CHAPTER X

ETCHING OF DIAMONDS

10.1 Introduction

Detailed knowledge of the processes taking place on diamond surfaces is highly desirable due to the extensive use of diamond in industry. Heat generated during drilling and grinding processes as well as the high temperatures generally used during diamond tool manufacture could increase the possibility of graphitization and oxidation which would in turn increase the rate of wear of the diamonds in the first instance and secondly weaken the bond between the matrix and the diamond. Therefore the studies of the etch patterns produced on diamond surfaces is of much importance. A great deal of work has so far been done on the etching of diamond, a brief review of which is given in the next section.

10.2 A review of the existing information

Natural etch figures in the form of solution cavities produced by magma are rarely observed on the octahedron faces of diamond. The earliest report in this connection is by Rose (1872).

Luzi (1892) carried out experiments on corrosion of diamond in molten blue ground. He exposed the crystals for 20 to 30 minutes at a very high temperature of 1770°C in a Kimberlite flux. The results thus obtained were very poor and instead of getting triangular marks, he obtained irregular and oval scars. The corrosion was considered to be due to the presence of oxygen in the fuse, and the results of the experiment proved otherwise that the blue ground was the original matrix of the diamond.

Fersmann and Goldschmidt (1911) carried out experiments on the etching of diamond, to investigate experimentally whether etching and solution produced the surface and reflection phenomena, which they suspected to be the solution phenomena on the natural crystals. Their method was to plot the reflected light signals from the crystal surfaces on a goniometric projection, when growth structure was supposed to be represented by points and straight lines, and the solution structure by bent lines. They had in mind that the rounded forms of diamond crystals were due to solution. The experiments of Fersmann and Goldschmidt consisted in heating the diamond octahedra and the octahedral cleavages to about 900° C in potassium nitrate or soda fluxes. The duration of the attack lasted for a long time, in some cases for several hours. They certainly produced triangular and rounded etch marks on the diamond surfaces, but because they were mainly interested in their theory of hemihedrism, no measurements were made and all the drawings were made by hand.

Williams (1932) introduced photomicrography to the study of diamond surfaces and the etch phenomena. He in collaboration with John Perry subjected a diamond octahedron to the fusion of potassium nitrate at the temperature of 900° C. During the time of 2 hours of etching the crystal lost one third of its weight. The photomicrograph imparted nothing that was not known from the earlier experiments and certainly the drawings made by hand looked more impressive.

Wilcock (1951) realising that the previous experiments on etching of diamond were of a damaging nature started etching at low temperatures. Nothing of special importance was observed by him.

Tolansky and Omar (1952) reported etch spiral in the form of a row of triangular pits making the shape of one turn of a spiral. The pseudo spiral was not one corresponding to the growth spiral which is the consequence of crystal growth by spiral mechanism. It was the result of preferential etching along surface flaws.

Custers (1954) by etching (111) cleavage face in air at 1400° C for two minutes reported the formation of bridges starting from the centres of the sides of the etched triangular pit and meeting at the centre.

Omar, Pandya and Tolansky (1954) carried out etching of octahedral faces in KNO_3 at temperatures ranging from 500° C to 700° C. They found that the concentration of etch pits within any growth trigons was less than elsewhere and this they attributed to a lower concentration of dislocations within the trigons. At 700° C the whole of the crystal face was eaten away and a striking block formation resulted.

Pandya and Tolansky (1954) from their studies of the etch patterns on cleavage (111), polished (110) and (100) faces of diamond have reported the formation of crystallographically oriented straight line patterns, which have revealed for the first time, the sectional history of growth of diamond. A wide report of the etching of diamond carried out by Tolansky and his team of workers has been given by Tolansky (1955).

Emara and Tolansky (1956) have shown that dodecahedral faces are much more susceptible to etch in nature than the octahedral faces.

Patel and Tolansky (1957) established that the rectilinearity of pits formed by etching octahedral faces of diamond depended in a sensitive manner on the temperature and rate of etch. Slow etching in potassium nitrate at 475° C produced sharp rectilinear pits while at 525° C etching was much more faster and the pits were rounded off.

Patel and Tolansky (1957) studied in detail the etch patterns on octahedral cleavages of diamond.

They established that the etch pits were distributed in three ways (i) random small pits (ii) striking linear arrangements and (iii) individual isolated pits usually larger than the others. By etching cleaved blocks a striking stratigraphy was revealed and it was proved that the individual stratigraphical sheets went right through the whole crystal. Hence the etch strata revealed for the first time the whole growth history of diamond.

Omar and Kenawi (1957) etched diamonds by heating them on a molybdenum filament in a low pressure (about 2.5 μ of mercury) oxygen. The etch figures obtained were sharply triangular. Frank and Puttick (1958) made an attempt to produce negatively oriented etch pits by heating octahedra in steam, chlorine and wet hydrogen at 800° C but did not succeed in their attempt. They did however, produce such pits by heating in fused kimberlite at about 1450° C.

Evans and Sauter (1961) etched octahedral, cubic and dodecahedral faces of diamond in various oxidising gases at reduced and at atmospheric pressures in the temperature range of 800° C to 1400° C. They observed a change in the orientation of the etch pits as the temperature was increased. They also considered the formation of surface graphite at temperatures below 1400° C.

Phaal (1962) examined the mechanism of etch pit formation on diamond in greater detail during a study of the kinetics of diamond oxidation and came to the conclusion that the reversal in orientation of the etch pits was in fact due to an attack by carbon dioxide which was one of the reaction products.

Evans and Phaal (1962) have studied the pressure dependence of the diamond oxygen reaction at a number of fixed temperatures. They determined the relative etch rates for the various faces of diamond and found that below 1000° C the rate of etching was the slowest on the (100) face. An explanation for the different etch rates observed on different faces was also given by them.

Patel (1961) studied the etch pits formed on octahedral cleavages of diamond. He found that although the shape of the pits was same, their structures differed.

Eccentricity observed in the case of some pits was explained by postulating inclined linear dislocation lines in the body of the crystal. Patel (1962) proposed a new mechanism of etching to explain the formation of etch figures of various shapes and orientation observed on octahedral faces. This mechanism also explained (1) how trigons were converted into hexagons while etching in a flux of potassium nitrate and (2) the displacement of the cleavage lines without any visible formation of etch pits during etching.

Patel and Ramanathan (1962) by etching natural (111) and polished (100) faces of diamonds in strong oxidising agents like potassium chlorate, obtained the pits of both the orientations and discussed the mechanism of their formation. They showed it for the first time that the etch could be initiated at such a low temperature as about 380° C and even at this temperature pits could be formed of negative orientation on octahedral faces. Patel and Ramanathan (1964) and Ramanathan (1963) have shown that in order to explain the formation of the two types of pits produced by the same etchant at same temperature one should take into account the energy of the surface around the dislocation in relation to the energy of the etchant.

Seal (1962), (1963) and recently (1965) has reported a study of the internal structures of some diamonds as revealed by etching polished sections. Fused potassium nitrate was used as an etchant in all his experiments. He has shown that there have been different types of diamond growth, that some diamonds have grown and then partially dissolved and then regrown, that there is a relation between the kind of the etch structure which is found and the type of diamond material. He has made an attempt to classify the structures which have been observed and given some interpretation of their significance, he could not find any correlation between the internal structure of natural diamond and its geographic origin.

Harrison and Tolansky (1964) used the stratigraphical etch patterns obtained on diamond surfaces to reveal the structure within the diamond. They have given the description of the past growth history of a clear apparently good quality octahedron diamond, which was arrived at by successive sectioning and study of the sectioned slabs by an etch technique.

Varshavskii (1965) carried out experiments for revealing dislocation sites in diamonds by etching them at high temperatures in air.

Recently Phaal (1965) reported the oxidation rates for the (111), (110) and (100) crystal faces of diamond single crystals at temperatures between 650° C and 1350° C. He has shown that the diamond oxygen reaction is not simply oxidization of diamond to gaseous CO_2 or CO but involves an intermediate process in which a carbon film forms on the diamond surface.