MME 415
Physical Metallurgy

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EXPERIMENT-1: RECOVERY AND RECRYSTALLIZATION

OBJECTIVE: To study the recrystallization behavior of pure metal (<u>Iron</u>).

THEORY: When metals are cold worked, most of the energy expended in the process appears as heat but a few percent is stored in the deformed metal structure. This stored energy acts as thermodynamic driving force which tends to return the metal to the undeformed state, provided the metal is at a temperature where the required reaction can occur at an observable rate.

Initially more gradual property changes may take place in the absence of appreciable change in microstructure. This phenomenon is recovery, which may be defined as property changes produced in cold-worked metal by heat-treating with times and temperatures that do not causes appreciable change in microstructure. During recovery, cold worked metals are heated at the relatively low temperatures during which more mobile imperfection like vacancies, interstitial existing in slip band are eliminated and that some dislocations of opposite sign may undergo annihilation. The relatively minor structure changes during recovery have pronounced effect on residual stresses. Thus, recovery may affect the course of subsequent recrystallization of a cold worked metal since in tendency towards recrystallization is lowered when appreciable recovery has occurred.

RECRYSTALLIZATION:

The energy stored during cold working of metal induces the state of transformation in the cold worked sample into a state tree from defects. One of the modes, in which this transformation, occurs involves the appearance of small defect free regions, called nucleons and the increase in the' size of these regions by the migration of their boundaries into the cold-worked region is called growth. Formation of the defect free states from the cold worked state in this mode is called recrystallization. Various parameters of the recrystallization reaction are considered below:

1. TIME: The volume fraction of the recrystallized region "X" can be approximated by the Johonson-Mehl equation:

$$X = 1-\exp(-kt^n) \qquad (1)$$

.... n = time exponent

Equation 1 suggests that the x vs t curve is sigmoidal. This equation can be written as:

$$\ln k \ldots\ldots + n \ln t = \ln [\ln \frac{1}{1-x}] \qquad (2)$$

Thus plotting $\ln t$ vs $\ln [\ln \frac{1}{1-x}]$ the exponent 'n' can be calculated.

TEMPERATURE: The recrystallization temperature can be defined as the temperature at which 50 % recrystallization occures in one hour. It mostly depends on the melting point and the impurities present in the metals. Generaly for pure metals recrystallization temperature is in the range of approximately 0.3 to 0.4 T_m and for alloys it is in the 0.5 T_m (T_m is the melting point). Fig (1) shows the various stages in recryatallization of strain free grain inside the deformed metal.
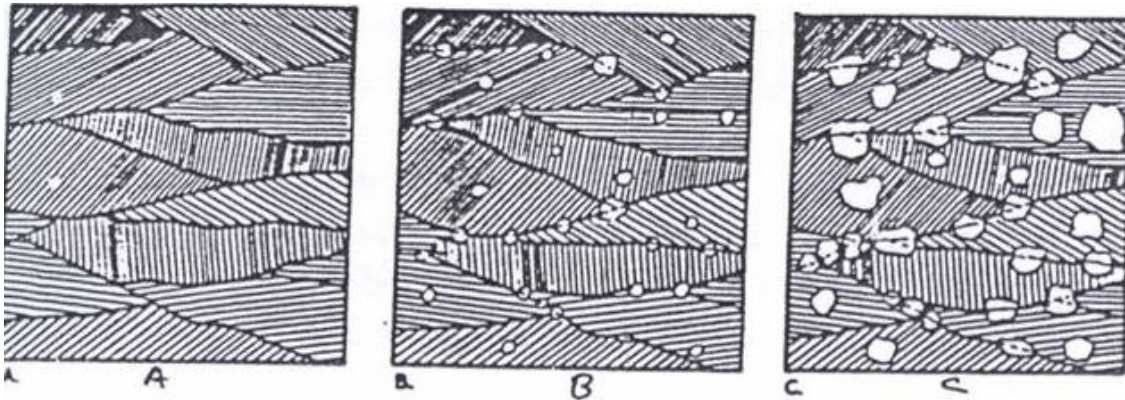

Figure: 1

Recrystallization process is an activated process and can be written as.

$$\frac{1}{t} = k e^{-Q/RT}$$

Hence plotting 1/t vs 1/T the effective activation energy "Q" can be obtained from the slop of the linear plot.

PRE-TREATMENT: Three sets of samples (9 samples) of Metal annealed at 800°C for ½ hour and deformed/cold worked by 50% reduction. These samples are then recrystallized at 600°C, 650°C and 700°C for different times at each temperature.

PROCEDURE: Polish the given sets of samples (3 sets) on 1/0, 2/0, 3/0 and 4/0 emery papers. Further final polishing is done with velvet cloth using alumina suspension on a rotating wheel till mirror like surface finish is obtained. The samples are then etched with nital solution (3% HNO_3 in alcohol).

OBSERVATIONS: Observe the microstructures of the samples under the microscope and note the following:

(1) Draw the microstructure of each sample in order with increasing temperature and time with all the details like magnification, temperature, time.

(2) Measure percentage recrystallization in each sample by quantitative metallography (systematic point counting technique.)

Plot ln t vs ln [ln $\frac{1}{1-x}$] and find the exponent n from the slope.

(3) Find the time (t) for 50 % recrystallization in each case and then by plotting 1 /t $_{0.5}$ vs 1/T, calculate effective activation energy Q from the slope.

EXERCISE:

1. Why recovery and recrystallization occur?
2. Write down the microstructural features changes during recovery and recrystallization of the sample under study?
3. What is the effect of cold working on the recrystallization temperature?
4. How will you determine the recrystallization temperature (without using metallography)?
5. How do you identify between hot working and cold working?

EXPERIMENT- 2: GRAIN GROWTH

OBJECTIVE: To study the effect of time and temperature on grain size of a metal (Cu sample).

THEORY: If the annealing temperature is above the re-crystallization temperature of the metal, the newly formed crystals will continue to grow by absorbing each other by cannibal fashion, until the structure is structure is relatively coarse grained as shown in figure. 1. Since the crystal boundaries have the higher energy than the interior of the crystal, a polycrystalline mass will reduce its energy if some of the grain boundaries disappear (Figure.1 shows the tendency of the movement of the curve grain boundaries during grain growth). Consequently, at temperature above that of re-crystallization, large crystals grow by absorbing small ones. The extent of grain growth is dependent to a large degree on following factors:

(a) The annealing temperature
(b) The duration of annealing process
(c) The degree of previous cold work
(d) The use of certain additives in a metal or alloy

Direction of movement of Crystal Boundary

Crystal Growing

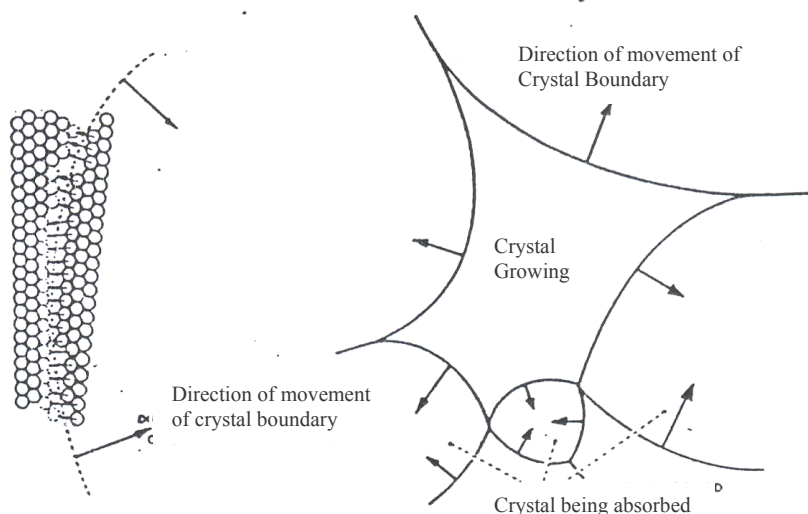Direction of movement of crystal boundary

Crystal being absorbed

FIG. 1.—The 'cannibalising' of small crystals by larger ones.

If a metallic grain growth is assumed to occur as a result of surface energy considerations and the diffusion of atoms across a grain boundaries occur, then it is to be expected that at any given constant temperature a grain growth law given below is followed:

$$D^{1/n} - D_0^{1/n} = kt \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

Where, 'D' is final average grain size (diameter). 'D_0' is the initial average grain size (diameter), 'n' is grain boundary exponent, 't' is time & 'k' is constant. 'n' is less than

0.5 and tend to increase with temperature and approaches 0.5. If the diffusion of atoms across a grain boundary is considered to be a simple activation process, then 'k' is given by

$$k = k_0 \exp(-Q/RT)..(2)$$

When 'Q' is the effective activation energy of the growth process, 'T' is the temperature in Kelvin and 'R' is the gas constant. Thus plotting ln D v/s ln t, the exponent n can be obtained from the slop for each temperature. Then using equation (1), find the values of 'k' of each samples. Similarly by plotting ln (k) v/s 1/T the effective activation energy 'Q' for the grain growth process can be obtained from the slop.

PRE-TREATMENT: Six sets of cold worked samples (each set consists of 3 samples) with 50 % reduction (9 samples) of single phase metal are annealed at 800°C for ½ hour for complete re-crystallization. Three set of 3 samples which will be subjected to micro structural observation are then annealed at 600°C, 700°C and 800°C for ½ hour, 1 hour, $1\frac{1}{2}$ hour for grain growth. Remaining Three set of 3 samples which will be subjected to Hardness measurement are also annealed at 600°C, 700°C and 800°C for ½ hour, 1 hour and $1\frac{1}{2}$ hour for grain growth.

PROCEDURE: Polish the first 3 set of samples (each set consists of 3 samples) on 1/0, 2/0, 3/0 & 4/0 emery papers followed by velvet cloth polishing in alumina powder suspension till the mirror like surface finish is obtained. Etch the samples in ferric chloride solution (4 gms. ferric chloride in 100 ml water) with chimose leather. Observe the microstructures under microscope. Remaining 3 set of samples are subjected to hardness measurement.

OBSERVATIONS:
   (1) Draw the microstructure of each sample in the increasing order of temperature and time.
   (2) a. Measure the average grain size of re-crystallized samples by linear intercept method.
       b. Plot grain size v/s time relation for each given temperature.
   (3) Plot ln D v/s ln t and find n from the slop at each temperature.
   (4) Plot a chart of 'k' of each samples using equation (1).
   (5) Plot ln (k) v/s 1/T and calculate Q from the slop for the grain growth process.
   (6) Measure the Hardness (R_B) of each sample on Rockwell Hardness Tester using the scale B.

EXERCISES:
   (1) What is the grain growth mechanism taking place in our 'Cu' sample?
   (2) What are the factors affecting the extent of grain growth in a given sample?

(3) Is there any change in the hardness of your samples? Explain why. (Hint: relate this to the grain size)

EXPERIMENT-3: NUCLEATION AND GROWTH

OBJECTIVE: To study the nucleation rate and growth rate of pearlite in eutectoid steel.

THEORY:: Phase changes occur in two ways, such as homogeneous transformation where every region of parent phase undergoes change such that its free energy decreases and the parent phase gradually approaches the product phase. Another mode of transformation, which is observed in most of the industrially important alloys, consists of the appearance of microscopic regions of the product phase in the discrete sites of the parent phase and growth of these regions by the migrations of their interfaces. Such transformation is known as heterogeneous transformations. The initiation of the transformation at discrete sites is called nucleation and the propagation of the interface of the nucleated regions in the parent phase is called growth of the nucleated region. The rate of a heterogeneous transformation is determined by the rate of nucleation ($\dot{N}$) and the rate of growth ($\dot{G}$). The rate of nucleation $\dot{N}$ is usually expressed as the number of nuclei formed per unit time per unit volume. The rate of growth $\dot{G}$ is expressed in cm. per second.

When the probability of the appearance of a nuclei in any small volume of the parent phase is same as that in any other small volume of the parent phase, nucleation occurs randomly all over the parent phase at the same rate (homogeneous nucleation). However, if high-energy sites are present in the parent phase nucleation may occur preferably on this high-energy sites (heterogeneous nucleation). Grain boundaries, inclusions, free surface, dislocations etc. are some of the heterogeneous sites found in metals.

The pearlite transformastion in eutectoid steels occurs by nucleation and growth. The nucleation and growth of pearlite occurs as if it is a single phase material. Grain boundaries are the common nucleation sites for pearlite. Figure-1 (b)shows the hypothetical nature of pearlite growth.

The nucleation and growth rate can be obtained if a sample of a coarse grained steel is cooled after austenitization to a temperature below the eutectoid temperature and held there for transformation to occur. After a certain time nuclei will appear and grow. The growth rate of pearlite is same in all directions. Therefore the nuclei grow into spherical particles. When a partially transformed sample is quenched the untransformed austenite transforms into martensite and nearly circular patches of pearlite appear in the microstructure. When the time is small these pearlite colonies are separated . each of these circular pearlite patches grow out of a single nucleus. Therefore the number of circular pearlite patches give the number of nuclei. From these data, rate of nucleation can be calculated.

Similarly the radius or diameter of the circular patch (pearlite colony) is due to the growth of this patch between the time at which the corresponding nuclei appeared and the time of final quench. Therefore the largest circular patch must represent the first nuclei and its radius or diameter can be used to calculate the growth rate.

PRE-TREATMENT

5 samples of 0.7% carbon steel (nearly of eutectoid composition) are austenised at 1000^oC for half an hour. These are then separately quenched in lead bath kept at 690^oC and soak them for 3,5,7,8 and 30 minutes. After soaking they are finally quenched in water. In this treatment, austenite (γ phase) at 1000^oC when cooled to 690^oC. pearlite starts nucleating on the grain boundaries. The nucleated pearlite then grows with time, till the complete austenite phase transforms into pearlite for 0.8% carbon steel. However for 0.7% carbon steel alpha(α) ferrite will appear along the grain-boundaries.

PROCEDURE

Polish the samples on 1/0,2/0,3/0 and 4/0 emery papers followed by velvet cloth cloth polishing in alumina powder suspension on rotating wheel till the mirror like surface finish is obtained. Etch the samples with 3% Nital (3% HNO_3 in ethanol). Observe the microstructures and take the diameter or size of pearlite colonies in different regions randomly in all the 5 samples. Take at least 10 readings for each sample.

OBSERVATION

1. Measure the number of pearlite nodules over a known area with the help of a square grid fitted in eyepiece.Take 10 such readings at least over different areas. Calculate the number of nuclei in unit area, which gives the nucleation volume. Plot the nucleation volume vs. time. Draw tangent at different times in the plot and measure the slopes. Plot slopes (which are nucleation rates $\dot{N}$) vs. time to give nucleation rate in different times..
2. For each sample measure the size of pearlite nodules (preferably bigger sizes) by linear intercept method with the help of a micrometer in the eyepiece. Take 10 such readings at least over different areas. Plot the size of the pearlite nodules with time to find growth rate $\dot{G}$ from its slope.

QUESTIONS

1. Why does pearlite nucleate on the grain-boundary?
2. How can you find the incubation-time from the data?
3. If volume-fraction data are given how can you correlate the nucleation and growth rate with "k" in rate-law given in experiment no-1?

(a)

(b)

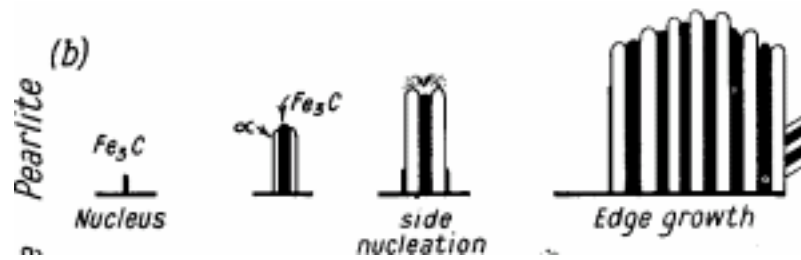Pearlite

Fe₃C
Nucleus

α — Fe₃C

side
nucleation

Edge growth
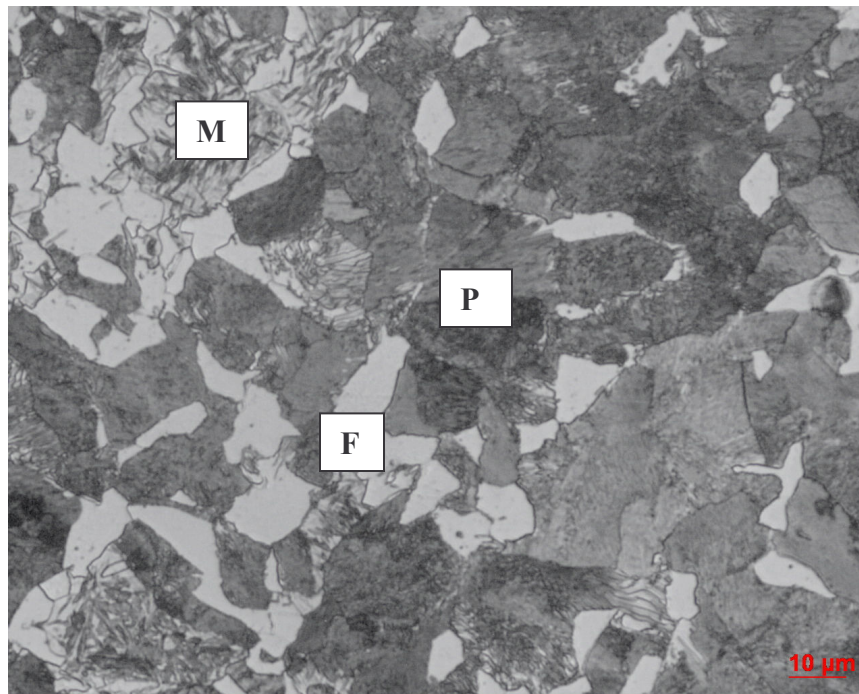
Figure-1 (a)A typical micrograph consisting of ferrite , pearlite and martensite (denoted as F, P & M respectively) (b) The mechanism of austenite-pearlite transformation

EXPERIMENT-4: CARBURIZING

OBJECTIVE: To measure the diffusion coefficient of carbon in steel

THEORY: If a steel specimen is exposed to a carbonaceous atmosphere (CO gas) at an elevated temperature, carbon dissolves in the surface of the specimen building up the carbon concentration at the surface and then diffuses inside under the influence of carbon concentration gradient (between the surface and the inside). Such a process is known as carburization. Here, the following reaction takes place at the surface:

$$2CO \text{ (g)} \quad = \quad CO_2 \text{ (g)} \quad + \quad C \text{ (steel)}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..1$$

If the carbon content of the carburizing atmosphere remains constant, it would give rise to a constant carbon concentration C_s (solubility limit of carbon in steel at the carburizing temperature) at the surface of steel.
If we assume that the diffusion is unidirectional, the process of carbon diffusion can be described by Fick's second law

$$\frac{dc}{dt} \quad = \frac{d}{dx}\left[D\frac{dc}{dx}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..2$$

Where D is the coefficient of diffusion of the diffusing element, dc/dt and dc/dx are concentration gradients with time and distance, respectively.

If $D \neq D(c)$ then
$$dc/dt = D \ (d^2c/dx^2)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..3$$

The solution to this equation (3) is of the general form in case of the diffusion couple consisting of a constant concentration on the surface (C_s i.e. for carburizing process) is given by

$$\frac{C_S - C(x,t)}{C_S - C_0} \quad = \quad \text{erf} \ \frac{x}{2\sqrt{Dt}} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..4$$

Where Cs   = surface carbon concentration

C (x, t)   = carbon concentration at depth "x" after time "t"

C_0 = initial carbon concentration of the given steel sample

Thus knowing C_0 = 0.2, C (x, t) = 0.4, Cs   = 0.8, erf (y) can be obtained [y = x/2√Dt]. Hence knowing x and t from the experiment D can be calculated.

PRE-TREATMENT: 0.2% Carbon steel is packed carburized in carburizing mixture (30-32% coke, 53-55% charcoal and 2-3% $Na_2 Co_3$, 10-12% $Ba_2 Co_3$ and 3-4% $Ca Co_3$) at 930^{0C} C (austenitic region) for 4hrs, 6hrs, 8hrs, 10hrs and 12hrs. For this purpose a stainless steel box is filled with the carburizing mixture and the samples are kept inside the mixture. The box then is sealed with high temperature cement to prevent the exposure of the carburizing mixture and the samples to the atmosphere to prevent possible oxidation.

EXPERIMENTAL PROCEDURE: The samples with the above treatment are polished by 1/0, 2/0, 3/0and finally on 4/0 emery papers. They are further polished on the polishing wheel on the velvet cloth with alumina suspension, till the mirror like surface is obtained. To reveal the microstructure, the samples are etched with nital solution (3% nitric acid in alcohol)

The microstructure show the carburized zone on the surface (indicated with complete pearlitic structure with cementite along the grain boundaries). Carbon content gradually decreases towards the center (amount of pearlite decreases towards center of the specimen as shown in figure)
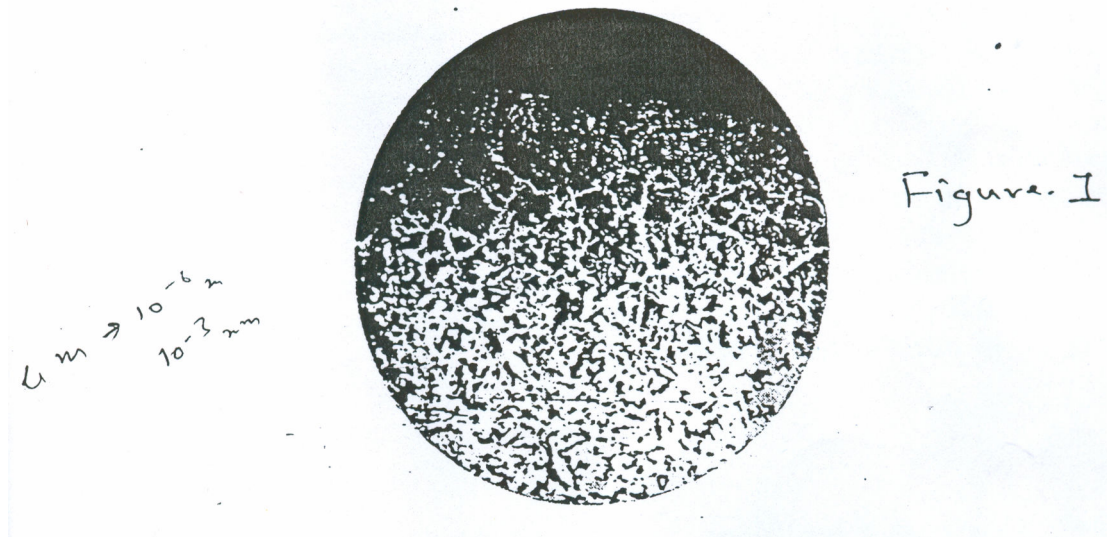

Figure: - 1.

Locate the depth (x) of 50% pearlite (c=0.4) with the help of micrometer eyepiece fitted in the microscope. Take nearly 10 readings of this depth for each sample ar different locations. Then the average depth (x) of 50% pearlite can be calculated. Knowing initial concentration $C_0 = 0.2$, surface concentration $C_s = 0.9$ to 1.0 and C (x, t) = 0.4 and "x" (in microns) as measured from the location of 50% pearlite. Knowing all the required carbon concentrations in the equation 4, the "erf" x/√Dt can be obtained, and knowing "x" and "t", the diffusion coefficient "D" can be calculated. The Data in then tabulated in the following format:

Sample	Time	x	erf (y)	D

Calculate the average "D" value of the diffusion coefficient from the set of reading. Compare your result with the value of diffusion coefficient "D" from the literature.

EXERCISE:
1. What are the factors on which D will depend?
2. Find out the diffusion rate of carbon through ferrite and austenite. Why are they different?
3. At what temperatures do surface, grain boundary, and volume diffusion predominate? Can you distinguish these by doing some careful experiments? Give details.
4. What is the atomic mechanism of diffusion for carbon in iron? (Hint: Do some research and report).

EXPERIMENT –5: HARDENABILITY OF STEEL

OBJECTIVE: To study the susceptibility of a steel to hardening by quenching.

THEORY: The susceptibility to hardening refers to the depth of hardening or the size of the piece which can be hardened to a given level under given cooling conditions.

Hardenability is directly related to the isothermal transformation diagrams. A steel with low critical cooling rate will harden deeper on quenching than a steel with a high critical cooling rate. Even though a center of a large bar cools slower than the surface, the center cooling rate may be equal to or greater than the critical rate, hence full hardening will result. Any condition that shifts the isothermal transformation curve to the right will improve hardenability, e.g., a steel can be made to harden deeper by coarsening the austenite grain size. Alloying of steel is another way of improving the hardenability.

The hardenability of a steel may be obtained by determining the diameter of bar that will just harden through to the center. The size of bar in which zone of 50% martensite occurs at the center is taken as the critical diameter. This is a measure of the hardenability of the steel for the particular quenching medium employed.

It is preferable to express the hardenability of steel in such way that the quenching medium is not a qualifying factor. This can be done if some standard quenching condition is taken for reference. The quenching condition can be expressed quantitatively by means of thermodynamic considerations involve in heat-transfer. The severity of quench is indicated in heat-transfer. The severity of quench of "H" is indicated by the heat transfer equivalent and is given by relation

$$H = f/K$$

Where f is hat transfer factor in cal/cm^2 – sec- $_0$ C and K the thermal conductivity in cal/cm – sec- $_0$ C.

The most rapid cooling rate would be with a severity of quench "H" = ∞ (infinity). Therefore, the inherent harednability of a steel can be expressed as the diameter of bar that will form a structure with 50% matensite at the center when quenched at H= ∞. This diameter is called ideal critical diameter (D_1). The relation between critical diameter (D), ideal critical diameter (D_1) and severity of quench can be determined from thermodynamic considerations. The relation are represented in figs. These relations provide a method of obtaining value of D_1 from the quenching procedure used to determined the critical diameter, provided H is known. Typical values for different quenching conditions are given in the table1.

The most common method of determining the hardenability of a steel is the end-quench test called Jominy Test. In this a bar of steel is machine to the dimensions given in Fig.2. The sample is heated to the proper austenitizing temperature90^0 held there for a proper length of time (one hour) and then it is quickly placed in a fixture shown in Fig.2. A quick acting valve admits water at a constant pressure through in orifice of a standard size. The water impinges on one end of the specimen. The end quenching continues until the bar is cooled nearly to room temperature. A 0.015 in deep flat is ground on the surface of the specimen.

Rockwell hardness values are determined at every 1/16 inch along 1inch length and at every 1/8 of the remaining specimen from the quenched – end. Plot the hardness vs distance with reference to end point.

The end – quench test does not provide directly a single figure indicating the hardenability of the steel. However, it is possible to calculate ideal critical diameter from the end – quench results. This may be done by determining the distance from water quenched end of the end – quench bar at which a structure consisting of 50% martensite is attained. The diameter of round bar that will produce the same structure its center when quenched with severity of the "H" = ∞ can then be determined by using the fig.2. The values so obtained is ideal critical diameter.

A direct comparison of the end – quench curves may be used for comparison of hardenability. The position of infletion point in terms of distance from the quenched end may be used in some instances for comparison.

EQUIPMENT AND MATERIALS:
1.   Samples of medium or high carbon steel or alloy steel, machined to the shape shown fig.1.
2.   Quenching tank to hold the hot specimen vertically with its lower end above the open end of a vertical water pipe.
3.   Suitable tongs to hold the bar firmly.
4.   Furnace with temperature controller, for temperatures up to 1000^{0C}.
5.   Rockwell hardness tester.
6.   Microscope.
7.   Mettalographic polishing equipment.
8.   Belt grinder.

PROCEDURE:
1.   Heat the sample in the furnace and bring to a temperature of 900^{0C}.
2.   Soak for 15 minutes at the temperature and then remove it to the quenching apparatus.
3.   Immediately turn on the water to impinge on the bottom of the hot bar at pre-set flow rate.
4.   After the entire sample has cooled to room temperature, turn of the water, remove any scale (iron oxide) and grind the sample along the axis to get a flat side.

5.   Measure hardness along the entire length at an interval of 1/8 inch (close to quenched –end) and at interval of ¼ inch elsewhere. (Fig.3 for reference).
6.   Polish the flat side metallographically, observe the structure and determined the approximately the distance from the quenched end at which the 50% martensite occurs.

RESULTS:
Plot Hardness (R_c) vs Distance curve.
Determine D_1 with the help of fig.2.

Table-1 Values of Severity of Quench (H)

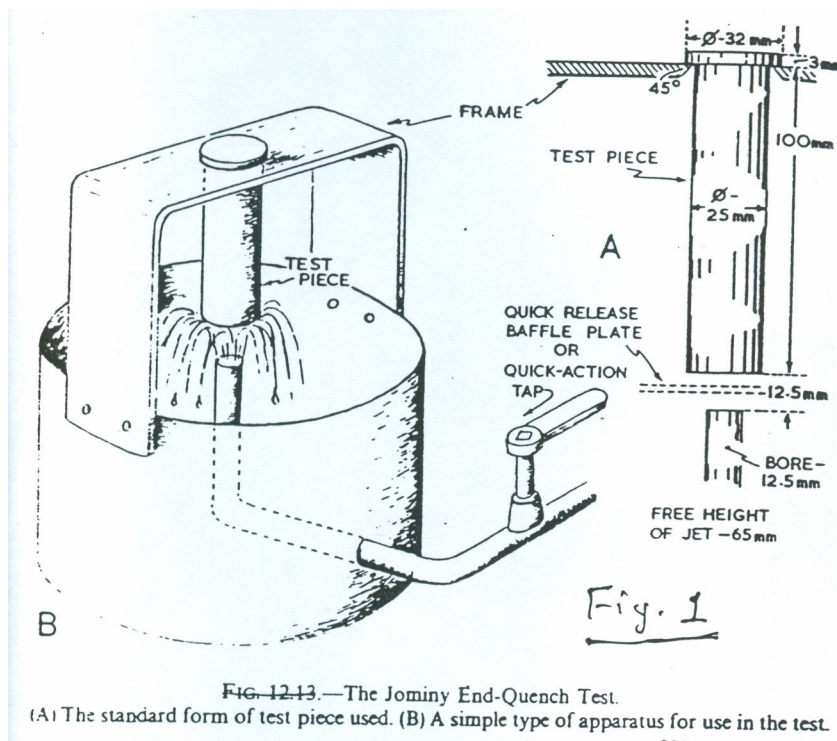|	Air	Oil	Water	Brine
No Circulation	0.02	0.03	1.0	2.2
Moderate Movement	____	0.4-0.6	1.5-3	____
Violent movement	____	0.6-0.8	3-6	7.5
Violent spray	____	1-1.7	6-12	____

Figures:

FIG. 12.13.—The Jominy End-Quench Test.
(A) The standard form of test piece used. (B) A simple type of apparatus for use in the test.

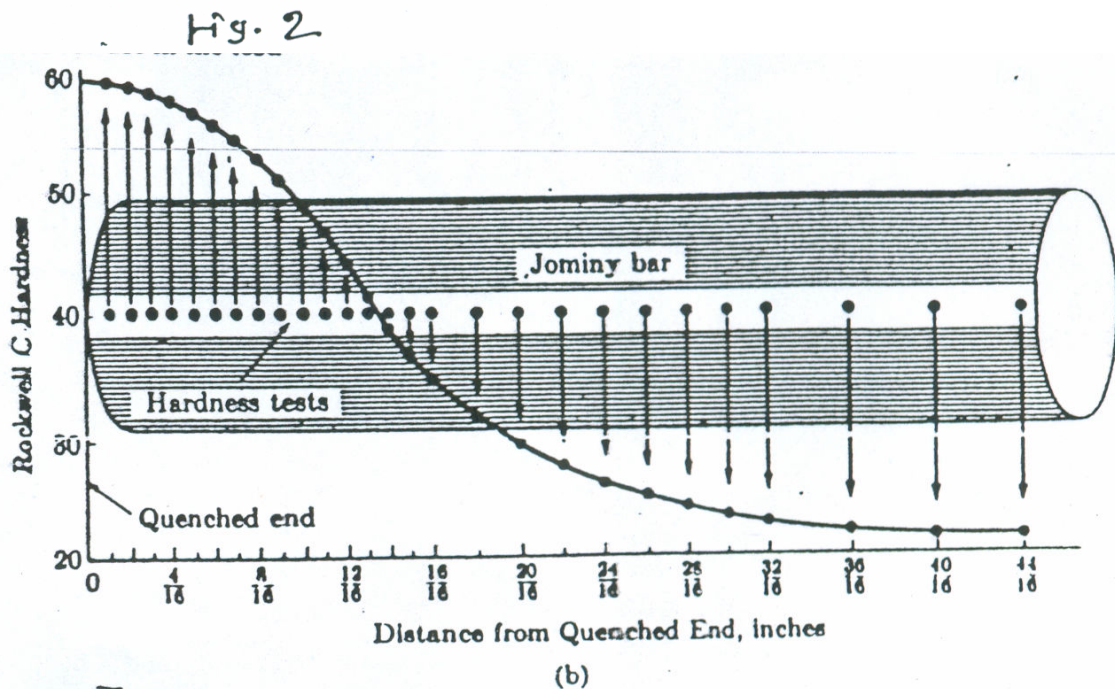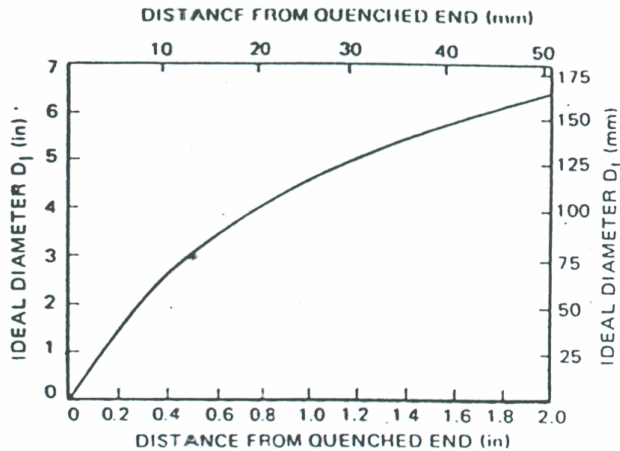Fig. 2

Distance from Quenched End, inches

(b)

Fig. 3. The steps in obtaining a Jominy curve. (a) Procedure for end quenching a Jominy bar after transfer to the quenching jig from the austenitizing furnace. (b) Jominy curve obtained by plotting the hardness values measure

EXERCISE:

1. What are the precautions one should take during this experiment?
2. Differentiate between hardness and hardenability?
3. Why Jominy-end-quench test is better than ideal-critical diameter test to determine hardenability?
4. Why hardenability test is important?
5. What is the effect of alloying elements on hardenability?
6. What is semi-martensitic zone?

EXPERIMENT-6: EUTECTOID TRANSFORMATION IN 0.7 % STEEL.

AIM: To estimate the inter-lamellar spacing and volume fraction of Pearlite.

THEORY: When steel containing about 0.8 wt % C is cooled from austenite (>800^{0}C) to a temperature below 723^{0}C the high temperature phase **austenite (γ)** transforms in to an aggregate of alternate layers of ferrite and cementite which is known as Pearlite and this transformation is known as the eutectoid transformation. The free energy change ΔG associated with the eutectoid transformation is zero at eutectoid temperature, but below this temperature ΔG= ΔS (T-T$_e$) where the entropy change ΔS is positive and nearly constant and the temperature T$_e$ is the equilibrium (eutectoid) temperature. Thus at less than the eutectoid temperature ΔG <0 and austenite tends to form into Pearlite. The factors effecting this transformation are as follow:

1. Time: The eutectoid reaction occurs by the nucleation and growth mechanism. Pearlite colonies nucleate at discrete sites in the austenite and these nuclei grow by the migration of their interface in the austenite. The growth rate has been experimentally found to be constant. Assuming the nucleation rate to be nearly constant the volume fraction of Pearlite X at any instant of time t can be expressed by the Johnson-Mehl equation:

$$X = 1 - \exp(-kT^4)$$

The time required for the formation of X amount of pearlite can be obtained from the following equation:

$$t_x = \left[\frac{\ln(1/\ 1-x)}{K} \right]^{1/\ 4}$$

Time t$_x$ is known as the incubation period. It is infinite at T$_e$ and 0^{0}K and has a finite value at 0^0 K < T < T$_e$ and is minimum at an intermediate temperature.
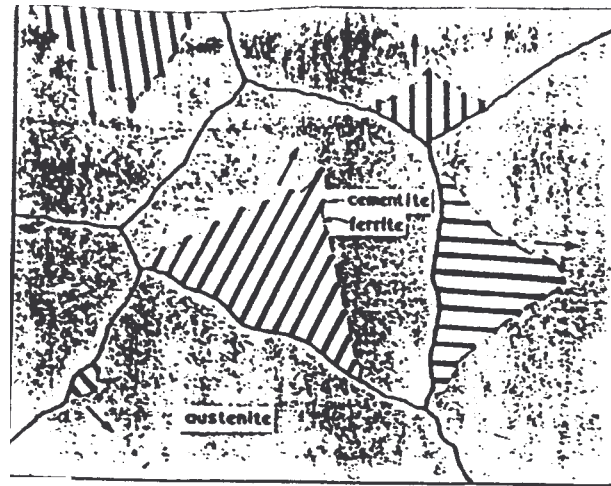The empirical activation energy for this transformation may be defined by:

$$K^{1/\ 4} = K_o \exp\left(\frac{-Q}{kT}\right)$$

2. Temperature: Below eutectoid temperature we have ΔG = ΔS (T-T$_e$). Thus ΔG is a function of temperature difference (T-T$_e$). The rate of transformation is zero at T$_e$, increases with decrease in temperature, is maximum at an intermediate temperature and then decreases with decrease in temperature.

3. Pearlite Morphology: In the eutectoid reaction the austenite is of uniform composition, but the product pearlite contains two phases whose carbon content differs considerably. This implies that the mechanism of formation of pearlite must involve

segregation of carbon by diffusion and the diffusion distance must be related to the inter-lamellar spacing δ of pearlite as shown in following figure.

Fig. —The mechanism of the austenite → pearlite transformation.

When the inter-lamellar spacing is less the diffusion distance is less and the diffusion flux is more. But simultaneously the interfacial energy within Pearlite becomes more and the net driving force for the reaction ΔG becomes less. It is shown that the growth rate is maximum when the inter-lamellar spacing is given by the following equation:

$$\delta = -\frac{4\sigma}{\Delta S(T - T_e)}$$

Here σ is the energy of the interface between ferrite and cementite. The equation suggests that the interlamellar spacing decreases with decrease in temperature.

PRE TREATMENT: Carbon steel samples (8 No) of 0.7 % C composition are austenitized at 900^0C for ½ hr and then transformed at two different temperatures i.e. 660^0C (4 samples) and 690^0C (4 samples) in lead bath for 5, 10, 30 and 60 minute. The samples treated are then quenched in water. The transformed products in each case at 660^0C and 690^0C is pearlite and its fraction depends on the transformation time. Similarly the inter-lamellar spacing depends on the transformation temperature (temperature difference, $T - T_e$.).

PROCEDURE: Polish the given samples (2 sets, 4 samples in each set) with 1/0, 2/0, 3/0 and 4/0 emery papers. Final polishing is done with 5 micron alumina slurry on polishing cloth (rotating wheel) followed by etching with nital (4 % HNO_3 solution in alcohol) followed by washing and drying.

OBSERVATIONS AND MEASUREMENTS: Observe the samples under microscope and note the following:

1. Draw the microstructures of one of the sets of the samples.

2. Measure the inter lamellar spacings (δ) of the samples with the help of the calibrated scale (graticule) provided in the eyepiece of the microscope. Present the data in table form.

3. Measure the volume fraction of Pearlite transformed at two different temperatures (by a systematic point counting technique). Compare the fractions transformed for the same time at two different temperatures (660^0 C and 690^0 C).

Exercise:

1. What is eutectoid temperature?
2. What are the other invariant reactions occur in Fe-C diagram?
3. What are the factors affecting inter-lamellar spacing in pearlite?

EXPERIMENT-7: TEMPERING OF MARTENSITE

AIM: To study the decomposition of martensite during tempering.

THEORY: Steels that have undergone a simple hardening by quenching are usually mixture of austenite and martensite, with the latter constituent predominating. Both of these structures are unstable and slowly decompose in to stable phases. The steel with a simple martensitic structure are of little useful value, and a simple heat treatment called TEMPERING is almost always used to improve the physical properties of quenched steel. In this treatment, the temperature of the hardened steel is raised to a value below the eutectoid temperature (723^0C), held there for a fixed length of time, after which the steel is cooled again to room temperature. The obvious intent of tempering is to allow diffusion process time to produce both dimensionally more stable structure and one that is inherently less brittle.

It is common practice to subdivide the reaction that occurs during tempering in to five categories, called the five stages of tempering. In the first stage, carbide which is not cementite precipitates in the Martensite. In consequence, the carbon content of the Martensite is reduced and a two-phase structure of carbide (called epsilon carbide which contains more carbon than that in cementite) and low-carbon Martensite results. This reaction occurs at rates that can be measured in the temperature interval between room temperature and approximately 200^0C. The second stage corresponds to the decomposition of retained austenite to bainite. The bainite reaction becomes measurable at about 300^0C. The microstructure of bainite that forms consists of ferrite and epsilon carbide. The formation of ferrite and cementite from the reaction products of stages one and two constitute what is known as the third stage of tempering. Formation of rods of cementite and dissolution of epsilon carbide occur. This reaction occurs in a reasonable length of time at temperature around 400^0C (rod like cementite). The fourth stage involves the growth of cementite particles. At 400^0C and above, the rod-shaped carbide dissolve and are replaced by a spheroidal cementite (Fe_3C) precipitate. The end result of tempering in plain carbon steel is an aggregate of equiaxed ferrite grains containing a large number of spheroidal iron carbide particles called cementite. In further heating, the spheroidal carbide particles grow. This is accomplished by diffusion process (a phenomenon called particle coarsening). Estimation of hardness is considered to be an important parameter to study the different stages of tempering in the laboratory.

The stages can be summarized as follow:
1. At 200-300^{0}C: Epsilon carbide.
2. At 300-400^{0}C: Acicular bainite or secondary troostite.
3. At 400-500^{0}C: Spherodized cementite in ferrite matrix.
4. At 500^{0}C above: Growth of cementite in ferrite matrix (coarsening).

PRE-TREATMENT: Plain carbon steel samples (6 Nos) containing about 0.7 % carbon are austenitised at 900^{0}C for ½ hr. These are then quenched in water to get maximum amount of Martensite. The samples are then tempered (heated) one each at

200, 300, 400, 500, 600, 700^{0}C temperatures for a fixed duration (1 hour). Depending on the temperature each sample will attain a different stage of tempering (decomposition of Martensite) as described above.

PROCEDURE: Polish the given samples with 1/0, 2/0, 3/0 and 4/0 emery papers. Final polishing is done with 5 micron alumina slurry on polishing cloth (rotating wheel) followed by etching with nital (4 % HNO_3 solution in alcohol), washing and drying.

OBSERVATIONS: Observe the samples under microscope (using relatively high magnification: 500x, 1000X) and note the following:

1. Draw the microstructure of each sample with all the possible details. Note how the martensite is gradually decomposed and the precipitation of the carbide particles in the ferrite matrix takes place.

2. Measure the hardness of each sample on Rockwell "HRC" hardness scale and plot the hardness vs tempering temperature.

Exercise:

Q1) Why tempering is required. List at least four points?

Q2) What is the tempered martensite?

Q3) What are the important properties that are affected by tempering and on what factors they depend?

Q4) What is secondary hardening?

EXPERIMENT 8 : ELECTRICAL RESISTIVITY OF ALLOY (Ge-SEMI CONDUCTOR)

AIM: To calculate the band gap energy (E_g) in Germanium (Ge) semiconductor.

THEORY: Solids are classified into three main groups namely metals, insulators and semiconductors, on the basis of their energy bands. Energy bands of any solid are obtained from solution of Schroedingers's equation for that solid, and represent the electron eigen-energies as a function of the electron wave vector [i.e. momentum].

Figure.1 contains the results of a hypothetical quantum-mechanical calculation of electron energy as a function of the lattice spacing for silicon. This schematic is very instructive for qualitative understanding of the occurrence of energy bands and forbidden energy gaps. In an ideal gas, each isolated atom has its discrete electron energy levels . These eigen energies expand into energy bands, as we decrease the interatomic spacing to form a solid. As the interatomic spacing is reduced, the interaction between atoms takes place, and keeps increasing. Finally, in a solid, atoms very strongly interact with each other, and the valence [the outermost] electrons can not claim to belong to any particular atom. What this means is that if the solid has N atoms, each atomic level must split [to remove degeneracy] into N sub-levels, very closely spaced to each other [as N is a very large number] to accommodate electron levels of N atoms. This is how an energy band of very closely spaced sub-levels evolves. The energy range between the allowed energy bands is the forbidden energy gap or band gap E_g. In the quantum –mechanical picture, electrons cannot have any energy in the forbidden energy range.

The highest completely filled [i.e. occupied with electrons] energy band at 0 K is called valence band, and the next higher band is called the conduction band. Figure.2 illustrates the basic differences between the 3 classes of solids in terms of the valence and conduction bands.
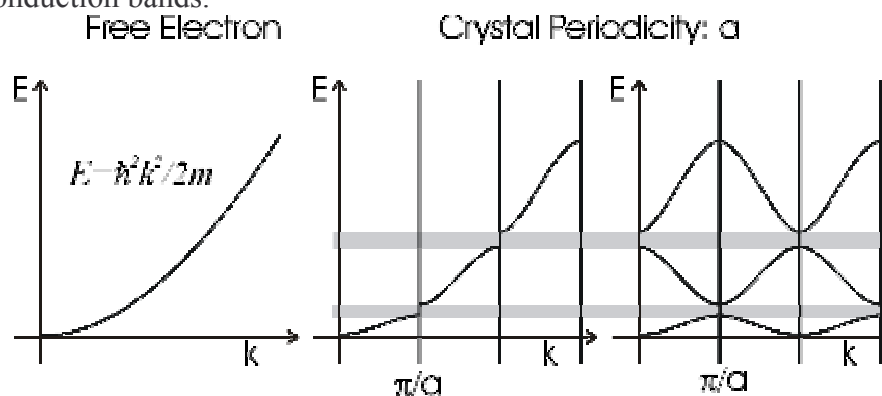

Figure-1 Electron energy (E) as a function of lattice spacing (a)

In Fig.2, the abscissa is some x- direction in the solid, while the ordinate is the electron energy. As Fig.2a indicates, the metals are characterized by overlapping conduction and

valence bands or partially filled conduction bands. The shaded area represents energy levels occupied by electrons. The non-metals, i.e. semiconductors and insulators, are characterized by completely empty conduction bands at 0 K. Semiconductors have lower bandgap than insulators, as indicated in Figs. 2b and 2c.

When an electron or a hole [i.e. a missing electron] responds to an applied electric field, it accelerates, and gains kinetic energy. [A force acts on a charge carrier in an electric field.] This means that it is excited to a higher energy state. So, only those electrons and holes can respond to an applied electric field, that have empty higher states available for excitation. [Note that Pauli's exclusion principle requires that no two electrons can have the same eigen energy, that too, only if they have opposite spins.] In a moderate electric field, gain in the kinetic energy is a very small fraction of the band gap energy. For this reason, the valence electrons in a non-metal at
0 K cannot respond to an applied electric, as they see no higher states to which they can be excited. For this reason, a non-metal is a perfect insulator at 0 K, as it has no conduction electrons or free carriers. [A free carrier is free to respond to an applied electric field.]

At room temperature [i.e. 300K], thermal vibrations break a minute fraction of the covalent bonds in a semiconductor. In other words, the thermal energy kT excites a very small fraction of valance, electrons in a semiconductor
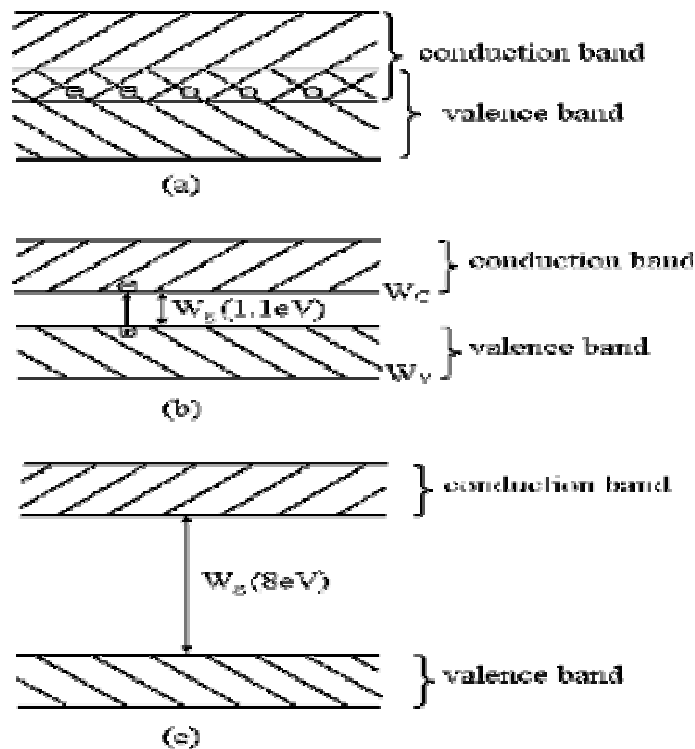

Figure-2 Various possible electeron band structure in the solids

over the band gap Eg into the conduction band. This fraction naturally depends upon the values of Eg and kT. This is known as thermal generation of free carriers. So thermal generation always gives rise to electron-hole pairs, i.e. equal numbers of conduction electrons and holes are created. The number of such pairs per unit volume is known as the intrinsic carrier density, n_i, which is given by:

$$n_i = C \exp\left[\frac{-E_g}{2kT}\right]$$ (1)

C is a constant and has same unit as n_i, i.e. cm^{-3}, k is Boltzmann's constant, and T is absolute temperature. From equation [1], it follows that for a semiconductor at 300K, the conduction band is slightly filled with electrons, and the valance band is slightly empty for electrons, or slightly filled with holes, as illustrated in Fig.2. A conduction electron is free carrier because it has empty higher states to which it can be excited to by gain in kinetic energy. A hole [which is always in the valance band] is also a free carrier, as it can be excited to all states filled by electrons. Note that in the energy band diagram, going up increases the electron potential energy, -q.V, but decreases the hole potential energy, q.V, where V is the electrostatic potential. When a conduction electron has no kinectic energy, the it is at the conduction band lower edge, E_C. Similarly, when a hole has no kinetic energy, then it is at the valance band upper edge, E_v.

The free carrier density in the pure semiconductor is n_i . The conductivity of a pure semiconductor is therefore proportional to n_i, while the resistivity, ρ, will be inversely proportional to it. Therefore:

$$\rho = K \exp\left[\frac{E_g}{2kT}\right]$$ (2)

K is a constant. A plot of ln (ρ) versus 1/T will therefore be a straight line, whose slope will be $E_g/2kT$. Hence the band gap of a semiconductor can be determined from measurement of resistivity, ρ as a function of temperature T.

FOUR POINT PROBE RESISTIVITY MEASUREMENT

The resistivity of a solid is obtained experimentally by passing a current through the solid, and measuring the current through and the voltage drop across the solid. This measurement is easier for metal. But for non-metal, the contact between metal current lead and non-metal sample act as high resistance junction. A metal semiconductor contact is a Schottky barrier diode. This a complication, because if the voltage is measured between the two current leads, then this will not only include the voltage drop across the semiconductor , but also the large voltage drop across the two metal semiconductor contacts. For this reason the semiconductor resistivity measurements involves four equidistant probes, as shown in Fig.3. The two outer probes carry the current from a constant current generator, while the two inner probes are used for

voltage measurement by a very high input resistance, then, there is no current flowing through the voltmeter. Ideally the voltmeter should infinite resustance, then,there is no current flowing through the voltmeter, hence there will be no voltage drop across the metal- semiconductor contacts at the voltage probes. This will ensure correct measurement of the voltage drop in the semiconductor in the region between the two inner probes.

Note the current enters/leaves the semiconductor at the probes flowing vertically, while in the central region the two outer probes, it flows horizontally. Also, the current flux density is not uniform. These complications result in the following relation between the resistivity q, the probes spacing d, the current I, and the voltage V between the two inner probes.

$$Q = 2\pi \left(\frac{dV}{I} \right) * \text{correction factor} \qquad (3)$$
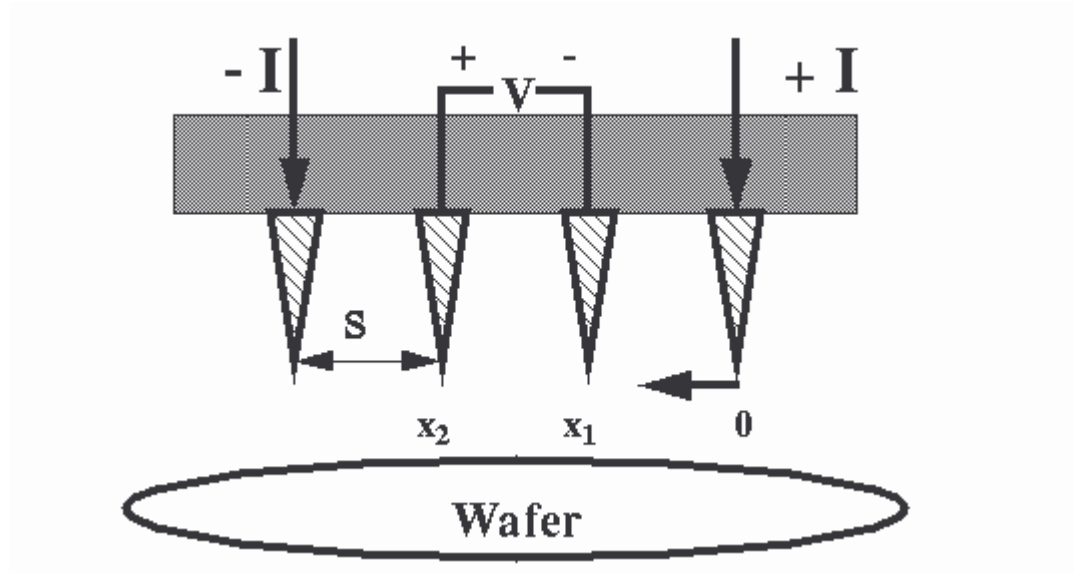

Figure-3 A schematic of four-point probe configuration

EXPERIMENTAL SETUP:

The semiconductor sample in the wafer form and is Ge, whose bandgap is about 0.66 at 300K. The four-probe set is spring-loaded, with collinear and equally spaced probes, and Zn-coated probe tips. The set is mounted on a stand, current and voltage leads are provided [see Fig4]. The probe set and the sample stage are arranged in a small box- type oven. The oven temperature can be varied from 300 to 475 K. The control cabinet has three units: [i] constant current generator; [ii] digital millivoltmeter (with high input resistance) cum milliammeter; and [iii] oven power supply.

PROCEDURE:

1. Set the current to 5-6 mA.

2. Switch in the oven on L_0 setting.

3. Wait till the temperature is approximately 70^0 C.

4. During the rise of the temperature of the furnace from 70-170^{0}C (343 K-443 K, at X-10 setting), note the voltage (mV) from the digital display with the interval of 10^0C rise in temperature (10 readings)].

5. Repeat the observation during the cooling of the sample.

6. Calculate the resistivity, ρ using the following relation:

$$\rho = 1.81\left(\frac{V}{I}\right)$$

   where V is in volt and I is in mA. (The value of ρ would be in ohm.cm).

7. PLOT "$\log_{10} \rho$" vs "1000/T" and calculate the slope.

   [Please note that the above equation is obtained from eq.(3) for d = 0.2 cm, a correction factor of 0.145]

8. From the slope of the linear region of this plot, calculate E_g by the following relations:

$$\rho = K \exp\left[\frac{E_g}{2kT}\right]$$

$$E_g = 0.4\left[\frac{d \log \rho}{d(1000 / T)}\right]$$

[In the above equation ρ is in ohm.cm and T in K].

Questions

1. Estimate the temperature at which diamond will have the same conductivity as silicon at room temperature.

2. Derive the expression $\rho = 1.81\left(\frac{V}{I}\right)$ which you have used in this experiment.

3 How does the impurity affect the conductivity of the semiconductor material.

EXPERIMENT : ELECTRICAL CONDUCTIVITY OF IONIC SOLIDS (NaCl)

AIM: To calculate the formation energy of vacancy pairs (Ø) and activation energy of vacancy migration (E$_m$).

THEORY: Electrical conductivity in ionic solids usually arises from the migration of ions under the influence on an electric field. Experiments show that in the alkali halides the positive ions are much more mobile than the negative ones. The mobility of ions in a perfect lattice (a lattice in which all sides are occupied by the ion) is extremely low. This is because of the high energy barrier preventing interchange of atoms. Hence, the presence of some lattice defects (viz. vacancies or interstitials) is essential for the occurrence of ionic conductivity. Such defects are indeed present in ionic crystals (and in metals also) and provide a thermodynamically stable state for the solid. The defect concentration is dependent on temperature. Thus the expression for the concentration of a pair of positive and negative ion vacancies is given by:

$$n = C \exp\left(\frac{-\phi}{2kT}\right)$$ --- (1)

where: n is the number of pairs of vacancies
     Ø is the formation energy of such a pair
     C is a constant
     K is the Boltzmann constant
     T is the temperature in Kelvin

The positive ions surrounding a positive ion vacancy will have a finite probability of jumping into it. As a result, the vacancy will move through the crystal by virtue of positive ions jumping into it and diffusion (i.e. ion movement without any external field applied) becomes possible. When an electrical field is applied to the solid, the probabilities of ion jumps in the direction parallel and antiparallel with the field are altered so that there is an effective movement of positive ion vacancies toward the anode. This means that there is a net effective movement of positive charge toward the cathode. The expression of conductivity, σ , derived on this basis is of the following form:

$$\sigma = A \exp\left[\frac{-(E_m + \phi/2)}{kT}\right]$$ --

(2)

Where 'A' is a constant for a particular crystal
     E$_m$ is the activation energy for migration
     Ø is the formation energy of vacancy pairs
     k is the Boltzmann constant

T   is the temperature in Kelvin

Thus, from the plot of $\log_{10} \sigma$ vs $1/T$ one can calculate the value of $(E_m + \emptyset/2)$. Plots of this sort for real alkali halides typically have the form of figure shown below:
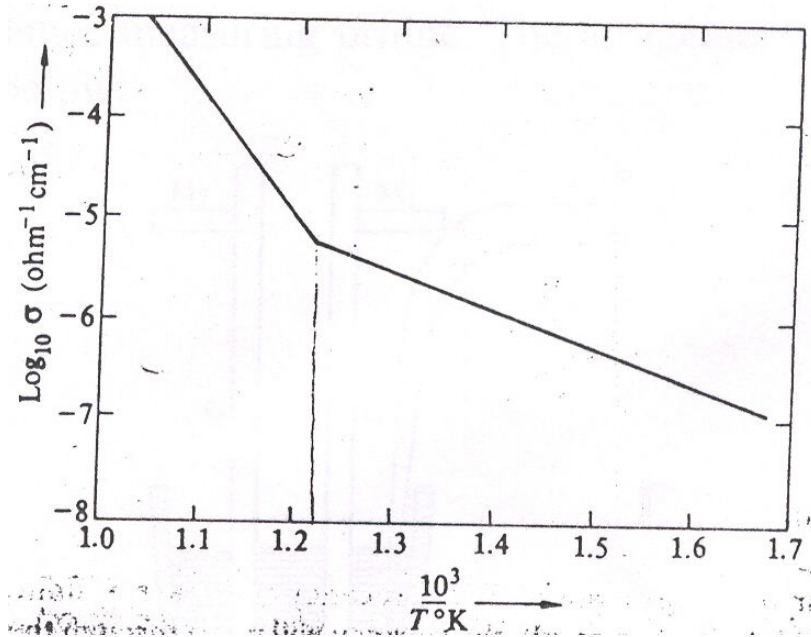

Fig.(1): Typical ionic conductivity curve for NaCl

There is a break observed somewhere in the temperature range of 400 to 700^0C depending on the purity of the crystal. This is known to arise from divalent positive impurities in the crystal. By the electrical neutrality condition, for each divalent positive ion present, there must be a positive ion vacancy. Thus, at lower temperature such crystals may contain more positive ion vacancies than would be expected on the basis of thermal equilibrium alone. In fact, below a critical temperature essentially all the vacancies arise because of the divalent impurities. The number thermally generated (Equation. 1) becomes insignificantly small. Thus the number of vacancies becomes temperature independent and the temperature dependence of the conductivity is controlled only by the mobility energy E_m. Above this temperature the number of thermally produced vacancies would predominate over the number due to the impurity atoms and consequently the conductivity will depend on the energy $(E_m + \emptyset/2)$. This means that the slop of $\log_{10} \sigma$ vs $1/T$ should be E_m and $(E_m + \emptyset/2)$ respectively in the two temperature ranges. Hence, by determining these slopes, the values of E_m and $\emptyset$ can be calculated.

EQUIPMENT: Furnace, Variac, Potentiometer, Temperature controller, Resistance measuring bridge. The arrangement is shown in the Figure (2) below:
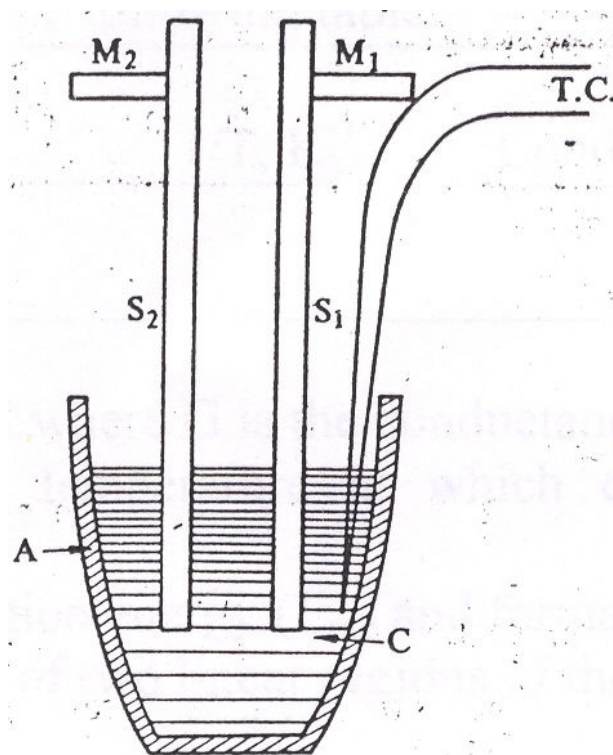
Fig.(2): Schematic diagram of the equipment

A is alumina crucible; C is polycrystalline sodium chloride specimen. S_1 and S_2 are two mild-steel plates for electrical connectivity and act as electrodes. T.C. represents the chromel-alumel thermocouple wires.

PROCEDURE:

1. Fused NaCl salt in a crucible is heated to 700-750^{0}C (below its melting point 805^{0}C).

2. It is then allowed to cool in a slow manner from around 700^{0}C to around 450^{0}C (by putting the power off to the furnace).

3. Measure the resistance of the fused salt (NaCl) in kΩ with the otentiometer connected across the two electrodes put into the salt in the furnace. Measure the resistance at the interval of 10^{0}C fall of temperature with a millivoltmeter (mV).

OBSERVATIONS:

1. Report the data in the following table:

Temperature (T) in K	$1/T$, K^{-1}	Conductance, G in mhos

2. Plot $\log_{10} G$ vs $1/T$ where G is the conductance ($G = 1/R$).
3. Note the critical temperature at which change of slop is observed.
4. Estimate the activation energy (E_m) and formation energy ($\emptyset$) in eV from the slopes of two linear regions of the graph.

EXERCISE:

1. What is the distinction between electronic and ionic conductivity?
2. Write down the factors affecting ionic conductivity of the ionic solids?
3. For a pure ionic solid sketch the conductivity graph vs. temperature.
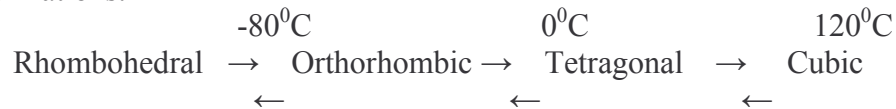
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EXPERIMENT-10 DIELECTRIC BEHAVIOR OF BARIUM TITANATE, (BaTiO$_3$)

AIM: To calculate dielectric constant (ξ) and the Curie-Weiss Temperature (T_c) of Barium Titanate.

THEORY: Barium titanate, BaTiO$_3$, exhibits the following polymorphic transformations:

$$\text{Rhombohedral} \xrightarrow{-80^0C} \text{Orthorhombic} \xrightarrow{0^0C} \text{Tetragonal} \xrightarrow{120^0C} \text{Cubic}$$
$$\leftarrow \quad\quad\quad \leftarrow \quad\quad\quad \leftarrow$$

The tetragonal-cubic phase change at 120^0C is studied in the present experiment. The cubic BaTiO$_3$, stable at temperatures over 120^0C, has the perovskite structure as shown in figure 1:

On cooling below 120^0C, one of the cubic edges becomes elongated so that the material assumes tetragonal symmetry (a=b≠c; α=β =γ= 90^0). At room temperature, c/a = 1.01; the c axis is elongated by 1 percent. The titanium ion is centrally located with respect to the six surrounding oxygen ions in the cubic phase. The equidistant tetragonal distortion produces a perturbation in the crystalline potential within the unit cell so that the titanium ion, instead of remaining equidistant from the two oxygen ions in the c-direction, moves closer to one oxygen ion or another. This non –centrosymmetric location of the titanium ion sets up a permanent dipole and causes spontaneous ionic polarization. When the direction of the spontaneous polarization of a material can be reversed by an applied electric field, the material is called a ferroelectric and the phenomenon, ferroelectricity. A ferroelectric material (e.g. BaTiO$_3$) exhibits the following characteristics:

(i)   High dielectric constant, 10-10,000, compared to 1-10 for most materials.
(ii)   A hysteresis loop between the dielectric displacement, D, and the electric field, E, analogous to the *B-H* hysteresis loop of a ferromagnetic material.
(iii)   A critical temperature, called the Curie temperature, beyond which the spontaneous polarization is lost and the material becomes paraelectric.

(iv)   A sharp peak in the dielectric constant-temperature plot, occurring at the Curie temperature.

(v)   Domains, or volume elements in which the direction of polarization is uniform.

(vi)   Domain growth: under the influence of an applied electric field, favorably oriented domain grow at the expense of those less favorably oriented, through domain wall motions.

(vii)   Curie-Weiss temperature dependence: above the Curie temperature, the dielectric constant (ξ) varies with temperature (T) as stated in the Curie-Weiss Law:

$$\xi \ (T - T_C) = C$$

where C is called the Curie constant and T_C is the Curie-Weiss temperature.

(viii) Piezoelectricity: electric charge is generated by the application of mechanical pressure and conversely, crystal dimension can be changed by applying an electric field.

The chief application of ferroelectric material such as . $BaTi_3$ arise from these properties. For example, ferroelectric materials are used for miniature capacitors because of their high dielectric constant: for memory devices because of their *D-E* hysteresis loops : or for electro-mechanical transducers because of their piezoelectric behavior.

EQUIPMENTS:

Electroded ceramic disk of barium titanate. Micrometer, sample holder, a tube furnace. Chromel-alumel thermocouple and potentiometer (millivolt meter), Capacitance meter.

EXPERIMENTAL SET-UP IS AS FOLLOWS:

PROCEDURE:

1. Measure the diameter and the thickness of the specimen with a micrometer. These are given (see the lable on the furnace)
2. Place the sample disk in the specimen holder and the specimen holder in the tube furnace. (It is already placed in the furnace as shown in the figure)
3. Connect the specimen holder to the capacitance bridge.(It is connected as shown in the figure)
4. Heat the furnace from room temperature to 150^0C.
5. Measure capacitance (pF) at a temperature of 10^0C intervals (rise) up to 150^0C. Plot the capacitance (pF) vs temperature (^{0}C).
6. Repeat the measurements on cooling the sample.

From the dimensions of the crystal the dielectric constants (ξ) can be calculated as follow:

$\xi = C (d/A\ \xi_0)$ C= is measured capacitance in farads
A= CROSS SECTION AREA (Squ. meters)
d = THICKNESS (meter)
$\xi_0 = 8.85 \times 10^{-12}$ farad/m.

Estimated the Curie-Weiss Temperature T_C both from the heating and cooling curve. Find the average.

Questions:

1. A 100pF barium titanate capacitor is how much smaller than a titania capacitor (K' =80)? (Assume the same dielectric strength for both materials and negligible electrode volume.)
2. Explain different features of Capacitance vs temperature plot that was obtained in this experiment .

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