

2016 Fall

“Phase Transformation *in* Materials”

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Eun Soo Park

Office: 33-313

Telephone: 880-7221

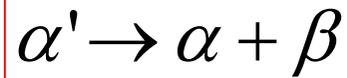
Email: espark@snu.ac.kr

Office hours: by an appointment

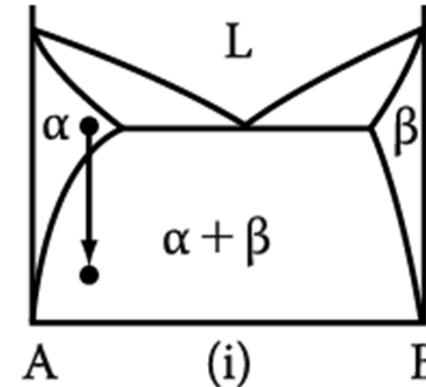
5. Diffusion Transformations in solid

: diffusional nucleation & growth

(a) Precipitation



Metastable supersaturated
Solid solution



Homogeneous Nucleation

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

Heterogeneous Nucleation

$$\Delta G_{het} = -V(\Delta G_V - \Delta G_S) + A\gamma - \Delta G_d$$

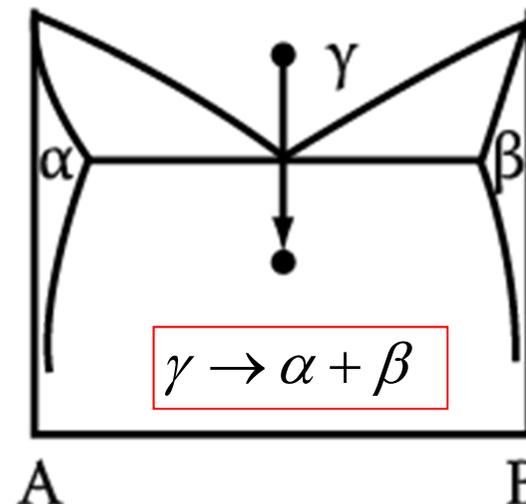
$$N_{hom} = \omega C_0 \exp\left(-\frac{\Delta G_m}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right)$$

→ suitable nucleation sites ~ nonequilibrium defects
(creation of nucleus ~ destruction of a defect (- ΔG_d))

(b) Eutectoid Transformation

Composition of product phases
differs from that of a parent phase.
→ **long-range diffusion**

Which transformation proceeds
by short-range diffusion?



Growth of Pearlite: analogous to the growth of a lamellar eutectic

Min. possible: $(S^*) \propto 1/\Delta T$ / Growth rate : mainly lattice diffusion $v = kD_c \gamma (\Delta T)^2$

Interlamellar spacing of pearlite colonies : mainly boundary diffusion $v = kD_b (\Delta T)^3$

Relative Positions of the Transformation curves for Pearlite and Bainite in Plain Carbon Eutectoid Steels.

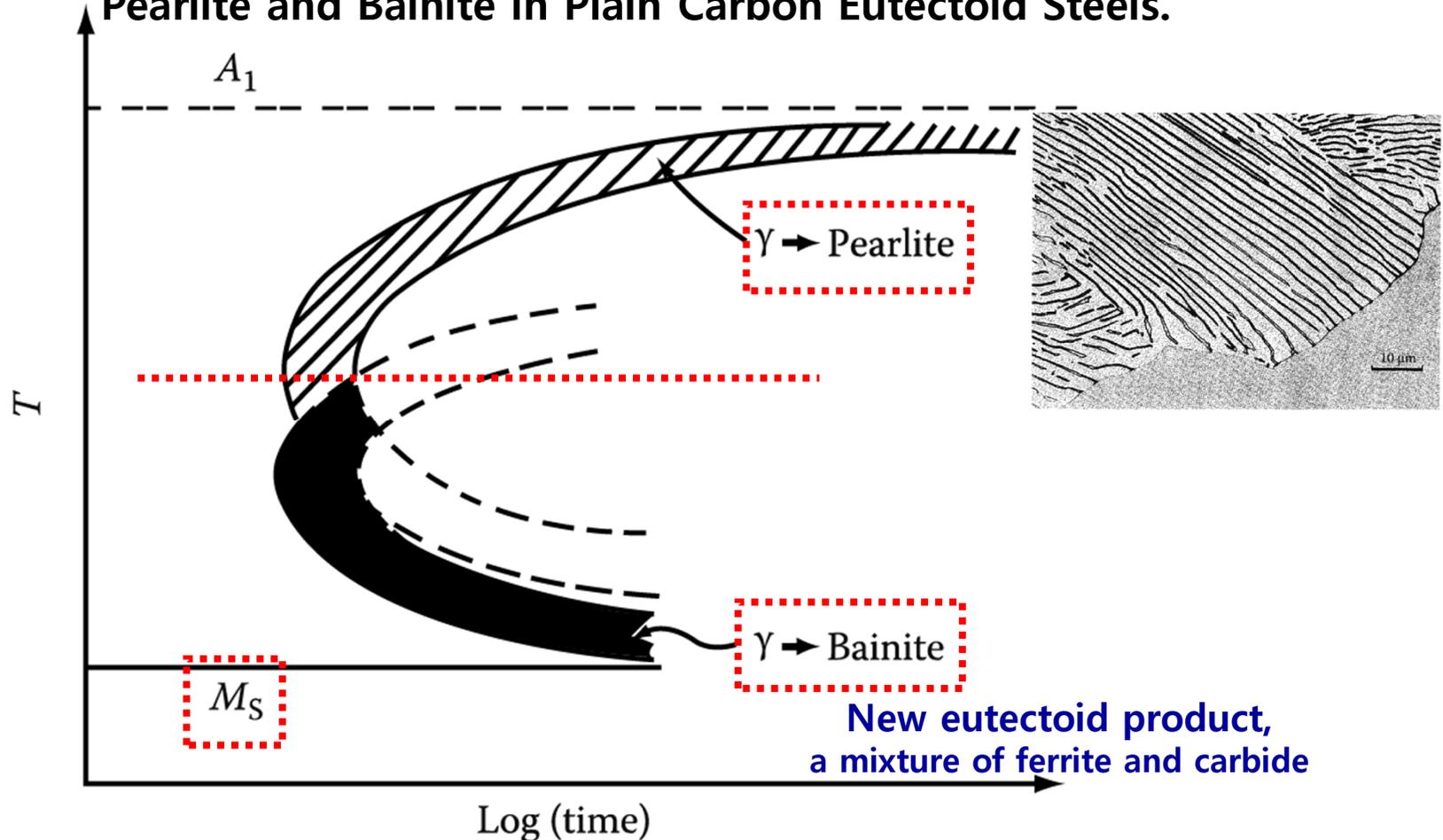
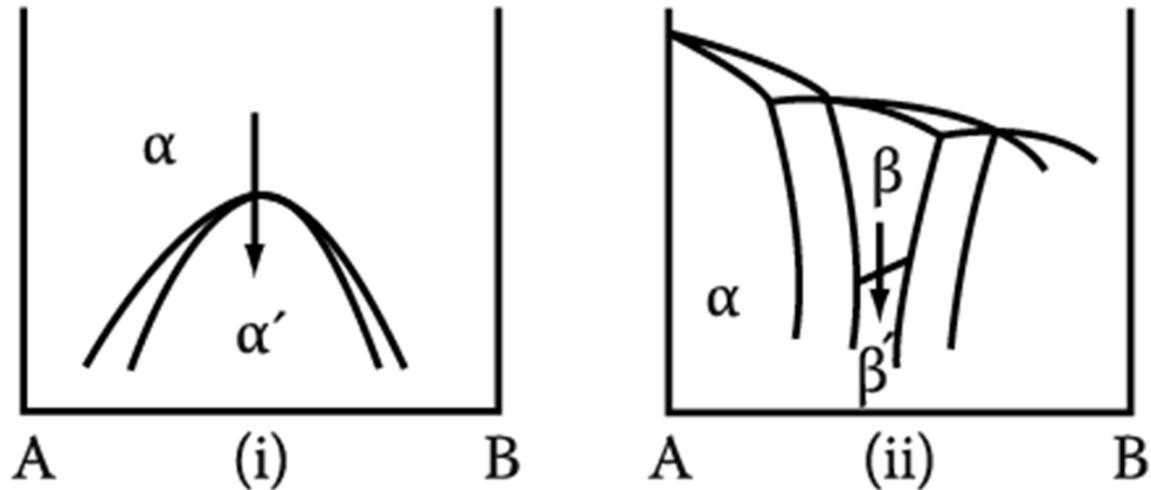
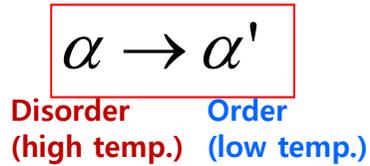


Figure 5.64 Schematic diagram showing relative positions of the transformation curves for pearlite and bainite in plain carbon eutectoid steel.

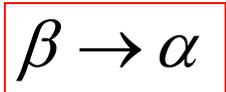
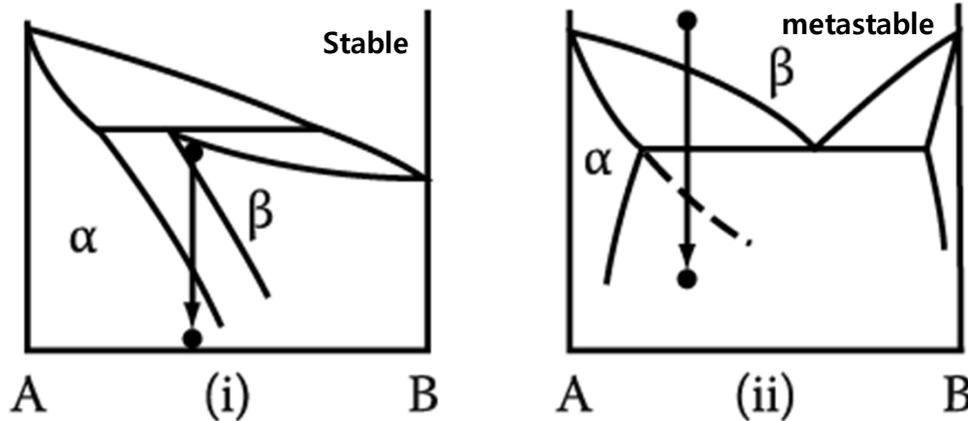
5. Diffusion Transformations in solid

(c) Order-Disorder Transformation

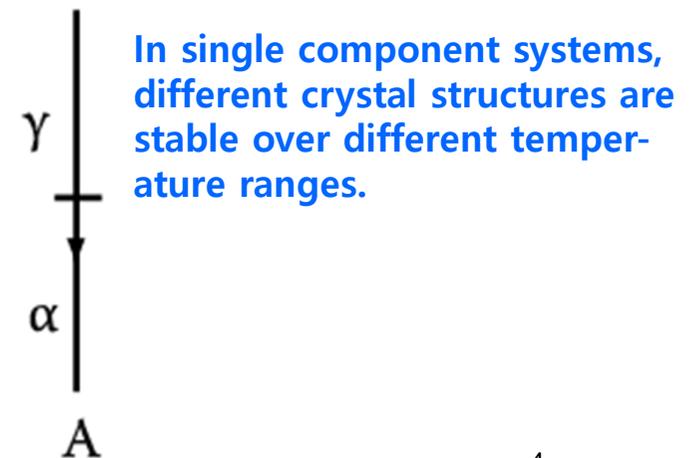


(d) Massive Transformation

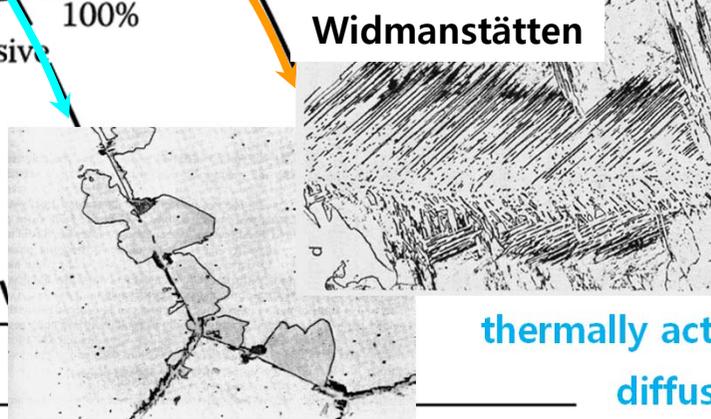
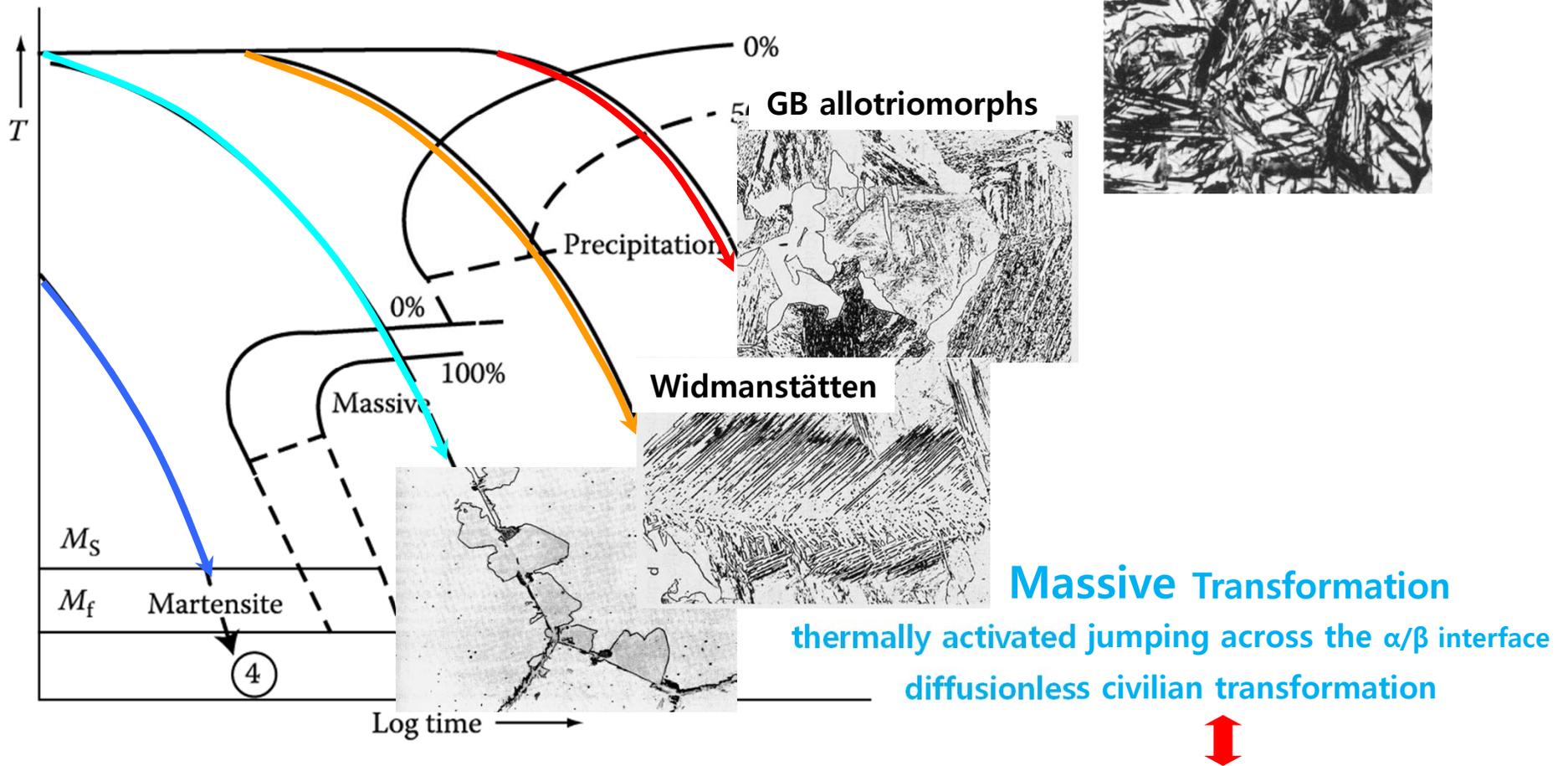
: The original phase decomposes into one or more new phases which have the same composition as the parent phase, but different crystal structures.



(e) Polymorphic Transformation



* Massive, Martensite Transformation



thermally activated jumping across the α/β interface
diffusionless civilian transformation



β is sheared into α by the cooperative movement of atoms across a glissile interface
diffusionless military transformation
Martensite Transformation

Fig. 5.75 A possible CCT diagram for systems showing a massive transformation. Slow cooling (1) produces equiaxed α . Widmanstätten morphologies result from faster cooling (2). Moderately rapid quenching (3) produces the massive transformation, while the highest quench rate (4) leads to a martensitic transformation.

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

Military Transformations

- What is a martensitic transformation?

Most phase transformations studied in this course have been diffusional transformations where long range diffusion is required for the (nucleation and) growth of the new phase(s).

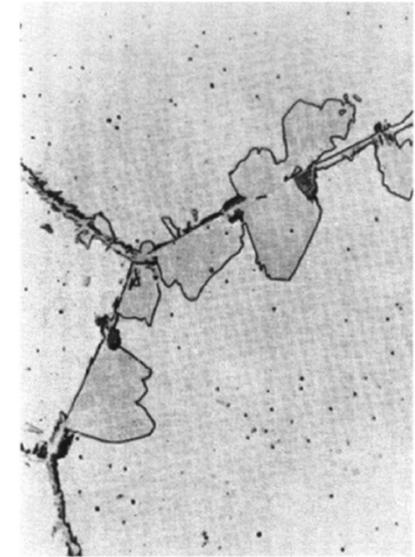
- There is a whole other class of *military transformations* which are *diffusionless transformations* in which the atoms move only short distances (**less than one interatomic spacing**) in order to join the new phase.
- These transformations are *also* subject to the constraints of nucleation and growth. They are (almost invariably) associated with *allotropic transformations* (동소변태).

Classification of Transformations

| | Civilian | Military |
|---------------------------|--|--|
| Diffusion Required | Precipitation, Spinodal Decomposition | ? |
| Diffusionless | Massive Transformations | Martensitic Transformations |

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 **diffusionless 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. There is always a ③ change in shape which means that there is a strain associated with the transformation. The strain is a general one, meaning that all six (independent) coefficients can be different.



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**.

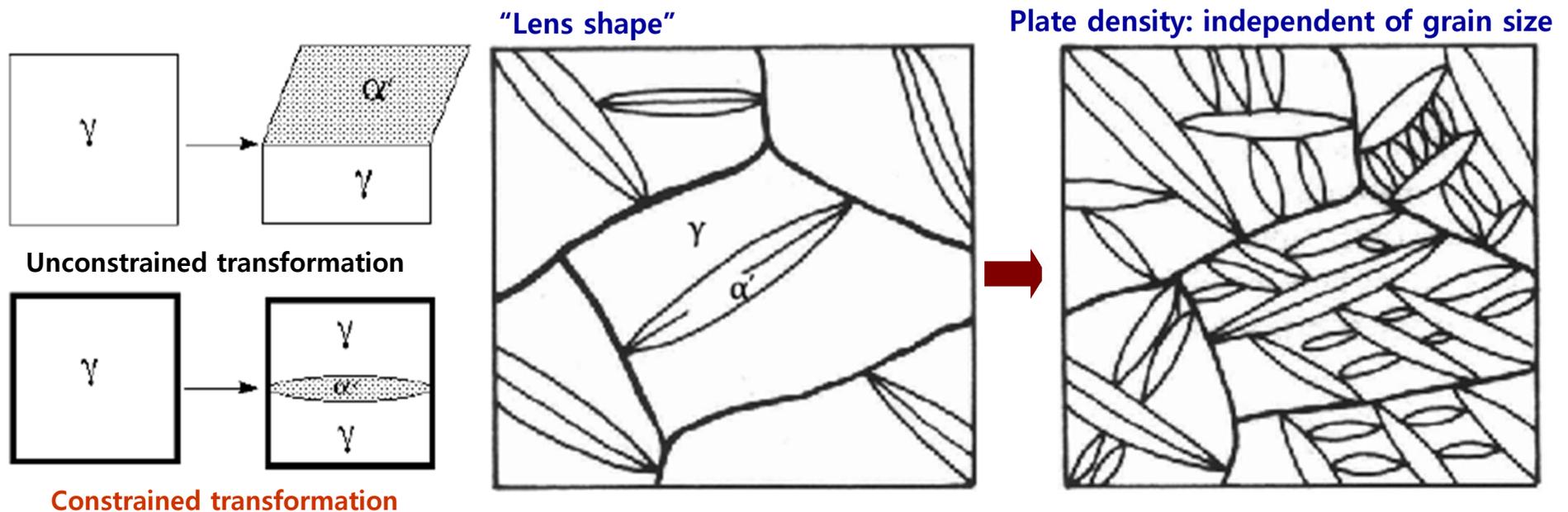


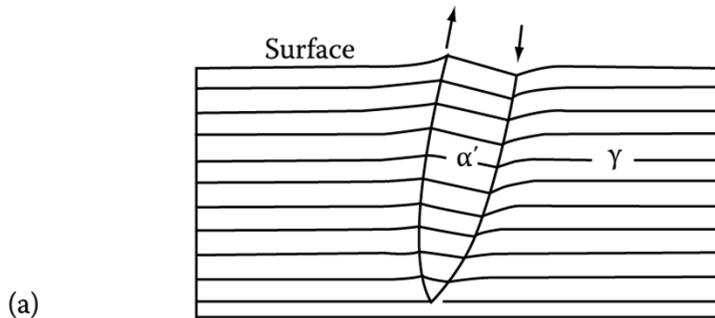
Fig. 6.1 Growth of martensite with increasing cooling below M_s .
→ Martensite formation rarely goes to completion

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**.

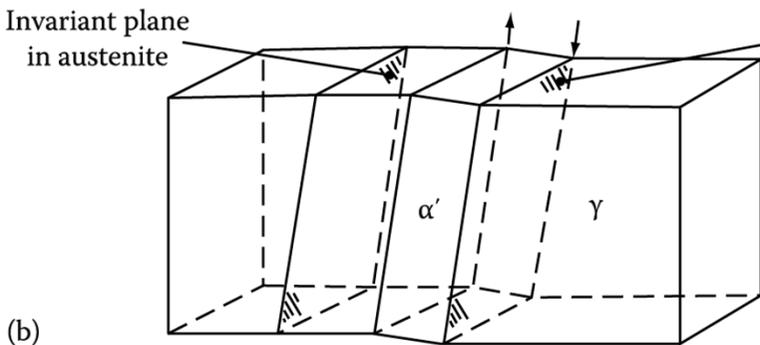
strain associated with the transformation

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



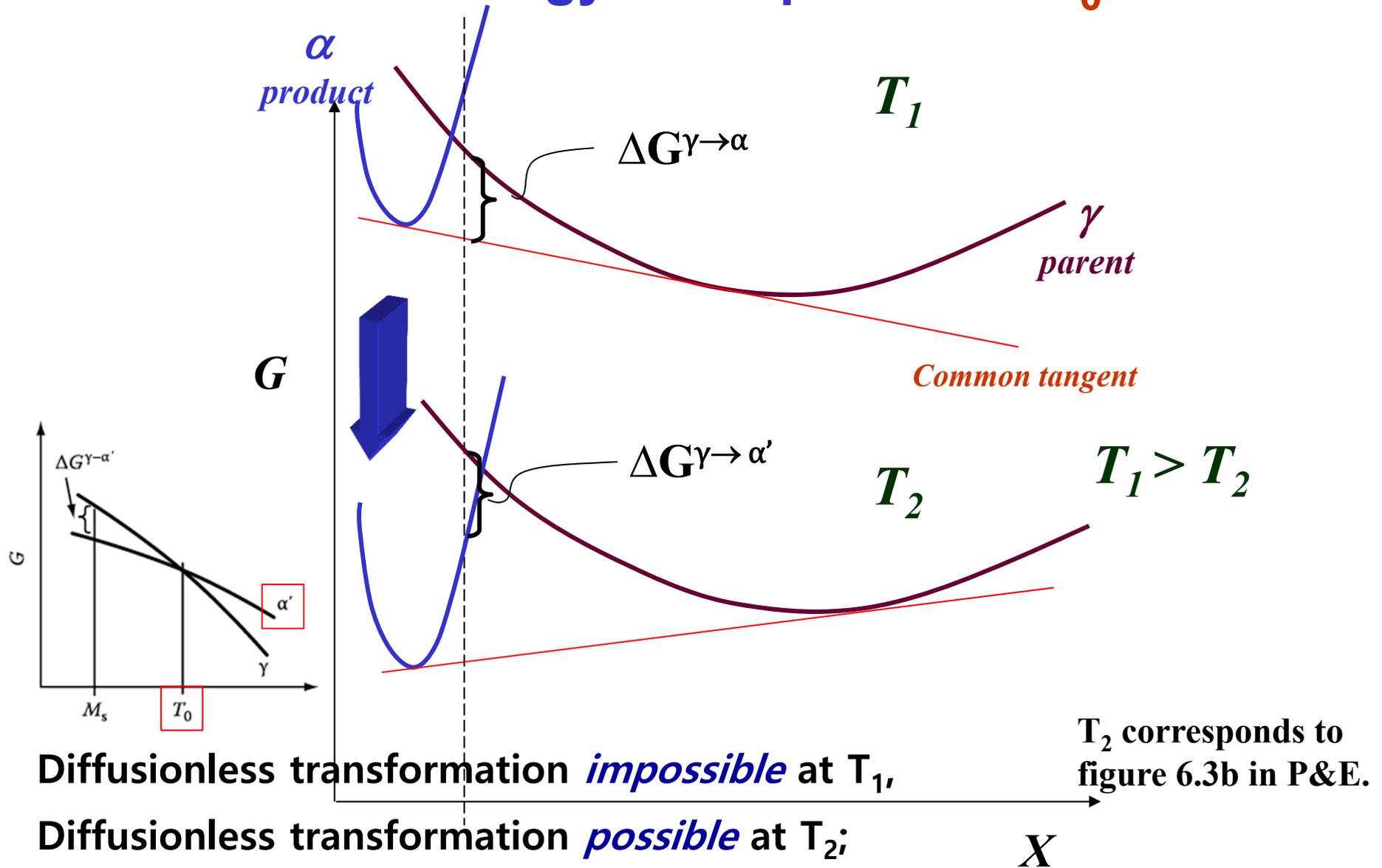
: difficult process to study M nucleation and growth experimentally

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

Driving Forces

- These transformations require **larger driving forces** than for diffusional transformations. (= large undercooling, ΔT)
- Why? In order for a transformation to occur without long range diffusion, it must take place **without a change in composition**.
- This leads to the so-called **T_0 concept**, which is the temperature at which the new phase can appear with **a net decrease in free energy at the same composition as the parent (matrix) phase**.
- As the following diagram demonstrates, the temperature, T_0 , at which segregation-less transformation becomes possible (i.e. a decrease in free energy would occur), is always less than the liquidus temperature.

Free Energy - Composition: T_0



“ T_0 ” is defined by no difference in free energy between the phases, $\Delta G=0$.

Driving Force Estimation

- The driving force for a martensitic transformation can be estimated in exactly the same way as for other transformations such as solidification.
- Provided that an enthalpy (latent heat of transformation) is known for the transformation, the driving force can be estimated as proportional to **the latent heat** and **the undercooling below T_0** .

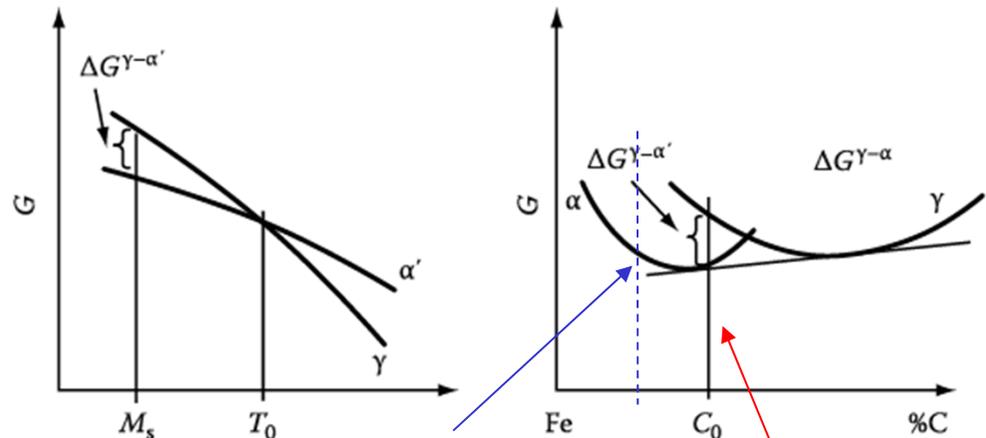
$$\Delta G = \frac{L\Delta T}{T_m} \Rightarrow \Delta G^{\gamma \rightarrow \alpha'} = \Delta H^{\gamma \rightarrow \alpha'} \Delta T / T_0 = \Delta H^{\gamma \rightarrow \alpha'} \frac{(T_0 - M_s)}{T_0}$$

| Alloy | $\Delta H^{\gamma \rightarrow \alpha'}$ (J mol ⁻¹) | $T_0 - M_s$ (K) | $-\Delta G^{\gamma \rightarrow \alpha'}$ (J mol ⁻¹) |
|------------|---|-----------------|---|
| Ti-Ni | 1550 | 20 | 92 |
| Cu-Al | 170-270 | 20-60 | 19.3 ± 7.6 |
| Au-Cd | 290 | 10 | 11.8 |
| Fe-Ni 28% | 1930 | 140 | 840 |
| Fe-C | | | 1260 |
| Fe-Pt 24% | 340 | 10 | 17 |
| Ordered | * Large differences in $\Delta G^{\gamma \rightarrow \alpha'}$ btw disordered and ordered alloys (a relatively small ΔT) | | |
| Fe-Pt | 2390 | ~150 | ~1260 |
| Disordered | | | |

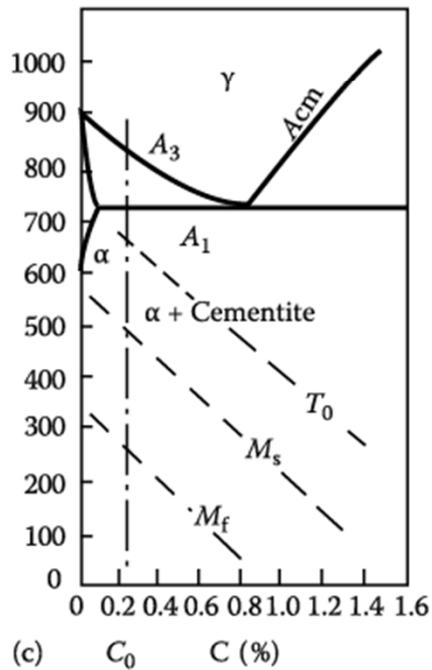
Source: From Guénin, G., PhD thesis, Polytechnical Institute of Lyon, 1979.

Table 6.1. Comparisons of Calorimetric Measurements of Enthalpy and Undercooling in some M alloys

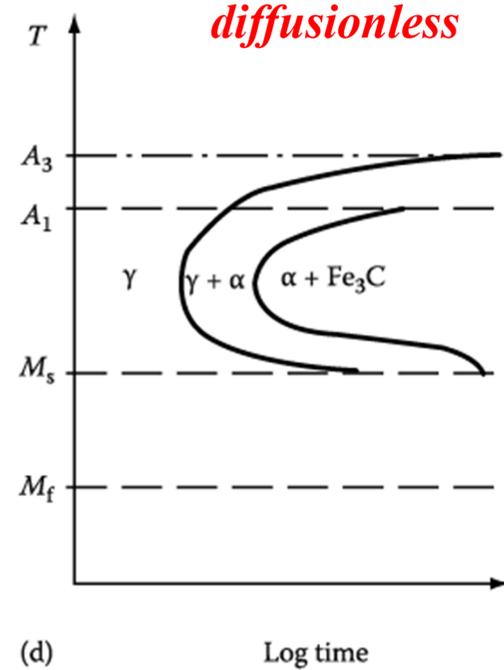
Various ways of showing the martensite transformation



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



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



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

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

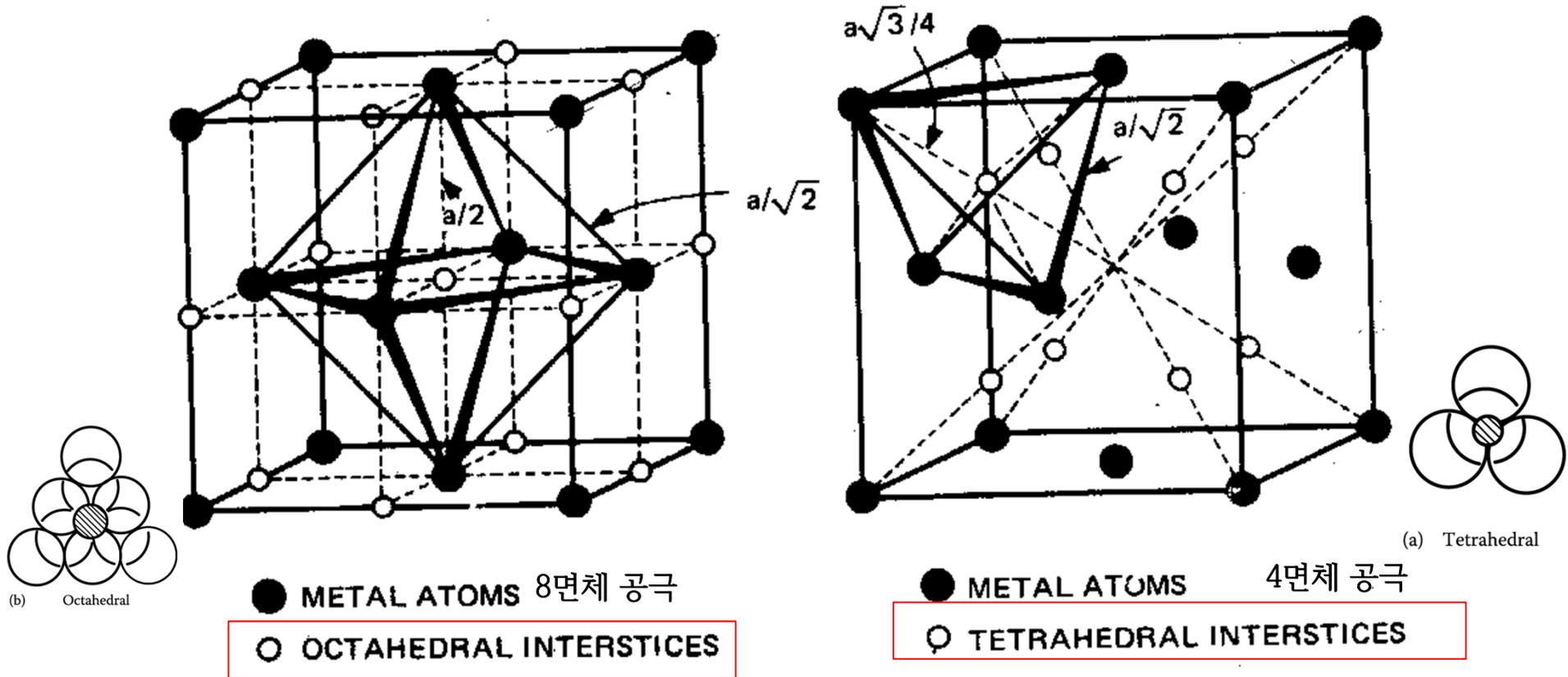
Some retained austenite can be left even below M_f . In particular, as much as 10%-15% retained austenite is a common feature of especially the higher C content alloys such as those used for ball bearing steels.

Mechanisms for martensitic transformations

- The mechanisms of martensitic transformations are not entirely clear.
- Why does martensite require heterogeneous nucleation?
The reason is the large critical free energy for nucleation outlined above
- Possible mechanisms for martensitic transformations include
 - (a) dislocation based
 - (b) shear based
- (a) • ***Dislocations*** in the parent phase (austenite) clearly provide sites for heterogeneous nucleation.
 - Dislocation mechanisms are thought to be important for ***propagation/growth of martensite platelets or laths***.
- (b) • Martensitic transformations **strongly constrained** by crystallography of the parent and product phases.
 - This is analogous to **slip (dislocation glide)** and twinning, especially the latter.

6.1.1 Solid Solution of carbon in Iron (철의 탄소고용체)

Figure 6.4 Illustrating possible sites for interstitial atoms in the fcc or hcp lattices.



Six nearest neighbors/ $d_6 = 0.414D = 1.044 \text{ \AA}$ surrounded by four atoms/ $d_4 = 0.225D = 0.568 \text{ \AA}$

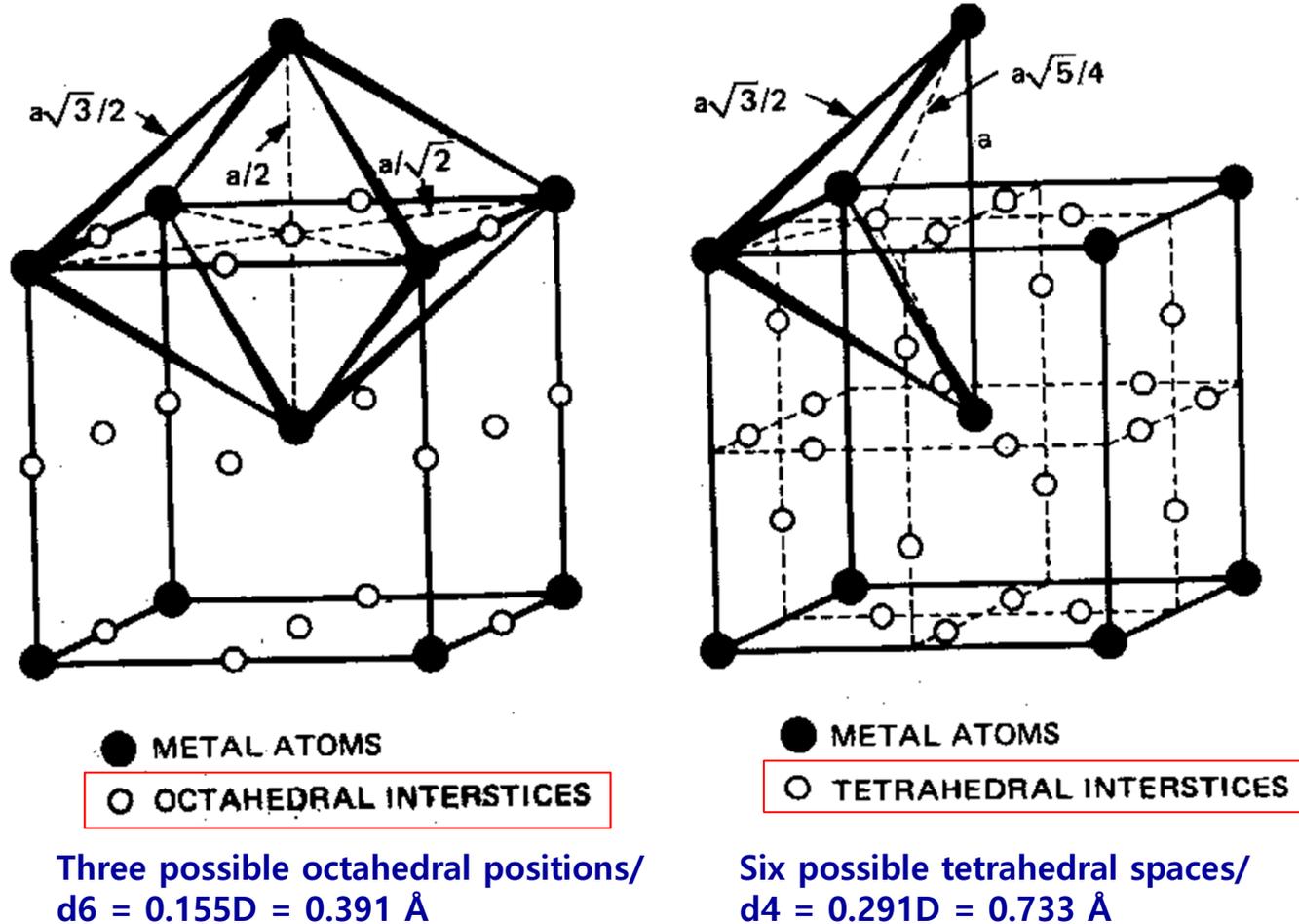
D is the diameter of the parent atoms/ d_4 and d_6 are the maximum interstitial diameters

Diameter of a carbon atom: 1.54 Å

: This means that **considerable distortion** of the γ austenite lattice must occur to contain carbon atoms in solution and that the **octahedral interstices should be the most favorable.**

6.1.1 Solid Solution of carbon in Iron

Figure. Illustrating possible sites for interstitial atoms in the bcc lattices.



D is the diameter of the parent atoms/ d_4 and d_6 are the maximum interstitial diameters

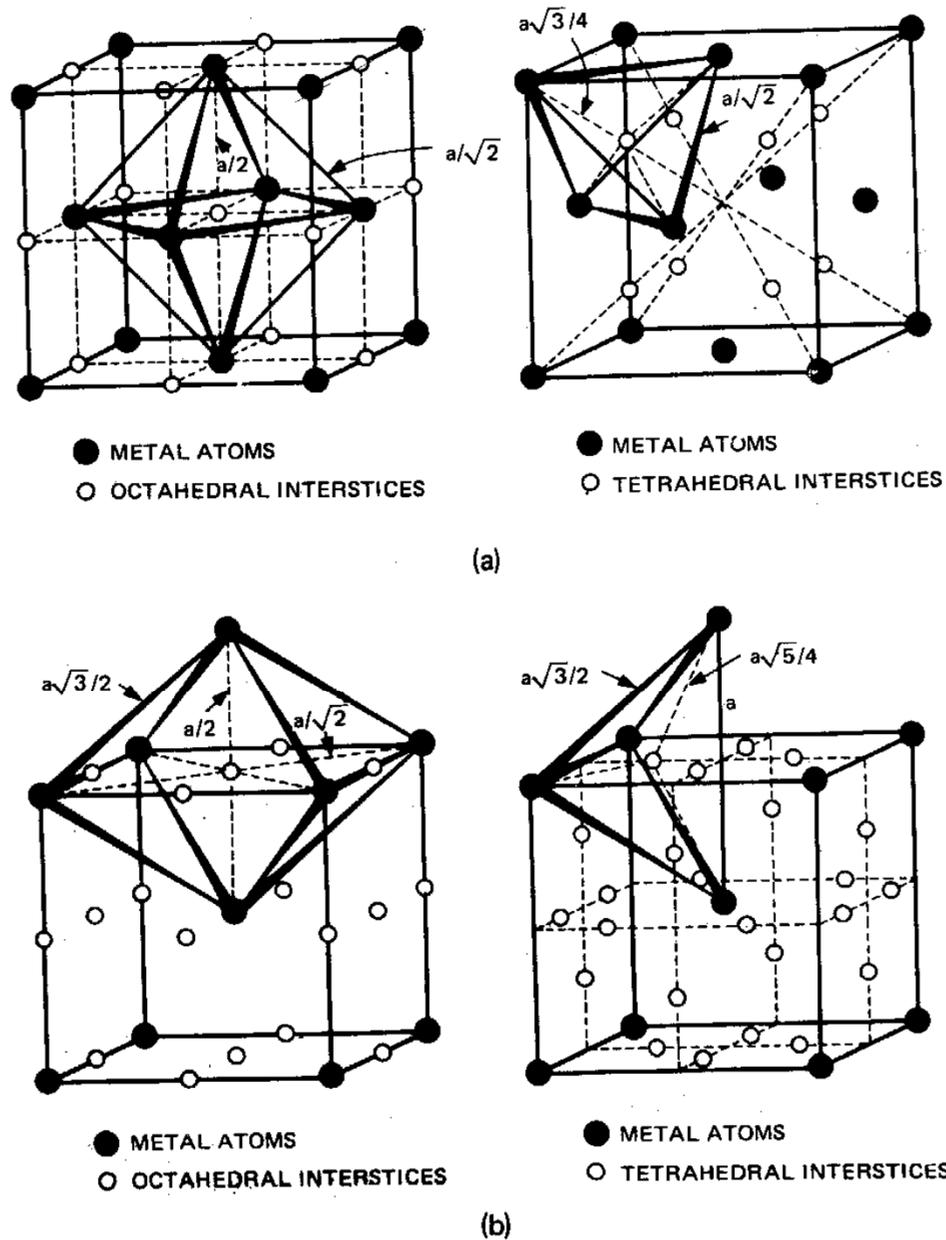
Free space: FCC < BCC but space available per interstitial: FCC > BCC

- * **In spite of $d_6 < d_4$, C & N prefer to occupy the octahedral positions in BCC.**
 → **required considerable distortion but <100> directions~weaker** due to the lower number of near and next nearest neighbors compared to the tetrahedral interstitial position

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.

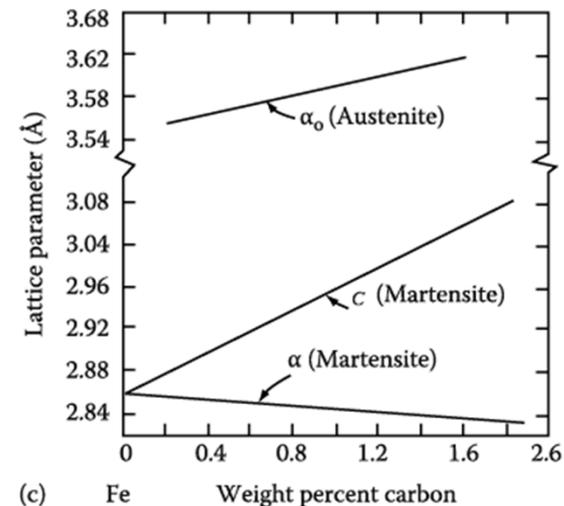
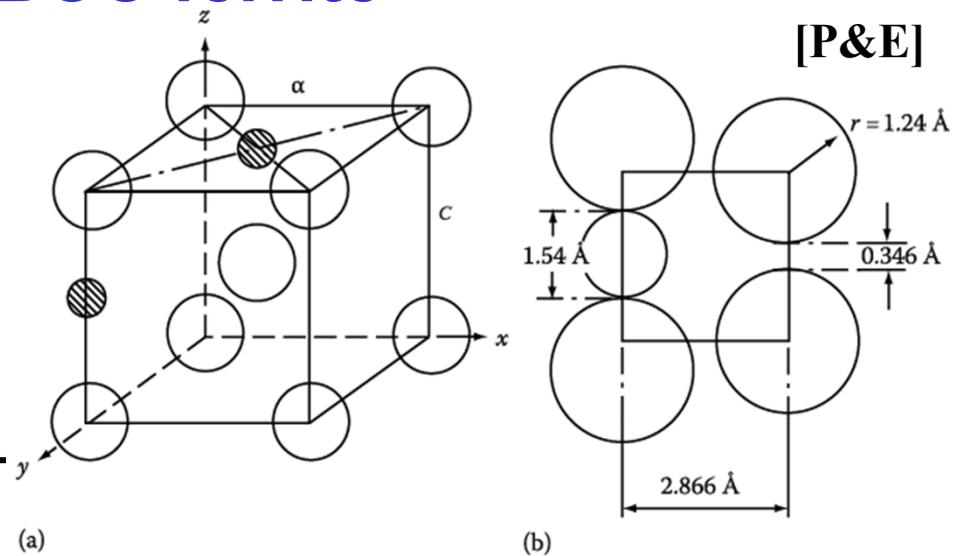


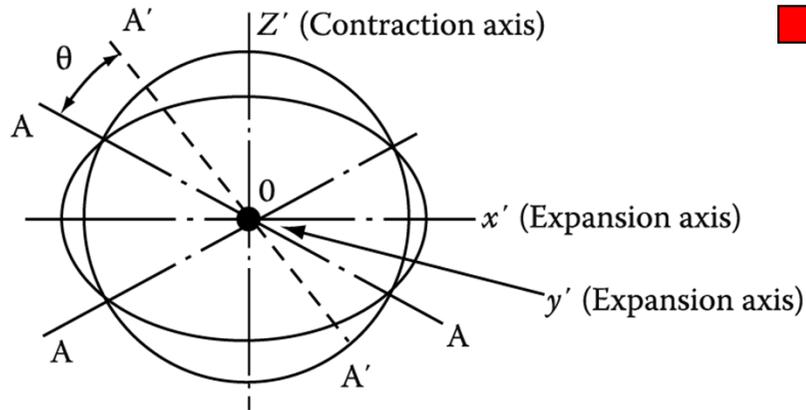
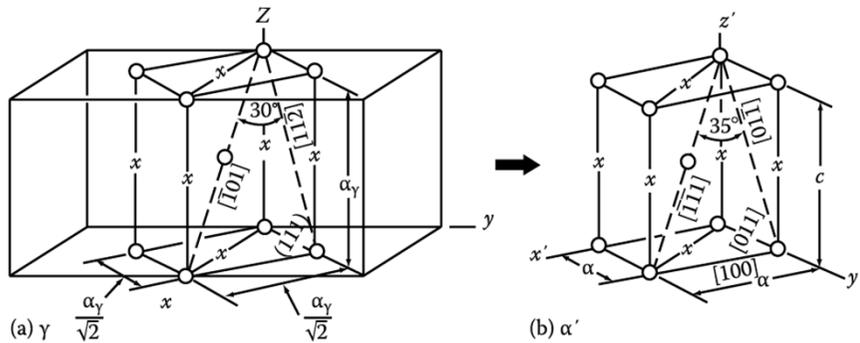
Fig. 6.5 Illustrating (a) possible sites for interstitial atoms in bcc lattice, and (b) the large distortion necessary to accommodate a carbon atom (1.54 \AA diameter) compared with the space available (0.346 \AA). (c) Variation of a and c as a function of carbon content.

Why tetragonal Fe-C martensite?

- At this point, it is worth stopping to ask why a tetragonal martensite forms in iron. The answer has to do with the preferred site for carbon as an interstitial impurity in bcc Fe.
- Remember: Fe-C martensites are unusual for being so strong (& brittle). Most martensites are not significantly stronger than their parent phases.
- Interstitial sites:
 - fcc: octahedral sites radius= 0.052 nm
tetrahedral sites radius= 0.028 nm
 - bcc: octahedral sites radius= 0.019 nm
tetrahedral sites radius= 0.036 nm
- Carbon atom radius = 0.08 nm.
- Surprisingly, it occupies the octahedral site in the bcc Fe structure, despite the smaller size of this site (compared to the tetrahedral sites) presumably because of the low modulus in the <100> directions.

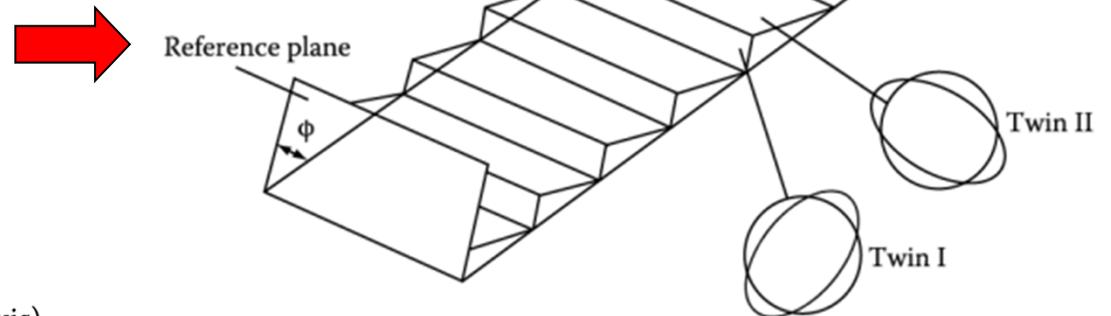
6.2. Martensite crystallography (Orientation btw M & γ)

- $\gamma \rightarrow \alpha'$:
- (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.

Possible atomic model for martensitic transformation: the Bain Model: fcc \rightarrow bct transformation

- For the case of **FCC Fe transforming to BCT ferrite** (Fe-C martensite), there is a basic model known as the **Bain model**.
- The essential point of the Bain model is that it accounts for the structural transformation with a *minimum of atomic motion*.
- Start with two FCC unit cells: contract by 20% in the z direction, and expand by 12% along the x and y directions.

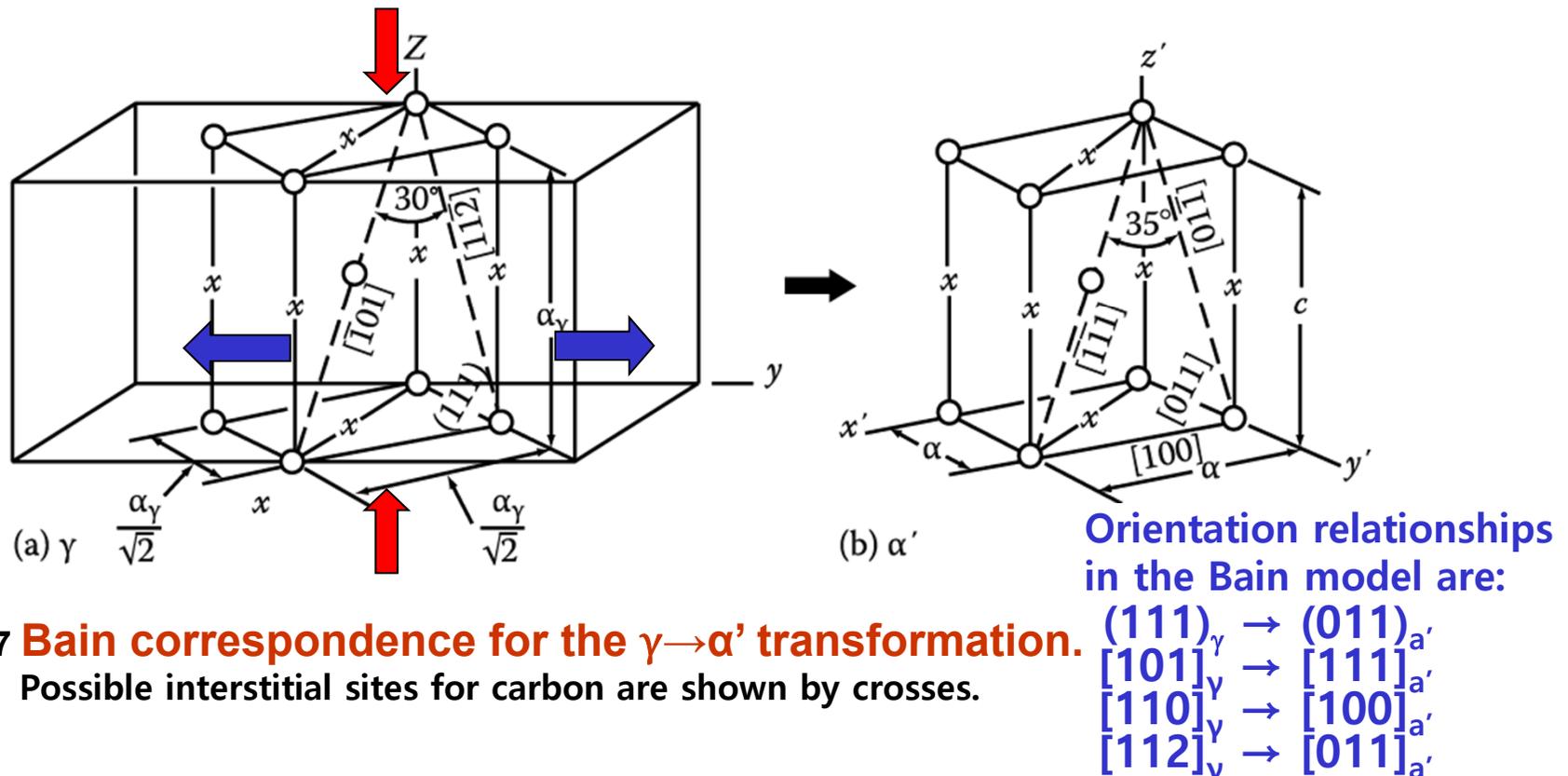


Figure. 6.7 **Bain correspondence for the $\gamma \rightarrow \alpha'$ transformation.**
Possible interstitial sites for carbon are shown by crosses.

Crystallography, contd.

- Although the Bain model explains several basic aspects of martensite formation, additional features must be added for complete explanations (not discussed here).
- **The missing component of the transformation strain is an additional shear that changes the character of the strain so that an invariant plane exists.** This is explained in fig. 6.8.

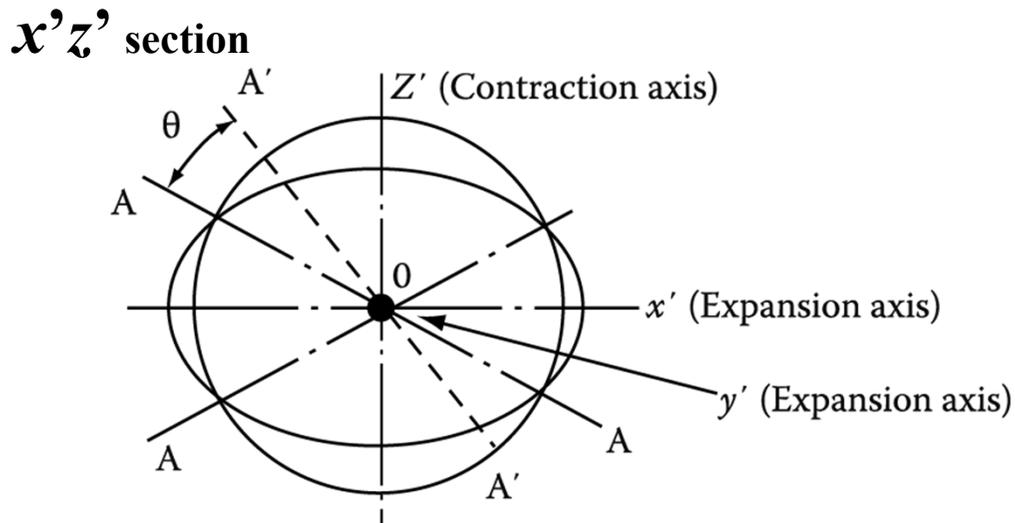


Fig. 6.8 Bain deformation is here simulated by the pure deformation in compressing a sphere elastically to the shape of an oblate ellipsoid. **As in the bain deformation, this transformation involves two expansion axes and one contraction axis.**

Bain deformation = Pure deformation

In this plane, the only vectors that are not shortened or elongated by the Bain distortion are OA or $O'A'$.

However, the vector OY' (perpendicular to the diagram) must be undistorted.

This is clearly not true and therefore **the Bain transformation does not fulfill the requirements of bringing about a transformation with an undistorted plane.** * 변형되지 않는 평면 설명 못함

Hence, the key to the crystallographic theory of martensitic transformations is to postulate an additional distortion which reduces the extension of y' to zero (in fact a slight rotation, θ , of the AO plane should also be made as shown in the figure).

→ The second deformation can be in the form of dislocation slip or twinning.

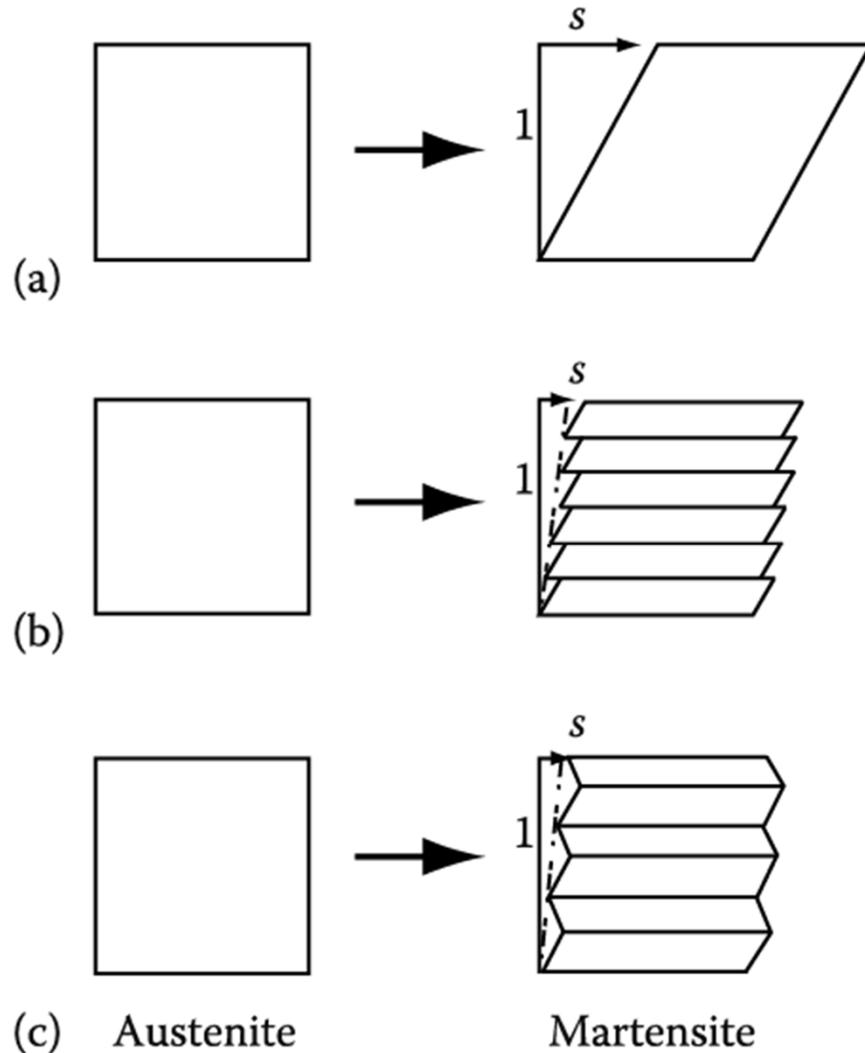
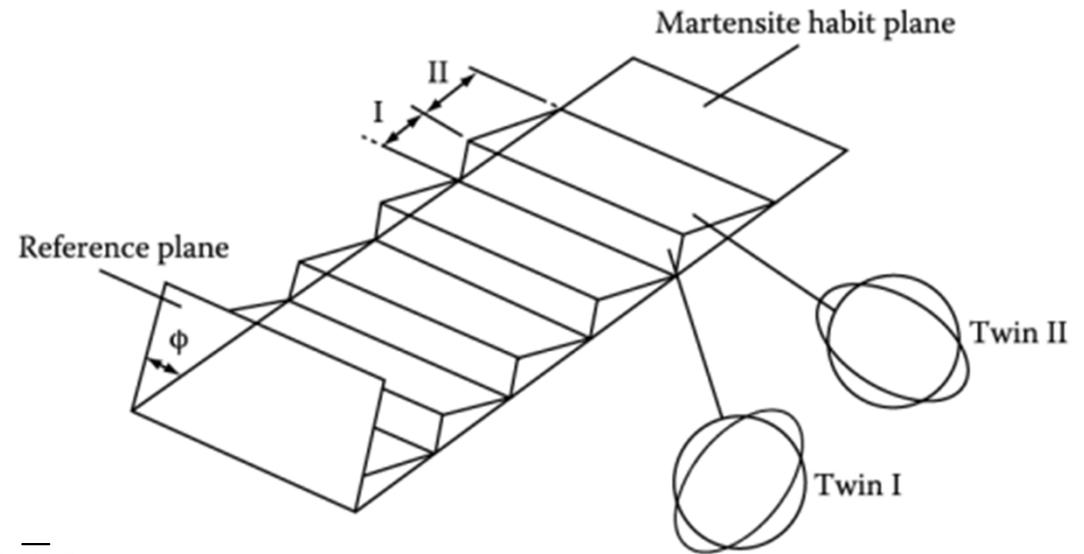
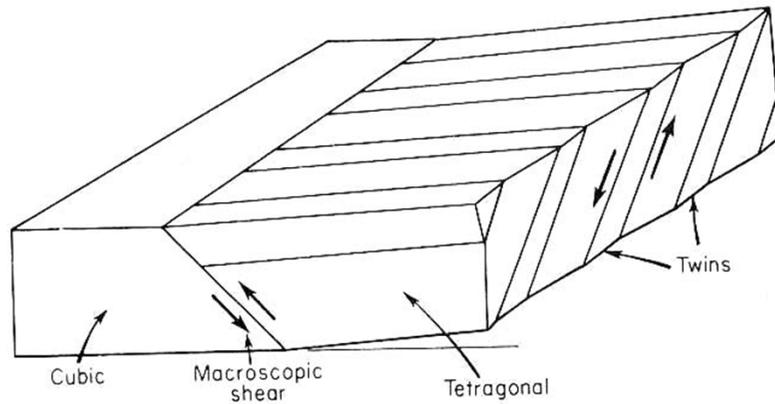


Figure. 6.9 Schematic illustration of how dislocation glide or twinning of the martensite can compensate for a pure lattice deformation such as a Bain deformation and thereby reduce the strain of the surrounding austenite. The transformation shear (s) is defined. Note how s can be reduced by slip or twinning.

Applying the twinning analogy to the Bain model,
the physical requirements of the theory are satisfied.



Slip or Twinning on
 $\{11\bar{2}\} \langle 111 \rangle$ in α $\{110\} \langle 1\bar{1}0 \rangle$ in γ

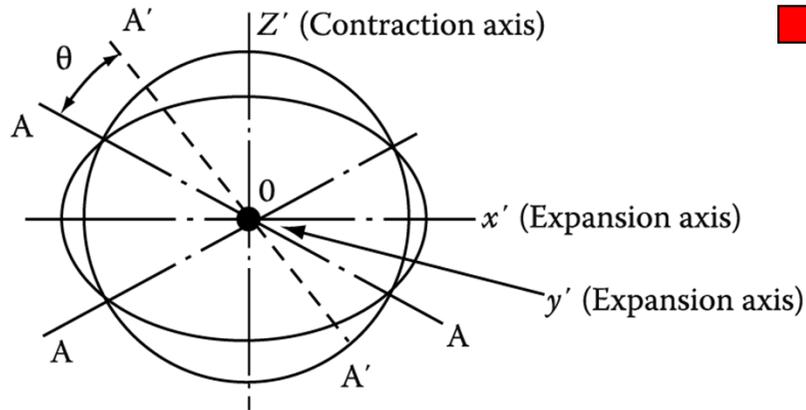
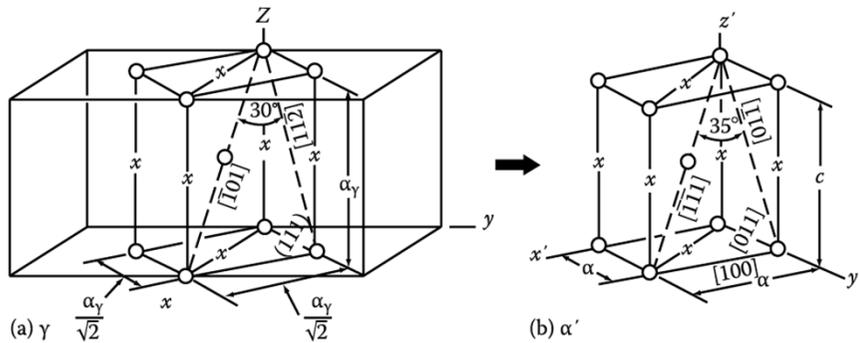
Twins in Martensite

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

- On the basis, the habit plane of the M plate can be defined as a plane in the austenite which undergoes **not net (macroscopic) distortion (=average distortion over many twins is zero)**
- Local strain E by twins at the edge of the plate, but if the plate is very thin (a few atomic spacings) this strain can be relatively small.

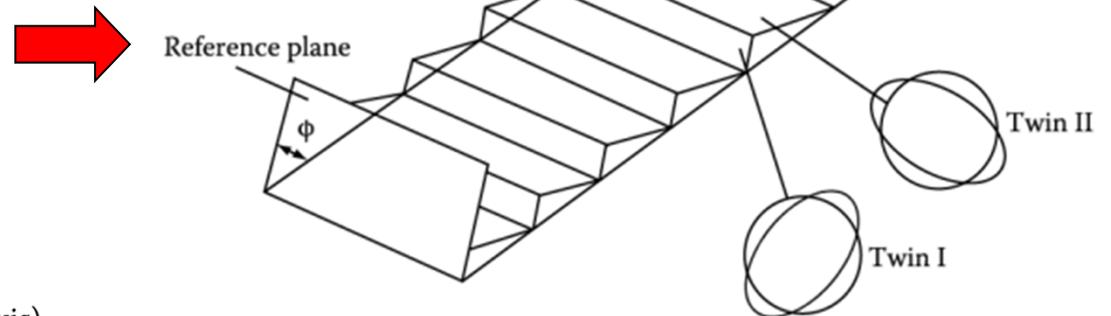
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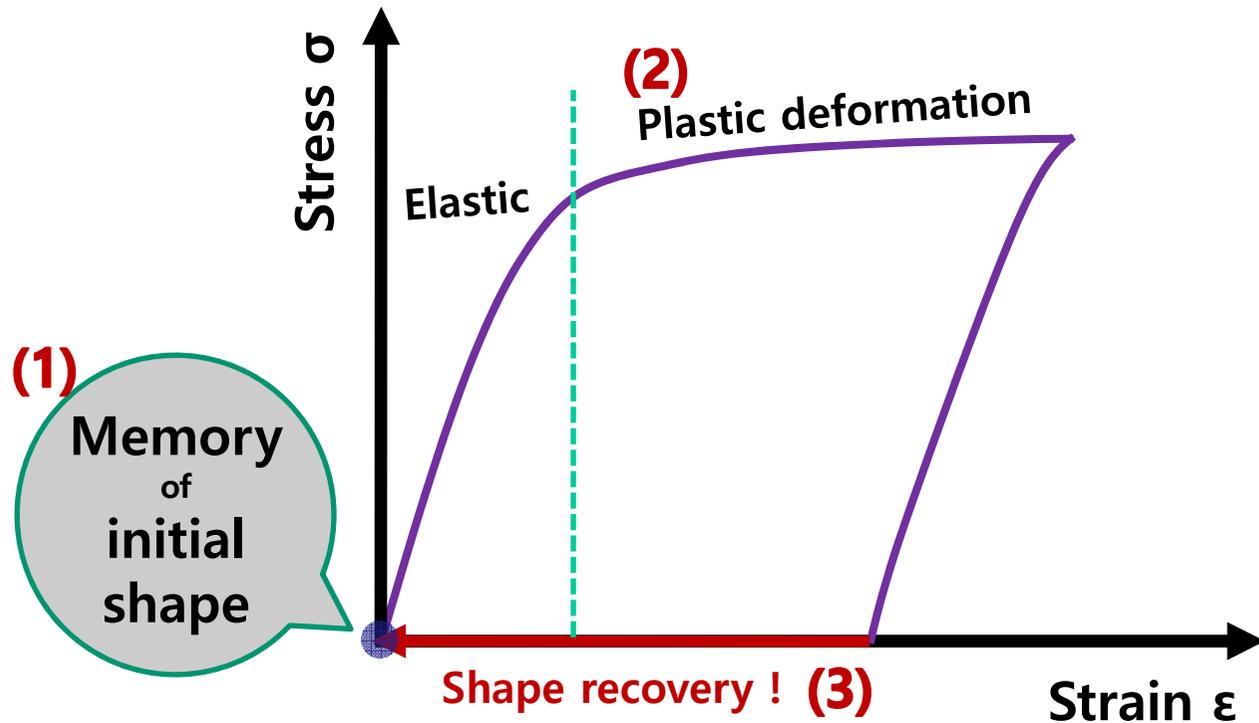
Representative Diffusionless Transformation

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) |

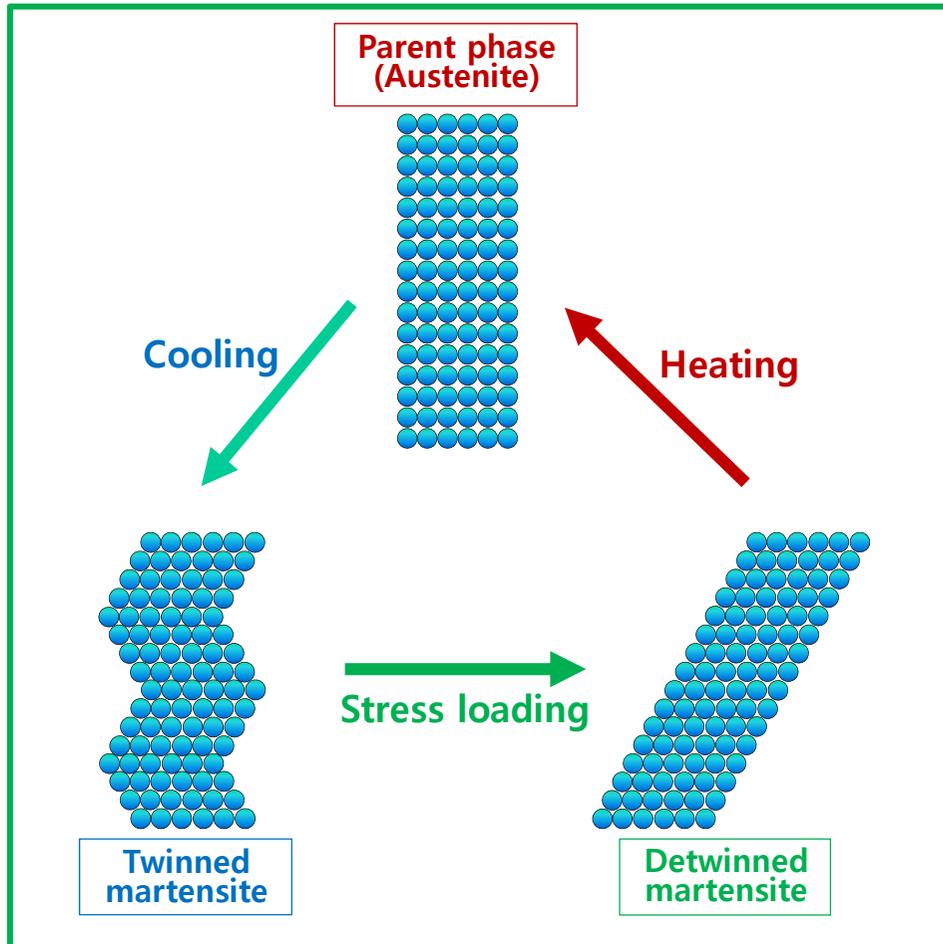
Principles

How can shape memory effect occur?

Principles

How can shape memory effect occur?

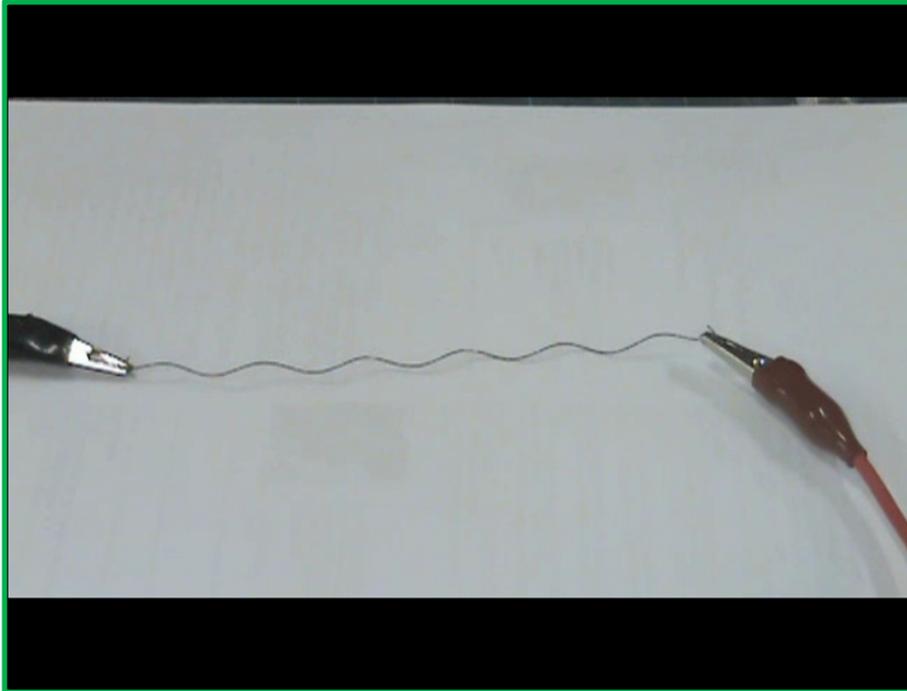
Principles- shape memory process



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

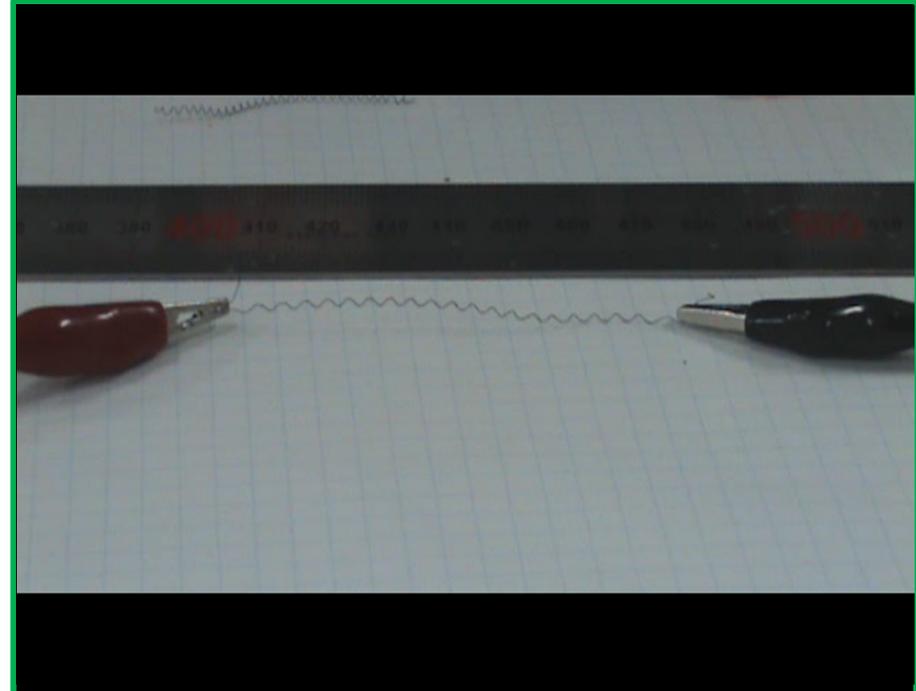
▼ One-way SME



↳ A_f 이상의 고온 형상만을 기억

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

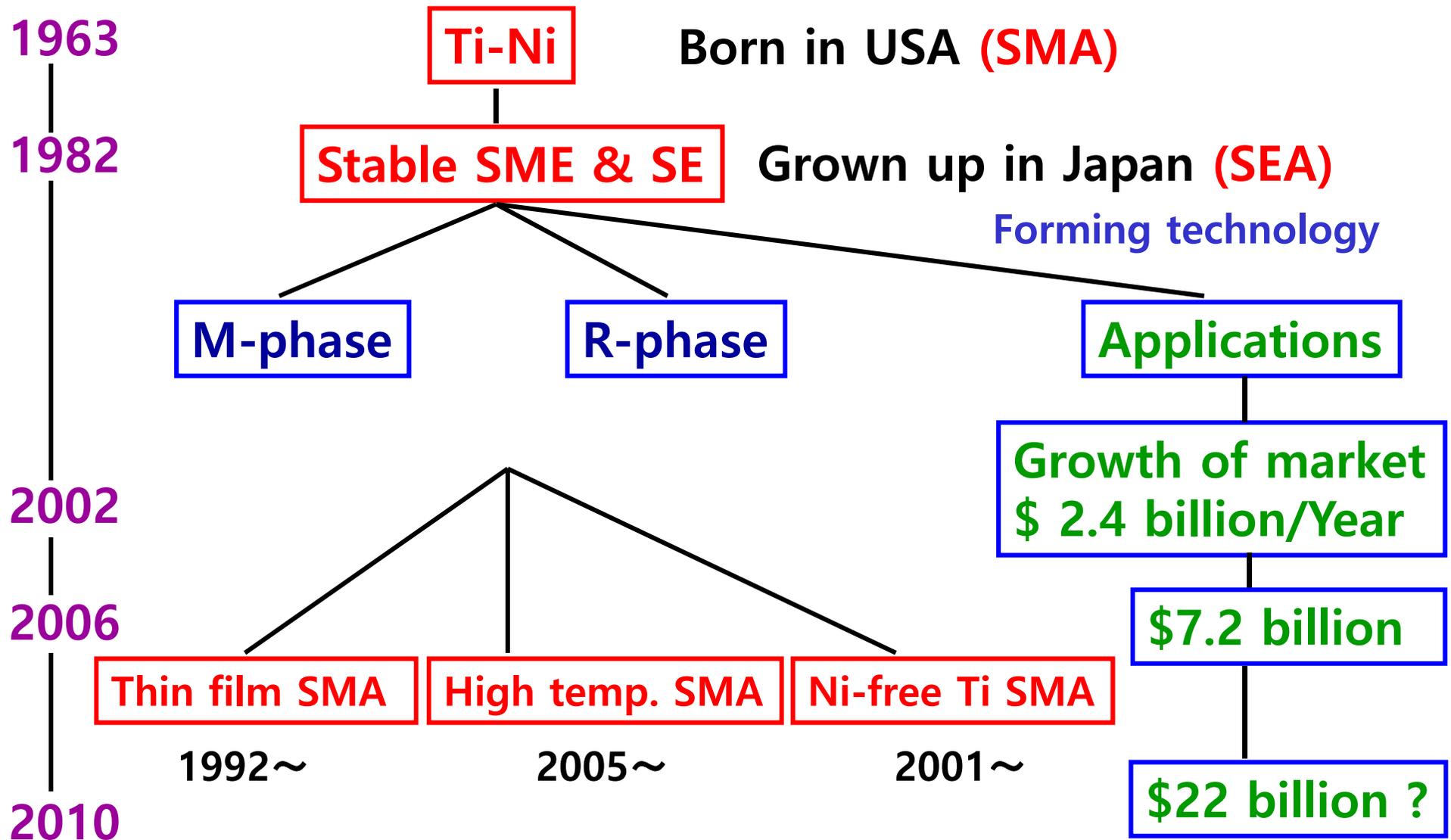
▼ Two-way SME



↳ 고온($> A_f$) 형상과 저온($< M_f$) 형상을 모두 기억

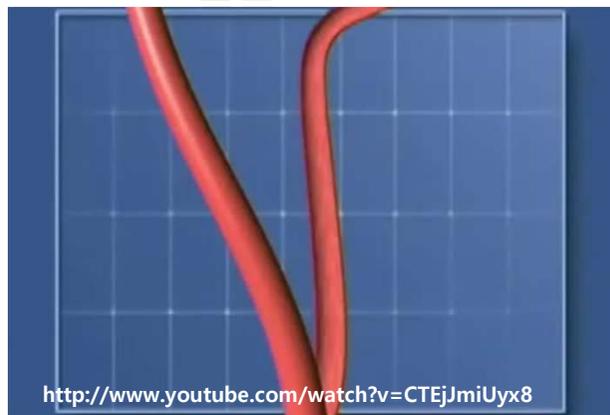
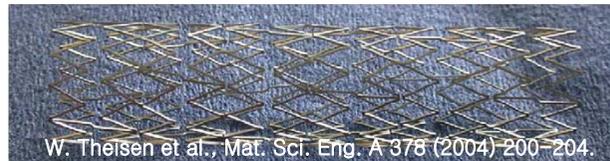
- 반복적인 변형으로 인한 형상기억합금 내 전위 밀도의 상승 & 특정방향 응력장의 형성
- 저온에서 반복소성변형 방향으로 회복

Summary



* Application of SMAs

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



▲ 생체의료 부문: 첨단의료재료
(stent, 치열교정용 강선 등)



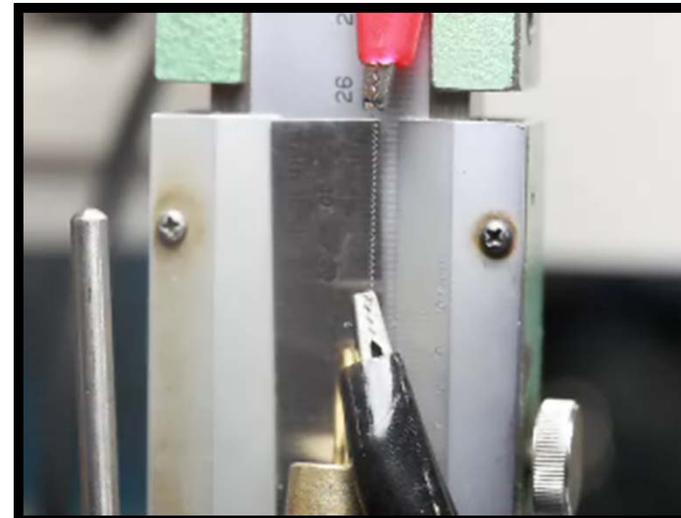
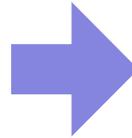
▲ 심해저/우주항공 부문: 극지재료
(잠수함, 태양전지판 등)

* SMA Actuator

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

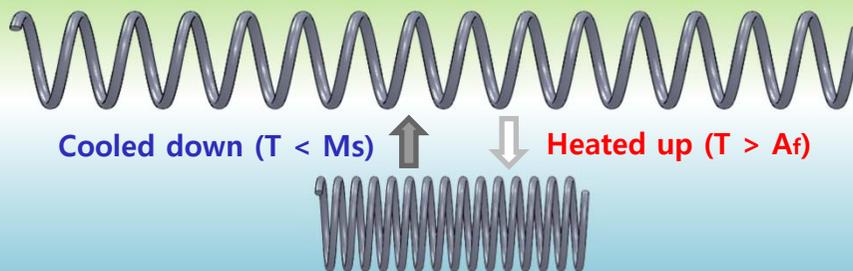


▲ 기존의 매크로 스케일 액츄에이터 (모터-기어 방식)



▲ SMA 스프링 액츄에이터

SMA Spring Actuator



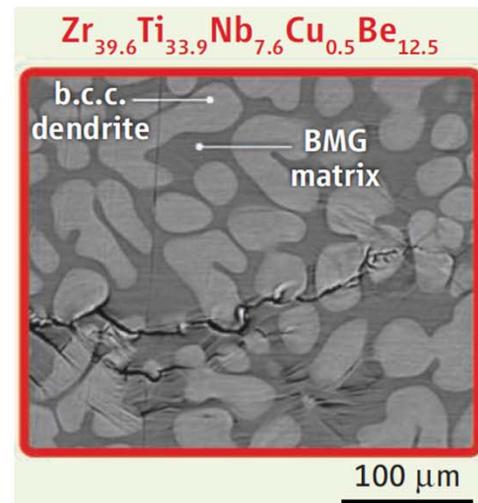
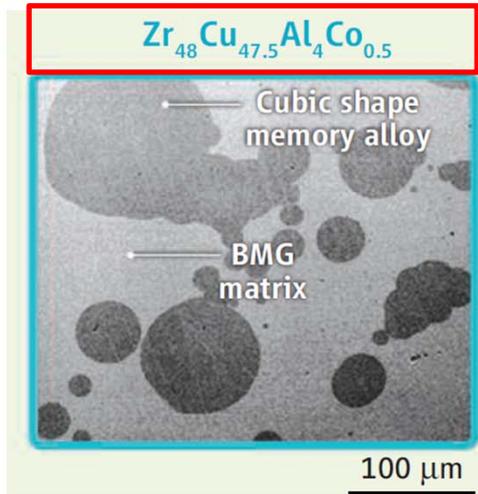
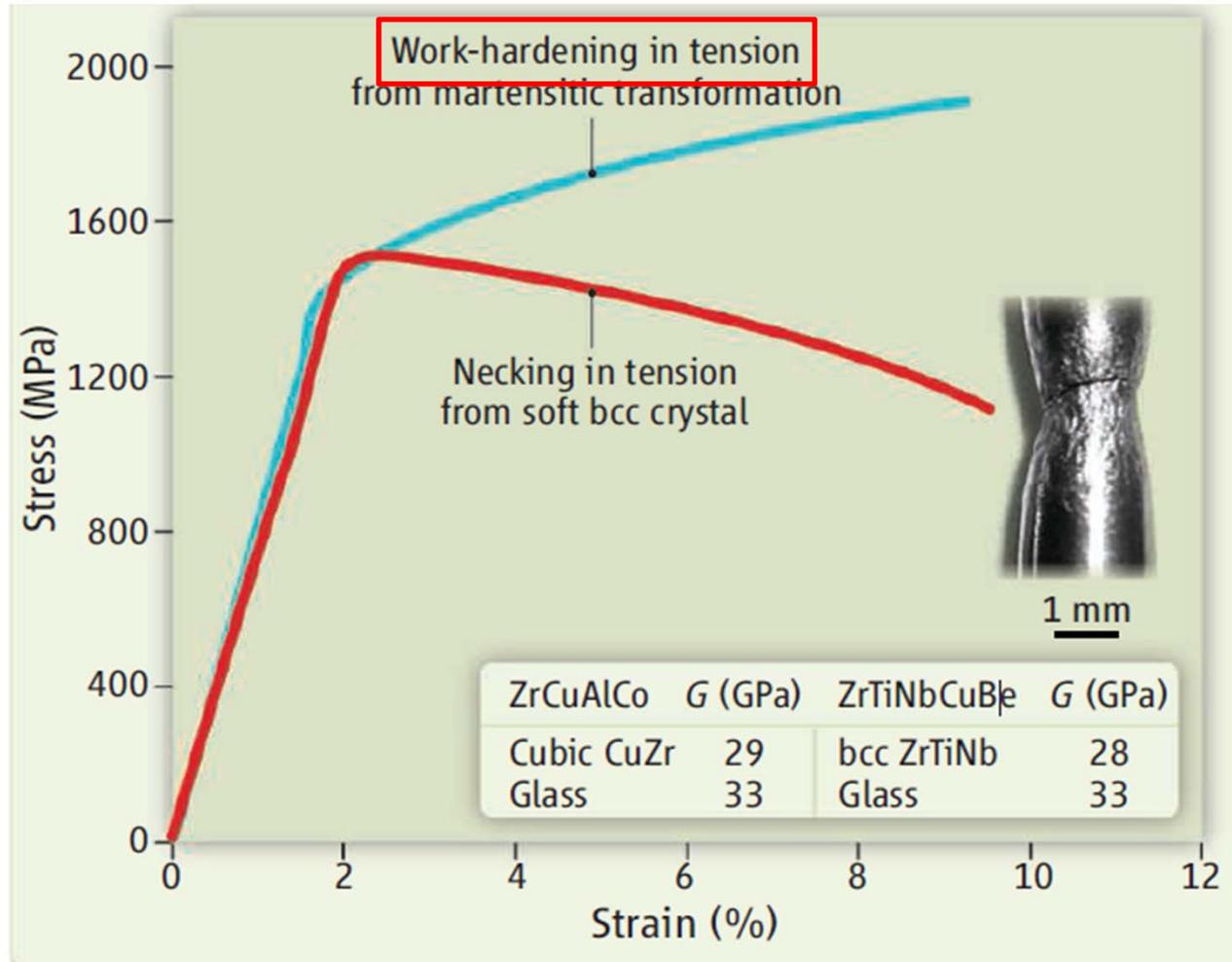
재료의 수축과 신장을 통하여 기계적인 동작을 가능하게 함.

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

Shape Memory Bulk Metallic Glass Composites

Douglas C. Hofmann

Glass-forming and shape memory metals may provide a route to fabricating materials with enhanced mechanical properties.



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

▶ Alloy system Cu-Zr-Al system

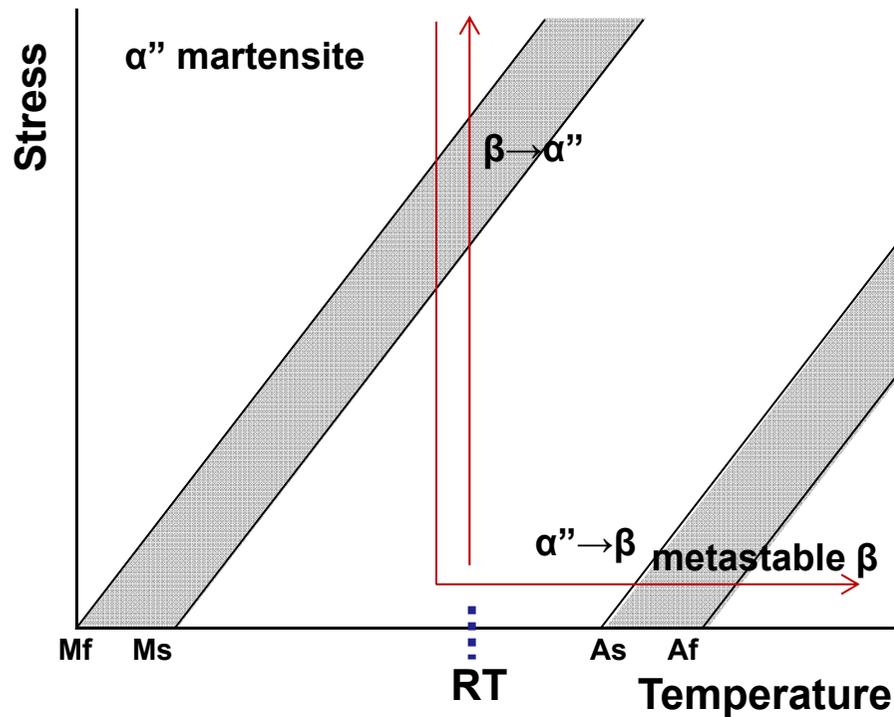
Secondary phase CuZr
Metastable B2 phase at RT
"Shape Memory Behavior"



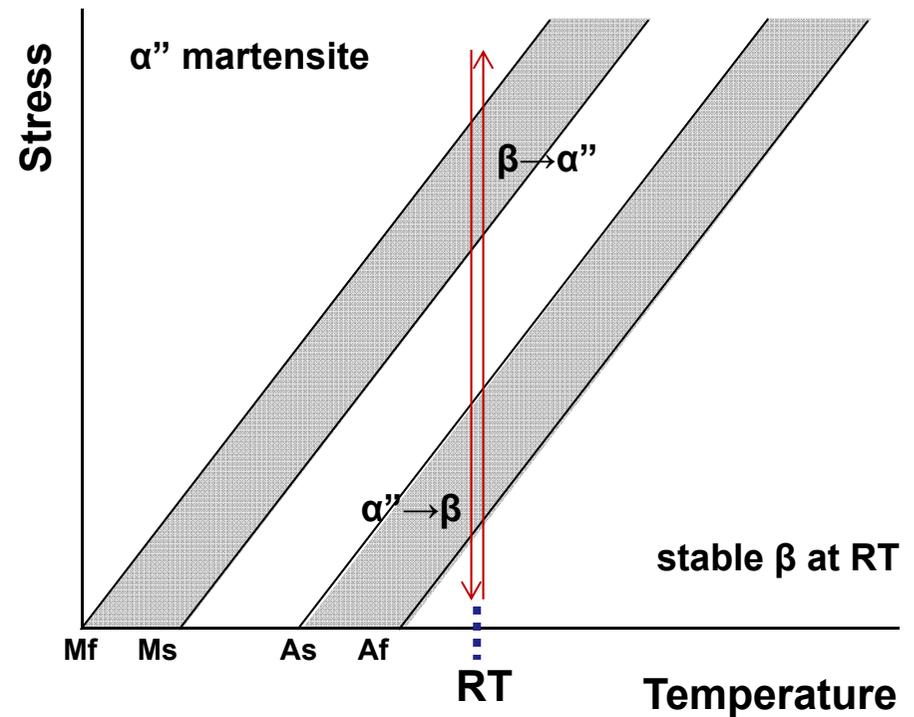
Ti-Cu-Ni system

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:
 Ti_{49} -Cu-Ni-X

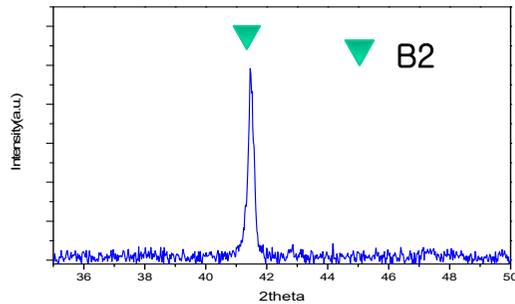
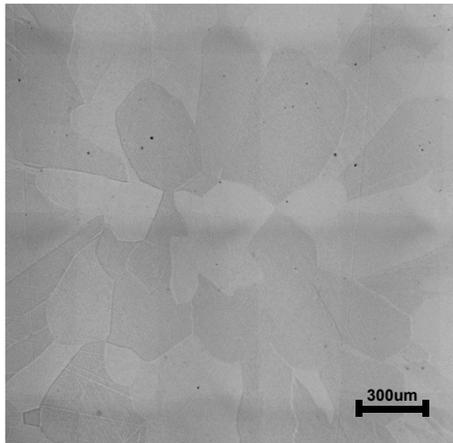
$\Phi 3mm$ suction casting
-Fully crystalline B_2

► **Stress-induced** phase transformation

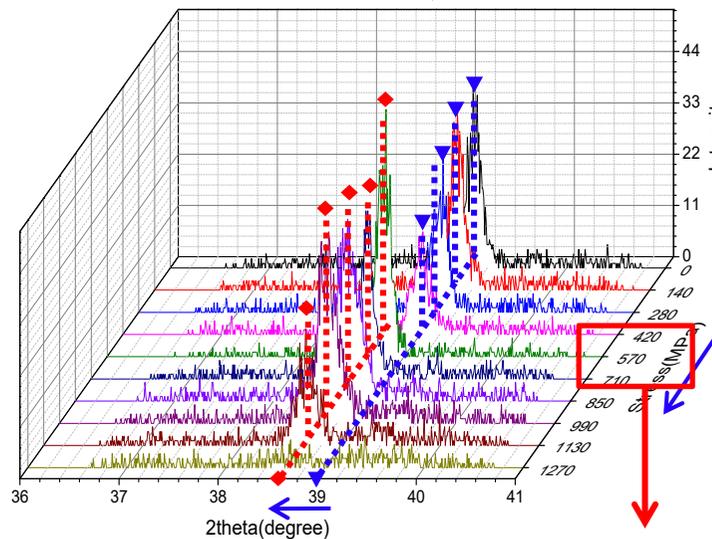
In-situ neutron diffraction measurement during compression

► **Temperature-induced** phase transformation

DSC measurement (during cooling)

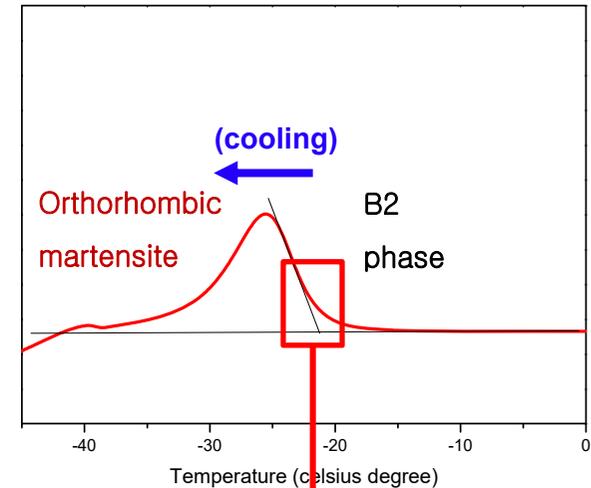


▼ B_2 phase
◆ Orthorhombic martensite phase



Phase transformation stress

= 570MPa



Martensite start T (Ms)

= -22°C

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

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 6.1-6.6 (pages 434-435)
until 16th December (before exam)**

Good Luck!!

FINAL (16th December, 9 AM-1PM)

Place: 33-328 & 330

**Scopes: Text: page 146 (chapter 3.3) ~
page 397 (chapter 6.2)/**

Teaching notes: 12~23/

QUIZ and Homeworks

Good Luck!!