2014 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

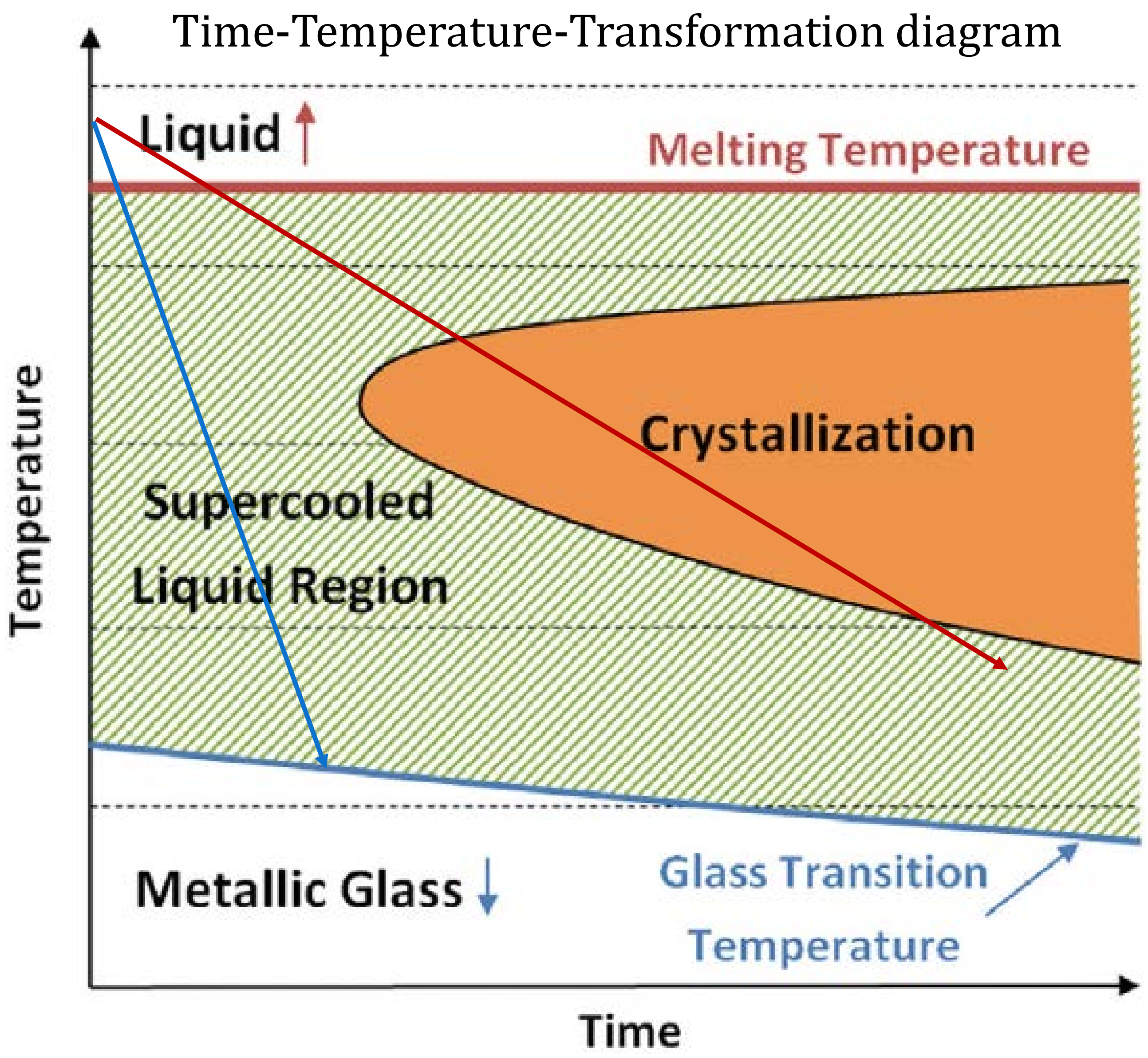
→ Completely new materials

" Stronger, Stiffer, Lighter and Hotter..."

: Nanocrystalline Materials, High Temperature Superconductors,

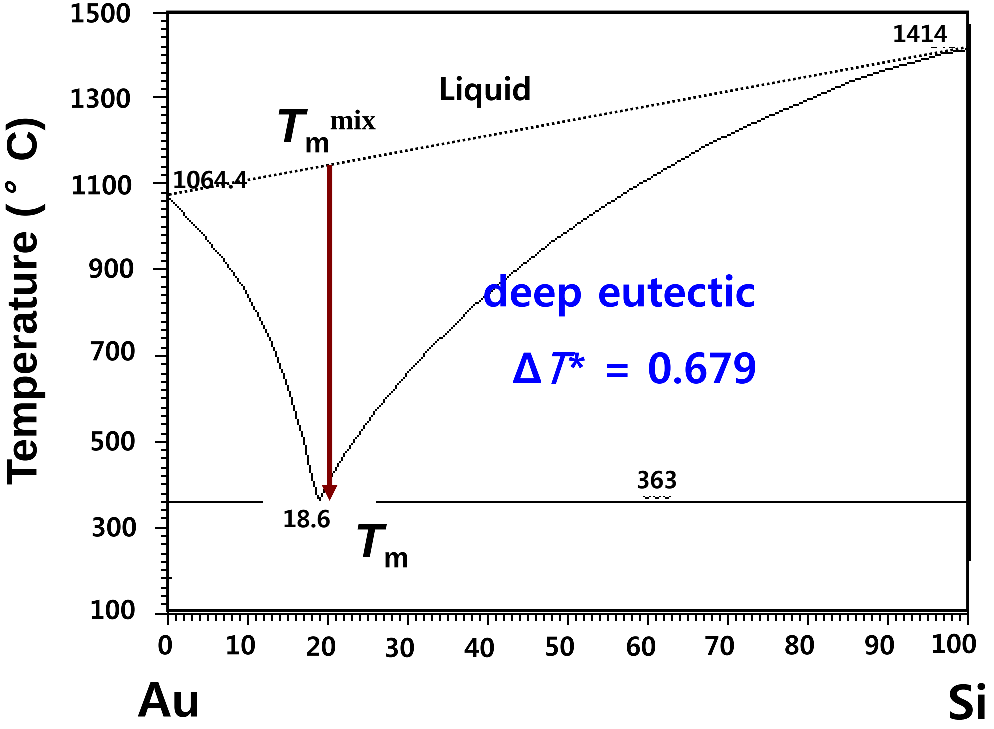
Metallic Glass (1960), Quasi-crystal (1984), Gum Metal (2003), High Entropy Alloy (2004)

(a) Bulk Metallic Glasses

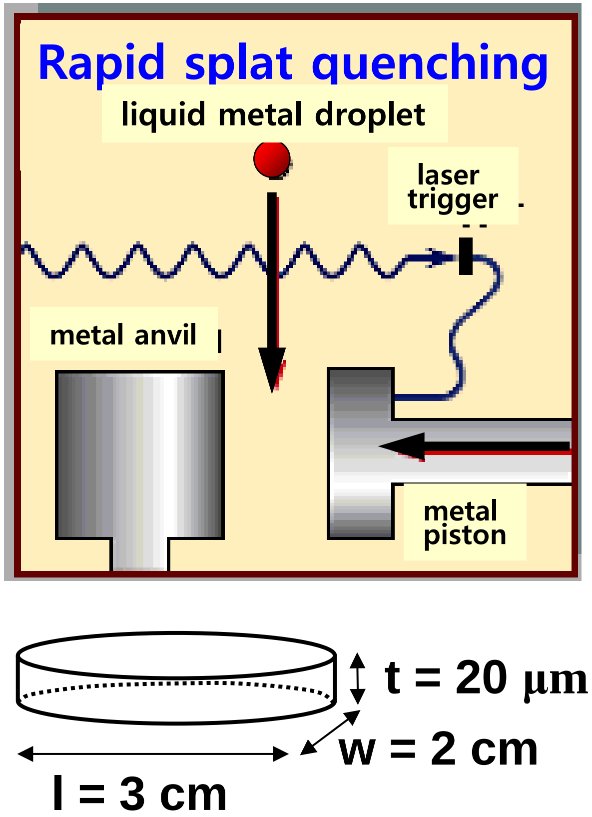


Glass formation : stabilizing the liquid phase & rapid quenching

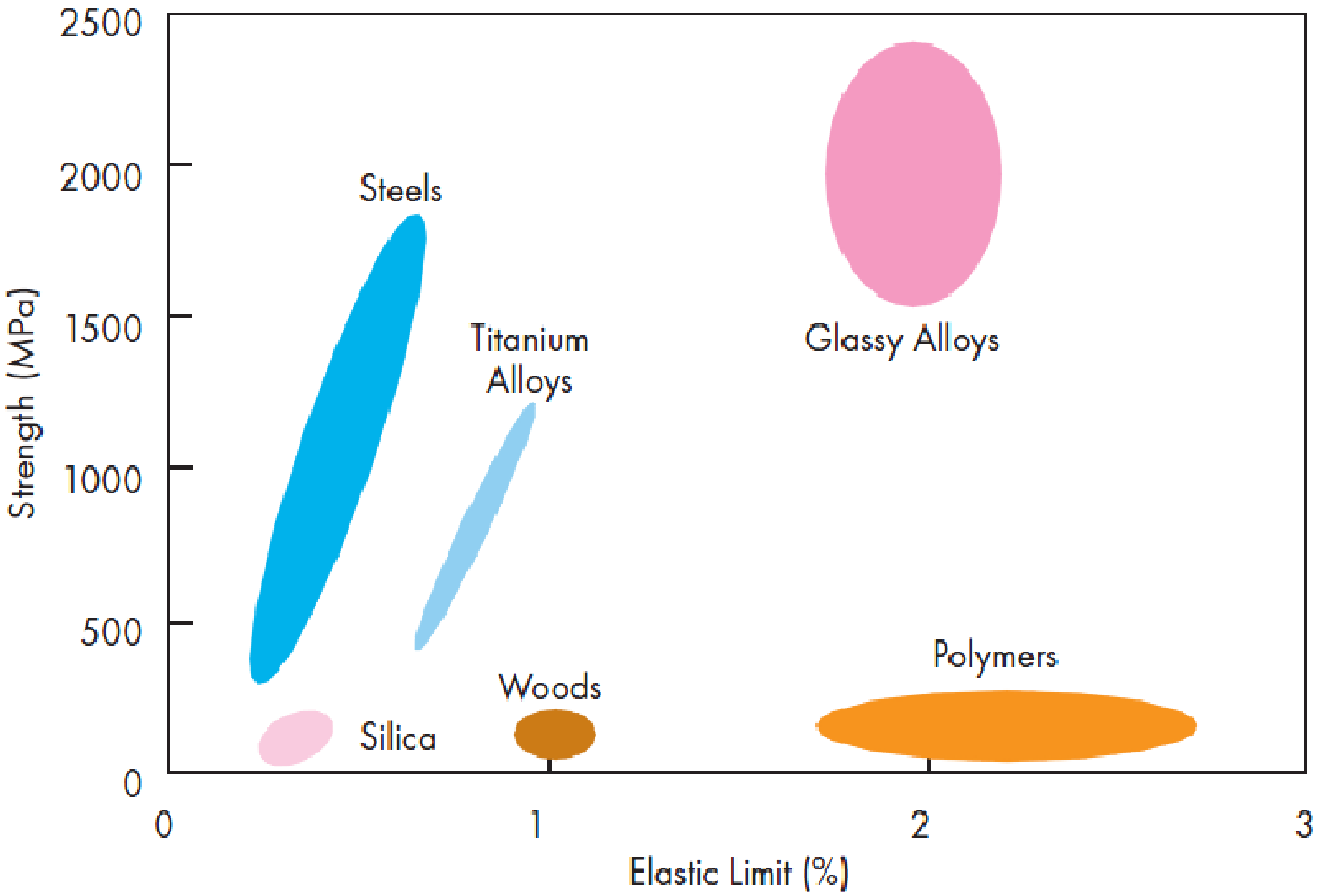
- First **metallic glass** ($Au_{80}Si_{20}$) produced by splat quenching at Caltech by Pol Duwez in 1960.



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

(b) Quasicrystals (Impossible Crystals)

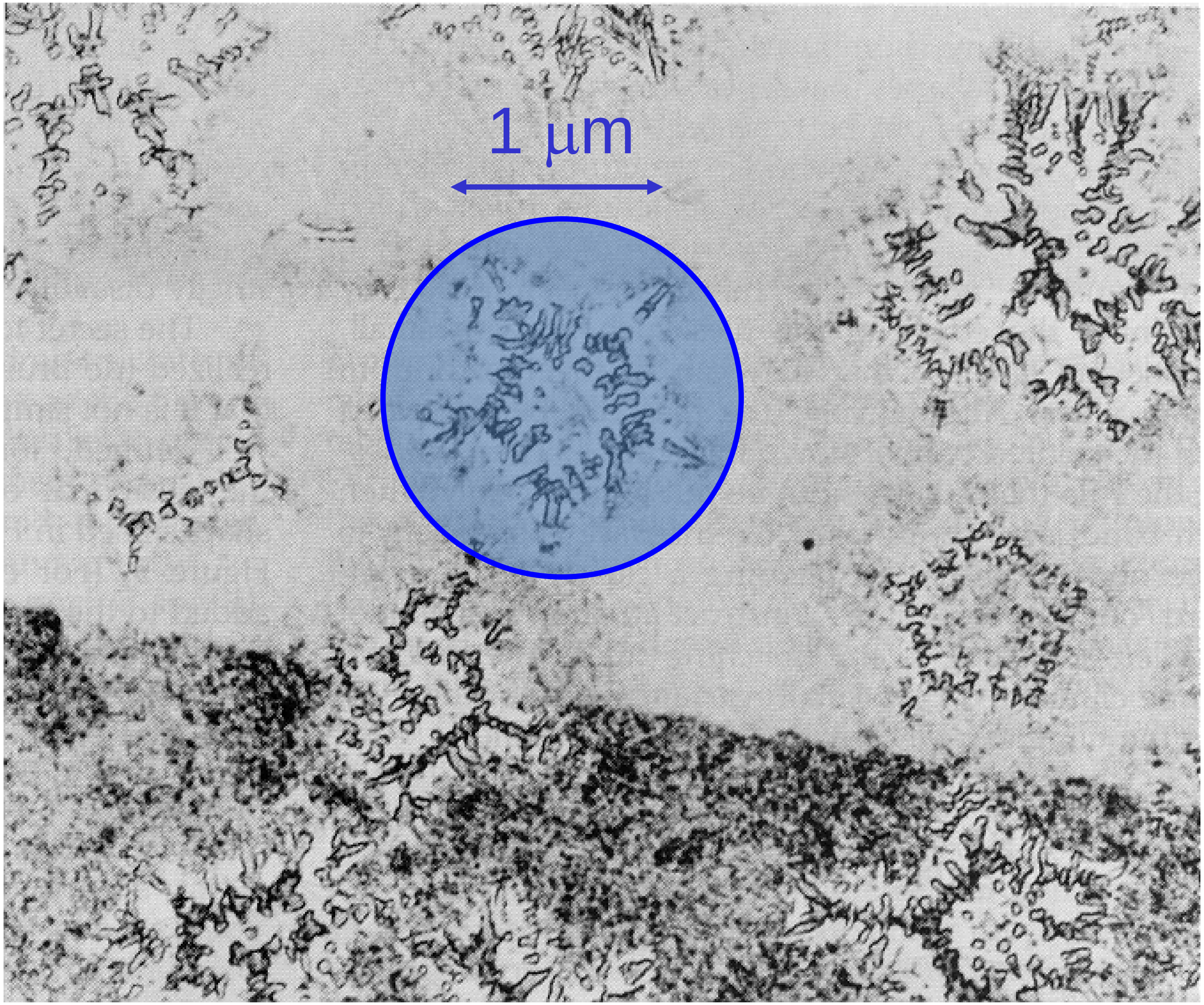
were first discovered in the laboratory by

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)

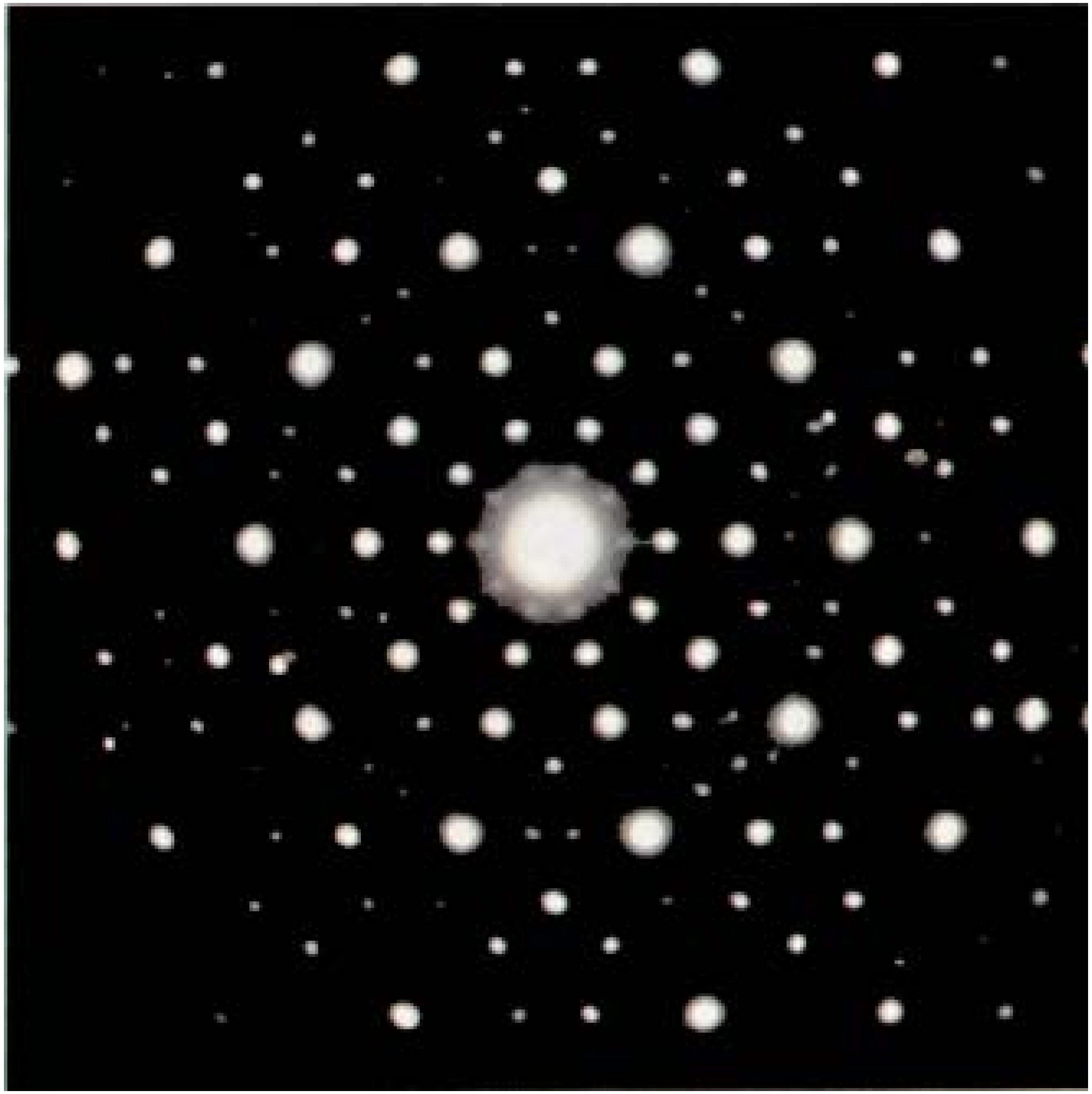
Al_6Mn



Their surprising claim:

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

Al_6Mn



2011 노벨화학상 수상자 대니얼 셰시트먼 박사

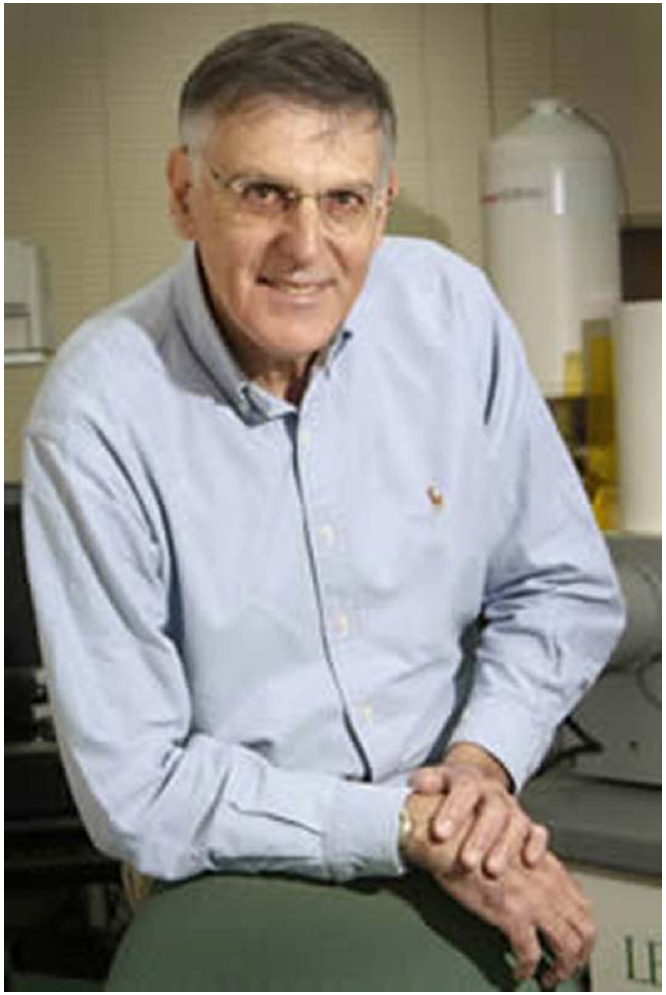
이스라엘 테크니온 공대의 대니얼 셰시트먼 박사(70·사진)가 2011년 노벨 화학상 수상자로 선정됐다.

스웨덴 왕립 과학아카데미는 5일(현지시간) 대니얼 셰시트먼 박사가 준결정(quasicrystal) 발견에 대한 공로를 인정받아 2011년 노벨 화학학상 수상자로 선정했다고 발표했다.

위원회는 "일반적으로 결정(crystal)은 원자가 같은 형태를 반복하면서 이뤄진다"며 "하지만 셰시트먼 박사는 결정 안에 원자들이 반복되지 않는 배열로 존재 할 수 있다는 사실을 발견했다"고 밝혔다.

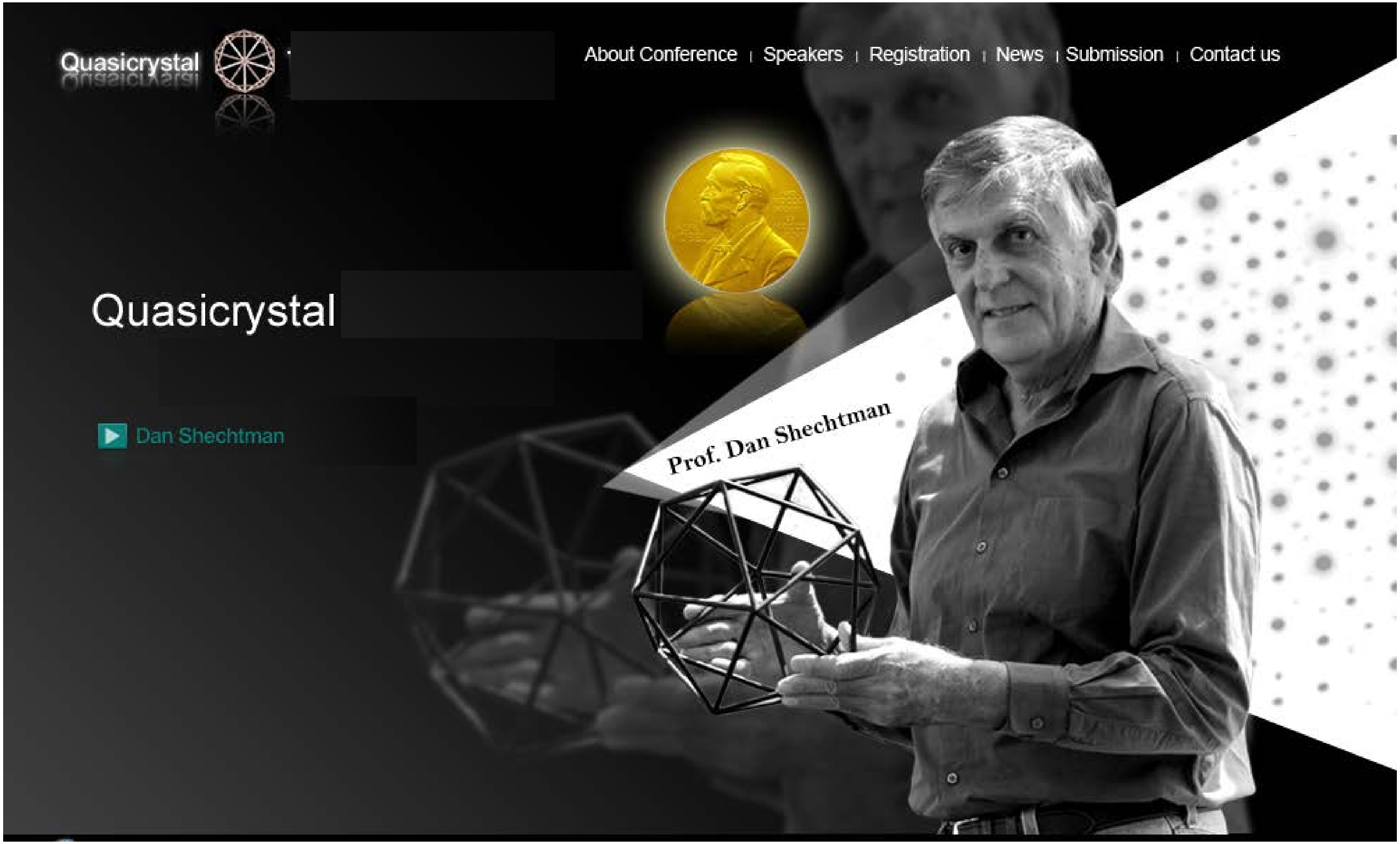
위원회는 또 "액체와 고체의 중간 상태인 준결정 연구를 통해 고체물질에 대한 이해를 바꿔놨다"고 수상 이유를 밝혔다.

셰시트먼 교수는 지난 1982년 세계 최초로 1982년 4월 특정무늬가 반복되지 않는 배열의 준결정을 발견했다.



2011 노벨 화학상 수상자 대니얼 셰시트먼 박사

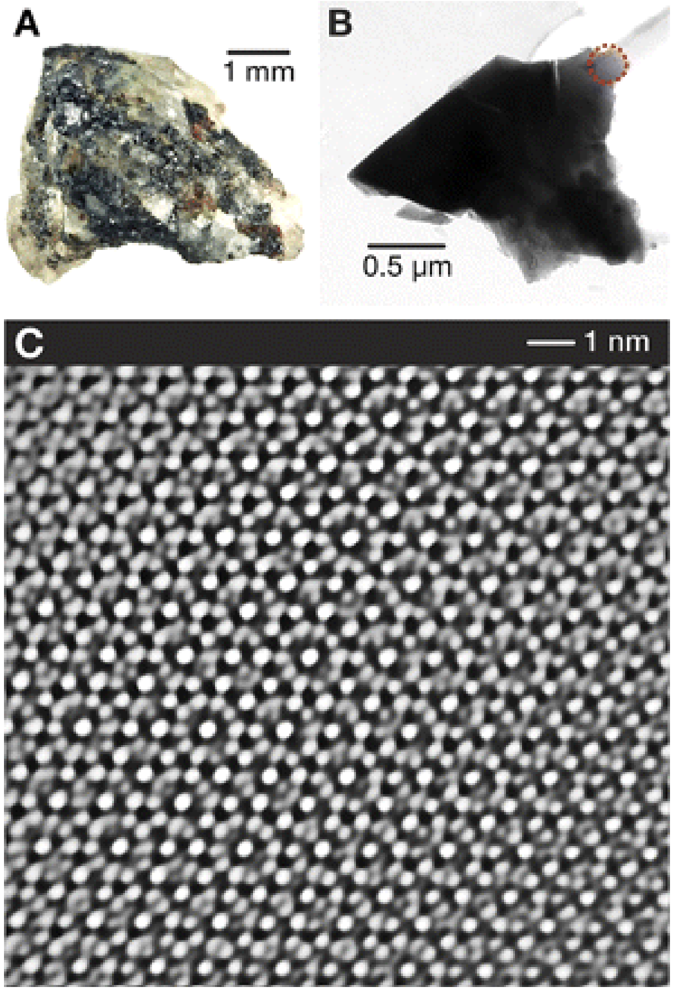
2011 노벨 화학상: Quasicrystal

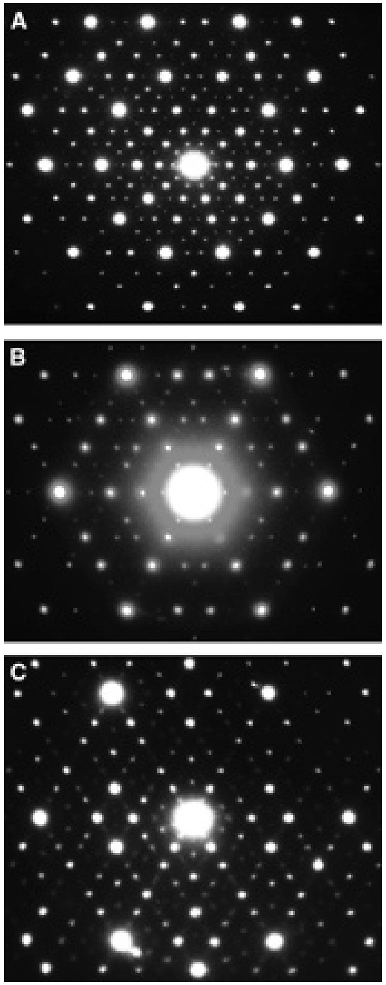


A new ordered phase showing the apparent fivefold symmetry was observed by Sastry et al. [Mater. Res. Bull. 13: 1065-1070] in 1978 in a rapidly solidified Al-Pd alloy, but was interpreted to arise from a microstructure Consisting of a series of fine twins. This was later shown to be a two-dimensional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

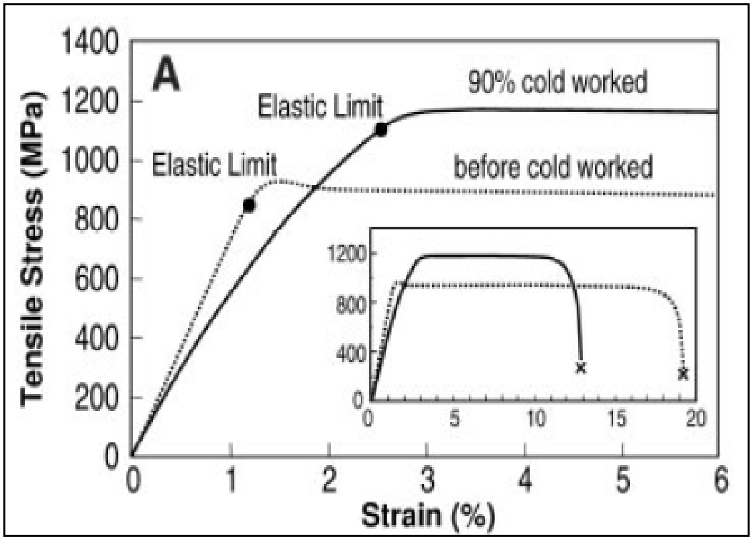
http://www.youtube.com/watch?v=k_VSpBI5EGM

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

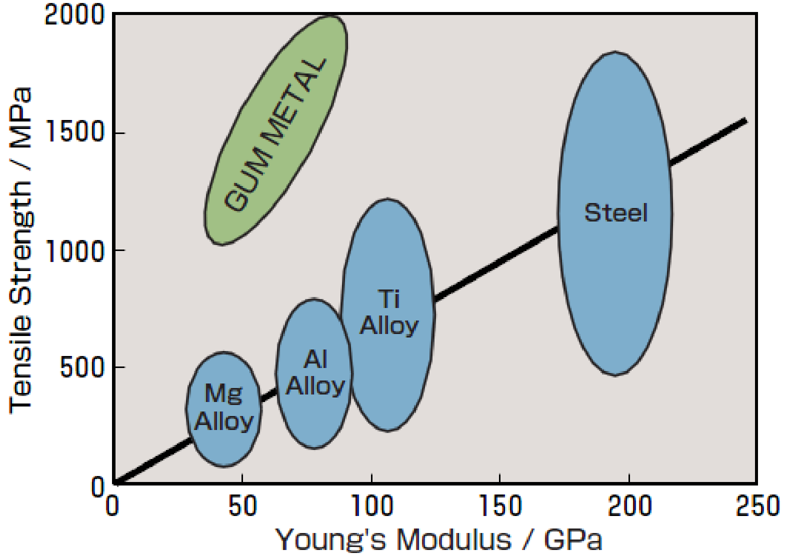
Metastable Beta-Ti alloy에 속함, 대표적으로
Ti-12Ta-9Nb-3V-6Zr-O, Ti-23Nb-0.7Ta-2Zr-O
등의 조성이 있음

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

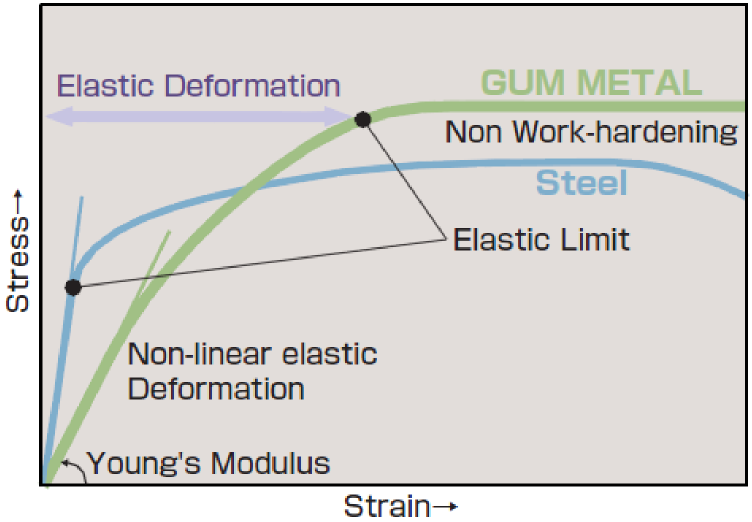
- Non-linear elastic deformation
- Non-work hardening
- No dislocation, No twinning, but large plasticity by giant fault (shear band와 비슷한)



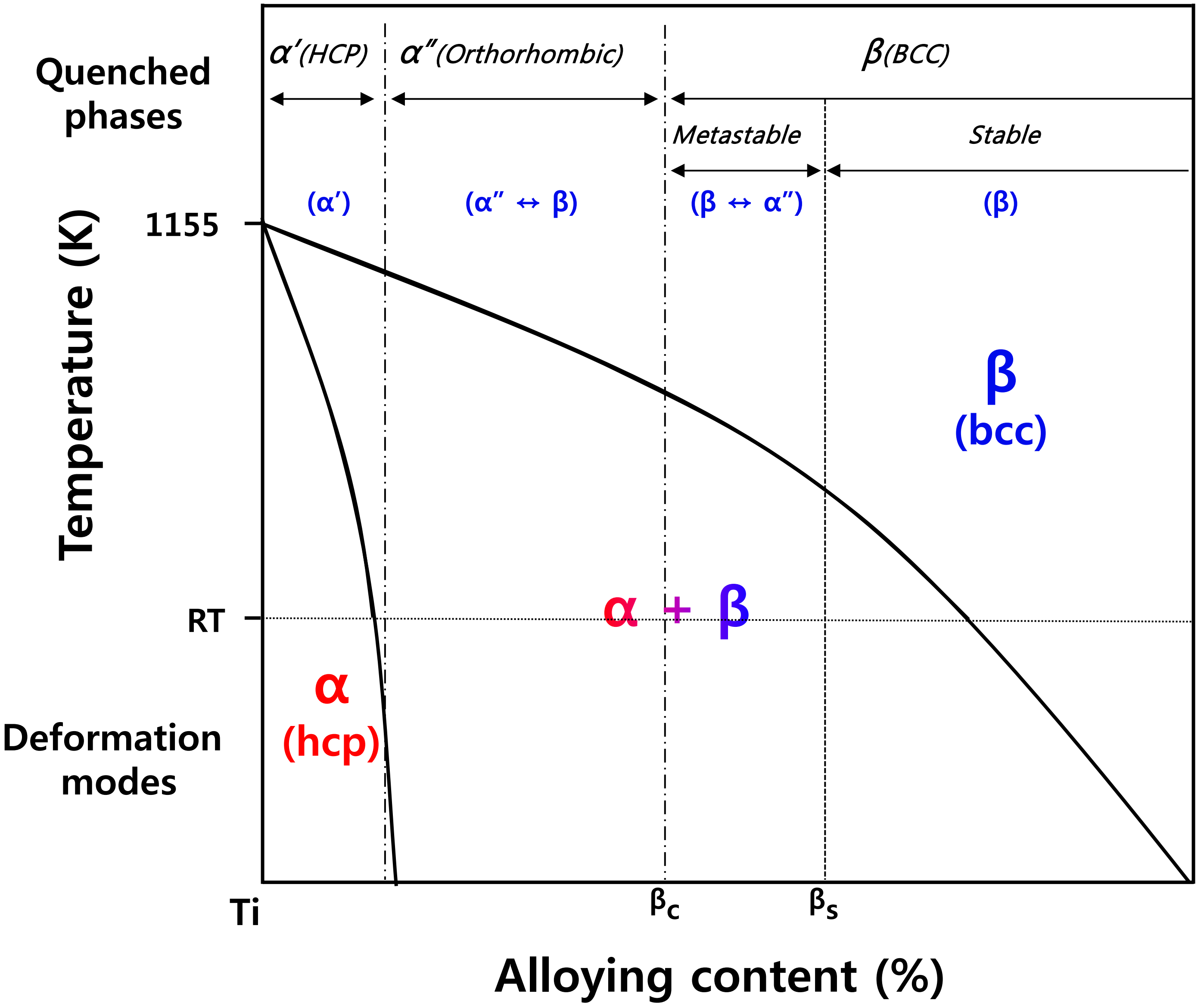
[Fig.1] Position of Young's Modulus and Strength of GUM METAL



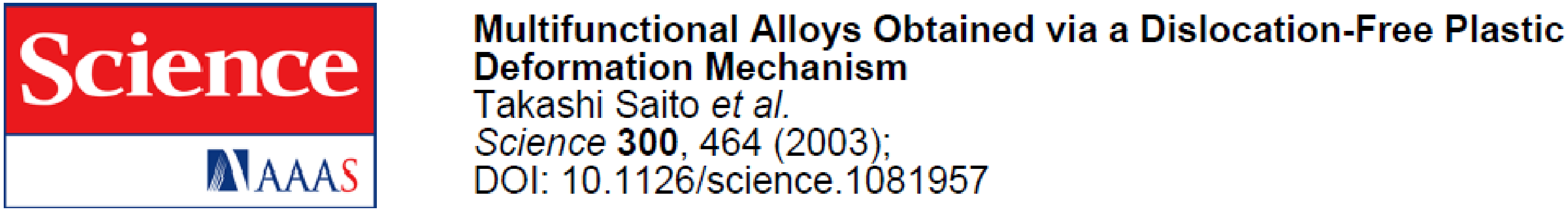
[Fig.2] Stress-Strain Curve of GUM METAL



Ti-based alloys



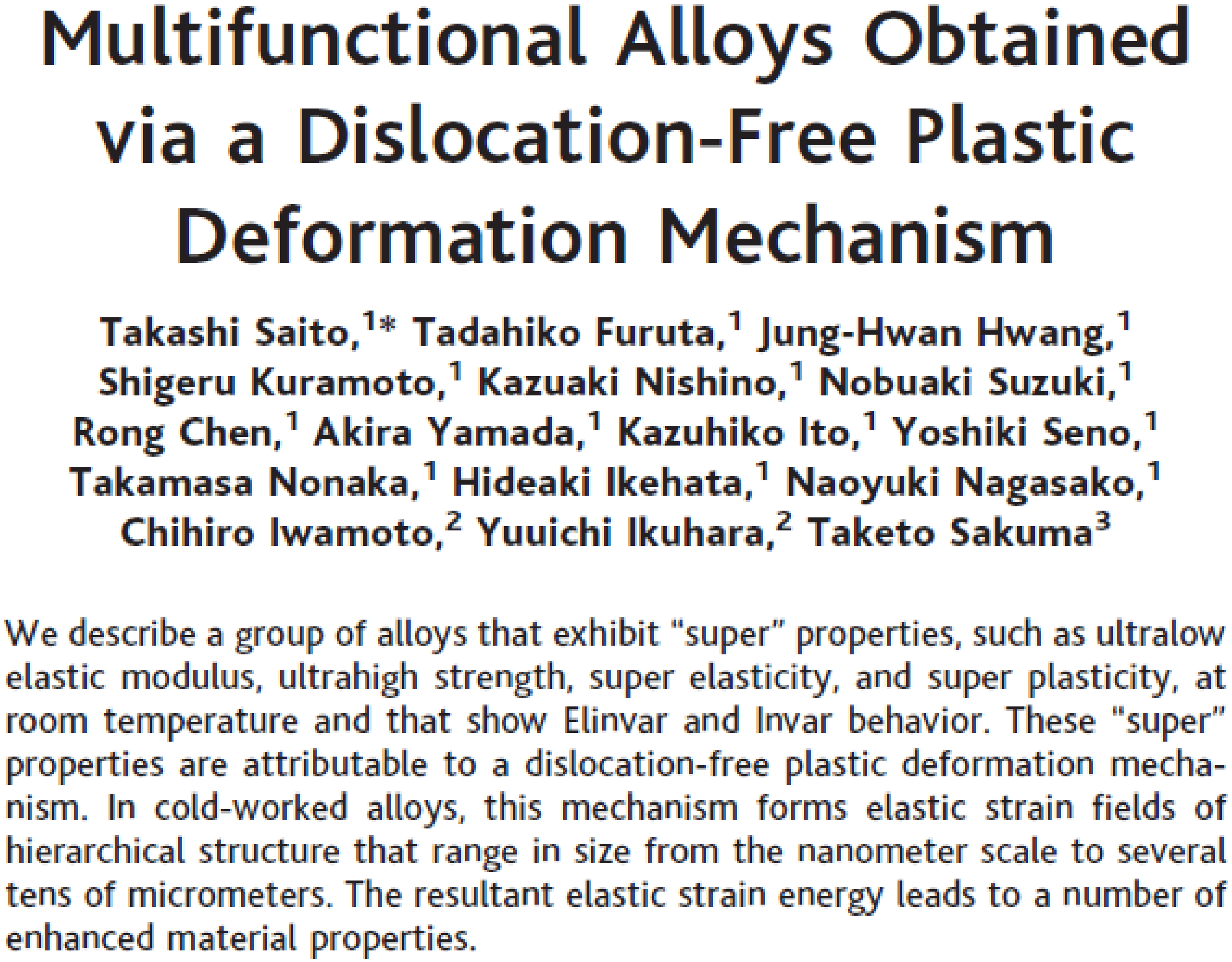
Gum metal - Science (2003)



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

- 다른 β-Ti alloy의 경우 Martensitic transformation (β↔α") 을 통해 super-elasticity를 보이는 반면, Gum metal은 martensitic transformation (β→α") 없이 재료의 intrinsic한 "true super-elasticity"를 보임.

- In-situ XRD 측정을 통해 non-linear elastic limit을 확인함.

In-situ XRD
- elastic limit 확인

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

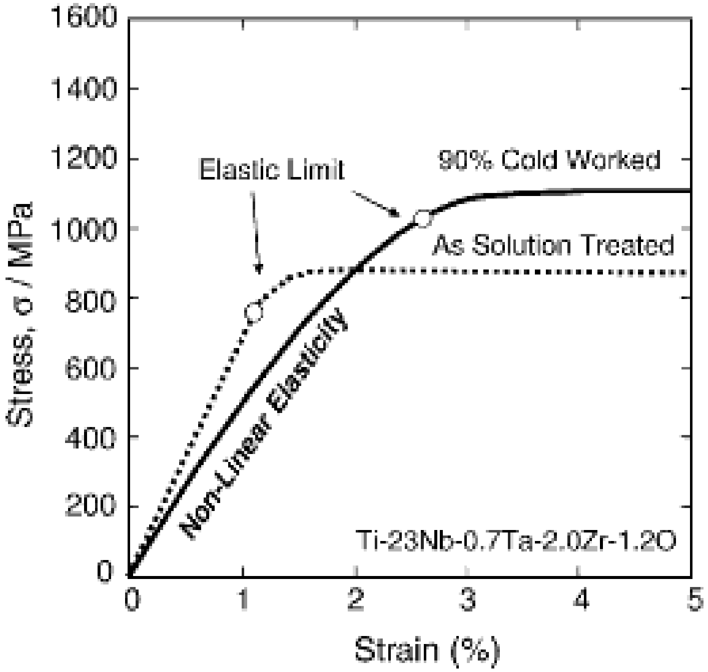


Fig. 1. Change in tensile stress-strain curve of specimen at room temperature both before and after cold working with a 90% reduction in area.

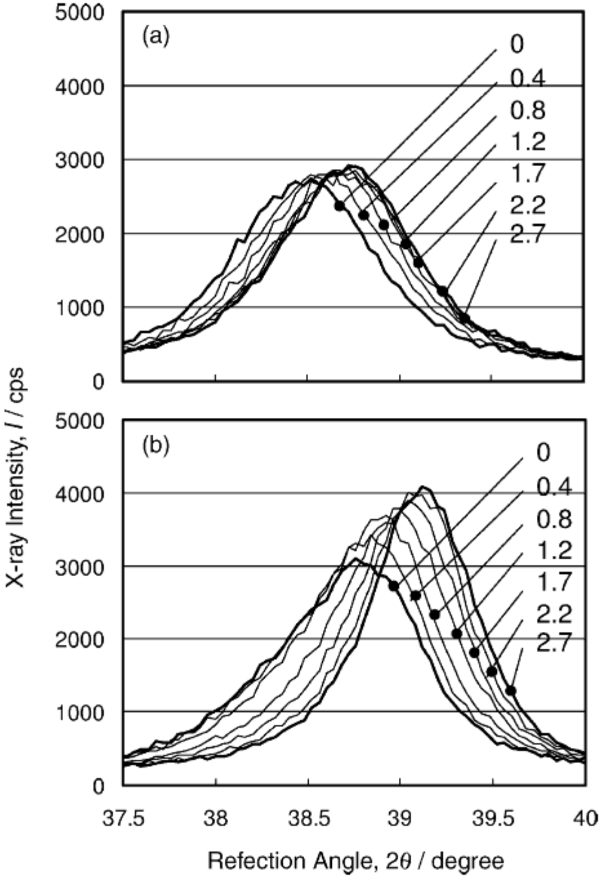
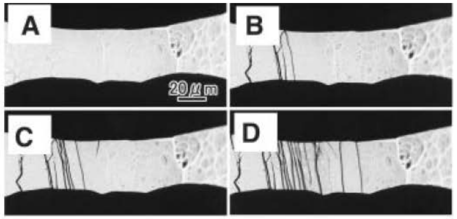


Fig. 4. Changes in X-ray profile during tensile deformation. Amounts of tensile strain (%) are indicated in the figure: (a) solution treated and (b) cold worked.

Gum metal - plastic property

- Dislocation / twin 과 관련된 모든 소성 변형기구가 없으며 마치 shear band와 유사한 giant fault에 의한 소성 변형을 하며 변형 후에는 매우 독특한 microstructure를 가짐.



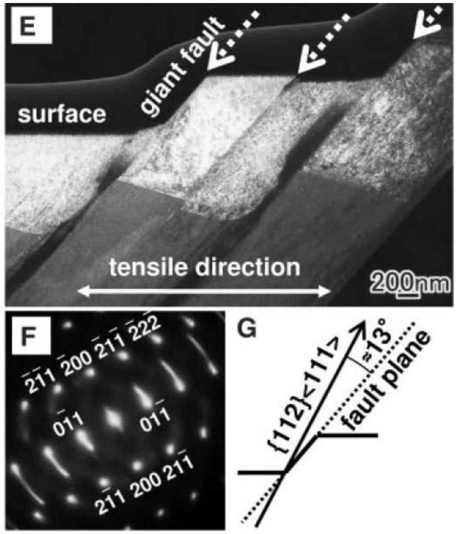
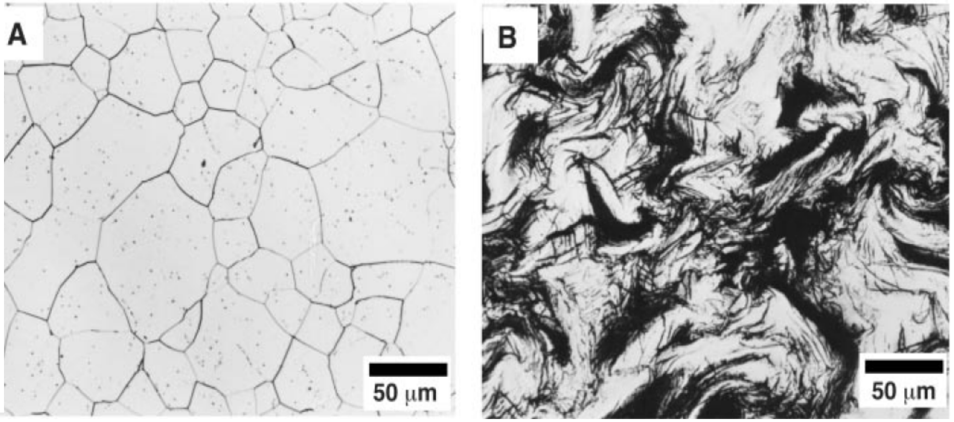


Fig. 3. (**A** to **D**) Changes in surface morphology of a tensile specimen of annealed Ti-23Nb-0.7Ta-2Zr-1.2O alloy. The amounts of deformation are (A) 0, (B) 4.3%, (C) 6.1%, and (D) 10.3%. (**E**) A TEM image near the surface of the specimen and (**F**) the corresponding electron diffraction pattern, 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.

Cold working 후의
독특한 미세구조

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

: giant fault 주변에 국부적으로 elastic strain energy가 축적됨. 즉 재료의 elastic mechanism 에 의하여 plastic deformation까지 이루어짐.

Gum metal - Science (2003) (Gum metal 제조 조건)

(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

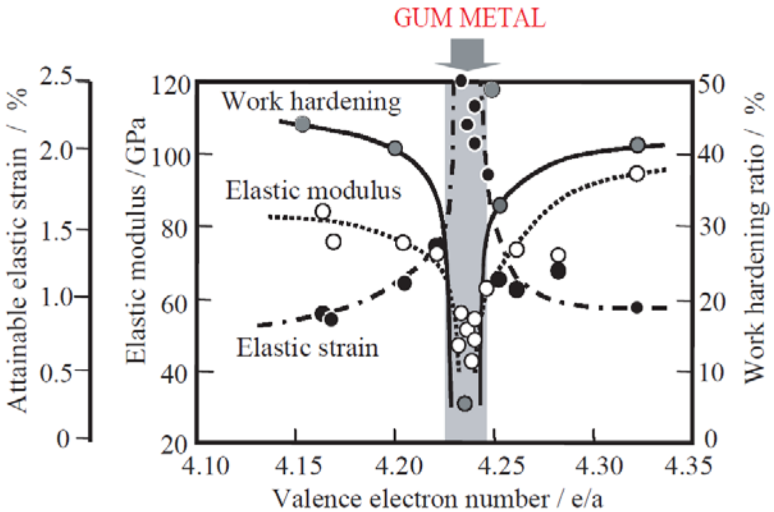
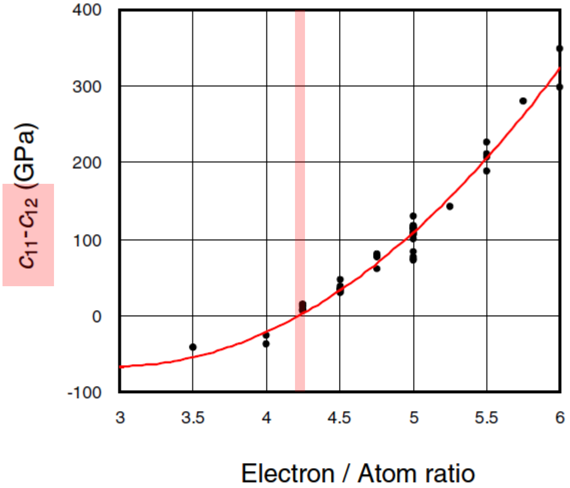


Fig. 3 Anomaly in properties of Ti-Nb-Ta-Zr-O alloys.



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

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

Magic number를 만족하는 조성의 합금을 simple BCC (A2) structure로 만들고 cold work 할 것. ex) Ti-12Ta-9Nb-3V-6Zr-O/ Ti-23Nb-0.7Ta-2Zr-O (O: 0.7~3 mol%)

Gum metal - Science (2003)

- 합금에 Oxygen 및 Zirconium 이 들어가야 gum metal이 되는 이유?

→ O이 Zr 주변에서 cluster를 형성하여 dislocation 활성을 방해함.

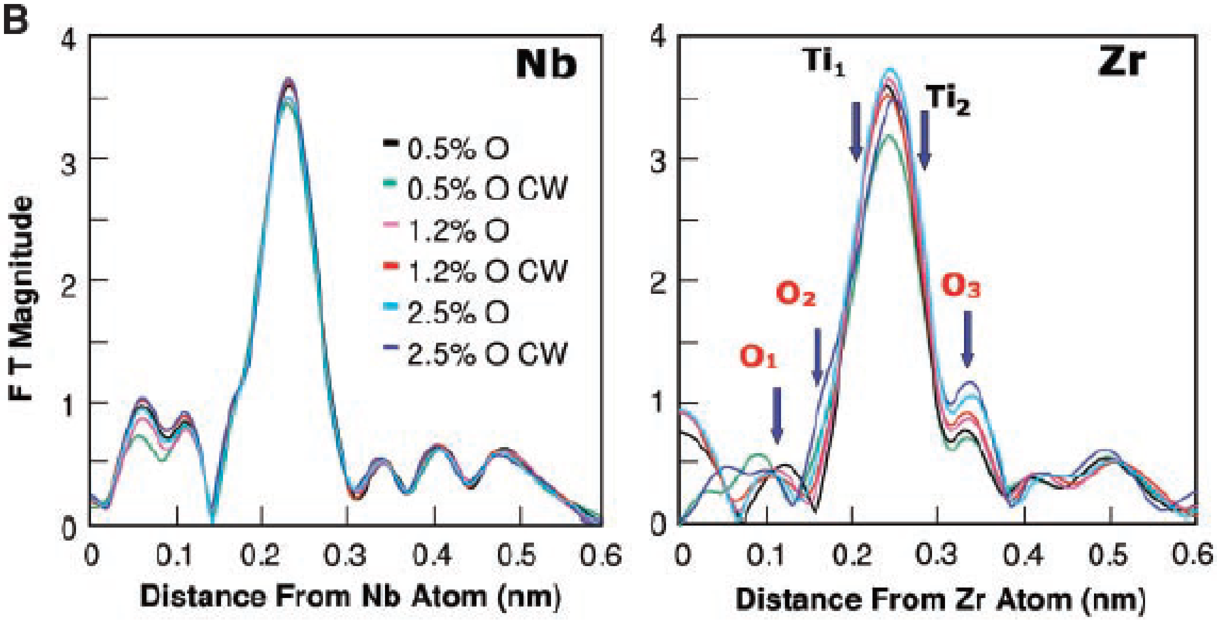


Fig. 4. (A) A distribution of alloying elements in the 90% cold-worked Ti-23Nb-0.7Ta-2Zr-1.2O alloy by EELS using a 200-kV TEM and a TEM image of the same magnification. (B) Comparison of the Fourier transferred spectra calculated from the K-edge EXAFS spectra for niobium and zirconium atoms using 8-GeV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

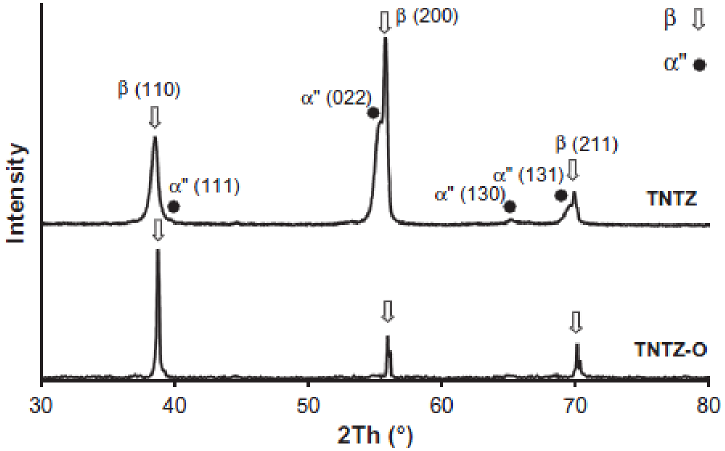


Fig. 2. XRD from the TNTZ and TNTZ-O alloys in the recrystallized/quenched state.

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

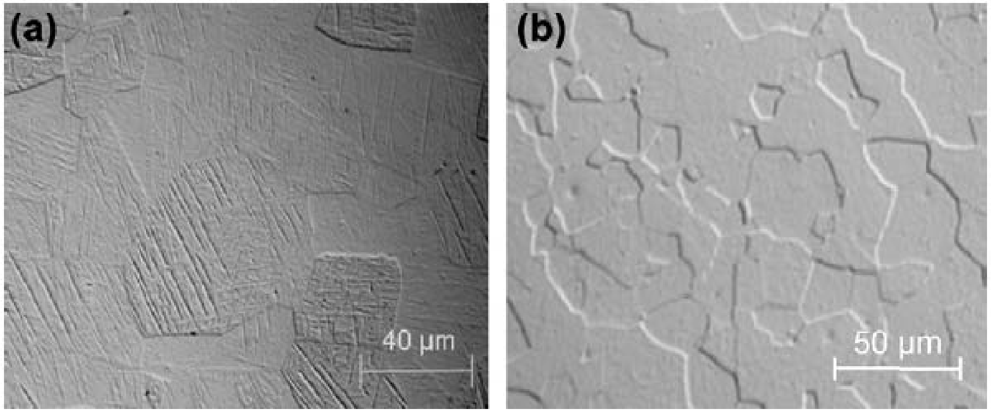
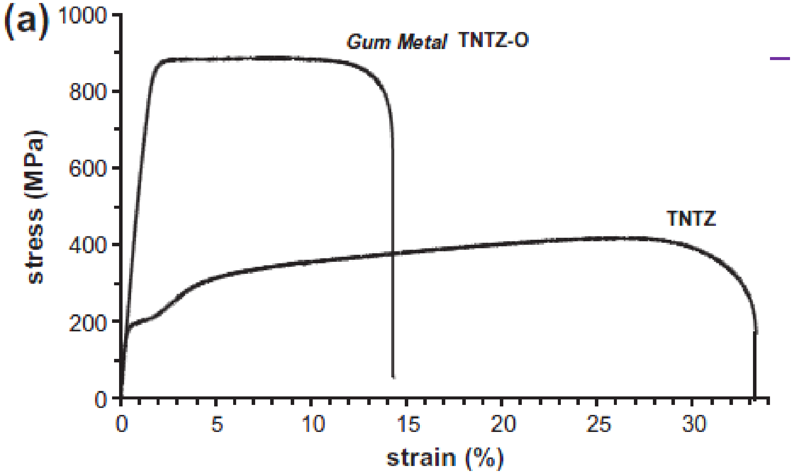


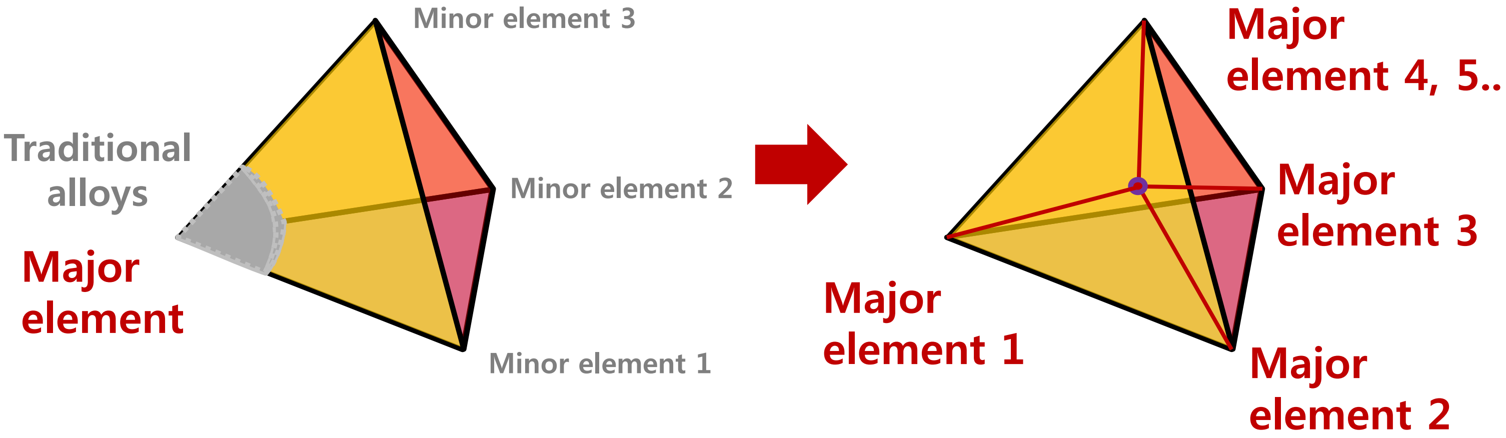
Fig. 1. Microstructures of the TNTZ (a) and TNTZ-O (b) alloys observed by optical microscopy.



- Oxygen 으로 인한 strengthening 효과
- Phase transformation의 억제로 인한 strengthening

➡ 일반적인 β-Ti alloy의 deformation mechanism에서 크게 벗어나지 않으며 Oxygen clustering에 의한 효과가 다소 독특함.

(d) high entropy alloy (HEA)



Conventional alloy system

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

High entropy alloy system

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

High entropy alloy_5개 이상 원소 포함, 5%~35% 사이의 원소 함량 가짐

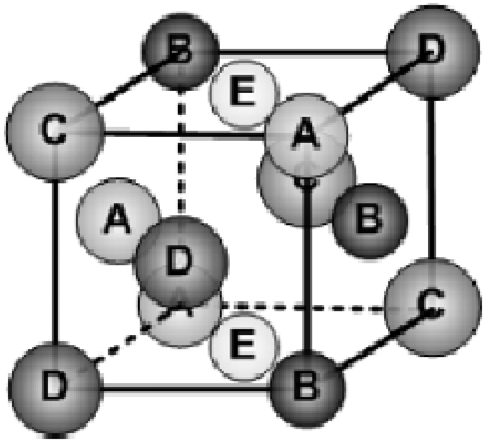
- Equimolar: AlCoCrCuFeNi
- Nonequimolar: AlCo0.5CrCuFe1.5Ni1.2
- Minor addition: AlCo0.5CrCuFe1.5Ni1.2B0.1C0.15

→ 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

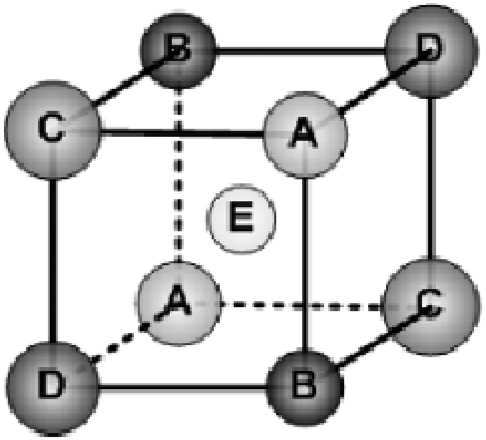


FCC type HEA Solid Solution

CoCrCuFeNi=HEA,

Yeh, MMTA, 2004;

BCC: 5 principal elements



BCC type HEA Solid Solution

AlCoCrFeNi=HEA ,

Zhou, APL, 2007

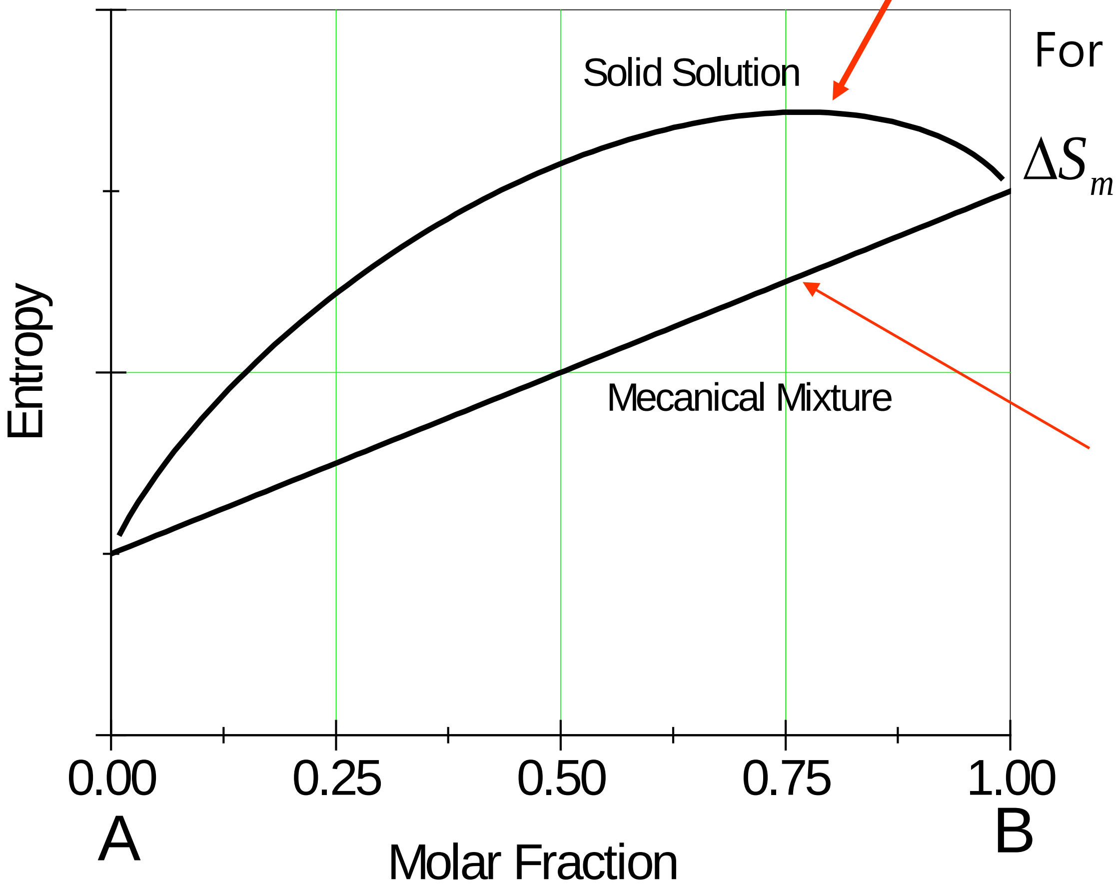
$Al_{20}[TiVMnHEA]_{80}$,

Zhou, MSEA, 2007

Basic concepts of high entropy alloy (HEA)

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

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

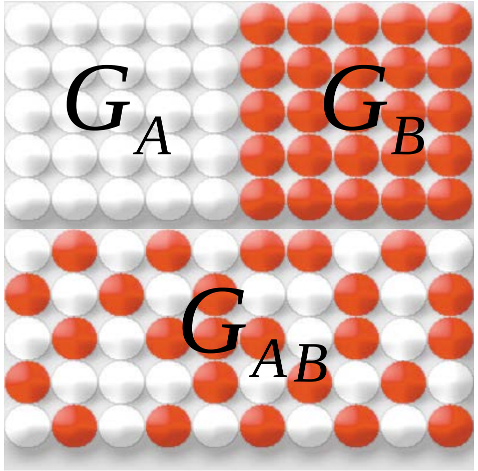


For the regular solution:

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

$$S = X_A S_A + X_B S_B$$

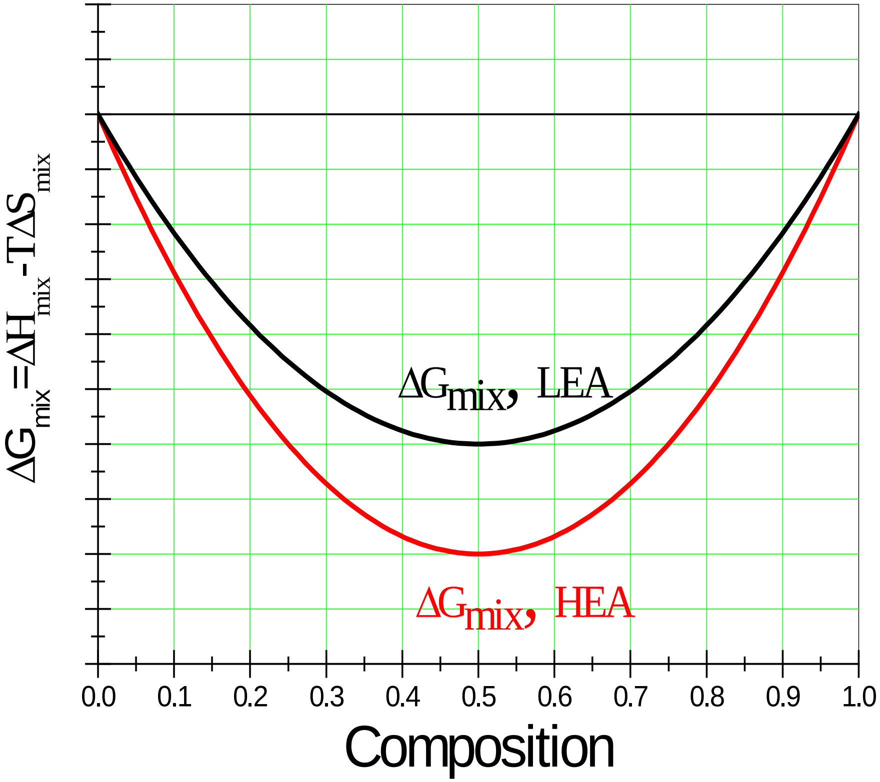
Basic concepts of high entropy alloy (HEA)

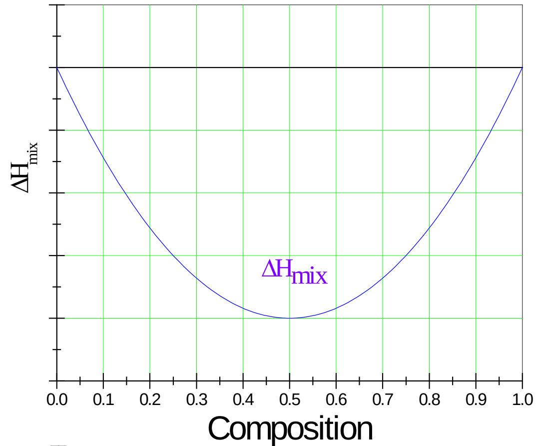


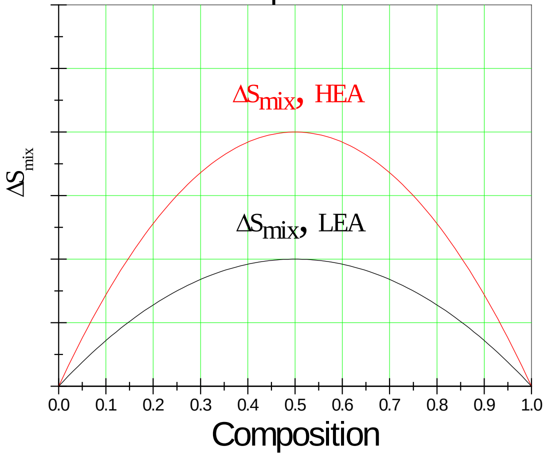
Gibbs Free Energy

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

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







Basic concepts of high entropy alloy (HEA)

(1) Thermodynamic : high entropy effect

high entropy of mixing enhance mutual solubility among elements and stabilizes solid solution phase_결정상 복잡하지 않음

(2) Kinetics : sluggish diffusion effect

cooperative diffusion of many elements is required to form new phase

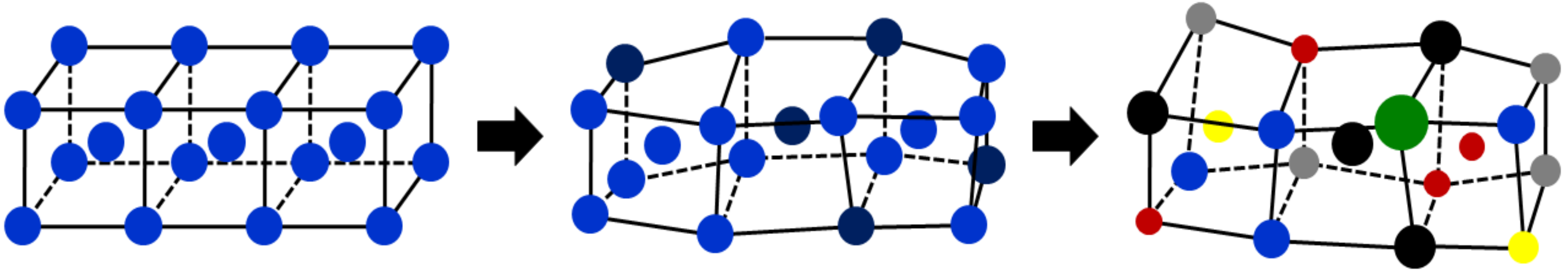
→ slow phase transformation rate

→ supersaturation 혹은 nano-precipitation 얻기 쉬움/ 높은 재결정 온도/ 느린 growth rate/ 느린 particle coarsening rate

(3) Structure : severe lattice distortion effect

원자반경차 ↑ 면 lattice distortion 증가

→ diffusion scattering 증가/ Hardness and strength 증가/ electrical or thermal conductivity 감소



Yong Zhang et al., Adv. Eng. Mat. P534-538, 2008

(4) Property : cocktail effect

come from the basis features of the composing elements and their mutual interactions

Basic concepts of high entropy alloy (HEA)

1. High Strength; *Zhou, APL, 2007;*
2. High wear resistance; *Lin, Surface Coating technology, 2008.*
3. High corrosion resistance; *Lee, Thin Solid Films, 2008;*
4. High thermo-stability; *Tsai, APL, 2008.*

* Application 일 예

1) High temp structural alloy:

$AlCoCr_2FeMo_{0.5}Ni$_1000℃ H_v~450_Supper alloy 보다 3배 큼

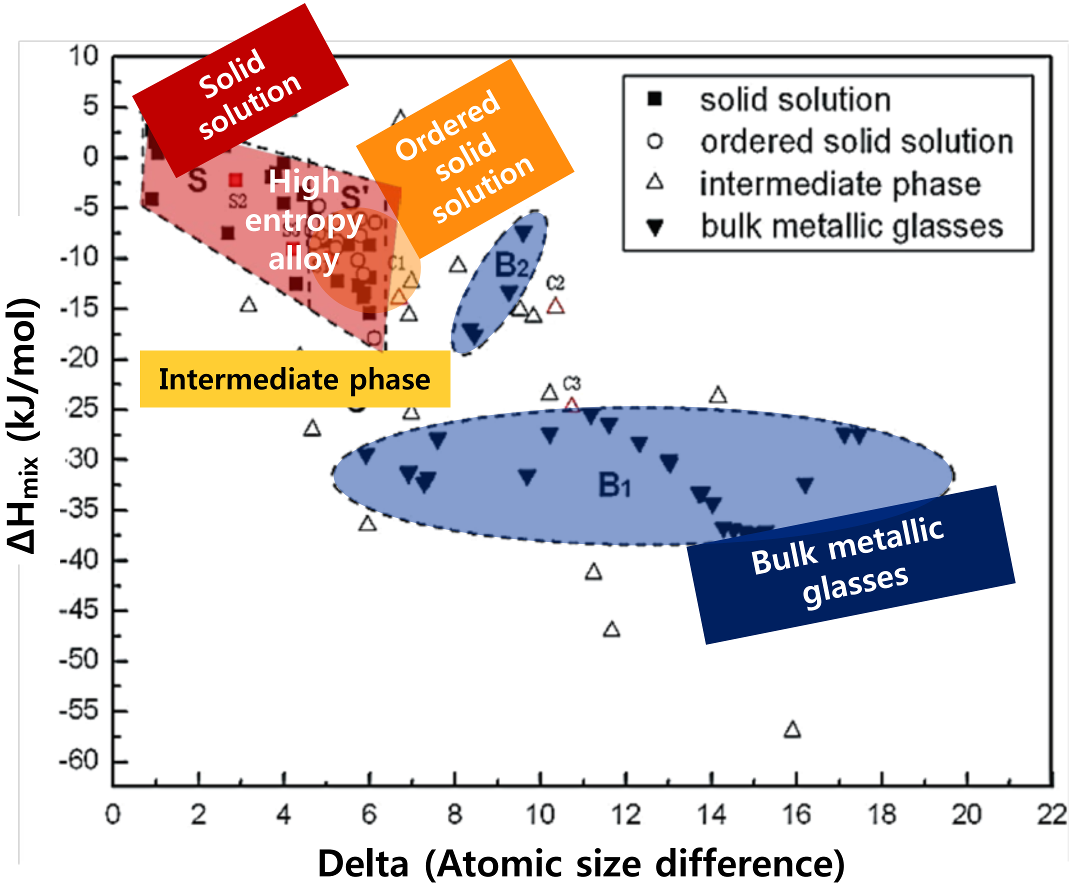
2) Thermal sprayed coating_oxidation resistance

3) Highly-workable alloy: AlCrFeMnNi 4900% 연신

4) HEA binders for cermeted carbides and cermets

Empirical rules: high entropy alloy vs bulk metallic glass

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

* Development strategy of completely new materials

a. Alloyed pleasures: Multi-metallic cocktails

b. Synthesize metastable phases

Equilibrium conditions → Non-equilibrium conditions

: non-equilibrium processing = “energize and quench” a material

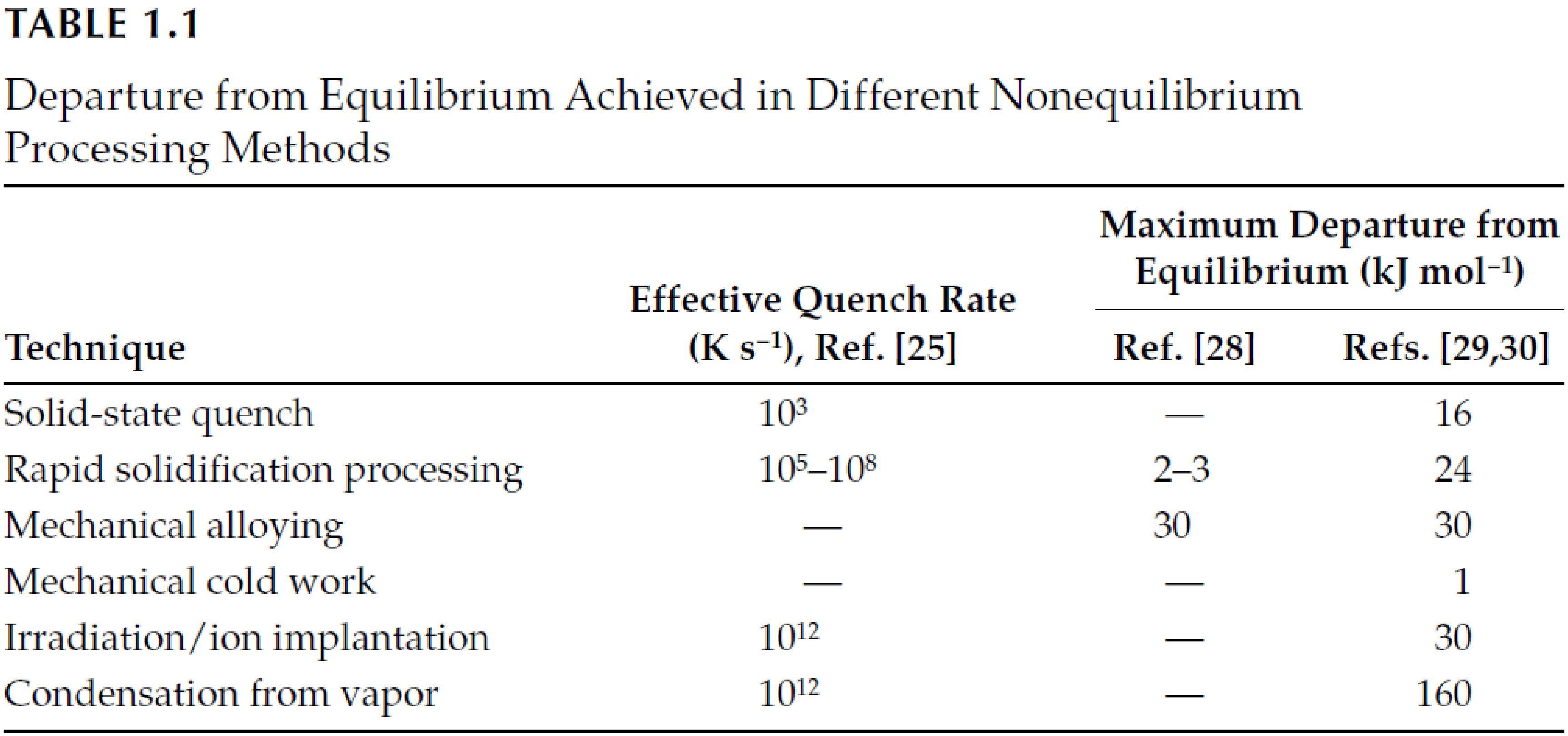
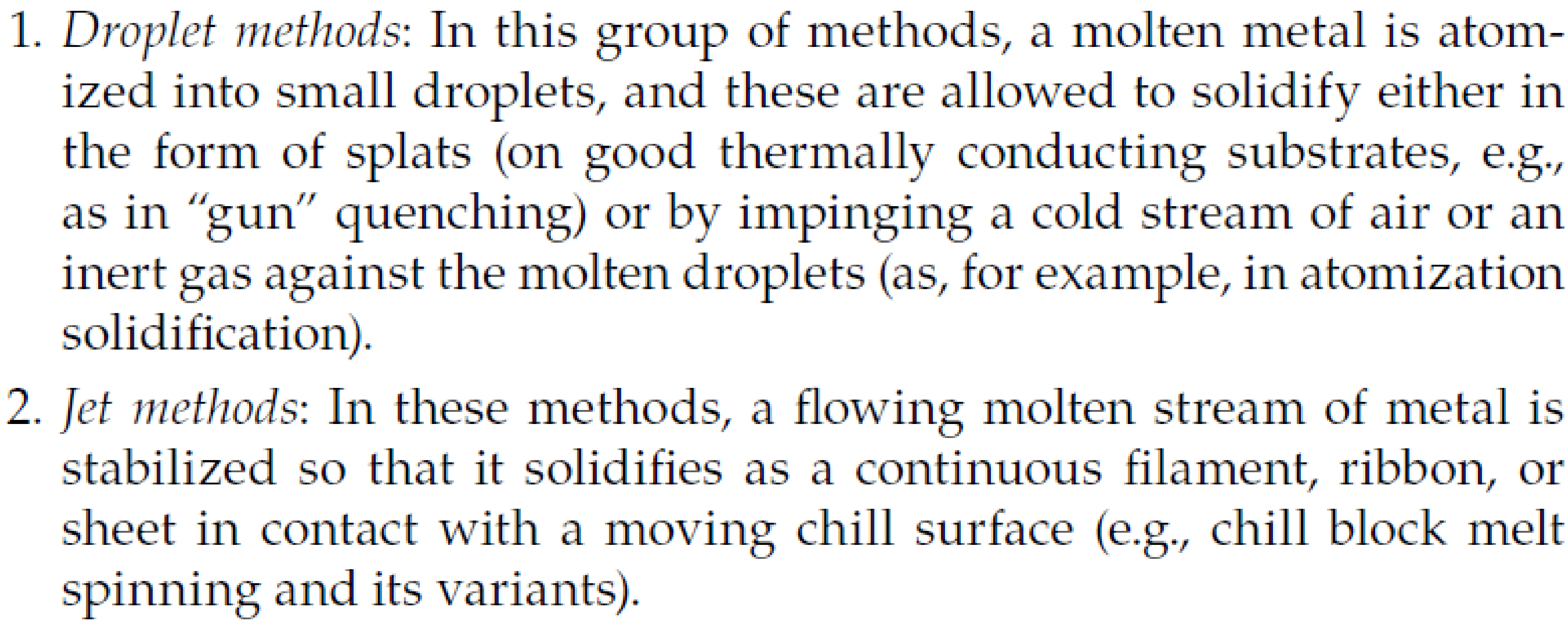


TABLE 1.1

Departure from Equilibrium Achieved in Different Nonequilibrium Processing Methods

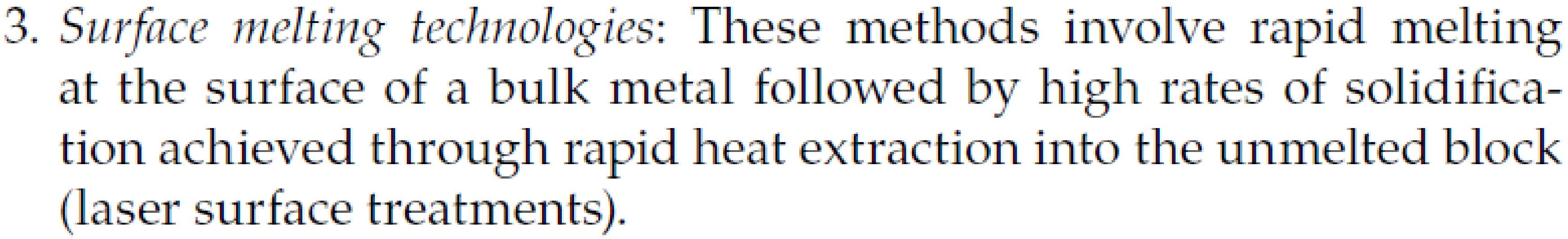
Technique	Effective Quench Rate (K s^{-1}), Ref. [25]	Maximum Departure from Equilibrium (kJ mol^{-1})	
		Ref. [28]	Refs. [29,30]
Solid-state quench	10^3	—	16
Rapid solidification processing	10^5–10^8	2–3	24
Mechanical alloying	—	30	30
Mechanical cold work	—	—	1
Irradiation/ion implantation	10^{12}	—	30
Condensation from vapor	10^{12}	—	160

1.3 Rapid Solidification Processing



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.

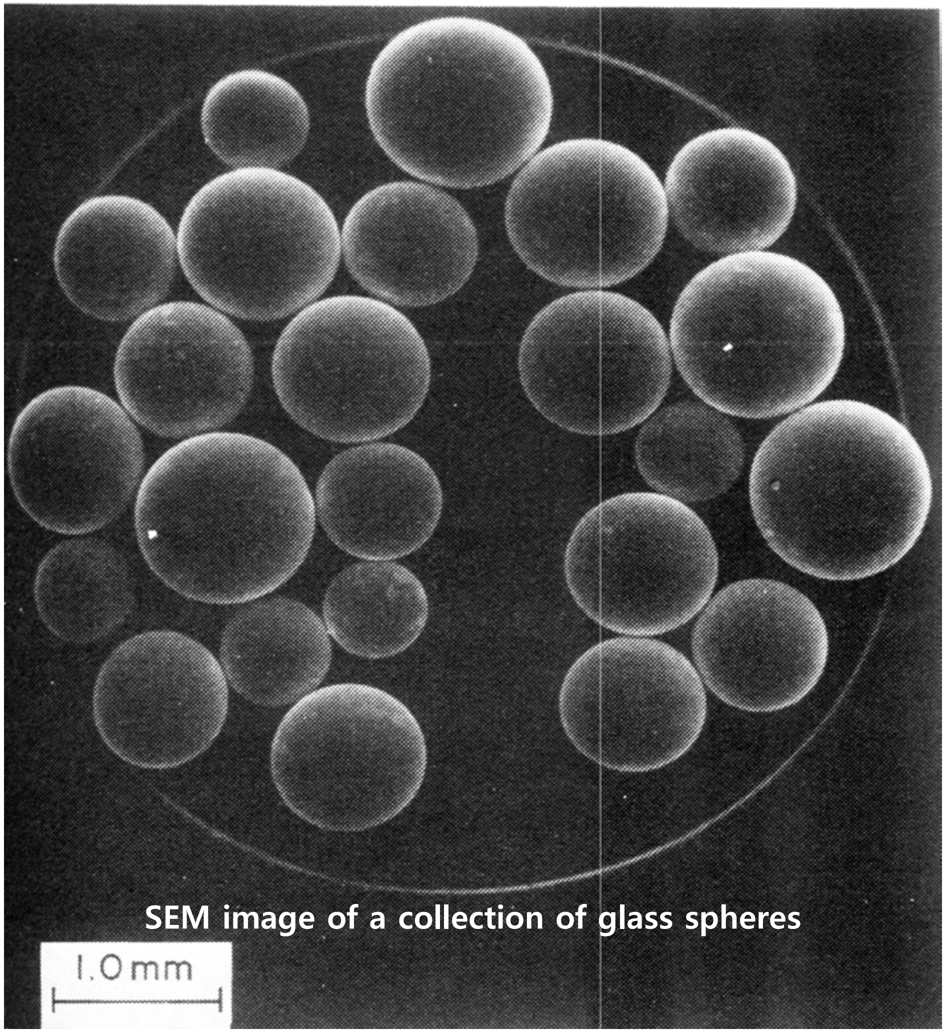


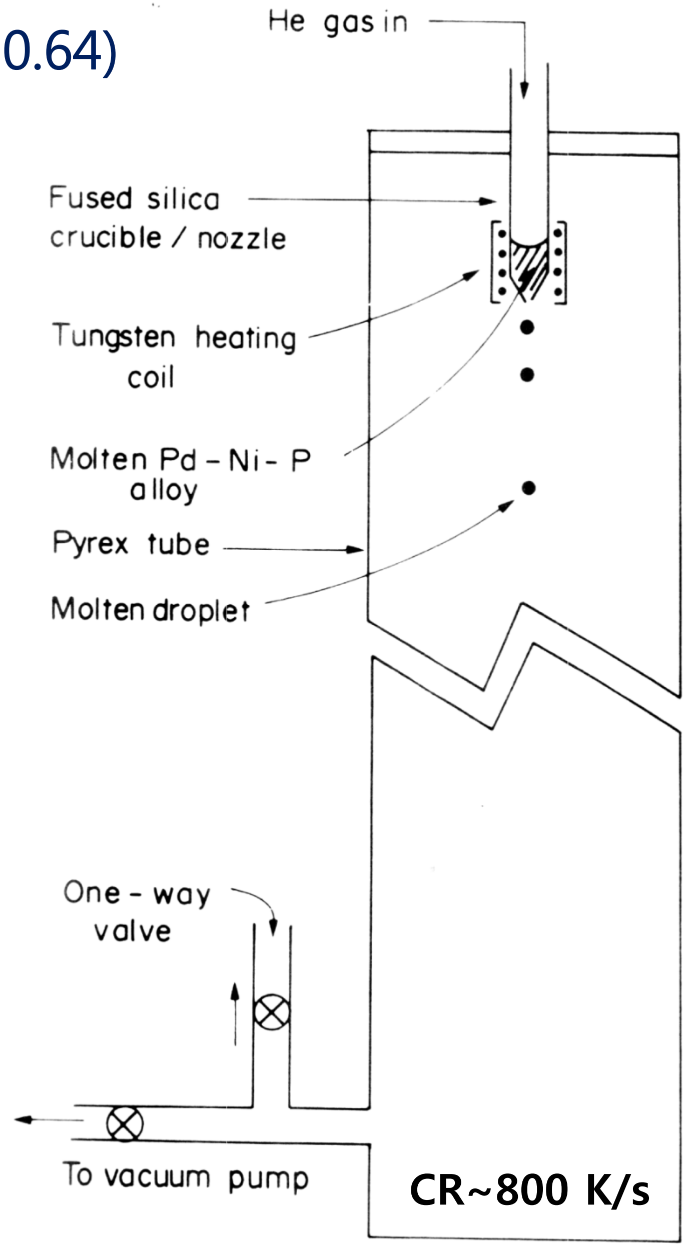
3. *Surface melting technologies*: These methods involve rapid melting at the surface of a bulk metal followed by high rates of solidification achieved through rapid heat extraction into the unmelted block (laser surface treatments).

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)

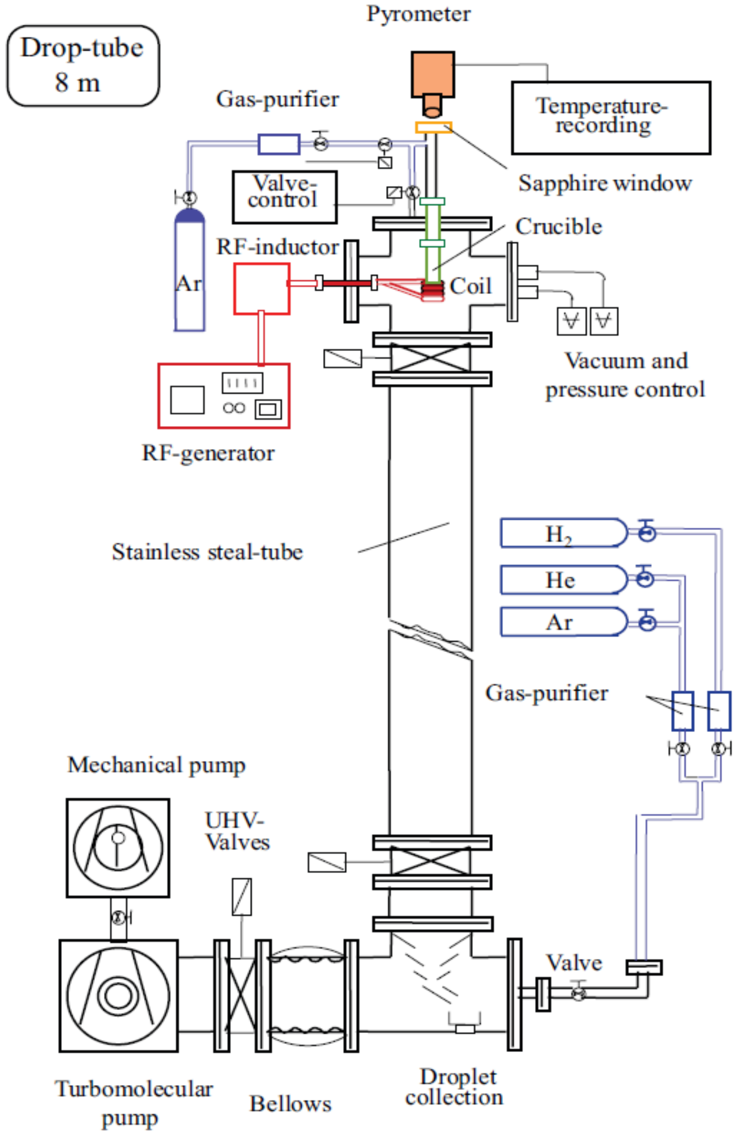




CR~800 K/s

Realizing heterogeneous nucleation

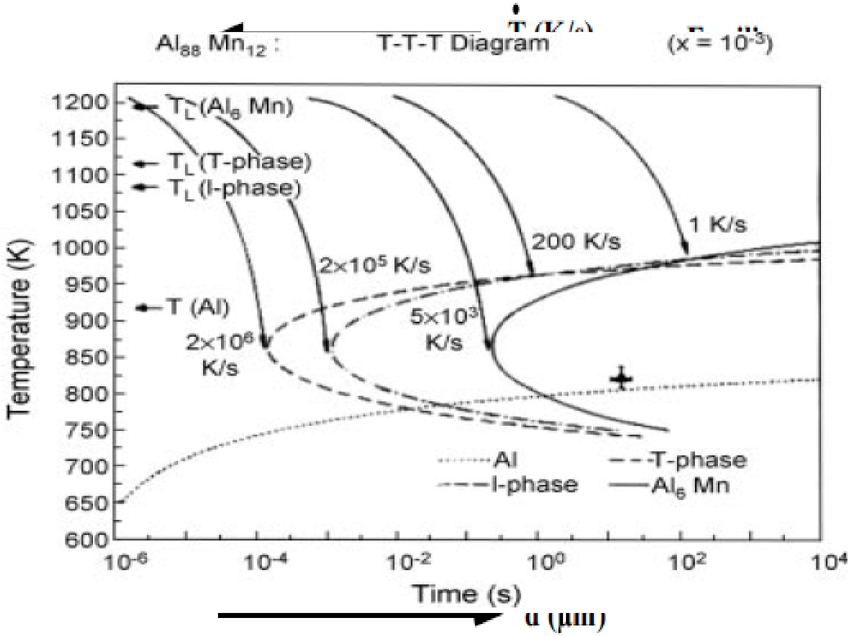
Solidification of containerless undercooled Melts, edited by Dieter M. Herlach and Douglas M. Matson, 2012, p.1-7



- Schematic view of DLR drop tube

Drop tube technique

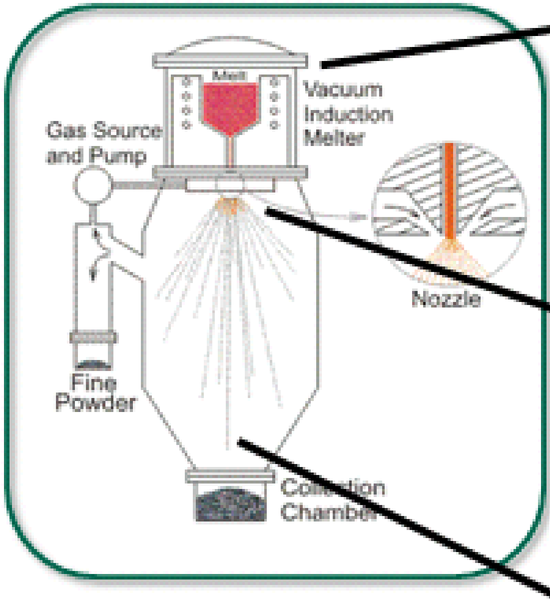
- rapid cooling of small particles by dispersion of the melt
- reduction of heterogeneous nucleation by containerless processing

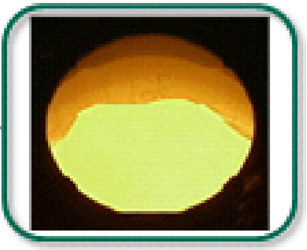


- TTT diagrams of the various phases involved in the solidification of undercooled droplets of $Al_{88}Mn_{12}$
- Phase mixture in droplets of $Al_{88}Mn_1$ alloy as a function of droplet diameter

Gas Atomization

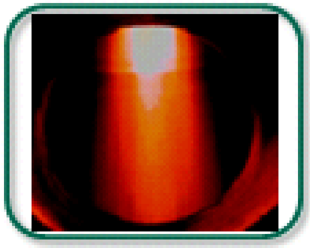
Components of Atomizer





- **Furnace**

  Melting Metal or Ceramics



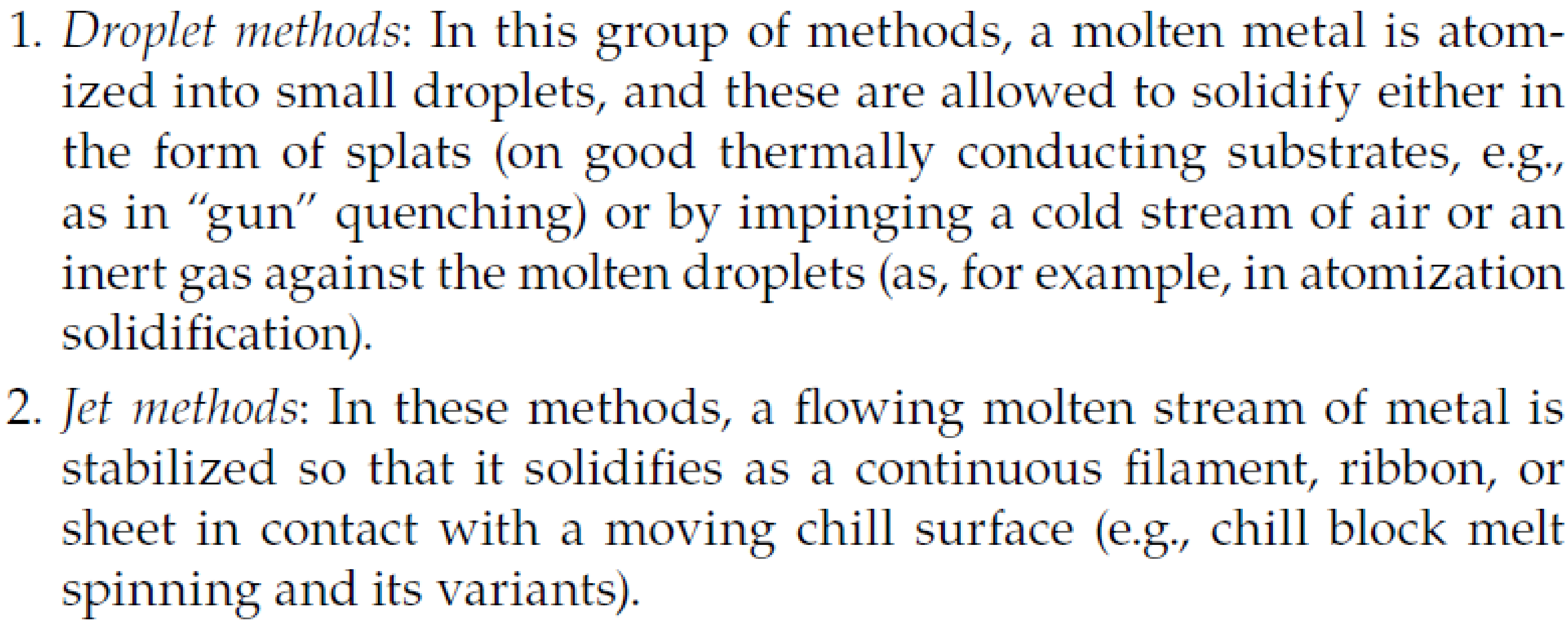
- **Pump and Spray Nozzle**

  Inert gas flows out with breaking bulk liquid.

- **Chamber**

  Powder is Stored in a chamber.

1.3 Rapid Solidification Processing



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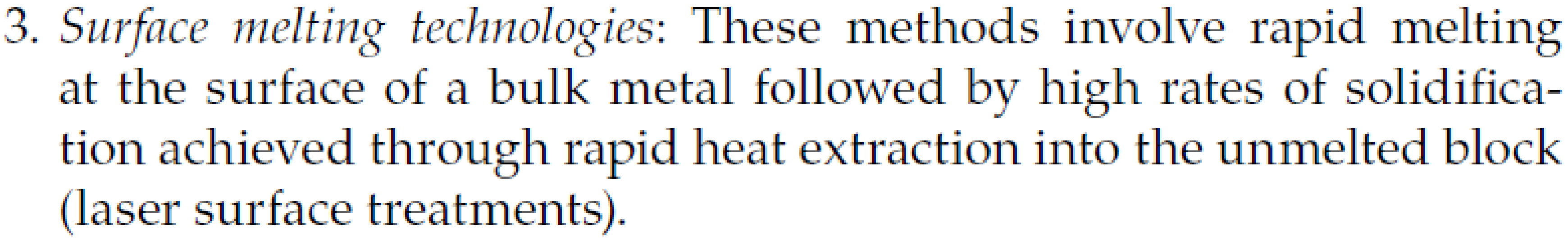
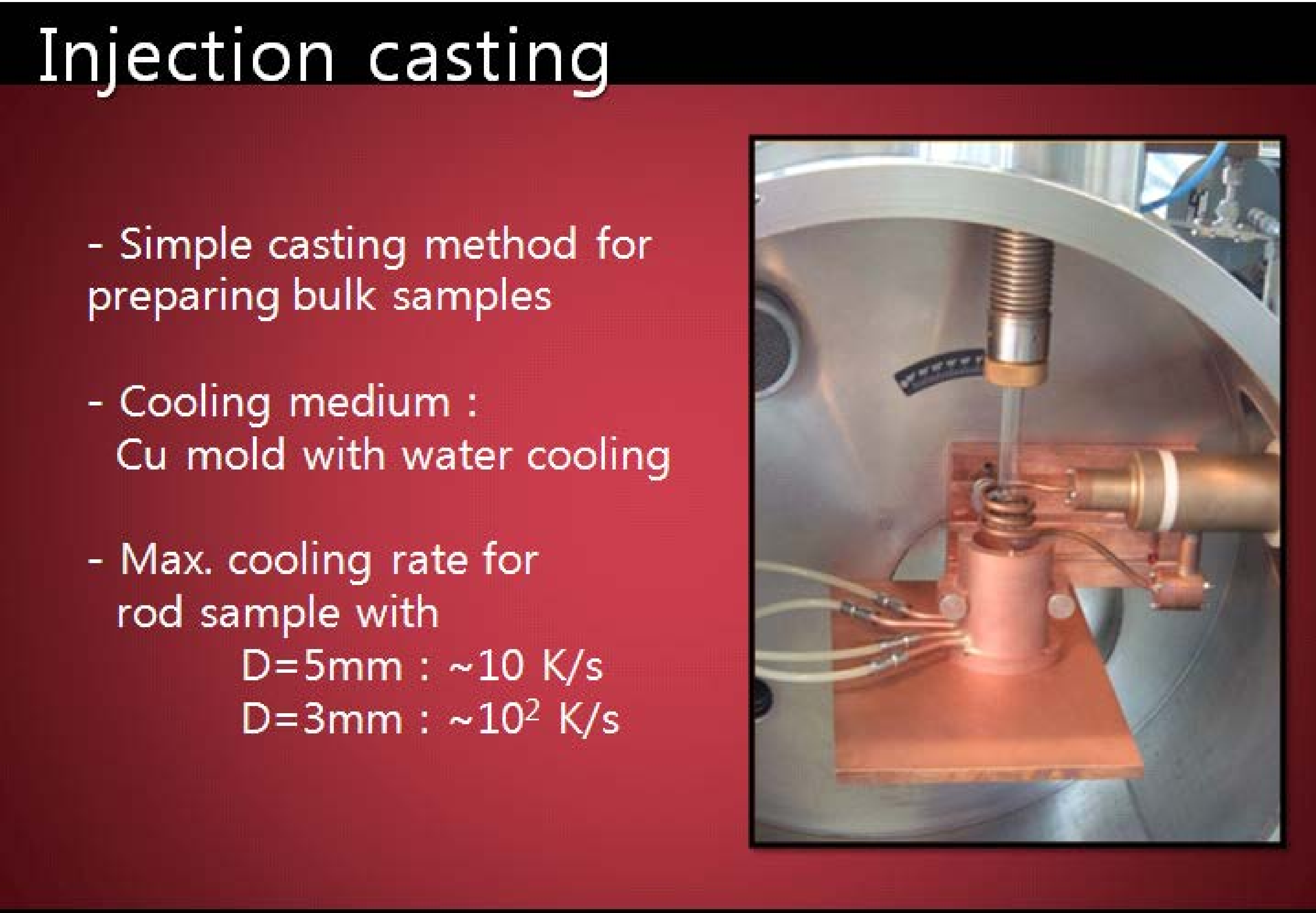


3. *Surface melting technologies*: These methods involve rapid melting at the surface of a bulk metal followed by high rates of solidification achieved through rapid heat extraction into the unmelted block (laser surface treatments).

Glass formation : Rapid quenching of liquid phase

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

Bulk sample: rod



Injection casting

- Simple casting method for preparing bulk samples

- Cooling medium :
  Cu mold with water cooling

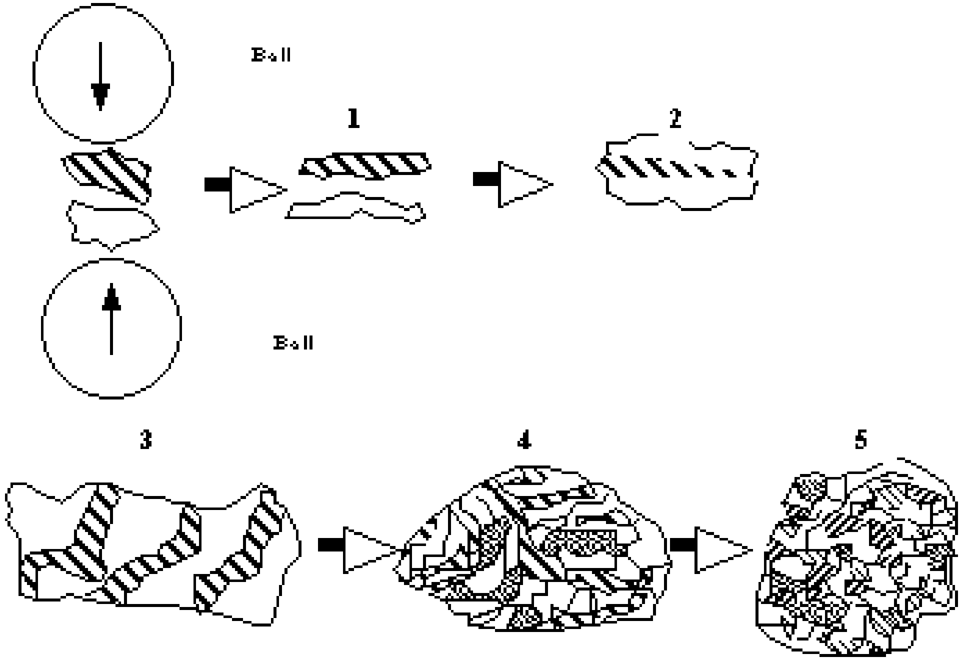
- Max. cooling rate for
  rod sample with
  D=5mm : ~10 K/s
  D=3mm : ~10^2 K/s

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.

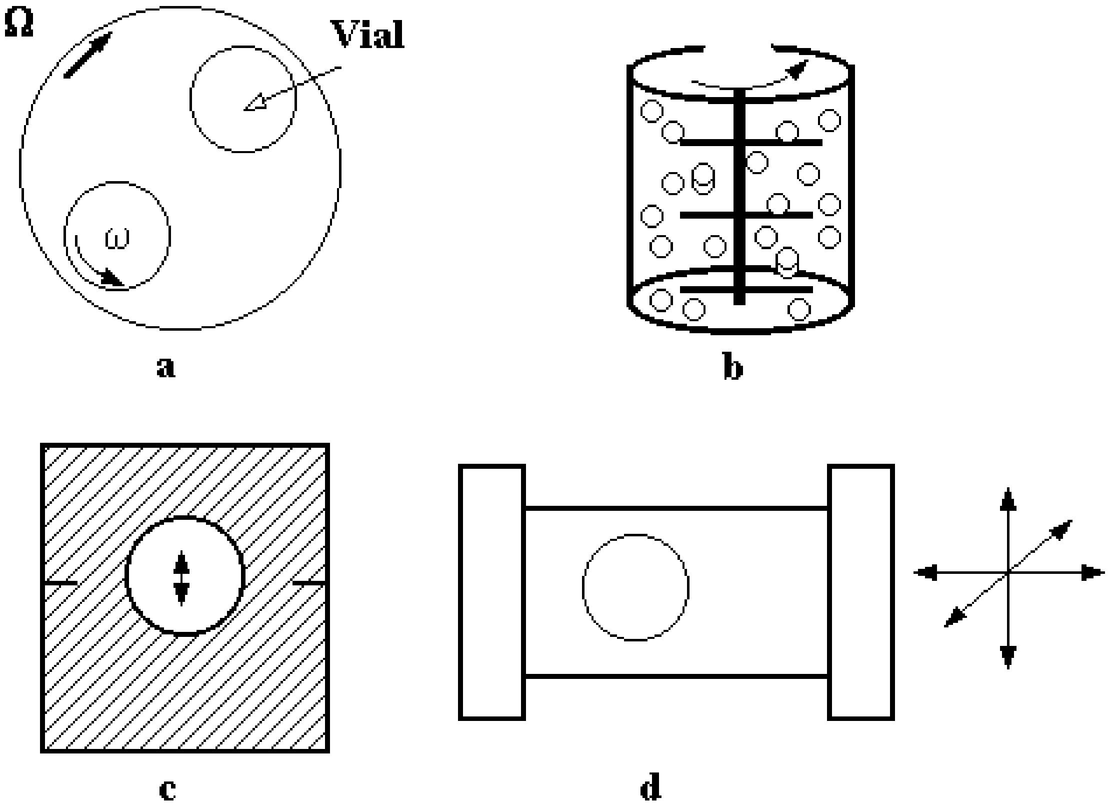
It is a method that can produce extremely small grain size (to below 10 nm), metastable phases (both crystalline and amorphous), and high concentration of lattice defects.

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.

History of mechanical alloying

- Developed to produce oxide dispersion strengthened nickel alloys, INCO Alloys, Gilman and Benjamin, 1968
- Ball milling can produce amorphous alloys, C.C. Koch, UNC, 1983 (top photo)
- Mechanically induced self-sustaining reactions, MSR, P.G. McCormick, 1989
- The first comprehensive book on mechanical alloying, C Suryanarayana, UCF, 2004 (bottom photo)
- Research on the chemical effects of mechanical milling has been ongoing since the 1950s, but the two areas did not have contact until the 1990s.

* 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.

→ consolidated to full density by conventional or advanced methods
such as vacuum hot pressing, hot extrusion, hot isostatic pressing, or shock consolidation, or combinations of these and obtain bulk samples