2015 Fall

“Phase Transformation *in* Materials”

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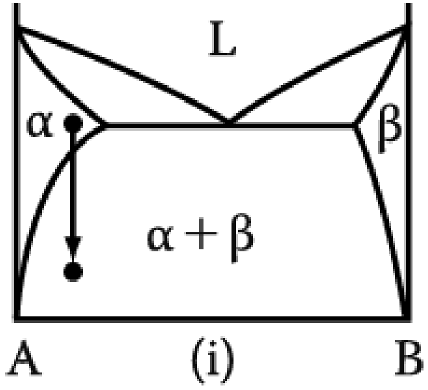
5. Diffusion Transformations in solid

: diffusional nucleation & growth

(a) Precipitation : long range diffusion

$$\boxed{\alpha' \rightarrow \alpha + \beta}$$

Metastable supersaturated
Solid solution



Homogeneous Nucleation

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

Heterogeneous Nucleation

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

Ex) 5.6 The Precipitation of Ferrite from Austenite (γ→α)

5.5.5 Spinodal Decomposition

5.5 Precipitation in Age-Hardening Alloys: transition phases

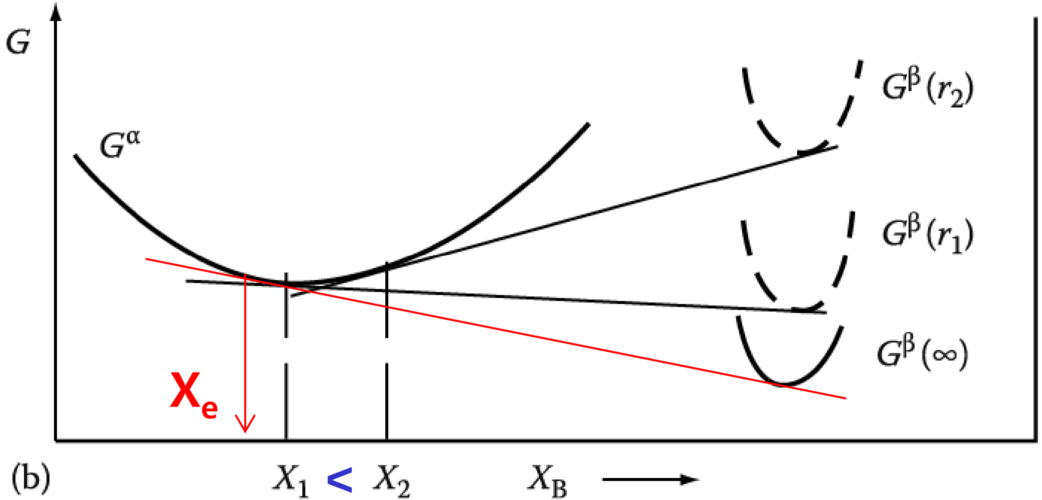
Microstructure of a two phase alloy is always unstable if the total interfacial free E is not a minimum. →

5.5.6. Particle Coarsening

(smaller total interfacial area→loss of strength or disappearance of GB pining effect→ particular concern in the design of materials for high temp. applications)

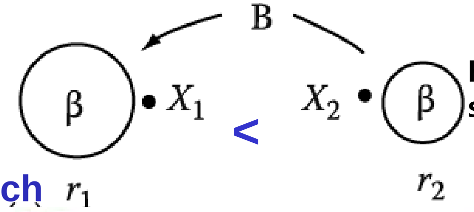
Two Adjacent Spherical Precipitates with Different Diameters

(Gibbs-Thomson effect: radius of curvature↓ → X_B ↑)



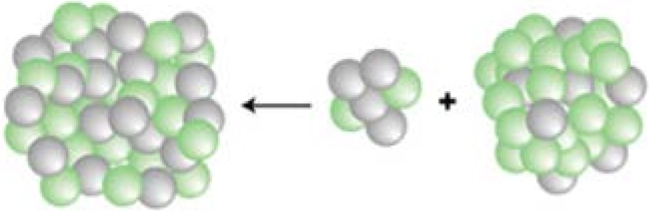
A-rich **B-rich**

Lower density of larger particles



High density of small precipitates

A-rich **B-rich**



Assumption: volume diffusion is the rate controlling factor

$$(\bar{r})^3 - r_0^3 = kt$$

Average radius

where $k \propto D\gamma X_e$

(X_e: Equil. solubility of very large particles)

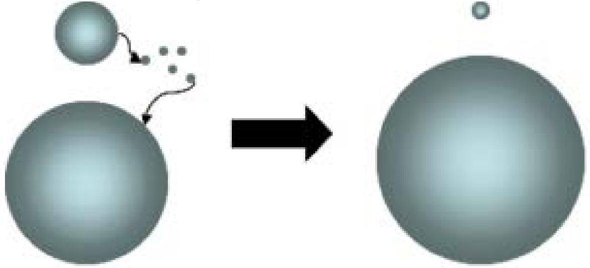
Coarsening rate

$$\boxed{\frac{d\bar{r}}{dt} \propto \frac{k}{\bar{r}^2}}$$

$\left(\begin{array}{l} D \text{ and } X_e \sim \exp(-Q/RT) \\ \bar{r} \end{array} \right.$ ↑ ↓ ⇨ **CR** ↑

Rapidly increase with Increasing temp.

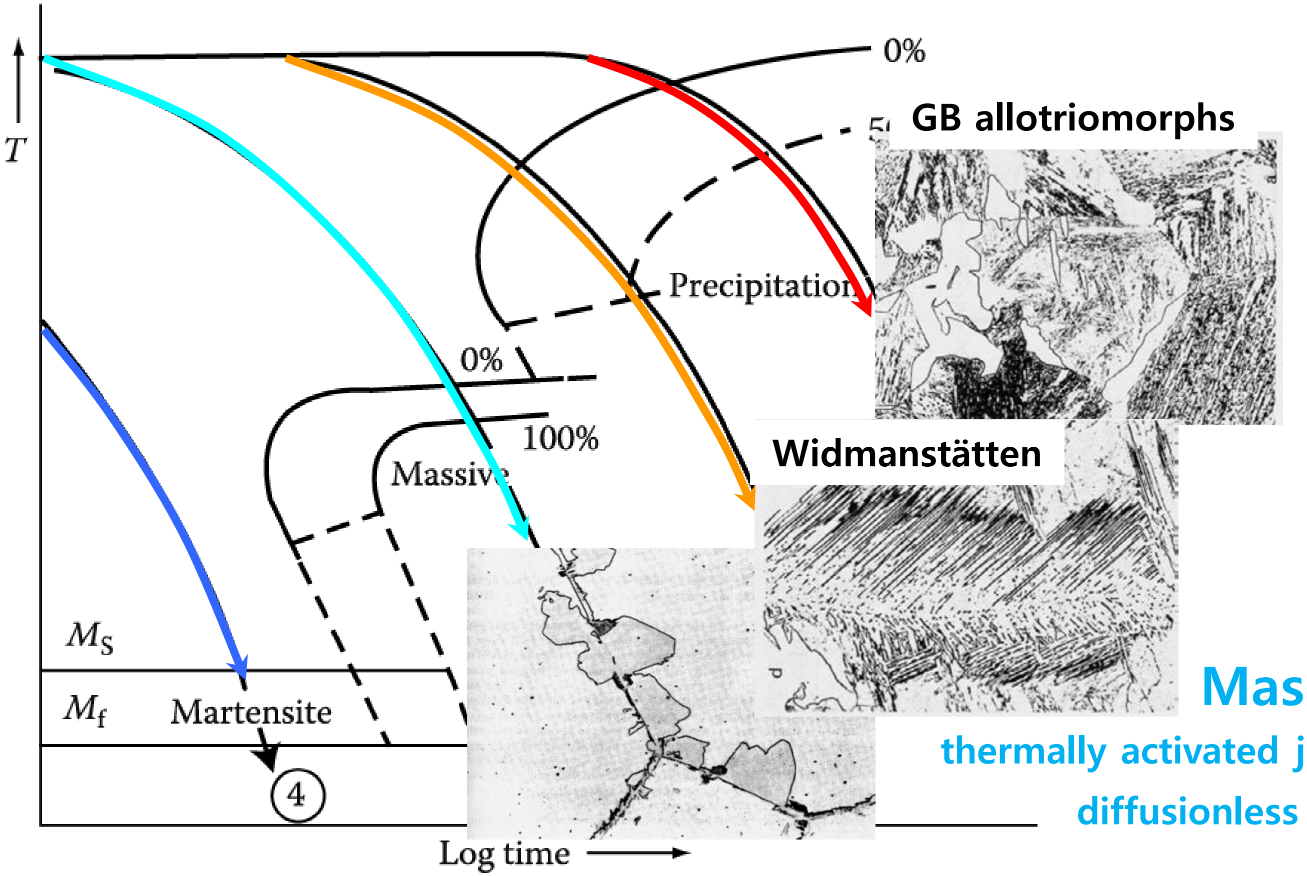
(Ostwald Ripening)



: Concentration gradient in matrix→diffusion→small particle_shrink/ large particle_grow

Ex) 5.6 The Precipitation of Ferrite from Austenite (γ→α)

* Massive, Martensite Transformation



Martensite

Fig. 5.75 A possible CCT diagram for systems showing a massive transformation. Slow cooling (1) produces equiaxed α. Widmanstatten 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.

Massive 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

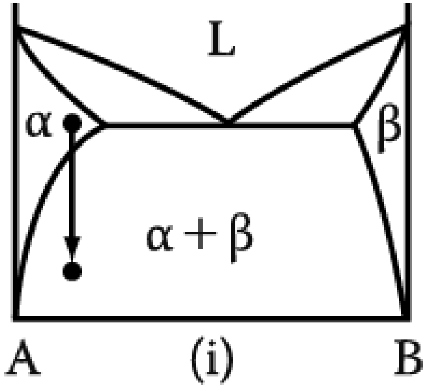
5. Diffusion Transformations in solid

: diffusional nucleation & growth

(a) Precipitation

$$\boxed{\alpha' \rightarrow \alpha + \beta}$$

Metastable supersaturated
Solid solution



Homogeneous Nucleation

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

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

Heterogeneous Nucleation

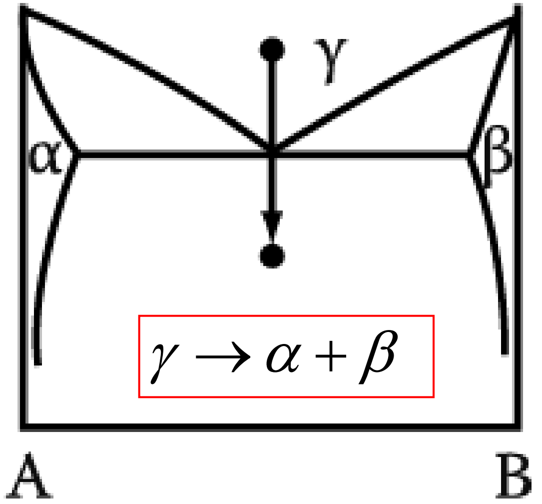
$$\boxed{\Delta G_{het} = -V(\Delta G_V - \Delta G_S) + A\gamma - \Delta G_d}$$

➡ suitable nucleation sites ~ nonequilibrium defects
(creation of nucleus~destruction of a defect($-\Delta G_d$))

(b) Eutectoid Transformation

Composition of product phases differs from that of a parent phase.

→ long-range diffusion



$$\boxed{\gamma \rightarrow \alpha + \beta}$$

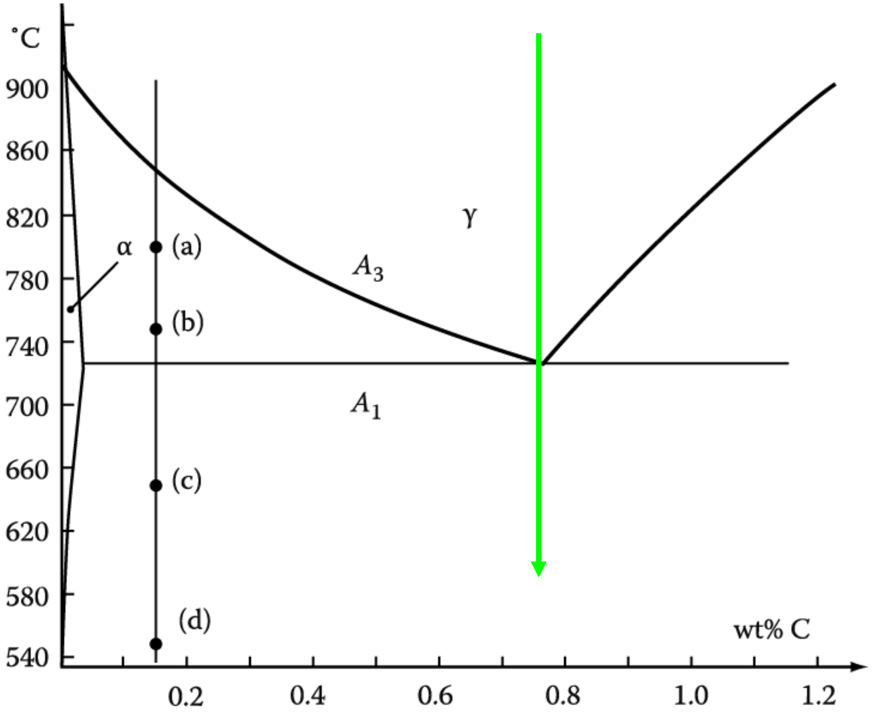
5.8. Eutectoid Transformation

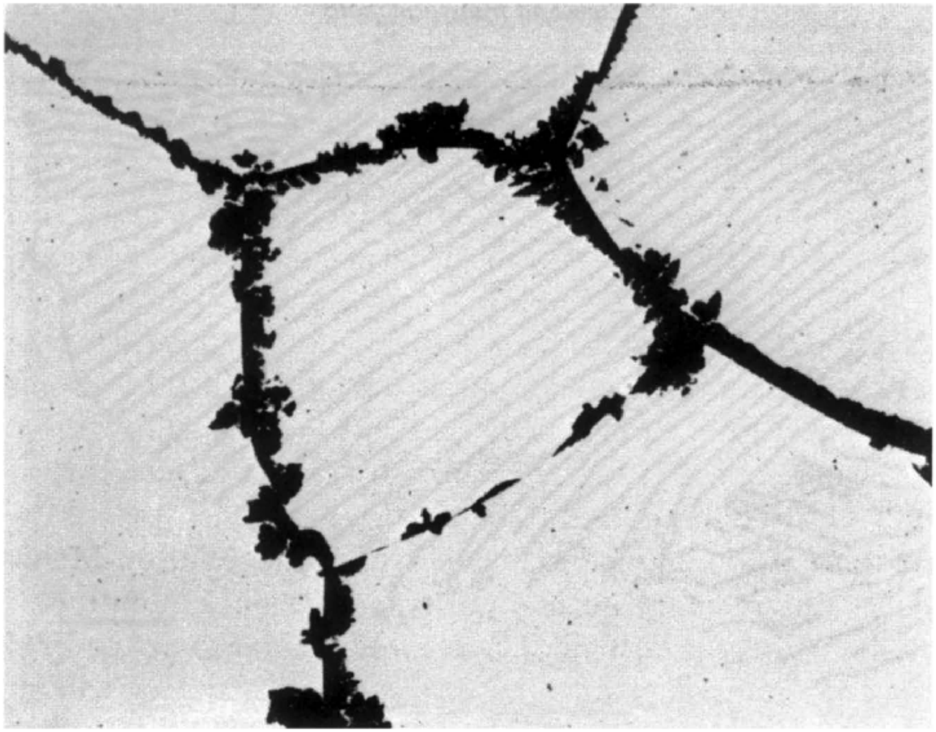
5.8.1 Pearlite Reaction in Fe-C Alloys

$$\gamma \rightarrow \alpha + Fe_3C$$

Very similar to a eutectic transformation

Pearlite nodule nucleate on GBs and grow with a roughly constant radial velocity into the surrounding austenite grains.





*** At large undercooling,**

: the nucleation rate is much higher and site saturation occurs, that is all GBs become quickly covered with nodules which <u>grow together forming layers of perlite</u>, Figure 5.61.

*** At small undercooling below A_1,**

: the number of pearlite nodules that nucleate is relatively small, and the nodules can grow as <u>hemispheres or spheres</u> without interfering with each other.

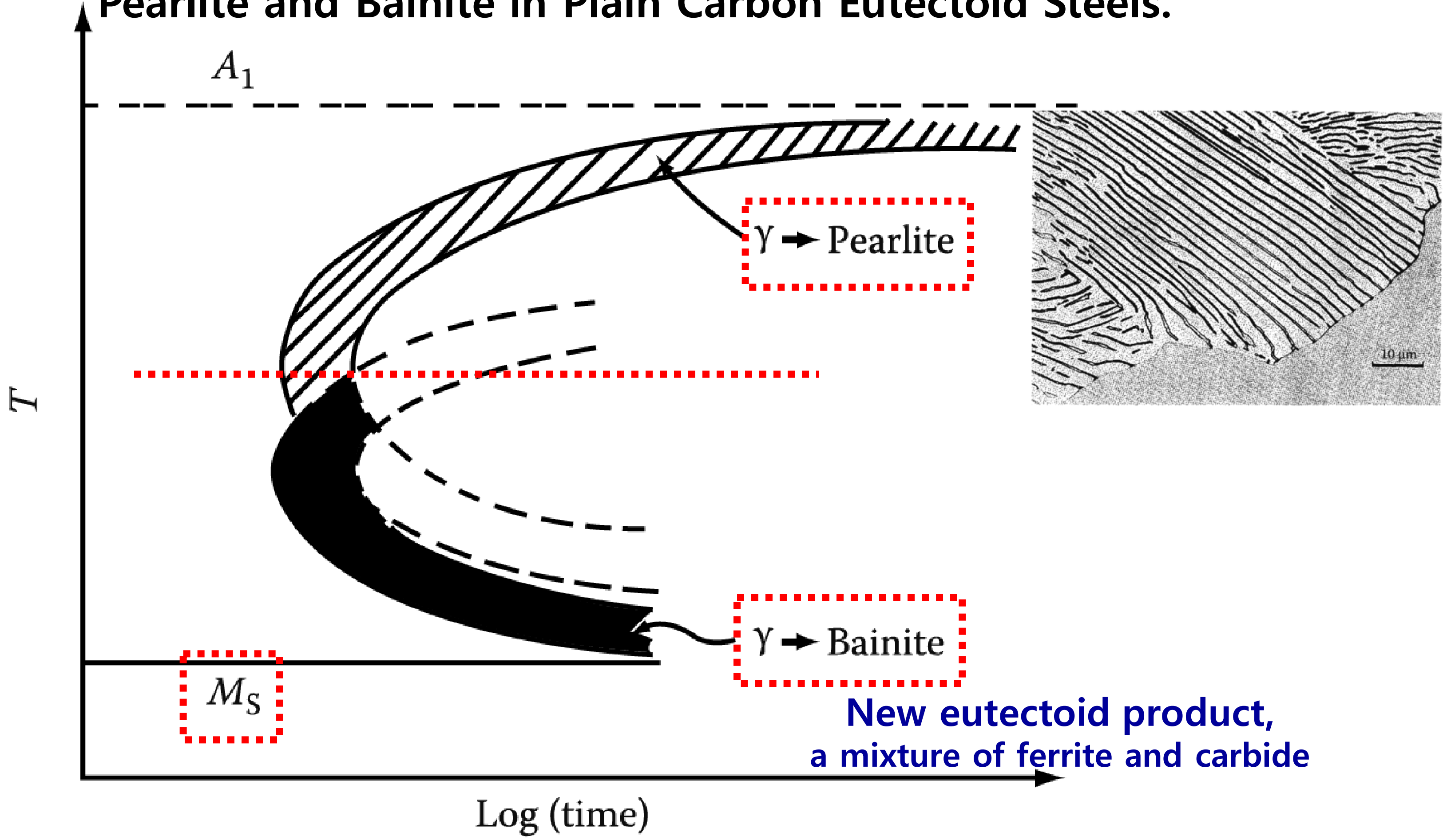
Growth of Pearlite: analogous to the growth of a lamellar eutectic

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

Interlamellar spacing

mainly boundary diffusion $v = kD_b(\Delta T)^3$

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



New eutectoid product,
a mixture of ferrite and carbide

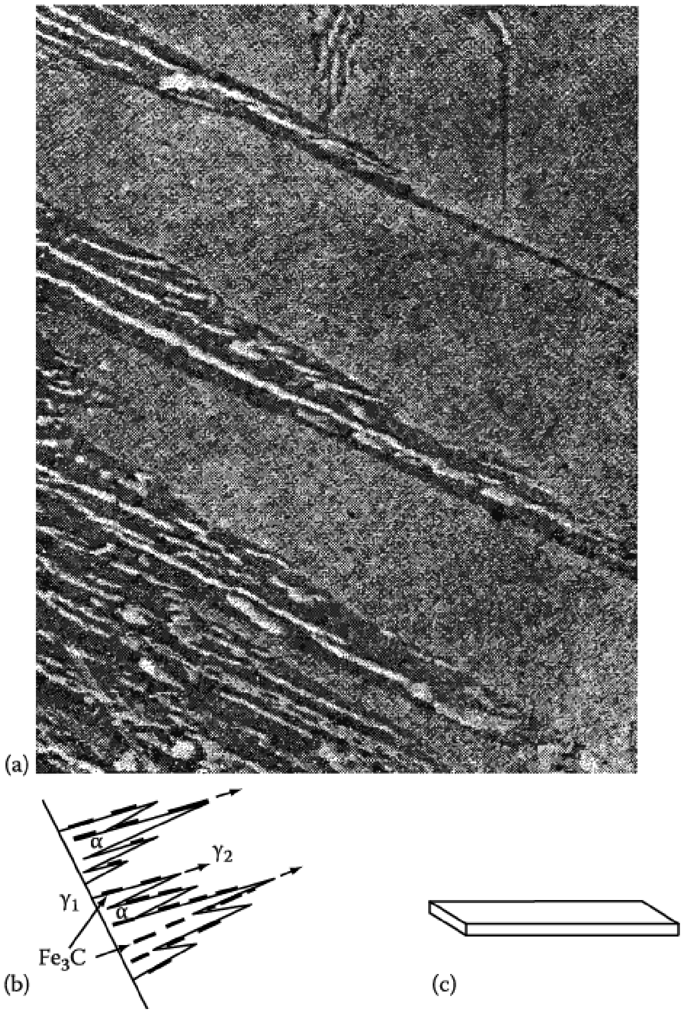
Figure 5.64 Schematic diagram showing relative positions of the transformation curves for pearlite and bainite in plain carbon eutectoid steel.

5.8.2 Bainite Transformation

The microstructure of bainite depends mainly on the temperature at which it forms.

Upper Banite in medium-carbon steel

At high temp. 350 ~ 550°C, ferrite laths, K-S relationship, similar to Widmanstäten plates

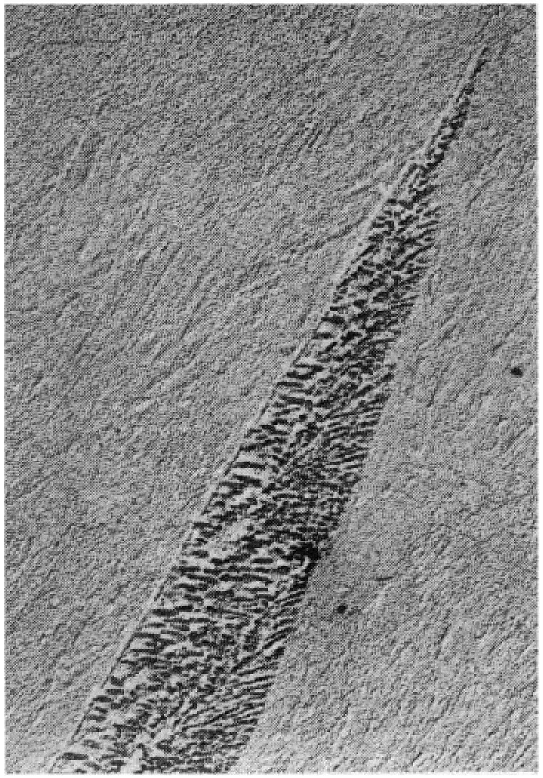


(b) Schematic of growth mechanism. Widmanstatten ferrite laths growth into γ_2. Cementite plates nucleate in carbon-enriched austenite.

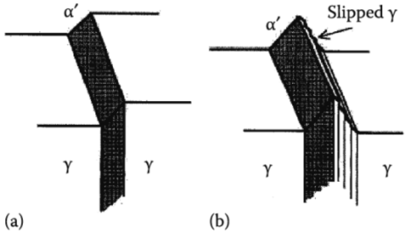
Lower Bainite in 0.69wt% C low-alloy steel

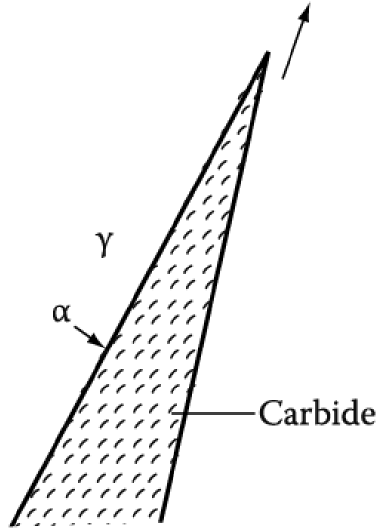
At sufficiently low temp. laths → plates

Carbide dispersion becomes much finer, rather like in tempered M.



(a)





(b)

Surface tilts by bainite trans. like M trans.
Due to Shear mechanism/ordered military manner

(b) A possible growth mechanism. α/γ interface advances as fast as carbides precipitate at interface thereby removing the excess carbon in front of the α.

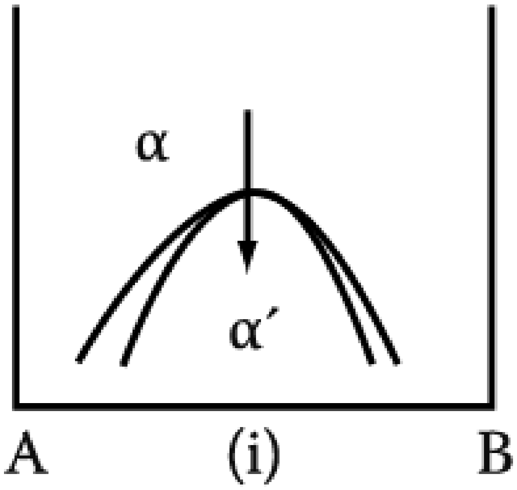
5. Diffusion Transformations in solid

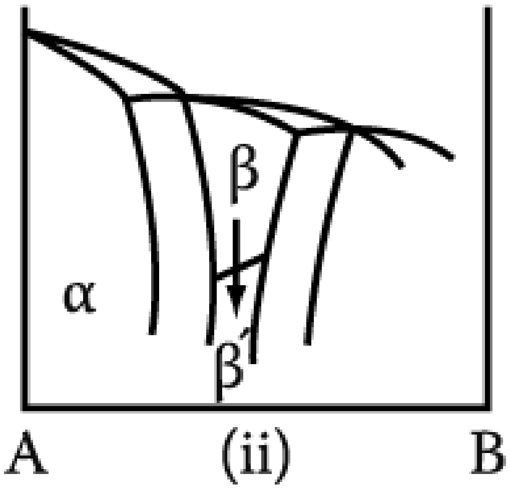
→ Short-range diffusion

(c) Order-Disorder Transformation

$$\boxed{\alpha \rightarrow \alpha'}$$

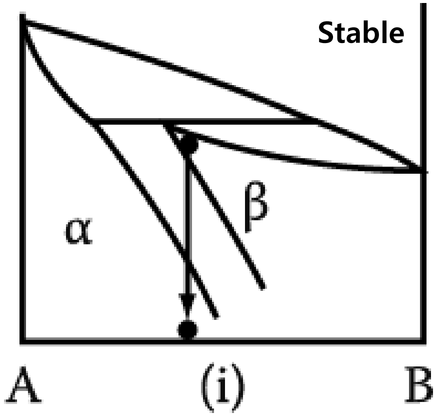
Disorder (high temp.)   Order (low temp.)



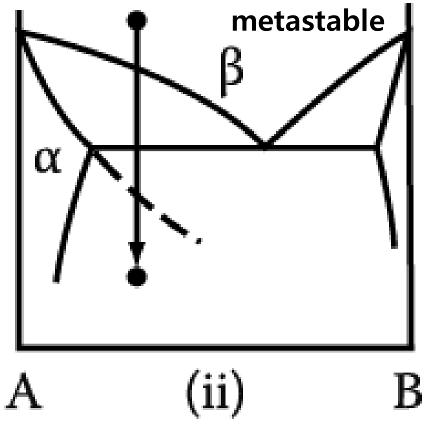


(d) Massive Transformation

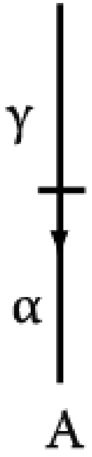
: The original phase decomposes into one or more new phases which have the same composition as the parent phase, but different crystal structures.



$$\boxed{\beta \rightarrow \alpha}$$



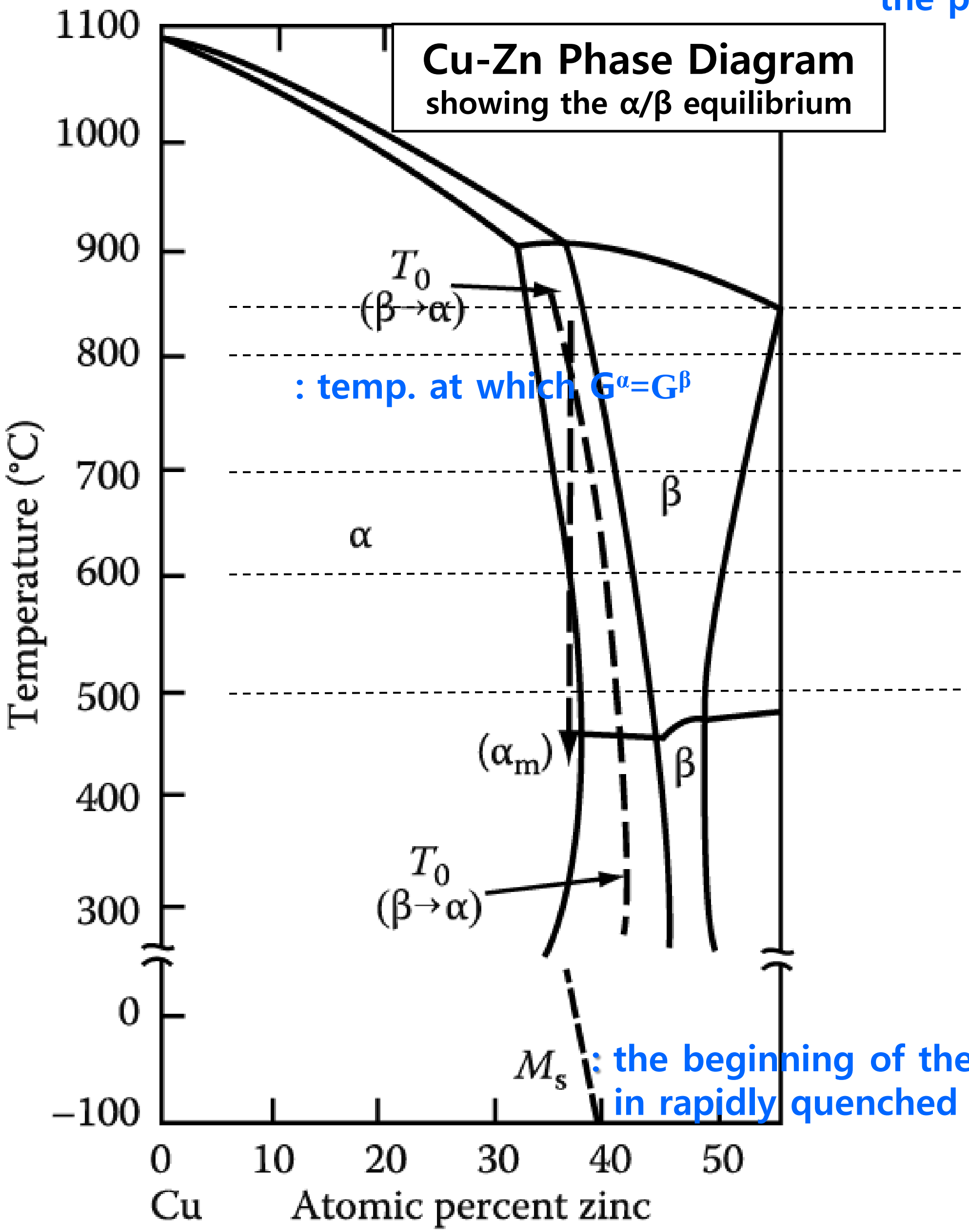
(e) Polymorphic Transformation



In single component systems, different crystal structures are stable over different temperature ranges.

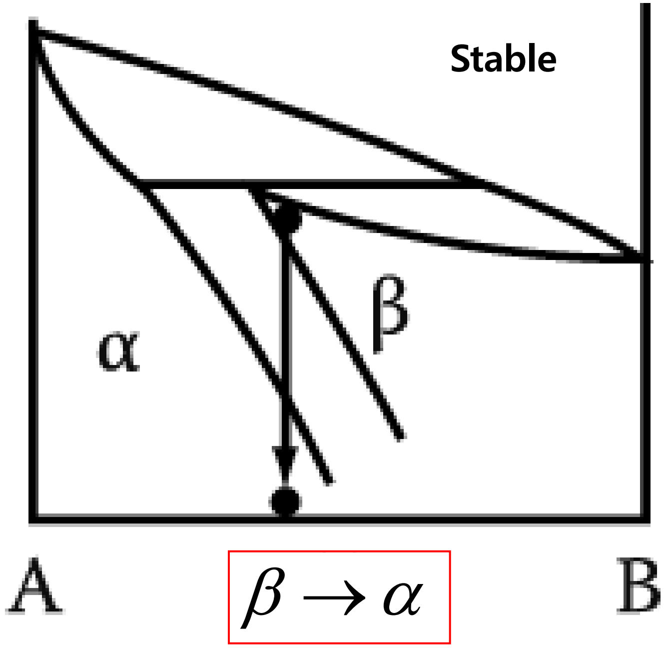
5.9 Massive Transformation

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



: temp. at which $G^\alpha = G^\beta$

M_s : the beginning of the M transformation in rapidly quenched specimens.



Free energy-composition curves for α and β at 850°C, 800°C, 700°C and 600°C?

5.9 Massive Transformation

Free energy-composition curves for α and β

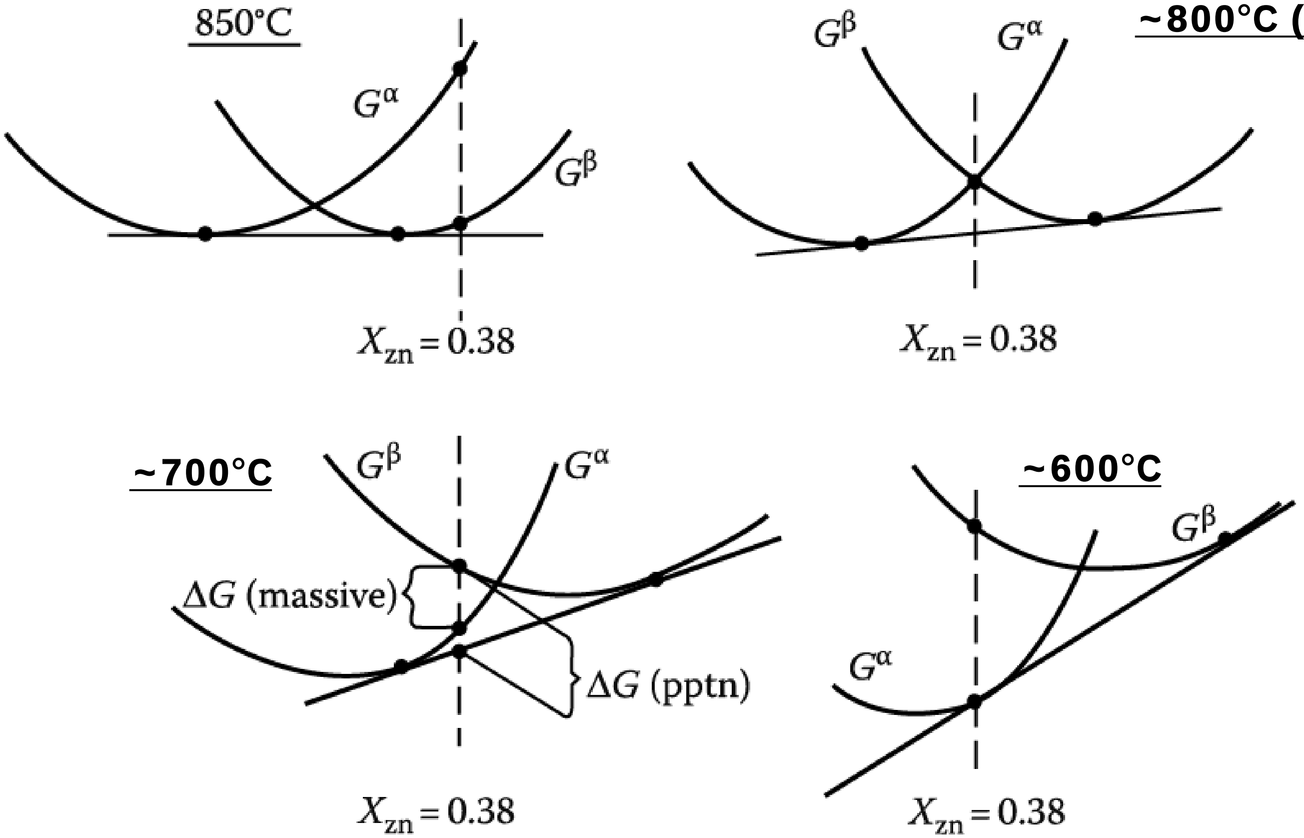


Fig. 5.86 A schematic representation of the free energy-composition curves for α and β in the Cu-Zn system at various temperatures.

At the thermodynamic point of view, it may possible for a massive trans. to occur within the two-phase region of the phase dia. anywhere below the T_0 temp.. But, in practice, there is evidence that massive trans. usually occur only within the single-phase region of the phase diagram

5.9 Massive Transformation

Massive α formed at the GBs of β and grow rapidly into the surrounding β

: a diffusionless civilian transformation (change of crystal structure without a change of composition)

Migration of the α/β interfaces~ very similar to the migration of GBs during recrystallization of single-phase material but, driving force ~ orders of magnitude greater than for recrystallization→ rapid growth: a characteristic irregular appearance.

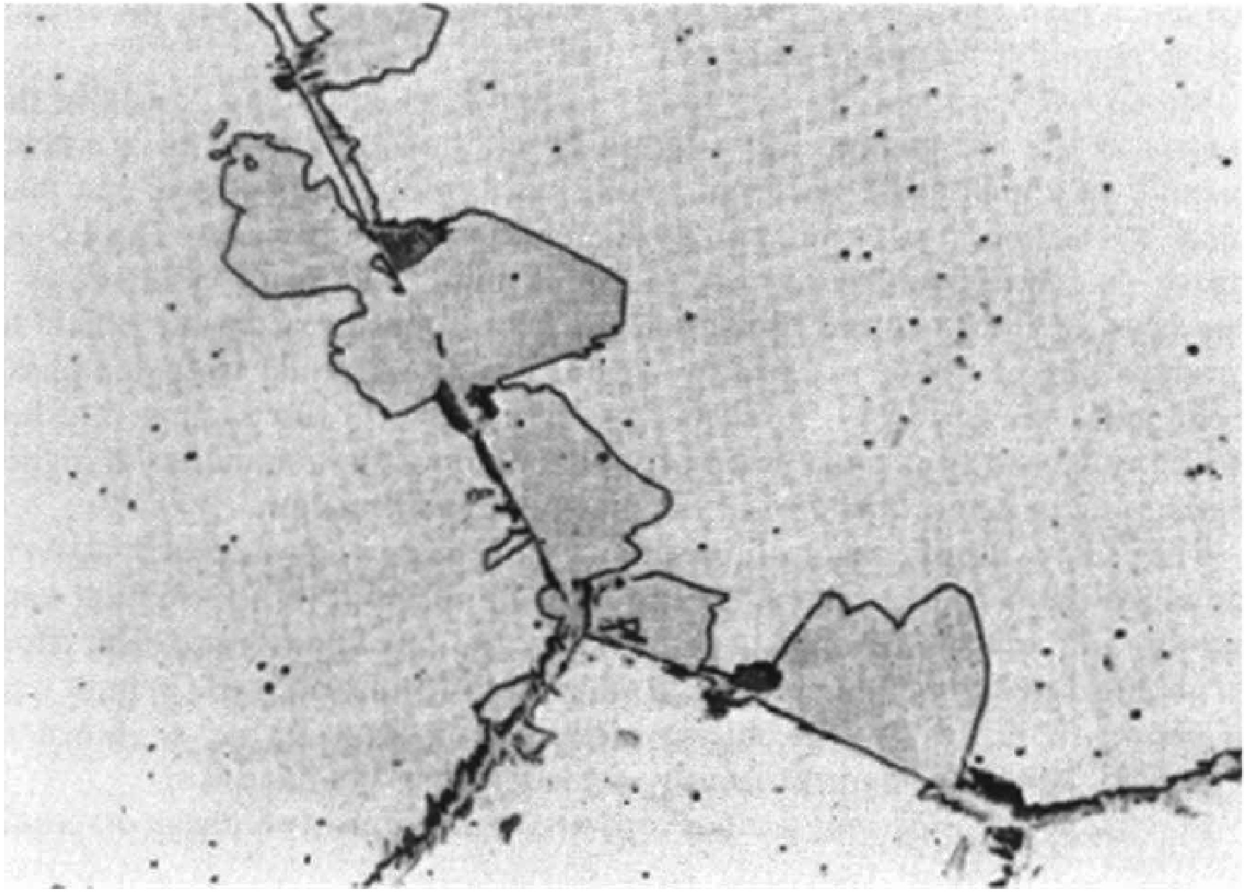
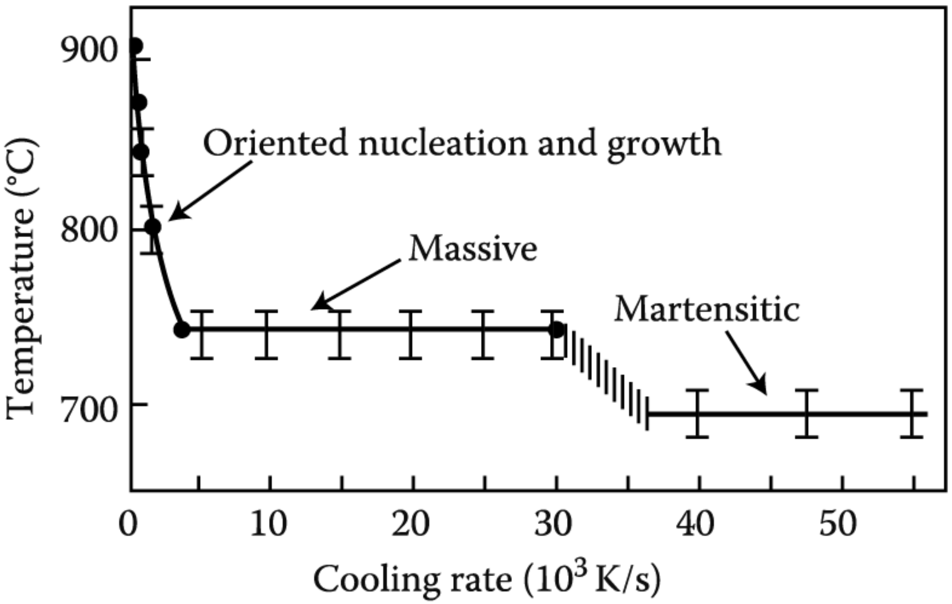
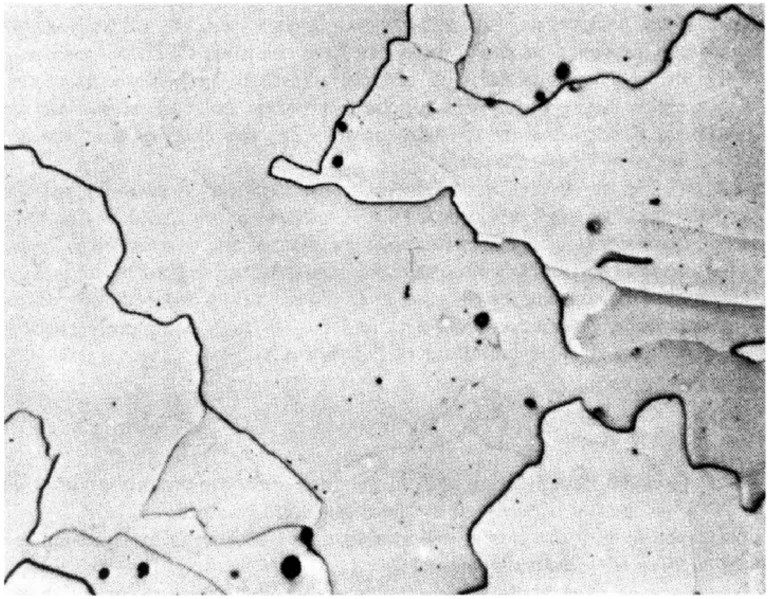


Figure 5.85 Massive a formed at the GBs of β in Cu-38.7wt% Zn quenched from 850℃ in brine at 0℃. Some high temperature precipitation has also occurred on the boundaries.

5.9 Massive Transformation : γ→α transformation in iron and its alloy

Effect of Cooling Rate on the Transformation Temperature at which transformation starts in pure iron



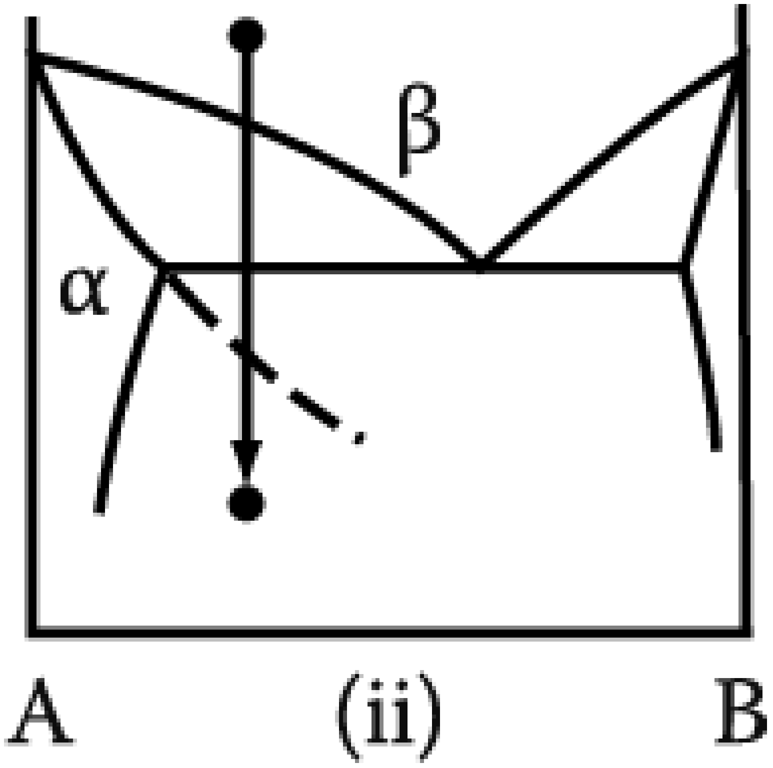


Massive a in an Fe-0.002wt%C

Quenched into iced brine from 1000 °C

: characteristically irregular α/α GBs.

5.9 Massive Transformation



Metastable phases can also form massively.

It is not even necessary for the transformation product to be a single phase: two phases, at least one of which must be metastable, can form simultaneously provided they have the same composition as the parent phase.

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

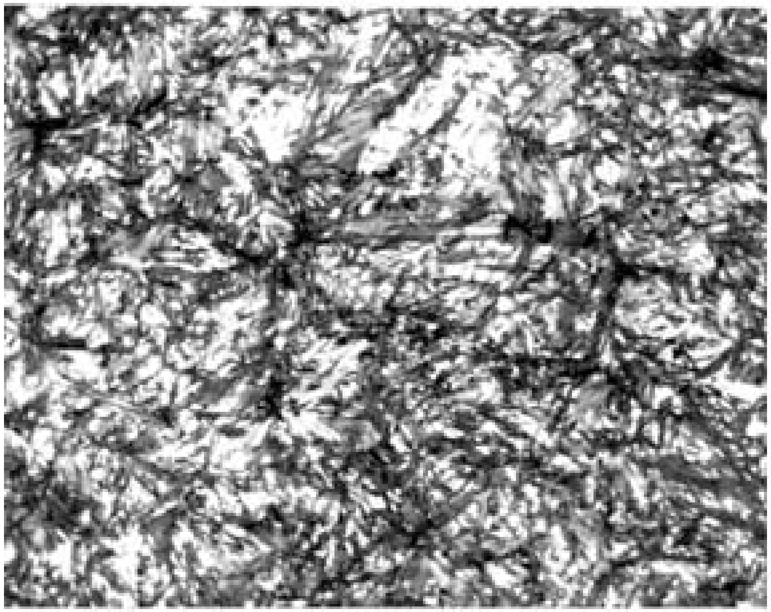
- **(Ch4) Solidification: Liquid → Solid**
- **(Ch5) Diffusional Transformations in Solid: Solid → Solid**
- **(Ch6) Diffusionless Transformations: Solid → Solid**

One of the most important technological processes is the hardening of steel by quenching.

Chapter 6 Diffusionless Transformation

Individual atomic movements are less than one interatomic spacing.

→ Martensite Transformation



(γ→α) Martensite with some retained austenite

"Needle like" Structure of martensite

Supersaturated solid solution of carbon in α-Fe

Named for the German metallurgist Adolph Martens, Martensite is the hardened phase of steel that is obtained by cooling Austenite fast enough to trap carbon atoms within the cubic iron matrix distorting it into a body centered tetragonal structure. Now, martensite is used in physical metallurgy to describe any diffusionless trans. product.

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).

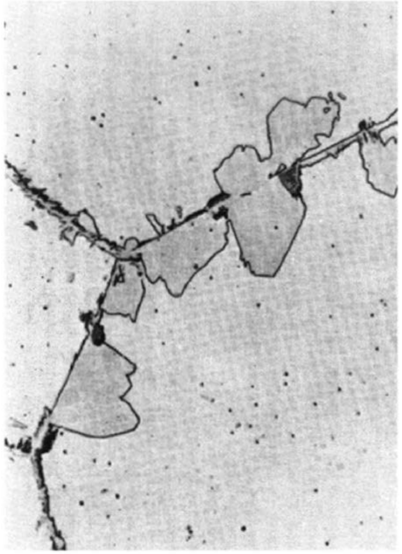
- **There is a whole other class of *military transformations* which are *diffusionless transformations* in which the atoms move only short distances (less than one interatomic spacing) in order to join the new phase.**

- **These transformations are *also* subject to the constraints of nucleation and growth. They are (almost invariably) associated with allotropic transformations (동소변태).**

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.

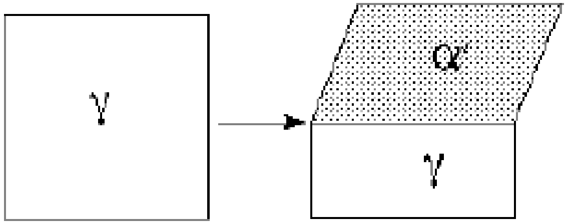
Classification of Transformations

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

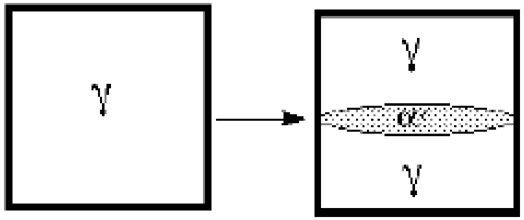
Microstructure of Martensite

- The microstructural characteristics of martensite are:
  - **the product (martensite) phase has a <u>well defined crystallographic relationship with the parent (matrix)</u>.**

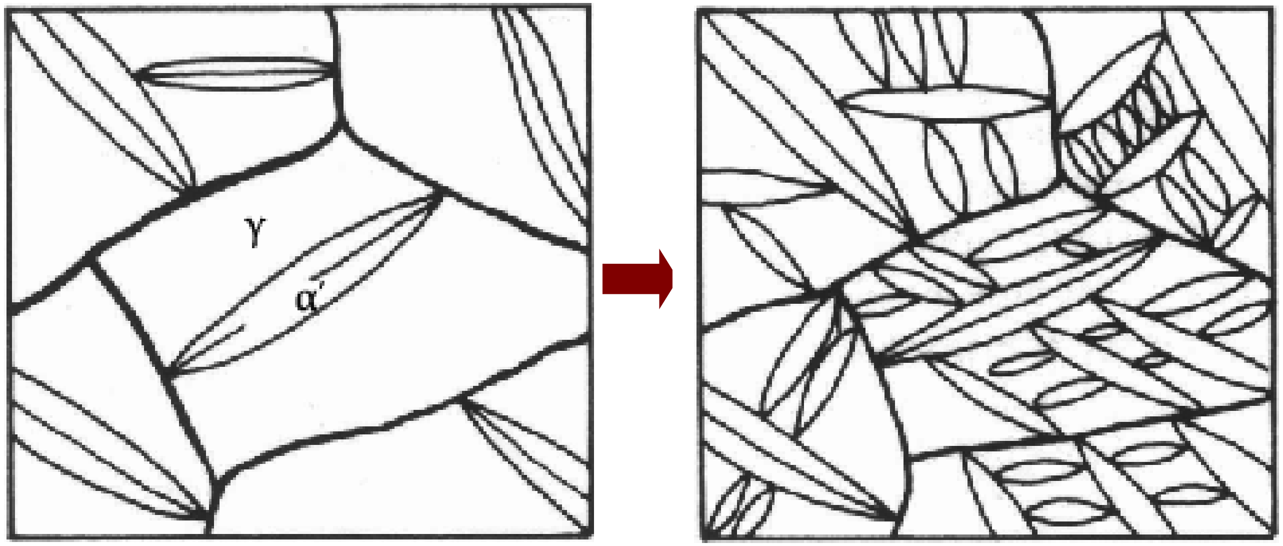
1) martensite(designated α') forms as platelets within grains.



Unconstrained transformation



Constrained transformation



"Lens shape"

Plate density: independent of grain size

Fig. 6.1 Growth of martensite with increasing cooling below Ms.

<u>→ Martensite formation rarely goes to completion</u>

Microstructure of Martensite

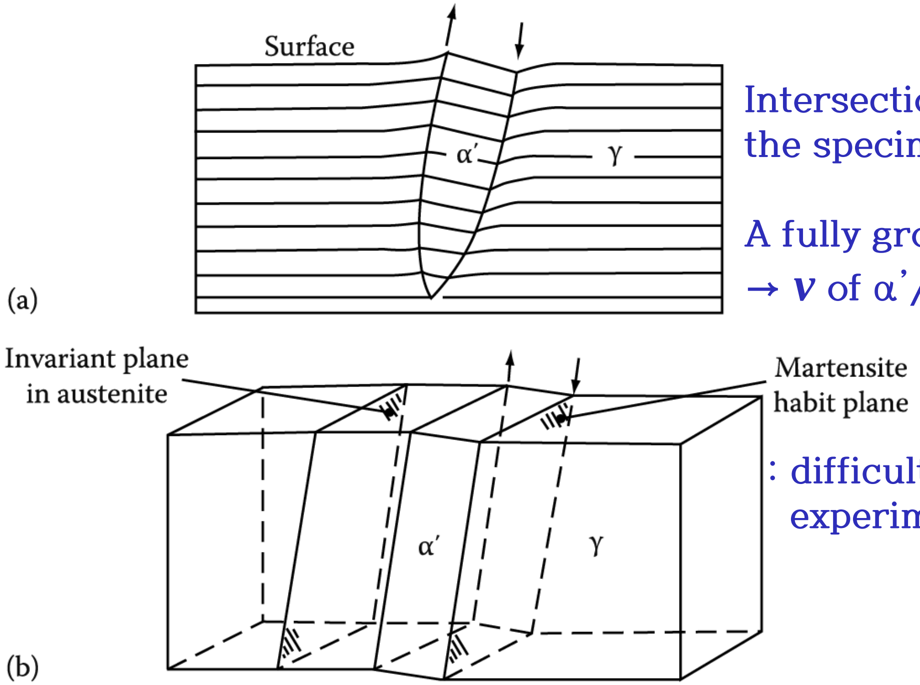
- The microstructural characteristics of martensite are:

2) 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 ~10^{-7} sec

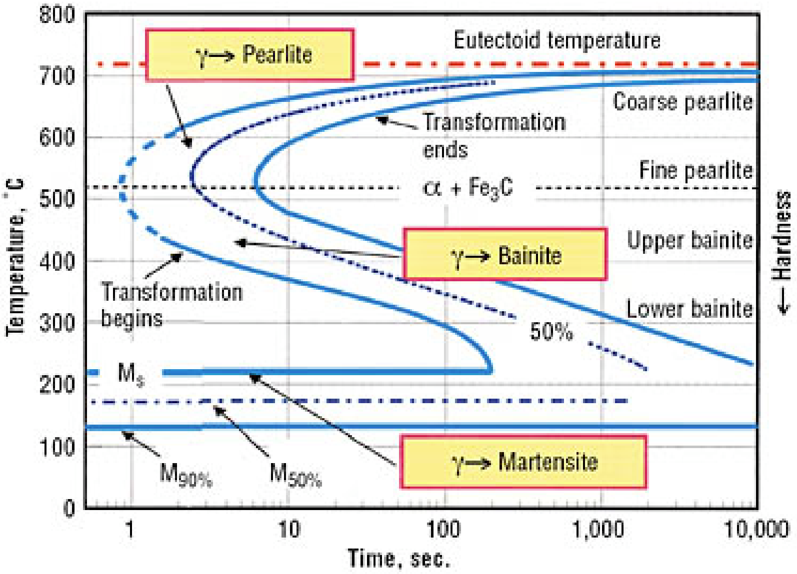
→ v of α'/γ interface $\propto$ speed of sound in solid

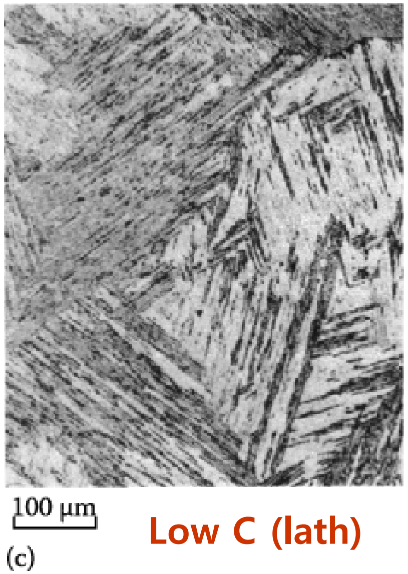
: difficult process to study M nucleation and growth experimentally

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

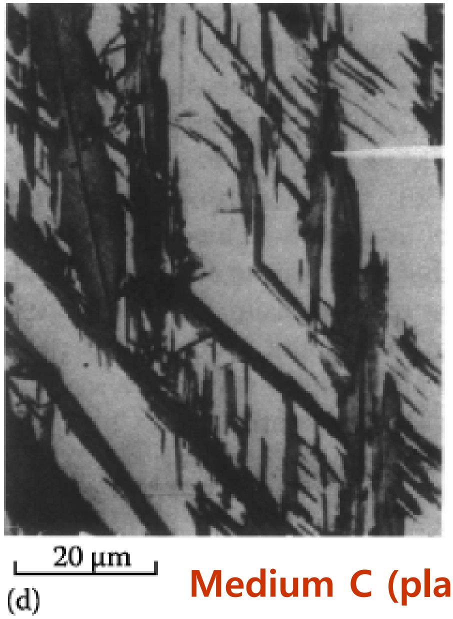
Microstructures

M_f temperature (M finish) corresponds to that temperature
Below which further cooling does not increase the amount of M.
→ 10-15% retained γ: common feature of higher C content alloys





Low C (lath)



Medium C (plate)

Fe-Ni (plate, some isothermal growth)

Fig. 6.1 (c-e) Different martensite morphologies in iron alloys

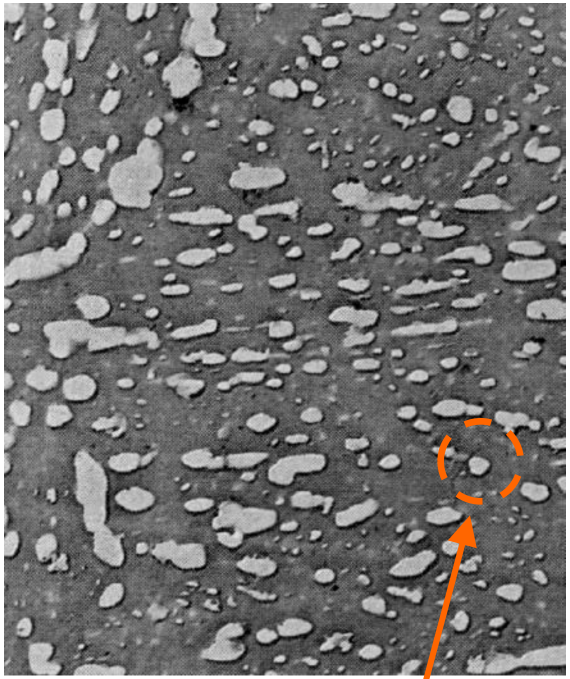
Control of Mechanical Properties
By Proper Heat Treatment in Iron-Carbon Alloy

Martensite

- **Tip of needle shape grain**
- → **Nucleation site of fracture**
- → **Brittle**

→

Proper heat treatment (tempering)



Tempered martensite

- → **Very small & spherical shape grain**
- → **Good strength, ductility, toughness**

Driving Forces

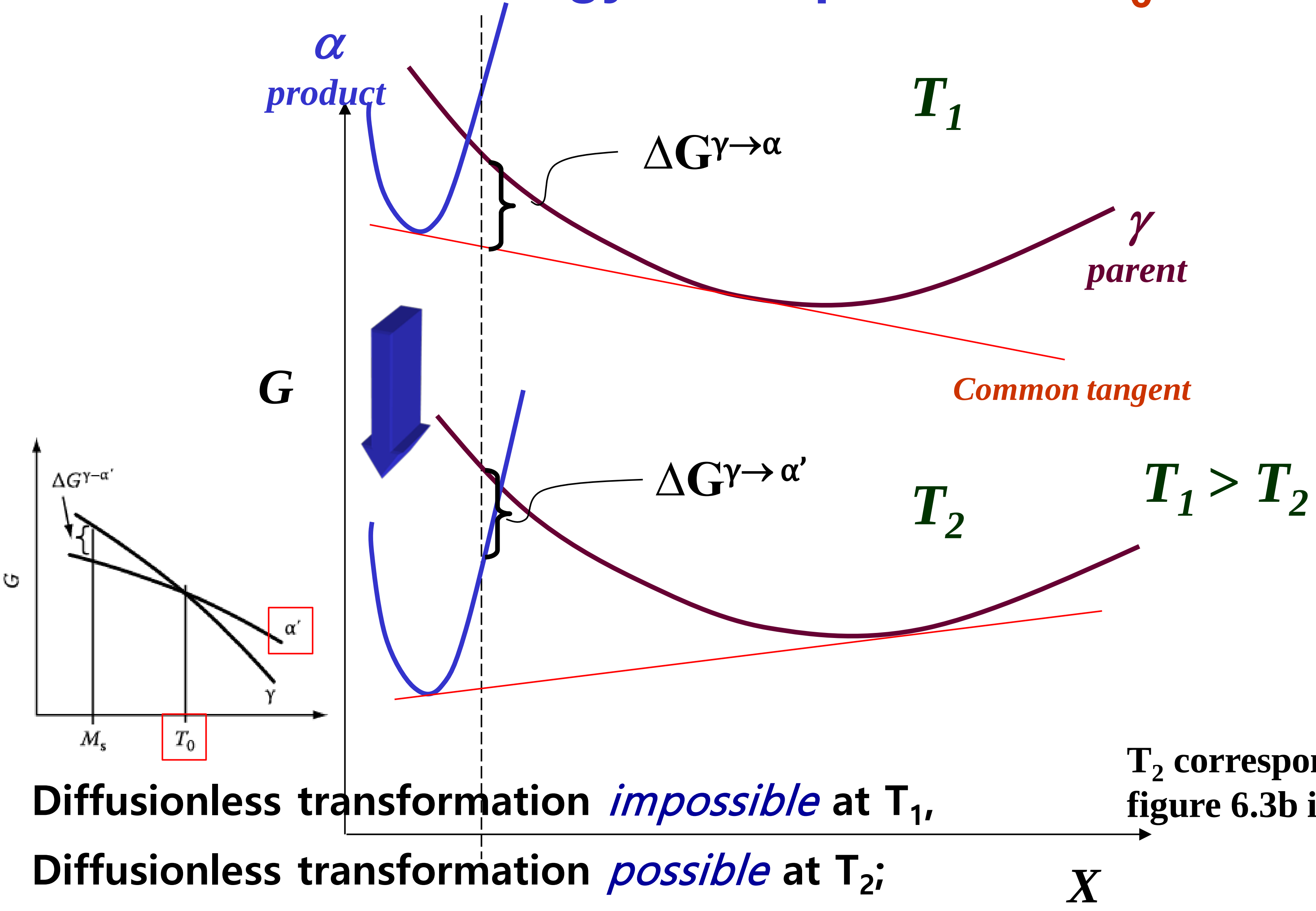
- These transformations require ***larger driving forces*** than for diffusional transformations. **(= large undercooling, ΔT)**

- 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_2 corresponds to figure 6.3b in P&E.

Diffusionless transformation *impossible* at T_1,

Diffusionless transformation *possible* at T_2;

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

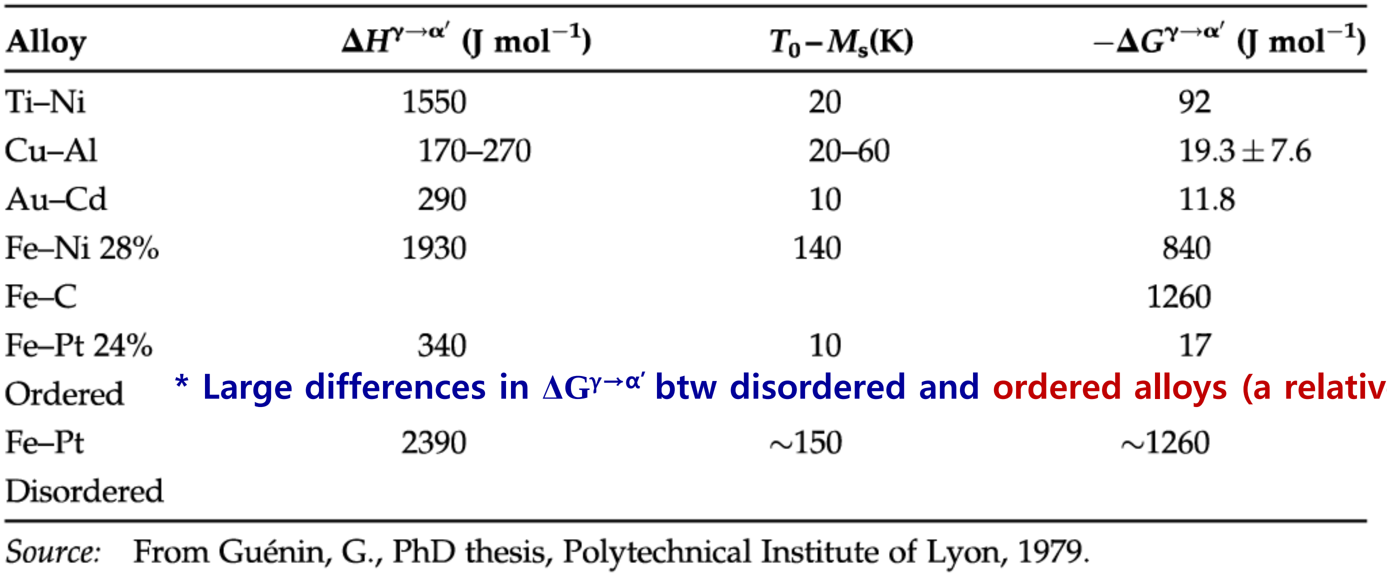
Driving Force Estimation

- 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**.

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

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



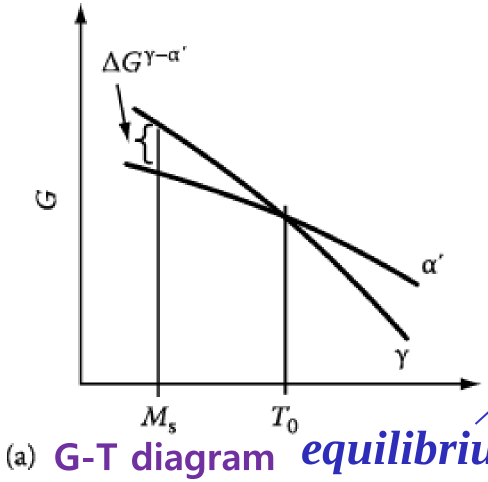
Alloy	$\Delta H^{\gamma\to\alpha'}$ (J mol^{-1})	$T_0 - M_s$(K)	$-\Delta G^{\gamma\to\alpha'}$ (J mol^{-1})
Ti–Ni	1550	20	92
Cu–Al	170–270	20–60	19.3 ± 7.6
Au–Cd	290	10	11.8
Fe–Ni 28%	1930	140	840
Fe–C			1260
Fe–Pt 24% Ordered	340	10	17
Fe–Pt Disordered	2390	~150	~1260

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

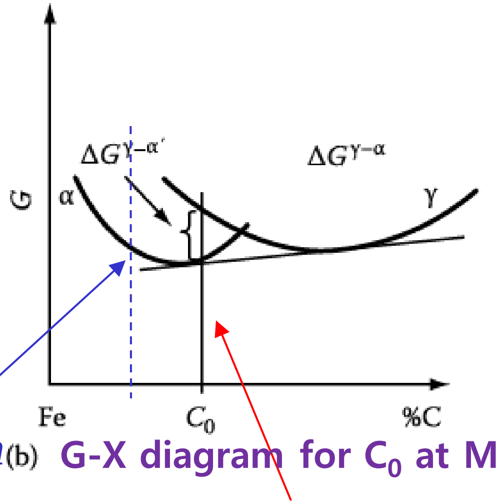
*** Large differences in $\Delta G^{\gamma\to\alpha'}$ btw disordered and ordered alloys (a relatively small ΔT)**

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

Various ways of
showing the martensite transformation



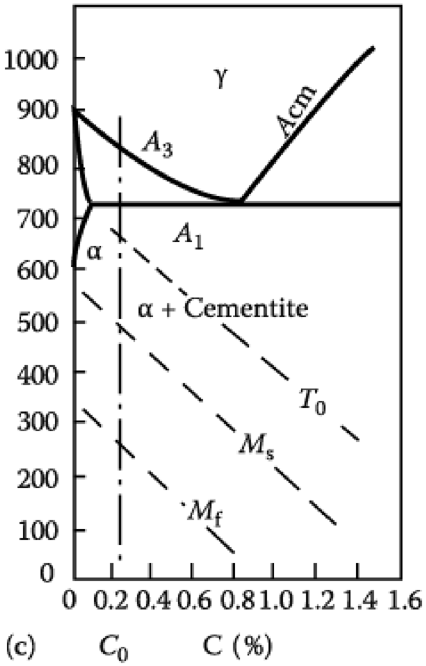
G-T diagram



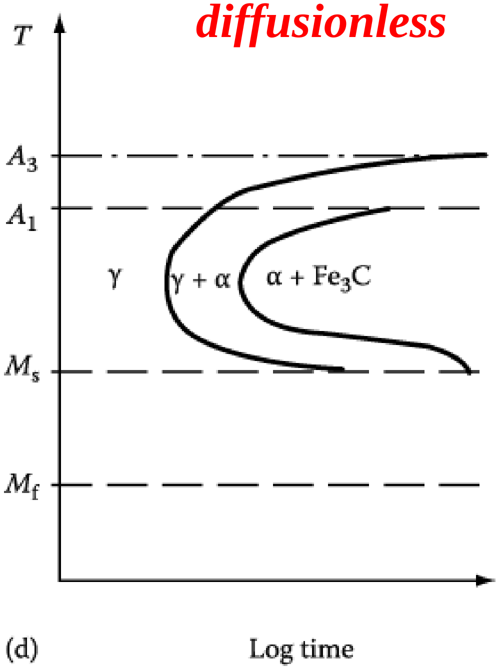
G-X diagram for C_0 at M_s

equilibrium

diffusionless



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



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 transfomrations

- The mechanisms of military 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

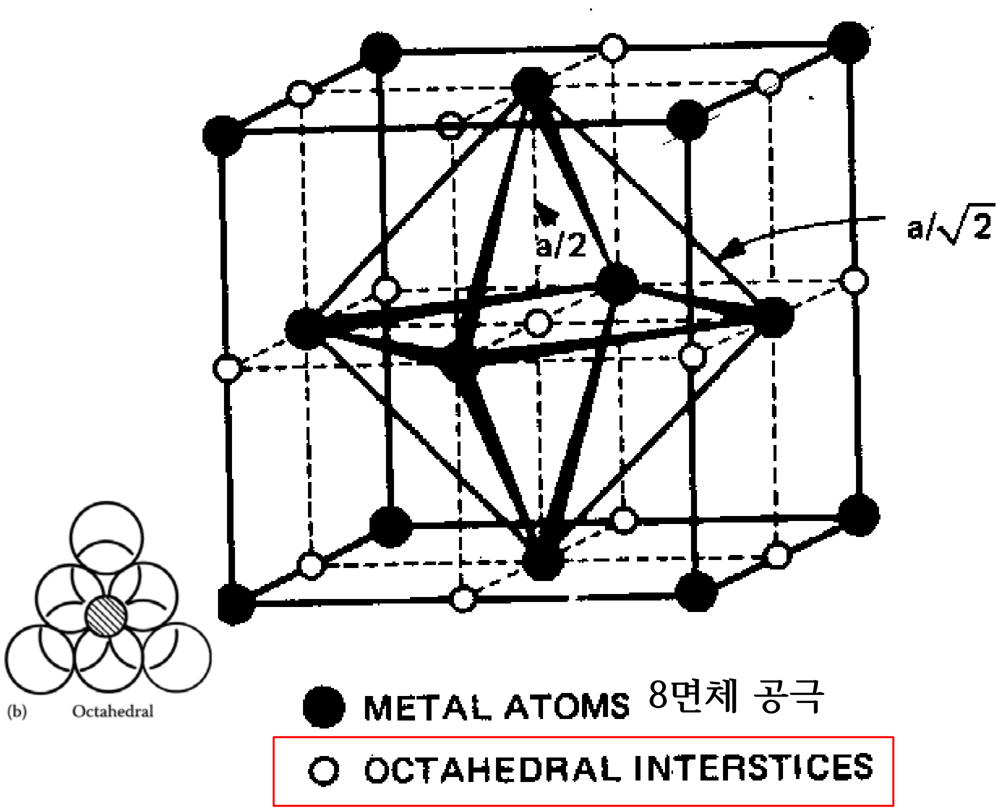
  (a) dislocation based
  (b) shear based

(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*.**

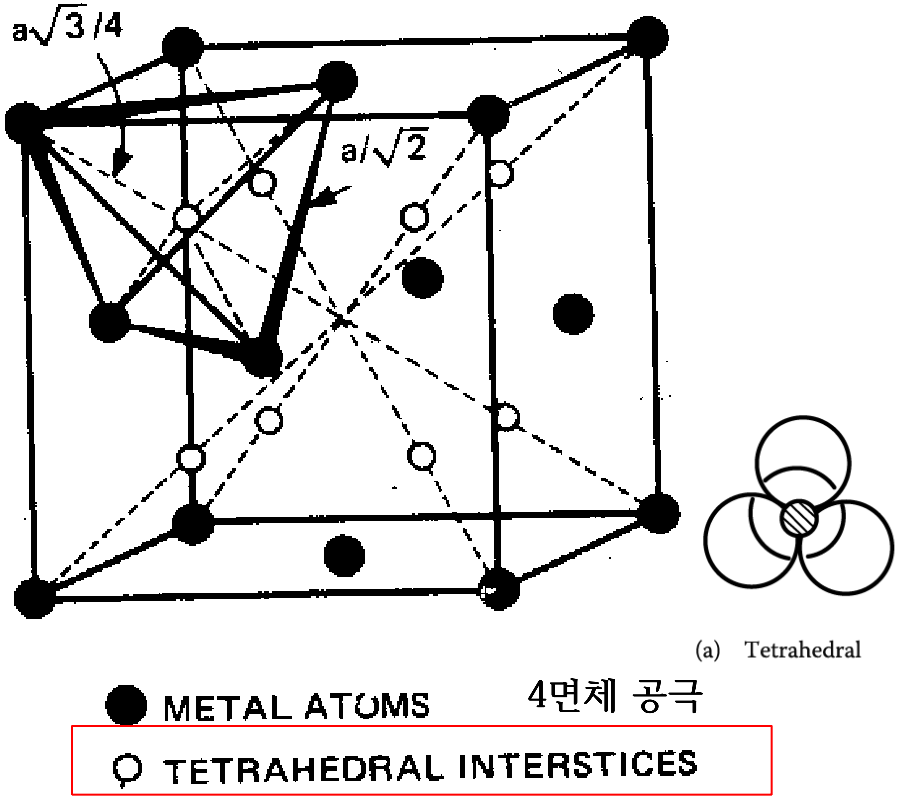
(b)
- Martensitic transformations strongly constrained by crystallography of the parent and product phases.
- This is analogous to slip (dislocation glide) and twinning, especially the latter.

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/ d6 = 0.414D = 1.044 Å



surrounded by four atoms/ d4 = 0.225D = 0.568 Å

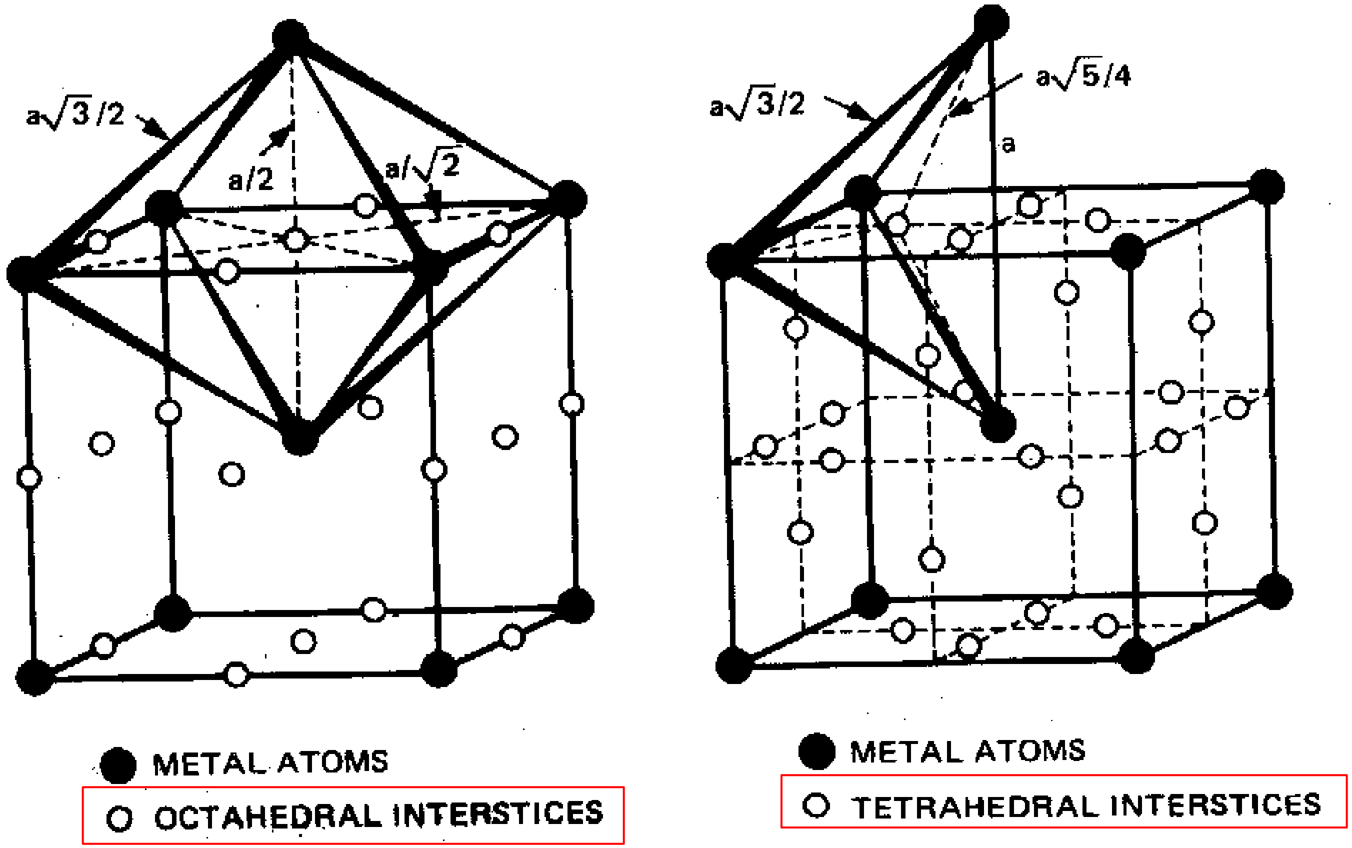
D is the diameter of the parent atoms/ d4 and d6 are the maximum interstitial diameters

Diameter of a carbon atom: 1.54 Å

: This means that considerable distortion of the γ austnite 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.



Three possible octahedral positions/
d6 = 0.155D = 0.391 Å

Six possible tetrahedral spaces/
d4 = 0.291D = 0.733 Å

D is the diameter of the parent atoms/ d4 and d6 are the maximum interstitial diameters

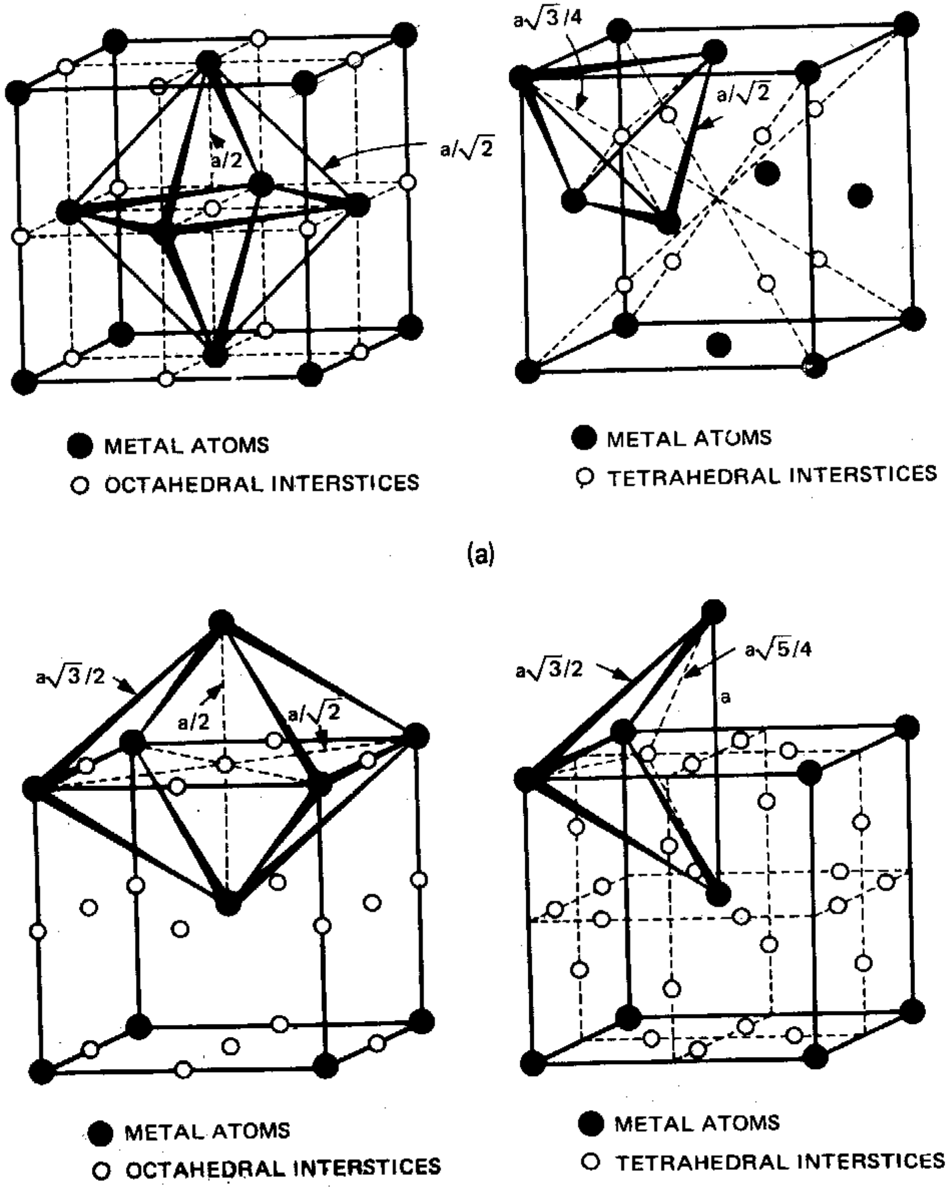
Free space: FCC < BCC but space available per interstitial: FCC > BCC

* In spite of d6<d4, 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



(a)

(b)

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.)

[Leslie]

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.

[P&E]

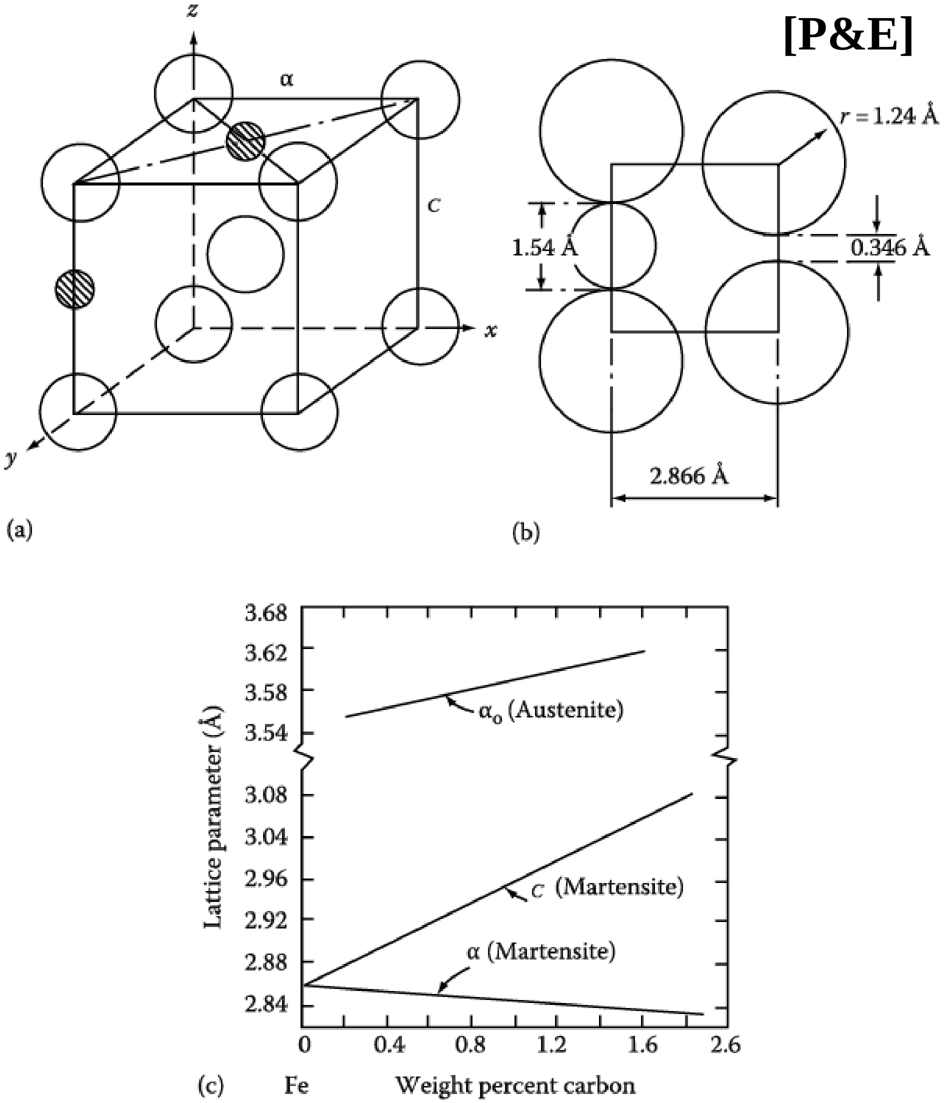


Fig. 6.5 Illustrating (a) possible sites for interstitial atoms in bcc lattice, and (b) the large distortion necessary to accommodate a carbon atom (1.54 Å diameter) compared with the space available (0.346 Å). (c) Variation of a and c as a function of carbon content.

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.

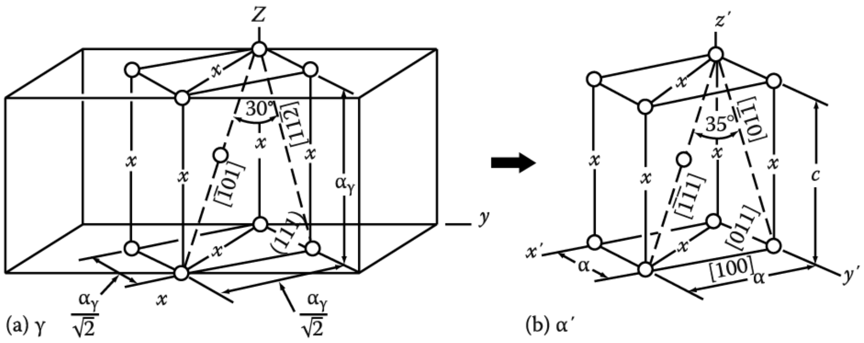
- Surprisingly, it occupies the octahedral site in the bcc Fe structure, despite the smaller size of this site (compared to the tetrahedral sites) presumably because of the low modulus in the <100> directions.

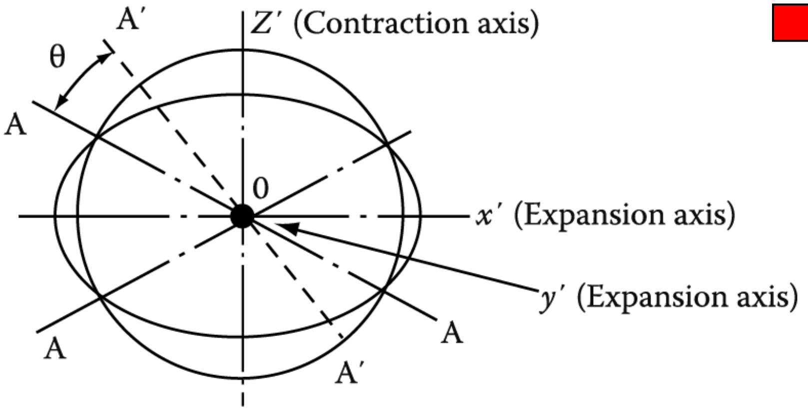
6.2. Martensite crystallography (Orientation btw M & γ)

γ→α′: (1) Habit plane of M: not distorted by transformation

(2) A homogeneous shear (s) parallel to the habit plane

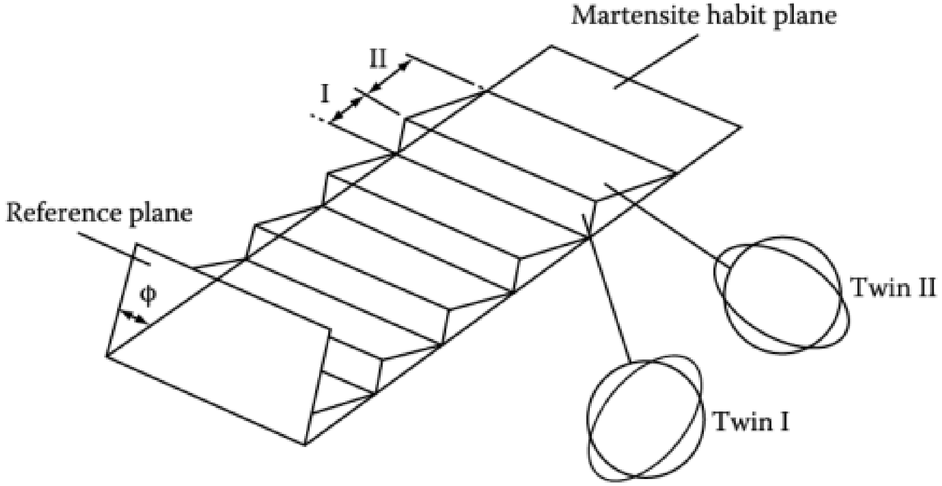
(3) ~4% expansion_dilatation normal to the habit plain (lens)





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.

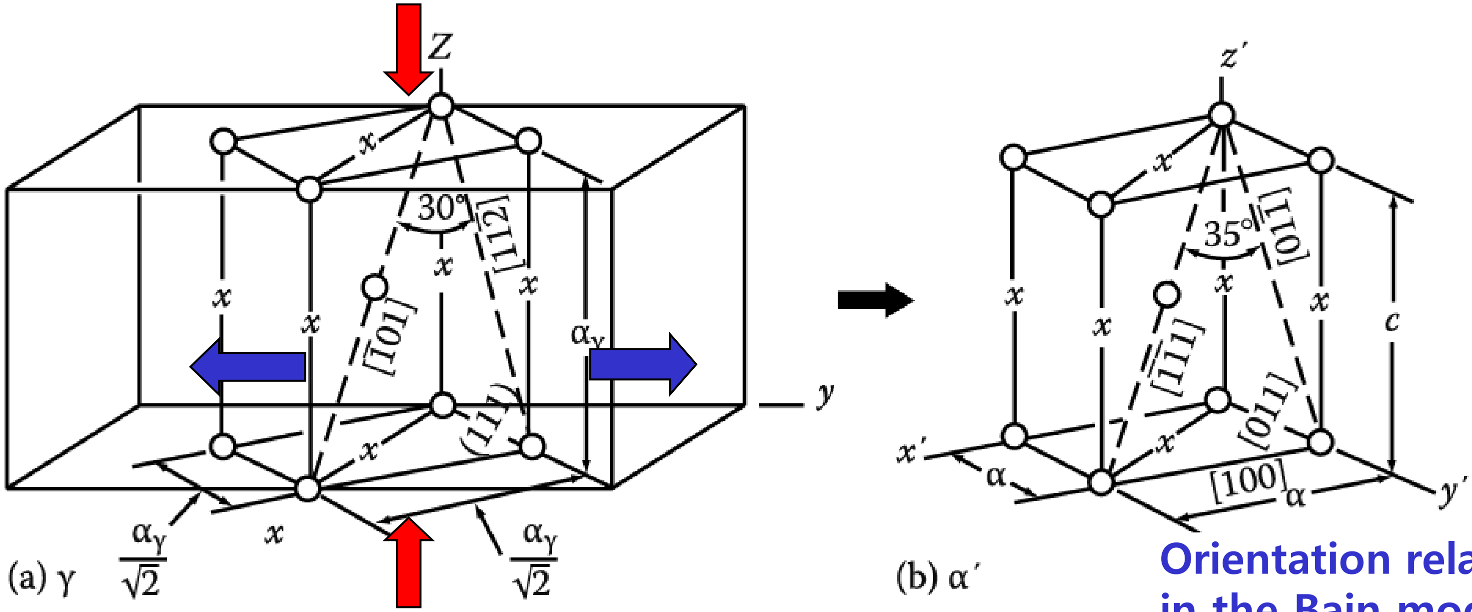


Figure. 6.7 **Bain correspondence for the γ→α’ transformation.**
Possible interstitial sites for carbon are shown by crosses.

Orientation relationships in the Bain model are:

$(111)_\gamma \rightarrow (011)_{a'}$
$[101]_\gamma \rightarrow [111]_{a'}$
$[110]_\gamma \rightarrow [100]_{a'}$
$[112]_\gamma \rightarrow [011]_{a'}$

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.

x'z' **section**

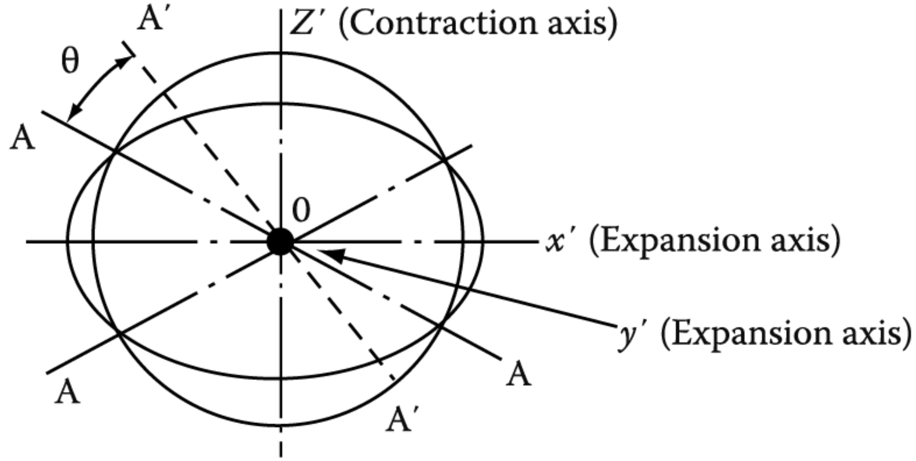


Fig. 6.8 Bain deformation is here simulated by the pure deformation in compressing a sphere elastically to the shape of an oblate ellipsoid. As in the bain deformation, this transformation involves two expansion axes and one contraction axis.

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 brining 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.

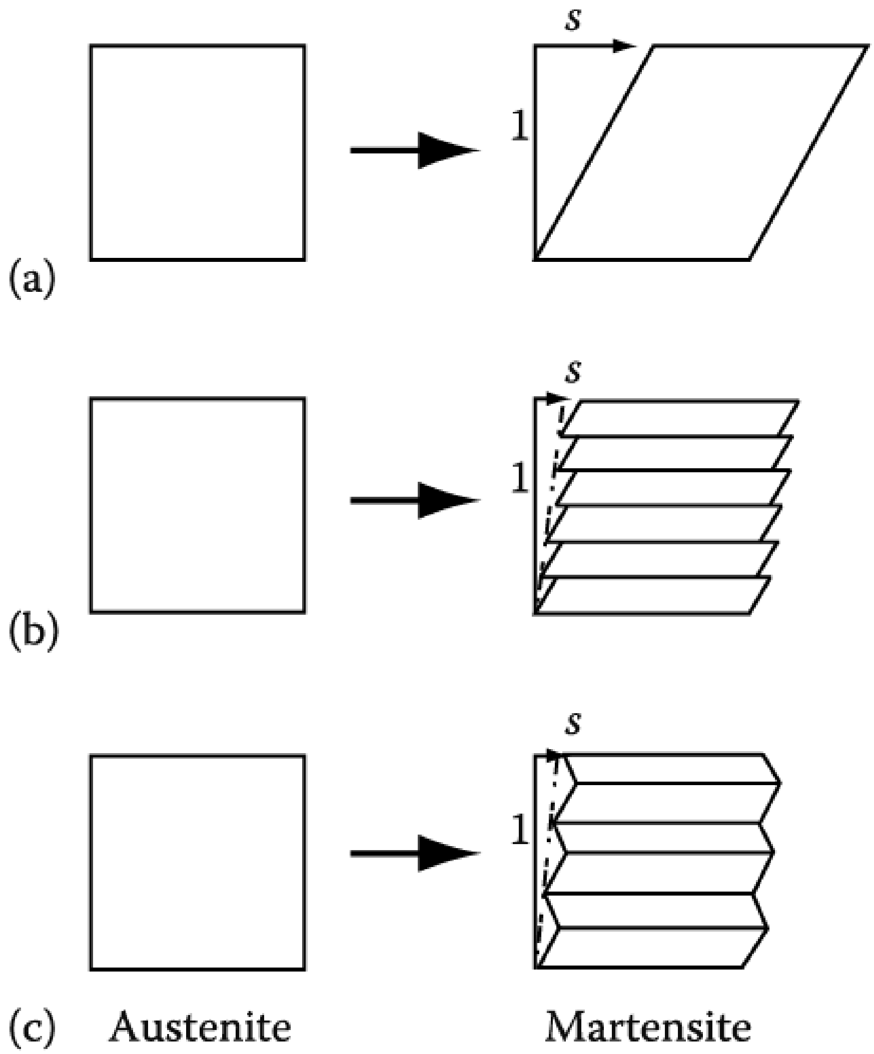
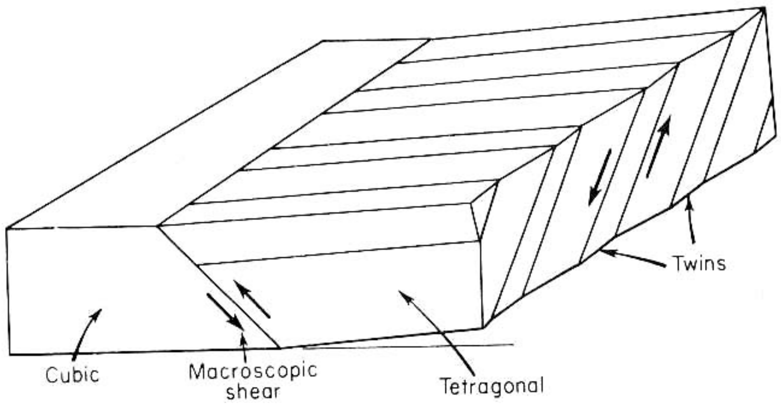
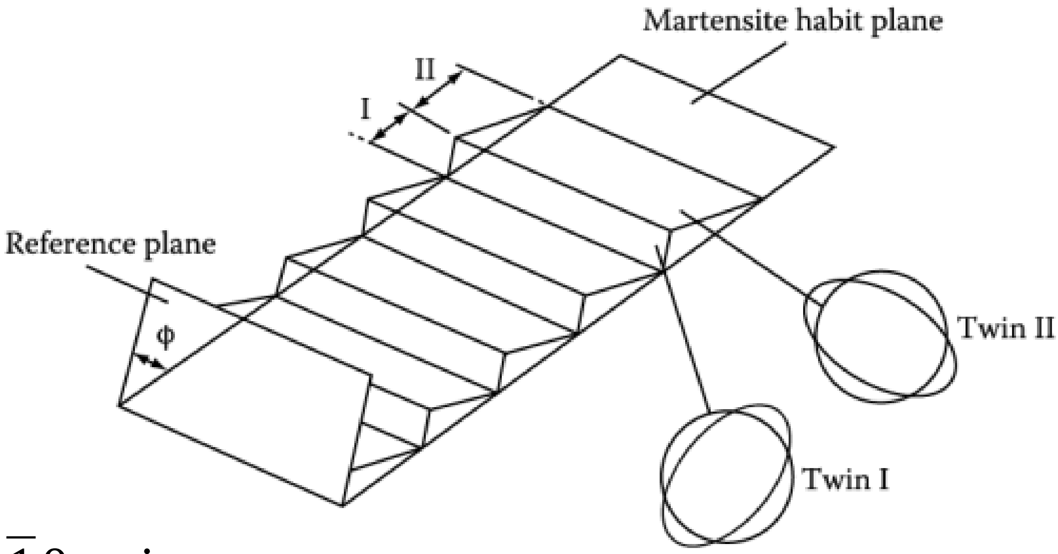


Figure. 6.9 Schematic illustration of how dislocation glide or twinning of the martensite can compensate for a pure lattice deformation such as a Bain deformation and thereby reduce the strain of the surrounding austenite. The transformation shear (s) is defined. Note how s can be reduced by slip or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

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





Slip or Twinning on

$\{11\bar{2}\}<111>$ *in* α $\quad \{110\}<1\bar{1}0>$ *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.

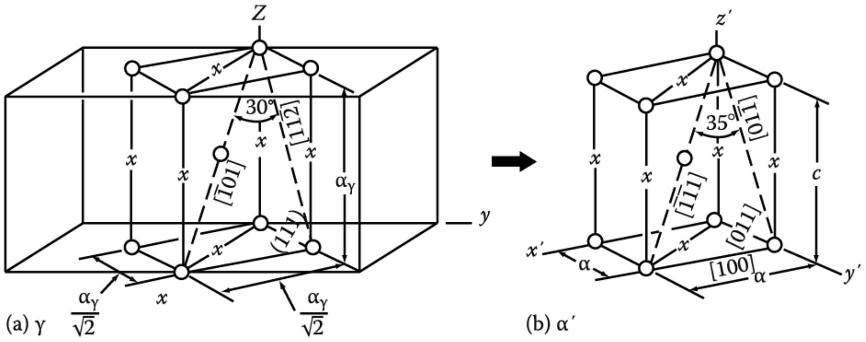
6.2. Martensite crystallography (Orientation btw M & γ)

γ→α′:

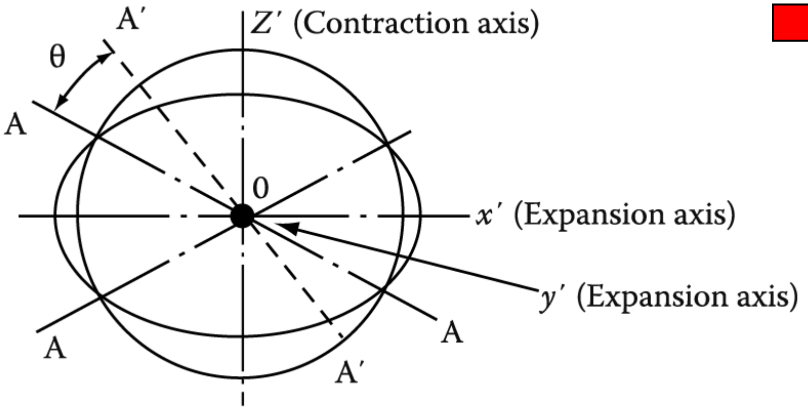
(1) Habit plane of M: not distorted by transformation

(2) A homogeneous shear (s) parallel to the habit plane

(3) ~4% expansion_dilatation normal to the habit plain (lens)

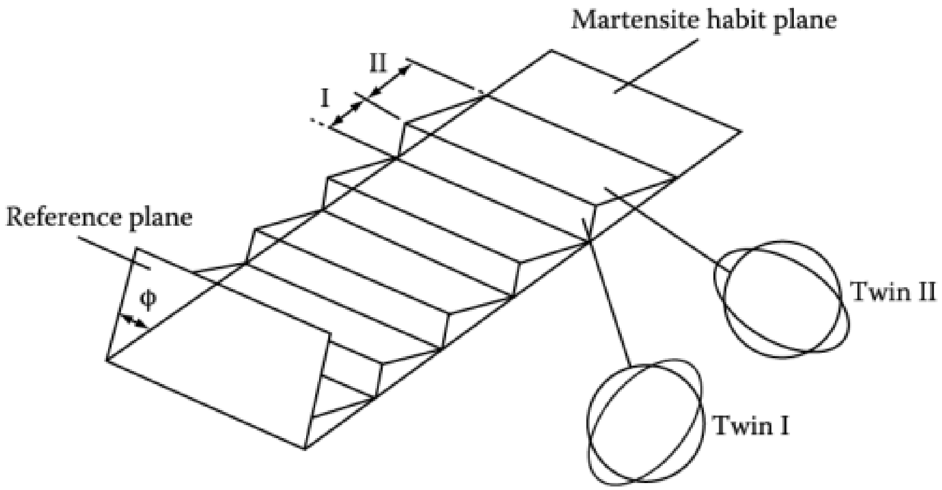


(a) γ (b) α′



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.

Representative Diffusionless Transformation

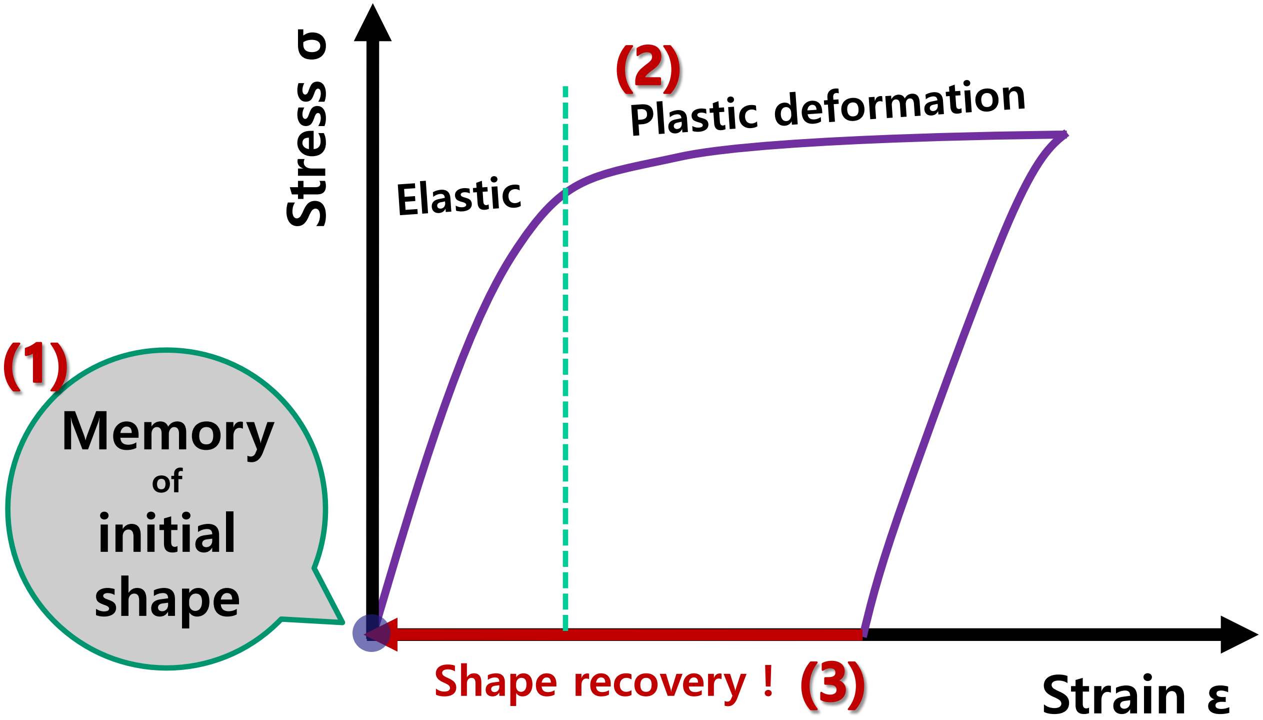
Martensitic transformation in Ni-Ti alloy ;

55~55.5 wt%Ni - 44.5~45 wt%Ti (“Nitinol”)

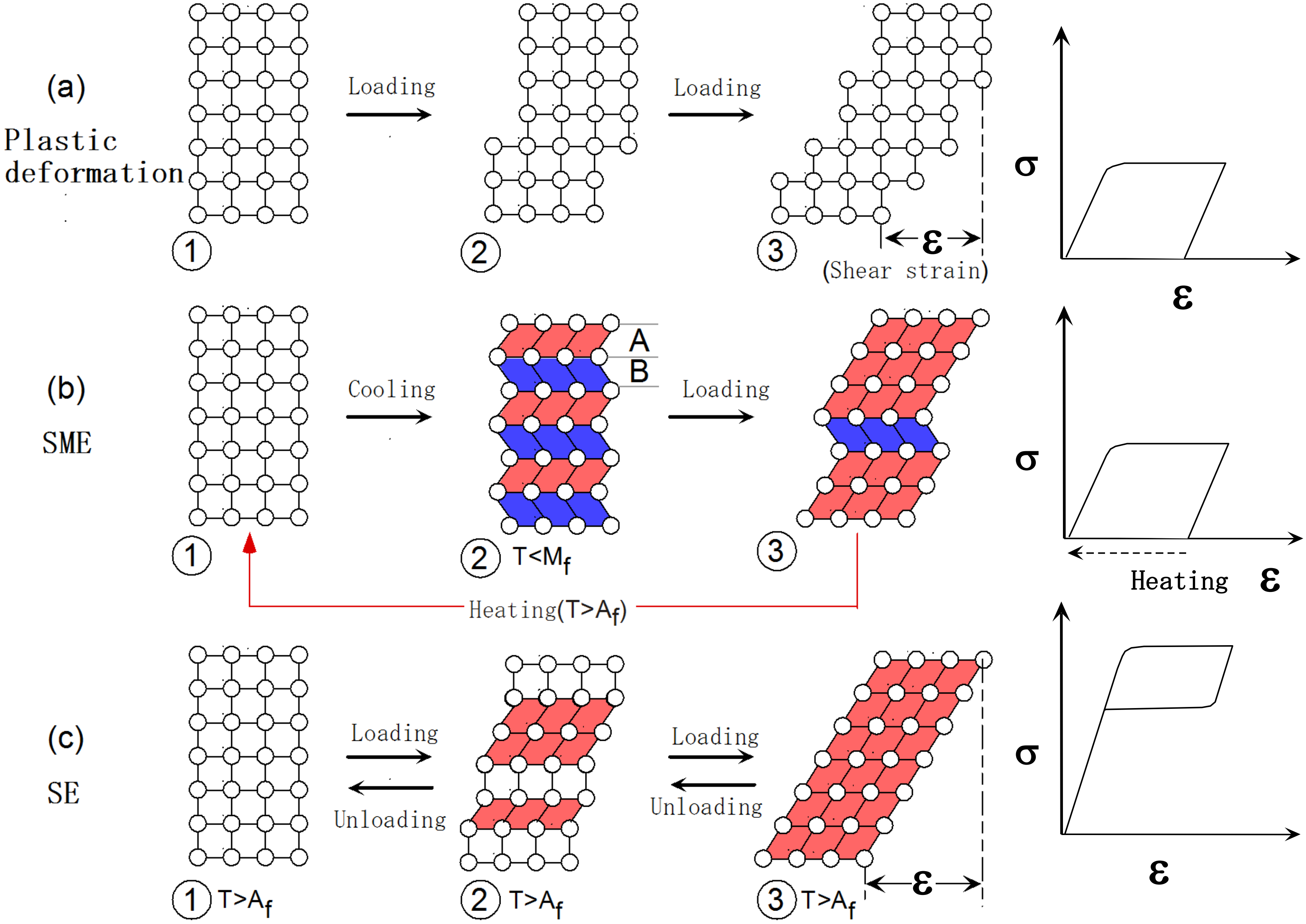
Ex) Shape memory alloy

Introduction - Shape memory effect

Stress-Strain cycle



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


(a)
Plastic deformation
Loading
Loading
①
②
③
ε
(Shear strain)
σ
ε
(b)
SME
Cooling
A
B
Loading
①
② T<M_f
③
Heating(T>A_f)
σ
Heating
ε
(c)
SE
Loading
Unloading
Loading
Unloading
① T>A_f
② T>A_f
③ T>A_f
ε
σ
ε

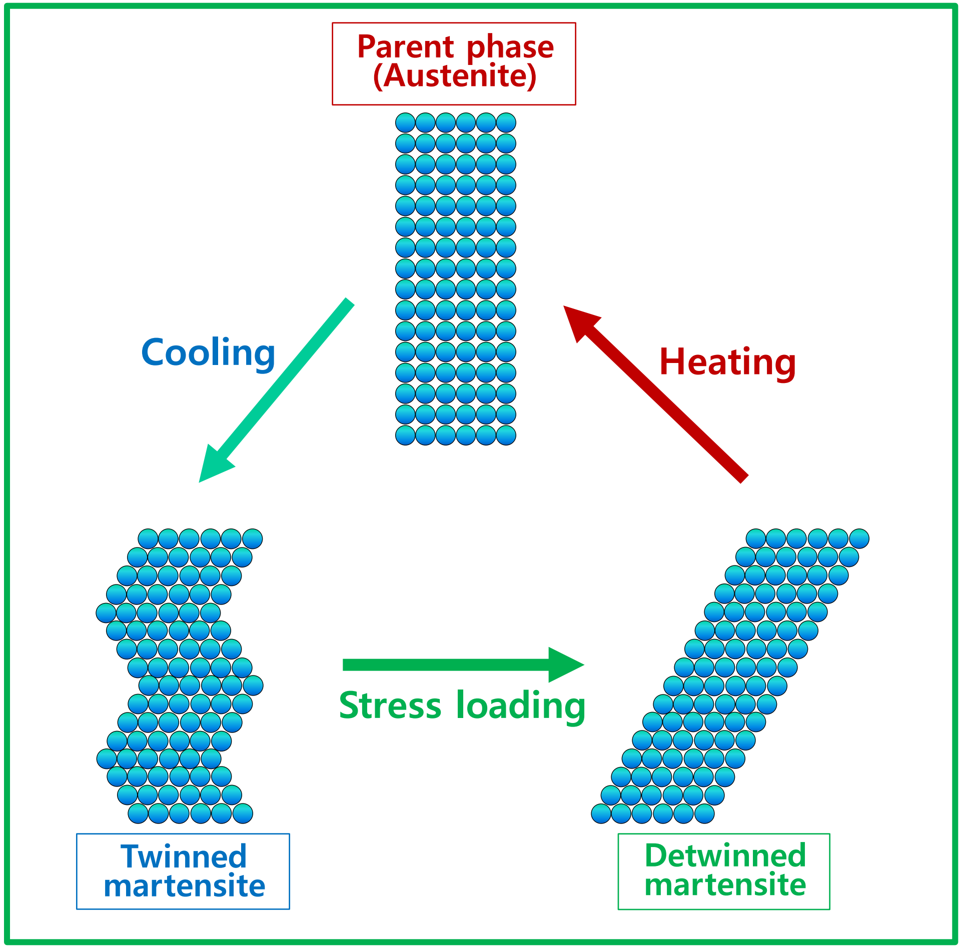
Principles

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

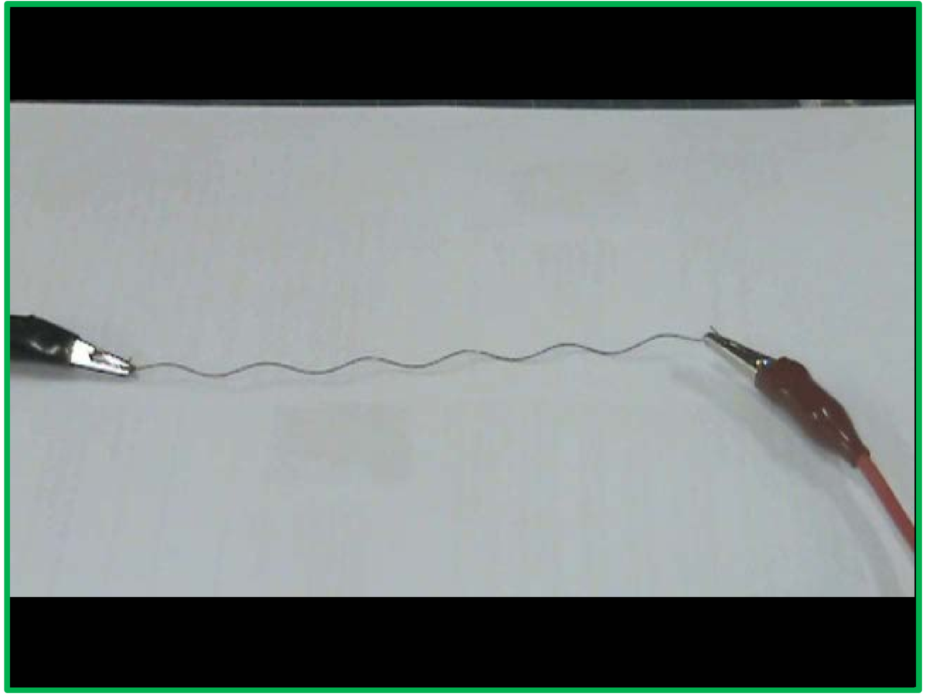
2. M_s 이하의 온도로 냉각시
   Twinned martensite 생성

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

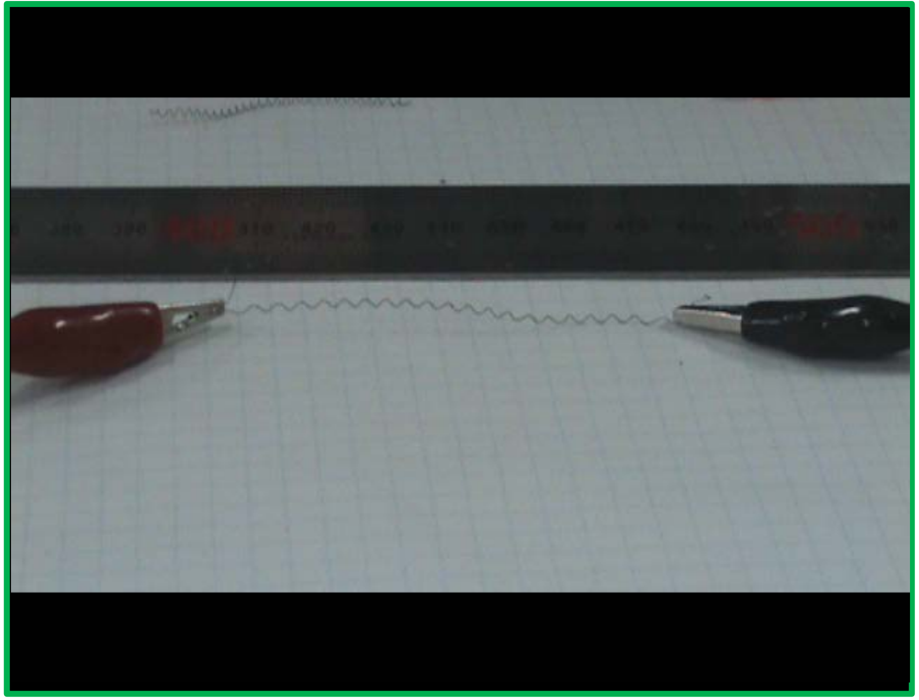


↳ A_f 이상의 고온 형상만을 기억

➡ 저온(< M_f)에서 소성변형 후
A_f 이상의 고온으로 가열

➡ 기억된 고온 형상으로 회복

▼ Two-way SME

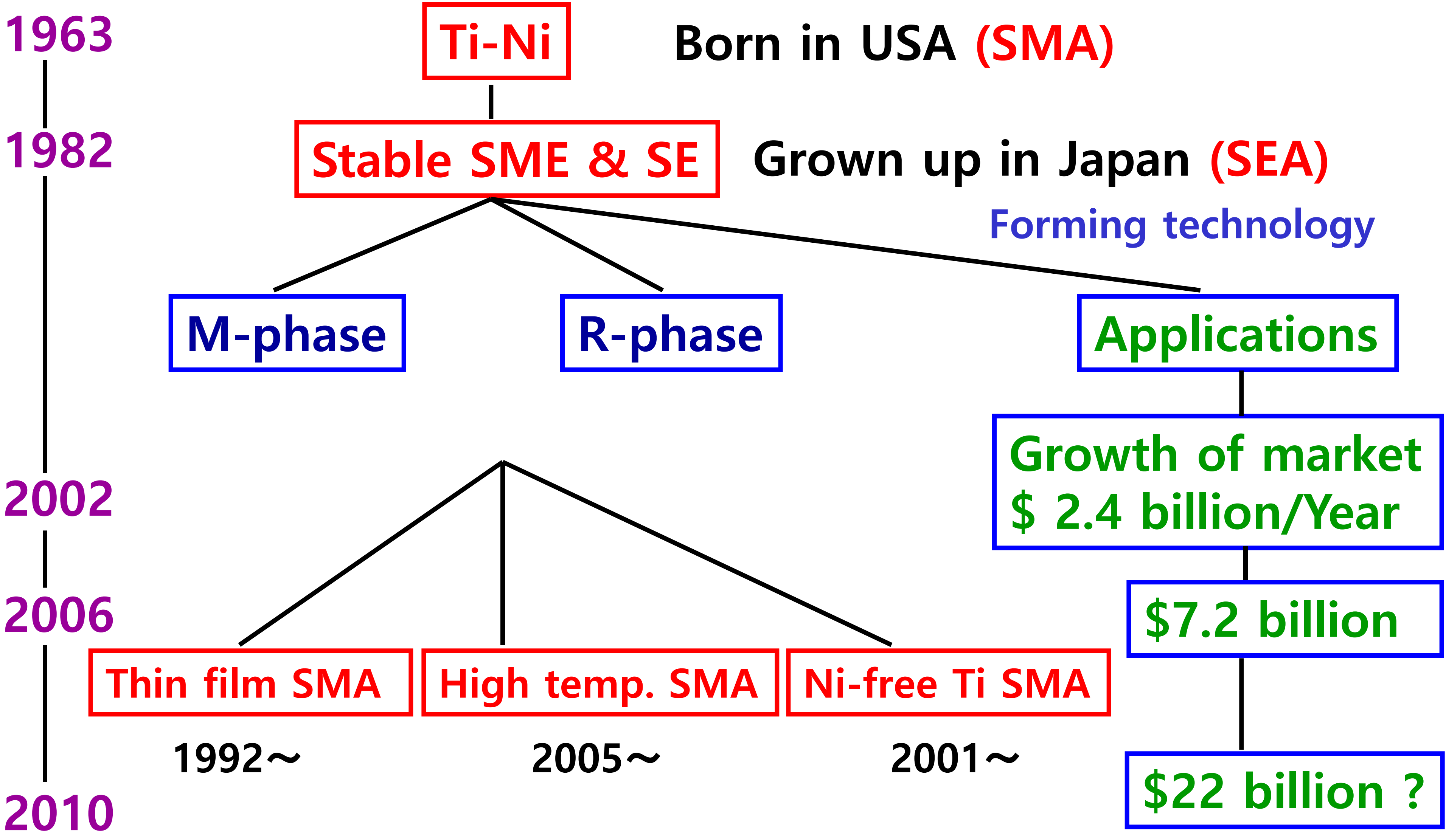


↳ 고온(> A_f) 형상과 저온(< M_f) 형상을 모두 기억

➡ 반복적인 변형으로 인한 형상기억합금 내
전위 밀도의 상승 & 특정방향 응력장의 형성

➡ 저온에서 반복소성변형 방향으로 회복

Summary



1963 Ti-Ni Born in USA (SMA)

1982 Stable SME & SE Grown up in Japan (SEA)

Forming technology

M-phase

R-phase

Applications

Growth of market
$ 2.4 billion/Year

2002

2006 $7.2 billion

Thin film SMA 1992～

High temp. SMA 2005～

Ni-free Ti SMA 2001～

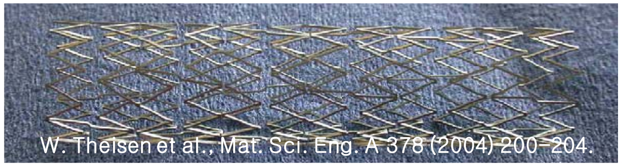
2010 $22 billion ?

* Application of SMAs

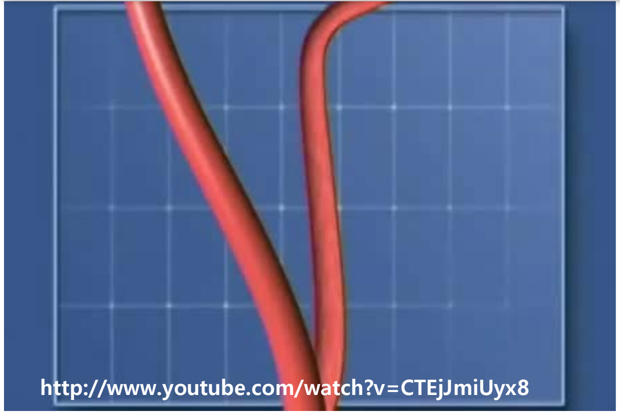
▼ **산업 부문: 부품소재** (파이프 이음, 스위치소자나 온도제어용 장치 등)

http://www.intrinsicdevices.com/

http://www.intrinsicdevices.com/



W. Theisen et al., Mat. Sci. Eng. A 378 (2004) 200–204.



http://www.youtube.com/watch?v=CTEjJmiUyx8

http://www.youtube.com/watch?v=fDNbGOwT2hI

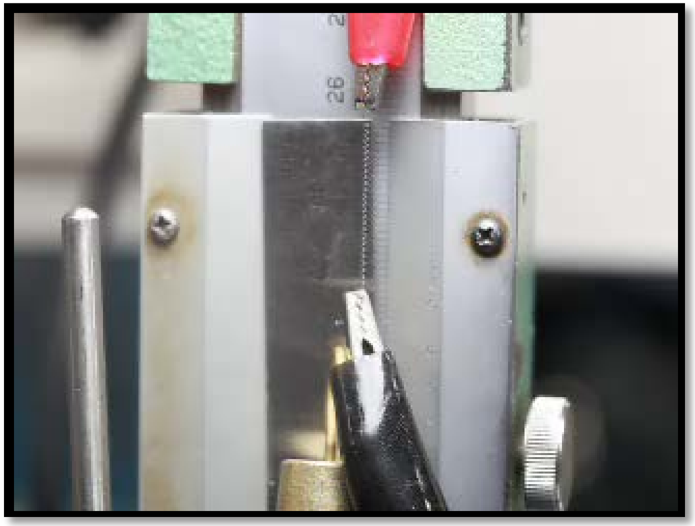
▲ **생체의료 부문: 첨단의료재료**
(stent, 치열교정용 강선 등)

▲ **심해저/우주항공 부문: 극지재료**
(잠수함, 태양전지판 등)

* SMA Actuator

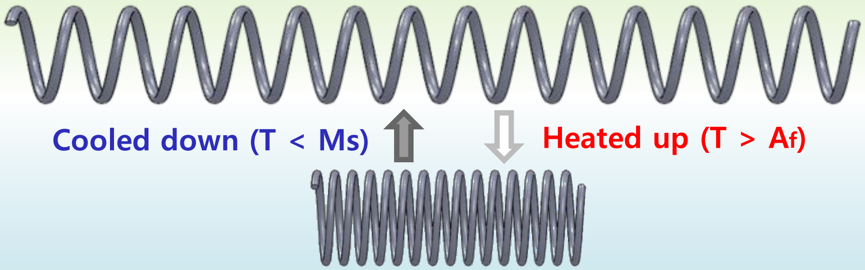
- 액츄에이터(Actuator) : 전기 에너지, 열에너지 등의 에너지원을 운동에너지로 전환하여 기계장치를 움직이도록 하는 구동소자

▲ 기존의 매크로 스케일 액츄에이터 (모터-기어 방식)



▲ SMA 스프링 액츄에이터

SMA Spring Actuator



재료의 수축과 신장을 통하여 기계적인 동작을 가능하게 함.

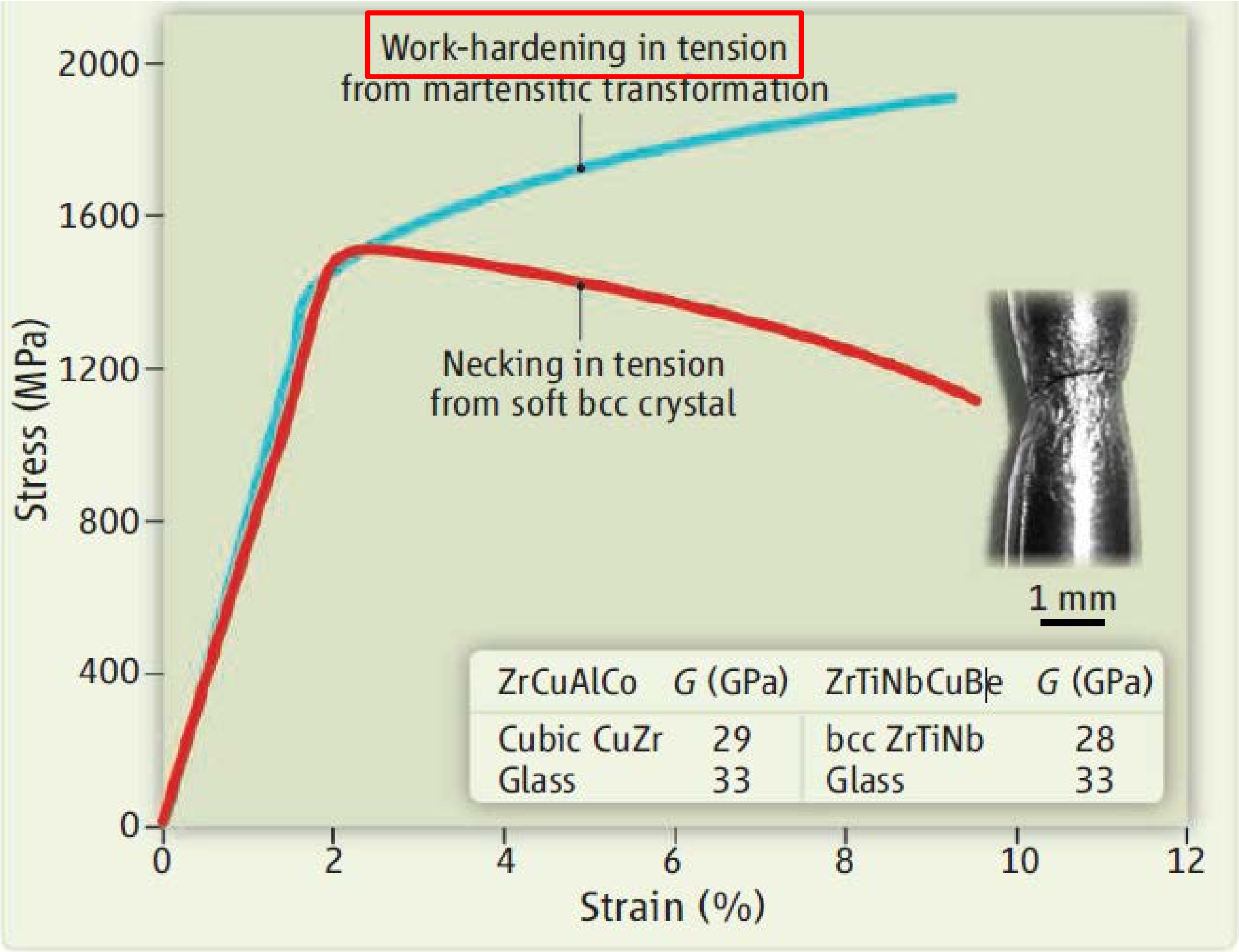
1. 단위 체적당 출력이 높음
2. 모터 구동에 비해 매우 단순한 구조
3. 온도에 의한 제어가 용이
4. 소형화가 쉬움.

MATERIALS SCIENCE

Shape Memory Bulk Metallic Glass Composites

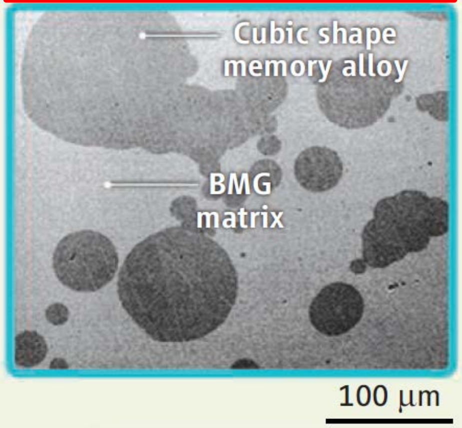
Glass-forming and shape memory metals may provide a route to fabricating materials with enhanced mechanical properties.

Douglas C. Hofmann

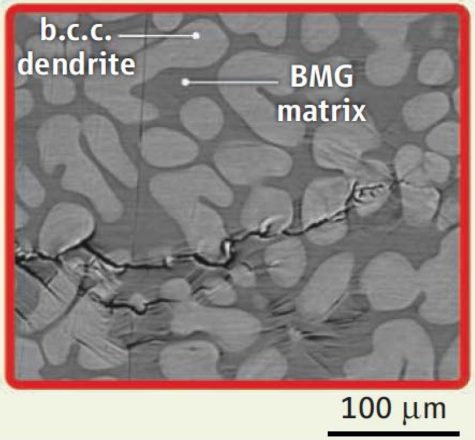


ZrCuAlCo	G (GPa)	ZrTiNbCuBe	G (GPa)
Cubic CuZr	29	bcc ZrTiNb	28
Glass	33	Glass	33

$Zr_{48}Cu_{47.5}Al_{4}Co_{0.5}$



$Zr_{39.6}Ti_{33.9}Nb_{7.6}Cu_{0.5}Be_{12.5}$



Douglas C. Hofmann, SCIENCE VOL 329 10 SEPTEMBER 2010

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

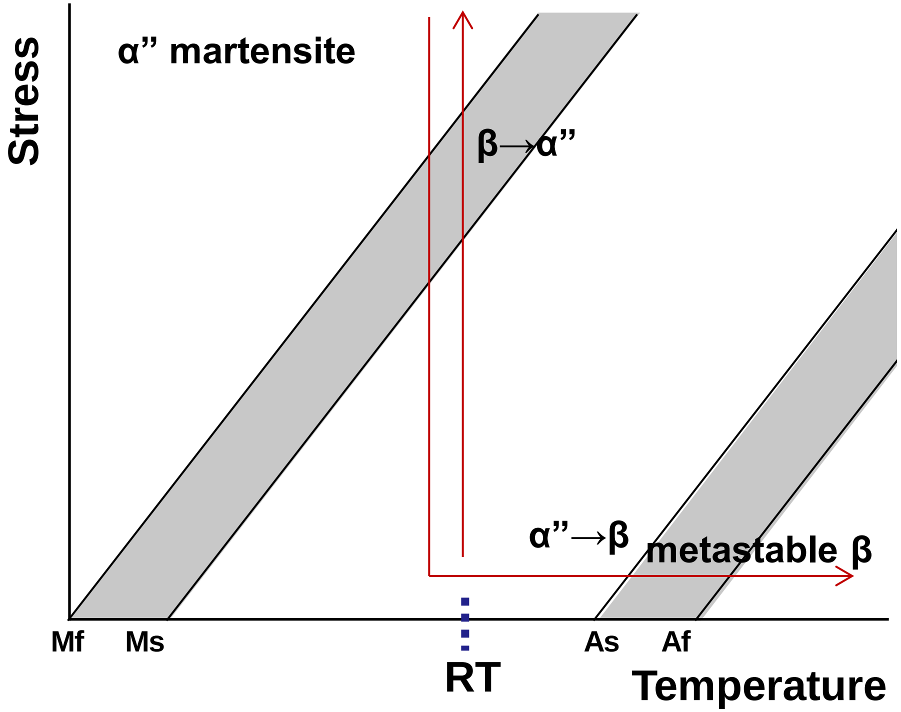
- **Alloy system** **Cu-Zr-Al system** → **Ti-Cu-Ni system**

Secondary phase

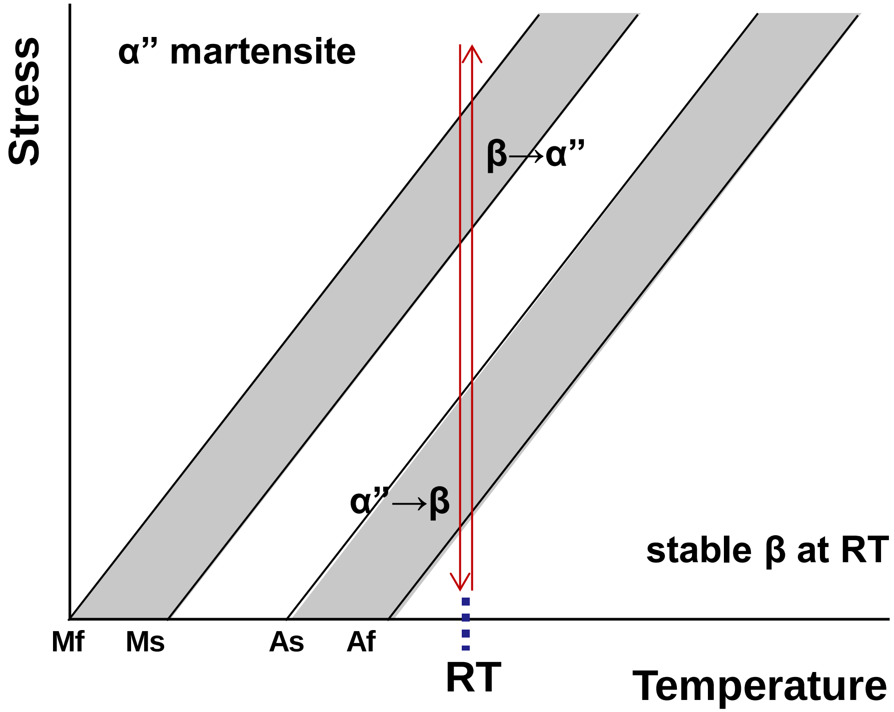
CuZr
Metastable B2 phase at RT
"Shape Memory Behavior"

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

Shape Memory Alloy (SMA)



Super-Elastic Alloy (SE alloy)

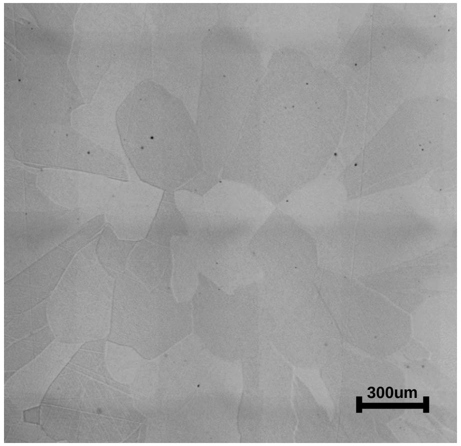


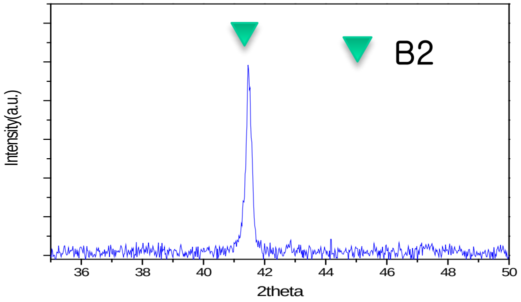
ESPark Research Group

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

- **Alloy composition:** **Ti_{49}-Cu-Ni-X**

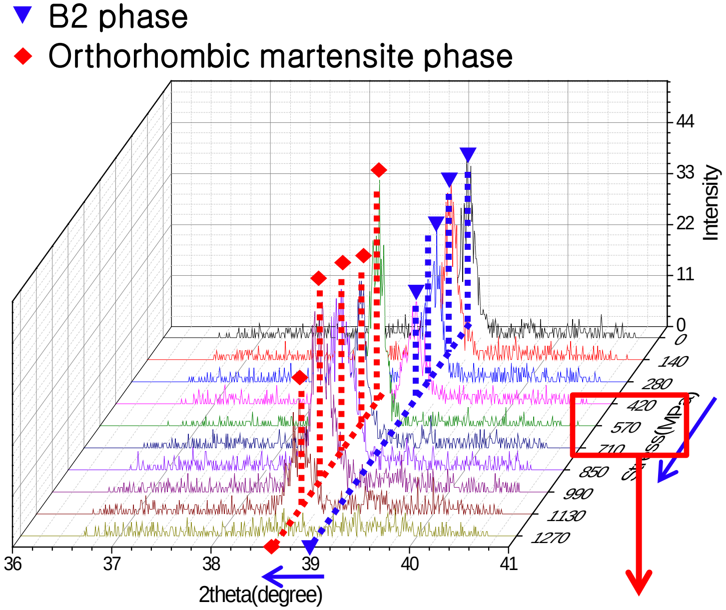
Φ3mm suction casting
-Fully crystalline B2





▷ Stress-induced phase transformation

In-situ neutron diffraction measurement during compression

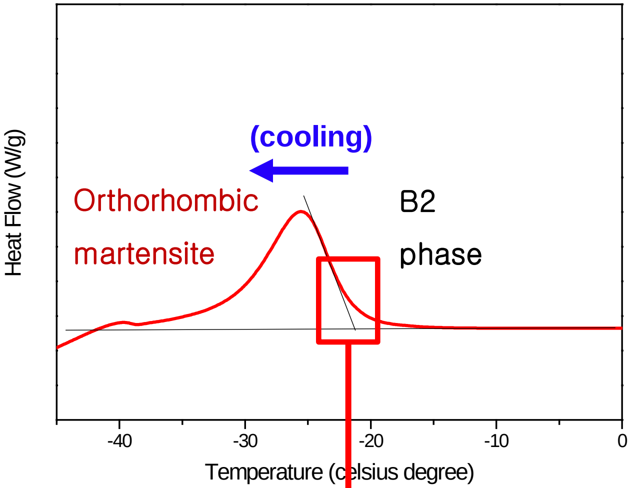


Phase transformation stress

= 570MPa

▷ Temperature-induced phase transformation

DSC measurement (during cooling)



Martensite start T (Ms)

= −22℃

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

ESPark Research Group

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 → Solid
- (Ch5) Diffusional Transformations in Solid: Solid → Solid
- (Ch6) Diffusionless Transformations: Solid → 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)

Good Luck!!

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

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

Teaching notes: 14~25/

QUIZ and Homeworks

Good Luck!!