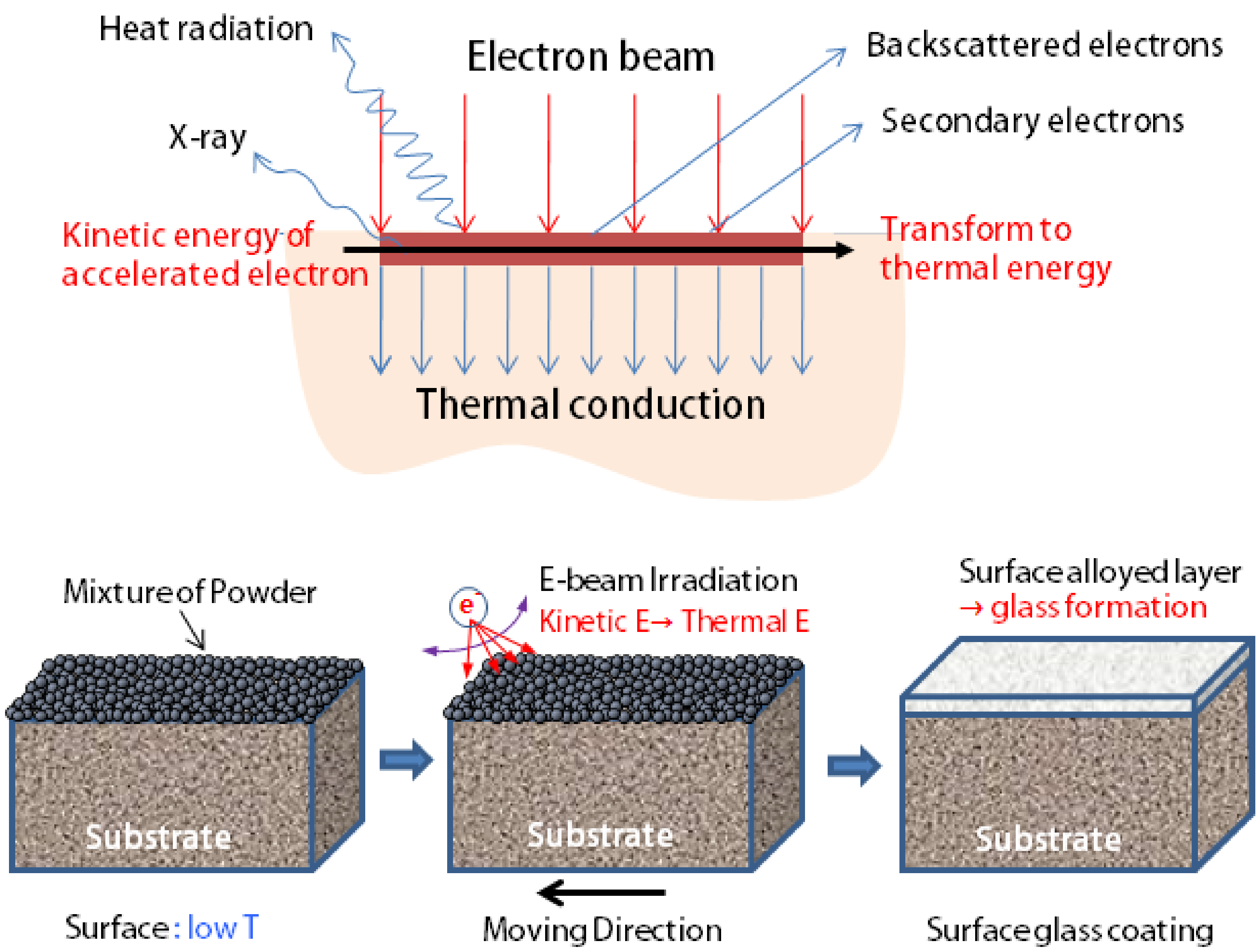
Heat radiation
Electron beam
Backscattered electrons
Secondary electrons
X-ray
Kinetic energy of
accelerated electron
Transform to
thermal energy
Thermal conduction
Mixture of Powder
E-beam Irradiation
Kinetic E→ Thermal E
Surface alloyed layer
→ glass formation
e
Substrate
Substrate
Substrate
Surface : low T
Moving Direction
Surface glass coating

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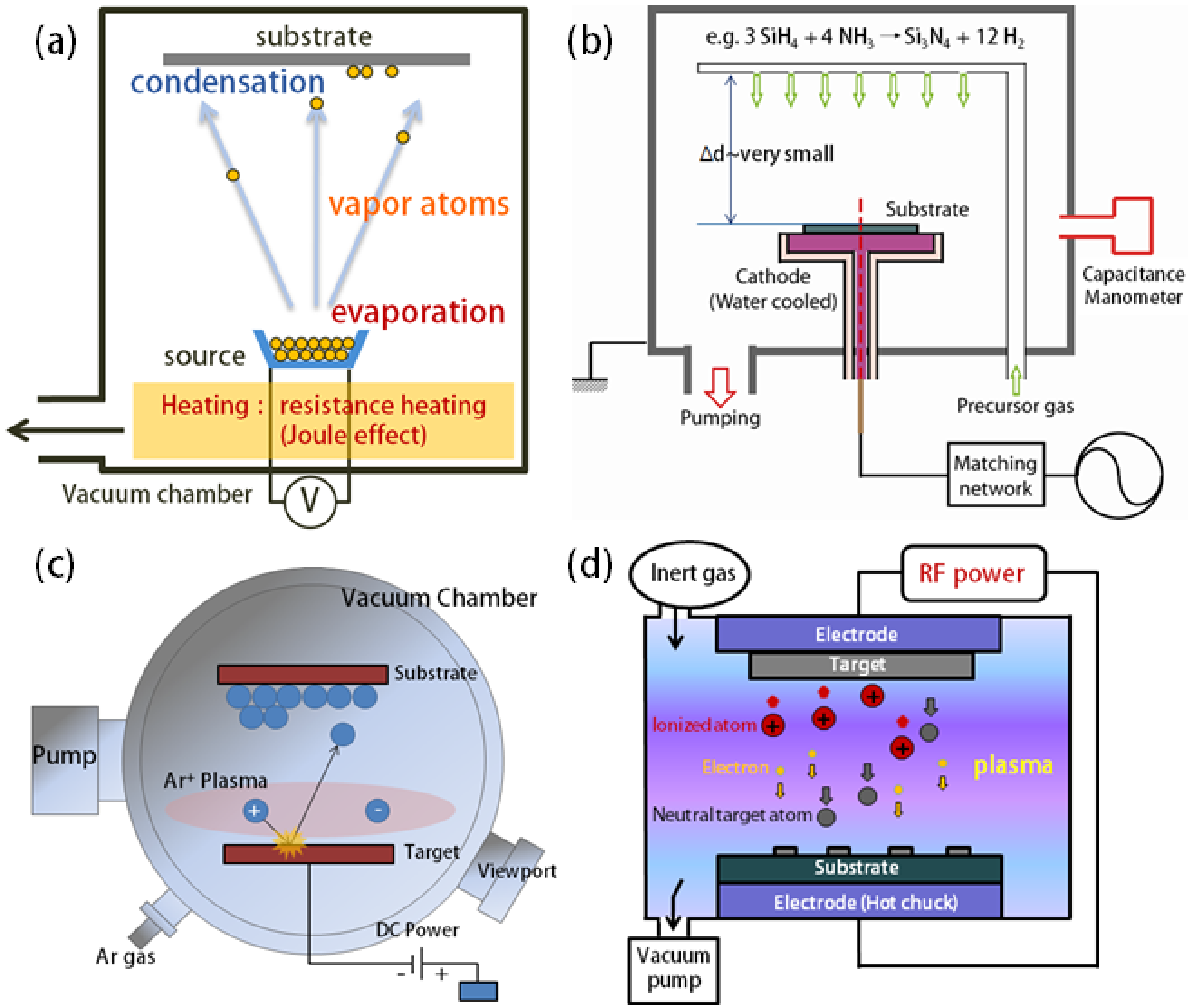
Chemical vapor deposition Sputtering



Electron beam evaporation Ion implantation