Phase transformation and Kinetics

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Phase transformation

- Transition from one phase to another
- Change in composition or structure or both of a phase
- Solidification is important for metallurgical operations
- Metals come from ores and extraction of metals at high temperature leads to liqid metal
- Casting followed with thermomechanical processing to achieve optimum microstructure

Callister

Phase transformation

- Solid state phase transformation important
- Nucleation and Growth by transport of mass
- Sudden transformation
- Austenite to martensite transformation
- Solutionizing and aging
- Eutectoid transformation

Solidification

Homogeneous

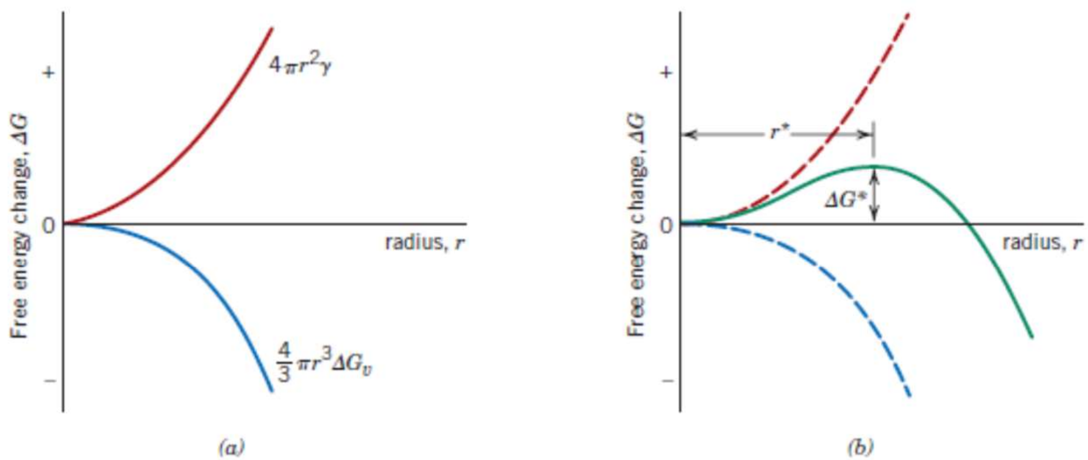
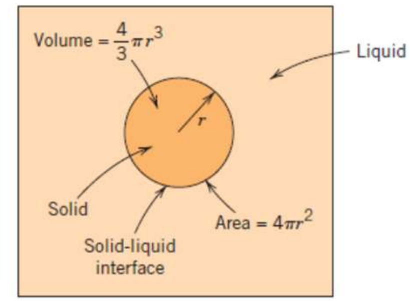


Figure 10.2 (*a*) Schematic curves for volume free energy and surface free energy contributions to the total free energy change attending the formation of a spherical embryo/nucleus during solidification. (*b*) Schematic plot of free energy versus embryo/nucleus radius, on which is shown the critical free energy change (ΔG^*) and the critical nucleus radius (r^*).

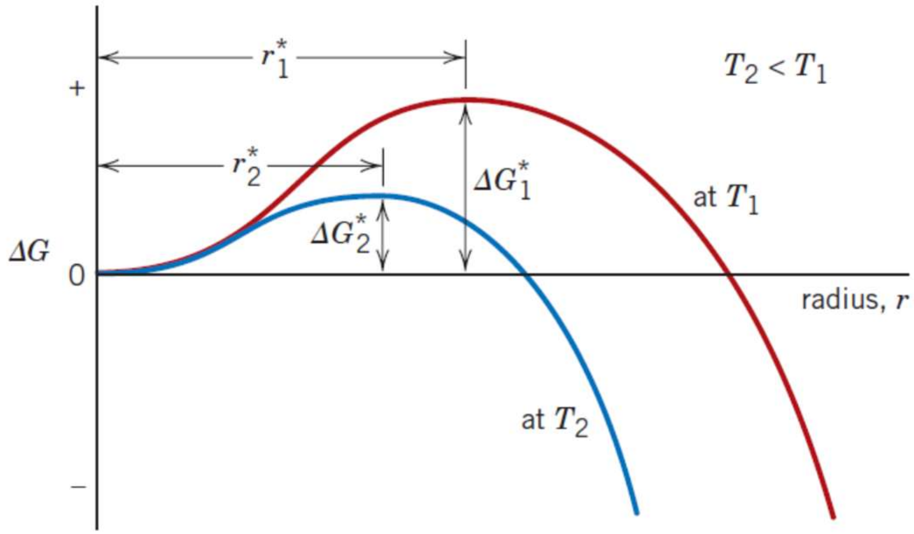


$$\Delta G = \tfrac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

$$\frac{d(\Delta G)}{dr} = \tfrac{4}{3}\pi \Delta G_v(3r^2) + 4\pi\gamma(2r) = 0$$

$$r^* = -\frac{2\gamma}{\Delta G_v}$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$$

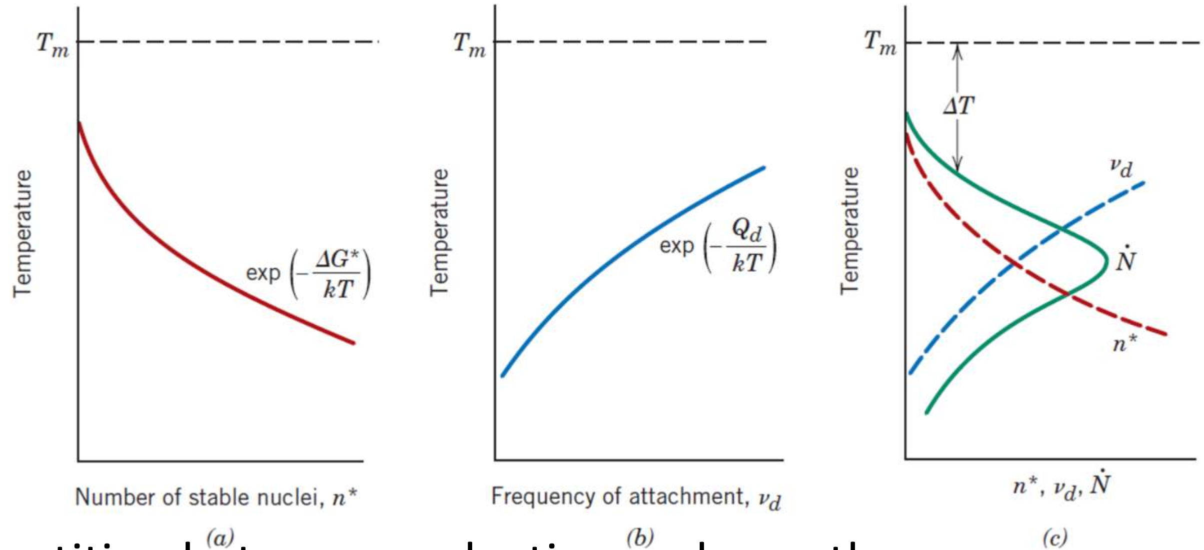


$$\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m}$$

$$r^* = \left(- \frac{2\gamma T_m}{\Delta H_f} \right) \left(\frac{1}{T_m - T} \right)$$

$$\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2} \right) \frac{1}{(T_m - T)^2}$$

$$n^* = K_1 \exp\left(- \frac{\Delta G^*}{kT} \right)$$



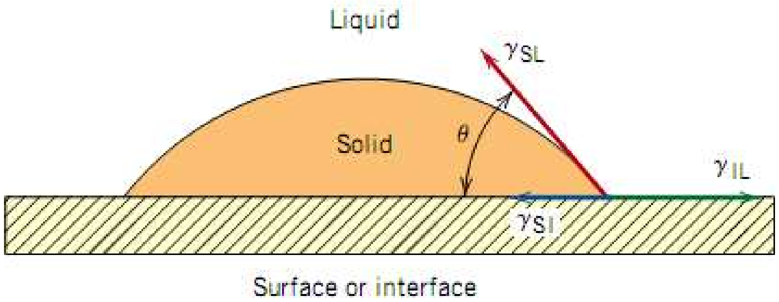
- Competition between nucleation and growth
- Number of nuclei increases with degree of undercooling
- Attachment of more atoms to the nuclei is necessary to achieve critical size
- Balance between nucleation and growth
- Higher nucleation rate and smaller growth rate leads to smaller grain size and vice versa

Table 10.1 **Degree of Supercooling (ΔT) Values (Homogeneous Nucleation) for Several Metals**

Metal	ΔT (°C)
Antimony	135
Germanium	227
Silver	227
Gold	230
Copper	236
Iron	295
Nickel	319
Cobalt	330
Palladium	332

Source: D. Turnbull and R. E. Cech, "Microscopic Observation of the Solidification of Small Metal Droplets," *J. Appl. Phys.*, **21,** 808 (1950).

Heterogeneous



$$\gamma_{IL} = \gamma_{SI} + \gamma_{SL}\cos\theta$$

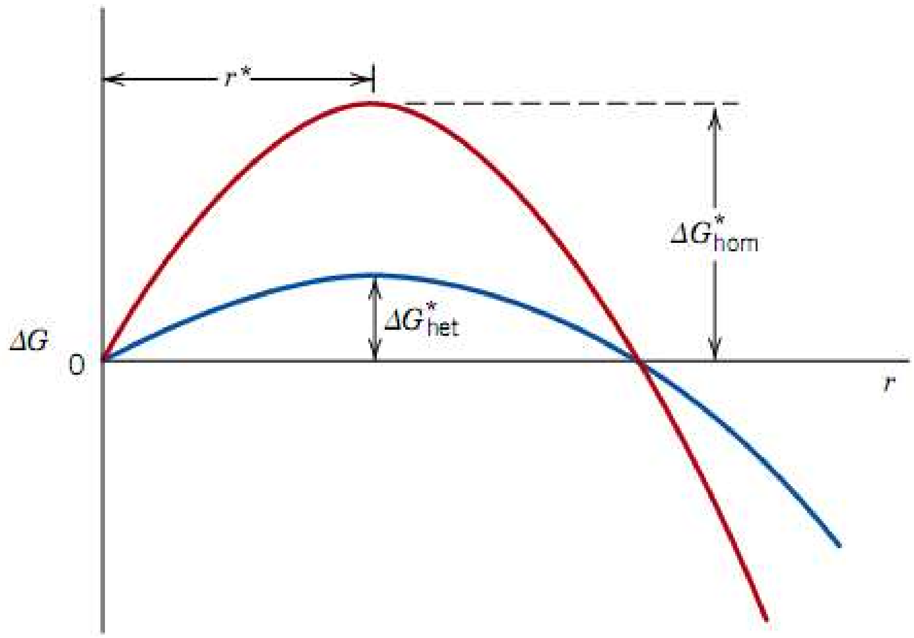
$$r^* = -\frac{2\gamma_{SL}}{\Delta G_v}$$

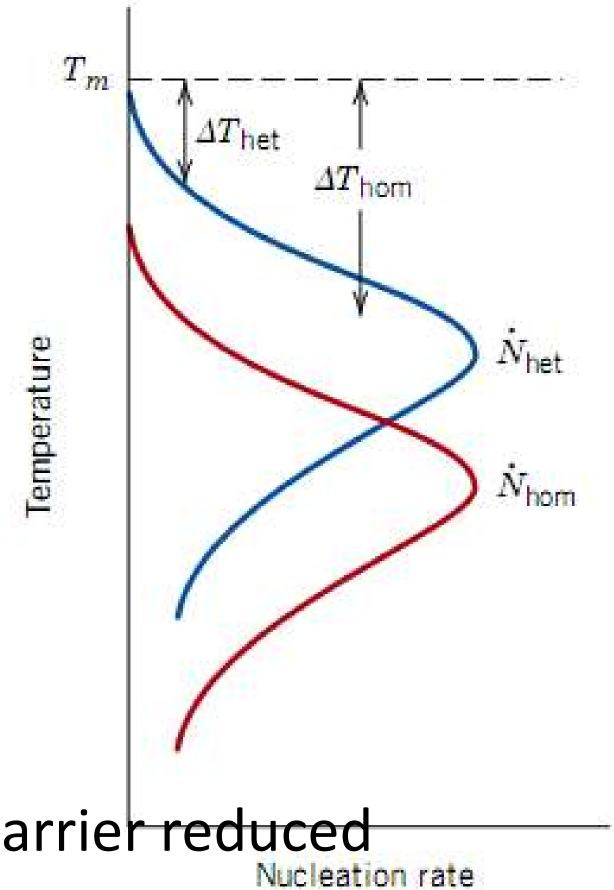
$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2}\right)S(\theta)$$

$$\Delta G_{het}^* = \Delta G_{hom}^* S(\theta)$$

Grain refiners in solidification of metals and alloys

TiB_2 in aluminium



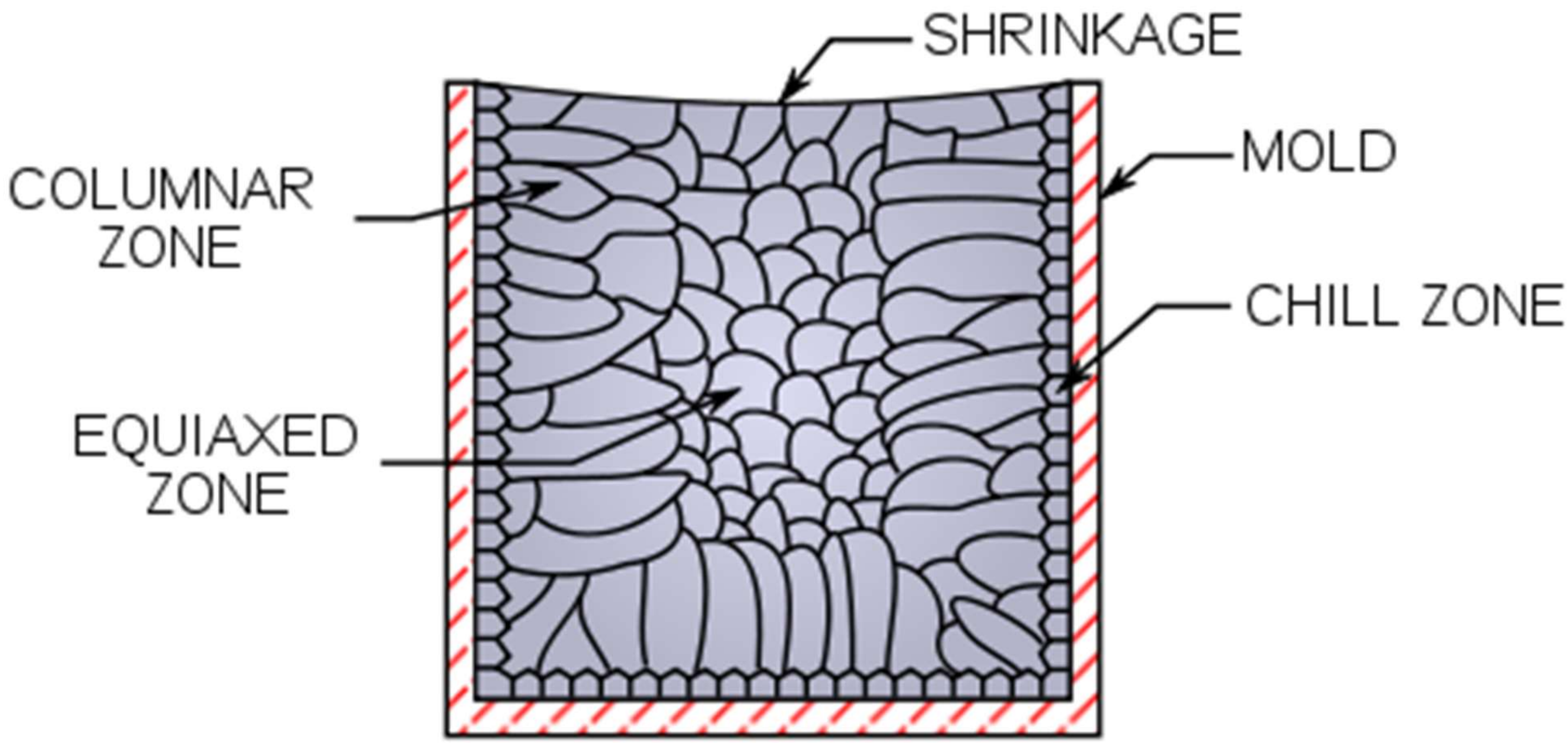


Critical radius is constant but energy barrier reduced

Nucleation rate is faster

Solidification grain size reduces

Solidification in a mould



Industrial castings from solidification of melt

Many engineering issues

- Levitation experiments for studying homogeneous nucleation
- Low gravity or magnetic levitation
- Different techniques to grow single crystal
- Coke and mentos experiment
- Cloud seeding

Growth or transformation rate

$$\dot{G} = C \exp\left(-\frac{Q}{kT}\right)$$

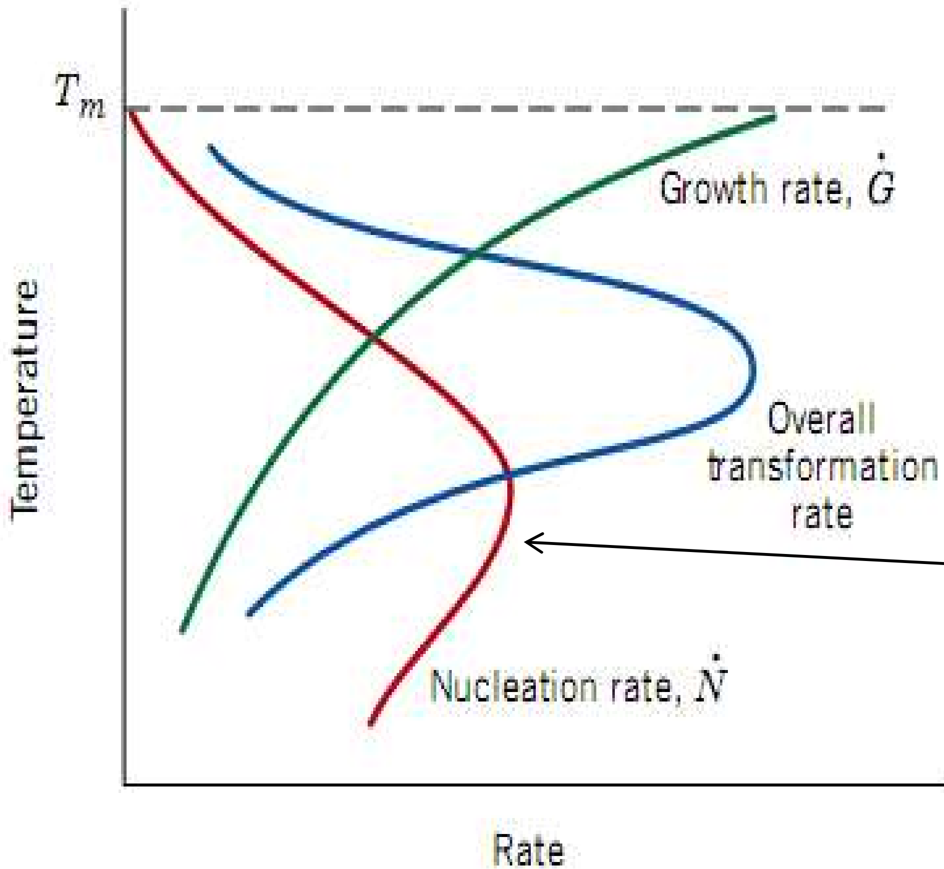
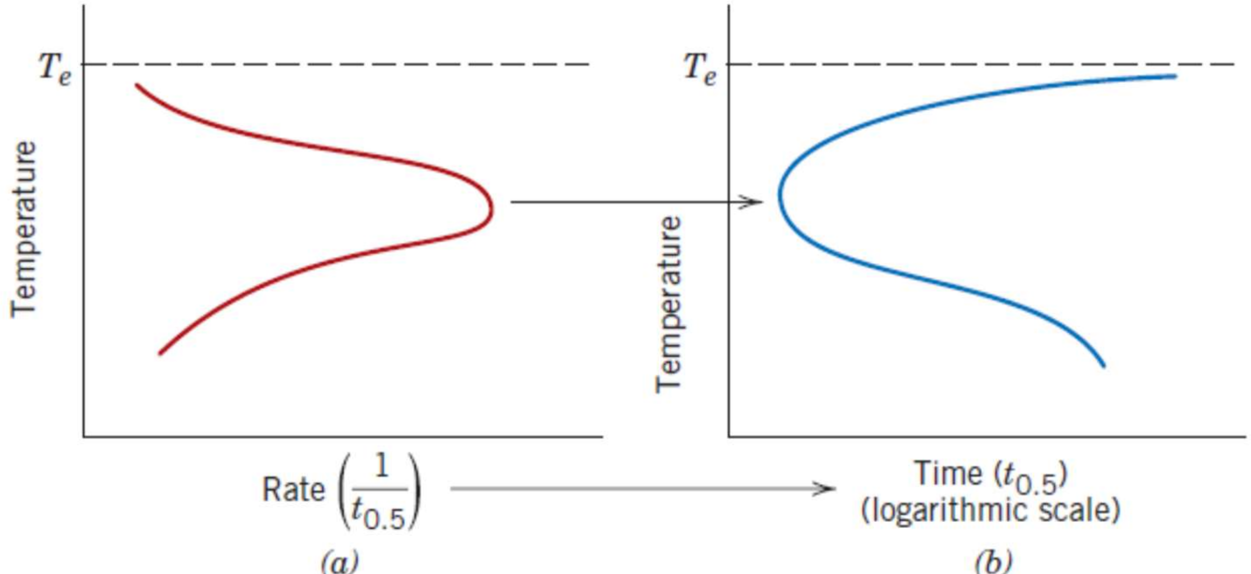


Figure 10.8 Schematic plot showing curves for nucleation rate ($\dot{N}$), growth rate ($\dot{G}$), and overall transformation rate versus temperature.

Nucleation rate for Heterogeneous nucleation



- Monitoring of nucleation and growth rate is difficult
- Easy to monitor time for completion of transformation
- Time for 50% or 100% transformation is plotted
- Mirror image

Avrami equation

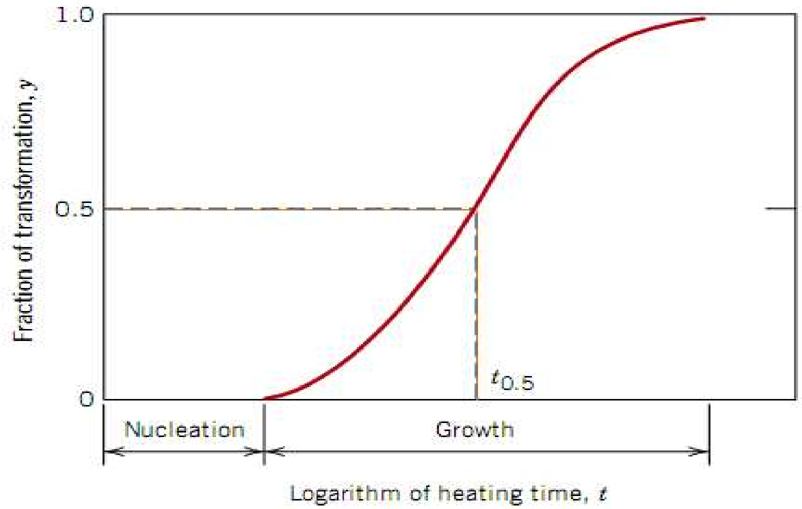
The fraction of original phase that has transformed into another phase can be given by following expression

$$y = 1 - \exp\left(-kt^n\right)$$

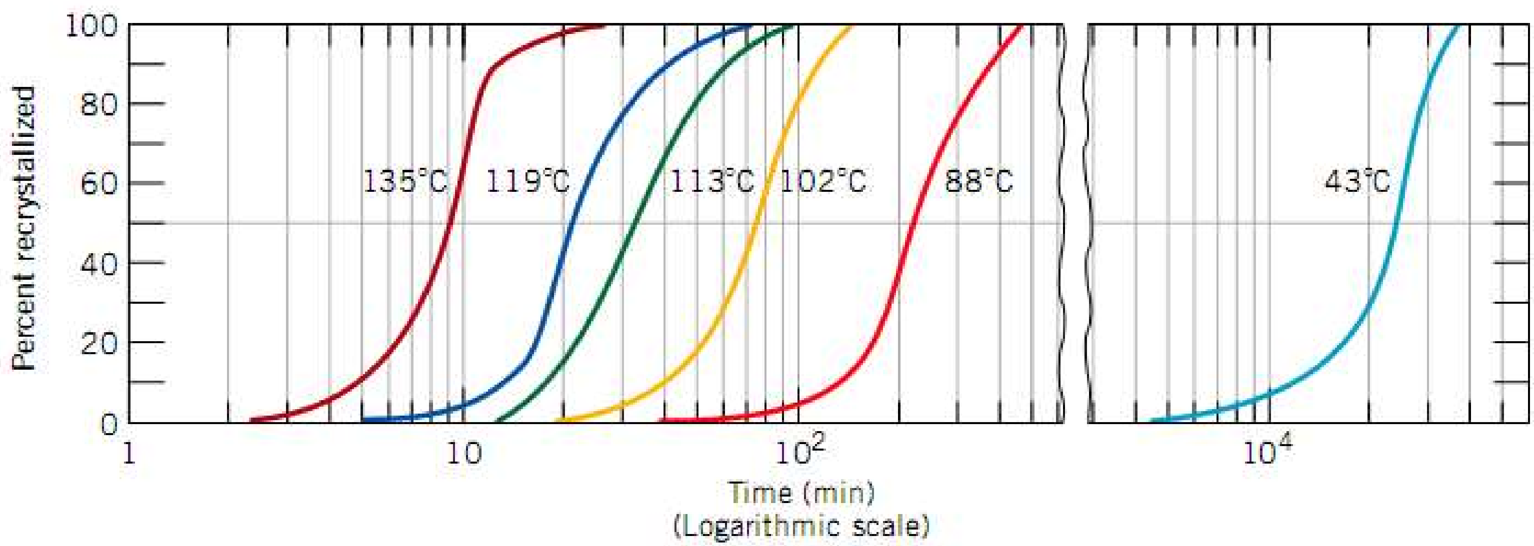
time independent constants for a particular transformation

The fraction that has transformed, at the given temperature lower that the Equilibrium temperature, i.e. at a given undercooling

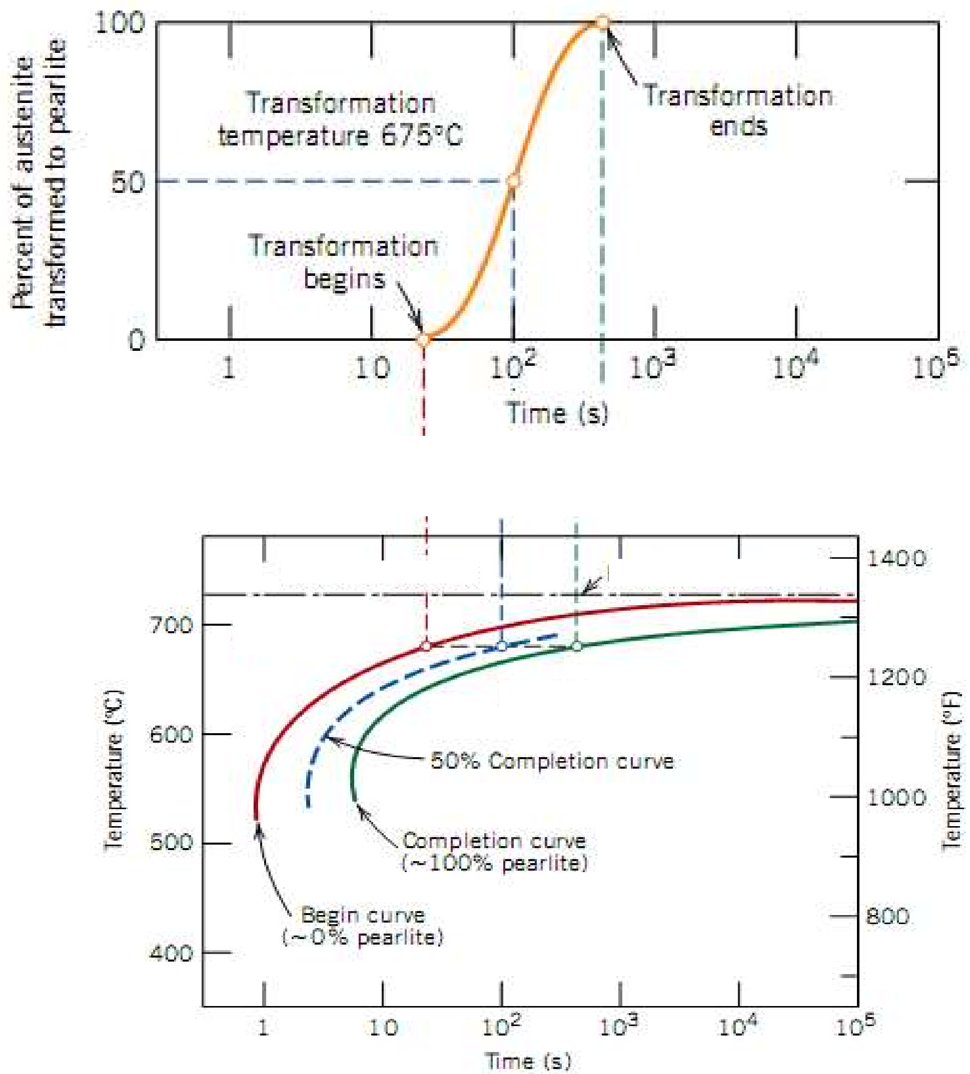
Time interval measured from the starting of the growth phase



Fraction transformed as a function of time and temperature



Time-Temperature-Transformation (TTT) Diagram



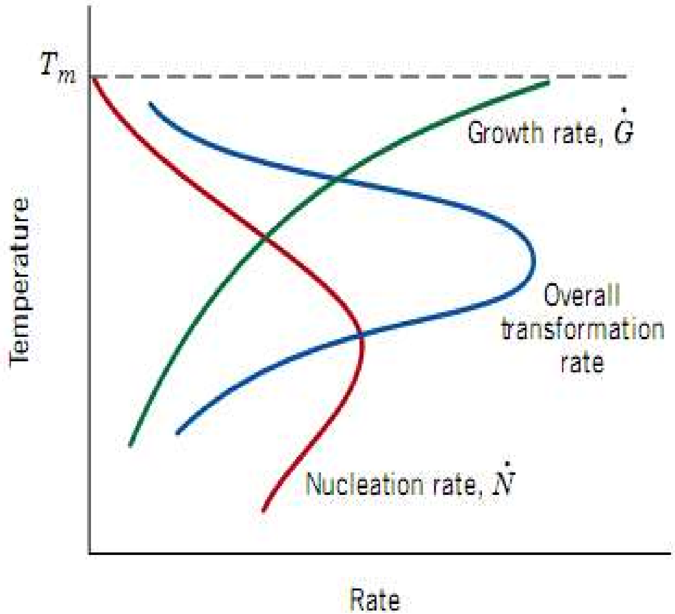
Isothermal heat treatment

Fraction transformed using microscopy or X-ray diffraction

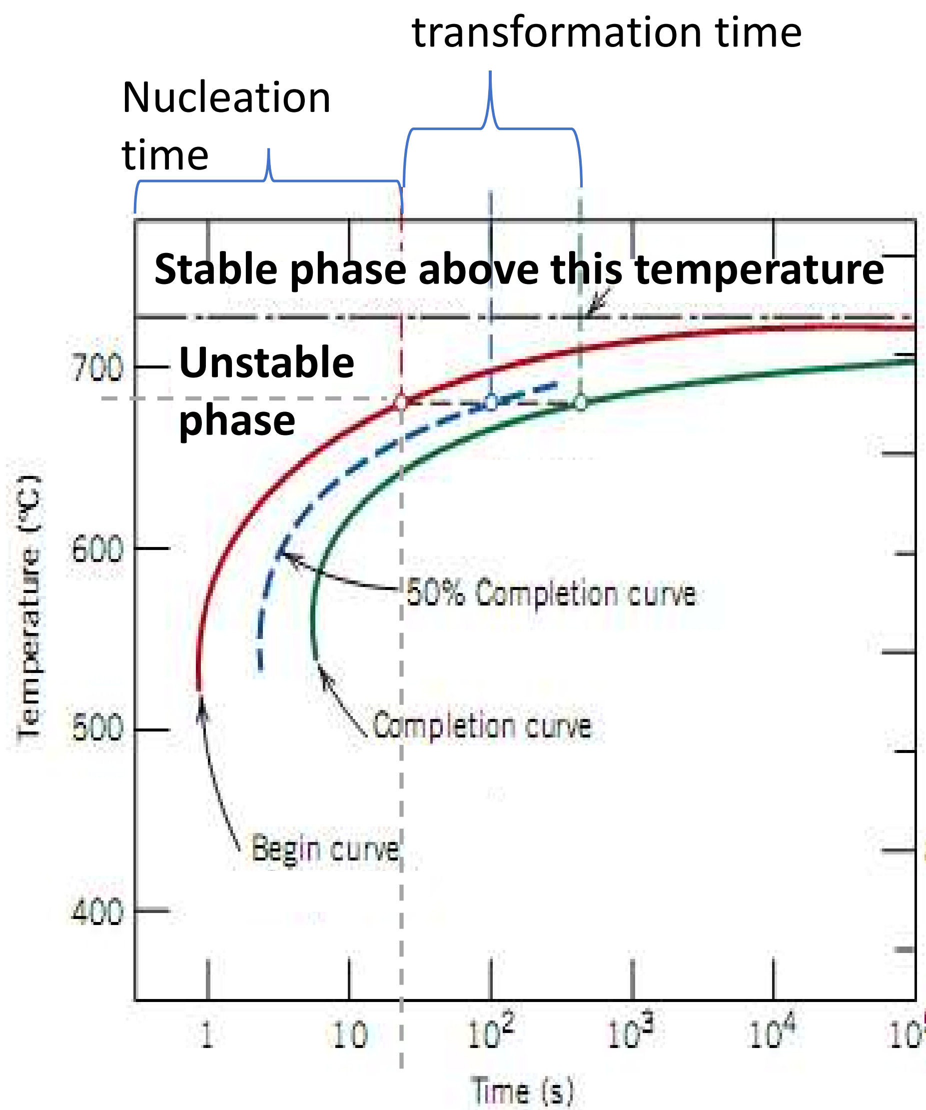
Tedious process

Information on Avrami kinetics

Different value of "n" indicates different growth mechanisms



T_m
Growth rate, $\dot{G}$
Overall transformation rate
Nucleation rate, $\dot{N}$
Temperature
Rate



transformation time
Nucleation time
Stable phase above this temperature
Unstable phase
700
600
500
400
Temperature (°C)
50% Completion curve
Completion curve
Begin curve
1
10
10^2
10^3
10^4
Time (s)

The iron-carbon phase diagram

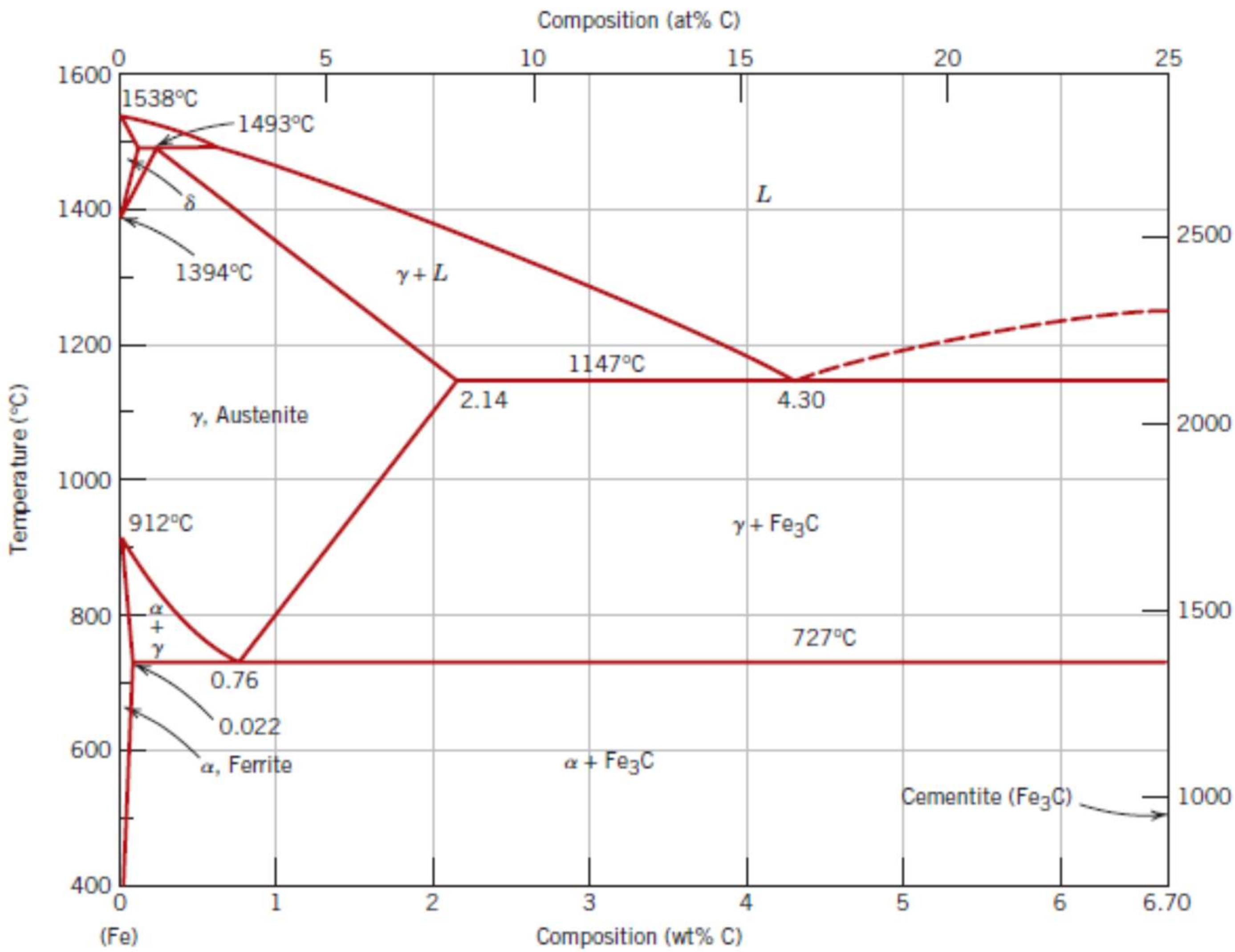


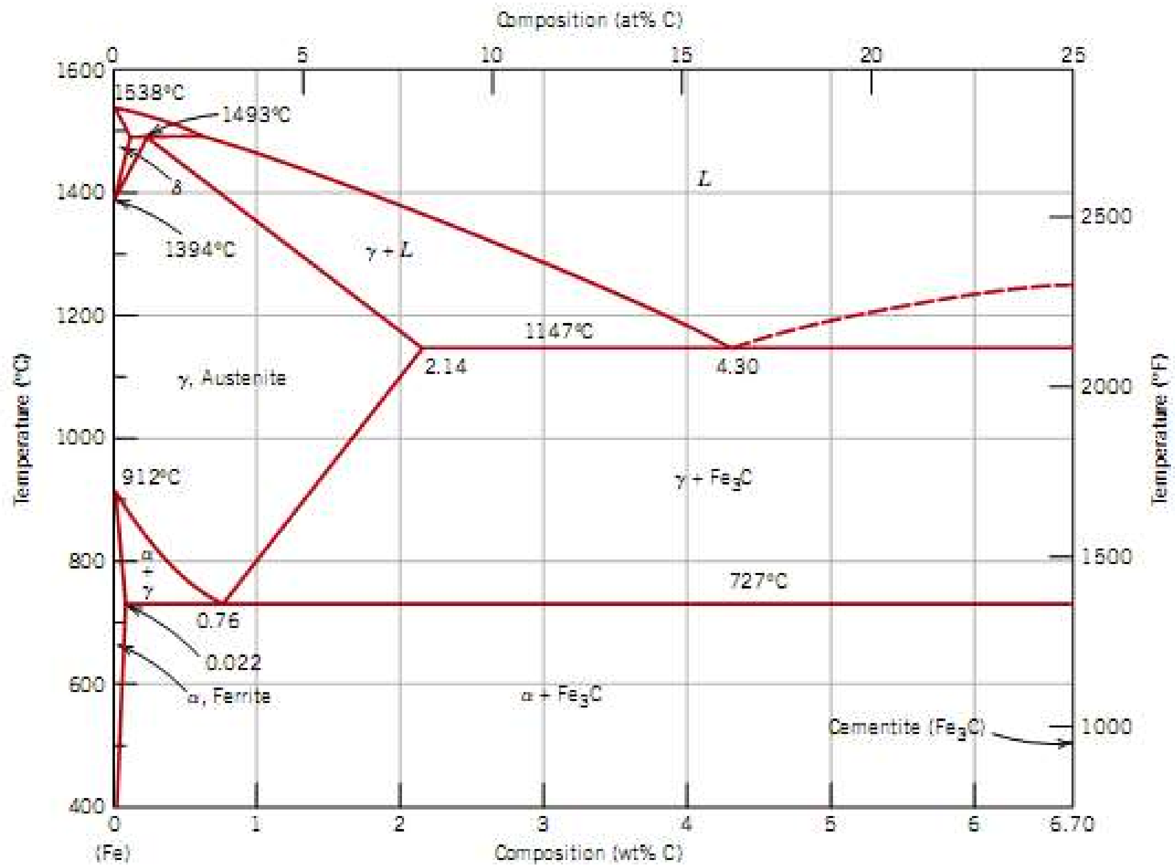
Figure 9.24 The iron–iron carbide phase diagram. [Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

- Iron has 3 allotropes
- Alpha ferrite (BCC), Gamma austenite (FCC) and Delta ferrite (BCC)
- Beta is ferro to paramagnetic transformation of alpha at K
- Carbon goes in interstitial site lower in BCC, higher in FCC
- Fe_3C intermetallic
- Higher percentage of carbon shows mostly graphite phase
- Three reactions till 7wt.% carbon

- Peritectic reaction at 1495 °C and 0.18%C,
  - δ-ferrite + $L \leftrightarrow \gamma$-iron (austenite)
- Eutectic reaction at 1147 °C and 4.3 %C,
  - $L \leftrightarrow \gamma$-iron + Fe_3C (cementite) [ledeburite]
- Eutectoid reaction at 727 °C and 0.77%C,
  - γ-iron $\leftrightarrow$ α–ferrite+Fe_3C (cementite) [pearlite]

- Steels and cast iron (>2 wt.% carbon)
- Hypo and hyper eutectoid steel
- Cementite is orthorhombic hard intermetallic phase
- Microstructural engineering for controlling strength, ductility and toughness

Thermodynamically governed
(i.e. Stable phases corresponding to the lower Gibbs Free energy

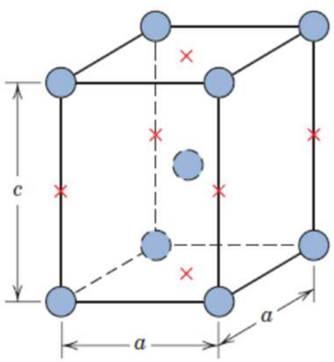


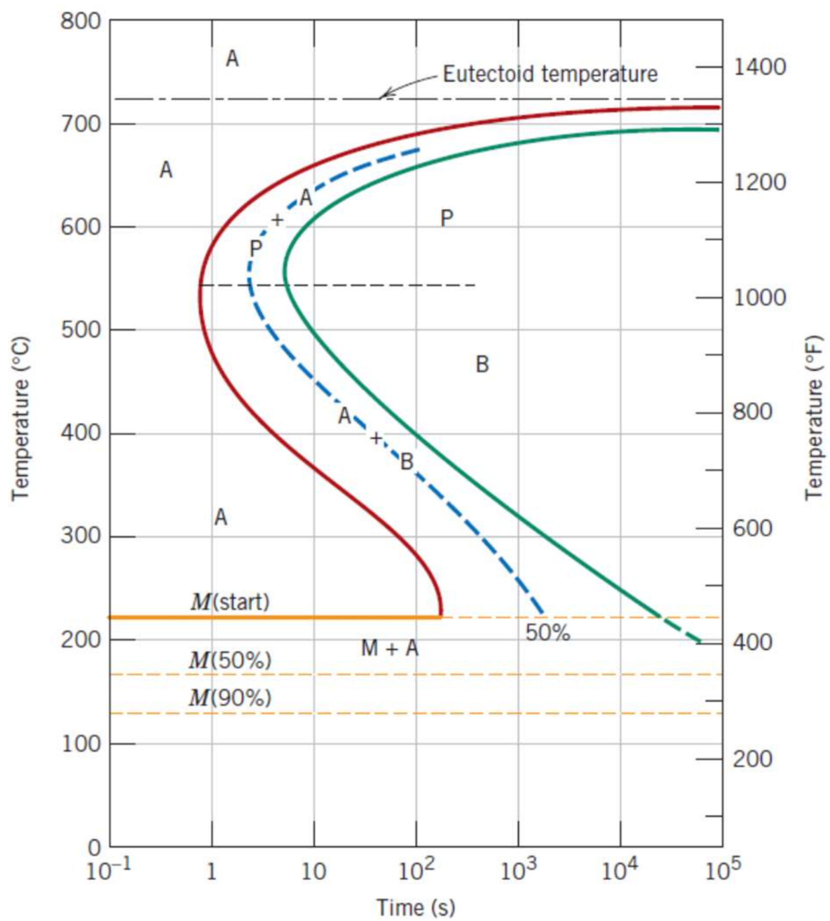
Phases and Microstructure governed by Kinetics (Metastable phases could also be present)

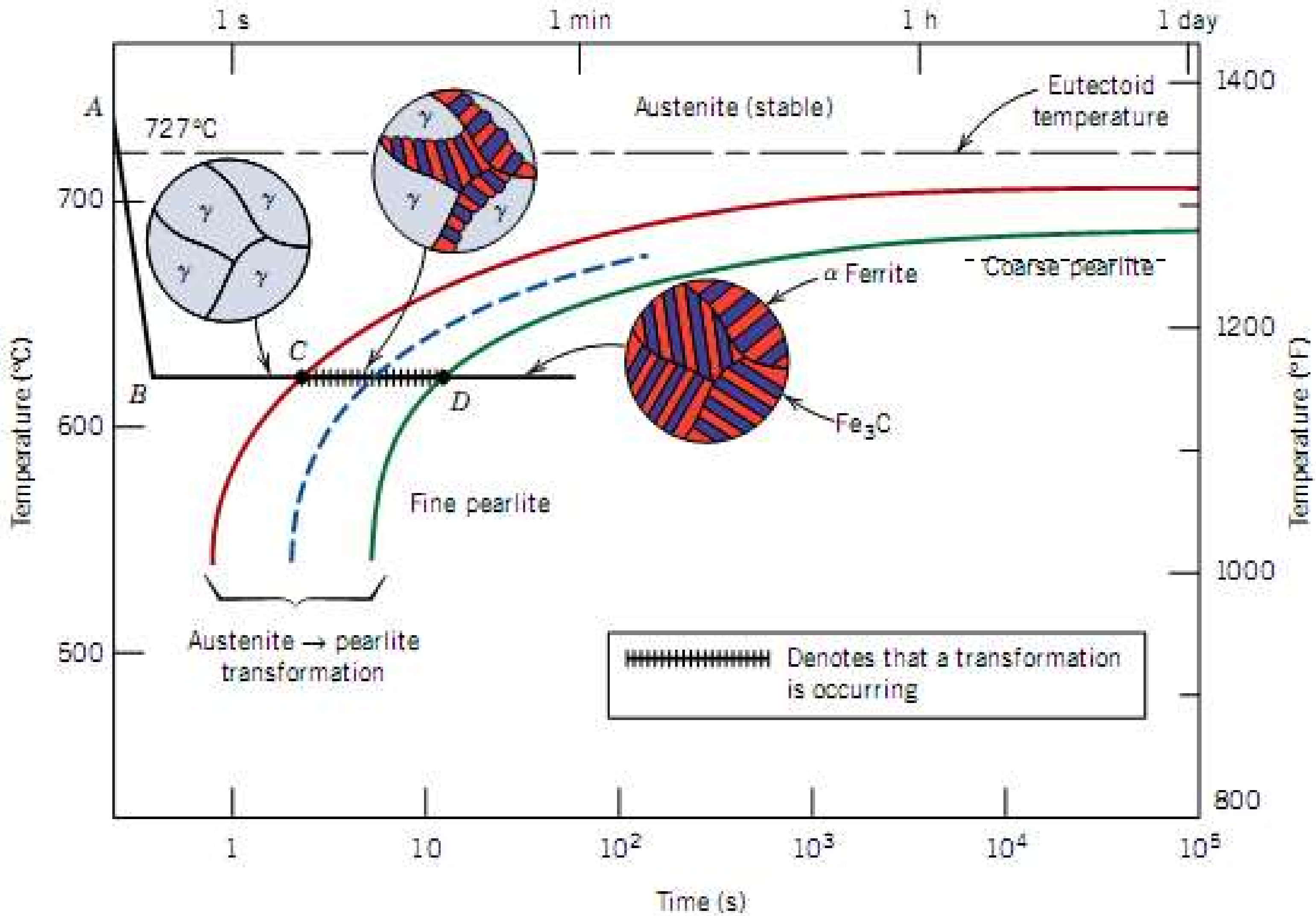
Martensite is BCT phase with high carbon content

Athermal transformation

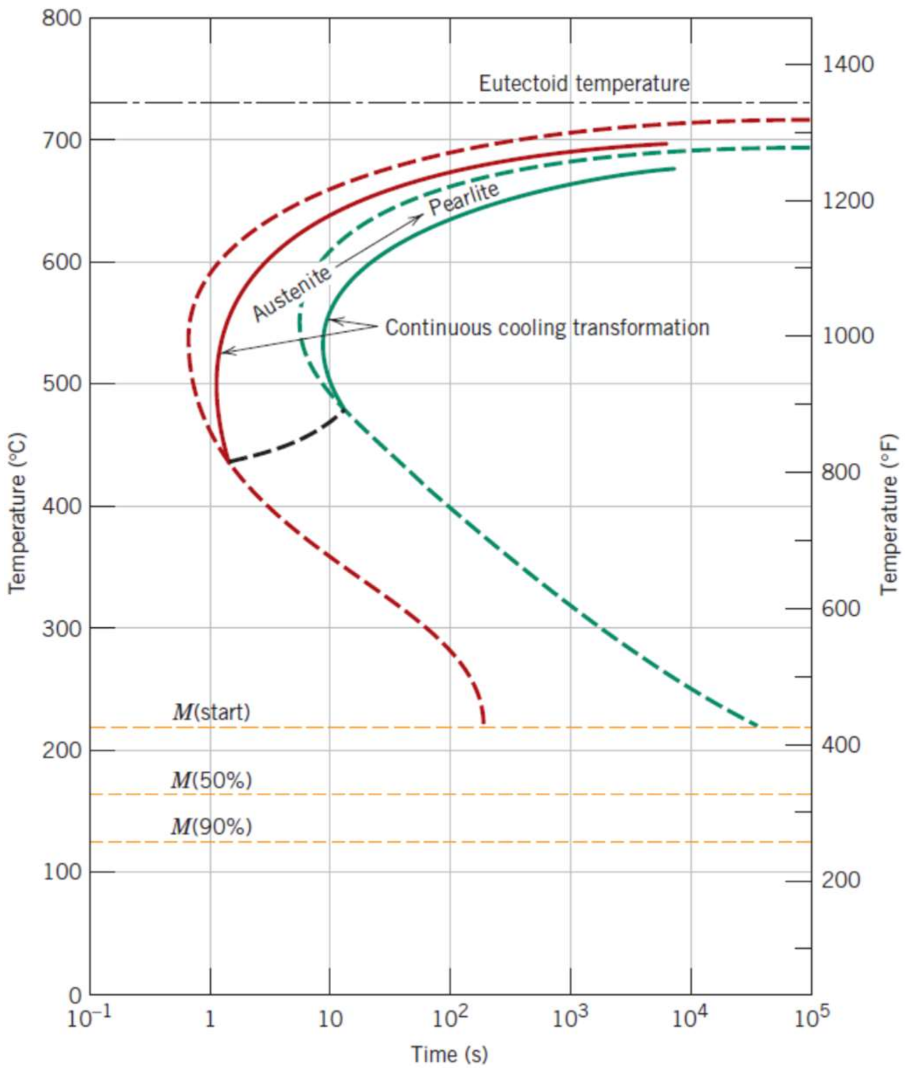
Bain distortion






1 s
1 min
1 h
1 day
A
727°C
Austenite (stable)
Eutectoid temperature
1400
700
γ
C
B
D
600
α Ferrite
Coarse pearlite
1200
Fe3C
Fine pearlite
1000
Austenite → pearlite transformation
500
Denotes that a transformation is occurring
800
1
10
10^2
10^3
10^4
10^5
Time (s)
Temperature (°C)
Temperature (°F)

Continuous-Cooling-Transformation (CCT) Diagram

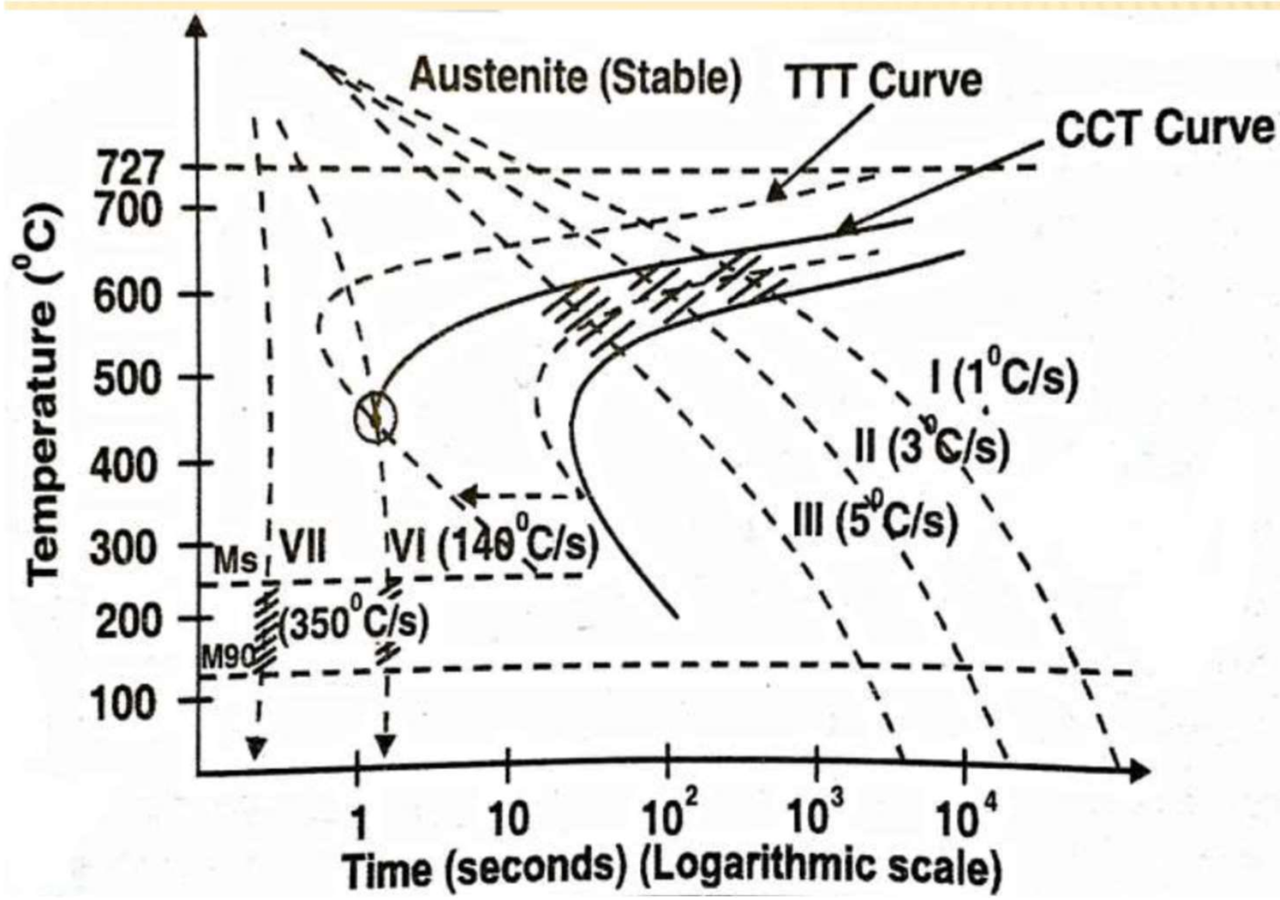


Difficult to follow isothermal heat treatment on shop floors

Industrial conditions of continuous cooling

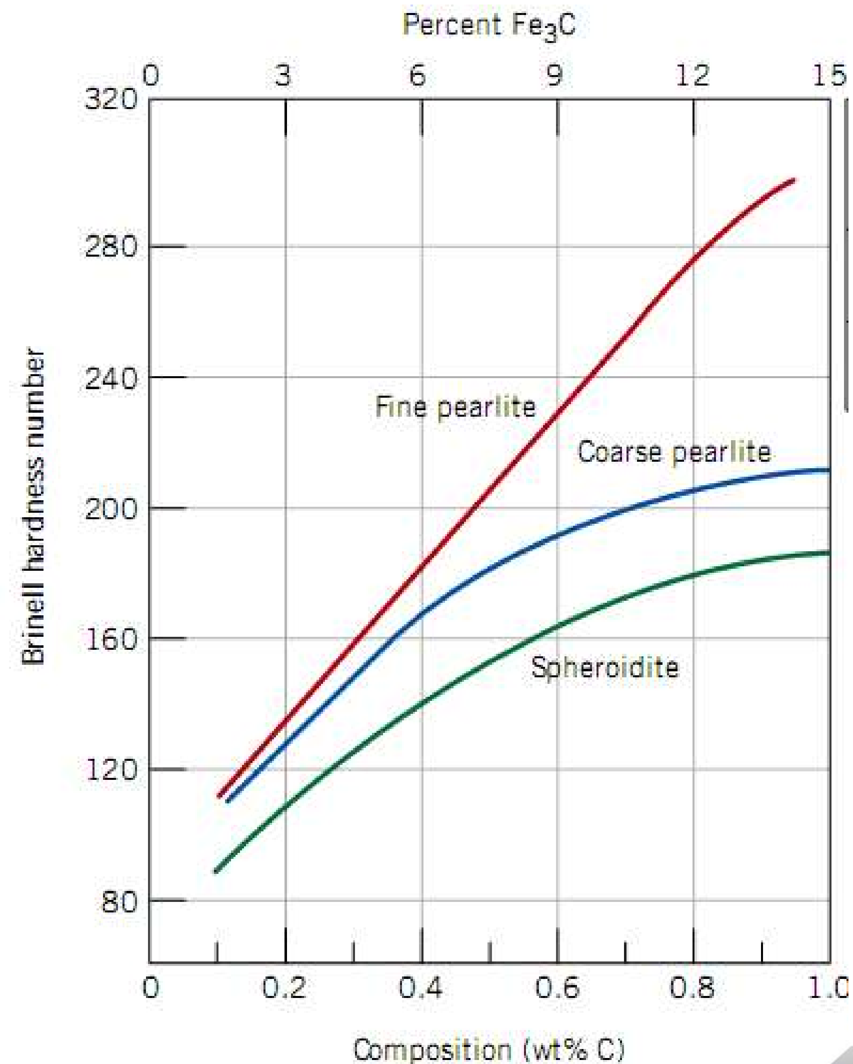
CCT have practical applications

Shifted to right of TTT



Austenite (Stable)
TTT Curve
CCT Curve
727
700
600
500
400
300
200
100
Temperature (°C)
I (1°C/s)
II (3°C/s)
III (5°C/s)
VI (140°C/s)
VII
(350°C/s)
Ms
M90
1
10
10²
10³
10⁴
Time (seconds) (Logarithmic scale)

- Mechanical property-microstructure correlation
- Multiple strengthening mechanisms
- More carbon more hardness (resistance to plastic deformation)
- Higher fraction of pearlite
- More interfaces-more obstacles to dislocation motion-higher hardness



Microstructural control in Al-4wt% Cu alloy

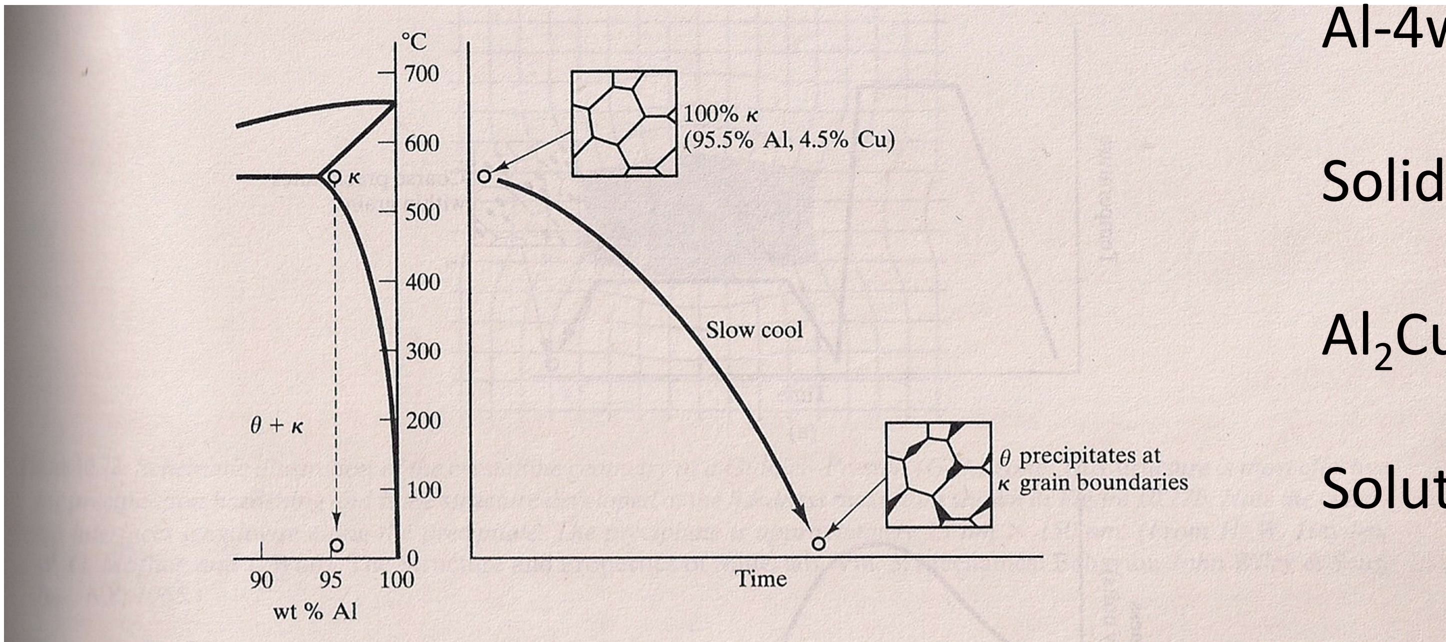


Figure 10.25 *Coarse precipitates form at grain boundaries in an Al–Cu (4.5 wt %) alloy when slowly cooled from the single-phase (κ) region of the phase diagram to the two-phase (θ + κ) region. These isolated precipitates do little to affect alloy hardness.*

Al-4wt% Cu

Solid solution

Al_2Cu precipitate at gb

Solutionizing

Supersaturated solid solution

Ageing experiment to control precipitate size, shape character, crystallography

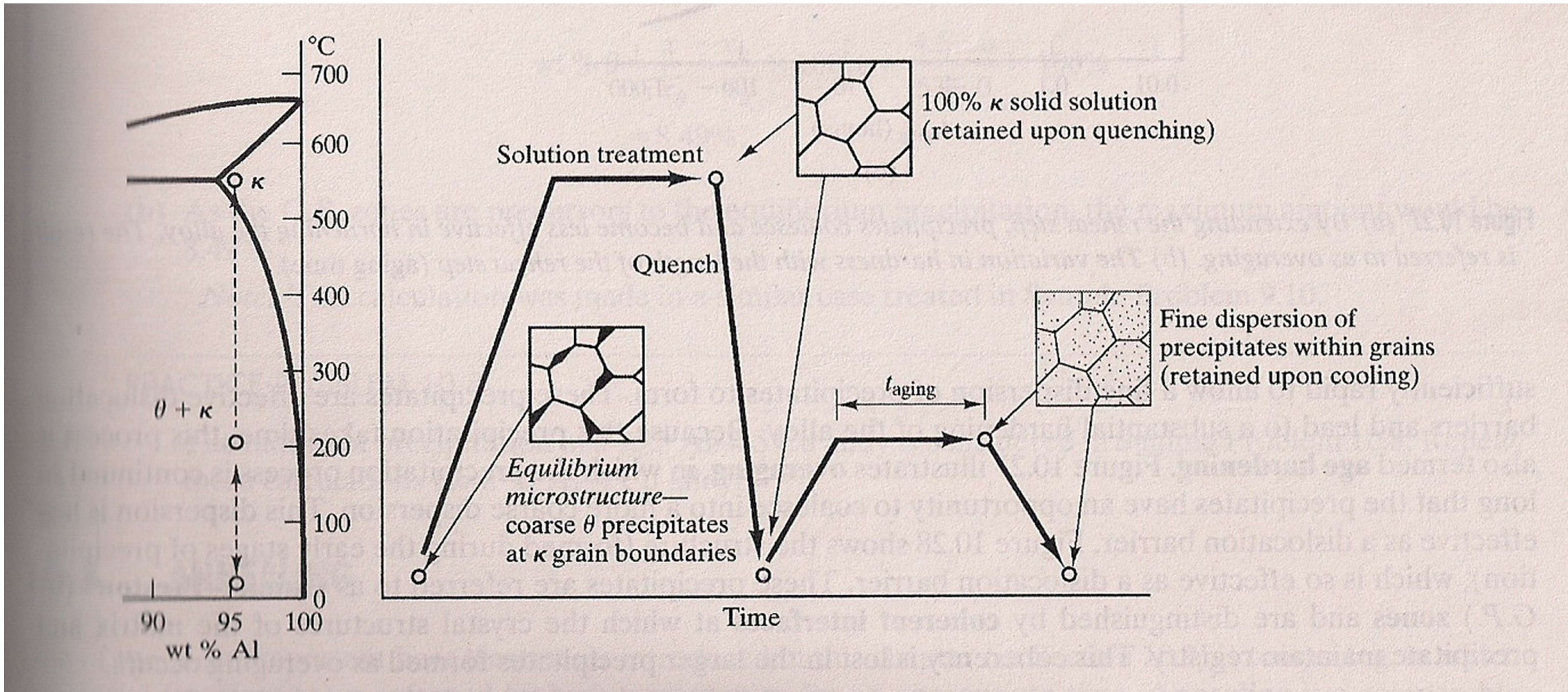


Figure 10.26 *By quenching and then reheating an Al–Cu (4.5 wt %) alloy, a fine dispersion of precipitates forms within the κ grains. These precipitates are effective in hindering dislocation motion and, consequently, increasing alloy hardness (and strength). This process is known as precipitation hardening, or age hardening.*

Ageing treatment to precipitate out copper followed with formation of Al_2Cu

Uniform distribution and control of interface with matrix

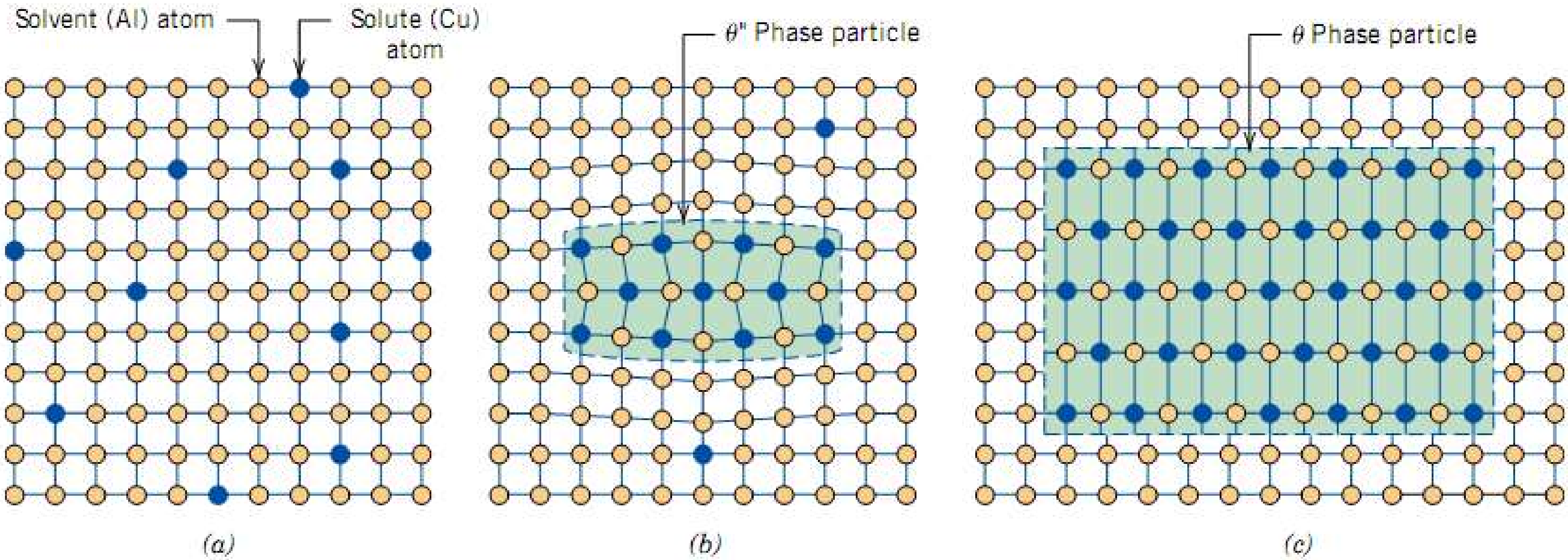
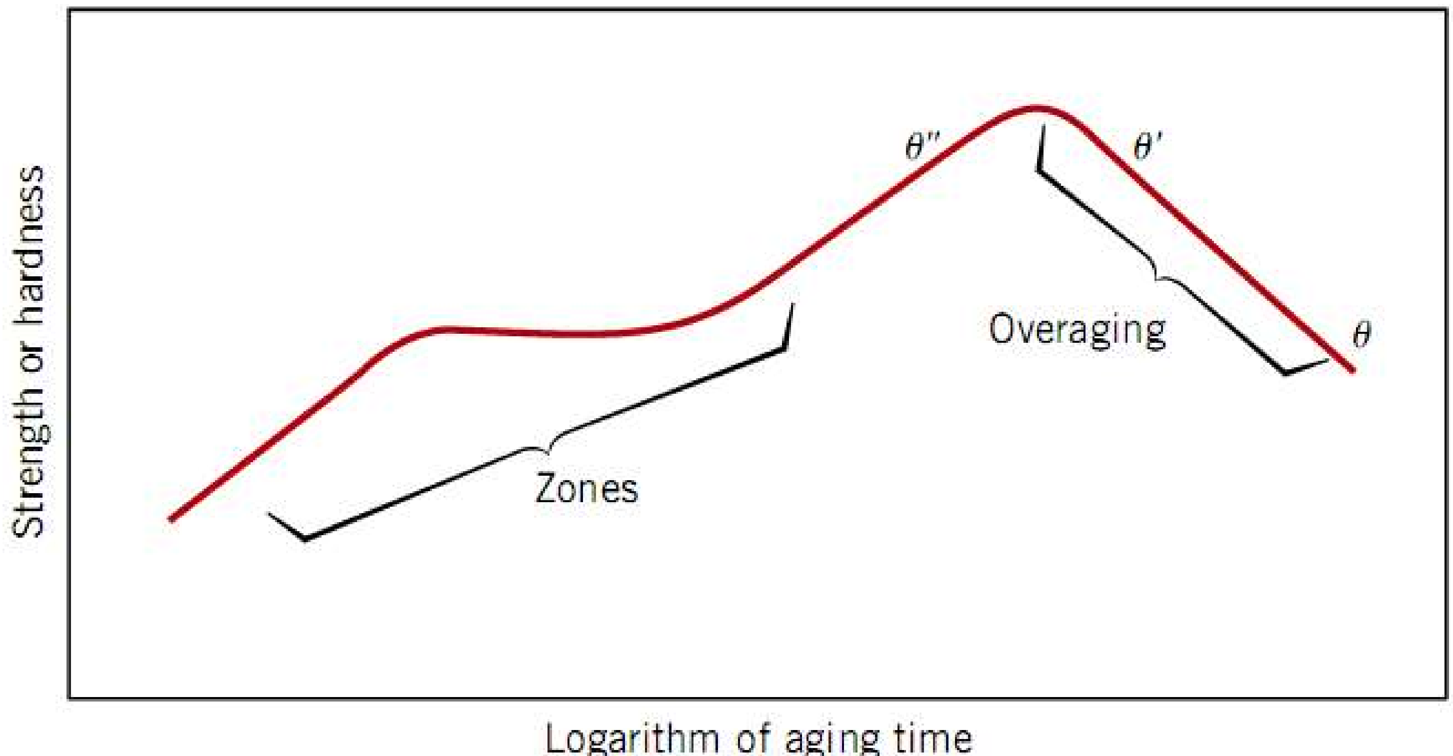


Figure 11.25 Schematic depiction of several stages in the formation of the equilibrium precipitate (θ) phase. (*a*) A supersaturated α solid solution. (*b*) A transition, θ'', precipitate phase. (*c*) The equilibrium θ phase, within the α-matrix phase.

Growth of coherent precipitate

Growth accompanied with loss of coherency at later stage of ageing

Improvement in hardness



More on this when we talk about strengthening mechanisms

Structure-Processing- Property linkage in structural materials like aluminium and steel

Gold nano particles (NPs)

Increasing particle size from tens to hundreds of nm

Gold nanoparticle synthesis by wet chemical route

Reduction of salts

Different colour of colloidal suspension depends on size of NPs

Absorption of light of particular wavelength by formation of surface plasmons

https://www.sigmaaldrich.com/technical-documents/articles/materials-science/nanomaterials/gold-nanoparticles.html

Applications

The range of applications for gold nanoparticles is growing rapidly and includes:

1. **Electronics** - Gold nanoparticles are designed for use as conductors from printable inks to electronic chips.[1] As the world of electronics become smaller, nanoparticles are important components in chip design. Nanoscale gold nanoparticles are being used to connect resistors, conductors, and other elements of an electronic chip.
2. **Photodynamic Therapy** - Near-IR absorbing gold nanoparticles (including gold nanoshells and nanorods) produce heat when excited by light at wavelengths from 700 to 800 nm. This enables these nanoparticles to eradicate targeted tumors.[2] When light is applied to a tumor containing gold nanoparticles, the particles rapidly heat up, killing tumor cells in a treatment also known as hyperthermia therapy.
3. **Therapeutic Agent Delivery** - Therapeutic agents can also be coated onto the surface of gold nanoparticles.[3] The large surface area-to-volume ratio of gold nanoparticles enables their surface to be coated with hundreds of molecules (including therapeutics, targeting agents, and anti-fouling polymers).
4. **Sensors** - Gold nanoparticles are used in a variety of sensors. For example, a colorimetric sensor based on gold nanoparticles can identify if foods are suitable for consumption.[4] Other methods, such as surface enhanced Raman spectroscopy, exploit gold nanoparticles as substrates to enable the measurement of vibrational energies of chemical bonds. This strategy could also be used for the detection of proteins, pollutants, and other molecules label-free.
5. **Probes** - Gold nanoparticles also scatter light and can produce an array of interesting colors under dark-field microscopy. The scattered colors of gold nanoparticles are currently used for biological imaging applications.[5] Also, gold nanoparticles are relatively dense, making them useful as probes for transmission electron microscopy.
6. **Diagnostics** - Gold nanoparticles are also used to detect biomarkers in the diagnosis of heart diseases, cancers, and infectious agents.[6] They are also common in lateral flow immunoassays, a common household example being the home pregnancy test.
7. **Catalysis** - Gold nanoparticles are used as catalysts in a number of chemical reactions.[7] The surface of a gold nanoparticle can be used for selective oxidation or in certain cases the surface can reduce a reaction (nitrogen oxides). Gold nanoparticles are being developed for fuel cell applications. These technologies would be useful in the automotive and display industry.

Structure-Processing- Property linkage in functional gold NPs

https://www.sigmaaldrich.com/technical-documents/articles/materials-science/nanomaterials/gold-nanoparticles.html