

MEM 6102 Alaşım Tekniği

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KMA 214

Salı 14:00-16:50

Yer: KMD-330

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Phase Transformation

- The development of microstructure in alloys involves phase transformation:
 - Phase transformation need **time, and cooling rate** greatly modify the phase transformation.

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Phase Transformation Basic Concepts

- **Phase transformation** as well as the **transformation rate** are important to develop a specific microstructure which in turn affect the mechanical properties of materials.
- For example, the tensile strength of Fe-C eutectoid alloy can be 700 MPa to 2000 MPa depending on heat treatment condition.

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Phase Transformation Basic Concepts

- Three classifications of phase transformations:
 - No change in composition, simple diffusion-dependent transformation
 - Composition change, diffusion-dependent transformation
 - Diffusionless transformation

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The 1st kind of phase transformation

- No change in composition, simple diffusion-dependent transformation
 - Solidification
 - Allotropic transformation ($\alpha \rightarrow \gamma$)
 - Recrystallization and grain growth
- No change in composition of phases.

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The 2nd kind of phase transformation

- Composition change, diffusion-dependent transformation
 - Eutectoid reaction ($\gamma \rightarrow$ pearlite)

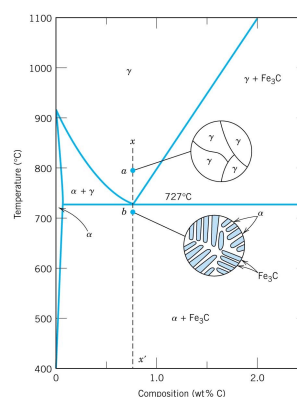


FIGURE 9.23 Schematic representations of the microstructures for an iron-carbon alloy of eutectoid composition (0.76 wt% C) above and below the eutectoid temperature.

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The 3rd kind of phase transformation

- Diffusionless transformation
 - Metastable phase
 - Martensitic transformation

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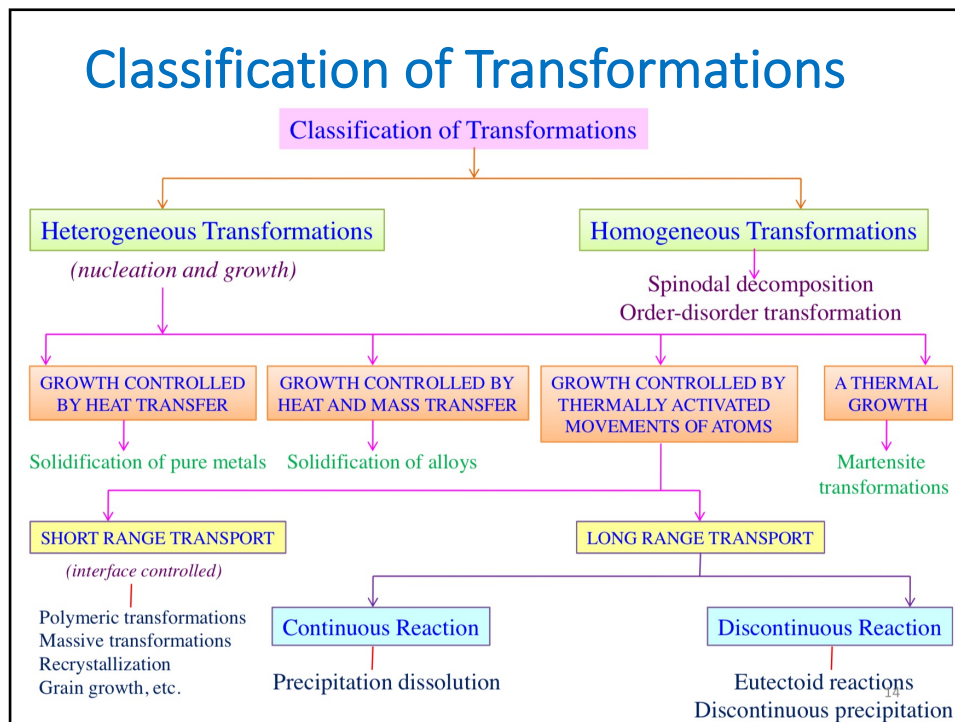
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The Kinetics of Phase Transformation

- The progress of a phase transformation can be broken down into two distinct stages:
 - Nucleation
 - Growth
- There are two types of nucleation :
 - Homogeneous
 - Heterogeneous
- The growth begins once an embryo has exceeded the critical size, r^*

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Classification of Transformations

- ❑ Phase transformations can be classified as homogeneous (transformations which take place through spinodal mechanism in which transformation takes place throughout the material) and heterogeneous (transformations which take place through nucleation and growth mechanism in which transformation takes place heterogeneously at a few places in the material at the start of the transformation).
- ❑ Transformations can also be classified as diffusional (or, so called, 'civilian') and diffusionless (or, so called 'military') depending on the mechanism. In civilian transformations, the nucleation and growth take place via diffusion assisted atomic motion. On the other hand, in the military transformation, the nucleation and growth is by shear and shuffle of atoms by less than one atomic displacement and the movement of all the participating atoms is coordinated.
- ❑ There are transformations which are thermally activated (which typically are based on diffusion) while there are others which are athermal.
- ❑ The transformations can also be diffusion controlled or interface controlled.
- ❑ Transformations can also be differentiated based on whether the interfaces formed are glissile or nonglissile.
- ❑ In some transformations there are compositional changes while in some other there are no composition changes.
- ❑ Further, transformations which are diffusional can either involve long range diffusion or short range diffusion.

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Fe-Fe₃C phase diagram

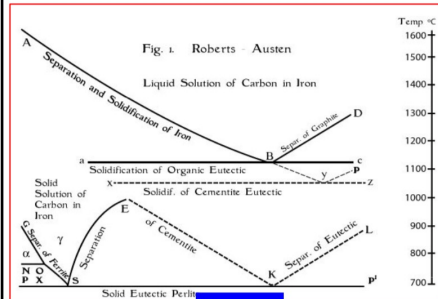


Figure 1

- Iron – carbon (Fe-C) diagram and first phase diagram of any alloy to be established, done by Roberts –Austen in 1898 after whom austenite came to be named. (Figure 1)

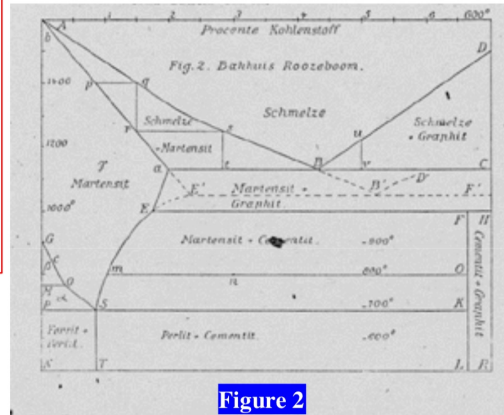


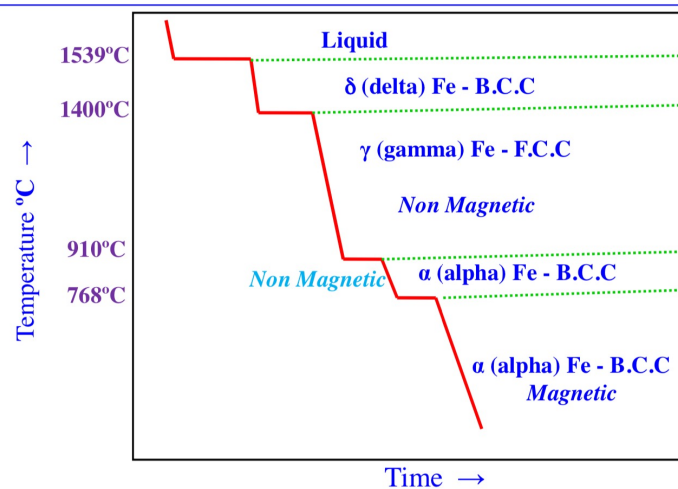
Figure 2

- The Iron Carbon diagram, adjusted by Bakhuis-Roozeboom in 1900. Notice line A-a and the temperature range between 1000 and 1100°C, where carbide formation was supposed to take place as the result of a chemical reaction between graphite and austenite (at that time called martensite)! (Figure 2)

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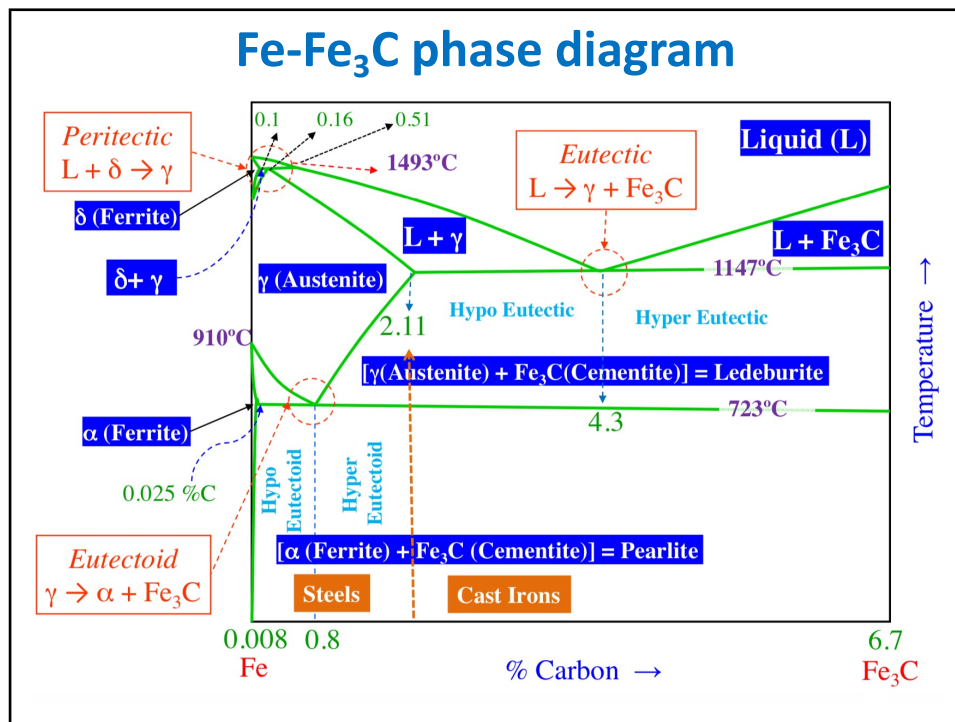
Allotropic Transformation in Iron

- Iron is an allotropic metal, which means that it can exist in more than one type of lattice structure depending upon temperature. A cooling curve for pure iron is shown below:



Can be other allotropic structures are possible....?

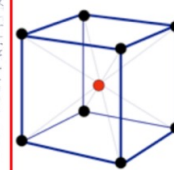
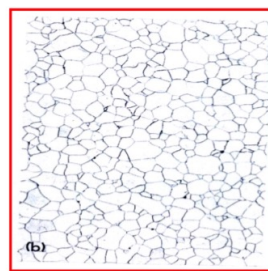
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Ferrite (α)

- Ferrite is known as α solid solution phase.
- It is an interstitial solid solution of a small amount of C dissolved in α (BCC) iron.
- stable form of Fe below 912 °C
- The maximum solubility is 0.025 % C at 723°C and it dissolves only 0.008 % C at room temperature.
- It is the softest structure that appears on the diagram.

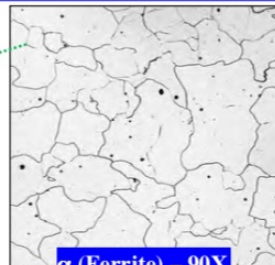
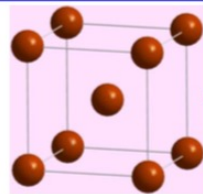


Ferrite

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Ferrite (α)

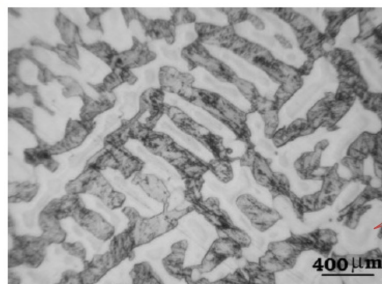
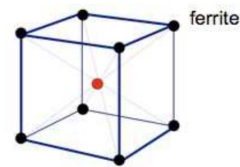
- ❑ It is an interstitial solid solution of a small amount of carbon dissolved in α iron. The maximum solubility is 0.025%C at 723°C and it dissolves only 0.008%C at room temperature. *It is the softest structure that appears on the diagram.*
- ❑ Ferrite is ferromagnetic at low temperatures but loses its magnetic properties with the rise of temperatures with major loss at curies temperatures, 768°C and above this temperature, it becomes non magnetic (paramagnetic).
- ❑ The crystal structure of ferrite (α) is B.C.C
- ❑ Tensile strength – 245 Mpa, Yield strength 118 Mpa
- ❑ Elongation – 40-50% in 2 in.
- ❑ Hardness - 95 VPN



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Ferrite (δ)

- ❑ Interstitial solid solution of carbon in iron of body centered cubic crystal structure. (δ iron) of higher lattice parameter (2.89Å) having solubility limit of 0.09 wt% at 1495°C with respect to austenite. The stability of the phase ranges between 1394-1539°C.
- ❑ It is a high temperature phase and is a high temperature manifestation of α ferrite.
- ❑ This is not stable at room temperature in plain carbon steel. However it can be present at room temperature in alloy steel specially duplex stainless steel.



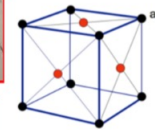
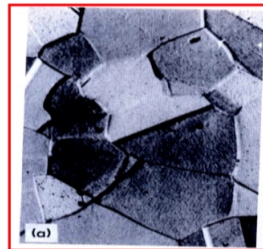
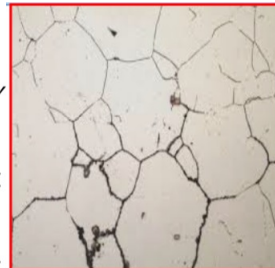
δ -ferrite in dendrite form
in as-cast Fe-0.4C-2Mn-
0.5Si-2 Al0.5Cu

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Austenite (γ)

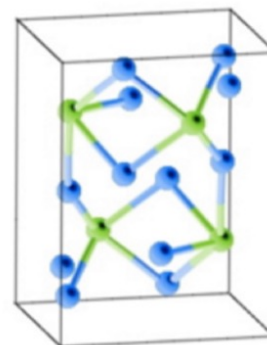
- **Austenite** is an interstitial solid solution of Carbon dissolved in γ (FCC.) Fe.
- Maximum solubility is 2.0 % C at 1130°C.
- High formability, most of heat treatments begin with this single phase.
- It is normally not stable at room temperature. But, under certain conditions it is possible to obtain austenite at room temperature.



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Cementite (Fe_3C)

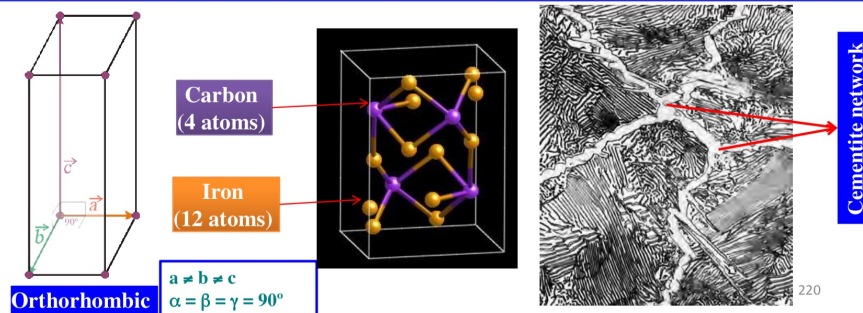
- **Cementite** or iron carbide, is very hard, brittle **intermetallic compound** of iron & carbon, as Fe_3C , contains 6.67 % C.
- It is the hardest structure that appears on the diagram, exact melting point unknown.
- Its crystal structure is **orthorhombic**.



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Cementite (Fe_3C)

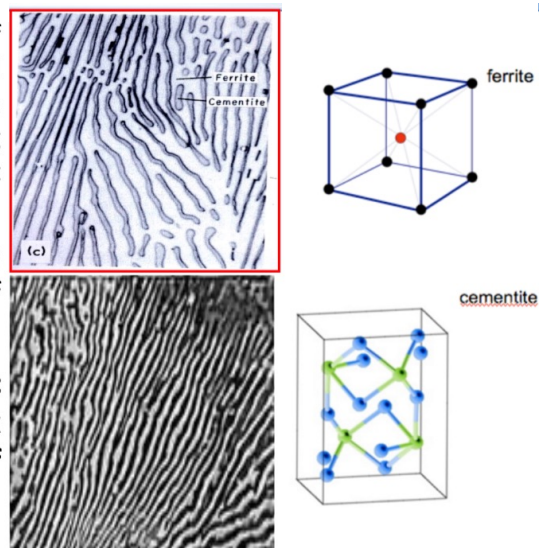
- ❑ Cementite or iron carbide, chemical formula Fe_3C , contains 6.67% C by weight and it is a metastable phase.
- ❑ It is typically hard and brittle interstitial compound of low tensile strength (35 Mpa) but high compressive strength and high hardness ~800 VHN.
- ❑ It is the hardest structure that appears on the diagram.
- ❑ It has a complex orthorhombic crystal structure with 12 iron atoms and 4 carbon atoms per unitcell.
- ❑ It is slightly ferromagnetic up to 210°C and paramagnetic above it. Melting point around 1227°C.



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Pearlite

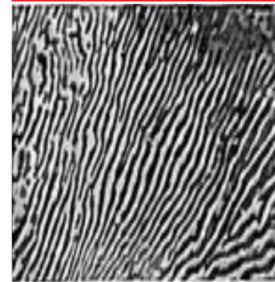
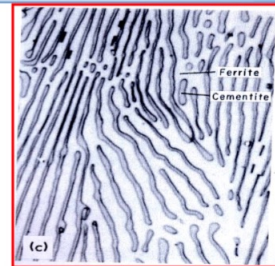
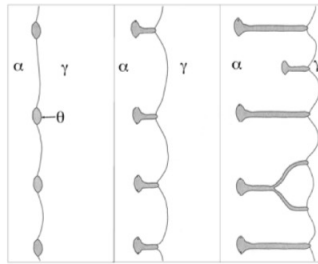
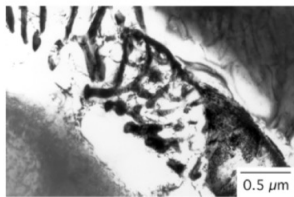
- **Pearlite** is in fact a mixture of two phases, ferrite and cementite (Fe_3C) and is the eutectoid mixture containing 0.80 % C and is formed at 723°C on very slow cooling.
- It is a very fine plate-like or lamellar mixture of ferrite and cementite.
- The **white ferritic background** or matrix contains **thin plates of cementite (dark)**.



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Definition of structures

Initiation of pearlite
(Howell)



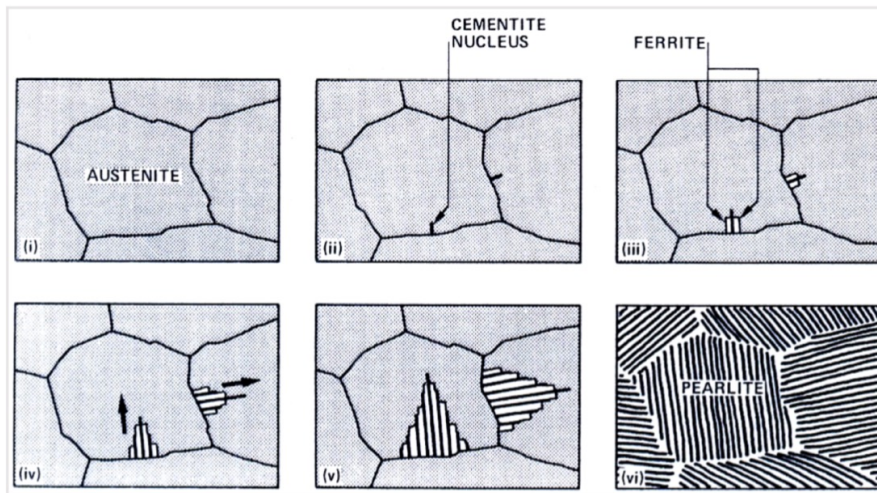
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Schematic Picture of the formation and growth of pearlite



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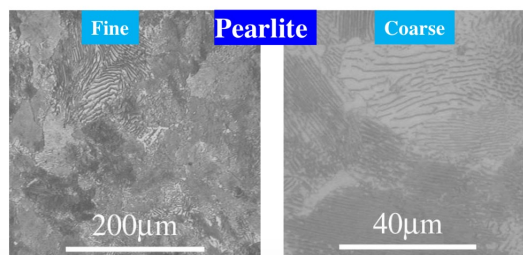
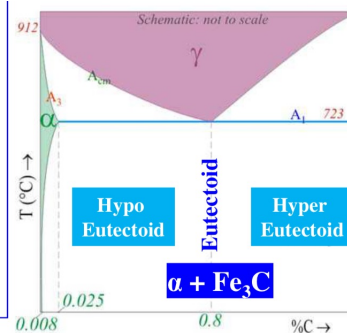
Nucleation & growth of pearlite



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Pearlite ($\alpha + \text{Fe}_3\text{C}$)

- ❑ Pearlite is the eutectoid mixture containing 0.80 %C and is formed at 723°C on very slow cooling.
- ❑ It is very fine platelike or lamellar mixture of ferrite and cementite. The fine fingerprint mixture called pearlite is shown in below figure.
- ❑ The weight % of these two phases are thus in ratio 8:1
- ❑ Tensile strength – 120,000 psi or 825 Mpa
- ❑ Elongation – 20 percent in 2 in.
- ❑ Hardness – HRC 20, HRB 95-100, or BHN 250-300



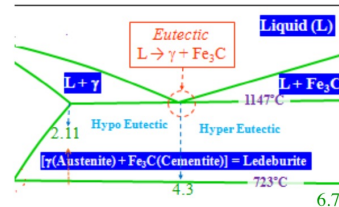
Remember...!
Pearlite is not a phase but combination of two phases (ferrite + cementite)

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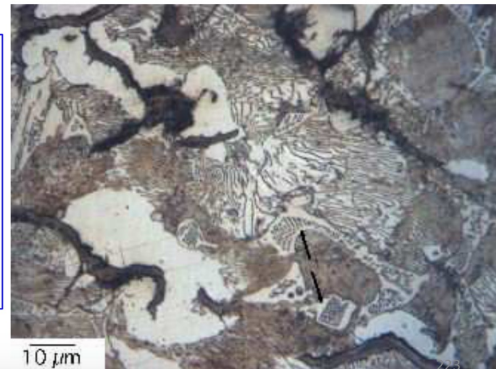
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Ledeburite ($\gamma + \text{Fe}_3\text{C}$)

- ❑ Ledeburite is the eutectic mixture of austenite and cementite. It contains 4.3%C and is formed at 1147°C
- ❑ Structure of ledeburite contains small islands of austenite are dispersed in the carbide phase.
- ❑ Not stable at room temperature

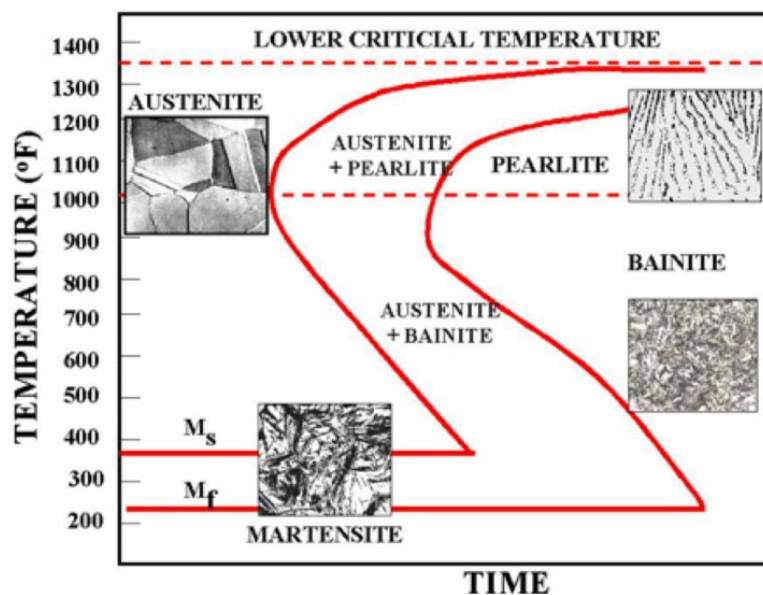


The pearlite is resolved in some regions where the sectioning plane makes a glancing angle to the lamellae. The ledeburite eutectic is highlighted by the arrows. At high temperatures this is a mixture of austenite and cementite formed from liquid. The austenite subsequently decomposes to pearlite.



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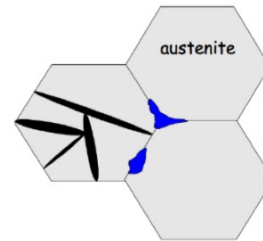
Temperature-Time-Transition Diagram



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Martensite

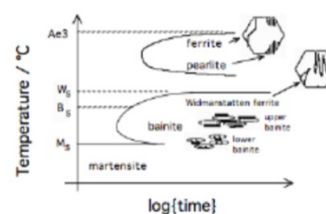
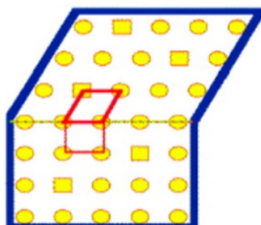
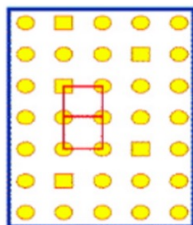
- **Martensite** - a super-saturated solid solution of carbon in ferrite.
- It is formed when steel is cooled so rapidly that the change from austenite to pearlite is suppressed.
- The interstitial carbon atoms distort the BCC ferrite into a BC-tetragonal structure (BCT).; responsible for the hardness of quenched steel



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Martensite

Martensite transformation begins when austenite is cooled to a temperature below M_s on the time-temperature-transformation diagram. It is a diffusionless transformation achieved by the deformation of the parent lattice into that of the product.



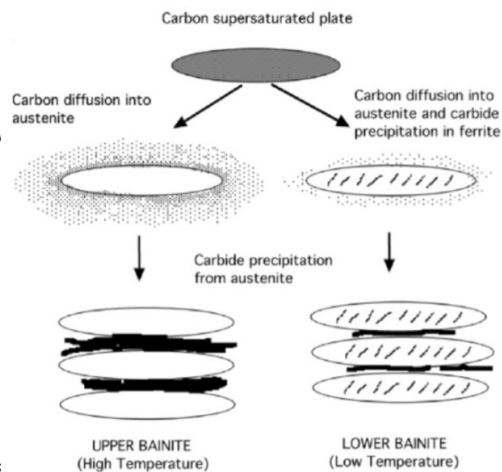
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Bainite

Bainite- The atomic mechanism of bainite is similar to that of martensite.

Plates of bainite form without any diffusion, but shortly after transformation, the carbon partitions into the residual austenite and precipitates as cementite between the ferrite platelets - this is the structure of upper bainite

Lower bainite is obtained by transformation at a lower temperature; the carbon partitioning is then slower, so some of the excess carbon has an opportunity to precipitate inside the ferrite plates and the rest of it precipitates from the carbon-enriched austenite as in upper bainite, Fig. 34.



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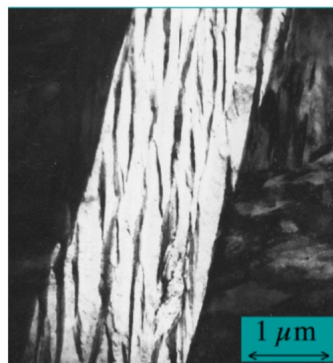


Figure 34: Upper bainite; the phase between the platelets of bainitic ferrite is usually cementite.

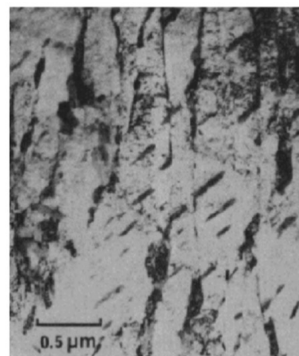



Figure 35: Lower bainite, with cementite inside the platelets and also between the platelets of bainitic ferrite.

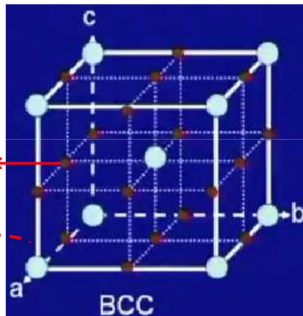
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Carbon solubility in Fe system

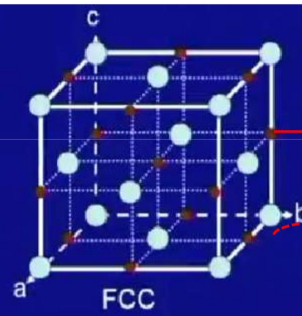


Solubility of carbon in Fe = f (structure, temperature)

Where is carbon located in iron lattice ?



BCC



FCC

Octahedral sites

6 faces sharing with two sides $(6/2)=3$
 12 edges sharing with four sides $(12/4)=3$
 Total sites is $(3+3)$, 6 per unit cell
 Every one Fe atom we have 3 interstitial sites

Octahedral sites

One interstitial site in center plus
 12 edges sharing with four sides $(12/4)=3$
 Total sites is $(1+3)$, 4 per unit cell
 Every one Fe atom we have 1 interstitial site

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Why concentration of carbon in α -Fe with BCC structure is less than γ -Fe with FCC structure?

- ❑ **FIRST LET US CONSIDER FCC STRUCTURE (γ -Fe)**
- ❑ Packing factor of FCC lattice 0.74
- ❑ This indicates the presence of voids. Let us discuss it more elaborately.
- ❑ In a FCC crystal there are mainly two types of voids:
- ❑ Tetrahedral: coordination number (CN) is 4. That means the void is surrounded by 4 atoms.
- ❑ Octahedral: CN is 6. That means the void is surrounded by 6 atoms.
- ❑ There are 8 tetrahedral voids in a unit cell. That means 2 voids per atom.
- ❑ There are 4 octahedral voids in a unit cell. That means 1 void per atom.
- ❑ However, impurities prefer to occupy octahedral voids.
- ❑ Because the ratio of the radius of the tetrahedral void to atom is 0.225 and the same for the octahedral void is 0.414.
- ❑ The ratio of the radius of the carbon atom (size is 77 pm) to Fe (when it has FCC crystal) is 0.596.
- ❑ So when a carbon atom occupies any void, lattice will be distorted to increase the enthalpy.
- ❑ Distortion will be less if it occupies the octahedral voids.
- ❑ Although it increases the enthalpy, carbon atoms will be present up to a certain extent because of the gain in entropy, as explained previously, which decreases the free energy ΔG .

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Carbon solubility in Fe system

FCC

Size of Fe atom
CCP crystal $r_{Fe}^{Fe} = 1.292 \text{ \AA}$

Size of the OV $x_{Fe}^{Fe}(oct) = 0.534 \text{ \AA}$

Size of Carbon atom $r^C = 0.77 \text{ \AA}$

BCC

Size of Fe atom
BCC crystal $r_{Fe}^{Fe} = 1.258 \text{ \AA}$

Size of the TV $x_{Fe}^{Fe}(d.tet) = 0.364 \text{ \AA}$

Size of the OV $x_{Fe}^{Fe}(d.oct) = 0.195 \text{ \AA}$

Relative sizes of voids w.r.t atoms

Note the difference in size of the atoms

Relative sizes of voids w.r.t atoms

Remember

❑ **FCC** Size of the largest atom which can fit into the tetrahedral is 0.225 and octahedral void is 0.414

❑ **BCC** Size of the largest atom which can fit into the *d.tetrahedral* is 0.29 and *d.octahedral* void is 0.154

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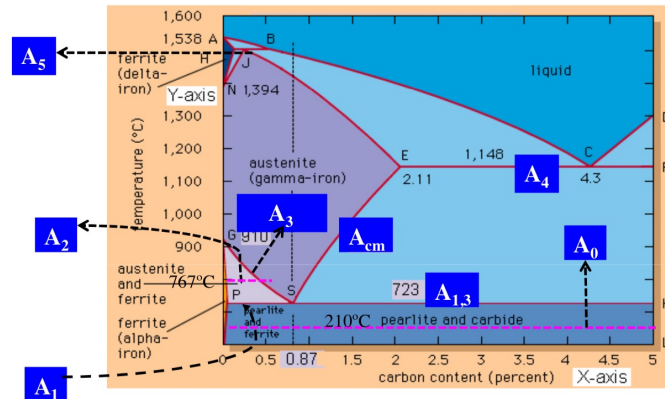
Why concentration of carbon in α -Fe with BCC structure is less than γ -Fe with FCC structure?

- ❑ **NOW LET US CONSIDER THE BCC UNIT CELL (α - Fe)**
- ❑ Packing factor of BCC lattice 0.68. So total void in a BCC unit cell is higher than FCC cell.
- ❑ However, there are 12 (6 per atom) tetrahedral and 6 (3 per atom) octahedral voids present. This number is higher than the number of voids present in a FCC unit cell.
- ❑ Unlike voids in FCC lattice, in a BCC lattice the voids are distorted. That means if an atom sits in a void, it will not touch all the host atoms.
- ❑ The ratio of the radius of tetrahedral void to atom is 0.29 and the radius of octahedral void to atom is 0.155.
- ❑ The ratio of the radius of the C atom (size is 77 pm) to Fe (when it has BCC crystal) is 0.612. So it is expected that in a BCC unit cell, impurities should prefer tetrahedral voids.
- ❑ However, although the octahedral void size is small, planar radius which has 4 atoms on the same plane is 79.6 pm, which is larger than the C atom size. That means it needs to distort only other two atoms.
- ❑ On the other hand if C sits in the tetrahedral void it has to distort all four atoms. So in α - Fe with BCC unit cell C occupies the octahedral voids
- ❑ Now the octahedral void size in γ -Fe (FCC) is higher than α -Fe (BCC). So naturally the distortion in a BCC cell will be higher and the activation energy for impurities to occupy a void in a BCC cell also will be higher.
- ❑ This is the reason that we find much lower solubility limit of C in α -Fe.

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Critical Temperature lines



- ❑ In general, A_0 – Subcritical temperature, A_1 – lower critical temperature, A_3 – upper critical temperature, A_4 – Eutectic temperature, A_5 – Peritectic temperature and A_{cm} – γ/γ +cementite phase field boundary.
- ❑ While heating we denoted as Ac_1, Ac_2, Ac_3 etc., 'c' stands for *chauffage* (French word), which means heating and while cooling we denoted as Ar_1, Ar_2, Ar_3 etc., 'r' stands for *refroidissement*, (French word) which means cooling.

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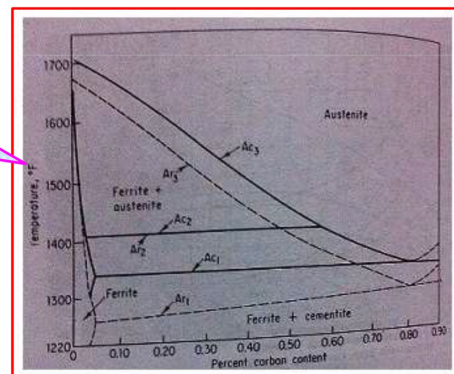
Critical Temperature lines

- ❑ The upper – and lower critical temperature lines are shown as single lines under equilibrium conditions and are sometimes indicated as A_{e3}, A_{e1} etc. When the critical lines are actually determined, it is found that they do not occur at the same temperature.
- ❑ The critical line on heating is always higher than the critical line on cooling. Therefore, the upper critical line of a hypo eutectoid steel on heating would be labeled A_{c3} and the same line on cooling A_{r3} . The rate of heating and cooling has a definite effect on the temperature gap between these lines.

The results of thermal analysis of a series of carbon steels with an average heating and cooling rate of 11°F/min are shown in figure.

Final word...! with infinitely slow heating and cooling they would probably occur at exactly the same temperature.

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