

Notation

T_0 := Eq. Temp. for 2 phases at same composition

ΔT := undercooling

ΔS := entropy of transformation

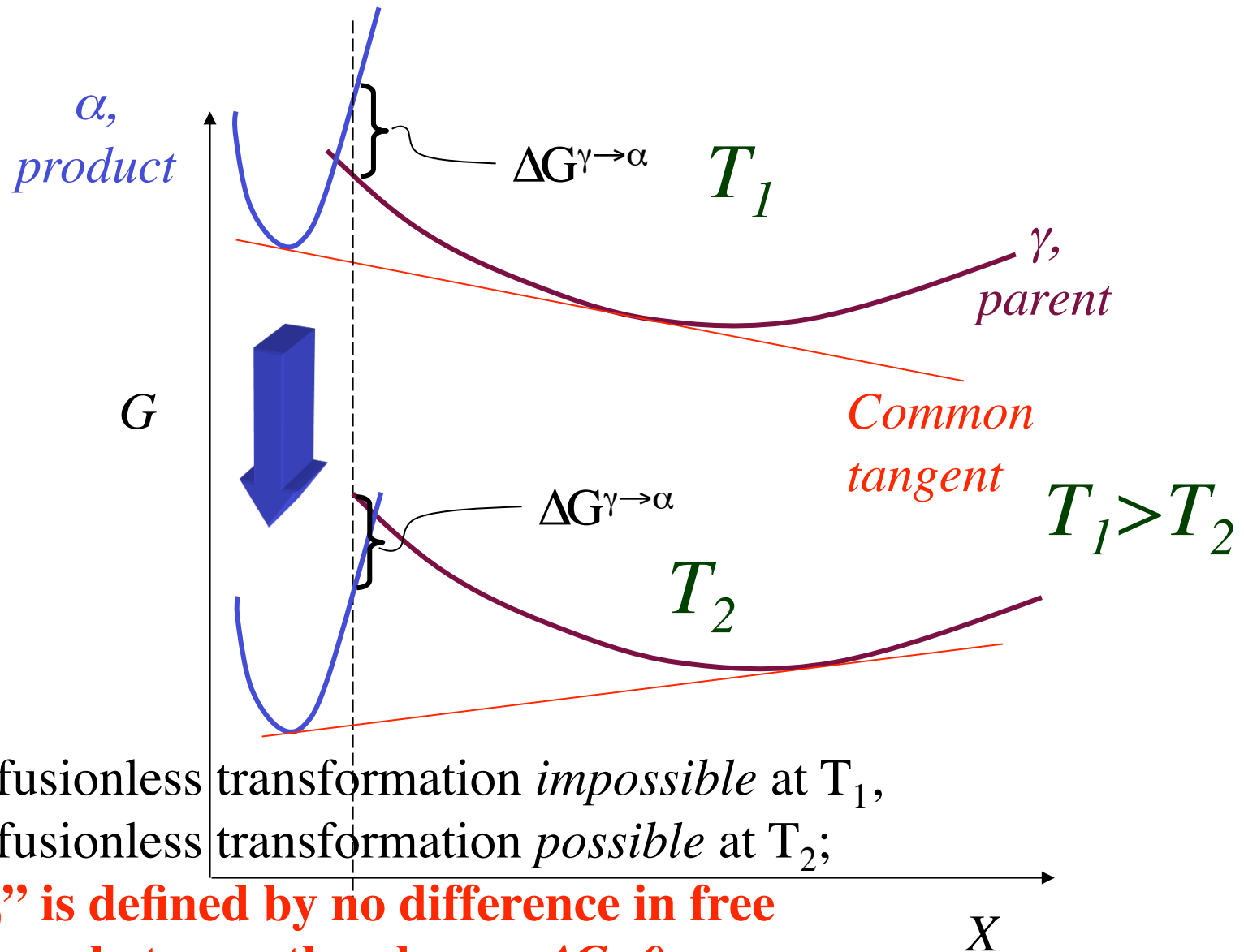
ΔH := enthalpy of transformation

ΔG := Gibbs free energy

ε := transformation strain

γ := Interface energy

Free Energy - Composition: T_0



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, $\Delta G=0$.

Phase relationships

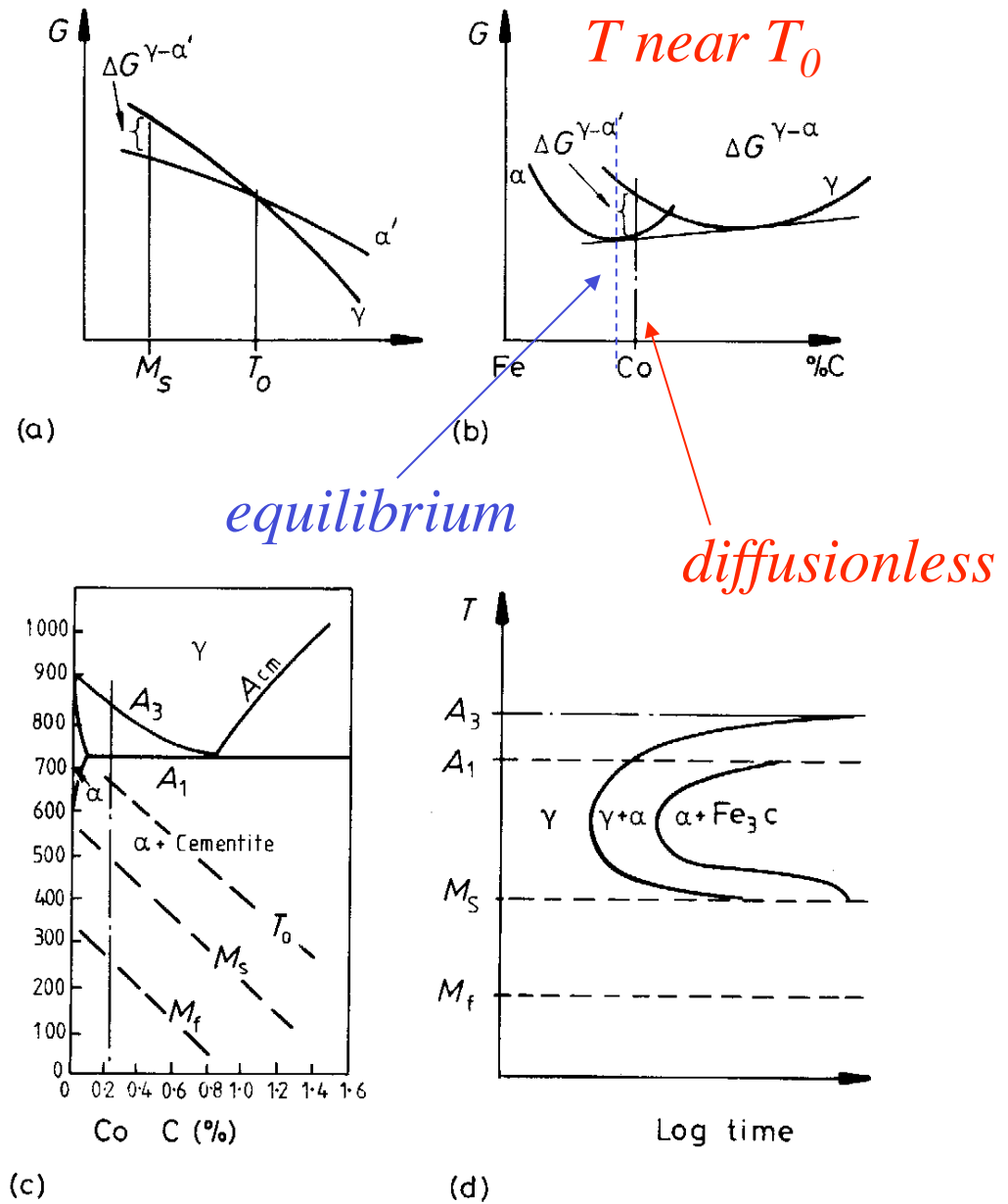


Fig. 6.3 Various ways of showing the martensite transformation. (a) Free energy-temperature diagram for austenite and martensite of fixed carbon concentration (c_0 in (b)). (b) Free energy-composition diagram for the austenite and martensite phases at the M_s temperature. (c) Iron-carbon phase diagram with T_0 as defined in (a), M_s and M_f superimposed. (d) M_s and M_f in relation to the TTT diagram for alloy C_0 in (c).

Microstructures

Martensite formation rarely goes to completion because of the strain associated with the product that leads to back stresses in the parent phase.

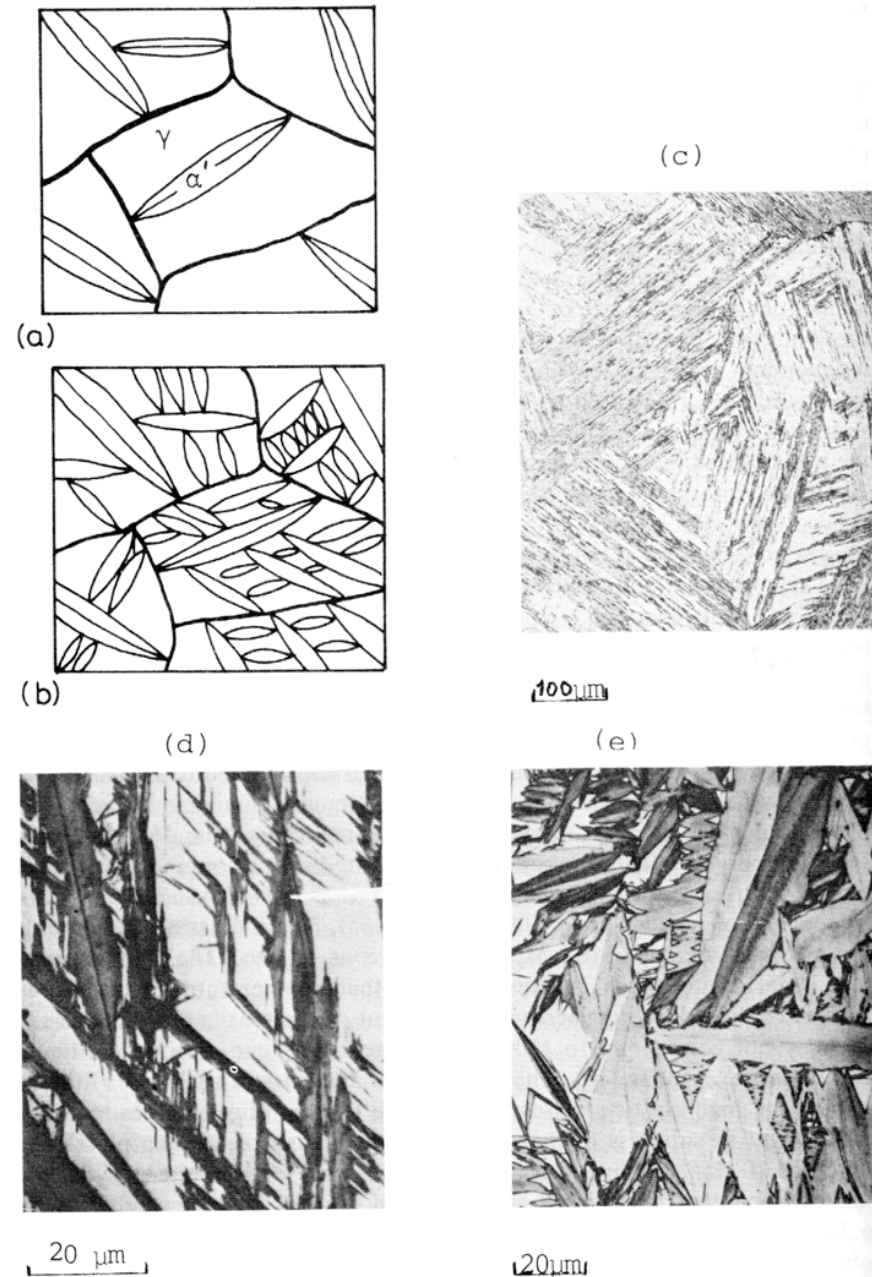


Fig. 6.1 (a), (b) Growth of martensite with increasing cooling below M_s . (c)–(e) Different martensite morphologies in iron alloys: (c) low C (lath), (d) medium C (plate), (e) Fe–Ni (plate).

Self-accommodation by variants

- A typical feature of martensitic transformations is that each colony of martensite laths/plates consists of a stack in which different variants alternate. This allows large shears to be accommodated with minimal macroscopic shear.

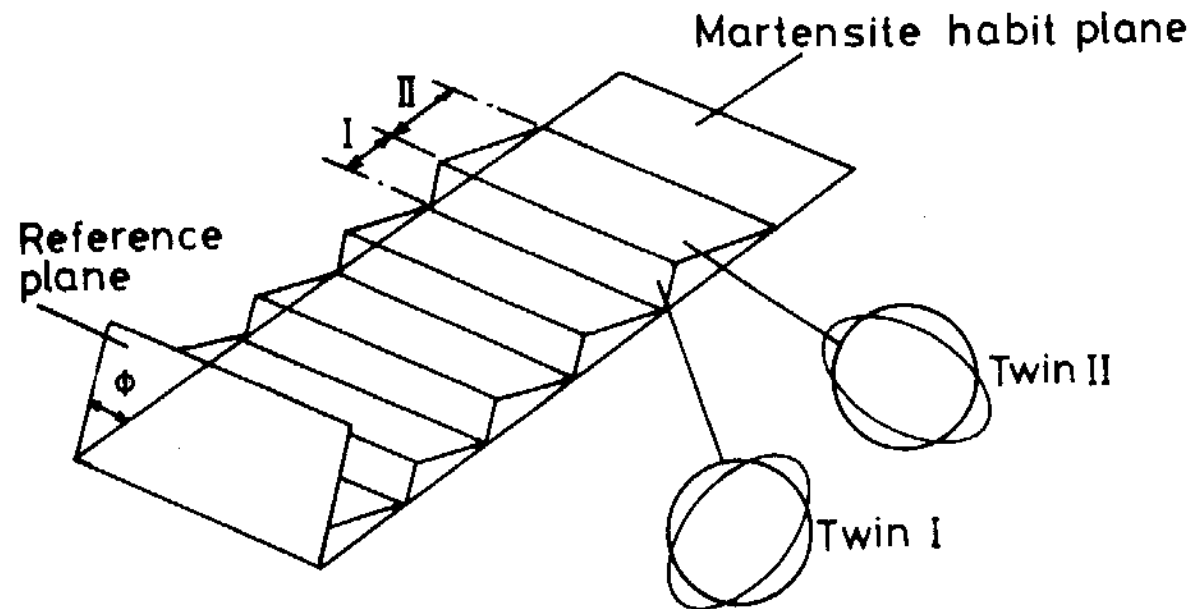


Fig. 6.10 Twins in martensite may be self-accommodating and reduce energy by having alternate regions of the austenite undergo the Bain strain along different axes.

Bain model

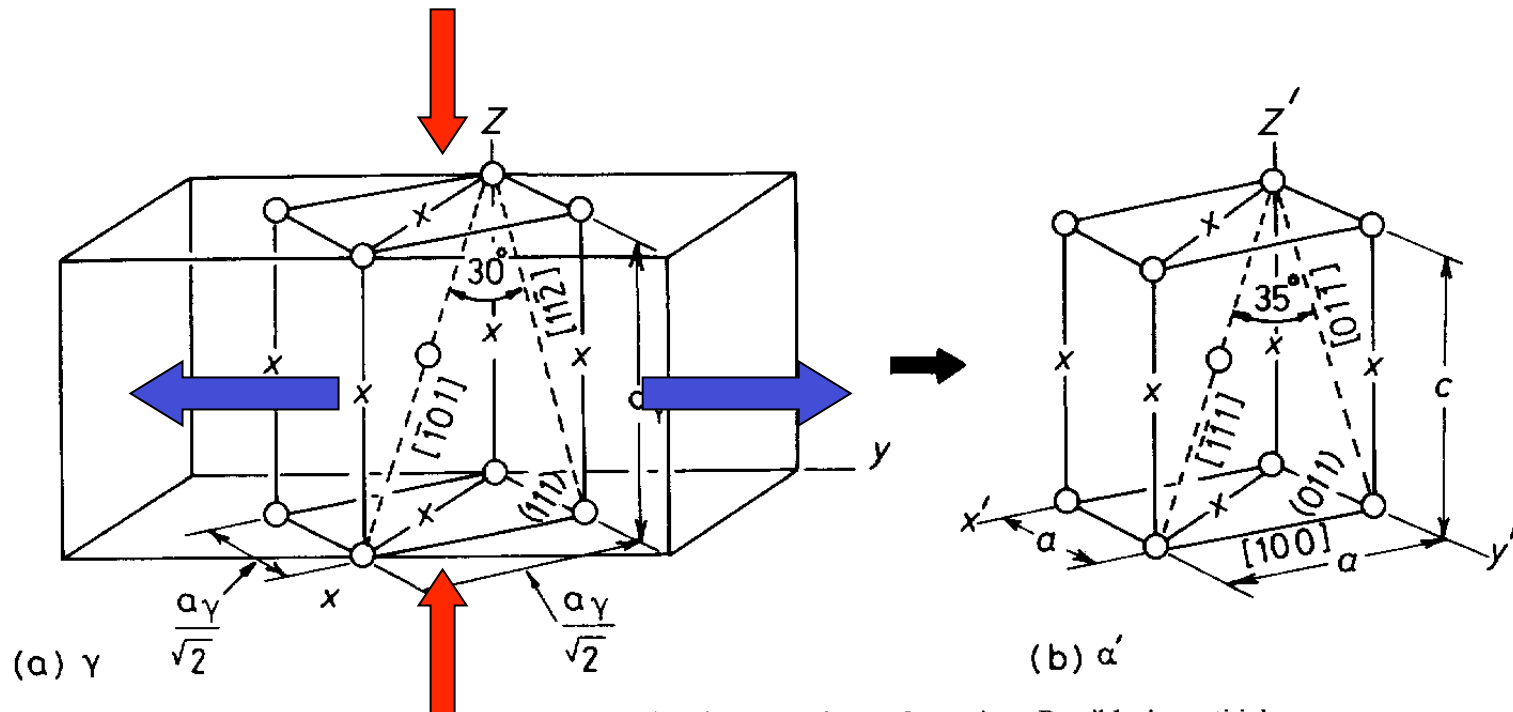


Fig. 6.7 Bain correspondence for the $\alpha \rightarrow \alpha'$ transformation. Possible interstitial sites for carbon are shown by crosses. To obtain α' the γ unit cell is contracted about 20% on the C axis and expanded about 12% on the a axes.

- Orientation relationships in the Bain model are:

$$(111)_\gamma \Leftrightarrow (011)_{\alpha'}$$

$$[101]_\gamma \Leftrightarrow [111]_{\alpha'}$$

$$[110]_\gamma \Leftrightarrow [100]_{\alpha'}$$

$$[112]_\gamma \Leftrightarrow [011]_{\alpha'}$$

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 $\langle 100 \rangle$ directions.

Interstitial sites for C in Fe

fcc: carbon occupies the octahedral sites

bcc: carbon occupies the octahedral sites

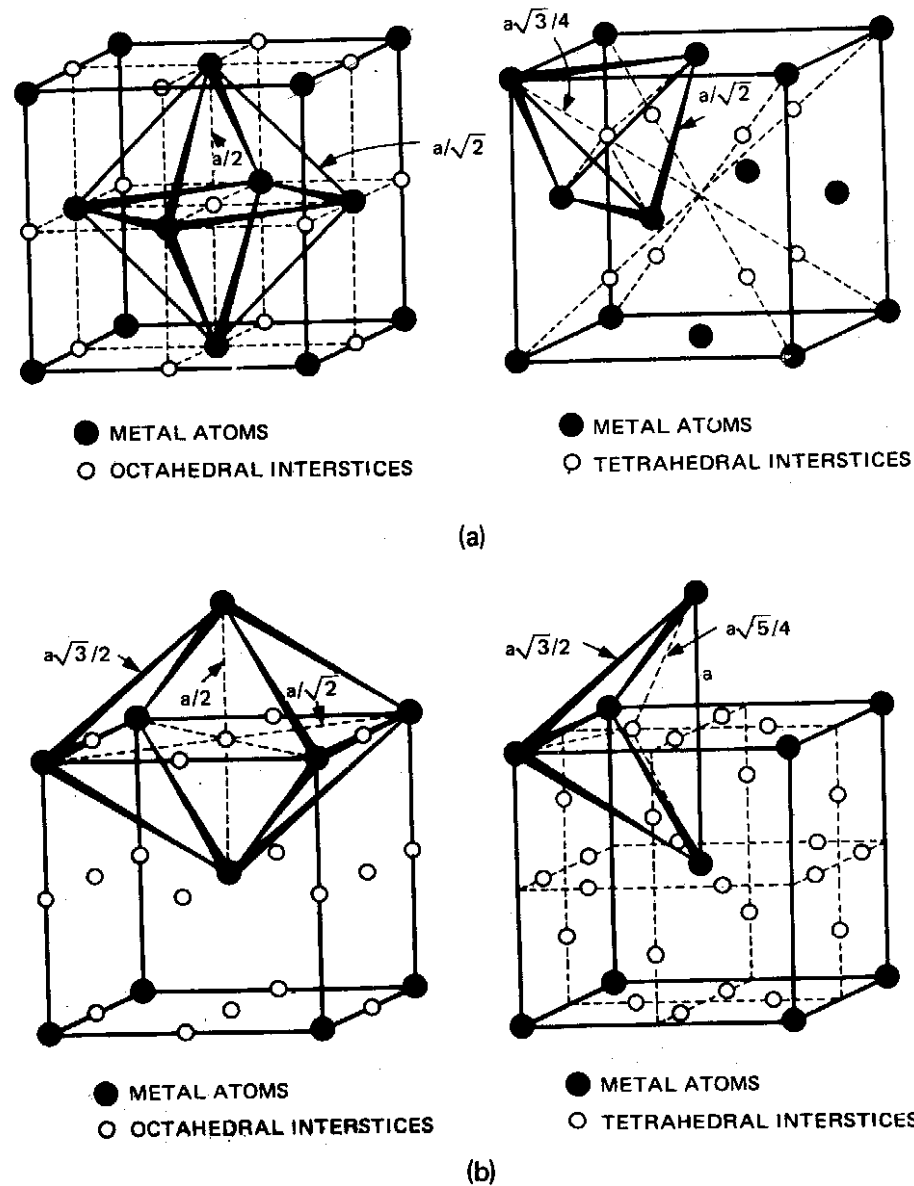


Figure II-1. Interstitial voids in iron. (a) Interstitial voids in the fcc structure, octahedral (1) and tetrahedral (2). (b) Interstitial voids in the bcc structure; octahedral (1) and tetrahedral (2). (From C.S. Barrett and T.B. Massalski, *Structure of Metals*, 3d ed., copyright 1966, used with the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

[Leslie]

Carbon in 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.

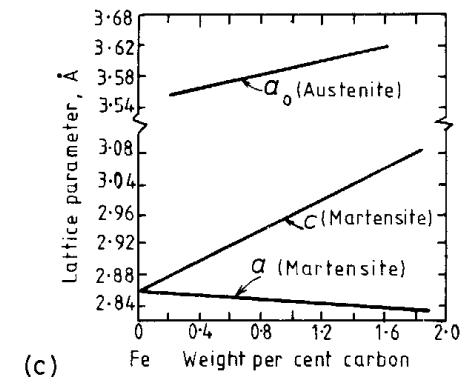
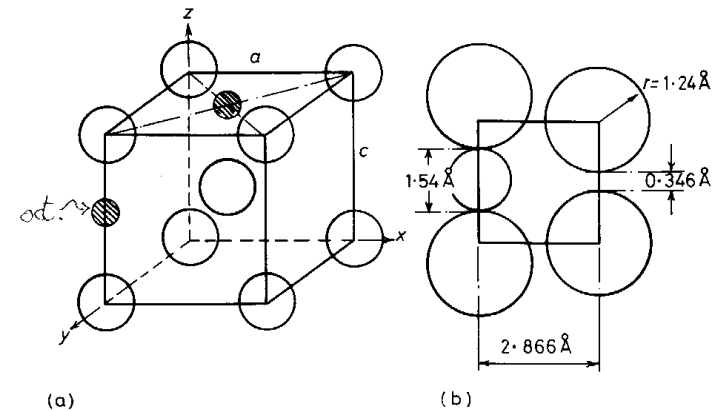
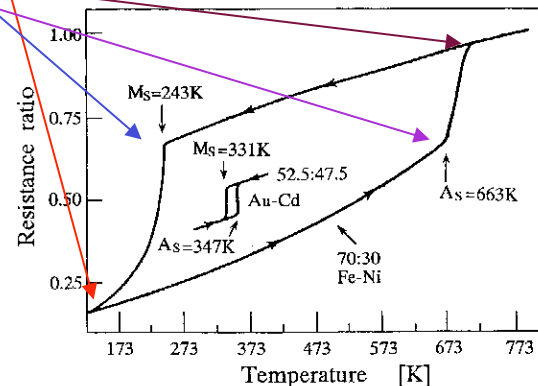


Fig. 6.5 Illustrating (a) possible sites for interstitial atoms in bcc lattice, and (b) the large distortion necessary to accommodate a carbon atom (1.54 Å diameter) compared with the space available (0.346 Å). (c) Variation of a and c as a function of carbon content. (After C.S. Roberts, *Transactions AIME* **191** (1953) 203.)

Shape Memory Effect (SME)

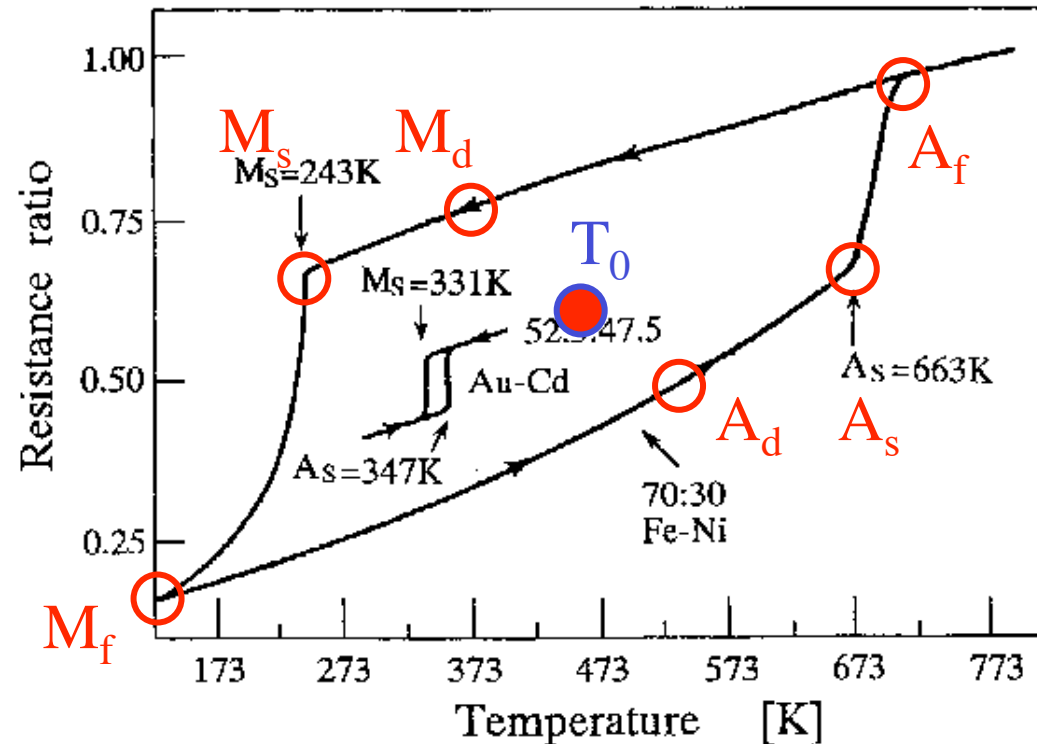
- General phenomenon associated with martensitic transformations.
- Characteristic feature = *strain induced martensite* (SIM), capable of *thermal reversion*.
- *Ferroelasticity* and *Superelasticity* also possible.
- $M_d, A_f, A_s, A_d, M_s, M_f$ temperatures.



[Shape
Memory
Materials]

Fig. 1.16. Electrical resistance changes during cooling and heating Fe–Ni and Au–Cd alloys, illustrating the hysteresis of the martensitic transformation on cooling, and the reverse transformation on heating, for non-thermoelastic and thermoelastic transformations respectively. (After Kaufman and Cohen³⁷)

Temperatures



The M_d and A_d temperatures bracket T_0 because they define the on-cooling and on-heating temperatures at which the transformation is possible with allowance for the effect of strain energy.

SME Definitions

- M_d : SIM possible below M_d .
- A_f : reversion of SIM complete above A_f (*heating*).
- A_s : reversion of SIM starts above A_s (*heating*).
- A_d : formation of parent phase possible above A_d .
- M_s : martensite start temperature (*cooling*).
- M_f : martensite finish temperature (*cooling*).

SME, contd.

- Classic alloy = Nitinol = NiTi
 - alloying for control of M_s .
- Stress for SIM must be less than yield stress for plastic deformation.
- SME depends on incomplete transformation and elastic back stresses to provide memory ($>M_s$).
 - SME more effective in single xtals.
- Alloying permits variations in the equilibrium transformation temperature, for example (critical for bio applications, for example). Also variations in the maximum strain that can be recovered are possible.

Super-elasticity

- Super-elasticity is simply reversible (therefore “elastic”) deformation over very large strain ranges (many %).
- Example: Ti-50.2%Ni.

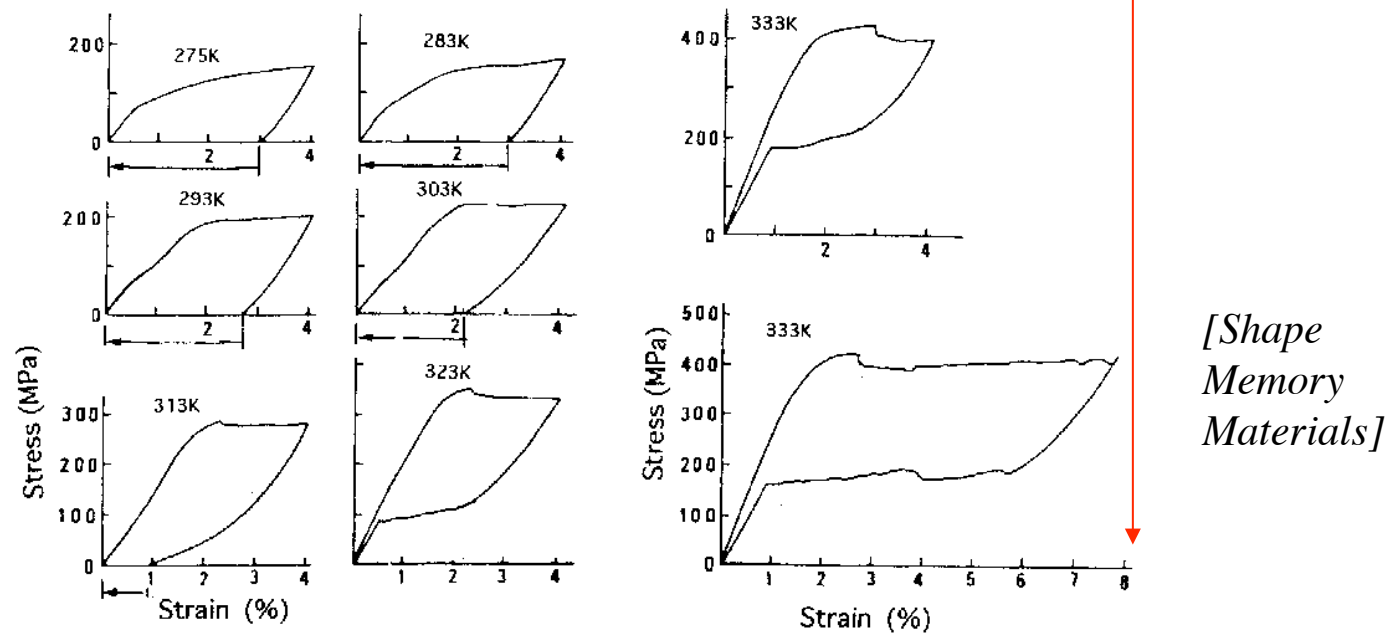


Fig. 3.12. Stress-strain curves of the Ti-50.2at% Ni alloy annealed at 313 K (400°C) for 3.6 ks after 25% cold-rolling. (After Saburi *et al.*⁴⁸)

Self-accommodation

- Micrograph with diagram shows how different variants of a given martensitic phase form so as to minimize macroscopic shear strains in a given region.

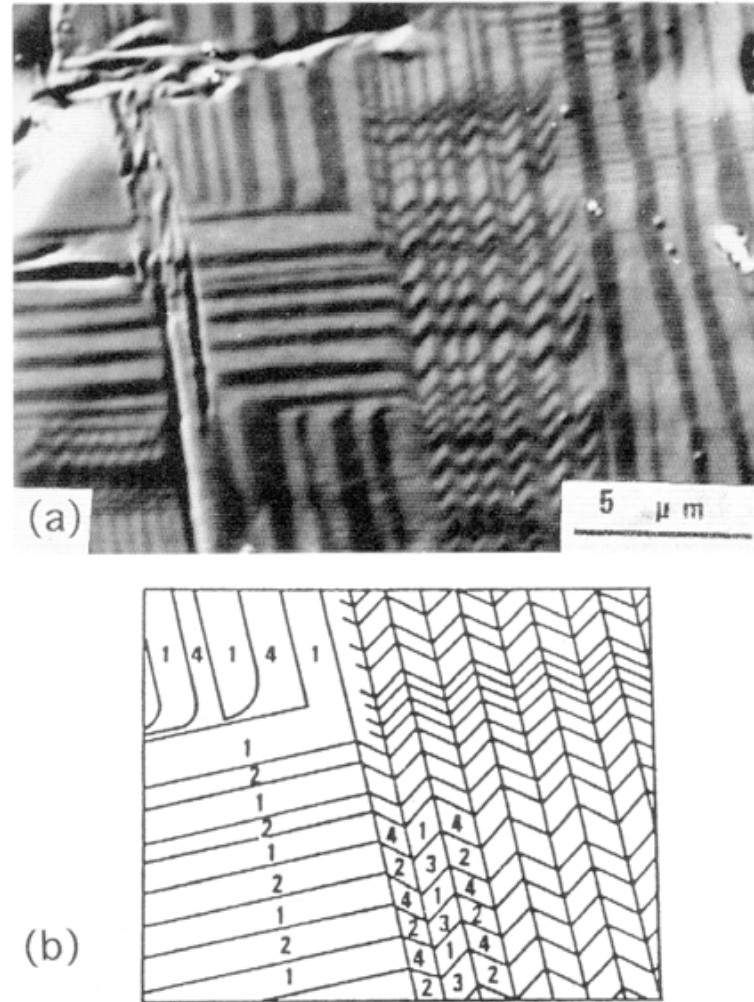


Fig. 3.33. Optical micrograph of self-accommodation of the R-phase (Ti-48.2Ni-1.5Fe (at%) alloy). (After Fukuda *et al.*³⁴)

Shape Memory Effect

- Demonstration of shape memory effect (SME) in a spring
- Mechanism of SME:
 - 1) transformation;
 - 2) martensite, self-accommodated;
 - 3) deformation by variant growth;
 - 4) heating causes re-growth of parent phase in original orientation

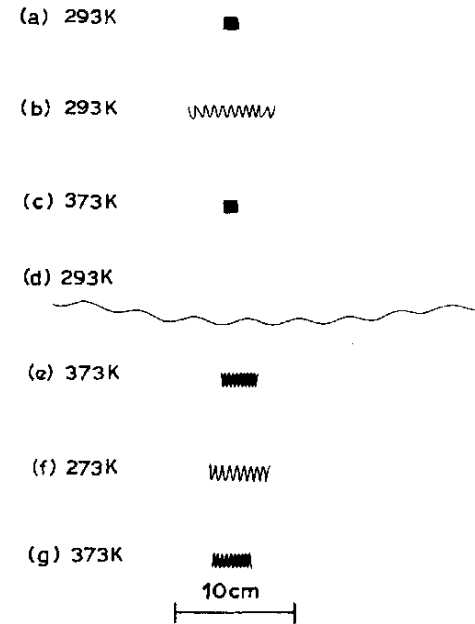


Fig. 2.10. Demonstration of shape memory effect (a–c) and two-way shape memory effect (d–g) in Ti-50.0 at% Ni alloy. (After Otsuka and Shimizu¹⁶)

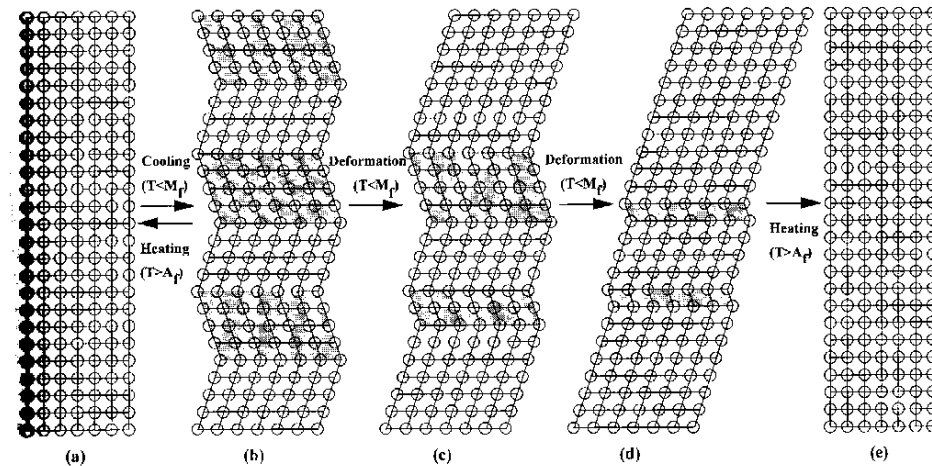


Fig. 2.11. Mechanism of shape memory effect; (a) original parent single crystal, (b) self-accommodated martensite, (c–d) deformation in martensite proceeds by the growth of one variant at the expense of the other (i.e. twinning or detwinning), (e) upon heating to a temperature above A_p , each variant reverts to the parent phase in the original orientation by the reverse transformation. (After Otsuka¹⁷)

Surface Relief

Micrographs show a sequence of temperatures with surface relief from the martensite plates.

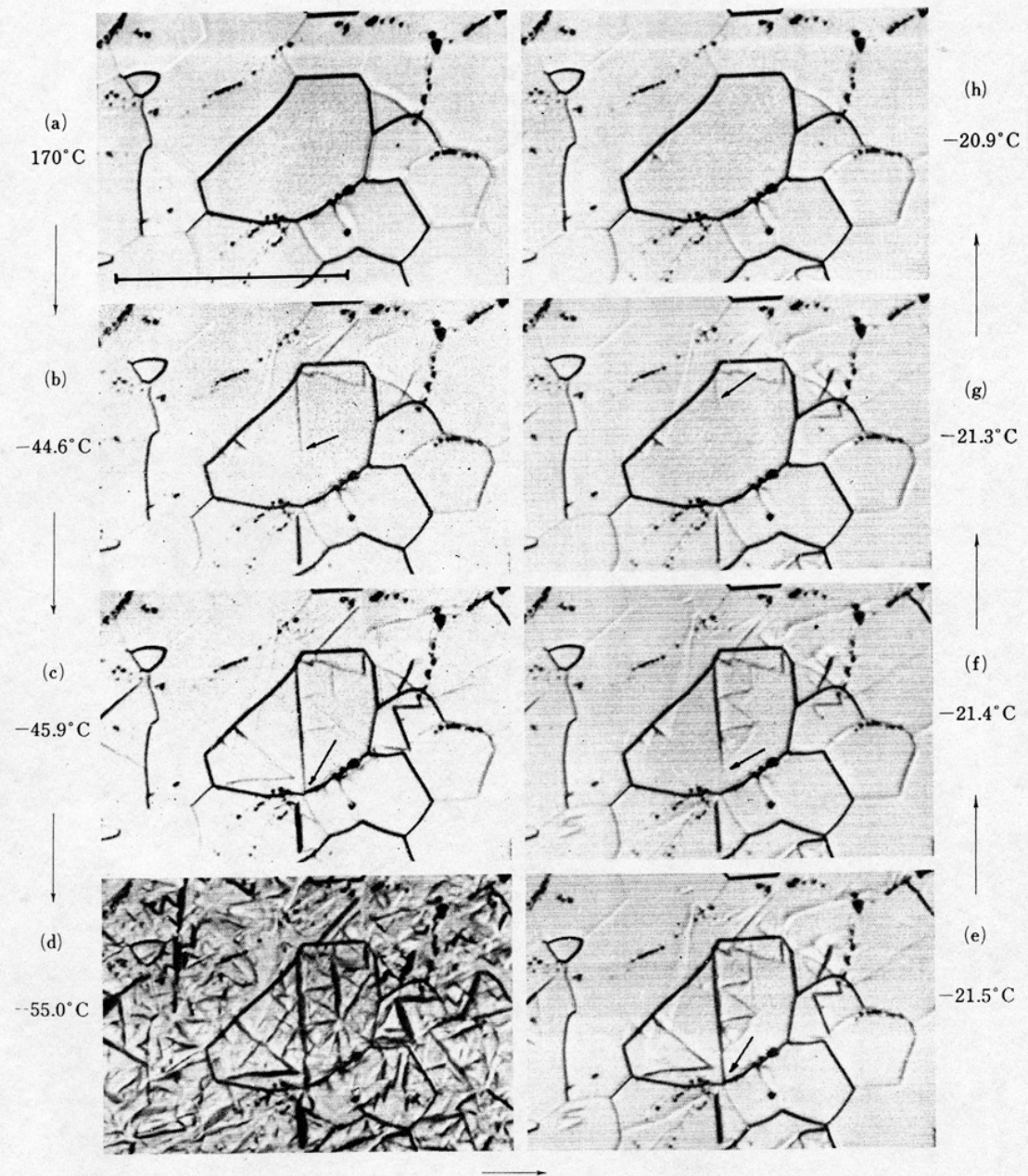
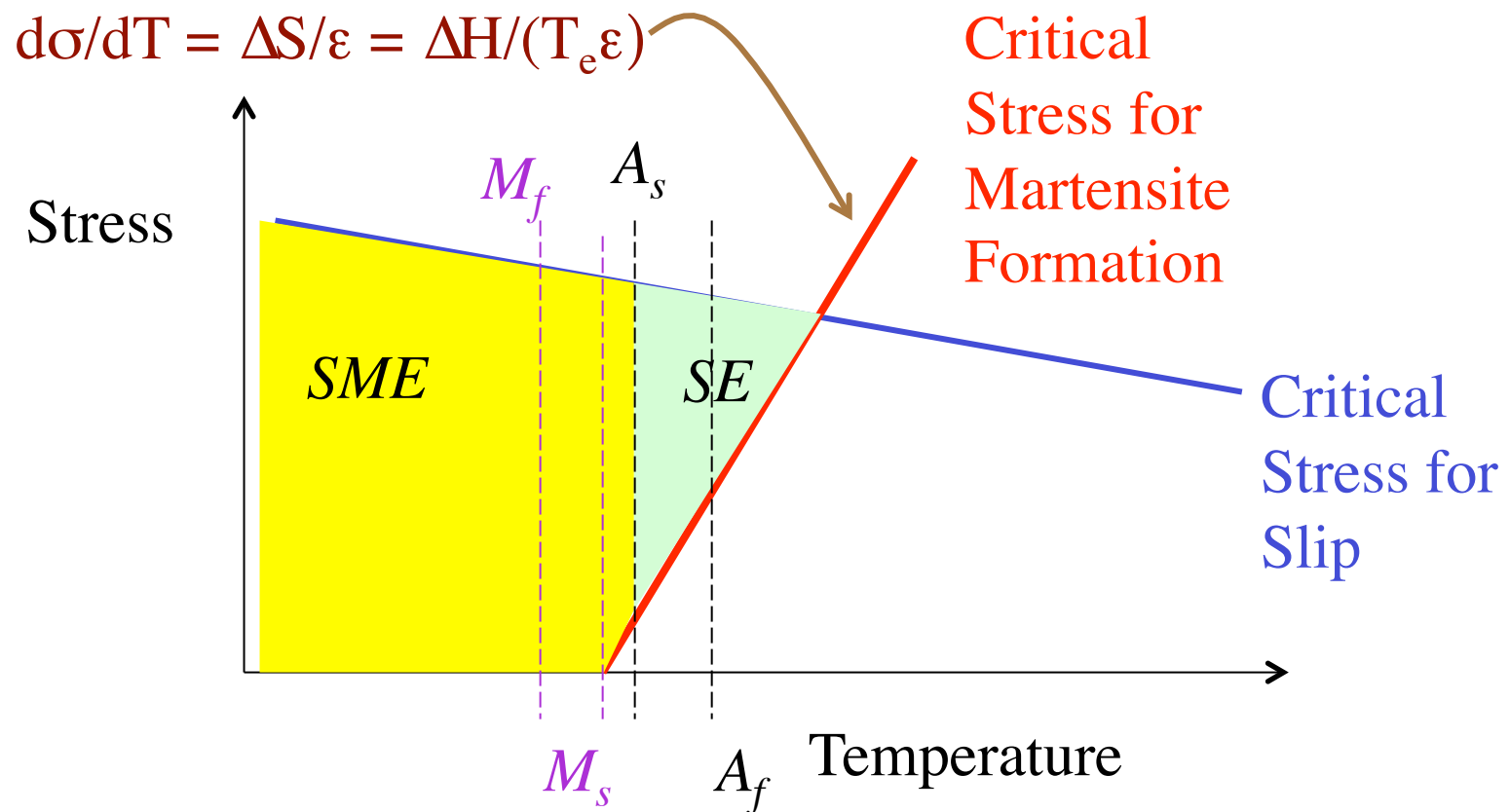


FIG. 2.81 Continuous observation of the surface relief from the thermoelastic growth and shrinking of the martensite in Ti-49.75 at. % Ni. (a)-(d) Cooling. (e)-(h) Heating. (After Otsuka *et al.*³¹²)

Stress versus Temperature

- The stress applied to the material must be less than the critical resolved shear stress for dislocation motion, because the latter is not recoverable;
SME = Shape Memory Effect; *SE* = Superelasticity



Ni-Ti Alloys

[Wasilewski, SME in Alloys, p245]

X	M_s	M_f	A_s	A_f
V	> 25	< -140	< -64	> 25
Cr	-100	< -180	< -58	> 25
Mn	-116	< -180	< -63	> 10
Fe	No information	< -180	-30	> 25
Co	No information	No information	0	> 25
Cu	> 25	< -100	?	> 25
TiNi_{0.95}	70	60	108	113
TiNi	60	52	71	77
Ti_{0.95}Ni	-50	< -180	?	20 (?)

SME Requirements

- For achieving a strong or technologically useful SME, the following characteristics are required.
- **High resistance to dislocation slip** (to avoid irreversible deformation).
- **Easy twin motion in the martensitic state** so that variants can exchange volume at low stresses.
- **Crystallographically reversible transformation** from product phase back to parent phase. Ordered structures have this property (whereas for a disordered parent phase, e.g. most Fe-alloys, multiple routes back to the parent structure exist.)

Photo-stimulated SME!

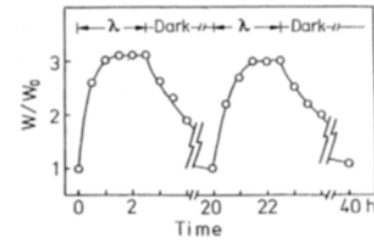


Fig. 9.10. Photostimulated reversible shape changes of a polyacrylamide gel having pendant triphenylmethaneleucohydroxide groups in water at 25°C. $\lambda = 270$ nm.¹²

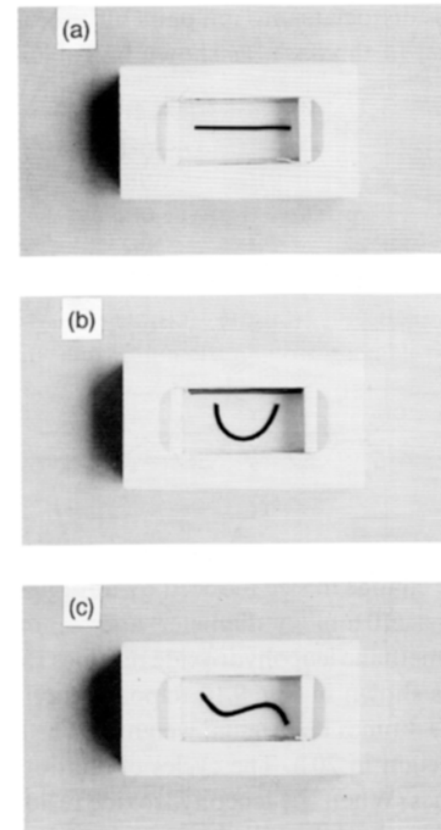


Fig. 9.11. Photostimulated shape changes of a rod-shape polyacrylamide gel having pendant triphenylmethane leucohydrocyanide groups in water at 25°C: (a) before photoirradiation; (b) one side of the gel was irradiated; (c) two spots of the gel were irradiated.

Summary

- Martensitic transformations are characterized by a diffusionless change in crystal structure.
- The lack of change in composition means that larger driving forces and undercoolings are required in order for this type of transformation to occur.
- The temperature below which a diffusionless transformation is possible is known as " T_0 ".
- Martensitic transformations invariably result in significant strains with well defined (if irrational, in terms of Miller indices) crystallography.
- Technological applications abound - quenched and tempered steels, Nitinol shape memory alloys etc.