

## Lecture 31 - 36:

Heat treatment of steel: T-T-T diagram, Pearlitic, Martensitic & Bainitic transformation, effect of alloy elements on phase diagram & TTT diagram, CCT diagram, Annealing, normalizing, hardening & tempering, hardenability

### Questions:

1. If a piece of steel having 0.2% carbon is quenched after soaking at a temperature just above A1 what type of structure will you get? Estimate approximate constituents of phases present and their compositions.
2. In a hypothetical experiment on steel having 0.2%C, a sample after soaking above A3 is quenched in a lead bath at 800°C and the structural change is followed with time. Assume that after some time austenite ( $\gamma$ ) boundary is covered by a thin layer of ferrite ( $\alpha$ ) and it continues to grow. This is known to be a diffusion controlled process. (a) Draw carbon profile perpendicular to  $\alpha/\gamma$  interface after some time has elapsed. (b) Derive an approximate expression for the thickness of ferrite as a function of time (c) If diffusivity of carbon in austenite at 800°C is  $3 \times 10^{-12} \text{ m}^2/\text{s}^2$  plot thickness as a function of time.
3. Carbon atoms occupy octahedral interstitial sites in austenite and ferrite. Estimate fraction of these sites that are occupied in these if carbon contents are 0.1 and 0.01wt% respectively.
4. Use Fick's first law to derive an expression for growth rate of pearlite nodule.
5. Show that the inter-lamellar spacing of pearlite is inversely proportional to the degree of under cooling.
6. Microstructure of isothermally transformed pearlite should have identical spacing in all colonies. However often its microstructure often shows that lamellar spacing varies from colony to colony. Why is it so?
7. Use the extended volume concept to show that if diffusion controlled transformation proceeds at constant nucleation rate (N) and constant growth rate (G) to show that fraction transformed (f) in time t is given by  $f = 1 - \exp\left(-\frac{\pi}{3}NG^3t^4\right)$
8. The growth of pearlite nodule at a give temperature in eutectoid steel is known to follow the following relationship:  $f = 1 - \exp\left(-\frac{\pi}{3}NG^3t^4\right)$  where f is fraction transformed, t is time, N is nucleation rate and G is growth rate. Use this to explain the characteristic shape of TTT diagram and show that the average nodule size of Pearlite is proportional to:  $\left(\frac{G}{N}\right)^{\frac{1}{4}}$ .
9. Use the concept of Bain distortion to estimate maximum displacement experienced by iron atom during martensitic transformation. Lattice parameters of austenite and ferrite are 0.356nm & 0.286 respectively. Assume c/a ratio of martensite to be 1.15.
10. Name three most important characteristics of martensitic transformation in steel.
11. Explain why bainite does not form during continuous cooling in plain carbon steel.
12. Why do not you have long carbide plates like Pearlite in Baintite?

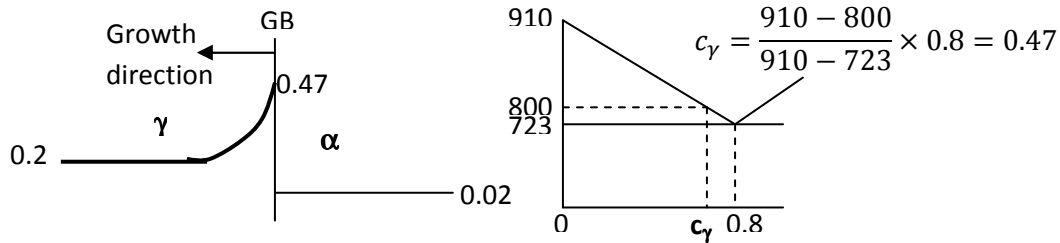
13. Use the equation given in the lecture note for total free energy change for nucleation of martensite and find out the expressions for critical nucleus size and activation hill.
14. Use the above expressions to estimate critical nucleus size and activation hill if  $\Delta G_v = -180\text{MJ/m}^3$ ,  $A = 3\text{ GPa}$ ,  $\gamma = 18\text{ mJ/m}^2$ .
15. Suggest a simple experimental method for determination of  $M_s$  temperature of steel if you have only facility for heat treatment and metallographic examination.
16. Which of the two would require more severe cooling rate to get fully hardened structure? (a) 0.8 % carbon steel (b) 1.0 % C steel.
17. A piece of steel which was quenched after prolonged holding at  $700^\circ\text{C}$  was found to have ferrite martensite structure. Explain when would you expect this to happen?
18. List the factors that determine the strength of properly hardened steel.
19. 0.2 % plain carbon steel in annealed condition has 25% coarse pearlite. If it is normalized (heat treatment) what changes would you expect in its microstructure?
20. A thin strip of 1.2% carbon steel is quenched in water from its fully austenitic state. What structure would you expect in this steel?
21. Cooling rate at the center of a steel rod on quenching in oil from  $850^\circ\text{C}$  is given by  $1.4 \times 10^4 \times d^{-1.9}$   $^\circ\text{C/s}$ , where  $d$  is diameter in mm. Which of the following steel would have 100% martensite at its centre if its diameter is 50mm? Critical cooling rate (CCR  $^\circ\text{C/sec}$ ) of steel to get 100% martensite is a function of composition. Assume that it is given by  $\log(\text{CCR}) = 4.3 - 3.3C + (Mn + Ni + Cr + Mo)/1.6$  (a) AISI 4340 steel having 0.4C, 0.7Mn, 1.8Ni, 0.8Cr, 0.25Mo (b) AISI 3130: 0.3C, 0.7Mn, 1.3Ni, 0.6Cr
22. Find out the diameters of the above steels (see problem 21) that would have 100% martensite at its center on quenching in the same medium.
23. Explain why thicker sections are more susceptible to cracking during hardening heat treatment.
24. Critical diameter of a certain grade of steel for oil quench, water quench and ideal quench are  $D_o$ ,  $D_w$  and  $D_i$  respectively. Arrange these in descending order.
25. List the factors that determine hardenability of steel. Which of these are preferred? Give reasons.
26. What is meant by severity of quench? List the factors that determine this. What is its dimension?
27. Give example of a shallow hardening and a deep hardening steel.
28. Martensite in Fe-30% Ni alloy is reversible but in most common grades of steel it is not reversible. Explain why it is so.
29. Hardness of a quenched and tempered steel is reported to be Rc 35. What additional test will you recommend to know that it has indeed been given this heat treatment?
30. It is apprehended that a hardened and tempered steel has become brittle. Suggest a suitable test to check if it is so.
31. Microstructure of a steel consists of 100% coarse pearlite. Its carbon content is reported to be 0.65%. Is this possible?
32. Diameter of a hardened 1.0% carbon steel rod is found to have increased on tempering. What will you infer from this?

33. A hardened steel has become embrittled on tempering. Can this be de-embrittled?

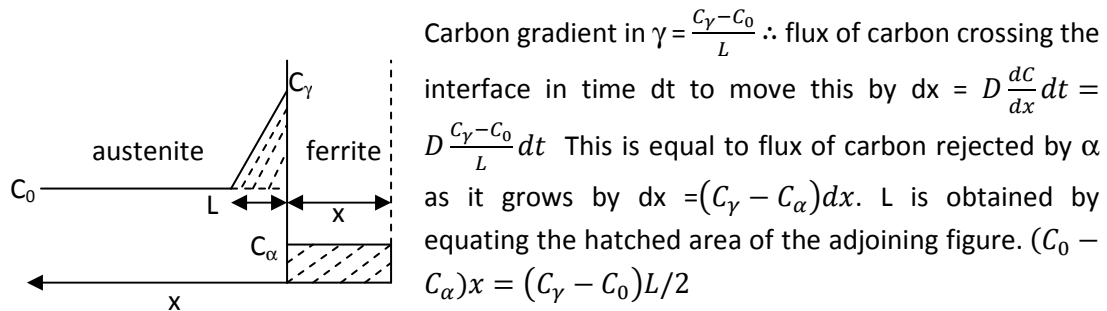
Answer:

1. A piece of steel when kept at just above A1 temperature will have ferrite and austenite. % ferrite =  $(0.8-0.2)/0.8 \times 100 = 75\%$ . Assumption: %C in austenite = 0.8% where as that in ferrite is negligible. If quenched 25% austenite present at soaking temperature will convert into Martensite. The structure at room temperature will consist of 75% ferrite and 25% Martensite having 0.8% carbon.

2. (a) Carbon profile on the two sides of  $\alpha/\gamma$  interface is as follows:



(b) To derive a simple relation we assume: densities of austenite and ferrite are the same. Therefore wt % = vol %. Area of interface = 1. Carbon gradient in austenite is constant. This is given by following sketch



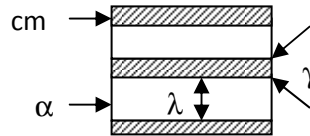
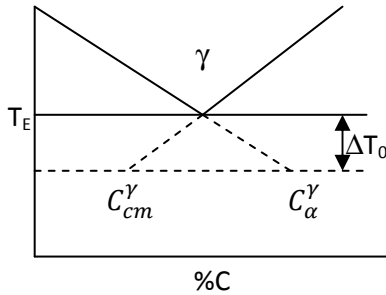
From the above one gets:  $(C_\gamma - C_\alpha)dx = D \frac{C_\gamma - C_0}{L} dt$  On substituting  $L : \frac{dx}{dt} = \frac{D}{2} \frac{C_\gamma - C_0}{C_\gamma - C_\alpha} \frac{C_\gamma - C_0}{C_0 - C_\alpha} \frac{1}{x}$  On integration thickness of ferrite layer at any time  $t = X^2 = D \frac{(C_\gamma - C_0)^2}{(C_\gamma - C_\alpha)(C_0 - C_\alpha)} t$

(c)  $X^2 = 10^{-12} \frac{(0.47-0.2)^2}{(0.47-0)(0.2-0)} t = 2.33 \times 10^{-12} t$  or  $X = 1.53 \times 10^{-6}$  Note that this estimate is valid only for short time.

3. Number of octahedral site in austenite = 1 / atom of Fe. Atomic wt of carbon = 12 and Fe = 56. Atom fraction carbon in austenite =  $\frac{0.1/12}{0.1/12 + 99.9/56} \approx \frac{0.1}{12} \times \frac{56}{100} \approx 0.0047$ . In one unit cell there are 4 Fe atoms and 4 interstitial sites. Fraction of these that are occupied = 0.0047. This mean amongst 100 unit cell the number of carbon atom is approximately 2 ( $\sim 100 \times 0.0047$ ).

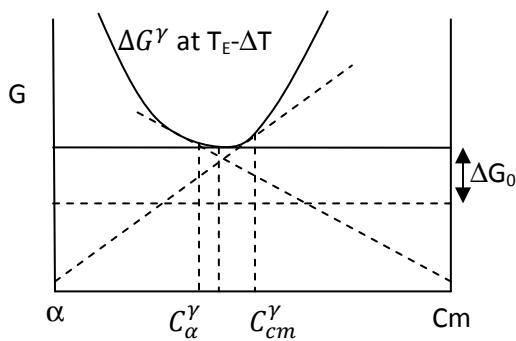
Whereas in ferrite the number of such sites / Fe atom = 3. Atom fraction carbon  $\approx \frac{0.01}{12} \times \frac{56}{100} = 0.00047$ . In one unit cell there are 2Fe atoms. Number of carbon atom = 0.00094. There are 6 sites / unit cell. Fraction of these that are occupied =  $0.00094/12 = 7.8 \times 10^{-5}$ . This means there is approximately one carbon atom in approximately 1000 unit cells.

4. Super cooling is necessary for Pearlite to nucleate:



Pearlite colony grows as carbon diffuses from  $\alpha / \gamma$  interface to  $cm / \gamma$  interface. Flux of C / unit area =  $G = D_C^{\gamma} \frac{C_{\alpha}^{\gamma} - C_{cm}^{\gamma}}{\lambda}$

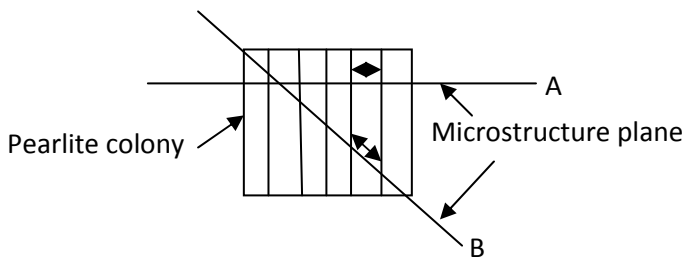
5. Super cooling is necessary to overcome activation hill arising due to creation of new surface.



For inter-lamellar spacing of  $\lambda$  the total interface area =  $2/\lambda \text{ m}^2 / \text{unit volume}$ .  $\Delta G$  for this to form is given by  $\Delta G_{\lambda} = -\Delta G_0 + \frac{2\sigma V_m}{\lambda}$  where  $V_m$  is molar volume,  $\sigma$  is surface energy and  $\Delta G_0$  is free energy for formation of pearlite having infinite inter lamellar spacing. The transformation will not occur unless  $\Delta G_{\lambda} < 0$ . Thus:

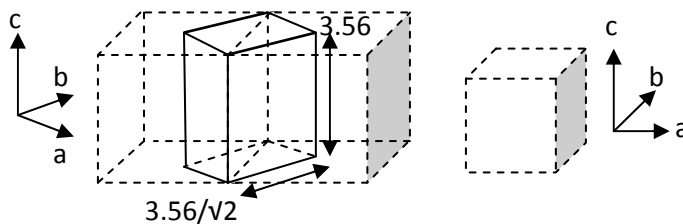
$$\lambda = \frac{2\sigma V_m}{\Delta G_0} = \frac{2\sigma V_m T_E}{\Delta H \Delta T_0}$$

6. Pearlite is made of alternate layers of ferrite and cementite. Ferrite plates being 7 times wider than cementite. Microstructure gives a sectional view. Colonies of Pearlite in a microstructure are randomly oriented. The plane of microstructure may intersect these at different angles. Wherever the plane is perpendicular to ferrite / cementite plates the spacing between two plates will be the minimum. Whereas those intersected at an angle will appear to have larger spacing. This is shown pictorially as follows:



On plane B spacing would appear significantly larger. If transformation occurs at a fixed temperature the minimum spacing is the correct estimate of lamellar distance.

7. Assume the shape of nuclei to be spherical. If both N & G are constant at any instant t. Number of new nuclei formed in time dt = Ndt. If G is the average growth rate the average radius of preexisting nuclei = Gt. Therefore increase in extended volume due to transformation:  $df_{ext} = \frac{4\pi}{3}(Gt)^3 Ndt$ . Since  $df = (1-f)df_{ext} \therefore df = (1-f)\frac{4\pi}{3}NG^3t^3$  Or, on integration  $f = 1 - \exp\left(-\exp\left(-\frac{\pi}{3}NG^3t^4\right)\right)$ .
8. Nucleation rate (N) depends on the degree of super cooling. Lower the transformation temperature higher is the magnitude of N. Whereas G depends on diffusion of carbon atoms in austenite which become slow if temperature is low. Therefore rate of transformation is the highest at intermediate temperature. It is reflected in the C shape of TTT diagram. To estimate nodule size assume that transformation is nearly complete say 95%. If it happens in time  $t_{0.95}$   $Gt_{0.95}$  is the average nodule radius. Since  $f = 1 - \exp\left(-\frac{\pi}{3}NG^3t^4\right)$  or,  $\left(\frac{\pi}{3}NG^3t^4\right) = \ln\left(\frac{1}{1-f}\right)$  Average diameter of nodule  $D = 2Gt$ . When  $f = 0.95$   $\ln\left(\frac{1}{1-f}\right) \approx 3$  &  $\frac{\pi}{3}NG^3t^4 = \frac{\pi}{48}\left(\frac{N}{G}\right)(2Gt)^4$ . Therefore on equating the two:  $D = \left[\frac{144G}{\pi N}\right]^{\frac{1}{4}}$ . We get finer nodule G is small & N is large. Finest Pearlite nodule is expected at the knee of the TTT diagram.
9. The following diagram shows how fcc austenite gets transformed into bct martensite. The cubes drawn in dotted line is austenite lattice. The tetragon drawn with firm line is bct unit cell with higher c/a ratio. It changes to martensite unit cell by contraction along c axis and expansion along the other two axes.



$$\text{Martensite: } c = 1.15 \times 2.86 = 3.29 \text{ \AA}$$

$$\Delta c = a_{\gamma} - c_M = 3.56 - 3.29 = 0.27$$

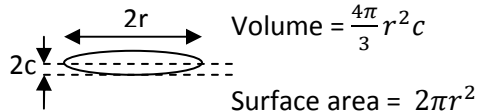
$$\Delta a = \frac{a_{\gamma}}{\sqrt{2}} - a_M = \frac{3.56}{\sqrt{2}} - 2.86 = -0.34$$

$$\text{Maximum displacement} = \sqrt{\Delta c^2 + \Delta a^2} = \sqrt{0.27^2 + 0.34^2} = 0.43 \text{ \AA}$$

10. Three most important characteristics of martensitic transformation in steel are (a) it is diffusion less there is no change in composition (b) it is athermal: takes place when temperature goes below a critical temperature and it processes as long as temperature decreases (c) it results in a product having very fine structure and high hardness.
11. Bainite is a low temperature eutectoid transformation. For it to form in steel it must be cooled below a critical temperature. This corresponds to the knee of TTT diagram. During continuous cooling once you avoid the knee unless you allow isothermal holding Bainite cannot form as it needs longer hold time since the reaction is very slow.

12. Bainite forms at low temperature where rate of carbon diffusion is very slow although nucleation rate is high because of high degree of super cooling. You have situation where there are more nuclei and limited (short) diffusion distance over which movement of carbon atom is possible. This is why you have platelets of cementite in Bainite.

13. Assuming that martensite nucleus has the shape of an oblate spheroid the expression for total free energy change is given by  $\Delta G = \frac{4\pi}{3}r^2c \Delta G_v + 2\pi r^2\phi \gamma + \frac{4\pi}{3}r^2cE_s$  where  $\gamma$  is surface energy and  $E_s$  is strain energy / unit volume.  $E_s$  is a function of the shape of nucleus:  $E_s = A \frac{c}{r}$ . Differentiating  $\Delta G$  with respect to  $r$  and  $c$  and equating these to zero one gets the critical size of nucleus.



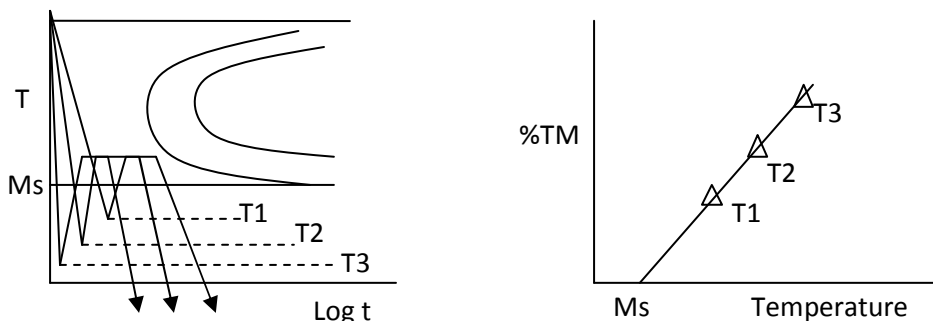
$$\frac{\partial \Delta G}{\partial r} = \frac{8\pi}{3}rc + 4\pi r\gamma + \frac{4\pi}{3}c^2A = 0$$

$$\frac{\partial \Delta G}{\partial c} = \frac{4\pi}{3}r^2 + \frac{8\pi}{3}c rA = 0$$

Solving the two equations one gets:  $c^* = -\frac{2\gamma}{\Delta G_v}$  and  $r^* = \frac{4\gamma A}{(\Delta G_v)^2}$  On substituting these in the expression for  $\Delta G$  one gets activation hill:  $\Delta G_v^* = \frac{32\pi}{3} \frac{A^2\gamma^3}{(\Delta G_v)^4}$

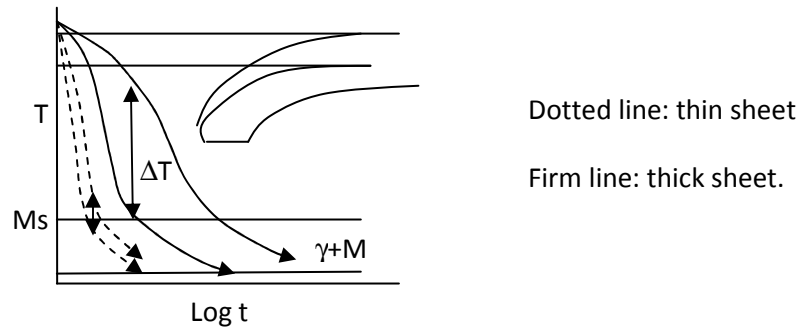
14. On substitution of the numerical values  $c^* = \frac{2 \times 18 \times 10^{-3}}{180 \times 10^6} = 0.2 \text{ nm}$ ,  $r^* = \frac{4 \times 18 \times 10^{-3} \times 3 \times 10^9}{180 \times 180 \times 10^{12}} = 6.6 \text{ nm}$  and  $\Delta G_v^* = \frac{32\pi}{3} \frac{9 \times 10^{18} \times 18 \times 18 \times 18 \times 10^{-9}}{(180 \times 10^6)^4} = 1.7 \times 10^{-18} \text{ J/nucleus} = 17 \text{ eV}$ . Note that such a large amount of energy is difficult to be provided by thermal fluctuation. At 700°K it amounts to  $kT = 0.06 \text{ eV}$  where  $k$  is Boltzmann constant. This indicates that homogeneous nucleation of Martensite is not possible. There is plenty of evidence that it takes place heterogeneously. Dislocations are the preferred sites. It is well known that cold work raises  $M_s$  temperature.

15. Austenitize a steel specimen, quench in baths maintained at a temperature close to its expected  $M_s$ , heat it again but placing it in another bath maintained at a little higher temperature, and then quench in water after holding it for some time. Repeat the same steps with different combination of the intermediate holding temperatures. Polish etch and examine the microstructures under microscope. If martensite forms at the first step cooling it will get tempered when it is put in higher temperature bath. Tempered martensite etches easily and it appears dark under microscope. Amount tempered martensite can be estimated. Plot % tempered martensite against intermediate quenching temperature. Extrapolate it to 0% tempered martensite. This gives an estimate of  $M_s$ . The experimental scheme is shown in the following figure for eutectoid steel.



16. Austenitization temperatures for both are same for hardening heat treatment. (a) being an eutectoid steel will have homogeneous austenite before quenching. Where as in (b) there will be cementite globules present which would provide sites for nucleation of pearlite. Therefore the latter would need more severe quenching to get fully hardened structure.
17. Eutectoid temperature of steel is a function of its composition. For plain carbon steel it is around 720°C. To get martensite the steel should be heated beyond this temperature. However presence of alloying elements which stabilize austenite (such as Mn, Ni) can bring down eutectoid temperature. In this case steel must be an alloy steel whose eutectoid temperature is less than 700°C. Therefore it must have been quenched from ferrite – austenite region and the austenite on quenching got transformed to martensite resulting in a ferrite – martensite structure.
18. A steel has maximum strength if has 100% martensite. This is obtained by quenching steel from austenitic state. Strength of martensite depends primarily on its carbon content. However the cooling rate needed to get 100% martensite in plain carbon steel is often difficult to achieve. Presence of additional alloy elements decreases critical cooling rate. Alloy steels are easy to harden. Therefore strength of hardened steel would depend on its carbon content, section size (thickness) and other alloy elements present & their amounts in the steel.
19. As against furnace cooling in the case of annealing the job is allowed to cool in air while normalizing. This being significantly faster normalized structure would have finer pearlite and a little less amount of ferrite. However the total amount of cementite would still be the same. Only the carbon content and therefore the amount of cementite in pearlite would decrease.
20. On quenching the microstructure of steel will consist of martensite and some retained austenite. Both  $M_s$  &  $M_f$  temperature of steel decreases with % carbon. Steels having beyond 0.7%C has subzero  $M_f$  temperature.
21. Cooling rate at the centre =  $1.4 \times 10^4 \times 50^{-1.9} = 8.28 \text{ }^\circ\text{C}/\text{sec}$ . CCR of the two steels are (a) 5.8  $^\circ\text{C}/\text{s}$  (b) 48.4  $^\circ\text{C}/\text{s}$ . Cooling rate is higher than CCR of (a) but lower than that of (b). Therefore (a) will have 100% martensite at its center.
22. (a)  $5.8 = 14000 \times d^{-1.9} \therefore d = \left(\frac{14000}{5.8}\right)^{1.9} = 60.5\text{mm}$  (b)  $d = \left(\frac{14000}{48.4}\right)^{1.9} = 20\text{mm}$
23. The difference in cooling rate between the centre and the surface is much more in a thicker section. As soon as the temperature at the surface crosses  $M_s$  temperature, martensite forms accompanied by volume expansion. The core is still soft austenite and can accommodate deformation if required. However later when its temperature goes below  $M_s$  it would expand, when outer core which is already transformed is hard and cannot accommodate deformation. A tensile stress therefore develops at the surface and it becomes prone to cracking. If thickness is

less the difference in temperature is not large. Transformation takes place almost simultaneously with little chance of developing high tensile stress at the surface. The following sketch illustrates this.



24.  $D_i, D_w, D_o$

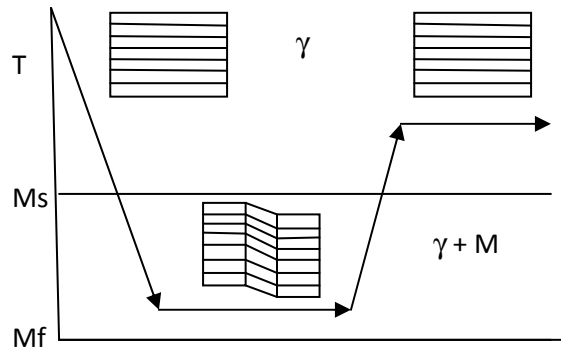
25. Hardenability increases with increasing carbon content, alloy addition (except cobalt), lower inclusion content and coarse austenite grain size. The first three are preferred. Finer grain size gives better crack resistance (toughness). Martensite formed in coarse austenite grain is more prone to cracking.

26. It is a measure of the rate at which heat can be extracted from the quenched steel. It is defined as the ratio of  $h/2k$  where  $k$  is the thermal conductivity of steel and  $h$  is convective heat transfer coefficient between steel and quenching medium. Dimension =  $\frac{\text{Joule}}{\text{m}^2 \text{K s}} \times \frac{\text{m}^2 \text{K}}{\text{Joule} \times \text{m}} = \frac{1}{\text{m}}$ . Therefore note that HD is a dimensionless quantity.

27. Most low carbon steels are examples of shallow hardening. Most alloy steels for tools and dies are examples of deep hardening steel. Many of these exhibit air hardening characteristics.

28. Martensitic transformation takes place through shear when temperature goes below  $M_s$ . There is no diffusion or change in composition. Therefore if the temperature is again raised beyond  $M_s$  it should go back to austenitic state. Most commercial steel has carbon. Martensite in these steel is susceptible to tempering if temperature is raised. Carbon precipitates as carbide. As a result composition changes. Therefore question of reverse martensitic transformation does not arise. However Fe-30Ni has little carbon. Here there is no precipitation. This is why it exhibits reverse martensitic transformation where it regains its original shape. Such alloys are known as shape memory alloys. This is shown schematically in the following sketch.





29. Examine its microstructure to see if it has tempered martensitic structure. Fine pearlite can also give similar hardness.
30. Best test to know if it has been embrittled to find out is the Charpy V notch impact test. If it has become brittle its CVN value will be low and fractured face will be predominantly cleavage with little notch root contraction.
31. Only eutectoid steel can have 100% pearlitic structure. Carbon content of eutectoid steel is a function of other alloying elements present in steel. It must be an alloy steel. Relatively fast cooling or isothermal transformation could give 100% pearlite. This possibility is ruled out since the pearlite is coarse.
32. 1% carbon steel is austenitized at 760°C and subsequently quenched during hardening. Since it has high carbon content it is likely that its Mf temperature is lower than room temperature. Therefore it would have some amount of retained austenite having a much more close packed structure than martensite. On tempering retained austenite would decompose to martensite. This transformation is accompanied by volume expansion. This is the most likely reason for increase in diameter.
33. Certain alloy steel on tempering at 350°-550°C may become embrittled. This is known as temper embrittlement. To de-embrittle the steel it must again be hardened and tempered at 600°C followed by quenching. Fast cooling will help avoid exposure to the temperature range susceptible to such embrittlement.