

2018 Fall

“Phase Transformation *in* Materials”

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Contents in Phase Transformation

Background
to understand
phase
transformation

(Ch1) Thermodynamics and Phase Diagrams

(Ch2) Diffusion: Kinetics

(Ch3) Crystal Interface and Microstructure

Representative
Phase
transformation

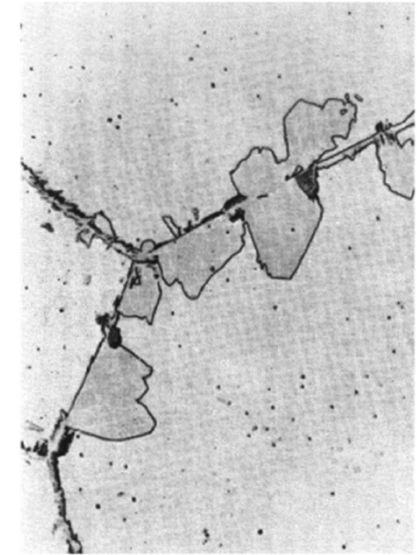
(Ch4) Solidification: Liquid \rightarrow Solid

(Ch5) Diffusional Transformations in Solid: Solid \rightarrow Solid

(Ch6) Diffusionless Transformations: Solid \rightarrow Solid

Massive vs. Martensitic Transformations

- There are two basic types of diffusionless transformations.
- One is the **massive transformation**. In this type, a diffusionless transformation takes place ① without a definite orientation relationship. The **interphase boundary (between parent and product phases)** migrates so as to allow the new phase to grow. It is, however, a ② **civilian transformation** because the atoms move individually.
- The other is the **martensitic transformation**. In this type, the change in phase involves a ① definite orientation relationship because the atoms have to ② move in a coordinated manner. (Military transformation) There is always a ③ change in shape which means that there is a strain associated with the transformation.



Microstructure of Martensite

- The microstructural characteristics of martensite are:
 - the product (martensite) phase has a well defined crystallographic relationship with the parent (matrix).
- 1) martensite (designated α') forms as **platelets within grains**.

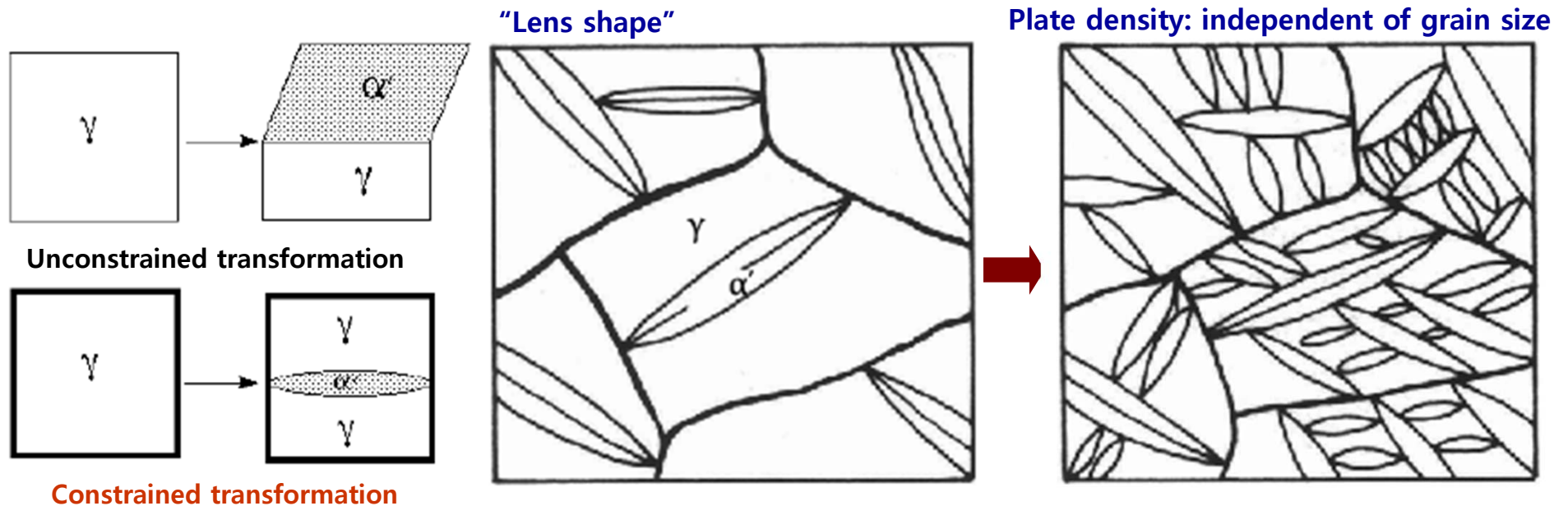


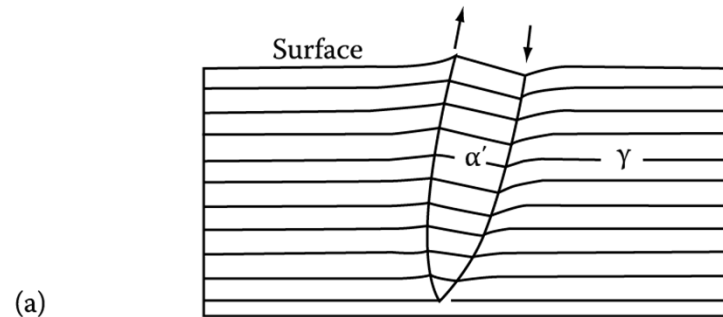
Fig. 6.1 Growth of martensite with increasing cooling below M_s .
→ Martensite formation rarely goes to completion

Microstructure of Martensite

- The microstructural characteristics of martensite are:
 - each platelet is accompanied by a **shape change**.
 - the shape change appears to be a **simple shear parallel to a habit plane** (the common, coherent plane between the phases) and a **“uniaxial expansion (dilatation) normal to the habit plane”**.

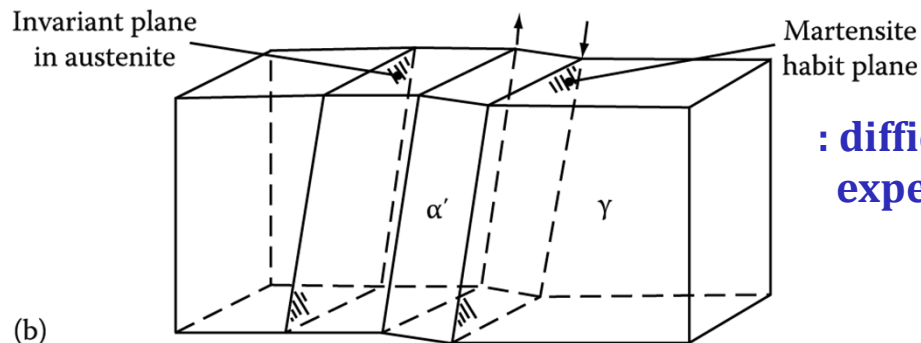
strain associated with the transformation

Polished surface_elastic deformation or tilting
→ but, remain continuous after the transformation



Intersection of the lenses with the surface of the specimen does not result in any discontinuity.

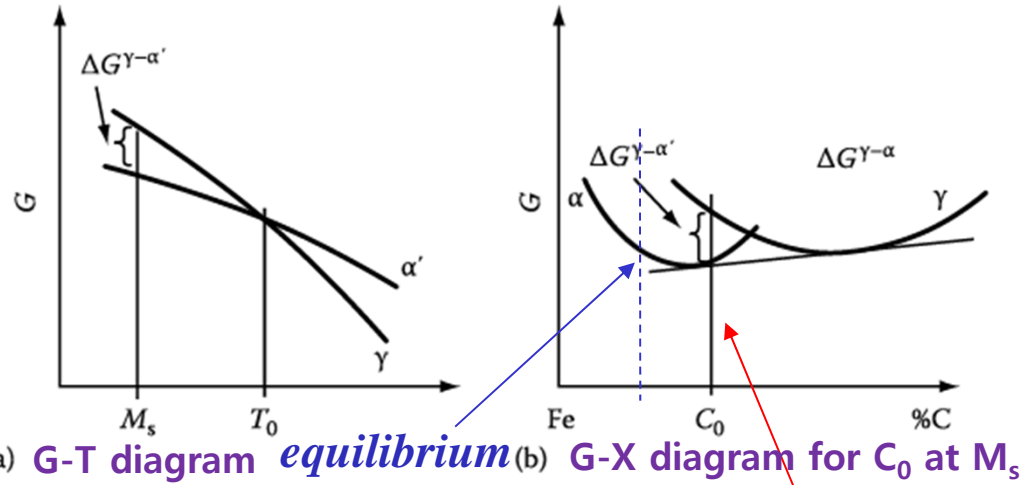
A fully grown plate spanning a whole grain $\sim 10^{-7}$ sec
→ V of α'/γ interface \propto speed of sound in solid



: difficult process to study M nucleation and growth experimentally

Fig. 6.2 Illustrating how a martensite plate remains macroscopically coherent with the surrounding austenite and even the surface it intersects.

Various ways of showing the martensite transformation

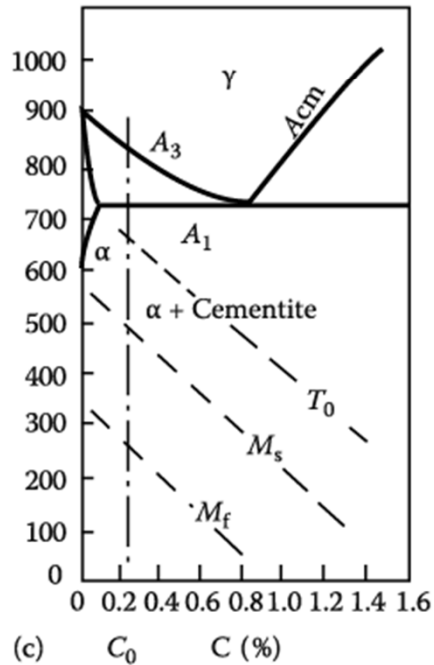


(a) G-T diagram *equilibrium* (b) G-X diagram for C_0 at M_s

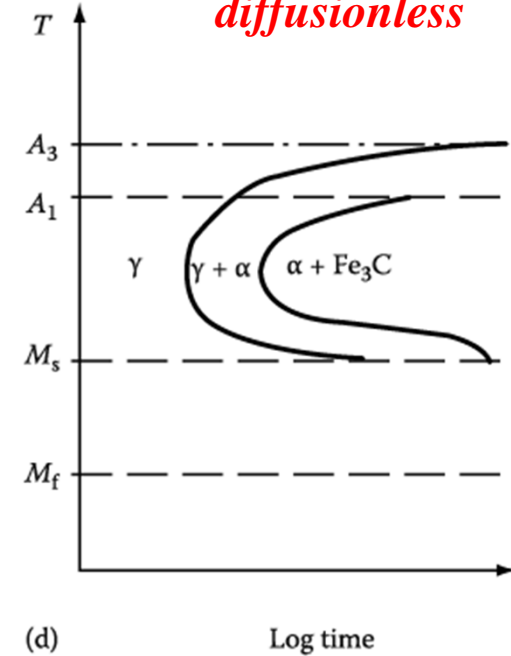
diffusionless

Note that the M_s line is horizontal in the TTT diagram; also, the M_f line.

Some retained austenite can be left even below M_f . In particular, as much as 10%-15% retained austenite is a common feature of especially the higher C content alloys such as those used for ball bearing steels.



(c) Fe-C phase diagram
Variation of $T_0/M_s/M_f$

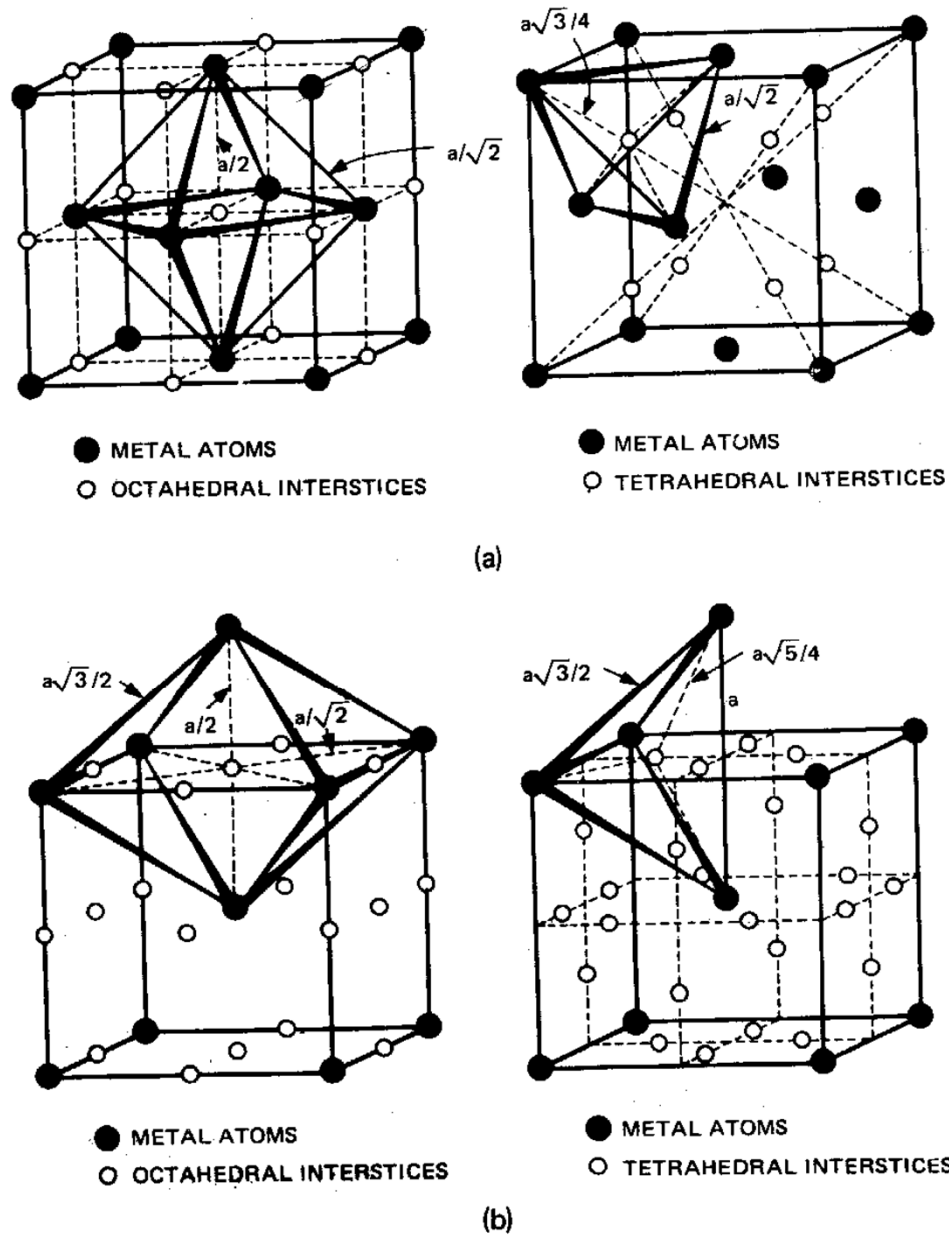


(d) TTT diagram
for alloy C_0 in (c)

Interstitial sites for C in Fe

fcc:
carbon occupies
the **octahedral**
sites

bcc:
carbon occupies
the
octahedral sites



[Leslie]

Figure II-1. Interstitial voids in iron. (a) Interstitial voids in the fcc structure, octahedral (1) and tetrahedral (2). (b) Interstitial voids in the bcc structure; octahedral (1) and tetrahedral (2). (From C.S. Barrett and T.B. Massalski, *Structure of Metals*, 3d ed., copyright 1966, used with the permission of McGraw-Hill Book Co., New York.)

Carbon in BCC ferrite

- One consequence of the occupation of the octahedral site in ferrite is that the carbon atom has only two nearest neighbors.
- Each carbon atom therefore distorts the iron lattice in its vicinity.
- The distortion is a tetragonal distortion.
- If all the carbon atoms occupy the *same type of site* then the entire lattice becomes tetragonal, as in the martensitic structure.
- Switching of the carbon atom between adjacent sites leads to strong internal friction peaks at characteristic temperatures and frequencies.

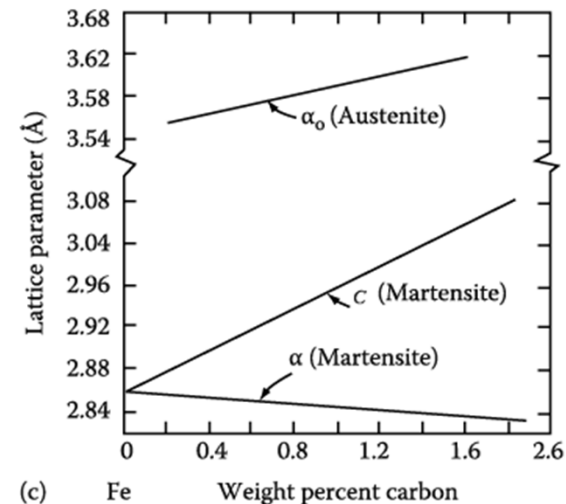
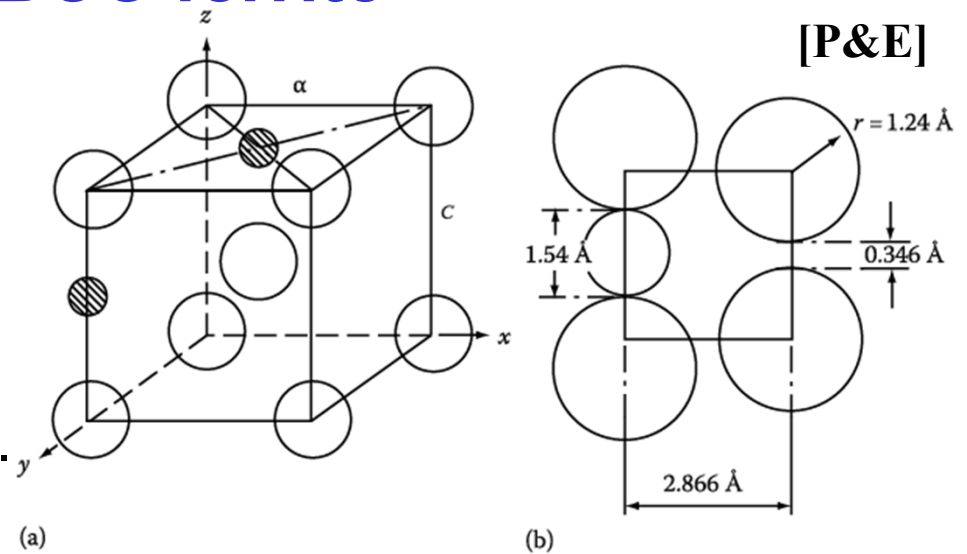
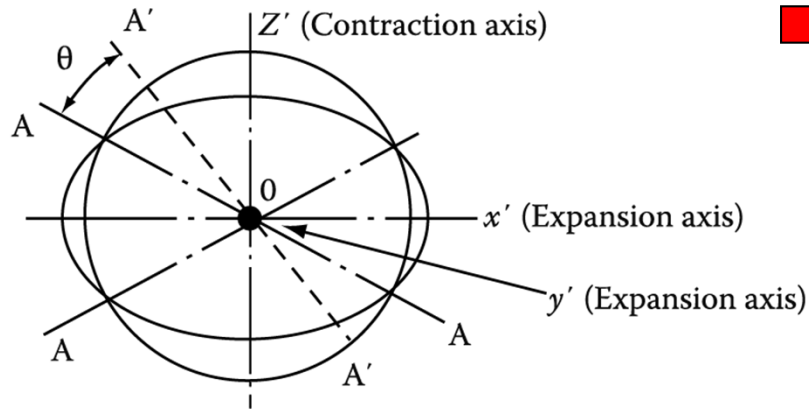
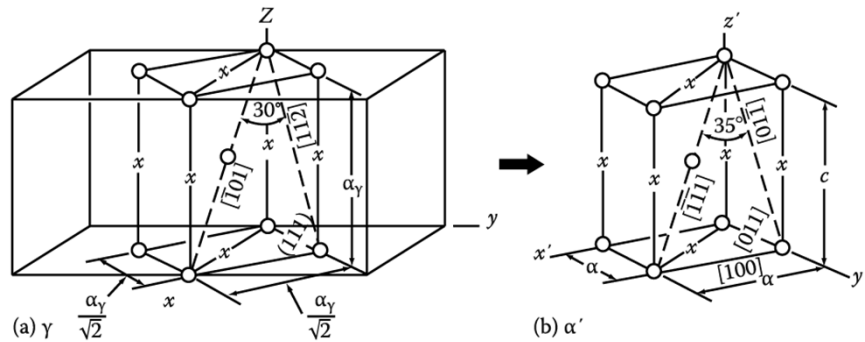


Fig. 6.5 Illustrating (a) possible sites for interstitial atoms in bcc lattice, and (b) the large distortion necessary to accommodate a carbon atom (1.54 \AA diameter) compared with the space available (0.346 \AA). (c) Variation of a and c as a function of carbon content.

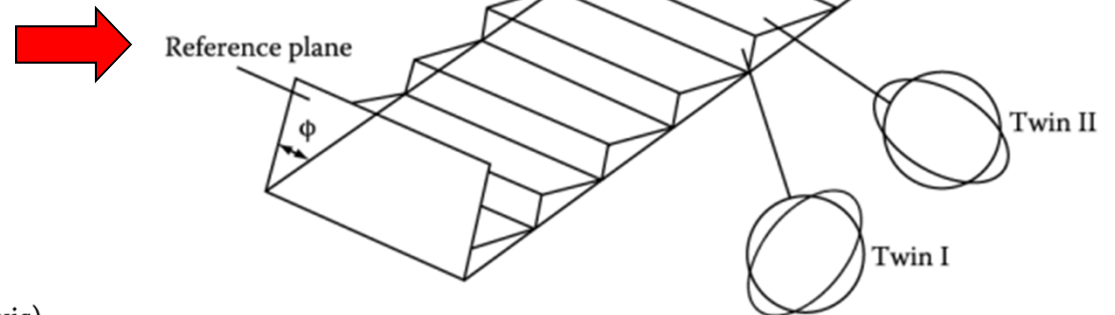
6.2. Martensite crystallography (Orientation btw M & γ)

- $\gamma \rightarrow \alpha'$:
- (1) Habit plane of M: not distorted by transformation
 - (2) A homogeneous shear (s) parallel to the habit plane
 - (3) $\sim 4\%$ expansion_dilatation normal to the habit plain (lens)



Bain Model for martensite

Applying the twinning analogy to the Bain model,



Twins in Martensite

may be self-accommodating and reduce energy by having alternate regions of the austenite undergo the Bain strain along different axes.

6.3.1 Formation of Coherent Nuclei of Martensite (Homogenous nucleation)

for thin ellipsoidal nucleus (radius **a**, semi thickness **c** and volume **V**),

$$\Delta G = A\gamma + V\Delta G_s - V\Delta G_v$$

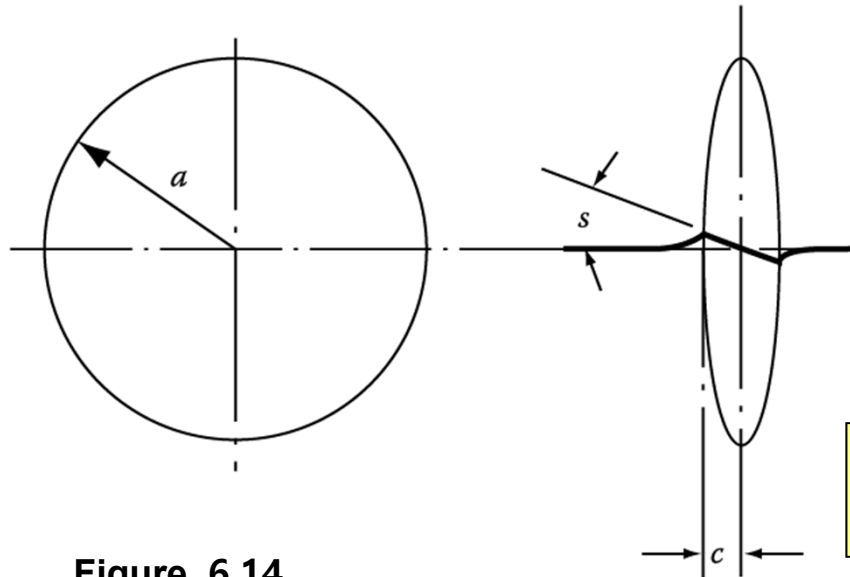


Figure. 6.14
Schematic representation of a M nucleus.

Assumption: 1) Nucleation does not necessarily occur at grain boundaries.
2) Nucleation occurs homogeneously without the aid of any other types of lattice defects.

→ The Nucleus forms by a simple shear, S , parallel to the plane of the disc, and complete coherency is maintained at the interface.

$$\Delta G = 2\pi a^2 \gamma + 2\mu V (s/2)^2 \frac{2(2-\nu)}{8(1-\nu)} \pi c / a - \frac{4}{3} \pi a^2 c \cdot \Delta G_v$$

If $\nu=1/3$,

$$\Delta G = \underbrace{2\pi a^2 \gamma}_{\text{Surface E}} + \underbrace{\frac{16\pi}{3} (s/2)^2 \mu a c^2}_{\text{Elastic E (shear component of strain only)}} - \underbrace{\frac{4\pi}{3} a^2 c}_{\text{Volume E}} \cdot \Delta G_v$$

Eq. (6.7)

6.3.1 Formation of Coherent Nuclei of Martensite

By differentiating Eq. (6.7) with respect to **a** and **c**, respectively

→ **Min. free energy barrier to nucleation: extremely sensitive to “ γ , ΔG_v and s ”**

$$\Delta G^* = \frac{512}{3} \cdot \frac{\gamma^3}{(\Delta G_v)^4} \cdot (s/2)^4 \mu^2 \pi \quad (\text{joules/nucleus})$$

→ **Critical nucleus size (c^* and a^*): highly dependent to “ γ , ΔG_v and s ”**

$$c^* = \frac{2\gamma}{\Delta G_v}$$

$$a^* = \frac{16\gamma\mu(s/2)^2}{(\Delta G_v)^2}$$

Eq. (6.9) & (6.10)

For steel, 1) typically $\Delta G_v = 174 \text{ MJm}^{-3}$, and

2) s (varies according to whether the net shear of a whole plate (e.g. as measured from surface markings) or shear of fully coherent plate (as measured from lattice fringe micrographs)
= 0.2 (macroscopic shear strain in steel)

3) $\gamma = 20 \text{ mJm}^{-2}$ (fully coherent nucleus)

→ **$c^*/a^* \sim 1/40$, $\Delta G^* \sim 20 \text{ eV}$: too high for thermal fluctuation alone to overcome (at 700 K, $kT = 0.06 \text{ eV}$)**

→ **“M nucleation = heterogeneous process” : possibly in dislocation**
(#= 10^5 per 1 mm^2)

6.3.2 Role of Dislocations in Martensite Nucleation

① atomic shuffles within the dislocation core

M transformation induced by half-twinning shear in fcc mater.

- **It is thus seen that some types of M can form directly by the systematic generation and movement of extended dislocations.**

→ M_s temperature : a transition from positive to negative SFE

- **However, 1) this transition type cannot occur in ① high SFE nor in ② thermoelastic martensites → need to consider alternative way in which dislocations can nucleate martensite other than by changes at their cores.**

2) this transition is also difficult to understand ③ twinned martensite, merely on the basis of dislocation core changes.

6.3.3 ② Dislocation strain energy assisted transformation : help of the elastic strain field of a dislocation for M nucleation

- Assumption: coherent nuclei are generated by a pure Bain strain, as in the classical theories of nucleation

The strain field associated with a dislocation can in certain cases provide a favorable interaction with the strain field of the martensite nucleus, such that one of the components of the Bain strain is neutralized thereby reducing the total energy of nucleation.

→ the dilatation associated with the extra half plane of the dislocation contributes to the Bain strain.

→ Alternatively, the shear component of the dislocation could be utilized for M transformation.

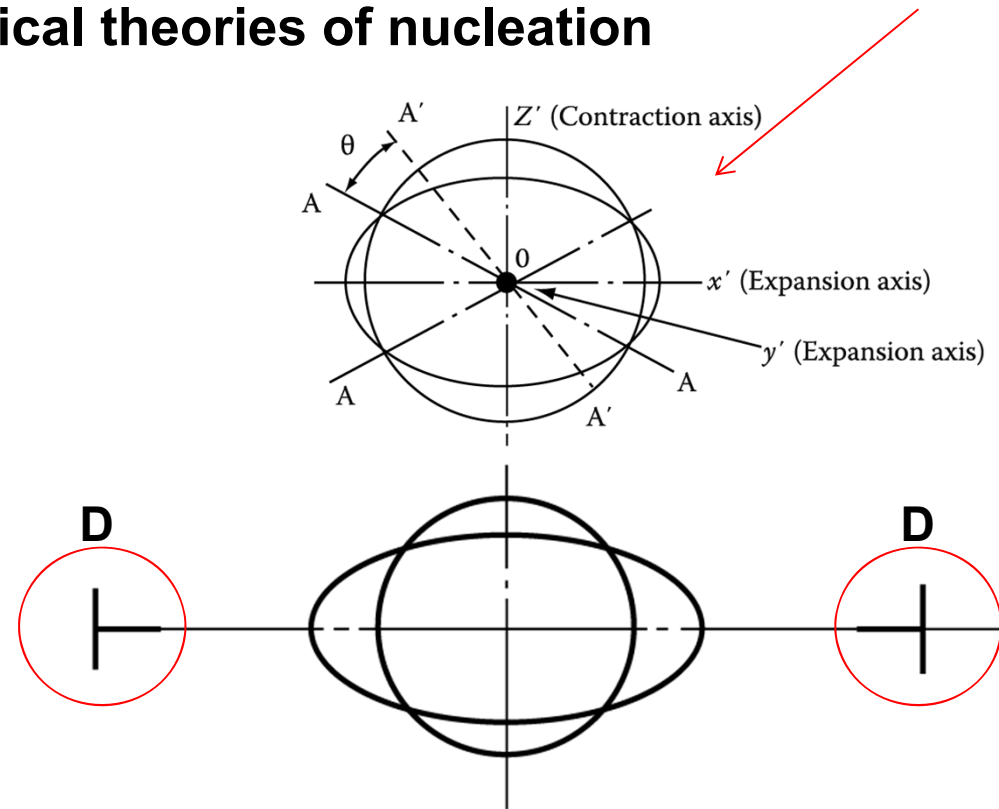


Figure. 6.19 Illustrating how one of the strain components of the Bain deformation may be compensated for by the strain field of a dislocation which in this case is tending to push atom planes together.

6.3.3 ② Dislocation strain energy assisted transformation : help of the elastic strain field of a dislocation for M nucleation

$$\Delta G = A\gamma + V\Delta G_s - V\Delta G_v - \Delta G_d$$

Creation of nucleus~destruction of a defect(- ΔG_d)

→ Dislocation interaction energy which reduces the nucleation energy barrier

$$\Delta G_d = 2\mu s\pi \cdot ac \cdot \bar{b}$$

where \bar{b} = Burgers vector of the dislocation,
s = shear strain of the nucleus

$$\Delta G = 2\pi a^2\gamma + \frac{16\pi}{3}(s/2)^2\mu ac^2 - \frac{4\pi}{3}a^2c \cdot \Delta G_v - 2\mu s\pi ac \cdot \bar{b} \quad \text{Eq. (6.16)}$$

전단변형과 bain 변형 포함

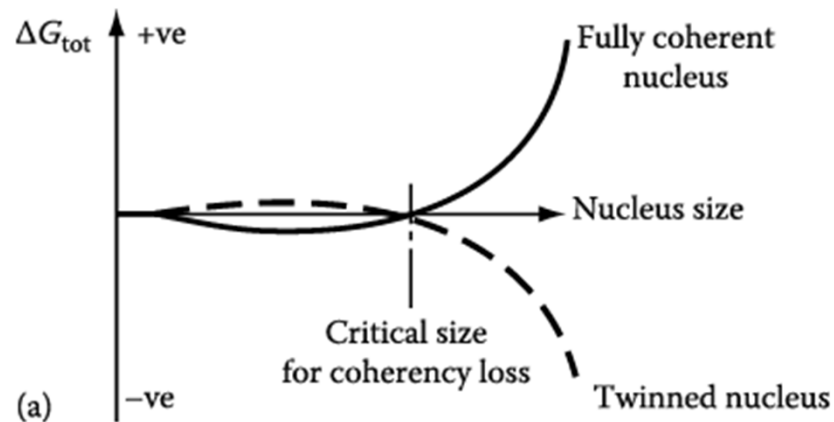


Figure. 6.20 (a) schematic diagram based on Eq. 6.16, illustrating the need for the nucleus to twin if it is to grow beyond a certain critical size.

- Total energy of martensite nucleus:
as a function of 1) diameter and thickness (a, c)
(whether it is twinned or not (this affect "s"))
2) Degree of assistance from the strain field of a dislocation (or group of dislocations)

e.g. A fully coherent nucleus from partial interaction with the strain field of a dislocation ~ 20 nm dia. & 2-3 atoms in thickness → further growth need to twin and slip formation

6.3.3 ② Dislocation strain energy assisted transformation

: help of the elastic strain field of a dislocation for M nucleation

Burst phenomenon

: autocatalytic process of rapid, successive M plate formation occurs over a small temperature range , e.g. Fe-Ni alloys

(Large elastic stresses set up ahead of a growing M plate → Elastic strain field of the M plate act as the interaction term of elastic strain field of dislocation in Eq. (6.16) → reduces the M nucleation energy barrier)

In summary,

- we have not dealt with all the theories of martensite nucleation in this section as recorded in the literature, or even with all alloys exhibiting martensitic transformations.
- Instead we have attempted to illustrate some of the difficulties associated with explaining a complex event which occurs at such great speeds as to exclude experimental observation.
- A general, all embracing theory of martensite nucleation has still evaded us, and may not even be feasible.

6.4 Martensite Growth

- Once the nucleation barrier has been **overcome**, the chemical volume free energy term (ΔG_v) is so large that **the martensite plate grows rapidly until it hits a barrier such as another plate or a high angle grain boundary.**
- High speed of M growth \rightarrow interface btw austenite and M must be a **glissile semi-coherent boundary** consisting of a set of parallel dislocations or twins with Burgers vector common to both phases, i.e. transformation dislocations \rightarrow dislocation motion brings about required **lattice invariant shear transformation** (may or may not generate an irrational habit plane)
- **Increased alloying lowers the Ms temperature** and that it is the temp. of transformation **that dictates the mode of lattice invariant shear.**
 - \rightarrow **Slip-twinning transition in a crystal at low temperatures:** increased difficulty of nucleating whole dislocations needed for slip, but not so temp dependence (as the Peierls stress for a perfect dislocation) of critical stress needed for the nucleation of a partial twinning dislocation & chemical energy for transformation \sim independent of M_s temp.
 - \rightarrow **When Ms temperature is lowered, the mechanism of M transformation chosen is governed** ① by the growth process having least energy.
Other factor affecting mode of growth = ② how the nucleus forms

* Two main cases of rational (lath) and irrational (plate) M growth in steel

6.4.1 Growth of Lath Martensite

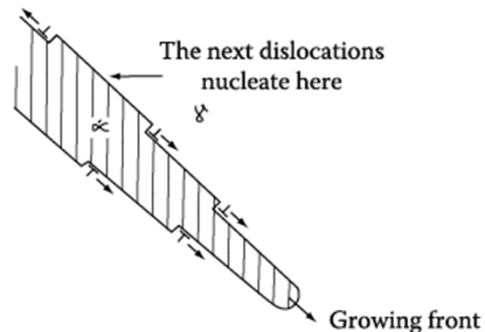


- Morphology of a lath with dimensions $a \gg b \gg c$ growing on a $\{111\}\gamma$ plane → **thickening mechanism involving the nucleation and glide of transformation dislocations** moving on discrete ledges behind the growing front, e.g. NiTi M and steel M
- Due to the **large misfit** between the bct and fcc, lattices dislocations could be **self-nucleated at the lath interface**. → the stress at the interface exceeds the theoretical strength of the material.

- **Eshelby's approach: for thin ellipsoidal plate ($a \gg c$)**
Maximum shear stress at the interface btw M and γ due to shear transformation

$$\sigma \cong 2\mu s c / a \quad \mu = \text{shear modulus of } \gamma$$

- ~Sensitive to ① shape (c/a) and ② angle of shear (s)
- : Of course in practice it is very difficult to define the **morphology of M** in such simple c/a terms, but this gives us at least a qualitative idea of what may be involved in the growth kinetics of M.



(b)

Figure. 6.20 (b) Lattice image of the tip of a martensite plate in a Ti-Ni alloy. The first interfacial dislocation behind the growing front is indicated.

6.4.1 Growth of Lath Martensite

- **Lath M growth by shear loop nucleation** ($\because \sigma/\mu > \text{threshold stress}$) :
by nucleating dislocations at the highly strained interface of the laths, the misfit energy reduced and the lath M can continue to grow into γ

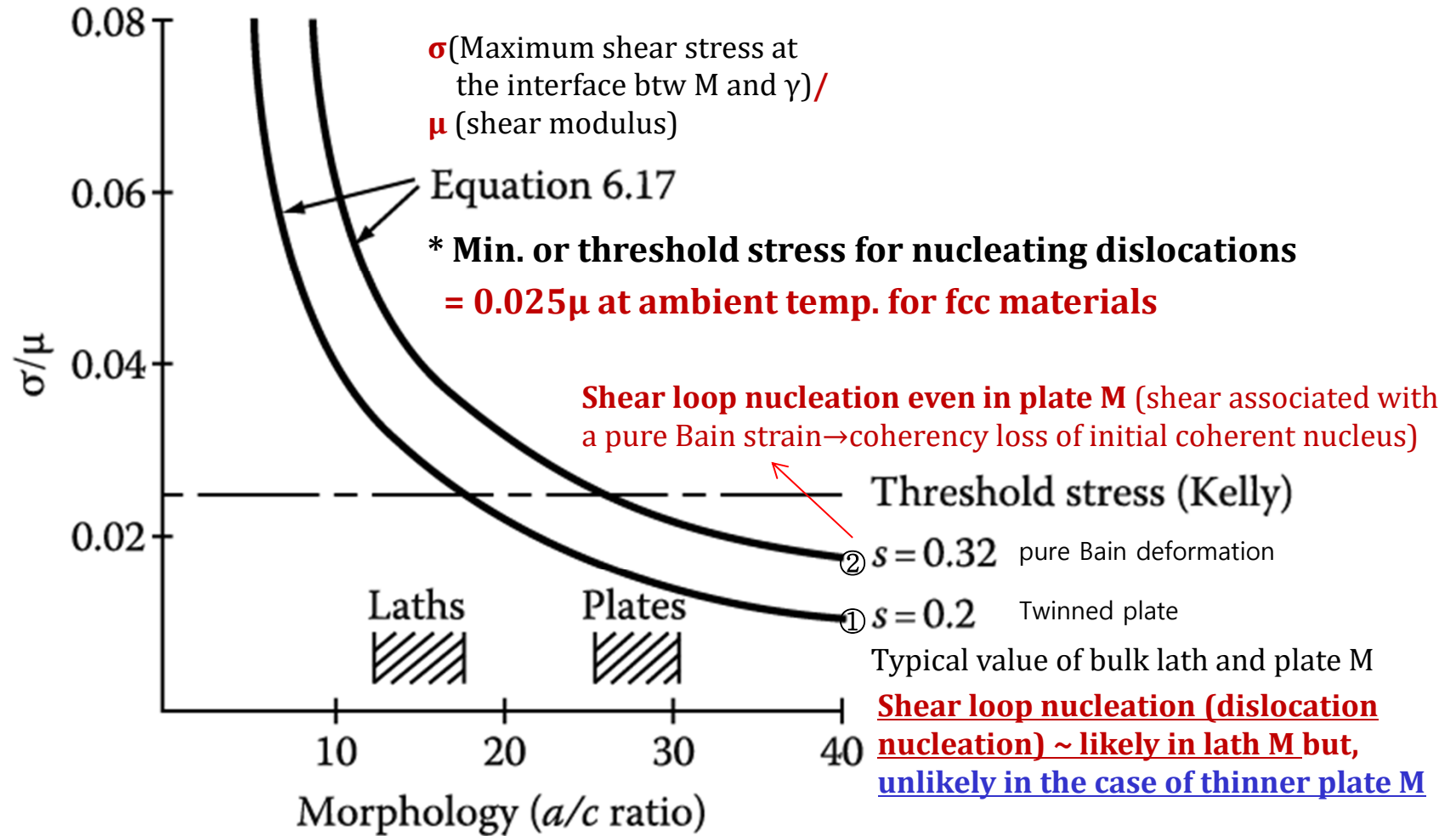
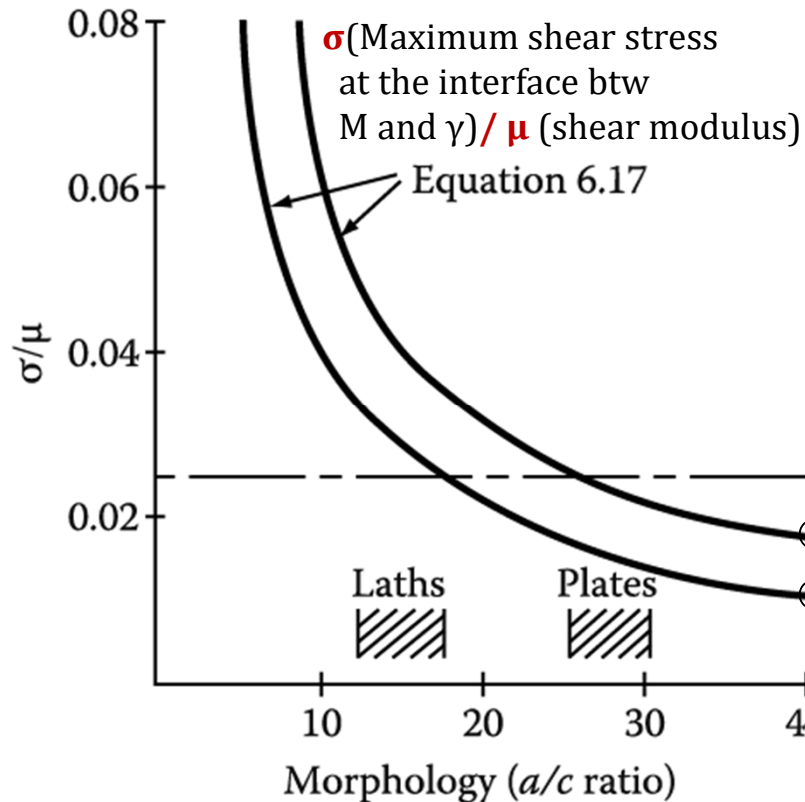


Figure. 6.21 Eq. 6.17 plotted for two values of shear corresponding to a pure Bain deformation ($s=0.32$) and a twinned plate ($s=0.2$)

6.4.1 Growth of Lath Martensite

- **Lath M growth by shear loop nucleation** ($\because \sigma/\mu > \text{threshold stress}$) : by nucleating dislocations at the highly strained interface of the laths, the misfit energy reduced and the lath M can continue to grow into γ



- By internal friction measurements,

Density of carbon in lath M : cell walls > within cell suggesting that **limited diffusion of carbon** takes place following or during the transformation

- **M transformation (at least at higher Ms like lath M)** → produce adiabatic heating which may affect ① diffusion of carbon and ② dislocation recovery (by dislocation climb and cell formation). ~ **a certain relationship between lower bainite and M**

Threshold stress (Kelly)

- ② $s = 0.32$ Shear loop nucleation lath M and plate M
- ① $s = 0.2$ Shear loop nucleation in lath M

- **High growth speed of lath M**

→ interface of predominantly screw dislocation

- **Volume of retained γ ~relatively small in lath M** (important to the mechanical properties of low-carbon steel) due to **sideways growth of screw dislocation not too difficult**

* **Figure. 6.21** Eq. 6.17 plotted for two values of shear corresponding to a pure Bain deformation ($s=0.32$) and a twinned plate ($s=0.2$)

6.4.2 Plate Martensite

- In medium and high carbon steels, or high nickel
Morphology: Lath M → Plate M (lower M_s temp. and more retained γ)
much thinner than lath M or bainite

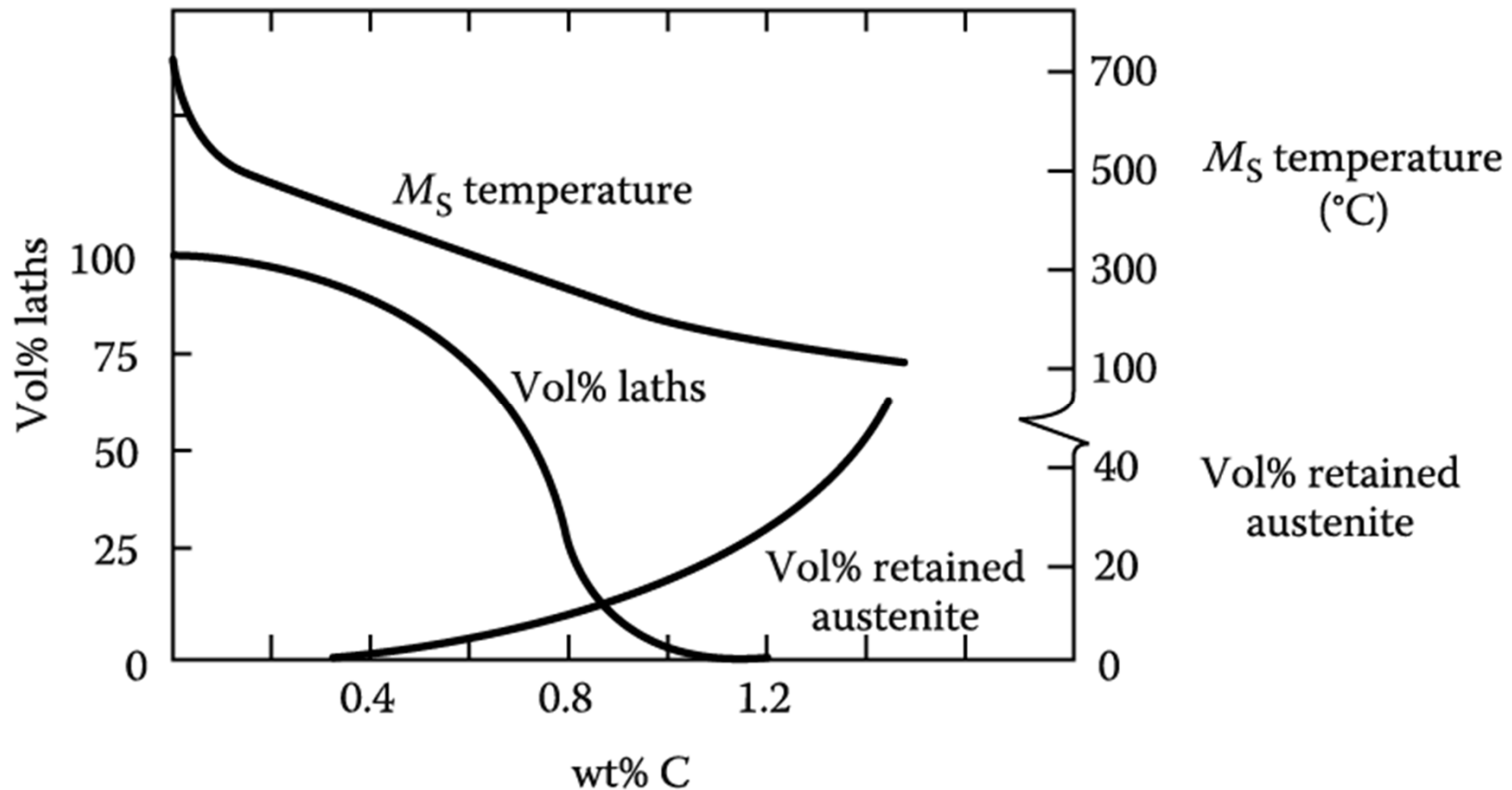


Figure. 6.22 Approximate relative percentages of lath martensite and retained austenite as function of carbon content in steels.

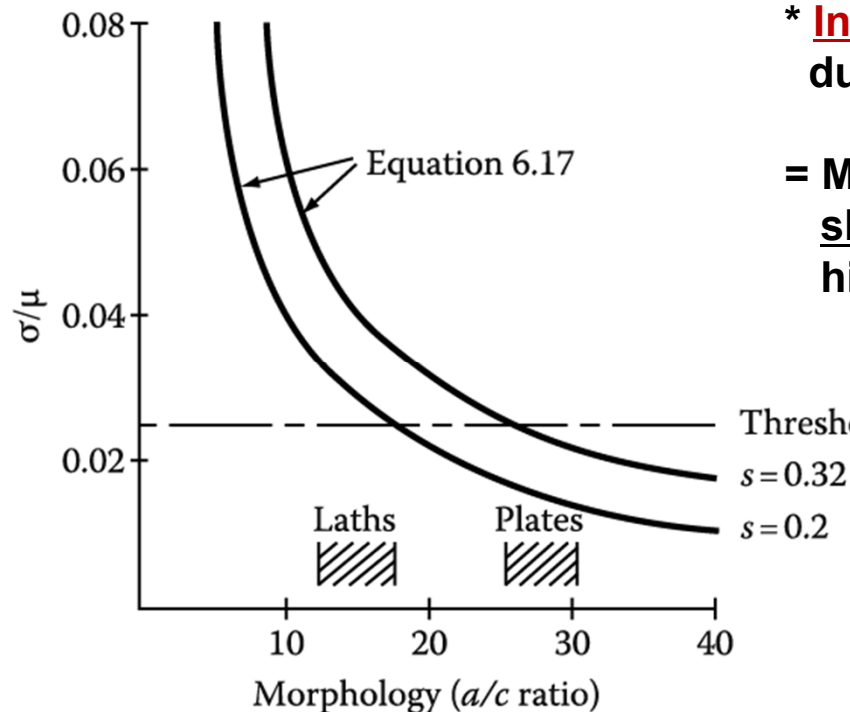
6.4.2 Plate Martensite

- In medium and high carbon steels, or high nickel
Morphology: Lath M \rightarrow Plate M (\because lower M_s temp. and more retained γ)
much thinner than lath M or bainite

- Transition from plates from growing on $\{225\}_\gamma$ planes to $\{259\}_\gamma$ planes with increasing alloy contents (habit 면 변화)

In lower carbon or nickel, $\{225\}_\gamma$ M = plates with a central twinned 'midrib', the outer (dislocation) regions of the plate being free of twins

In high carbon and nickel, $\{259\}_\gamma$ M = completely twined & less scattered habit plane



* In Midrib M, transition from twinning \rightarrow dislocations due to a change in growth rate after the midrib forms

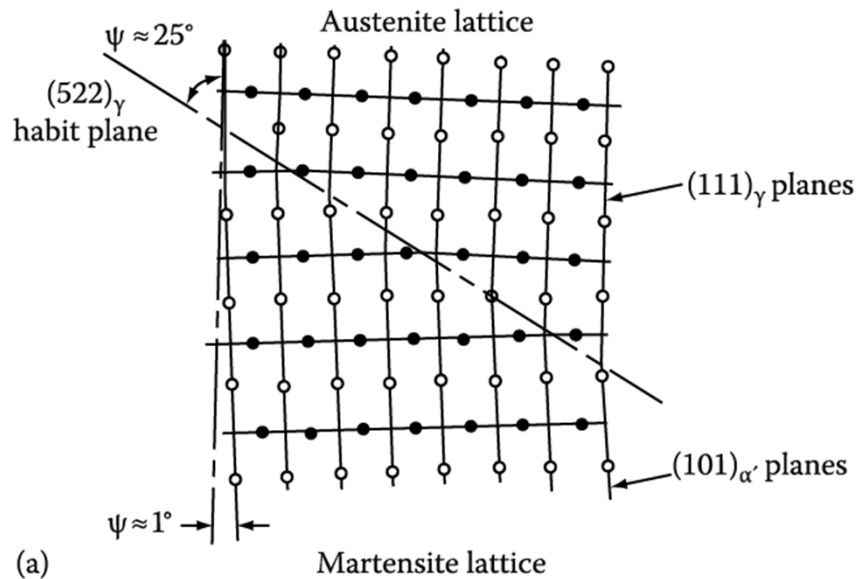
= M formed at higher temp. or slower rates grows by a slip mechanism, while M formed at lower temp and higher growth rates grows by a twinning mode.

- 1) $s=2$, problem in nucleating whole dislocations in the case of growing plate M, but **partial twinning dislocations evidently can nucleate**.
 \rightarrow Once nucleated, twinned M grows extremely rapidly, but the mechanism is unclear.

6.4.2 Plate Martensite

빠른 M growth 설명: 정상탄성파가 쌍정전위를 생성시키고 이로 인해 판상의 빠른 성장

* Dislocation generated {225}γ M (Frank)



Close-packed plane

: slight misfit along the $[01\bar{1}]_\gamma$ & $[11\bar{1}]_{\alpha'}$

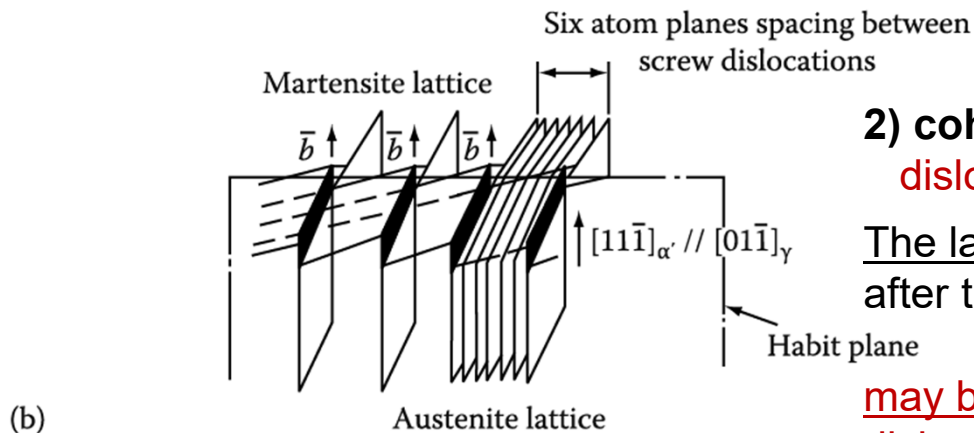
= M lattice parameter is ~2% less than that of γ

→ Insertion of an array of screw dislocations

with a spacing of six atom planes in the interface

* In terms of the min. shear stress criterion (Fig. 6.21), when the midrib reaches some critical a/c ratio **further expansion and thickening of a {225}γ twinned midrib by a Frank dislocation interface** could occur.

→ “No detailed explanation”



2) coherent nucleus with s=0.32: possible for dislocation nucleation to occur to relieve coherency.

The larger amount of chemical free energy, available after the critical size for growth has been exceeded,

may be sufficient to homogeneously nucleate dislocations particularly in the presence of the large strain energy of the rapidly growing plate.

Figure. 6.23 Model for the {225}γ habit austenite-martensite interface in steel.

- * Other factors for affecting the growth of M: ③ phenomenon of stabilization, ④ external stresses, and ⑤ grain size

6.4.3 Stabilization

- * In intermittent cooling between Ms and Mf, transformation does not immediately continue, and the total amount of transformed M is less than obtained by continuous cooling throughout the transformation range.

6.4.4 Effect of External Stresses

$$\Delta G = -V\Delta G_V + A\gamma + V\Delta G_S - ES$$

- * In view of the dependence of M growth on dislocation nucleation, it is expected that an externally applied stress (ES) will aid the generation of dislocations and hence the growth of M.

- a) ES lowers the nucleation barrier for coherency loss of second phase precipitates.
- b) ES aid M nucleation if the ① external elastic strain components contribute to the Bain strain.
→ Ms temperature can be raised. But, if plastic deformation occurs, there is an upper limiting value of Ms defined as “the Md temperature”.
- c) ② Under hydrostatic compression, Ms temperature can be suppressed to lower temp.
(P ↑ → stabilizes the phase with the smaller atomic volume (close-packed austenite) → lowering the driving force ΔG_V for the transformation to M)
- d) ③ large magnetic field can raise the Ms temperature on the grounds that it favors the formation of the ferromagnetic phase.
- e) Plastic deformation of samples can aid both nucleation and growth of M, but too much plastic deformation may in some cases suppress the transformation (nucleation ↑ & nuclei growth ↓).
* **Ausforming process** : plastically deforming the austenite prior to transformation → number of nucleation sites and hence refining M plate size → High strength (fine M plate size + solution hardening (due to carbon) and dislocation hardening)

- * Other factors for affecting the growth of M: ③ phenomenon of stabilization, ④ external stresses, and ⑤ grain size

6.4.5 Role of Grain Size

- * Martensite growth ~ maintaining a certain coherency with the surrounding austenite
 - high-angle grain boundary is an effective barrier to plate growth.
 - While grain size does not affect the number of M nuclei in a given volume, the **1) final M plate size** is a function of the grain size.
- * **2) Degree of residual stress** after transformation is completed.
 - In large grain sized materials: dilatation strain associated with the transformation
 - Large residual stresses to built up btw adjacent grains
 - **GB rupture (quench cracking)** and substantially increase of dislocation density in M
 - In fine grain-sized metals: dilatation strain associated with the transformation
 - more self-accommodating & smaller M plate size
 - **stronger & tougher material**
- * In summary, theories of M nucleation and growth are far from developed to a state where they can be used in any practical way – such as helping to control the fine structure of the finished product. It does appear that nucleation is closely associated with the presence of dislocations (dislocation density) and the process of ausforming (deforming the austenite prior to transformation) could possibly be influenced by this feature if we know more of the mechanism of nucleation. However, growth mechanisms, particularly by twining, are still far from clarified.

6.5, 6.6 & 6.7 Skip

**IH: Summarize the pre-martensite phenomena and
the tempering behavior of Ferrous martensite.
(until 20 th December before final exam)**

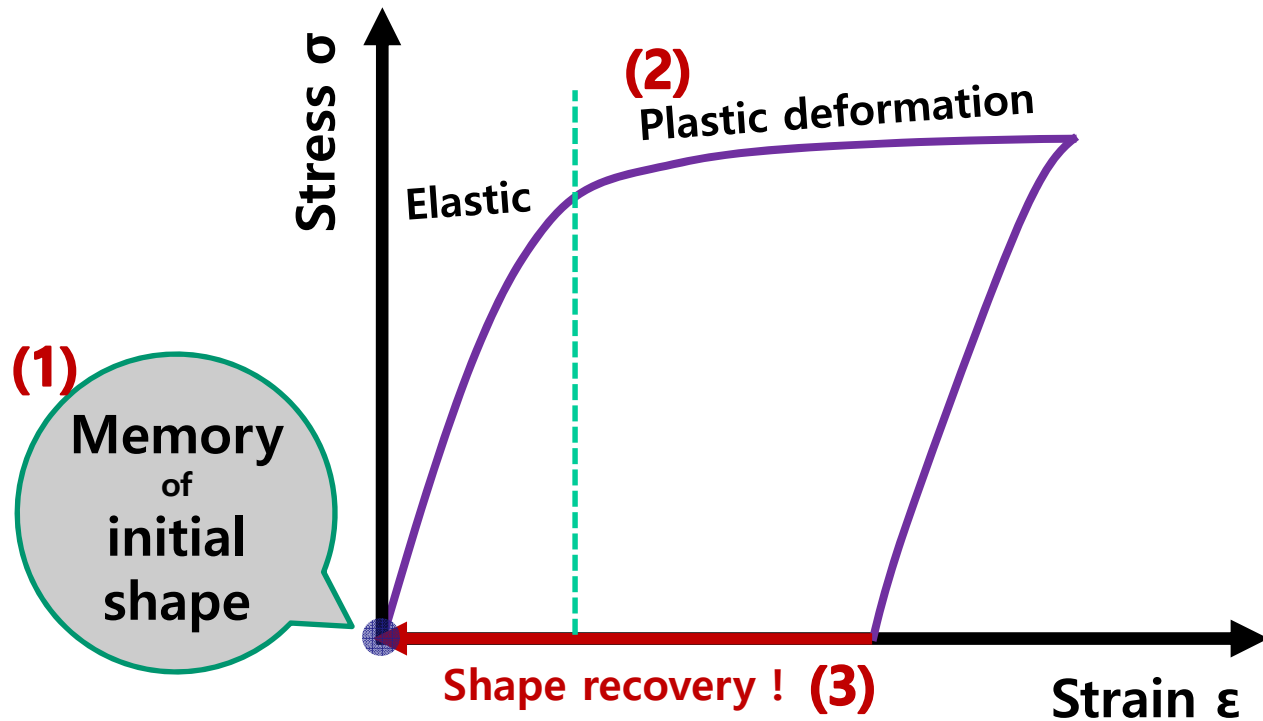
Representative Diffusionless Transformation

Martensitic transformation in Ni-Ti alloy ;
55~55.5 wt%Ni - 44.5~45 wt%Ti (“Nitinol”)

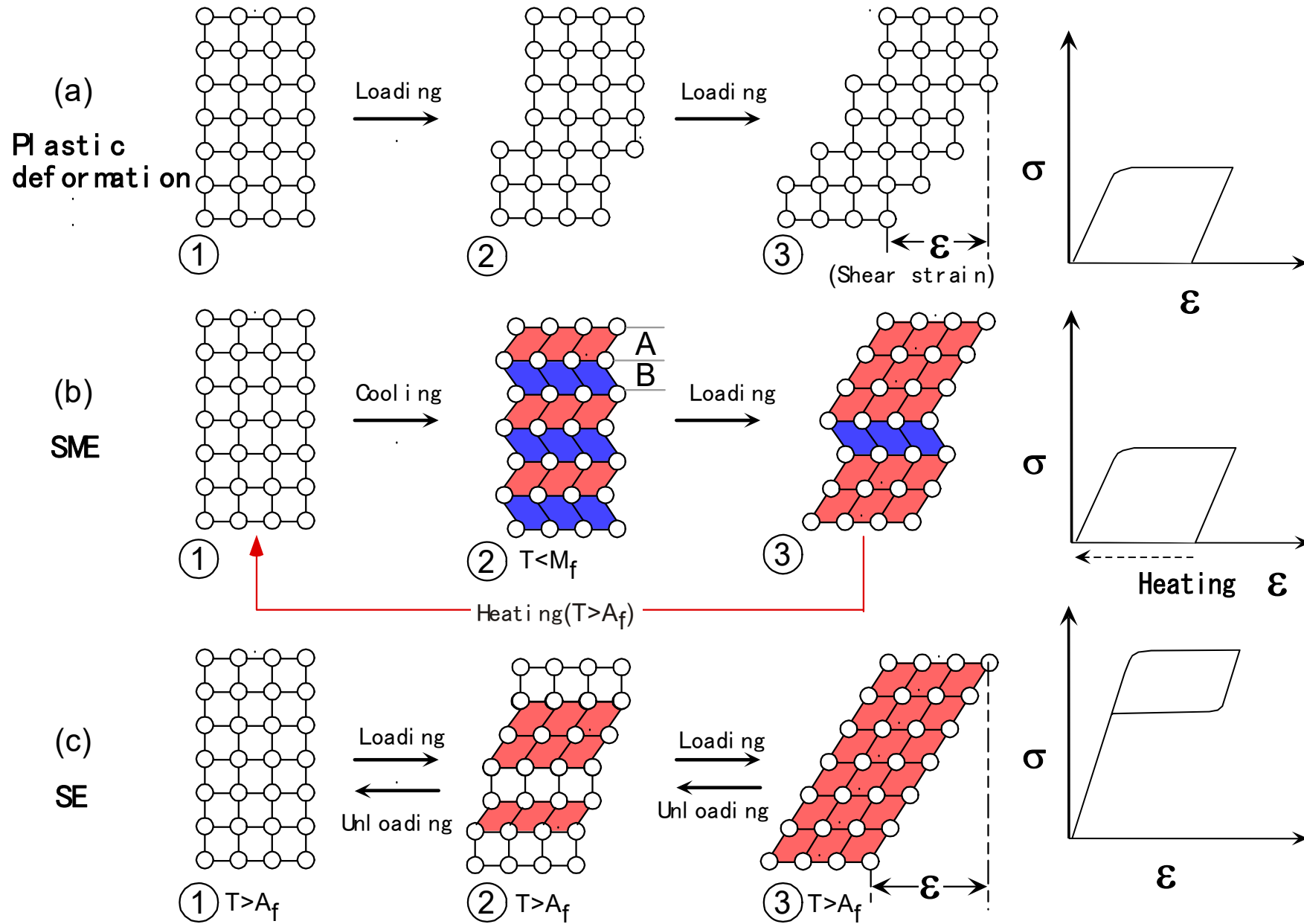


Ex) Shape memory alloy

Introduction - Shape-Memory Effect



	Elastic Deformation	Plastic Deformation	Transformation Deformation
Ceramics	○	×	×
Conventional Metals, Alloys & Plastics	○	○	×
Shape Memory Alloys	○	○	○
	<u>Recoverable</u> Small Deformation ↓ Elasticity	Permanent <u>Large Deformation</u> ↓ Plasticity	<u>Recoverable</u> Large Deformation ↓ Shape Memory Effect Superelasticity (Pseudoelasticity)



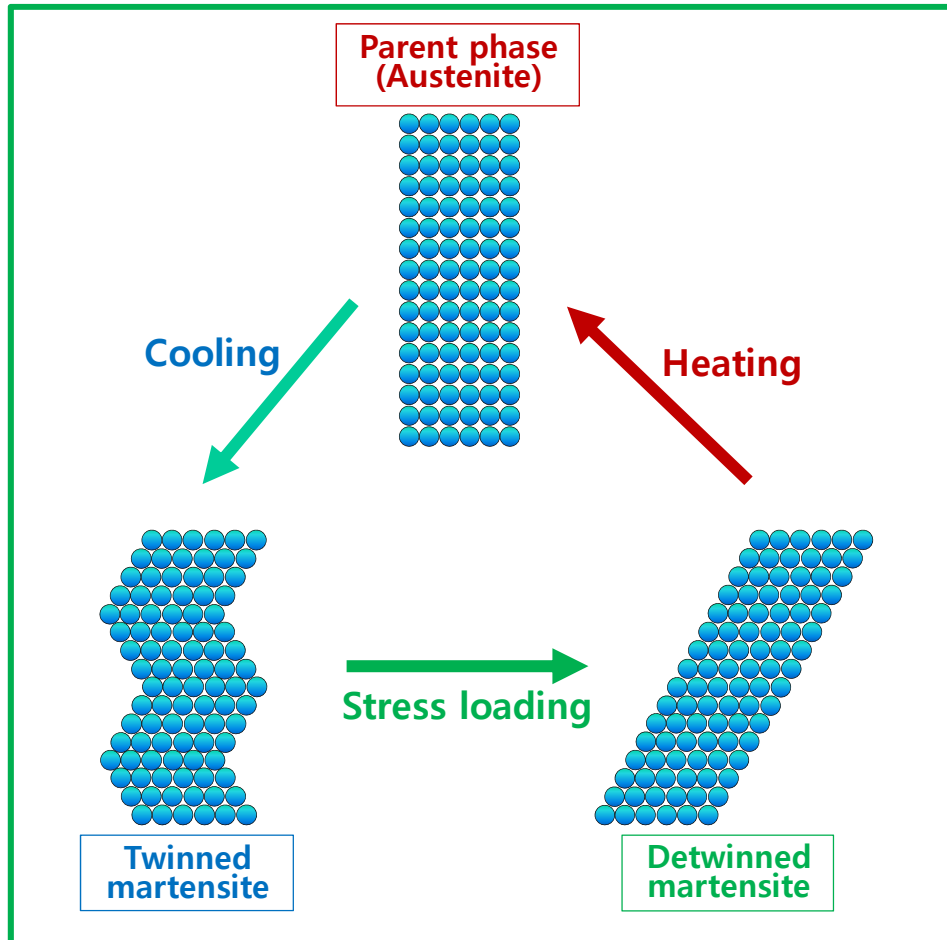
Principles

How can shape memory effect occur?

Principles

How can shape memory effect occur?

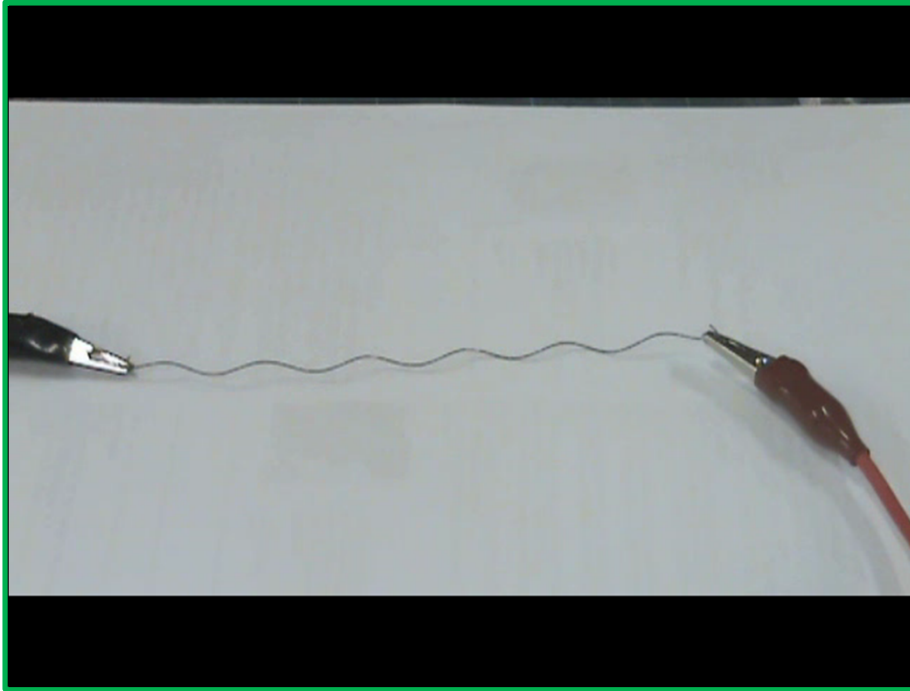
Principles- shape memory process



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 martensite 에서 다시 Austenite로 변태
 → 기억된 형상으로 회복

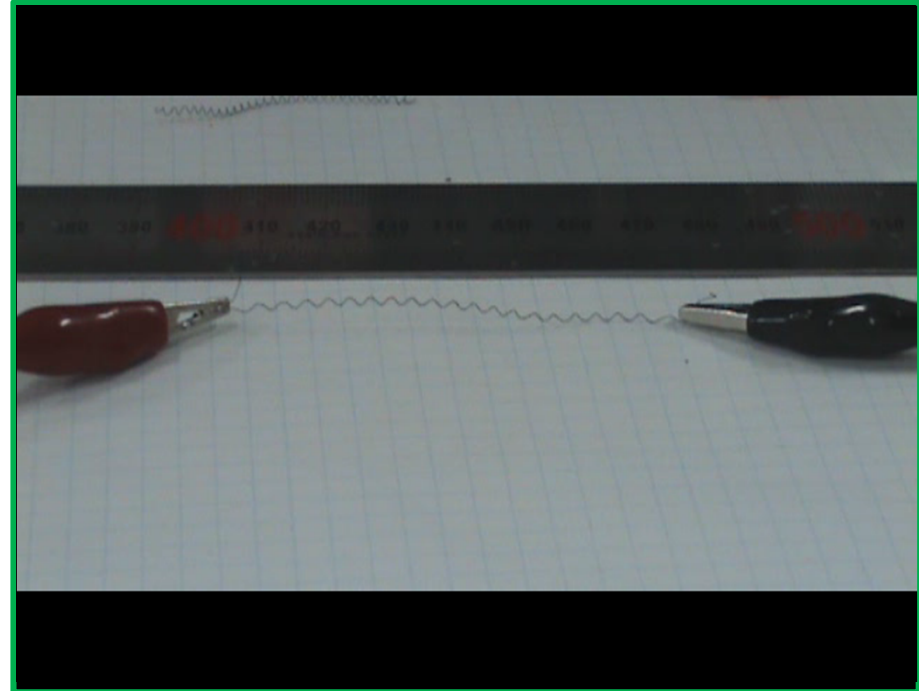
* One-way / Two-way shape memory effect

▼ One-way SME



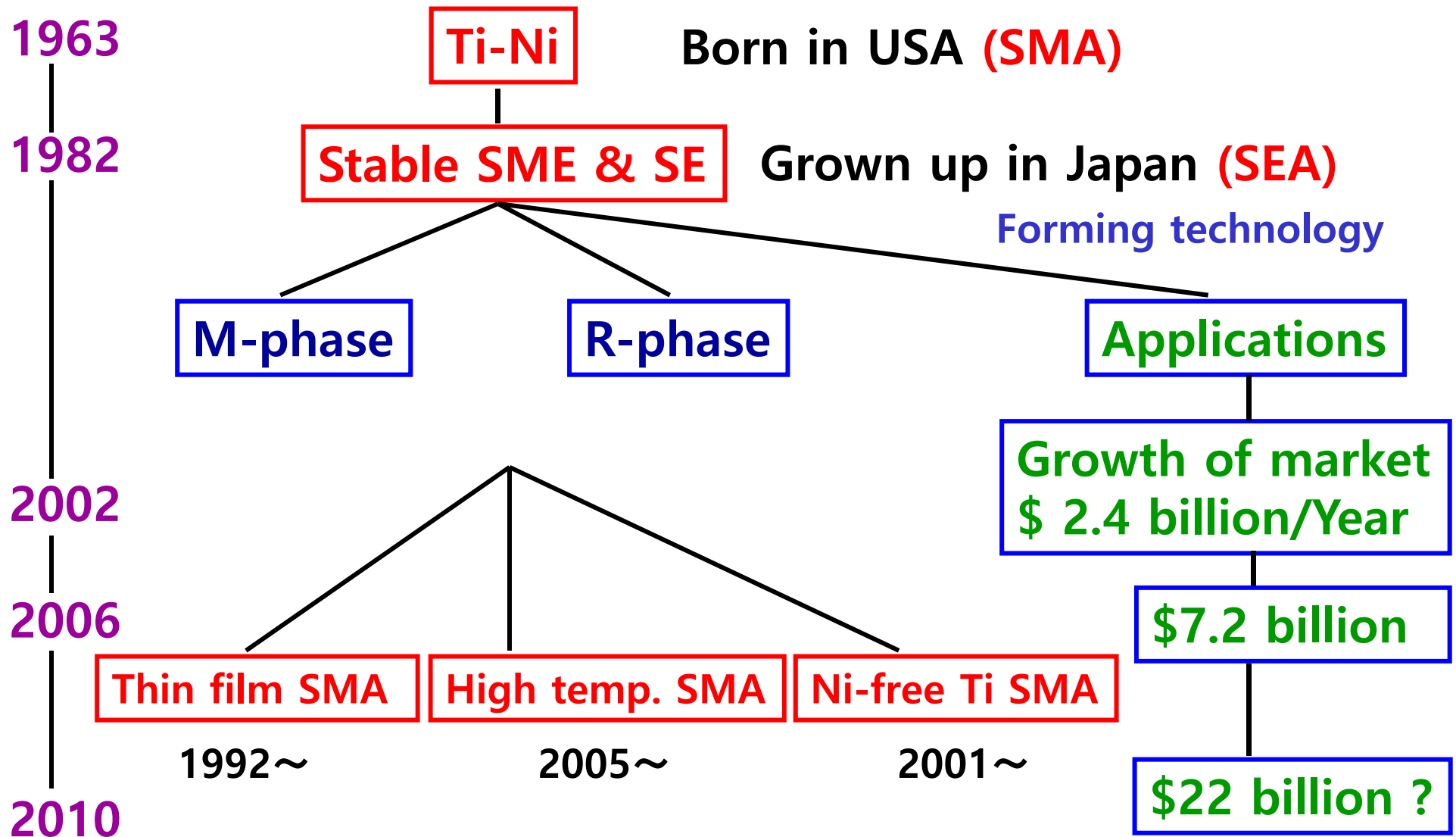
- ↳ A_f 이상의 고온 형상만을 기억
 - 저온($< M_f$)에서 소성변형 후 A_f 이상의 고온으로 가열
 - 기억된 고온 형상으로 회복

▼ Two-way SME



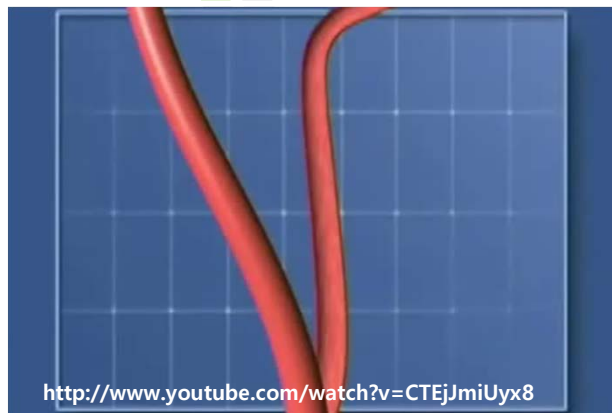
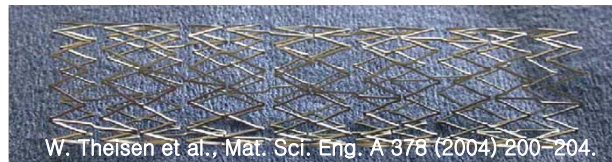
- ↳ 고온($> A_f$) 형상과 저온($< M_f$) 형상을 모두 기억
 - 반복적인 변형으로 인한 형상기억합금 내 전위 밀도의 상승 & 특정방향 응력장의 형성
 - 저온에서 반복소성변형 방향으로 회복

Summary



* Application of SMAs

▼ 산업 부문: 부품소재 (파이프 이음, 스위치소자나 온도제어용 장치 등)



▲ 생체의료 부문: 첨단의료재료
(stent, 치열교정용 강선 등)



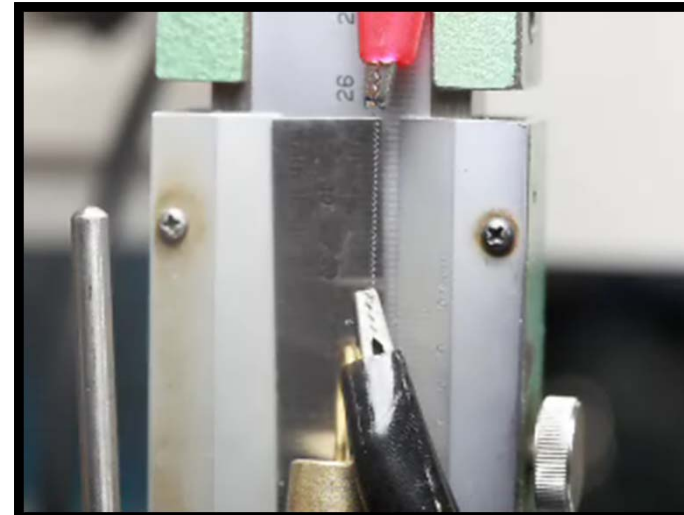
▲ 심해저/우주항공 부문: 극지재료
(잠수함, 태양전지판 등)

* SMA Actuator

▶ 액츄에이터(Actuator) : 전기 에너지, 열에너지 등의 에너지를 운동에너지로 전환하여 기계장치를 움직이도록 하는 구동소자

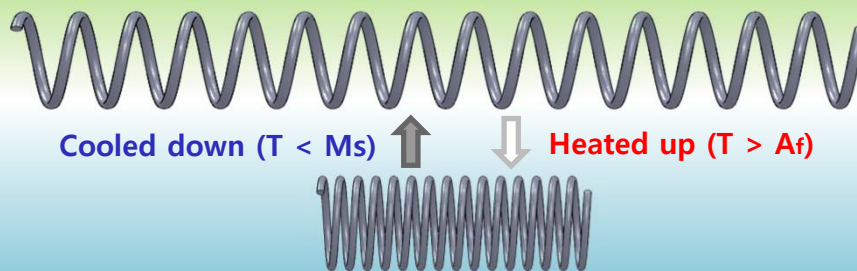


▲ 기존의 매크로 스케일 액츄에이터 (모터-기어 방식)



▲ SMA 스프링 액츄에이터

SMA Spring Actuator



재료의 수축과 신장을 통하여 기계적인 동작을 가능하게 함.

1. 단위 체적당 출력이 높음
2. 모터 구동에 비해 매우 단순한 구조
3. 온도에 의한 제어가 용이
4. 소형화가 쉬움.



자가 치유가 가능한 금속

Self-healing Metallic Materials

Materials design for reuse

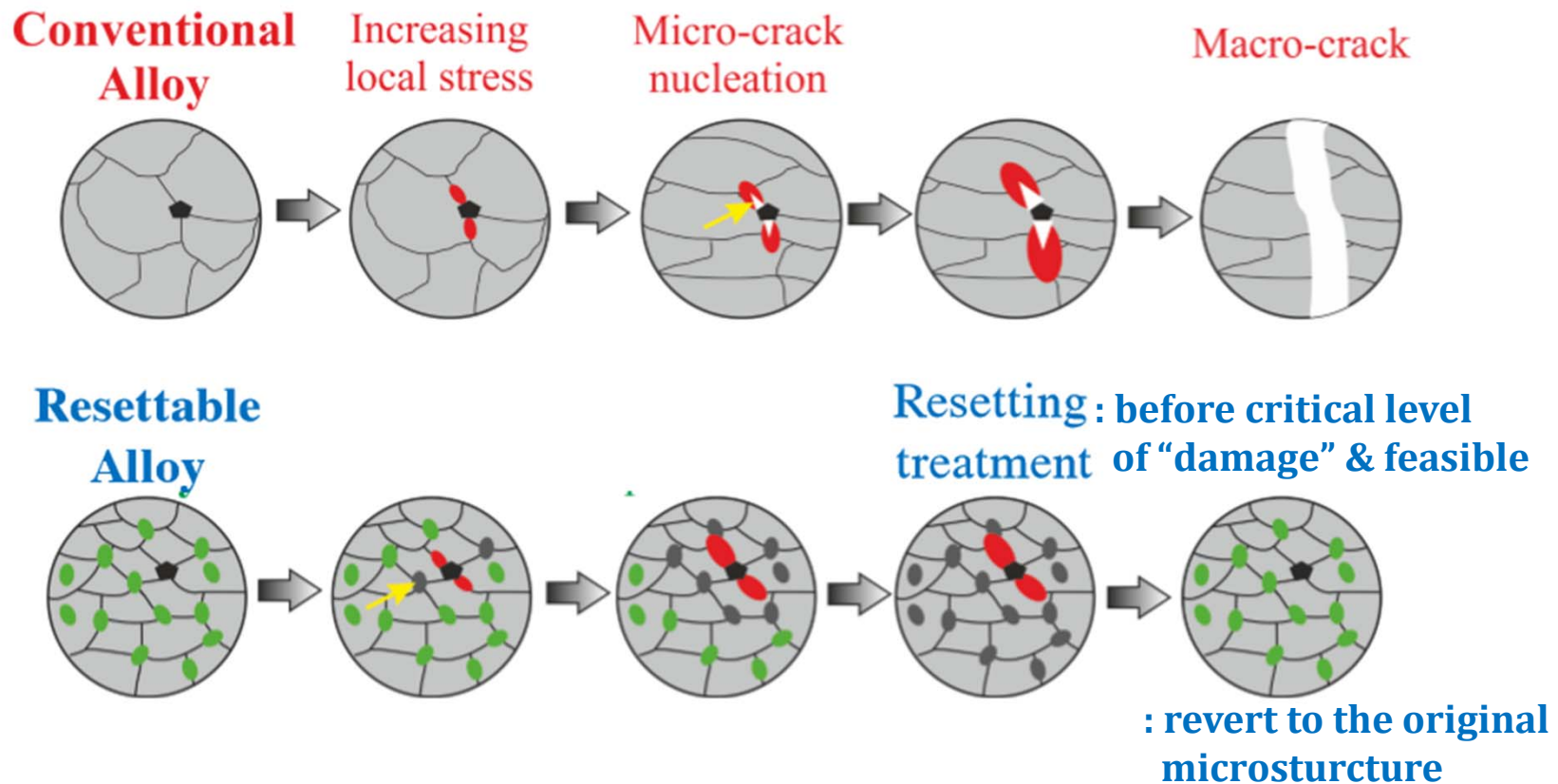
Damage process is incremental, and often local → repair opportunity

Two damage repair options possible:

- The metal autonomously repair damage → *Self-healing*
- Damage is repaired by an external treatment → *Resetting*

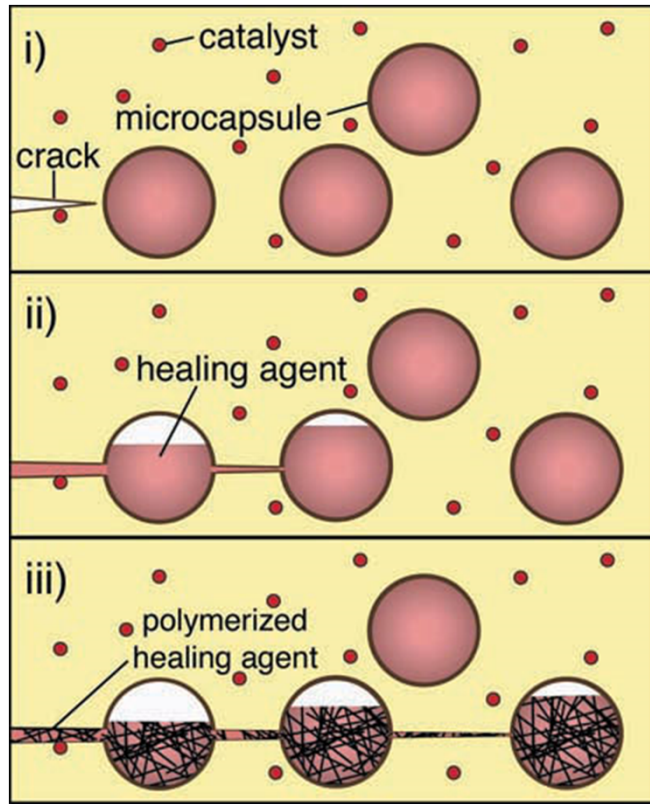
Self-healing metals vs Resettable alloys

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

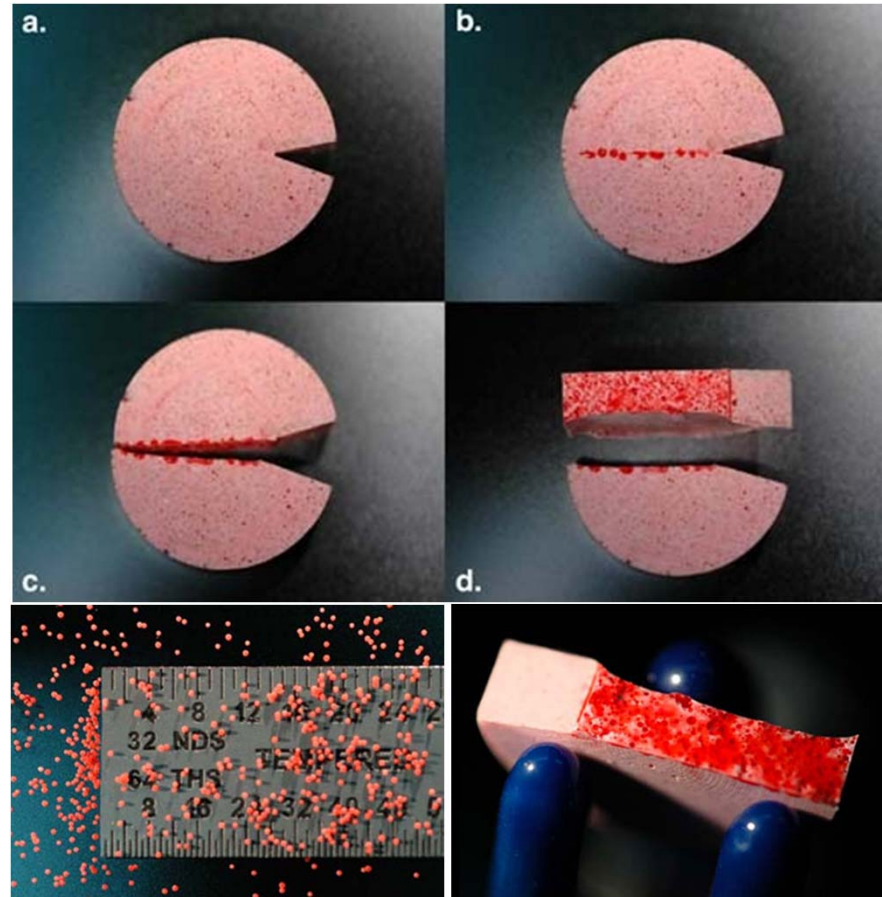


Different failure mechanisms require different resetting strategies

Self-healing : Microencapsulation approaches



Healing agent + catalyst

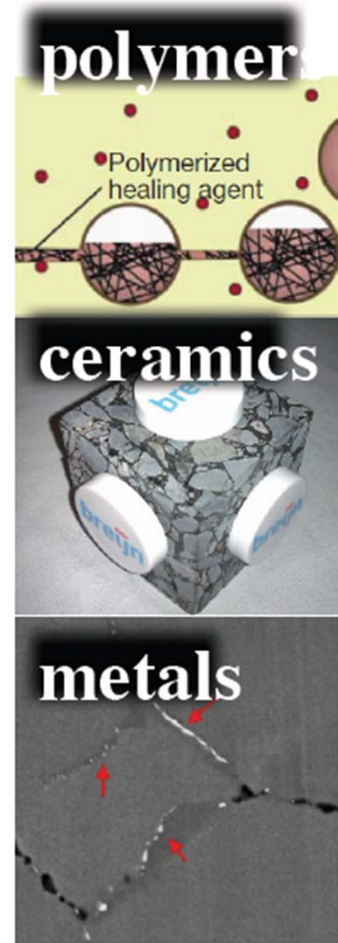
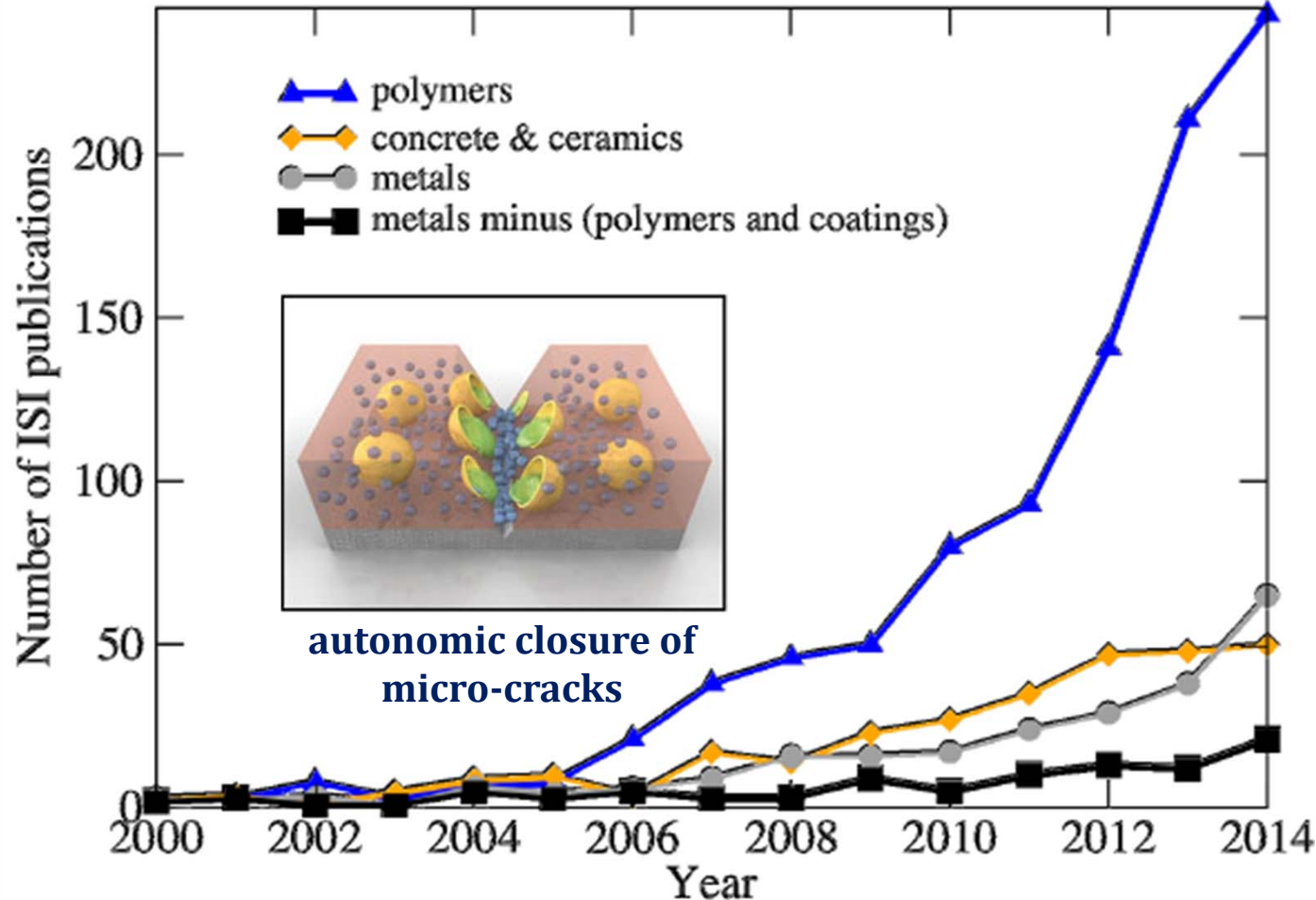


• White et al, 409, Nature, 794-797, 2001

구조소재 개발 新 패러다임 : 자가치유 Self-healing



White et al, Nature, 409, 794-797 (2001)



“자가치유”의 개념은 폴리머 등의 활성화 공정을 통해 제안되어 개발되고 있음!



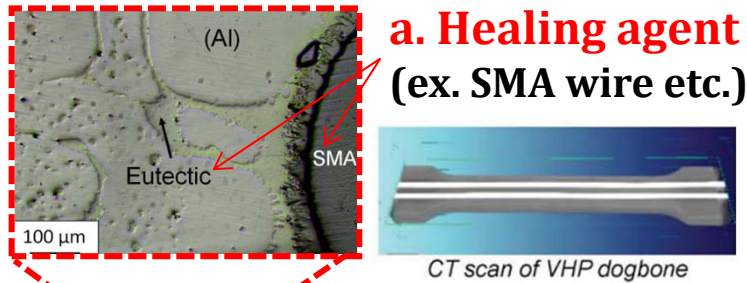
자가치유금속 (Self-healing metals): 현 기술수준



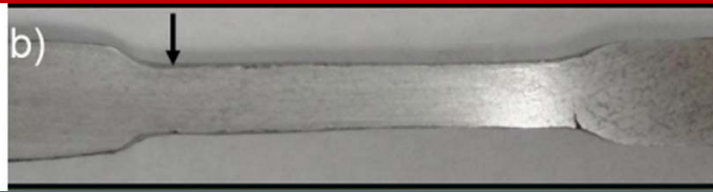
Grabowski & Tazan, *Self-healing Metals* (2016)

Healing agent 기반 Macro-crack 전파 방지

Al-3at% Si composite reinforced with 2vol% NITI SMA wire

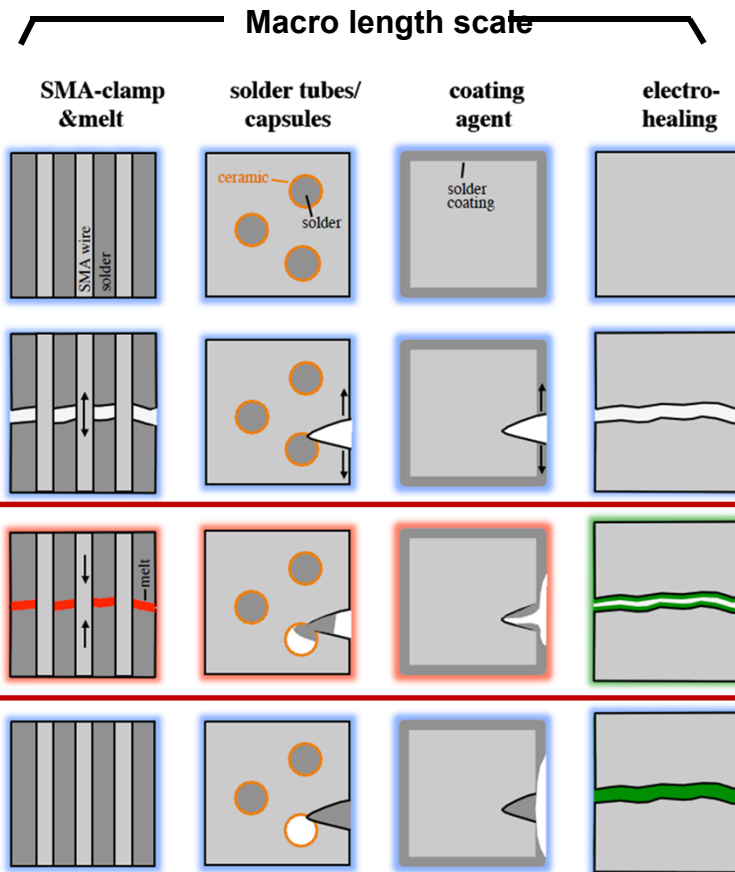


a. Healing agent
(ex. SMA wire etc.)



b. Healing Treatment & **c. Local melting**
(ex. Aging, electro pulse etc.) (ex. Eutectic phase, Sn etc.)

➔ 생성된 Macroscale crack 전파 방지



금속의 경우 상온에서 자가치유를 위한 열역학/동역학적 "구동력이 제한적"임!





1) “Super-elastic Bulk Metallic Glass Composite”

**Self-healing Metallic Materials
with Recoverable 2nd phase**

Development of **New Ti-based BMGC** with High Work-hardenability

▶ Alloy system **Cu-Zr-Al system**

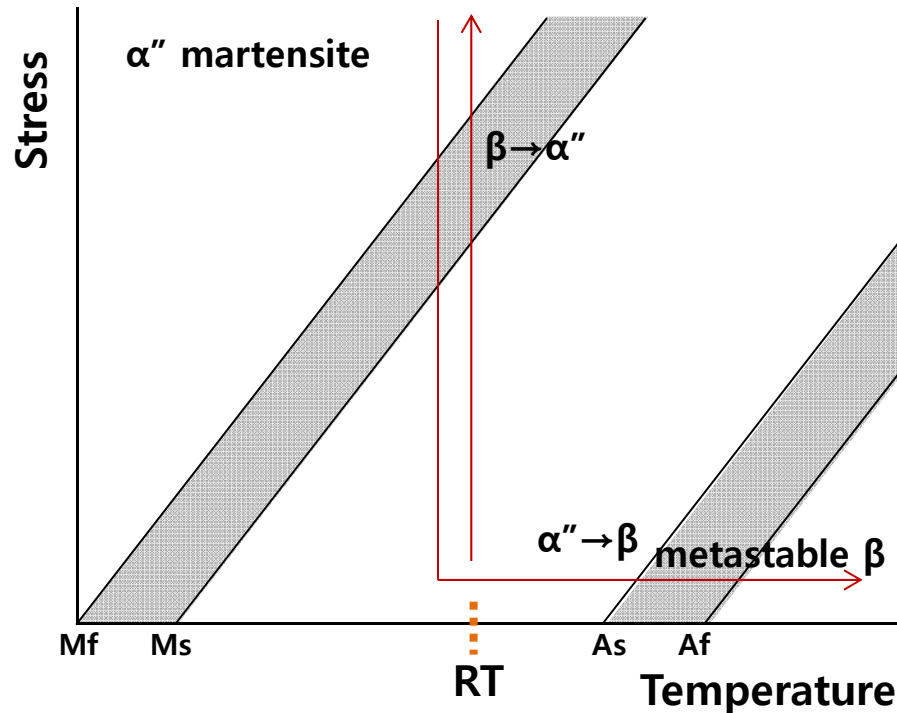
Secondary phase **CuZr**
Metastable B2 phase at RT
"Shape Memory Behavior"



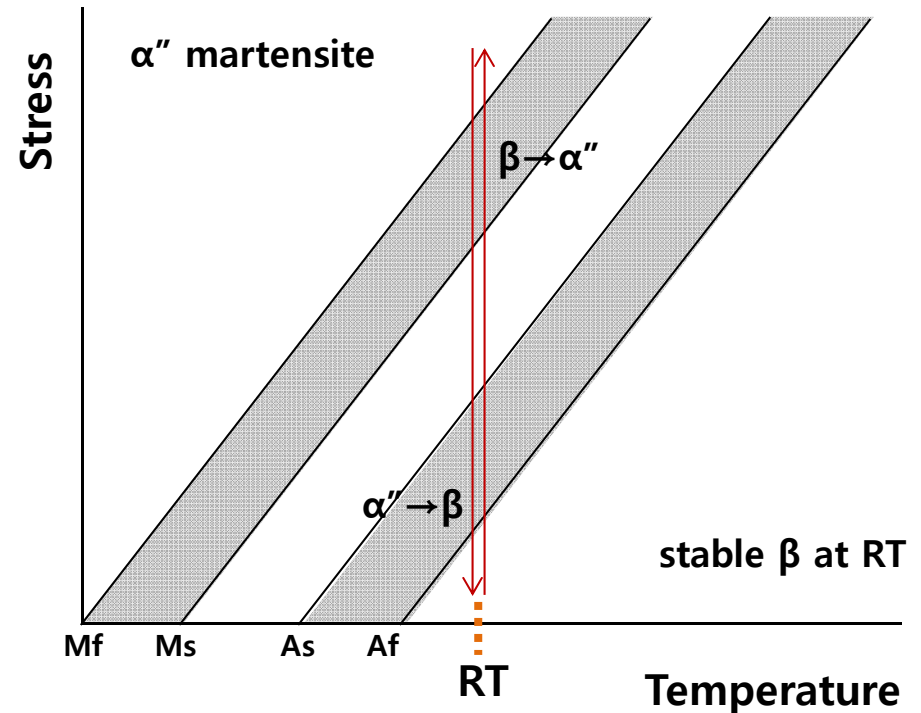
Ti-Cu-Ni system

Ti-X
Stable B2 phase at RT
"Superelastic behavior"

Shape Memory Alloy (SMA)



Super-Elastic Alloy (SE alloy)



Phase transformation in Ti-based alloys : $B_2 \rightarrow M \rightarrow B_2$

- Alloy composition:
Ti₄₉-Cu-Ni-X

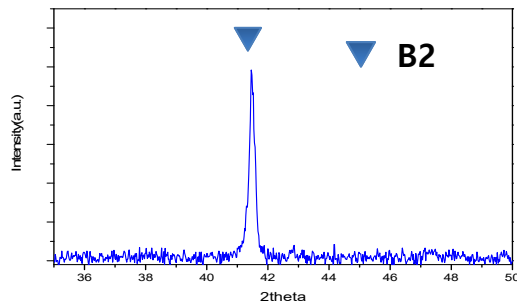
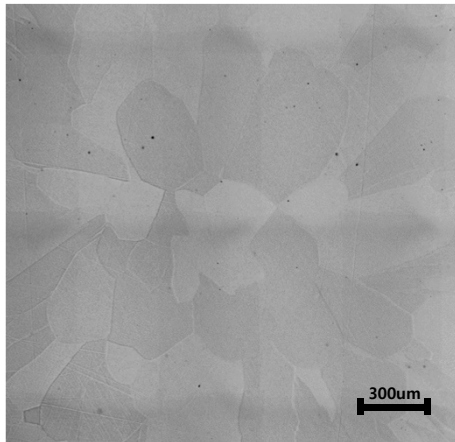
Φ3mm suction casting
-Fully crystalline B2

► **Stress-induced** phase transformation

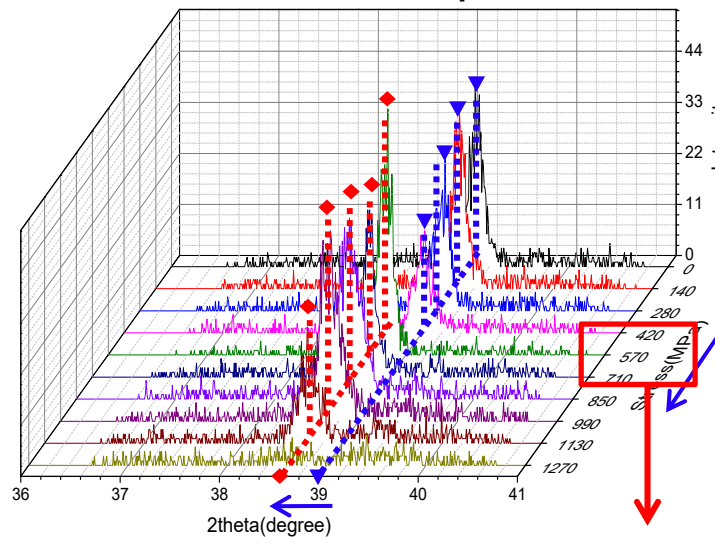
In-situ neutron diffraction measurement during compression

► **Temperature-induced** phase transformation

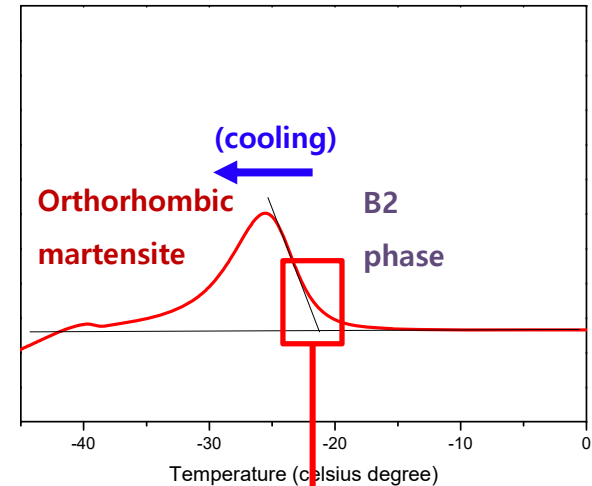
DSC measurement (during cooling)



▼ B2 phase
◆ Orthorhombic martensite phase



Phase transformation stress
= 570MPa



Martensite start T (Ms)
= -22°C

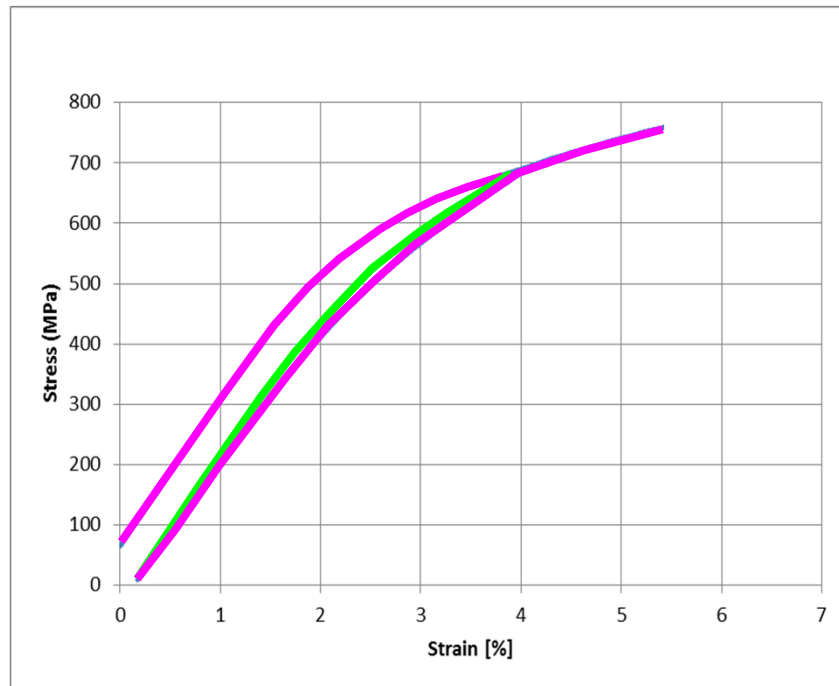
➔ **Novel Ti-based Super-elastic Crystalline Alloy**

In-situ synchrotron diffraction analysis during tensile test

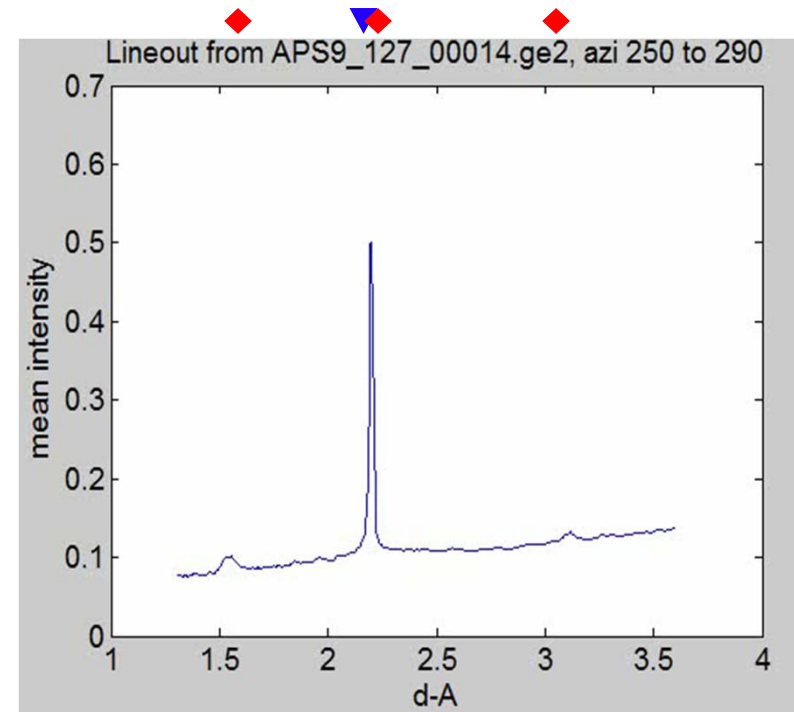
► Superelastic BMG composite: Reversible Phase Transformation Behavior

Ti-Cu-Ni-X Φ 3mm
Water cooled Cu mold suction casting,

Loding → Unloading → Reloading



- ▼ Initial BCC phase in as-cast sample
- ◆ Deformed martensite phase



at APS beam line, ANL





2) “TWIP/TRIP High Entropy Alloy”

- Stress-induced phase transformable HEA -

극지 개발의 글로벌 이슈



남극 장보고 과학기지 조감도



북극 항로 개척 및 활용

시베리아-베링 해협을 잇는 해상 수송 루트 개척 및 활용을 위한 첨단 선박 기술



극지 에너지 자원 개발

북극 오일샌드, 해양 플랜트, 시베리아 유전 개발에 따른 구조물 및 파이프라인 건설



극지 인프라 구축

생태, 환경 및 천체관측용 과학기지 건설에 따른 인프라(건축, 항만, 도로, 공항, 상하수도 등) 구축



극지운용 장비 및 용품 개발

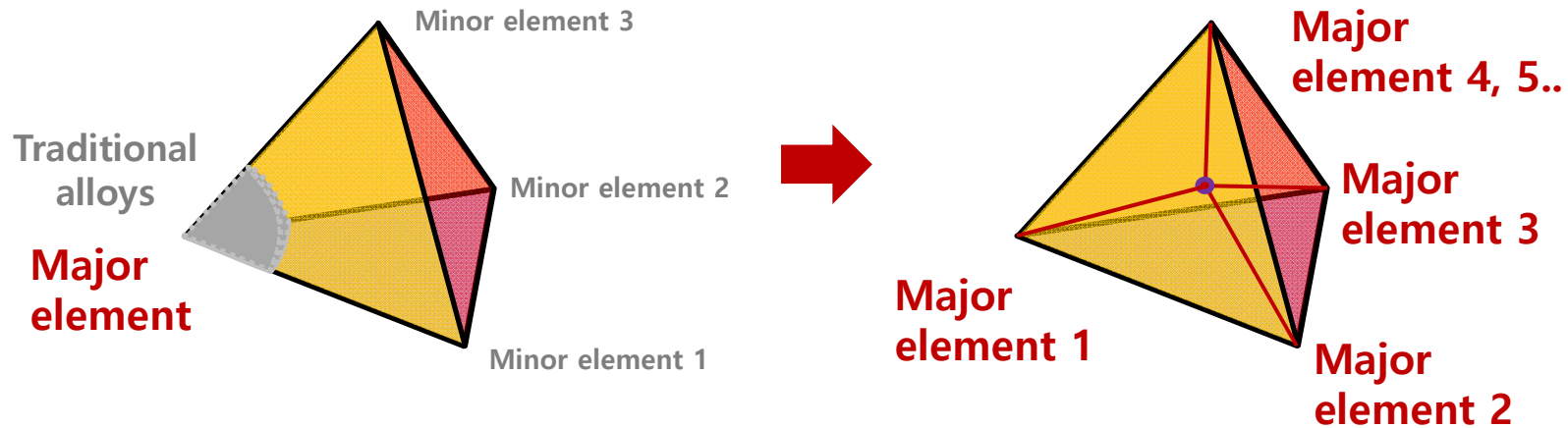
극지 건설/운영장비/관측장비, 운송/이동/탐사 수단 및 관련 용품 개발



METAL MIXOLOGY

306 | NATURE | VOL 533 | 19 MAY 2016

Basic concepts of high entropy alloy (HEA)



Conventional alloy system

Ex) 304 steel - $\text{Fe}_{74}\text{Cr}_{18}\text{Ni}_8$

High entropy alloy system

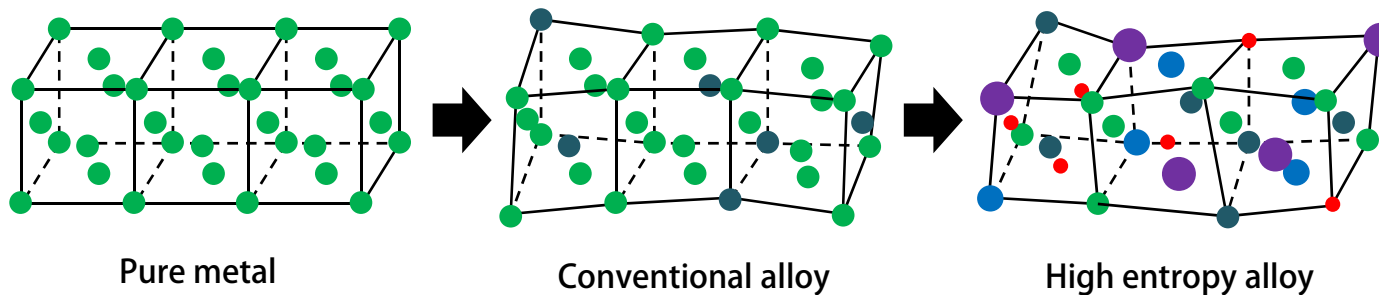
Ex) $\text{Al}_{20}\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{20}\text{Ni}_{20}$

(1) Thermodynamic : high entropy effect

(2) Kinetics : sluggish diffusion effect

(3) Structure : severe lattice distortion effect

(4) Property : cocktail effect

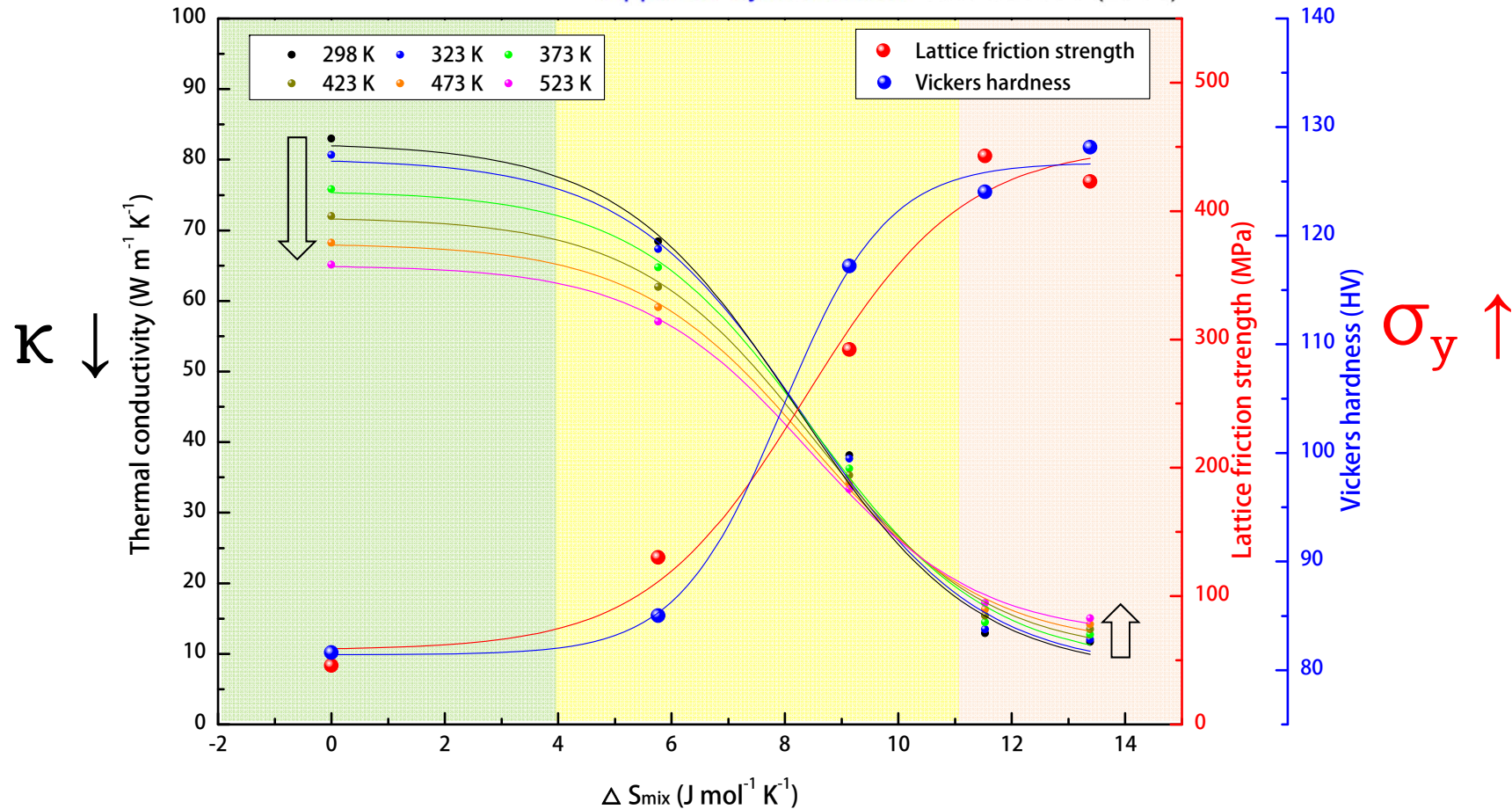


Severe lattice distortion → Sluggish diffusion & Thermal stability

차세대 극지구조용 신소재 : “하이엔트로피 합금”

우수한 σ_y/κ ratio

Applied Physics Letters **109**, 061906 (2016)



하이엔트로피 합금화를 통한 저온 고인성 합금의 개발가능

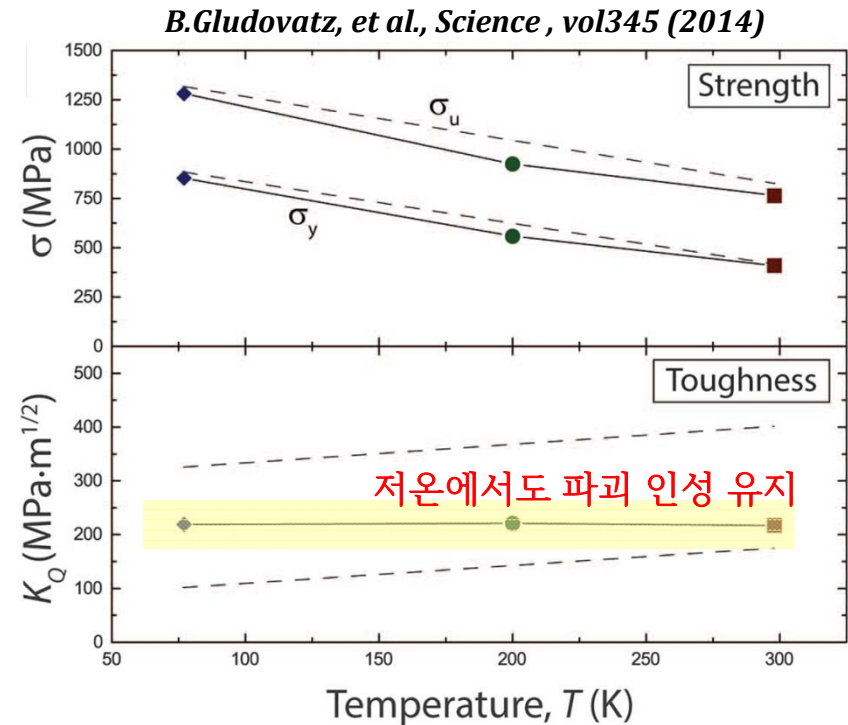
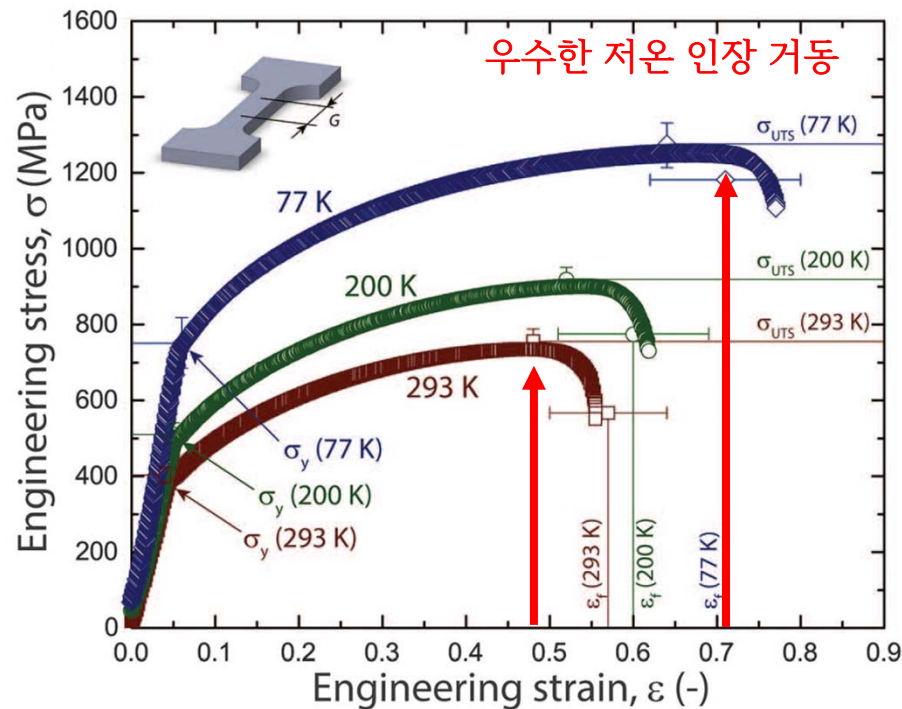


차세대 극지구조용 신소재 : “하이엔트로피 합금”

▶ FCC 하이엔트로피 합금의 극저온 특성

1) 우수한 극저온 파괴 인성 ($\sim 200 \text{ MPa}\cdot\text{m}^{1/2}$)

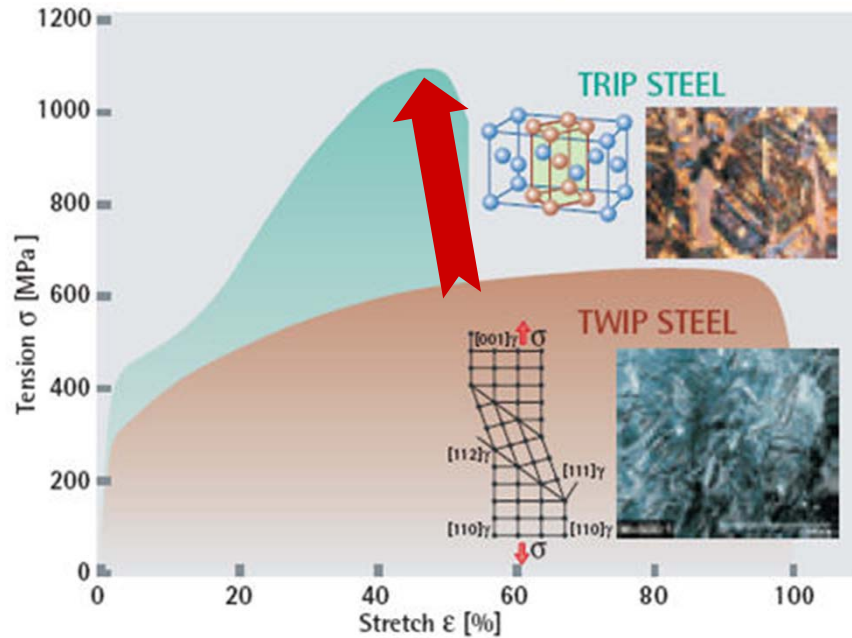
2) Nano-twin 작동으로 일반적 상용합금과는 다르게, 저온에서도 상온의 파괴 인성이 유지됨



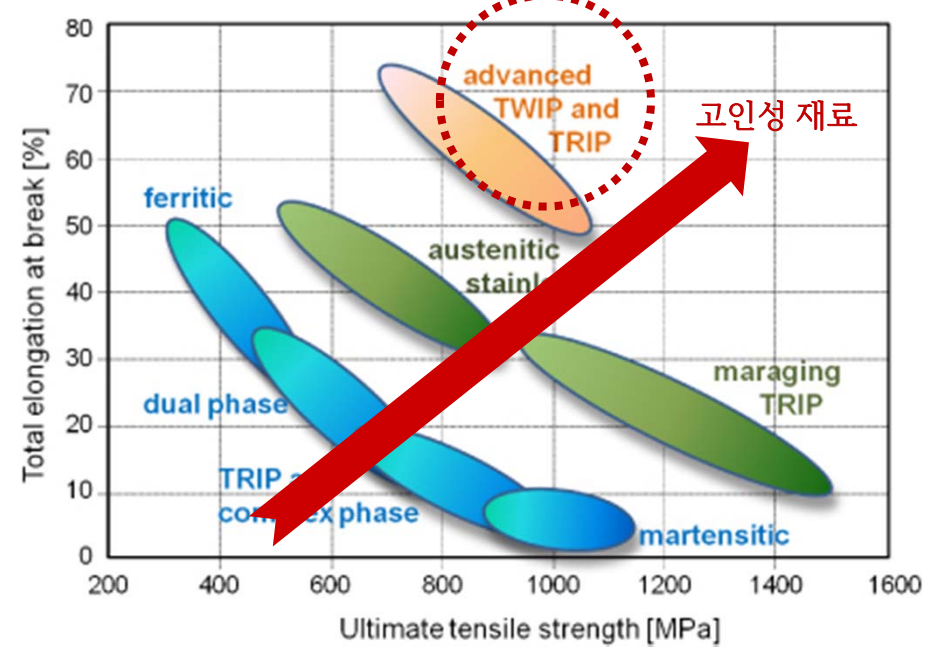
“하이엔트로피 합금화를 통한 저온 고인성 합금의 개발 가능”

TWIP/TRIP 효과 도입을 통한 기계적 물성 향상

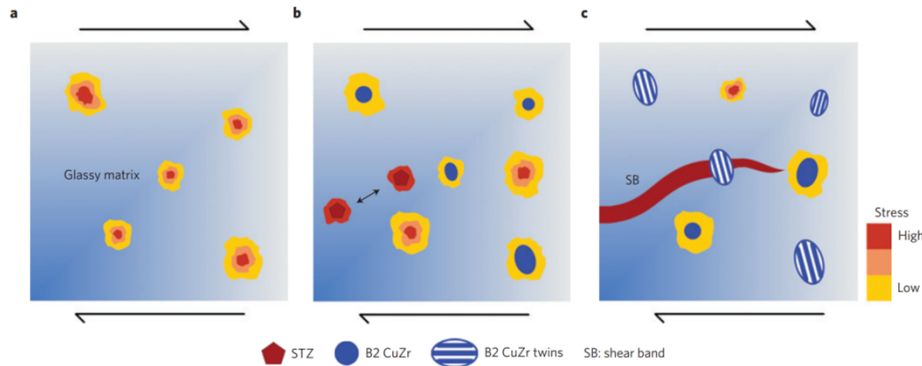
▶ TWIP/ TRIP 효과



▶ TWIP 및 TRIP Steel의 특성



▶ TRIP에 의한 균열 전파의 방지 거동

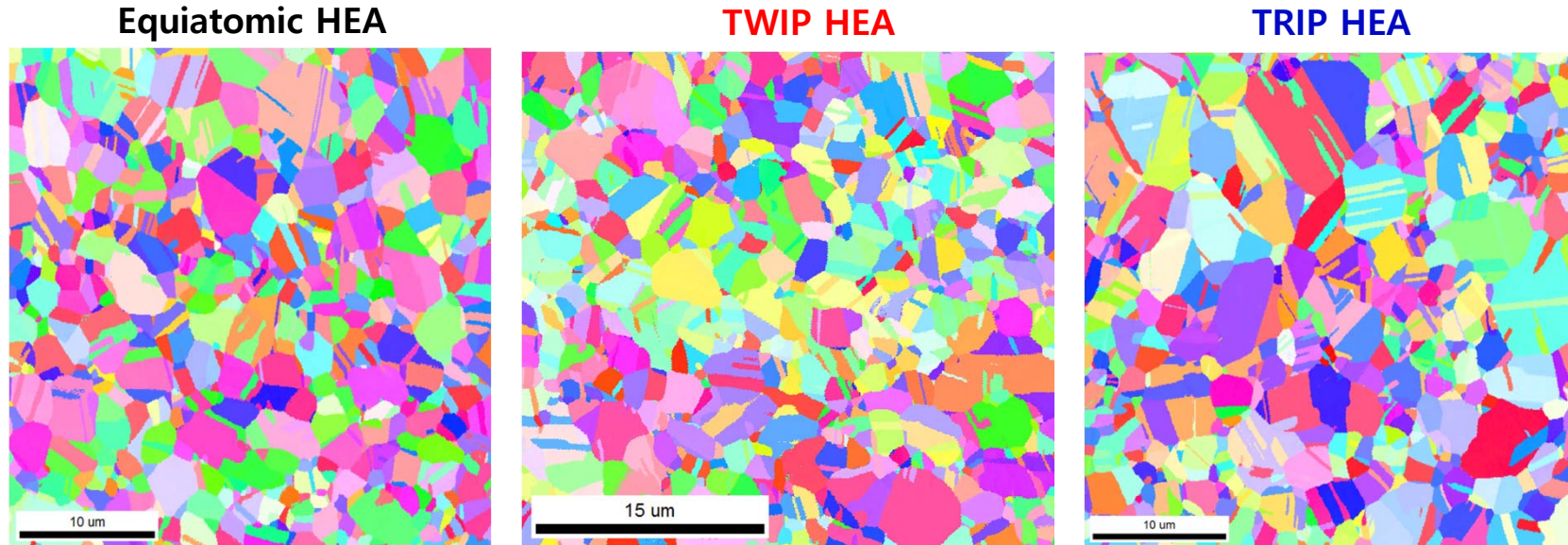


균열부 주변에서 다수의 쌍정유기소성(TWIP), 또는 상변화유기소성(TRIP)을 통한 고인성 구현

“극지 환경 피로파괴 저항성이 큰 TRIP 하이엔트로피 합금 개발”

Development of TWIP/TRIP High Entropy Alloy

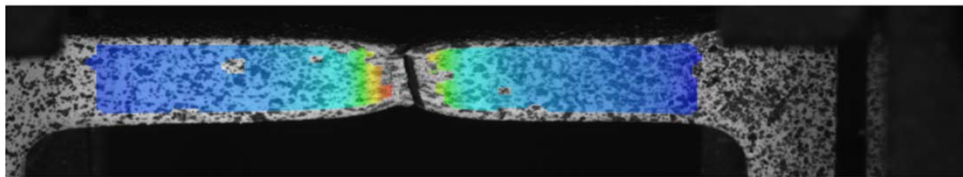
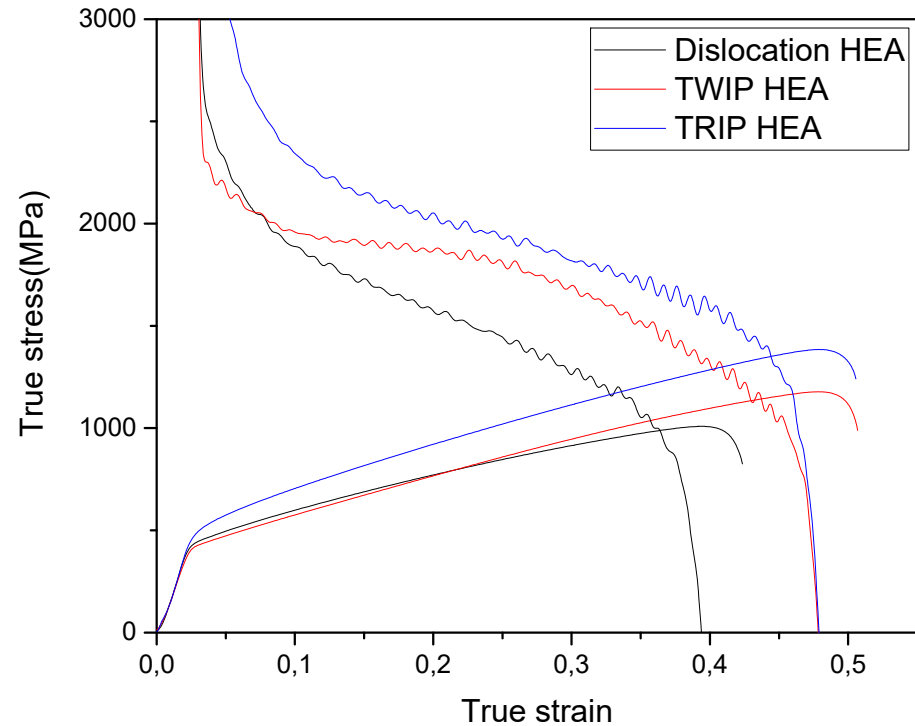
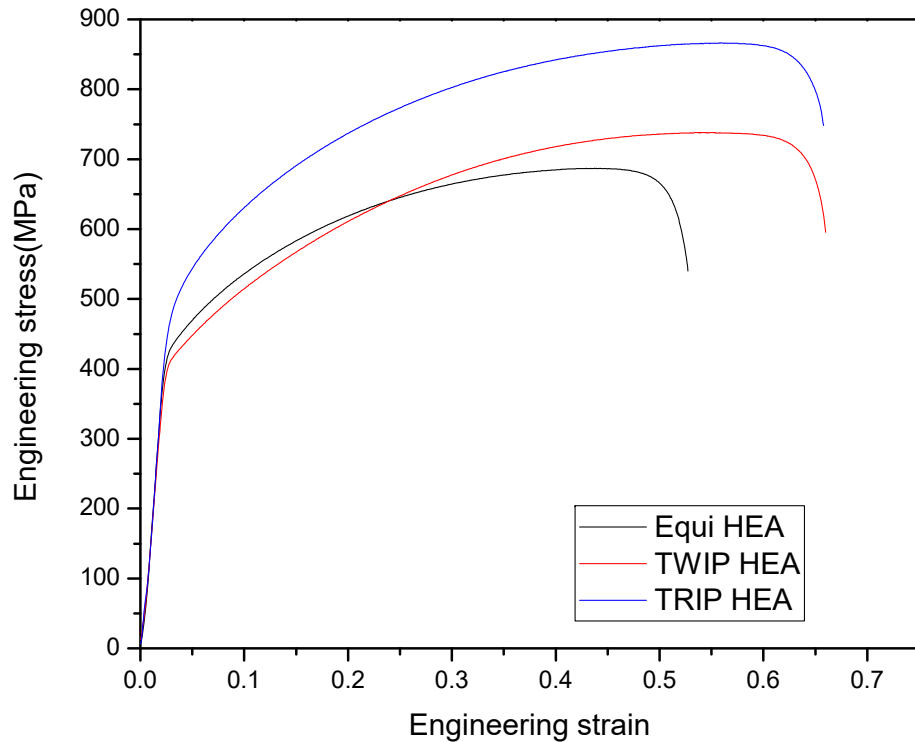
- Design of TWIP/TRIP high entropy alloy **without losing yield strength**



	Composition	Grain size (μm)
1	Equiatomic HEA	3.8
2	TWIP HEA	3.6
3	TRIP HEA	4.3

Development of TWIP/TRIP High Entropy Alloy

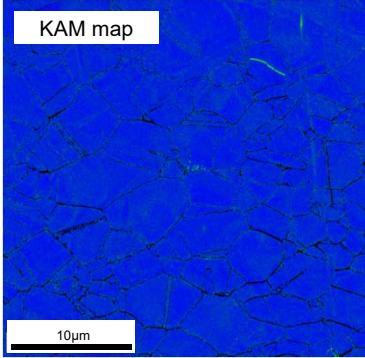
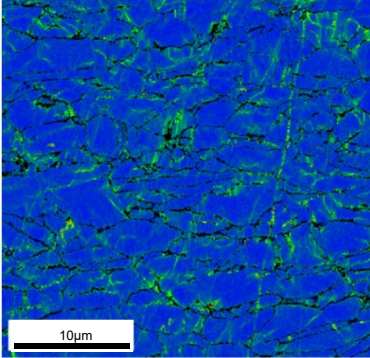
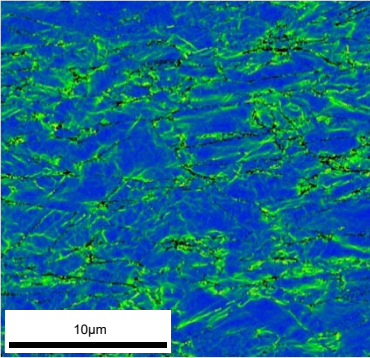
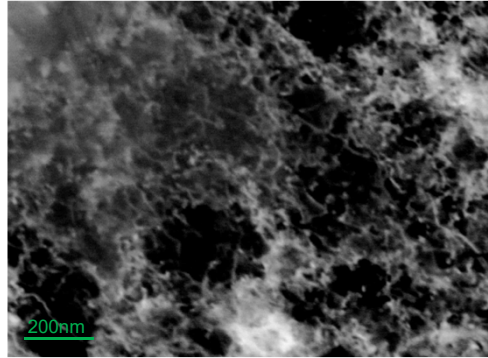
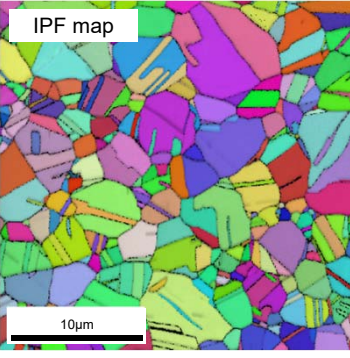
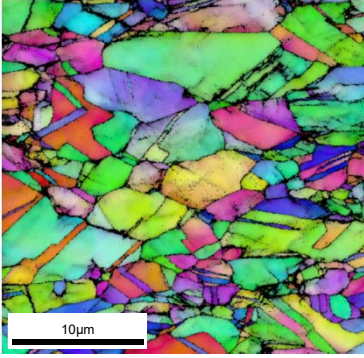
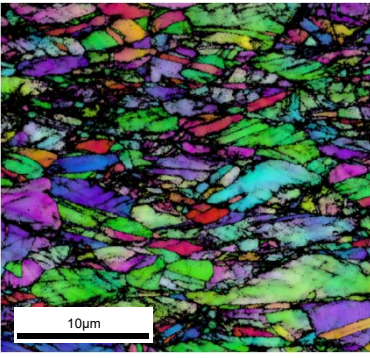
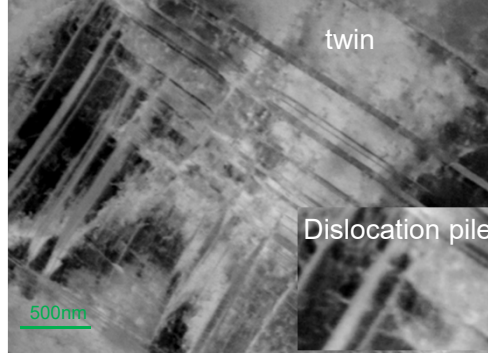
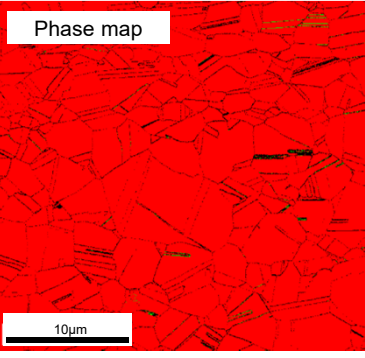
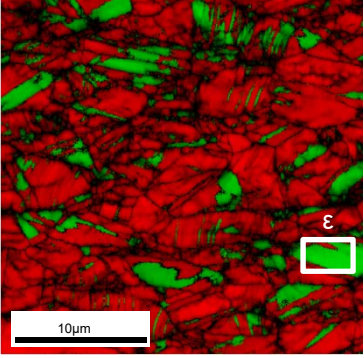
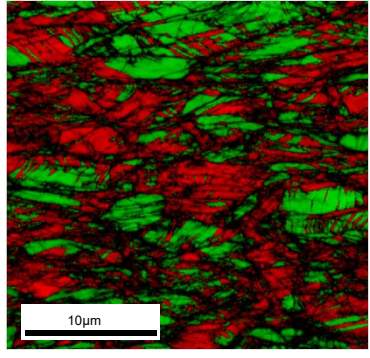
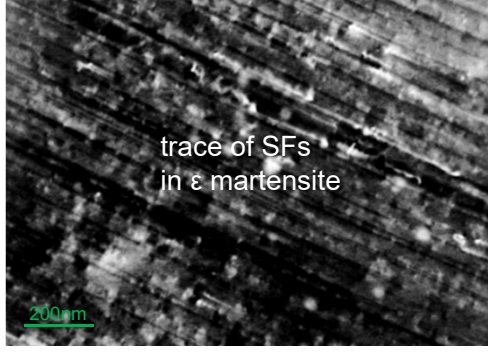
Ni-Co-Fe-Cr-Mn high entropy alloy



Considered criteria

$$\sigma = \frac{\partial \sigma}{\partial \varepsilon} : \text{Necking}$$

Development of TWIP/TRIP High Entropy Alloy

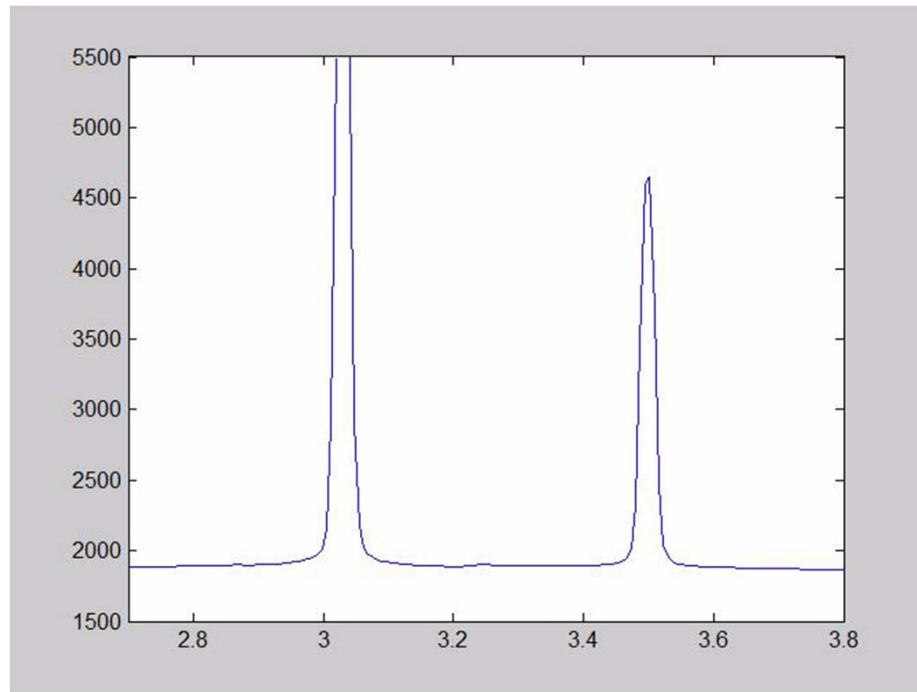
Strain	0%	30%	60%	ECCI
Equi HEA	 <p>KAM map</p> <p>10µm</p>	 <p>10µm</p>	 <p>10µm</p>	 <p>200nm</p>
TWIP HEA	 <p>IPF map</p> <p>10µm</p>	 <p>10µm</p>	 <p>10µm</p>	 <p>twin</p> <p>Dislocation pile</p> <p>500nm</p>
TRIP HEA	 <p>Phase map</p> <p>10µm</p>	 <p>ε</p> <p>10µm</p>	 <p>10µm</p>	 <p>trace of SFs in ε martensite</p> <p>200nm</p>



Development of TWIP/TRIP High Entropy Alloy

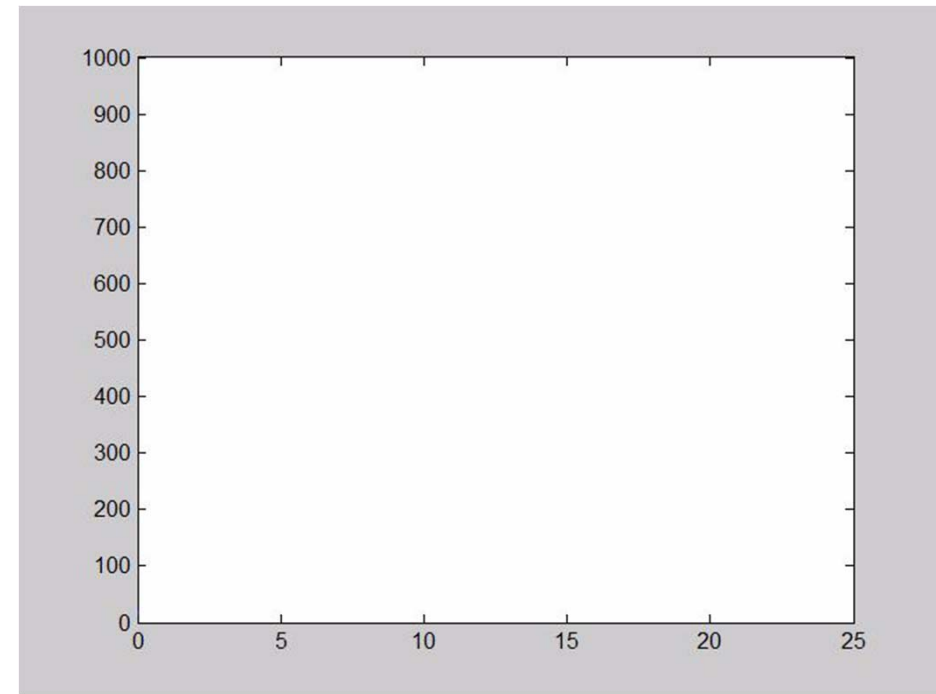
TRIP HEA

ϵ γ ϵ γ



I(Q) vs. Q

Stress-strain curve



Stress (MPa) vs. Strain (%)

at APS beam line, ANL



Contents in Phase Transformation

Background
to understand
phase
transformation

(Ch1) Thermodynamics and Phase Diagrams

(Ch2) Diffusion: Kinetics

(Ch3) Crystal Interface and Microstructure

Representative
Phase
transformation

(Ch4) Solidification: Liquid \rightarrow Solid

(Ch5) Diffusional Transformations in Solid: Solid \rightarrow Solid

(Ch6) Diffusionless Transformations: Solid \rightarrow Solid

Microstructure-Properties Relationships

Alloy design &
Processing

Performance

“Phase Transformation”

Microstructure
down to atomic scale

Properties

“Tailor-made Materials Design”

*** Homework 6 : Exercises 6**

until 20th December (before exam)

FINAL (20th December, 10 AM-1 PM)

Place: 33-225

**Scopes: Text: page 189 (chapter 4) ~
page 433 (chapter 6)/**

Teaching notes: 16~25/

Good Luck!!