P A R T V

MICROHARDNESS OF CALCITE CLEAVAGES

CHAPTER 10

MICROHARDNESS OF CRYSTALS (GENERAL)

10.1 Introduction:

Although hardness is a term which is quite familiar to the people working in various fields, it has not been possible to define it precisely so as to include all the various characteristics of a material which have been referred to as "hardness". Though the concept of hardness is different to different people, in different fields, hardness is felt by the resistance to a cut, a scratch, penetration etc. Tuckerman explained hardness as a hazily conceived aggregate or conglomeration of properties of 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".

10.2 Definitions and measurements:

From time to time many definitions have been given for hardness but none has been found to be satisfactory. The general definition of indentation hardness which relates to the various forms of the indenters is the ratio of the load applied to the surface area of the indentation. Meyer (1908) proposed that hardness should be defined as the ratio of the load to the projected area of the indentation. So the hardness has the dimension 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 inter atomic forces (Tertsch, 1948). Attempts towards a physical definition of hardness were made by Friedrich (1926), Goldschmidt (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 Meyer's law $W = ad^n$

for spherical indenters, he derived a formula for the measurement of hardness 'H'. According to Plendl and Gielisse (1962) hardness can be defined as a pressure or force per square centimeter, and thus it can be conceived as an energy per unit volume e.g. the ratio between the imput energy and the volume of indentation. They have come to the conclusion that resistance is a function of the lattice energy per unit volume and called it the volumetric lattice energy ($\frac{U}{V}$) having the dimensions ergs/cm^3. 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 the ease 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.

All the definitions of hardness imply resistance to deformation. There are many ways of deforming a body and hence any resistance to deformation involves many factors e.g. elastic limit, elastic moduli, yield point, tensile

strength etc. There are many methods of finding the hardness of a substance. In almost all methods the substance is deformed upto plastic range and this involves considerable plastic deformation. For only this reason, it is believed that hardness of a substance is bound up primarily with their plastic properties and only to a secondary extent with the elastic properties.

There are basically four different methods to determine hardness of a substance (1) scratch (2) abrasive (3) dynamic (4) static indentation method.

10.21 Scratch hardness:

Scratch hardness is an earlier method developped by mineralogists and depends upon the ability of one solid to scratch another or to be scratched by another solid. Moh (1822) has introduced a scale of hardness for minerals by selecting ten minerals as standards. The modifications of this method were over shadowed by other sensitive methods and experiments.

10.22 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. For ferromagnetic materials hardness measurements have been made with attempts to associate them with the magnetic properties. It is generally found that materials with large magnetic coercive force are mechanically deformed to a greater extent than the material with less magnetic coercive force. It is found that hardness varies generally in the same way as the electrical resistivity.

10.23 Dynamic hardness:

This type of hardness measurement involves the dynamic deformation of the specimen under study. Here a steel sphere or a diamond cone is dropped from a given height, the depth and size of the impression produced and the energy of the impact gives the hardness of the substance, i.e. hardness is given as the ratio of the energy of impact to the volume of indentation mark. 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.

10.24 Static hardness:

This test is probably the simplest and is a very sensitive method of measuring (empirically) the strength of materials. This involves the formation of a permanent indentation mark on the surface of the specimen to be examined. Here the stressing force producing the indentation is applied slowly, and after a certain time of application, is carefully removed. The hardness of the material is then defined as the ratio of the applied load to the area of the indent mark or the depth of the indentation formed. The hardness values so obtained vary with the indenter and the method of calculations.

The static indentation hardness has been measured by pressing a hard indenter of known geometrical shape under a given load into the flat surface of the specimen and measuring the dimensions of the resulting impression. Various types of indenters such as spherical indenter, [Brinell (1900)] conical indenter, [Ludwick (1908)], double cone indenter, [Grodzinski (1952)], triangle pyramid indenter, [Benninghoff (1950)] diamond pyramidal indenter, [Smith and Sandland (1922); Knoop et al (1939)] etc. were given from time to time. Excellent literature on different types of indenters is given by Mott (1956).

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, the hardness studies were made only from the view of material research but as the expansion in the 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 initate the dislocations and their motion is not understood clearly. When an indenter is pressed on the surface of a solid, the stresses are not simply tensile or compressive in nature. Stresses in various directions are set up and 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 the crystal relative to another along certain definite crystallographic planes. The movement is concentrated in a succession of planes having the intermediate 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) describes 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 single 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 occur during twin formation. 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 crystal with the

help of Knoop and Vickers indenter. When indented crystal is etched by a dislocation etchant rosettes are formed on some crystals (usually alkali halides) indicating the dislocation distribution around an indentation. Dislocation loops are also formed around the indentation mark in caesium 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 piling up of dislocations on the slip plane. Breidt et al (1957) observed that crack formation is less at higher temperatures (375°C) than at lower temperatures (25°C). The cracks are usually observed to propagate from the corners of the impression.

The interferometric studies of indented surfaces 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 and 1952)

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 the differences 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 the samples, and has nothing to do with the orientation of the square of the indentation. They (1952) concluded that the convex sides, corresponding to the extended wings in interference pattern were 'piled-up' regions and the concave sides were 'sink-in' regions. Satyanarayan (1956) observed barrel or pin-cushion shape of indentation marks interferometrically and gave idea about 'sinking-in' which occurs mostly at the faces with very little along the diagonals of the indentation mark.

10.3 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. But this is not completely true. It is clear that during a hardness test the formation of

indentation mark leads to an increase in the effective hardness of the material and so the hardness number obtained is not the actual hardness of the material in the initial state. This is mainly due to the 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 summarized below: Knoop et al (1937), Bernhardt (1941) etc. observed an increase in hardness with the decrease in load whereas Campbell et al (1948), Mott et al (1952) etc. observed a decrease in hardness with the 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 the applied load. There are two ways of studying this relationship. One is to study P and ~~the~~ H_v directly, and other

way of studying this relationship is by plotting the graph of log. P and log. d. Kick (1885) has given an empirical rule $P=ad^n$ (1). Here P and d mean load and diameter (diagonal) of the impression respectively while 'a' and 'n' are the constants of the material under test. From the definition of Vickers hardness number

$$H_v = \frac{2 \sin 68^\circ P}{d^2} = \text{Constant} \left(\frac{P}{d^2}\right) \quad (2)$$

From the above two equations $H_v = a_1 d^{n-2}$

or $H_v = a_2 P \left\{\frac{n-2}{n}\right\}$.

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

Schulz and Hanemann (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 2.0) 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 the actual results obtained by different workers revealed disparities amounting to 30 - 50%. Due to this variation in the results, a low load region was selected which led to the 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) eqn. i.e. $P = ad^n$ is not valid.

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

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

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 term low load hardness for the above term. This confusion has arisen because these ranges have not been defined sharply. However, three possible regions of vickers diamond pyramid indentation

testing can be defined as follows:

(1) Microhardness: From the lowest possible loads upto a maximum of 200 gms and diameter of the indentation upto 30 - 50 microns. The most characteristic region comprises of loads from 1 to 50 gms (5-15 microns diagonal length).

(2) Low-load hardness: Loads from 200 gms - 3 kgms and diameter of indentations upto about 300 microns. The most characteristic region comprises of loads from 200 gms to 1 kg.

(3) Standard hardness: Loads of over 3 kgms. This test is also referred to as the microhardness testing.

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

In the recent work done by many workers (1960 onwards) the hardness has been found to be increasing at lower loads, then remaining constant for a range of higher loads. Many workers reported the variation of microhardness with load for many crystals e.g. Boyarskaya (1960), on

sodium chloride crystals; Yoshino (1965) on aluminium and magnesium, Berzina (1965) on alkali halide crystals, Gune and Cox (1970) on gold crystals. They found that microhardness increased rapidly at first with the increase of load then decreased gradually and finally became independent of load.

Upit et al (1968) studied hardness variation from the relation $P = ad^n$ and found the value of n = 1.86 ($\pm$ 0.02) which is of course in agreement with that of Dolidge (1959). The value of n is independent of the temperature, while temperature effects the value of constant "a". They further observed that value of microhardness had some relation with the motion and initiation of dislocations.

Hardness variation with respect to impurity content, temperature effect, loading time and depth and thickness variation was studied by many workers e.g. Atkins et al (1966), Nabutovskaya et al (1966), Nekrasov (1966), Shaskolskaya et al (1969). Winner et al (1963) observed an increase in hardness with the increase in composition of NaCl-NaBr solid solution single crystals. Caffyn and Matkin (1963) studied the effect of divalent impurities on the hardness of sodium chloride crystals. They observed increase in hardness at room temperature by addition of calcium impurity in sodium chloride, single crystals. They correlated

hardness with dislocations and their motions. They redefined hardness as a measure of the rate at which dislocations dissipate energy when moving through a crystal lattice.

10.4 Orientation Variation:

The variation of hardness on different faces of the same crystal is an established fact. If the indentations are made along different direction on the same face, values of hardness are not usually found same, though the shape of the indentation mark remains practically same in a few cases. Different values of hardness on the same face are attributed to the anisotropic nature of the crystal surface.

Bergsman (1945) observed a little variation in hardness values with respect to change in orientation of indenter for single crystals having high symmetry. However, Henriques (1957) reported the dependence of hardness with the crystallographic directions for sphalerite. Boyarskaya and Volkovskaya (1962) has shown that the shape of the indentation mark is dependent on the orientation of the indenter with respect to the indented surfaces of cubic crystals.

There are many opinions about the cause of this phenomenon change in the shape, hardness value etc. with the orientation of the indenter with respect to a given direction on a crystal face. Mokievskii (1960) and others related the nonsquare shape of the indentation mark to the anisotropy of elastic properties of the crystals, while Boyarskaya and his group (1962) related it to the anisotropy of the plastic property. The hardness anisotropy was studied on super pure and polycrystalline aluminium crystal with the help of three different indenters by Petty (1962). He observed peaks for the regular interval of 90^{o}. The variation was attributed to the pressure resolved in the surface. Partridge and Roberts (1963) reported the asymmetrical shape of diamond impression on magnesium and zinc crystals and attributed this to the basal slip, pyramidal slip and twinning produced due to indentation. For barilium and wurtzite compounds hardness variation with orientation were reported by Kahn and Cline (1963). Hardness maxima have a relation with the symmetry of the particular face. This was shown for various faces of silicon ferrite and basal plane of zinc by Dunn and Daniels (1949). Lendvay (1969) observed microhardness anisotropy in cubic and hexagonal zinc sulphide crystals. Brookes et al (1971) confirm that the nature of anisotropy in hardness is essentially determined by the crystal structure and primary

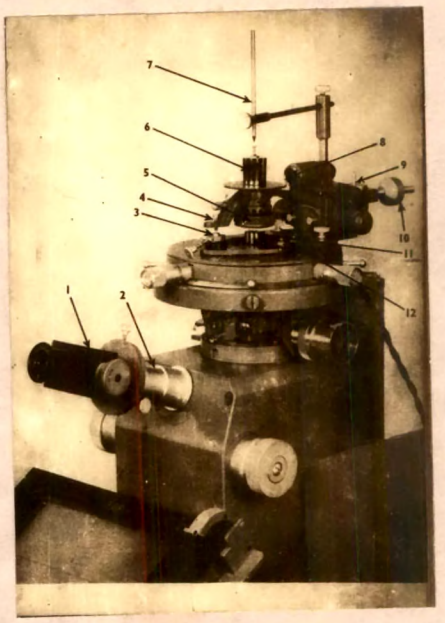

Fig. 10.1

slip systems which accomodate dislocation motion during indentation from the knoop indentation measurements on single crystals.

The present work on microhardness of calcite cleavage faces was undertaken to examine critically the applicability of Kick's law viz. $P = ad^n$. The microhardness was studied by indenting the freshly cleaved faces of calcite crystals by using diamond pyramidal indenter of Vickers hardness tester, which will now be discribed briefly in the following pages.

10.5 Indentation Technique:

The diamond pyramidal indenter equipment employed for the indentation work in the present study, is used with vicker projection microscope. Fig. 10.1 shows the complete assembly of this equipment. The various parts are as follows:

1. Filar micrometer eyepiece in centering mount.
2. Tube length scale used for magnification setting.
3. Base plate contact anvil.
4. Beam contact tip.
5. Collet chuck securing specimen.
6. Calibrated weights used to apply load.

7. Load center indicator.
8. Red signal lamp.
9. Auxiliary counter weights.
10. Counter weights.
11. Diamond indicator objective.
12. Electricity supply terminals.

The whole equipment (i.e. pivoted beam unit) is fixed to the stage plate of the microscope by means of two finger screws. On unscrewing these, it can be removed and placed to one side.

The support block for the load position is next removed on releasing the finger screw and is secured in the pocket at the back of the microscope slide.

The socket for the vertical pillar should be to the left hand side, as one faces the microscope. The vertical pillar, horizonal bar and central pin are assembled in position. The vertical position of the main bar is checked and if necessary adjusted by the use of the screw, which is afterwards locked by means of the grub screw provided.

The diamond indenter objective, assembled in its

centering mount, is placed in position in the universal illuminator. Adequate care is taken to see that the objective is accurately centered to the optical axis of the instrument. Further the load position indicator pin is carefully lowered, taking care that its movement is truely vertical and its point centered over the diamond indenter. The horizontal bar is locked by its clamp screw and the set screw limiting the rotation of the vertical pillar is locked by its nut. The pin will now indicate the position of the indenter within the range of its vertical movement and may be clamped at any desired height just to clear off the weight placed on the beam plate. The electrical connection to the transformer or battery is then made to complete the circuit for the 4V (1.2W) lamp.

The specimen to be tested is mounted with either araldite or galva cement on a bakelite or aluminium circular disc (1 inch in diameter) to fit exactly in the collet provided. The surface to be tested should, of course, be normal to the axis of the cylindrical mount. The mounted specimen is then inserted into the collet and the milled ring tightened with the aid of the double pin key until it is firmly gripped into the holder. The collet is then registered in the 'V' sideway and locked by means of the clamp screw. The filar micrometer (reading to 0.01 mm on

the micrometer drum) in its centering mount is assembled and clamped to the end of the instrument eye piece tube. The hinged lock screw should now be released and when electrical contact is made, the lamp will illuminate the red window. The beam must now be balanced and this is accomplished by the removal or addition of counter weights in the pocket provided and the adjustments of the counter weight of the screwed spindle. The vibrations due to the fan etc. should be stopped, till the completion of the experiment, as the flickering of the indicator lamp is of great assistance while balancing for making the setting sensitive, i.e. the counter weights should be adjusted in such a way that contact can just be maintained. Under these conditions, the contact will break on gently tapping the main casing of the instrument with the fingers. The sensitivity in the present case was maintained for 100 mg.

Care is taken to see that the weights are placed just above the diamond indenter with the help of pre-set vertical pin indicating load position.

The selection of the load depends upon the material to be tested. Very light loads are used for soft materials or for minute crystalline structures. Generally, a load selected must give an impression of at least

10 μ diameter.

The region to be indented is scanned with the help of the reading objective and then the diamond indenter is placed properly in the centering mount. After ensuring that the fine motion mechanism is near the lower limit, the stage is lowered by course motion slide until the surface is approximately in focus and then clamping the slide, the fine motion mechanism is used to raise the indenter diamond objective until the diamond makes contact with the specimen surface and lifts it sufficiently to break the contact between the conductors as denoted by the extinction of the red light. The speed of this fine motion drum should be maintained at 15 μ per second, in order to maintain the static nature (basis) of the test. Strict count of the revolutions should be kept as fine motion is advanced, the clearance of the indenter should be 7 revolutions. The tube length should be kept at 242 mm and the contact of the diamond indenter with the specimen surface should be maintained for about 15 to 30 seconds (depending upon the test material). On reversing, the indenter speed should be the same (15 μ per sec.) then the indented region is examined by the reading objective through the filar eyepiece (total magnification x 80).

When a series of indentations are to be made on a

crystal surface, the distance between any two consecutive indentations should not be less than twice the length of the diagonal. In the present work this distance is kept eight times ~~and~~ the diagonal length. The precaution is taken to present completely the interference of plastic flow around the impressions.

It is important that the impression produced by the diamond, should be a square and if an error exists in the axial setting of the pyramid or the levelling of the sample to be tested, it should be checked first. The anisotropy of crystal surface may play a part and the impression may not be a square, then it should be symmetrical, i.e. it should be elongated along a diagonal in a symmetrical fashion.

This hardness tester was utilized by the present author to study (i) variation of hardness with load and (ii) effect of orientation of indenter with respect to a given direction on crystal face on its microhardness. These observations will now be reported in the next chapter.