Iron-Iron carbide (Fe-Fe₃C) Phase Equilibrium Diagram

In this diagram weight % C is plotted along horizontal axis and temperature along vertical axis. The diagram shows the phases present at various temperatures for very slowly cooled Fe-C alloys with carbon content up to 6.67%.

Information given by the diagram:

1. Solid phases in the phase diagram
2. Invariant reactions in the phase diagram
3. Critical temperatures
4. Eutectoid, hypoeutectoid and hypereutectoid steels

1. **Solid phases in the Fe-Fe₃C phase diagram**: Four solid phases, namely α-Ferrite, Austenite, Cementite (Fe₃C), and δ-Ferrite.

(a) **α-Ferrite**: The solid solution of carbon in α-iron is called α-ferrite or simply ferrite.
- Stable between -273 -910 ºC.
- The phase has BCC structure
- Maximum solubility of carbon in α-ferrite (i.e. 0.025%) is at 723 ºC. The solubility of carbon in α-ferrite decreases with decreasing temperature until it is about 0.008% at 0 ºC.
- It is soft, ductile and highly magnetic.
- Density is 7.88 gm/cm³ and tensile strength is ~ 310 MPa.

(b) **Austenite**: The solid solution of carbon in γ-iron is called austenite.
- Stable between 910-1401ºC (2554 ºF).
- The phase has FCC structure
- The solubility of carbon in austenite reaches a maximum of 2% at 1130 ºC and then decreases to 0.8% at 723 ºC.
- It is soft and ductile
- Not ferromagnetic at any temperature.

(c) **Cementite or Iron carbide**: It is an intermetallic iron-carbon compound.
- Carbon in excess of solubility limit forms a separate phase called iron carbide (Fe₃C).
- In cementite crystal lattice the No. of Fe atoms are three times more than carbon atoms.
- Has negligible solubility limits and contains 6.67% C and 93.3% Fe.
- Has orthorhombic crystal structure with 12 Fe atoms and 4 C atoms per unit cell.
- Density is 7.6 gm/cm³
- As compared to ferrite and austenite, cementite is extremely hard and brittle.
- Magnetic below 210 ºC.

(d) **δ-Ferrite**: Solid solution of carbon in δ-iron is called δ-Ferrite.
- Stable between 1401-1539 ºC.
- Has BCC crystal structure.
- Maximum solubility of carbon in δ-Ferrite is 0.1 % at 1493 ºC.

(e) **Pearlite**: Pearlite is a 2 phased lamellar (layered) structure composed of alternating layers of ferrite (87.5 weight %) and cementite (12.5 weight %) that occurs in some steel and cast irons. When austenite is cooled below eutectoid temperature i.e. 723 C, it separates into
eutectoid mixture of ferrite and cementite called pearlite. At 0.8 %C the structure is completely pearlite.

2. Invariant reactions (Reactions with zero degree of freedom): an invariant reaction for a binary alloy is one occurring when 3 phases are in equilibrium at constant pressure. It has no degree of freedom and therefore, composition of phases and temperature of reaction are fixed.

(a) Eutectic reaction: involves liquid-solid transformation

\[
\text{Liquid (liquid solution of fixed composition)} \leftrightarrow \text{Solid 1 + Solid 2}
\]

\[
\begin{align*}
L & \leftrightarrow \alpha + \beta \\
\text{(cooling/heating)} & \text{(cooling/heating)}
\end{align*}
\]

In Fe-Fe\textsubscript{3}C phase diagram:

\[
L \leftrightarrow \gamma + \text{Fe}_{3}\text{C}
\]

(cooling/heating)

**Eutectic temperature** (the temperature below which the material is fully solid for all composition) = 1130 °C

**Eutectic composition** (the composition which remains fully liquid up to eutectic temperature during cooling) = 4.3 % C + 95.7 % Fe

(b) Eutectoid reaction: Reaction occurring in entirely solid state where liquid phase is replaced by a third solid phase \(\gamma\) is called as eutectoid reaction.

\[
\begin{align*}
\text{Solid 1} & \leftrightarrow \text{Solid 2 + Solid 3} \\
\gamma & \leftrightarrow \alpha + \beta \\
\text{(cooling/heating)} & \text{(cooling/heating)}
\end{align*}
\]

Number of solids formed are same as the number of components in the system.

In Fe-Fe\textsubscript{3}C phase diagram:

\[
\gamma \ (0.8 \% \text{C}) \leftrightarrow \alpha \ (0.025\% \text{C}) + \text{Fe}_{3}\text{C}
\]

(cooling/heating)

**Eutectoid temperature:** 723 °C

**Eutectoid composition:** 0.8 % C + 99.2 % Fe

(c) Peritectic reaction: Occurs during the solidification of some alloys.
In Fe-Fe$_3$C phase diagram:

\[
\begin{align*}
\delta + L & \xleftrightarrow{\text{(cooling/heating)}} \gamma \\
L + \beta & \xleftrightarrow{\text{(cooling/heating)}} \alpha
\end{align*}
\]

**Peritectic temperature:** 1493 °C  
**Peritectic composition:** 0.18 % C + 99.82 % Fe

(c) **Peritectoid reaction:** Transformation of two solids into a third solid. Peritectoid reactions are relatively rare. It does not occur in Fe-Fe$_3$C system, real example of this reaction are Co-W, Ni-Mo, FeO-Al$_2$O$_3$ systems.

\[
\begin{align*}
\text{Solid 1} + \text{Solid 2} & \xleftrightarrow{\text{(cooling/heating)}} \text{Solid 3} \\
\gamma + \beta & \xleftrightarrow{\text{(cooling/heating)}} \alpha
\end{align*}
\]

3. **Critical temperatures:**  
(a) **Upper Critical temperature** (A$_3$): Temperature below which ferrite starts to form as a result of ejection from austenite in hypoeutectoid alloys.  
(b) **Upper Critical temperature** (A$_cm$): Temperature below which cementite starts to form as a result of ejection from austenite in hypereutectoid alloys.  
(c) **Lower Critical temperature** (A$_1$): Temperature below which austenite does not exist.  
(d) **Magnetic transformation temperature** (A$_2$): Temperature below which $\alpha$-ferrite is ferromagnetic.

4.  
(a) **Eutectoid steel:** Steel containing 0.8 % C  
(b) **Hypoeutectoid steel:** Steel containing < 0.8 % C  
(c) **Hypereutectoid steel:** Steel containing > 0.8 % C (up to 2 % C)  
(d) **Eutectic cast iron:** Cast iron containing 4.3 % C  
(e) **Hypoeutectic cast iron:** Cast iron containing 2 - 4.3 % C  
(f) **Hypereutectic cast iron:** Cast iron containing 4.3 - 6.67 % C