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Heat treatment of diamond grains for bonding strength improvement

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The heat treatment of synthetic cubo-octahedral diamond grains to produce tight bonding by making their surface rough is reported. In order to obtain a rough surface, a thermal etching technique at atmospheric pressure in air at 700 to 1100° C is applied. The shape, surface features and surface area are investigated, then in order to examine the effect of the roughened diamond surface on bonding strength, peeling and bending tests were carried out. The results obtained showed that: rough surfaces may be obtained by thermal etching at atmospheric pressure in air; on etching at 700 to 1000° C, the etch rate of the {1 1 1} face is higher than that of the {1 0 0} face, and in particular, diamonds etched at 700 to 1000° C have a hollow {1 1 1} face; the surface area of one grain can be increased by etching – on etching at 900° C for 15 min, surfaces become fully covered with clear etch pits and the surface area shows maximum value; the surface area seems to have an influence on bonding strength, and when diamond grains are bonded with phenol resin or electroless plating nickel, bonding strength improves by about 10%.

1. Introduction
Diamond grains play important roles in drill bits, dressers, grinding wheels and other tools. In these cases, bare or metal-coated grains are used by burying them in resinoid or metallic matrix materials. These grains must be tightly bonded to the matrix materials to prevent tool wear which is caused by popping out, and to maintain the accuracy of a machined workpiece.

In order to improve bonding strength, surface roughening processes are sometimes adopted. These processes may also be applied to diamond grains. From this point of view, irregular shaped grains may be used, but synthetic diamond grains which have a high strength are block-shaped cubo-octahedrons having plain surfaces, and thus they cannot always achieve a high bonding strength.

There are many methods in which to make a surface rough. However, it is difficult to make diamond grain surfaces rough by mechanical processing, because diamond is the hardest material on earth. Therefore, we have proposed the idea of covering the plain surfaces with etch pits.

Many studies on diamond etching have been carried out, for example, by Evans and co-workers in oxygen [1], Tolansky and co-workers in KNO_3 [2], Kanda and co-workers in ultra-high pressure and high-temperature water [3]. These studies were carried out to elucidate the growth process of diamond by observing etched features, and not the trials for the industrial uses of etch pits.

In this study, in order to improve bonding strength of cubo-octahedral diamond grains, a method of making their surfaces rough by etching was studied.

2. Diamond grains and the etching process
The diamond grains tested are well-crystallized cubo-octahedral synthesized grains with plain surfaces. Their average weight and the size of a grain are 26 μg and 280 μm, respectively.

Atmospheric pressure of air was selected as an etchant in a furnace shown in Fig. 1. This furnace does not have any special air supplying system. A monolayer of 0.2 g grains were spread in an alumina capsule and placed in the heated furnace at certain temperatures for certain durations. The etching temperatures were 700, 800, 900, 1000 and 1100° C, with 15 and 30 min holding times. After the holding time had passed, they were removed from the furnace and cooled in air at room temperature. Then etched grains were washed in a boiling mixed acid of H_2SO_4 and HNO_3, and cleaned ultrasonically in an alcohol bath.

3. Shape changes by etching
3.1. Mass and size changes
In order to examine the effects of the etching temperature on the mass change, 1.8 to 2.0 mg grains were weighed before and after etching with a microgram balance. Their numbers were also counted on an enlarged projection. The mass divided by the number gave the average mass of one grain before, M_0, and after, M_e, etching. The percentage mass decrease, $(M_0 - M_e)/M_0 \times 100$, was calculated and plotted against etching temperature and shown in Fig. 2. Mass loss is recognized even at 700° C, but above 900° C this rate becomes higher in proportion to the etching temperature.

Fig. 3 shows the micrographs of the diamond grains

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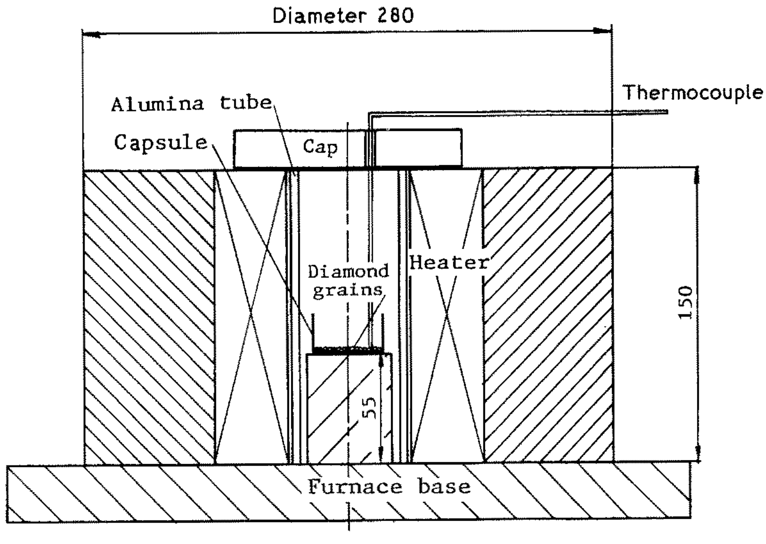

Figure 1 The furnace used for etching.

before and after etching. Fig. 3a shows non-etched grains, and Fig. 3 shows the grains etched at 900° C for 15 min. The former look glossy while the latter look grey; however, little difference in the grain size can be recognized.

3.2. Surface observations by SEM

As shown in Fig. 3, glossy surfaces change to grey. This is evidence that the plain surface becomes rough on etching. SEM observations of the grains were carried out. After etching for 15 min, macro- and micro-observations were made as shown in Figs 4 and 5, respectively.

Before etching, the diamond grain is a well-defined cubo-octahedron and both {1 1 1} and {1 0 0} faces seem to be plain and smooth. At 700° C, a little mass loss was observed as shown in Fig. 2, some irregularly shaped pits could be observed only on the {1 1 1} face while no macroscopic change could be found.

At 800° C, a little macroscopic change may be seen. The {1 0 0} face is covered with small pits and the {1 1 1} face is also covered with triangular pits with sides of 2 μm.

At 900° C, the shape change becomes significant and the corners become more pronounced. The {1 0 0} face is covered with square pits with sides 5 μm long and the {1 1 1} face is also covered with various sizes of triangular pits.

At 1000° C, the etching process progresses further and the square pits on the {1 0 0} face become circular. At 1100° C, the faces look less rough and the shape changes to round.

Fig. 6 shows the SEM observations of the shapes and {1 0 0} surfaces etched at 800° C for varying etching time from 15 to 120 min. When the etching temperature is constant, the shape becomes hollow and the {1 0 0} surface becomes covered with clear etch pits in proportion to the etching time. This process is similar to that shown in Figs 4 and 5.

Phaal [4] reported in his study on etching of natural diamond that in 0.4 mm Hg oxygen, the etch rate of the {1 1 1} face was higher than that of {1 0 0} in the etching temperature range 700 to 1000° C, and above these temperatures, the etching rate of the two faces was almost the same.

In this study on synthetic diamond etching, only {1 1 1} face changes were observed at 700° C, and grains showed edge-line remains in the range of 800 to 1000° C. Therefore, it can be said that synthetic diamond has the same characteristics as natural diamond concerning its etching rate in air. However, at 1100° C, no edge-line remains could be recognized. The reason why etching proceeded rapidly may be because of too high a temperature.

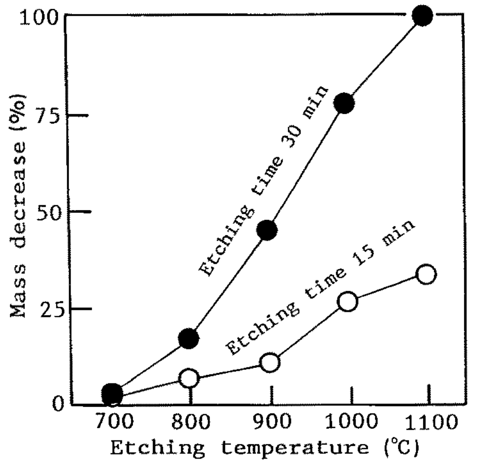

Figure 2 The effect of etching temperature on mass decrease.

3.3. Surface area

The BET method is well-known as a means of measuring the specific surface area of a powder. We tried to estimate the surface area of a diamond grain by the BET method using krypton for a 2 g diamond, but a reliable value could not be obtained, because the diamond surface area was very small. Therefore, in this study, the surface area of one grain was estimated by the following procedure.

1. The mass of one grain was measured by the above method.

2. The diamond grains were covered by a thin plating film.

3. The mass gain of one grain was calculated from the results of 1 and 2.

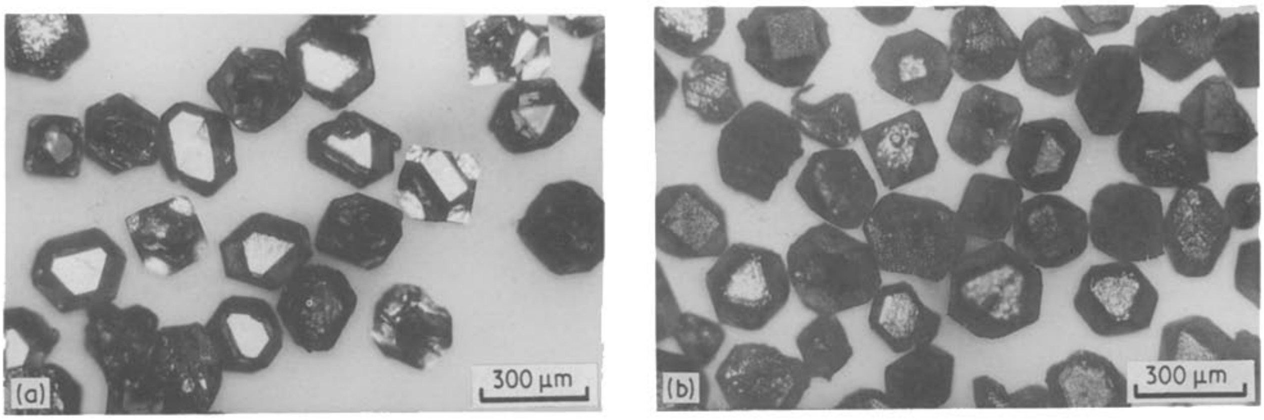

Figure 3 Micrographs of (a) un-etched and (b) etched diamond.

4. The mass of one plated grain was also measured in a similar way as 1.

5. The volume of one grain by plating is calculated from the mass gain obtained.

6. Supposing that the thickness of the plated layer is regular, the volume gain is divided by the measured thickness of the plated layer to give the surface area of one grain.

Electroless nickel plating was adopted, because diamond is non-conductive and by this method a regular thick plated layer can be obtained regardless of the surface state of the mother material. A 2 μm thick layer was obtained under the plating conditions of 85° C for 10 min. Fig. 7 shows a plated grain used for measuring the surface area. Even if plated, the etch pits can still be observed, and it is clear that the plated layer covers the roughened surface.

The relation between the surface area and etching temperature with etching duration is shown in Fig. 8. For both etching conditions the surface area of one grain becomes large in proportion to etching temperature, and then falls after showing a maximum value at a certain etching temperature. In general, the higher the etching temperature and the longer is the

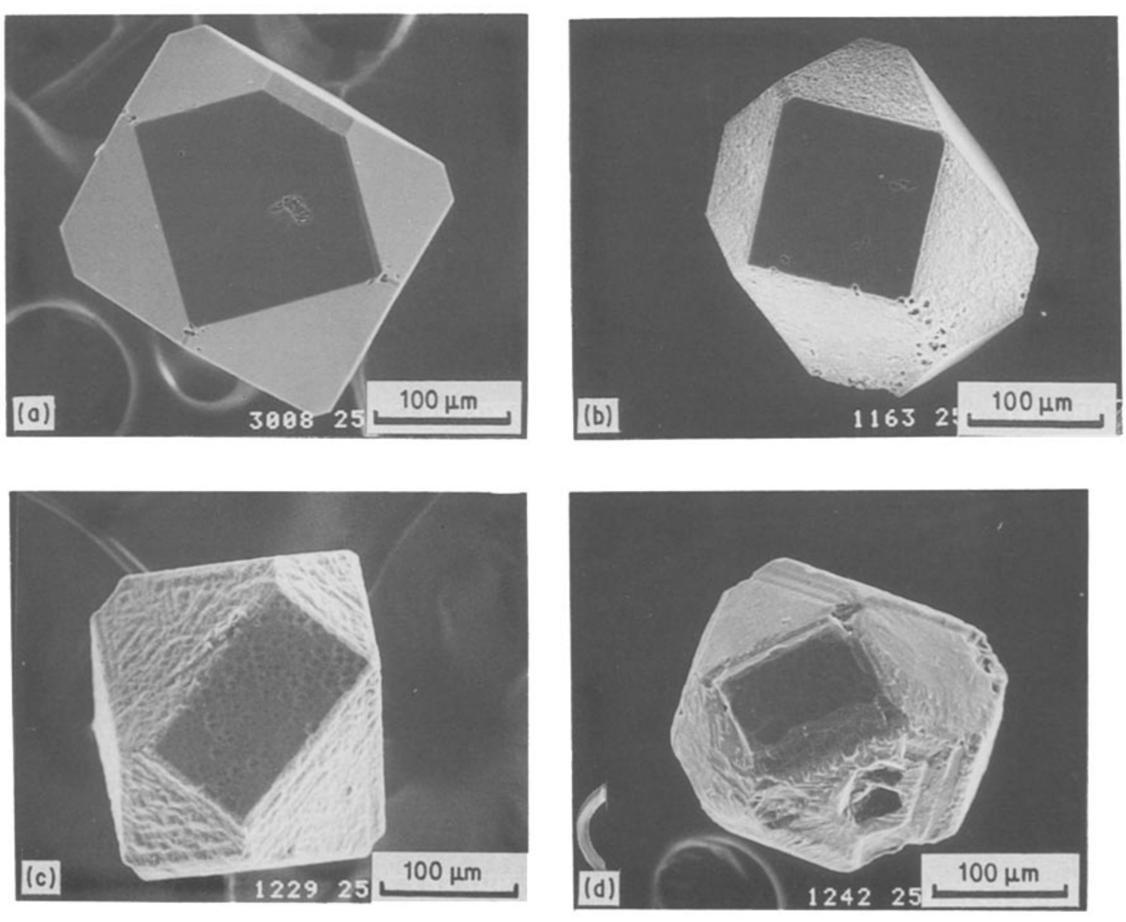

Figure 4 Macro-observations of etched features for various etching temperatures, and an etching time of 15 min. (a) Before etching, (b) etched at 800° C, (c) etched at 900° C, (d) etched at 1000° C.

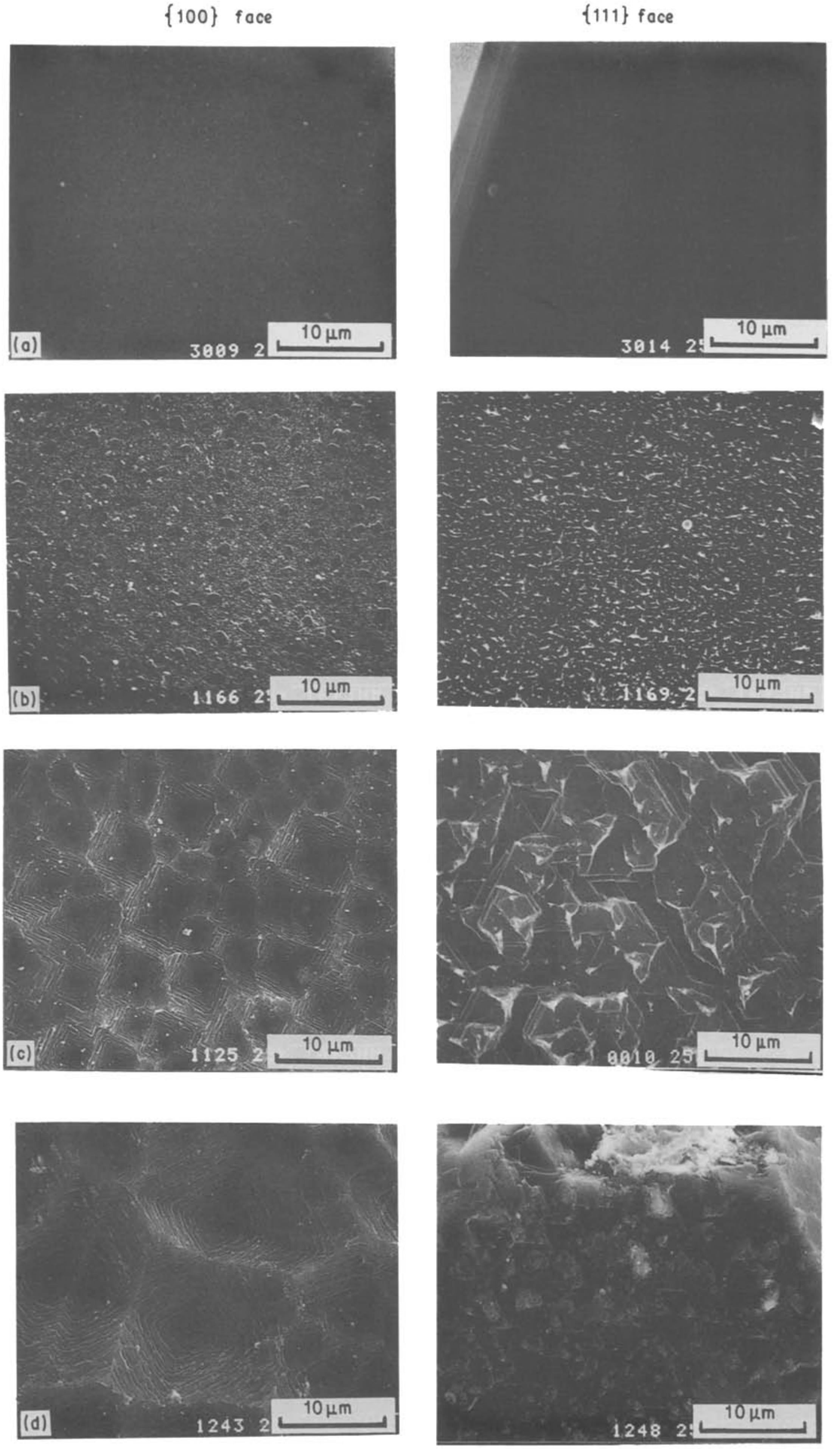

Figure 5 Micro-observations of etched surfaces for various etching temperatures, and an etching time of 15 min. (a) Before etching, (b) etched at 800° C, (c) etched at 900° C, (d) etched at 1000° C.

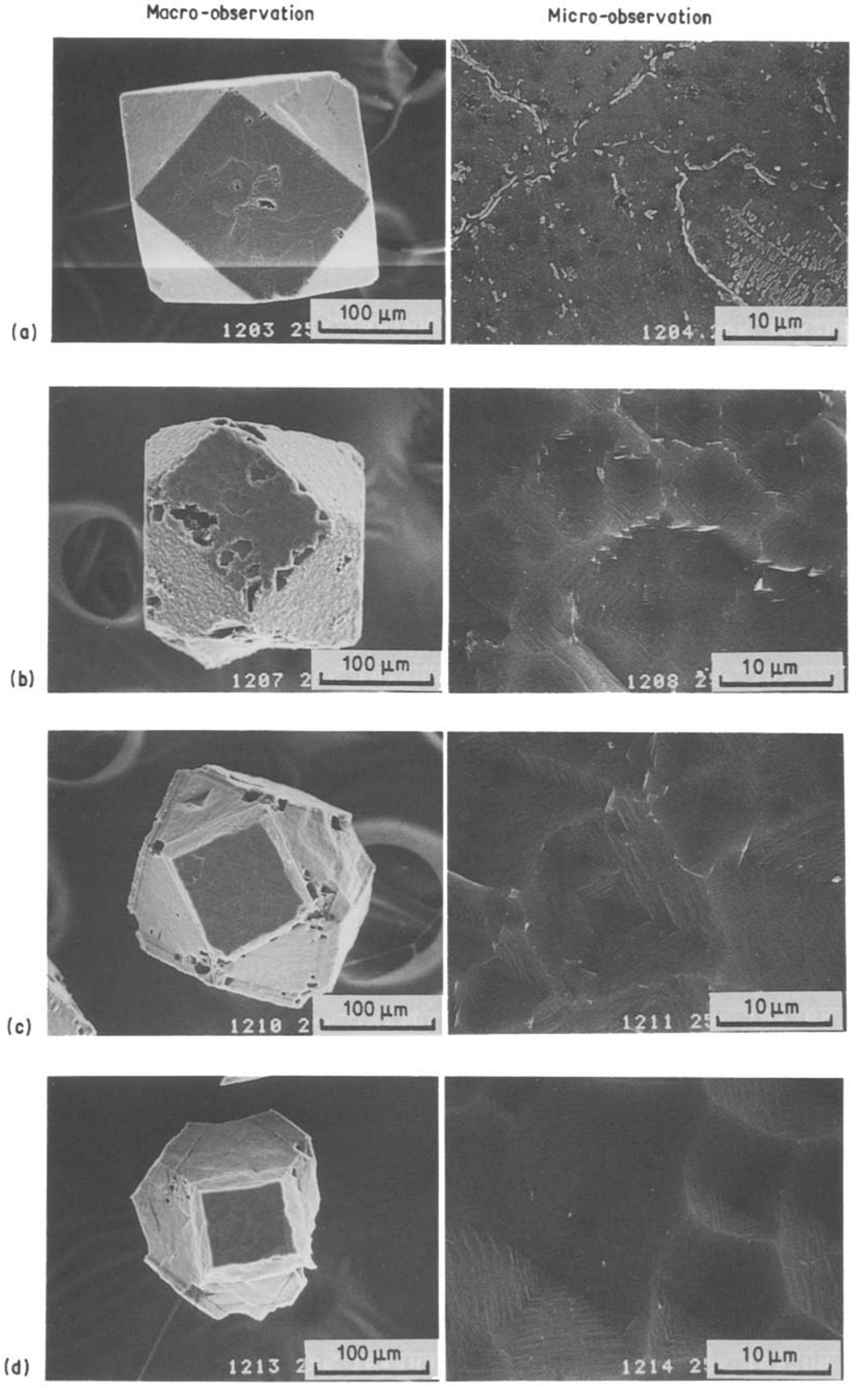

Figure 6 SEM observations of etched features and {1 0 0} surfaces for various etching times, at an etching temperature of 800° C. (a) 30 min, (b) 60 min, (c) 90 min, (d) 120 min.

etching duration and the smaller are the grain size and area. However, in the case of a diamond, as shown in Fig. 8, increasing surface area can be observed.

From the SEM observations above, attempts have been made to model the surface features and shape changing process of a diamond heated in air for 15 min, as shown in Fig. 9. In (1), a non-etched grain, both {1 0 0} and {1 1 1} faces are flat and smooth. After etching at 700° C (2), small etch pits can be seen only on the {1 1 1} face; macroscopic shape changes can rarely be observed. After etching between 800 and 1000° C (3), the difference in etching rates between the

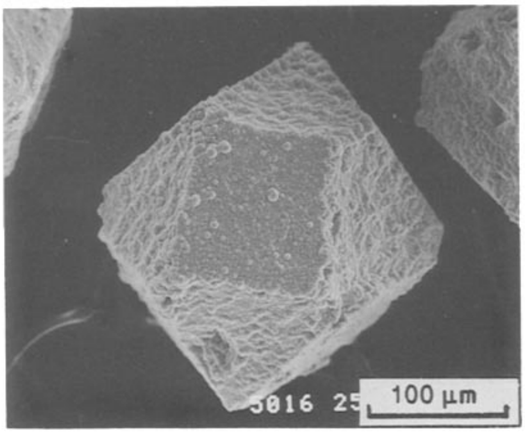

Figure 7 A diamond grain coated with electroless plating nickel used for measuring the surface area.

two facets produces angular grains and at this time surfaces are covered with clear etch pits. On etching above 1000° C (4), the difference in etch rate between the two facets cannot be observed, the angular shape disappears and every facet becomes relatively smooth as a result of the etching process.

4. Bonding strength

In order to examine the effect of roughened diamond surfaces on bonding strength, two tests were carried out. One was a peeling test and the other was a bending test.

4.1. Estimation by the peeling test

Diamond grains for the peeling test were prepared with a 10 μm thick nickel alloy coating by electroless plating. The coated grains were packed into a glass bottle with a cemented carbide bar 5 mm diameter and 16.5 mm long. After rotation for 3 h at 60 r.p.m., grains whose coating had peeled off were selected from the grains tested. The percentage of "peeled-off" grains, N_p, was plotted against the total number of grains tested, N_0 as shown in Fig. 10. In all etching

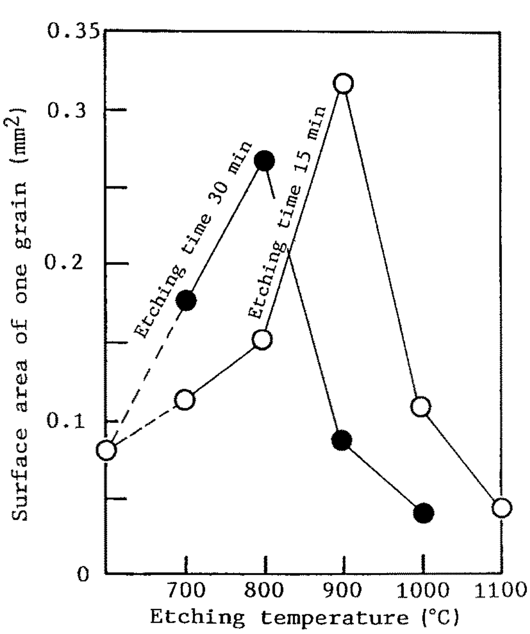

Figure 8 The relation between surface area and etching temperature.

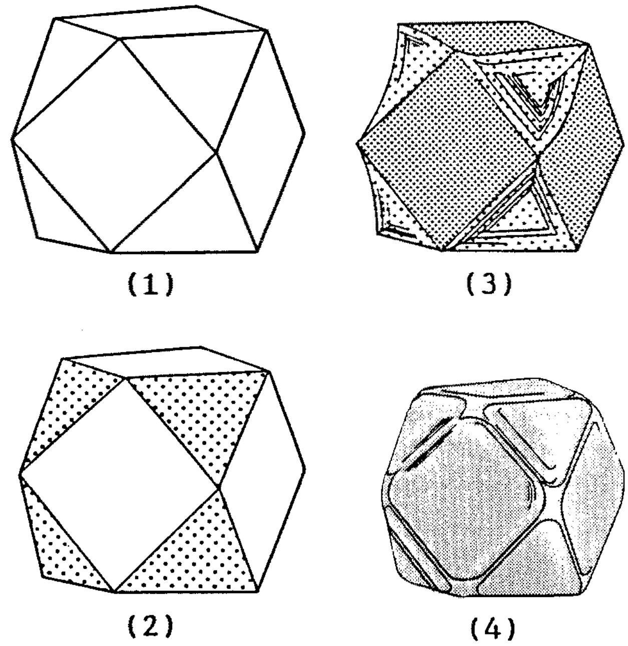

Figure 9 An etching process model of a diamond in air.

conditions the percentage of etched grains is not as high as that of un-etched grains, and the minimum percentage, that is those most difficult to peel off, is obtained under the etching conditions of 900° C for 15 min. Comparing these observations with the surface area results shown in Fig. 8, it was found that there are some correlations.

Fig. 11 shows two typical grains after the peeling test. Fig. 11a shows un-etched diamond with the plated layer peeling off from the edgeline, like peeling the skin off an orange. Fig. 11b shows an etched diamond; however, the plated layer does not peel off like orange skin, and some plated layer remains. It is understood that bonding strength has been improved by the etching.

4.2. Estimation by the bending test

A bending test was carried out on two types of test pieces made by different binders. Both un-etched grains and those etched at 900° C for 15 min which showed maximum bonding strength in the peeling test were used.

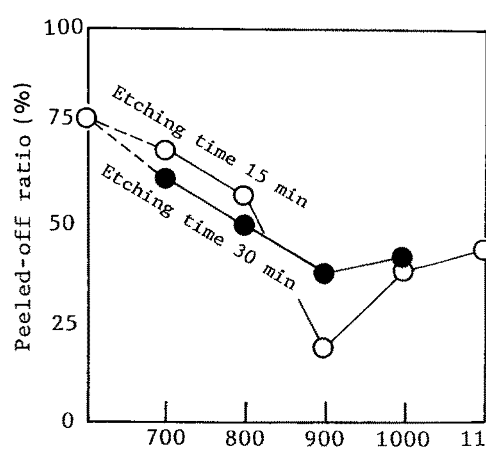

Figure 10 The relation between bonding strength and etching temperature as estimated by the peeling test.

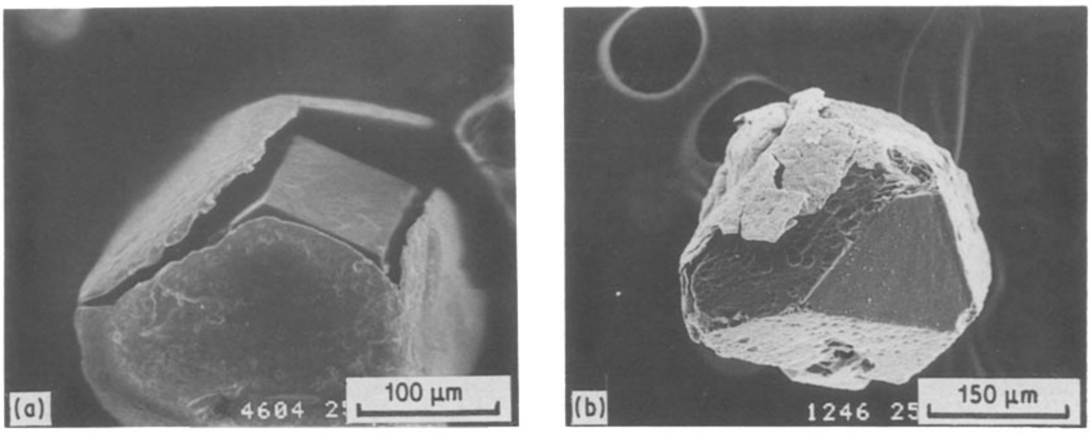

Figure 11 Diamonds after the peeling test: (a) un-etched, (b) etched.

One type of test piece was prepared by electrolessly plating a 10 μm thick layer of nickel on the grains which were then hot-pressed under a compression pressure of 10 MPa at 800° C for 30 min in nitrogen.

The other type of test piece was bonded by phenol resin by imaging a resin-bonded diamond wheel of diamond concentration 100. These test pieces were also made by hot-pressing at 170° C under a compression pressure of 50 MPa for 15 min in air.

Both types of test piece were 30 mm long, 10 mm wide and 5 mm thick. Two test pieces were prepared for each condition. The bending test was carried out by three-point bending, and the results are shown in Table I.

The bending strength on both types of test pieces with etched grains exceeds that of un-etched grains by about 10%.

SEM observations of fractured surfaces from the bending test are shown in Fig. 12. Fig. 12a-1 shows an un-etched diamond, when large-scale peeling is observed. On the other hand, as shown in Fig 12a-2, large-scale peeling cannot be observed in the fractured surface when etched grains are used. A fractured surface bonded by phenol resin with non-etched diamonds is shown in Fig. 12b-1; here, the trace of a diamond grain on the resin looks flat. In the case using etched grains, as shown in Fig. 12b-2, many etch pit marks of the diamond can be observed on both the bottom and side of the trace. It is believed that they are evidence of improvement of the bonding strength obtained by using etched diamonds.

4.3. Effects of surface roughening

From the above observations, roughening the diamond

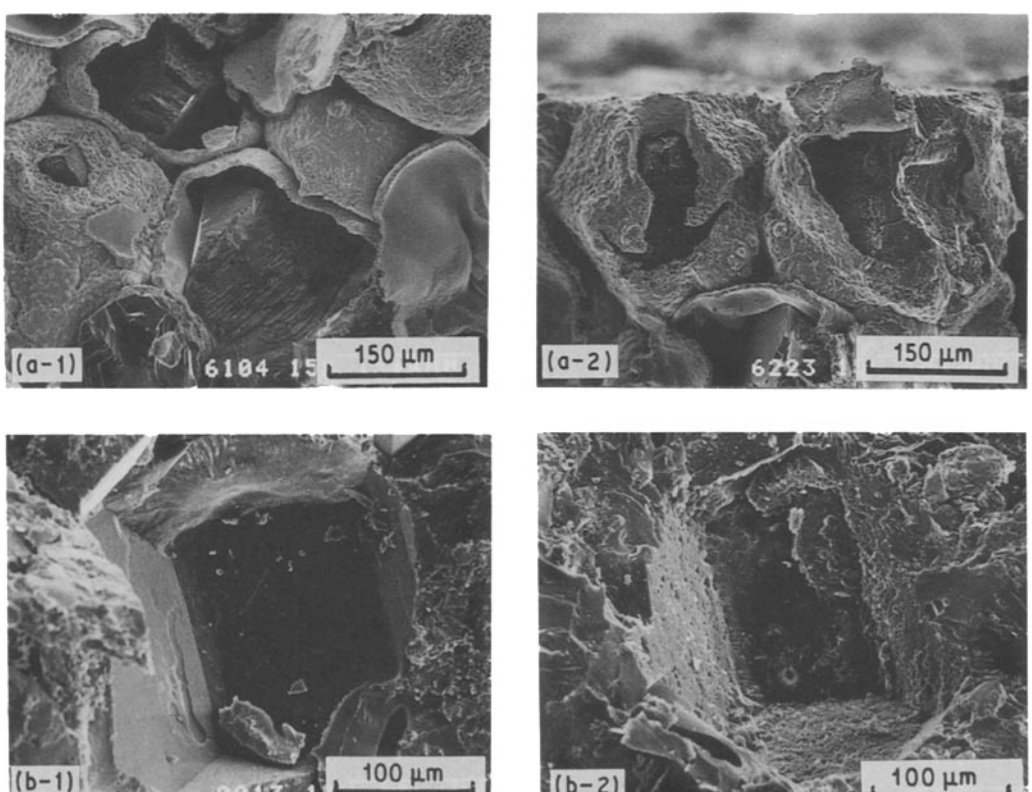

Figure 12 Fractured surfaces obtained by the bending test: (a) bonded with electroless plating nickel; (b) bonded with phenol resin. (a-1), (b-1) un-etched; (a-2), (b-2) etched.

TABLE I Bonding strength of the diamonds bonded with electroless plating nickel or phenol resin

Treatment	Bonding material	
	Electroless-plating nickel	Phenol resin
Un-etched	200	55
Etched 900° C, 15 min	214	65

surface improves the bonding strength between diamonds and other materials. Therefore surface roughening has a slight effect on bonding strength.

Generally, bonding strength cannot always be improved by surface roughening, because adhering media cannot completely fill up the hole and air pores may easily be included; in this case a rough surface is not always advantageous. When chemical bonding is strong, a rough surface has rather bad effects on bonding strength. In this experiment, however, the pit marks remaining on the adhering media indicated that the anchor effect, as shown in Fig. 13, is expected even on diamonds.

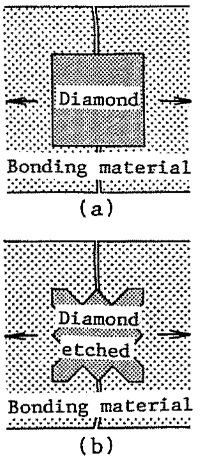

Figure 13 A tight-bonding model: (a) un-etched diamond; (b) etched diamond.

5. Conclusions

In order to improve the bonding strength of diamond grains, a surface roughening process was proposed and carried out by a thermal etching technique. Thermal etching was carried out at atmospheric pressure in air at 700 to 1100° C. The shape, surface features and surface area were investigated. Diamond grains were then bonded with electroless plating nickel or phenol resin and bending tests were carried out to estimate the effect of surface roughening on the bonding strength.

The following results were obtained.

1. Rough surfaces are obtained by thermal etching at atmospheric pressure in air.

2. Or etching at 700 to 1000° C, the etch rate of the {1 1 1} face is higher than that of the {1 0 0} face, and in particular, diamonds etched at 700 to 1000° C have a hollow {1 1 1} face.

3. The surface area of one grain can be increased by etching. On etching at 900° C for 15 min, the surfaces are completely covered with clear-cut etch pits and the surface area shows a maximum value.

4. Surface area seems to have influence on bonding strength and when diamond grains are bonded with phenol resin or electroless plating nickel, the bonding strength improves by about 10%.

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