CHAPTER VII
ELECTROLYTIC ETCHING OF DISLOCATIONS IN BISMUTH-ANTIMONY CRYSTALS

In the previous chapter, study of the chemical etching of Bi-Sb cleavages, development of a new dislocation etchant and the superiority of the new etchant over the known etchants were reported. This chapter is devoted to a systematic study of electrolytic etching of Bi-Sb cleavages. The development of the electrolytic etchant is discussed and the results obtained are compared with those of the new chemical etchant. Some interesting conclusions are presented in this chapter. As there is no information on the electrolytic etching
of dislocations in Bi-Sb crystals, the present work was undertaken.

There is a great amount of literature on various techniques for revealing dislocations in non-metals, and after getting success with ionic crystals, many workers have developed different techniques for making dislocations visible in metals and alloys. Out of these, the etching technique is often employed for the determination of dislocation densities and assessing the crystal perfection.

Various workers employed electrolytic etching technique for revealing dislocations in metal and alloy crystals. Hannibal used electrolytic etching technique for revealing dislocations in Fe-Ni alloys. An electrolytic etching technique was employed by Demkin for revealing dislocations in monocrystalline Molybdenum. He used methyl alcohol solution of sulphuric acid, with the surface inclined at 12° to the (010) plane, which showed subgrain boundaries below as well as on the surface. Three boundaries appeared as dislocations jointed in the etch grooves. It was shown that small variation in parameter of electrolytic etching of Mo single crystals created conditions under which the movement of dislocation took place in the absence
of external stresses. The dislocations moved in a discontinuous manner, leaving behind discrete series of flat bottomed etch pits. Cross slip dislocation was also observed and the slip planes of individual dislocation were identified.

Experimental results about dislocation etch pits on the \{100\}, \{111\} and \{110\} surfaces of Molybdenum single crystals were reported by Pong Duan et al.\(^4\). Electrolyte used was a mixture of methyl alcohol, sulphuric acid and chloric acid. The arrangement of dislocation lines in space from observed etch figures was deduced by them. The successive etching technique was employed to study the arrangement of dislocations in space. Using the etching, polishing and etching technique the correspondence between the etch figures and the sites of the emergence of dislocation lines was studied (by them). It was also reported that, when the angle between the dislocation and the observation plane was less than certain critical value \((15^\circ-24^\circ)\), no etch pits developed. The significance of the results of the etch pit figures has been discussed and compared with other methods of direct observation of dislocation lines. It has been shown that the etch figure method is superior to all other existing methods in the study of dislocations in metal crystals.
Kolontsova et al.\textsuperscript{5,6} in their study of Aluminium crystals found that electrolytic etching occurs in the wetting boundary layer on immersion of the crystal in an electrolyte of the same composition as that used for polishing (1 part per-chloric acid, $d = 1.55$ for 1.9 parts acetic acid) with a current density approximately 15 mA/cm$^2$. It was reported that for etching a definite portion of a crystal it was necessary to measure carefully the depth of immersion of the crystal in the electrolyte. The etching process is capricious and does not always result in the formation of etch pits. Layer by layer chemical etching of the Aluminium crystals further indicated that the etch pits disclosed by the method suggested by previous workers\textsuperscript{7,8,9} correspond to decorated dislocations. A search for etch method by means of which 'fresh' defects - undecorated dislocations could be revealed, was conducted by them and it was found that electrolytic etching and etching by ionic bombardment reveal not only decorated dislocations, but also 'fresh' ones, acquired by the crystal in the process of deformation by shear. Polishing of the deformed crystal surface followed by etching, revealed etch pits along the shear stress. They have also reported that the chemical etching revealed grown-in dislocations only, and not dislocations produced by deformation, while electrolytic
and ion-bombardment etching revealed dislocations of both the types.

Berlec from his detailed study on electrolytic etching of Tungsten crystals has shown that etch pits can be produced only on the planes of certain crystallographic orientation. When the plane of polish is a cubic plane, the etch pit traces pointing in \(\langle 100\rangle\) directions form a square. If the crystal is rotated from this orientation, the shape of the pit changes, and if the angle of rotation is greater than 35° no well defined pits are produced. Further, he showed that if the plane of etching is \((111)\), or nearly \((111)\), careful etching will produce pyramids at the dislocation sites. Capability of the etchant for revealing fresh dislocations was established by the polygonization study. Etching, polishing and etching experiments were employed to check the reliability of the etchant for revealing dislocations. It was also reported that the increase in the current density was associated with the increase in the pit density. The detailed study of etching of Tungsten crystals of different impurities showed that the presence of carbon could markedly affect the size, shape and density of etch pits. Instead of crystallographic pits, striations consisting of very small
pits were observed on crystal surface if the metal contained high impurity.

Morr described a simple electropolishing technique for Lead-Telluride. It was used at room temperature and thus avoided the risk of cracking due to thermal shock associated with technique at 100°C. The electrolyte consisted of 20 gm KOH in 45 cc of water with 200 cc of glycol and 20 cc of ethanol added to it. Ground samples were etched using a platinum foil cathode at a current density of about 0.2 Amp/cm².

A study has been made on the etch pits formed chemically and electrolytically on (100) and (111) faces of Silver by Kawabuchi et al. On (100) faces, changes in orientation of etch pits and re-orientation within etch pits have been obtained by the electrolytic etching carried out in the aqueous solution of KCN. On (111) faces triangular etch pits were obtained by the electrolytic etching in the aqueous solution of KCl and AgNO₃. The results were interpreted on the basis of kink.

Doerschel has reported the study of dislocation in Antimony and Antimony rich Bismuth alloys by using electrolytic etching technique. The present work is concerned with the electrolytic etching of Bi-Sb cleavages.
The experimental arrangement used for electrolytic etching is shown in Fig. VII-1. A freshly cleaved specimen (C) to be etched was made the anode of an electrolytic bath. The circuit was assembled as shown in Fig. VII-1. The stainless steel cathode (D) was of much greater size than the anode. The distance between anode and cathode was kept minimum to lower the cell voltage and thereby reducing the heating effect.

The electrolyte (E) in the present case consists of,

- 66% methyl alcohol,
- 19% sulphuric acid,
- 9% hydrochloric acid, and
- 4% diethylene glycol (% by volume).

A cold water bath (F) was kept surrounding the cell and the surface (111) - cleavage plane to be etched was kept horizontal, about 10 mm below the cathode.

Voltage was supplied across the bath from a d.c. supply and was increased in small steps from zero to about 0.8 V. The current at each step was noted and a graph of current against voltage was plotted. The nature of the graph is shown in Fig. VII-2.
For the current and voltages corresponding to the line AB on the graph, electrolytic etching takes place and for higher values of voltages (CD) polishing takes place. The parameters were so adjusted that conditions on the part AB of the graph may prevail during etching experiments.

Before switching off the current the etched specimen was removed and washed immediately in water, then in industrial methylated spirit and finally dried in a warm draught from a hair dryer. This electrolyte has been reported by Yim et al. for polishing Bi-Sb alloy crystals.

Results obtained are given in a tabular form in Table VII-1.

Critical value of etching time is essential for revealing sharp and point bottomed etch pits. By increasing the etching time more than the fixed minimum value, it was observed that almost all the pits increased in size but the number and shape of the pits remained the same.

The behaviour of the surface on successive etching on increasing current density in step is likely to give useful information of an electrolytic etchant. Fig.VII-6
### TABLE VII-1
DETAILS OF ELECTROLYTIC ETCHING EXPERIMENTS

<table>
<thead>
<tr>
<th>Sr. Current No.</th>
<th>Current density amp/cm²</th>
<th>Cell voltage in Volts</th>
<th>Etching time in Sec.</th>
<th>Pit shape</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.005</td>
<td>0.3</td>
<td>10</td>
<td>Irregular - shape of etch pit is not clear.</td>
<td>VII-3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.005</td>
<td>0.3</td>
<td>25</td>
<td>Slightly elongated etch pits with rounded edges.</td>
<td>VII-4</td>
</tr>
<tr>
<td>3</td>
<td>0.005</td>
<td>0.3</td>
<td>45</td>
<td>Sharp, point bottomed etch pits [pyramidal pits (with an equilateral triangular outline), elongated pyramidal pits (with isosceles triangular outline) &amp; pentagonal pits] with random distribution.</td>
<td>VII-5</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>0.4</td>
<td>25</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>0.015</td>
<td>0.5</td>
<td>15</td>
<td>&quot;</td>
<td>-</td>
</tr>
</tbody>
</table>
represents random distribution of pentagonal, elongated and pyramidal etch pits obtained by etching the cleavage surface $(\text{III})$ for a few seconds at a current density of $0.005 \text{ amp/cm}^2$, and cell voltage $0.3 \text{ V}$. The photomicrograph (Fig.VII-7) shows the same area of Fig.VII-6 after further etching at a current density of $0.015 \text{ amp/cm}^2$ and cell voltage $0.5 \text{ V}$. Almost all the pits have increased in size but the shape and density of etch pits have remained unaltered. This indicates that the shape and density of the etch pits are independent of current density. However, it has been reported by Berlec in his study of electrolytic etching of Tungsten that the increase in the pit density was associated with the increase in the current density.

The morphology of different shaped etch pits and planes developed on etching are shown schematically in Fig.VII-8. An attempt was made to determine the planes of the etch pits by using optical goniometric method, but since the faces of the pit slopes are insufficiently flat to give an adequate goniometric signal, the author could not determine the indices of the etch pit planes, by goniometric method. Hence, the stereographic method of three trace analysis (Reed-Hill) was employed to determine the planes and directions of the edges of the
et’ch figures. The results obtained are given in a tabular form (Table VII-2).

The salient features of the above observations can be summarised as follows:-

(i) When all the experimental conditions are kept the same, etch pits are observed for all values of current density in the etching region.

(ii) Shape of the etch pit is independent of the current density.

(iii) Density of etch pit is independent of current density.

(iv) Shape of the etch pit is independent of the etching time.

Figures VII-9(a) and 9(b) represent the etch pattern on the oppositely matched cleavage faces after etching the specimen for 15 seconds at the current density of 0.015 amp/cm² and cell voltage 0.5 V. The general correspondence of sharp point bottomed elongated triangular etch pits is observed, but some deviation from the perfect match is visible. This may be due to the bending of a dislocation line at or near the cleavage plane during the act of cleavage.
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Pit shape</th>
<th>Planes developed</th>
<th>Directions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pyramidal etch pits</td>
<td>(111), (111), (111)</td>
<td>&lt;110&gt;</td>
</tr>
<tr>
<td>2</td>
<td>Elongated triangular</td>
<td>(111), (122), (122)</td>
<td>One edge is parallel to [110] direction and the other two are in non-crystallographic directions.</td>
</tr>
<tr>
<td>3</td>
<td>Pentagonal</td>
<td>(111), (111), (111), (122) and (122)</td>
<td>Three edges are parallel to &lt;110&gt; directions and two edges are in non-crystallographic directions.</td>
</tr>
</tbody>
</table>
Figures VII-10(a) and 10(b) are good examples where triangular elongated and pentagonal etch pattern on the oppositely matched cleavage faces appear identical. Exact one to one correspondence between the pentagonal etch pits represented by 'A' is observed on the matched cleavage faces. Quite a few discrepancies from a perfect match are clearly visible in the photomicrograph.

For further confirmation, that all the three types of etch pits developed by the electrolytic etching are at the sites of dislocations, successive etching experiments were carried out. Figures VII-11(a) and 11(b) show pyramidal and elongated triangular etch pits developed after etching the specimen for 45 seconds and 70 seconds respectively. Almost all the pits have increased in size but the density and shape of the etch pits remain practically constant.

Rows of triangular etch pits and intersecting rows of etch pits are also observed. Above results show that the etch pits are at the specific defects like dislocations.

To understand the mechanism responsible for the production of etch pits of different shapes on electrolytic etching, the results are compared with those of chemical
etching developed in this laboratory\textsuperscript{15}. The results are reported as follows.

In order to bring out the differences and actions at preferential sites one cleavage face was etched electrolytically [Fig.VII-12(a)] and its counter part was etched in the chemical etchant [7 parts saturated solution of tartaric acid + 4 parts nitric acid (70\% A.R. Quality) + 1 part water] (Fig.VII-12(b)). Another example of etching the oppositely matched cleavage faces, one electrolytically and its counterpart chemically is shown in Fig.VII-13(a) and 13(b), respectively. The etch pattern of the above photomicrographs reveal the following:-

(i) The etch pits developed on electrolytic etching are of different shapes - pyramidal (with an equilateral triangular outline), elongated pyramidal (with an isosceles triangular outline) and pentagonal [Fig.VII-12(a) and 13(a)].

(ii) Almost all the pits are point bottomed and randomly distributed. All the pits produced on chemical etching are triangular pyramidal in shape [Figs.VII-12(b) and 13(b)].

(iii) There is almost one to one correspondence in the position of the etch pits on oppositely matched cleavage faces.
Fig.VII-12(a) shows triangular pyramidal and pentagonal etch pits observed after etching the cleavage face electrolytically. The surface was deeply polished electrolytically and re-etched as before. Fig.VII-14(a) shows the etch pattern on the same area of Fig.VII-12(a). There is no change in the appearance of the etch pattern indicating thereby that the shape of the etch pits is not due to some surface heterogeneity but is associated with some dislocation structure.

The same crystal surface was polished electrolytically and then etched in a chemical dislocation etchant. The etch pattern of the same area of Fig.VII-12(a) is shown in Fig.VII-14(b). It is interesting to note that all the etch pits are triangular in shape but the position and the number of etch pits are identical with those observed on electrolytic etching. Polishing effect of the etchant is also visible in the photomicrograph.

To understand the cause responsible for the development of different shaped etch pits observed on etching the crystals electrolytically, various experiments were undertaken, and the results are reported as under.
Freshly cleaved specimen was indented by Vickers Pyramidal Indentor and subsequently etched electrolytically. Fig. VII-15 shows cluster of triangular etch pits near the indentation mark and rows of triangular etch pits in \(\langle 110\rangle\) slip directions. It is interesting to note that the pits which are aligned along the slip traces are all triangular pyramidal in shape and elongated and pentagonal shaped etch pits are randomly distributed.

The cleavage face of the specimen crystal was bent about \([111]\) axis. The specimen was kept at about 250°C in vacuum \((10^{-4} \text{ mm of Hg})\) for about three days and was slowly cooled to the room temperature. It was then etched electrolytically. Fig. VII-16 shows the resulting etch pattern observed on the specimen surface after the above treatment. It is observed that the pyramidal pits are aligned along \(\langle 112\rangle\) direction during polygonization while the other shaped pits (B,C) are randomly distributed.

A double etch technique was employed to study the dislocation motion. The cleaved surface of the specimen was first etched electrolytically to reveal the positions of the dislocations. Then a low stress was applied to the specimen. The specimen was then re-etched electrolytically. A second etch will both reveal the new positions
of dislocations and enlarge the old pits representing the original dislocations. Fig. VII-17 shows the new (A) and old (B) triangular pyramidal etch pits. It is observed in the photomicrograph that such type of motion is observed only in the case of triangular pyramidal etch pits. Here also it is noteworthy that, elongated triangular and pentagonal pits do not show any movement indicating thereby that the dislocations revealed by these pits have not moved at all under applied stress.

Matched pair of cleavage faces were etched, one electrolytically and the other in the chemical etchant. They were then annealed at 250°C for three days in vacuum of about $10^{-4}$ mm of mercury, and re-etched as before. Fig.VII-18(a) shows the etch pattern on one cleavage face etched electrolytically and Fig.VII-18(b) shows the etch pattern on the oppositely matched cleavage face etched in the chemical etchant. Pyramidal pits (A) developed on the matched cleavage face showing observable movement, is clearly visible in the photomicrograph. Another example of etching the oppositely matched cleavage faces, one electrolytically and its counterpart chemically as above, is shown in Fig.VII-19(a) and 19(b), respectively. It is interesting to note that the elongated pyramidal (A)
and pentagonal (B) pits [Fig.VII-19(a)] have not moved at all. Triangular pyramidal pits [Fig.VII-19(b)] denoted by (A and B) corresponding to elongated pyramidal and pentagonal pits [Fig.VII-19(a)] do not show any movement.

The results of the above experiments lead the author to believe that the triangular etch pits developed on electrolytic etching are at the sites of fresh and unpinned dislocations, while elongated pyramidal and pentagonal etch pits are probably at the dislocation sites pinned by the precipitation of impurities around them.

It is known that the dislocation core energy is different at different dislocation sites depending upon the nature of the surface surrounding the dislocations. This may give rise to difference in dissolution rates at different dislocation sites. It seems that the electrolytic etchant is critical in differentiating between pinned and unpinned dislocations on account of ionic bombardment on the crystal surface, which results in the development of elongated and pentagonal pits at the sites of the aged dislocations pinned by the impurities and pyramidal pits at the sites free from impurities. Contrary to this, chemical etchant is not critical, the etchant will produce only pyramidal pits. Patel and Desai and Bhagavan Raju
and Bansigir\textsuperscript{17} have reported similar results in CaF\textsubscript{2} and NaCl crystals respectively.

**Conclusions:**

(1) The electrolytic etchant is capable of revealing dislocations intersecting the cleavage plane.

(2) The etch pit density is independent of the current density.

(3) The shape of the etch pit is independent of the current density and etching time.

(4) The etchant is critical in differentiating between pinned and unpinned dislocations. The unpinned dislocations are revealed as pyramidal triangular etch pits while elongated pyramidal and pentagonal etch pits reveal the sites of emergence of dislocations pinned by precipitation of impurities around them.

The chemical etchant produces only pyramidal triangular etch pits. It seems that the chemical etchant is incapable of differentiating between pinned and unpinned dislocations by producing pits of different shapes.

(5) The shape of the etch pit developed on electrolytic etching depends upon the nature of the surface surrounding the dislocation.
REFERENCES

4. Fong Duan, Ming-Maben and Lichi (1965) Scientia Sinica (China), 14, 1130.