

**2015 Fall**

# **“Phase Transformation *in* Materials”**

**12.09.2015**

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**Office hours: by an appointment**

# 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

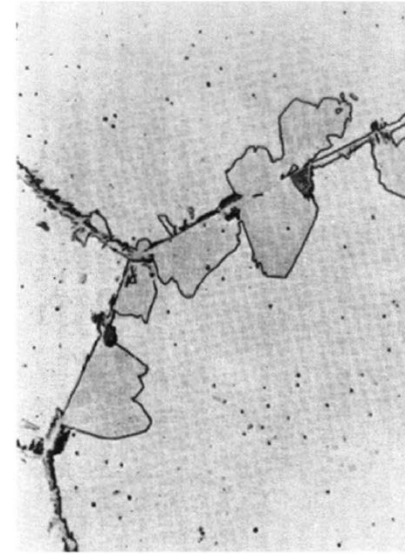
(Ch4) Solidification: Liquid  $\rightarrow$  Solid

(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. 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  $\alpha'$ ) forms as **platelets within grains**.

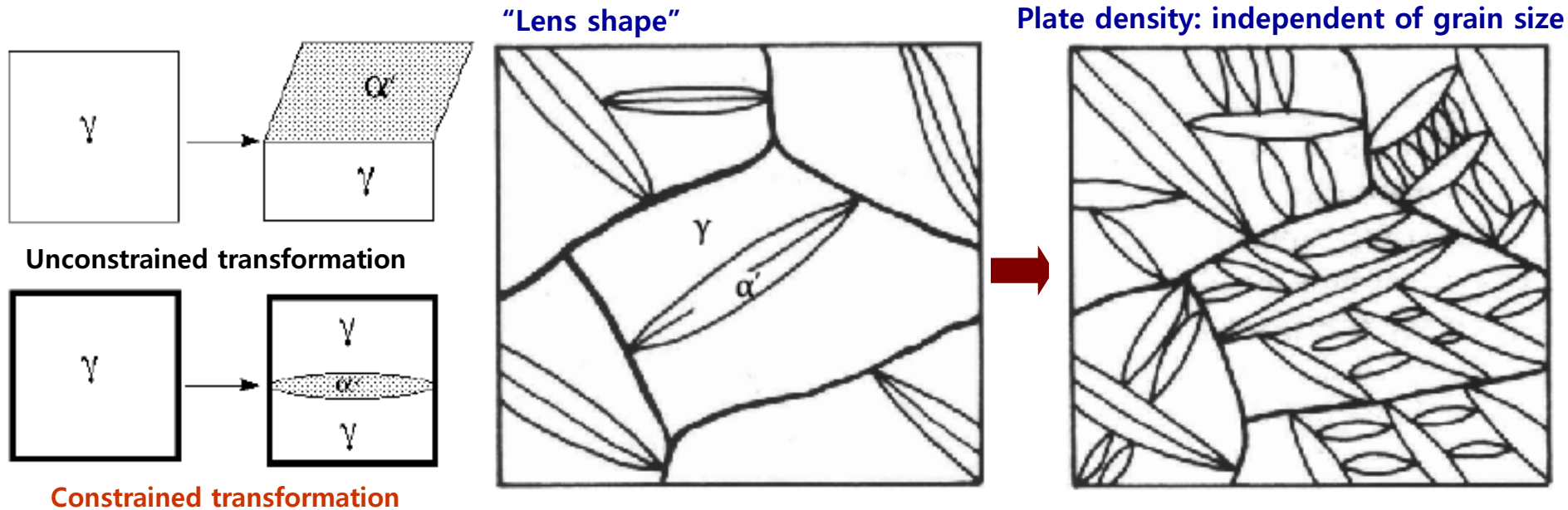


Fig. 6.1 Growth of martensite with increasing cooling below  $M_s$ .

→ Martensite formation rarely goes to completion

# 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  $T_0$** .

$$\Delta G = \frac{L\Delta T}{T_m}$$

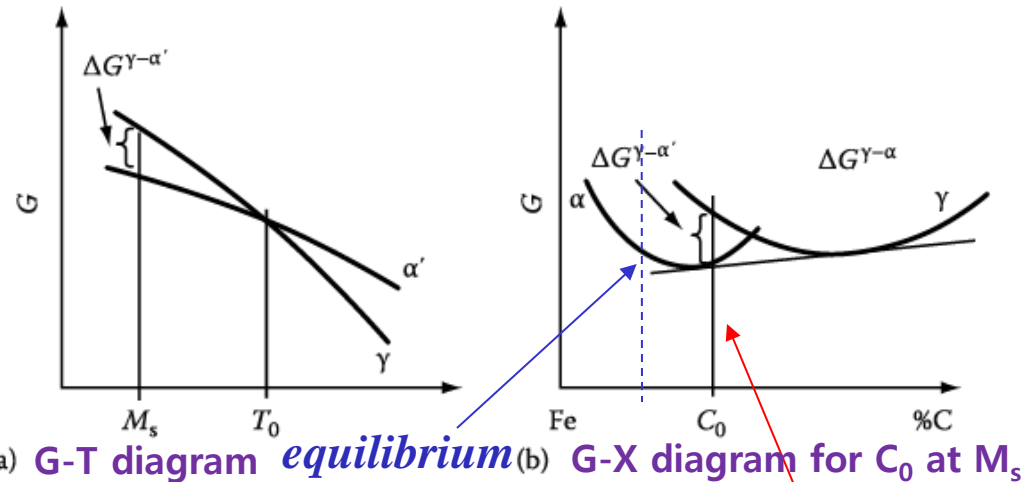


$$\Delta G^{\gamma \rightarrow \alpha'} = \Delta H^{\gamma \rightarrow \alpha'} \Delta T / T_0 = \Delta H^{\gamma \rightarrow \alpha'} \frac{(T_0 - M_s)}{T_0}$$

Alloy	$\Delta H^{\gamma \rightarrow \alpha'}$ (J mol <sup>-1</sup> )	$T_0 - M_s$ (K)	$-\Delta G^{\gamma \rightarrow \alpha'}$ (J mol <sup>-1</sup> )
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	<b>* Large differences in <math>\Delta G^{\gamma \rightarrow \alpha'}</math> btw disordered and ordered alloys (a relatively small <math>\Delta T</math>)</b>		
Fe-Pt	2390	~150	~1260
Disordered			

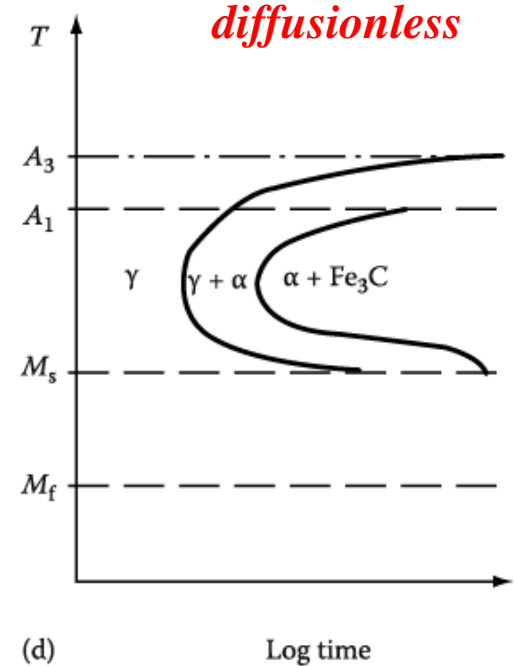
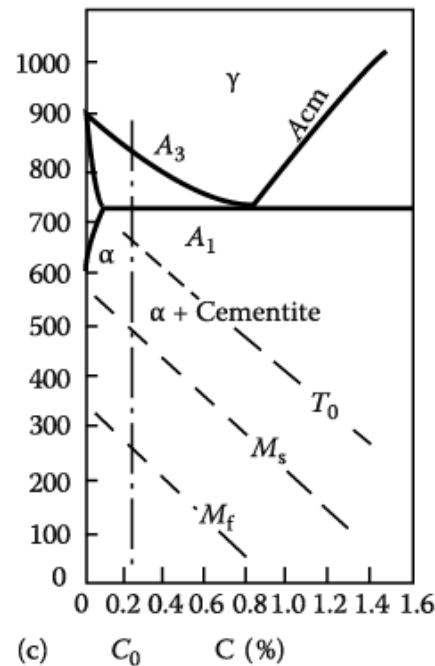
Source: From Guénin, G., PhD thesis, Polytechnical Institute of Lyon, 1979.

# Various ways of showing the martensite transformation



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

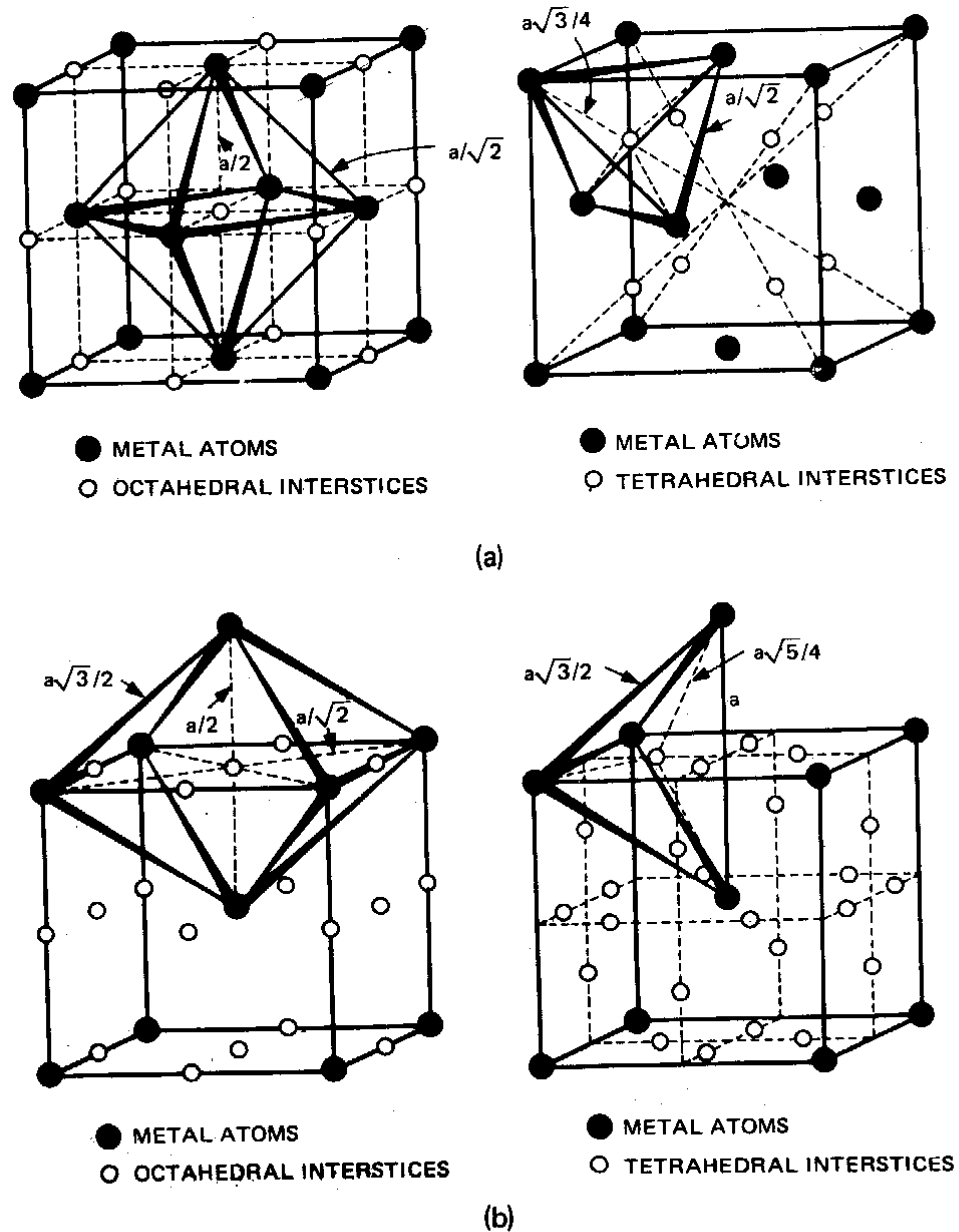
Some retained austenite can be left even below  $M_f$ . In particular, as much as 10%-15% retained austenite is a common feature of especially the higher C content alloys such as those used for ball bearing steels.



# 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.)

# 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.



# 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.

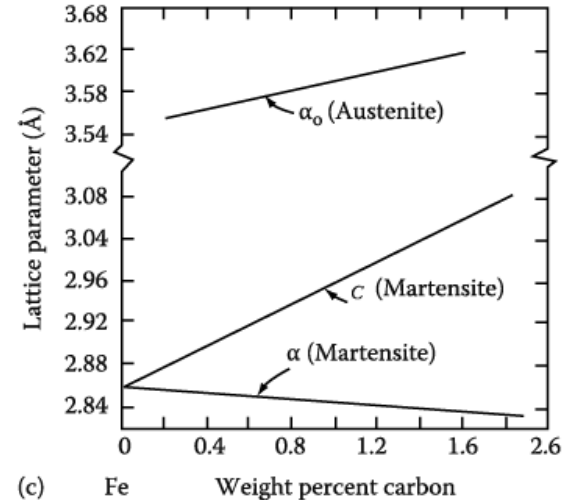
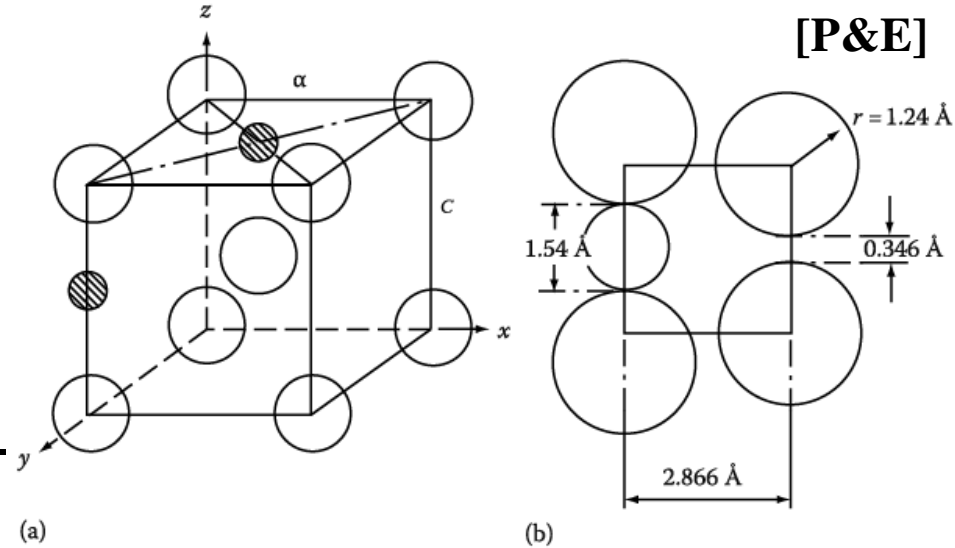
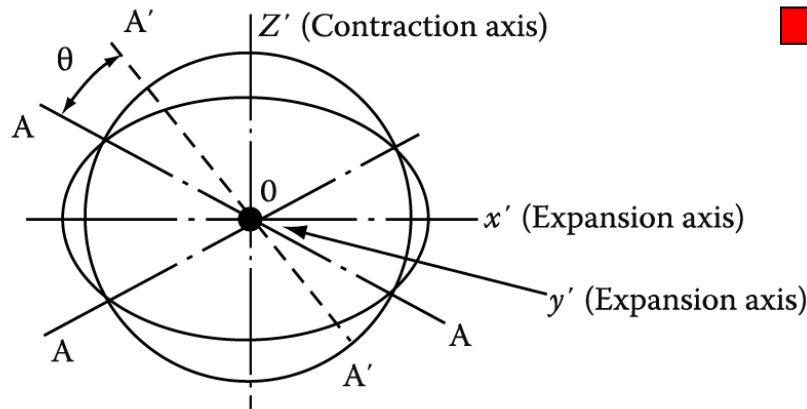
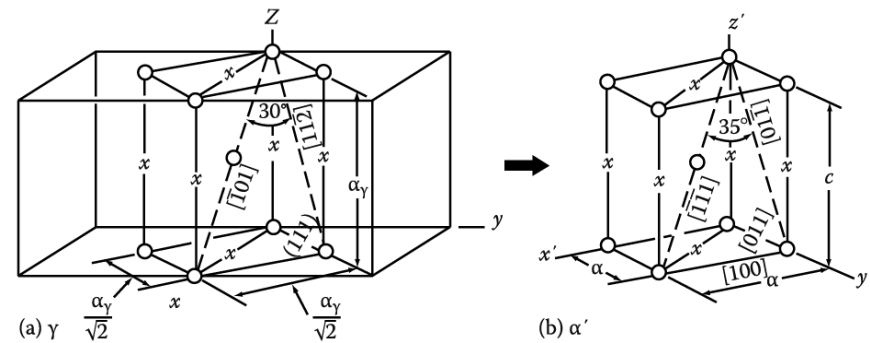


Fig. 6.5 Illustrating (a) possible sites for interstitial atoms in bcc lattice, and (b) the large distortion necessary to accommodate a carbon atom (1.54 Å diameter) compared with the space available (0.346 Å). (c) Variation of  $a$  and  $c$  as a function of carbon content.

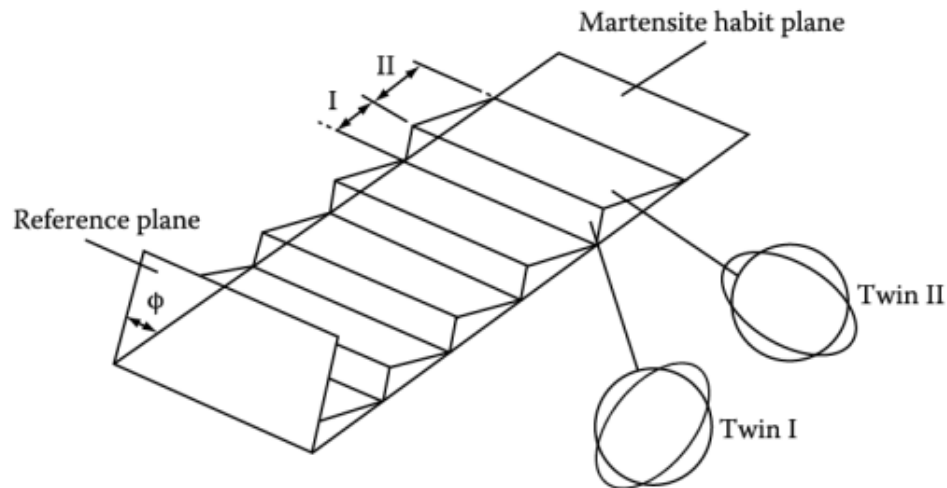
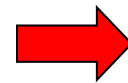
## 6.2. Martensite crystallography (Orientation btw M & $\gamma$ )

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

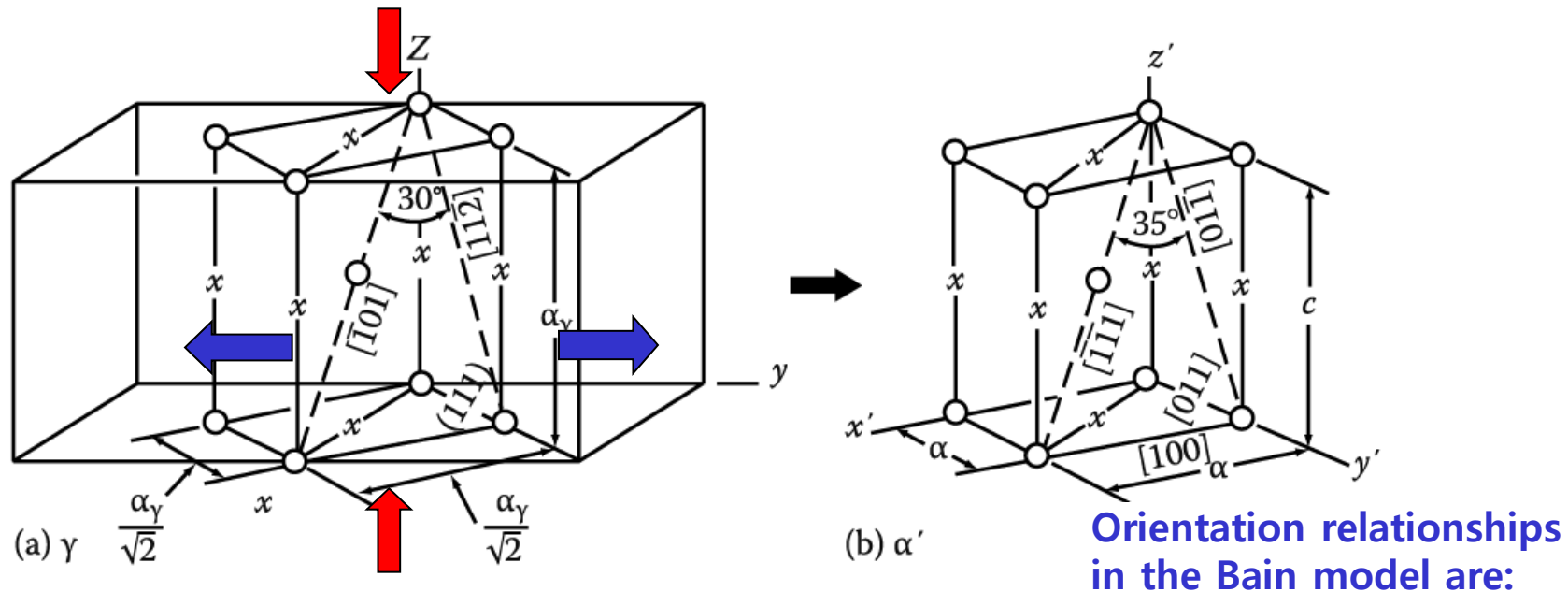


Figure. 6.7 **Bain correspondence for the  $\gamma \rightarrow \alpha'$  transformation.**  
Possible interstitial sites for carbon are shown by crosses.

$$\begin{aligned}
 [111]_\gamma &\rightarrow [011]_{\alpha'} \\
 [101]_\gamma &\rightarrow [111]_{\alpha'} \\
 [110]_\gamma &\rightarrow [100]_{\alpha'} \\
 [112]_\gamma &\rightarrow [011]_{\alpha'}
 \end{aligned}$$

# 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.

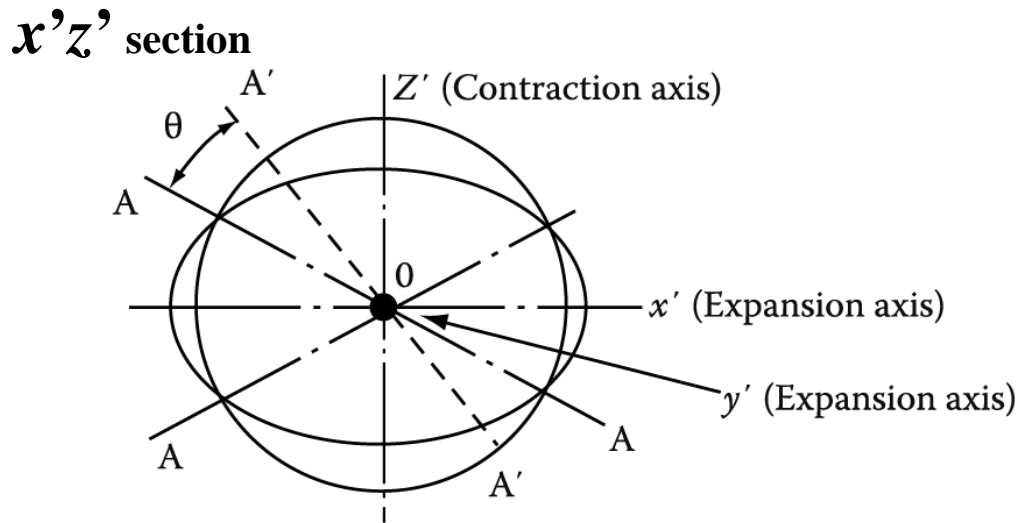


Fig. 6.8 Bain deformation is here simulated by the pure deformation in compressing a sphere elastically to the shape of an oblate ellipsoid. **As in the bain deformation, this transformation involves two expansion axes and one contraction axis.**

**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,  $\theta$ , 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.

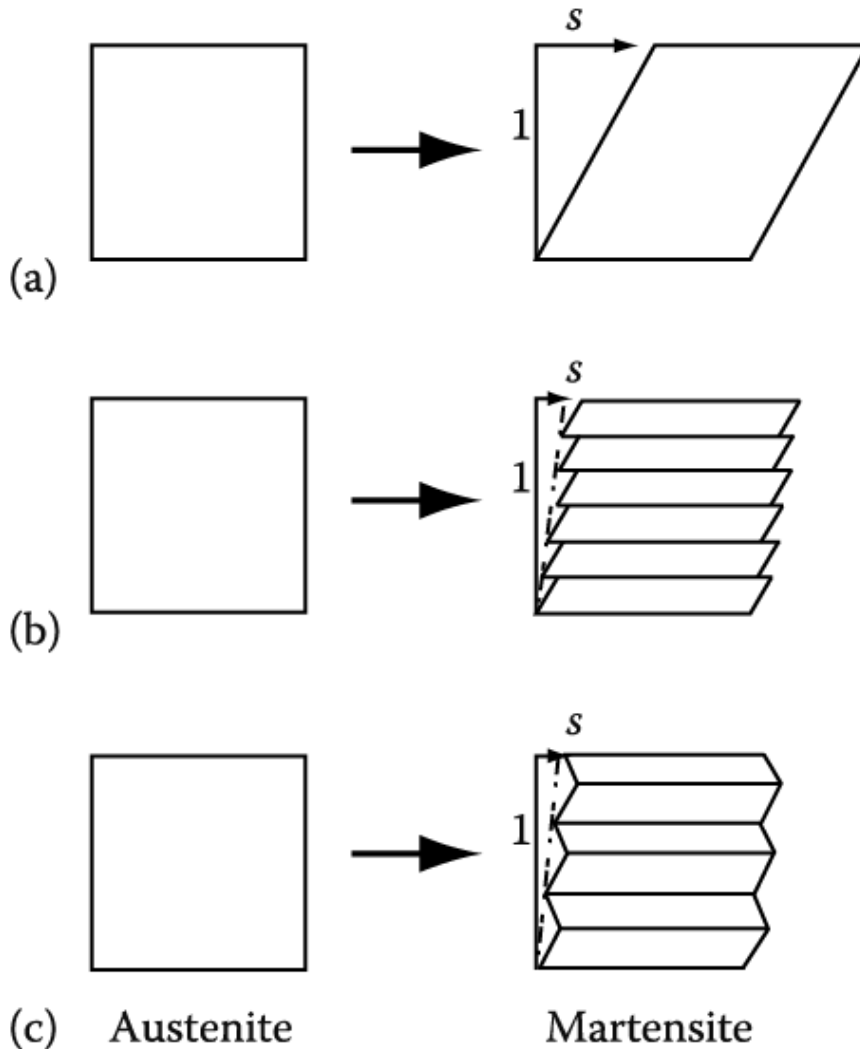
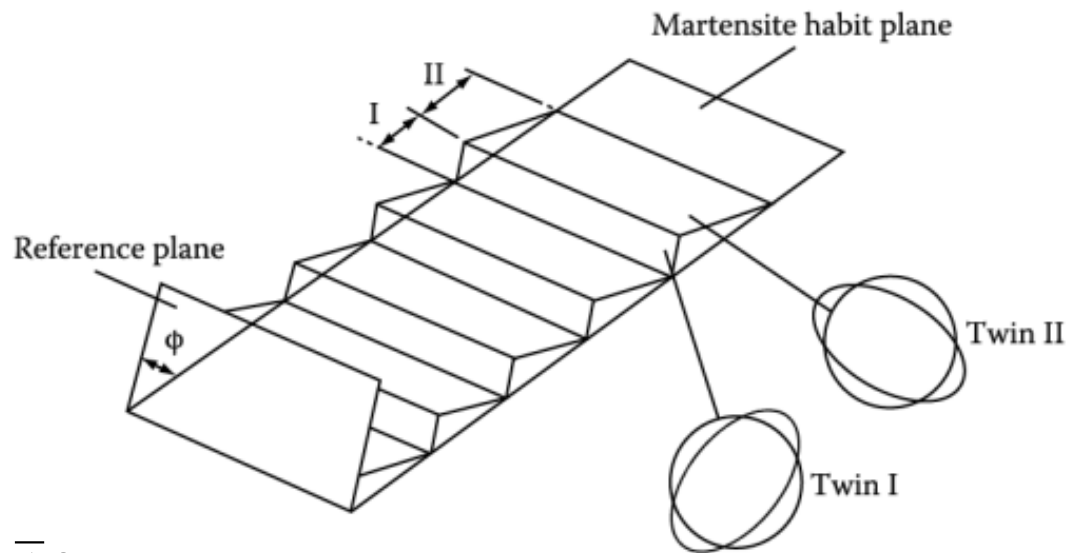
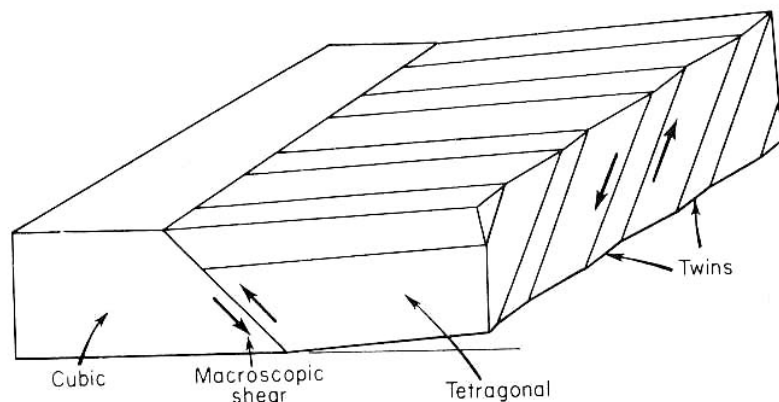


Figure. 6.9 Schematic illustration of how dislocation glide or twinning of the martensite can compensate for a pure lattice deformation such as a Bain deformation and thereby reduce the strain of the surrounding austenite. The transformation shear ( $s$ ) is defined. Note how  $s$  can be reduced by 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  $\alpha$        $\{110\} \langle 1\bar{1}0 \rangle$  in  $\gamma$

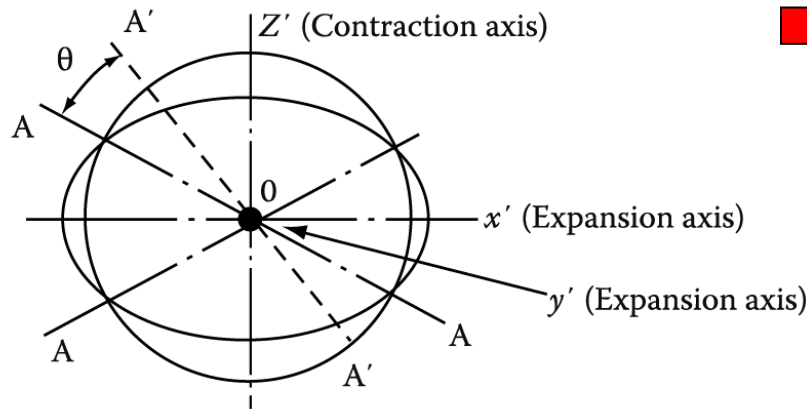
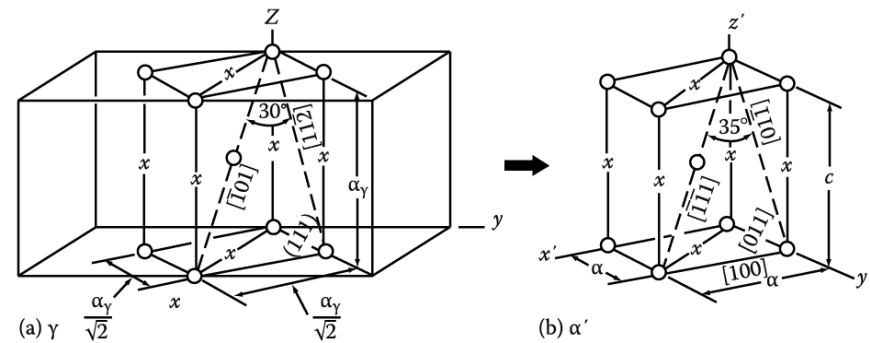
## Twins in Martensite

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.

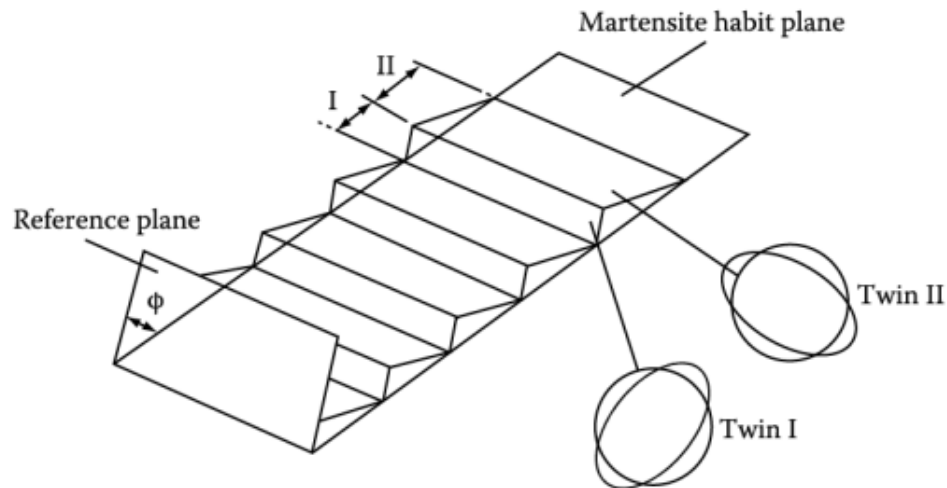
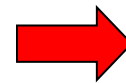
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**Bain Model for martensite**

Applying the twinning analogy to the Bain model,



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# Representative Diffusionless Transformation

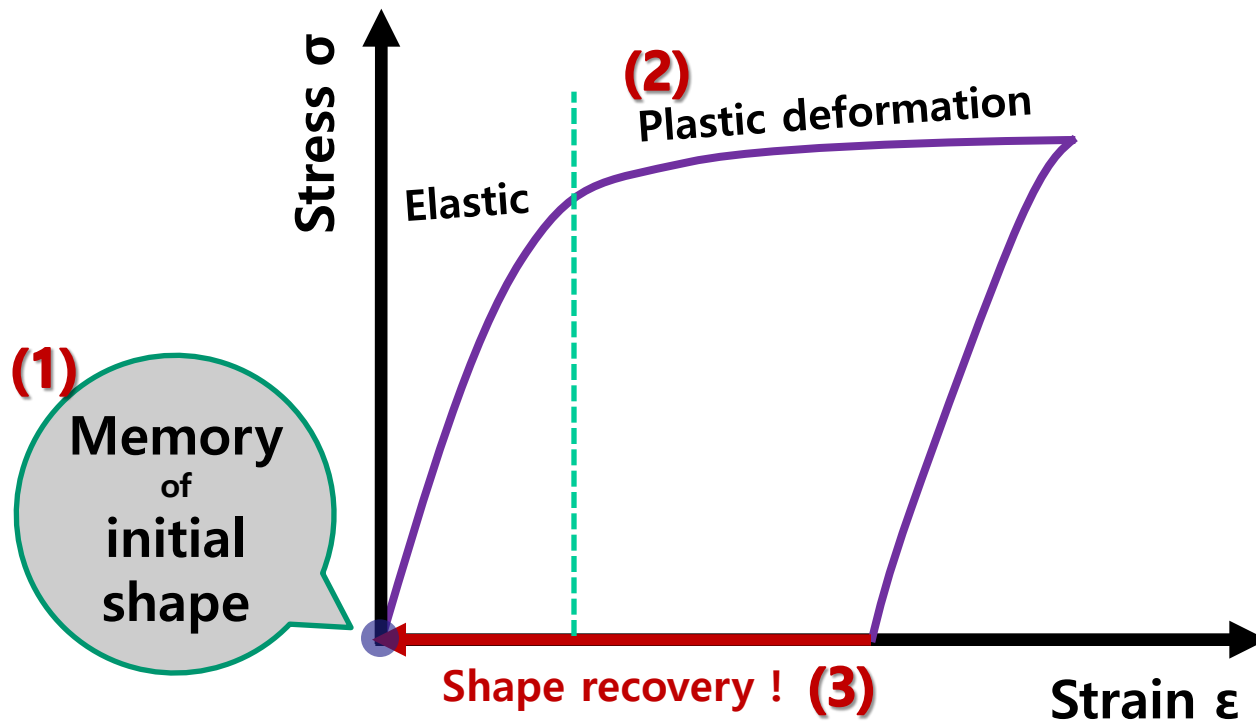
**Martensitic transformation in Ni-Ti alloy ;**  
**55~55.5 wt%Ni - 44.5~45 wt%Ti (“Nitinol”)**



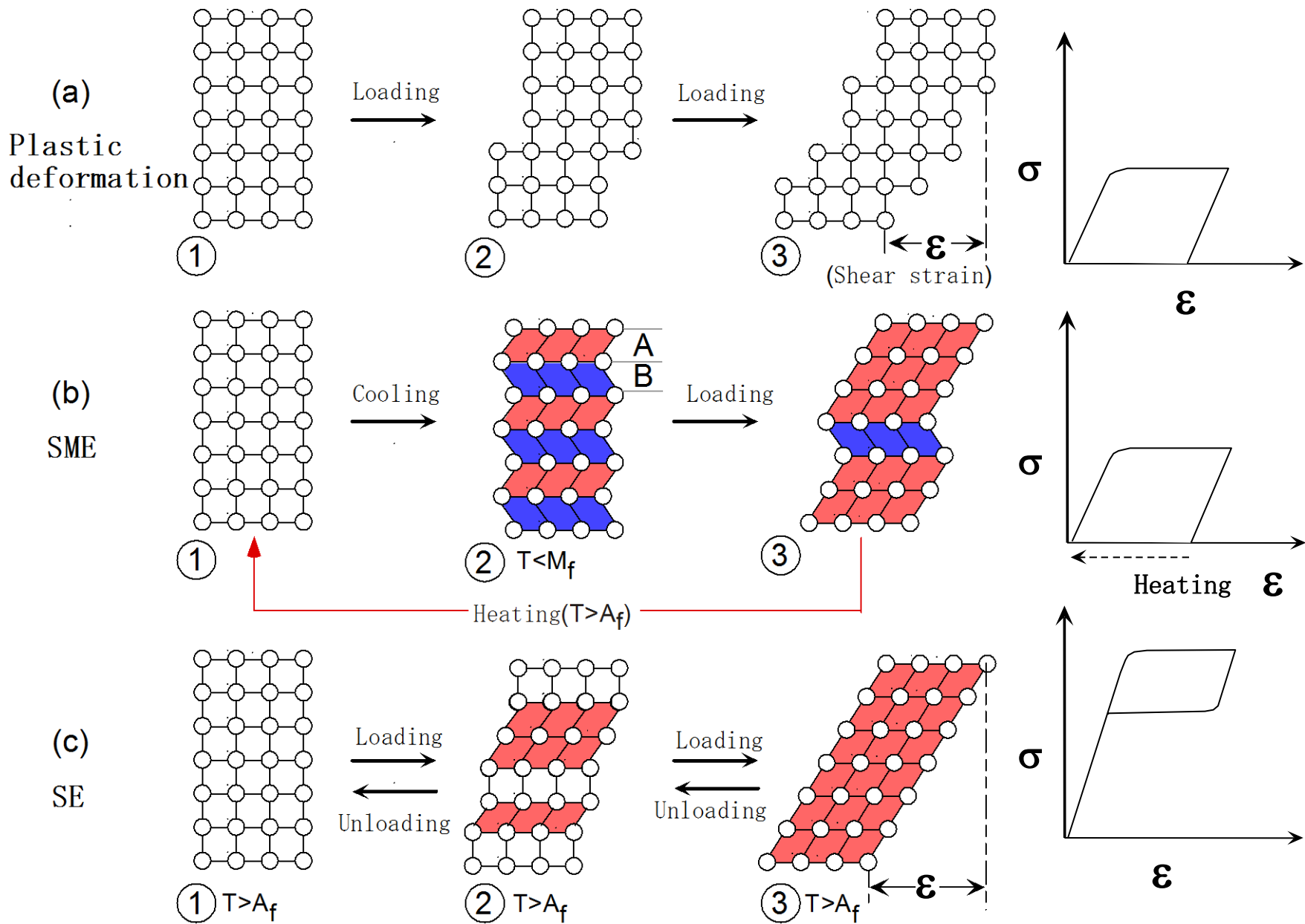
**Ex) Shape memory alloy**



# 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)



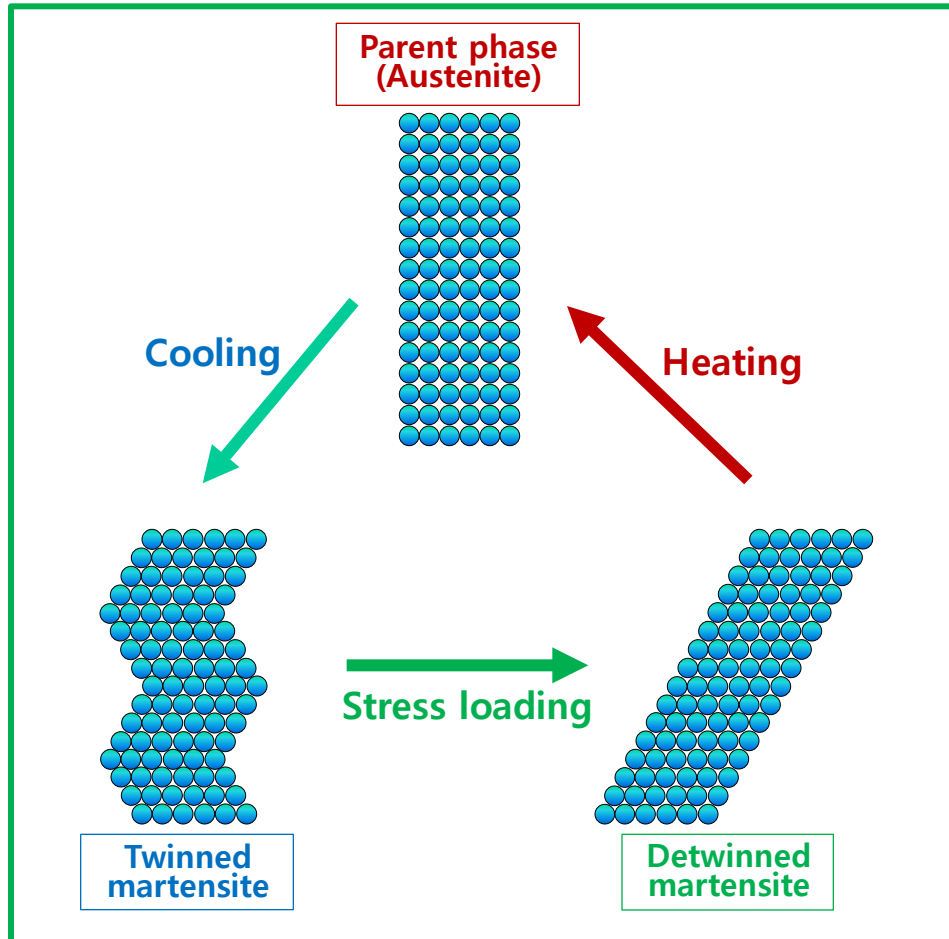
# Principles

How can shape memory effect occur?

# Principles

How can shape memory effect occur?

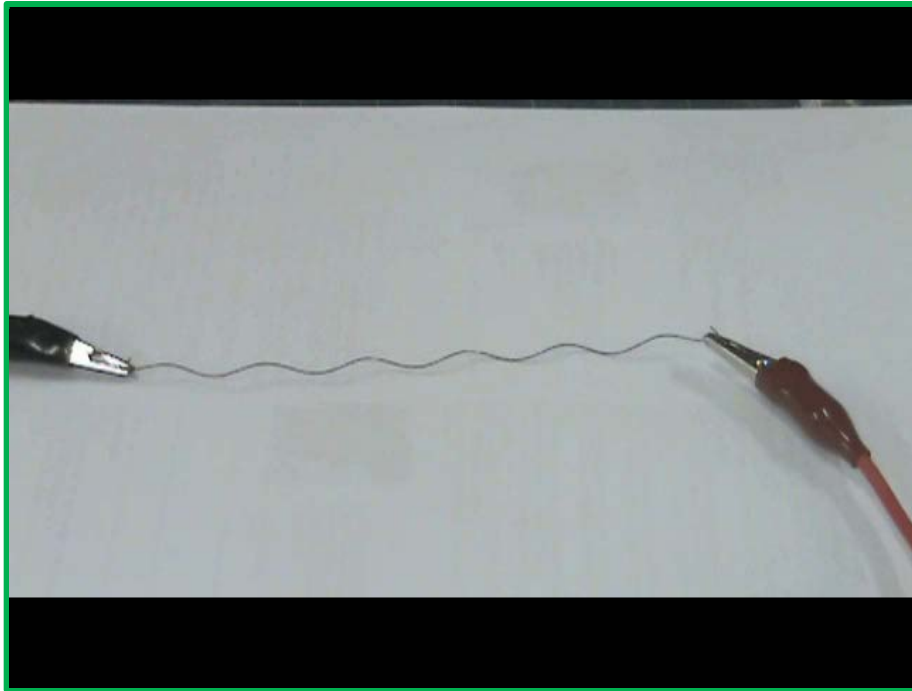
# Principles- shape memory process



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

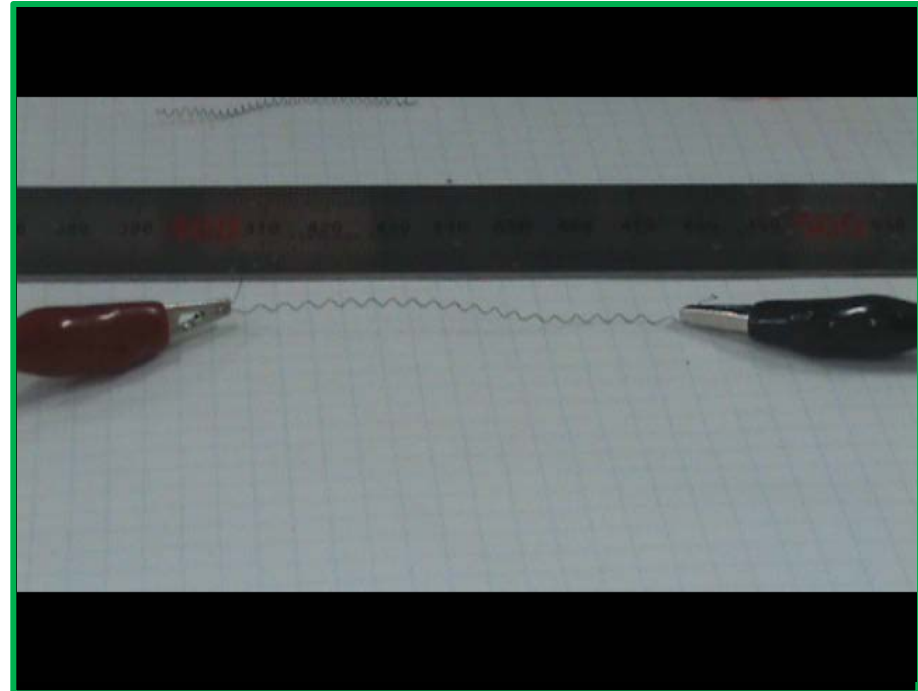
# \* One-way / Two-way shape memory effect

## ▼ One-way SME



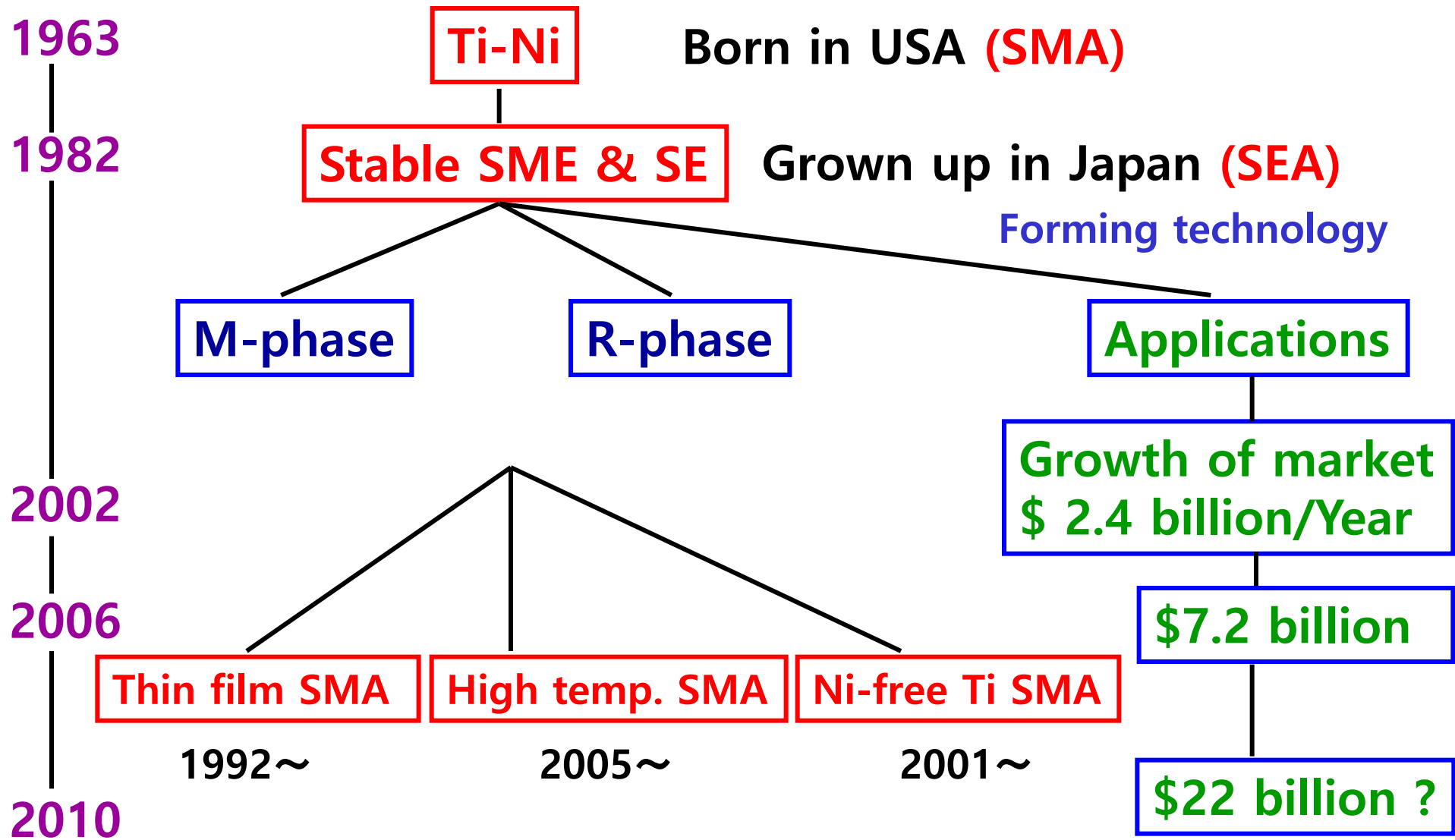
- ↳  $A_f$  이상의 고온 형상만을 기억
  - 저온( $< M_f$ )에서 소성변형 후  $A_f$  이상의 고온으로 가열
  - 기억된 고온 형상으로 회복

## ▼ 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

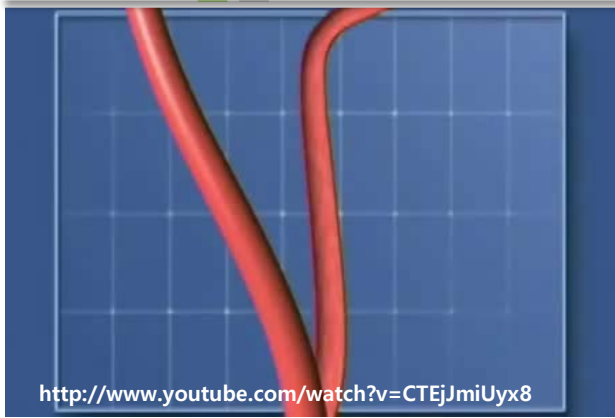
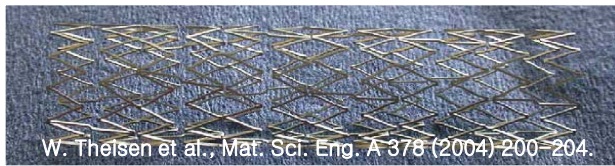
# Summary





# \* Application of SMAs

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



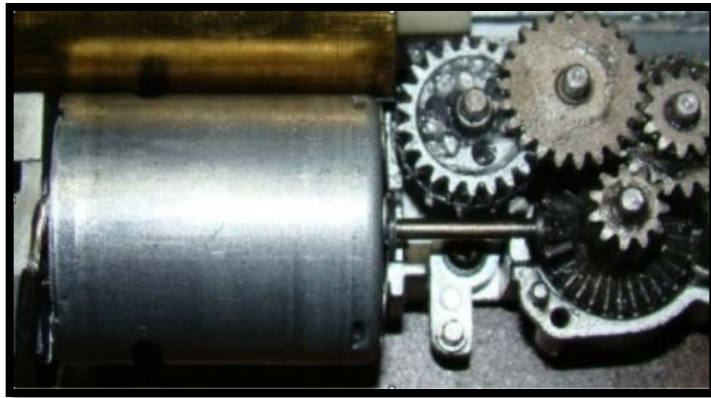
▲ 생체의료 부문: 첨단의료재료  
(stent, 치열교정용 강선 등)



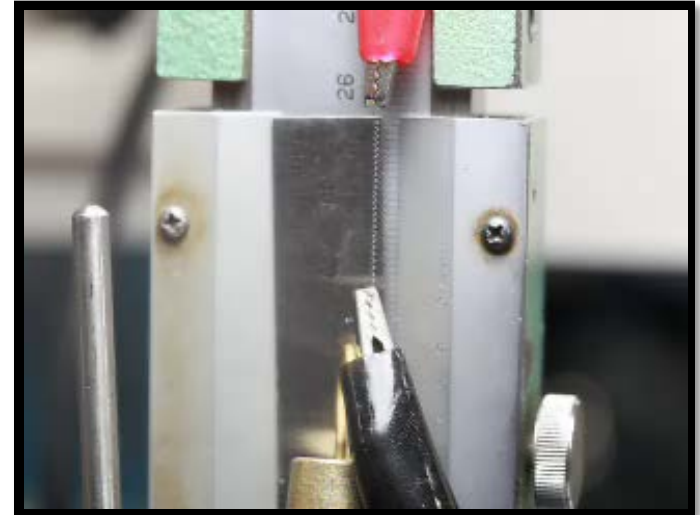
▲ 심해저/우주항공 부문: 극지재료  
(잠수함, 태양전지판 등)

# \* SMA Actuator

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

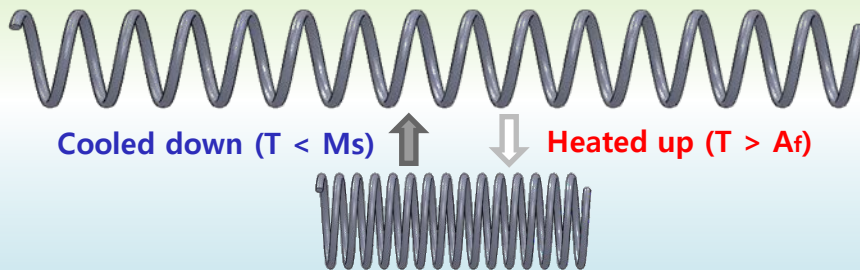


▲ 기존의 매크로 스케일 액츄에이터 (모터-기어 방식)



▲ SMA 스프링 액츄에이터

## SMA Spring Actuator



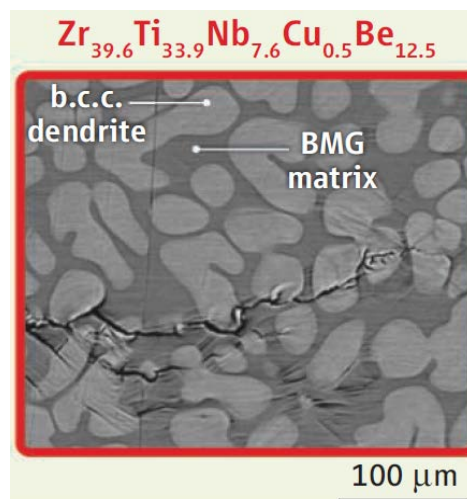
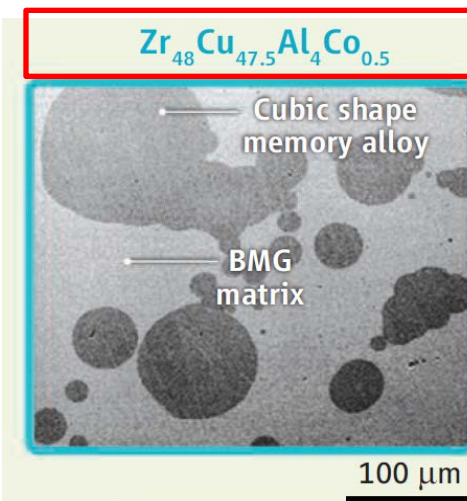
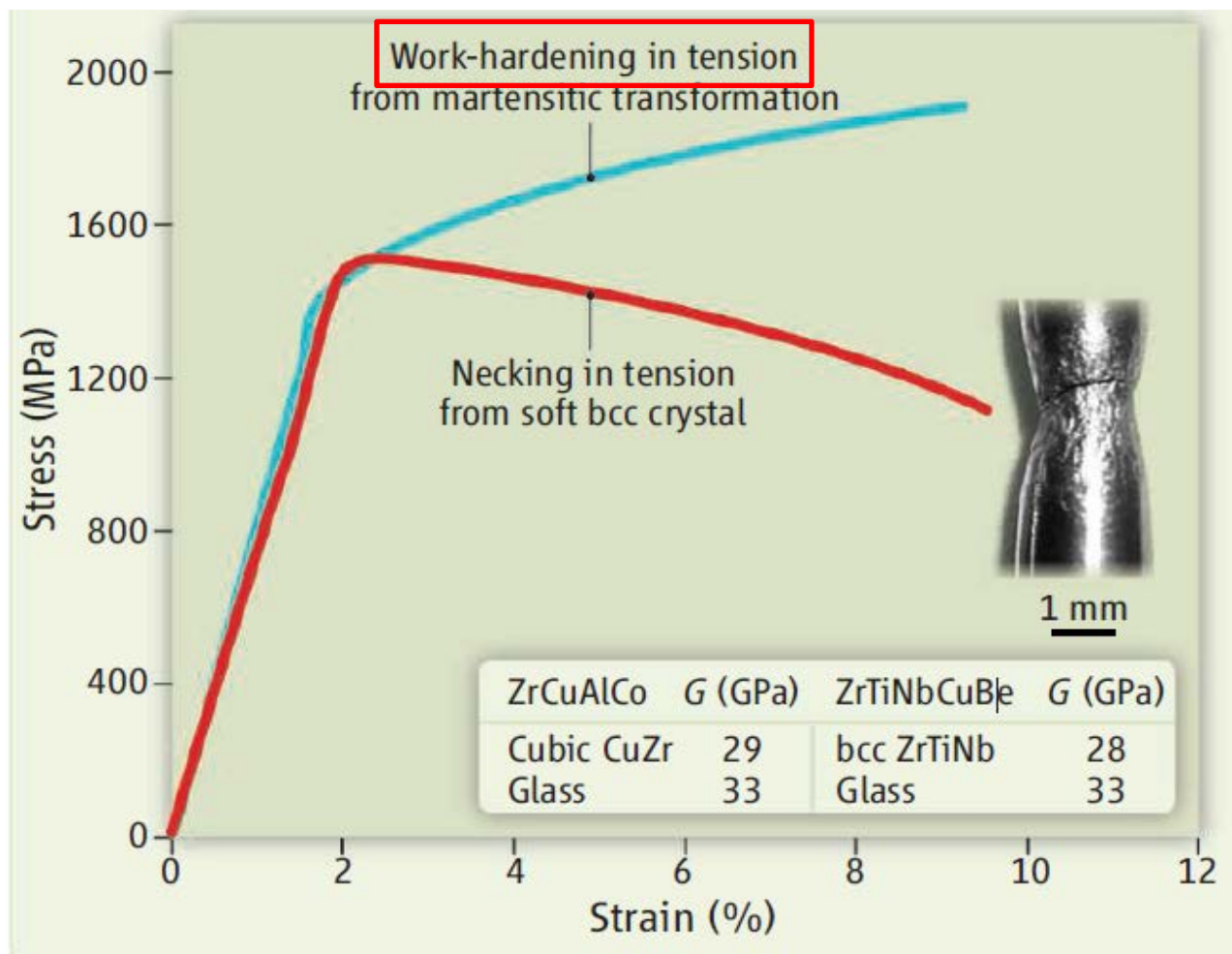
재료의 수축과 신장을 통하여 기계적인 동작을 가능하게 함.

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

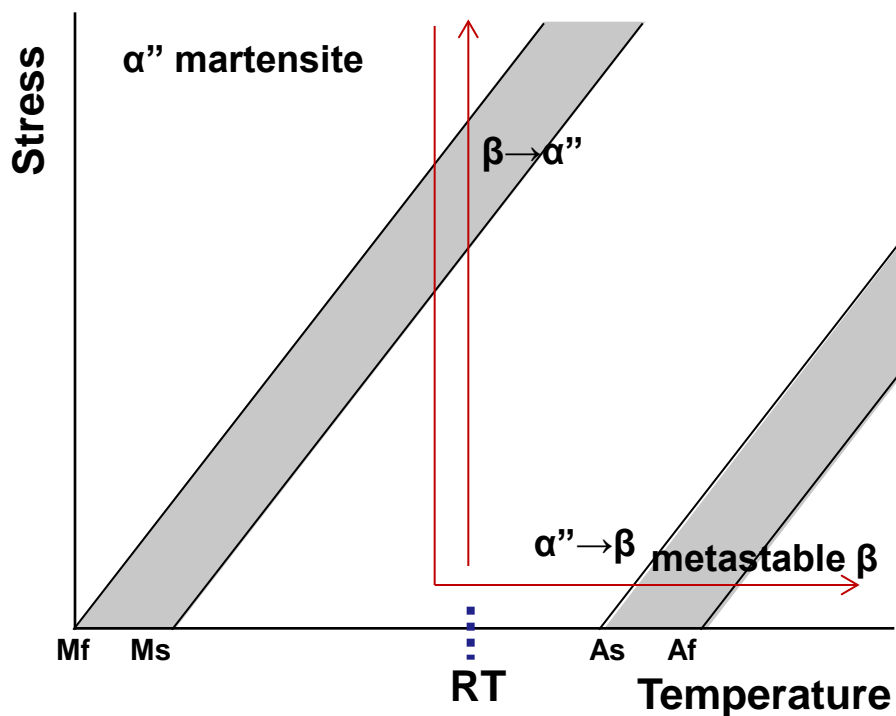
Secondary phase CuZr  
Metastable B2 phase at RT  
"Shape Memory Behavior"



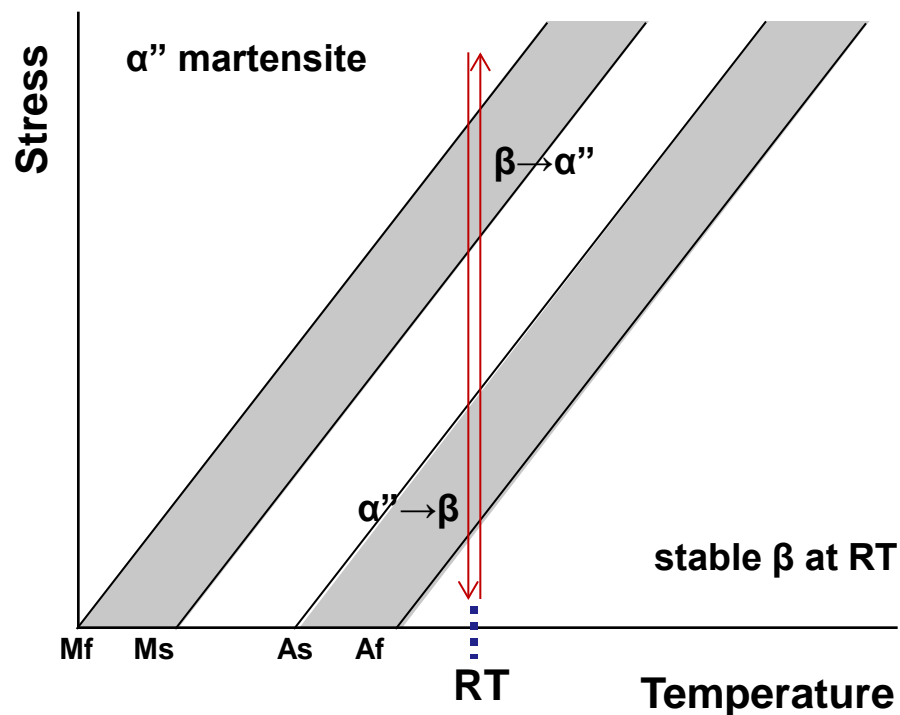
Ti-Cu-Ni system

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

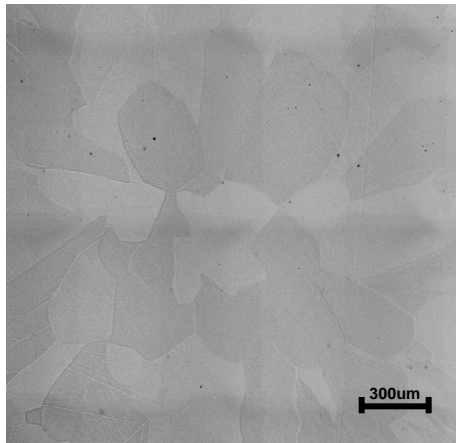
$\Phi 3mm$  suction casting  
-Fully crystalline  $B_2$

► **Stress-induced** phase transformation

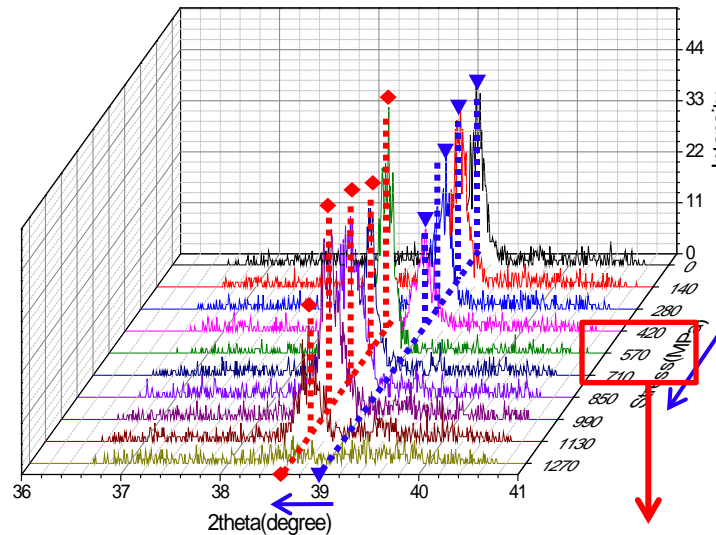
In-situ neutron diffraction measurement during compression

► **Temperature-induced** phase transformation

DSC measurement (during cooling)

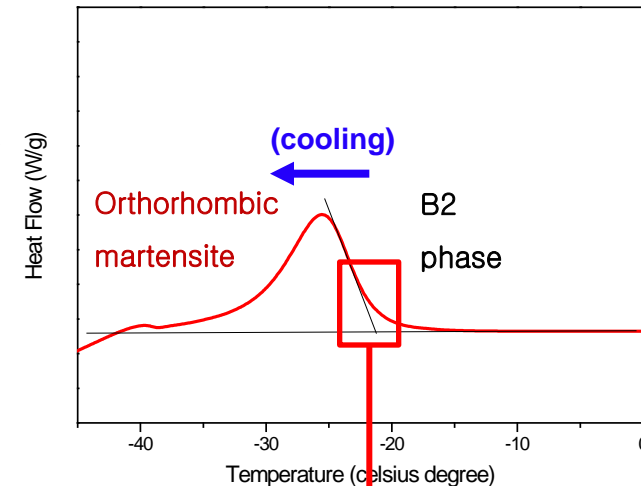


▼  $B_2$  phase  
◆ Orthorhombic martensite phase



Phase transformation stress

= 570MPa



Martensite start T ( $M_s$ )

=  $-22^\circ C$

➡ **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 14th December (before exam)**

**\* IH: Summary of Martensite nucleation & growth**

**Good Luck!!**



**FINAL (14th December, 7 PM-10PM)**

**Scopes: Text: page 146 (chapter 3.4) ~  
page 397 (chapter 6.2)/**

**Teaching notes: 14~25/**

**QUIZ and Homeworks**

**Good Luck!!**