T-T-T Diagram & Basics of Heat Treatment

Objective of this Lecture

- The trainee should be able to understand:
  - Relevance of T-T-T Diagram in metallurgy.
  - Heat Treatment & its purpose.
  - Some Basic Heat Treatment Processes.

Introduction

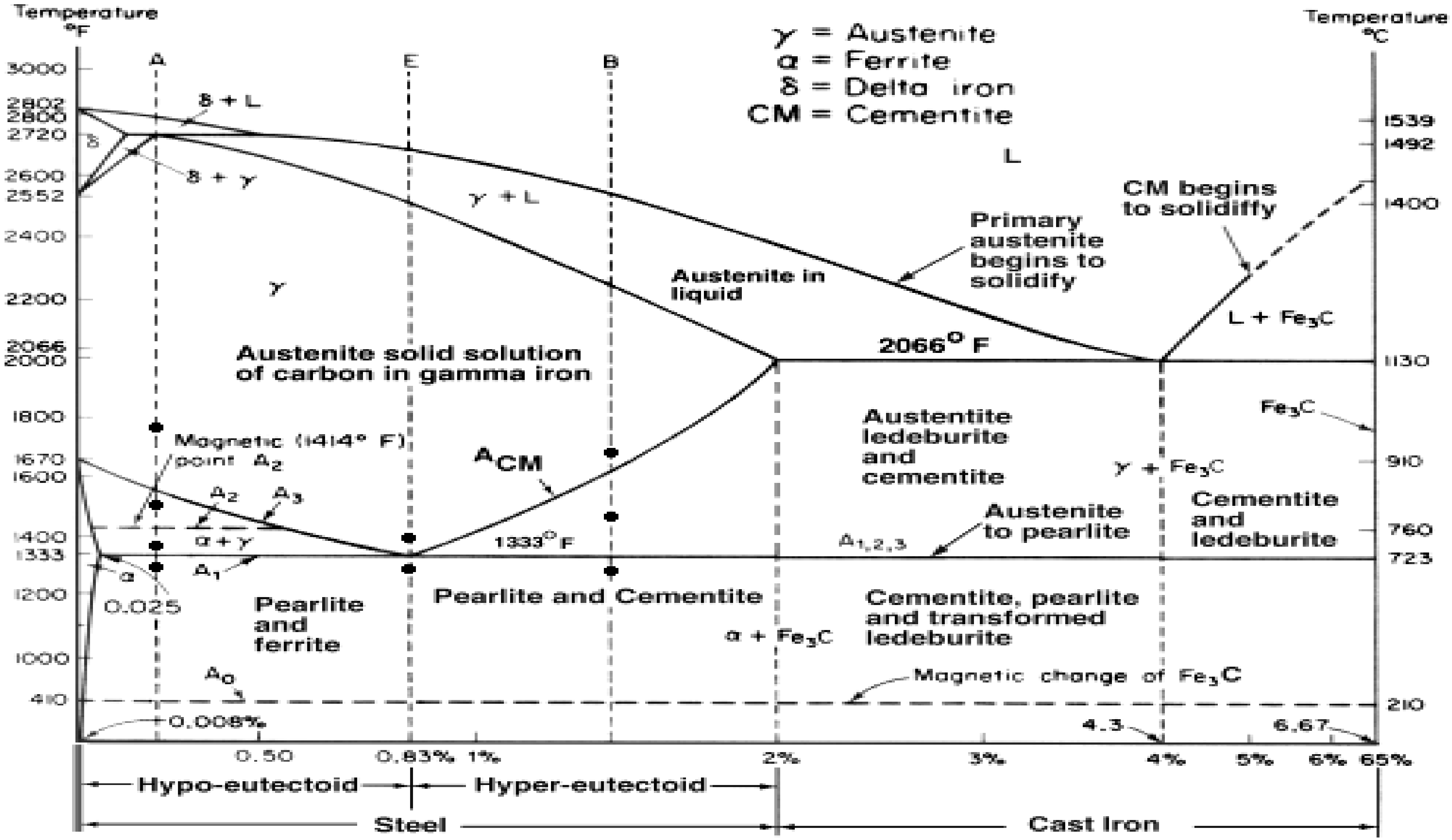
- Fe-C diagram shows the ideal phases when:
  - The system is held at a temp. for sufficiently long time.
  - All diffusions are complete to ideal lattice position.
- Not the practical situation, where steel is heated or cooled at a definite rate.
- So, all the changes are either not started or not completed.
- The practical situation is studied at TTT Diagram.

Introduction

- Both temperature & time i.e. rate of cooling is taken in consideration
- TTT – Time Temperature Transformation
- A plot of temperature versus log of time
- Steel alloy of definite composition.
- Determines when transformations begin and end for an isothermal (constant temp.) phase transformation of a previously austenitized alloy.

Note: **T-T-T curves are accurate only for phase transformations in which temperature of the alloy is held constant through out the duration of the reaction. This means these reactions are isothermal**

Iron Carbon Diagram



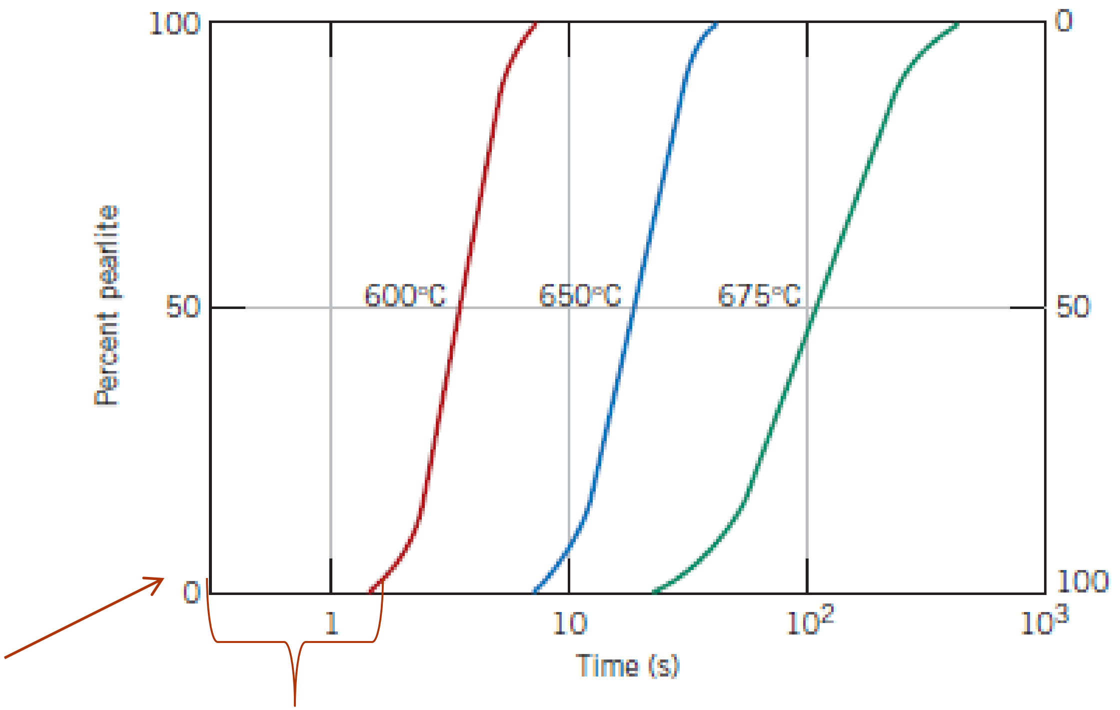


Figure 10.12 For an iron–carbon alloy of eutectoid composition (0.76 wt% C), isothermal fraction reacted versus the logarithm of time for the austenite-to-pearlite transformation.

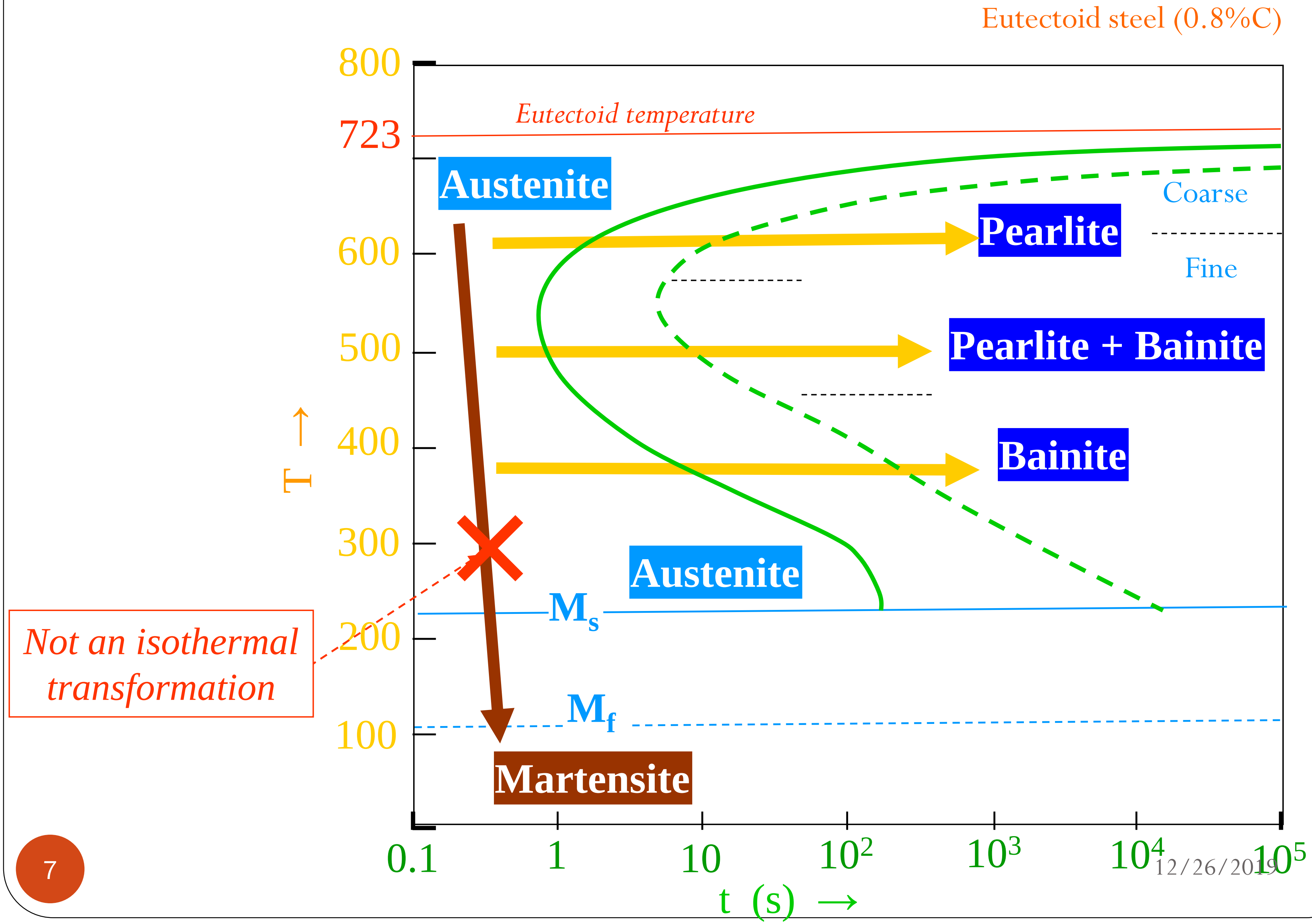
Incubation time

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

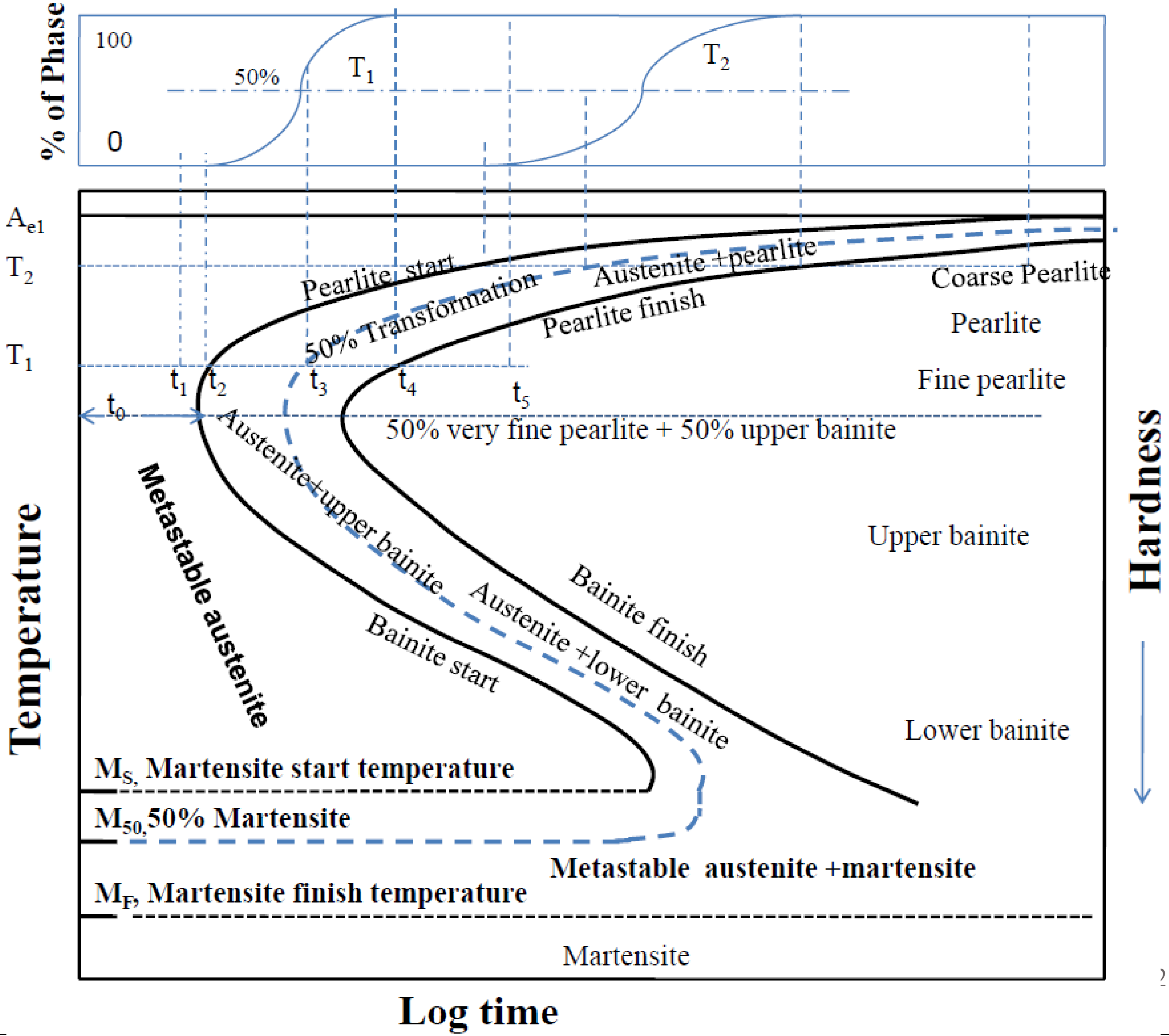
$$y = 1 - \exp(-kt^n)$$

$$\text{rate} = \frac{1}{t_{0.5}}$$

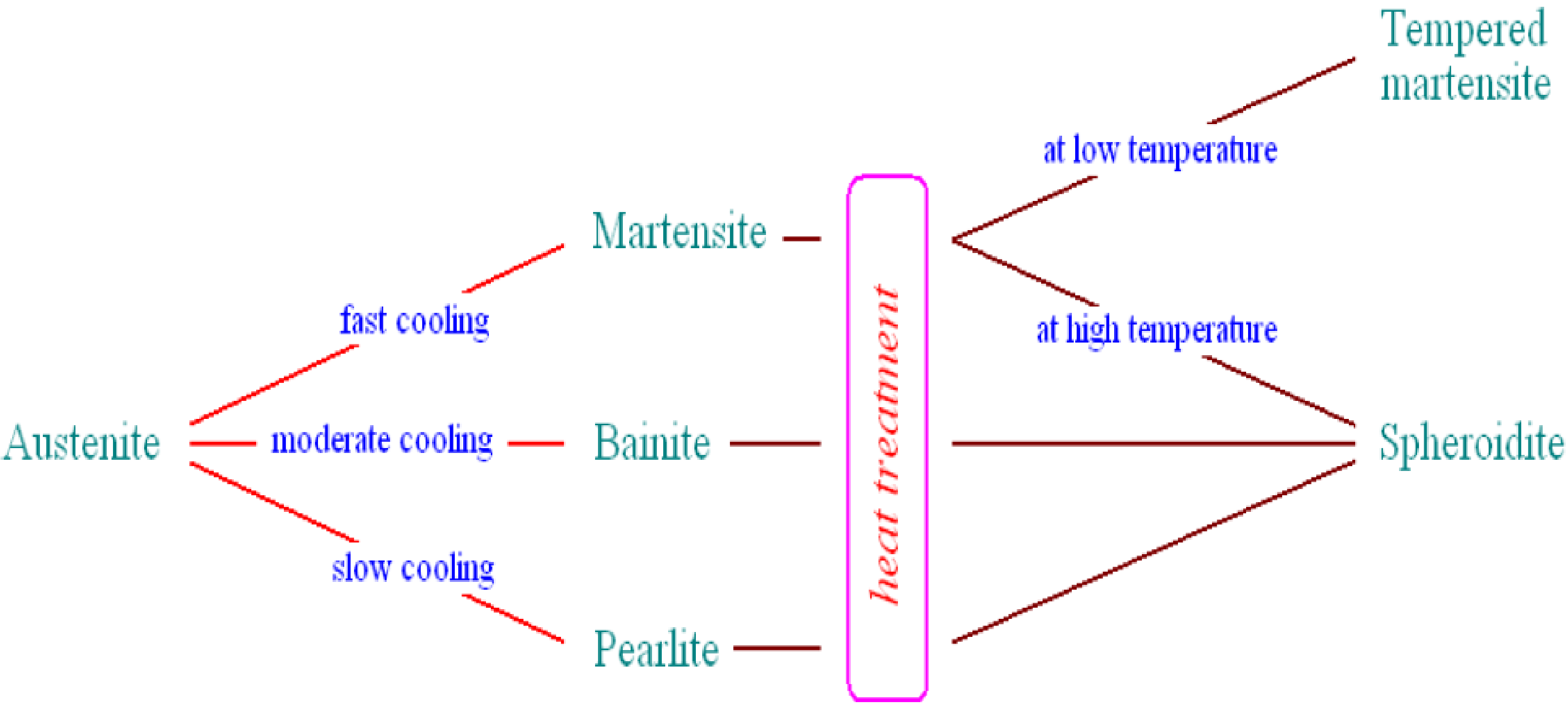
Time- Temperature-Transformation (TTT) Curves – *Isothermal Transformation*



T-T-T Diagram

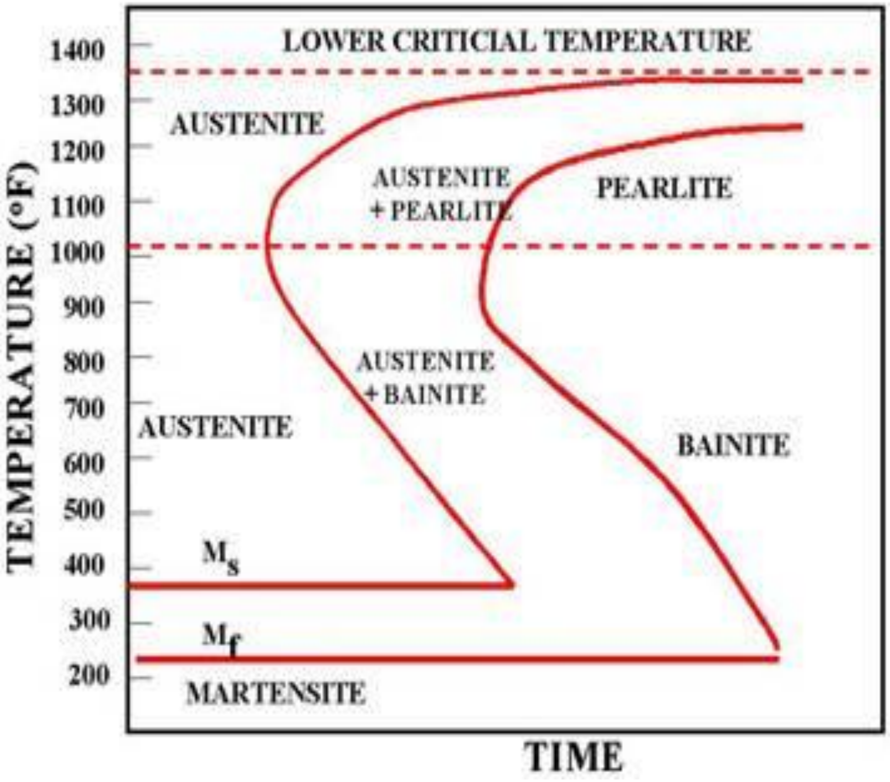

% of Phase
100
0
50%
T1
T2
Ae1
T2
T1
t0
t1
t2
t3
t4
t5
Pearlite start
50% Transformation
Austenite +pearlite
Pearlite finish
Coarse Pearlite
Pearlite
Fine pearlite
50% very fine pearlite + 50% upper bainite
Austenite+upper bainite
Upper bainite
Bainite finish
Bainite start
Austenite +lower bainite
Lower bainite
Metastable austenite
MS, Martensite start temperature
M50, 50% Martensite
Metastable austenite +martensite
MF, Martensite finish temperature
Martensite
Temperature
Log time
Hardness

Transformations involving austenite for Fe-C system



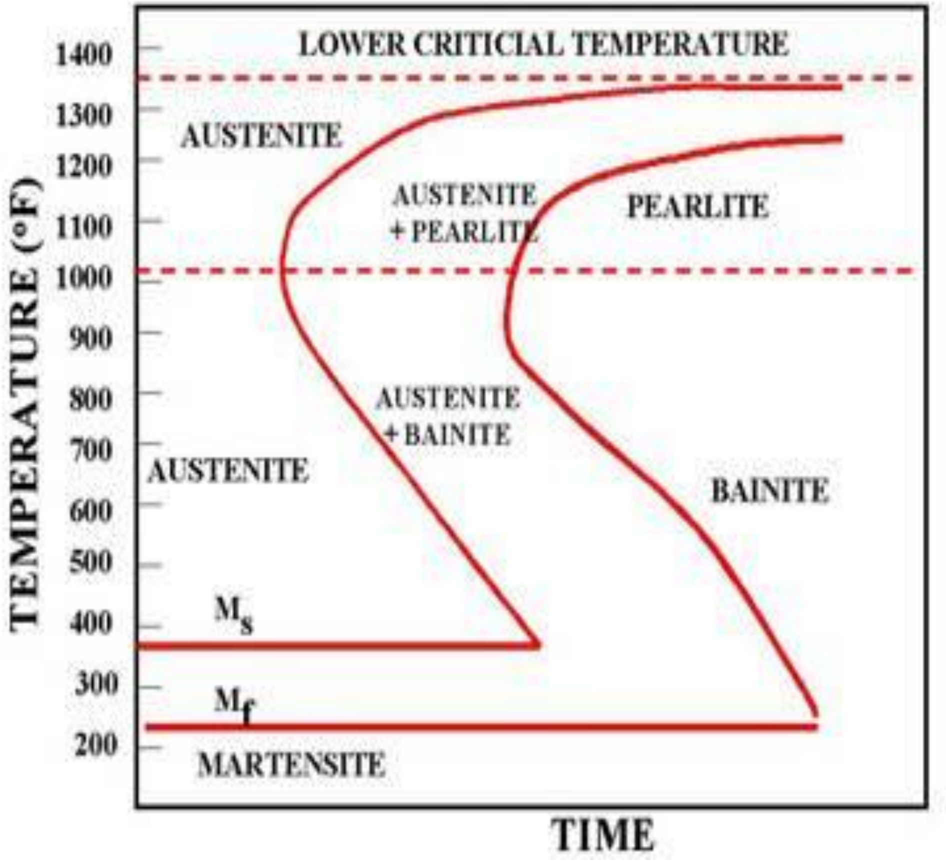
TTT Diagram

- Area on the Left is austenite region.
- Austenite stable above LCT but unstable below LCT
- Left curve start of transformation
- Right curve finish of transformation



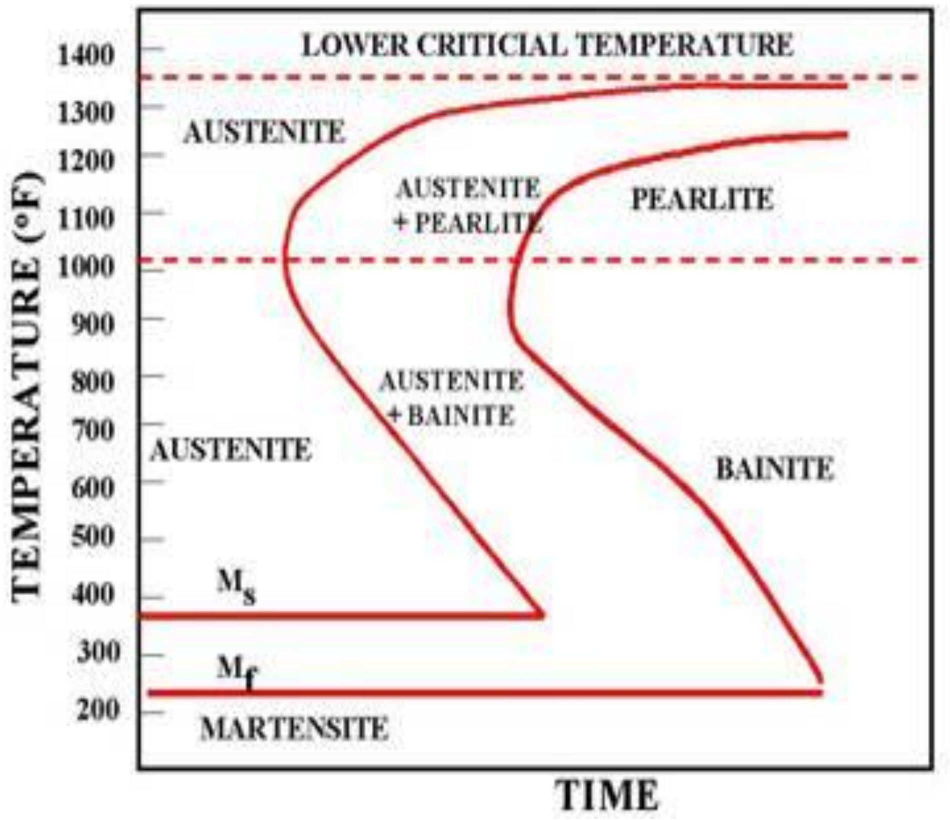
TTT Diagram

- Area between the two curves indicates the transformation of austenite to different types of crystal structures (Pearlite, Martensite, Bainite)



TTT Diagram

- In slow cooling as annealing process, the end product is 100% Pearlite.
- If the cooling curve passes through the middle of the transformation area, the end product is 50% Pearlite and 50% Martensite



Pearlite & Bainite

- Both are decomposition product of ע iron

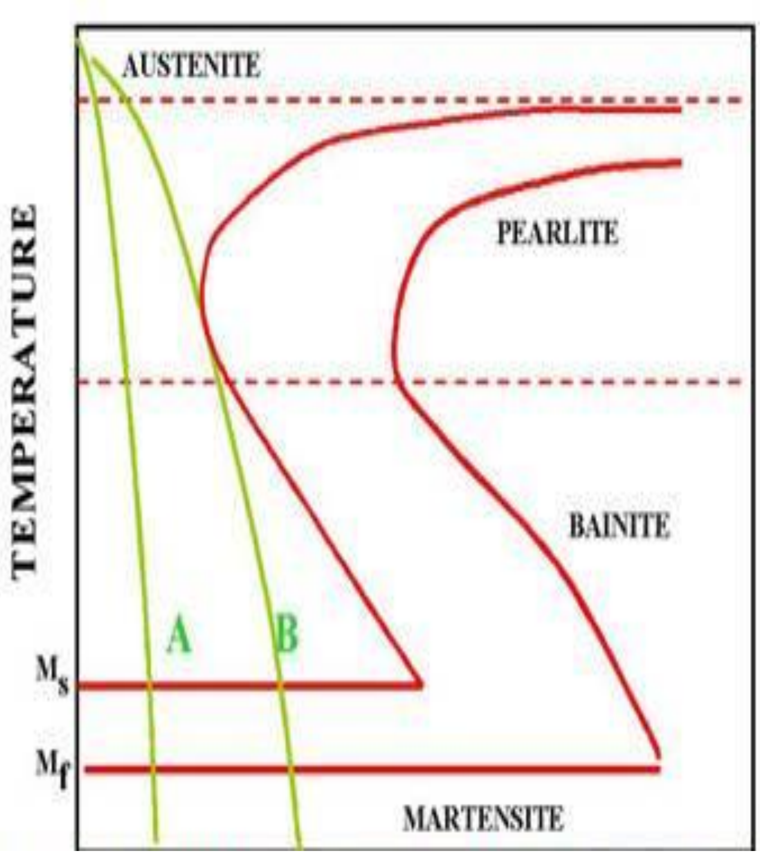
  Coarse Pearlite → Fine Pearlite (Troostite) → Upper Bainite → Lower Bainite etc.
- At temp below 550^0C, movement of iron atom practically stops.
- Bainite forms around 400–550 °C in sheaves of ferrite plates (*sub-units*) separated by retained austenite, martensite or cementite.
- Bainite is an intermediate of pearlite and martensite in terms of hardness and kinetics of diffusion.

Nose of TTT

- As seen in diagram, at a particular level of under cooling the transformation takes least time to start and finish (around 550^{0}C).
  - Above that, the urge is less (temperature difference)
  - Below that, ability (diffusion kinetics/time) reduces!
  - That point is known as 'Nose of TTT'
- During quenching, the cooling rate must be fast enough to avoid the nose.

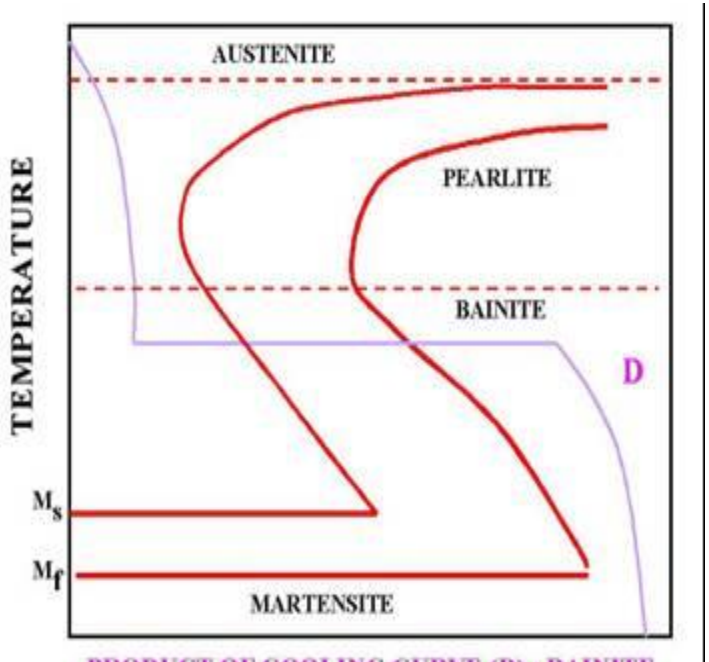
Quenching

- If cooling rate is very high, all Austenite will transform to Martensite
- Higher cooling rate (Rate A)
  - Higher distortion
  - Higher stresses than cooling rate B.
- The end product of both cooling rates is martensite.
- Cooling rate B is also known as the Critical Cooling Rate



Austempering

- Quenching process checked by immersing in a molten salt bath and soaking
- Curve passes through Bainite region of TTT diagram
- End product is Bainite
  - Not as hard as Martensite
  - More dimensional stability
  - Less distortion
  - Less internal stress



PRODUCT OF COOLING CURVE (D) : BAINITE

Effect of Alloying Elements

- All alloying elements(except Co) increases the stability of super-cooled austenite and retard both pro-eutectoid and the pearlitic reaction and then shift TTT curves of start to finish to right or higher timing.
- This is due to quenching possible at much slower cooling rate
- i) low rate of diffusion of alloying elements in austenite as they are substitution elements,
- ii) reduced rate of diffusion of carbon as carbide forming elements strongly hold them.
- iii) Alloyed solute reduce the rate of allotropic change, i.e. $\gamma \rightarrow \alpha$, by solute drag effect on $\gamma \rightarrow \alpha$ interface boundary.
- Additionally those elements (Ni, Mn , Ru , Rh , Pd, Os, Ir, Pt, Cu ,Zn, Au) that expand or stabilize austenite, depress the position of TTT curves to lower temperature.
- In contrast elements (Be ,P, Ti,V,Mo,Cr,B,Ta,Nb,Zr) that favor the ferrite phase can raise the eutectoid temperature and TTT curves move upward to higher temperature.
- However Al, Co, and Si increase rate of nucleation and growth of both ferrite or pearlite and therefore shift TTT diagram to left.

Martensite

- Supersaturated solution of carbon trapped in a FCC lattice forming distorted body centered tetragonal structure (BCT).
- Hardening in martensite is not due to microstructure but due to blockage to the movement of dislocation.
- Highly stressed condition.
- Too brittle for any practical purpose.
- Quenching is always followed by tempering to
  - Reduce the brittleness.
  - Relieve the internal stresses caused by hardening.

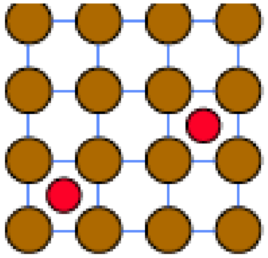


Figure 4. Representation of an Interstitial Solution

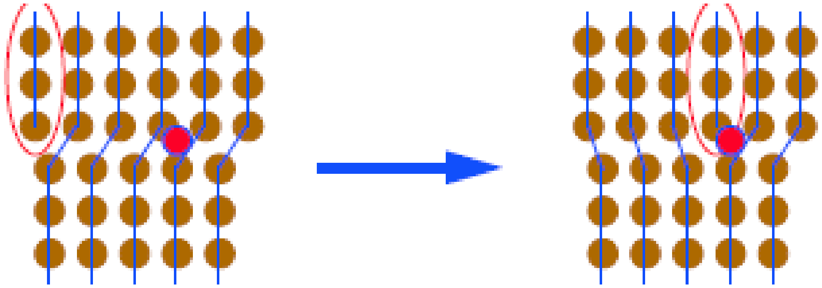
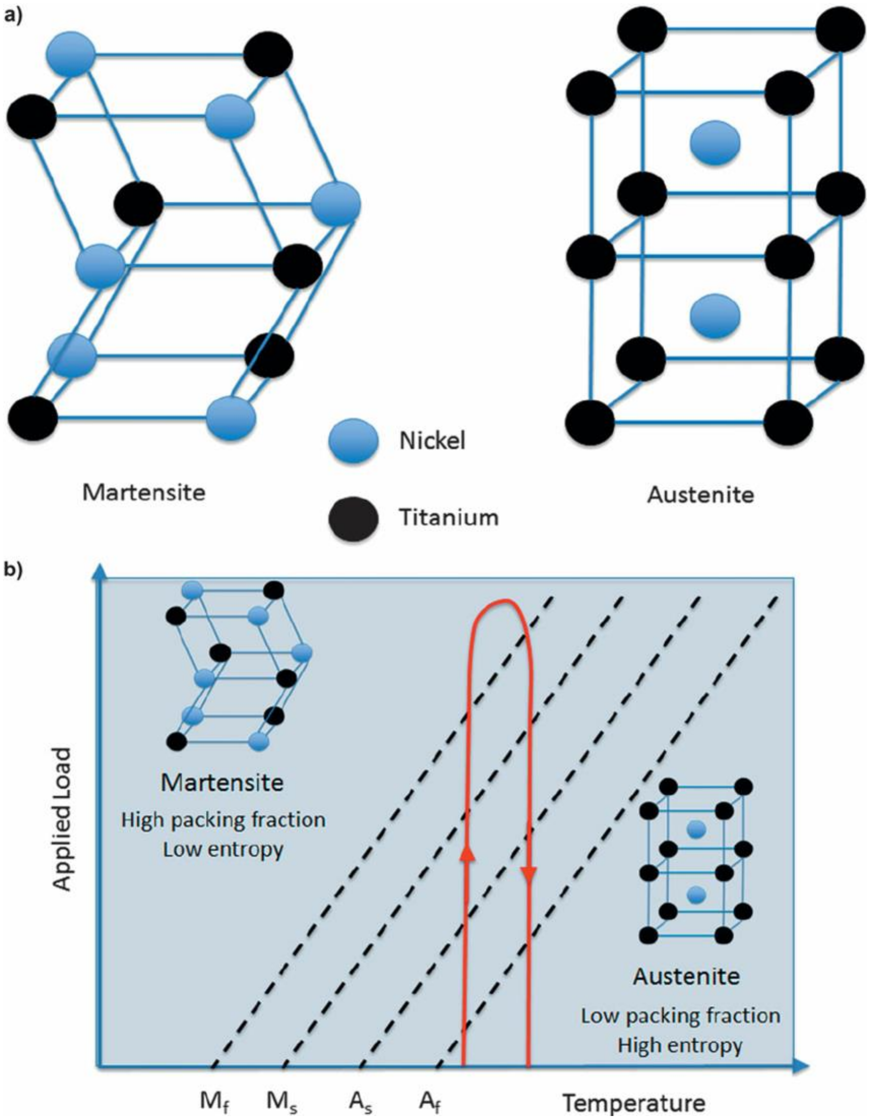


Figure 5. Representation of a Dislocation Stopped by an Interstitial Atom

Martensite


a)
Martensite
Nickel
Titanium
Austenite
b)
Applied Load
Martensite
High packing fraction
Low entropy
Austenite
Low packing fraction
High entropy
M_f
M_s
A_s
A_f
Temperature

Heat Treatment

Introduction

- Heat Treatment is the process of controlled heating and cooling of metals
  - To alter their mechanical properties
  - Without changing the product shape
- Heat Treatment sometimes takes place inadvertently due to manufacturing processes such as welding or forming
- Sometimes HT becomes integral part of manufacturing as in TMT (Thermo Mechanical Treatment)

Introduction

Definition - **Metal Hand Book (ASM)**

- A combination of heating & cooling operation timed & applied to a metal or alloy in solid state in a way that will produce desired properties

Objectives of Heat Treatment

- Increasing the service worthiness of material
  - Hardening.
  - Softening.
  - Property modification
- **Obtain certain manufacturing objectives like**
  - Improve machinability & formability
  - Restore ductility
  - Recover Grain Size etc.
  - Then known as Process Heat Treatment

Objectives of Heat Treatment

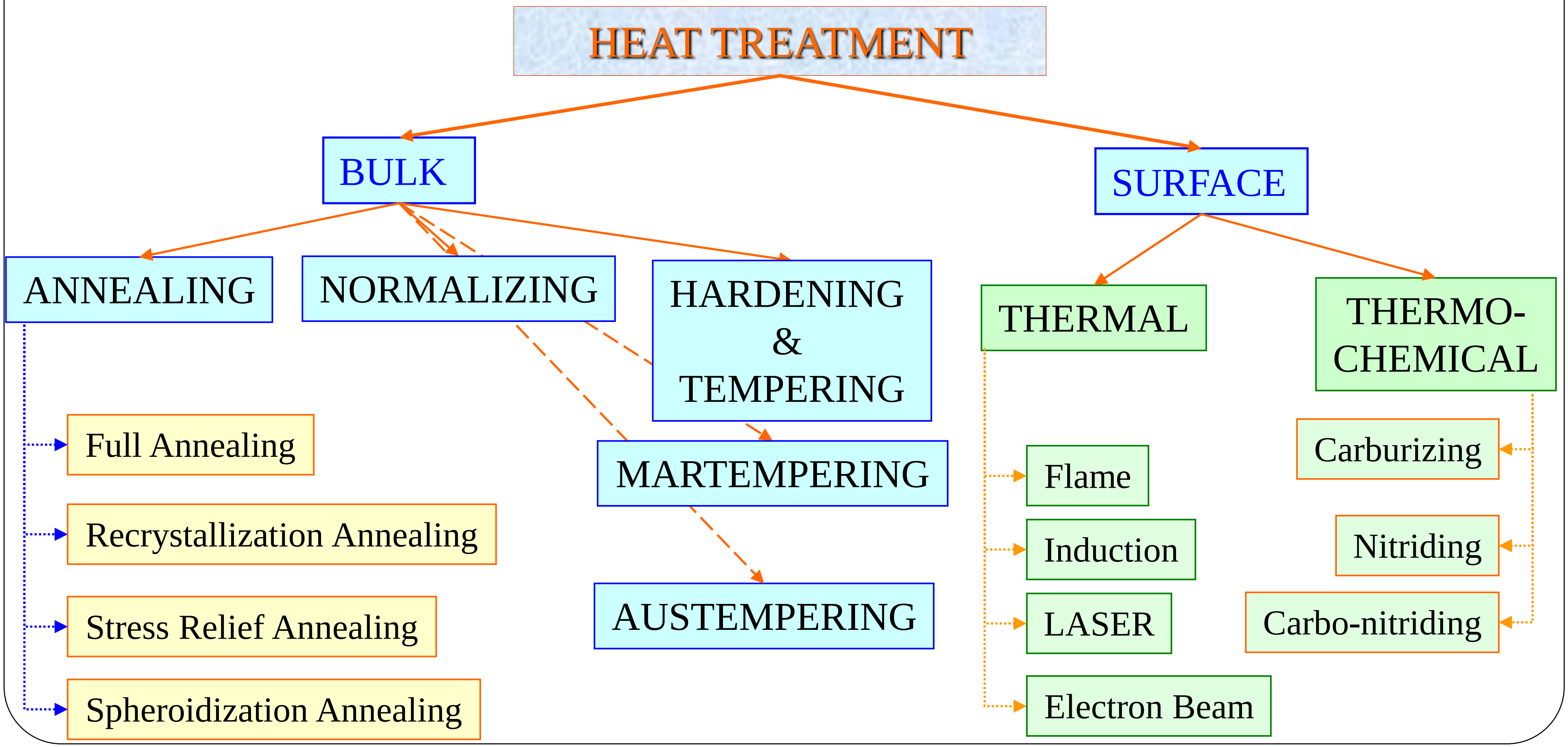
- **Softening**:
  - reduce strength or hardness,
  - remove residual stresses,
  - improve toughness,
  - restore ductility,
  - refine grain size or change the electromagnetic properties of the steel.
  - Annealing —
  - Full Annealing
  - Process,
  - spheroidizing,
  - normalizing and tempering — austempering, martempering are the principal ways by which steel is softened.

Objectives of Heat Treatment

- **Hardening**:
- *the strength and wear properties.*
- *sufficient carbon and alloy content* is required.
- **Material Modification**:
  - modify the behavior of the steels in a beneficial manner to maximize service life, e.g., stress relieving , or strength properties, e.g., cryogenic treatment, or some other desirable properties, e.g., spring aging.

An overview of important heat treatments

- A broad classification of heat treatments possible are given below. Many more specialized treatments or combinations of these are possible.



HEAT TREATMENT

BULK

SURFACE

ANNEALING

NORMALIZING

HARDENING & TEMPERING

THERMAL

THERMO-CHEMICAL

Full Annealing

Recrystallization Annealing

Stress Relief Annealing

Spheroidization Annealing

MARTEMPERING

AUSTEMPERING

Flame

Induction

LASER

Electron Beam

Carburizing

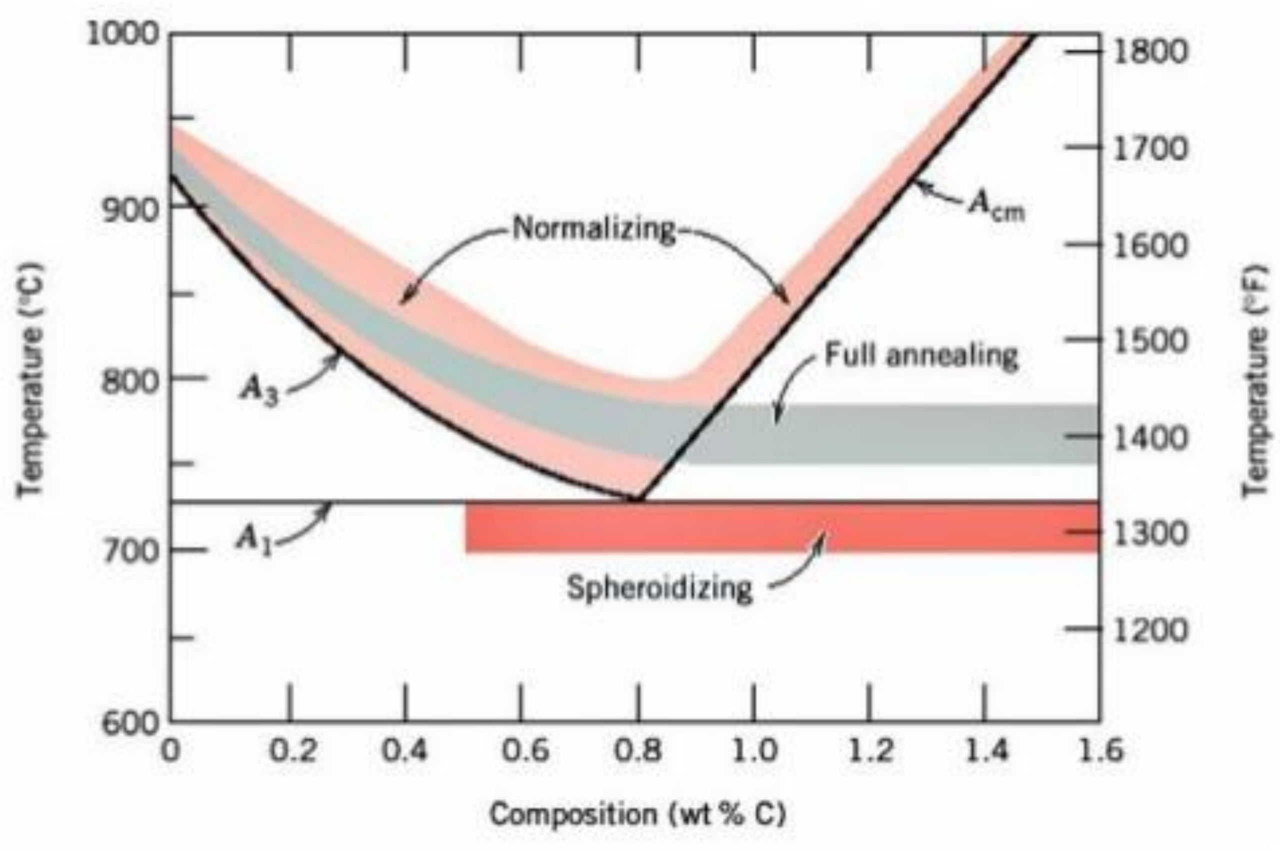
Nitriding

Carbo-nitriding

Some common terminologies

- **Upper critical temperature (point) A_3** is the temperature, below which ferrite starts to form as a result of ejection from austenite in the hypoeutectoid alloys.
- **Upper critical temperature (point) A_{CM}** is the temperature, below which cementite starts to form as a result of ejection from austenite in the hypereutectoid alloys.
- **Lower critical temperature (point) A_1** is the temperature of the austenite-to-pearlite eutectoid transformation. Below this temperature austenite does not exist.
- **Magnetic transformation temperature A_2** is the temperature below which α-ferrite is ferromagnetic.

Fe-Fe_3C phase diagram indicating heat treating temperature ranges for plain carbon steel



Characteristics of Heat Treatment

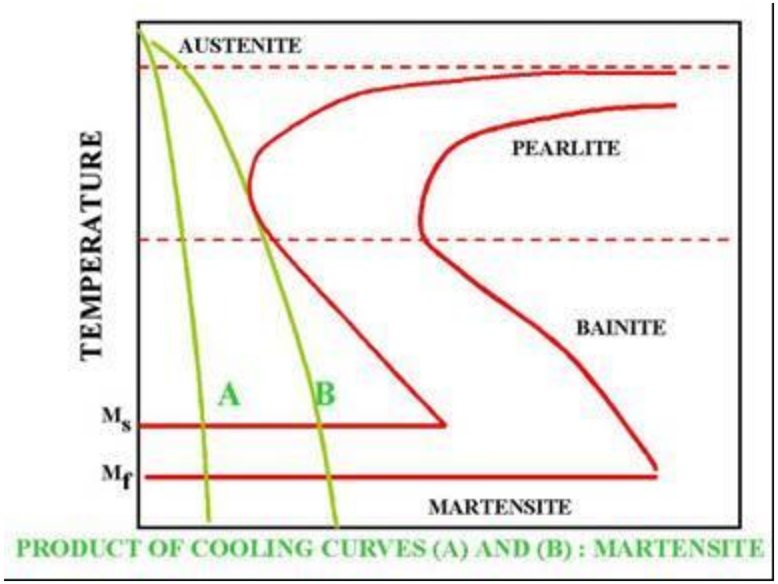
- Hardening HTs particularly suitable for Steels
  - Many phase transformation/ inter-metallic compound precipitation involved even in PCS or LAS.
  - Normal phase transformation or precipitation characteristics modified.
  - Not applicable to Steels having Single phase structure like Austenetic or Ferritic SS.
- Other type of heat treatments equally applicable to ferrous & non-ferrous alloys.

Hardening Heat Treatments

- Hardening (normally quenching followed by Tempering) is intended to improve the strength and wear properties of steel.
- Generally increases hardness at the cost of toughness
- Can be of two types
  - Through hardening → about same hardness from surface to core
  - Surface hardening → Sharp drop in hardness after few mm from surface

Requirement of Hardening HT

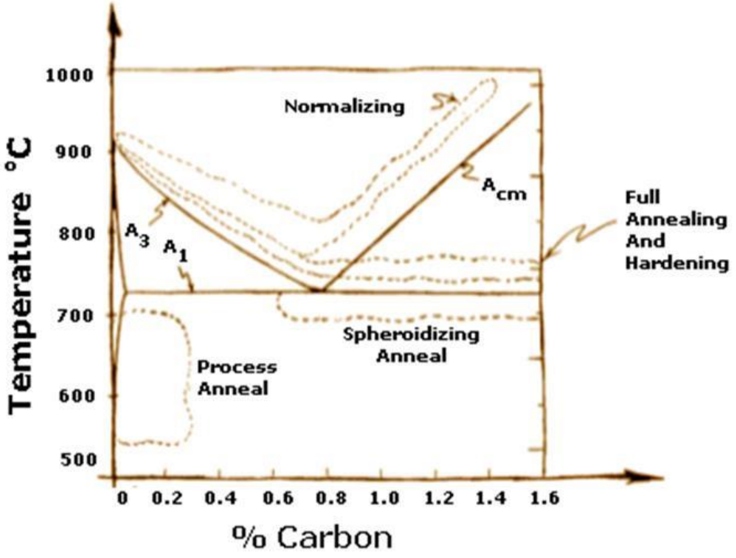
- Steel should have enough C and/or other alloys to
  - Shift TTT curve to right.
  - To avoid 'Nose' in practical quenching line.
- If both conditions are satisfied, both type of hardening is possible
- If not, only surface can be carburized and hardened.



PRODUCT OF COOLING CURVES (A) AND (B) : MARTENSITE

Through Hardening HT

- Steps
  - Heating to γ → Soaking → Quenching to martensite → Tempered to tempered martensite

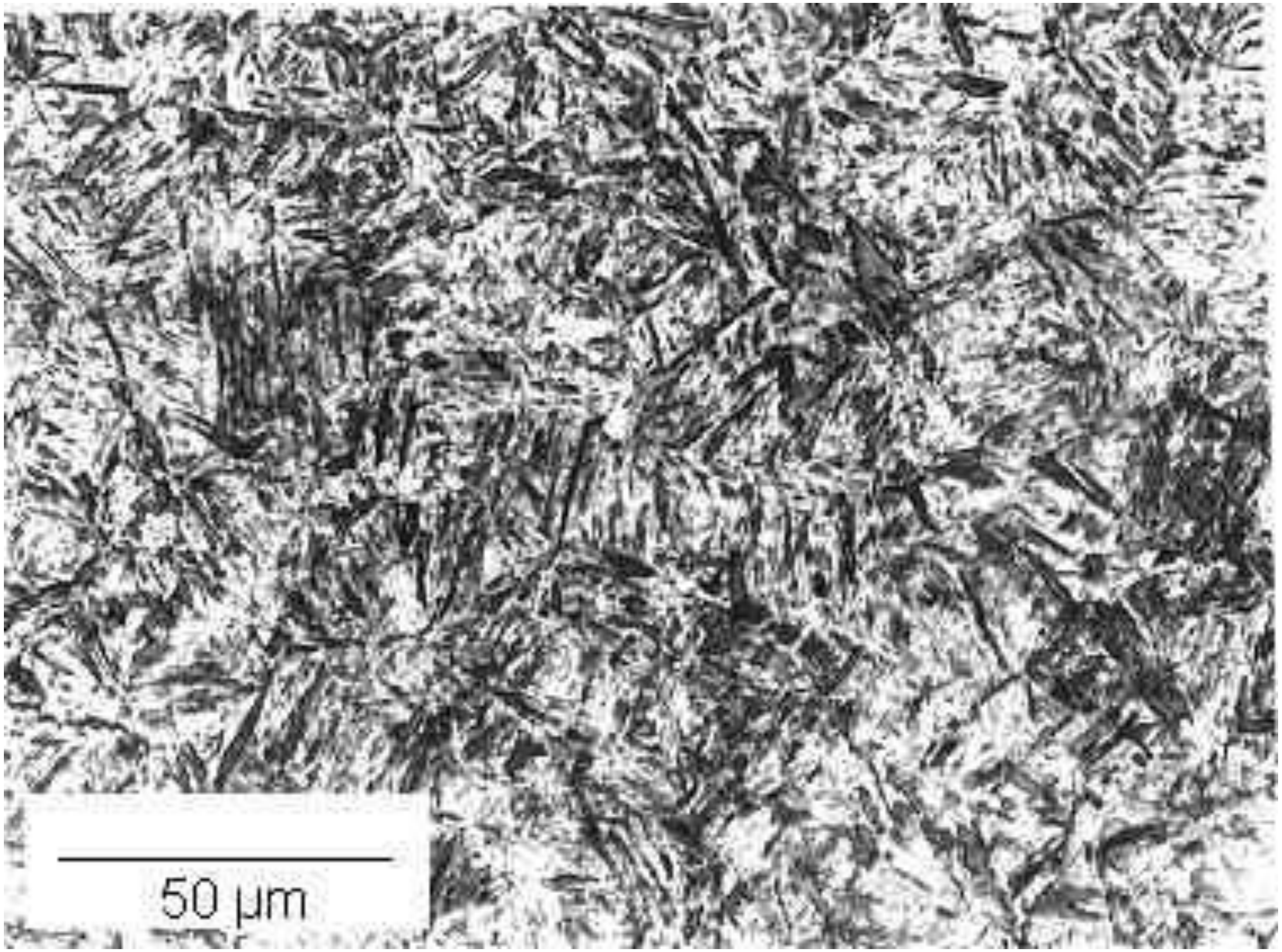


HEAT TREATMENT PROCESS

Through Hardening HT

  - Heating to austenizing range i.e. 30 – 50^{0}C above Ac_3 (Hypoeutectoid) or Ac_1 (Hypereutectoid).
  - Holding sufficiently long time for full transformation (1hr/per inch of maxm. thickness).
  - Dipping in Quenching Medium.
  - Raising temp in 300^{0}C -500^{0}C range.
  - Holding for predetermined time.
- To obtain tempered martensite of required hardness & toughness as demanded in service.

Martensite Photo



Tempering

- Tempering means subsequent heating
  - to a specific intermediate temperature.
  - holding for specific time.
- Tempering leads to the partial decomposition of martensite into ferrite-cementite mixture.
- At low tempering temperature (up to 200^0C or 250^0C),
  - Hardness changes only to a small extent
  - True tensile strength increases
  - Bending strength increases

Tempering

- Exhaustive tempering temperature range 200^0C - 600^0C
- Holding time varies from 30 min. to 2hrs.
- Temp & time depends on the hardness-toughness combination required in service.
  - Higher time/temp → Reduced hardness & increased toughness.
- Carbon separates out from martensite lattice(retained austenite)as Cementite.
  - Reduction in stress & accicularity (becoming needle shaped).
    - Drop in hardness, increase in toughness

Tempering

- Higher tempering temperature reduces
  - Hardness
  - True tensile strength
  - Yield point
  - relative elongation.
- This is due to formation of ferrite and cementite mixture.

Tempering

- At still higher temperature or holding time
  - Spherodisation of cementite.
  - Coarsening of ferrite grains.
  - Fall in hardness as well as toughness.
  - In certain cases machinabilty improves.
- In high alloyed steel, retained austenite decomposes.

Temper Embrittleness

- A sharp fall in Impact strength when:
- Holding or slowly cooling alloy steels which were previously tempered between 400-660 degree celsius.
- Tempering as quenched alloy steels in the temperature range 250 - 400 degree celsius.
- All steels, in varying degree, suffer from this
  - Carbon steels display slight loss of toughness.
  - Observed specifically in steels with phosphorous, antimony, tin and arsenic
  - For alloy steel reduction by 50% to 60% (steels containing Cr,N
  - Plain carbon Steels with Mn less than 0.5% are not susceptible to temper embrittlement
- The reason associated with
  - Precipitation of alloy carbides
  - Decomposition of retained austenite.
- It can be eliminated by heating steel above the embrittlement range followed by rapid cooling.
- Mo, Ti, Zr, W can be added so as to suppress embrittlement.

Quenching Media

- Quenching media with increased degree of severity of quenching
  - Normal Cooling
  - Forced Air or draft cooling
  - Oil
  - Polymer
  - Water and
  - Brine

Quenching Media

- Quenching medium depends on
  - Material composition
  - Weight of job
- Aim is to have a cooling rate just bye-passing the nose of TTT curve for
  - minimum stress
  - minimum warping/crack during quenching.
- Cooling rate varies from surface to core: slower cooling towards centre.

Severity of quench values of some typical quenching conditions

- ❑ Before we proceed further we note that we have a variety of quenching media at our disposal, with varying degrees of cooling effect. The severity of quench is indicated by the ‘H’ factor (defined below), with an ideal quench having a H-value of ∞.

Severity of Quench as indicated by the heat transfer equivalent H

$$H = \frac{f}{K} \qquad [m^{-1}]$$

f → heat transfer factor
K → Thermal conductivity

Process	Variable	H
Air	No agitation	0.02
Oil quench	No agitation	0.2
"	Slight agitation	0.35
"	Good agitation	0.5
"	Vigorous agitation	0.7
Water quench	No agitation	1.0
"	Vigorous agitation	1.5
Brine quench (saturated Salt water)	No agitation	2.0
"	Vigorous agitation	5.0
Ideal quench		∞

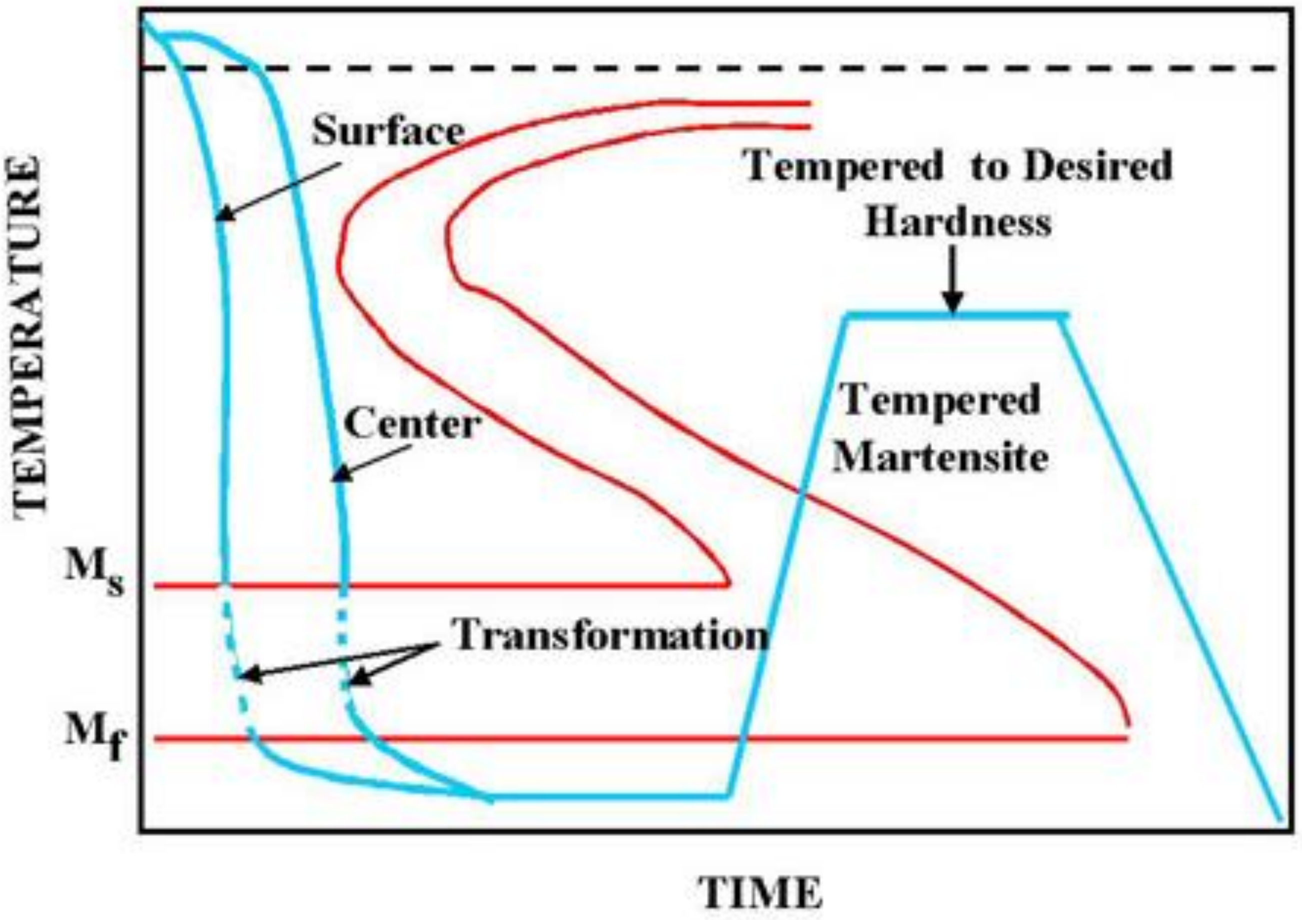
Increasing severity of quench

Note that apart from the nature of the quenching medium, the vigorousness of the shake determines the severity of the quench. When a hot solid is put into a liquid medium, gas bubbles form on the surface of the solid (interface with medium). As gas has a poor conductivity the quenching rate is reduced.

Providing agitation (shaking the solid in the liquid) helps in bringing the liquid medium in direct contact with the solid; thus improving the heat transfer (and the cooling rate).

The H value/index compares the relative ability of various media (gases and liquids) to cool a hot solid. Ideal quench is a conceptual idea with a heat transfer factor of ∞ (⇒ H = ∞).

Standard Quenching & Tempering



Surface Hardening

- Objective is to harden the surface & subsurface selectively to obtain:
  - Hard and wear-resistant surface
  - Tough impact resistant core
  - The best of both worlds
- Case hardening can be done to all types of plain carbon steels and alloy steels

Surface Hardening

- Selectivity is achieved

  a) For low carbon steels

  - By infusing carbon, boron or nitrogen in the steel by heating in appropriate medium
  - Being diffusion controlled process, infusion is selective to surface and subsurface
    - Thus making the area responsive to HT

  b) For medium & High carbon or Alloy steel

  - By heating the surface selectively followed by quenching

Case Carburizing

- Heating of low carbon steel in carburizing medium like charcoal
- Carbon atoms diffuse in job surface
- Typical depth of carburization; 0.5 to 5mm
- Typical Temperature is about 950^0C
- Quenching to achieve martensite on surface and sub-surface
- If needed, tempering to refine grain size and reduce stresses

Case Nitriding

- Heating of steel containing Al in nitrogen medium like Nitride salt, Ammonia etc.
- Typical temperature is about 530^0C
- Nitrogen atoms diffuse in job surface
- Forms AlN, a very hard & wear resistant compound on surface & sub-surface
- Typical use is to harden tubes with small wall thickness like rifle barrel etc.

Case Carbo-nitriding

- Heating of low carbon steel containing Al in cynide medium like cynide salt followed by Quenching
- Typical temperature is about 850^0C
- Nitrogen & Carbon atoms diffuse in job
- Typical case depth 0.07mm to 0.5mm
- Forms very hard & wear resistant complex compounds, on surface & sub-surface
- If needed, tempering to refine grain size and reduce stresses

Induction and Flame Hardening

- Employed for medium & high carbon steel or alloy steels
- Local heating of the surface only either by flame or induction current
- Heating to austenizing range, 30 – 50^{0}C above Ac$_3$ (Hypoeutectoid) or Ac$_1$ (Hypereutectoid)
- Quenching in suitable quenching media
- If needed, tempering to refine grain size and reduce stresses

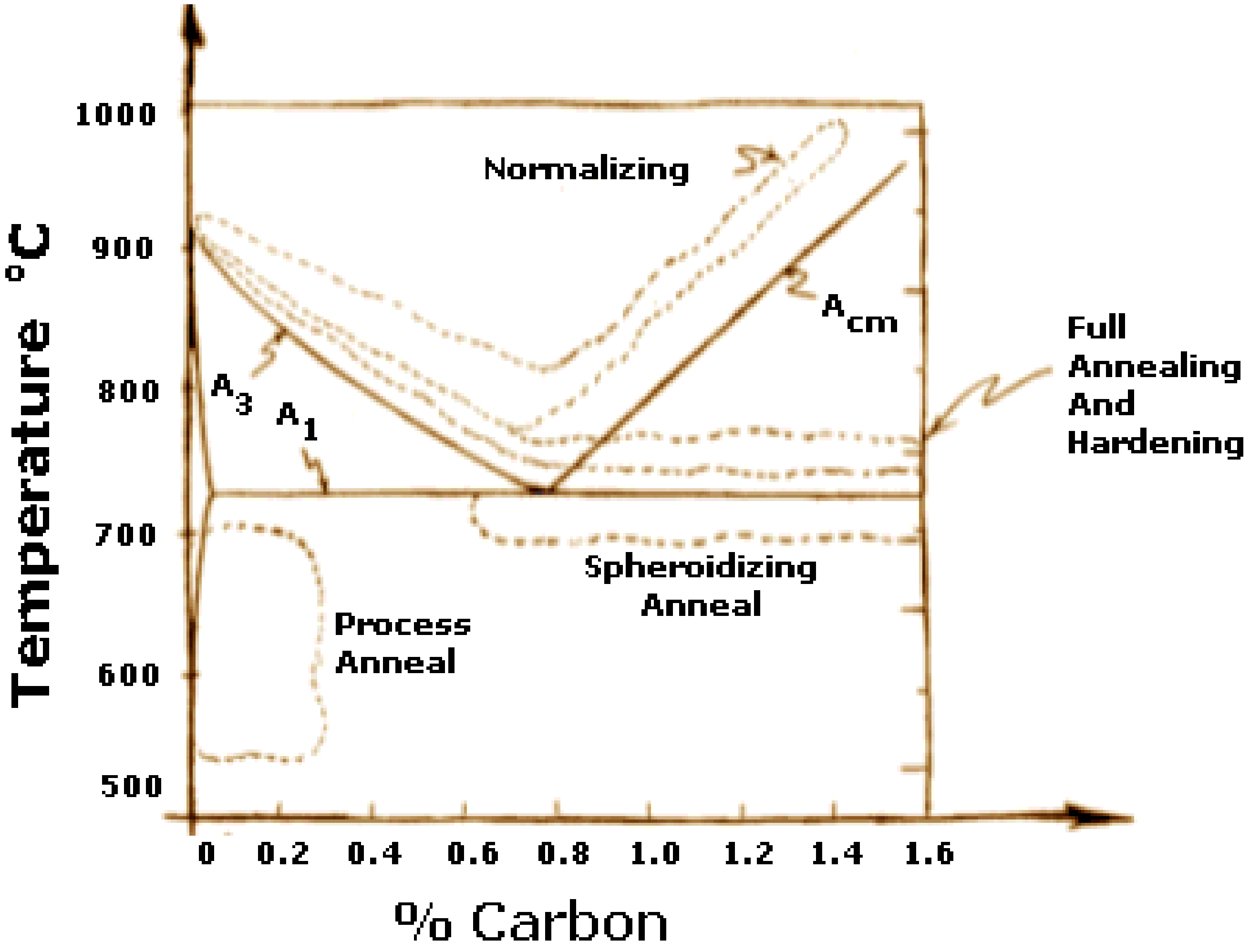
Softening Heat Treatment

- Softening Heat Treatment done to:
  - Reduce strength or hardness
  - Remove residual stresses
  - Restore ductility
  - Improve toughness
  - Refine grain size
- necessary when a large amount of cold working, such as cold-rolling or wire drawing been performed

Softening Heat Treatment

- Incomplete Annealing
  - Stress Relieving
  - Process Annealing
  - Spherodising
- Full Annealing
- Normalizing

Softening HT Temperatures



Stress Relieving

- To reduce residual stresses in large castings, welded and cold-formed parts.
- Such parts tend to have stresses due to thermal cycling or work hardening.
- Parts are
  - heated to 600 - 650ºC (1112 - 1202ºF)
  - held for about 1 hour or more
  - then slowly cooled in still air.

Process Annealing

- Used to treat work-hardened parts made out of low-Carbon steels (< 0.25% Carbon).
- In process heat treatment
- Allows the parts to be soft enough to undergo further cold working without fracturing.

Process Annealing

- Temperature raised near the lower critical temperature line A_1 i. e. 650ºC to 700ºC
- Holding for sufficient time, followed by still air cooling.
- Initially, the strained lattices reorient to reduce internal stresses (recovery)
- When held long enough, new crystals grow (recrystallisation).
- Used to treat work hardened parts made from Low carbon steels (<0.25% carbon)

Process Annealing

- Material stays in the same phase through out the process
  - Only change in size, shape and distribution of the grain structure
- This process is cheaper than either full annealing or normalizing
  - As material is not heated to a very high temperature or cooled in a furnace.

Spheroidization

- Used for high carbon steels (Carbon > 0.6%) that will be machined or cold formed subsequently.
- Cycle multiple times between temperatures above and below 727 degree celsius.
- Be done by one of the following ways:
- Heat just below the line A_1 (727 ºC)
- Hold for a prolonged time
- Followed by fairly slow cooling

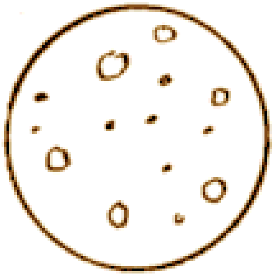
Spheroidization

- Temperatures slightly above and below the A_1 say 700 and 750ºC
- Slow cool.

Or

- For tool and alloy steels
  - heat to 750 to 800ºC
  - hold for several hours
  - followed by slow cooling.

Spheroidization



SPHEROIDITE

- Results formation of small globular cementite (spheroids)
- Dispersed throughout the ferrite matrix.
- Improved machinability
- Improved resistance to abrasion

Full Annealing

An act of

- Heating to austenizing range, 30 – 50^{0}C above Ac_3 (Hypoeutectoid) or Ac_1 (Hypereutectoid)
- Holding sufficiently long time for full transformation (1hr/per inch of maxm. Thickness)
- Cooling slowly upto 500^{0}C
- Normal cooling to room temperature

Full Annealing

- Cooling rate varies from 30°C/hr to 200°C/hr depending on composition
- Enable the austenite to decompose fully
- Higher the austenite stability, slower the cooling to ensure full decomposition.
- Thus, alloy steels, in which austenite is very stable should be cooled much slower than carbon steel.
- The microstructure is coarse Pearlite with ferrite or Cementite (depending on whether hypo or hyper eutectoid).

Full Annealing

- Full annealing hyper eutectoid steel is required only for restoring grain size
  - When hot working (rolling or forging) finished at high temperature resulting in coarse grained structure.
- For hot working finished at a normal temperature, incomplete annealing OK
- Hypoeutectoid hot worked steel (rolled stock, sheet, forgings, etc), castings of carbon & alloy steels, may undergo full annealing.

Normalizing

- Refine grain structure before hardening .
- To harden the steel slightly.
- Raising the temperature to 60ºC (140 ºF) above line A_3 (hypo) or line A_{CM} (hyper)fully into the Austenite range.
- Held at this temperature to fully convert the structure into Austenite
- Removed from the furnace
- Cooled at room temperature under natural convection.
- Results a grain structure of fine Pearlite with pro-eutectoid Ferrite or Cementite.
- Normalizing is normally carried out at a temperature 50 degree Celsius above annealing.

Normalizing Vs. Annealing

Normalising

- considerably cheaper
- No added cost of blocking the furnace. & at times, power
- Comparatively harder
- Non-uniform hardness
  - Machinability

Annealing

- Costlier in terms of fuel and furnace. time
- Cost of blocking the furnace. & at times, power
- Softest possible structure in that composition
- Uniform hardness in all section thickness
  - Uniform machinability

Thank you