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Etching of diamond octahedrons at high temperatures and pressure with controlled oxygen partial pressure

S. YAMAOKA, H. KANDA, N. SETAKA
National Institute for Researches in Inorganic Materials, Namiki-1 chome, Sakura-mura, Niihari-gun, Ibaraki 300-31 Japan

Etching of a natural diamond octahedron was carried out at temperatures of 800 to 1400° C and at pressures of 15 and 40 kbar under controlled oxygen partial pressure in the range 10^{-17} to 10^{4} atm by use of oxygen buffers. Well-defined etch pits of equi-angular triangule outline were formed. When the results were plotted based on log P_{O_2} versus $1/T$, reversal of the pit orientation clearly occurred on a boundary curve expressed by an equation, $\log P_{O_2} = -9.0 \times 10^4/T + 63$, where P_{O_2} (atm) and T (K) are oxygen partial pressure and temperature, respectively. Etch pits with the same orientation as an octahedral face were produced in a low temperature and high P_{O_2} region, and those with the opposite orientation, i.e. the same as for natural "trigon", were produced in the other region.

1. Introduction

On natural diamond octahedral faces are often seen small depressions bounded by equi-angular triangules, which are called "trigons". The vertices of a trigon point in opposite directions to the vertices of the octahedral face. This is termed negative orientation [1]. Their ubiquitous nature and similarity in appearance from stone to stone indicate that they arise from some common process during the formation or subsequent transport of the diamond. On the other hand, positively oriented triangular pits have been formed by etching natural diamond octahedrons with an oxidizing agent such as KNO_3 and $KClO_3$ at high temperature and normal pressure [2]. This is the main reason why controversy has lasted until recently over whether the trigons were caused by an etch or growth [2–5].

Because diamonds are formed deep under the earth, it is reasonable to carry out etching experiments at high temperature and pressure. The authors recently etched diamond octahedrons using water as an etchant at high temperatures of 1100 to 1300° C and at high pressures of 50 kbar. The etched features formed on an octahedral face were almost the same as the trigons seen on natural diamonds and no positively oriented pits were produced [6].

Now the problem is: what causes an etched triangular pit to be reversed in its orientation? Evans and Sauter [7] etched natural diamonds by heating them in air and found a change in the orientation of the etch pits: a positively oriented pit was formed at temperatures below 900° C and a negatively oriented one at temperatures above 1000° C. The authors carried out a preliminary etching experiment at high temperature and pressure using transition metal oxides as etchants. In this experiment as well, triangular pits with both orientations were obtained: a negative pit or trigon was formed at higher temperature and a positive one at lower temperature. The temperature where the orientation became opposite was varied by etchants. Because transition metal oxides have a specific partial pressure oxygen, P_{O_2}, in a closed system, P_{O_2} could be thought to be one of the factors which controlled etched features.

It is the object of the present paper to make clear the role of P_{O_2} for the etched features of diamond octahedrons.

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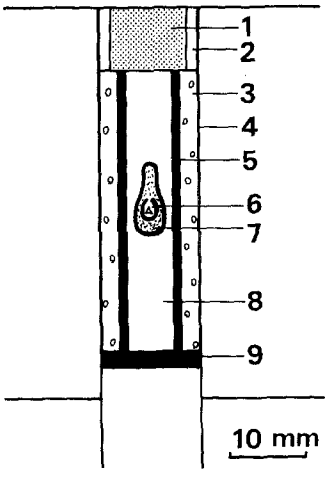


Figure 1 A sample assembly used in the present experiment (1) steel, (2) pyrophillite, (3) talc, (4) lead foil, (5) graphite heater, (6) sample in an inner capsule, (7) oxide mixture in a sealed outer capsule, (8) BN, (9) graphite end plate.

2. Experimental details

Small natural octahedral diamonds 0.5 to 1 mm in edge length were used as starting samples. They were colourless and transparent having very few or sometimes no trigons on each face. Two sample stones were put into a small platinum capsule 2 mm diameter and 4 mm long with one end sealed. The capsule was then filled with fine quartz powder to prevent diamond stones from contacting each other and the capsule wall during an experiment. The small capsule was placed with an oxide mixture into a large platinum capsule 4 mm diameter and 10 mm long. The latter capsule was sealed by d.c. arc welding. The double capsules were finally placed into a furnace assembly of a piston-cylinder type high-pressure apparatus [8] as shown in Fig. 1.

The following two-phase coexisting systems of Fe–O and Mn–O were adopted as oxide mixtures. They were mixtures of FeO and Fe_3O_4, Fe_3O_4 and Fe_2O_3, Mn_3O_4 and Mn_2O_3, and Mn_2O_3 and MnO_2. As long as these two condensed phases coexist in equilibrium, the system is kept under a fixed oxygen partial pressure at a certain temperature and total pressure. Therefore, the oxide mixtures served as oxygen buffers to a sample in a closed system. An inner capsule was used as a separator between the oxides and the diamond stones to prevent direct reaction between them.

An etching experiment was carried out at temperatures of 800 to 1400° C and at a total pressure of 15 kbar by use of a piston-cylinder type high-pressure apparatus. When a mixture of Mn_2O_3 and MnO_2 was used, experiments were preformed at a total pressure of 40 kbar and at temperatures below 1300° C. This stems from the fact that oxygen partial pressure increases to 39 kbar at 1300° C in this system [9]. The experimental procedures were the same as that described before [6]. The etching time was varied from 5 min to 5 h according to the experimental conditions. Temperature and total pressure are considered to be accurate within ± 20° C and ± 1 kbar, respectively.

After an experiment, surface structure changes of an octahedral face were examined by a differential interference microscope. X-ray powder diffraction data of an oxygen buffer were also taken to determine whether an oxygen partial pressure had been kept constant during an experiment.

3. Results

A triangular etch pit became opposite in its orientation at a certain temperature when the same oxygen buffer was used. A positively oriented pit was formed at lower temperature and a negatively oriented one at higher temperature. The latter cannot be distinguished from natural trigons. Because an oxygen buffer gives a specific oxygen partial pressure, P_{O_2} (atm) at constant temperature, T (K), and total pressure, P_T, and $\log P_{O_2}$ is generally proportional to $1/T$, the experimental results were plotted based on $\log P_{O_2}$ versus $1/T$. The relations of $\log P_{O_2}$ and $1/T$ of

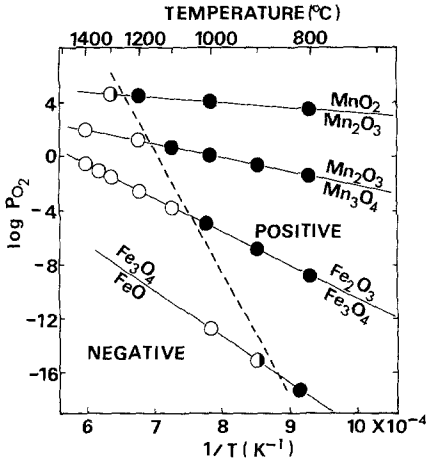


Figure 2 Experimental results based on the plots of $\log P_{O_2}$ versus $1/T$. • positive orientation, ○ negative orientation.

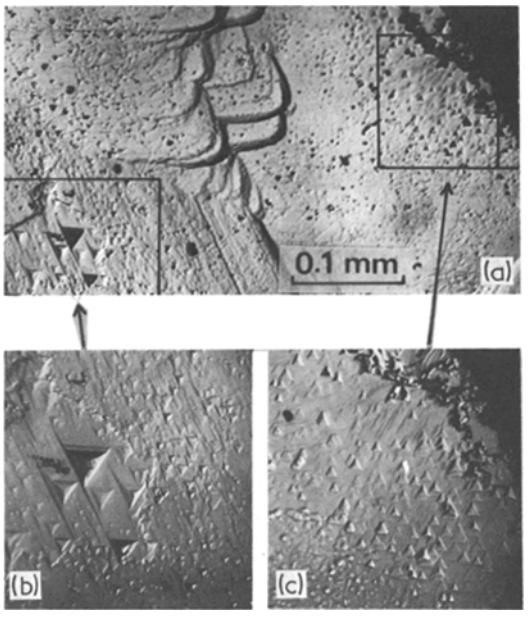


Figure 3 (a) An octahedral face etched near the boundary curve at 1300° C, 40 kbar for 5 min in MnO_2–Mn_2O_3 oxygen buffer. (b) The area where negative pits were produced, and (c) the area where positive pits were produced.

the oxygen buffers were taken from the literature [9–11], and were used without correction of total pressure because the effect of P_T on P_{O_2} is very small [12].

The experimental results are summarized in Fig. 2. The area of the positive pit formation was separated clearly from that of the negative pit formation by a boundary curve which exists at about 1000° C. The curve was linear with a negative slope and was expressed by an equation, $\log P_{O_2} = -9.0 \times 10^4/T + 63$. No negative pits were seen on any face etched at temperatures below the boundary, and vice versa. In some runs near the boundary, however, triangular pits with both orientations were formed even on the same face. Fig. 3 shows an octahedral face after etching at 1300° C and 40 kbar for 5 min in the oxygen buffer MnO_2–Mn_2O_3, where triangular pits with both orientations are seen.

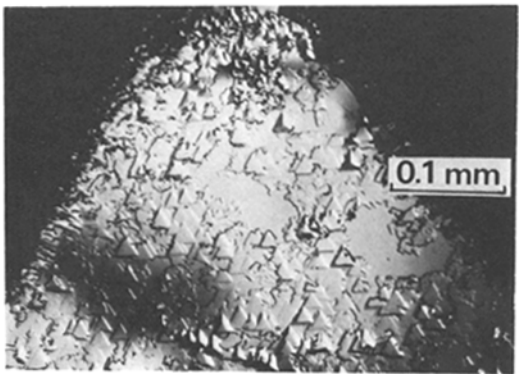
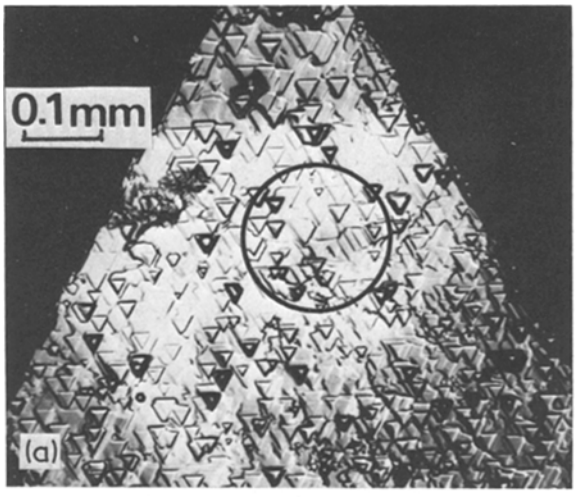


Figure 4 An octahedral face etched at 1100° C, 15 kbar for 30 min in Mn_2O_3–Mn_3O_4 oxygen buffer, where positive pits were produced.



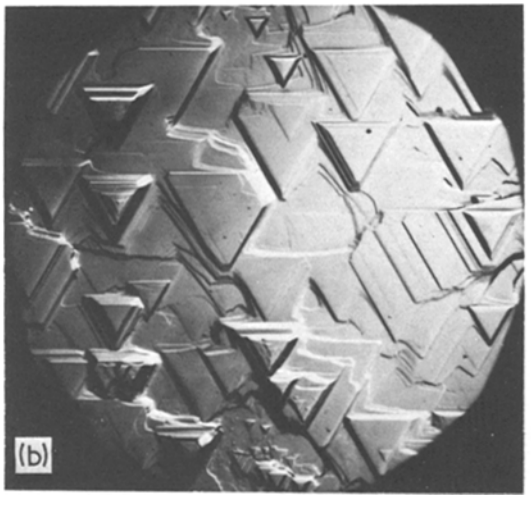


Figure 5 (a) An octahedral face etched at 1100° C, 15 kbar for 45 min in Fe_2O_3–Fe_3O_4 oxygen buffer, where negative pits were produced, and (b) an enlargement of the area circled in (a).

Figs. 4 and 5 show typical examples of the (1 1 1) faces with positive and negative etch pits, respectively. The former was etched at 1100° C, 15 kbar for 30 min in Mn_2O_3–Mn_3O_4 oxygen buffer, and the latter at 1100° C, 15 kbar for 45 min in Fe_2O_3–Fe_3O_4 oxygen buffer. Both flat-bottomed and pyramid-type triangular etch pits

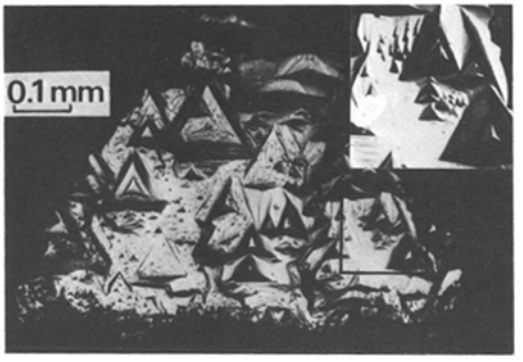


Figure 6 An octahedral face overetched at 1200° C, 40 kbar for 10 min in Mn_2O_3–MnO_2 oxygen buffer, where positive pits were produced. The area within the square is shown enlarged at the upper right.

interesting and useful for considering the etching mechanism of diamond surface. The reversal of the pit orientation was observed for the first time by Evans and Sauter [7]. They explained this phenomenon by a change in the relative velocities of the two different types of steps, step 1 and step 2 as shown in Fig. 8.

Although both types of step are atomically identical to each other, the edges of step 1 consist of atoms which are trebly bonded to the lattice, whereas atoms at step 2 are doubly bonded to the lattice. When step 1 moves at a higher velocity than step 2, positive etch pits result, whereas when the reverse is the case, negative pits are formed. They indicated that the relative step velocities

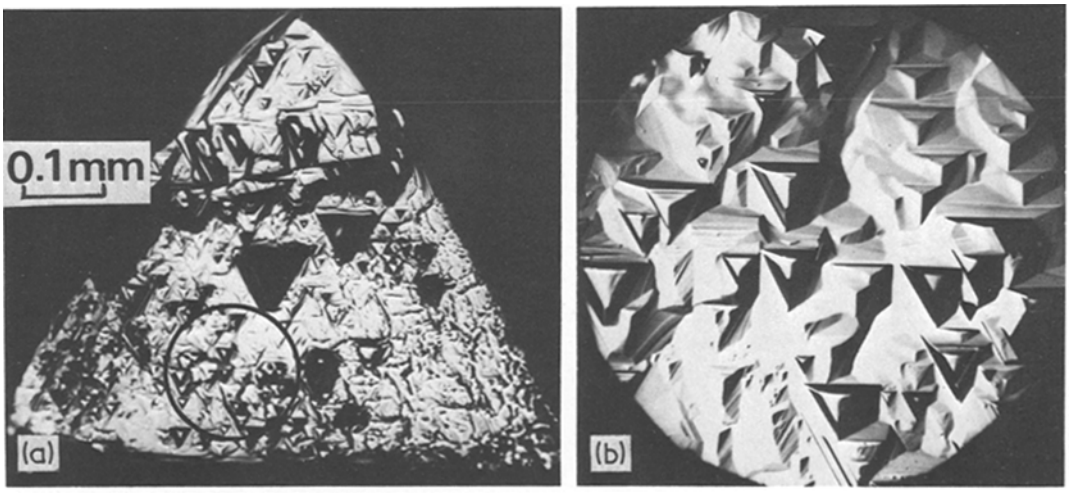


Figure 7 (a) An octahedral face overetched at 1300° C, 15 kbar for 30 min in Fe_2O_3–Fe_3O_4 oxygen buffer, where negative pits were produced, and (b) an enlargement of the area circled in (a).

[3] were observed not only in the negative orientation but also in the positive orientation. Etching proceeded vigorously with increasing temperature and P_{O_2}, and some etch pits grew large by consumption of neighbouring smaller ones. Figs. 6 and 7 show the surface structures of (1 1 1) faces vigorously etched at 1200° C, 40 kbar for 10 min in Mn_2O_3–MnO_2 oxygen buffer, and at 1300° C, 15 kbar for 30 min in Fe_2O_3–Fe_3O_4 oxygen buffer, respectively.

4. Discussion

From the present experimental results, oxygen partial pressure, P_{O_2}, was found to determine the orientation of the triangular etch pits on the octahedral face of diamond. This fact is very

were determined by the relative stabilities of the different oxygen–carbon complexes formed at the steps, and that step 2 was strongly stabilized by oxygen atoms forming bridges between carbon

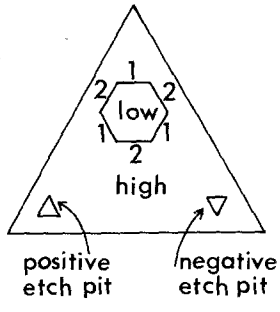


Figure 8 Steps 1 and 2 on an octahedral face of diamond.

atoms at temperatures below 900° C, producing positive etch pits. At temperatures exceeding 1000° C, the observation of negative pit formation could be explained by a reduction in the stabilization by bridge formation at these temperatures such that the lifetime of the oxygen–carbon complex on step 2 was less than the different type of complex formed on step 1.

The present experimental results support their explanation. Because oxygen partial pressure corresponds to oxygen concentration around a diamond surface, the dissociation temperature of the oxygen–carbon complex formed on step 2 can be increased with increasing P_{O_2}. Therefore, the higher the P_{O_2}, the higher the reversal temperature.

Evans and Sauter [7] observed the change in etch-pit orientation in a temperature range of 900 to 1000° C. Because their experiments were performed in air, P_{O_2} and P_T were 0.21 and 1 atm, respectively. The reversal temperature in the present result, on the other hand, was 1130° C at P_{O_2} of 0.21 atm and P_T of 15 kbar, which was higher than the former by about 130 to 230° C. The difference might come from that in total pressure. One reason is that diamond is not thermodynamically stable at atmospheric pressure, and this might have some effect on a surface reaction between carbon and oxygen atoms.

Almost all the triangular pits seen on natural diamond octahedral faces have the negative orientation, which shows that diamonds were etched under the earth with the conditions corresponding to a negative region in Fig. 2. Because diamonds sometimes have mineral inclusions with Fe^{2+} such as olivine $[(Mg, Fe)_2SiO_4]$, enstatite $[(Mg, Fe)SiO_3]$, and garnet $[(Mg, Fe)_3Al_2(SiO_4)_3]$ [13], showing that they were formed under fairly low oxygen partial pressure [14], the present result is consistent with our knowledge of diamond formation. Besides, the stability of these mineral inclusions depends on temperature, total pressure and oxygen partial pressure, and gives important information on the growth condition of natural diamonds. The present experimental results also give useful information about it.

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