PART THREE

MICROINDENTATION HARDNESS OF CALCITE CLEAVAGES

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CHAPTER - VI

MICROHARDNESS OF CRYSTALS (GENERAL)

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6.1 INTRODUCTION :

Of all the mechanical properties of materials, hardness is least understood property. It may be broadly defined as the ability of one body to resist penetration by another. It is by definition a relative property of a material and depends on the elastic and plastic properties of both the penetrated body and the penetrator. In addition, the comparative hardness of different materials is strongly dependent upon the method of measurement. All hardness tests measure some combination of various material properties, namely elastic modulus, yield stress (which denotes the onset of plastic behaviour or permanent distortion), physical imperfection, impurities and work-hardening capacity. The latter is a measure of the increase in stress to continue plastic flow as strain increases. Since each hardness test measures a different combination of these properties, hardness itself is not an absolute quantity and, to be meaningful, any statement of hardness of a body must include the method used for measurements.

6.2 DEFINITIONS AND MEASUREMENTS :

From time to time many definitions have been given for hardness but none has been found to be satisfactory for quantitative interpretation of the processes taking place in indented materials. Tuckerman (1929) explained hardness

as a hazily conceived aggregate or conglomeration of properties of a material more or less related to each other. Best general definition is given by Ashby (1951), " Hardness is a measure of the resistance to permanent deformation or damage ". The general definition of indentation hardness which is related to the various forms of the indenters is the ratio of load applied to the surface area of the indentation. Mayer (1908) proposed that hardness should be defined as the ratio of load to the projected area of the indentation. Hence the hardness has the dimensions of stress. Spaeth (1940) suggested that hardness should not be defined as stress but as the resistance to indentation in the form of the ratio of the specific surface load to the unrecovered deformation. In short, the hardness of a solid is defined by the resistance against lattice destruction and is considered to be a function of inner atomic forces (Tertsch, 1948). Attempts towards a physical definition of hardness were made by Friedrich (1926), Goldsmith (1927) and Chatterjee (1954).

Chatterjee (1954) defined indentation hardness as the work done per unit volume of the indentation in a static indentation test for a definite angle of indentation. On the basis of this definition and Mayer's law $P = ad^n$ for spherical indenters, he derived a formula for measurement of hardness. According to Plendl and Gielisse (1962) hardness

can be defined as pressure or force per square centimeter, and thus it can be conceived as an energy per unit volume. e.g. the ratio between the input energy and volume of indentation. They have concluded that resistance is a function of the lattice energy per unit volume and called it volumetric lattice energy (U/V) having the dimension ergs/c.c. U is the total cohesive energy of the lattice per mole and V is the molecular volume defined as M/S, where M is a molecular weight and S is specific heat. The hardness was thus considered to be the absolute overall hardness. Matkin and Caffyn (1963) from their studies on hardness of sodium chloride single crystals containing divalent impurities, correlated hardness with the dislocation theory. They redefined hardness in terms of generation and/or movement of dislocations associated with indentation, or it is the measure of the rate at which the dislocations dissipate energy when moving through a crystal lattice. It is now realized that (Westbrook and Conard, 1973) hardness is not a single property but rather a whole complex of mechanical properties and at the same time a measure of the instrinsic bonding of the material.

Hardness measurements :

There are basically four methods to determine hardness of materials. They are as follows :

(1) Scratch hardness tester

(ii) Abrasive method

(iii) Dynamic method and

(iv) Static indentation method.

They are briefly reviewed here.

(i) Scratch hardness :

An early method of measuring scratch hardness still in wide use today by minerologists was developed by Friedrich Mohs in 1822. This gives a relative ranking of minerals based simply on their ability to scratch one another. The Mohs method is not suitable for a general use with materials of hardness greater than 4, since in this range the intervals are rather closely and unevenly spaced. The modifications of this method were overshadowed by other sensitive methods and experiments.

(ii) Abrasive hardness :

Abrasive hardness is defined as the resistance to mechanical wear, a measure of which is the amount of material removed from the surface under specific conditions. The hardness may be found by the depth of penetration.

(iii) Dynamic hardness :

The hardness measurement in this method involves the dynamic deformation of specimen under study and is determined by following different considerations : (a) Here a steel sphere or a diamond-tipped hammer is dropped from a given height, and the height to which the ball or hammer,

rebounds is read on a scale. This is taken to be the measure of hardness. The kinetic energy of a ball or hammer is used up partly in plastically deforming the specimen surface by creating a slight impression and partly in rebound. This test is sometimes referred to as 'dynamic rebound test'. (b) Here a steel sphere or dimond-tipped hammer is dropped from a given height, the depth and size of the impression produced and the energy of impact gives the hardness of the substance, i.e. hardness is given as ratio of the energy of impact to the volume of indentation mark. (c) Chalmers (1941) assessed the surface hardness in terms of the reduction in optical reflectivity when a known amount of sand was allowed to impinge on the surface under standard conditions.

(iv) Static identation hardness :

The most widely used method of hardness testing is the indentation method. This is the simplest and a very sensitive method in which a hard indenter (e.g. diamond, sapphire, quartz or hardened steel) of a particular geometry is applied slowly, and after a certain time of application, is carefully removed, leaving behind a permanent indentation mark on the surface of specimen. Measurement is made either of the size of the indentation resulting from a fixed load on the indenter or the load necessary to force the indentor

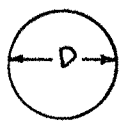
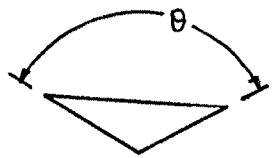
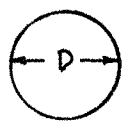
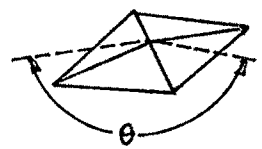
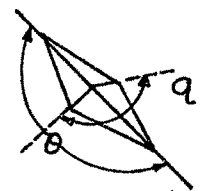
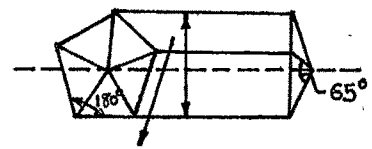
down to a predetermined depth and the hardness of material is then defined as the ratio of the load to the area of the indentation mark. The hardness values so obtained vary with the indenter geometry and with the method of calculations.

Many combinations of indenter, load, loading procedure, and means of indentation measurement are used among the various tests in order to accommodate various shapes, sizes and hardnesses of specimens, and this has resulted in a proliferation of hardness scales. The most commonly used indenters are described in table 6.1. Diamond indenters must be used for hard materials in order to minimize errors due to elastic distortion of the indenter. In case ball indenters are used, the hardness number will be independent of load only when the ratio of load to indenter diameter is held constant. For cone and pyramidal indenters, hardness number will be independent of load for all loads above a certain minimum value depending upon specimen material.

6.3 GENERAL INFORMATION ON HARDNESS :

The hardness study undertaken, so far for studying the strength of solids and the effect of various treatments on the hardness of a solid, have proved somewhat useful. Most of the work has been reported on alkali halides and metals. Previously, hardness studies were made only from the view of material research but as the expansion in the

Table 6.1

	Brinell	Rockwell		Vickers	Knoop	Broken & Moxley
Material of which indenter is made	Hardened steel or tungston carbide	Diamond	Hardened steel	Diamond	Diamond	Diamond
Shape of indenter	Sphere	Conc	Sphere	Square based pyramid	Rhomb based pyramid	Pentagonal
Dimensions of indenter	 D = 10mm.	 θ = 120°	 D = 1/16 in. 1/8 in. 1/4 in. 1/2 in.	 θ = 136°	 q = 130° θ = 172°30'	 ZERO AZIMUTH.
Characteristics	1. Geometrically similar impressions are not obtained	1. Prepares the surface upon which the further penetration due to major lead is based. 2. Hardness is read directly on the dial gauge. 3. Hardness value may be appreciable in error due to large amount of recovery along depth.		1. Geometrically similar impressions are obtained	1. Hardness of upper most surface layers can be found. 2. Sensitive to anisotropy of crystals. 3. Shorter diagonal undergoes recovery.	1. Eliminates the anisotropy normally observed in hardness with all other indenters.

field of scientific research increased, the study on hardness helped in understanding various other mechanical properties of solids. Gilman and Roberts (1961) correlated indentation hardness with the elastic modulus by gathering the data for various materials. Their empirical linear relation shows that elastic modulus is an important factor which determines plastic resistivity against the dislocation motion. The behaviour of the indented region during the propagation of stresses which initiate dislocations and their motion is not understood clearly. When an indenter is pressed on surface of a solid, the stresses which initiate the dislocations and their motion is not understood clearly. When an indenter is pressed on surface of a solid, the stresses are not simply tensile or compressive in nature. Stresses in various directions are set up and the one should treat the resultant plastic flow as a result of these combined stresses. It is also observed that the fundamental mechanisms of deformation can be either slip or twin or both or at times fracture.

(i) Slip is the most common mode of plastic deformation, which is characterised by the displacement of one part of crystal relative to another along certain definite crystallographic planes. The slip planes are usually of low indices and the slip directions are those of closely packed ones in a crystal structure.

(ii) Certain crystals may also deform by twinning, a mechanism by means of which a portion of a crystal may change lattice orientation with respect to the other in a definite symmetrical fashion. Schmidt and Boas (1955) described the twinning as the simple sliding of one plane of atoms over the next, the extent of the movement of each plane being proportional to its distance from the twinning plane. Partridge (1964) studied the microhardness anisotropy of magnesium and zinc crystals. He observed twin in above crystals and concluded that the resolved shear stress criterion is insufficient to account for the observed distribution of twins and any analysis which attempts to relate deformation twinning with hardness anisotropy must take into account the dimensional changes which occure during twin deformation. Indenting diamond flats with diamond indenter Phaal (1964) reported the slip and twinning of diamonds. Vahldick et al. (1966) studied the slip systems and twinning in molybdenum carbide single crystals with the help of knoop and vickers indenters. When the indented crystal is etched by a dislocation etchant rosettes are formed on some crystals (usually alkali halide) indicating the dislocation distribution around an indentation. Dislocation loops are also formed around the indentation mark in ceasium iodide and sodium chloride. (Urusovskaya, 1965 and Kubo, 1970).

Many workers have proposed some or other explanation for the microcrack formation during indentation of a crystal surface. Smakula and Klein (1951) from their punching experiments on sodium chloride explained the crack formation on the basis of shear on slip planes. Gilman (1958) attributed these microcracks which have a definite crystallographic direction to the pilling up of dislocation on the slip plane. Breidt et al. (1957) observed that crack formation is less at higher temperatures (375^{o}C) than at lower temperatures (25^{o}C). The cracks are usually observed to propagate from the corners of the impression.

The interferometric studies of indented surface have revealed the nature of the deformation and the history of the sample under test. Votava et al. (1953) were the first to study the deformed region on the cleavage faces of mica and sodium chloride. Tolansky and Nickols (1949) studied the indented surfaces of steel, tin and bismuth. They observed maximum distortion along the medians bisecting sides of the square and minimum along diagonals, showing thereby that no distortion projects beyond the diagonal. They could easily show that difference between 'piling-up' and the 'sinking-in' with the help of FECO fringes. They established interferometrically that the asymmetry in the fringe pattern is purely crystallographic and depends on the previous history of samples, and has nothing to do with

the orientation of the square of indentation. They (1949) concluded that the convex sides, corresponding to extended wings in the interference pattern were 'piled-up' regions and the concave sides were 'sinked-in' regions. Satyanarayan (1956) observed barrel or pin-cushion shape of indentation marks interferometrically and gave idea about 'sinking-in' which occurs mostly at faces with very little along the diagonals of the indentation mark.

In crystalline materials plastic deformation or slip occures through the movement of line imperfections called dislocations. As dislocations are multiplied (by one of several mechanisms) during deformation, their spacing decreases and they interact and impede each other's motion, thus leading to work hardening. The strength of dislocation interference depends on the nature of the crystal and on the ratio of temperature of deformation to the melting point of the crystal.

In general, hardening of crystals can be accomplished by the introduction of any barrier to dislocation motion. This can occure by (a) work hardening (b) impurity hardening (impurities tend to segregate to dislocations and pin them) (c) decreasing grain size in a polycrystal (grain boundries are barriers to dislocation motion) (d) dispersion of fine particles of second phase in the crystal and (e) Phase transformations (by quenching).

It can be seen from this brief summary that the amount of plastic deformation induced in a material by an indenter under load depends in a complicated way on variety of factors which defy simple analysis.

6.4 VARIATION OF HARDNESS WITH LOAD :

For geometrically similar shapes of the indent marks for all loads, it can be shown that the hardness is independent of load. However this is not completely true. It is clear that during a hardness test the formation of indentation mark leads to an increase in effective hardness of the material and so the hardness number obtained is not the actual hardness of the material in the intial state. This is mainly due to work hardening of the substance during the process of indentation which will be varying with the load. Attempts have been made to determine the absolute hardness by eliminating work hardening. This can be done only, if the method does not appreciably deform the substance plastically. Absolute hardness was found to be one third of the normal hardness by Harrise (1922).

A large number of workers have studied the variation of hardness with load and the results given are quite confusing. Their findings are summarised below : Knoop et al. (1937) ; Bernhardt (1941) etc. observed an increase in hardness with the decrease in the load whereas Campbell et al. (1948), Mott et al. (1952) etc. observed a decrease in

hardness with decrease in load. Some authors e.g. Taylor (1948), Bergsman (1948) reported no significant change of hardness with load. In view of these different observations it has become rather difficult to establish any definite relationship of general validity between microhardness values and applied load.

There are two ways of studying relation between hardness (H) and applied load (P) or relation between load (P) and diagonal (d) of the indentation mark. Kicks (1885) has given an empirical formula

$$P = ad^n \qquad \text{----------} \quad (6.1)$$

where 'a' and 'n' are constants of the material under test. From the definition of hardness number

$$H = \frac{r\,P}{d^2} \qquad \text{----------} \quad (6.2)$$

where r is a constant and depends upon the geometry of the indenter. The combination of the above equations yields

$$H = a_1 d^{n-2} \qquad \text{----------} \quad (6.3)$$

$$H = a_2 P^{\frac{n-2}{n}} \qquad \text{----------} \quad (6.4)$$

where

$$a_1 = r\,a \qquad \text{----------} \quad (6.5)$$

and

$$a_2 = r\,a^{2/n} \qquad \text{----------} \quad (6.6)$$

It has been shown that in case of Vickers microhardness the value of the exponent n is equal to 2 (Kick's law, 1885) for all indenters that give geometrically similar impressions. This implies a constant hardness value for all loads.

Hanemann and Schulz (1941) from their observations concluded that in the low load region 'n' generally has a value less than two. Onitsch (1947) found such low values of n (1 to 2) by observing variation of hardness with load while Grodzinski (1952) found variation of n values from 1.3 to 4.9 ; the value of n was nearly found to be 1.8. The standard hardness values thus obtained were expected to yield constant results, but actual results obtained by different workers revealed disparities amounting to 30-50%. Due to this variation in the results, a high load region was selected which led to definition of an independent region of microhardness. The hardness values so obtained for this region again showed scattered results even though the apparatus had a good mechanical precision. The scattered observations may be attributed to the following reasons :

(1) Equation i.e. $P = ad^n$ is not valid.

(2) Microstructures exercise a considerable influence on measurements involving very small indentations.

(3) The experimental errors due to mechanical polishing, preparation of specimen, vibrations, loading rate, shape of indenter, measurement of impression, effect the hardness measurements considerably.

The term connected with the above test, microhardness means the microindentation hardness, as it actually refers to the hardness measurement on the microscopic scale. Some authors prefer the terms low load hardness for the above term. This confusion has arisen because these ranges have not been defined sharply. However, three possible regions can be defined as follows :

(1) Microhardness : From lowest possible loads upto maximum of 200 gms.

(2) Low load hardness : Loads from 200 gms to 3 Kg. The most characteristic region comprises of loads from 200 gms to 1 Kg.

(3) Standard hardness : Loads over 3 Kg.

Since the present study is made in the region of microhardness as defined in (1) above ; the following presents a brief review of the work reported on microhardness of various crystals.

In the recent work reported by many workers (1960 onwards) the hardness has been found to be increasing at low loads, then remaining constant for a range of higher loads. Murphy (1969) studied hardness anisotropy in copper crystal ; the variation in hardness by plastic deformation is shown to be in part due to the escape of primary edge dislocations.

Sugita (1963) while studying the indentation hardness of Ge crystal, found that occurrence of ring cracks was suppressed relative to radial cracks as the temperature increased and the load required to produce the observable cracks was increased as the temperature is raised. The temperature at which the microscopic slip lines become observable was higher in heavily doped crystals than in high purity crystals, indicating that dislocation multiplication was strongly affected by impurities.

Kosevich & Bashmakar (1960) studied the formation of twins produced in Bi, Sb, Bi-Sb, Bi-Sn and Bi-Pb single crystals under action of concentrated load by diamond pyramid microhardness tester. They showed that the length (l) of twins was proportional to the diagonal (d), of the indentation and the intensity of the twinning thus given by the coefficient α in the equation $l = a + \alpha d$. The value of α was more for homogeneous alloys and was

increased with Sb content and remains constant for higher concentration of Sn and Pb.

The variation of hardness with load was also studied by Shah and Mathai (1969), who explained hardness in terms of slip taking place due to deformation in the crystal (tellurium). Edelman (1964) showed that microhardness of InSb and GaSb single crystals decreased exponentially with temperature. The presence of deflection points on the curves at 0.45 - 0.50 Tm indicate the deformation by slip. The activation energy for plastic flow in InSb and GaSb was estimated to be 0.6 ev.

Samsonov et al. (1970) studied temperature dependence of microhardness of titanium carbide in the homogeneity range and found that the hardness decreased with decrease in carbon content in carbide and also determined the activation energies of dislocation movement by plastic deformation.

Hardness variation was also studied with respect to the impirity content, dislocation density and the change in mobility of dislocation by various workers. Mil'vidski et al. (1965) observed decrease in hardness with increase in concentration of impurity and dislocation density in silicon single crystal. Kuz'memko et al. (1963) showed decrease in hardness due to change in mobility of dislocations as result of excitation of electrons during

lighting and their transition to higher energetic zone in titanium iodide and termed this a 'Photomechanical effect'. Beilin and Vekilov (1963) observed decrease in the hardness upto 60% illumination in Ge and Si. Decrease in the hardness was attributed to the induced photo-conductivity, which altered the widths of the dislocation cores at the sample surface and in turn altered the plasticity.

Westbrook and Gilman (1963) studied electrochemical effect in number of semiconductors. They observed decrease in resistance of semiconducting crystals to mechanical indentations in the presence of a small electric potential (0.05 to 10 V) between the indenter and the crystal surface. This was found to be due to significant enhancement of the surface photovoltage by a longitudinal electric field.

The anisotropic nature of microhardness of semiconductor was studied by Tsinzerling et al. (1969). They observed that the anisotropy was connected with anisotropic bonding and with the position of the cleavage planes relative to the movement of the indenter.

The variation of hardness in number of semiconductors was studied in terms of concentration of charge carrier, mobility and their interaction by many workers. Osvenskii et al. (1968) observed decrease in microhardness due to

increase in carrier concentration for different contents of donor and acceptor impurities for GaAs and InSb semiconductors. In addition to this they also showed that decrease in hardness was independent of the type of carrier. Smirnov et al. (1969) studied the temperature dependence of carrier density and mobility of Ge crystals after irradiation with electrons and during various stages of annealing. They observed that the microhardness of such crystals did not recover fully their initial value and this was attributed to the interaction between radiation, defects and dislocations, which could act as sinks or condensations for components of Frankel pairs. Seltzer (1966) who studied the influence of charged defects on mechanical properties of lead sulphide found that the rosette wing length and hardness were nearly independent of concentration of free electrons in n-type, while had marked dependence on concentration of holes in p-type. For a hole concentration about 8×10^{-7} cm^{-3}, rapid hardening was observed with an attendent decrease in rosette size. It was suggested that this behaviour results from an e.s. interaction between charged dislocations and acceptor point defects.

Perinova and Urusovskaya (1966) studied the hardening of NaCl single crystals by X-rays and found the increase in microhardness by irradiation due to pinning of dislocations

in irradiated samples and that the pinning was not destroyed by illumination. The effect of irradiation was also studied by Berzina and Berman (1964) who gave a relationship between the length of rays of etch figure star and proton irradiation dose in LiF, NaCl and KCl single crystal.

Because of substantial effect of surface layers on the microhardness, the increase in the microhardness was observed when applied load was reduced (Upit et al, 1969). They showed the ratio P/l^2 (where l is the length of rays in dislocation rosette around the indentation mark) was not constant (P against l^2 was not linear) at low loads due to retarding influence of the surface on the motion of dislocations. Further (1970) they estimated the change of the mechanical properties of the crystal as the indentation depth decreased on the basis of correlation between the size of an indentation mark and the length of dislocation beam.

The distribution of dislocations arround an indentation mark was studied using chemical etch pit technique by Urusovskaya and Tyagaradzhan (1965). They found large number of prismatic loops. They examined the process of interaction of dislocations in crystals having CsCl lattice. Shukla and Murthy (1968) also studied the distribution of dislocations in NaCl single crystals. They found increase in the distance travelled by leading

dislocation with increase in load. They further observed that impurity had little effect on the dimensions of the indentation but had a pronounced effect on length of the edge rays of the 'star pattern' and the ratio of the mean diagonal length to mean length of edge rays was nearly constant. Matkin and Caffyn (1963) observed increase in the hardness with increase in Ca^{++} concentration in NaCl, while the distance travelled by leading dislocation was observed to decrease.

The effect of impurity on hardness was also studied by various workers. Dryden et al. (1965) studied the hardness of alkali halides when low concentration of divalent cations are incorporated in the crystal lattice on the basis of dielectric measurement of doped alkali halide crystals. They observed following effect of the state of aggregation of the divalent impurities on critical resolved shear stress (1) the increase in critical shear stress was proportional to $C^{2/3}$, where C is the concentration of divalent ion-vacancy pairs, (2) there was no increase in hardness as these divalent ion-vacancy pairs aggregate into groups of three (trimers), (3) in NaCl : Mn^{++}, KCl : Sr^{++} and KCl : Ba^{++} there was no increase in hardness as these trimers grow into large aggregate, (4) in LiF :Mg^{++} there was a large increase in hardness as the trimers grow into larger aggregates and (5) in NaCl : Ca^{++} the hardness

increases as a second region of dielectric absorption appears. They have also concluded that the structure of the trimer was same in all these crystals and the trimer can grow in two ways, one of which produces an increase in the resistance to movement of dislocations. Urusovskaya et al. (1969) investigated the influence of impurity on the strength of crystals, microhardness, length of dislocation rosette rays and velocity of dislocation movement in CsI crystals. Takeuchi and Kitano (1971) reported the softening of NaCl crystal due to introduction of water molecules. The plastic resistance was almost independent of dislocation velocity except at very high velocities. It was, however, strongly influenced by temperature, impurities, radiation damage and structure of core of dislocation. Gilman (1960) observed a sharp drop in plastic resistence of covalent crystal at roughly about two-third of the melting temperature and suggested that the drop was because the cores of dislocation in covalent crystal 'melt' at this temperature.

Temperature dependence of microhardness was also studied by Sarkozi and Vannay (1971). They concluded that besides thermal stress the observed hardening may be due to dislocations piled-up at various impurities, to complexes in solid solution and vacancy clusters which were developed at high temperature. And by quenching the clusters become distributed in the crystals as fine dispersions.

Temperature dependence of microhardness was also studied by Shah (1976) who found that hardness of calcite cleavage faces increases with the temperature. Acharya (1978) found that the hardness of Zn and KBr decreases with the quenching temperature while the hardness of TGS increases with the quenching temperature.

Comparative study of Vickers and Knoop hardness numbers has been investigated in detail by Mohrnheim (1973) on metallic materials. An analysis of Knoop microhardness was studied by Hays and Kendall (1973) where authors have modified Kick's law which correlates applied load to the long Knoop diagonal by a term that considers the resistance offered by the test specimen itself. The theory was applied to nine test specimens of varient hardness and proven valied by graphical methods. Results were discussed for usage of modified Kick's law to obtain Knoop hardness numbers independent of applied load. Comparative study of Knoop and Vickers hardness numbers is also reported by Tietz and Troger (1976).

The above represents a brief review of the work done on hardness of various crystals. The present work is centred on the study of the variation of load with diagonal length of the indentation mark, of variation of hardness with load of natural calcite crystals at various quenching temperatures by using Knoop and Vickers diamond pyramidal indenters.