HOMEWORK

List and describe the primary strengthening mechanisms are in Pearlite. For help consult the following article:
JOM, v. 54 (2002) p. 25-30

Module #20

Particle Hardening
(i.e., Precipitation and Dispersion Hardening)

READING LIST

DIETER: Ch. 6, pages 212-220

How can dispersed particles influence strength?

- Dispersed particles can increase the strength of a solid by impeding dislocation motion.

- The particles can be *precipitates*, which are natural. They can also be things like *dispersed* oxide or carbide *particles* which are not necessarily natural.

- *Particle hardening is generally a more potent way to strengthen a material* than solid solution hardening. Precipitates and dispersoids are usually more effective barriers to dislocation penetration than single solutes.

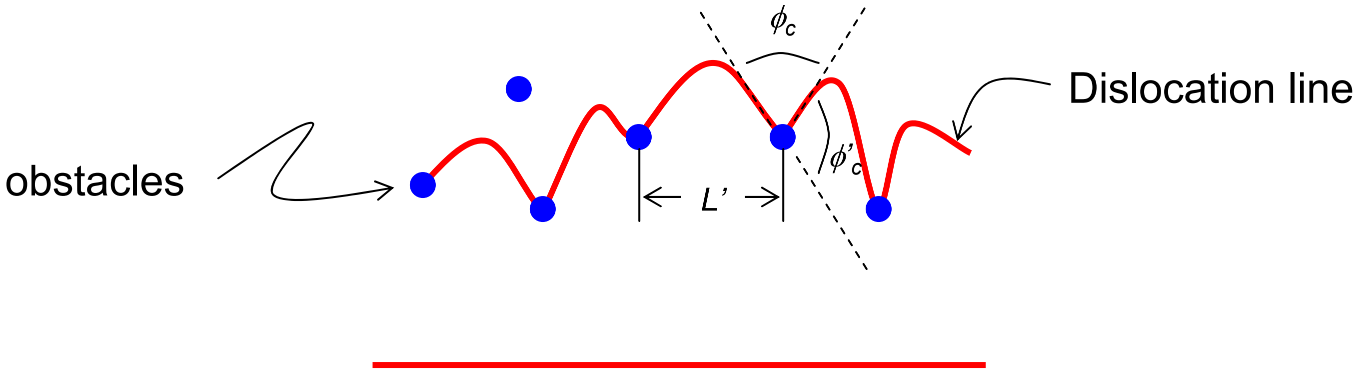
★ NOTE: Most structural materials utilize some sort of particle hardening in conjunction with the other hardening mechanisms to achieve high strengths.

What determines the degree of strengthening?

- Particle size
- Particle volume fraction

These things define the mean particle spacing *L*

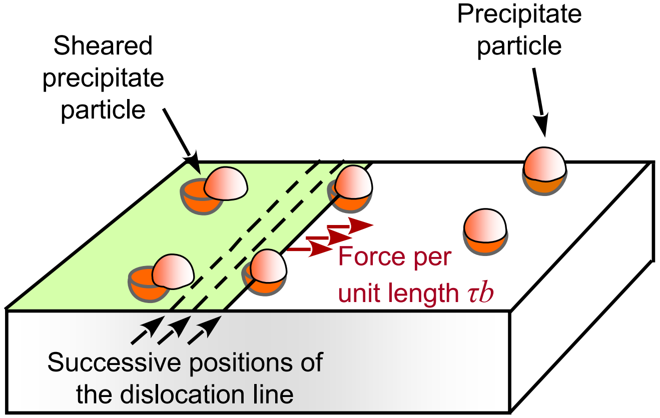
- Particle shape
- Nature of the interface between the particle and the matrix
- Structure of the particle



For deformation to proceed dislocations must:

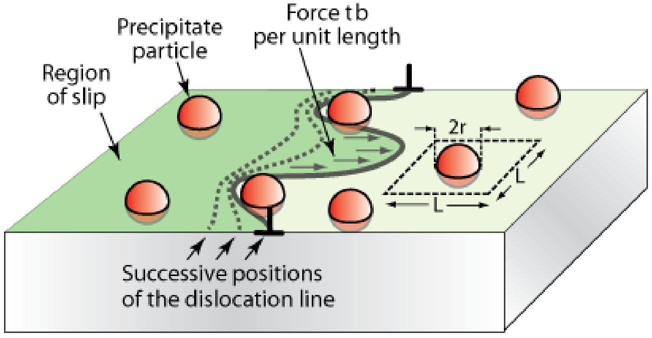
Cut through particles
("shearing" or "cutting")

[Weaver]

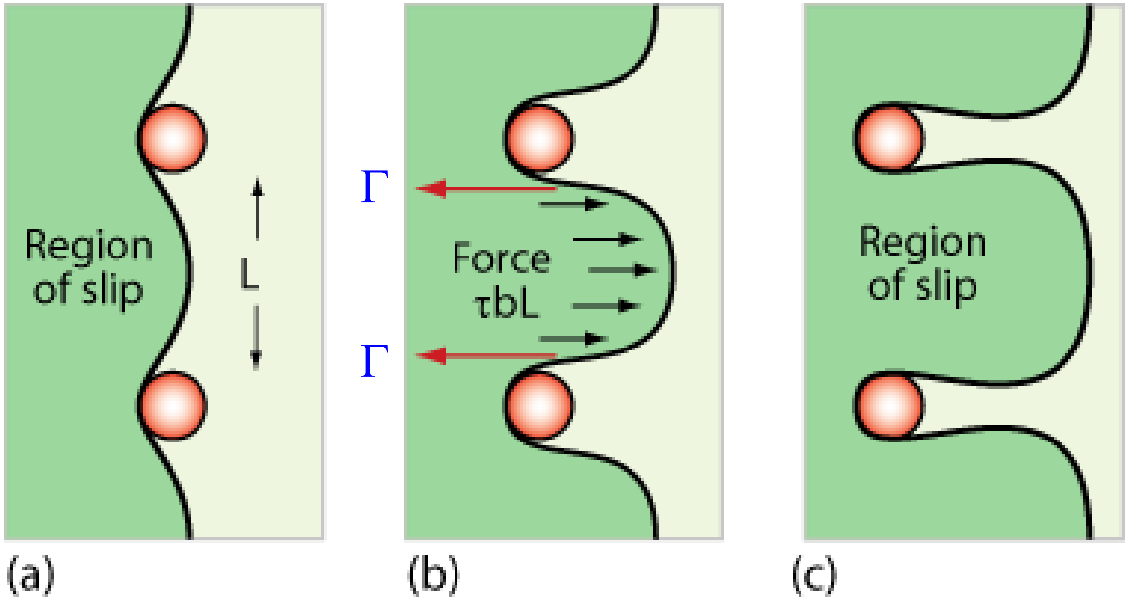


or

Extrude between particles
("bowing" or "Orowan looping").



[Ashby, Shercliff, & Cebon, p. 129]



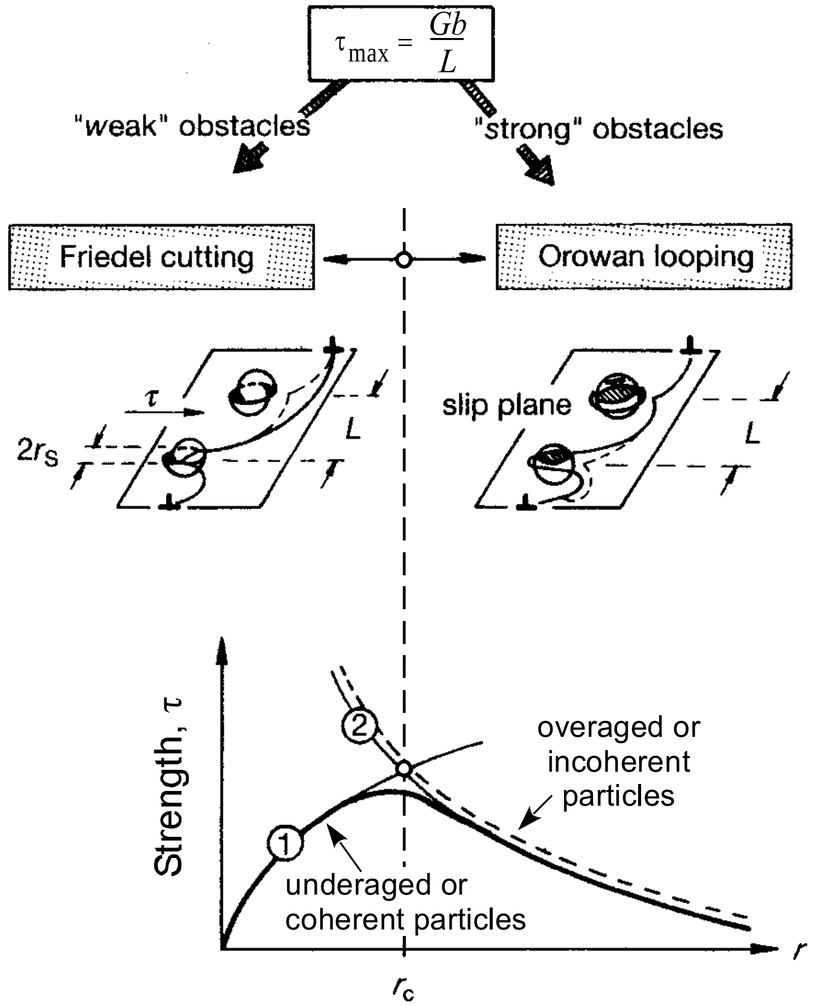
[Ashby, Shercliff, & Cebon, p. 131]

$$2\Gamma = \tau_o bL$$

Stress on ppt.
Derived from line tension.

$$\tau_{ppt} = \frac{2\Gamma}{bL} \approx \frac{\alpha G b}{L}$$

What dictates the mechanism?

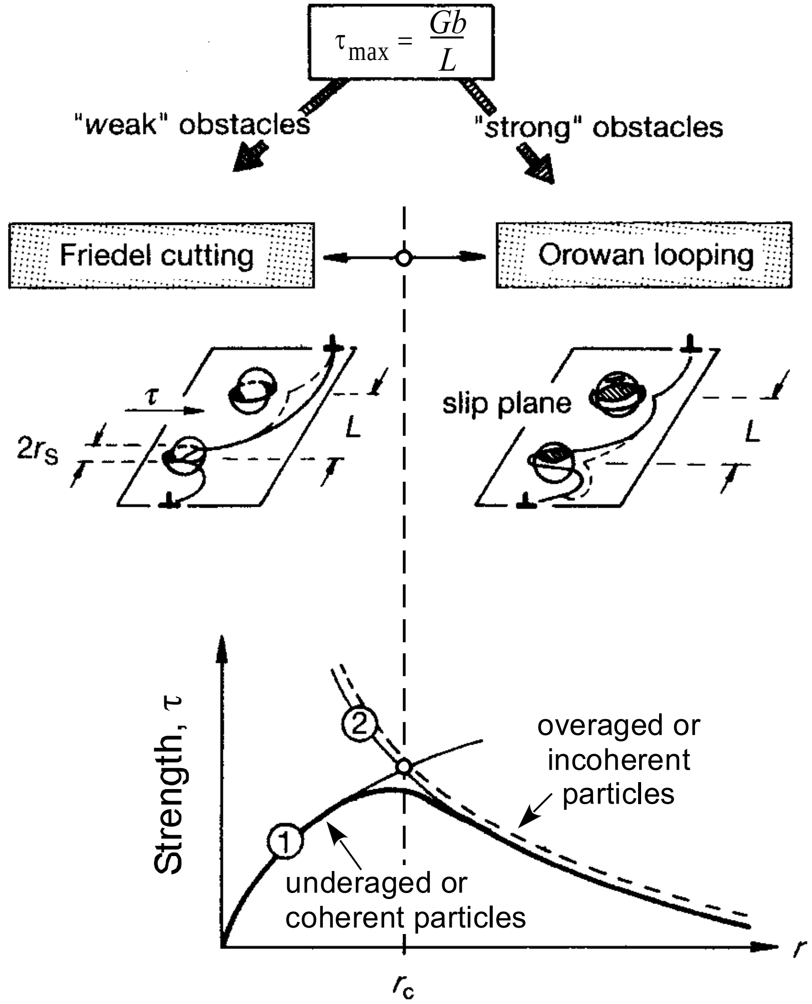


Adapted from Reppich, in *Plastic Deformation and Fracture of Materials,* VCH, (1992).

What dictates the mechanism?

- Type of interaction
- Properties of particles
- Particle distribution

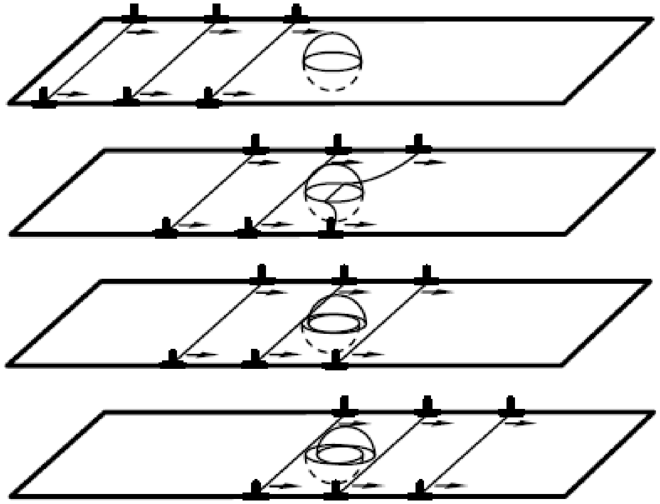
B*



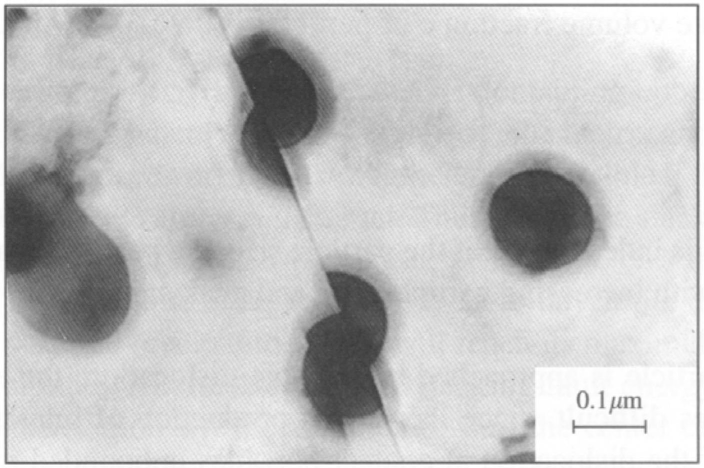
Adapted from Reppich, in *Plastic Deformation and Fracture of Materials,* VCH, (1992).

Particle shearing/cutting

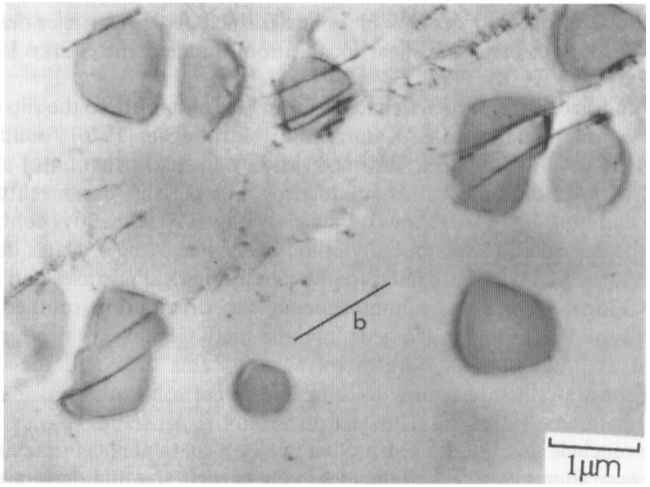
What determines whether or not this process occurs?



[Roesler, Harders, Baeker, p. 191]



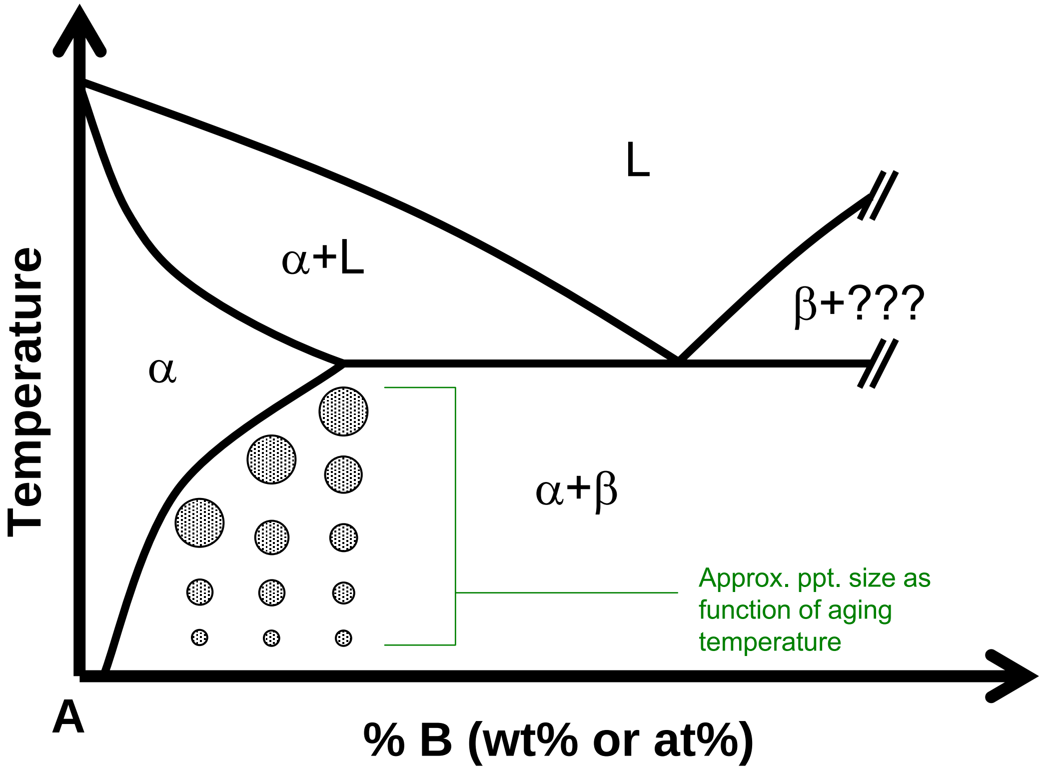
[Argon, Strengthening Mechanisms in Crystal Plasticity., p.221.]



[Humphreys and Hatherly, Recrystallization and Related Annealing Phenomena, 2nd Ed., p.49.]

Precipitation

As you learned in Physical Metallurgy and Thermodynamics, precipitates are generally very small in the early stages of precipitation. They coarsen with time at temperature.

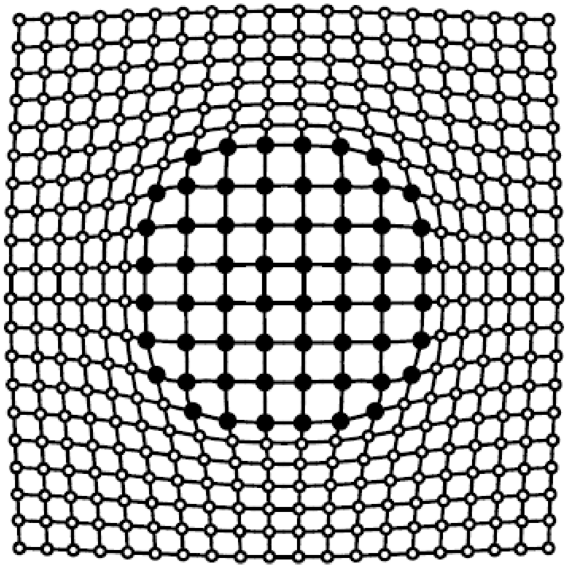


Precipitate size scales with composition, time and temperature.
THUS
Properties change with time at temp.

1. Small particles are generally *coherent* with the matrix
2. Intermediate particles are often *semi-coherent* with the matrix
3. Large particles are generally *incoherent* with the matrix

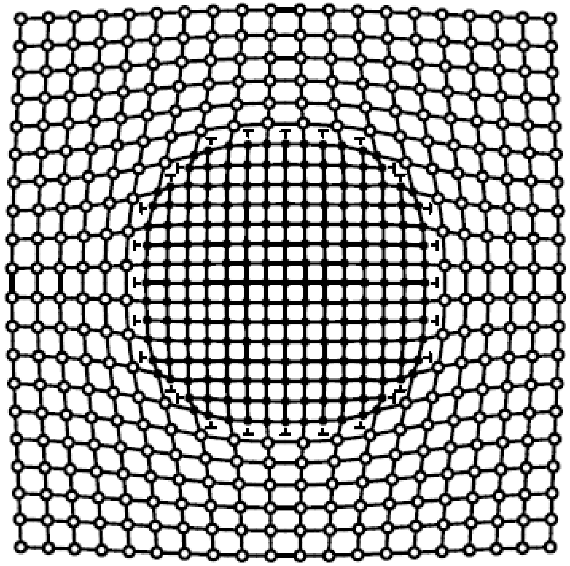
Properties scale with precipitate size and spacing for a constant precipitate volume fraction

Types of interfaces



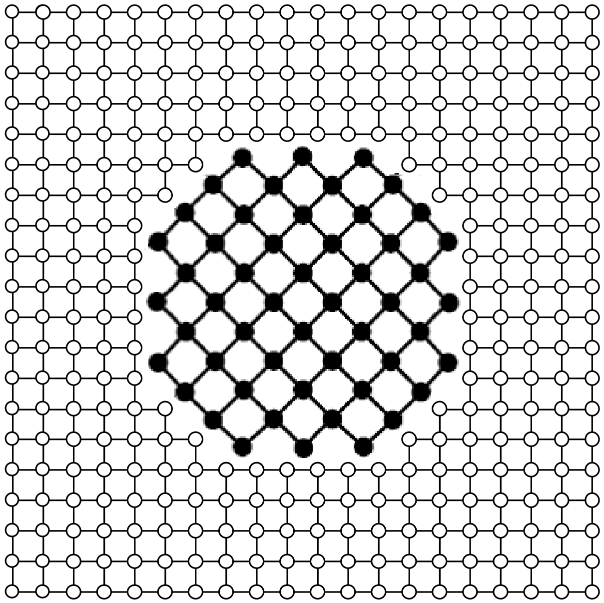
Coherent

All crystal planes line up



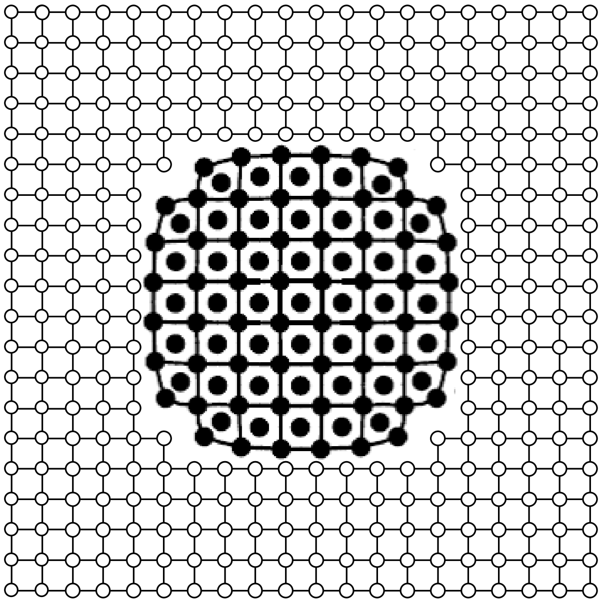
Semi-coherent

Come crystal planes line up



Incoherent

Different crystal orientations



Incoherent

Different crystal structures

Adapted from Roesler, Harders, Baeker, p. 15,16

Effect of Interface Character

- Precipitates <u>can</u> have stress fields associated with them.

- Stress fields around particles, when present, creates a larger effective particle volume.

★ Dislocations will interact with the stress fields surrounding coherent particles in the same way that they do with the stress fields around solute atoms (i.e., just like solid solution hardening).

Coherency Strain

- Dislocations interact with the stress fields that surround coherent particles in the same way that they interact with the stress fields surrounding solid solution atoms.
  - *Coherency strains* develop that reduce dislocation velocity (remember the Taylor-Orowan equation?) and increase strength. The increase in resolved shear stress is:

$$\boxed{\tau_{coh} \cong 7\left|\varepsilon_{coh}\right|^{3/2} G\sqrt{\frac{rf}{b}}}$$

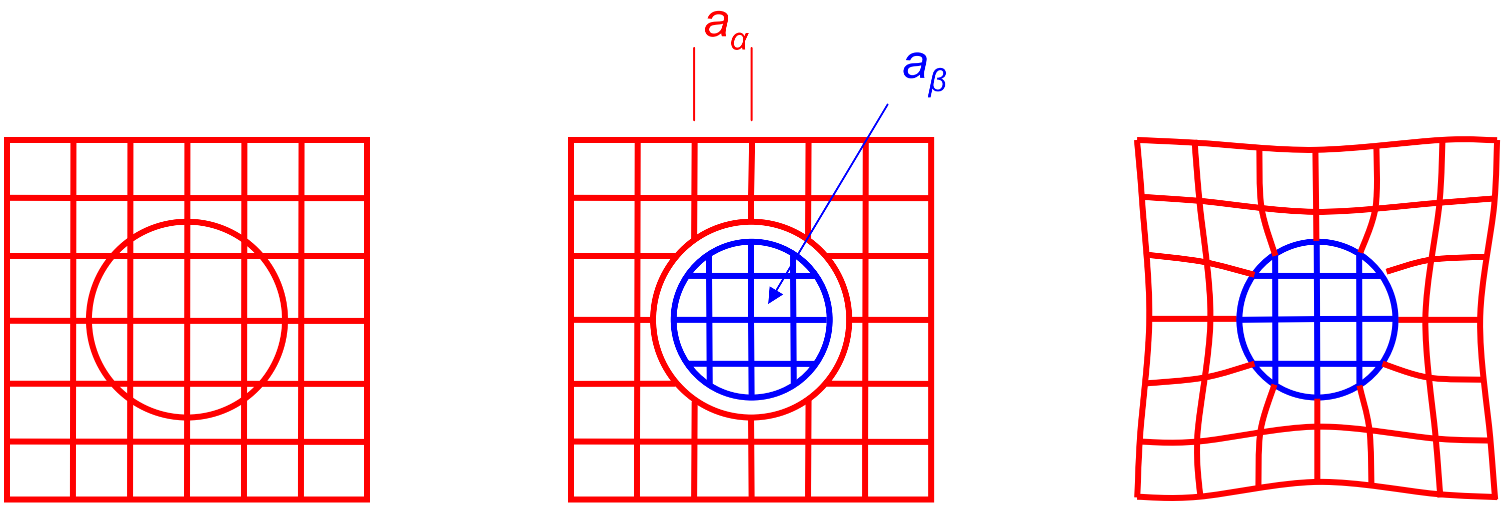
where

$$\varepsilon_{coh} = \frac{a_{ppt} - a_{matrix}}{a_{matrix}}$$

  - In this equation, the *rf/b* term ∝ to solute concentration in that *f* is the precipitate volume fraction (i.e., “precipitate concentration”).

Origin of coherency strains in precipitation strengthened material

Just a convenient way to visualize it.



$a_\beta < a_\alpha$

$$\varepsilon_{coh} = \frac{a_{ppt} - a_{matrix}}{a_{matrix}} = \frac{a_\beta - a_\alpha}{a_\alpha}$$

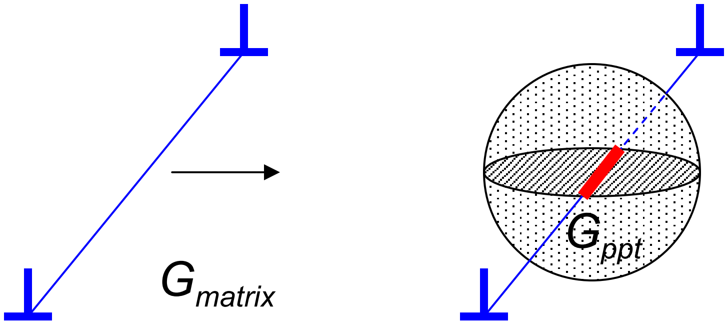
Notice that the number of lattice points inside the hole is conserved

Other factors to consider when particles are coherent (1)

- Modulus hardening
  - When a *precipitate* has a *shear modulus* that *is different from that of the matrix*, the *line tension on a dislocation* that enters a precipitate *is altered*.
  - This is analogous to solid solution hardening. The modulus change induces a *local change in the elastic strain energy* of the line segment (i.e., the *dislocation*). The resulting hardening has been equated (by Courtney) as:

$$\boxed{\tau_{Gppt} = 0.01 G \varepsilon_{Gppt}^{3/2} \sqrt{\frac{fr}{b}}}$$

  - This equation only provides an approximate estimate in the early stages of precipitation.

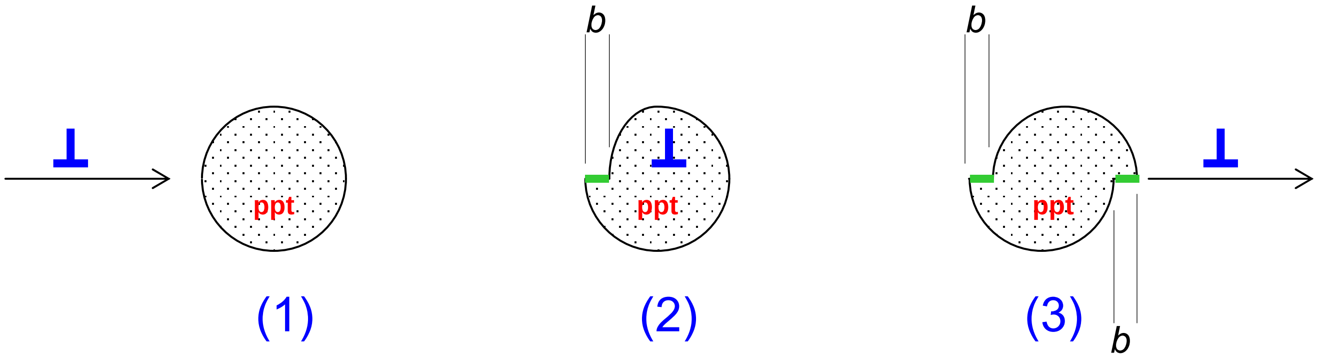


Change in line tension on cutting dislocation segment

$$= \frac{(G_{ppt} - G_{matrix}) b^2}{2} (2r)$$

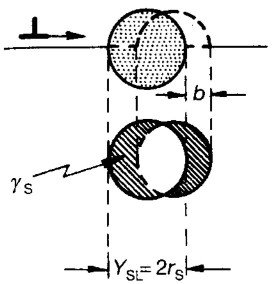
Other factors to consider when particles are coherent (2)

- Chemical strengthening
  - When a dislocation passes through a particle, a new region of particle-matrix interface is produced. There is a surface energy associated with this new interface. Work must be done to produce it. The strengthening associated with this is called chemical strengthening.



$$\boxed{\tau_{chem} = 2G\left(\frac{\gamma_s}{Gr}\right)^{3/2}\sqrt{\frac{fr}{b}} = 2G\varepsilon_{chem}^{3/2}\sqrt{\frac{fr}{b}}}$$

  - Chemical strengthening does not play as large a role in precipitation hardening as other mechanisms.

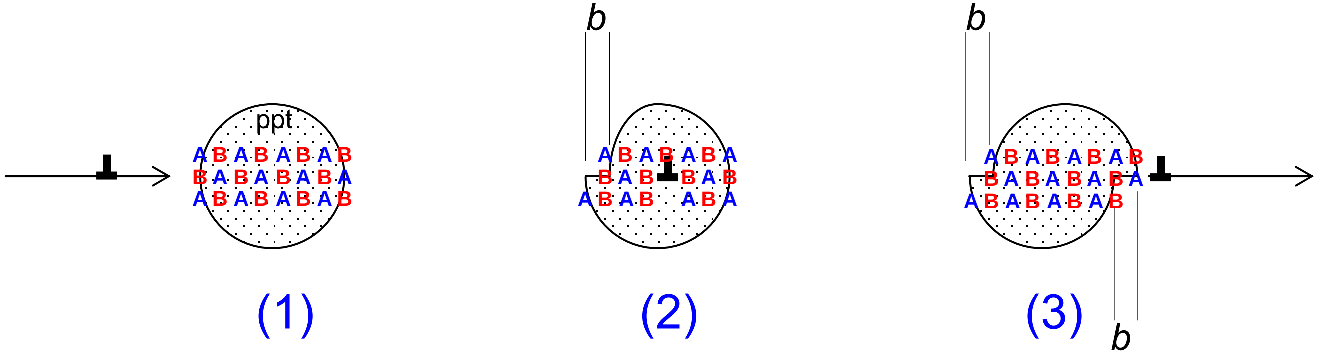


Reppich, in *Plastic Deformation and Fracture of Materials,* VCH, (1992) p. 325.

Figure 7-7. Chemical (surface) strengthening: edge dislocation shearing a spherical particle creates the (hatched) new particle-matrix interphase of area $2r_s\boldsymbol{b}$.

Other factors to consider when particles are coherent (3)

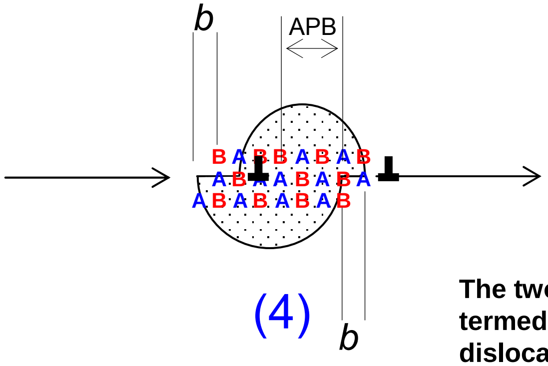
- Order strengthening and stacking fault strengthening
  - When the stacking fault energies of the particle and matrix are different, dislocations will be impeded because the equilibrium separation of the partial dislocations is different in the matrix and the particle.
  - When a particle has an ordered structure, like bonds (i.e., A-A, B-B, etc.) will form when a single dislocation passes through the precipitate. These are called *anti-phase boundaries (APBs)*. This represents a higher energy state than the desired A-B type bonding. The energy increase is the APB energy.



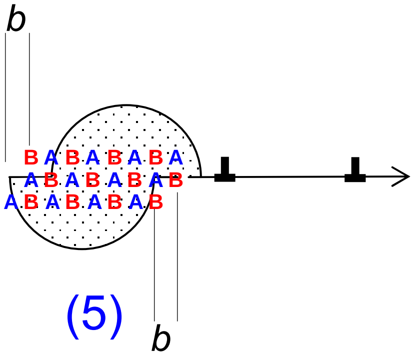
$$\boxed{\tau_{order} = \frac{\pi \gamma_{APB} f}{2b}}$$

Other factors to consider when particles are coherent (4)

- Order strengthening and stacking fault strengthening (cont'd)
  - A second dislocation must pass through the precipitate to return the lattice to its preferred stacking sequence.
  - The second dislocation is attracted to the particle because it "removes" the APB created by the passage of the first. Separation between the dislocations bounding the APB is quite complicated.



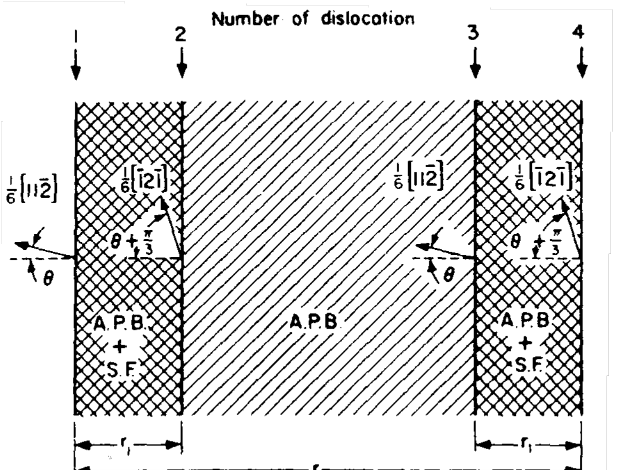
(4)



(5)

The two dislocations are termed superlattice dislocations or "superdislocations"

  - Keep in mind that each individual dislocation can also dissociate into a partial dislocations separated by stacking faults <u>and</u> APBs. One such example in Ni_3Al is illustrated to the right.
  - We'll address this more in the ordered alloys lecture module.



[Soboyejo, p. 203]

Other factors to consider when particles are coherent (5)

- For low APB energies (wide dislocation separation) in the early stages of precipitation:

$$\tau_{ord} \cong 0.7G\varepsilon_{ord}^{3/2}\sqrt{\frac{fr}{b}}, \text{ where } \varepsilon_{ord} = \frac{\gamma_{APB}}{Gb}$$

- For high APB energies (smaller dislocation separation) in the early stages of precipitation:

$$\tau_{ord} \cong 0.7G\left[\varepsilon_{ord}^{3/2}\sqrt{\frac{fr}{b}} - 0.7\varepsilon_{ord}f\right]$$

- For low APB energies (wide dislocation separation) in the late stages of precipitation:

$$\tau_{ord} \cong 0.44G\varepsilon_{ord}\sqrt{f}$$

- For high APB energies (smaller dislocation separation) in the late stages of precipitation:

$$\tau_{ord} \cong 0.44G\varepsilon_{ord}\left[\sqrt{f} - 0.92f\right]$$

Loss of coherency

- When precipitate particles grow, coherency can be lost.

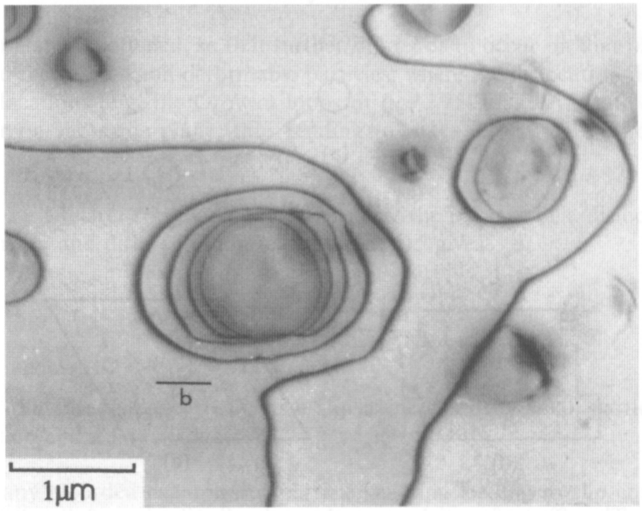
- The energy of the strained interface between the particle and matrix becomes greater than the energy for an incoherent interface. This occurs when the particle size exceeds a critical value. You should recall this from Physical Metallurgy. See a physical metallurgy text such as Reed-Hill and Abbaschian for more details.

- When you lose coherency, you lose the coherency strain and associated hardening. This same thing occurs in dispersion hardening materials where there is no coarsening and no coherency.

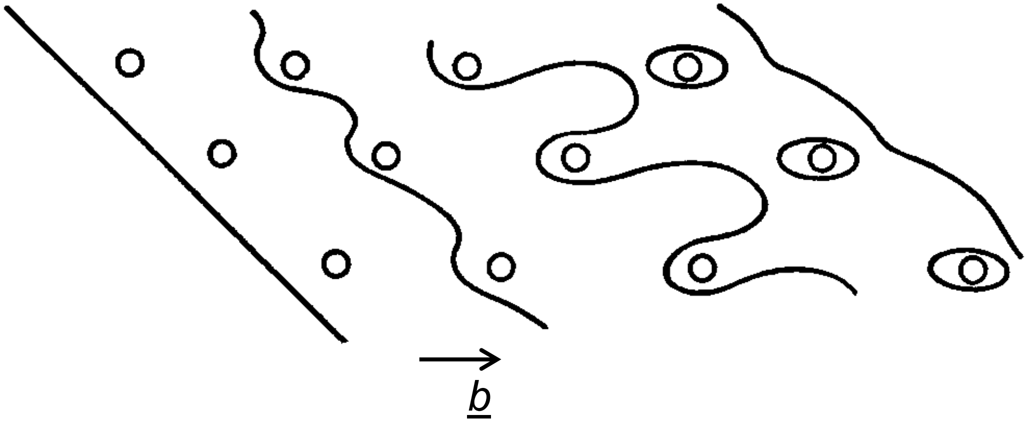
- Strength still increases anyway (up to a point)! WHY?

Orowan Looping

What determines whether this process occurs?



[Humphreys and Hatherly, Recrystallization and Related Annealing Phenomena, 2nd Ed., p.49.]

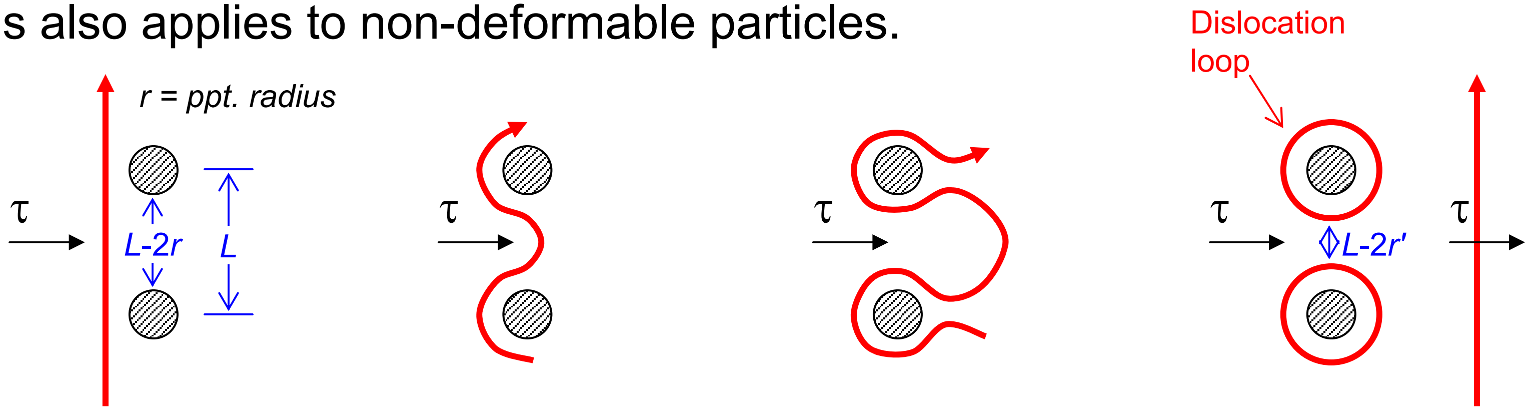


[C.R. Barrett, W.D. Nix and A.S. Tetelman, The Principles of Engineering Materials, Prentice Hall, Englewood Cliffs, NJ (1973) p.263.]

Orowan bypass mechanisms

- Particles can bypass incoherent precipitates by looping/bowing around them.

- This also applies to non-deformable particles.



- Dislocation bowing will *occur when the volume of particle phase* increases above some critical value *or* when the *interface boundary is incoherent*.

- The shear stress required to cause bowing is given by:

$$\tau_{bowing} = \frac{Gb}{(L-2r)} = \frac{Gb}{L'}$$

- This stress will increase after a loop forms around a particle because a subsequent dislocation would have to “squeeze through” a smaller region in between the two loops. The end result is an increase in strength.

Orowan loops as they appear in an electron microscope

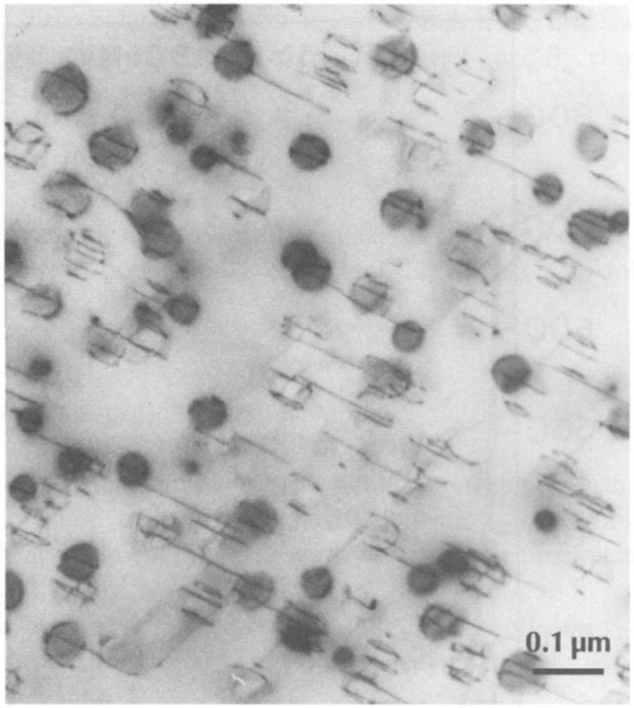
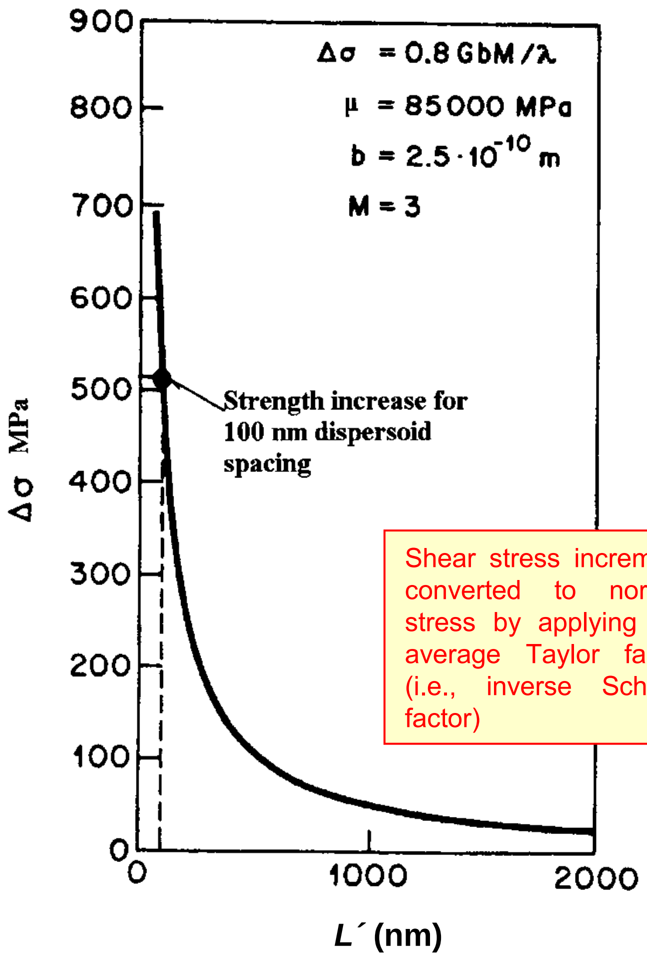


Fig. 2.16 TEM image of Orowan loops surrounding γ′ particles in a precipitation-hardened austenitic steel deformed 1% at 650°C.

Strengthening caused by Orowan looping



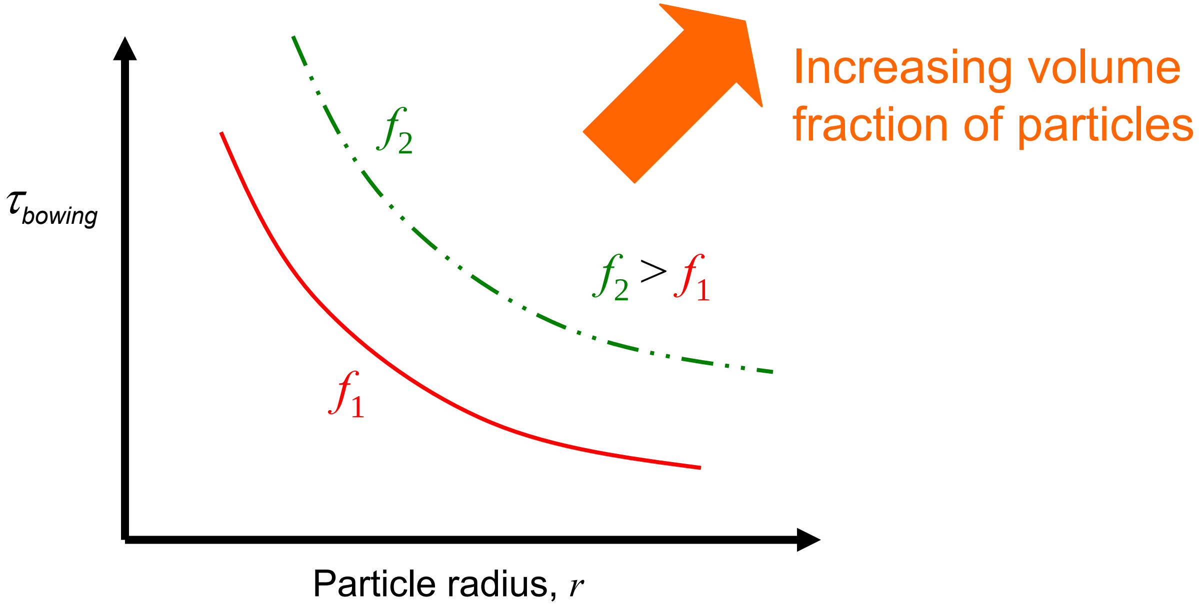
Shear stress increment converted to normal stress by applying the average Taylor factor (i.e., inverse Schmid factor)

Fig. 2.17 The Orowan stress as a function of the interparticle spacing for a nickel matrix.

[Martin, Precipitation Hardening, 2nd Ed.]

Does the bowing stress change with particle volume fraction (f)?

- YES! For a fixed volume fraction of particles, the bowing stress decreases with increasing particle radius r. This is accompanied by an increased particle spacing.

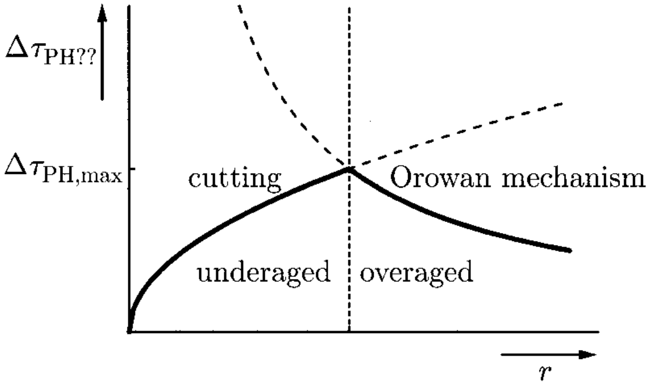


- Increasing f also increases the bowing stress. How does this relate to structure?
- What happens if we increase the resistance to dislocation penetration after bowing commences?

Transition from cutting to bowing

- Assuming a constant precipitate volume fraction, the following events occur.

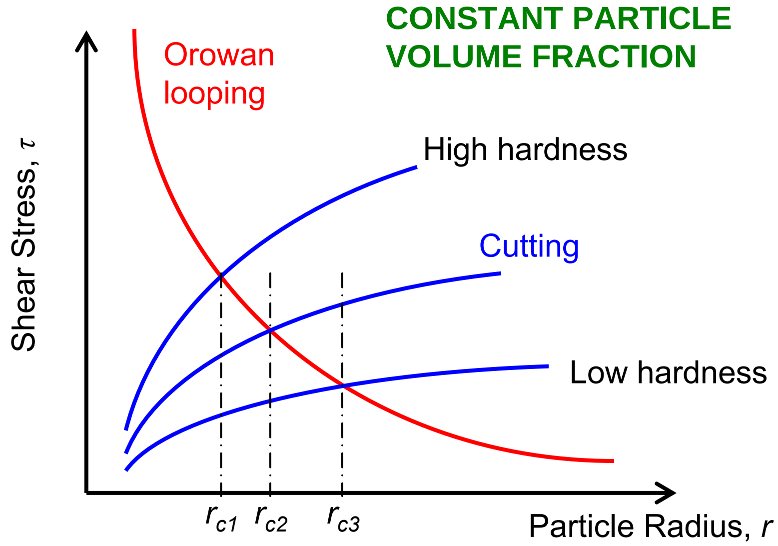
[Roesler]



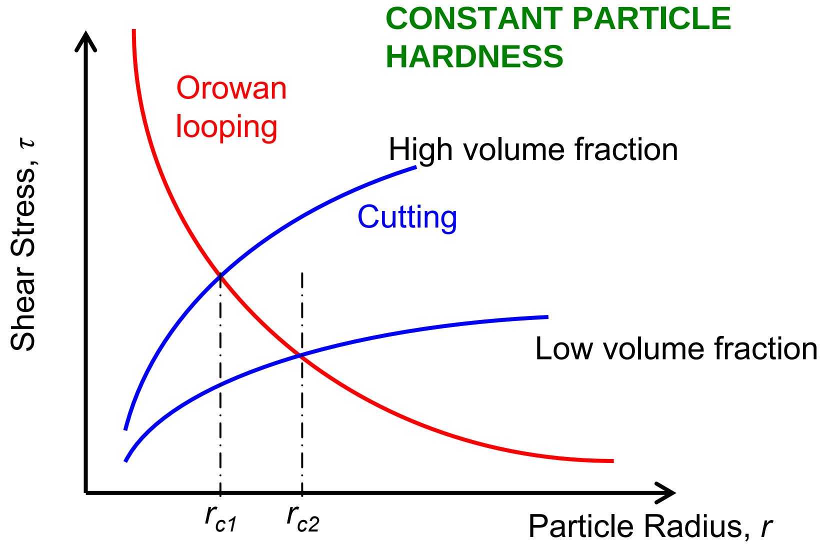
- As particle size increases, it becomes more difficult for cutting to occur. This means it becomes more difficult for dislocations to pass through particles. Coherency is also lost.
- The difficulty of cutting arises from:
  - The increase in the amount of work that is required to shear a larger precipitate.
  - Also, the mean spacing between particles increases which causes the shear stress required to cause bowing to decrease.
- In general, particles that are smaller than some critical size are “sheared.” This means that dislocations cut through them. When particles are larger than the critical size, they are bypassed by “Orowan looping/bowing.”

Do variations in volume fraction and precipitate hardness influence strength?

- Constant volume fraction of particles
  - Increase precipitate hardness → increase strengthening; decrease precipitate radius where bowing begins.
- Constant particle hardness
  - Increase precipitate volume fraction → increase strengthening; increase precipitate radius where bowing begins.



Change in shear stress with increasing particle hardness and radius



Change in shear stress with increasing particle volume fraction

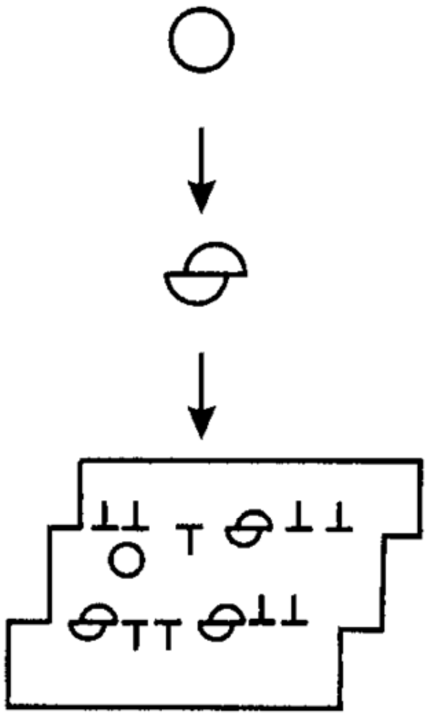
Precipitation hardening and work hardening rates

- The extent of work hardening depends upon whether or not dislocations cut through or bow/loop around precipitates.

- <u>Deformable particles</u>

  Easily sheared.

  Work hardening is very similar to that of materials without precipitates. Dislocations cut precipitates repeatedly. This does not yield a dramatic increase in dislocation density. It also makes it easier for subsequent dislocations to pass through.



Deforming particles lead to slip concentration. [Adapted from Humphries & Hatherly, <u>Recrystallization and Related Annealing Phenomena, 2nd Edition</u>, (Elsevier, Amsterdam, 2004) p. 50]

Precipitation hardening and work hardening rates

- The extent of work hardening depends upon whether or not dislocations cut through or bow/loop around precipitates.

- Non-deformable particles

  Can’t be sheared. Must bypass (Orowan looping).

  Work hardening rate is much greater
  than that of a material without precipitates. Plastic deformation causes loops to form around precipitates which leads to a decrease in the precipitate spacing and an increase in the stress to cause further plastic deformation (bowing).

- The Cu-Be alloy contains coherent shearable particles. The precipitates are bypassed by particle shearing. This results in a dramatic increase in strength but in virtually no increase in work hardening above pure copper.

- The Cu-BeO alloy, however contains non-deformable BeO particles. They are bypassed via the Orowan looping mechanism. This results in a smaller increase in strength at low strains compared to materials where particle shearing occurs; however, the work hardening rate is much higher because dislocation motion is constrained to the region between particles.

- What is the influence of particle spacing?

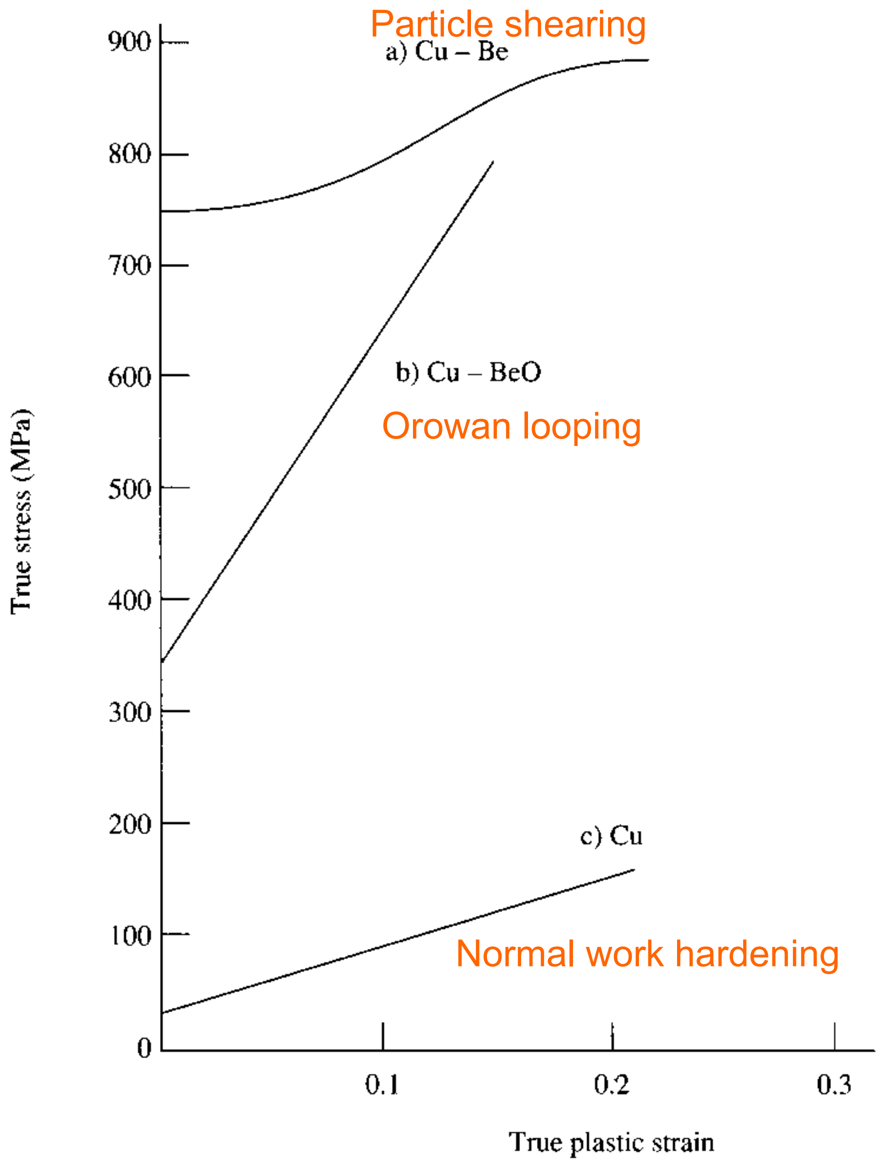
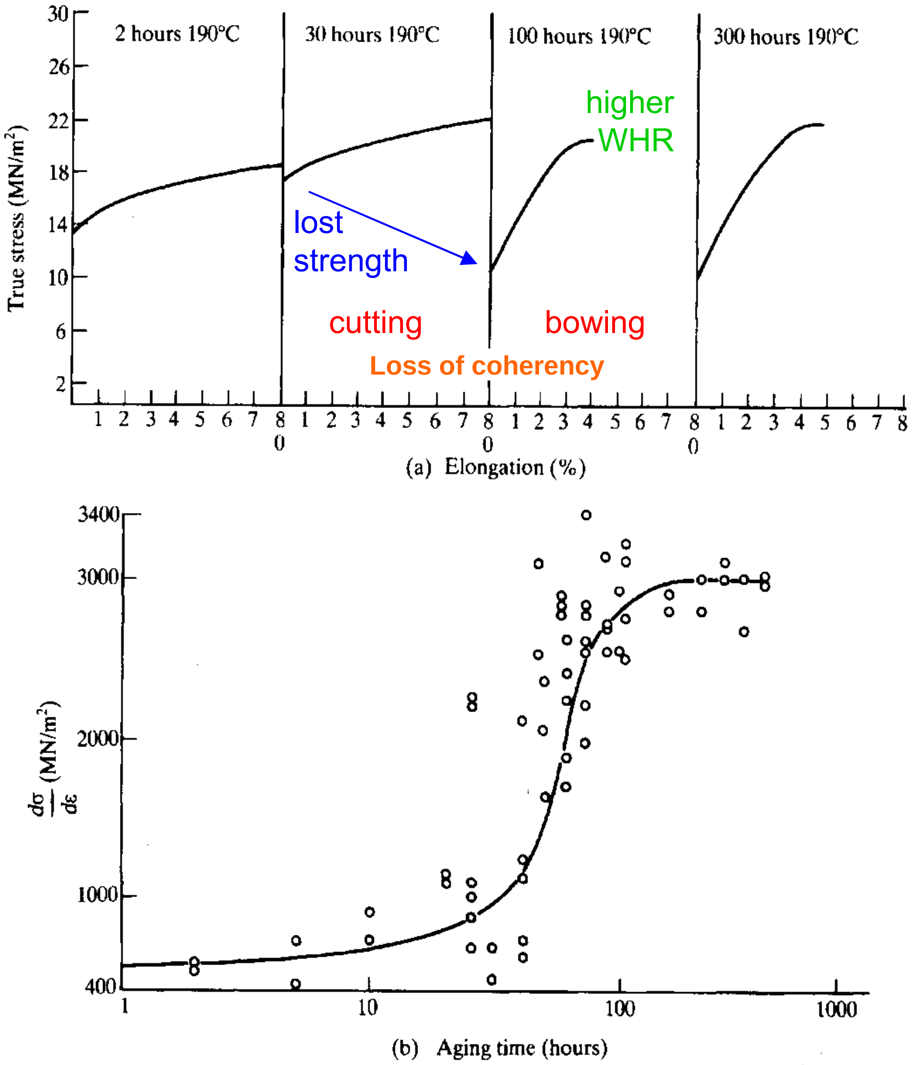


Figure 5.29

[Courtney]



[Courtney]

Figure 5.34
(a) Room-temperature stress-strain curves for Al-1.6 wt.% Cu alloys aged for various times at 190°C. For aging times of 30 hours or less, plastic deformation takes place by particle shearing; for aging times of 100 hours or more, it occurs by dislocation bowing. Dislocation bowing is associated with lower yield strengths. However, work-hardening rates are much greater when bowing is the slip mechanism. This is illustrated further in (b) where the work-hardening rate (at 2 percent strain) is plotted vs. aging time. The transition from dislocation cutting to bowing is accompanied by a substantial increase in this rate. (*From Prog. Matls. Sc., 10, "Precipitation Hardening," A Kelly and R. B. Nicholson, 151, Copyright 1963, with permission from Elsevier Science.*)

- Classical examples of materials where both mechanisms occur are the 2000 series aluminum alloys (Cu is the major alloying element). Nice model systems are the Al-Cu and Al-Ag systems. Al-Cu is shown to the left.

- Precipitate coherency is lost between 30 and 100 hours at 190°C. You can see that the strength decreases at low strains but the work hardening rate increases dramatically when we transition from cutting to bowing.

Example: Al-Cu alloys

- Precipitation sequence:

  α → GP → θ″ → θ′→ θ

- GP zones → shearable
- θ″ → shearable
- θ′ → semi-shearable
- θ → not shearable

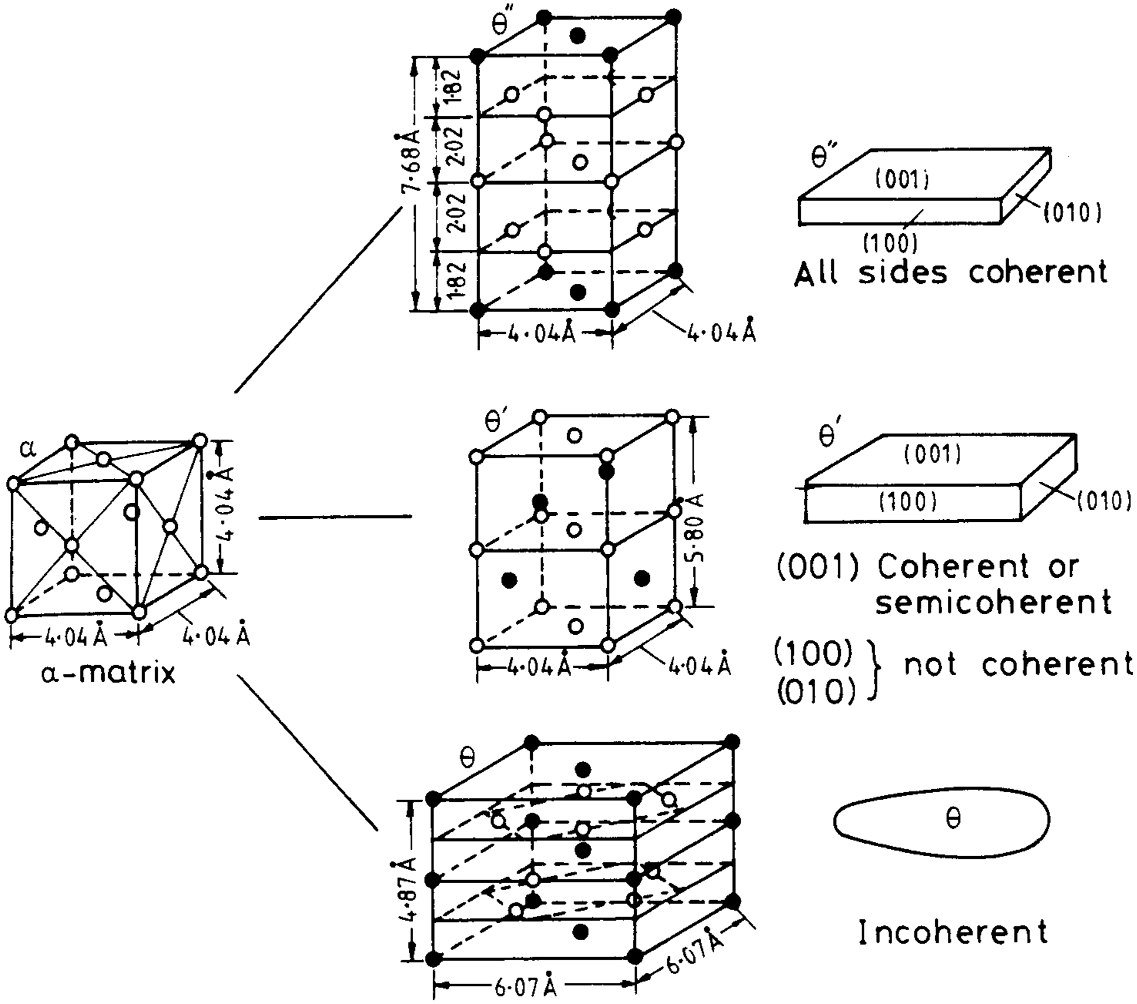
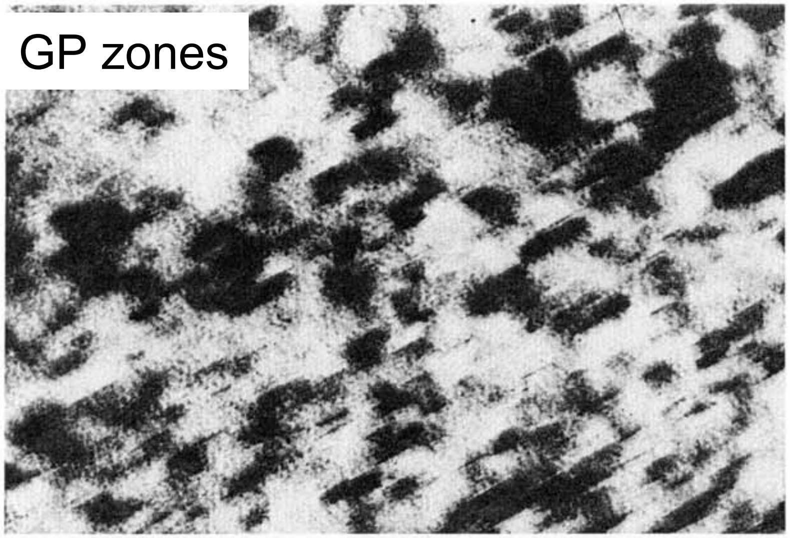


Fig. 5.29 Structure and morphology of θ″, θ′ and θ in Al–Cu (○ Al, ● Cu).

[Porter & Easterling]

GP zones



θ″

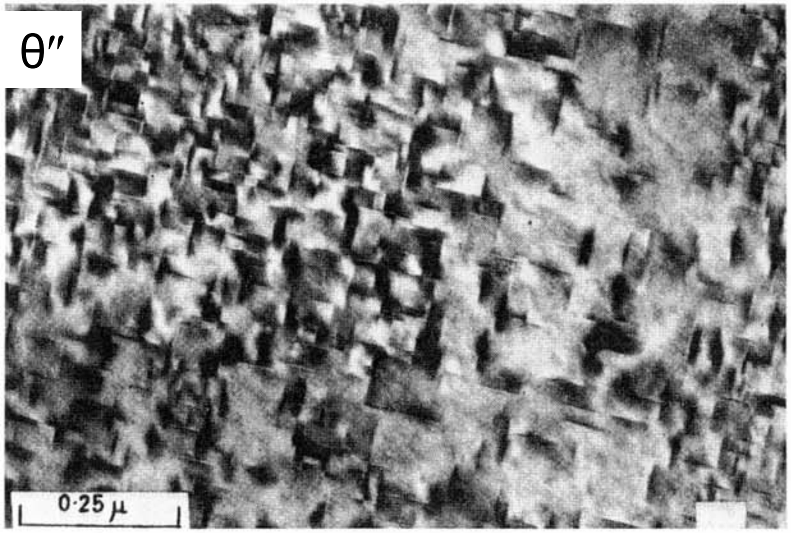
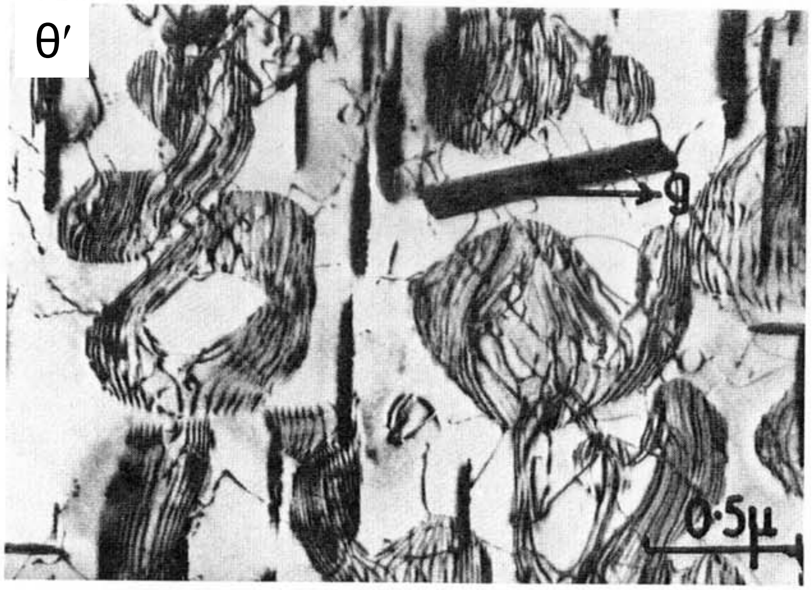


Fig. 5.30 Microstructures at different stages during ageing of Al–Cu alloys. (a) GP zones × 720 000. (b) θ″ × 63 000. (c) θ′ × 18 000. (d) θ × 8000. [(a) After R.B. Nicholson and J. Nutting, *Philosophical Magazine* **3** (1958) 531. (b) R.B. Nicholson, G. Thomas and J. Nutting, *Journal of the Institute of Metals* **87** (1958–1959) 431. (c) G.C. Weatherly and R.B. Nicholson, *Philosophical Magazine* **17** (1968) 813. (d) G.A. Chadwick, *Metallography of Phase Transformations*, Butterworths, London, 1972, from C. Laird.]

[Porter & Easterling]

θ′



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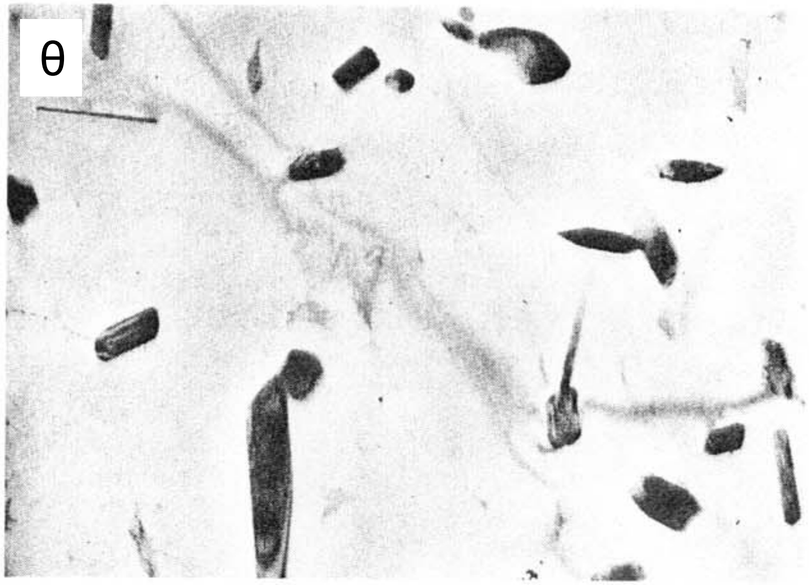

Summary of hardening/strengthening mechanisms for crystalline solids

Hardening Mechanism	**Nature of Obstacle**	**Strong or Weak**	**Hardening Law**
Work hardening	Other dislocations	Strong	$\Delta\tau = \alpha G b \sqrt{\rho}$ (see [1])
Grain size / Hall-Petch	Grain boundaries	Strong	$\Delta\tau = k'_y / \sqrt{d}$ (see [2])
Solid solution	Solute atoms	Weak (see [3])	$\Delta\tau = G\varepsilon_s^{3/2} c^{1/2} / 700$ (see [4])
Deforming particles	Small, coherent particles	Weak (see [5])	$\Delta\tau = CG\varepsilon^{3/2}\sqrt{\frac{fr}{b}}$ (see [6])
Non-deforming particles	Large, incoherent particles	Strong (see [7])	$\Delta\tau = \frac{Gb}{(L-2r)}$

[1] α equals about 0.2 for FCC metals and about 0.4 for BCC metals.

[2] k'_y scales with inherent flow stress and/or shear modulus; therefore k'_y is generally greater for BCC metals than for FCC metals.

[3] Exception to weak hardening occurs for interstitials in BCC metals; the shear distortion interacts with screw dislocations leading to strong hardening.

[4] Equation apropos to substitutional atoms; parameter ε_s is empirical, reflecting a combination of size and modulus hardening.

[5] Coherent particles can be "strong" in optimally aged materials.

[6] Constant C depends on specific mechanism of hardening; parameter ε relates to hardening mechanism(s). Equation shown applies to early stage precipitation. Late stage precipitation results in saturation hardening.

[7] Highly overaged alloys can represent "weak" hardening.

SYMBOLS : $G =$ shear modulus; $b =$ Burgers vector; $\rho =$ dislocation density ; $d =$ grain size; $c =$ solute atom concentration (at.%); $f =$ precipitate volume fraction; $r =$ precipitate radius; $L =$ spacing between precipitates on slip plane.

Table adapted from Courtney, *Mechanical Behavior of Materials*, 2nd edition, p. 232.