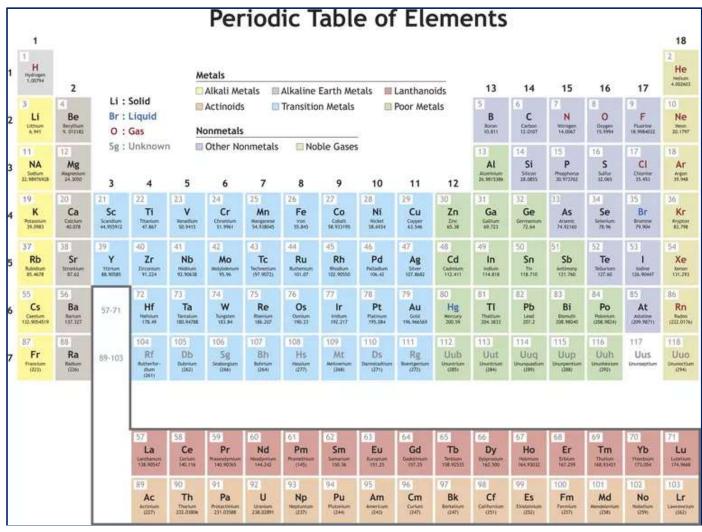
Material Science: Annealing



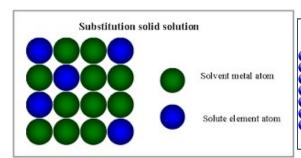
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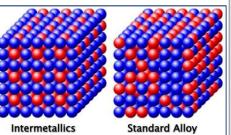
Alloys: An alloy is a blend of metallic elements prepared by mixing the molten components and then cooling the mixture to produce a metallic solid. Alloys may be homogeneous solid solutions, where atoms of one metal are distributed randomly among the atoms of the other, or they may be compounds with a definite composition and internal structure. Alloys typically form from two electropositive metals. Solid solutions are classified as either 'substitutional' or 'interstitial'.

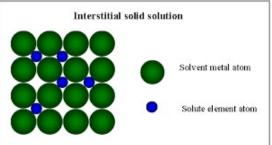
A substitutional solid solution is a solid solution in which atoms of the solute metal occupy some of the locations of the solvent metal atoms. E.g. brass An interstitial solid solution is a solid solution in which the solute atoms occupy the interstices (the holes) between the solvent atoms. E.g. carbon steel Substitutional solid solutions must fulfil these three criteria:

- 1. The atomic radii of the elements are within about 15% of each other.
- 2. The crystal structures of the two pure metals are the same: this similarity indicates that directional forces between the two types of atom are compatible with each other.
- 3. The electro(+ve) characters of the two elements are similar; otherwise compound formation, where e-s are transferred between species, would be more likely.

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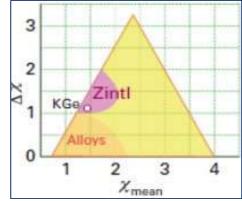






<u>Intermetallic compounds</u>: The third type of alloy are those_

in which the structure adopted is different from the structures of either component metal. E.g. β -brass (CuZn) and compounds of composition MgZn₂, Cu₃Au, NaTl, and Na₅Zn₂₁. Intermetallic compounds containing a very electropositive metal in combination with a less electropositive metal (eg, Na/ Zn), and in a Ketelaar triangle



Ketelaar triangle

lie above the true alloys are called Zintl phases. These compounds are not fully ionic.

E.g. KGe. The Ketelaar triangle is an equilateral triangle with vertices designated metallic (M), ionic (I), & covalent (C), which quantifies the Periodic Table based on types of chemical bonding plotted with mean electronegativity vs.

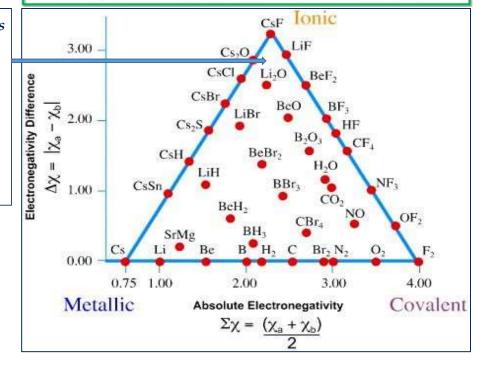
Gold difference in electronegativity.

These intermetallic compounds have higher melting point than either of the parent metal This higher melting point indicates the high strength of the chemical bond in intermetallic compounds

Intermetallics are compounds of two (or more) metallic elements that are held together by metal bonds. They show long range ordering, in other words they have a regularly repeating pattern. Compounds consist of a fixed ratio of atom.

Intermetallics tend to be brittle

Binary ionic materials have large electronegativity differences, typically $\Delta x > 3$, thus found at the top corner of Ketelaar triangle.



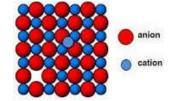
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Defects and their types: defects are formed because they introduce disorder into the lattice and the entropy rises. Formation of defects is endothermic and increases as the melting points of solids are reached. Defects are of two types:

1. Intrinsic point defects:

Schottky defect is a point defect in which an atom or ion is missing from its normal site in the structure. They occur in more ionic materials.

Frenkel defect is a point defect in which an atom or ion has been displaced onto an interstitial site. They occur in more covalent materials with low coordination numbers.



A third type is an atom-interchange or anti-site defect, which consists of an interchanged pair of atoms: neutral atoms exchange metal atoms in metal alloys.

2. Extrinsic point defects: are defects introduced into a solid due to doping with an impurity atom. E.g. introduction of As into Si to enhance the latter's semiconducting properties.

Defects in Heat Treatment

Heat treatment of steels or aluminium can lead to several defects. The principal types of defects found in quenching of steels are internal, external cracks in work, distortion & warping.

<u>Crack</u>: When the internal tensile stresses exceed the resistance of the steel to separation the crack occurs. The insertion of the tools in the furnace without preheating for tempering is one of the main causes of crack propagation. The crack formation is reduced by preheating the tool between 200°Cto 300°C.

<u>Distortion</u>: occurs due to uneven heating, too fast cooling, part incorrectly supported in furnace, incorrect dipping in quenching and stresses present before preheating. Distortion can be prevented by preheating the tool or check furnace capacity, reduce the hardening temperature, and by reviewing the method of dipping.

Warping: Asymmetrical distortion of the work is often called warping in heat-treating practice. Warping is usually observed upon non-uniform heating or over heating for hardening. It also occurs when the work is quenched in the wrong position and when the cooling rate is too high in the temperature range of the martensite transformation. An elimination of these causes should subsequently reduce warping.

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Design Guidelines in Heat Treatment

- 1. The properties required in the heat treated part are obtained without the parts being distorted beyond the acceptable limits.
- 2. The ideal design for a heat treatable part is the shape that when heated (or cooled) would have the same temperature at every point with in the part.
- 3. Abrupt change in the section sizes must be avoided.
- 4. Long thin parts like connecting rods are recommended to have symmetrical and rounded cross sections to reduce stresses.
- 5. Holes in a part are centred so that mass of metal surrounding them is equally balanced.
- 6. All internal corners in a part should be rounded, and non-cutting holes should have radii at the top or bottom surfaces.
- 7. The irregular shaped /unbalanced die sections are recommended for 2 piece construction.
- 8. The rounded corners at the base of the gear and ratchet teeth and at the bottom of keyways reduce heat treatment stress concentrations.
- 9. A sectional sprocket or gear design avoids stresses due to unbalanced sections.
- 10. Through holes provide more uniform section thickness and reduce heat treating problem course Instructor: Dr Bhar Saha

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Different heat treatment processes comprising heating and cooling operations or the sequence of two or more such operations are applied to any material in order to modify its metallurgical structure and alter its physical, mechanical, magnetic, electrical & chemical properties. Usually it consists of heating the material to some specific temperature, holding at this temperature for a definite period and cooling to room The basic steps of heat treatment are:

temperature or below with a definite rate.

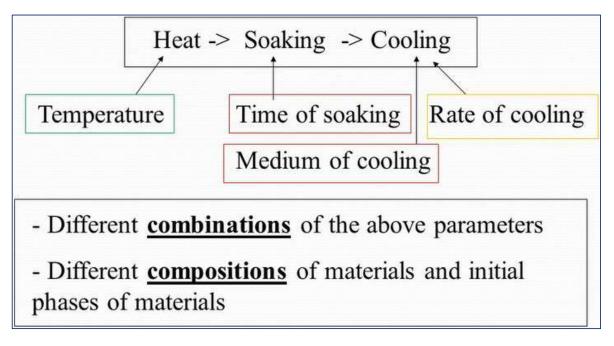
Heating — Soaking — Cooling

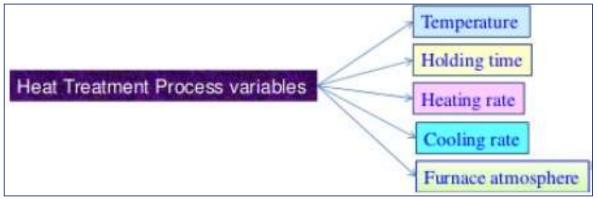
The four widely used heat treatment processes that affect the structure and properties, and carried out to meet the specific requirements are:

- Annealing
- Normalizing
- Hardening
- Tempering

The key to improve the material property is to change its structure **at atomic level**. This can be achieved through (i) **alloying** and (ii) controlled heat and cooling basically – **heat treatment**

Steels being the most widely used materials in major engineering fabrications, undergo various heat treatment cycles depending on the requirements. Also aluminium and nickel alloys are exposed to heat treatment for enhancement of properties.





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Quenching

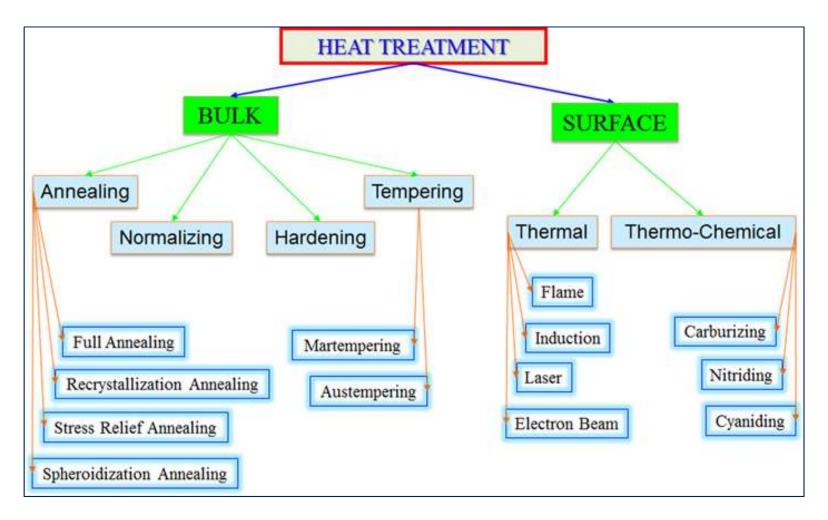
2,00000000				
Process	Variable	H Value		
Air	No agitation	0.02		
Oil quench	No agitation	0.2		
"	Slight agitation	0.35		
и	Good agitation	0.5		
"	Vigorous agitation	0.7		
Water quench	No agitation	1.0		
	Vigorous agitation	1.5		
Brine quench (saturated Salt water)	No agitation	2.0		
"	Vigorous agitation	5.0		
Ideal quench		00		

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 ∞ (\Rightarrow H = ∞) Severity of Quench as indicated by the heat

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

transfer equivalent H

 $f \rightarrow heat transfer factor$ $K \rightarrow Thermal conductivity$ Course Code: SC202
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The major objectives of heat treatment processes are:

- 1. To increase strength, harness and wear resistance (bulk hardening, surface hardening)
- 2. To increase ductility and softness (tempering, recrystallization annealing)
- 3. To increase toughness (tempering, recrystallization annealing)
- 4. To obtain fine grain size (recrystallization annealing, full annealing, normalising)
- 5. To remove internal stresses induced by differential deformation by cold working, non-uniform cooling from high temperature during casting and welding (stress relief annealing)
- 6. To improve machinability (full annealing and normalising)
- 7. To improve cutting properties of tool steels (hardening and tempering)
- 8. To improve surface properties (surface hardening, corrosion resistance-stabilising treatment and high temperature resistance-precipitation hardening, surface treatment)
- 9. To improve electrical properties (recrystallization, tempering, age hardening)
- 10. To improve magnetic properties (hardening, phase transformation)

Theory of annealing process

Annealing occurs by the diffusion of atoms within the steel material, so that the steel material progresses towards its equilibrium state. Heat increases the rate of diffusion by providing the energy needed to break bonds. The movement of atoms has the effect of redistributing and destroying the dislocations in the steel material. This alteration in dislocations allows steel material to deform more easily, so increases its ductility.

The amount of process initiating Gibbs free energy in a deformed steel material is also reduced by the annealing process. This reduction of Gibbs free energy is termed also as stress relief.

The relief of internal stresses is a thermodynamically spontaneous process. However, at room temperatures, it is a very slow process. The high temperature at which annealing occurs serve to accelerate this process.

The reaction that facilitates returning the cold worked steel material to its stress free state has many reaction pathways, mostly involving the elimination of lattice vacancy gradients within the body of the steel material.

The creation of lattice vacancies is governed by the Arrhenius equation, $k=Ae^{-\frac{E_a}{RT}}$ or $\ln k=-\frac{E_a}{RT}$ and the migration/diffusion of lattice vacancies are governed by Fick's laws of diffusion.

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Fick's first law relates the diffusive flux to the concentration under the assumption of steady state. It postulates that: the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient (spatial derivative), or in simplistic terms the concept that a solute will move from a region of high concentration to a region of low concentration across a concentration gradient. In one (spatial) dimension, the law is:

$$J = -D \, \underline{d\varphi}$$
$$dx$$

where

J is the "diffusion flux," of which the dimension is amount of substance per unit area per unit time, so expressed in such units as mol m^{-2} s^{-1} .

D is the diffusion coefficient or diffusivity. Its dimension is area per unit time, so units are m^2/s . φ (for ideal mixtures) is the concentration, of which the dimension is amount of substance per unit volume. It might be expressed in units of mol/m^3 .

x is position, the dimension of which is length. It might thus be expressed in the unit m.

Fick's second law predicts how diffusion causes the concentration to change with time.

It is a partial differential equation in one dimension:

$$\frac{d\varphi}{dt} = D \, \frac{d^2\varphi}{dx^2}$$

Where φ is the concentration in dimensions of [(amount of substance) length⁻³], mol/m³; $\varphi = \varphi(x,t)$ is a function that depends on location x and time t [s]

D is diffusion coefficient in dimensions of [area time⁻¹], m^2/s ; x is the position [length], m In two or more dimensions we must use the Laplacian $\Delta = \nabla^2$, which generalizes the second derivative, obtaining the equation

$$\frac{d\varphi}{dt} = D \Delta \varphi$$

$$\frac{d}{dt}$$
Linear expansion
$$\frac{\Delta L}{L_0} = \alpha \Delta T$$

$$\alpha_L = \frac{1}{L} \frac{dL}{dT}$$

$$\alpha_A = \frac{1}{A} \frac{dA}{dT}$$

$$\alpha_V = \frac{1}{V} \frac{dV}{dT}$$

$$\alpha_V = \frac{1}{V} \frac{dV}{dT}$$

Substances that expand at the same rate in every direction are called isotropic

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Steels: are alloys comprising iron, carbon, and some other elements.

They are classified according to the percentage of carbon they contain:

- 1. Mild steels contain up to 0.25 atom per cent C
- 2. Medium-carbon steels contain 0.25 to 0.45 atom per cent C
- 3. High-carbon steels contain 0.45 to 1.50 atom per cent C.

The addition of other metals to these carbon steels can have a major effect on the structure,

properties, and therefore applications of the steel.

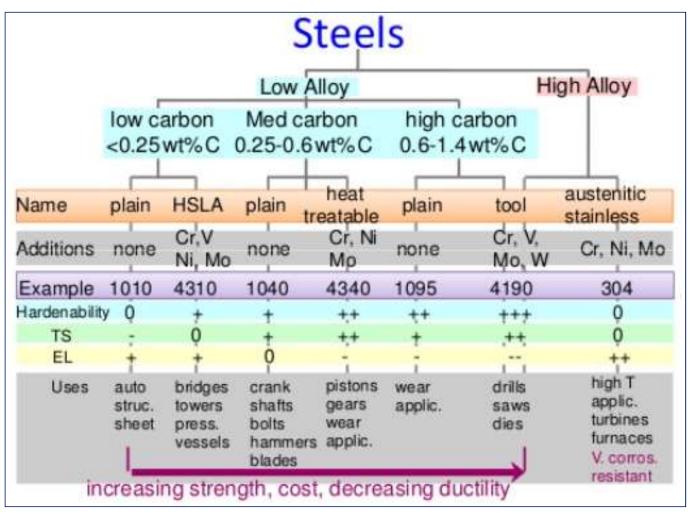
Metal	Atom percentage added	Effect on properties
Copper	0.2-1.5	Improves atmospheric corrosion resistance
Nickel	0.1-1	Benefits surface quality
Niobium	0.02	Increases tensile strength and yield point
Nitrogen	0.003-0.012	Improves strength
Manganese	0.2-1.6	Improves strength
Vanadium	Up to 0.12	Increases strength

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CLASSIFICATION OF STEELS

	Compositions, such as carbon (or non alloy), low-alloy, and alloy steels
	Manufacturing methods, such as converter, electric furnace, or electroslag remelting methods
0	Application or main characteristic, such as structural, tool, stainless steel, or heatresistant steels.
	Finishing methods, such as hot rolling, cold rolling, casting, or controlled rolling and controlled cooling.
	Product shape, such as bar, plate, strip, tubing, or structural shape
	Oxidation practice employed, such as rimmed, killed, semikilled, and capped steels.
	Microstructure, such as ferritic, pearlitic, martensitic, and austenitic
	Required strength level, as specified in the American Society for Testing and Materials (ASTM) standards.
	Heat treatment, such as annealing, quenching and tempering, air cooling (normalization), and thermo-mechanical processing.
	Quality descriptors and classifications, such as forging quality and commercial
	quality. Course Code: SC202 Presented by Course Instructor: Dr Bhar Saha

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Stainless steels are also classified by their crystalline structures, which are controlled by factors such as the rate of cooling following their formation in a furnace and type of added metal. Pure iron adopts different polymorphs depending on temperature and some of these high-temperature structures can be stabilized at room temp in steels or by quenching (cooling very rapidly).

Austenite is a solid solution of carbon and iron that exists in steel above 723°C and is ccp iron $(\gamma$ -Fe) with about 2 per cent of the octahedral holes filled with carbon. On cooling, it breaks down into other materials including ferrite and martensite as the solubility of carbon in the iron drops to below 1 atom per cent.

Ferrite is α -Fe with only a very small level of carbon, less than 0.1 atom %, with a bcc iron crystal structure. They contain between 10.5 and 27 atom per cent Cr and some Mo, Al, or W. **Martensitic** crystal structure is closely related to ferrite but the unit cell is tetragonal not cubic.

Cementite, Fe_3C , is a major constituent of steel and cast iron.

Utilize heat treatments to design optimum microstructures and mechanical properties (strength, ductility, ardness....)

Strength in steels correlates with how much martensite remains in the final structure

Iron Carbide (Fe₃C) or CEMENTITE which is important in the study of Iron- Carbon diagrams is an example of an interstitial compound.

The majority of steels rely on just two allotropes of iron: (1) α -Fe, which is **body-centered cubic** (BCC) ferrite, and (2) γ -Fe, which is **face-centered cubic** (FCC) austenite. At ambient pressure, BCC ferrite is stable from all temperatures up to 912 °C (the A_3 point), when it transforms into FCC austenite. It reverts back to ferrite at 1394 °C (the A_4 point). This high-temperature ferrite is labeled δ -Fe, even though its crystal structure is identical to that of α -Fe. The δ -Fe remains stable until it melts at 1538 °C. Regions with mixtures of two phases (such as ferrite + cementite, austenite + cementite, and ferrite + austenite) are found between the single-phase fields. At the highest temperatures, the liquid phase field can be found, and below this are the two-phase fields (liquid + austenite, liquid + cementite, and liquid + δ -ferrite). In heat treating of steels, the liquid phase is always avoided.

The **steel portion** of the Fe-C phase diagram covers the range between 0 and 2.08 wt. % C. The **cast iron** portion covers the range between 2.06 and 6.67 wt. % C.

The **steel portion** of the metastable Fe-C phase diagram can be subdivided into 3 regions:

- **1.** *Hypoeutectoid* (0 < wt. % C < 0.83 wt. %),
- **2.** Eutectoid (C = 0. 83 wt. %), &
- **3.** Hypereutectoid (0. 83 < wt. % C < 2.06 wt. %).

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- ❖ Alloys, containing up to 0.51% of carbon, start solidification with formation of crystals of δ-ferrite. Carbon content in δ-ferrite increases up to 0.09% in course solidification, and at 2719 °F (1493°C) remaining liquid phase and δ-ferrite perform peritectic transformation, resulting in formation of austenite.
- ❖ Alloys, containing carbon more than 0.51%, but less than 2.06%, form primary austenite crystals in the beginning of solidification and when the temperature reaches the curve ACM primary cementite stars to form.

Iron-carbon alloys, containing up to 2.06% of carbon, are called steels.

- ❖ Alloys, containing from 2.06 to 6.67% of carbon, experience eutectic transformation at 2097 °F (1147 °C). The eutectic concentration of carbon is 4.3%. In practice only hypoeutectic alloys are used. These alloys (carbon content from 2.06% to 4.3%) are called *cast irons* When temperature of an alloy from this range reaches 2097 °F (1147 °C), it contains primary austenite crystals and some amount of the liquid phase. The latter decomposes by eutectic mechanism to a fine mixture of austenite and cementite, called ledeburite.
- ❖ All iron-carbon alloys (steels and cast irons) experience eutectoid transformation at 1333 °F (723°C). The eutectoid concentration of carbon is 0.83%. When the temperature of an alloy reaches 1333 °F (733°C), austenite transforms to pearlite (fine ferrite-cementite structure, forming as a result of decomposition of austenite at slow cooling conditions).

Hypocutectoid steels (carbon content from 0 to 0.83%) consist of primary proeutectoid) ferrite (according to the curve A3) and pearlite.

Eutectoid steel (carbon content 0.83%) entirely consists of pearlite.

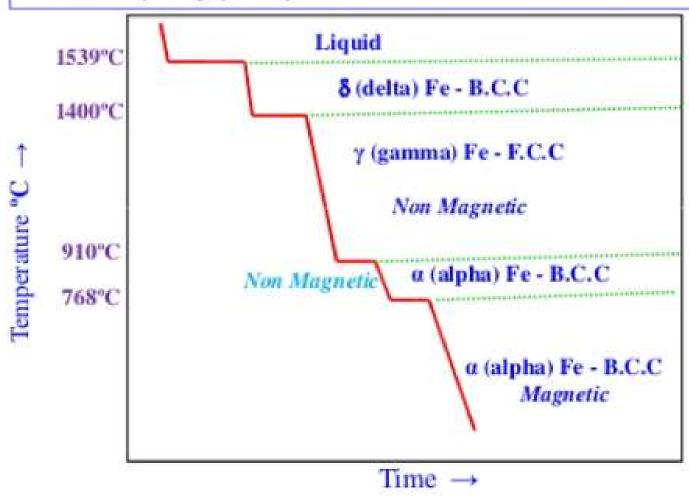
Hypereutectoid steels (carbon content from 0.83 to 2.06%) consist of primary (proeutectoid) cementite (according to the curve ACM) and pearlite.

Cast irons (carbon content from 2.06% to 4.3%) consist of proeutectoid cementite C2 ejected from austenite according to the curve ACM, pearlite and transformed ledeburite (ledeburite in which austenite transformed to pearlite.

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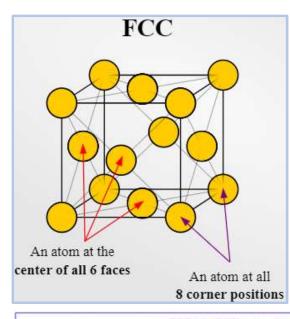
DIFFERENT ALLOTROPES OF IRON

Iron is an allotropic metal, which means that it can exist in more than one type of lattice structure depending upon temperature.



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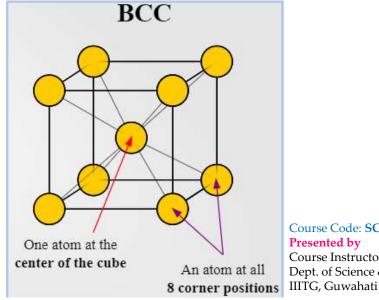


FCC STRUCTURE (y-Fe)

- 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
- 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.

BCC UNIT CELL (a - 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 that 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 g-Fe (FCC) is higher than a-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 a-Fe.



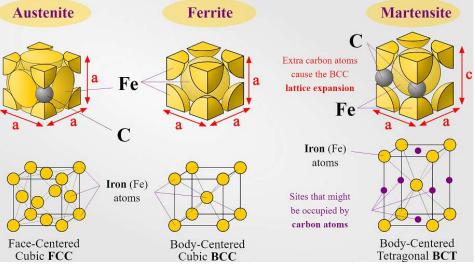
There are two types of interstitial voids that may become sites for carbon atoms in bcc and fcc structures.

In austenite, assuming spherical Fe atoms in contact, an octahedral site could accommodate an atom 0.052 nm (0.52 A°) in radius, but a tetrahedral site could accommodate an atom only 0.028 nm (0.28A°) in radius In ferrite, because of the limited number of carbon atoms that can be accommodated, the lattice remains essentially cubic.

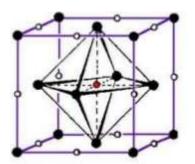
If large numbers of carbon atoms present in austenite are trapped in bcc octahedral sites by in the octahedral voids even though some rapid cooling, the cubic structure may actually lattice expansion is required. become tetragonal.

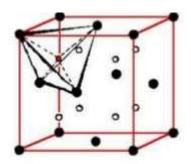
The latter structure typifies the phase "martensite".

Carbon atoms have radii of 0.07 nm (0.7 A°), and are therefore more readily accommodated



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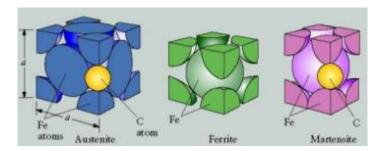
		Radius	Radius in iron (Å)
bec	Tetrahedral	0.29r	0.37
	Octahedral	0.15r	0.19
fcc	Tetrahedral	0.23r	0.28
	Octahedral	0.41r	0.51

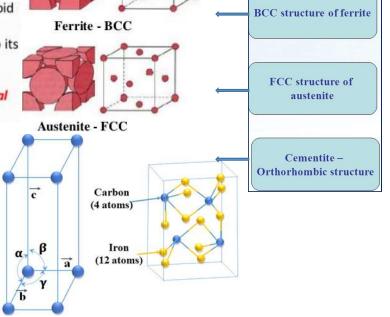
Octahedral Site

Tetrahedral Site

 Carbon goes into the octahedral sites (both in BCC and FCC) to avoid strain due to surrounding Fe atoms in Tetrahedral sites.
 (Strain due to C in octahedral site is less than tetrahedral sites due to its large size)

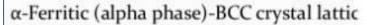
 Solubility of C in Austenite is larger than Ferrite because Octahedral site is larger in FCC than BCC.



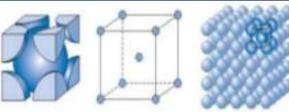


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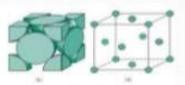


$$a = b = c$$
 $\alpha = \beta = \gamma = 90$



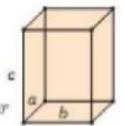
γ-Austenite (gamma phase)-FCC crystal lattice

$$a = b = c$$
 $\alpha = \beta = \gamma = 90^{\circ}$



δ- (delta phase)-BCC crystal lattice

$$a = b = c$$
 $\alpha = \beta = \gamma = 90^{\circ}$

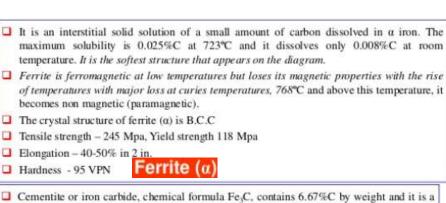


Fe₃C - Cementite phase - Orthorhombic

	A
$a \neq b \neq c$	$\alpha = \beta = \gamma = 90$

Туре		Crystal Structure	Temperature
Ferrite	α-iron	BCC	Room Temperature (Stable Form)
Austenite	γ-iron	FCC	@ 912 °C – 1394 °C
δ-ferrite		BCC	@ 1394 °C – 1538 °C
Liquid		No Crystal Structure	@1538 °C - above
Cementite	Fe_3C	Compound	

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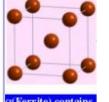
It is typically hard and brittle interstitial compound of low tensile strength (35 Mpa) but

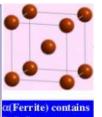
It has a complex orthorhombic crystal structure with 12 iron atoms and 4 carbon atoms per

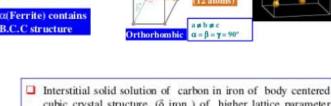
It is slightly ferromagnetic up to 210°C and paramagnetic above it. Melting point around

Cementite (Fe₂C)

- 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. Ferrite (δ)
- It is a high temperature phase and is a high temperature manifestation of α ferrite.







Carbon

(4 atoms

- It is an interstitial solid solution of a small amount of carbon dissolved in y iron and has FCC crystal structure. The maximum solubility is 2.1%C at 1147°C.
- Austenite is soft, ductile tough and malleable (FCC structure) and non magnetic (paramagnetic).
- Steels are commonly rolled and forged above about 1100°C when they are in austenite state due to its high ductility and malleability, which is also due to its FCC structure.
- Tensile strength 150,000 psi or 1035 Mpa
- Elongation 10% in 2 in.

metastable phase.

1227°C.

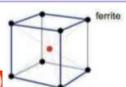
Hardness - 395 VPN and Toughness is high.

- Austenite (y)
- Liquid (L) Eutectic L -> y + Fe;C L+y Hypo Estectic Hyper Entertie [y(Austraite) + Fe3C(Cementite)] - Ledeburit
- Ledeburite is the eutectic mixture of austenite and cementite. It contains 4.3%C and is formed at 1147°C

high compressive strength and high hardness ~800VPN.

It is the hardest structure that appears on the diagram.

- Structure of ledeburite contains small islands of austenite are dispersed in the carbide phase.
- Not stable at room temperature Ledeburite (y+



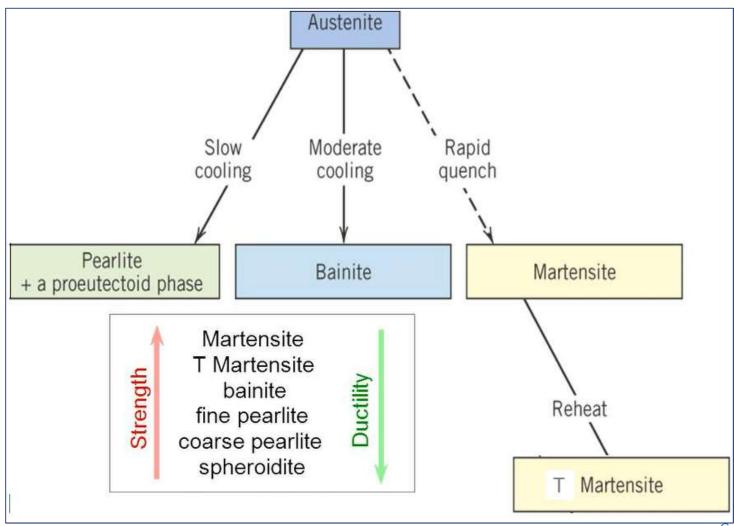
Pearlite (α+Fe₂C

- 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

Tensile strength - 120,000 psi or 825 Mpa Elongation - 20 percent in 2 in.

Hardness - HRC 20, HRB 95-100, or BHN 250-300 Code: SC202

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Microconstituent	Phases Present	Arrangement of Phases	Mechanical Properties (Relative)
Spheroidite α Ferrite + Fe ₃ C Relatively small Fe ₃ C sphere-like particles in an α -ferrite matrix		Soft and ductile	
Coarse pearlite	α Ferrite + Fe ₃ C	Alternating layers of α ferrite and Fe ₃ C that are relatively thick	Harder and stronger than spheroidite, but not as ductile as spheroidite
Fine pearlite	α Ferrite + Fe ₃ C	Alternating layers of α ferrite and Fe ₃ C that are relatively thin	Harder and stronger than coarse pearlite, but not as ductile as coarse pearlite
Bainite	α Ferrite + Fe ₃ C	Very fine and elongated particles of Fe ₃ C in an α-ferrite matrix	Hardness and strength greater than fine pearlite; hardness less than martensite; ductility greater than martensite
Tempered martensite	α Ferrite + Fe ₃ C	Very small Fe ₃ C sphere-like particles in an α-ferrite matrix	Strong; not as hard as martensite, but much more ductile than martensite
Martensite	Body-centered tetragonal, single phase	Needle-shaped grains	Very hard and very brittle

Properties of Different Phases of Steel				
Туре	Tensile Strength (psi)	Hardness (Rockwell)	Elongation (2 in.)	
Ferrite	40,000	C 0 or B 90	40 %	softest structure on the diagram small amount of carbon dissolved in α (BCC) iron Ferromagnetic & Fairly ductile
Pearlite	120,000	C 20 or B 95-100	20 %	α-Ferrite + Cementite
Austenite	150,000	~ C 40	10 %	normally not stable at room temperature. But, under certain conditions it is possible to obtain austenite at room temperature Carbon dissolved in γ (F.C.C.) iron Non-magnetic & ductile
Cementite	~ 5,000	Hardest struct Classified as o Orthorhombic	eramic in pure	

Microconstituent	Phases Present	Arrangement of Phases	Mechanical Properties (Relative)
Spheroidite	a-Ferrite + Fe ₃ C	Relatively small Fe ₃ C spherelike particles in an α -ferrite matrix	Soft and ductile
Coarse pearlite	α-Ferrite + Fe ₃ C	Alternating layers of α-ferrite and Fe ₃ C that are relatively thick	Harder and stronger than spheroidite, but not as ductile as spheroidite
Fine pearlite	a-Ferrite + Fe ₃ C	Alternating layers of α-ferrite and Fe ₃ C that are relatively thin	Harder and stronger than coarse pearlite, but not as duetile as coarse pearlite
Bainite	α-Ferrite + Fe ₃ C	Very fine and elongated particles of Fe ₃ C in an α-ferrite matrix	Harder and stronger than fine pearlite; less hard than martensite; more ductile than martensite
Tempered martensite	α-Ferrite + Fe ₃ C	Very small Fe ₃ C spherelike particles in an α-ferrite matrix	Strong: not as hard as martensite, but much more ductile than martensite
Martensite	Body-centered, tetragonal, single phase	Needle-shaped grains	Very hard and very brittle

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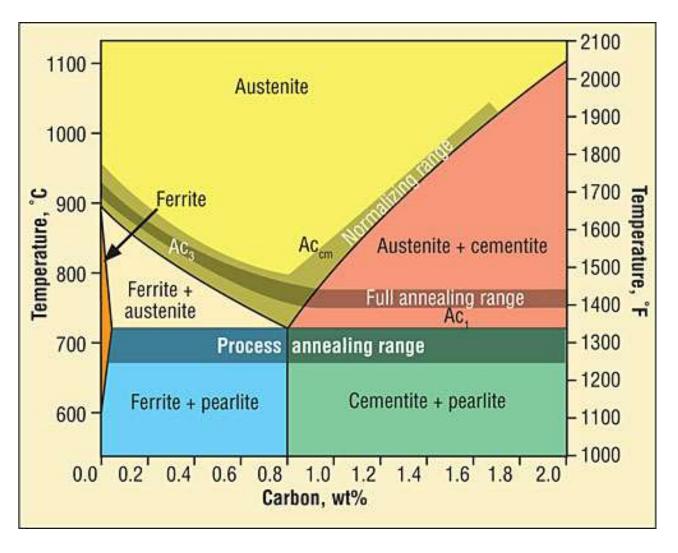
Phase Transformations

- By varying Temperature, Composition, and the external Pressure
- Temperature Changes by means of Heat Treatments are most conveniently utilized
- Crossing a Phase Boundary on the Composition–Temperature phase diagram as an alloy of given composition is heated or cooled
- Most phase transformations require some finite time to go to completion (to get the equilibrium state) – need to wait to finish
- The speed or rate is often important in the relationship between the heat treatment and the development of microstructure
- One limitation of phase diagrams is their inability to indicate the time period required for the attainment of equilibrium

Equilibrium vs Metastable

- The rate of approach to equilibrium for solid systems is so slow.
- Equilibrium conditions are maintained only if heating or cooling is carried out at extremely slow and unpractical rates.
- For other-than-equilibrium cooling, transformations are shifted to lower temperatures than indicated by the phase diagram. (Supercooling)
- for heating, the shift is to higher temperatures (Superheating)
- For many technologically important alloys, the preferred state or microstructure is a metastable one (e.g. Martensite)
- Intermediate between the initial and equilibrium states
- It thus becomes imperative to investigate the influence of time on phase transformations.

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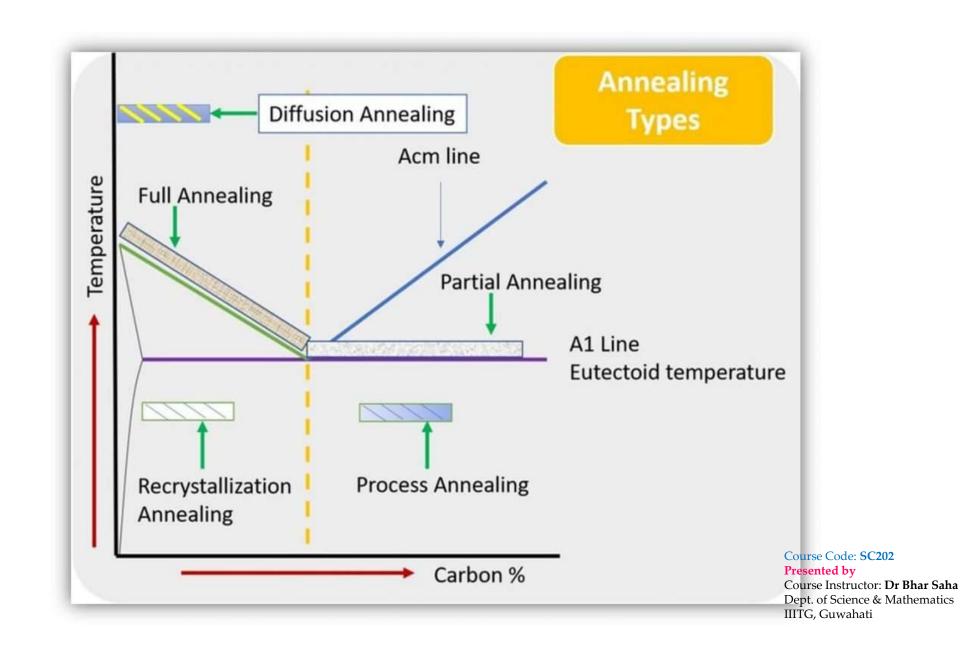
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A very important phase change in the metastable Fe-C phase diagram occurs at 0.68 wt. % C. The transformation is eutectoid, and its product is called **pearlite** (ferrite + cementite):

 γ -Fe (austenite) \rightarrow α -Fe (ferrite) + Fe₃C (cementite).

Some important boundaries at single-phase fields have include:

 A_1 — The so-called **eutectoid temperature**, which is the minimum temperature for austenite.

 A_3 — The lower-temperature boundary of the austenite region at low carbon contents; i.e., the gamma / gamma + ferrite boundary.

 A_{cm} — The counterpart boundary for high-carbon contents; i.e., γ -Fe / γ -Fe + Fe₃C boundary. Sometimes letters c, e, or r are also included:

 Ac_{cm} — In **hypereutectoid steel**, the temperature at which the solution of cementite in austenite is completed during heating.

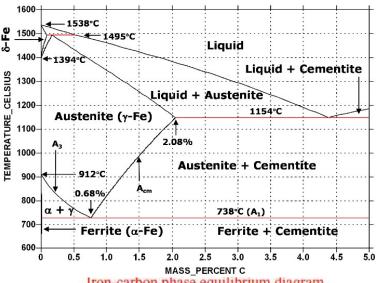
 Ac_1 — The temperature at which austenite begins to form during heating, with the c being derived from the French chauffant.

 Ac_3 —The temperature at which transformation of ferrite to austenite is completed on heating.

• Ae_{cm} , Ae_1 , Ae_3 — The temperatures of phase changes at equilibrium.

molybdenum, tungsten, etc) increase the A_1 temperature.

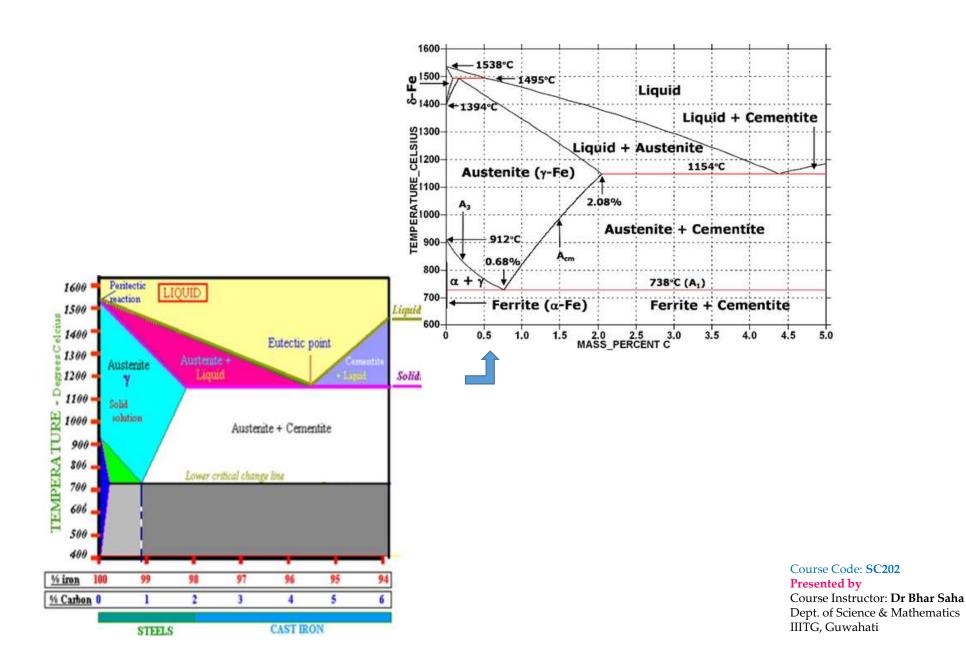
- Ar_{cm} In hypereutectoid steel, the temperature at which precipitation of cementite starts during cooling, with the \mathbf{r} being derived from the French refroidissant.
- Ar_1 The temperature at which transformation of austenite to ferrite or to ferrite plus cementite is completed during cooling.
- Ar_3 The temperature at which austenite begins to transform to ferrite during cooling.
- Ar_4 The temperature at which delta-ferrite transforms to austenite during cooling. If alloying elements are added to an iron-carbon alloy (steel), the position of the A_1 , A_3 , and A_{cm} boundaries, as well as the eutectoid composition, are changed. In general, the **austenite-stabilizing elements** (e.g., nickel, manganese, nitrogen, copper, etc) decrease the A_1 temperature, whereas the **ferrite-stabilizing elements** (e.g., chromium, silicon, aluminium, titanium, vanadium, niobium,
- M_s The highest temperature at which transformation of austenite to martensite starts during rapid cooling.
- \bullet M_f The temperature at which martensite formation finishes during rapid cooling.

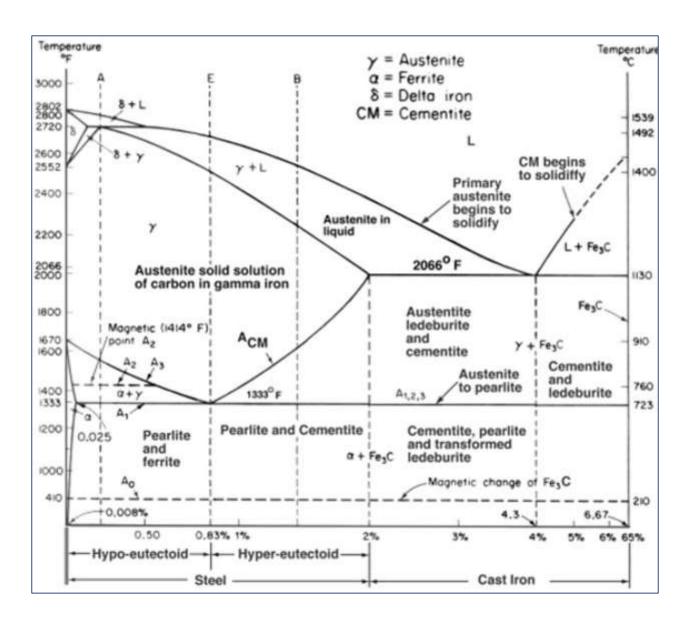


The Fe-C phase diagram shows which phases are to be expected at metastable equilibrium for different combinations of carbon content and temperature. The metastable Fe-C phase diagram is calculated using Thermo-Calc [software package based upon a powerful Gibbs Energy Minimizer], coupled with PBIN thermodynamic database.

At the low-C end, we find ferrite (α -Fe), which can at most dissolve 0.68 wt. % C at 738°C, and austenite (γ -Fe), which can dissolve 2.08 wt. % C at 1154°C. The much larger phase field of γ -Fe (austenite) compared with that of α -Fe (ferrite) indicates clearly the considerably greater solubility of carbon in γ -Fe (austenite), the maximum value being 2.08 wt. % at 1154°C. The hardening of carbon steels, as well as many alloy steels, is based on this difference in the solubility of carbon in α -Fe (ferrite) and γ -Fe (austenite). At the C-rich side of the metastable Fe-C phase diagram we find cementite (Fe₃C). Of less interest, except for highly alloyed steels, is the δ -Fe at the highest temperatures.

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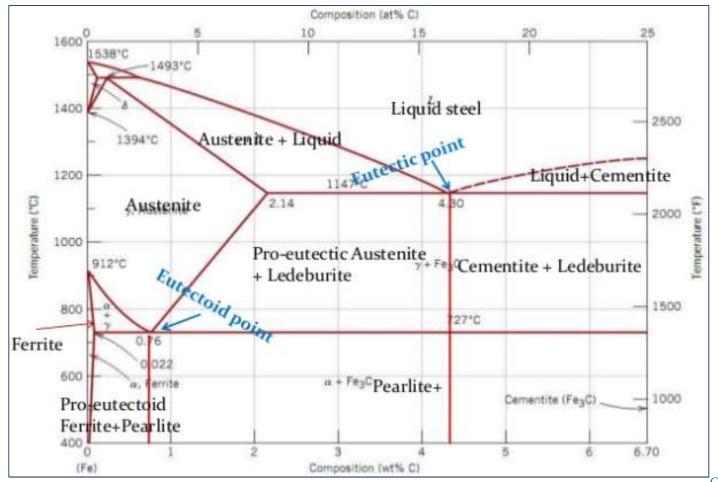
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Each C wt% on the X-Axis is a different alloy system

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Annealing

Annealing refers to a wide group of heat treatment processes and is performed primarily for homogenization, recrystallization or relief of residual stress in typical cold worked or welded components. Depending upon the temperature conditions under which it is performed, annealing eliminates chemical or physical non-homogeneity produced of phase transformations.

Important variants of annealing are:

- 1. Full annealing/ Conventional annealing
- 2. Isothermal annealing,
- 3. Spheroidize annealing,
- 4. Recrystallization annealing, &
- 5. Stress relief annealing

Defects in metals include holes (vacancies), dislocations and interstitial atoms. Annealing will promote the movement and eventual removal of these defects. This recovery generally takes place in discrete stages at certain temperatures corresponding to the annealing out of each type of defect. Recovery is complete after treatment at recrystallization temperature.

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Annealing: a heat treatment in which a material is exposed to an elevated temperature for an extended time period and then slowly/controlled cooled.

Causes

- Thermal factors (e.g., thermal stresses caused by temperature gradients within the workpiece during heating or cooling)
- 2. Mechanical factors (e.g., cold-working)
- 3. Metallurgical factors (e.g., transformation of the microstructure)

 Stress Relief: Reduce stress caused by:
 -plastic deformation

nonuniform cooling
 phase transform.

Spheroidize (steels):
 Make very soft steels for good machining. Heat just below T_E & hold for 15-25 h.

Types of Annealing Full Anneal (steels):
 Make soft steels for good forming by heating to get γ, then cool in furnace to get coarse P.

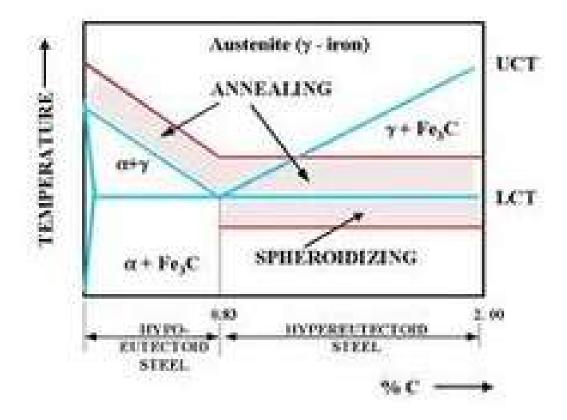
Process Anneal:
 Negate effect of cold working by (recovery/ recrystallization)

Normalize (steels):
 Deform steel with <u>large</u> grains, then normalize to make grains small.

Annealing temperature and the control cooling rate depend on the alloy composition and the type of the annealing treatment.

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Schematic representation of annealing operation

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Full Annealing

- For compositions less than eutectoid, the metal is heated above
 As line to form austenite
- For compositions larger than eutectoid, the metal is heated above A1 line to form austenite and Fe3C
- Cooled slowly in a furnace instead in air as in Normalizing.
 Furnace is switched off, both metal and furnace cool at the same rate

-Microstructure outcome: Coarse

Usually applied for low and medium C steel

Pearlite. In Normalizing, structure?

- -Structure is relatively softer than that in Normalizing
- -Full annealing is normally used when material needs to be deformed further.

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All structural changes from hardening, normalizing and tempering are eliminated by annealing.

- Relieving stresses
- Increasing softness, ductility, and toughness
- Producing a specific microstructure (homogenization)

Annealing process consists of

- 1. Heating to the desired temperature
- 2. Holding at a specified temperature
- 3. Cooling to room temperature

Full annealing /conventional annealing:

- 1. Heating the metal to above A_3 (upper critical temperature for ferrite) for hypoeutectoid steels (C content up to 0.83%) and above A_1 (lower critical temperature) for hypereutectoid steels (C content 0.83-2.00%) by 30-50°C.
- 2. Holding the steel component at this temperature for a definite soaking period of at least 20 mins/cm of the thick section to ensure temperature equalization through the cross-section of the component and complete austenization. Cool the hot steel component to room temperature slowly in the furnace (furnace cooling).

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Isothermal Annealing

- Hypoeutectoid low-carbon steels as well as medium-carbon structural steels are often isothermally annealed, for best machinability
- An isothermally annealed structure should have the following characteristics:
- 1. High proportion of ferrite
- 2. Uniformly distributed pearlite grains
- 3. Fine lamellar pearlite grains
- Austenitizing followed by a fast cooling to the temperature range of pearlite formation (usually abt 650°C.)
- Holding at this temperature until the complete transformation of pearlite
- and cooling to room temperature at an arbitrary cooling rate

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Isothermal annealing

- 1. Heating the steel components similar as in the case of full annealing.
- 2. Slightly fast cooling from usual austenitizing temp to a constant temp just below A_1 .
- 3. Holding at this reduced temp for sufficient soaking period for completion of transformation.
- 4. Cooling the steel component to room temperature in air. Figure depicts the heat treatment cycles of full annealing and isothermal annealing. The terms α , γ , P, P_S and P_F refer to ferrite, austenite, pearlite, pearlite starting and pearlite finish, respectively.

Isothermal annealing has distinct advantages over full annealing:

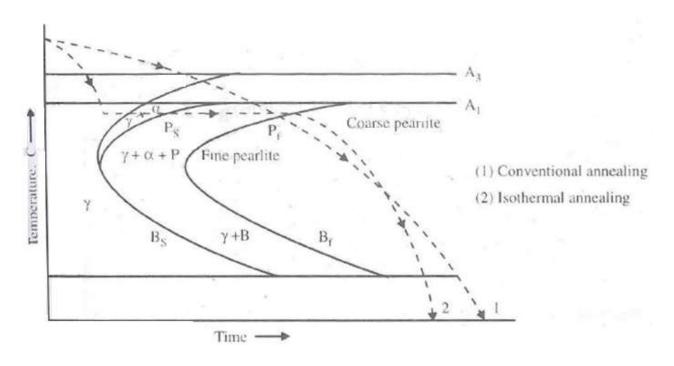
- Reduced annealing time, especially for alloy steels which need very slow cooling to obtain the required reduction in hardness by the full annealing.
- More homogeneity in structure is obtained as the transformation occurs at the same time throughout the cross section.
- Improved machinability and surface finish is obtained after machining as compared to that of the full annealed components.

Isothermal annealing is primarily used for medium carbon, high carbon and some of the allogourse Code: SC202

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Heat treatment cycles of full annealing and isothermal annealing

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Spheroidizing Annealing

- It is also called as Soft Annealing
- Any process of heating and cooling steel that produces a rounded or globular form of carbide
- It is an annealing process at temperatures close below or close above the A_{C_1} temperature, with subsequent slow cooling
- Such a soft structure is required for good machinability of steels having more than • Hold for several hours, o.6%C and for all cold-working processes • Slow cooling. that include plastic deformation.
- Spheroidite steel is the softest and most ductile form of steel

Process: A

- Heat the part to a temperature just below the Ferrite-Austenite line, line A₁ 727 °C.
- Hold the temperature for a prolonged time,
- · Fairly slow cooling. Or

Process: B

- Cycle multiple times between temperatures slightly above and slightly below the 727 °C line, say for example between 700 and 750 °C,
- Slow cooling, or

Process: C

- For tool and alloy steels heat to 750 to 800 °C,

The aim is to produce a soft structure by changing all hard constituents like pearlite, bainite, and martensite (especially in steels with carbon contents above 0.5% and in tool steels) into a structure of spheroidized carbides in a ferritic matrix

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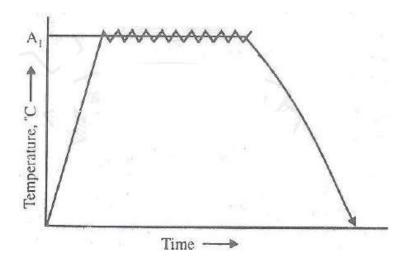
Spheroidizing - Mechanism

- The physical mechanism of soft annealing is based on the coagulation of cementite particles within the ferrite matrix, for which the diffusion of carbon is decisive
- Globular cementite within the ferritic matrix is the structure having the lowest energy content of all structures in the iron-carbon system
- The carbon diffusion depends on temperature and time
 - By heating alloy at a temp just below A1 (700C). If pre-cursor structure is pearlite, process time will range b/w 15 & 25Hrs
 - Heating alloy just above A1 line and then either cooling very slowly in the furnace or holding at a Temp just below A1
 - Heating & cooling alternatively within ±50C of the A1 line.

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Spheroidize annealing: is one of the variants of the annealing process that produces typical microstructure consisting of the globules (spheroids) of cementite or carbides in the matrix of ferrite. The following methods are used for spheroidize annealing: Holding the steel component at just below the lower critical temperature (A_1) transforms the pearlite to globular cementite particles. But this process is very slow and requires more time for obtaining spheroidized structure.



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Stress-Relief Annealing Process

- For plain carbon and low-alloy steels the temperature to which the specimen is heated is usually between 450 and 650°C, whereas for hotworking tool steels and high-speed steels it is between 600 and 750°C
- This treatment will not cause any phase changes, but recrystallization may take place.
- Machining allowance sufficient to compensate for any warping resulting from stress relieving should be provided
- In the heat treatment of metals, quenching or rapid cooling is the cause of the greatest residual stresses
- To activate plastic deformations, the local residual stresses must be above the <u>yield strength</u> of the material.
- Because of this fact, steels that have a high yield strength at elevated temperatures can withstand higher levels of residual stress than those that have a low yield strength at elevated temperatures
- Soaking time also has an influence on the effect of stress-relief annealing

New stresses that may be induced during cooling depend on the (1) **cooling rate**, (2) on the **cross-sectional size** of the workpiece, and (3)on the **composition of the steel**

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Recrystallization annealing

Recrystallization annealing process consists of heating a steel component below A_1 temperature i.e. at temperature between 625°C and 675°C (recrystallization temperature range of steel), holding at this temperature and subsequent cooling. This type of annealing is applied either before cold working or as an intermediate operation to remove strain hardening between multi-step cold working operations. In certain case, recrystallization annealing may also be applied as final heat treatment. The cold worked ferrite recrystallizes and cementite tries to spheroidize during this annealing process. Recrystallization annealing relieves the internal stresses in the cold worked steels and weldments, and improves the ductility and softness of the steel. Refinement in grain size is also possible by the control of degree of cold work prior to annealing or by control of annealing temperature and time.

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Tempering

Tempering is a heat treatment that reduces the brittleness of a steel without significantly lowering its hardness and strength. All hardened steels must be tempered before use The mechanism of tempering depends on the steel and the tempering temperature.

Tempering results in a desired combination of hardness, ductility, toughness, strength, and structural stability.

Martensite is a somewhat unstable structure.

- When heated, the Carbon atoms diffuse from Martensite to form a carbide precipitate and the concurrent formation of Ferrite and Cementite, which is the stable form.
- Tool steels for example, lose about 2 to 4 points of hardness on the Rockwell C scale. Even though a little strength is sacrificed, toughness (as measured by impact strength) is increased substantially.

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Tempering is achieved by heating hardened steel to a temperature below A_1 , which is in the range of 100° C to 680° C, hold the component at this temperature for a soaking period of 1 to 2 hours (can be increases up to 4 hours for large sections and alloy steels), and subsequently cooling back to room temperature.

The tempering temperature is decided based on the type of steel. Highly alloyed tool steels are tempered in the range of 500°C - 600°C, hold the component at this temperature for a soaking period of 1 to 2 hours (can be increases up to 4 hours for large sections and alloy steels), and subsequently cooling back to room temperature.

Low alloy construction steels are tempered above 400°C to get a good combination of strength and ductility.

Tempering process

- Tempering at temperatures 300°C 400°C.
- Soaking time varies (2 to 8 hr)s depending on the parts size.
- At these temperatures martensite transforms to trostite (very fine mixture of ferrite and cementite).
- Trostite is softer than martensite and more ductile.
- Tempering at temperatures higher than 400°C but lower than lower critical point (A₁).
 - Soaking time varies (2 to 8 hrs) depending on the parts size.
 - At these temperatures martensite transforms to sorbite (fine mixture of ferrite and cementite).
 - Sorbite and trostite are principally similar structures differing only in the particles size.
 - Sorbite is more more ductility and toughness, and less strong than trostite.

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- Tempering is done to toughen the metal by transforming brittle martensite or bainite into a combination of ferrite and cementite or sometimes Tempered martensite
- Tempered martensite is much finer-grained than just-quenched martensite
- The brittle martensite becomes tough and ductile after it is tempered.
- Carbon atoms were trapped in the austenite when it was rapidly cooled, typically by oil or water quenching, forming the martensite
- The martensite becomes tough after being tempered because when reheated, the microstructure can rearrange and the carbon atoms can diffuse out of the distorted bodycentred-tetragonal (BCT) structure.
- After the carbon diffuses out, the result is nearly pure ferrite with body-centred structure.

- Phase diagrams only show stable phases that are formed during slow cooling
- If cooling is rapid, the phase diagram becomes invalid and metastable phases may form
 - In the case of steel, the formation of ferrite and cementite requires the diffusion of carbon out of the ferrite phase.
- What happens if cooling is too rapid to allow this?
- The crystal lattice tries to switch from fcc (austenite) to bcc (ferrite).

Excess carbon → distorted body centred lattice (BCT)



Austempering

- Material is quenched above the temperature when Martensite forms M_s, around 215 °C (Eutectoid steel)
- Hold longer at this temperature, the Austenite transforms into Bainite
 - Tendency to crack is severely reduced.

Martempering

- Martempering is similar to
 Austempering except that the part is slowly cooled through the martensite transformation.
 - The structure is martensite, which needs to tempered just as much as martensite that is formed through rapid quenching.
 - The biggest advantage of Martempering over rapid quenching is that there is less distortion and tendency to crack.

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Hardening and Tempering

- Hardenability: is the ability of the Fe-C alloy to be hardened by forming martensite. Hardenability is not "hardness".
 - It is a qualitative measure of the rate at which hardness decreases with distance from the surface because of decreased martensite content.
- Hardenability depends on
 - Carbon content
 - Alloying elements
 - Geometry
 - Cooling media

Direct Hardening – Austenitizing and quench

- Austenitizing again taking a steel with .6% carbon or greater and heating to the austenite region.
- Rapid quench to trap the carbon in the crystal structure – called martensite (BCT)
- Quench requirements determined from isothermal transformation diagram (IT diagram).

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Conventional hardening process consists of four steps.

The first step involves heating the steel to above A_3 temperature for hypoeutectoid steels and above A_1 temperature for hypereutectoid steels by 50° C.

The second step involves holding the steel components for sufficient socking time for homogeneous austenization.

The third step involves cooling of hot steel components at a rate just exceeding the critical cooling rate of the steel to room temperature or below room temperature.

The final step involves the tempering of the martensite to achieve the desired hardness.

Applications of annealing:

Applications of annealing include design of engineering machinery and aircraft equipment

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Normalizing

- A heat treatment process consisting of austenitizing at temperatures of 30–80°C above the A_{C3} transformation temperature followed by slow cooling (usually in air)
- The aim of which is to obtain a fine-grained, uniformly distributed, ferrite-pearlite structure
- Normalizing is applied mainly to unalloyed and low-alloy hypoeutectoid steels
- For hypereutectoid steels the austenitizing temperature is 30–80°C above the A_{C1} or A_{Cm} transformation temperature

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The properties of normalized components are not much different from those of annealed components. However, normalizing takes less time and is more convenient and economical than annealing and hence is a more common heat treatment in industries. Normalizing is used for high-carbon (hypereutectoid) steels to eliminate the cementite network that may develop upon slow cooling in the temperature range from point A_{cm} (upper critical temperature for cementite) to point A_1 . Normalizing is also used to relieve internal stresses induced by heat treating, welding, casting, forging, forming, or machining. Normalizing also improves the ductility without reducing the hardness and strength.

The variation in the properties of the annealed and normalized components

Annealed Normalized

Slightly more hardness, tensile strength

Pearlite is coarse and usually gets resolved

by the optical microscope.

Grain size distribution is more uniform.

Less hardness, tensile strength and toughness.

Pearlite is fine and usually appears

unresolved with optical microscope.

Grain size distribution is slightly less

uniform.

Internal stresses are slightly more.

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Internal stresses are least.

T T T DIAGRAM TIME TEMPERATURE TRANSFORMATION

T (Time) T(Temperature) T(Transformation) diagram is a plot of temperature versus the logarithm of time for a steel alloy of definite composition. It is used to determine when transformations begin and end for an isothermal (constant temperature) heat treatment of a previously austenitized alloy. When austenite is cooled slowly to a temperature below LCT (Lower Critical Temperature), the structure that is formed is Pearlite. As the cooling rate increases, the pearlite transformation temperature gets lower. The microstructure of the material is significantly altered as the cooling rate increases. By heating and cooling a series of samples, the history of the austenite transformation may be recorded. TTT diagram indicates when a specific transformation starts and ends and it also shows the percentage of transformation of austenite at a particular temperature

TTT curve – principle for Martensite Formation

- eutectoid composition

- preheat or heat up alloy to austenite.

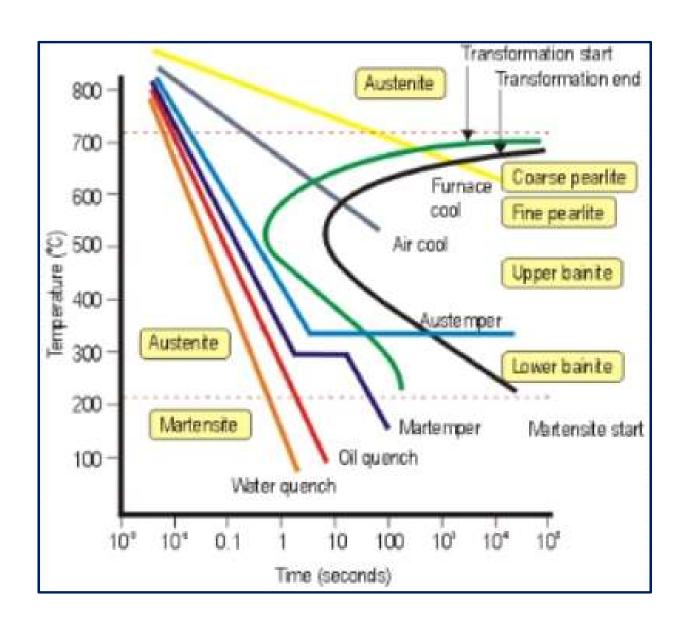
- austenite to various phases: cooling rate.

Pearlite, P; Bainite, B: alternative forms of ferrite-carbide mixtures

Martensite, M

Also called Isothermal Transformation Diagram

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Materials and equipment

Large ovens or furnaces are used for the annealing process.

Once the annealing process is successfully completed, metals/alloys are sometimes left in the oven so the parts cool in a controllable way.

Once removed from the oven, the metals/alloys are often quickly cooled off in a process known as quench hardening. Typical methods of quench hardening materials involve media such as air, water, oil, or salt. Salt is used as a medium for quenching usually in the form of brine (salt water). Brine provides faster cooling rates than water.

Surface heat treatment

Thermo chemical treatment
 Composition of part surface altered by addition of other elements
 Adding of carbon, nitrogen, or other elements
 Carburizing
 Nitriding

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