PART II

MICRO-HARDNESS ALONG TRI-CRYSTAL BOUNDARIES IN TIN CRYSTALS
(1) Introduction

Hardness as applied to metals has long been the subject of discussion among engineers, physicists, metallurgists and mineralogists and there are all sorts of conceptions as to what constitutes hardness. The overwhelming difficulty of defining hardness is that it is not a fundamental property of the material. There is hardness as measured by resistance to cutting by scratching, by penetration, by electrical and magnetic properties. L. B. Tuckerman has rightly put "Hardness is a hazily conceived conglomerate or aggregate of properties of materials more or less related to each other". However, the hardness measurements are of very great practical importance and it will be instructive to make a closer survey of the meaning and measurement of hardness.

(2) Definitions and Measurements

All definitions of hardness imply a resistance to deformation. There are many ways of deforming a body and hence any resistance to deformation involves many factors.
The phase contrast picture is as shown in Fig. (61, x 360). Interesting points in the photograph are (i) clusture of pits (ii) the alignment of pits in rows in definite directions and (iii) the regions free of etch pits. Such features were also observed when etched by the new etchant.

All these points justify the importance of new etchant in revealing definite structural defects and these defects appear to be dislocations.

Furthermore, it should be emphasized that the density of etch pits is of the same order as the density distribution of growth hillocks (Pandya and Balasubramaniam 1962) observed on the natural faces of antimony single crystals (Fig. 46) grown from the gaseous phase. This further points to the effectiveness of the new etchant.

Conclusions:

A new etchant was developed in the laboratory. It possesses most of the desirable characteristics discussed above. A good deal of evidence regarding the concentration of pits, etch pit count along intersecting boundaries and deformation studies of crystals suggest the pits to be at dislocations emerging on the cleavage surfaces of the crystals.
Scratch hardness is the oldest form of hardness measurement and was probably first developed by mineralogists. It depends upon the ability of one material to scratch another or to be scratched by another. This goes to Reaumer who produced a metal bar whose hardness increased from one end to the other. The hardness was determined by the position of the bar which the metal being tested would scratch.

Mohs (1822) introduced a scale of hardness for minerals by selecting ten minerals as standards beginning with talc (Scratch hardness 1) and ending with diamond (Scratch hardness 10). Each mineral, all those in the scale would scratch below it. The Mohs hardness scale has been widely used by mineralogists. It is not however, well suited for metals since the intervals are not of equal value in the higher ranges of hardness. Further, the actual values obtained may depend in an unpredictable way on the experimental procedure, in particular on the inclination and orientation of the scratching edge.

A modern development of scratch hardness is of the micro-character. It consists of a sharp diamond stylus and is drawn across the surface to be tested, under a fixed pressure and the width of
the scratch determines the hardness. The scratching process depends in the complicated way on the elastic, plastic and frictional properties of the surface. Hence the test has not achieved wide-spread use.

**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 specified conditions. Abrasion between two surfaces depends on many factors such as the coefficient of friction, surface conditions, cold working, testing speed and other factors. Hence it is not possible to define a method of measuring abrasive hardness which will be suitable for all the practical applications for which such a quantity is required.

**Static Indentation Hardness**

Reaumer in 1722 performed the first static indentation hardness test by applying pressure to two triangular prisms whose cones were at right angles to each other. From the depth of the two indentations made, he judged the relative hardness of the two materials.

Since 1900, the static indentation hardness has been measured by pressing a hard indenter of
known geometrical shape, under a given load, in to the flat surface of specimen and measuring the resulting impression. 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 force to the surface area of indentation. The hardness values so obtained vary with the indenter and the method of calculation. This had led to the compilation of many hardness conversion tables connecting one scale with another. They are not satisfactory for all materials and are all based on empirical results.

Dynamic Hardness

In the most direct case a hard indenter is dropped on to the surface of the specimen and the hardness is expressed in terms of the energy of impact and the size of the resulting indentation produced on the surface. Also the hardness may be expressed in terms of the height of rebound of the indenter as in the Shore Scleroscope (Shore 1918).

The value of dynamic hardness depends on the way in which it is defined and the velocity of impact of the indenter. Under ordinary experimental
conditions the dynamic yield pressure (the ratio of the energy of impact to the volume of indentation) is of the same order of magnitude as the static yield pressure (the ratio of the load to the projected area of the indentation) and dynamic yield pressure will invariably be slightly higher than the static yield pressure. With soft metals the difference is more marked and will increase with the velocity of impact.

In conclusion it is worth mentioning the opinion of two experts. Roudie (1930) has said that the elasticity and hardness are two inseparable manifestations of molecular energy which dynamic methods alone can define and measure. But Meyer whose researches on indentation hardness are universally accepted was of the opinion that dynamic effects should be eliminated from the concepts of indentation hardness.

**Magnetic Hardness**

The magnetic properties of ferro-magnetic materials have been of considerable value from the hardness measurement point of view, for it is generally found that materials with large magnetic coercive force are also mechanically deformed so that when the coercive force is changed, the mechanical hardness is changed in the same sense. Magnetic methods provide
hardness tests for suitable materials without causing damage to the specimens. Now, ferrous metal and alloys on cold working and alloying produce important changes in their magnetic susceptibilities which may in turn be correlated with their hardness behaviour. Hardness may also be considered in relation to electrical properties. For example the electrical resistivity of a metal at room temperature is changed when another element is alloyed with it and it is found that the hardness varies generally in the same way as the resistivity.

Again the electrical resistivity and hardness both increase in most metals when mechanically deformed. It must be remembered that the parallelism between resistivity and hardness ceases with respect to change in temperature.

The above survey of measuring hardness serves to illustrate the complexity of the concept of hardness. Further complications arise, however, when one considers the structure and properties of the material under which tests are made. The material under test may be crystalline or amorphous, isotropic or anisotropic, all of which raise new questions of interpretation. The nature of the plastic properties of crystalline materials, in relation to particular planes of crystals lattice leads to the directional
effect on the hardness values of single crystals.

Microscopic Indentation

In this section a review of the development of the static indentation hardness measurements will be given.

Spherical Indenter

J. A. Brinell (1900) proposed the first important indentation hardness test which has served as basis for all subsequent test of this type. In the Brinell hardness test a hard spherical indenter of diameter 10 m.m. is pressed slowly under a fixed normal load on to the smooth surface of the metal. When equilibrium has been reached, after 15-30 seconds, the load and the indenter are removed and the diameter of the permanent impression measured. The Brinell hardness number (B.H.N.) is then expressed as the ratio of load $W$ to the curved area of indentation.

Thus B.H.N. = \[ \frac{2W}{WD^2 \left[1 - \sqrt{1 - \left(\frac{d}{D}\right)^2}\right]} \]

where $W$ = load in Kgm$s$. $D$ = the diameter of the indenter in m.m. and $d$ the diameter of the indentation in m.m. The diameter of the impression should be the average of the two readings at right angles.
The B.H.N. is not constant for a given metal, but varies with the load and the size of the indenter. On general physical principles we should expect that for geometrically similar indentations, whatever their actual size, the hardness number should be constant and this is found to be true. That is, if a ball of diameter $D_1$, produces an indentation of diameter $d_1$, and another indenter of diameter $D_2$ produces an indentation of diameter $d_2$, the hardness number will be the same if the two indentations are geometrically similar in which case:

$$\frac{d_1}{D_1} = \frac{d_2}{D_2}$$

Further the B.H.N. is not a satisfactory physical concept, for though at first it would seem that the ratio of the load to the surface area of the indentation is equal to the mean pressure over the surface, in fact it is not. Tabor (1951) has shown that the mean pressure is equal to the ratio of the load to the projected area of indentation i.e.

$$P = \frac{W}{\pi a^2}$$

where $2a = d$, the chordal diameter of the indentation. E. Meyer (1908) proposed, this mean pressure as a measure of the hardness and is referred to as the Meyer Hardness Number (M.H.N.):

$$M.H.N. = \frac{4#}{\pi D^2}$$

Meyer Law
This law states that for a ball of fixed diameter $W = \alpha d^n$ where $W = $ load in kg, $d =$ diameter of indentation in m.m. and $\alpha$ and $n$ are constants for material under test.

**Strainless Indentation**

During the hardness test the formation of the indentation itself leads to an increase in the effective hardness of the metal so that the hardness number obtained is not the actual hardness of the metal in the indented state. This is due to work hardening of the metal during the process of indentation. Attempt has been made to determine the absolute hardness by eliminating work hardening. This can only be done if the method does not appreciably deform the metal plastically. Two methods have been attempted first by Harris (1922) and other by Mahin and Foss (1939). They found that the absolute hardness was about one third of the normal hardness.

**Conical Indenters**

A conical diamond indenter for hardness measurement was first introduced by Ludwick in 1908. He used a sharp pointed diamond cone of included angle $90^\circ$ and defined the hardness as the ratio of the load to the area of curved surface of the indentation. Thus if for a load $W$, the diameter of the
impression is \( d \), then the Ludwick hardness number is given by

\[
H_L = \frac{4W}{\sqrt{2} \pi d^2}
\]

The Ludwick hardness number is independent of load, as well the indentations are geometrically similar, but varies considerably with the angles of the cone. This is probably because friction becomes increasingly important as the included angle of the cone decreases.

Rockwell Test

This test is based on the measurement of the depth of the penetration. A minor load is first applied followed by a major load which is then removed and with the minor load still applied the additional depth of penetration is measured directly on a dial gauge. The value obtained may be correlated with Vicker or Brinell hardness value. There are two scales of Rockwell hardness utilising different major loads and indenters. For softer materials a spherical indenter is used (Rockwell B) and for harder metals a conical indenter with a hemispherical tip (Rockwell C) is used.

The Pyramidal Indenter

The diamond pyramidal indenter was first used
by Smith and Sandland (1922) and was later developed by Messrs. Vickers Armstrong Ltd. The indenter is in the form of a square pyramid, the opposite faces making an angle of $136^\circ$ with one another. The diamond pyramid hardness method follows the Brinell principle in that, an indenter of definite shape is pressed slowly into the material e to be tested, the load removed, and the diagonals of the indentation measured and the hardness number is defined as the ratio of the load to the surface area of indentation. It also follows the Brinell test in the choice of the shape of the pyramid. In the Brinell test using the ball of diameter $D$, the range of indentation diameter is allowed to vary between 0.25$D$ and 0.5$D$. The average of these is 0.375$D$ and tangents drawn to a circle at the ends of a chord of length 0.375 $D$, include an angle of $136^\circ$ (Fig.I) hence the angle between the faces of the pyramid indenter. The geometry of the indenter is such that the base of the pyramid has an area equal to 0.927 times the surface area of the faces.

The diamond pyramid hardness (D.P.H.) also known as Vicker hardness ($H_v$) is defined by the formula:

$$H_v = \frac{2WSin^2}{d^2}$$

where $W$ is the load in Kg, $d$ is the diagonal of the impression in m.m. and $\theta$ is the angle between the
Fig: (I).

Fig: (II).

Fig: (III).
opposite faces of the indenter ( = 135°) 

\[ Hv = \frac{1.854 W}{d^2} \]

The Vickers hardness number is expressed in \( \text{Kg/mm}^2 \) and for normal use the accuracy may be better than 1/2 per cent. There are two advantages of this test. The first is that the indentations are geometrically similar for all the loads and hence the hardness is independent of the load for a homogeneous material. The second is that the load can be varied from 1 to 120 Kg, which means that all hardness variations obtained with metals can be measured on the same hardness scale.

Although the indenter, being made of diamond, suffers very little deformation during the formation of the indentation, it is generally found that when the indenter is removed the impression is not a perfect square. For annealed metals the impression has concave boundaries (pincushion appearance) corresponding to "sinking in" of the metal around the flat faces of the pyramid. For highly worked materials the indentation has convex boundaries (barrel shaped appearance) corresponding to "piling up" of the metal around the faces of the indenter. The length of the diagonal is affected by this but to much lesser extent than if the measurements were made to the centre of the sides. The
deformation will be small along the edges of the pyramid compared with the deformation at the centre of the faces.

The main difficulty in the Diamond Pyramid hardness test is that the specimen requires careful preparation and must be set horizontally to the axis of the pyramid, otherwise the impression obtained will not be symmetrical.

Micro-Hardness

The term micro-hardness means micro-indentation hardness as it actually refers to small indentations. This type of testing is used for thin materials; small precision parts, exploring hardness variations over small areas, and has been of great use in measuring the hardness of different electroplates.

Micro-hardness testers fall into two groups, the scratch method and the indentation method. Most scratch hardness testers are of historical interest only and because of the limitations of the scratch test metallurgists prefer indentation methods.

The first indenter for micro-hardness testing of metals was developed by Knoop (1939) and is called Knoop indenter. This indenter is a diamond pyramid in which the included conical angles, subtended by the longer and shorter edges respectively, are $172^\circ$, $30^\circ$
and $130^\circ$ respectively. The indentation formed has the shape of a parallelogram in which the longer diagonal is about 7 times as large as the shorter diagonal. The Knoop hardness number is defined as the ratio of the applied load to the unrecovered projected area i.e.

$$H_K (K.H.N.) = \frac{W}{L^2 C}$$

where $W = \text{load in Kg}$, $L = \text{length of long diagonal in m.m.}$ $C = \text{constant relating to projected area}$.

The double cone indenter as developed by Grodzinski (1952) consists of two cone faces joined on equal bases, the axis being in a line. The indenter has V shaped section in one plane and a circular cross-section in the perpendicular plane. The hardness is given by

$$H_{D.C.} = \frac{W}{A}$$

where $W = \text{load in Kg}$ and $A = \text{area of uncovered impression in sq. m.m}$.

For micro-hardness measurements along Tri-crystal boundaries in Tin, the present author has used diamond pyramidal indenter which can be fitted on the Vicker's projection microscope. The experimental techniques employed will be discussed in the chapter on techniques.

In the present investigation the micro-hardness measurements were made on the grain boundaries, it is necessary to give a brief review of the existing theories of grain boundaries in metals.
Grain Boundaries

The nature of the boundary between adjoining grains in a polycrystalline aggregate has been a favourite subject for discussion by metallurgists and physicists for many years. The early work of Rosenhain and Beilby (1957) supported the idea that an amorphous film some 100 atoms in thickness existed between the grains. Later Hargreaves and Hills (1929) proposed a "transition lattice", theory in which the boundary was considered to be a narrow region of transition, only a few atoms wide, across which the pattern of atomic sites changes from that of one crystal to that of the other. King and Chalmers (1949) have discussed in detail these two conceptions of the crystal boundary and the controversy arose round them.

If the boundary is a narrow region of transition some of its properties should depend on the difference in orientation between the adjoining crystals. Definite evidence for such effects have now been obtained. Forsyth et al (1946) have shown with Cu-Be and Al-Mg alloys that the extent of precipitation at a grain boundary changed abruptly wherever a change occurred in the relative orientations across the boundary. Lacombe and Yannaquis (1947) observed that the rate of attack of hydrochloric acid on grain boundaries in high purity
aluminium depended on the relative orientations of the adjoining grains and of the orientations of the boundary itself. Boundaries where the grains were of almost the same orientations or were in twin relationships to one another resisted the attack particularly well.

The attractiveness of the transition lattice idea stimulated interest in the problem of what form a boundary should have, in order to join crystals with the minimum amount of disarrangement. It has now become clear that, for small differences in orientation at least, this boundary will in fact consist of a row of dislocations. Burgers (1939) and Bragg (1940) first proposed the models of grain boundaries in terms of dislocations. The theory was later developed in detail by Shockley and Read (1949, 1950) and Van der Merwe (1950). Fig. (II) shows the very simple type of tilt boundary in which two crystals of simple cubic arrangement, slightly misaligned to each other are joined along the plane $x = 0$. The crystals are rotated by equal and opposite amounts about the $Z$ axis and differ in orientation by the angle $\Theta = Z \tan^{-1}(b/2h)$. The boundary consists of a sheet of parallel edge dislocations of the same sign whose lines are parallel to the $Z$ axis and are spaced at intervals 'h' along the $y$ axis. Provided that $\Theta$ is less than about $5^\circ$ the spacing of
the dislocations is large compared with the lattice constant and individual dislocations in the boundary can be clearly recognized. On the other hand, when $\theta$ exceeds about $15^\circ$ neighbouring dislocations lie within a few atom spacing of one another. In these large angle boundaries, the dislocations are so closely spaced that it is difficult to recognize individuals in the array, the description in terms of dislocations is then rather formal. In spite of this, the energy of a large angle boundary agrees surprisingly well with that calculated from the dislocation model.

A general grain boundary has five degrees of freedom, three of which result from the fact that the adjoining crystals can be rotated with respect to each other about three perpendicular axes, the other two being the degrees of freedom of the orientation of the boundary surface itself with respect to the crystals.

In fig. (III) is shown a 'twist boundary' i.e. a plane boundary between the halves of a crystal that are rotated relative to one another about an axis perpendicular to the boundary. This is formed from two intersecting sets of screw dislocations lying along perpendicular axes, the spacing of the dislocations being the same in each set. A single set of parallel screw dislocations is unstable because it causes a shear
strain in the crystals which extends a long way from the boundary. By introducing a second set of dislocations this far-reaching shear can be cancelled, so forming a stable boundary between two oppositely rotated crystals. Frank (1948) and Wilman (1950) have discussed the possibility of the formation of a twist boundary on a slip plane by means of 'rotational slip'. Experimental evidence for rotational slip has been put forward by Evans et al (1951) and Jilson (1950).

More dislocations have to be introduced in the case of a boundary which lies unsymmetrically with respect to the axes of the adjoining crystals. The reason for this is that when the boundary lies unsymmetrically, the crystal spacing of the two grains measured along the direction of the boundary are different. As such extra dislocations whose Burgers vectors are inclined to those of the first set are needed to take up this misfit. Lomer and Nye (1952) have confirmed this effect in bubble rafts experiment. They have shown that when all the dislocations in a boundary had parallel Burgers vectors, they formed a row perpendicular to these vectors, and that a boundary involving dislocations on non-parallel slip planes always had a well defined orientation for any given arrangement of physically distinct dislocations.

When the angle between adjoining crystals is
very small the spacing between the dislocation lines in a simple boundary is large enough to be resolvable by a microscope, so that a dislocation structure in this type of boundary should be detectable. Lacombe (1948) in study of 'Veining' in aluminium found that a net work of faint lines or veins existed in a crystal, which were revealed as rows of separate etch pits after etching treatment. Each etch pit was formed at the point of emergence of a dislocation line. It is interesting that the order of magnitude of the orientation difference across the veins was $10^{-3}$ radians or less, while the spacing of etch pits was about $3 \times 10^{-4}$ cm. or less. These values are broadly consistent with the dislocation relation $h = b/\theta$ when a reasonable value for $b$ is used.

Whatever the precise structure of grain boundaries the fact that there is departure from the perfect crystal structure means that each boundary atom on the average has more total energy than a grain interior atom. It does not immediately follow that each boundary atom on the average also has more free energy. However, calculations suggest that this is so and experiment confirms it.

An important feature which is made use of to determine grain boundary tension is the equilibrium
arrangement where grain boundaries meet. If a piece of polycrystalline metal is heated at a temperature high enough to ensure atomic mobility, the tension acting in each grain boundary will pull into equilibrium with those acting in the adjoining boundaries. Grain boundaries nearly always meet three at a time. At a triple junction the situation is as shown in fig. (IV). If there is equilibrium, and if the junction line is normal to the plane of the paper, then by applying a virtual work argument to the junction, it has been shown by Read (1953) that:

\[
\frac{E_1}{\sin \alpha_1} = \frac{E_2}{\sin \alpha_2} = \frac{E_3}{\sin \alpha_3}
\]

where \(E_1, E_2, E_3\) are free energies per unit area and \(\alpha_1, \alpha_2, \alpha_3\) are the equilibrium dihedral angles.

A generalization of this formula to take account of the orientation of the boundary with respect to the crystal lattice has been given by Herring (1950). By measuring the angles the relative free energies can be determined. This method has been used to study the variation of the energy of grain boundaries with the angle between the grains by Dunn and Lionett (1949) and by Aust and Chalmers (1950). Smith (1948) has shown by a statistical analysis of grain boundary angles in
metals that the observed values are generally consistent with a single energy for the boundaries.

A good account of the theory of grain boundaries is given by McLean (1957), Cottrell (1953) and Read (1953).