

**Chapter Outline: Phase Transformations in Metals**

**Heat Treatment (time and temperature) ⊃  
 ⊃ Microstructure ⊃ Mechanical Properties**

- Kinetics of phase transformations
- Multiphase Transformations
- Phase transformations in Fe-C alloys
- Isothermal Transformation Diagrams
- Mechanical Behavior
- Tempered Martensite

*Not tested:  
 10.6 Continuous Cooling Transformation Diagrams*

**Phase transformations. Kinetics.**

**Phase transformations** (change of the microstructure) can be divided into three categories:

- **Diffusion-dependent with no change in phase composition or number of phases present** (e.g. melting, solidification of pure metal, allotropic transformations, recrystallization, etc.)
- **Diffusion-dependent with changes in phase compositions and/or number of phases** (e.g. eutectoid transformations)
- **Diffusionless phase transformation** - produces a metastable phase by cooperative small displacements of all atoms in structure (e.g. martensitic transformation discussed in later in this chapter)

Phase transformations do not occur instantaneously. Diffusion-dependent phase transformations can be rather slow and the final structure often depend on the rate of cooling/heating.

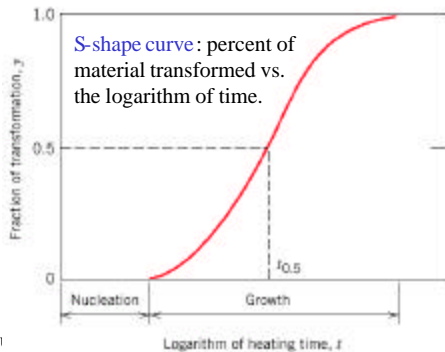
**We need to consider the time dependence or kinetics of the phase transformations.**

**Kinetics of phase transformations**

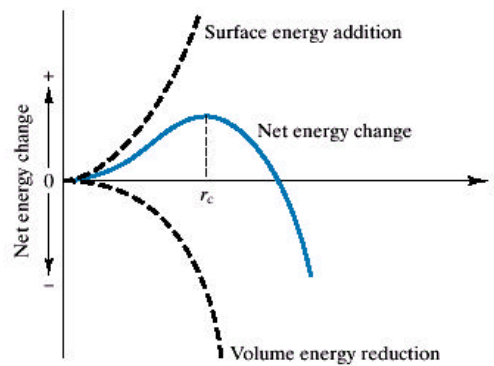
Most phase transformations involve change in composition ⇒ redistribution of atoms via diffusion is required.

The process of phase transformation involves:

- **Nucleation** of the new phase - formation of stable small particles (nuclei) of the new phase. Nuclei are often formed at grain boundaries and other defects.
- **Growth** of new phase at the expense of the original phase.



**Nucleation**



A nucleus is only stable if further growth reduces the energy of the system. For  $r > r_c$  the nucleus is stable.

### Rate of phase transformations

Rate of transformation can be defined as reciprocal of time for transformation to proceed halfway to completion:

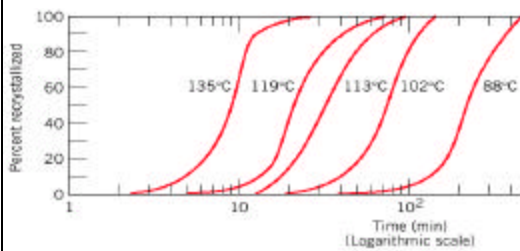
$$r = 1/t_{0.5}$$

Rate increases with temperature according to Arrhenius equation, characteristic for thermally activated processes:

$$r = A \exp(-Q_A/kT) = A \exp(-Q_m/RT)$$

Per atom

Per mole

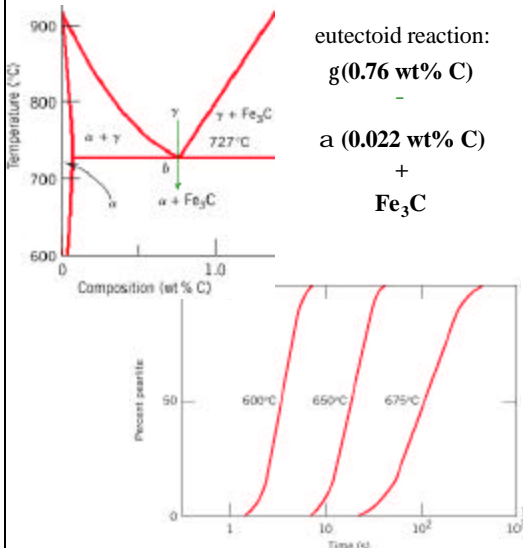


Percent recrystallization of pure copper at different T

### Superheating / supercooling

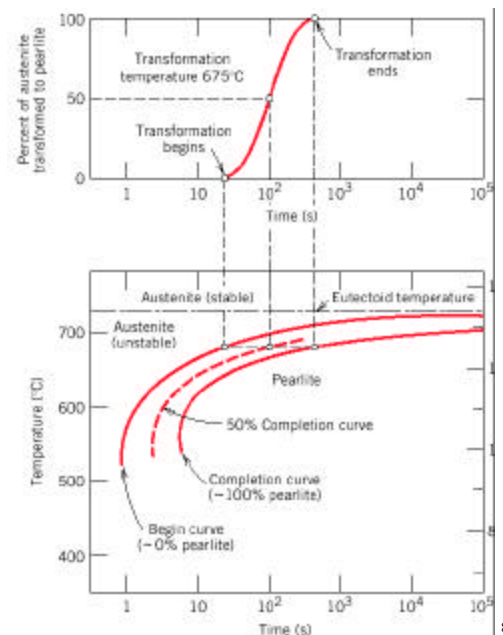
- Upon crossing a phase boundary on the composition-temperature phase diagram phase transformation towards equilibrium state is induced.
- But the transition to the equilibrium structure takes time and transformation is delayed.
- During cooling, transformations occur at temperatures less than predicted by phase diagram: **supercooling**.
- During heating, transformations occur at temperatures greater than predicted by phase diagram: **superheating**.
- Degree of supercooling/superheating increases with rate of cooling/heating.
- **Metastable states** can be formed as a result of fast temperature change. **Microstructure is strongly affected by the rate of cooling.**
- Below we will consider the effect of time on phase transformations using iron-carbon alloy as an example.

### Let us consider eutectoid reaction as an example

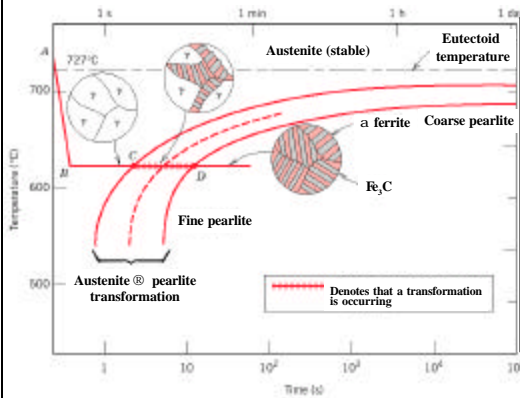


The S-shaped curves are shifted to longer times at higher T showing that the transformation is dominated by nucleation (nucleation rate increases with supercooling) and not by diffusion (which occurs faster at higher T).

### Isothermal Transformation (or TTT) Diagrams (Temperature, Time, and % Transformation)



### TTT Diagrams

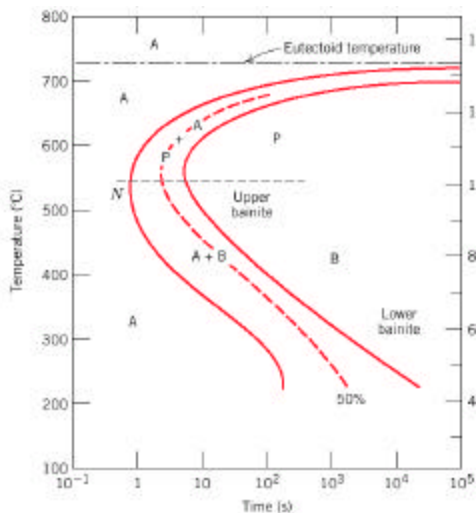


The thickness of the ferrite and cementite layers in pearlite is ~ 8:1. The absolute layer thickness depends on the temperature of the transformation. The higher the temperature, the thicker the layers.

### TTT Diagrams

- The family of S-shaped curves at different T are used to construct the TTT diagrams.
- The TTT diagrams are for the **isothermal** (constant T) transformations (material is cooled quickly to a given temperature before the transformation occurs, and then keep it at that temperature).
- At low temperatures, the transformation occurs sooner (it is controlled by the rate of nucleation) and grain growth (that is controlled by diffusion) is reduced.
- Slow diffusion at low temperatures leads to fine-grained microstructure with thin-layered structure of pearlite (**fine pearlite**).
- At higher temperatures, high diffusion rates allow for larger grain growth and formation of thick layered structure of pearlite (**coarse pearlite**).
- At compositions other than eutectoid, a proeutectoid phase (ferrite or cementite) coexist with pearlite. Additional curves for proeutectoid transformation must be included on TTT diagrams.

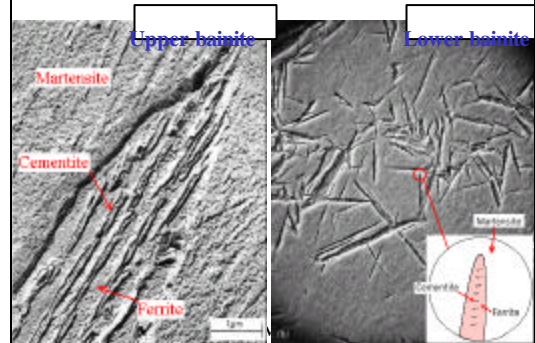
### Formation of Bainite Microstructure (I)



If transformation temperature is low enough ( $\leq 540^\circ\text{C}$ ) bainite rather than fine pearlite forms.

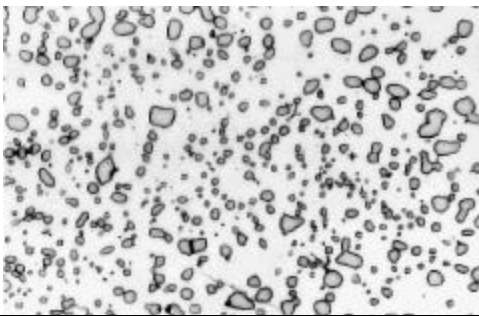
### Formation of Bainite Microstructure (II)

- For  $T \sim 300\text{-}540^\circ\text{C}$ , **upper bainite** consists of needles of ferrite separated by long cementite particles
- For  $T \sim 200\text{-}300^\circ\text{C}$ , **lower bainite** consists of thin plates of ferrite containing very fine rods or blades of cementite
- In the bainite region, transformation rate is controlled by microstructure growth (diffusion) rather than nucleation. Since diffusion is slow at low temperatures, this phase has a very fine (microscopic) microstructure.
- Pearlite and bainite transformations are competitive; transformation between pearlite and bainite not possible without first reheating to form austenite



### Spheroidite

- Annealing of pearlitic or bainitic microstructures at elevated temperatures just below eutectoid (e.g. 24 h at 700 C) leads to the formation of new microstructure – **spheroidite** - spheres of cementite in a ferrite matrix.
- Composition or relative amounts of ferrite and cementite are not changing in this transformation, **only shape of the cementite inclusions is changing**.
- Transformation proceeds by C diffusion – needs high T.
- Driving force for the transformation - reduction in total ferrite - cementite boundary area



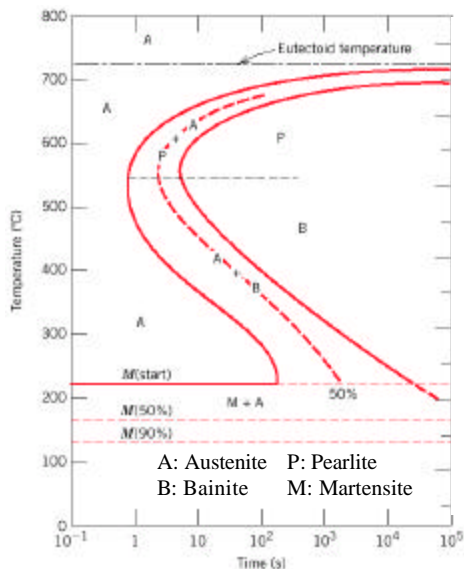
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### Martensite (I)

- Martensite forms when austenite is rapidly cooled (**quenched**) to room T.
- It forms nearly instantaneously when the required low temperature is reached. The austenite-martensite **does not involve diffusion** → no thermal activation is needed, this is called an **athermal transformation**.
- Each atom displaces a small (sub-atomic) distance to transform FCC  $\gamma$ -Fe (austenite) to martensite which has a Body Centered Tetragonal (BCT) unit cell (like BCC, but one unit cell axis is longer than the other two).
- Martensite is **metastable** - can persist indefinitely at room temperature, but will transform to equilibrium phases on annealing at an elevated temperature.
- Martensite can coexist with other phases and/or microstructures in Fe-C system
- Since martensite is metastable non-equilibrium phase, it does not appear in phase Fe-C phase diagram

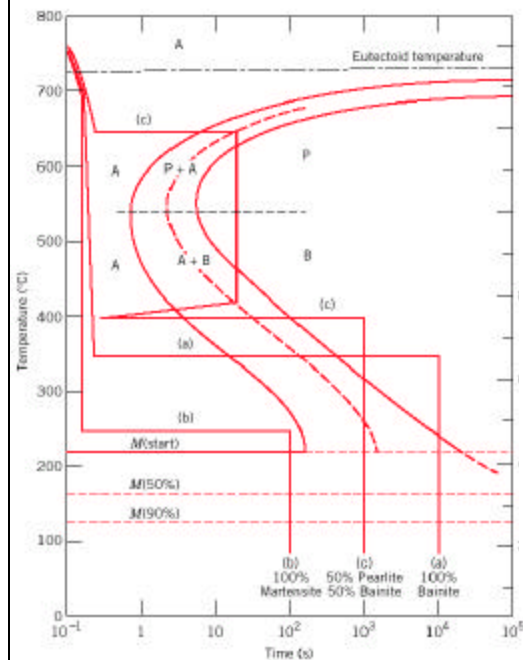
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### TTT Diagram including Martensite



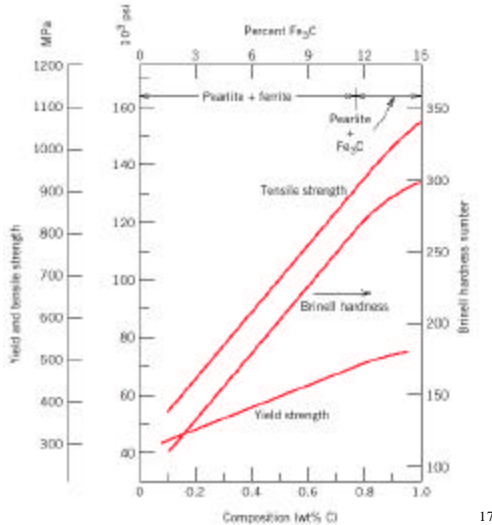
Austenite-to-martensite is diffusionless and very fast. The amount of martensite formed depends on temperature only.

### Time-temperature path – microstructure



### Mechanical Behavior of Fe-C Alloys (I)

Cementite is harder and more brittle than ferrite - increasing cementite fraction therefore makes harder, less ductile material.



### Mechanical Behavior of Fe-C Alloys (II)

The strength and hardness of the different microstructures is inversely related to the size of the microstructures (fine structures have more phase boundaries inhibiting dislocation motion).

#### Mechanical properties of bainite, pearlite, spheroidite

Considering microstructure we can predict that

- Spheroidite is the softest
- Fine pearlite is harder and stronger than coarse pearlite
- Bainite is harder and stronger than pearlite

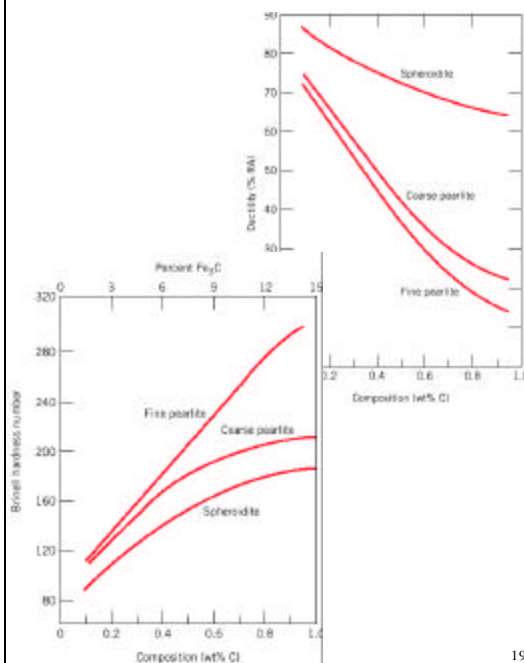
#### Mechanical properties of martensite

Of the various microstructures in steel alloys

- Martensite is the hardest, strongest and the most brittle

The strength of martensite is not related to microstructure. Rather, it is related to the interstitial C atoms hindering dislocation motion (solid solution hardening, Chapter 7) and to the small number of slip systems.

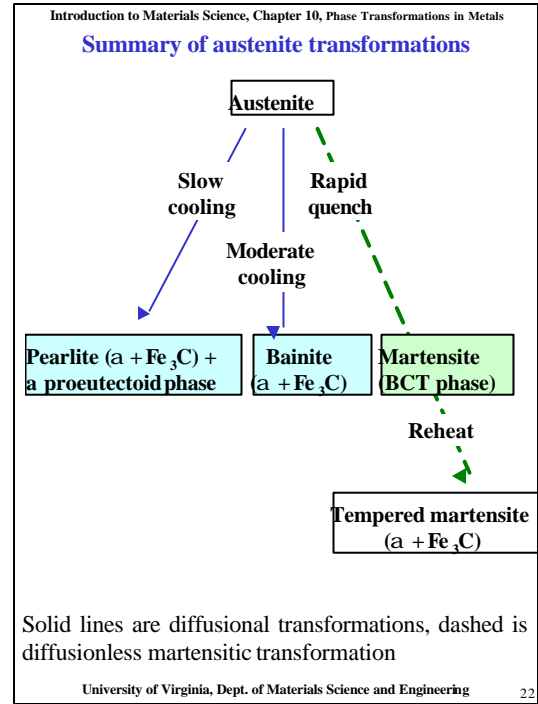
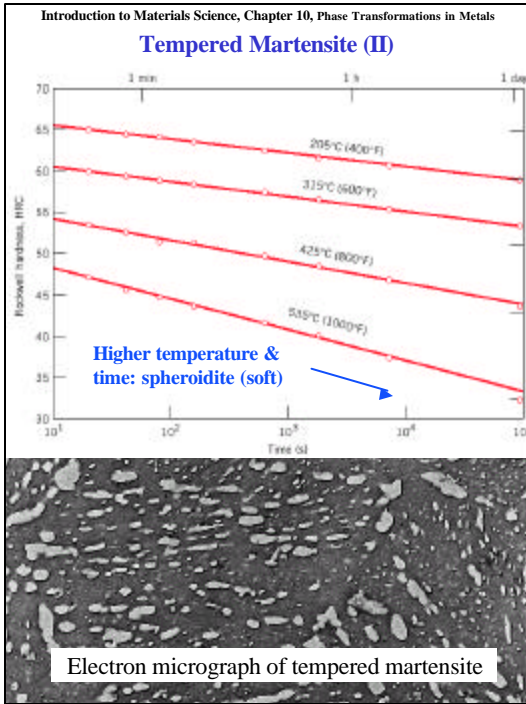
### Mechanical Behavior of Fe-C Alloys (III)



### Tempered Martensite (I)

Martensite is so brittle that it needs to be modified for practical applications. This is done by heating it to 250-650 °C for some time (tempering) which produces **tempered martensite**, an extremely fine-grained and well dispersed cementite grains in a ferrite matrix.

- Tempered martensite is less hard/strong as compared to regular martensite but has enhanced ductility (ferrite phase is ductile).
- Mechanical properties depend upon cementite particle size: fewer, larger particles means less boundary area and softer, more ductile material - eventual limit is spheroidite.
- Particle size increases with higher tempering temperature and/or longer time (more C diffusion) - therefore softer, more ductile material.



- Introduction to Materials Science, Chapter 10, Phase Transformations in Metals
- ### Summary
- Make sure you understand language and concepts:
- Alloy steel
  - Athermal transformation
  - Bainite
  - Coarse pearlite
  - Fine pearlite
  - Isothermal transformation diagram
  - Kinetics
  - Martensite
  - Nucleation
  - Phase transformation
  - Plain carbon steel
  - Spheroidite
  - Supercooling
  - Superheating
  - Tempered martensite
  - Thermally activated transformation
  - Transformation rate
- University of Virginia, Dept. of Materials Science and Engineering 23

- Introduction to Materials Science, Chapter 10, Phase Transformations in Metals
- ### Reading for next class:
- #### Chapter 11: Thermal Processing of Metal Alloys
- Process Annealing, Stress Relief
  - Heat Treatment of Steels
  - Precipitation Hardening
- University of Virginia, Dept. of Materials Science and Engineering 24