5.1 Introduction

The hardness of a substance is an important parameter to define the strength of a material. The concept of hardness depends on the sphere of activity and hence has different meanings to different people. To a fitter, it is the case with which a thick material can be swan filed or drilled, to a metallurgist it is the resistance to wear and tear, to a design engineer it is a measure of flow stress, to a mineralogist it is the resistance to scratching, to a machinist it is resistance to cutting and so on. In the case of urinary crystals, it may decide the frequency of impulse to be given for crushing the crystals from biological systems.

Hardness is a measure of resistance that the lattice offers to the flow of dislocations when impinched by a load and it measures the opposition to the lattice deformation. These properties are basically related to the crystal structure of the materials or in other words, the way in which atoms are packed and the electronic factors operating to make the structure stable. The elastic deformation developed in the material when subjected to an indentation is directly proportional to the plastic deformation. Bernhardt suggested that a part of the energy absorbed during indentation is used in producing plastic deformation and the rest increases the surface free energy.
Hardness value depends on the method of measurement that in turn determines the scale of hardness obtained. In metals, polymers and organic molecular solids, an indenter is pressed into the surface and the size of the permanent indentation mark formed is measured. In certain materials, an indenter is pressed into the material and the hardness is determined by the extent to which it has penetrated under load. In the case of minerals and brittle solids, hardness is calculated on the basis of scratch produced in one material by another of specific hardness number.

Hardness of a material depends on its elastic and plastic deformation characteristics, therefore no method of measuring hardness is dependent on a single physical property. Hardness property of a material may change appreciably as the test is applied. In an indentation test the initial penetration of the indenter increases the resistance of the material to further indentation. In a wear test, the surface may become work hardened and offer more resistance to further abrasion. Materials having the same hardness number may have varying physical properties like forging, drawing, stretching or rolling. Chemical forces in crystal also resist the motion of dislocation as it involves the displacement of atoms. Such resistance is known as the intrinsic hardness of a crystal.

For classifying materials, hardness tests are widely employed, mainly because it can be performed easily. It is a non-destructive method with the help of which we can check the uniformity of the product and assess the success of a given method of fabrication or heat treatment.

5.2 Various Testing Methods

There are many methods for measuring hardness of materials but the most commonly used form of measuring hardness of these is the indentation type. An elaborate description of these methods with their advantages and limitations are discussed by Tabor (6).
(i) Static Indentation Tests: In these tests, a ball cone or pyramid is used as an indenter, which is forced into the surface and the load per unit area of the impression measures the hardness of the surface. The Brinell, Vickers, Rockwell, Monotron and Knoop tests are of this type.

In the Brinell Hardness Test [7], a hard spherical indenter is pressed under a fixed normal load on to the smooth surface of the material under examination. When equilibrium has been reached the load and the indenter are removed and the diameter of the impression is measured. The Brinell hardness number $H_B$ is defined as the maximum applied load per contact area. Another type of indenter, which is most commonly used, is the conical or pyramidal indenter in the Ludwick and Vickers Hardness Testers. In the Knoop indenter, the indentation is in the form of an elongated pyramidal impression, its length being seven times its width. This indenter is particularly suitable for the study of anisotropy in hardness.

(ii) Scratch Tests: In this test it is observed whether one material is capable of scratching another. If a material is able to scratch the other it is said to be harder than it.

(iii) Plowing Tests: In these tests a blunt element (usually diamond) is moved across a surface under controlled conditions of load and geometry and the width of the groove is the measure of hardness. The Bierbaum Test is of this type.

(iv) Rebound Tests: In these tests, an object of standard mass and dimension is bounced from the tests surface and the height of rebound is taken as the measure of hardness. The Shore Sceloroscope is an instrument of this type.

(v) Damping Tests: In these tests, a change in amplitude of a pendulum having a hard pivot resting on the test surface is the measure of hardness. The Herbert pendulum test is of this type.
(vi) Cutting Tests: In these tests, a sharp tool of given geometry is used to remove a chip of standard dimensions.

(vii) Abrasion Test: In this test, hardness is defined as the resistance to mechanical wear, a measure of which is the amount of material removed under specified conditions. For example, a specimen under test is loaded against a rotating disc and the rate of wear is a measure of hardness.

(viii) Erosion Tests: In these tests, sand or abrasive grain is made to strike the specimen under standard condition and the loss of material in a given time is taken as a measure of hardness. This method is used to measure the hardness of grinding wheels. Recent reports have shown that an ultrasonic hardness tester consisting of the modification of the Brinell indenter has been developed which enables instantaneous automatic readout using ultrasonics [8].

5.3 Microhardness and Crystal Defects

The theory that hardness is independent of load is valid only for high load indentations. In small loads, the hardness number of some materials may increase with load, since less number of dislocations becomes available for slip in such small volumes of the crystal. If more than one slip system exists, increasing the load may activate a secondary system, thereby decreasing the hardness of the material.

Hardness is also dependent on time, especially for ductile materials. If stress is applied to such a material over a long period of time, creep processes come into play. Therefore, contact time must remain constant from one indentation test to another.

Slip line field and elastic theories are the two main models that have been postulated for deformation below an indenter. The slip theory was first explained by Prandtl [9], who calculated the mean stress for the onset of plastic flow upon indentation. This theory assumes
the existence of a plastic region below the indenter, surrounded by a rigid material. The upward flow in the material accounts for the volume displaced by the indenter.

The elastic theory predicts the development of an elastic region beyond the plastic boundary. The displaced materials are accounted for, by an elastic decrease in the volume of the material. When the indentation load is removed, there is a second plastic action over a smaller volume in the opposite direction. This theory corresponds more closely to the flow pattern of a blunt indenter. The stress field which develops around an indenter is complex; but the understanding of the mechanism of slip is simplified by the fact that hydrostatic pressure plays no part in the mechanism of slip.

Fragmentation of stones has become an invasive technique of stone therapy. The stones can be crushed inside the bladder, ureter or kidney. Hardness of the stones stumbles the process of such bloodless surgery. A proper knowledge of the hardness of these crystals will be useful in managing the disease more effectively. The variations of hardness on the different types of urinary crystals are discussed in this chapter. Micro hardness measurements have aided the determination of the elastic constants of the crystal. Knowledge of the elastic properties of stones is also essential in optimising the parameters like frequency and intensity required for stone fragmentation by ultrasound lithotripsy.

5.4 Experimental

Micro hardness studies on smooth plane surfaces were carried out using Leitz hardness tester type P1191 fitted with a Vicker’s pyramidal diamond intender. Indentations were made on selected faces of the grown crystals using the diamond intender. The indentation time was maintained at 30 seconds. The load was varied from 5 to 200 grams. For each load five indentations were made at a distance greater than 4 times the length of diagonal. The Vicker’s micro-hardness number Hv was calculated for different loads using the relation
where $P$ is the applied load in grams and $d$ is the average diagonal length of the Vicker's impression in mm after unloading. The variations of hardness with load have been studied on a large number of materials. For some materials, the microhardness increases with applied load (10-13). For some other materials, the microhardness decreases with applied load (14-17). For a third group of materials the variations assume a complex nature (18).

The variations of microhardness with applied load are plotted for all the five samples. The curves describe the following nature. For whewellite the microhardness increases with load up to a load of $p=100$ gms and then for further increase of load microhardness acquires a constant value (figure 5.1).

![Variations of microhardness with load for whewellite](image)

**Figure 5.1:** Variations of microhardness with load for whewellite

For brushite, the microhardness although increases initially, it attains a constant value at lesser load than for whewellite. Around $p = 40$ gms, the pure and doped brushites attain constant value of microhardness (figure 5.3).
Struvites shows a variation in microhardness with load similar to that of brushites (figure 5.5). The random distribution of the doped ions produces an internal stress field interaction that changes the microhardness of the doped crystals from that of the pure one.

Figure 5.3: Variations of microhardness with load for pure and doped brushites

Figure 5.5: Variations of microhardness with load for pure and doped struvites
The nature of the variation of microhardness with applied load is different for uric acid and cystine (figures 5.7 and 5.9).

**Figure 5.7:** Variations of microhardness with load for uric acid

**Figure 5.9:** Variations of microhardness with load for cystine

For these crystals the microhardness initially decreases with load and finally attains a constant value in the high load region. All
these variations can be explained by the proportional resistance model (PSR model) proposed by Li and Brat [19]. The theory has extensively been applied to a number of systems. [20-26]. In the PSR model micro hardness has two contributions. The indentation load independent part and indentation load dependent part.

Mayer's power law [27] can be applied to this part, which is in the low load region.

\[ P = A d^n \] (5.2)

A plot of 'log p' versus 'log d' graph provides a straight line, the slope of which gives the work hardening coefficient n. A is a constant parameter for a given material. These graphs for the different crystals are represented in figures 5.2, 5.4, 5.6, 5.8 and 5.10.

**Figure 5.2:** log p Vs log d graph for whewellites
**Figure 5.4:** $\log p$ Vs $\log d$ graph for pure and doped brushites

**Figure 5.6:** $\log p$ Vs $\log d$ graph for pure and doped struvites
Figure 5.8: log p Vs log d graph for uric acid

Figure 5.10: log p Vs log d graph for cystine

Table 5.1 depicts the work hardening coefficient of all the crystals. The work hardening coefficient is the highest for brushites,
closely followed by that for struvites, whewellites and the least for uric acid and cystine crystals. According to the Onstrich concept [28], the lattice is soft if \( n > 2 \) and if \( n < 2 \) the lattice is hard. A hard lattice will show brittle characteristics in the high load region. Interestingly no crack lengths were observed when the samples were subjected to different loads. Thus all the crystals can be assigned with soft lattices.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Work Hardening Coefficient-( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Whewellites</strong></td>
<td>3.1547</td>
</tr>
<tr>
<td><strong>Brushites</strong></td>
<td></td>
</tr>
<tr>
<td>Pure Brushites</td>
<td>3.4665</td>
</tr>
<tr>
<td>Nickel doped Brushites</td>
<td>1.228</td>
</tr>
<tr>
<td>Cadmium doped Brushites</td>
<td>1.881</td>
</tr>
<tr>
<td>Magnesium doped Brushites</td>
<td>4.8264</td>
</tr>
<tr>
<td>Lead doped Brushites</td>
<td>2.1599</td>
</tr>
<tr>
<td><strong>Struvites</strong></td>
<td></td>
</tr>
<tr>
<td>Pure Struvites</td>
<td>3.2336</td>
</tr>
<tr>
<td>Nickel doped Struvites</td>
<td>4.1058</td>
</tr>
<tr>
<td>Cadmium doped Struvites</td>
<td>3.4646</td>
</tr>
<tr>
<td>Lead doped Struvites</td>
<td>3.8060</td>
</tr>
<tr>
<td>Uric Acid</td>
<td>1.5700</td>
</tr>
<tr>
<td>Cystine</td>
<td>1.3511</td>
</tr>
</tbody>
</table>

**Table 5.1:** Mayer's law parameters determined for different crystals
In the high load region classical Mayer’s law is insufficient to explain the variations as the microhardness tends to be load independent.

In this region the indentation test load $P$ is related to indentation size $d$ as per the polynomial equation

$$P = a_1 d + a_2 d^2 - a_3 d + (P_c/d_0^2) d^2 \quad \text{(5.3)}$$

where $a_1$ is the proportionality constant in the load dependent region and $a_2$ that in the load independent region, $P_c$ is the critical applied test load above that the microhardness becomes load independent and $d_0$ is the corresponding diagonal length. The first term in equation (5.3) represents the surface energy contribution while the second term represents the volume energy contribution. Equation (5.3) can be rearranged to give

$$(P/d) = a_1 + (P_c/d_0^2) d \quad \text{(5.4)}$$

Hence a plot of $P/d$ versus ‘d’ will give a straight line and the slope of which gives the value of load independent microhardness $(P_c/d_0^2)$, when multiplied this by the Vicker’s conversion factor 1.854 gives the load independent microhardness $H_o$. The values are tabled in table 5.2.

Interestingly $H_o$ is the highest for whewellites followed by struvites, brushites, uric acid and the least for cystine. This is in agreement with results obtained from natural samples [29].

The first order elastic stiffness coefficient $C_{11}$ of the samples are calculated using Wooster’s empirical relation [30].

$$C_{11} = H_o^{7/4} \quad \text{(5.5)}$$
5.5 Effect of Dopents on Urinary Crystals

Investigations of urinary stones show 14 different trace elements [31]. The prominent among these are cadmium, nickel, lead and magnesium. These trace elements enter the body through atmospheric pollutants and food. The presence of these impurity elements in stones changes their properties especially the hardness. Since crystal hardness is a measure of resistance to local deformation, a co-relation between the microhardness and the impurities present in the crystals can give important information regarding the nature of secondary nucleation phenomenon in these crystals [32]. The variations of micro hardness on doping the crystals of brushites and struvites have been carried out. The micro hardness of doped struvites and brushites has considerable variation from there respective pure samples. In the case of brushites, doping with magnesium decreases the $H_o$ value whereas all other dopents like lead, cadmium and nickel increased the $H_o$ value when
compared to the pure brushites. The inhibiting nature of magnesium and the decrease of micro hardness with increase in concentration has been reported by Kalkura et.al [33]. The doped crystals of struvites too show increase in $H_0$ values compared to the pure samples. Thus the dopents have a considerable influence on the hardness of the urinary crystals. There may be chances for their incorporation as the kidney filters out these two elements. As the pollutants like Nickel, lead and Cadmium increase in the body the hardness of the formed stones increases making it difficult for the removal by shock wave lithotripsy.

References

2) Ashby N.A; N. Z. Engg. 1951, 6, 33.
28) Onstrich; Microskopie, 1947, 2, 131.