CHAPTER-2

HARDNESS OF CRYSTALS

Hardness of a material may be broadly defined as its ability to resist penetration by another particular material. Thus it is a relative property of a material which depends on the elastic and plastic properties of both the penetrated body and the penetrator. In addition to this, hardness of a material depends strongly upon the method of measurement which usually combines in itself various material properties, like elastic modulus, yield stress (which is a measure of plastic behavior or permanent distortion), physical imperfection, impurities and work-hardening capacity. Imperfections created by thermal or mechanical stresses at the time of crystal growth or after it, bear their effect on microscopic properties like electrical resistivity and on macroscopic properties like mechanical strength and in understanding the fracture mechanics, particularly in ductile metals and alloys, etc. In the case of solid solution alloys, to accommodate substitute atoms of greater or smaller size, a change in average inter-atomic spacing may take place and the solvent lattice may suffer plastic deformation. The distorted lattice causes increased frictional stress to the free movement of dislocations when the alloy is sheared. This means an increase in general hardness.

Single crystals are known to deform by the process of slip, deformation twinning, crack and fracture. Slip is displacement of one part of crystal relative to another along certain definite crystallographic planes and directions. Usually the slip planes and directions are of low indices and of close packing.

HARDNESS:

Many definitions have been given for hardness from time to time but none has been found proper with enough quantitative interpretation and understanding. Tuckerman[1] explained hardness as a hazily conceived aggregate or conglomeration of properties of a material more or less related to each other. Ashby[2] defined hardness as a measure of 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. Meyer[3] proposed that hardness should be defined as the ratio of load to the projected area of the indentation. Hence hardness has the dimensions of stress. Thus, the hardness of a solid is defined in general as resistance to deformation. The deformation in turn is a function of interatomic forces (Tertsch)[4].

Chatterjee[5] further defined indentation hardness as the work done per unit volume of the indentation in a static indentation test for a definite orientation of indenter. On the basis of this definition and Meyer's law, $P = ad^n$ for spherical indenters, he derived a formula for calculation of hardness. Plendl et al[6] defined hardness as the pressure or force per square centimeter, which can be conceived as an energy per unit volume and it is in short, the ratio of the input energy and volume of indentation. They further concluded that the resistance itself is a function of the lattice energy per unit volume which is called volumetric lattice energy (U/V), having dimension of ergs/cc. where "U" is total cohesive energy of the

lattice per mole and "V" is the molecular volume defined as M/S where "M" is the molecular weight and "S" is the specific heat. Matkin et al[7] suggested a correlation of hardness with the dislocation theory. They gave a definition of hardness on the basis of generation and movement of dislocations associated with indentation. Later, Westbrook et al[8] concluded that hardness is not a single property but it is a rather whole complex of mechanical properties and at the same time a measure of the intrinsic bonding of the material. Gilman[9] defined hardness as the strength determining parameter which gives information regarding elastic, inelastic, plastic, viscous and fracture properties of both the isotropic and anisotropic solids.

Though the basic meaning of hardness remains the same, i.e., a measure of resistance to plastic deformation, it carries different meaning to different people: for a metallurgist it is resistance to penetration, for a lubrication engineer, it is resistance to wear, for a mineralogist it is resistance to scratching etc. Therefore hardness can be determined by various methods:

1. Scratch method
2. Abrasive method
3. Plowing method
4. Rebound method
5. Damping method
6. Cutting method
7. Erosion method and
8. Static indentation method

1) **Scratch method**: In this method, whether one material is capable of scratching another or not is observed. The mohs and file hardness tests are of this type.

2) **Abrasive method**: Here, a specimen is loaded against a rotating disc and the rate of wear is taken as the hardness measure.

3) **Plowing method**: Here, a blunt element (usually diamond) is moved across a surface under controlled conditions of load and geometry. The width of the groove produced is taken as the measure of hardness. The Bierbaum test is of this type.

4) **Rebound method**: Here, an object of standard mass and dimensions, e.g. a steel ball, is bounced from the test surface and the height of rebound is taken as the measure of hardness. The scleroscope is a hardness tester of this type.

5) **Damping method**: In this method, the change in amplitude of a pendulum having a pivot resting on the test surface is the measure of hardness.

6) **Cutting method**: In this method, a sharp tool of specific geometry is made to remove a chip of standard dimensions from the test specimen.

7) **Erosion method**: Here, sand or abrasive grain is caused to impinge upon the test surface under standard conditions and loss of material in a given time is taken as the measure of hardness.

8) **Static Indentation method**: In this method, a ball, a pyramid or a cone is forced into a surface and the load per unit area of the permanent

impression formed is taken as the measure of hardness. The Brinell, Vickers, Rockwell and Knoop tests are of this type.

STATIC INDENTATION METHOD:

This is the most popular research method of hardness measurement. A hard indenter of specific geometry is slowly pressed under a load into the surface to be examined and after a certain time of application, it is carefully removed leaving behind a permanent indentation mark on the surface. The ratio of applied load to the area of the mark is termed as the hardness of the specimen indented. In this case the hardness value, apart from other factors, also depends on the geometry of the indenter and if the specimen is anisotropic, complicated effects like ridging and sinking, especially with pyramidal indenters (O'Neill)[10] occur requiring correction in the formula used to calculate hardness. To accommodate various shapes, sizes and hardnesses of the specimens, a combination of indenter, load, loading procedure and means of indentation measurement is used. Diamond indenters are always used for hard materials in order to minimize errors due to elastic distortion of the indenter. In the case of ball indenters, the hardness number will be independent of load only if 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. Knoop indenter with rhomb – based pyramid is used to study the hardness anisotropy of a crystal and, to

eliminate anisotropy effect, pentagonal indenter is used Brookes et al[11]. The description of various indenters shows that the method of indentation can easily be applied to all kinds of crystalline materials under their own suitable conditions of temperature and environment.

Though the static indentation method is very simple, it results in a complex development of the stress fields especially in the crystalline materials. Mott[12] and Gilman et al[13] have shown that the indentation hardness value depends on the crystal structure, nature of bonding and elastic modulus of the crystal and it can be used to determine plastic resistivity against the dislocation motion. It has also been observed that the fundamental mechanism of deformation due to indentation tests, can be one or both of slip and twin.

Among the factors not inherent to the materials, which can increase resistance to dislocation motion and hence the observed hardness value, the main ones are,

1. Work hardening
2. Impurity hardening
3. Variation of grain size in polycrystalline materials
4. Dispersion of second phase particles and
5. Phase transformation

The hardness dependence on surface treatment, dopant and orientation of crystal has been established by Pamukchiera[14]. Gilman[9] has observed, in the case of CdS crystals, that the local pressure created below the indenter may induce phase change of the test material and can affect the measured value of hardness. Various workers have studied

hardness variation with respect to impurity content, dislocation density and change in mobility of dislocation. In Si single crystal, hardness was found to decrease with increase in concentration of impurity and dislocation density[15]. Many workers have studied the Vickers microhardness of $Cd_xHg_{1-x}Te$ alloy at room temperature as a function of x and have found hardness to increase with increasing Cd content

The materials with high dislocation mobility are harder than those with low dislocation mobility. For example, it has been found that the semimetals have small microhardness and low dislocation mobility[16]. From the above description, plastic deformation induced in a material by an indenter under load, depends on various factors in a complicated way defying simple analysis.

VARIATION OF HARDNESS WITH LOAD:

From the geometrically similar shape of the indentation marks for various loads, it can be shown that the hardness is independent of load, though it is not true experimentally for certain ranges of applied load. The hardness obtained by the indentation tests is not the actual hardness prior to indentation. This is so because the indentation process deforms the indented region of the sample. The deformation has to bear its effect in responding to the progressive penetration of the indenter. Usually at low applied loads, the deformation causes work hardening of the surface layers. Hence, the measured hardness is more than the actual. The main findings in this respect are briefly given below.

The variation of hardness with load was explained in terms of slip in Te crystals[17], Knoop[18] and Bernhardt[19] observed increase in hardness with decrease in load. Campbell et al [20] and Mott et al[21] observed decrease in hardness with decrease in load. Taylor[22] and Bergsman[23] observed no significant change in hardness by varying load.

Due to this variation in the results, a high load region has to be selected which leads to the definition of a load independent region of microhardness. The microhardness values so obtained for this region again show scattered results even though the apparatus used may be of a good mechanical precision. The scattered results may be attributed to the following reasons:

1. Microstructures exercise a considerable influence on measurements involving very small indentations.
2. The experimental errors due to mechanical polishing, preparation of specimen, vibrations, loading rate, shape of indenter and measurement of impression affect the hardness measurements considerably.

The term microhardness refers in principle to micro indentation hardness, as it actually refers to the hardness measurement on the microscopic scale. Some workers prefer the term 'low load hardness'. However, the range of macro and micro indentation are not practically definable.

But three possible regions can be crudely defined as follows:

1. **Microhardness:** From the lowest possible loads up to maximum of 200 gm.

2. **Low load hardness:** Loads from 200 gm to 3 kg. The most characteristic region comprises of loads from 200 gm to 1 kg.

3. **Standard hardness:** Loads over 3 kg.

Hardness variation was also studied with respect to the impurity content, dislocation density and the change in mobility of dislocation by various workers. Milvidski et al[15] observed decrease in hardness with increase in concentration of impurity and dislocation density in silicon single crystals. Kuz'menko et al[24] observed decrease in hardness due to change in mobility of dislocation as a result of excitation of electrons during lighting and transition to higher energetic zone in titanium iodide and termed this a 'photochemical effect". Beilin et al[25] observed decrease in the hardness up to 60% by illumination in Ge and Bi. The decrease in hardness was attributed to the induced photoconductivity, which altered the widths of the dislocation cores at the sample surface and in turn altered the plasticity.

A detailed account of the work carried out by the present author, on microhardness of $Bi_{1-x}Sb_x$ (where x = 0.05, 0.10, 0.15,0.20,0.25,0.30) single crystals, is given in chapter-7.

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