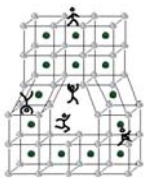
Time-Dependence



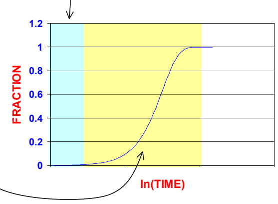
Monday,
Oct. 12, 2003

MATS275: INTRODUCTION TO MATERIALS SCIENCE

- Phases - Recap
- Nucleation and Growth
- The Avrami Relationship
- Diffusionless Transformations
- Quenching of Irons
- Phases and Microstructures
  - Cementite, Ferrite, Pearlite, Bainite, Martensite, and Spheroidite
- Hardenability
- Alloying of Steel

The Next Dimension : Time

- No phase transformation occurs instantly.
  - Nucleation
    - Homogeneous
    - Heterogeneous
  - Growth



Homogeneous Nucleation

- Surface must form between phases
- Surfaces have high energy
- Energy gained by phase change must offset this

Related to volume

Related to surface area

Free Energy Released by Phase Change

$$\Delta G_n = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 (\Delta G_v)$$

Free energy/area of surface

Nucleation Energy

The Critical Radius

- Smaller than r* and particles redissolve, larger than r* and they grow on and on...

$$\frac{d}{dr}(\Delta G_n) = 8\pi r\gamma + 4\pi r^2(\Delta G_v)$$

$$8\pi r^*\gamma + 4\pi r^{*2}(\Delta G_v) = 0$$

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

The Effect of Temperature

- Remember what the Gibb's Free Energy is...

$$\Delta G_v = \Delta H_v - T\Delta S$$

At equilibrium $\Delta G_v = \Delta H_v - T_E\Delta S = 0$

$$\Delta S = \frac{\Delta H_v}{T_E}$$

$$\Delta G_v = \Delta H_v - T_E\frac{\Delta H_v}{T_E} = \Delta H_v\frac{T - T_E}{T_E}$$

$$\Delta G_v = \left(\frac{\Delta H_v}{T_E}\right)\Delta T$$

The Effect of Temperature

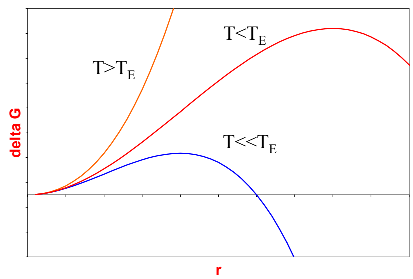
$$r^* = \frac{-2\gamma}{\Delta G_v} = \frac{-2\gamma T_E}{\Delta H\Delta T}$$

$$\Delta G_n = 4\pi r^2\gamma + \frac{4}{3}\pi r^3(\Delta G_v)$$

$$\Delta G_n = 4\pi\left(\frac{-2\gamma T_E}{\Delta H\Delta T}\right)^2\gamma + \frac{4}{3}\pi\left(\frac{-2\gamma T_E}{\Delta H\Delta T}\right)^3\left(\frac{\Delta H}{T_E}\Delta T\right)$$

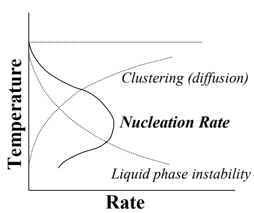
$$= \frac{16\pi\gamma^3 T_E^2}{3\Delta H^2}\left(\frac{1}{\Delta T}\right)^2$$

Free Energy Change vs. r



Competing Mechanisms

- But there is also the need to diffuse...



Nucleation Mechanisms

- Homogeneous
- Heterogeneous
  - Coherent (lattice match across interface)
  - Semicoherent
  - Incoherent

Growth

- Growth proceeds from nucleation.
- Avrami relation...

$$X = 1 - e^{-(kt)^n}$$

Fraction transformed

0.5 < n <5.0 typ.

k is a rate constant

The Transformation Rate

$$r = \frac{1}{t_{1/2}}$$

At a given temperature

Temperature dependence

$$\boxed{r = Ae^{-Q/RT}}$$

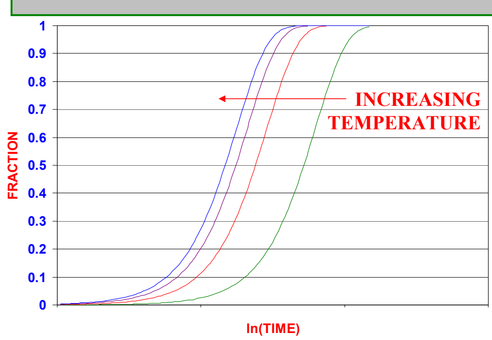
Q - Activation Energy

T - Absolute Temperature

R - Gas Constant

A - Pre-exponential Constant

TEMPERATURE DEPENDENCE



Crystallization of Cu

- At 900°C, the growth rate of of Cu is 10^6 times as large as at 400°C. What is the activation energy?

$$\frac{G_{900}}{G_{400}} = \frac{Ae^{-Q/R(1173\,K)}}{Ae^{-Q/R(673\,K)}} = e^{-\frac{Q}{R}\left(\frac{1}{1173}-\frac{1}{673}\right)}$$

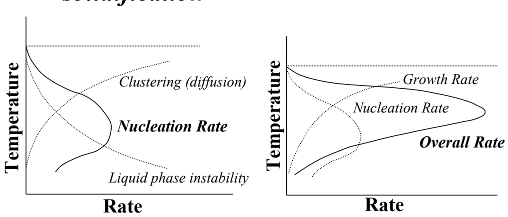
$$ln\left(10^6\right) = -\frac{Q}{R}\left(\frac{1}{1173}-\frac{1}{673}\right)$$

$$13.8 = \frac{Q}{8.314\frac{J}{mol\cdot K}}\left(6.33\times10^{-4}\right)$$

$$Q = 181\,\frac{kJ}{mol}$$

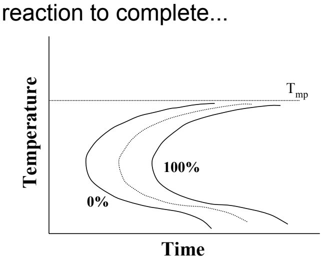
Competing Mechanisms

solidification



Flipping the Rate

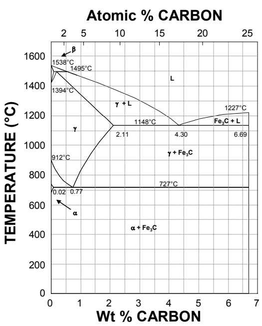
- The inverse of the rate is the time it takes for the reaction to complete...



Types of Transformations

- Diffusional
  - solidification, recrystallization, grain growth
  - eutectic (change of phase composition)
- Diffusionless
  - Martensitic

$Fe-Fe_3C$ Phase Diagram



α - Ferrite - BCC iron

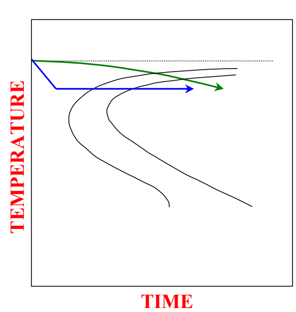
β - high temperature BCC iron

γ - Austenite - FCC iron

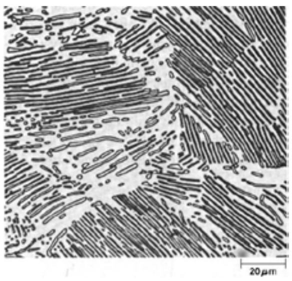
Fe_3C - Cementite or Carbide

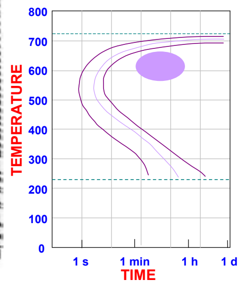
Slow Cooling

- Slow cool
- Cool and hold at 650°C
- Forms coarse pearlite.



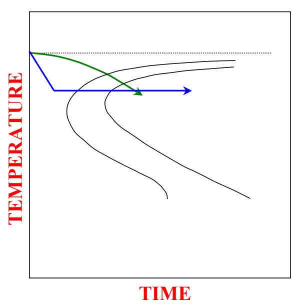
Pearlite





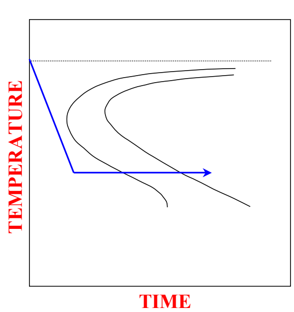
Faster Cooling

- Moderate cool
- Cool and hold at 575°C
- Forms fine pearlite.

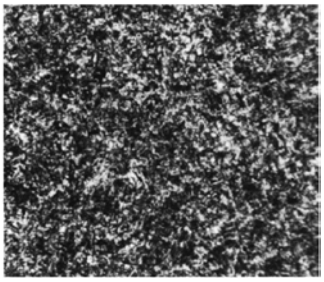


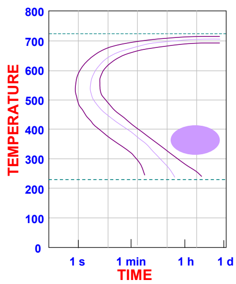
Even Faster Cooling

- Cool and hold at 300°C
- Forms Bainite.



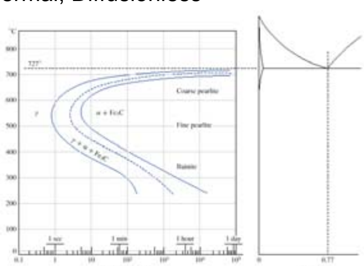
Bainite



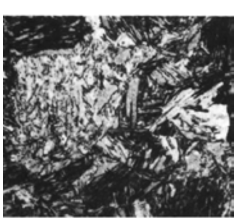


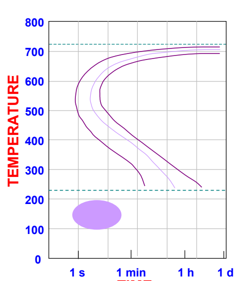
Martensitic Transformation

- Athermal, Diffusionless



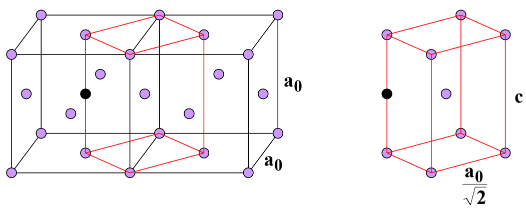
Martensite





Martensitic Transformation

- Austenite to Martensite



FCC BCT

How Much Are We Talking About?

- How many Carbon interstitials are we talking about in eutectoid steel (0.76 % C)?

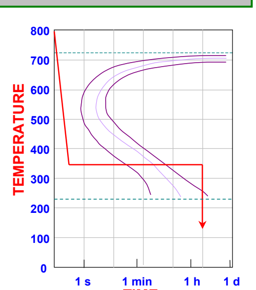
$$0.0076 = \frac{m_C}{m_C + m_F} = \frac{(12.001\,u)n_C}{(12.001\,u)n_C + (55.85\,u)n_F}$$

$$= \frac{(12.001\,u)}{(12.001\,u) + (55.85\,u)\frac{n_F}{n_C}}$$

$$\frac{n_F}{n_C} = \frac{\frac{(12.001\,u)}{0.0076} - (12.001\,u)}{(55.85\,u)} = 7.02$$

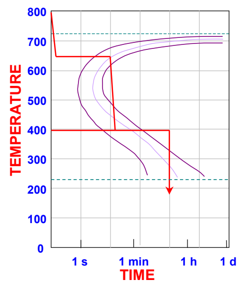
Example

- Quench to 350°C
- Hold for 3 hrs
- Quench to RT



Example

- Quench to 650°C
- Hold for 20 s
- Quench to 400°C
- Hold 17 min
- Quench to RT



Example

- Quench to 250°C
- Hold for 2 min.
- Quech to RT