CHAPTER XIII

STUDIES ON ETCH RATES OF DIFFERENT FACES OF NATURAL DIAMONDS

13.1 Introduction

The importance of etching in the case of diamond and the work done on this aspect by the various investigators has already been described in chapter X, on the etching of diamond surfaces. It appears that a little work has so far been done on the comparative oxidation rates of different faces of diamond. Evans and Phaal (1962), Phaal (1962,1965) have reported that they measured the oxidation rates for the (111), (110) and (100) faces of single crystals of diamond at temperatures between 650° C and 1350° C. The oxidation of the diamond surfaces in their experiments was carried out by allowing a fast flowing stream of previously purified oxygen over the faces to be oxidised at the required temperature. For these experiments they selected different faces not on the same crystal but on different crystals. Since similar faces of different crystals usually etch differently even when etched under the same conditions, it was thought that such experiments when performed on different faces of the same crystal would give more reliable information on the oxidation rate than the information obtained by oxidising different faces of different crystals. This chapter, therefore, deals with studies made on the comparative oxidation rates on different faces of the same crystal. The oxidation experiments in the present work were carried out in hot KNO_3 (Analar grade) at 580° C.

Since it is very difficult to find a diamond having good (111), (100) and (110) faces on the same crystal, suitable for investigation, some of these faces were obtained by grinding and polishing them on some good quality crystal. The surfaces so ground were within 1° of the low index plane and almost free of polishing marks. These crystals were obtained on request from Dr. Custers, of the Diamond Research Laboratory, Johannesburg.

The observations made on different crystals are described below.

13.2 Etching of Crystal No. 1

This crystal had four natural (111) octahedral faces, two (110) and two (100) polished faces. The (110) and (100) faces were lapped so smooth that no polish marks could be seen. Etching was carried out until pits of measurable size were produced on each face. The oxidation rates on different faces were compared by measuring the rate at which pits grew during etching.

After the crystal was etched for seven hours at 560° C in the fused potassium nitrate, it was taken out for observation. During this period of etching triangular pits of measurable size were produced on octahedral faces whereas very little etching had taken place on the cubic (100) and the dodecahedral (110) faces. Thus figure 111 (X 500) represents the etch pattern produced on the (111) faces. The same crystal was etched for a further six hours at the same temperature, during which time the pits on the octahedral faces grew bigger in size and pits of measurable size appeared on both the cubic faces as well as dodecahedral faces. These patterns are shown respectively in figure 112 (X 500) and figure 113 (X 500). Thus the same crystal was successively etched for different periods and the sizes of the pits were measured on each face after a regular interval of time. All the measurements made on octahedral (111), cubic (100) and dodecahedral (110) faces on some six typical pits on all faces are given in Table Nos. 13.1, 13.2 and 13.3.

TABLE NO. 13.1 : OCTAHEDRAL FACE

Pit No.	10 hrs.etch at 580° C.	14 hrs.etch at 580° C.	18 hrs.etch at 580° C.	Increase in size of the pit per hour	
	Pit size in microns				
	I stage	II stage	III stage	II - I	III - II
1.	22.3	34.5	46.6	3.05	3.02
2.	24.4	36.7	48.6	3.07	2.98
3.	21.7	33.8	46.1	3.02	3.07
4.	24.2	36.1	48.5	2.98	3.10
5.	23.0	34.8	46.5	2.98	2.92
6.	23.6	35.6	47.7	3.00	3.02

TABLE NO. 13.2 : CUBIC FACE

Pit No.	14 hrs.etch at 580° C.	18 hrs.etch at 580° C.	22 hrs.etch at 580° C.	Increase in size of the pit per hour	
	Pit size in microns				
	I stage	II stage	III stage	II - I	III - II
1.	15.1	23.2	31.4	2.02	2.05
2.	15.4	23.6	31.7	2.05	2.02
3.	15.6	23.6	31.5	2.00	1.98
4.	14.8	22.7	30.7	1.19	1.95
5.	13.1	20.9	28.5	1.95	1.90
6.	16.1	24.4	32.8	2.07	2.10

TABLE NO. 13.3 : DODECAHEDRAL FACE

Pit No.	16 hrs.etch at 580^{o} C.	20 hrs.etch at 580^{o} C.	24 hrs.etch at 580^{o} C.	Increase in size of the pit per hour	
	Pit size in microns				
	I stage	II stage	III stage	II - I	III - II
1.	7.8	11.6	15.2	0.95	0.90
2.	7.5	11.1	14.3	0.90	0.80
3.	7.6	11.0	14.8	0.85	0.87
4.	8.0	11.3	15.0	0.82	0.92
5.	7.3	10.9	14.7	0.80	0.95
6.	7.8	11.3	14.7	0.89	0.85

From these tables it is clear that :

(1) The etch rate on the different faces is not the same.

(2) The rate of increase in the size of the pit on any face is independent of the initial size of the pit.

(3) The etch rate on the octahedral faces is fastest whereas that on dodecahedral faces is the slowest.

(4) The etch rate of cubic faces is less than that of the octahedral faces and more than the dodecahedral faces.

(5) Pits appear first on octahedral faces and then later on cubic and dodecahedral faces respectively.

13.3 Etching of Crystal No. 2

This crystal had five natural octahedral, two polished dodecahedral, and one polished cubic face. In order to confirm the observations made on crystal no. 1, experiments similar to those described above were carried out on crystal no. 2. The observations on this crystal are given in Table Nos. 13.4, 13.5 and 13.6. The observations are in complete agreement with those on crystal no. 1.

TABLE NO. 13.4 : OCTAHEDRAL FACE

Pit No.	10 hrs. etch at 580° C.	14 hrs. etch at 580° C.	18 hrs. etch at 580° C.	Increase in size of the pit per hour	
	Pit size in microns				
	I stage	II stage	III stage	II - I	III - II
1.	18.1	29.4	40.8	2.82	2.85
2.	18.1	29.5	40.8	2.85	2.82
3.	18.3	29.6	40.9	2.82	2.82
4.	18.7	30.1	41.5	2.85	2.85
5.	18.2	29.4	40.7	2.80	2.82
6.	18.3	29.5	40.7	2.82	2.80

TABLE NO. 13.5 : CUBIC FACE

Pit No.	14 hrs.etch at 580° C.	18 hrs.etch at 580° C.	22 hrs.etch at 580° C.	Increase in size of the pit per hour	
	Pit size in microns				
	I stage	II stage	III stage	II - I	III - II
1.	12.6	20.2	27.7	1.90	1.87
2.	12.4	19.9	27.5	1.87	1.90
3.	12.8	20.3	27.8	1.87	1.87
4.	13.0	20.6	28.0	1.90	1.85
5.	12.3	19.8	27.4	1.87	1.90
6.	12.8	20.2	27.7	1.85	1.87

TABLE NO. 13.6 : DODECAHEDRAL FACE

Pit No.	16 hrs.etch at 580° C.	20 hrs.etch at 580° C.	24 hrs.etch at 580° C.	Increase in size of the pit per hour	
	Pit size in microns				
	I stage	II stage	III stage	II - I	III - II
1.	6.2	9.4	12.5	0.80	0.77
2.	6.1	9.2	12.4	0.77	0.80
3.	6.0	9.2	12.3	0.80	0.77
4.	6.8	9.9	13.1	0.77	0.80
5.	6.5	9.7	12.9	0.80	0.80
6.	6.3	9.5	12.8	0.80	0.82

13.4 Etching of the cleavage faces from different sources

A comparative study on the etch rates of similar faces of crystals obtained from different deposits was also carried out. For this work, the octahedral cleavages of South African as well as Panna (Indian) diamonds were selected from our stock. These cleavages were etched under the same conditions, in hot potassium nitrate solution at 580° C. The experimental technique was the same as that described above for the polished faces of diamonds. These experiments were carried out on three pairs of Panna and South African diamond cleavages, independently etching one pair at a time. Table Nos. 13.7, 13.8 and 13.9 represent the measurements made on these pairs. It is clear from the tables that :

(1) As before, the rate of increase in the size of the pits on any crystal is independent of the initial size of the pits.

(2) The etch rate of Panna cleavages in each case is faster than that of South African cleavages.

In the present case the pit depths were also measured on both pairs. These observations are shown in Table No. 13.10. The depths were measured by the depth of

TABLE NO. 13.7

PANNA

Pit No.	Pit size in microns		Increase in size of the pit per hour
	Ist stage 7 hrs. at 580° C.	IInd stage 9 hrs. at 580° C.	
1.	5.60	7.74	1.070
2.	6.80	8.93	1.065
3.	7.20	9.35	1.075
4.	7.50	9.64	1.070
5.	8.21	10.38	1.085
6.	9.72	11.86	1.070

SOUTH AFRICAN

1.	3.01	4.21	0.60
2.	4.02	5.20	0.59
3.	3.30	4.48	0.59
4.	4.21	5.39	0.59
5.	3.90	5.10	0.60
6.	2.81	3.98	0.585

TABLE NO. 13.8

PANNA

Pit No.	Pit size in microns: Ist stage 7 hrs. at 580^{0} C.	Pit size in microns: II nd stage 9hrs. at 580^{0} C.	Increase in size of the pit per hour
1.	6.71	8.21	0.75
2.	6.92	8.43	0.755
3.	7.50	8.99	0.745
4.	10.53	11.03	0.75
5.	9.71	11.21	0.75
6.	9.61	11.11	0.75

SOUTH AFRICAN

1.	5.02	5.92	0.45
2.	3.91	4.82	0.455
3.	3.63	4.52	0.445
4.	3.03	3.93	0.45
5.	4.221	5.11	0.445
6.	4.16	5.06	0.45

TABLE NO. 13.9

PANNA

Pit No.	Pit size in microns I stage 8hrs.etch	II stage 10hrs.etch	III stage 12hrs.etch	Increase in size of the pit per hour II-I	III-II
1.	7.13	9.34	11.61	1.10	1.13
2.	7.50	9.70	11.90	1.10	1.10
3.	8.23	10.42	12.63	1.09	1.10
4.	8.34	10.60	12.80	1.13	1.10
5.	8.22	10.46	12.67	1.12	1.10
6.	7.86	10.06	12.26	1.10	1.10

SOUTH AFRICAN

1.	5.03	6.31	7.69	0.64	0.64
2.	4.86	6.14	7.43	0.64	0.645
3.	4.63	5.92	7.23	0.645	0.655
4.	5.05	6.35	7.64	0.65	0.645
5.	5.09	6.39	7.67	0.64	0.64
6.	5.01	6.29	7.57	0.64	0.64

TABLE NO. 13.10

PANNA

Pit No.	Depth of the pit in microns		
	Ist set	IInd set	IIIrd set
1.	2.12	1.91	2.41
2.	2.14	1.92	2.39
3.	2.16	1.93	2.40
4.	2.18	1.94	2.42
5.	2.20	1.90	2.38
6.	2.13	1.98	2.39

SOUTH AFRICAN

1.	1.52	1.20	1.62
2.	1.51	1.19	1.63
3.	1.55	1.18	1.61
4.	1.60	1.21	1.57
5.	1.54	1.23	1.59
6.	1.53	1.21	1.64

focus method and confirmed by Light Profile Microscopy. It is clearly seen from the table that the pits on Panna cleavages are deeper compared with those formed on South African Cleavages.

13.5 Conclusions

The two sets of observations taken on polished (100), (110) and natural (111) faces of diamonds suggest that the rate of dissolution is different on different faces of diamond when they are etched in potassium nitrate. It is clear that the rate of dissolution is fastest on the octahedral faces while it is slowest on dodecahedral faces of diamond. The cubic faces have dissolution rates intermediate between the two other faces. Thus the octahedral faces appear to be the most susceptible to etching. It is also observed that all the octahedral faces are characterised by triangular depressions called trigons. It is conjectured that these trigons may be the result of the dissolution of octahedral faces in nature. Absence of micro-disc patterns on the octahedral faces similar to those observed by Tolansky and Pandeya (1961) on dodecahedral faces also indicates that these faces might have been subjected to dissolution in nature for a longer period, during which, if such discs are formed, they are washed out as reported by Patel and Goswami (1962). Thus the findings described in this chapter also support the absence of micro-disc patterns on the octahedral faces.

The observations on the comparative etch rates of octahedral cleavages obtained from Panna diamonds and South African diamonds suggest that Panna cleavages are more susceptible to etch than the South African cleavages. It is therefore clear that diamond cleavages obtained from diamonds from different deposits etch differently.

A comparison of Tables 13.1 and 13.4 and 13.7, 13.8 and 13.9 shows that for the same crystal, natural octahedral faces etch at a faster rate than cleaved octahedral faces.

CHAPTER XIV

CLEAVAGE AND ETCHING OF DIAMOND BOARTS

14.1 Introduction

It seems that no work has so far been reported on the cleavages of boarts or on etch patterns produced on them. This may be due to the fact that the cleavages obtained from boarts are usually very rough and uneven.

Since boart diamond is of immense industrial importance it was thought worthwhile to pursue the etching technique (reported in the earlier chapter) to the studies of boarts and their cleavages. This chapter describes such studies made on boart diamond.

The crystals for the present investigation were selected from our stock and were cleaved in the usual manner. Some crystals already cleaved, were supplied on request by Dr. Custers of Diamond Research Laboratory, South Africa.

14.2 Interferometric study of the cleavage faces

Figure 114(a) (X 40) represents the cleavage face of a diamond boart obtained from South Africa. It is seen from the photograph that the surface is highly uneven and only portions show some nice cleavage, the rest of the surface shows uneven fracture. In order to study the nature of the cleavage surface, a multiple beam interferogram was taken over the region of figure 114(a), which is shown in figure 114(b) (X 40). The dispersion could not be increased beyond a certain limit because of some projections on the surface.

The interferogram reveals that the cleavage is not very smooth, there is no regular step formation. It also reveals that the cleavage face has a slight curvature.

In order to obtain a large dispersion in the interferogram, a small cleavage face was selected. Figures 115(a) (X 75) and 115(b) (X 75) represent the face and its interferogram. This interferogram supports the observations made from figure 114 above.

14.3 Etching of the cleavage faces

The cleavages, were etched in molten potassium nitrate in a nickel crucible in a muffle furnace.

Figure 116 (x 350) represents the etch pattern produced by etching for 12 hours at 560° C while figure

118 (x 600) represents the etch pattern produced in 36 hours at 500° C. Figures 117 (X 350) and 119 (X 600) represent typical etch patterns produced on good quality octahedral cleavages given here for comparison. The comparison of the etch patterns in figures 116 and 118 with figures 117 and 119 reveals that :

(1) The etch pattern on boart cleavages consists of a number of isolated triangular pits not very much different from the etch patterns of figures 117 and 119.

(2) The etch pits in figures 116 and 118 are smaller in size as compared to that shown in figures 117 and 119.

(3) The pits on boart cleavages are rectilinear, having sharp corners in contrast to the pits observed on the good quality octahedral cleavages.

In order to make the numerical measurements on the etch rates of boart cleavages as compared to that on good quality crystals, three pairs of boart and good quality diamond cleavages were taken. Each pair was independently etched for three successive periods under the same conditions, in hot KNO_3 melt at 560° C. Table Nos. 14.1, 14.2 and 14.3

TABLE NO. 14.1

GOOD QUALITY DIAMOND CLEAVAGE

Pit No.	Pit size in microns			Increase in size of pit per hour	
	I stage 10 hrs.	II stage 12 hrs.	III stage 14 hrs.	II-I	III-II
1.	7.63	10.83	14.03	1.60	1.60
2.	7.24	10.44	13.64	1.60	1.60
3.	6.93	10.03	13.23	1.55	1.60
4.	8.02	11.22	14.32	1.60	1.55
5.	7.31	10.51	13.71	1.60	1.60
6.	6.84	9.94	13.04	1.55	1.55

BOART CLEAVAGE

1.	5.32	7.32	9.32	1.0	1.0
2.	4.38	6.38	8.28	1.0	0.95
3.	5.76	7.66	9.56	0.95	0.95
4.	6.08	8.18	10.08	1.05	0.95
5.	3.82	5.82	7.82	1.0	1.0
6.	5.02	7.02	9.02	1.0	1.0

TABLE NO. 14.2

GOOD QUALITY DIAMOND CLEAVAGE

Pit No.	Pit size in microns			Increase in size of pit per hour	
	I stage 10 hrs.	II stage 12 hrs.	III stage 14 hrs.	II-I	III-II
1.	5.86	9.26	12.66	1.70	1.70
2.	6.02	9.42	12.82	1.70	1.70
3.	7.34	10.74	14.24	1.70	1.75
4.	6.31	9.61	12.91	1.65	1.65
5.	8.42	11.72	14.92	1.65	1.60
6.	5.90	9.30	12.70	1.70	1.70

BOART CLEAVAGE

1.	3.86	6.06	8.26	1.10	1.10
2.	4.08	6.18	8.38	1.05	1.10
3.	5.61	7.81	10.01	1.10	1.10
4.	4.38	6.68	8.78	1.15	1.05
5.	4.22	6.42	8.62	1.10	1.10
6.	3.84	6.04	8.24	1.10	1.10

TABLE NO. 14.3

GOOD QUALITY DIAMOND CLEAVAGE

Pit No.	Pit size in microns			Increase in size of pit per hour	
	I stage 10 hrs.	II stage 12 hrs.	III stage 14 hrs.	II-I	III-II
1.	6.32	10.22	14.22	1.95	2.0
2.	7.24	11.14	15.04	1.95	1.95
3.	8.34	12.24	16.14	1.95	1.95
4.	5.92	9.72	13.62	1.90	1.95
5.	6.01	10.01	14.01	2.0	2.0
6.	7.82	11.72	15.62	1.95	1.95

BOART CLEAVAGE

1.	2.98	5.58	8.08	1.30	1.25
2.	3.34	5.84	8.34	1.25	1.25
3.	3.84	6.34	8.84	1.25	1.25
4.	2.86	5.36	7.96	1.25	1.30
5.	4.32	6.92	9.42	1.30	1.25
6.	3.98	6.58	9.18	1.30	1.30

represent the measurements made on them. It is clear from the tables that :

(1) The size of the pit on any crystal increases independently of its initial size.

(2) The etch rate of good quality octahedral cleavages in each case is more than that of the boart cleavage.

The nature of the boart cleavage after etching [redacted] was studied by multiple beam interferogram, shown in figure 120(b) (X 175) taken on the region shown in figure 120(a) (X 175). The interferogram clearly reveals that the surface has undergone a general dissolution and this dissolution has clearly taken place by micro pit formation.

In the present investigations, it was many a times observed that the etch pattern on the cleavage face of a boart shows the regions of different pit density. This is clear from the photomicrograph of figure 121 (X 175) which is typical. It may be noted that in some regions the pits are isolated, while in some other region they are so much crowded that they can not be resolved.

14.4 Stratigraphical etch patterns

During the present investigations, the stratigraphical etch patterns, so commonly observed on good quality crystals, were also observed on boart cleavages. A typical stratigraphical pattern on boart cleavage is shown in figure 122 (X 250). In order to see if this stratigraphical pattern extends right through the body of the crystal, a thin flake 0.98 mm. thick was etched in KNO_3. Figures 123(a) (X 200) and 123(b) (X 200) represent the etch patterns thus produced on the opposite faces of a thin plate. From the figures, it is quite clear that there is a considerable amount of correspondence in the etch patterns on the two sides. This suggests that the stratigraphical sheets go right through the body of the crystal.

14.5 Conclusions

It is very clearly seen from the cleavage faces and their corresponding interferograms that the boart cleavages are usually very rough, uneven and have a little curvature.

The comparative study of the etch patterns on the boarts and good quality octahedral cleavages has shown that in order to produce the pits of the same size as observed on the good quality cleavages, the boart cleavages should either be etched for a longer period at the same temperature or they should be etched at a still higher temperature. It is therefore conjectured that the boart cleavages are more resistant to etch than good quality diamonds. From the tables it is quite clear that the oxidation rates of the good quality crystal cleavages is more than that of boart cleavages.

The regions of different pit density may be due to the fact that cleavage is smooth in some parts and rough in others.

The study of stratigraphical etch pattern suggests that the boart crystals have also grown up by layer deposition as some good quality diamond crystals.