Module #25

Martensitic Transformations and Strengthening

READING LIST

► DIETER: Ch. 6, pp. 226-228.

- Chapter 11 in Meyers & Chawla.
- Chapter 13 in P. Haasen, Physical Metallurgy, 3rd Edition, Cambridge University Press (1996).
- Chapter 6 in D.A. Porter and K.E. Easterling, Phase Transformations in Metals and Alloys, 2nd Edition, CRC Press (1992).
- Ch. 5 of G. Krauss' Steels: Processing, Structure, and Performance, 2nd Edition, ASM, Materials Park, OH (2005)

Introduction

- It has long been recognized that some materials can be significantly strengthened by quenching them and inducing the formation of a metastable phase that has a different crystal structure than the parent material.

- One type of phase than can form and lead to significant increases in strength is called *martensite*.

- The phase transformations in this case are called *martensitic transformations*.

- Martensite is important for more than just its strength. Martensitic transformations are also key elements in *shape memory effect* and the *superelastic effect*.

Martensite

- Named after German metallurgist Adolf Martens. Described a hard microstructure found in quenched carbon steel.

- More recent emphasis placed on the nature of the phase transformation, which is displacive (not diffusive).

- Martensitic transformations occur in a wide array of materials systems.

Goal of Module

- In this Module, our goal is not to exhaustively review the physical metallurgy of martensite.

- Our goal will be to briefly (very briefly) address the strengthening that can be obtained from martensitic transformations and the role of martensitic transformations in deformation. We will relate everything to the fundamentals that we have discussed already.

- Listen carefully as I may say more in your lectures than I have written down here!

Introduction (3)

- Martensites are one of the most technologically interesting and complicated classes of materials when considering strength.

- Martensites invoke several (combined) strengthening mechanisms like most structural materials. Martensitic transformations are extremely important in a variety of materials.

- Martensitic transformations also play a critical role in many deformation processes such as the aforementioned shape memory and superelastic effects.

Some alloy systems where martensitic transformations are known to occur

Alloy(s)	Transformation
Co, Fe-Mn, Fe-Cr-Ni	FCC ↔ HCP
Fe-Ni	FCC ↔ BCC
Fe-C, Fe-Ni-C, Fe-Cr-C, Fe-Mn-C, etc.	**FCC ↔ BCT**
In-Tl, Mn-Cu	FCC ↔ FCT
Au-Cd	BCC ↔ Orthorhombic
ZrO_2	Tetragonal ↔ Monoclinic
Ti-Al-Nb, Ti-Al-Ta, etc	B2 ↔ Ordered HCP
TiNi (Nitinol)	B2 ↔ Monoclinic

Kinetics/Thermodynamics of Martensitic transformation

- Martensitic transformations are *diffusionless* structural changes that have a *dominant deviatory component* and an *associated change in shape* such that *strain energy* dominates the kinetics and morphology of the transformation.

- More simply put, thermodynamic considerations induce a shear of the lattice into a metastable state during quenching.

Kinetics/Thermodynamics of Martensitic transformation

- There are many different morphologies for martensites. Some are shown on the next slide.
  - Plate
  - Lath
  - Acicular
  - Lenticular
  - Twinned
  - Etc.

- Acicular martensite (BCC or BCT structure) has a significant impact on strength.
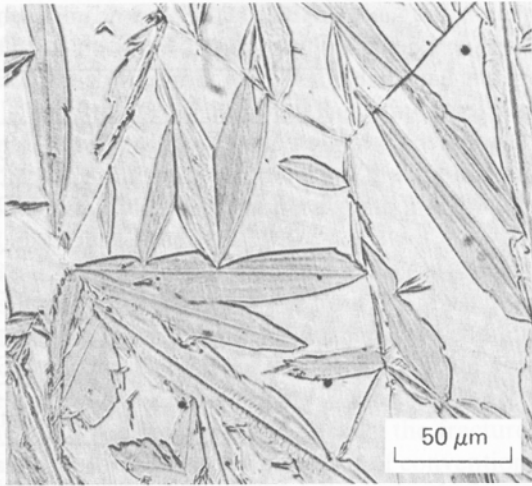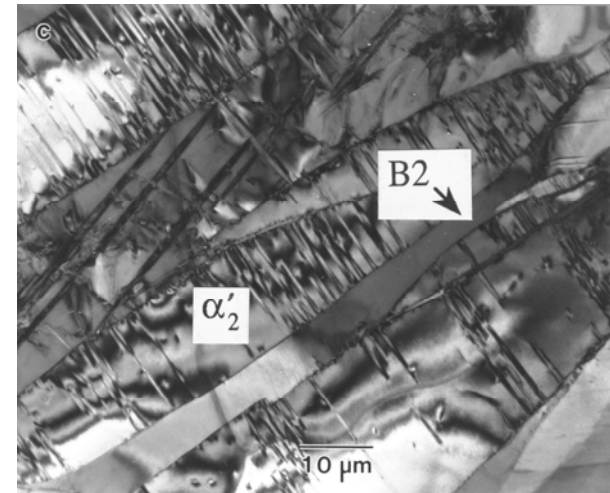
What do they look like?

Figure 11.2(a) Lenticular martensite in an Fe–30% Ni alloy. (Courtesy of J. R. C. Guimarães)

[Meyers & Chawla]
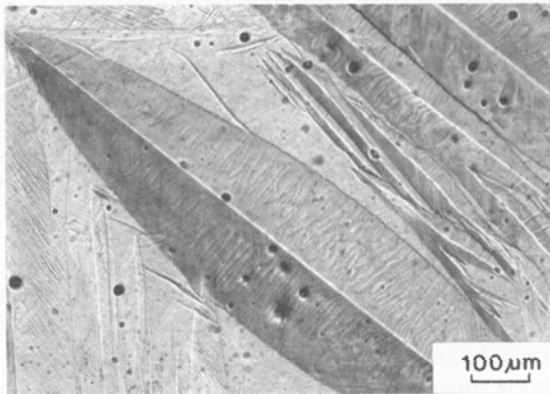

B2

α'_2

[Weaver & Kaufman]

Figure 11.2(b) Lenticular (thermoelastic) martensite in Cu–Al–Ni alloy. (Courtesy of R. J. Salzbrenner)
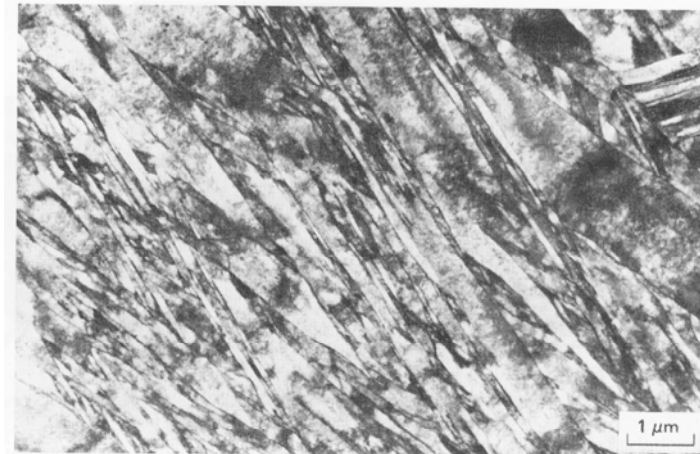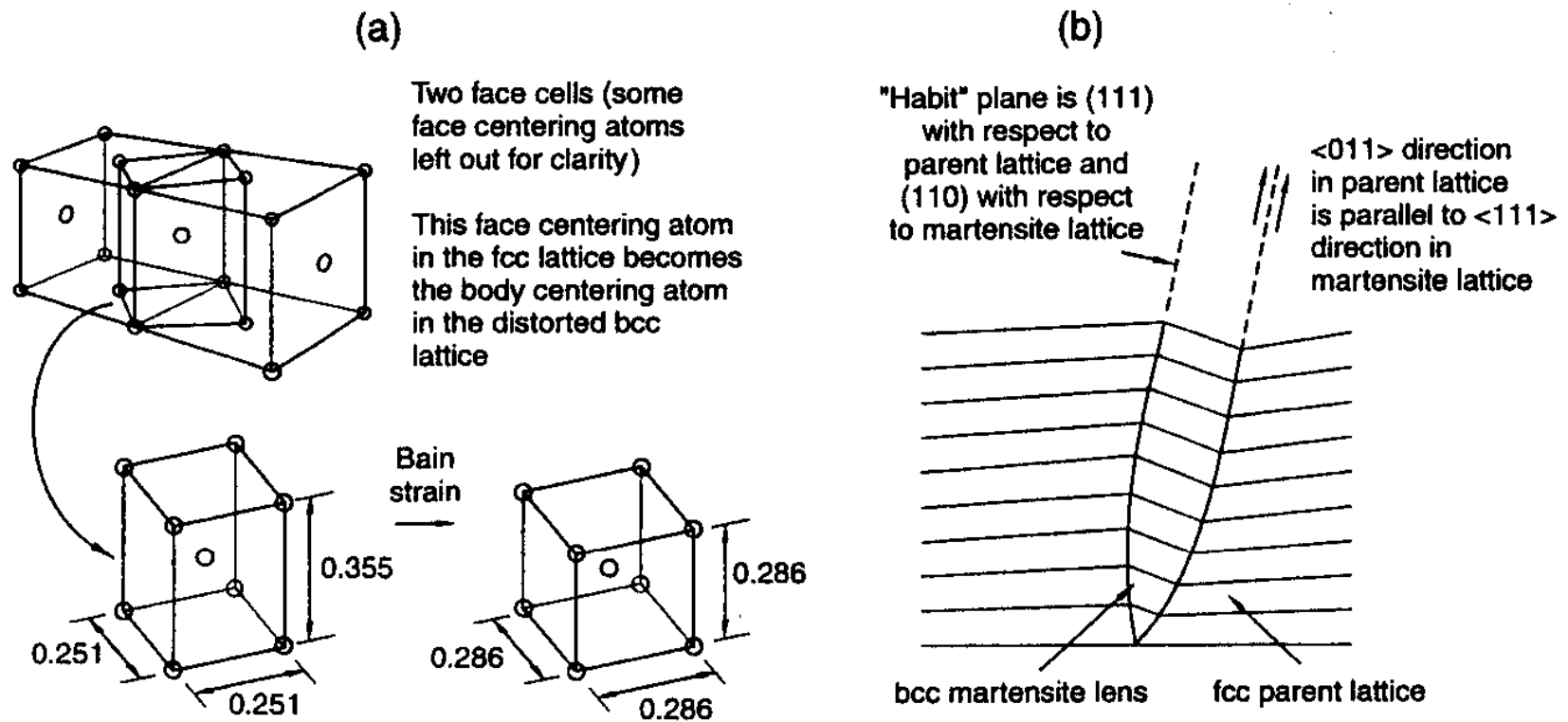
[Meyers & Chawla]

Figure 11.3 Lath martensite. (Reprinted with permission from C. A. Apple, R. N. Caron, and G. Krauss, *Met-Trans.*, 5 (1974) 593)

[Meyers & Chawla]

Martensites have a wide variety of morphologies.
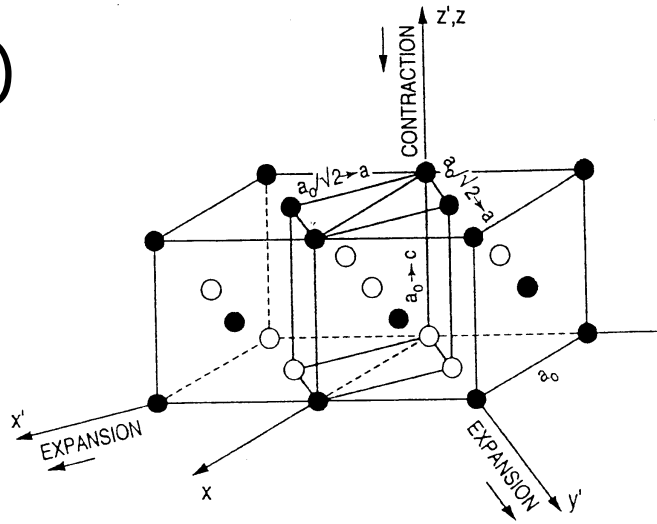All have a few features in common.

FIGURE 2.21 Formation of martensite: (a) local shuffling brings two f.c.c. lattices together (note that the Bain strain is needed to restore undistorted cubic cell; (b) coherent thin martensite plate. (Adapted from Ashby and Jones, 1994. Reprinted with permission from Pergamon Press.)
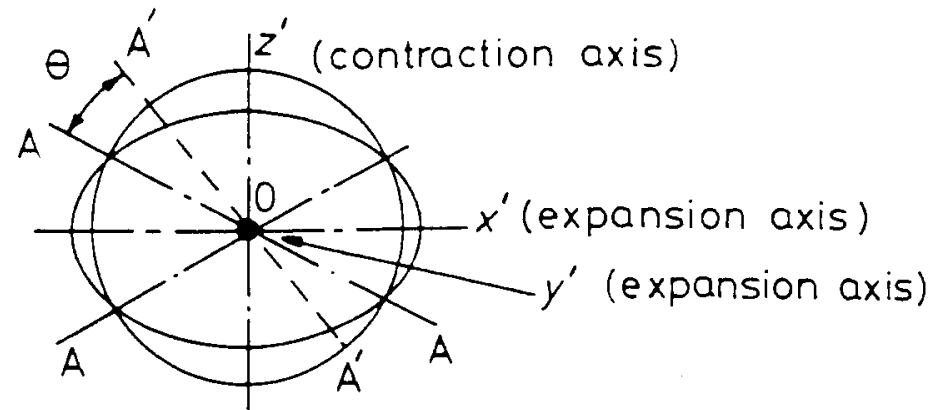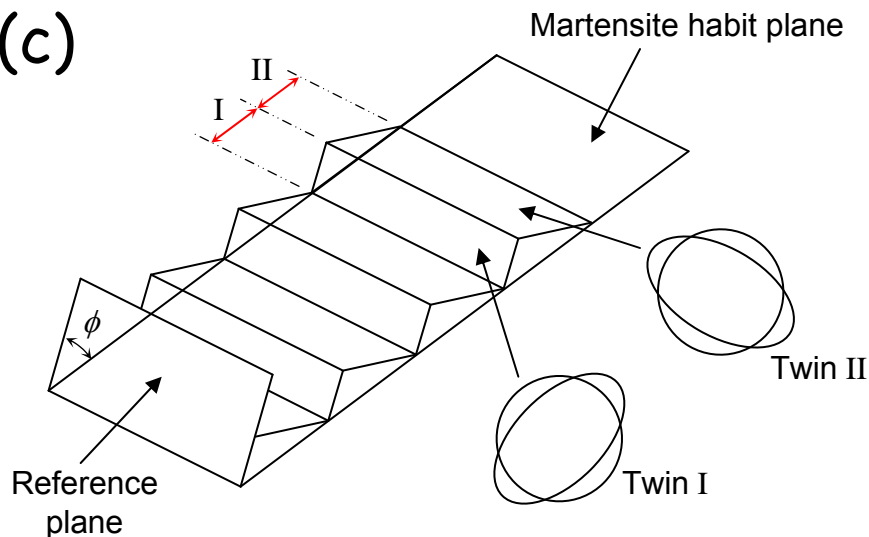
The Bain strain and twinning in martensite

(a)

The Bain deformation

(b)

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

(c)

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

[Figures (b) and (c) from Porter & Easterling. (b) p. 394 and (c) p. 395.]

Common features for all martensites

- The existence of an *undistorted* and *unrotated plane* (i.e., *habit plane*). There is always a plane that has the same indices in both structures.

- There will be a crystallographic orientation relationship between them. Some famous ones are the Kurdjumov-Sachs relationship and the Nishiyama-Wasserman relationship. They occur in steels.

  - KS relationship

    $$(111)_A \parallel (011)_M$$
    $$[10\bar{1}]_A \parallel [01\bar{1}]_M$$

  - NW relationship

    $$(111)_A \parallel (011)_M$$
    $$[11\bar{2}]_A \parallel [01\bar{1}]_M$$

Region of plastic accommodation in austenite

Tilted martensite surface

Original austenite surface

Austenite

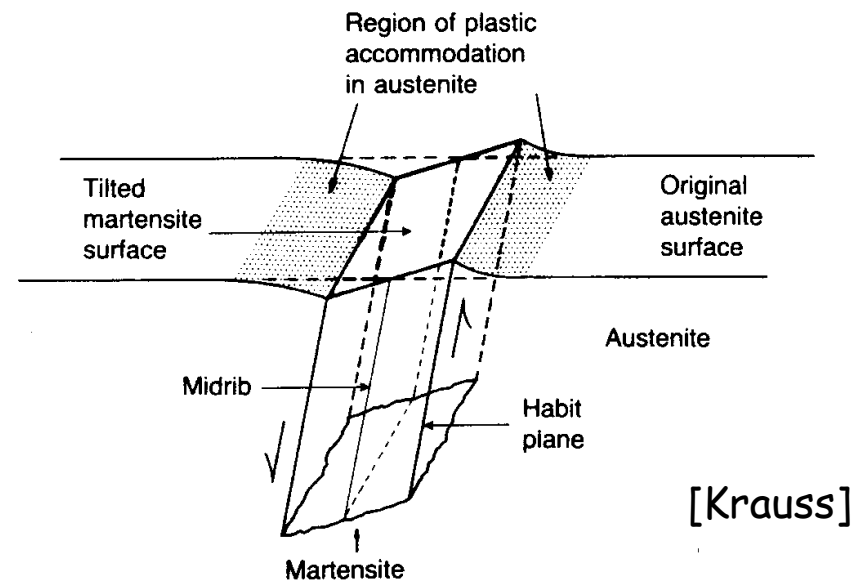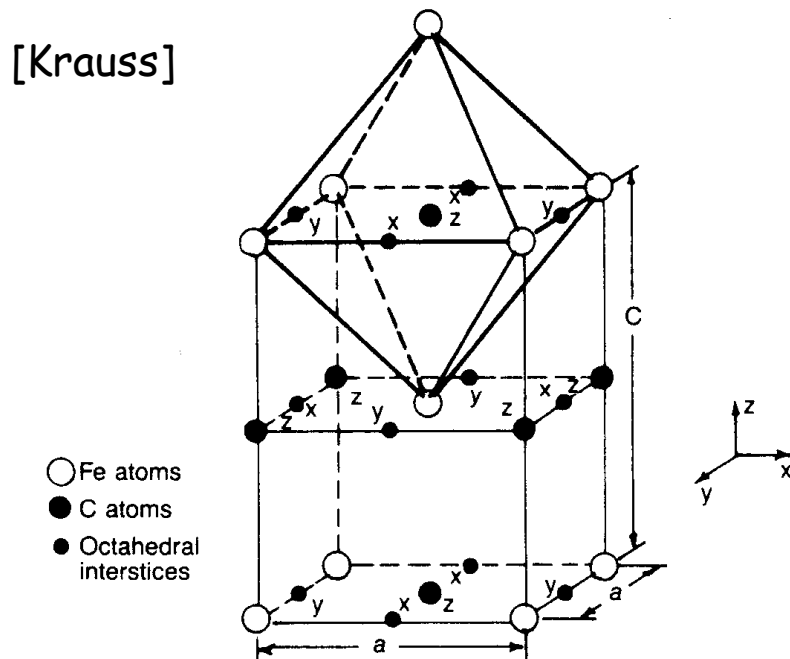Midrib

Habit plane

Martensite

[Krauss]

Fig. 5.3 Schematic of shear and surface tilt associated with formation of a martensite plate. Adapted from Ref 5.7, courtesy of M.D. Geib, Colorado School of Mines, Golden

Strength of martensite (1)

- Martensitic transformations strengthen steels significantly.
- Strengthening is not as significant in other materials.

[Krauss]

Fe atoms
C atoms
Octahedral interstices

Fig. 5.1 Body-centered tetragonal crystal structure of martensite in Fe-C alloys. Carbon atoms are trapped in one set (z) of interstitial octahedral sites. The x and y sites are unoccupied. Source: Ref 5.5

In Fe-based alloys, the martensite forms when Fe containing some concentration of C or N tries to transform from FCC to the BCC form. The presence of these interstitials distorts the lattice to BCT.

Martensite strength
depends upon a number of factors

- **Grain size** of the Austenite phase from which it forms.

- **Solute concentration**

  - Substitutional solid solution hardening

  - Interstitial solid solution hardening

- **Precipitation** hardening

- **Substructure** (includes dislocation) hardening

Grain size effect in martensite

- Martensite grain size is determined by the prior austenite grain size.

- Martensite forms in "packets" (bundles) that evolve from shear transformation of austenite grains (e.g., FCC→BCT).

- For normal grain sizes, the yield strength will increase as the martensite plate size or packet size *decreases*. This is in accordance with the Hall-Petch relationship. See the diagram on the right.
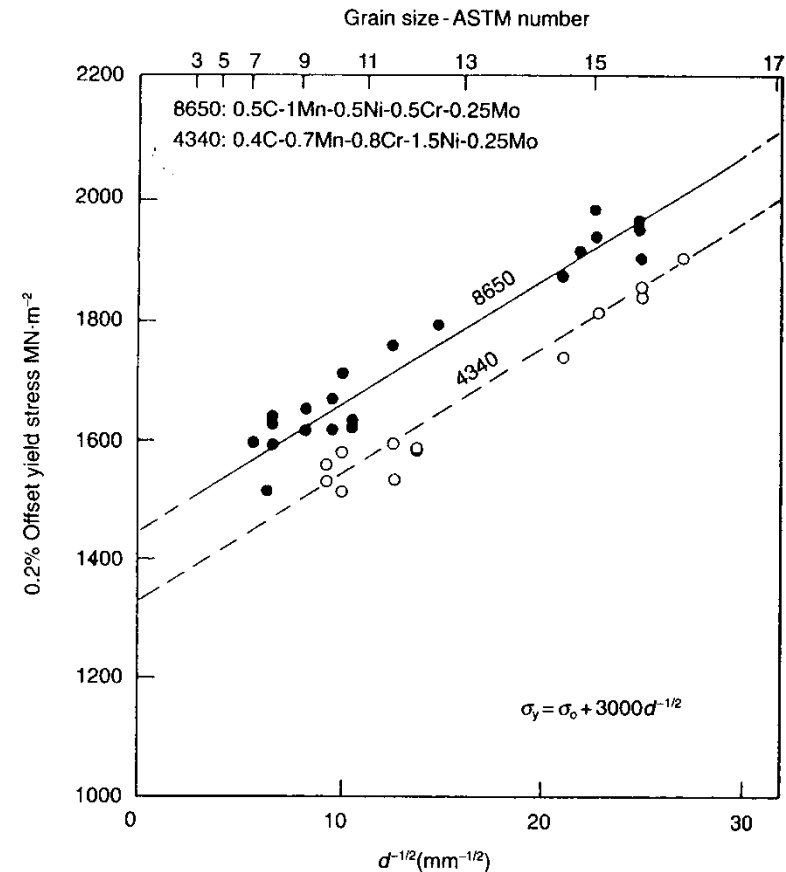

Grain size - ASTM number

8650: 0.5C-1Mn-0.5Ni-0.5Cr-0.25Mo
4340: 0.4C-0.7Mn-0.8Cr-1.5Ni-0.25Mo

8650

4340

$\sigma_y = \sigma_o + 3000 d^{-1/2}$

0.2% Offset yield stress $MN \cdot m^{-2}$

$d^{-1/2} (mm^{-1/2})$

FIGURE 8.48   The effect of prior austenite grain size on the yield strength of two commercial martensitic steels.[224] (*Reprinted by permission of ASM International, Materials Park, Ohio.*)

Substitutional solid solution hardening of martensite

- Substitutional solutes contribute very little (directly) to the strength of ferrous martensites.

- Substitutional solute do contribute indirectly through their effects on grain size, martensite start (M_s) temperature, hardenability, and percent retained austenite. For example, Mn contributes to strengthening ~35 Pa per %Mn above 5%.

Interstitial solid solution hardening of martensite

- Fleischer[*] has investigated solid solution hardening of martensite. He assumed a model of dislocation bending away from solute atoms with short-range interactions. His expression for flow stress is:

$$\sigma = \sigma_o + \frac{2}{3} G \Delta \varepsilon \sqrt{c}$$

- In this relationship, $\Delta\varepsilon$ is the difference between the longitudinal and transverse strains caused by the interstitial atom. This equation predicts a stress strain curve with a slope ranging from G/15 to G/20.

- More recent experimental work has verified similar relationships for the different types of martensite. They are detailed in the following references:

  – G.R. Speich and H. Warlimont, *JISI*, vol. 206 (1968) p. 385.
  – J.M. Chilton and P.M. Kelly, *Acta Metallurgica*, v. 16 (1968), p. 637.
  – M.J. Roberts and W.S. Owen, *JISI*, vol. 206 (1968) p. 375.
  – M.J. Roberts and W.S. Owen, in *Physical Properties of Martensite and Bainite*, Special Report 93, Iron and Steel Institute, London (1965) pp. 171-178.

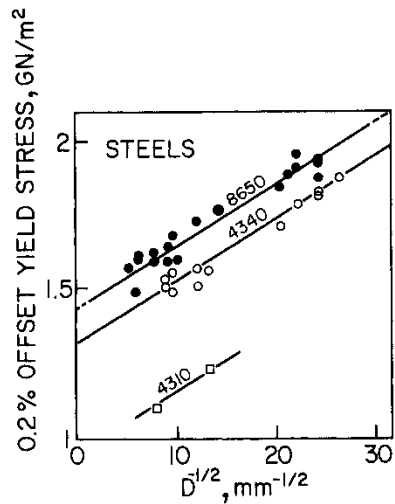[*] R.L. Fleischer, *Acta Metallurgica*, v. 10 (1962) pp. 835-842.

Figure 11.8 Effect of prior austenite grain size on the yield stress of three commercial martensitic steels. (Adapted with permission from R. A. Grange, *Trans. ASM,* 59 (1966) 26)
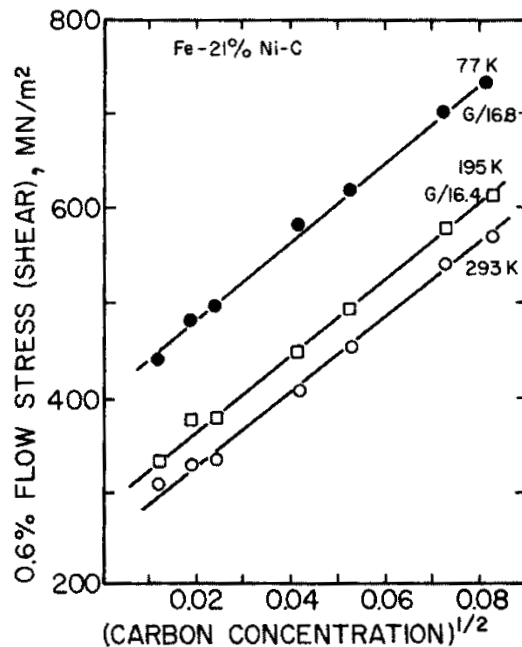

Figure 11.9 Plot of 0.6% proof stress (one-half of tensile stress) versus $C^{1/2}$ for Fe–Ni–C lath martensite at various temperatures. The slopes are shown as fractions of the shear modulus, which is denoted by G. (Adapted with permission from M. J. Roberts and W. J. Owen, *J. Iron Steel Inst.,* 206 (1968) 37)

Solution hardening of martensite – cont'd

- Alternatively, we can regard martensite as a supersaturated solid solution of carbon in ferrite. In that event, the strengthening can be described as[*]:

$$\tau_o = \left(1 - \frac{\phi'}{5\pi}\right) G \left(\frac{F_{max}}{2T}\right)^{3/2} \sqrt{3c}$$

F_{max} = maximum force exerted by an obstacle on dislocation

T = tension of dislocation line

ϕ' = angle turned through by the dislocation right before it breaks free from obstacle

[*] See A.J.E. Foreman & M.J. Makin, *Philosophical Magazine*, v. 14 (1966), p. 191.

Substructure strengthening of martensite

- High-carbon martensites have fine twinned substructures. It has been proposed that these structures can provide a major contribution to strength. However, this proposition has been poorly received.

- In *lath martensites*, which are untwinned but densely dislocated, it has been shown that the increase in dislocation density leads to large increases in strength. Dislocation density can be increased by increasing the carbon content. Norstrom[*] has developed the following expression for lath martensite:

$$\sigma_{ys} = \sigma_o + \sigma_i + k_y \sqrt{d} + \alpha Gb \sqrt{\rho_\perp}$$

where

σ_o = Peierls stress

σ_i = Solid-solution hardening effect

σ_o = Hall-Petch constant

α = Constant

$$\rho_\perp = \rho_o + K(c) + \frac{\theta}{b}\frac{2}{w}$$

where

w = lath width

c = carbon concentration

ρ_o = dislocation density in laths

K = constant

θ = misorientation between laths

* L.A. Norstrom, *Scandanavian Journal of Metallurgy*, v. 5 (1976), p. 159.

Contributions to the strength of martensite in 0.4% carbon steel

|	
Boundary strengthening	620 MPa
Dislocation density	270 MPa
Solid solution hardening by carbon	400 MPa
Rearrangement of C during quench (i.e. Cottrell atmospheres, Snoek effect, solute clustering, etc.)	750 MPa
Other effects	200 MPa
Total	2,240 MPa

Shape Memory Effect

- Some alloys after being deformed at one temperature can recover their original shape upon heating to a second temperature.

- Materials:
  - NiTi (NiTiNOL),
  - NiAl,
  - AgCd,
  - Cu-Al
  - Certain ferrous alloys,
  - Etc…

- Uses:
  - Stents,
  - Sensors,
  - Toys,
  - Etc…

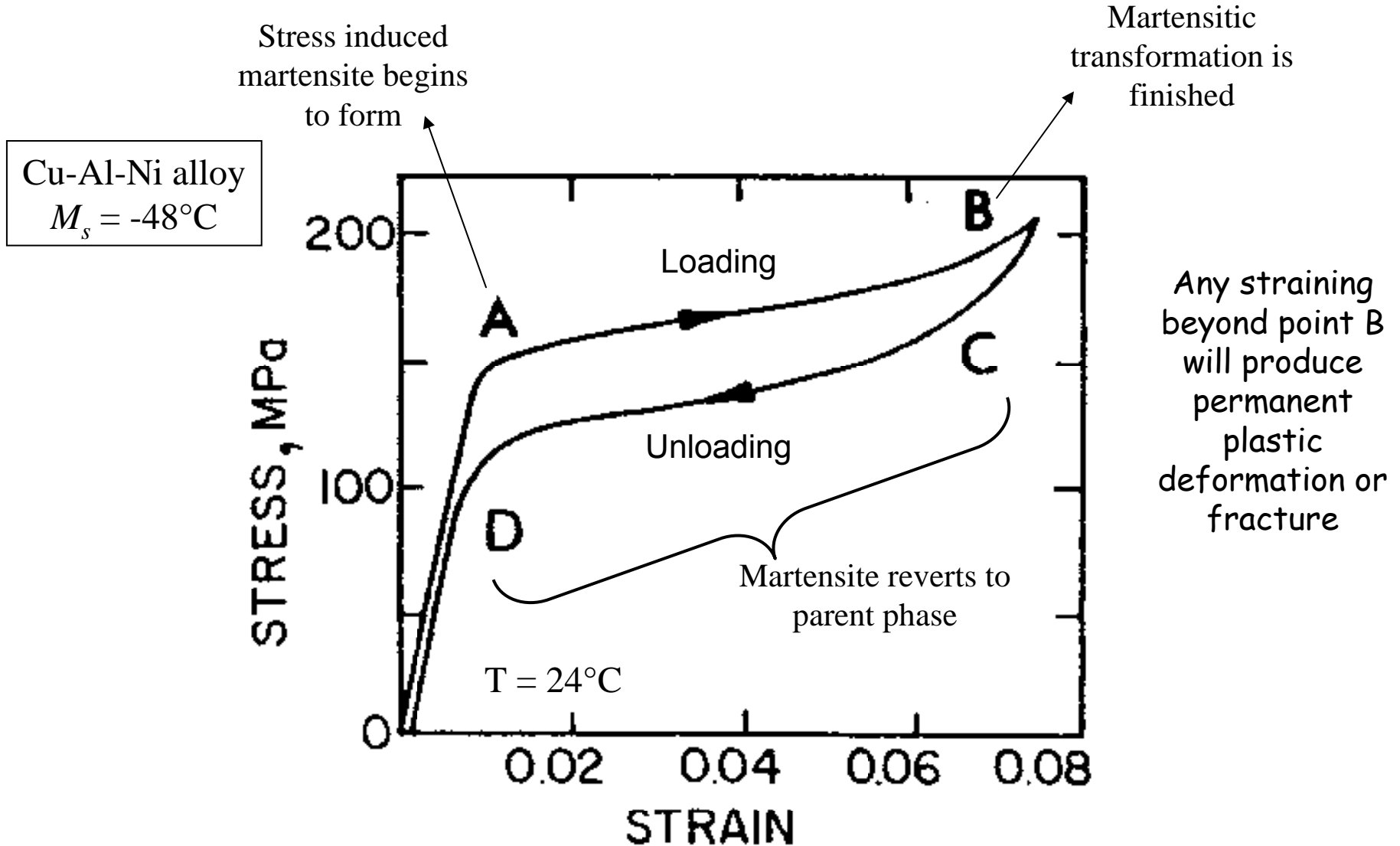High Temp. Phase
↓↑
Martensitic Phase
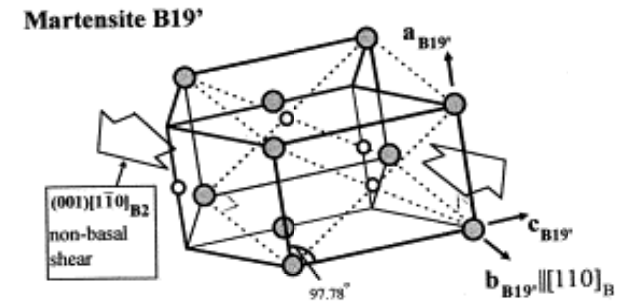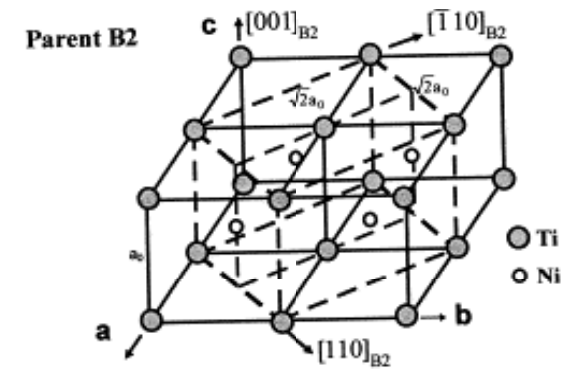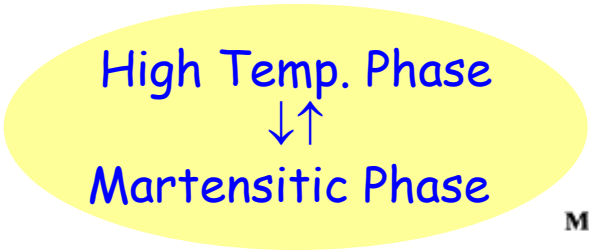
Some Decent SME References

- K. Otsuka and X. Ren, "Recent developments in the research of shape memory alloys" *Intermetallics* 7 (1999) p. 511-528

- K. Otsuka and X. Ren, "Physical metallurgy of Ti-Ni-based shape memory alloys" *Progress in Materials Science* 50 (2005) p. 511-678

SME Characterized By

- Pseudoelasticity (superelasticity)

  – Results from a stress-induced martensitic phase transformation in a tensile test that reverts to the parent phase upon unloading.

- Strain-memory effect

 – When "pseudoelastic" deformation becomes irreversible.

Pseudoelastic stress-strain curve

Stress induced martensite begins to form

Martensitic transformation is finished

Cu-Al-Ni alloy
M_s = -48°C

Any straining beyond point B will produce permanent plastic deformation or fracture

Martensite reverts to parent phase

Any unloading below point D will result in a return to the original sample geometry

[Meyers & Chawla, p. 512]

Temperature dependence of pseudoelastic stress-strain curves

Cu-Al-Ni alloy

$M_s = -140°C$
$M_f = -150°C$
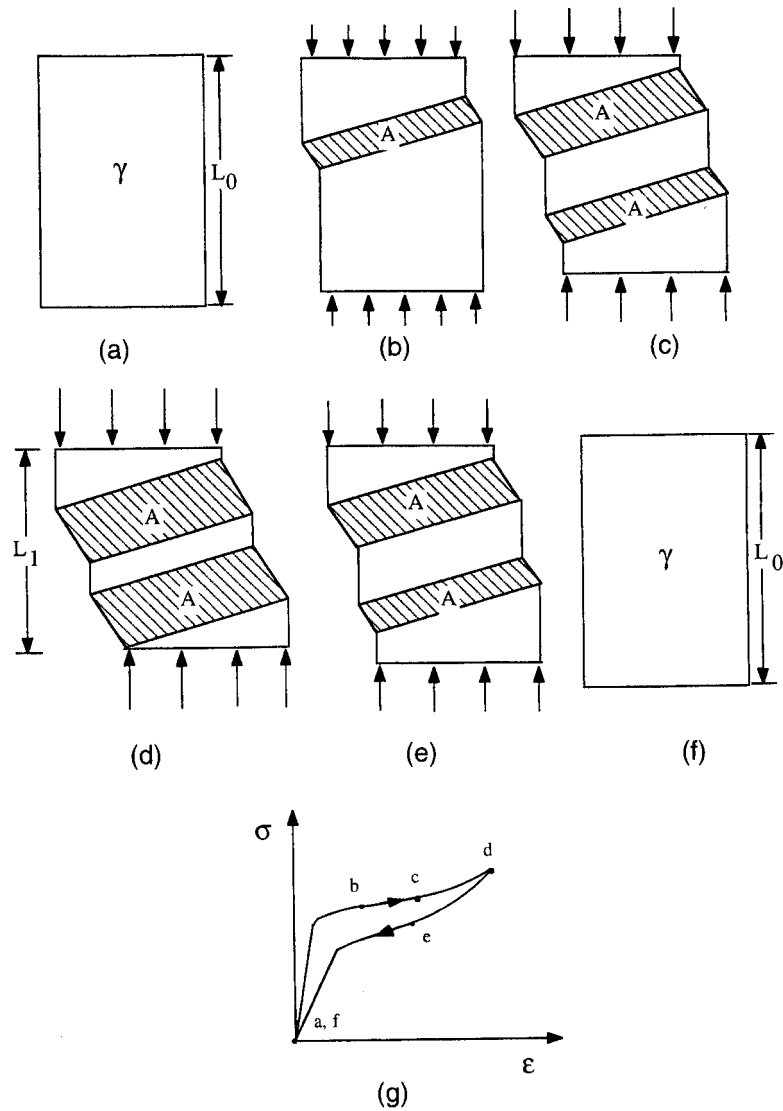$A_s = -109°C$
$A_f = -90°C$
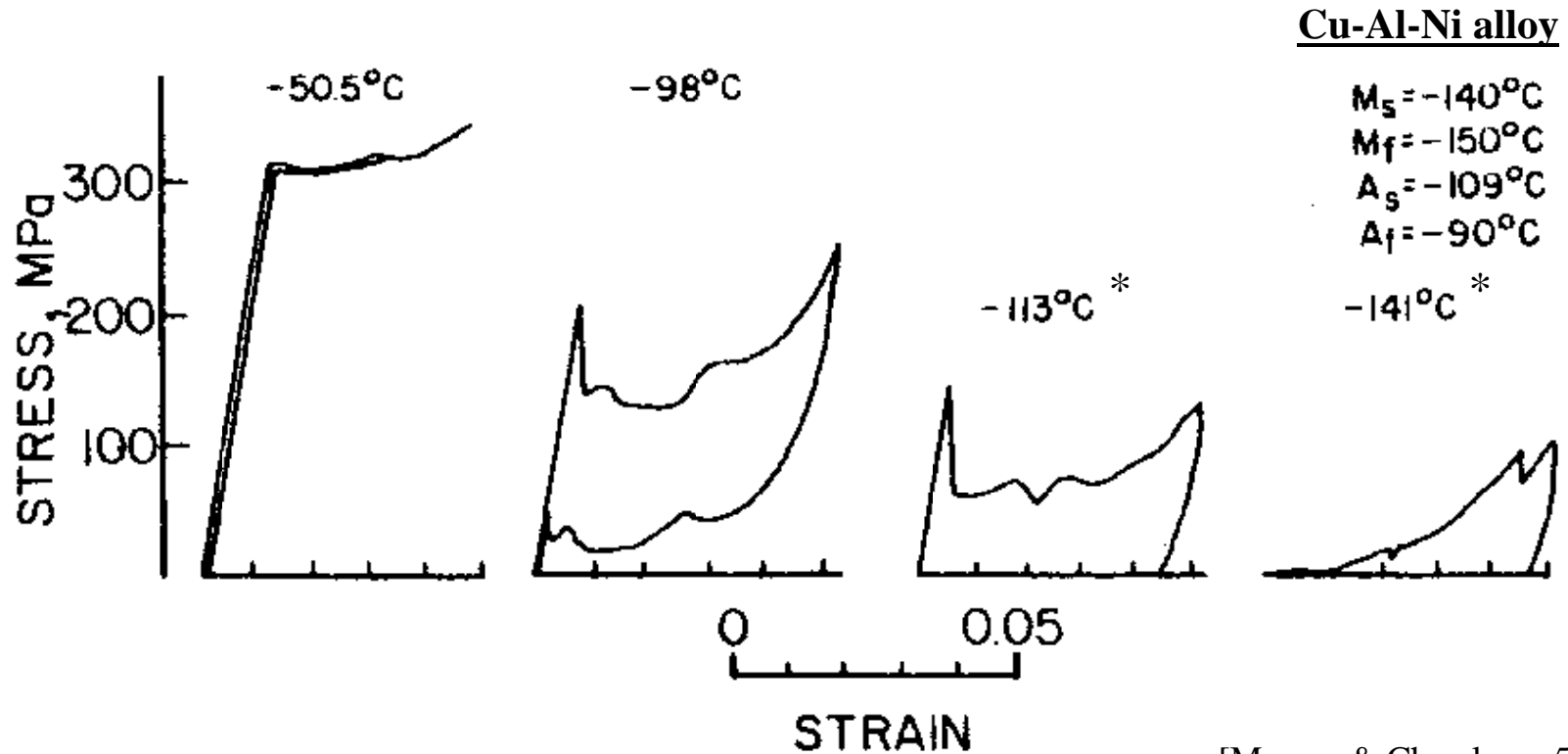
[Meyers & Chawla, p. 512]

*If tests are conducted below the Austenite start temperature (A_s), the martensite will not revert to austenite upon unloading

Stress to form martensite gets higher as T increases

Pseudoelastic effect

Figure 11.17 Schematic representation of pseudoelastic (or superelastic) effect. (a) Initial specimen with length L_0. (b, c, d) Formation of martensite and growth by glissile motion of interfaces under increasing compressive loading. (e) Unloading of specimen with decrease in martensite. (f) Final unloaded configuration with length L_0. (g) Corresponding stress–strain curve with different stages indicated.

[Meyers & Chawla, p. 513]
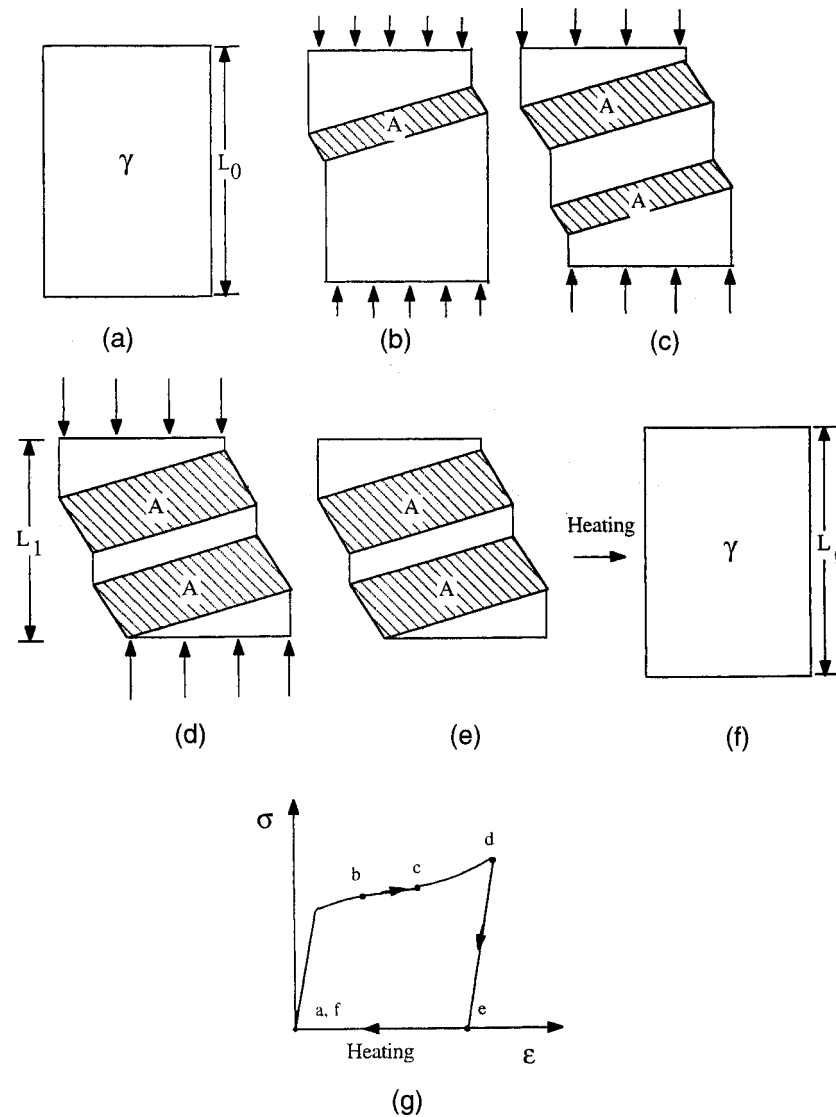
Strain-memory effect

Figure 11.20 Schematic representation of strain-memory effect. (a) Initial specimen with length L_0. (b, c, d) Formation of martensite and growth by glissile motion of interfaces under increasing compressive stresses. (e) Unloading of specimen. (f) Heating of specimen with reverse transformation. (g) Corresponding stress–strain curve with different stages indicated.

[Meyers & Chawla, p. 516]

Transformation Toughening

- Can be used to enhance toughness of brittle materials. The most important example is in zirconia (ZrO_2) ceramics. The phase transformation is tetragonal-to-monoclinic.

- In regions surrounding a propagating crack, a stress-induced martensitic transformation occurs.

- The transformed region has dilatational and shear strain components that work against the stress field generated by the crack.

- This decreases the stress intensity factor and thus increases the toughness of the ceramic.