

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.

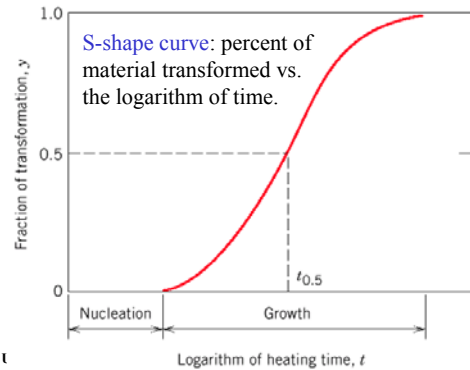
We need to consider the time dependence or kinetics of the phase transformations.

Kinetics of phase transformations

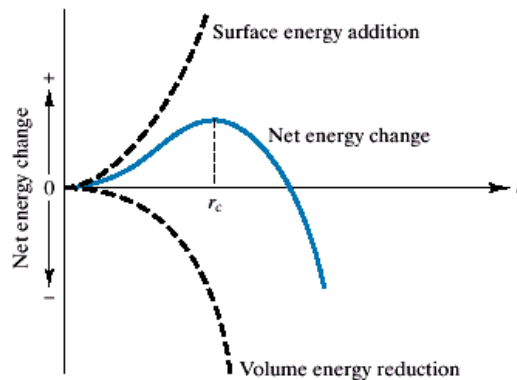
Most phase transformations involve change in composition
 ⇒ redistribution of atoms via diffusion is required.

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:

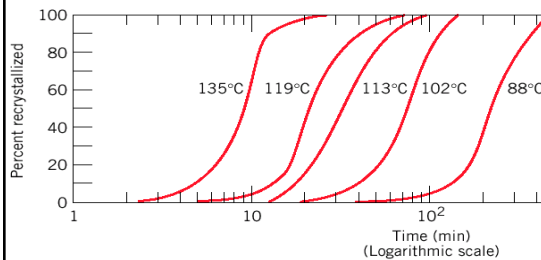
$$r = 1 / t_{0.5}$$

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

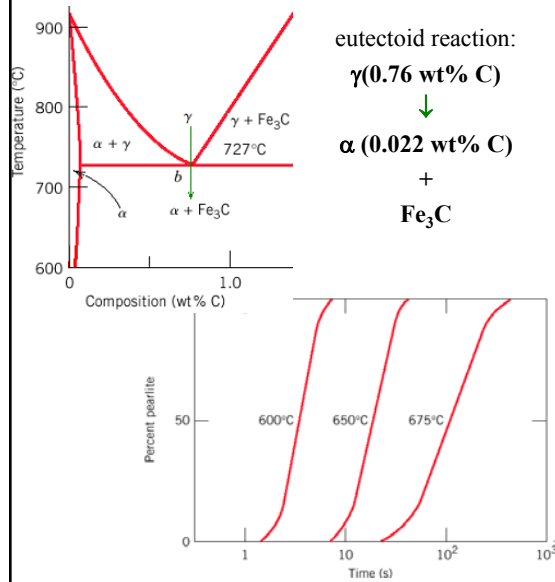


Percent recrystallization of pure copper at different T

Superheating / supercooling

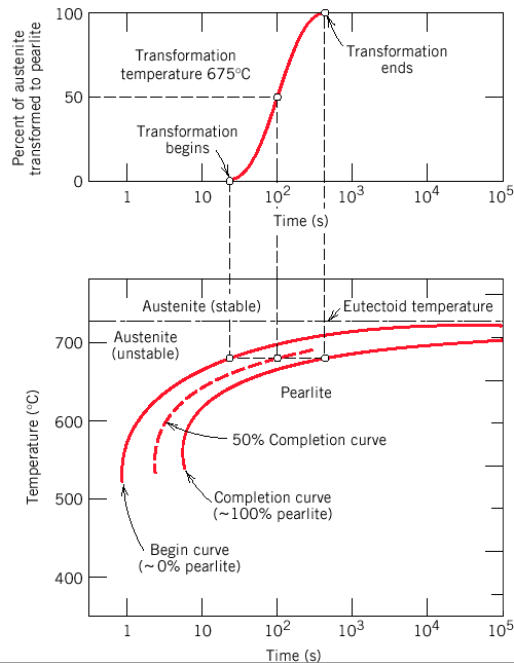
- Upon crossing a phase boundary on the composition-temperature phase diagram phase transformation towards equilibrium state is induced.
- But the transition to the equilibrium structure takes time and transformation is delayed.
- During cooling, transformations occur at temperatures less than predicted 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

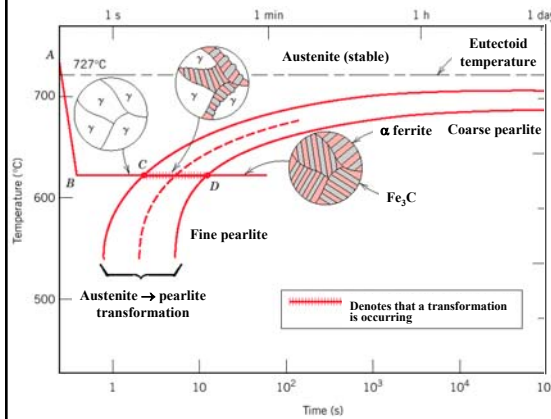


The S-shaped curves are shifted to longer times at higher T showing that the transformation is dominated by nucleation (nucleation rate increases with supercooling) and not by diffusion (which occurs faster at higher T).

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



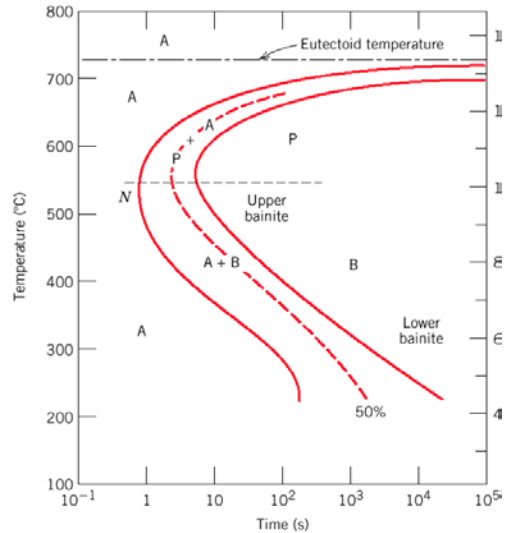
TTT Diagrams



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

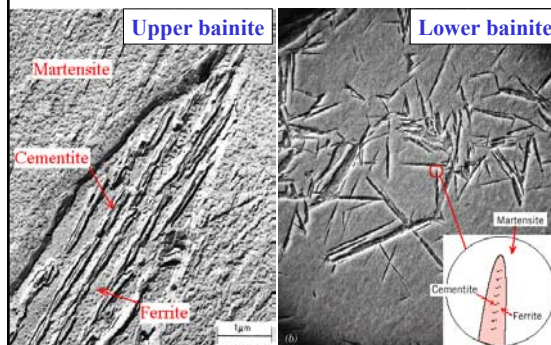
- The family of S-shaped curves at different T are used to construct the TTT diagrams.
- The TTT diagrams are for the **isothermal** (constant T) transformations (material is cooled quickly to a given temperature before the transformation occurs, and then keep it at that temperature).
- At low temperatures, 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.

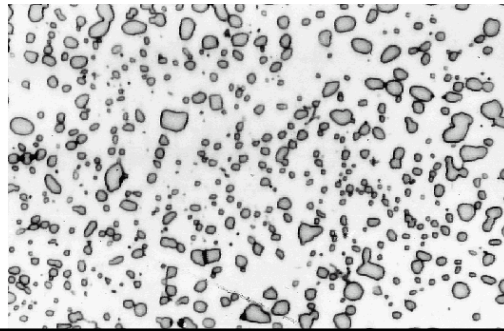
Formation of Bainite Microstructure (II)

- 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

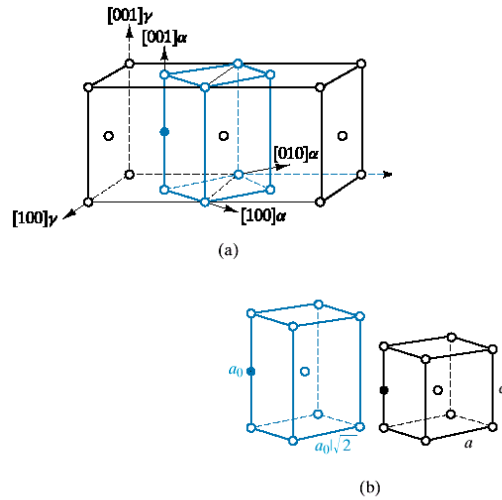
- Annealing of pearlitic or bainitic microstructures at elevated temperatures just below eutectoid (e.g. 24 h at 700 C) leads to the formation of new microstructure – **spheroidite** - spheres of cementite in a ferrite matrix.
- Composition or relative amounts of ferrite and cementite are not changing 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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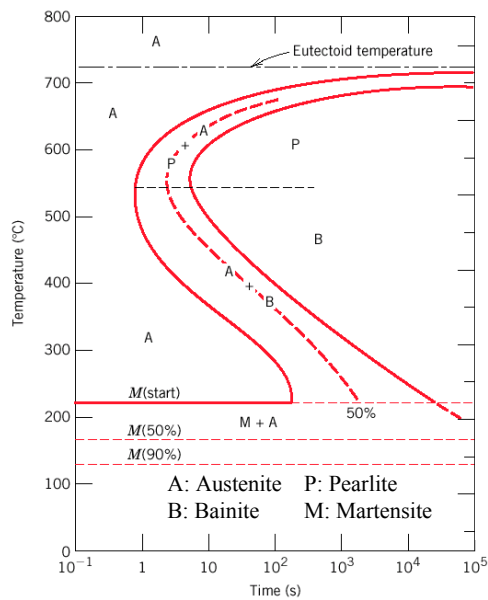
Martensite (I)

- 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 γ -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



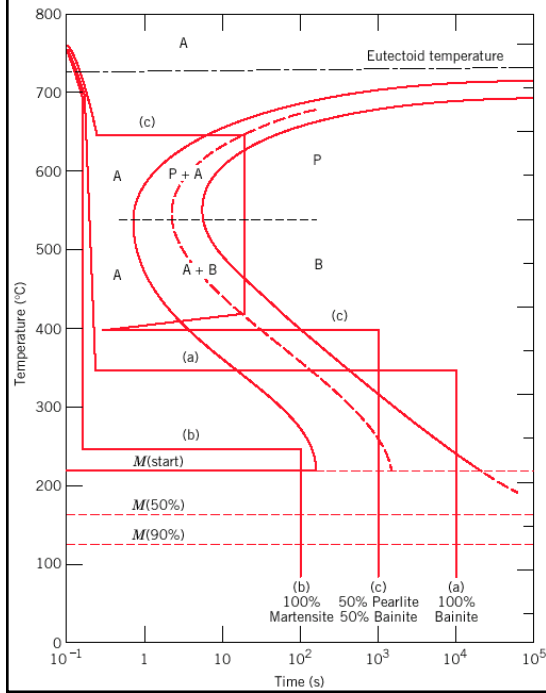
The martensitic transformation involves the sudden reorientation of C and Fe atoms from the FCC solid solution of γ -Fe (austenite) to a body-centered tetragonal (BCT) solid solution (martensite).

TTT Diagram including Martensite



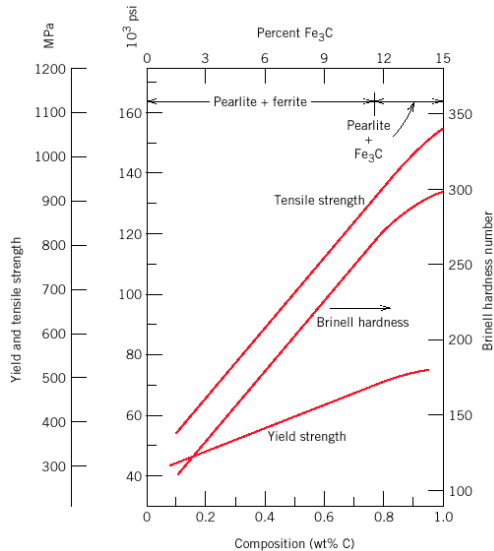
Austenite-to-martensite is diffusionless and very fast. The amount of martensite formed depends on temperature only.

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

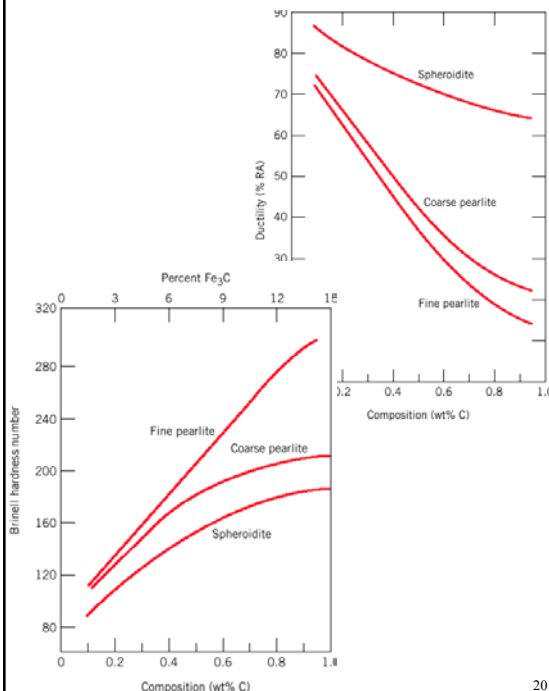
Mechanical properties of martensite

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)

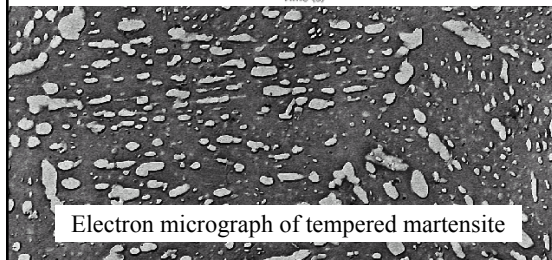
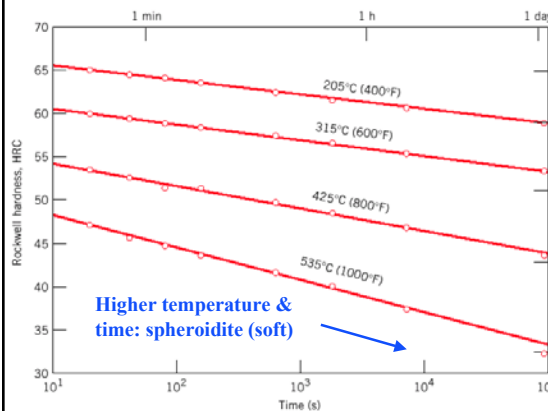


Tempered Martensite (I)

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.

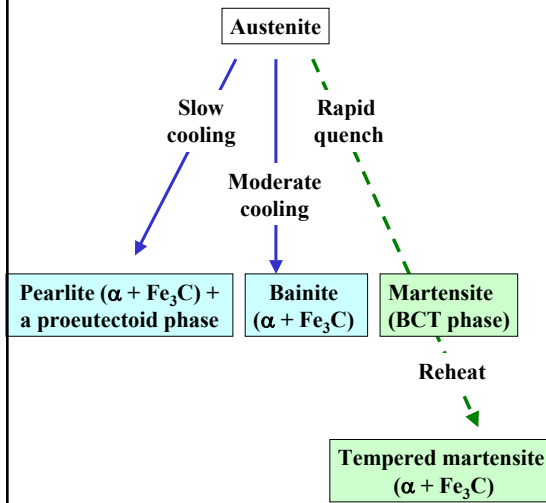
- Tempered martensite is less hard/strong as compared to regular martensite but has enhanced ductility (ferrite phase is ductile).
- Mechanical properties depend upon cementite particle size: fewer, larger particles means less boundary area and softer, more ductile material - eventual limit is spheroidite.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

Tempered Martensite (II)



Electron micrograph of tempered martensite

Summary of austenite transformations



Solid lines are diffusional transformations, dashed is diffusionless martensitic transformation

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

Reading for next class:

Chapter 11: Thermal Processing of Metal Alloys

- Process Annealing, Stress Relief
- Heat Treatment of Steels
- Precipitation Hardening