CHAPTER – 3

DEFORMATION AND HARDNESS OF CRYSTALS

CHAPTER – 3

DEFORMATION AND 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, namely, elastic modulus, yield stress (which is a measure of plastic behavior or permanent distortion), physical imperfection, impurities and workhardening 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 interatomic 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.

Deformation in some crystals is dominated by twinning. In this case, a crystal changes the lattice orientation at deformation sites, with respect to the undeformed matrix. Twinning is simple sliding of one plane of atoms over another plane and the movement of each plane is proportional to its distance from the twinning plane[1]. In the study of microhardness anisotropy of zinc and magnesium single crystals, Partridge et al[2] observed deformation twins and the resolved shear stress criterion was found insufficient to account for the observed distribution of twins. Any analysis, which attempts to relate deformation twinning with hardness anisotropy, must take into account the dimensional changes which occur during twin deformation. The slip and twinning of diamond were reported by Phaal[3], with a diamond indenter indenting on the flat and smooth surface of diamond. Similar results were observed in the case of molybdenum carbide single crystals using Knoop and Vickers indenters[4]. Tolansky et al[5] studied the Vickers indented surfaces of steel, tin and bismuth and using interferometry, observed maximum distortion along the medians bisecting the sides of the square mark and

minimum along the diagonals. They finally conclude that the symmetry in the fringe pattern is purely crystallographic and it has nothing to do with the orientation of the square of the indentation mark. They also concluded that in the interference pattern, convex sides corresponding to extended wings were "Piled – up" regions and concave sides were "Sinked – in" regions. Though plastic deformation is known classically as the permanent deformation left after removal of load or deforming stress, the present day trend defines plastic deformation as the deformation in which creation or motion of dislocations is involved. The phenomena of crack and fracture are classified as ductile or brittle according as whether or not they involve plastic deformation in their nucleation and propagation. In addition to these, there are other deformation phenomena involving lattice reorientation as in deformation twinning; but unlike deformation twinning, these phenomena occur in an irregular way producing inhomogeneous deformation. However, these are not considered as independent mechanisms. Irrational twins, kink bands, deformation bands, Brillantov – Obreimov bands etc. are of this type. Crocker and Abell[6] have pointed out that the phenomenon know as kinking and for a long time known to be governed by slip processes in Zn[7] and in Ni[8], can be considered as a deformation mechanism in its own right. The occurrence and amount of deformation produced by different mechanisms depend on various factors such as crystal structure,

nature of atomic bonds, strain rate, temperature, impurities, method of deformation, crystallographic orientation of the deforming stress axis with respect to the crystal, etc. Various authors [9 – 12] have treated the general aspects of deformation by slip and twinning. The basic theory of crack and fracture has been reviewed extensively and treated in various reports[13-14].

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[15] explained hardness as a hazily conceived aggregate or conglomeration of properties of a material more or less related to each other. Ashby[16] 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[17] 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)[18].

Chatterjee[19] 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[20] 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/c.c. 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[21] 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[22] 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[23] defined hardness as the strength determining parameter which gives information regarding elastic, anelastic, 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 minerologist 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.

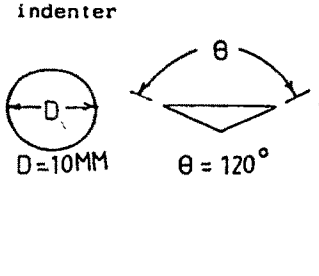
7) Erosion method : Here, sand or abrasive grain is caused to impinge upon the test surface under standard conditions and loss of material in a given time is taken as the measure of hardness.

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)[24] 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. The most commonly used indenters are described in Table-1. 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

Table - 1

	Brinell	Rockwell		Vickers	Knoop	Brookes & Moxley
Material of which indenter is made	Hardened steel or tungston carbide	Diamond	Hardened steel	Diamond	Diamond	Diamond
Shape of indenter	Sphere	Cone	Sphere	Square based	Rhomb based	Pentagonal
Dimensions of indenter						
Characteristics	1. Geometrically similar impressions are not obtained	1. Prepares the surface upon which the further penetration due to major load 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.

eliminate anisotropy effect, pentagonal indenter is used (Brookes et al)[25]. 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.

The measurement of hardness of single crystals as well as polycrystals is very essential from the academic, engineering and industrial viewpoints. Though the static indentation method is very simple, it results in a complex development of the stress fields especially in the crystalline materials. Mott[26] and Gilman et al[27] 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.

On the basis of correlation between hardness anisotropy and slip behavior of single crystals, Hannink et al[28] studied and reported the slip behavior and slip system in cubic carbides by the method of hardness anisotropy measurements. Boyarskaya et al[29] reported the shape of the indentation mark depending on the orientation of the indenter with respect to the indented surface in cubic crystals. Mokievskii[30] reported the non – square shape of the indentation mark related to the anisotropy of elastic properties of the crystals whereas Boyarskaya et al[31] related the non –

square shape to the anisotropy of plastic properties of the crystals. In the case of aluminum single crystals, Petty[32] attributed the variation in hardness value for different orientations to the pressure resolved in the surface. Shimotori[33] has given a mathematical expression for Knoop hardness anisotropy of cubic crystals. Brookes et al[34] have reported the effect of plastic anisotropy by establishing a correlation between the effective resolved shear stress and the hardness values obtained.

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[35]. Gilman[23] 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[36]. Many workers have studied the Vickers microhardness of $Cd_xHg_{1-x}Te$ alloy at room temperature as a function of x and their findings are as follows :

1. The hardness increases as a function of composition up to x = 0.75[37].
2. Increase in hardness with increase in x from about 220 MPa at x = 0 to 440 MPa at x = 1, exhibiting a maximum of about 850 MPa at x = 0.75. Also hardening rate dH/dt depends on the composition[38].
3. Similar results of increase in hardness with composition have been reported for $Hg_{1-x}Cd_xTe$ alloys[39].

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[40]. 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[41]. Knoop[42] and Bernhardt[43] observed increase in hardness with decrease in load. Campbell et al[44] and Mott et al[45] observed decrease in hardness with decrease in load. Taylor[46] and Bergsman[47] 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 microindentation 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 microindentation 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.

Inspite of all these, the hardness indentation has been very fruitfully used to study plastic deformation. For example, Murphy[48] studied hardness anisotropy in copper crystals and the anisotropic variation in hardness and hence the plastic deformation has been shown to be partly due to escape of primary edge dislocations. Sugita[49] has studied the indentation hardness of Ge crystal and found occurrence of ring cracks and radial cracks and that the load required to produce the observable cracks increased with the temperature. 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 et al[50] studied the formation of twins produced in Bi, Sb, Bi-Sb, Bi-Sn and Bi-Pb single crystals under the 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 twinning is given by the coefficient α in the equation, $l = a + \alpha d$, where "a" is a constant. The value of α was more for homogeneous alloys and increased with Sb content and remained constant for higher concentrations of Sn and Pb. The variation of hardness with load was also studied by Shah et al[41] who explained hardness in terms of slip taking place due to deformation in the tellurium crystals. Edelman[51] found that the microhardness of InSb and GaSb single crystals decreased exponentially with temperature. The presence of deflection on the curves at 0.45 – 0.50 T_m indicates deformation by slip. The activation energy for plastic flow in InSb and GaSb was estimated to be 0.6 eV. Dyer[52] using slip-line and etch pit observations, on copper, studied possible dislocation interactions in fcc crystals and their effect on the deformation process. Sestak et al[53] provided an account of the complex nature of slip in bcc metals by performing indentation in Si-Fe alloys.

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[36] observed decrease in hardness with increase in concentration of impurity and dislocation density in silicon single crystals. Kuz'menko et al[54] 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[55] 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.

Samsonov et al[56] have studied temperature dependence of microhardness of titanium carbide in the homogeneity range and reported that hardness decreases with decrease in carbon content. Acharya[57] reported that the hardness of Zn and KBr decreases with the quenching temperature while the hardness of TGS increases with the quenching temperature. Thus the hardness of a material depends on applied load, impurity, composition, crystal orientation and general mechanical state of the crystal. Over and above, the time dependence of plastic deformation, (i.e., creep), plays a prominent role in hardness measurements. The time dependent behavior has been found in many cases to be closely parallel to the creep characteristics of the material in unidirectional stress tests. These characteristics are intimately associated with temperature. At the

same time the nature and amount of plastic deformation and the measured hardness itself depend on the temperature. Recently in 1992, Fujiwara et al[58] have studied the indentation creep deformation by pencil glide in tin crystals. The investigation was on the deformation mechanism of [001] pencil glide in the crystals at the temperatures of 298, 333 and 373 K using a Vickers microhardness tester. They reported that the size of the impression produced increased with increasing load and temperature. It was concluded that the steady state deformation due to pencil glide was rate – controlled probably by cross slip between planes containing the [001] slip vector. Many workers have analyzed the creep characteristics. However, most significantly, Atkins et al[59] on the basis of kinematic analysis have given a successful hardness–time relation in terms of temperature and creep activation energy.

A detailed account of the work carried out by the present author, on microhardness of $InBi_{1-x}Sb_x$ and $InBi_{1-x}Se_x$ (where x = 0.2, 0.3, 0.4) single crystals, is given in chapter-8.

REFERENCES

1. Schmidt, E. and Boas, W., Naturwiss, 20 (1955) 416
2. Partridge, P.W., Nature, 203u (1964) 634 – 5
3. Phaal, C., Phil. Mag., 10 (1964) 887 – 91
4. Vahldick, F.W., Jap., J. Appl. Phys., 5 (1966) 663
5. Tolansky, S. and Nicholas, D.G., Nature, 164 (194) and Phil. Mag., 43 (1952) 410
6. Crocker, A.G. and Abell, J.G., Phil. Mag., 33 (1976) 305
7. Hess, J. and Barrett, C.S., Trans AIME, 185 (1949) 599
8. Flewitt, P.E. J, Phil. Mag., 34 (1976) 877
9. Van Bueren, H.G., Imperfections in Crystals (North Holland) (1960)
10. Cottrell, A.H., Dislocations and Plastic Flow in Crystals (Oxford Univ.) (1953)
11. Reed – Hill, R.E., Physical Matallurgy Principles (Van Nostrand), (1964)
12. Barett, C.S., Dislocations and Mechanical Properties of Crystals, eds., J.C. Fisher et al (Wiley), (1965)
13. Lawn, B.R. and Wilshaw, T.R., Fracture of Brittle Solids (Cambridge Univ.), (1975)
14. Taplin, D.M.R.(ed), Rep. 4th Int. Conf. on Fracture, Waterloo (1977)

15. Tuckerman, L.B., Mech. Eng., 47 (1925) 53 – 5

16. Ashby, N.A., N.Z. Engng., 6 (1951) 33

17. Meyer, E.Z., Verdeutsch Ing., 52 (1908) 645

18. Tertsch, H., Z. Krist., 92 (1935) 39 – 48 and Neus Jahrb. Mineral, Monatsh, (1951) 73 – 87

19. Chatterjee, G.P., Ind. J. Phys., 28 (1956) 9-20

20. Plendl, J.N. and Gielisse, P.J., Phys. Rev., 125 (1962) 828 – 32

21. Matkin, D.I. and Caffyn, J. E., Trans. Britt. Ceram. Soc., 62 (1963) 753 – 61

22. Westbrook, J.H. and Conrad, H., The Science of Hardness and its Research Applications, American Soc. For Metals, Ohio, (1973)

23. Gilman, J.J., The Science of Hardness Testing and its Research Applications, eds. J.H. Westbrook and H.Conred (ASM, Ohio), (1973) 51

24. O'Neill, H., Hardness Measurements of Metals And Alloys, Chapman and Hall Ltd. (London), (1967)

25. Brookes, C.A. and Moxley, B., J. Phys. E8 (1975) 456

26. Mott, B.W., Micro – Ind. Hardness Testing (Butter – Worths Publ.) London, (1956)

27. Gilman, J.J. and Roberts, B.W., J. Appl. Phys., 32 (1961) 1405

28. Hannink, R.J.H., Kohlstedt, D.L.K. and Murray, M.J., Proc.,

Roy. Soc., A326 (1972) 409

29. Boyarskaya, Yu. S. and Val'kovskaya, M.I., Sov. Phys. Cryst., 7 (1962) 202

30. Mokievskii, Sov. Phys. Cryst., 4 (1960) 381

31. Boyarskaya, Yu. S., Keloglu, Yu. P., Bologa, M.K. and Dunaeva, S.M., Sov. Phys. Cryst., 5 (1960) 188

32. Petty, E.R., J. Inst. Metals (GB), 91 (1962) 254

33. Shimotori, K., J. Jap. Inst. Met., 38 (1974) 942

34. Brookes, C.A., O'Neill, J.B. and Redferm, A.W., Proc. Roy. Soc., A322 (1971) 73

35. Pamukchiera, Cryst. Res. And Tech., 28 1 (1993), 119 – 23

36. Milvidski, M.G., Osvenskii, V.B., Stolyarov, O.G. and Shylakov D.B., Fiz. Metallovi, Metallovendenie, 20 (1965), 150 –1

37. Bhrvit, J.F., Rivand, G. and Desayer, J.C., J. Mater. Sci. (UK), 23 5 (1988) 1655 – 9

38. Fessel, A., Schek, M. and Engel, A., Cryst. Res. Technol. (East Germany), 24 5 (1989) 557 – 65

39. Andrews, R.N., Walck, S.D., Price, M.W., Szofran, F.R. Su, C.H. and Lehoczky S.L., J.Cryst. Growth (Netherlands), 99 1 – 4 (1990) 2, 717 – 21

40. Boyarskaya, Yu. S., Cryst. Res. And Tech. (Germany), 16 (1981) 441

41. Shah, B.S. and Mathai, M.B., Current Sci. (India), 38 (1969) 4780

42. Knoop, F., Tech. Blatter, 27 (1973) 472

43. Bernhardt, E.O., Z. Metalk, 33 (1941) 135

44. Campbell, R.F., Honderson, O., and Donleavy, M.R., Trans. ASM , 40 (1948) 954

45. Mott, W.B., Ford, S.D. and Jones, I.R.W., AERE, Harwell Report IR, 1 (1952) 017

46. Taylor, E.W., J. Instr. Metals, 74 (1948) 493

47. Bergsman, E.B., Met. Progr., 54 (1948) 183

48. Murphy, R.J., Scripta Metallurgica (U.S.A.), 3 (1969) 905 – 10

49. Sugita, Y., J. Appl. Phys. (Japan), 10 (1963) 951

50. Kosevich, V.M. and Bashmakov, V.I., Fiz. Metallovi, Metallovendenie, 9 (1960) 288 – 93

51. Edelman, F.L., Phys. Status Solidi (Germany), 7 (1964) K 65-66

52. Dyer, L.D., Trans. ASM, 58 (1965) 620

53. Sestak, B. and Libovicky, S., Czech. J. Phys., 11 (1961) 444

54. Kuz'menko, P.P., Novykov, N.N. and Ya. Horydko, N., Ukveyin, Fiz. Zn. (USSR), 8 (1963) 116 – 20

55. Beilin, V.M. and Vekilov, Yu Kh., Fiz. Tverdogo, Tela., 5 (1963) 2372 – 4

56. Samsonov, G.V., Kovalchenko, V.V., Dzemedinskii and

Upadhyay, G.S., Fiz Tekh., Paluprevachikov, 3 (1969) 1760 – 5

57. Acharya, C.T., Ph.D. Thesis, M.S. Univ. Of Baroda, (1978)

58. Fujiwara, M. and Hirokawa, T., J. Jpn, Inst. Met. (Japan), 56 2 (1992) 155 – 60

59. Atkins, A.G., Silverio, A. and Tabor, D., J. Inst. Met., 94 (1966) 369