CHAPTER IV

ANTIMONY

Introduction:

There can be little doubt that antimony was known in ancient times, either in the form of the metal or in compounds. Antimony is regarded as one of the commonest elements, but it is neither widely nor abundantly distributed in nature. In order of abundance of metals in the earth's crust, it is rated as less than arsenic and about the same as mercury and cadmium, occurring to the extent of somewhat less than 0.0001 per cent. Over a hundred minerals contain antimony but commercial ores are limited to only a few. The principal ores of antimony contains the mineral known variously as stibnite, antimonide or antimony glance. Other antimony minerals occasionally found in ores that are commercially valuable include cervaltite or antimony/ochre kermesite, valentinite, white antimony or antimony bloom and senarmontite. Native antimony occurs in too small quantity to be commercially available. It is found in coal, river sands, some silver veins, in animal tissues and also with sphalerite, pyrite, quartz etc.

Antimony, with chemical symbol Sb, has an atomic number of 51, an atomic weight of 121.76 and isotopes of mass 121 (56 per cent) and 123 (44 per cent). It is in group V of the periodic table, in the sub-group that also
contains nitrogen, phosphorus, arsenic and bismuth, with 5 electrons in the outershell of the atom, permitting valence numbers of +3, +5 and -3. It is more metallic in both chemical and physical properties than any other member of the sub-group except bismuth. In addition to the normal crystalline metal, it exists in black, yellow and explosive forms. The stable modification of antimony melts at 630.5°C, boils at 1440°C and has a density of 6.7 gm/c.c. The metal in the normal crystalline form is silverly white, very brittle, but rather soft. It has low ductility which restricts its use to alloys such as lead and tin-base alloys in which the increased hardness and strength it imparts are desired. It possesses metallic lustre, is feebly pleochroic and weekly anisotropic. In polished sections, it is brilliantly white with very strong reflectivity, the percentage reflectivity, for green, orange and red being respectively 67.5 per cent, 58 per cent, and 55 per cent. Its hardness on Moh’s scale is 3 to 3.5.

Crystallographically it belongs to hexagonal scalenohedral class of the hexagonal system with space group 32/m and cell constants \( a = 4.501 \pm 0.003, \alpha = 57^\circ 05' \) and containing 2 Sb atoms. For hexagonal axes \( a_0 = 4.301, c_0 = 11.26 \) and the cell contains 6 Sb. Four well established forms \{01\overline{1}2\}, \{0001\}, \{10\overline{1}4\} and \{10\overline{1}1\} are known. It has a perfect cleavage
parallel to \{0001\}, sometimes distinct along \{10\overline{1}1\}, imperfect along \{10\overline{1}4\} and indistinct along \{1120\}. Along any other direction it gives uneven brittle fracture. Twinning on \{10\overline{1}4\} is common, is formed in complex groups of four layers and six layers. It also exhibits poly-synthetic twinning.

From X-ray analysis it is deduced that the structure consists of two interpenetrating face-centred lattices, the symmetry being that of a rhombohedron. The length of the unit edge of the rhomb is 6.20 A and the shortest distance between two atoms is 2.92 A. The angle between any two edges of the rhombohedron is 86° 58' and the angle between the (100) and (010) faces is 92° 55'.

The more important application of antimony are in the formations of alloys containing antimony, such as various type metals, bearing metals, lead-storage battery plates, Britania metal, calile coverings, hard lead sheets, pipes, collapsible lead tubes, soft-solder and in castings. Substantial amounts of antimony are consumed in making antimony oxide and other antimony compounds. The compounds of antimony are toxic, but metallic antimony is generally considered to be non-toxic. It is used in medicine, in making pigments and paints.

Because of its poor mechanical properties pure antimony is used only to slight extent in castings, as for metal trimming on coffins. Likewise, antimony rich
alloys are of little importance, hence it is as an addition to other metals that antimony has found its place in physical metallurgy. Of these, the soft metals lead and tin are by far the most important host metals.

The stable modification, metallic antimony forms brittle silvery-white rhombohedral crystals which are considerably less volatile than those of arsenic. Single crystals of antimony have been prepared, the methods adopted being, in general, similar to those employed for bismuth. Among the properties of such single crystals that have been investigated are the mechanical properties (Gough & Cox 1930), the electrical resistance (Bridgman 1929), the thermoelectric properties (Bridgman 1928) and the magnetic susceptibility (Mchennan & Cohen 1929, Versbaum 1927).

Growing Single Crystals of Antimony:

The artificial crystals of antimony are easily obtained in various ways, such as the reduction of SbCl₃ by hydrogen. Various allotropic modifications are known, but the rhombohedral is the stable form, the only one found in nature. The present author has not studied any natural crystals, but crystals were prepared in the laboratory by the technique described in Chapter II.

While embarking upon growing single crystals of antimony from the melt, one obvious difficulty was
encountered, viz. the melting point of antimony being 630.5°C, the pyrex tube which begins to soften at about this temperature could not be used for growing crystals in the vertical temperature gradient furnace. Moreover, there were no available means to make the silica tube as per requirements, it was necessary to use some other crucible, which is not attacked by antimony and which can withstand this temperature. The choice fell on carbon crucible. Moreover, instead of vertical furnace, horizontal furnace was used and the carbon crucible containing the required amount of antimony was placed in a long horizontal silica tube firmly fixed in the clamps and which was connected to a rotary pump to create a fairly good vacuum of the order of $10^{-2}$ m.m. of mercury in the tube, the other end being tightly closed. Throughout the formation of the crystal the rotary pump was operated. Small but quite good crystals were obtained after about 24 hours' operation. Unlike bismuth single crystals, the size of the crystals was limited because of the changed set up, the size of the crucible and the silica tube.

The crystals so grown were taken out of the crucible and were immersed in the liquid air and after the crystals had attained the liquid air temperature, they were cleaved along the (111) plane. The cleavage surfaces thus obtained were examined under the Vickers projection microscope. The present work is chiefly concerned with the etching of cleavage faces, but it was thought
desirable to study the oppositely matched cleavage faces, before they were subjected to etching. During this study some new features were found on the cleaved surface and as a result a new series of experiments were required to be carried out.

Figures (40a, b, x 105) show the features on the oppositely matched faces. Similarly another pair of oppositely matched faces are shown in Figs. (41a, b, x 105). It is interesting to note that there is general correspondence of features on both the photographs, but the detailed study of these photographs reveal that, at many places, the features are not completely reflected whereas at some, places - there is a complete reflection of cleavage markings. One such pair is shown in photomicrographs (Figs. 42a, b, x 105) taken at high magnification. It should be noted that there is perfect correspondence so far as all typical features are concerned. Such regions of exact correspondence are quite rare. This might be due to the fact that plastic stresses are introduced while cleaving the crystals and hence both the faces are deformed to different degrees. Moreover, distortion of the lattice by thermal stresses during growth from the melt, and thereby resulting in plastic deformation is typical about crystals grown from the melt. It is known that the simplest way of reducing thermal stresses is to ensure that the interface between melt and ingot remains plane throughout the growth of the crystal. Solidification in a horizontal boat such
as this employed in the present case occurs over an inter-
face which is rather distorted by the lack of radial 
symmetry of the heat flow.

Figures (43, x 105; 44, x 175) show phase contra-
st photomicrographs of freshly cleaved surfaces. These 
photomicrographs show clearly the very flat triangular 
features which are of particular interest. It is hard to 
understand as to how such features could be observed on 
cleaved specimens. Such features are also observed on 
 oppositely matched cleavage faces (Figs. 45a, b x 105). In 
this case also, as mentioned above, there is general 
correspondence between the features on both the surfaces 
on a microscopic scale, but detailed study of microstructu-
res reveal that such is not the case. One interesting 
feature on these photomicrographs is the perfect reflect-
ton of a triangular pattern in the centre of both the 
photomicrographs. Such features were found on a few 
samples, but their occurrence is very rare. A light 
profile study shows clearly the feature to be an elevation 
on the surface. A close examination of the triangular 
pattern reveals the following important characteristics:

(i) Extreme linearity of the edges of the 
triangular figure.

(ii) The step formation of the walls of the 
pyramidal depression.
edges of the main face have been observed.

The typical photomicrograph of the natural faces of the vapour grown single crystals of antimony are shown.
Fig. (47) x900.

Fig. (48) x900.
Figure (46) shows the rows of triangular growth features arranged in a direction normal to (111) plane. The most important point about these rows of triangular patterns is that it obeys the equation $n_A = n_B + n_C$. For two intersecting rows $n_B = 0$, hence $n_A = n_C$.

This relation was found to hold in several cases. This, therefore, leads one to conclude that they represent dislocation tilt boundaries. This conclusion was confirmed by studying the etch features on the natural faces. Figure (47) shows three intersecting boundaries and triangular patterns on the natural faces. The triangular features have close correspondence with the features observed on the cleaved surfaces of the crystals grown from the melt (Figs. 43, 44) and therefore, it is very likely that during the formation of the crystals some such triangular facets might have been included at some cavities which are revealed during the act of cleavage. The etching of the features of Fig. (47) is represented by the photomicrograph, Fig. (48, x 900). This photomicrograph discloses clearly the etching of the three boundaries and the disappearance of the triangular patterns. This shows that the triangular patterns are elevations and not depressions. This further supports the idea presented above, namely, during the formation of the crystal from the melt the triangular facets might have been trapped at the cavities. The boundaries which are revealed by the etching appear
to be tilt boundaries because the etch pits count on these boundaries obey the well-known relation \( n_A = n_B + n_C \). It should be emphasized that this relation is true only for dislocations boundaries revealed by appropriate etching. One more interesting point is that the etch pits so formed are oppositely oriented to the growth triangles. At high magnification a typical photomicrograph obtained by etching the natural face is shown in Fig. (49, x 540). This photomicrograph very clearly shows the lineage boundaries obeying the above relation.

It should be noted that various workers have reported the revealing of dislocations by etching method using different etchants. The above etch patterns obtained by etching the natural faces are all produced by the etchant which was developed, after several trials and errors in this laboratory by the present author. The detailed discussion of the development of the etchant and the study of etch patterns so obtained is given below.

**ETCHING**

**Introduction:**

For investigations on the physical properties of crystals, it is very important to know about the perfection of their structures and the type of defects occurring in them. It is now recognized that one method of investigating the perfection of crystals is by etching their
surfaces with appropriate etchants. Defects in the crystal lattice gives rise to differences in the speed of etching, and as a result etch figures arise. Thus etch pits under favourable conditions of etching can nucleate on dislocations and other surface defects.

The investigation in the present work concerns with the study of dislocations by etching techniques in single crystals of antimony grown in this laboratory. Experiments on etching of antimony have been reported by a number of workers. (Wernick et al 1958, Shigeta and Hiramastu 1958, Kosevich 1960, Soifer and Startsev 1960). A preliminary investigation on the etching of the cleavages faces of single crystals of antimony is already reported (Pandya and Bhatt 1961).

Wernick et al studied the etching of cleavage surfaces of single crystals of zone-refined antimony. The etching was carried out by etchants having composition ranging between the CF$_4$ and the Dash etchants. They concluded from their observations on etch pit data for intersecting boundaries, plastic deformation and annealing that the pits were nucleated at dislocation sites. Shigeta and Hiramastu reported the study of chemical as well as thermal etch pits, on single crystals of antimony prepared by zone-melting, chemical etch pits being produced by an etchant consisting of 10 gm. FeCl$_3$, 30 c.c.of HCl and 120 c.c.
of H₂O at temperatures ranging from 25° to 45°C for one to several minutes; whereas the thermal etch pits were produced by keeping the crystal at a temperature of 400°C under a pressure of 10⁻² to 10⁻⁴ m.m. of mercury. Their observations indicated the chemical pits to be at the sites of dislocations emerging from the grains. Using dilute nitric acid as an etchant, Soifer and Startsev (1960) studied dislocation etch pits on the cleavage surfaces of antimony single crystals.

**Experimental Procedure:**

Single crystals of antimony grown from the melt were cooled to the liquid air temperature and cleaved with a sharp blade along the (111) plane, the only perfect and easy cleavage plane of antimony. The cleaved surface was highly polished and smooth. They were then examined under a microscope and were subsequently etched at room temperature by a variety of etchants. Among them are:

1. Inorganic acids like HCl, HNO₃, H₂SO₄ and chromic acid of various concentrations.
2. Organic acids like citric, acetic, and tartaric acids of various concentrations.
3. Acidic and alkaline salts.
4. Suitable combinations of acids, salts etc. as shown below:
(a) CP$_4$ etchant.
(b) 28 parts glacial acetic acid + 5 parts HNO$_3$ + 4 parts HF + 3 parts Br$_2$.
(c) Dil. HNO$_3$
(d) 10 gm. FeCl$_3$ + 30 c.c. HCl + 120 c.c. water.
(e) 2 c.c. HF + 1 c.c. HNO$_3$ + 2 c.c. AgNO$_3$.
(f) 30 parts CH$_3$COOH + 5 parts HNO$_3$ + 4 parts HF + 3 parts Br$_2$.

The time of etch was adjusted to each etchant so as to obtain well developed pits. Immediately after etching for appropriate time, crystals were washed in running distilled water and dried. The etch patterns thus obtained were studied by using high resolution microscopic techniques described in Chapter II.

Observations:

It soon became apparent that the few successive etching of the crystal, the surfaces made them mottled and black, the blackness being the result of corrosion which started immediately within few multiple etches. The mottled character of the surface is obviously due to the inherent property of selective etching of the specimen, but the blackness of the surface effectively prevents one from taking further observations, because the reflectivity of the surface is greatly deteriorated, so as to escape the detailed microtopographical analysis and to defeat the use
of high resolution optical techniques described in Chapter II. This, therefore, limits the study of crystal surfaces in the depth direction. Because of these primary difficulties, it was decided to study in detail the various aspects of several etchants and if possible to develop an etchant which would be free from such undesirable properties and at the same time which would be helpful in studying defect structures - particularly line singularities by delineating them. It is, therefore, worthwhile to examine in detail the ideal and desirable characteristics of an etchant with reference to the nature of surfaces which are about to receive it. These aspects are carefully considered in the following section.

Development of an Etchant:

The inhomogeneities in a crystal are revealed by etching only because they react at inherently different rates with the usual etching reagents. The structural defects (e.g. point defects, line defects etc.), inclusions segregated area etc. are selectively attacked by the etching reagent and as a consequence their precise locations are manifested finally by some visible etching characteristic, such as cavities, striations, local discolouration etc. Before etching many of the inhomogeneities and defects associated with the section of interest may be extremely small in size - even entirely invisible. However, during etching the areas occupied originally by certain
of these inhomogeneities will increase in size far beyond their original dimensions and eventually reach a size which will be visible and amenable to detailed study under a variety of optical techniques.

The successful application of etching depends upon several factors. Among them the important factors are as follows:

(1) Condition of the metal surface that is to be etched.

(2) Chemical composition of the etching reagent selected.

(3) Temperature of etching reagent selected.

(4) The length of the time the specimen is etched.

As far as the etching reagent is concerned, it should possess the following characteristics:

(1) The reagent should be of such composition that it will give good all round results and reveal the greatest number and variety of structural characteristics, defects and irregularities present. At the same time, it should be able to distinguish its effect from those produced by any of the etchants which can attack on only definite types of defects. Thus this selective etching should enable one to study only specific defects.
(2) The reagent should be simple in composition and stable so that its concentration will not change appreciably upon standing or during use at room temperatures and also if possible at moderately higher temperatures.

(3) The reagent should have constant characteristics at a particular temperature so that the conditions of etching can be easily reproduced.

(i) **Temperature of etching:** The rate at which the etching reagent attacks the specimen depends upon the temperature at which etching takes place. The precise influence of temperature, however, varies according to the composition (amount of impurity present) and previous history of the specimen. It is, therefore, desirable for reproducible results to carry out etching experiments only at definite temperatures.

(ii) **Time of etching:** The time of etching is perhaps one of the most important factors contributing to successful etching and attendant appearance of the structure enabling their detailed study possible with the help of optical techniques. For example, if the time of etching is short as compared to that appropriate for a particular material, the
etched structure will not be completely developed nor will there be sufficient details revealed to permit accurate interpretation of the etched area. However, too long a time of etching is just as unsatisfactory as one too short, owing to details of the surface structure being thereby obscured to varying degrees and frequently some parts of the structure being completely obliterated. The time of etching depends upon the conditions of the metal (normalized, hardened, etc.) and the temperature and the reagent.

(4) The reagent, while acting on the specimen should not form products which will precipitate on the surface of the specimen considered, but must have such a composition that reaction products are immediately dissolved - chemically or physically - in the solution. They must possess closer affinity with the etchant than with the specimen.

(5) The reagent should be non-injurious and non-toxic to the person conducting the work.

(6) For orientation determination, the etchant should develop etch pits or facets with plane faces accurately parallel to the crystallographic planes of low index.
Looking to the above requirements of the etchant and the surface to receive it, (in the present case cleavage plane of antimony single crystals), it was found after several trials that the etchant developed by the present author possessed most of the properties discussed above and was well suited for revealing dislocations. Before arriving at this etchant, various combinations have been tried. The etchant developed in this laboratory consists of three parts of Nitric acid (concentrated and A.R.quality) nine parts of tartaric acid and 1 part of distilled water. This etchant, it appears, has two more important characteristics.

1. Starting of the reaction is characterized by the evolution of bubbles from the surface.

2. With the progressive etching of the specimen, the surface is not tarnished and does not become too coarse to be unsuitable for studies in depth and in extension.

The chemistry of the etchant can be explained as follows. The tartaric acid acts on antimony forming antimony tartarate which is soluble in nitric acid, thereby removing the reaction products so formed.

Vigorous agitation of etchant while acting on the specimen produces fairly good polish. This aspect has one typical interesting point, viz., good polishing appears to depend upon the content of impurity and the previous
Fig. (51) x 1800.

Fig. (52) x 360.

Fig. (53) x 360.
treatment of the specimen. Metals supplied by various firms contain different amounts of impurity and hence the crystals grown from one lot differ from another batch of crystals. As a result a solution prepared for one specific set of crystals was found to be unsuitable for another set. This is not the only case, but etching time to obtain pits of approximately the same size also varies with the amount of the impurity. This latter point was also found to be true in the case of etching of cleavage faces of the natural crystals of mica and calcite (Pandya & Pandya, 1958) Thus the impurity plays a very important part and the etchant was required to be slightly modified accordingly. It was found by experiments that in such cases use of HgO or instead of distilled water was more advantageous. The observations of etch patterns secured by this etchant along with other etchants are reported below:

Figures (50, 51, x 1800) represent the photomicrographs of the etch pits produced by the new etchant developed in this laboratory. This (Fig.50) shows the characteristic random distribution of etch pits. All the pits are not of the same sizes but they differ to a marked extent. Individual pits consist essentially of a hollow tetrahedron and have the outline of an equilateral triangle. (Fig.51) represents the advanced stage of etching showing the development of etch pits with multiple etching. The important point to be noted is that the pits do not preserve their shape, but with gradual etching they turn
Fig. (54) x1500.

Fig. (55) x360.

Fig. (56) x360.
into quadrilateral, pentagons and hexagons. Some of the pits also show terraced structure.

Figure (52, x 360) represents the etch pits produced by an etchant containing two parts of HF, one part of HNO$_3$, and two parts of 5 per cent aqueous solution of AgNO$_3$ for a period of one second. At high magnification, the phase contrast photomicrograph is shown in Fig.(53, x 360) which represents the same area etched for one more second. The photograph clearly shows the pits inside the pits forming a terrace, the etch pits being of two types, (1) flat bottomed and (2) point bottomed pits. This on further etching of one second gives rise to the formation of well-known block pattern observed on diamond, fluorite and calcite. It should be noted that pits are very sharp in outline but at the same time the etching time is too short to carry out detailed study. After about three seconds etch the surface is blackened and becomes useless for further study.

Figures (54, x 1500; 55, x 360) represent the phase micrograph and a simple photomicrograph of a freshly cleaved surface of antimony crystals. In these photomicrographs, attention is specifically drawn to the boundaries which do not appear to be of the same nature. This shows that the etchant is capable of revealing such boundaries. Details of such boundaries will be taken up in next section.
Origin of the Pits:

The most important aspect of etching experiments is to determine the origin of pits. Several experiments have been carried out in this connection. They will now be presented below.

(1) A freshly cleaved surface was etched by the new etchant and then a suitable easily identifiable area on the crystal surface was selected for studying the development of etch pits on successive etching. It was found that the density of etch pits revealed was found to be practically independent of the exposure time to the etchant. But after a certain time which depends upon the crystal prepared from different lots, it was observed that individual pits begin to overlap each other and the pattern became too complicated to be of any valuable analysis.

Thus the density of pits remains constant for a fairly good time of etching which clearly indicates the pits to be at some specific defects.

(2) Various rows of etch pits giving rise to boundaries are observed on the crystal surfaces. Some of the typical boundaries observed
as rows of etch pits are shown in Figures (56, x 360; 57, x 750; 58, x 750; 59 x 1800). All these patterns were obtained by etching with the new etchant. The etch patterns on Figures (56, 57, 58) are obtained by etching them for about one minute. The crystals were selected from different lots. The remarkable features of these photomicrographs are as follows:

(i) Although all the crystals have been etched under identical conditions of temperature and time of etching, the disclosure of the boundaries is of different degrees. It might be due to different amounts of impurity present in the crystals. However, it should be pointed out that the present author is not quite certain as to what extent the impurity plays a part in determining the dislocation content of the crystal, although, it is well-known that the impurities diffuse towards the defect structure of the crystals.

(ii) Very few isolated pits are observed on the surface, showing thereby the etchant has a marked action on the boundaries.
This preferential etching is one of the important characteristics of the new etchant. In other words the defect free surface offers greater resistance and therefore remains practically unaffected with the initial etching.

(iii) The etch pits on the boundaries obey the relation

\[ n_A = m_B + n_C \]

or \[ n_A = n_C \] when \( n_B = 0 \)

where the symbols have the usual meaning.

A high magnification photomicrograph of the etched boundaries is shown in Fig.(59) which enables one to count the etch pits along this intersecting low angle boundaries. This etch pit count obeys the above relation.

These observations, therefore, suggest that etch pits are the seat of dislocation lines meeting the surface of the crystal. Crystals were deformed in a number of different ways which are described in detail in the previous chapter on Bismuth. Local deformation was produced by scratching the freshly cleaved surface with a sharp needle. This surface was subsequently etched. The etch pattern (fig. 60, x 360) consists of slip traces and mechanical twins. Note also the scarcity of random pits. The second experiment was carried out by deforming the crystal which was then cleaved and etched by CP₄ etchant.